PRINCIPLES OF
ENERGY
STORAGE SYSTEMS

P. Jayarama Reddy

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Principles of Energy Storage Systems

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***by* Jayarama Reddy Puthalpet**

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Dedicated to

SAI

&

My Teachers

Preface

In an electric power system, predicting the electricity demand and operating power plants to meet that varying demand are involved in a complex way. Baseload coal-fired and nuclear plants operate almost at full output to meet the large constant electricity demand. The electricity demand, however, frequently changes which is instantly supplied by operating a range of small power plants. These are load-following or ‘cycling’ plants which are usually gas- or oil-fuelled plants or hydropower plants. These units are intermediate-load plants run to meet most of the day-to-day variable demand, and peaking units that take care of the peak demand, and often operate less than a few hundred hours per year. In addition to this daily cycling, frequency regulation and contingency reserves are also provided by partly loaded generators and responsive load.

The world is at a critical point today. Carbon pollution is increasing and the climate is changing in spite of best efforts by the world governments to minimize it. Some studies say there is also a danger of fossil fuels running out in the next few decades resulting in a dire need to find the alternatives to meet the world’s energy requirements. Modern technology has already provided us with alternatives like renewable energy sources such as solar photovoltaics, wind turbines, and biomass plants, and new generation nuclear plants. But these technologies except nuclear plants, unlike traditional power plants, produce much smaller amounts of electricity and that too intermittently because sun is not always shining nor the wind always blowing.

The global energy demand is huge and growing by about 3.6% annually. Technically, the amount of electricity fed into the power grid must remain the same and intermittent pumping of more electricity damage the grid. Situations are arising where the power production is higher than the consumption or the reverse. In such situations, energy storage technologies come into play as ‘key element’ to balance out the hitches.

In its most popular form, a solar-plus-storage project consists of a battery storage system connected to a solar PV plant such that the battery is charged from the solar power plant and then discharged to the grid at a later time when the energy is required most. Similar arrangement is done with a wind farm. The energy storage system helps mitigate the intermittency problem of solar or wind and also match energy supply with demand.

The need for electrical energy storage technologies in a future energy system mostly based on variable renewable energy sources is widely recognized. However, the issue is which storage technology is more suited. Several studies are made in this perspective and different technologies are suggested depending on the application.

Studies have shown that no energy storage technology scores high in all aspects. Each storage technology has its own performance characteristics that make it better suited comparatively for a specific grid application. The storage technology of choice depends particularly on the system capacity, application, marginal cost of peak electricity and so on. And a variety of complementing technologies are required to fully address the needs of an electric grid with large-scale integration of renewable energy.

Of the different technologies, *Pumped hydropower, electrochemical batteries, and hydrogen/SNG seem to emerge as the technologies of the future*. Pumped storage is a mature technology with a proven track record and is the cheapest option for large-scale energy storage (>50 MW). The lack of suitable installation sites and local environmental impact are the barriers to their further expansion. Battery systems have emerged as a feasible alternative for applications less than 50 MW. However, factors such as considerable uncertainty over the usable life, performance, safety, and cost remain as challenges for their widespread deployment. Hydrogen/SNG storage technology has the potential due to their high energy density and quick response time, but further research on concerns related to cost, safety, reliability, efficiency, physical infrastructure inadequacy are needed. Technology advances along with careful planning, design improvements, combined field demonstrations, standardization, and fair regulatory environment may result in lower cost of storage technology, higher revenues, increased user confidence, which eventually leads to large scale utilization.

Further, lifecycle cost of these technologies is critical to their widespread adoption. Significant research and development efforts need to be undertaken both at a component level and at a system level to make the storage technologies economically sustainable in the longer term. Interoperable components and systems, sophisticated communication and automation technologies and control algorithms must be ensured for successful project deployments (IEC Market Strategy Board, 2011).

In order to achieve the commitment made by the world countries at Paris Meet in 2015, renewable energies need to dominate the future energy supply system. As the renewable energy installations grow, the need for energy storage systems will increase. To ensure smooth connection of energy storage systems, potential issues related to their largescale integration to the electric grid coupled with renewable energy should be carefully investigated. Also, necessary technical specifications and regulatory frameworks need to be appropriately in place.

Of late, the importance of storage of electric energy in rechargeable batteries is increasing. The commercial lithium-ion battery which has steadily improved over the last decade and a half has been vital for the more sophisticated portable consumer electronics. Recently, advanced batteries have been used in more large-scale applications like electric and hybrid electric vehicles (EVs and HEVs), and energy buffering in the electricity grid. Storage in other forms of energy, for example, thermal energy has shown several applications. Cryogenic goods transportation, low temperature cooling, domestic space heating and sanitary hot water supply, industrial waste heat recovery, high temperature solar thermal power plant management are a few applications of thermal storage that provide economic advantage and likely larger energy utilization.

According to the International Energy Agency, the world will need 10,000 GW-hours of batteries and other forms of energy storage by 2040, a 50-fold increase on today, a formidable task for the energy storage sector.

Consumer electronics, electric vehicles and storage needs for intermittent wind and solar are primarily the drivers. The acceleration is facilitated by cost reductions in the last decade, of nearly 90% for lithium-ion batteries for

EVs, and by nearly two-thirds for stationary applications including electricity grid management. Despite considerable progress, the decision-makers still need a better comprehension of all the technologies and their role to meet the target.

The US Energy Storage Association (ESA) set a goal in August 2020 for the deployment of 100GW of new energy storage by 2030 using a range of technologies. It is considered as an ‘entirely reasonable and attainable’ goal, if ‘right policies and regulatory frameworks’ are brought in. Achieving the target would have an impact on the transition to renewable energy as well as on the wider global economy. The ESA contends the transition away from fossil fuels is now overwhelming, and a range of energy storage technologies will play an ever-increasing role because the energy storage can help to create reliable and cleaner grid cost-effectively by offering the flexibile services.

India has the ambitious goal of installing 225 GW of renewable energy by 2022. Battery-based energy storage provides flexibility and agility to better integrate intermittent solar and wind energy resources into India’s electric grid and ensure high-quality power for consumers.

New electricity grids will be self-balancing and self-healing networks, and they level and optimise energy production using demand-response algorithms and sophisticated prediction models. *Smart grids* and connected grid-energy storage allow power producers to send excess supply to temporary storage sites that become energy producers when demand for electricity is greater, optimising the production by storing off-peak power for use during peak times. Intermittent energy producers, not needing any local storage device, would be connected directly to the grid, which effectively becomes a giant battery. Solar energy could be stored for the night’s use, while wind power could be stored for quiet times.

On the demand side, grid operators and utilities plan to roll out *smart metering devices* in every household in most countries. This plan would help to harness valuable data about the consumption behaviors of endusers and consequently adjust the flows between baseload and intermittent power plants as well as smart grids and connected storage facilities.

This book on ‘Energy Storage Systems’ discusses several of these issues. Many of the technologies are under continuous development and/or testing and very few are matured. The book written comprehensively stressing on the principles, is expected to serve the study requirements of undergraduate students of engineering particularly electrical and power engineering as well as science students. In addition, the book meets the needs of those working in the field of energy storage and the decision makers. A large number of earlier and latest references are given at the end of each chapter that will provide enough base for the students wish to pursue further in this field of study which has tremendous potential.

The ‘Energy Storage News’ edited by Andy Colthorpe reports regularly the progress in energy storage technologies/ systems, and the installed and proposed energy storage projects worldwide. Students will be benefited by regularly perusing them.

- Author

Acknowledgement

Most of the energy storage technologies are under development or demonstration and deployment; only a few are at the commercial level and available for ready implementation. Several research papers and reviews from peer-reviewed journals, which are cited under ‘references’ were consulted in writing this book. The reports published from time to time by government Departments and Agencies such as the US Department of Energy (USDOE), International Energy Agency (IEA), International Renewables Agency (IRENA), Energy Storage Association (ESA) of the US, National Renewable Energy laboratory (NREL), European Commission (EC), Intl Electro-technical commission (IEC) and quite a few othersare a great source of R&D and commercial status of these technologies as well as operational experience. The brochures released by the manufacturers of the storage devices are highly informative. My sincere thanks to all the authors and publishers/agencies of these papers/documents.

My family members, particularly my young grand-daughters, research students, friends, and well-wishers have constantly provided cheer and support during the preparation of the manuscript despite the disturbances due to the Covid pandemic and consequent lockdown. My affectionate thanks to all of them. Special thanks to my research student, Dr. M. Sirajuddin, former Technical Director, Department of Defence Production, Government of India, for going through some parts of the text and offering valuable suggestions.

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I take responsibility for any lapses in the presentation of this growing subject.

- Author

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Abbreviations

AER	Absorption enhanced reforming
AGC	Automatic generation control
AGM	Absorbed glass mat
BESS	Battery energy storage systems
BTS	Base transceiver station
CAES	Compressed air energy storage
CCA	Cold cranking Amps
CES	Cryogenic energy storage
CHP	Combined heat and power
CNT	Carbon nanotube
COPV	Composite overwrapped pressure vessel
DER	Distributed energy resources
DESS	Distributed energy storage systems
EES	Electrical energy storage
EROI	Energy return on energy invested
ESS	Energy storage systems

EV	Electric vehicle
FACTS	Flexible AC transmission systems
FCAS	Frequency control ancillary services
FCEV	Fuel cell electric vehicles
FES	Flywheel energy storage
FRR	Frequency response reserve
HER	Hydrogen evolution reaction
HTF	Heat transfer fluid
HV	Hybrid vehicle
HVAC	Heating, ventilation and air-conditioning
IEA	International Energy Agency
LAES	Liquid-air energy storage
LCO	Lithium cobalt oxide
LCOS	Levelised cost of storage
LFP	Lithium iron phosphate
LHS	Latent heat storage
Li-ion	Lithium-ion
LMO	Lithium manganese oxide
LMP	Locational marginal prices

MAB	Metal-air battery
MOF	Metal organic framework
Ni-Cd	Nickel-cadmium
NCA	lithium nickel-cobalt-aluminum oxide
Ni-Fe	Nickel iron
$NaNiCl_2$	Sodium nickel chloride
NMC	lithium nickel-manganese-cobalt oxide
NiMH	Nickel metal hydride
Na-S	Sodium Sulphur
NiZn	Nickel zinc
OER	Oxygen evolution reaction
PAH	Polycyclic aromatic hydrocarbons
PAS	Polyacene
PCM	Phase change material
PEM	Proton exchange membrane
PEV	Plug-in electric vehicle
PHS	Pumped hydro storage
RFB	Redox flow battery
SCADA	Supervisory control and data acquisition

SHS	Sensible heat storage
SLA	Sealed lead-acid
SMES	Superconducting magnetic energy storage
SMG	Smart mini-grid
SMR	Steam-methane reforming
SNG	Synthetic/Substitute natural gas
SOFC	Solid oxide fuel cells
SRAM	Static random-access memory
SSB	Solid state battery
STH	Solar-to-hydrogen
TES	Thermal energy storage
TRS	Technology readiness level
VPP	Virtual power plant
VRFB	Vanadium redox flow battery
VRLA	Valve-regulated lead-acid
ZnAg	Zinc silver
ZnMn	Zinc manganese

CHAPTER 1

Introduction *(Electricity & Electrical Energy Storage)*

1.1 Energy

Energy is one of the most basic concepts in physics. It is stated as ‘the capacity for doing work.’ Actually, it is a complex conception and rather difficult to define. Everything in the world is one or the other energy (or matter) and it makes things happen. Energy exists in several forms: radiation, chemical, electrical, thermal, gravitational, nuclear, and so on.

All these forms of energy are categorized as ‘potential energy’ or ‘kinetic energy.’ Potential energy is ‘stored’ energy, and when used to do ‘work’, it is called ‘kinetic energy.’ So, the kinetic energy makes things to move or happen; that is, a moving object possesses kinetic energy. An object of definite mass and volume moving at a certain speed has kinetic energy. If a car and truck travel with the same speed both have kinetic energy, but the truck has a more kinetic energy than the car because of its more mass. There are numerous examples in nature showing several kinds of potential energy and several types of kinetic energy. For example, the motion of waves, atoms, molecules, electrons and objects are all kinetic energy. Let’s see each of these forms of energy: *‘Radiant energy’* is electromagnetic energy that includes visible light, X-rays, gamma rays, and radio waves. Sun’s radiation is radiant energy that sustains life on earth. Atoms and molecules in the materials are held together by bonds. And the energy stored in the bonds of atoms and molecules is called ‘*chemical energy.’* The chemical energy in gasoline, natural gas, coal, and biomass converts to thermal energy when they are burned. For instance, when biomass/wood is burned or when gasoline is burned in a vehicle’s engine. Batteries are used to store chemical energy. *Electrical energy* is a type of kinetic energy caused by moving charged particles such as electrons, and the speed of the charges decide the amount of energy they carry. The energy stored in an electric field is also electrical energy. For example, (a) lightening during a thunderstorm is the release of electrical energy stored in the atmosphere, (b) energy that is stored in a power plant’s generator is delivered to the consumer through transmission lines; (c) energy stored in a capacitor can be released to drive a current through an electrical circuit. Energy that an object possesses by virtue of its motion or position is called *mechanical energy.* The mechanical energy is termed as kinetic energy or potential energy: the former if the object is in motion or movement, and the latter due to its position (ie, it is stored energy). Examples of stored mechanical energy are compressed springs and a huge rock on a mountain cliff. *Nuclear energy* is the energy stored in the atom’s nucleus, the core of the atom, which is huge. This energy can be released by 2 main nuclear processes, fission and fusion. Nuclear energy is used to produce electricity. *Gravitational energy* is the potential energy stored in an object positioned above the Earth and is released (as kinetic) when the object falls. Climbing stairs and lifting objects is work done against gravitational force. This work done against the gravitational force goes into an important form of stored energy. Hydropower is a good example of gravitational energy, where gravity forces water down through a hydroelectric turbine to produce electricity. *Thermal energy* is the energy given by a hot (heated) substance using the process of conduction or convection or radiation. The best examples are heat from the sun’s radiation and geothermal energy. The internal energy of a thermodynamic system in equilibrium because of its temperature is an example. Thermal energy provided by concentrated solar radiation can be converted into electrical energy using a Stirling engine with a coupled generator.

Energy cannot be created or destroyed. Energy can be converted from one form to another, and can be ‘conserved.’ This is the most basic principle in physics, known as ‘conservation of energy’ or ‘first law of thermodynamics’ applicable in several physical and chemical processes.

All forms of energy cannot be stored. The forms that are difficult to store are converted into forms that are more suitable and economical and then stored. Some technologies offer short-term energy-storage, while others can sustain for a longer period.

1.2 The Power Problem

Electricity is generated at the central power generation sites such as coal and natural gas-fired power plants and nuclear plants. The (MW) high power current is transmitted to substations by power cables, where the power is step-down to medium voltage and distributed to all types of consumers, domestic to government to industrial and commercial consumers.

The conventional grid design is a considerably centralized set-up. A centralized power system is susceptible to costly line breakdowns; and once the power line is downed, there could be extensive power failures severely affecting all sectors including common customers. With continually increasing population and the people getting used to several types of electronic and other devices, the per capita electricity demand has increased. Consequently, the aging grid infrastructure is likely to become less stable and less reliable if the utilities and other operators do not upgrade the old infrastructure.

The most important problem of recent origin, the electric grid around the world facing, is the addition of power from renewable-energy sources. Sources such as coal, gas or nuclear plants provide a steady flow of energy to the grid, which enables the distribution of a fair quality of power to all sectors or regions. But, in the last few decades, renewable power sources like wind and solar, which are intermittent have been pumping electricity to the grid in large amounts. As a result, the power levels alter with time of the day or with changes in the day’s weather, creating several issues to the grid if directly pumped. The utility operators must stabilize the supply and demand constantly to keep up efficient flow of power and to meet the peak demand. As a result, it has become critical for most utility grids to utilize ‘energy-storage’ systems to store the excess energy generated by the renewables and discharge to the grid at the times of need.

The renewable solar and wind energy sources, though expensive to start with, are not only cheaper now but compete with fossil fuels without subsidy; hence, they are now preferred for electricity generation. Renewables already account for almost 30% of global electricity output, according to the International Energy Agency. The renewable costs have declined rapidly during the last decade, 2010–2019: solar PV by 82%, concentrated solar power (CSP) by 47%, onshore wind by 39% and offshore wind by 29%. The onshore wind and solar PV-generated power have both fallen below 5 US cents/kWh for the first time, and the fossil fuel thermal power generation is estimated to cost between 5 and 18 US cents/kWh according to IRENA [1a].

Following global trend, in India also, the cost of solar PV power generation has been falling and the recent 2GW solar auction in June 2020 by Solar Energy Corporation of India (SECI) had shown the renewable-energy tariff at Rs. 2.36/kWh, so far lowest in India, with zero indexation for 25 years [1b].

Each of these resources, however, has drawbacks. Though efficient and sustainable, they are intermittent because the sun shines in the day-time only and the wind resources are not ideal in many locations. These factors make the grid unstable as they try meeting demand. As a result, the grid needs frequency regulation. As the share of solar and wind energy increases with increased demand from the grid, extra flexibility is necessary for the entire system. This can be solved by a demand response and that is where the *energy-storage* helps. A large amount of solar or wind connected to the grid begin affecting voltage, and the energy-storage may help to balance the grid. For instance, in the U.S., the California state, which installed considerable solar power generation has zeroed in on storage as the key component of the smarter grid. The energy-storage, apart from providing frequency regulation on the grid and helping to stabilize intermittent solar and wind energy, can also provide other effects by moving to smarter grid. Energy storage not only accommodate this demand peaks but enables lesser investments in network expansion, thus avoiding high consumer costs. Storage, thus, offers one possible source of flexibility.

Challenges in modern electrical power systems: *A* range of ancillary services is already required by current power systems to guarantee a smooth and reliable operation. The supply-demand need to be synchronized to make sure the quality of power supply (e.g., constant voltage and frequency, energy control, peak demand, bi-directional power flow and so on), so that a smooth supply is sustained to all consumers and elude any damage to electrical applications. With the desired flexibility services available to power systems, the grid operators can respond to sudden changes in demand or to the loss of large volumes of supply (e.g. large stations tripping offline, loss of an interconnection, and so on). This flexibility also facilitates operators to expedite the reestablishment of system equilibrium [8; 2a].To address these issues, energy-storage systems, which have many remarkable value functions and benefits are utilized in different ways [e.g. 2b, c].

1.3 Energy Storage Benefits

Energy storage plays an important role in creating a more elastic and consistent grid system. Consider a situation when there is more supply than demand of power, say, during the night when power generating plants operate continuously. The excess electricity generated can be used to power/charge storage systems [8].

Energy storage allows de-coupling of energy production from consumption. Thus, it decreases the necessity for constant monitoring and prediction of consumer peak energy demands (Figure 1.1).

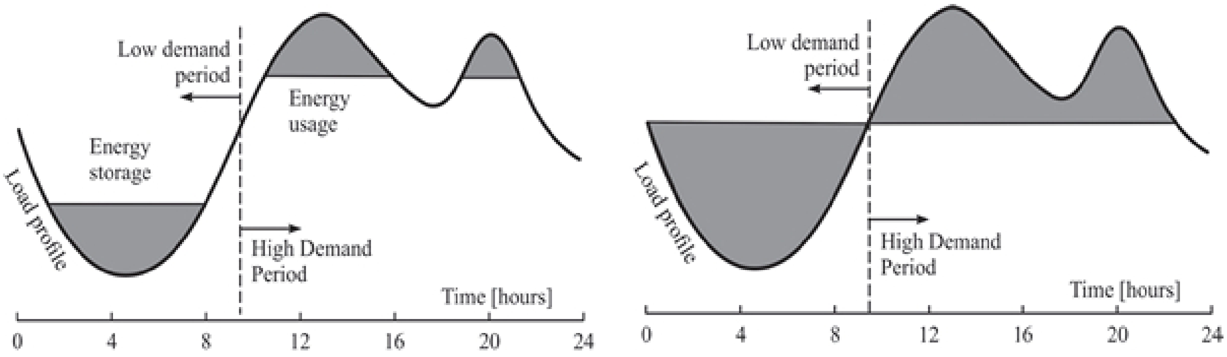

Figure 1.1:Energy demand (or load profile) over 24 hours of the day. (Left): figure shows a typical application of energy-storage; the energy-storage is load leveling, as shown in the figure on Right. (Source: [4])

Energy storage allows a decrease in energy production by the plant to meet average demands rather than peak demands. As a result, transmission lines and related equipment can be appropriately sized, thus saving financially.

Energy storage is particularly essential for the delocalized electricity production and to introduce fluctuating solar and wind energy sources. These intermittent sources make it more difficult to stabilize the power network, mainly due to a supply-demand imbalance. It is therefore convenient to generate the energy, convert it to suitable form, and store. The stored energy can then be drawn when required at a greater economic value or demand. More than ever, the storage of electrical energy has become a necessity with increased electricity generation from renewable-energy sources.

Long-duration storage can help avoid transmission and distribution improvements that involve huge capital cost. It would also add resilience and consistency by being available when the need is greatest, say, for peak demand conditions or supporting critical load during power outage.

Energy storage can provide back-up power during disruptions. The back-up idea can be extended to an entire building or even the grid in general. Energy storage offers flexibility for the grid to make sure continuous power supply to consumers, needed at any time and place. This flexibility is critical to both reliability and resilience. Energy storage supports achieving smart grids.

Energy storage is commonly used to smooth out the minor variations in energy output for small and large electricity generation sources.

Energy storage is also used in running electric vehicles (EVs) and trains, which further help reduce environmental effects.

Energy storage enables electricity to be saved for future days, when it is most needed. Storage makes the electric grid more efficient and capable, including the ability to reduce greenhouse gas emissions. It can increase the capacity factor of existing resources, and eliminate the need for constructing new peak power plants that contribute to pollution.

By introducing more flexibility into the grid, energy-storage can help integrate more solar, wind and distributed energy-resources (DERs).

As the energy supply mix becomes cleaner by including more low-carbon resources, energy-storage helps in developing such supply mix more easily and reliably.

Generally, energy-storage is a *technology* that allows for improved management of energy supply and demand. And a single unit of energy-storage set-up can provide multiple energy and power services.

In the coming years, as the grid progresses and adds new generation resources and consumption patterns, various combinations of capacity, power, reliability, and cost viability in storage technologies might prove useful [5].

Installations associated with grid and ancillary services are projected to grow by roughly 40 times over the decade, 2014 - 2024 (from 538.4 MW in 2014 to 20,800 MW in 2024) due to newly emerging factors such as renewables integration, energy demand, asset withdrawals, and technological innovation [6]. Energy storage among both commercial and residential users is expected to see much greater growth of about 70 times during the same period (from 172 MW in 2014 to 12,147 MW in 2024) due, in large part to the smart grid technology, *which optimizes power supply by using information on both supply and demand. The concept of smart grid is discussed in detail in later pages.* The range of storage technologies that fuel these exponential growth rates spans the states of energy and the principles of physics [6].

1.4 Energy Storage System Technology

Energy storage system technology is a method for converting energy from one form to a storable form and storing it in several media. The stored energy can be converted into electrical energy when needed [e.g. 2, 3]. The well-known battery is a simple device to store energy in the chemical form. The development of a technology to store electrical energy so that it can be available to meet demand whenever needed would represent a breakthrough in electricity distribution.

Energy storage technologies can be implemented on large- and small-scales allover the energy system. A few of these technologies are developed or near development, and most are still in the initial stages of progress.

Energy storage systems (ESS), however, have been expensive and non-viable economically on a commercial scale. However, continuous R&D in energy-storage technologies have led to gradual decreases in costs and improved technology applications, especially for Battery energy-storage systems.

Recently, high costs and low round trip efficiencies obstructed large-scale deployment of battery energy-storage systems. Nevertheless, increased use of lithium-ion batteries in consumer electronics and electric vehicles has led to a growth in worldwide production capacity, resulting in a significant cost decrease which is likely to continue over the next few years. Both the low cost and high efficiency of lithium-ion batteries have contributed to the surge of BESS deployments recently for both small-scale, behind-the-meter installations and large-scale, grid-level deployments [7].

1.5 Classification based on the Needs of the Grid[1]

It is the first grouping methodology differentiating the flexibility options based on their ability to balance the load and demand in the grid: (a) Electricity to electricity, (b) Electricity to non-electricity form, and (c) non-electricity form to electricity.

1.5.1 ‘Electricity to Electricity’ Storage Technologies

All storage systems, which ‘draw electrical power from the grid’ and ‘pump electrical power to the grid are referred to ‘electricity to electricity’ storage technologies.

As the grid is concerned, it is inappropriate how the energy is stored between these two functions. The main storage technologies under ‘electricity to electricity’ type storage systems, according to the *physical way* of storing the energy are the following. This sort of classification based on the ‘physical’ energy-storage is quite often used.

(i) *Electrical*: (a) Electrostatic fields, e.g. capacitors, super capacitors; and (b) Electrodynamic fields, e.g., superconducting coils

(ii) *Electrochemical:*

  (a) With *internal* energy-storage (here, power conversion and storage capacity are directly linked):

    - Redox-flow batteries [e.g., zinc-bromine with limited capacity due to material deposition in the stack during discharging]
    - Batteries (Pb-acid; Lithium-ion; Ni-Cd; Ni-Metal hydride; NaS & $NaNiCl_2$ batteries and several more)

  (b) With *external* energy-storage (here, power conversion and storage capacity are independent and not linked; sizing of power and energy capacity is separately possible):

- Redox-flow batteries (components: Stacks, redox pairs in liquid solution in tanks);
- Gas (components: electrolyzer for hydrogen production, optional: hydrogen to methane converter, gas storage system, fuel cells or gas turbines for generating power)

(iii) *Mechanical:* (a) Pumped Hydro Storage (PHS); (b) Compressed air energy-storage (CAES): diabatic; adiabatic; isothermal; isobar; and (c) Flywheels

(iv) *Thermal:* (a) Liquid air storage system, and (b) High-temperature thermal storage system

1.5.2 'Electricity to Non-electrical Energy' Storage [1]

This category has flexibility options allowing the consumption of electricity and converting it into another form and stored for other uses. The stored energy is not used for generating electricity. Electricity usage currently is about one-fourth to one-third of the total energy consumption. Transport and space heating are the major energy consuming sectors apart from the power sector.

To cut down carbon emissions, it is necessary to practice energy savings (energy efficiency measures) and to use clean energy in all sectors. Hence, the conversion of low-carbon electricity into other forms of energy is necessary.

'Electricity to nonelectrical form' technologies may include storage.

(i) Thermal energy technologies *with energy-storage*: (a) thermochemical heat storage; (b) cold storage; (c) sorption storage; (d) latent heat storage, and (e) sensible heat storage;

(ii) Electricity to gas (e.g., hydrogen, methane); (iii) electricity to chemicals (e.g., methanol);

(iii) Thermal energy technologies *without energy-storage*: (a) Thermal energy (e.g., electrical space heating); (b) Demand-side management (switching on electrical loads in industry or private houses); (c) Shutdown of renewable power generators (loss of energy)

1.5.3 ‘Non-electrical Energy form to Electricity’ Storage

This category includes power generation units using fuels, which can generate electricity on demand. But, capital costs are high and the operation is expensive if they are not regularly used.

(i) Conventional power plants utilizing fossil or nuclear fuels

(ii) Power plants using biogas or biomass

(iii) Demand-side management (shutdown of loads in industry or private houses, including shutdown of charging processes for electric vehicles)

(iv) Stored thermal energy for power generation (e.g. concentrated solar power plants)

There are other types of classification in practice, which are explained in the next chapter.

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CHAPTER 2

Overview of Energy Storage Technologies

2.1 Classification

Energy-storage systems (ESS) provide several technological approaches to manage power supply to create a more robust energy infrastructure as well as cost savings to both utilities and consumers.

ESS is categorized in terms of various criteria: suitable storage duration (short-, mid- or long-term, ranging from seconds to weeks), response time (the time it takes for a system to provide energy at its full rated power), scale (magnitude), or the form of stored energy. We have seen one based on the needs of the grid in the first chapter. One of the most widely used classification methods is based on the *form of energy stored* in the system [1a, 2a, 17] as shown in Fig. 2.1.

(a) *Mechanical energy-storage:* The systems in this category are ‘pumped hydroelectric storage (PHS)’, ‘compressed air energy-storage (CAES), and flywheel’;

(b) *Electrochemical energy-storage:* In this type, the systems are ‘conventional rechargeable batteries’, ‘high-temperature batteries’ and ‘flow batteries’;

(c) *Electrical/electromagnetic energy-storage*: The capacitors, super capacitors and superconducting magnetic energy-storage (SMES) systems belong to this type of energy-storage;

(d) *Chemical energy-storage:* The prominent in this type are ‘hydrogen storage with fuel cells

(e) *Thermal* energy-storage: This category comprises ‘sensible heat storage’ and ‘latent heat storage’;

(f) *Thermochemical storage:* ‘solar (fuel) hydrogen’ belongs to this type [2a].

If, at least 2 of these technologies are integrated, they are called ‘hybrid energy-storage’ required in certain situations.

Conventional and advanced batteries, and Capacitors and super-capacitors are together also referred to as ‘solid state batteries’ [3a].

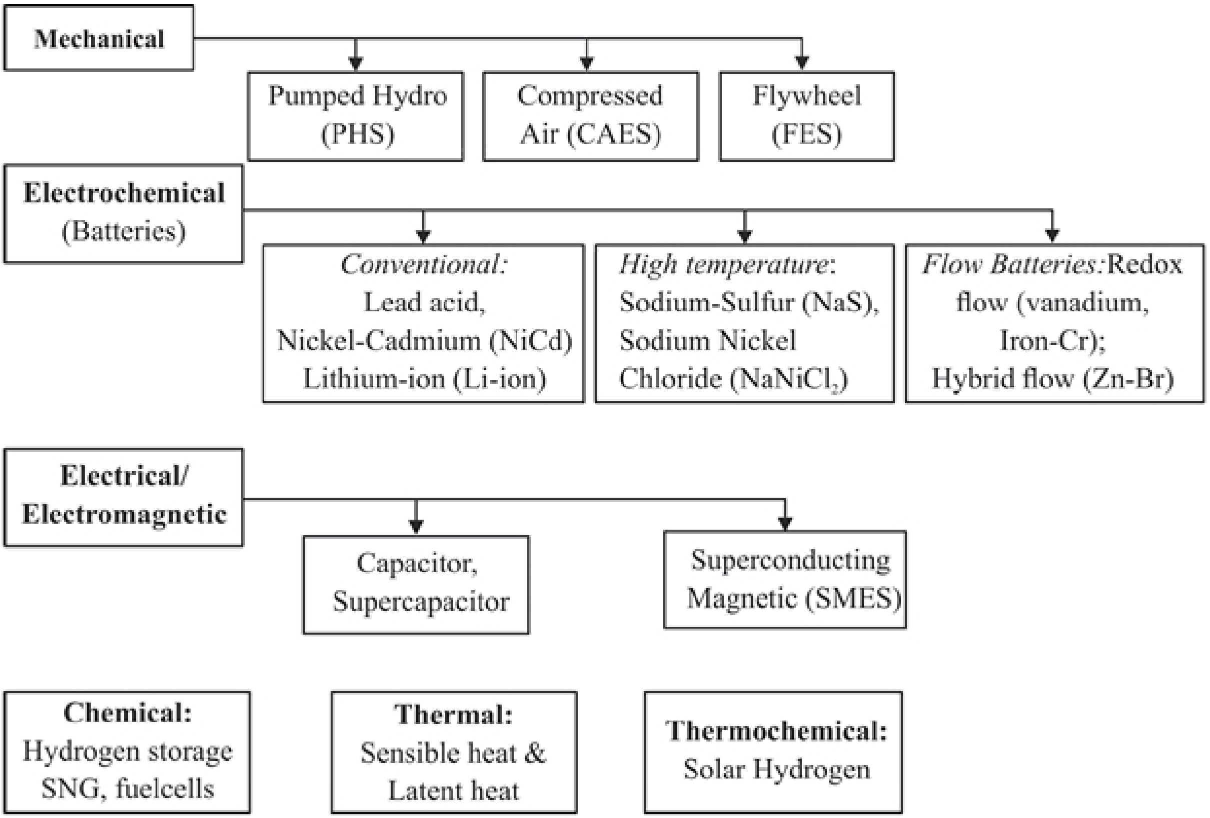


Figure 2.1: Classification of Energy Storage methods by the form of stored energy.

The ‘output’ and ‘energy density’ of the energy-storage devices describe their performance.

Figure 2.2 displays the classification of (a) applications according to the output, the period of usage, and the power requirement, and (b) energy-storage devices according to the period of usage, power generation, and system and/or network operation [2b].

The range of electricity storage technologies can be considered for providing an array of services to the electric grid and can be located around their power and energy relationship. This relationship is illustrated in Figure 2.3. The figure shows that the compressed air energy-storage (CAES) and pumped hydrostorage (PHS) have high discharge times, the order of tens of hours, and similarly high capacities achieving 1000 MW. However, several electrochemical batteries and mechanical flywheels have lower power and shorter discharge times, as clearly seen in the figure. However, many of the storage technologies shown here have expansive duration and power ratings. The contrasts in the figure are general and not rigid.

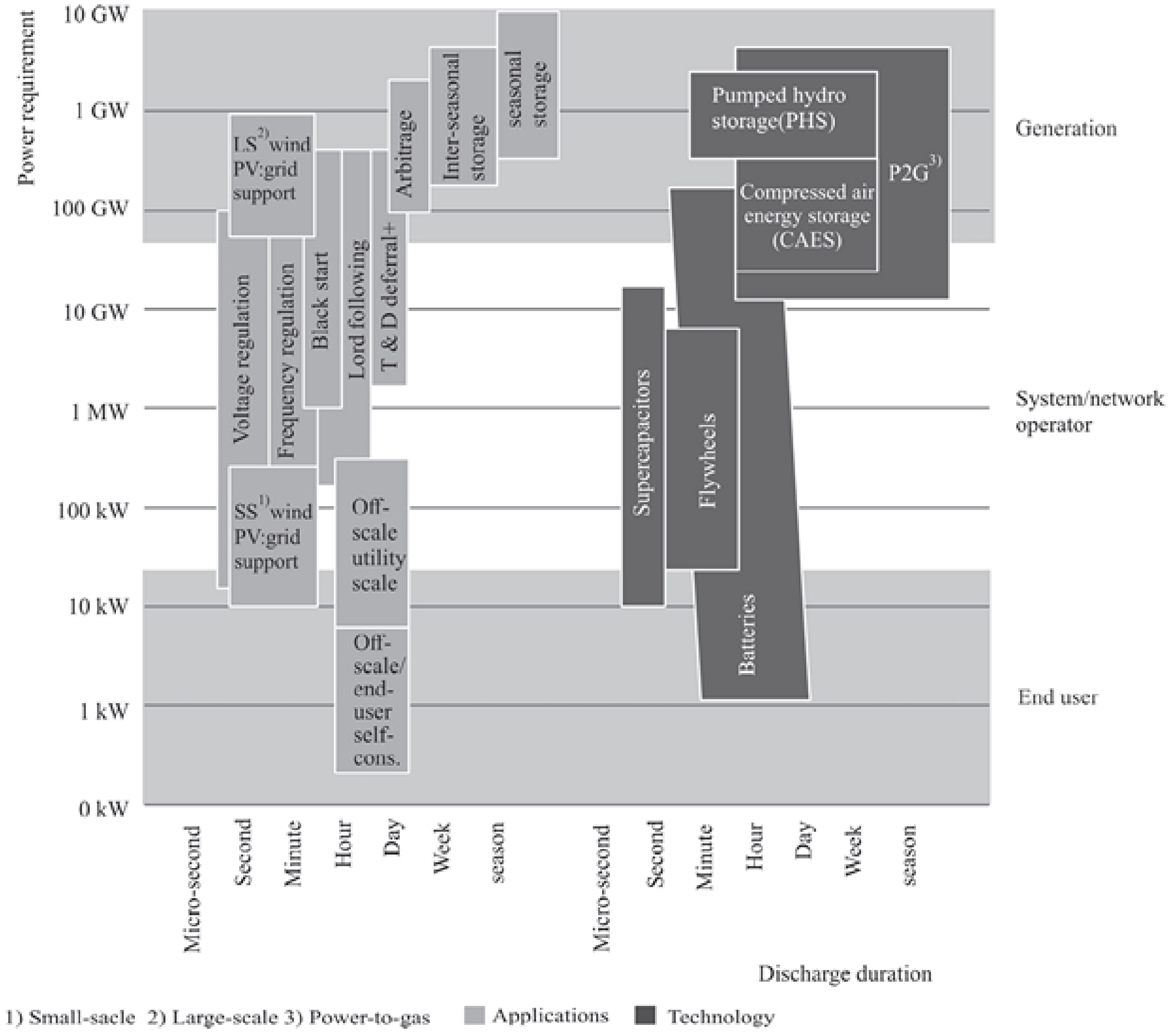


Figure 2.2 Various storage technologies for different purposes. (Source: [2b])

The high costs of the sites and construction of storage reservoirs and dams for pumped hydro (PHS) are a vital factor to be considered in choosing this technology. Hence, traditionally, the markets preferred the pumped hydro (PHS) be designed for higher storage times, more than 8 to 10 hours because it allows to pay off the costs. For example, Rocky Mountain Hydroelectric Plant built in the US, has over 10 hours of storage capacity and is rated at 1095 MW. Similarly, for the compressed air energy-storage

(CAES), large naturally occurring underground caves, or artificially generated caverns or large storage reservoirs on the ground constructed with steel assemblies must store the compressed air.

By comparison, flywheel and the array of batteries have low discharge duration times, ranging from a few seconds to about 6 hours, particularly sodium-sulfur battery systems and certain flow battery systems, not shown in the figure [2.3].

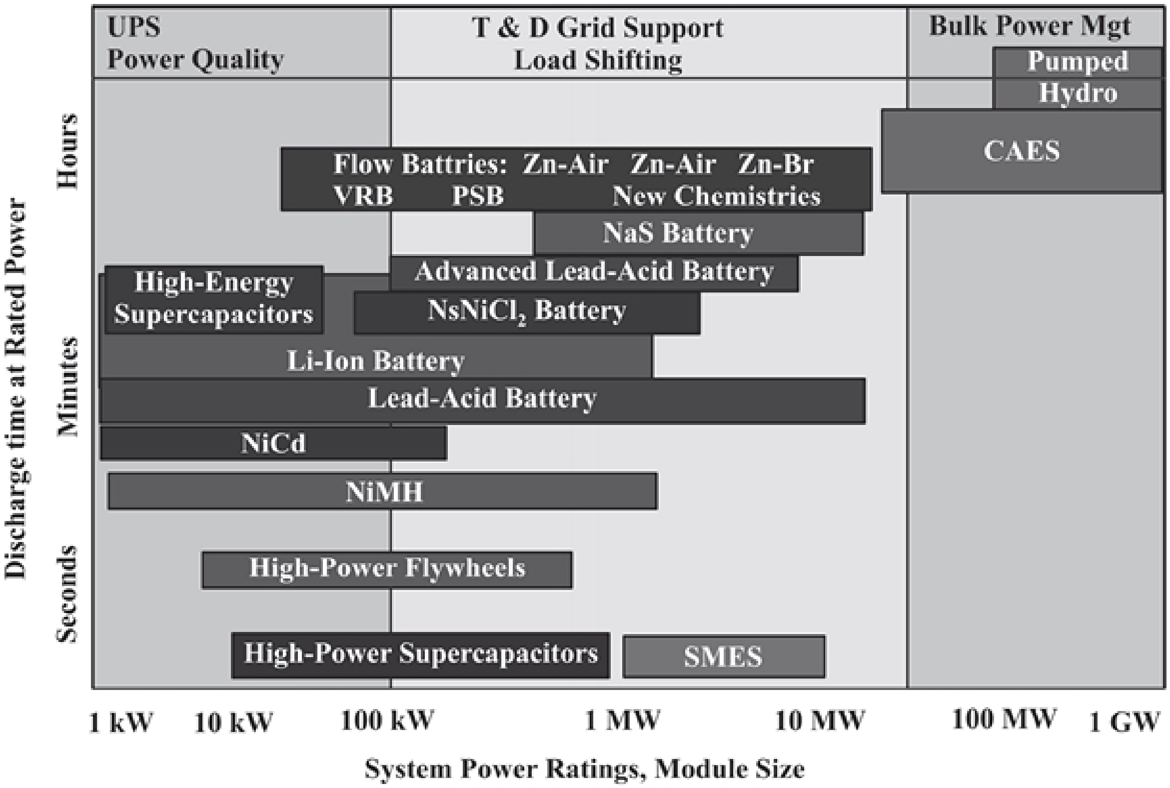


Figure 2.3: Positioning of Energy-storage technologies. (Source: [3b])

2.2 Overview

Extensive R&D have resulted in wide-ranging publications on Energy Storage systems due to their several value ideas in many areas - electricity generation, reliable grid supply, the transition to low carbon energy sources despite climate change mitigation and so on. Several laboratories worldwide are involved in this important field of study. These research articles are reviewed by several scientists from different perspectives: a comparative broad critical review of different energy-storage systems highlighting the overall need to store energy for improving power networks and maintaining load levels, their applications and deployment status [e.g. 1; 2a; 3b; 4a-c; 10; 11a-c;12a,b; 14; 15a-d; 16–18], exclusive appraisal of advanced materials for several ESS technologies [e.g. 14; 22; 35], and the strategies for development, particularly hydrogen storage, and lithium-ion battery materials [e.g. 31], and so on. There is a host of publications and what are mentioned here are representative.

As renewable energy sources started entering the energy sector for many of their merits, especially in reducing greenhouse gas emissions, reviews concentrating on ESS options for increased renewable applications have appeared; for example, wind power applications, and solar power applications [38–49].

Reviews of specific aspects are also published, like ESS in electric grid and the potential in distribution networks [e.g. 10], on battery energy-storage for grid uses [e.g. 24a-d, 25a, b], redox-flow batteries [e.g. 48 a, b; 49] and lithium-ion batteries [59–67], sodium-sulfur batteries [68–72], superconducting magnets [33a, b], fly wheel [49c, 33c-e], thermal storage [e.g.74a-d; 75a-c; 76a, b], developments, challenges in materials for electrochemical -relevant energy-storage [e.g. 27, 31, 32], and important applications [e.g. 49a-c; 76c; 77a-c; 78a-c]. With the electric vehicles increasingly entering the market, the related ESS technologies are the theme of several publications [e.g. 4a, 50–58].

Currently, there are 140 GW of large-scale electrical, grid-connected, energy-storage installed worldwide. Up to 99% of this is dominated by mechanical storage in the form of Pumped hydroelectric energy-storage (PHS) through its 270 sites globally, making it the largest type of energy-storage [1b, c; 5a; 6]. The remaining 1% consists mainly of a mixture of compressed air energy-storage (CAES), flywheel energy-storage (FES) and electrochemical energy-storage (EES) in the form of sodium-sulfur (Na/S) batteries and lithium-ion (Li-I) batteries [1b, c]. In terms of capacity, compressed air (440 MW), sodium-sulfur (316 MW), lead acid (35 MW), nickel cadmium (27 MW), flywheel (25 MW), lithium-ion (20 MW) and flow battery (3 MW) [5a; 7; 12a; 25b] are deployed. These numbers have been continuously changing with new installations and announcements of new projects.

Presently, the share of ‘battery energy-storage systems (BESS)’ in the total battery volumes in stationary applications is insignificant. However, this share is expected to grow fast to a capacity of 167 GW in 2030 [8; 9]. The total electricity storage capacity in terms of energy appears set for a 3fold increase by 2030, if countries keep on doubling the share of renewables in the global energy system [23a].

Storage system for a given application: In the selection of a storage system for a given application, 2 main approaches can be considered: (i) based on the storage system’s competence to deliver energy for a short or long time. Such an evaluation of storage systems (energy stored Vs power output, with delivery time limits) is shown in Figu re 2.4 [4]; and (ii) based on the efficiency and life cycle considerations of energy-storage systems as shown in Figure 2.5 [35]. This approach is appropriate (a) to evaluate the economics of the possible choices, and (b) for a particular application with limited available energy source requiring a high number of cycles.

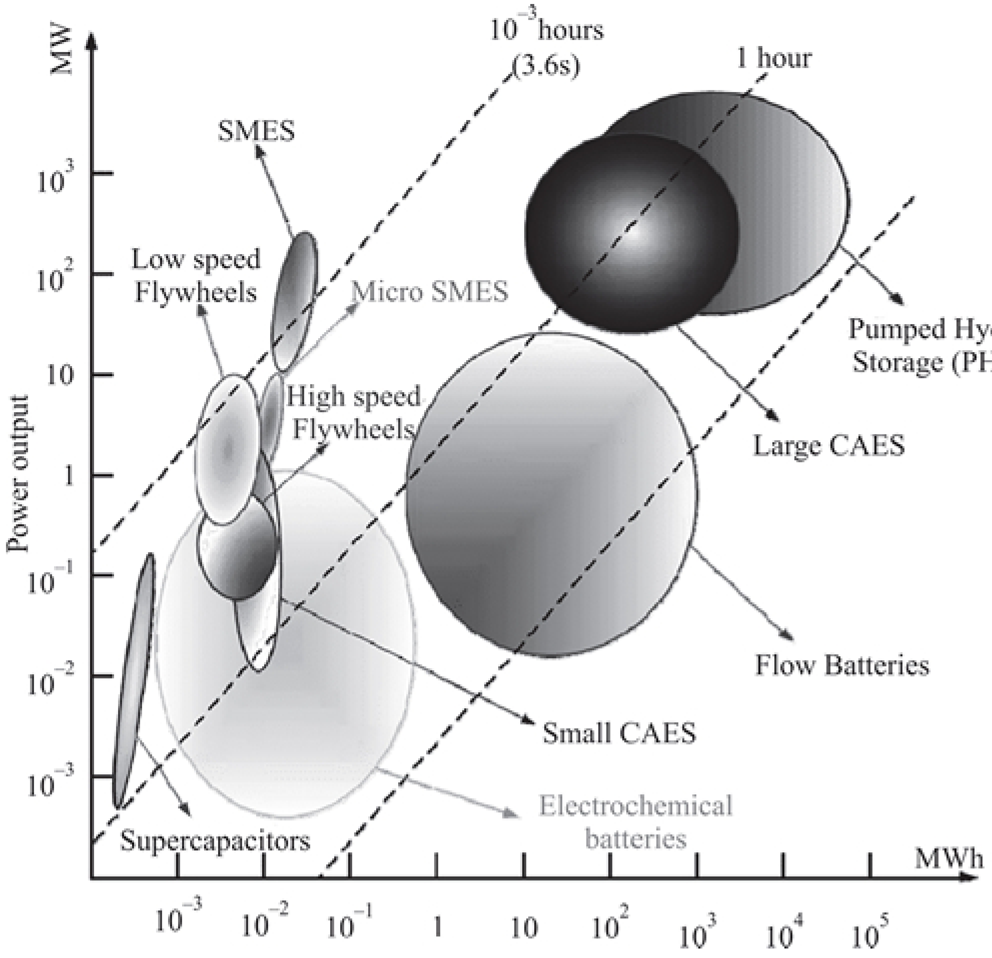


Figure 2.4: Energy-storage systems with different storage capacity. (Source: [4])

Using Figure 2.3, where power ratings of different storage systems are shown, a proper energy-storage system may be selected, in association with a comparison graph of efficiency vs life cycle shown in Figure 2.5 [35].

Flywheel and battery energy-storage are highly efficient and compressed air energy-storage and pumped hydrostorage is reasonably efficient and can be used in applications that require *high energy* with reasonable efficiency and significant life cycle.

For long-term storage and seasonal balancing of renewable energy sources, only chemical secondary energy carriers can be used currently. These are 'hydrogen' and carbon-based fuels such as 'substitute natural gas (SNG)'. Hydrogen and SNG can be generated from different renewable energy sources. Figure 2.6 shows the extraction volumes of underground gas storage together with conversion to electricity reaching 10 GW range, with cycle times extending from days to months. Therefore, they signify the only feasible choice for seasonal balancing of renewable energy of TWh range-capacity and converting it back into electricity when required. Additionally, chemical secondary energy carriers can be used in other application areas, notably in transport.

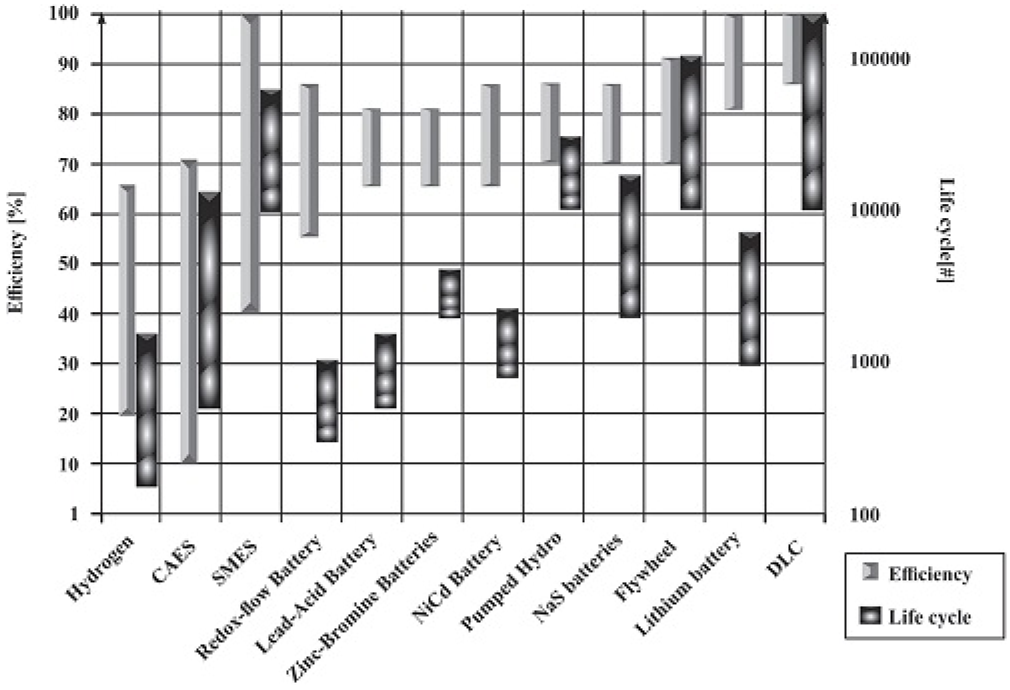


Figure 2.5: Energy-storage comparison, based on efficiency and life cycle. Source: courtesy [35].

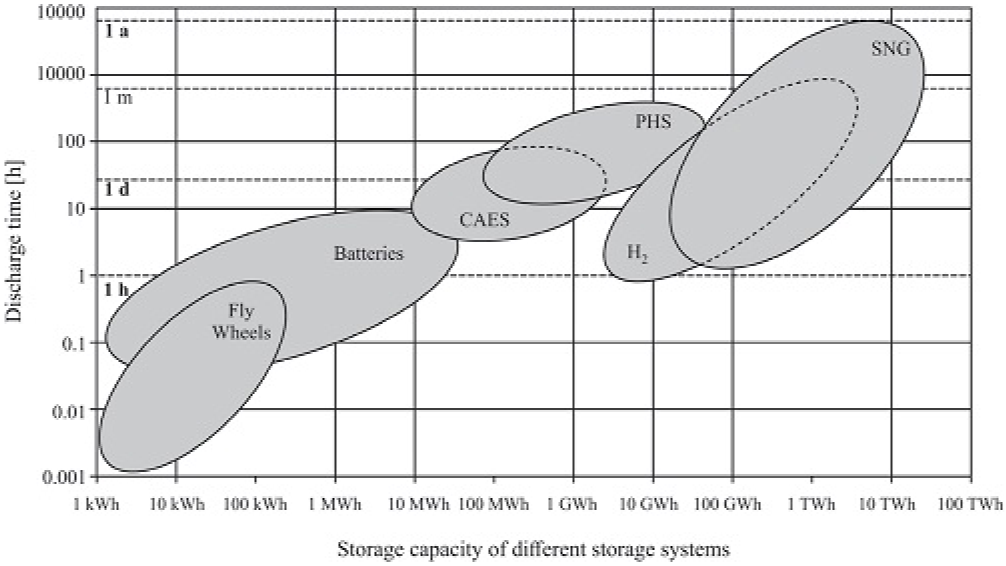
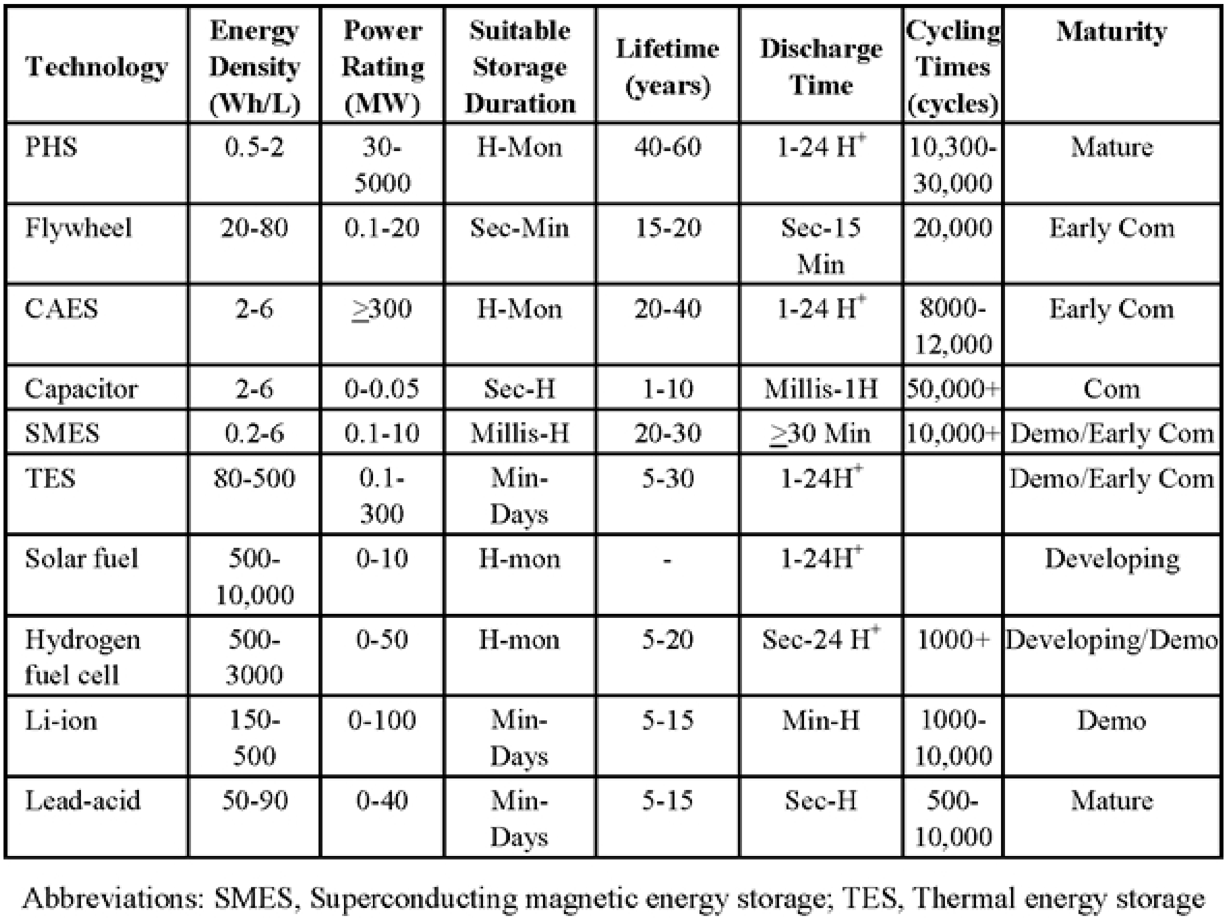


Figure 2.6: Discharge time and storage capacity of different ESS. (Source: [73])

The energy-storage technologies and their technical characteristics are presented in Table 2.1, collected from the references cited.

More discussion on the maturity and current status of these energy-storage systems is presented in chapter 8.

Table 2.1: Technical characteristics of Energy-storage technologies (Source: [20–23, 31, 34])



Technology	Energy Density (Wh/L)	Power Rating (MW)	Suitable Storage Duration	Lifetime (years)	Discharge Time	Cycling Times (cycles)	Maturity
PHS	0.5-2	30-5000	H-Mon	40-60	1-24 H^{+}	10,300-30,000	Mature
Flywheel	20-80	0.1-20	Sec-Min	15-20	Sec-15 Min	20,000	Early Com
CAES	2-6	≥300	H-Mon	20-40	1-24 H^{+}	8000-12,000	Early Com
Capacitor	2-6	0-0.05	Sec-H	1-10	Millis-1H	50,000+	Com
SMES	0.2-6	0.1-10	Millis-H	20-30	≥30 Min	10,000+	Demo/Early Com
TES	80-500	0.1-300	Min-Days	5-30	1-24H^{+}		Demo/Early Com
Solar fuel	500-10,000	0-10	H-mon	-	1-24H^{+}		Developing
Hydrogen fuel cell	500-3000	0-50	H-mon	5-20	Sec-24 H^{+}	1000+	Developing/Demo
Li-ion	150-500	0-100	Min-Days	5-15	Min-H	1000-10,000	Demo
Lead-acid	50-90	0-40	Min-Days	5-15	Sec-H	500-10,000	Mature

Abbreviations: SMES, Superconducting magnetic energy storage; TES, Thermal energy storage

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CHAPTER 3

Mechanical Energy Storage

Mechanical energy-storage is currently the most used energy-storage type in the world. Mechanical energy is either stored as potential energy or as kinetic energy. These types of energy storages are mainly used to increase the reliability of the electrical grid. They can also be used for large term energy-storage and hence is the leading technology now in the world [1b].

3.1 Pumped Hydroelectric Storage (PHS)

Pumped hydroelectric energy-storage is a large, mature, and commercial utility-scale technology currently used at many locations around the world. PHS utilizes gravity as well as the power of water, a highly intense renewable energy source. In pumped-hydro, water from a reservoir is pumped during off-peak times (when power is cheaper) to another reservoir at a higher altitude. When the demand for electricity arises, water is made to flow from the high altitude reservoir into the low reservoir through a hydroelectric turbine to generate electricity (Figure 3.1A).

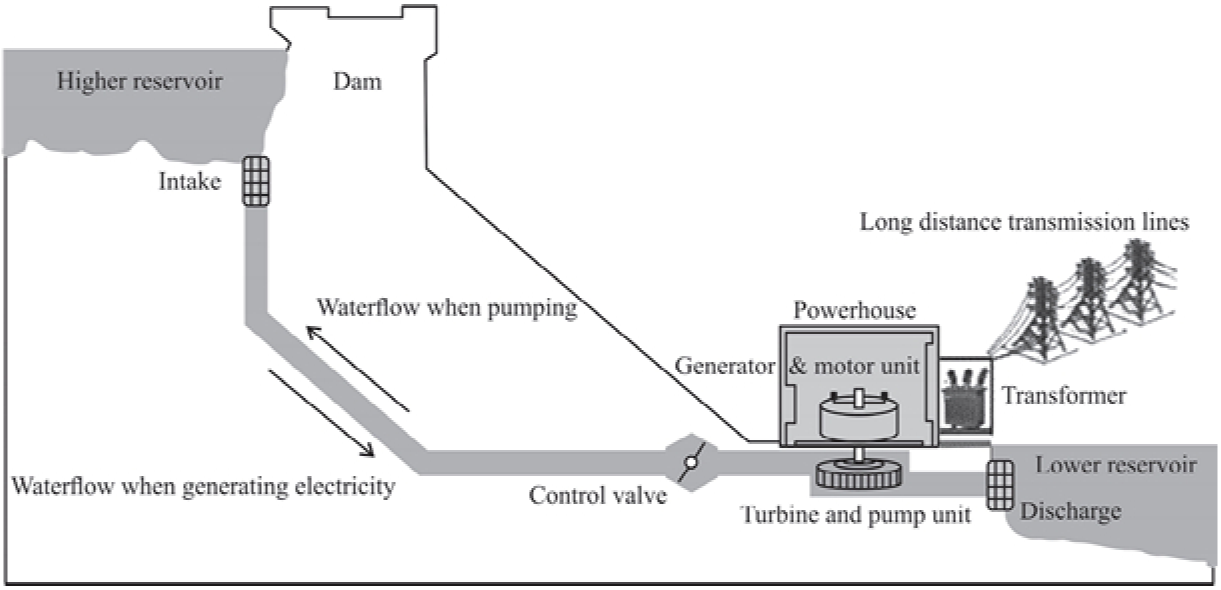


Figure 3.1A: Schematic of A Pumped Hydroelectric Storage Plant (PHS). (Source: [4])

The amount of stored energy is proportional to the height difference between the reservoirs and the mass of water stored, E = mgh [1]. This principle has the highest capacity of the energy-storage technologies assessed since its size is limited only by the size of the available upper reservoir. The rated power of PHS plants depends on the water pressure and flow rate through the turbines and rated power of the pump/turbine and generator/motor units.

Energy and Efficiency: The Bernoulli's theorem can be used to evaluate the energy of the PHS system. The Bernoulli equation "assumes a constant discharge rate, and states that the energy head at any point in the system is equal to any point downstream in the system plus intervening losses such as pipe friction losses, entrance losses, pump/turbine losses, " [2]. It is stated mathematically as follows:

$$(P_1/\gamma) + z_1 + (v_1^2/2g) = (P_2/\gamma) + z_2 + (v_2^2/2g) + h_L$$

Here, z = elevation head relative to a set datum for the system

v = velocity (m/s)

P = pressure (N/m^2)

h_L = total head losses between points 1 and 2 (m)

γ = specific weight (N/m^3)

The cycle *efficiency* of a pumped-storage hydropower project is the ratio between the energy output and energy input. Pumped-storage hydropower projects typically recapture about 70 to 80% of energy inputs [3]. It means, if 10 MWh of energy is invested, around 7 to 8 MWh is recaptured. The losses in the system are mostly the losses in the pump/turbine units and waterways.

Power (P), which is the utilized energy with respect to time, is the product of the specific weight of water, the discharge, and the change in hydraulic head ΔH [2].

$$P = \gamma \, Q \, \Delta H$$

Here

γ = specific weight of the fluid = ρg, where ρ is the density of water (kg/m^3) and ‘g’ is acceleration due to gravity (m/s^2),

Q = flow rate (m^3/s),

ΔH = change in head (m).

Using the Bernoulli equation, ΔH is calculated as follows [2]:

$$\Delta H = H_2 - H_1 = (P_2/\gamma) + z_2 + (v_2^2/2g) - (P_1/\gamma) + z_1 + (v_1^2/2g)$$

During the pumping operation, ΔH refers to energy applied to pump the water to the upper reservoir; and during turbine operation, ΔH is energy (weight) applied by fluid (water).

The power required to pump the water to upper reservoir is

$$P_{Pumping} = \gamma\ Q\ \Delta H/\eta = (\rho g)\ Q\ \Delta H/\eta$$

The power generated during turbine operation is calculated as the following:

$$P_{generating} = \eta\ \gamma\ Q\ \Delta H = \eta\ (\rho g)\ Q\ \Delta H$$

The total volume of water multiplied by the altitude difference between the reservoirs is proportional to the energy stored. It means, assuming an altitude change of 1,000 feet, a reservoir capacity of 10,000 acre-feet, and an efficiency generation of 90%, the system can provide a power of around 9,000 MWh to the grid [2].

Not only water, but other materials can also be raised to a higher altitude. Currently, by creating gravitational systems, gravel is moved up the side of a hill and use the same supporting principle. Here the gravel when released to generate power, its weight drives a mechanical system that pushes a turbine and generates electricity [5].

Pumped-storage stations differ from traditional hydroelectric stations. However, properly designed PHS plants are highly efficient and can prove advantageous in terms of balancing load within the overall power system.

Moreover, these facilities can be economical because of variations in peak and off-peak power price, and their potential in delivering critical ancillary grid services [5].

The technical data related to PHS are given in Table 3–1 along with other mechanical energy-storage systems. PHS has relatively low energy cost, high capacity, and long lifetime. Other features of PHS are short start-up time and flexibility in the production of electricity. Due to these characteristics, pumped hydroelectric are currently the main method for storing.

Installations: It is a mature technology and several tens of plants are operating worldwide. A recent analysis from 'Renewables 2018' by IEA [6] shows that by the end of 2017, the global cumulative installed capacity had reached 153 GW, out of which over 80% was installed in Europe, China, Japan and the U.S. Also, the capacity was estimated to increase almost one-fifth in the next 5 years because of the need for system flexibility to integrate power from intermittent renewable energy sources in China, Asia-Pacific countries, Europe, the Middle East and North Africa region [6].

A reservoir with an average head of 200 meters, diameter of one kilometer and a depth-of 25 meters would hold sufficient water to generate 10,000 MWh power.

Fig. 3.1B shows a machine-made upper reservoir of Tennessee Valley Authority's Raccoon Mountain Pumped Hydro Plant. The facility has been operational since 1979 and it can generate 1620 MW for up to 22 hours [7].

Projects may be sized up to 4000 MW and have long lives, order of 50 years [1, 8, 9, 10], low operating and maintenance costs and fast response times (within seconds). These features enable them to be used equally well in voltage and frequency regulation, spinning reserve, and non-spinning reserves markets, as well as energy arbitrage, reactive power, black-start capability and system capacity.

Seventeen variable-speed pump machines are currently in operation (totaling 3,569 MW) and 19 are under construction (totaling 4,558 MW). All of these units are located in Europe, China, India, or Japan.

Figure 3.1B: Man-made Upper Reservoir of Tennessee Valley Authority's Raccoon Mountain PH Plant: the facility can generate 1620 MW for up to 22 hours [7].

Figure 3.1C: Dinorwig pumped hydro asset is the fastest power generation unit in Wales, UK, with the ability to deliver 1.7GW in 16 seconds.

Pumped-storage are used to balance the load on a system, facilitating large thermal or nuclear plants to operate at peak efficiencies. A typical pumped-storage project is designed to have a hydraulic reservoir storage for 6 to 20 hours of operation. By designing a plant of increased capacity, size and number of units, PHS generation can be used during periods of highest power demand, when the power has the greatest value [5].

The turbine-generator can respond fast to frequency changes in the generating mode like the general hydroelectric generators, and increase the overall balancing and stability of the grid. And in both turbine and pump modes, generator excitation can be altered to contribute to reactive power load and voltage stabilization. In the absence of generating or pump modes, it can be operated in synchronous condenser mode or to provide spinning reserve, offering the capacity to quickly pick up load or balance excess generation. Pumped-storage at grid-scale can provide this type of a load-balancing advantage for time scales, ranging from seconds to hours, with the digitally controlled turbine governing systems and huge water reservoirs for bulk energy-storage [5].

Progress: Because of its technological and market position, PHS is significantly more advanced than other energy-storage technologies such as battery storage and flywheel [11]. In the long-term, apart from flexible production units and market conditions, the economic sustainability of PHS depends on the parallel development of economic storage technologies such as batteries, distributed production and smart-grids [12].

As the PHS technology progressed, some PHS plants using flooded mine shafts, underground caves and oceans as reservoirs were designed, and some are in operation in Japan and the U.S.

In Japan, Okinawa Yanbaru station, the world’s first pumped-storage facility to use sea-water with a maximum output of 30 MW was started in 1999 but dismantled in 2016 as the power demand in the area did not increase as expected.

In the U.S., 300 MW sea-water-based PHS plant in Hawaii, the Summit project in Ohio, and the Mount Hope project in New Jersey are in operation [13–15].

The wind or solar power generation coupled with PHS is being developed. This could help the integration of intermittent wind or solar in isolated or distributed networks [16a, 17]. For instance, the Ikaria Island power station in Greece, which is presently in the construction stage plans to integrate 3 900 kW capacity wind farms with a PHS facility. This will be one of the first wind-hydro-pumped-storage hybrid stations in the world [16a]. In Germany, the Gaildorf wind and hydroproject near Münster comprise 13.6 MWe of wind turbines and 16 MWe of hydrocapacity from pumped-storage. The details are discussed in reference [16b].

Other developments happening in PHS are building the hydroelectric unit with higher speed and larger capacity compared to the current technological status, installing centralized monitoring and using intelligent control systems [13, 18, 19]. The focus of R&D specifically includes the variable-speed pump-turbine, enabling increased flexibility, efficiency and reliability at the expense of initial cost [20–22].

Single- and Variable-speed pump-turbines: Despite significant advantages with variable-speed pump-turbines compared to fixed-speed pump-turbines, they involve extra equipment costs as well as the lack of recognition for the additional services provided by the equipment improvements (i.e., ancillary service market development). The power expended in the pumping mode can be varied with variable-speed machines over a range of outputs. The speed modification also allows the turbine to operate at highest efficiency over most of its operating time. The variable-speed technology is well suited to integrate the power from the intermittent renewables. As a result, these machines are being considered by many of the proposed new pumped-storage projects.

In a conventional, single-speed pump-turbine, under use since the 1960s, the magnetic field of the stator and that of the rotor rotate with the same speed and they are coupled. In the variable-speed pump-turbine, the magnetic fields are decoupled. Presently, a double-fed induction motor-generator is a typical design for variable-speed machines.

A major advantage of variable-speed pump-storage technology is regulating the grid frequency to provide grid stability and frequency regulation. This new additional service facility is needed to accommodate variable renewables, particularly for the wind at night.

The new installations of variable-speed PHS must be evaluated on an individual basis; market conditions must be appropriate for the technology to be economically viable, and its advantages must be evaluated with respect to a complex control scheme and greater unnecessary loads. For generating intermittent renewable energy, however, variable-speed technology can offer an extensive operating range and quicker start and reversal times than conventional PHS. It is an attractive alternative [5].

Prospects: While pumped-hydro is a highly useful, cost effective, and proven technology, its further expansion has been limited by its geographical requirements, environmental concerns, and high capital costs. For example, additional costs may occur due to the corrosive operational environment of sea-water pumped-hydro [22, 23]. However, reduced environmental impact, a larger energy capacity and reduced costs are expected from the proposed plans: (a) the hydraulic lifting of masses during charging, (b) discharge by releasing them gravitationally to sink, and (c) forcing water to pass through a turbine. Although these proposals appear technically and economically feasible, a demonstration plant would enable their market acceptability and contribution in a sustainable development pathway [24, 25].

3.2 Compressed-Air Energy Storage (CAES)

CAES is a power-to-power energy-storage option, which converts electricity to mechanical energy and stores it in the subsurface [26]. This technology uses electricity in the off-peak times to compress air at high pressures and store it in large underground caverns or depleted wells. The compressed air can also be stored aboveground using high-pressure pipes and/or vessels. Both processes are the same, the latter is small and above the ground.

When electricity is needed, the compressed air can be released and directed through turbines to generate power. Large amounts of heat released during compression if not stored but allowed to dissipate, the compressed air must be reheated in combustors before expansion in the turbine. This whole process is called ‘diabatic CAES’ and the round-trip efficiencies are generally less than 50%. Diabatic CAES technology is well established and highly reliable with moderate efficiency. The benefit of CAES is large in capacity, while the main disadvantage is geographic restriction of sites.

If the heat of compression is recovered and utilized to reheat the compressed air before directing through a turbine, there is no need to burn extra natural gas to reheat the compressed air in combustors. The efficiency then can reach up to 70%. This process where the heat of compression is recovered and used to reheat the air before expansion in the turbine is called ‘adiabatic’ CAES method. This is still under development and so far unproven.

CAES system configuration: CAES is a commercial technology available like PHS, capable of providing huge energy-storage (above 100 MW with single unit). Figure 3–2 shows a schematic of a CAES system [24]. Its 5 major components are (a) a motor/generator that engages alternately with the air compressors or turbines using clutches; (b) an air compressor of two (or more) stages attached to intercoolers and after-coolers, to accomplish compression at low-cost and to lessen the moisture quantity in the compressed air; (c) a turbine arrangement holding both high- and low-pressure turbines; (d) a cavern* for storing compressed air, and (e) other equipment and auxiliaries such as fuel storage and heat exchanger units [1]. {*cavern can be underground rock caverns produced by mining rock formations, salt caverns formed by solution- or dry-mining of salt growths, and porous media reservoirs made by water-bearing aquifers or depleted gas or oil wells, e.g. sandstone and fissured lime [1]}.

The working of CAES is similar to that of conventional gas turbine generation. It decouples the compression and expansion cycles of a conventional gas turbine and stores the energy as pliable potential energy of compressed air. During low power demand, energy is stored as highly compressed air in an air tight space, typically at 4.0–8.0 MPa. To generate power on demand, compressed air is drawn from the storage, heated and directed through a high-pressure turbine, which captures part of the energy in the compressed air. The air is then mixed with fuel and combusted with the exhaust expanded through the LP turbine. Both the high and low-pressure turbines are coupled to a generator to produce electricity. A recuperator placed before exhaust possibly captures the waste heat in the exhaust before being released into the atmosphere.

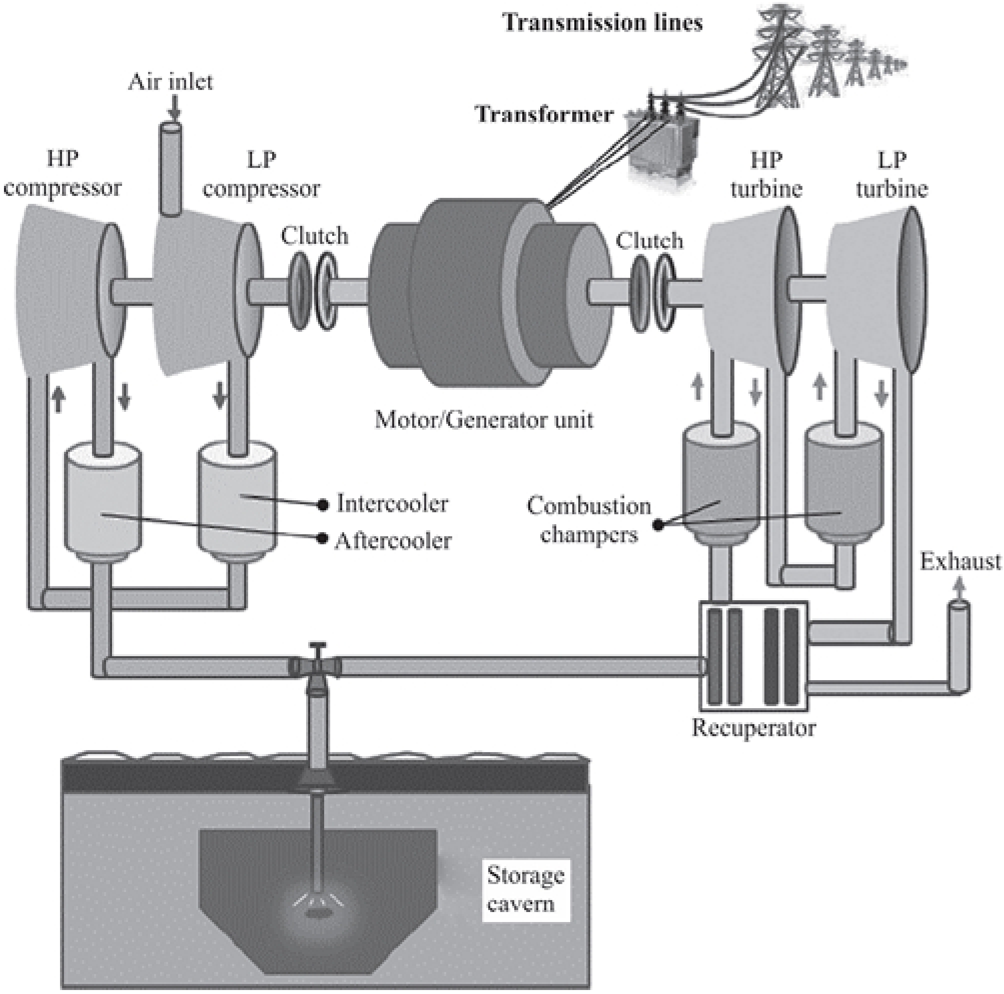


Figure 3.2: Schematic of CAES. (Source: [24])

So, by applying work to the compressor, energy can be stored in the form of high-pressure compressed air in a high-pressure reservoir (cavern) in a CAES system. The energy-storage process here follows the thermodynamic law of energy conversion for air. The stored energy depends on the volume, pressure, temperature of the reservoir, and how its energy conversion occurs, isothermal or adiabatic or isentropic.

The amount of work in a polytropic process is expressed as [27, 28]:

$$W = (n/n - 1)\ P_1\ V_1\ [(P_2 /P_1)\ (n\text{-}1/n) - 1]$$

Here ‘n’ represents the polytropic exponent (C_p /C_v), P_1 and P_2 are atmospheric and the tank pressure in a compression cycle, respectively. A polytropic process is a thermodynamic process that obeys the relation, pV^n = constant, where p is the pressure, V is the volume, and n is polytropic index. The polytropic process equation can describe multiple expansion and compression processes, which include heat transfer. The equation above indicates that the stored energy in a fixed volume is a direct function of the pressure ratio, and by increasing the pressure ratio both the stored energy and energy density, which is a critical parameter of a CAES system can be improved. The energy-storage density (*w*) can be expressed by the following equation:

$$w(\text{in kWh/m}^3) = [n\ N\ P_f\ /\ 3600\ (n\text{-}1)]\ [1\text{-}\ (P_a/\ P_f)^{(n-1)/n\ N}]$$

Here N is the number of stages, P_a is the atmospheric pressure and P_f is the final pressure.

Increasing the maximum pressure in the tank is essential to increase the energy density of the storage system. Further, the increase in the number of stages can improve the energy density characteristics of the storage system. But, after especially 5 stages, the influence of increasing the number of stages on the energy density will be decreased in all pressure ratios. This observation should be taken into account to decide the optimum number of stages and its working pressure in designing a CAES system [28].

CAES systems are designed to cycle daily and to operate efficiently even during partial load settings. Due to the daily cycle, CAES units swiftly fluctuate from generation to compression modes.

The capacity of CAES system range from 50 to 300 MW, which is much higher than other storage technologies except for PHS. The storage period, about one year, is also longer because of trivial losses, than other storage methods except for the PHS. The efficiency of the CAES is about 70–89%, and the capital costs depend on the underground storage conditions and vastly vary [1].

Storage Options: It is clear by now that huge storages are required because of the low storage density. Artificially built salt caverns in deep salt formations are desirable locations. Salt caverns also have several encouraging characteristics such as high flexibility, absence of pressure losses within the storage, and not reacting with the oxygen in the air and the salt host rock.

It is also possible to use natural aquifers. But, studies must know whether oxygen reacts with the rock and with any microbes in the aquifer rock formation because such reactions could encourage oxygen depletion or obstruct the pore spaces in the reservoir.

Another storage option for compressed air is ‘depleted natural gas fields’; further to the oxygen depletion and blocking concerns cited above, the mixing of residual hydrocarbons with compressed air need to be deliberated (Energy Storage Association).

Other geological structures, for example, porous formations are used in underground CAES technology. The different options are shown schematically in Figure 3.3 [29].

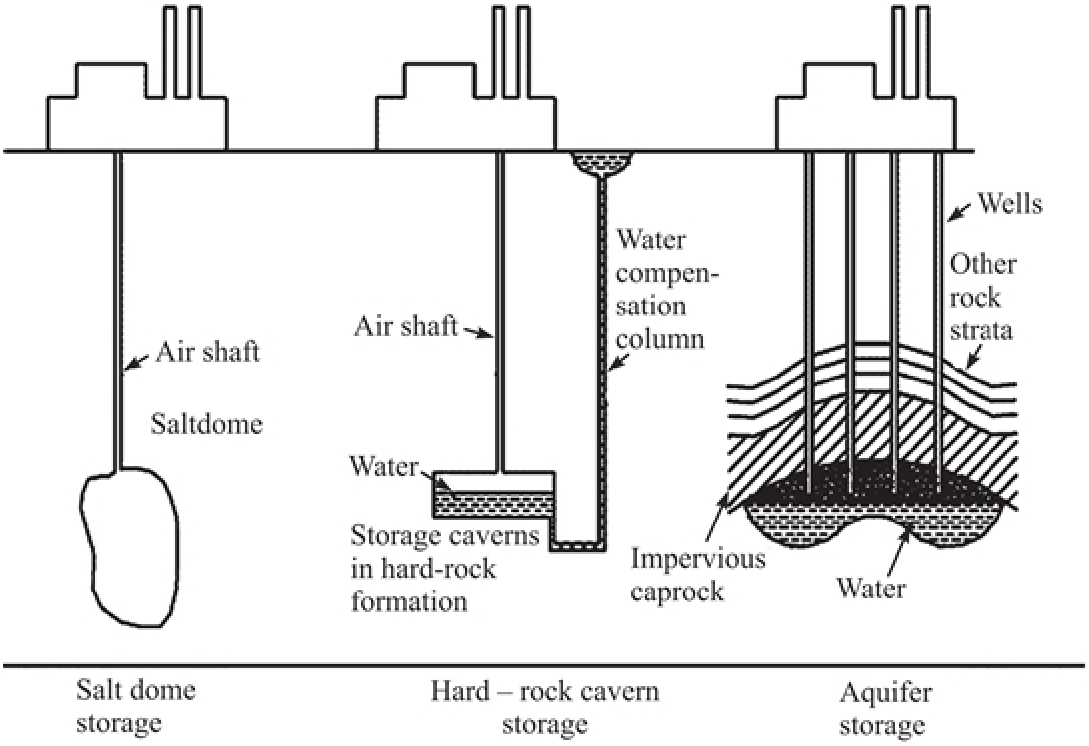


Figure 3.3: Different types of compressed air reservoirs (Source: [29])

The salt caverns can be mined at different depths within a suitable salt dome [30], which allows for a range of operation pressures, and porous formations have a much wider geological availability compared to rock salt suitable for caverns and may provide much larger storage capacities [31]. Besides, the storage volume of a porous formation can be stretched by injecting additional air to expand into a larger air reservoir, or extra wells can be drilled. But, with the increase in the cavern size, the risk of instability increases [35], leading to the construction of additional caverns if at all storage size is increased.

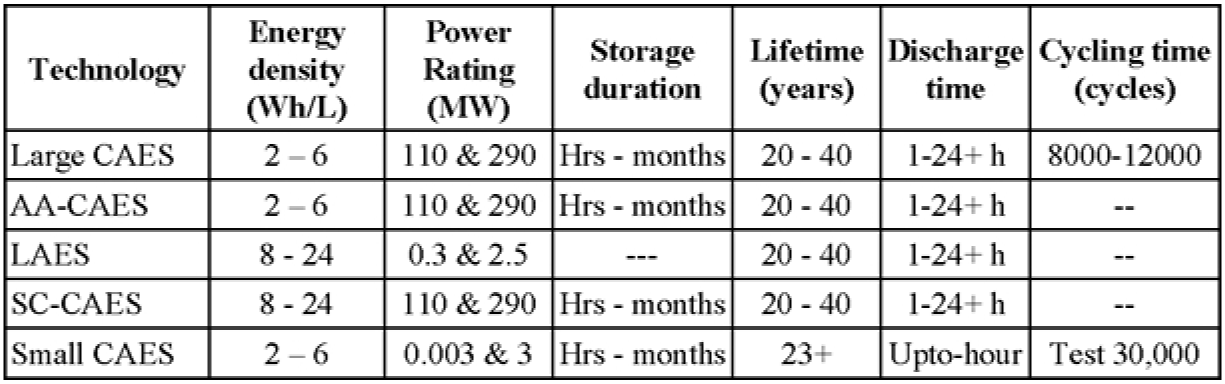
Benefits: CAES is valuable to the utilities with significant load varying during the daily cycle and substantial fluctuating costs with the level of generation or time of day.

CAES systems can respond to load changes to provide load following because they are intended to sustain frequent start-up/shut-down cycles. CAES systems have a relatively long storage period, high efficiency, and low capital costs.

3.2.1 Development of various CAES Technologies

Achieving energy sustainability and reducing greenhouse gas emissions are perhaps the drivers behind the development of CAES technology. This technology development, therefore, aims not to use fossil fuels in CAES systems. Table 3.1 presents the various CAES technologies currently under development. These variations are expected to improve the thermal process and integrate CAES with other subsystems to improve their efficiency [32].

Table 3.1: Comparison of various CAES technologies (Source: [33])



Technology	Energy density (Wh/L)	Power Rating (MW)	Storage duration	Lifetime (years)	Discharge time	Cycling time (cycles)
Large CAES	2 – 6	110 & 290	Hrs - months	20 - 40	1-24+ h	8000-12000
AA-CAES	2 – 6	110 & 290	Hrs - months	20 - 40	1-24+ h	--
LAES	8 - 24	0.3 & 2.5	---	20 - 40	1-24+ h	--
SC-CAES	8 - 24	110 & 290	Hrs - months	20 - 40	1-24+ h	--
Small CAES	2 – 6	0.003 & 3	Hrs - months	23+	Upto-hour	Test 30,000

3.2.1.1 Advanced Adiabatic CAES

Advanced Adiabatic CAES (AA-CAES) is an evolution of traditional CAES and based on integration with a thermal-energy-storage subsystem, which has no fuel combustion involved in the expansion mode [4, 35, 36]. The typical working principle of AA-CAES is schematically shown in Fig. 3.4 [33]. Here, the heat generated during compression is removed and stored separately, and used again during the expansion before running through the turbine. This method may increase the round-trip efficiency of the process considerably. One of the conceivable ways is to heat-exchange the compressed air with oil and store in an insulated container placed above the ground. If the compression is performed using multiple compressors in several stages, with heat-exchange occurring between each compression stage, the oil could be retained at a safe temperature for storage (e.g., below 600K).Hartmann et al. recently analyzed different adiabatic CAES plant configurations [37].

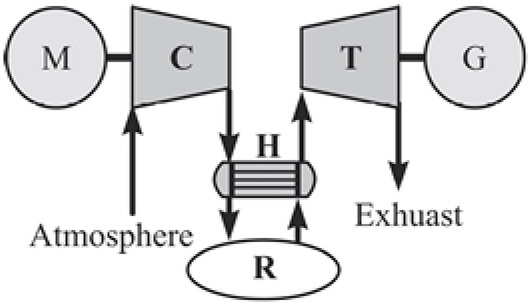


Figure 3.4: Schematic representation of the working principle of AA-CAES; C -compressor; T - turbine, G - generator, M - motor, H - heat storage, R - reservoir. (Source: [47c])

One variation of this scheme is to use wind turbines that are suitably designed to compress air directly utilizing mechanical linkage, which in theory improves efficiency and decreases the costs. Another variation is to employ expandable underwater bags to store the compressed air, which can be an alternative to storing in a cavern. This will allow air to be stored and recovered at constant pressure, resulting in improved operating characteristics.

Several AA-CAES schemes have been suggested which are all at the early stages of design.

However, the world’s first AA-CAES demonstration plant - ADELE -at Saxony-Anhalt in Germany (shown in Figure 3.5) was designed to have a storage capacity of 360 MWh and an electric output of 90 MW. The efficiency expected to achieve is approximately 70% [34]. Because wind energy powers the compression mode, the ADELE plant emits no carbon dioxide in a full-cycle. A global group headed by the German energy company RWE worked the development of the necessary components and the heat storage. A pilot plant was recently installed and experimental and numerical results from this world's first advanced adiabatic compressed air energy-storage (AA-CAES) pilot-scale plant were presented [38]. TWO experimental operations were performed with the pilot plant. The first experiment was performed using a sensible TES [38]. The second one was performed using a combined sensible/latent TES and was described by Becattini et al. [39].The pilot plant was put up in a tunnel of 4.9m diameter, which was not in use, in which 2 concrete plugs bordered a 120 m long unlined cavern. A 12 MWh_{th} capacity sensible thermal-energy-storage (TES) was placed inside the cavern. The plant was then operated with charging/discharging cycles of various durations, varying air temperatures of up to 550 °C, and reaching a maximum cavern gauge pressure of 7 bar. Due to the leaks that were traced mainly to the concrete plugs, higher pressures could not be reached. The measurements agreed well with the results of simulations using a coupled model of the TES and cavern. Cycle energy efficiencies of the TES were in the range, 76–90%. The round-trip efficiency of the pilot plant was estimated using the measured TES performance and assessed performances of the other components, which turned out to be 63–74%. These values compare very well with the usually cited figures of 60–75% for prospective AA-CAES plants.

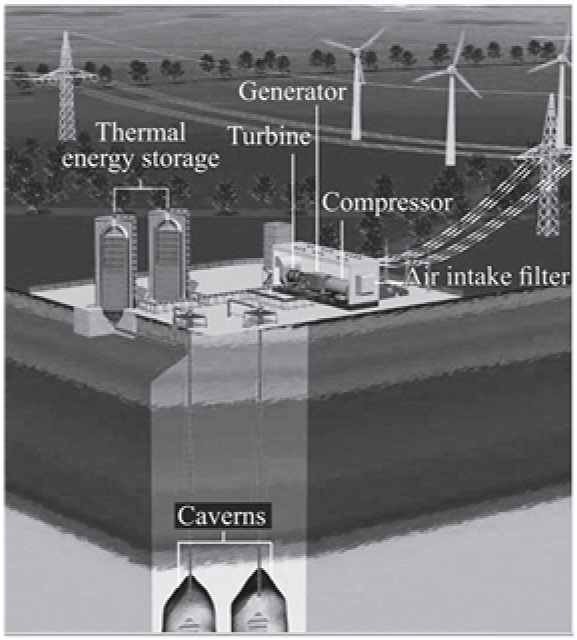


Figure 3.5: The world’s first AA-CAES demonstration plant - ADELE - at Saxony-Anhalt in Germany. (Source: RWE Power Brochure)

3.2.1.2 Isothermal CAES

Isothermal compressed air energy-storage (CAES) is a developing technology trying to eliminate some of the limitations of conventional CAES. In the conventional system, turbo-machinery is used to compress air to around 70 bar before storage, which would heat up air to around 900°K, making it impossible to process, if the intercooling is unavailable. Also, it is excessively costly to store the gas. As an alternative, the air is submitted to successive stages of compression and heat-exchange to reach a lower final temperature close to ambient. In AA- CAES the heat recovered from compression phase is stored separately and fed back into the compressed air during expansion, thereby eliminating the re-heating with natural gas.

For efficient performance of CAES, the pressure-volume (P-V) curve during compression and expansion needs to be controlled. If the P-V curve closely resembles an isotherm, the energy wasted in the process is less. Isothermal CAES technologies attempt to achieve true isothermal compression and expansion in situ, rather than employing numerous stages to compress, cool, heat and expand the air, to reach the improved round-trip efficiency at reduced capital costs. More so, the necessity to store the heat of compression by a secondary medium like oil is eliminated.

Isothermal CAES involves continuous removal of heat from the air during compression cycle and similarly continuous addition of heat during expansion stage to maintain the typical isothermal process. This is a technologically exciting task because transferring heat at a high rate with a minimal temperature difference requires a massive surface area of contact.

Currently, there are no commercial Isothermal CAES plants in operation. But, several promising solutions have been offered based on reciprocating machinery. A solution is to spray fine droplets of water inside the piston during compression. The high surface area of the water droplets combined with the high heat capacity of water relative to air allows the temperature to stay approximately constant within the piston; the water is removed and the cycle gets repeated. During the expansion also, similar process occurs.

The developers of Isothermal CAES systems anticipate a possible round-trip efficiency of 70–80%. In Isothermal CAES, the gas/air compresses and expands near-isothermally over several pressures, from atmospheric pressure to a maximum of about 2,500 psig. This wide operating pressure range combined with an isothermal expansion, reduces storage costs by almost 7 times compared to classical CAES in containers [Energy Storage Association].

The LightSail Energy Ltd. in the US is developing the facilities by using reversible reciprocating piston machines [34]. The Luminant and Shell-Wind Energy proposed in 2007 to evaluate the potential of incorporating CAES with the wind farm, and after a delay of 6 years, the project started with a set target of 317 MW of CAES [20, 34].

The first study of CAES using porous formation was conducted in Pittsfield, Illinois, USA, and showed that the concept was feasible at this site [40, 41].

In Japan, a 2 MW system, meant for field-test, used a concrete-lined tunnel in an abandoned mine [35, 42]. A test facility designed and prepared by Electric Power Research Institute and others utilized a hard-rock cavern with water compensation [43]. Italy’s Enel operated a porous rock based CAES facility of 25 MW capacity in Sesta, but the testing could not proceed because of a disturbed geothermal issue [35].

Succar and Williams [35] in their review discussed the technical and economic prospects of large-scale CAES storage sites integrated with wind farms and evaluated the potential to utilize a porous formation as a CAES storage reservoir. The Iowa Stored Energy Park project planned to use porous sandstone aquifers to build an underground reservoir for constructing a 270 MW CAES plant; but, the field-test results indicated that the existing geological structure could not obtain a fast enough flow for large-scale CAES. Hence, the project was abandoned [44].

3.2.1.3 Liquid-air or Cryogenic energy-storage (LAES or CES)

It is a new concept. It is similar to CAES facility, except that with LAES the heat lost to the atmosphere during air compression is stored in a phase change material. The principle is to use excess electricity to cool ambient air to -196°C where it becomes a liquid and store it in an insulated low-pressure container. When more electricity is needed on the grid, the stored liquid is converted back to the gaseous state by exposing it to ambient temperature and expanding in the turbine to produce electricity.

LAES comprises 3 main processes: (a) *Charging the system:* this is an air-liquefied unit that pulls air from the surrounding environment using electricity, then cleaning the air, and finally cooling the air to temperatures where the air liquefies. This is simply air liquefaction and large change in volume occurs, 700 liters of ambient air reduce to 1 liter of liquid-air; (b) *Energy storage:* The liquid-air is stored in a properly insulated tank or vessel at low-pressure, the tank/vessel functions as the energy-storage. This is a standard equipment used worldwide for many years for the storage of liquid nitrogen, liquid oxygen and LNG in vast quantities. The tanks that are used in the industry can hold up to GWh of stored energy; (c) *Power recovery*: When electricity is required, liquidair is released from the tanks and pumped to high-pressure. Then, the air is vaporized and superheated to normal (ambient) temperature, when a high-pressure gas is produced, which is then used to drive a turbine to generate power [44a].

Air Liquefaction is normally done in 2 processes: Linde-Hampson process and Claude process. In the Linde-Hampson process, air drawn from the atmosphere is compressed to a high-pressure of about 200 atm in a compressor. Then, the compressed air is run through a counter-flow heat exchanger, where its temperature is reduced. At high-pressure and low cryogenic temperature, this compressed air undergoes Joule-Thompson expansion through an insulated valve to a low-pressure. The resulting liquid-air is collected in storage tanks, and the cold gas is returned through a heat exchanger to cool the incoming air to the compressor. In the second process, Claude process, liquefaction is accomplished in stages, thereby reducing the pressure ratio requirements. Pressures of about 40 atm are required in the Claude process. The storage of liquid nitrogen also presents substantial challenge [44b-d].

LAES offers long storage duration and promising round-trip efficiency of up to 80% [24, 7]. Compressed-air storage requires a massive underground cavern but LAES requires a few low-pressure tanks. Moreover, LAES is one of the few storage technologies, which can offer large-scale storage without geographical restrictions [44e]. LAES can offer large-scale energy-storage, the order of hundreds of MW output. LAES can utilize industrial waste heat or cold from such applications as thermal plants, steel mills and LNG terminals to help improve system efficiency. The existing components with established long-life times of more than 30 years and performance, and affordable operation and maintenance costs are used by LAES.

Demonstration project: A first-of-its-kind 5MW/15MWh demonstration system was built in UK in 2015 by Highview Power Co., in Bury and connected to Pillsworth Landfill gas site. This LAES plant uses heat from the connected gas plant in the re-heating process. A propriety system is also developed to store the ‘waste cold’ that is created when air is discharged. This waste cold is used to increase the efficiency of the process that converts air into liquid [45a]. The storage tanks in this system are nearly 12 and a half meters tall, 3 meters in diameter, and 13 mm thick and weigh 16,230 kg when empty (Fig. 3.6a).

Figure 3.6A: Photo of the demonstration project. Credit: Highview Power [Source: Austen Adams, A Look at LAES Technology, Renewable Energy World, **19(4),** March 30, 2016]

The theoretical performance and detailed cycle analysis of the project was conducted using a classical analysis method by Morgan et al. [45b, c]. It was found that the thermal storage played a core role in improving the system efficiency on predicted lines. The links between the component characteristics and system performance were explained by Sciacovelli, et al. [45d]. Another objective of the project was to develop innovative designs such as thermal storage, with the prospective of removing any hitches for the next generation of LAES [33].

LAES is more environment-friendly compared to batteries as it involves no unusual metals and harmful chemicals. As the cold from liquid cryogen evaporation is not wasted, co-recovery of energy is possible in this technology. This ‘cold’ can be used again in numerous applications; for example, sustainable refrigeration industry, food processing, and so on. Warehouses that are cooled for storing chilled and frozen foods use large amounts of electrical energy. By reimburse some of the cold from the cryogen evaporation at temperatures around -120°C, reduce power consumption and could greatly enhance the cost-effectiveness of the whole operations.

3.2.1.4 Supercritical Compressed-Air Energy Storage (SC-CAES)

The SC-CAES system is a kind of new CAES system that incorporates the benefits in both AA-CAES and LAES systems such as high energy density, high thermal efficiency, and environmental safety.

Figure 3.6b shows the schematic of a typical SC-CAES system. The air is drawn from the atmosphere and is compressed to reach its supercritical state (at p > 37.9 bar, and temp. > 132° k). This is now stored in tanks after the compression heat is collected by a heat exchanger. When electricity is needed, the stored liquid-air is pumped to supercritical pressure and heated by heat exchangers; then it converts to its gas state, which can drive a turbine to generate power [46].

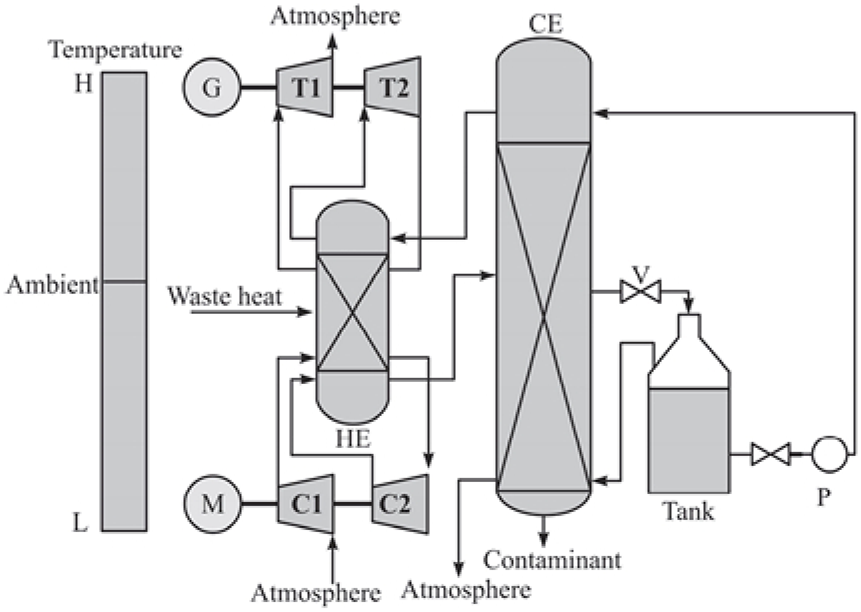


Figure 3.6B: Diagram of SC-CAES system (V—Throttle valve, C—Compressor, T—Turbine, G—Generator, M—Motor, P—Pump, HE—Heat storage & Exchanger, CE—Cold storage & Exchanger) (Source: [46])

The liquefaction can be done in 2 ways: using (a) throttle liquefaction valve or (b) liquefied expander as described in [46]. The throttle valve can use the cooled air to obtain liquid-air in the throttling process in which the temperature is reduced. Because it is a kind of typical irreversible process, it not only consumes large amounts of energy but also causes cavitation. Instead, the liquid expander can replace the throttle valve to achieve the throttling depressurization effect [46].

Guo et al (2013) built a thermodynamic model [46] to understand and improve the SC-CAES system, the studies by Guo et al (2016) found that the energy densities (3.2581–3.4602 x 10^5 KJ/m^3) could be 18 times higher than that of conventional CAES, and the round-trip efficiency could reach 67.41% [47].

A SC-CAES demonstration project of capacity, 1.5 MW, was designed in 2013 by Macao energy (Bijie) Industrial

Park Development Co. Ltd and Institute of Engineering Thermo-physics of the Chinese Academy of Sciences. All the performance indexes have reached or even exceeded the designed goals. By 2017, the 1.5 MW SC-CAES system had run for more than 3000 h successfully and the system efficiency were about 55% [33].

Applications: The application prospects of large-scale CAES in supporting the power system operation are widely recognized. For the supply side, the transmission and distribution network operators can use CAES for bulk energy reorganizing for maintaining load balance. CAES can regulate the electricity usage by consumers taken from the suppliers based on the energy price to reduce their energy bill. Other prospective applications of this technology are peak shaving and demand side management, frequency and voltage control, higher utilization and greater integration of renewable generation, provision of black-start services in a power shut-down condition, ancillary services including spinning reserve and MVAR generation, application to smart-grids, and so on [48, 33,44a].

As mentioned, the advantage of CAES to work with intermittent renewable energy, especially in smoothing the output power in the case of wind power, has driven the R&D groups and industrial units to evince interest in this technology [34, 49, 50].

The major obstacle for large-scale implementation of CAES technology lies in identifying appropriate geographical locations because the investment costs mostly depend on this aspect. Another concern is its relatively low round-trip efficiency compared to PHS and battery technologies.

Nevertheless, small-scale CAES has recently witnessed rapid development. These can replace the battery for applications such as UPS and back-up power units.

UK based Flowbattery (earlier known as Pnu Power) has developed compressed air battery systems to the stage of successful commercialization [4]. Air cylinders filled with compressed air were used in these systems to drive a combined structure of a scroll-expander and a generator to produce electric power [34, 51]. The guideline study for the efficient design and sizing of small-scale CAES pressure vessels aiming to lower the costs were reported [52]. Also, feasibility studies on the direct mechanical coupling of a wind turbine and a scroll-expander with smallscale CAES that include the on-site tests were undertaken at the University of Warwick [51, 53, 54].

Facilities in operation: Currently 2 commercial CAES facilities are operating: one in Huntorf in Bremen, Germany, and another one in McIntosh, Alabama, USA, both using subsurface salt caverns as reservoir for the compressed air [55].The 290 MW Huntorf Plant is the world’s first compressed air storage power station, operating since 1978 (Fig. 3.7). The plant arranges for peak shaving, spinning reserves and VAR support. About 11 million cft of air at pressures up to 1000 psi is stored in 2 underground salt caverns at a depth-of 2100–2600 feet below the surface. Twelve hours of off-peak power are needed to fully recharge, and then the unit supplies 290 MW, the total output, for up to 4 hours. This system operates a conventional cycle and earlier to expansion, burns natural gas. The efficiency of the plant is around 42%.

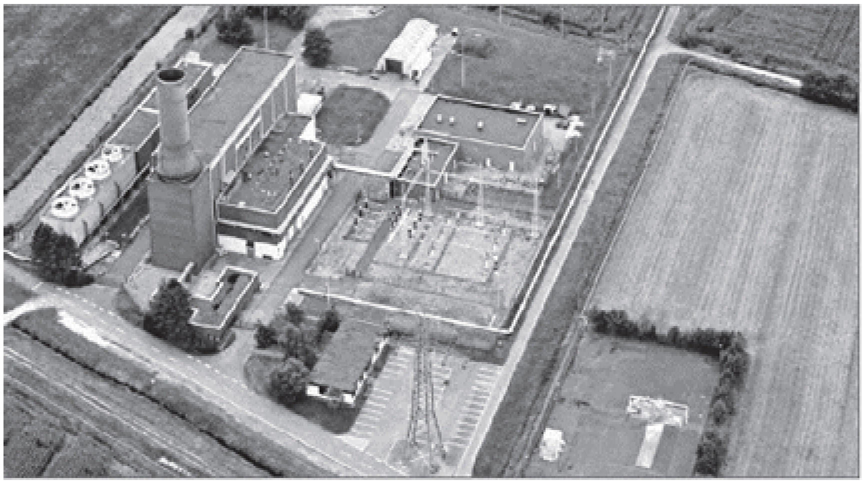


Figure 3.7: 290 MW Huntorf CAES plant. E.ON. [© SBC Energy Institute]

Alabama’s Electric Cooperative runs the 110 MW capacity McIntosh project from the time of installation in 1991. 19 million cft is stored at pressures up to 1080 psi in a salt cavern 2500 feet deep, and can deliver a full power output for a period of 26 hours. By recovering waste heat, this system reduces 25% of fuel consumption compared to the Huntorf System, and the efficiency of the plant is about 54%. This unit is utilized to store off-peak power, to generate peak power and to provide spinning reserve [1, 4, 32, 33, 36, 55, 56a]. The common feature of these 2 plants is the use of natural gas, a fossil fuel, which is undesirable when clean energies are strongly advocated in place of fossils. Another disadvantage is low energy conversion efficiency [33].

Wang et al. [33] outlines several CAES projects under development in China, Canada (Toronto), the US (Texas and islands of Washington-Oregon), and North Ireland (Antrim). The economic and technical feasibility of the integrated wind/CAES system has been studied by Fertig and Apt, using wind power data, hourly electricity prices, and monthly natural gas prices [56b].

3.2.1.5 Integrated and Hybrid CAES Systems

Minutillo et al., 2015 have studied the behavior and performance of a photovoltaic power system integrated with an adiabatic CAES unit. This unit supplies electric power to a small-scale off-grid BTS (base transceiver station) from solar PV resource. A thermal-energy-storage unit to recover the heat of compression to reheat before expansion without using extra fossil fuels is arranged to make sure the adiabatic condition of CAES. The power system is so designed such that a cooling effect from the cold air (3 °C) at the exit of the turbine is attained that can be useful for the cooling of the telecom equipment. The main aim of the study was to evaluate the ideal plant operating factors, with reference to the average storage pressure and air tank’s operating pressure range, allowing for plant installation in 3 different climatic zones. The study was conducted by presenting parameters such as storage efficiency, energy supply factor and cooling supply factor. The results obtained established that by selecting the lowest average storage pressure and the highest operating pressure range of the air tank, the best performance can be achieved. [57a]

Sun et al. 2015[57b] have conducted a feasibility study of a new hybrid system, ‘a wind turbine integrated with CAES. A mechanical transmission mechanism is applied for power integration within the hybrid system. A scroll-expander has served as an ‘air-machinery energy converter’. This can transmit extra driving power unspecified from the compressed air storage to the turbine shaft for smoothing the wind power fluctuation. A mathematical model originates for the total process and the control strategy examined for resultant cooperative operations. A prototype test rig for implementing the suggested mechanism is fabricated for the proof of the concept. Using both the simulated and experimental studies, the energy conversion efficiency is evaluated using the system submitted to different operation settings and modes. It is demonstrated that the suggested ‘hybrid wind turbine integrated into CAES’ is technically viable.

More publications on this important subject of integration of renewables with CAES are found in the literature [e.g. 58. 59a, b, 60].

3.3 Flywheel Energy Storage (FES)

Flywheel Energy Storage (FES) is based on an old concept, working of an outdated pottery wheel. Yet, it is a relatively new concept used to overcome the limitations of new energy sources, solar PV or wind, which is intermittent and do not produce electricity all through the day. FES can be regarded as a mechanical battery where it does not create electricity but simply converts and stores energy as kinetic energy until it is required for use. As electricity can be created from the spinning flywheel within seconds, it makes an ideal choice to help regulate supply in the electrical grid.

A flywheel-energy-storage system consists of a heavy rotor, the flywheel, and an electric motor that also serves as a generator. The motor spins the flywheel up to its operating speed and so stores kinetic energy in the form of angular momentum. Conversely, the flywheel can transfer rotational energy to the motor/generator, which then transforms it back into electrical energy. Such a system can generate several megawatts of power for a short time. Advanced high-strength materials are used to make the rotor. Flywheels get charged by drawing power from the electric grid to increase rotational speed, and get discharged by generating electricity as the rotation of the wheel slowed (Fig. 3.8).

In designing a flywheel, a few important aspects need to be examined, the most important are ‘bearings’. The bearings hold the shaft that links the device to the motor-generator in position, and assist the rotation. The mechanical bearings, however carefully they are made, create friction which results in a loss of energy as the flywheel spins. Mechanical bearings are being replaced now by magnetic bearings, which considerably reduce or eliminate the frictional losses [61–63].

Compared with other methods for storing electricity, FES systems have long lifetimes (lasting decades with little or no maintenance [64]; fullcycle lifetimes ranging higher than 10^5 up to 10^7 cycles of use [65] ; high specific energy, 100–130 Wh/kg [66]; and large maximum power output. The round-trip energy efficiency of flywheel is high and can reach nearly 90%. The capacities normally vary from 3 kWh to 133 kWh [64]. Charging of a system occurs fast in less than 15 minutes. The high specific energies often mentioned are deceptive because commercial systems in general have much less specific energy, around 11 Wh/kg [Wikipedia].

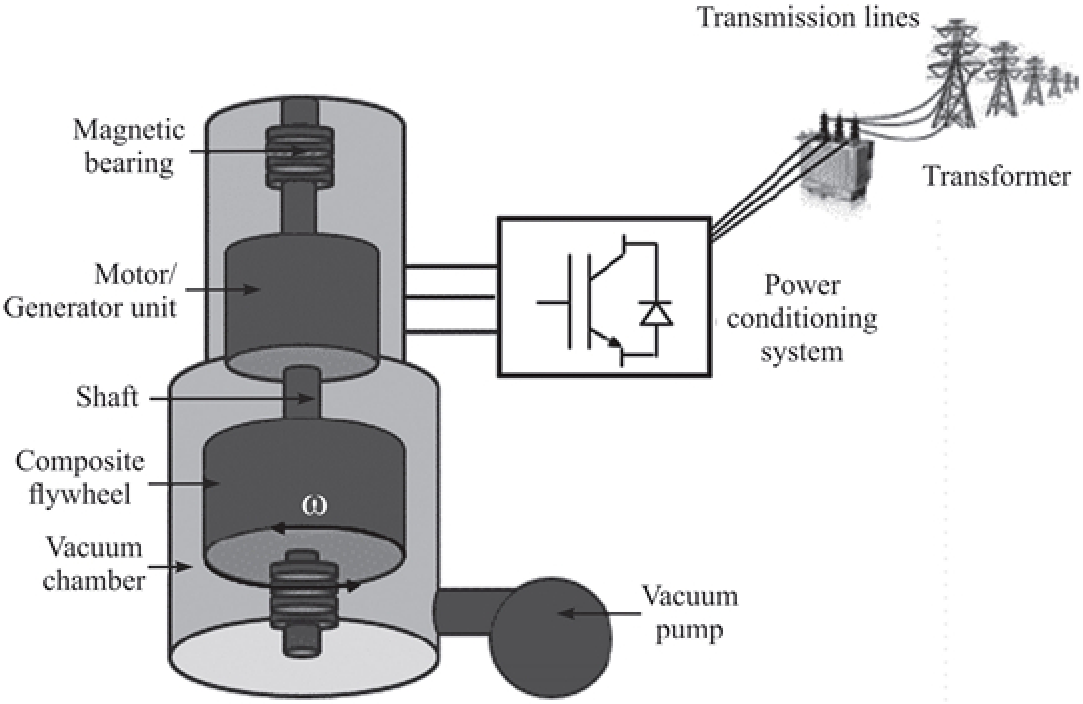


Figure 3.8: Flywheel Energy storage system. (Source: [91])

To determine how much energy a particular device may hold, consider the kinetic energy of a spinning mass: $E = \frac{1}{2} I\omega^2 = \frac{1}{4} m (r\omega)^2$.

Here I is the moment of inertia equal to $\frac{1}{2} mr^2$ for the rotating disc (m is mass and r is the radius of the disc), and ω is the rotational velocity. This is the ‘stored rotational energy.’ This implies that by increasing the maximum speed of the disc the energy capacity is significantly increased than by increasing the mass of the disc [67].

The highest specific energy of a flywheel rotor is largely dependent on: (a) the rotor's geometry, and (b) properties of rotor material. For single-material isotropic rotors, this relationship can be expressed as [68],

$$E/I = K.\ \sigma/\rho$$

Here, E is the kinetic energy of the rotor [in J], I is the rotor's moment of inertia [in kg.m^2], K is the rotor's geometric shape factor [in m^{-2}], σ is the tensile strength of the material [in Pa], ρ is the material's density [in units of kg/m^3]. For energy-storage, materials with high-strength and low density are desirable.

Flywheels have a quick response time of 4 milliseconds or less, can have a size of 100 kW to 1650 kW, and may be utilized for short duration times, up to 1 hour. They are shorter energy duration systems and are not preferable for large-scale grid support applications, which require many kWh or MWh of energy-storage. Their efficiencies are high, about 93%, with lifetimes estimated at 20 years [62].

Variations: These FES systems are categorized into low-speed and highspeed designs:

(i) Most low-speed designs are conventional metal rotor systems, which are typically made of extremely heavy steel discs and are 10,000 rpm or less. The shaft is either vertical or horizontal, and may have mechanical or magnetic bearings. These systems do not have the required energy and the standby losses are relatively large. They are normally used in applications with short-term (~10 to 100 s) durations, and having medium or high load. Germany’s Piller, and America’s Active Power, Satcon and Caterpillar are the leading commercial suppliers of the low-speed flywheels [69].

(ii) The high-speed designs operate above 10,000 rpm, some even more than 100,000 rpm. Because of the speeds, and associated fatigue failure risks, stronger materials including fabric composite materials such as composites of graphite or fiberglass are required, and magnetic bearings and a vertical shaft [67, 70]. The high directional strength properties of such composites combined with their relatively low density help in optimizing the overall configuration, hence specific energy and power.

Urenco Power Technologies (UPT) already supplied commercial units, and AFS-Trinity, Beacon Power, Piller, and a few others are in the process of development [69].

The specific energy of low-speed flywheel is ~5Wh/kg, and the highspeed composite rotor can achieve a specific energy of up to ~100Wh/kg [66a].Typical products are rated at 100–250 kWe with 3.3–25 kWh stored energy [71].

High-speed flywheel typically use 2 kinds of rims, made of solid steel or carbon composite. The material chosen to fabricate rims decides the system weight and size, performance and cost. Rims made of carbon composites are both lighter and stronger than that of steel, resulting in achieving much higher rotational speeds. The amount of energy that can be stored in a flywheel depends on RPM (a function of the square of the RPM); hence, desirable to make higher rotational speeds.

System Design Considerations**:** A flywheel’s speed decreases as its energy is discharged and to account for this, the generator’s AC output is converted to DC, then back to a 60 Hz AC using power electronics. This procedure ensures a steady output waveform without the flywheel spinning always at the right speed.

Another design concern is regarding frictional loss due to the fluid in which the device rotates. The frictional loss occurs whether the rotor is surrounded by air or a highly viscous fluid. The system is therefore often enclosed in a vacuum to lessen such frictional losses.

In sizing a system, power and energy capacity can be handled independently. Although the power capacity is decided by the power conversion system, and the motor-generator, the energy capacity is determined by the mass and speed of the flywheel. Many flywheels are designed to provide high-power output for short periods, 5 to 50 seconds [67]. A flywheel-energy-storage plant can be scaled up by adding more flywheel system modules.

Although the flywheel have power densities 5 to 10 times that of batteries, there are practical limitations to the amount of energy (kWh) that can be stored.

Operation and Maintenance: The bearings require most maintenance. Magnetic bearings are complex systems requiring some care to operate and maintain. Since these devices show hazardous failure, inspecting these devices for signs of fatigue is critical for preventing disastrous failure [61].

Advantages: Flywheels existed for centuries. They have several benefits and only over the past few decades, they are considered bulk energy-storage systems. FES systems can be applied from small micro-satellites to huge power networks. A simple form of kinetic energy-storage, these systems are extremely rapid in their response time and, with recent advances in bearing design (using magnetic bearings), can achieve high efficiencies (up to ~95% at rated power) for short durations of storage. Other favorable characteristics of FES are, relatively high-power density, high reliability, no depth-of-discharge effects, low-cost maintenance, and long-life, 15 to 20 years. Some flywheels are capable of well over 100,000 full discharge cycles and the newest designs are capable of even more, greater than 175,000 full depth-of discharge cycles [70, 72, 73].

The disadvantages are that they have a high rate of self-discharge due to frictional losses and high initial costs. Also, the relatively short duration, high frictional loss and low energy density restrain FES from the use in energy management [69].

Thus, flywheel systems are suitable mostly to short-term energy-storage applications requiring instant power delivery for meeting frequent load fluctuations as well as in power conditioning sectors.

Applications: The technology possess many favorable properties required to improve the present-day electric grid. The system can capture energy from intermittent energy sources over time, and deliver a constant supply power to the grid. The UPT Co. recently demonstrated the application of flywheel to the smoothing of the output of wind turbine systems and the associated stabilization of small-scale island power-supply networks [71, 74].

Flywheels can respond to grid signals instantly, delivering frequency regulation and electricity quality improvements.

The applications of high-speed Systems are constantly expanding, mainly in high-power quality and in short-term ride-through power service as in traction and the aerospace industry [75]. The rail traction industry utilize flywheel storage for trackside voltage support [76, 77].

The technology is environmentally sound; hence, its role in the transport sector is likely to increase by way of improving the overall efficiency and fuel economy in vehicles [78, 79].

Currently, high-power flywheel are used in many aerospace and UPS applications. Presently, 2 kW/6 kWh systems are being used in telecom. Mousavi et al recently presented a comprehensive review of FES systems for hybrid vehicles, railways, wind power systems, hybrid power generation system, power networks, marine, space and other applications explaining the advantages and disadvantages [80].

For utility-scale storage a ‘flywheel farm’ approach can be used to store megawatts of electricity for applications needing minutes of discharge duration [81].

Other typical applications include power quality, supplement to batteries in uninterrupted power-supply, and short-term and medium/high-power applications [69, 82].

Typical Operating Systems: A Flywheel Energy Storage System of 2 MW configuration is shown in Fig. 3.9. Table 3.2 lists selected FES facilities [83]. In June 2011, Beacon Power built and installed 20 MW modular plant for commercial operation in New York and regarded the largest advanced EES facility functioning in North America [84, 85]. 200 highspeed flywheel systems spinning at 16000 rpm are used to deliver fast response frequency regulation services to the grid, providing ~10% of the whole state frequency regulation demand [84, 85]. In March 2012, Rockland Capital acquired the assets of the Beacon Power Corporation and put up funding to develop a second 20 MW flywheel regulation plant in Pennsylvania (The Green Age @https://www.thegreenage.co.uk/tech/flywheel-energy-storage/).

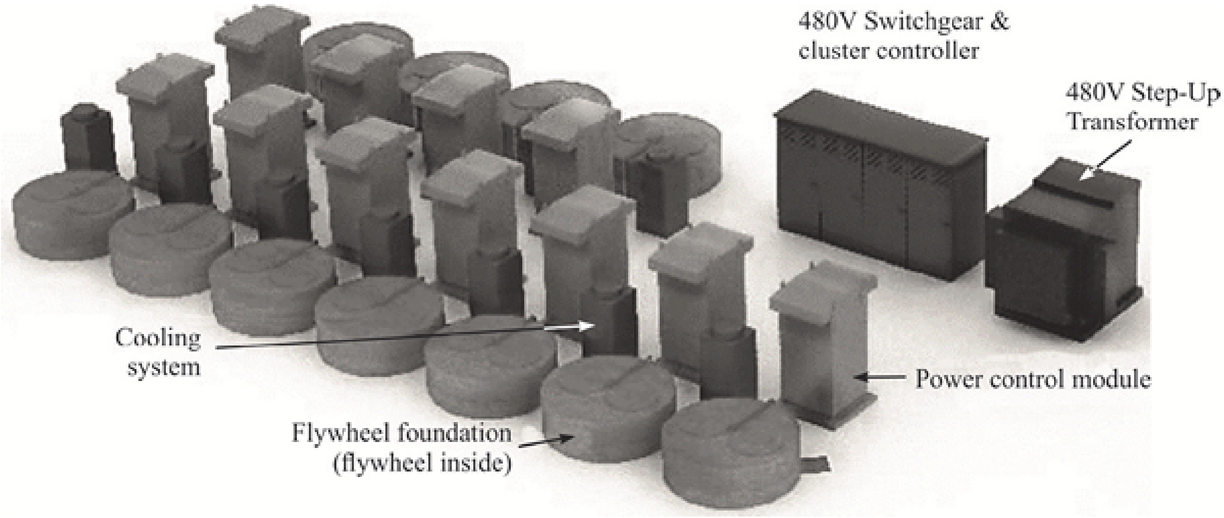
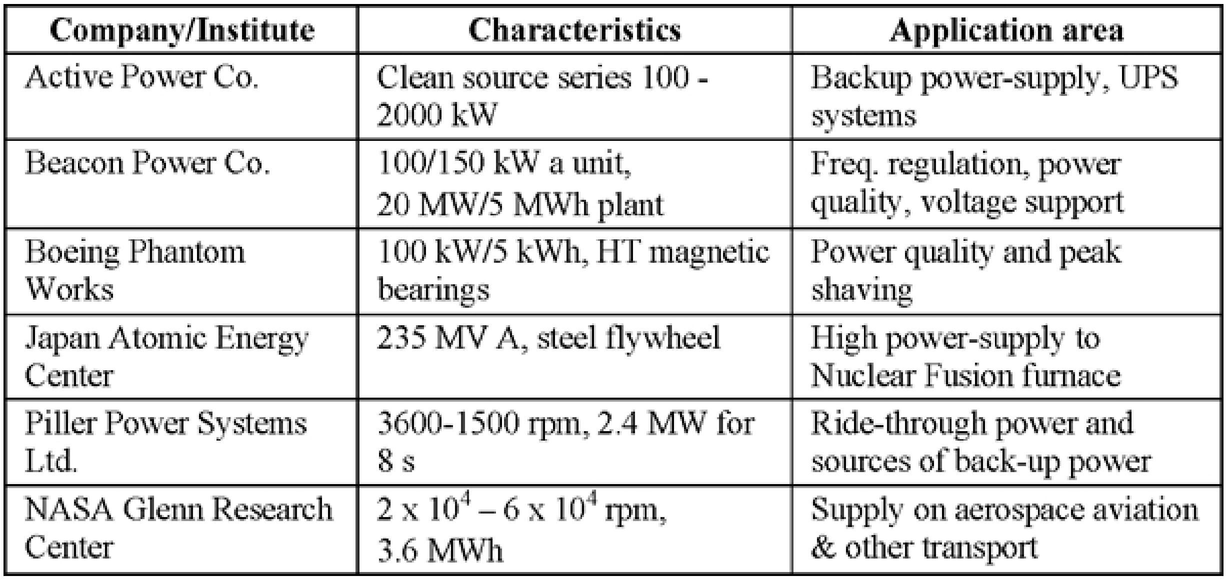


Figure 3.9: Representative Flywheel Energy Storage Systems: 2 MW configuration. (Source: [64d])

FES systems of limited capacity are effective in delivering adequate power in short durations. They are, therefore, not preferred as a standalone back-up power except when operated with other sources, fuel-fired power generation systems or batteries. The main problem of FES is, when on standby, it suffers from the idling losses, which can bring about a moderately high self-discharge, up to nearly 20% of stored capacity per hour [72].

Table 3.2: Selected FES facilities (Source: [70, 72, 73, 83, 84–86])



Company/Institute	Characteristics	Application area
Active Power Co.	Clean source series 100 - 2000 kW	Backup power-supply, UPS systems
Beacon Power Co.	100/150 kW a unit, 20 MW/5 MWh plant	Freq. regulation, power quality, voltage support
Boeing Phantom Works	100 kW/5 kWh, HT magnetic bearings	Power quality and peak shaving
Japan Atomic Energy Center	235 MV A, steel flywheel	High power-supply to Nuclear Fusion furnace
Piller Power Systems Ltd.	3600-1500 rpm, 2.4 MW for 8 s	Ride-through power and sources of back-up power
NASA Glenn Research Center	$2 \times 10^4 - 6 \times 10^4$ rpm, 3.6 MWh	Supply on aerospace aviation & other transport

Currently, the R&D efforts of FES focus on (a) finding the material for the flywheel to increase its rotation speed abilities and power densities, (b) high-speed electrical machines, (c) high carrying capacity of the bearings, and (d) the flywheel assemblage technology [83].

Recent progress in FES technology is a high-temperature superconductor (HTS) bearings, a favorable alternative for improving the performance of the bearing. Argonne National Laboratory in the US created a 2-kWh FES system using high-temperature superconductors and permanent magnets as passive bearings to perform a feasibility study [87].

Ammodo et al (2009) studied a model-based power flow control strategy for improving flywheel performance in high-power pulse systems [88].

FES was tested by the rail traction industry for application in trackside voltage support [77]. The International Techno-economic commission is studying ‘optimizing flywheel for relatively long-term operation (up to several hours) for use in vehicles and power plants [89].

The techno-economic parameters of FES systems drawn from several studies undertaken during the decade, 2000 to 2010 are presented by Bradbury [61].

Siemens has developed a reliable system and also inexpensive to operate. The Siemens system can deliver 125 KW of power for 15 seconds. This system is around one meter high and has a dia. of 60 cm. Its heart is a steel flywheel weighing 260 kg that is suspended by magnetic bearings and rotates 9,000 times per minute in a full vacuum. The magnetic-bearing suspension causes the flywheel to hover, which makes it virtually maintenance-free. A Siemens electric motor with a power electronics system is mounted above the flywheel and runs in atmospheric pressure. To couple the flywheel in the vacuum to the electric motor in ambient pressure, a magnetic reluctance coupling with 2 rotors is used. A ceramic plate serves as a vacuum barrier that separates the flywheel from the electric motor. There are also 2 toothed clutch-discs, each of which is located 3 millimeters from the ceramic plate. One clutch-disc is crushed onto the flywheel, and the other is fixed on the electric motor’s shaft. To release electrical energy from the FES, the motor is turned on and run up to the rotational speed of the flywheel, which is around 9,000 rpm. An electromagnet creates a magnetic field, which generates traction between the 2 clutch-discs. The vacuum plate doesn’t obstruct this process because it’s magnetically neutral. The traction engages the system and motor now operates as a generator that provides the desired amount of energy [63].

3.4 Comparison of PHS, CAES and FES

Mechanical energy-storage systems vary widely in terms of their efficiency, energy density, and capital costs. All 3 mechanical storage systems, Pumped Hydroelectric (PHS), compressed air (CAES) and flywheel systems (FES) all have a high cycle life, resulting in higher efficiencies. PHS, for instance, possess long service lives, exceeding 80 years. Some of the existing facilities have been in operation for more than 100 years.

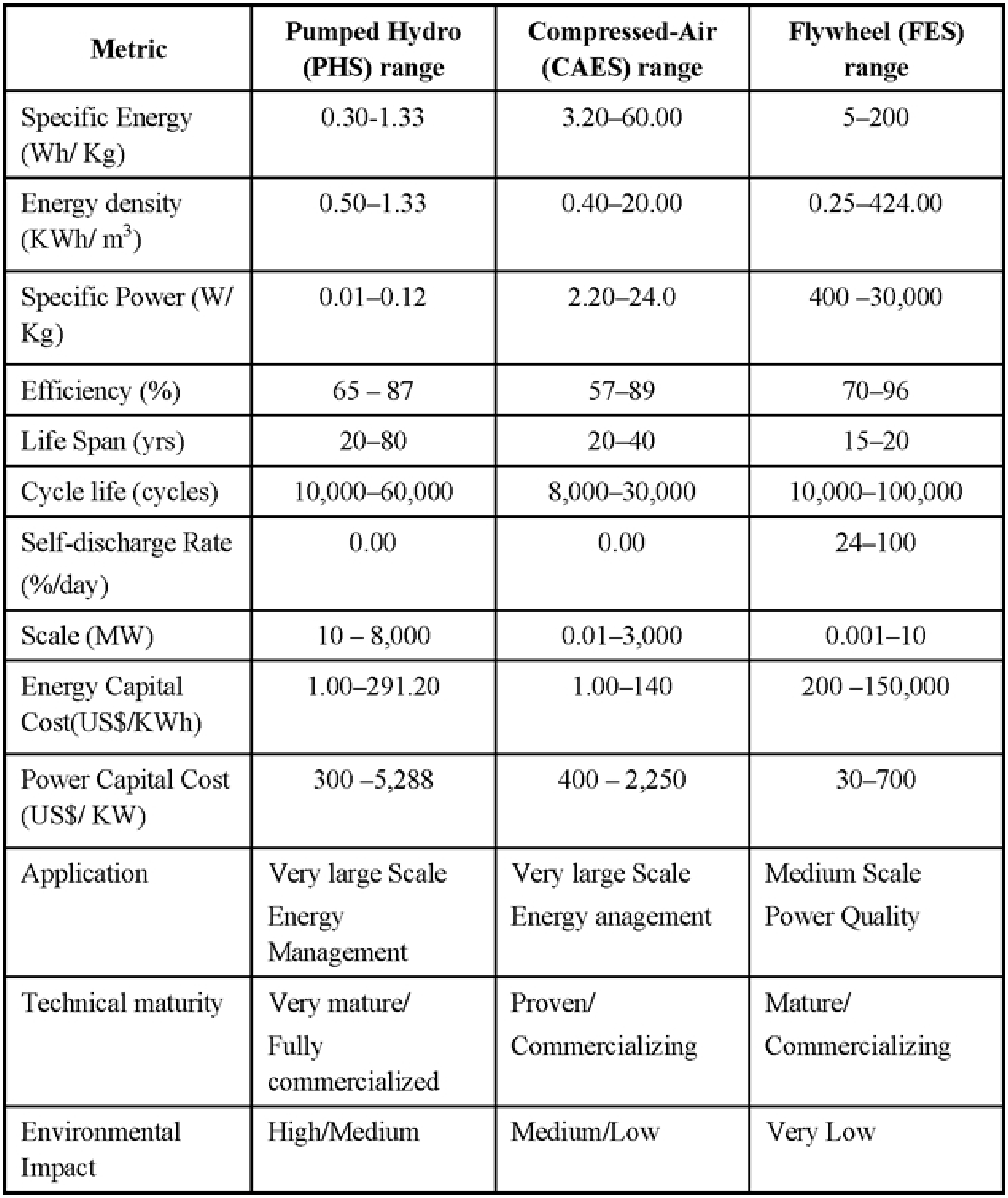
FES systems have higher efficiencies and energy densities; but, they are the most costly among the 3 MES. FES can be used for applications in the millisecond to minute range as in the case of electric storage systems, but in contrast to technologies with comparable energy densities.

PHS is an abundantly matured technology with low capital costs per installed unit of power. But at levels of around 75%, the efficiency of PHS is usual compared with other storage systems. The volumetric energy density is low, and grows marginally as the elevation of the upper reservoir rises with respect to lower reservoir. Because of this, the PHS system is restricted only to a few geographical locations. The advantage of PHS lies in its potential storage capacity, the largest among short-term storage systems.

The CAE systems are mostly similar to PHS about capital costs. The marginally larger energy densities, however, cannot compensate for their low efficiencies, below 55% because the compressed air storage systems presently operating rely on natural gas, a fossil fuel. Besides, conventional CAES can only be set up where caverns are located. The isothermal compressed air storage uses a combination of pneumatics and hydrology. These smaller, modular systems could be used for decentralized applications. The system is yet to be developed fully. These

3 mechanical energy-storage systems are compared in Table 3.3.

Table 3.3: Comparing mechanical storage based on several metrics (Source: [90])



Metric	Pumped Hydro (PHS) range	Compressed-Air (CAES) range	Flywheel (FES) range
Specific Energy (Wh/ Kg)	0.30-1.33	3.20–60.00	5–200
Energy density (KWh/ m^3)	0.50–1.33	0.40–20.00	0.25–424.00
Specific Power (W/ Kg)	0.01–0.12	2.20–24.0	400 –30,000
Efficiency (%)	65 – 87	57–89	70–96
Life Span (yrs)	20–80	20–40	15–20
Cycle life (cycles)	10,000–60,000	8,000–30,000	10,000–100,000
Self-discharge Rate (%/day)	0.00	0.00	24–100
Scale (MW)	10 – 8,000	0.01–3,000	0.001–10
Energy Capital Cost(US$/KWh)	1.00–291.20	1.00–140	200 –150,000
Power Capital Cost (US$/ KW)	300 –5,288	400 – 2,250	30–700
Application	Very large Scale Energy Management	Very large Scale Energy anagement	Medium Scale Power Quality
Technical maturity	Very mature/ Fully commercialized	Proven/ Commercializing	Mature/ Commercializing
Environmental Impact	High/Medium	Medium/Low	Very Low

[Ref: Sabihuddin, S: 2015. A numerical and graphical review of energy-storage and energy production technologies (dataset); @ http://figshare.com/articles/A_Numerical_and_Graphical_Reviewof_Energy_Storage_and_Energy_Production_Technolgies/1096289]

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CHAPTER 4

Electrochemical Energy storage

4.1 Battery Energy Storage Systems (BESS)

Battery technologies are mature and relatively easy to design and install in relation to other energy storage technologies. They are, therefore, one of the favorable storage systems for stationary applications [1a, b, 2, 3]. A significant number of publications on BESS were reviewed by several authors from different perspectives. To mention a few: overviews of large-scale battery systems for electricity storage, focusing on the types and operational characteristics as well as their applications in the integration of solar and wind energies [4–7]; the use of redox flow batteries for the storage of renewable energy [8]; application in household-demand smoothening in electricity-distribution grids [1, 9, 10]; evaluation of gridlevel adaptability for stationary applications in Europe [11]; progress in photovoltaics integrated with BESS and related feed-in tariff policies [1, 12], and several others. The references cited are only representative.

Although batteries, which use toxic materials pose threats to the environment and human health [13], environmental impact studies on BESS are not many. Recently, the life cycle environmental impact of batteries in a renewable energy system was analysed [14] using a standalone solar PV energy generation system and the mature, cost-effective and widely-used lead-acid battery for the study [15, 16]. This extensive study includes how the lifecycle, cycling capacity and the number of substitutions of the lead-acid battery cells contributes to the environmental effect of the system over the expected lifetime of 25 years [14].

Batteries are of 2 types: primary type, which are non-rechargeable, and secondary type, which are rechargeable. Rechargeable/secondary battery is the oldest form of electricity storage [17, 18], which store electricity in the form of chemical energy. A secondary battery consists of one or more electrochemical cells connected in series or parallel, and each comprising 2 electrodes immersed in a solid- or liquid- or viscous-state electrolyte. These electrodes are ionic conductors at the operating temperatures of the cell (19, 20), and they can store and provide energy by electrochemical reversible reactions. The electrically connected cells in series and parallel provide the desired battery voltage and current levels. Figs. 4.1 shows the simplified operational principle of a typical BES system. In discharge phase, electrochemical reactions occur at the 2 electrodes generating electrons that flow as current in an external circuit. The reactions are reversible and allow the battery to recharge by an external voltage applied to the electrodes.

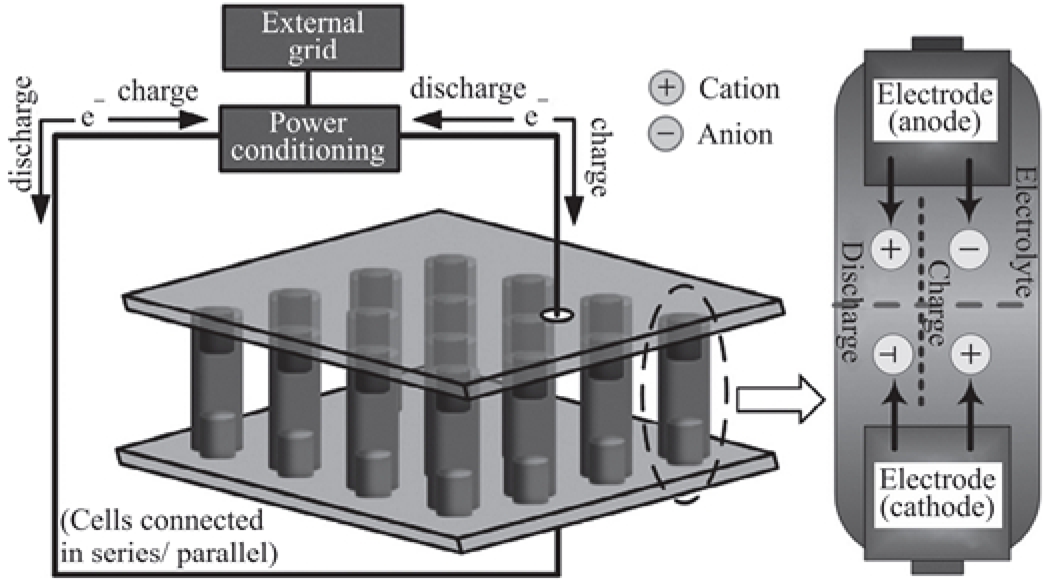


Figure 4.1: Cells in series/parallel (Source: [21]).

In more detail: the negative electrode gives up electrons to the external circuit and is oxidized during the electrochemical reaction. The positive electrode is the oxidizing electrode accepting electrons from the external circuit and is reduced during the reaction. The electrolyte is an ionic conducting medium (different from an electrical conducting medium) that transfer electrons as ions between the anode and the cathode. An electrical conductor is avoided as an electrolyte because that would make the cell useless by short-circuiting the electrodes.

Charge and Discharge: When the cell is connected to an external load, electrons flow from the negative terminal through the load to the positive terminal, that is, the cell discharges. Simultaneously within the cell, negative anions flow toward the negative electrode and positive cations flow toward the positive electrode to complete the circuit.

So, as the positive electrode becomes more negatively charged (or less positively charged), the cell looses energy, as expected during discharge. These actions/procedures get reversed when the cell recharges. From the viewpoint of the circuit, electrons originate at the anode and move toward the cathode. As the electric current is interpreted as the opposite of that of electron flow, current constantly flows from the cathode to the anode [22].

If the electrochemical cell is disconnected from the load, it is ‘opencircuit’ state; an electromagnetic potential energy difference (voltage) exists between the electrode with fewer electrons (the positive terminal) and the electrode with more electrons (the negative one). If, then, a load is connected externally completing the circuit, the voltage results in a force prompting electrons to flow from the negative electrode to the positive electrode (a current). This leads to a charge imbalance that leaves the positive and negative electrodes slightly less positively and negatively charged, respectively. As a result, the anion flow to the anode and cations to the cathode to establish chemical equilibrium in the system. In this process, there is a loss of chemical energy stored within the cells delivering to the load, leading to decrease in the potential difference between the 2 electrodes. During charge, a voltage is applied across the terminals so that the electron- and ion-flow directions are reversed, and the chemical energy that is lost during discharge may be returned from the input electrical energy retreating the chemical reaction [22].

To adjust *power generation to changing demand* many battery technologies have been proposed. Starting with the oldest lead-acid, others include nickel-cadmium, nickel-metal hydride, sodium-sulfur, sodiumnickel chloride, and lithium-ion. Batteries usually have low standby losses and can have a high-energy efficiency (60–95%).

Rating batteries: The batteries are graded with reference to their *energy* and *power capacities*. The power and energy capacities are prescribed during the design stage and are not free to alter.

The important characteristics of a battery are efficiency, the life span in terms of cycles, working temperature, depth of discharge, self-discharge when shelled and energy density [23].

Main assets of these systems are (a) low initial capital cost for most mature BESS, (b) cover all power systems size needs, and (c) short lead times, modularity, scalability and portability (24a, 25).

Key characteristics of battery energy storage systems [24b]

(a) *Rated power capacity*: the maximum rate of discharge that the system can accomplish beginning from a fully charged condition;

(b) *Energy capacity*: the highest amount of energy stored, expressed in kWh or MWh;

(c) *Storage duration*: the period that the storage system can discharge at its rated power capacity before run down its energy capacity;

(d) *Cycle life or lifetime*: the total time (or number of cycles) the system can offer regular charging and discharging before it fails or significantly degrades;

(e) *Self-discharge:* the decay in the charge of the battery either through internal chemical reactions, or energy lost without out-performing work;

(f) *State of charge:* level of charge at any time, from discharged state to fully charged state;

(g) *Round-trip efficiency*: the ratio of the energy needed to charge the battery to the energy discharged from the battery. The calculation includes self-discharge loss and other electrical losses. The manufacturers frequently refer to the DC-DC efficiency, though AC-AC efficiency is more important to utilities who are concerned with battery's charging and discharging from the point of linkage to the AC power system [24b].

Applications: Batteries are more appropriate for electrical energy storage. They afford fuel flexibility and are reasonably environmentally sound. Also deliver numerous important functional benefits to the power utilities. Their response to load changes is quick and take co-generated and/or third-party power to boost the system stability. Other areas of uses are power quality, energy management, ride-through power and transportation systems.

However, until recently, there have been limited *large-scale functional battery storage* systems because of their drawbacks such as low energy densities, lesser power capacity, high maintenance costs, short cycle life and restricted discharge capability. Besides, most batteries comprise toxic substances that produce ecological impact during their unchecked or unorganized disposal [26].

Currently, battery technology is going through substantial development. Many distinct types of batteries are emerging; a few of them at experimental status and a few at commercial readiness. In power system applications, deep-cycle batteries have been used so far (the type used in Electric vehicles) [27] having energy capacity varying from 17 to 40 MWh and having about 70–80% efficiencies. For power system applications, only a few of the battery technologies out of the various types available are more appropriate [27].

4.2 Lead-acid (Pb-acid) Battery

Globally, lead-acid (Pb-acid) batteries constitute the largest share in the secondary battery market. In spite of lesser performance compared to many accessible chemical batteries, factors such as low-cost, reasonable cycle life, high operating temperatures, relatively high power outputs and little maintenance, and simple charging methods make them appealing [1].

It is the oldest type of rechargeable battery, invented in 1859 by French physicist Gaston Plante, which has the largest number of applications. A lead-acid battery comprises 2 electrodes, lead metal and lead oxide, immersed in an electrolyte, nearly 37% (5.99 molar) sulfuric acid in the charged condition. In the discharged state, both electrodes convert to lead sulfate, with the electrolyte losing its sulfuric acid content and reducing primarily to water. The chemical reactions that occur during charge cycle and discharge cycle are schematically shown in the Figure 4–2. The chemical reactions at the electrodes can be represented as the following:

$$\text{Anode: } Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$$

$$\text{Cathode: } PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \leftrightarrow PbSO_4 + 2H_2O$$

A single cell will provide an open-circuit output voltage (V_{oc}) of about 2.13 volts when fully charged and when it drops to 1.95 volts, the cell is considered discharged. A battery may consist of a single lead-acid cell or several lead-acid cells connected. For example, a 12 volt Pb-acid battery comprises 6 lead-acid cells connected in series. The

V_{oc} from these cells when full charge is ~ 12.78 volts, and when it drops to 11.7 volts, the battery is considered to be fully discharged.

A lead-alloy is used to fabricate grid structure of this battery because pure lead is soft to support itself. Small quantities of other metals are alloyed with lead, not only to achieve the required mechanical strength but to improve electrical properties. Antimony, calcium, tin and selenium are the metals added, and in such cases, the batteries are often called ‘leadantimony’ and ‘lead—calcium’ batteries. However, they are accompanied by side effects, for eg, adding antimony while improving deep cycling, also increases water consumption; similarly adding calcium while reduces self-discharge, the positive lead-calcium plate grows due to grid oxidation when over-charged. The present lead-acid batteries use doping agents such as selenium, cadmium, tin and arsenic to reduce antimony and calcium content [28].

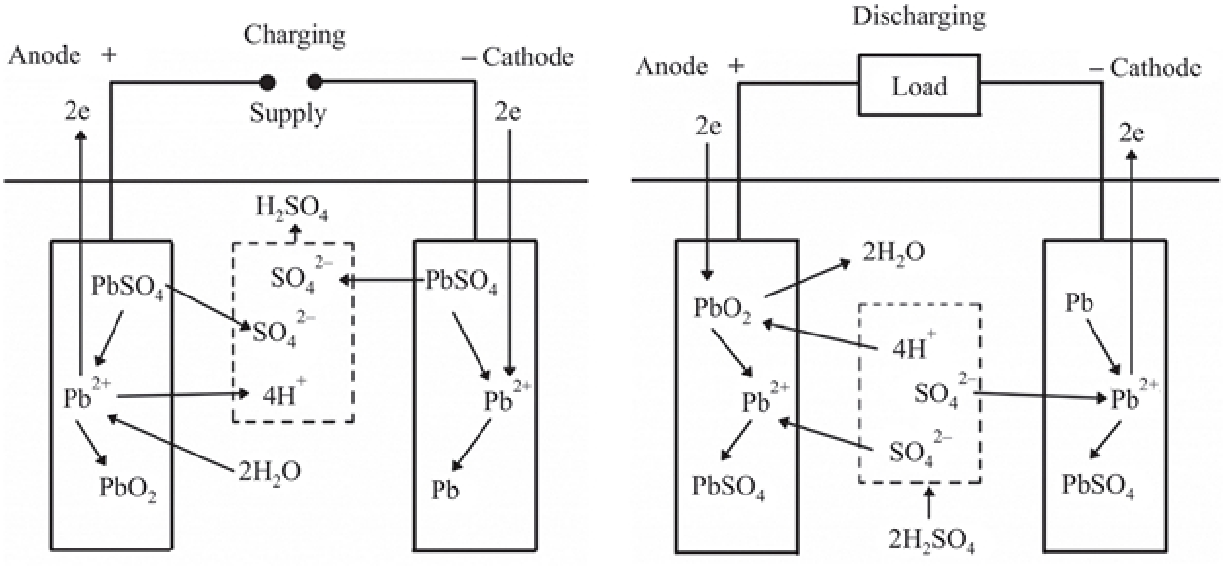


Figure 4.2: During ‘Charging’, lead oxide is formed at the anode, pure lead is formed at the cathode and sulfuric acid is liberated into the electrolyte causing the specific gravity to increase; and during ‘Discharging’ lead sulfate is

formed at both electrodes and sulfuric acid is removed from the electrolyte causing the specific gravity to reduce (Source: [29]).

There are several types of lead-acid batteries: each is designed for a particular application with specific charge and discharge characteristics. These battery types, explained below, are specifically planned for a designated end-application [29, 30].

1. Deep Cycle batteries

These are designed to discharge by as much as 80% of their capacity (depth of discharge) over thousands of charging and discharging cycles. A true deep-cycle battery is built for maximum capacity and a reasonably high cycle count. Deep-cycle batteries are marked in Ah or minutes of runtime. The capacity is typically rated a 5-hour and 20-hour discharge. These are used to store electricity in autonomous power systems (e.g., solar energy system) for emergency back-up as well as in electric automobiles where constant current for long periods are required. These are also extensively used in golf carts, mobility scooters, power banks, RV power banks.

‘Deep-cycle batteries’ are of 2 kinds: ‘Flooded Lead-acid’ type and ‘Sealed Lead Acid’ type or ‘valve-regulated lead-acid (VRLA) type. Sealed lead-acid (SLA) batteries use gelled electrolytes and thick glass fiber absorbent mats (AGM) to improve ruggedness.

(a) *Flooded type*: These batteries contain a conventional liquid electrolyte. Standard types have removable caps so that the electrolyte can be diluted and the specific gravity measured. They are supplied dry and distilled water need to be added. These are inexpensive and if they are kept topped up, they are not too sensitive to high charging voltages. These are extensively used in auto industry.

Flooded batteries are the oldest technology, and the number of types and sizes available is unlimited. They range in size from a small motorcycle battery to large 4000lb steel case varieties designed to operate electric forklifts and underground locomotives. Flooded batteries are made for engine starting, deep-cycle, traction, uninterruptable power systems, wheelchairs, marine and aircraft uses.

(b) *Sealed-type batteries*: Known as ‘valve-regulated lead-acid (VRLA)’ or Sealed Lead Acid (SLA) batteries, these are available in a few different formats. The internal structure is essentially similar to that of a flooded battery. The only alteration in the sealed-type is that the battery maker ensures that enough electrolyte is placed in the battery before sealing to withstand the chemical reaction under normal use all through the assured life of the battery. During stressful charge and rapid discharge, venting must be controlled, and hence, valves are included to let gases go if pressure builds up. Instead of submerging the plates in a liquid, the electrolyte is permeated into a moistened separator, which assists operating the battery in any physical orientation without leakage. Their main manufacturing process, including number of plates and plate thickness determines its designated end user application.

The most substantial benefit that a sealed-type battery offers is its capability to combine oxygen and hydrogen to create water and avoid dry-out during cycling. This occurs at a moderate pressure of 0.14 bar (2psi). The valve functions as a safety vent in case, the gas accrual rises. It is better to avoid repeated venting to prevent an eventual dryout. Sealed lead-acid batteries do not tend to degrade as easily as ‘flooded type’ and are regarded the safest lead-acid battery to use. VRLA batteries have been critical for virtually maintenance-free operation in some applications. Conical lead plate stacks have been used to produce round cell technologies for low maintenance operations [31].

(i) Absorbed Glass Mat (AGM) batteries:

These batteries use an Absorbed Glass Matt (AGM) process, which is superior to traditional flooded technology. Fine, highly porous, micro-fiber glass separators (boron-silicate mat) absorbs the electrolyte, increasing efficiency by lowering internal resistance, which in turn boost capacity. Lower internal resistance allows the battery to get recharged much faster than conventional flooded lead-acid batteries. These will not leak and are less sensitive to over-charging. They can stand for a long time, as much as 30 days in a discharged state and can still be recharged successfully. These batteries provide a much larger capacity in a smaller case size and can be mounted on their side and shipped using standard shipping processes.

AGM works best as a mid-range battery with capacities of 30 to 100Ah, and is less suited for large systems such as UPS. These batteries are commonly used in alarm and telecom industries, golf carts and trundlers, mobility vehicles, automotive and much more. Although the voltage, capacity, dimensions and ratings may be similar across a range, each AGM battery has a specific application that they should be used in.

(ii) Gel type

Gel VRLA batteries contain a jellified electrolyte and so they do not leak. Sulfuric acid is mixed with silica fume, which makes the resulting mass gel-like and immobile. This creates a complete maintenance-free, non-spill and good lead-acid battery. Unlike flooded batteries, these batteries do not require to be kept upright and can be shipped using standard shipping process.

These batteries possess greater resistance to extreme temperatures, shock, and vibration. They are capable of withstanding over discharging, unlike flooded and some AGM batteries. They have a low discharge rate (1% per month), but they require specific charging practices and need to be charged with a Gel-specific battery charger.

The capacity of AGM steadily declines with cycling and time of life; and the gel-type maintains high-performance for an extended time and drops abruptly toward the end of life. Gel type batteries are much more expensive than the AGM and Flooded types.

Gel batteries are not as common as AGM batteries, but are often found in deep discharge situations. They are ideal in applications where a constant current is required such as golf carts, mobility, power bank and RV power bank applications.

The sealed lead-acid battery, on the other hand, is aimed to have a low over-voltage potential to forbid it to attain its gas-generating potential during charge. If charged in excess, gassing, venting and ensuing water depletion occurs and eventually dry-out. As a result, gel and to some extent, AGM, are not charged to their full potential and the charge voltage maximum is fixed lower than that of a flooded type battery.

Regard to charging, the gel and AGM are not the straight alternatives for the flooded type.

Regardless of some benefits, the performance of lead-acid batteries has been low; more so, they are hard to store in the discharged state because of sulfation effects that restrict their lifetime [31]. Since it is challenging to plan small packages, they have limited application and are found in small portable electronics.

2. Start Batteries

Known also as Cranking batteries, these are used to start and run engines. They have numerous thinner plates to have maximum surface area and consequently low internal resistance; the current output is affected by the total surface area. These are specifically designed unlike deep-cycle batteries, to produce a large burst of current in a short period, which is particularly useful in engine starting applications. They can deliver a very large current in a short time, discharging by about 2 to 5%.

These batteries are grouped using their CCA (Cold Cranking Amps) ratings as basis. The total current a fully charged battery at -18°C can deliver for 30 seconds, without the voltage falling below 1.2 V per cell (7.2v for a 12v battery) is called CCA, which is usually around 1% of the battery's capacity. If the CCA rating is large for a battery, it can turn over a larger engine. These batteries are not planned to be deep cycled. If deep cycled, these batteries quickly degenerate and fail after 30–150 cycles because discharging start causing irreversible damage to the battery plates. This ultimately reduces its performance, total life span and in some cases even cause complete failure.

3. Marine batteries

Usually a hybrid battery that falls between deep-cycle and start/cranking batteries although some are true deep-cycle batteries. Hybrid batteries should not be discharged by over 50%.

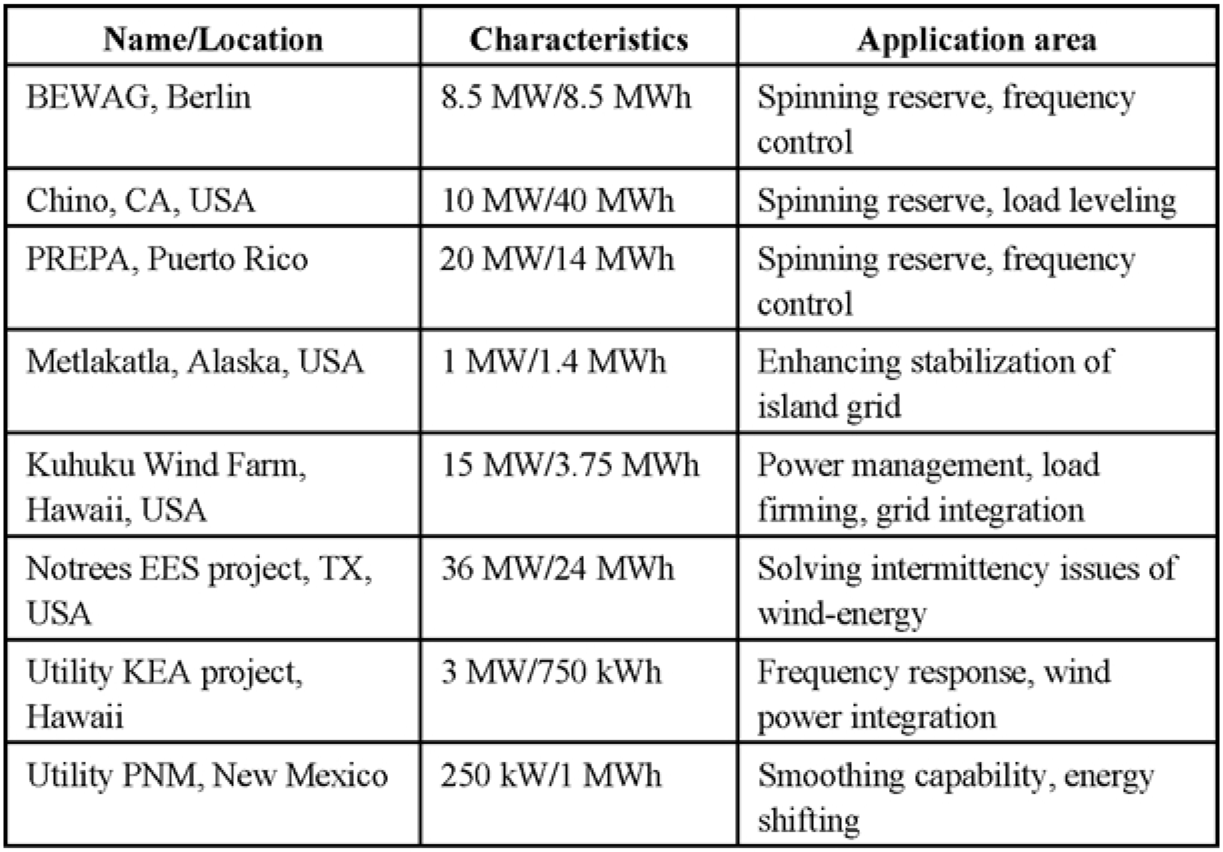
The production process is the critical aspect that enables this battery for use in marine applications.

Batteries experience a lot of stress and too much vibration in marine environment. A standard deep-cycle or start battery produces normal results for marine application in the short term. In the long term, tough marine conditions, too much vibration and deterioration damage the fragile lead-acid battery, finally leading to a reduced rated lifespan. Batteries that are designed for marine use are specifically labeled as Marine Grade. These are available in Flooded or Gel or AGM type.

Another category called ‘Standby Sealed Lead Acid batteries’ , which is the Sealed lead-acid type is designed only for standby applications to operate on a float (low) load, maintaining UPS, alarm systems, telecom and network systems. These batteries are generally of AGM variety.

Some of the electrochemical energy storage facilities using lead-acid batteries are listed in Table 4.1. The Stafford Hill Solar Farm and Microgrid facility (battery storage system of 4 MW/ 3.4 MWh) installed in Rutland, VT, USA is shown in Figure 4.3.

Table 4.1: Examples of EES facilities using lead-acid batteries.



Name/Location	Characteristics	Application area
BEWAG, Berlin	8.5 MW/8.5 MWh	Spinning reserve, frequency control
Chino, CA, USA	10 MW/40 MWh	Spinning reserve, load leveling
PREPA, Puerto Rico	20 MW/14 MWh	Spinning reserve, frequency control
Metlakatla, Alaska, USA	1 MW/1.4 MWh	Enhancing stabilization of island grid
Kuhuku Wind Farm, Hawaii, USA	15 MW/3.75 MWh	Power management, load firming, grid integration
Notrees EES project, TX, USA	36 MW/24 MWh	Solving intermittency issues of wind-energy
Utility KEA project, Hawaii	3 MW/750 kWh	Frequency response, wind power integration
Utility PNM, New Mexico	250 kW/1 MWh	Smoothing capability, energy shifting

(Source: [21, 33])

Figure 4.3: Stafford Hill Solar Farm (2.3 MW) and battery system (4 MW/ 3.4 MWh) in Rutland, VT; Photo: Green Mountain Power (Source: [32]).

In the early years, BESS was used simply to supplement the generation capacity for the utility to meet demands during periods of high usage. This application alone could not justify the cost of a BESS. The added applications in utility use, such as correcting ongoing power quality issues, providing a reserve of energy for uninterrupted power supply, peak shaving and load leveling support BESS, a viable alternative to other power management solutions. However, they are difficult to design in small packages and so have seen limited application in small portable electronics.

Recently, load leveling applications using lead-acid batteries combined with renewables have been investigated. The results show that further improvements are needed. Improved casing besides hybrid ultra-capacitor devices are expected to add to the performance by increasing specific power, recharge times and cycle life [1].

Thin film technologies, which enable low-cost manufacturing have recently come into the market. Titanium oxide supports have been suggested to increase specific energy and to fabricate bipolar batteries [28]. Also, acid circulation can be used to increase the application of active materials. Despite progress, the nature of materials used in these batteries continues to highly impact the environment at levels almost similar to those of Ni-Cd batteries, although larger collection and recycling rates have diminished a few of these impacts [34]. The lead-acid batteries have several advantages & disadvantages [28, 35]:

Advantages: (a) mature technology, (b) relatively cheap to manufacture and buy (they provide the lowest cost per unit capacity for rechargeable cells), (c) low self-discharge, (d) large current capability, (e) high specific power, capable of high discharge currents, (f) performance good at low and high temperatures, (g) tolerant of over-charging, (h) available for various applications in various sizes and specifications, and (i) many producers worldwide.

Disadvantages: (a) fails after a few years of use, lifespan typically 300 -500 cycles, deep cycling reduces battery life, (b) low specific energy; poor weight-to-energy ratio, (c) slow charge, full charging takes about 15 hours, (d) corrosive electrolyte (can cause burns to people and corrosion on metalwork), (e) acid needs careful disposal,(f) adverse environmental impact, (g) cannot always be used in various orientations, (h) must be stored in the charged state once electrolyte introduced, (i) typical charging efficiency only around 70%, (j) transportation restrictions on the flooded type.

Maintenance: Some of the Lead-acid batteries are aimed to be free of maintenance; these are sealed and cannot be refilled with the electrolyte. Sealed batteries that are not vented should not receive equalization charges. Some precautions need to be followed: (i) Batteries should not be left standing for any length of time, either charged or uncharged; these can’t be stored in discharged state due to sulfation effects that limit their lifespan [81b]; (ii) Batteries delivered dry can be shelved only for 2 to 3 years; (iii) Over-charging or discharging of the battery should not be by more 60% of their capacity; (iv) Batteries of same make and same model must constitute a battery bank, and no new batteries should be added once a battery bank functioned for more than a few weeks; (v) The electrolyte should be regularly added with distilled water to maintain the suggested specific gravity; (vi) equalization charges should be used for regularly cycled batteries atleast once in a month.

Safety: Lead-acid batteries vent hydrogen and oxygen while working and therefore, they can be dangerous. The following facts should be kept in mind: (i) In the flooded cells, the electrolyte must be kept with distilled water at the precise level, to allow good losses resulting from evaporation and gassing; (ii) Materials susceptible to acid attack are not used in the battery room. The acid spilled and/or vapourised would corrode rapidly the exposed metals other than lead. As far as possible, an asphalt floor shall be used and the wooden surfaces be coated with anti-acid paint; (iii) The battery room need to be well-ventilated, and if necessary, corrosion-proofed fans shall be used; (iv) Visible flames must be shunned in the room; and all circuits must be switched off to prevent sparking as the gases present are explosive; (v) The acid spilt need to be cleaned immediately, washing with soda solution; (vi) The eyes must be protected from acid; (vii) For the initial charging of new cells, acid mixture should be prepared by adding acid to water, and not the other way; (viii) The cell temperature must be observed, not exceeding 36°C, as too much heat damage the cells; (ix) The battery terminals must be always clean and coated with petroleum jelly; (x) Short-circuiting the battery or cell can create very high currents that may end up with fire or burns; (xi) Insulated tools must be used always, and great care must be taken to ensure that the terminals do not connect even by mistake.

4.3 Nickel Cadmium Batteries

Nickel cadmium (Ni-Cd) batteries had been in commercial use since about 1915 and still prevalent. Ni-Cd batteries contain a nickel hydroxidepositive electrode plate, a cadmium hydroxide-negative electrode plate, a separator, and an alkaline electrolyte. 30% solution of KOH in distilled water is the electrolyte. LiOH and NaOH are also suggested electrolytes, but they show a lower conductivity than KOH. Non-woven polyolefin with improved wettability is used for separators.

Ni-Cd batteries are normally sealed into a metal case with a sealing plate fitted with a self-sealing safety valve. The 2 electrode plates, positive and negative, that are shielded from each other by the separator, are curved into spiral shape inside the metal case. This design is branded as the jelly-roll design and assist the Ni-Cd cell to provide a much greater maximum current than an alkaline cell of comparable size.

In the charging state, they consist of a nickel oxy-hydroxide, [NiO(OH)] cathode, an anode made of metallic cadmium, a separator and an alkaline electrolyte [13]. During discharging, the cathode reacts with water available in the aqueous potassium hydroxide to generate $Ni(OH)_2$ and hydroxide ions at the anode. The chemical reactions (reversible) for the anode and cathode:

Oxidation of cadmium at the negative electrode:

$$Cd \rightarrow Cd^{2+} + 2e^-$$

Reduction of trivalent nickel ions to bivalent at the positive electrode:

$$Ni^{3+} + e^- \rightarrow Ni^{2+}$$

During charging both reactions are reversed.

At anode: $Cd + 2OH^- \leftrightarrow Cd\,(OH)_2 + 2e^-$

At cathode: $2NiOOH + 2H_2O + 2e^- \leftrightarrow 2Ni\,(OH)_2 + 2OH^-$

Combining, the net chemical reaction during discharge is

$$2NiO\,(OH) + Cd + 2H_2O \leftrightarrow 2Ni\,(OH)_2 + Cd(OH)_2$$

Electrical characteristics: Ni-Cd batteries have better advantages over those of lead-acid batteries. The average EMF of Ni-Cd battery is 1.2 V per cell. However, the EMF of a cell can go as high as 1.4 V on full charge. The typical charging voltage is 1.45 V, while the trickle charging rating is 1.35 V. The Ah efficiency under average operating settings is roughly 80%, whereas watt-hour efficiency is around 65%. The battery’s self-discharge rate is around 10% per month and energy density varies between 50 and 75 Wh per kg. The cycle life is relatively low, 1500–3000.

Types: Traditional Ni-Cd batteries are of the sealed-type, the charge gas is normally recombined and they release no gas unless severely over-charged or a fault develops. Vented cells have a vent or low pressure release valve that releases any generated oxygen and hydrogen gases when overcharged or discharged rapidly. This also means that the battery is not normally damaged by excessive rates of overcharge, discharge or even negative charge. Vented cell Ni-Cd batteries have reduced size and weight, and less maintenance requirements over other types of batteries.

Vented cell Ni-Cd batteries are a successful technical product. The battery is safer and has a simpler and more economical structure. Large battery systems using vented Ni-Cd batteries operate on a scale similar to lead-acid batteries, and are interchangeable with lead-acid batteries.

Merits: Ni-Cd batteries are rugged and have a robust reliability and low maintenance requirements. These devices can withstand significant mechanical and electrical abuse. They are great for high power outputs, have long life (up to 20 years or more depending on the type), have good low-temperature characteristics, wide temperature range (from -40° to 70 °C), excellent cycle life, flat voltage profiles, economic pricing and are generally maintenance-free [1a, 31]. Compared to lead-acid batteries, these batteries have a higher power density, a slightly greater energy density and higher number of cycles.

Demerits: Both its maximum capacity and whole life are subject to the memory effect and thus cannot be repeatedly recharged after being partially discharged [36]. However, with proper battery management procedures, this problem can be tackled. Applications requiring moderate discharge are, therefore, preferred. The electrolyte is corrosive and requires careful handling of the battery to avoid skin burns or eye irritation. Cadmium and nickel are toxic creating environmental issues, especially during battery disposal. The regulatory constraints have displaced these batteries in favor of NiMH and Li-Ion chemistry. Ni-Cd is now restricted primarily to specialized applications, for instance, in aerospace. Since 2006, they have been mostly avoided for consumer use [37].

Present status: Early Ni-Cd cells used pocket-plate technology that is still in production. In mid-20th century, in an attempt to increase power and energy density, a switch over to nickel products such as nickel foam and nickel fiber, and plastic bonded and sintered electrodes happened. Subsequently, the resilience of fiber-structured electrodes led to decrease in plate degradation [31].

Ni-Cd cells using pocket and fiber plates employ similar electrode design for both the nickel-positive electrode and cadmium-negative electrode. But sintered and foam positives are mostly used together with plastic- bonded negatives [38].

The pocket-plate type Ni-Cd batteries are the most reliable and rugged with a long float life, 20–25 years and are currently used. They have good charge retention and can withstand, to a great extent, overcharge or deep discharge or even accidental reverse charge. They can be stored in any state of charge [SBS LLC @ https://www.sbsbattery.com /products-services/by-product/batteries/nickel-cadmium-batteries-1/kp-kb-series-ni-cad-wet-pocket-plate.html].

Industrial designs: All commercial Ni-Cd designs favor vented type to drive away gases formed on overcharge. This requires, however, refill of some water to compensate. This has led to the production of ‘separator’ designs capable of allowing varying levels of recombination; some are designed for telecom and some for off-grid renewable energy applications, realizing near maintenance-free operation with reference to the electrolyte [38]. Most recent research has focused on reducing costs by more effective use of costly nickel and cadmium and streamlining manufacturing process.

To extend the life of Ni-Cd batteries, many precautions must be observed: (a) short-circuiting the cells must be avoided, lest large currents are drawn, which result in enormous heat generation. Also, the cells should not be discharged at high rates; (b) never overcharge the cells at rates equal to or higher than the usual charging current, and accept trickle charging; (c) do not reverse charge the cells, that generally happens when a battery with several cells in series is totally discharged; (d) at no time throw the cells in a fire; (e) advisable to operate within -20°C to +60°C temperatures [39].

Applications: These are widely-used in portable devices, emergency lighting, UPS, aviation, rail and mass transit, back for telecoms, power plants, photovoltaic, fire alarms, switchgear protection, instrumentation and process control, and generator starting depending on the capacity (Ah). Because of their relatively low internal resistance, they can deliver high surge currents. This advantage favors them for applications such as remote-controlled electric model airplanes, boats, cars, cordless power tools and, camera flash units.

Systems in operation: The Ni-Cd system established at Golden Valley, Fairbanks, Alaska, USA [40, 41] is the world's largest and most powerful battery system. The system contains 4 battery strings, each string consisting of 3440 cells, with a 5200 V string voltage. The system is graded at 27 MW for 15 min, and 40 MW for 7 min, with a final 46 MVA restriction enforced by the power converter. The batteries are estimated to perform 100 complete and

500 partial discharges in the design life of 20 years. The environmental conditions are -52^{o}C to +32°C. The electrical diagram of the system is shown in Figure 4.4. The system here provides critical spinning reserve functionality in what is effectively an 'electrical island.'

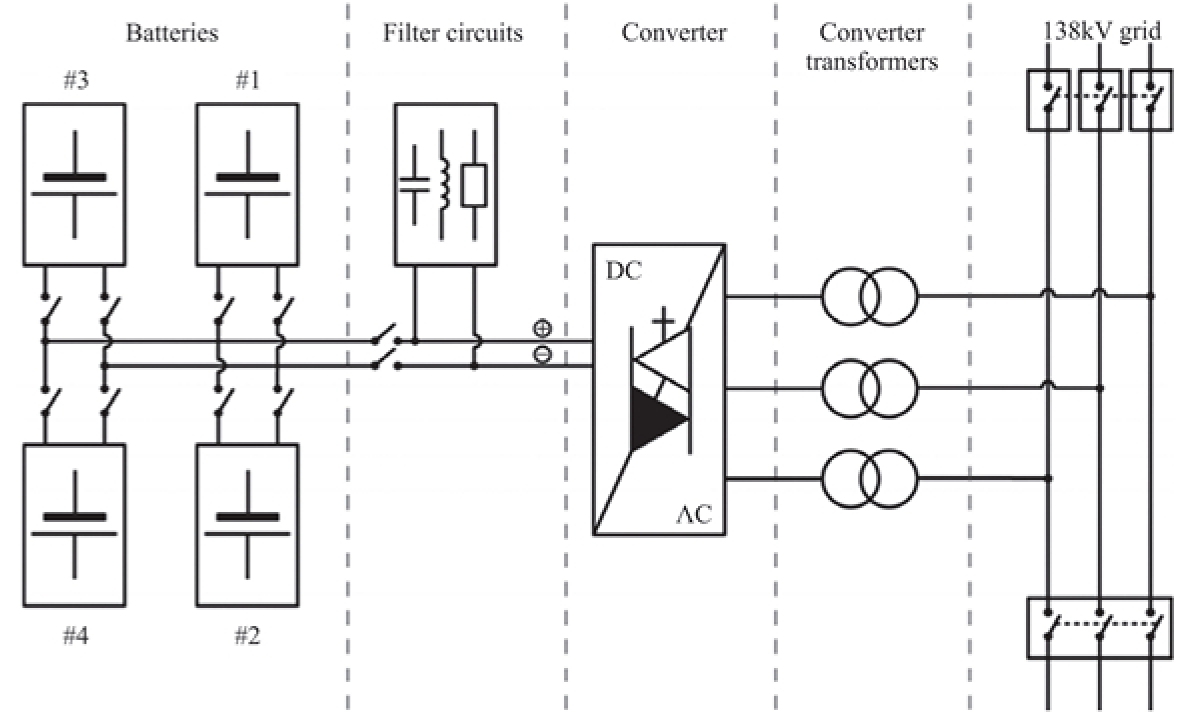


Figure 4.4: Electrical diagram of the BESS power conversion system [Credit: ABB Inc., www.abb.com/powereletronics].

Images of Ni-Cd batteries

Ni-Cd system of 3 MW was also commissioned for stabilizing wind-energy systems on the island of Bonaire in 2010. This was part of a project for the island to become the first community with 100% of its power derived from sustainable sources [38].

The reader may refer to manufacturer's manuals for more technical details and maintenance instructions, for example: SBS LLC manual or Alpha Technologies, 'Alpha Ni-Cd Pocket Plate Battery Technical Manual'.

4.3.1 Nickel Iron (NiFe) and Nickel Zinc (NiZn) Batteries

The NiFe battery consists of nickel (III) oxide-hydroxide plates as positive electrode and iron plates as negative electrode, with potassium hydroxide electrolyte. The active materials are placed in Ni-plated steel tubes or pouches with perforations. These batteries are robustly built, have extended cycle life and the utmost durability of all conventional chemical batteries. They are characterized by the highest deep discharge competences and most pliable charging schemes that make them most flavored chemistry for rough and harsh settings [31]. These batteries are rechargeble too.

Chemistry:

The half-cell reaction at the positive plate:

$$2\ Ni\ (OH)_2 + 2\ OH^- \leftrightarrow 2\ NiO(OH) + 2\ H_2O + 2\ e^-$$

at the negative plate:

$$Fe + 2\ OH^- \leftrightarrow Fe\ (OH)_2 + 2\ e^-$$

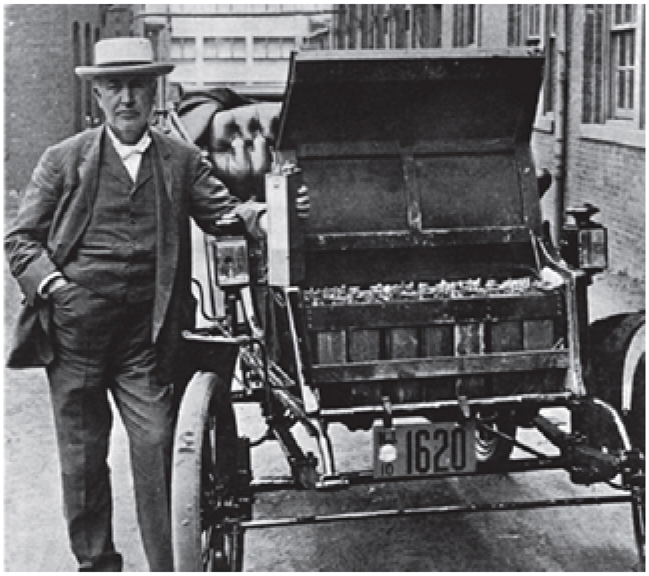
(left to right arrow is discharging, and right to left arrow is charging)

The open-circuit voltage (V_{oc}) is 1.4 volts and falls to 1.2 volts when discharging. The electrolyte is a blend of potassium hydroxide and lithium hydroxide, which is not used in charging or discharging. So, in contrast to lead-acid battery, the specific gravity of the electrolyte does not specify the state of charge [31]. To charge the NiFe battery, the voltage needed is 1.6 v per cell or more [Wikipedia, the free Encyclopedia, April 21, 2019]. Lithium hydroxide improves the performance of the cell. The equalization charge voltage is 1.65 volts.

Thomas Edison patented and marketed NiFe battery in 1901 in the United States and, proposed this battery as energy provider for electric vehicles, such as the Detroit Electric and Baker Electric. Edison asserted that the NiFe design was "far superior to batteries using lead plates and acid (Pb-acid)” [42].

However, because of certain disadvantages such as high production and upkeep costs, poor charge retention, large internal resistance, low specific energy and power densities, these batteries are replaced by lead-acid batteries when the latter entered the market. But, recent advances in NiFe have lowered the costs and enhanced energy and power-linked performance. Also, the recent versions are costlier than Pb-acid batteries but cheaper than Ni-Cd batteries. Their application in managing intermittent renewable power sources has come up again. Further, their use in electric vehicles known to run 150 Km on a single charge is increasing [31; 1].

Studies to improve NiFe batteries are now focused (a) on the sulfide, lithium and potassium additives, (b) on porous polymer separators, and (c) electro-precipitation methods for depositing nickel into porous and metal fiber electrodes efficiently. The main concerns still persistent with NiFe batteries are poor charge retention, heating issues during charge/discharge and some minor hydrogen venting problems [43].



Thomas A. Edison and his improved storage battery. Edison promoted Nickel-iron as being lighter and cleaner than lead-acid. Lower operational costs were to offset the higher initial cost. In 1901 Edison recognized the need for the electric car. He said that the same care should be given to the battery as the horse and railroad locomotive. [Credit: Scientific America New York, Jan. 14, 1911; @ https://batteryuniversity.com/learn/article/nickel_based_batteries]

Nickel Zinc batteries: NiZn battery comprises nickel oxide as the positive electrode and zinc metal as the negative electrode, and KOH as electrolyte. This type of battery shows a higher energy density than Ni-Cd batteries, by roughly 25%. Compared to traditional lead batteries, NiZn batteries have a higher energy-to-mass ratio and powerto-mass ratio. As a result, there is good potential for this battery system for application in intermittent renewable energy systems.

NiZn has a voltage of 1.6 V and is rechargeable. Though this battery type is known for nearly a century, the invention of a stabilized zinc electrode system has enabled this battery, in the last 2 decades, sustainable and economical compared to other rechargeable batteries in the market. [Wikipedia, free encyclopedia.]

Chemical reactions: At negative electrode:

$$Zn + 4\,OH^- \leftrightarrow Zn\,(OH)_4^{2-} + 2e^- \qquad (E^0 = -1.2\ V/SHE\ )$$

$$Zn\,(OH)_4^{2-} \leftrightarrow Zn(OH)_2 + 2OH^-$$

$$Zn\,(OH)_2 \leftrightarrow ZnO + H_2O$$

At positive electrode:

$$2\,NiO\,(OH) + 2\,H_2O + 2\,e^- \leftrightarrow 2\,Ni\,(OH)_2 + 2\,OH^- \quad (E^0 = +0.50\ V/SHE)$$

The complete reaction: $Zn + 2\,NiO\,(OH) + H_2O \leftrightarrow ZnO + 2\,Ni\,(OH)_2$

The specific energy of this chemistry is higher compared to other nickel-based batteries.

They can be discharged and charged quickly. They are sealed and maintenance-free, the environmental impact is insignificant, and can be fabricated with commonly obtainable materials [31]. But, the costs are high compared to lead-acid batteries and have low energy densities. The single biggest problem to adoption has been their short cycle life due to electrode shape change and dendrites, which reduce the cell discharging performance or, eventually, short out the cell. They have seen the primary application in small electric scooters and bicycles.

Recent research efforts have focused on improving the cycle life by examining the following approaches: (a) electrode and electrolyte additives, (b) upgraded separators, (d) changes in charging schemes, (e) changes in the synthesis of active materials. For instance, studies have shown that by adding mercury, heavy metals, and hydroxides, the stability of zinc electrode has enhanced and the loss of active material has decreased. Similarly, polymer binding has reduced shape change effects and consequently reducing zinc loss (and capacity loss) even more. Alkalinity reduction of electrolytes has displayed similar results. PVA film separators have improved flexibility without soaking and reduced shape change effects. Pulsed DC charging schemes are used to prolong life; and by using foams and nanomaterials for electrodes, the base capacities are enriched. Regardless of all these improvements, the cycle life of NiZn is still inadequate [43; 1].

Advantages: NiZn cells have a nominal voltage of 1.65 volts and full charge have an open-circuit voltage (V_{oc}) of 1.85V. This makes NiZn an exceptional substitute for electronic gadgets designed to use 1.5 V alkaline primary cells. The tools and apparatus designed for alkaline cells hardly operate correctly beneath an end-voltage based on 1.5 V when new. Both Ni-Cd and NiMH battery systems have nominal cell voltage of 1.2 V and get to this endpoint before they deliver all the charge they are capable of.

The cells manufactured in recent times are more potent with up to 800 cycles of lifespan, and can substitute Li-ion batteries in electric vehicles (EVs). Because of the higher cell voltage, smaller number of cells are enough for a given pack voltage than Ni-Cd and NiMH cells. They are characterized by low internal impedance, normally 5 milliohms, which facilitates high battery discharge rates, up to a temperature of 50°C.

NiZn batteries do not use materials that are difficult to recycle such as Hg, Pb, or Cd, or metal hydrides. Both elements, Ni and Zn are normally found in nature, and are fully reusable. NiZn cells do not use combustible active materials or organic electrolytes; the recently available cells use polymeric separators that lessen the dendrite formation. NiZn cells if appropriately designed can achieve high power density and low-temperature discharging, and ability to fully discharge 100% and recharge without any issues.

1,200Ah NiFe battery for solar homes
globalsources.com

1.6V 2500mAh NIZN Rechargeable
Battery gearbest.com In stock

4.3.2 Nickel-metal-hydride (NiMH)

A nickel-metal hydride battery, NiMH is a type of rechargeable battery. NiMH batteries were commercially introduced around 1995. The NiMH battery combines the proven positive electrode chemistry of the sealed Ni-Cd battery with the energy storage features of metal alloys developed for advanced hydrogen energy storage concepts [44a].

NiMH battery has the maximal nominal capacity, which is still 10 times less, compared to Ni-Cd and Pb-acid. In NiMH batteries, the negative electrode is mainly composed of hydrogen-absorbing alloy instead of cadmium. Usually, alloys of Lanthanum and rare earths that serve as a solid source of reduced hydrogen that can be oxidized to form protons are used. The substitution of Cd by hydrogen-absorbing alloy increases the battery’s electrical capacity (measured in Ah) for a given weight and volume and eliminates the toxic cadmium metal. Nickel hydroxide (NiOH) remains the positive electrode. The rest of the NiMH battery is similar to the Ni-Cd with a separator made of fine fibers, an alkaline electrolyte, a metal case and a sealing plate provided with a self-resealing safety vent. Slight changes in the application parameters between the 2 types of batteries exist.

The electrochemical reactions at the anode and cathode are represented as follows:

$$\text{Anode: } \mathrm{Ni\,(OH)_2 + OH^- \leftrightarrow NiO(OH) + H_2O + e^-}$$

$$\text{Cathode: } \mathrm{M + H_2O + e^- \leftrightarrow MH_{ab} + OH^-}$$

$$\text{Overall reaction: } \mathrm{Ni\,(OH)_2 + M \leftrightarrow NiO(OH) + MH_{ab}}$$

Here, M is hydrogen-absorbing alloy, and H_{ab} is absorbed hydrogen. The forward direction represents charging and reverse reaction, discharging.

As can be seen by the overall reaction, the principle behind a NiMH battery is while the cell is charging, H_2 travels from the positive to the negative electrode, and the opposite happens during discharge, and the electrolyte remains indifferent to the reaction; it means that the electrolyte neither increases nor decreases. Figure 4–5 shows the battery's charge and discharge mechanism. These are the valuable reactions happening at the respective boundary surfaces of the 2 electrodes; and the figure displays how the reactions proceed by the transfer of H+ ions (protons). The negative electrode made of hydrogen-absorbing alloy effectively decreases the gaseous oxygen emanating from the positive electrode (nickel hydroxide) during overcharge by enhancing the capacity of the negative electrode appropriately, as done in Ni-Cd batteries. If the battery's internal pressure is held persistent in this way, it is practicable to seal the battery.

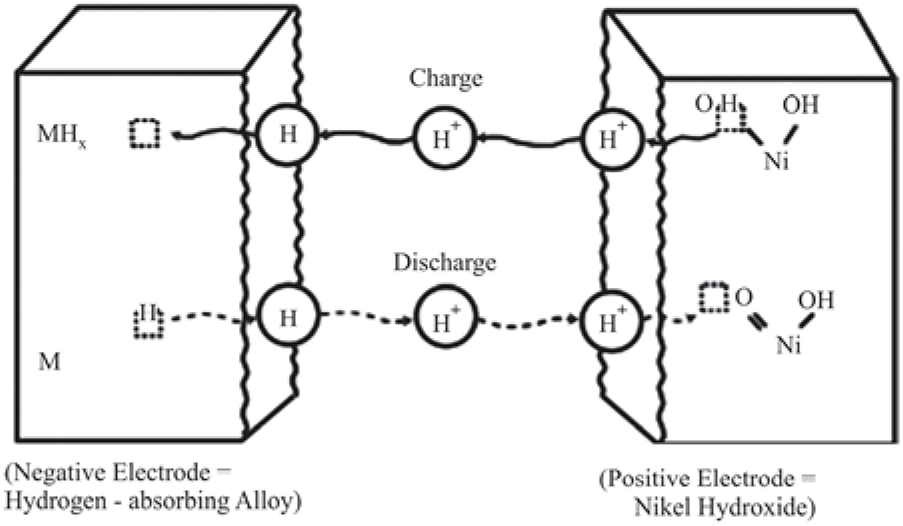


Figure 4.5: Charge and discharge mechanism in NiMH batteries (Source: [44b])

The concept of the NiMH battery-negative electrode originated in the 1970s, from studies on the storage of hydrogen for use as an alternative energy source.

The hydrogen-absorbong alloy combines 2 metals (A and B), one whose hydrides generate heat endo-thermically and the other whose hydrides generate heat exothermically to create the proper binding energy so that hydrogen can be sucked up and let go at or near normal temperature and pressure levels.

The alloys are categorized into the following types based on how metals A and B are alloyed: AB (e.g., TiFe), AB_2 (e.g., $ZnMn_2$), AB_5 (e.g., $LaNi_5$) and A_2B (e.g., Mg_2Ni). From the standpoint of charge and discharge efficiency and durability, these 2 types - AB_5 and AB_2 - are found appropriate. For instance, Panasonic focuses its attention on AB_5 type alloys, which feature high capacity, excellent charge and discharge efficiency, and excellent cycle life [44b].

A few metallic alloys were noticed to create hydrides that could absorb (and let go) hydrogen in volumes up to nearly a thousand times their own volume. A proper selection of the alloy constituents and quantities can ensure thermodynamics balance to allow the capture and release process to carry on at room ambient temperatures. More on this aspect will be seen in the later pages. The metal hydride electrode has a higher theoretical capacity, roughly 40%, than the cadmium electrode in a Ni-Cd battery. Hence, NiMH batteries offer higher energy densities by about 20% than the comparable Ni-Cd battery [45].

General features: NiMH differ from existing battery chemistry in that they rely on reactions with hydrogen-ion absorbing porous metal alloys.

NiMH systems are sealed, maintenance-free, have low internal resistance, have higher energy densities, about

50% better than Ni-Cd, long shelf life, cycle life of 3000 and rapid charge capabilities, can be deep cycled and operate well at temperatures, 0 to 50 C.

They are environmentally friendly, safer than Li-based cells in case of an accident or abuse due to the use of more benign active chemicals. This later property is particularly important in high power and automotive applications. Their expectancy life is typically 2 to 5 years.

Several factors such as battery capacity, working temperature, depth of discharge, charge and discharge current, excess charge and discharge, materials used in design, storage environment, and extent of life operation can affect NiMH (charge/ discharge) cycle life.

Some of these aspects can increase gas generation within the battery that can trigger the safety vent leading to lifelong weakening of the battery. Given the perfect controlled state of affairs, cycles up to 1000 can be realized. But, in practice, these factors can adversely impact the number of total cycles that may be accomplished [45]. Having the same voltage of 1.2 V as Ni-Cd cell, NiMH battery system can reach higher specific energy of around 75 Wh/kg, and decreased memory effect.

However, this battery undergoes drastic self-discharge, about 20% per day and lesser efficiency, thus becoming unattractive for electrical energy storage from intermittent renewable energy sources [46–49]. Moreover, they hold only moderate charge, and are much costlier than Li-ion batteries [1]. These drawbacks have caused a gradual shift to Li-ion cells. Nevertheless, the relative abundance of materials has favored them, on a larger scale, for use in electric vehicles (EVs) and low-power UPS systems [31].

Current studies in NiMH batteries mostly concentrate on improving the performance of the metal hydride electrode having characteristics such as long cycle life, high capacity, high rate of charge and discharge at a constant voltage, and retention capacity. Research focus in NiMH is also on aspects like improving specific power and performance at low temperatures [50]. Sintered plates are employed to increase porosity and charge retention [31]. Advances in materials are expected to change the electrode surface catalytic action at the interface of metal-electrolyte [50]. Exclusive activation processes are proposed for boosting power performance [51]. Substituting cobalt rich, zinc and manganese for nickel within the electrodes have upgraded temperature performance and minimized corrosion issues, resulting in increased cycle life [50, 51].If corrosion is well tackled, then decreasing the electrode particle size would improve power performance [51].

Applications: There is considerable interest in NiMH batteries for electric and hybrid vehicles. Since the sealed NiMH batteries are strong and much safer than Li-ion batteries, the hybrid vehicles (HVs) currently operate almost entirely with these batteries. The present-day costs of the NiMH batteries are about the same as lithium-ion batteries. In portable and mobile applications sealed NiMH batteries have been extensively replaced by lithium-ion batteries [37].

NiMH batteries find extensive application in the high-end portable electronic products, industrial standby applications such as UPS, combined solar applications, elevator safety systems, medical instruments and equipment, emergency lighting for buildings and trains, so on.

Safety Precautions: NiMH batteries are safe; however, like any other battery, they should be handled carefully with respect to these issues: (a) hydrogen generation under normal or foul circumstances should be treated as a potential safety issue to avert the buildup of hydrogen gas within the battery to hazardous levels, (b) generation of high currents on shorting (even by mistake!) are adequate enough to cause burns or ignite flammable materials, (c) the active materials in the negative electrode can flare up when exposed to air, and (d) the electrolyte being corrosive causes chemical burns. Therefore, battery should be preserved as an integral product [45]. Typical images if NiMH batteries are shown below.

4.3.3 ZnAg and ZnMn Batteries

Zinc silver oxide (ZnAg) batteries are familiar for their attractive features: (a) high-energy densities, (b) good low-temperature performance, (c) flat discharge curves (under high and low current drain), (d) low environmental impact, and (e) high durability. For larger scale applications, these batteries are not flavored due to the high cost of silver. So, their usage is restricted to small devices like hearing aids and watches [31], though, a few kilowatt-scale systems are in operation. These batteries are by and large single charge batteries with short lifetimes.

For military applications, to maintain a long back-up life, mechanical and automatic methods are used to actuate cells, thereby extending lifespan [31]. The progress in nanomaterials development resulted in extra advances in the design of cathode. The polymerization process has resulted in better-quality layered separators. In recent times, rechargeable ZnAg batteries of low cycle life are introduced for higher power mobile applications [52].

Zinc manganese dioxide (ZnMn) alkaline batteries are currently the most permeating primary battery useful for portable devices. This high usage has created more landfill waste, with low recovery rates of zinc, manganese and steel remain [53]. Their appropriate features such as low-temperature and low/high current drain performance as well as low internal resistance make them attractive and popular. Though the discharge curves are not as flat as in the case of ZnAg batteries, the costs are viable. Their long shelf life (but, shorter than ZnAg in un-activated state) makes them more suited for unrestrained storage in intermittent energy usage applications.

The new batteries in the market have larger resistance to internal pressure accumulation leading to leakage [31]. With the surge in power demands in portable electronics, investigations in high drain ZnMn battery chemistries have intensified; for instance, the application of nanomaterials is a major step in this direction [54]. Efforts to increase cycle life increase the fabrication of bipolar rechargeable ZnMn systems [55], and with the emergence of new devices, new charging schemes have emanated. Additions of bismuth have also been attempted to extend the cycle life of the battery [56].

Progress in 3D printing has created procedures for fabricating printable versions of ZnMn cells [57, 58]. Recent improvement efforts regard to flow-assisted alkaline batteries have also examined the possibility of large-scale grid-level applications [59].

Progress: Zinc-based electrochemical devices are receiving considerable attention for useful energy storage because they are distinct with respect to low-cost and high safety. However, their limited output voltage and insufficient energy density compared to more conventional Li-ion batteries have highly restricted their grid-scale application. Focused studies have been in progress addressing these issues. For instance, Chao et al. 2019 [60] suggested “a latent high-voltage MnO_2 electrolysis process in a conventional Zn-ion battery and report a new electrolytic Zn-MnO_2 system, via enabled proton and electron dynamics, that maximizes the electrolysis process. Compared with other Zn-based electrochemical devices, this new electrolytic Zn-MnO_2 battery has a record-high output voltage of 1.95 V and imposing a gravimetric capacity of about 570 mAh per gram, with a record energy density of approximately 409 Wh/kg, when both anode and cathode active materials are taken into consideration. The cost was conservatively estimated at <US$ 10 per kWh. This result opens a new opportunity for developing Zn-based batteries, and should be of immediate benefit for low-cost practical energy storage and grid-scale applications.”

4.4 Lithium-ion Batteries

A lithium-ion (Li-ion) battery technology is a highly mature technology in which lithium ions play a key role in the battery’s electrochemistry. During discharge time, lithium atoms in the anode are ionized, and the lithium ions leave the anode and pass through the electrolyte toward the cathode. There, they recombine with their electrons and electrically get neutralized. The lithium ions are too small to be able to move through a micro-permeable separator positioned between the anode and cathode. Li-ion batteries are characterized by a very high voltage and charge storage per unit mass and unit volume because of lithium’s small size.

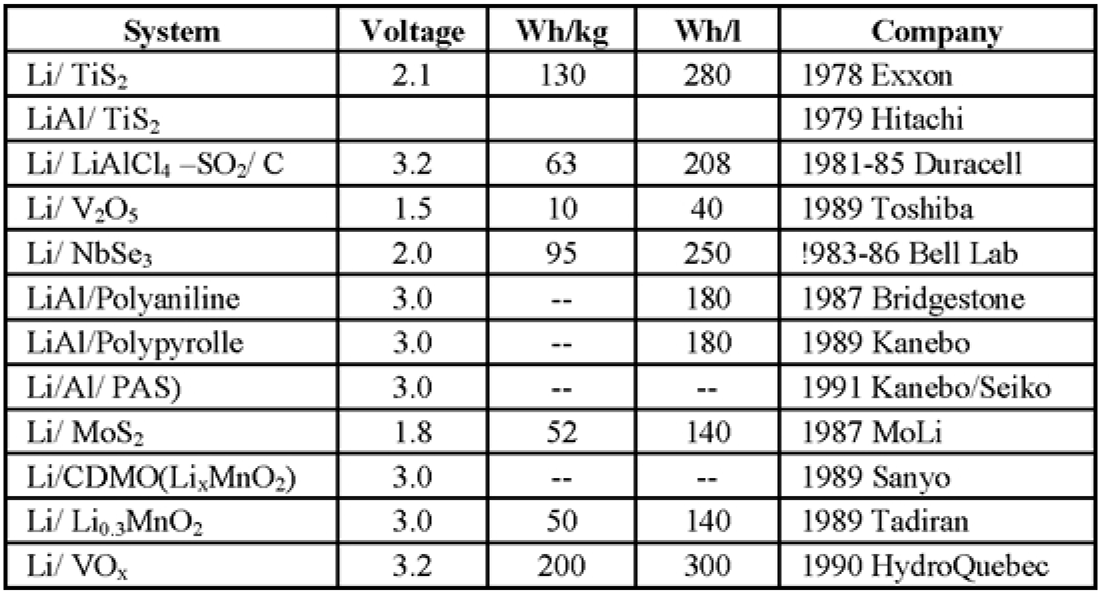
4.4.1 Lithium Metal Batteries

The rechargeable Pb-acid and the Zn-MnO2 batteries, which have a long history and advanced technical maturity are the major battery systems in use. Compared to lead and zinc in the traditional batteries, lithium has a low atomic number and high electrode potential that results in significantly high-energy density for a Li battery. However, the progress achieved in high-energy Li battery technology has not been unchallenging. An entirely a new system approach and evolution of innovative knowhow regard to new electrodes and non-aqueous electrolytes are most needed to carry on the consistent progress of Li- battery systems.

The research work of Harris in 1958 created interest in lithium batteries [61]. This work eventually led to the development and commercialization of various primary lithium cells during the 1970s. Primary batteries with lithium-metal anode using non-aqueous electrolytes such as propylene carbonate-lithium perchlorate and lithium-negative electrodes were fabricated in the 1970s. Matsushita presented a lithium-carbon monofluoride (Li-CF_x) primary cell in 1973, and Sanyo brought in primary Li-MnO_2 cells in 1975. These cells were used in applications such as LED fishing floats, hand cameras, and memory back-up situations.

Intense development studies were then started to transform the primary cells into high-energy density *rechargeable cells*. Table 4.2 provides the list of Li-metal battery systems developed by different organizations along with the corresponding parameters [62].

Table 4.2: Development of Li-metal battery systems by different Companies [62].



System	Voltage	Wh/kg	Wh/l	Company
Li/ TiS_2	2.1	130	280	1978 Exxon
LiAl/ TiS_2				1979 Hitachi
Li/ $LiAlCl_4$ –SO_2/ C	3.2	63	208	1981-85 Duracell
Li/ V_2O_5	1.5	10	40	1989 Toshiba
Li/ $NbSe_3$	2.0	95	250	!983-86 Bell Lab
LiAl/Polyaniline	3.0	--	180	1987 Bridgestone
LiAl/Polypyrolle	3.0	--	180	1989 Kanebo
Li/Al/ PAS)	3.0	--	--	1991 Kanebo/Seiko
Li/ MoS_2	1.8	52	140	1987 MoLi
Li/CDMO(Li_xMnO_2)	3.0	--	--	1989 Sanyo
Li/ $Li_{0.3}MnO_2$	3.0	50	140	1989 Tadiran
Li/ VO_x	3.2	200	300	1990 HydroQuebec

During the 2 decades, the 1970s and 1980s, the development focus was on ‘inorganic cathode compounds’. Conducting-type polymer materials, mainly polyacetylene, were produced as potential negative and positive electrode materials. But, these polymers had less density than water, and the batteries fabricated using these materials, except polyacene (PAS) battery, provided no advantage when it was enlarged. The low-density conducting-polymer cathodes were successfully used for coin cells used for memory back-up.

Also, this period witnessed the development of rechargeable lithium batteries using lithium insertion compounds as positive electrodes. The first cells of this type appeared when Exxon tried commercializing Li/TiS_2 system and later Li/MoS_2 system by Moli Energy. These were low voltage systems operating near 2 volts. Whittingham [63] reviewed the properties and preparation of many insertion compounds and discussed the intercalation reaction. The most prominent of these compounds to be used in batteries were V_2O_5, V_6O_{13} and MnO_2. All of these systems continued to use metallic lithium anodes. The real and obvious safety problems limited the commercial use of rechargeable lithium batteries that used metallic lithium anodes.

Li-metal anodes tended to form dendrites and powder deposits on recharging, which created main safety concerns. The high-performance perchlorate electrolyte was withdrawn from the battery fabrication from the safety point because dendrite formation and reactive fine powder deposits were noticed during recharge.

In 1989, the manufacturer, Moli Energy observed the heat generation concerning Li-metal in an AA-size cell. So, the anode material was shifted to lithium-aluminum (LiAl) alloy for greater safety in coin cells, though the metallurgy of the alloy proved undesirable for wound AA-size cells. Then, a dioxolane-based electrolyte that freely polymerized at temperatures above 110°C emerged [64a]. The rechargeable Li-metal cells are now limited mainly to small capacity coin cells.

An early lithium battery that is still in use is based on the electrochemical system LiAl-PAS. In association with a solar photovoltaic cell, this battery system offers an appropriate and compact power source. These power sources are now used widely for road sign night time illumination or similar applications in remote areas as a capacitor PAS-PAS or Li-doped PAHs-PAS hybrid battery. PAH (polycyclic aromatic hydrocarbons) is the reformed structure from PAS [64b, c]. Some other lithium alloys are also being developed for use as active materials for Li battery [62].

4.4.2 Emergence of Lithium-ion Cells

Meanwhile, Steele proposed graphite and layered sulfide as potential electrode materials for a lithium-ion battery working with a non-aqueous liquid electrolyte [65]. After experiencing with the transition metal chalcogenides, the higher voltage metal oxides (oxides of Ni, Co, or Mn) emerged [66a, b; 67], which are the source for most of the cathodes used in commercial lithium-ion cells. Almost simultaneously, the model of lithium-ion cells was examined with 2 insertion electrodes cycling lithium ions between them, without using a metallic lithium anode [68, 69].

Considerable R&D was witnessed in the following decade, on innovative battery systems based on the insertion and removal of lithium ions into host compounds that function as electrodes [66b]. Much of the research was related to finding a suitable material to host lithium ions as a battery-negative. This idea is old; Steele and Armand put forward this idea in the 1970s [65, 70, 71]. In 1991, finally the first lithium-ion cell based on C/ $LiCoO_2$ was brought into the market by Sony. These cells ensured a V_{OC} of 4.2 V and an operational voltage of 3.6 V [72].

Recently, portable power applications due to the miniaturization of electronic machines continue to drive R&D of advanced battery systems. Often, a system is considered based on the extra energy content and portability rather than economics. This has been true of Li battery technologies for the past 30 years and for the newly evolved Li-ion battery systems.

The chemistry of Li-ion battery: The lithium-ion battery was conceived and developed by Japanese company, Asahi Kasei [73]. It was first commercialized by Sony [74] in 1991, followed by A&T Battery Co., in 1992, and quickly became popular due to its high-energy density and good performance. In a Li-ion battery, the cathode is made of a lithium-metal oxide, such as $LiCoO_2$ earlier and $LiMO_2$ or $LiNiO_2$ later, and the anode is made of graphitic carbon. Carbon is a leading anode material in commercial Li-ion batteries because of its favorable electrochemical properties in addition to its attractive cost and easy availability. The chemical diffusion coefficient for lithium in carbon is of the order of 10 sq. cm/s. Amorphous carbons are favored as potential anode materials due to their numerous suitable properties: (i) higher lithium uptake, much higher than the maximum of 372 mAh/g that a graphite structure offers, (ii) their flexibility for alterations by changing the type of organic precursor and temperature pattern, and (iii) ability for proper cycling [66b].

The most commonly used combination is $LiCoO_2$ and graphite used in portable electronic devices. The electrolyte is normally a non-aqueous organic liquid such as $LiPF_6$ containing dissolved lithium salts, such as $LiClO_4$ [13, 75, 76]. A separator is placed to prevent short-circuit between the electrodes and accompanying risk of flame burst.

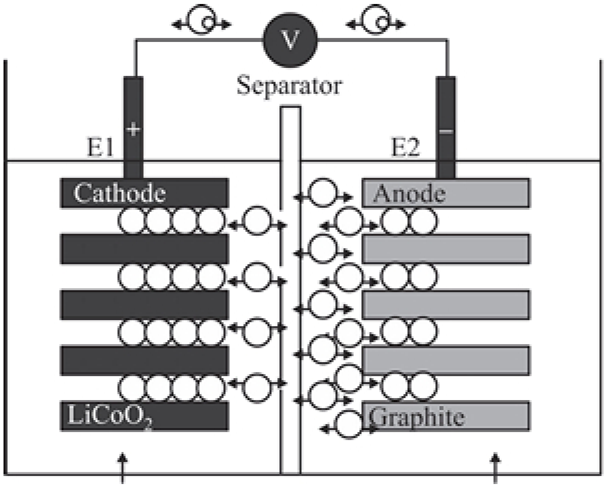


Figure 4.6: Principle of Li-ion battery; (Source: Sandia report [80])

During discharging, lithium atoms oxidized to lithium ions (Li^+). The released electron flow through the external circuit to the cathode, whereas lithium ions pass through the electrolyte to the cathode. There, Li^+ reacts with the cobalt oxide (CoO_2) and the electrons creating lithium cobalt oxide ($LiCoO_2$) [77]. The principle is schematically shown in Figure 4–6. The chemical reactions at the anode and cathode are

$$\text{At the anode, } LiC_6 \leftrightarrow Li^+ + e^- + 6C$$

$$\text{At the cathode, } CoO_2 + Li^+ + e^- \leftrightarrow LiCoO_2$$

If different lithium-metal oxides ($LiMO_2$) are used to form the cathode [78, 79], the reactions are shown in generalized form:

$$Li_xC \leftrightarrow Li^+ + xe^- + C$$

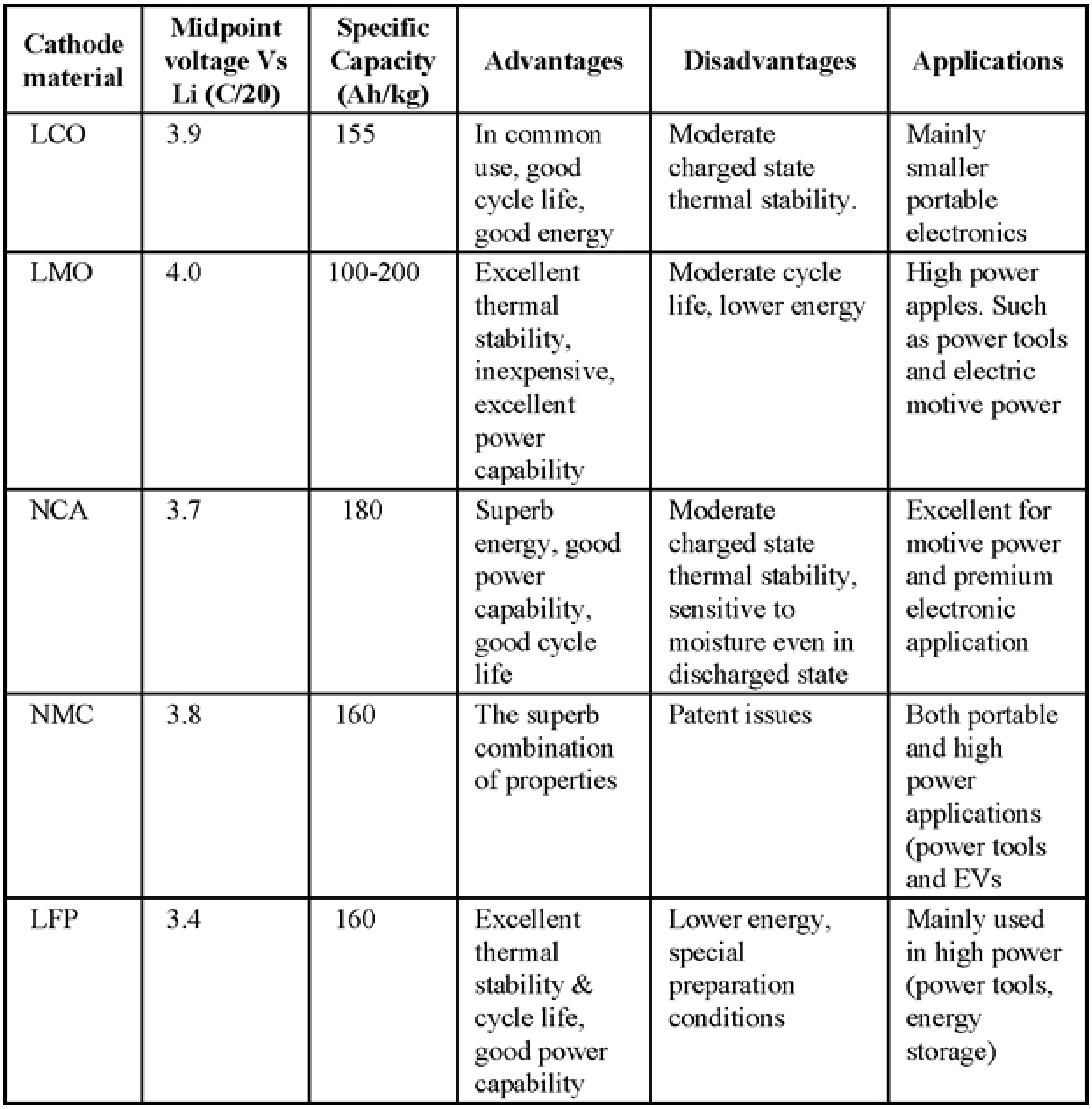
$$LiMO_2 + xLi^+ + xe^- \leftrightarrow Li_{1-x}MO_2$$

Specific energy, Specific power and storage efficiency: Lithium-ion batteries have better benefits over Ni-Cd and

Pb-acid batteries. Although the original Sony Li-ion battery with coke-negative electrode had specific energy (energy density) of 80 Wh/kg [81], with continuous progress in the improvement of negative electrode, the present commercial lithium-ion batteries provide better features: (a) highest energy density (265 Wh/kg) [Li-ion Battery: Clean Energy Institute], (b) specific power of 500–2000 W/kg and nominal voltage of 3.7 V, 3 times higher compared to Ni-Cd or NiMH systems, (c) energy storage efficiency of 97% [13, 82], (d) self-discharge rate of 0.03%, (e) no memory effect, (f) long life, (g) environmental- friendly operation and (h) extremely low maintenance [83 - 85a].

Cathode materials: A detailed analysis on cathode materials was given by Shukla et al. [66b]. The present cathode materials used in commercial lithium-ion batteries are the 2 original ones, $LiCoO_2$ (LCO) and $LiMn_2O_4$ (LMO), and newly emerged $LiNi_{0.8}Co_{0.15}Al_{0.05}$ (NCA), $LiNi_xMn_yCo_{1-x-y}O_2$ (NMC), and $LiFePO_4$ (LFP). Each of these materials has merits and demerits and has been applied to different applications, shown in Table 4.3.

Table 4.3: Various cathode materials used in commercial lithium-ion batteries. (Source: [86])



Cathode material	Midpoint voltage Vs Li (C/20)	Specific Capacity (Ah/kg)	Advantages	Disadvantages	Applications
LCO	3.9	155	In common use, good cycle life, good energy	Moderate charged state thermal stability.	Mainly smaller portable electronics
LMO	4.0	100-200	Excellent thermal stability, inexpensive, excellent power capability	Moderate cycle life, lower energy	High power apples. Such as power tools and electric motive power
NCA	3.7	180	Superb energy, good power capability, good cycle life	Moderate charged state thermal stability, sensitive to moisture even in discharged state	Excellent for motive power and premium electronic application
NMC	3.8	160	The superb combination of properties	Patent issues	Both portable and high power applications (power tools and EVs
LFP	3.4	160	Excellent thermal stability & cycle life, good power capability	Lower energy, special preparation conditions	Mainly used in high power (power tools, energy storage)

Li-ion with manganese spinel was first published in 1983. The structural design forms a 3D spinel structure that increases ion-flow on the electrode, which lowers internal resistance and enhances the current manipulation. High thermal stability and greater safety are other gains of the spinel structure; but the cycle life is restricted. One of the best Li-ion systems is a cathode combination of nickel-manganese-cobalt (NMC). Like Li-manganese, this system can be adjusted to function as energy or power cells. In 1996, researchers at the University of Texas and others revealed phosphate could be cathode stuff for rechargeable Li batteries. Li-phosphate (LFP) system with nanoscale phosphate cathode material provides good electrochemical behavior with low resistance. The main advantages of this system are high current rating, extended cycle life, satisfactory thermal stability, higher safety, and tolerance if neglected [85b].

According to Pillot [81], LCO is still the largest cathode material in use followed by NMC, which is growing. The others, LMO, LFP and LCO are used in that order. The fast increase in the usage of NMC is, to some extent, the material's flexibility for both high-energy and high power applications. It is also used regularly in consumer electronics because manufacturing is easier compared to NCA, and forming various cell geometries with this material are possible.

Advantages: Li-ion battery is considered a good option for applications where milliseconds response time, small dimension and/or weight of equipment is important [1, 13, 37, 84]. Their small size and low weight make them market leader for portable applications such as smartphones and laptops. They have also proved to be the most promising option in electric vehicles [6] from a clean energy perspective. Currently, the bestselling electric cars, the Nissan Leaf and the Tesla Model S, both use Li-ion batteries as their primary fuel source [Clean Energy Institute].

Li-ion batteries are earnestly contemplated for numerous utility gridsupport applications such as DESS (community energy storage), portable systems for gridsupport, marketable end-user energy management, household back-up energy controlling systems, frequency regulation, and smoothing of intermittent renewable power. Stationary markets for Li-ion batteries could exceed those for transportation [88].

The Li-ion battery applications broadly are in 3 main areas: consumer electronics and devices, transportation, and grid energy and industry.

(a) Consumer electronics and Devices consisting of smartphones, laptops, tablets, power tools and personal care (electric shaver, toothbrush etc) are a 'gradually saturated market';

(b) Transportation that involves cars, passenger buses, forklifts, autobicycles and so on is a 'growing' market, and

(c) Grid energy and industry consisting of grid energy, renewable energy, stationary energy storage and portable energy storage is also a 'growing' market.

Disadvantages: The main drawbacks, which restrict their use in large-scale applications are (a) the cycle depth of discharge, which can affect the battery's lifetime, and (b) the need for an on-board computer to manage its operation, which increases its overall cost [46]. Another disadvantage is their sensitivity to high temperatures and the need to provide with a battery management system at least to protect overvoltage, overtemperature and over-current [52, 90].The optimum temperature range of their operation is around -30° to 60°C [23].Lithium is corrosive and may create fires on exposure to moisture/dampness. The electrolyte used is toxic, and hence these units should be recycled with utmost care.

Li-ion batteries are typically available in preset sizes. In larger energy storage systems, they are typically connected in series/parallel groupings to get the desired power and energy capacity [22].

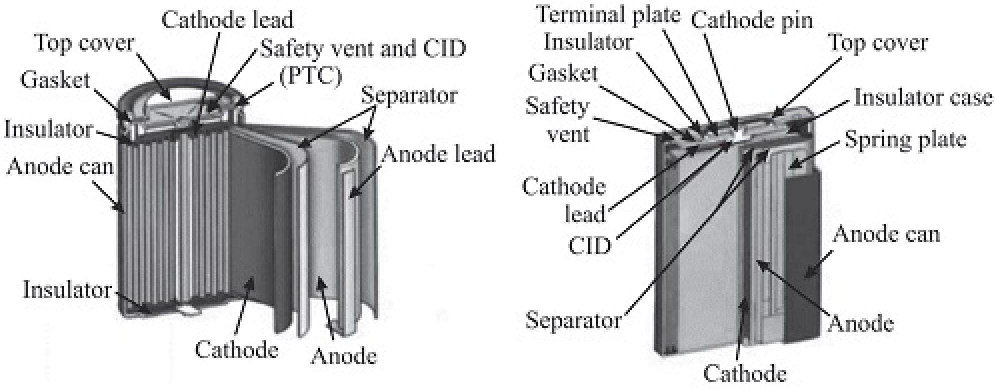


Figure 4.7: Schematic of cylindrical cell (left), and prismatic cell (right), (Source: [80])

Research focus: There are different Li-ion chemistry, each with specific power Vs energy characteristics. The focus of current research includes (a) improving battery power capability using nanoscale materials, and (b) boosting battery-specific energy by originating innovative electrode materials and electrolytes.

Facilities: Several firms are involved using Li-ion batteries in the utilityscale energy market. A few instances are cited here.

(i) AES Energy Storage of the US had been commercially operating a Li-ion BES system in New York, 8 MW/2MWh set up in 2010 enlarged to 16 MW in 2011, for supplying frequency regulation [93, 91]. AES also installed a 32 MW/8 MWh LiB system (Laurel Mountain) in 2011 for supporting a 98 MW wind generation plant [91, 92];

(ii) Cranborne Energy Storage, Somerset, UK, installed a 250 kW/500 kWh Tesla Powerpack Li-ion storage system to integrate with a 500 kW solar PV power generation system. According to Tesla, the powerpacks can be designed to deliver power and energy capacity to the grid as a stand-alone advantage, and provide a frequency regulation, voltage control, and spinning reserve facilities. The standard Tesla unit is 50 kW/210 kWh working with a round-trip efficiency of 88% [95].

(iii) In 2014, Toshiba supplied to Tohoku Electric Power Co. a 40 MW/20 MWh Li-ion battery system to regulate frequency changes caused by power output fluctuations from renewables. In Feb 2016, another 40MW/40MWh Li-ion battery energy storage system, one of the largest globally, started operating. This system is meant to manage and improve the balance of fluctuating renewable energy by storing renewable electricity when supply exceeds demand and release when the demand is high [96].

(iv) San Diego Gas & Electric installed a 30 MW/120 MWh Li-ion battery energy storage in Escondido, CA, USA; STEAG Energy Services began a 90 MW Li-Ion battery storage installation program in Germany; a 100 MW facility is being put up in Long Beach, CA, by Edison.

(v) Tesla 100 MW/129 MWh lithium-ion system was installed next to Neoen’s 309 MWe Hornsdale wind farm near Jamestown in Southern Australia. The state government contracted about 70 MW of the capacity to provide grid stability and system security that include frequency control ancillary services (FCAS) in time scales of 6 seconds to 5 minutes. The rest, 30 MW is used as load shifting by Neoen for the wind farm located nearby. It has established a speedy response for FCAS, providing up to 8 MW for about 4 seconds before FCAS intervenes while frequency dropped below 49.8 Hz. [95].

The Hornsdale Power Reserve, a 100 MW battery storage facility in South Australia. Credit: Tesla

(vi) Eneco (a Dutch utility) and Mitsubishi have set up a 48 MW/50 MWh lithium-ion battery in Jardelund, northern Germany to deliver primary reserve to the grid and enhance grid stability. This is the region where many wind turbines are working and faced with grid congestion issues.

(vii) SolarCity is using 272 Tesla Powerpacks (Li-ion storage system) for its 13 MW/52 MWh Kaua’i Island solar PV project in Hawaii, to meet evening peak demand. KIUC is also commissioning a project with 28 MWe solar farm and 20 MW/100 MWh battery system [95].

(viii) Li-ion batteries are widely used currently in electric vehicles (EVs) and hybrid electric vehicles. Auto analysts at Bernstein predicted in 2017 that EVs would have a share of 40% of global vehicle purchases in 2 decades' time. Since almost 100 million vehicles are now produced globally, the EV annual market will be 40 million, even if the total global vehicle production remains same. Supposing that battery prices reach parity with that of an IC engine (~$6000), a battery industry worth $240 billion is now in the creation [97]. See 'Battery systems for Electric Vehicles' below.

Prospects and Limitations: Li-ion batteries have specific energy and energy densities close to those of alkaline primary batteries, higher than most existing rechargeable batteries. Additionally, Li-ion devices have excellent charge retention, high cell voltages, excellent low temperature performance, long cycle life and high depth of discharge and rapidly lowering costs [31].

Simultaneously, with this battery chemistry, there are some concerns regarding safety. Surpassing maximum charge voltage or physical damage to the device can cause thermal runaway, venting, fire and finally outburst. Additionally, untimely discharge cut-off or deep discharge can produce long-lasting effects on battery capacity. This shows that charging circuitry is complex and necessitates single cell watching or checking.

The recycling of these batteries are challenging [98] and concerns over the readiness of enough resources for large-scale storage applications persist [99]. Nonetheless, they are more environmentally sound compared to other battery types.

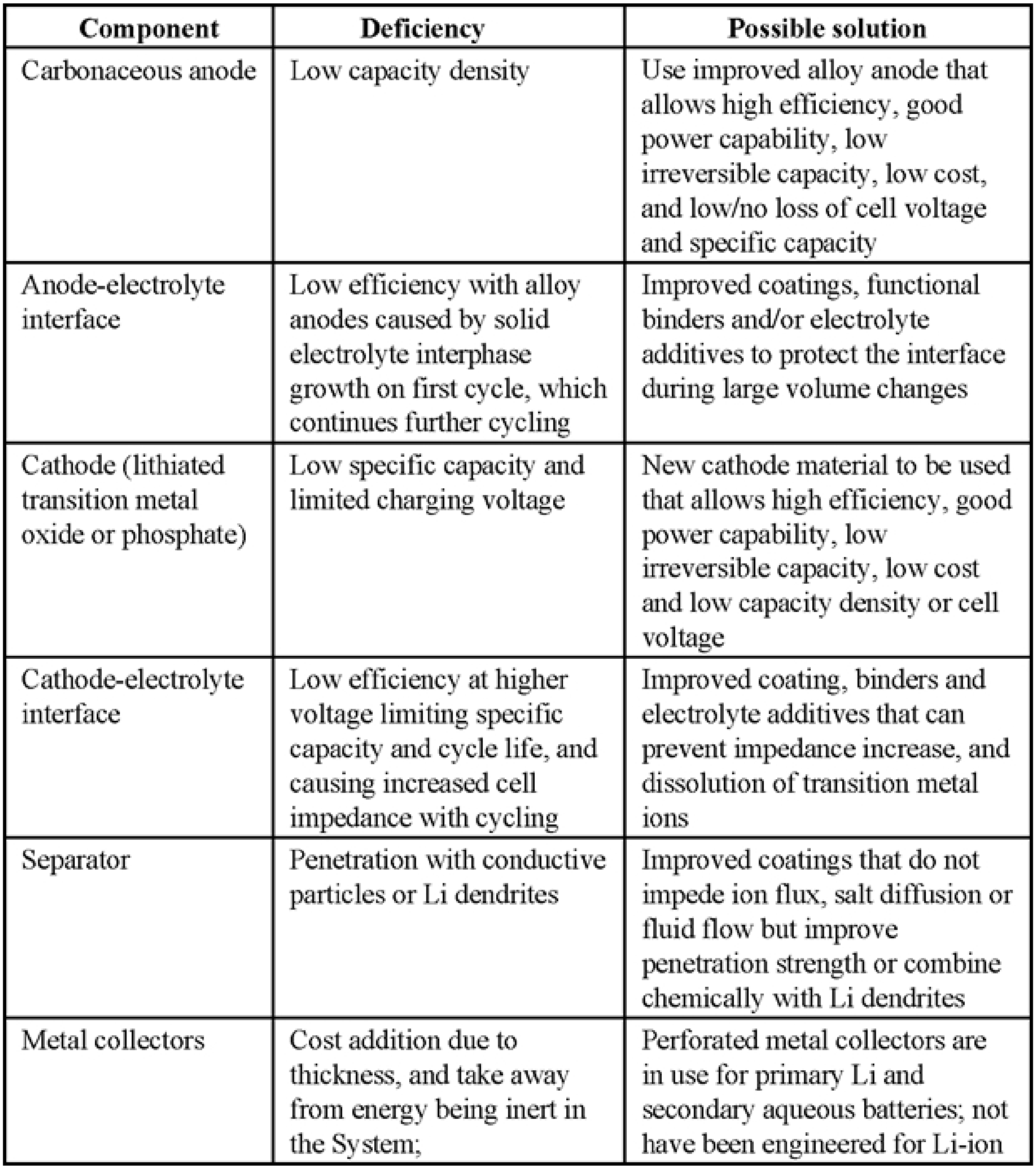
Carbon fiber and nanocomposite enhancements in anode materials are intended to achieve higher power, greater reversibility and longer cycle life [100]. Great interest has been evinced to employ carbon nanotubes (CNTs) as anodes in Li-ion batteries. Multi-walled carbon nanotubes (MWCNTs) are observed attractive as high-capacity anodes for these storage systems. CNTs have good chemical stability, and possess high tensile strength (~50 GPa) and shear strength (~500 MPa), which hold promise in improving the longevity of the anode [66b].

Using solid electrolytes and electrolyte salts has given rise to decreased acidity and greater stability, which support reducing safety risks [100]. Layered cathode usage besides incorporating internal electronics has been suggested for the recent battery designs [100, 101]. Research studies focus mainly on changes in electrolyte and negative electrode. These changes include the initiation of reversible intercalation, electrolyte polymerization (eg. plastic lithium-ion thin film batteries), gel-coated micro-porous separators (eg. lithium-ion polymer batteries) and several more. Further progress comprising the use of meso-porous materials and aerogels, and the use of metal oxides in positive electrodes allow more prospects [102, 100]. However, some researchers argue that lithium chemistry is in early stages and much room for improvement exists [102, 1].

Larger scale production of Li-ion batteries should trigger further manufacturing process innovation.

Recently Blomgren [86] discusses the development of Li-ion battery technology since it made its first entry into the market and the technology’s future. There has been significant progress in new materials, new battery concepts and cell designs and so on related to lithium-ion battery technology (See the next section). Table 4.4 shows the main deficiencies and possible remedies [86]. Successful results from the suggested studies could yield batteries having specific energies of 400 Wh/kg and reasonable power density. This would mean, about 60% improvement over the best cells of today [86].

Table 4.4: Main deficiencies and possible remedies [86].



Component	Deficiency	Possible solution
Carbonaceous anode	Low capacity density	Use improved alloy anode that allows high efficiency, good power capability, low irreversible capacity, low cost, and low/no loss of cell voltage and specific capacity
Anode-electrolyte interface	Low efficiency with alloy anodes caused by solid electrolyte interphase growth on first cycle, which continues further cycling	Improved coatings, functional binders and/or electrolyte additives to protect the interface during large volume changes
Cathode (lithiated transition metal oxide or phosphate)	Low specific capacity and limited charging voltage	New cathode material to be used that allows high efficiency, good power capability, low irreversible capacity, low cost and low capacity density or cell voltage
Cathode-electrolyte interface	Low efficiency at higher voltage limiting specific capacity and cycle life, and causing increased cell impedance with cycling	Improved coating, binders and electrolyte additives that can prevent impedance increase, and dissolution of transition metal ions
Separator	Penetration with conductive particles or Li dendrites	Improved coatings that do not impede ion flux, salt diffusion or fluid flow but improve penetration strength or combine chemically with Li dendrites
Metal collectors	Cost addition due to thickness, and take away from energy being inert in the System;	Perforated metal collectors are in use for primary Li and secondary aqueous batteries; not have been engineered for Li-ion

4.4.3 Batteries for Electrical Vehicles - Development Path

Nearly 25% of global energy-related GHG emissions at present are contributed by transport vehicles according to IEA. Therefore, alternate fuel-driven and electric vehicles (EVs) must be developed urgently.

The invention of rechargeable Pb-acid battery by Gaston Plante of France in 1859 [103] saw the cars to run on electricity. Though they were replaced gradually by gasoline-powered vehicles, which have better range, speed and relatively low cost since 1910, the oil embargo and the energy crisis in 1970s revived electric vehicles again [104]. In the next several decades, the EV market was protected by Pb-acid batteries (the first generation, General Motor's EV1 [105, 106] with a range 80–100 miles), and NiMH batteries (the second generation with range, 100–140 miles [107]) in succession.

NiMH batteries have greater energy density than Pb-acid ones, allowing the battery system to be contained within a smaller space. But NiMH batteries have somewhat lower charging efficiencies, and a major problem with self-discharge (which is up to 12.5% per day under ussual room temperature conditions) that make worse when they must work at high temperatures [109]. Due to this behavior, NiMH batteries are unfeasible for hotter situations/locations [108]. Additionally, poor sales and narrow competitiveness with conventional internal combustion engines, forced GM to cancel the EV1 project eventually.

In 1991, rechargeable Li-ion batteries (LIB) with energy density > 150 Wh per kg [110] entered the market and found to be the most suitable compared to Pb-acid or NiMH batteries for next-generation EVs because of their flexibility, higher energy and power densities, low self-discharge rate, lower costs, and smaller and lighter cell designs [111–113].

But, compared to internal combustion engine vehicles, LIB-driven EVs still suffer from battery issues such as ranges, charging rates, lifetime, high cost safety, reliability, limited charging infrastructures, thus slowing down their widespread adoption [100, 114].

Since battery performance and costs are the 2 main factors, a further increase in battery energy density to meet a driving range of at least 300 miles per charge and reduced battery costs of around $125 per kWh are obligatory in the near future. Additionally, progress in the battery lifetime (at least 10 years), safety, and reliability, and charging infrastructure, government incentives are also needed.

Many countries strongly support the development of EVs. For example, the USA has pledged $2.4 billion in federal grants to support the growth of batteries and next-generation EVs [115], and the European Union has invested EUR 43 billion in EV-related research (EVUE 2012), likely to increase to EUR 225 billion [116]. China is investing US$15 billion in the EV industry [117].

Major German carmakers, Volkswagen, Daimler and BMW Groups, committed in 2017 investments of EUR 50 billion to develop electric automobiles. Daimler’s Mercedes Benz plans to invest EUR 10 billion in electrification [118].

As for battery industry, Tesla is building new factories in Nevada (USA) with the projected capacity of 150 GWh per year [119]. The LIB production is rapidly expanding for the transportation sector, along with grid and industrial energy storage and consumer electronics and devices.

Battery Market and costs: Over the decade, 2006–2016, the LIB production increased six-fold, from 11 GWh to 78 GWh [120], and the global capacity is predicted to reach 125 GWh in 2022, 220 GWh in 2025 and 390 GWh in 2030 [121]. But the global market share of new plug-in EVs (PEVs) was low at 0.86% in 2016, up from 0.62% in 2015 and 0.38% in 2014 (IEA).Several countries have initiated incentive policies for pushing EV development and have given forecasts for future EV market, largely due to falling battery prices and increasing EV ranges. Swedish firm Volvo has indicated that it would only develop hybrid, plug-in hybrid or fully electric cars from 2019 [102].

The emerging market for electric vehicles (EVs) has been the primary driver of progress in Li-ion batteries recently, and this market will continue to provide an advantage over other technologies in the near future [123].

Despite these encouraging trends, the current EV production is still in its infancy and many future factors are uncertain. The governments, industry, and R&D and financial institutions must work together to overcome several barriers.

The EV market was valued US$ 171.26 billion in 2020, and it is expected to reach a value of US$ 725.14 billion by 2026, registering a CAGR of around 27.19% during 2021–2026 [Report Linker.com: Electric Vehicle market - Growth, Trends, COVID-19 impact and Forecasts (2021–2026), Oct 26, 2021].

Lithium and cobalt resources: The U.S Geological Survey (USGS) has estimated in 2011 that total Li resources are around 29 Mrs. Until recently, Li was used for various industrial purposes (lubricants, aluminum production, catalysts for rubber production etc.) [124]. But, the major use of lithium was for batteries, around 35%, in 2015 [125] and expected to grow to 70% in 2025 that includes 38% for automotive applications.

Cobalt is also a critical element in cathode materials because it enables increased energy density and structural stability, despite its toxicity, high price and limited production. Cobalt's use in the battery industry accounted for 50% of the total in 2017 [126].

State-of-the-Art Li-Ion chemistry for Automotive Batteries

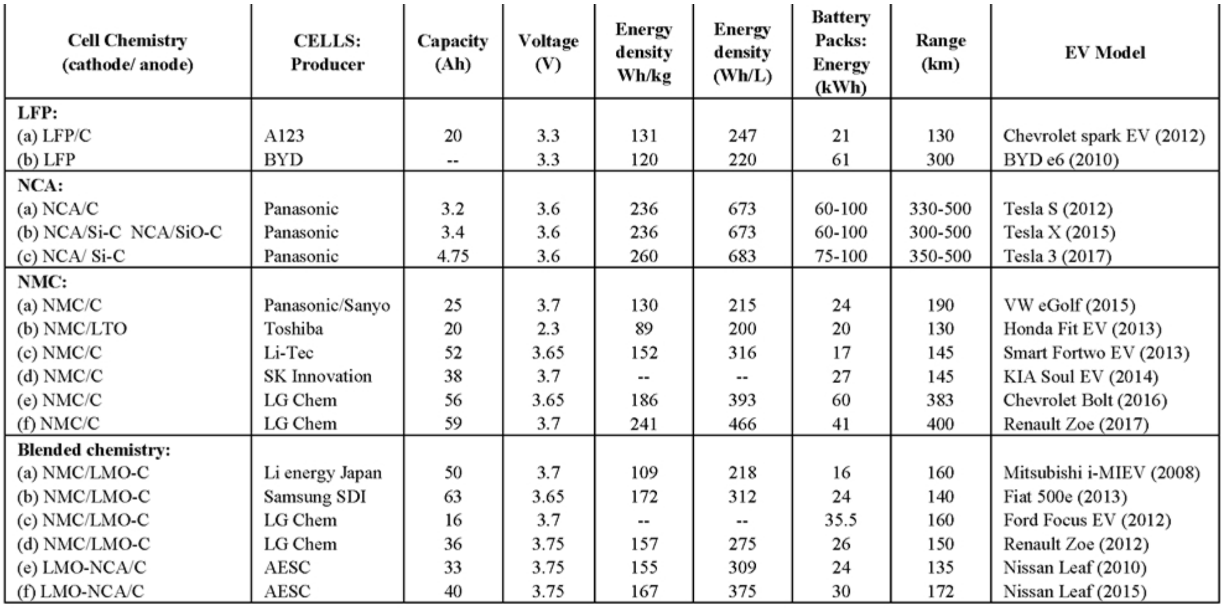
The lithium cobalt oxide (LCO) chemistry prevalent in consumer electronics is unsuitable for use in automobiles because of its innate structural volatility in the over-delithiated state, resulting in safety concerns [127]. Further, inadequate resources and high costs of cobalt are the main hurdles for its extensive application in EVs. Compared with LCO, other cathode materials including spinel LMO, NCA, NMC and LFP are most popular for EVs because their crystal structures are more stable, their resources are much more abundant and costs are lower. All battery chemistry require elaborate monitoring, balancing, and cooling systems to control the chemical release of energy, prevent thermal runaways and ensure safety and a long lifespan. Technically, LIB technology can be good for energy density, power density, safety, costs and life spans. On the market side, the cost is one of the major barriers. Hence, manufacturers should focus on low-cost battery materials and increase production volume, decreasing manufacturing costs and optimize cell design in the future.

As on today, these 4 battery technologies, LMO, LFP, NCA and NMC are effectively implemented by several automobile manufacturers that include Tesla, BMW, BYD, Chevrolet, GM, Mercedes Benz-Daimler, Volkswagen, Renault, Ford and Nissan. As the demand for electric cars grow in order to reduce oil consumption and to mitigate green house gas emissions, the production levels of these 4 battery cathode materials have enlarged similarly. In 2016, NMC, LFP and LCO accounted for 83% of the whole market share, which are mainly used for EV application except LCO.

Table 4.5 gives an overview of various cell chemistry (LFP, LMO, NCA, NMC and their blended systems) for automotive applications.

Next-Generation Li-Based Car Batteries: The layered lithium transition metal oxides (NMC) have become the most popular cathodes for automotive batteries. Further optimization of cathode materials in the NMC family will benefit because the related battery technology is reasonably mature. But, due to the limited theoretical capacity of NMC compounds, NMC-811 may only be a transitional Li-ion technology and to achieve higher energy densities, about 500 Wh/kg and above, new high-energy battery chemistry systems such as all-solid-state or Li-air or Li-S batteries, etc. need to be developed.

Table 4.5: Various LIB cell chemistry for EVs [100].



Cell Chemistry (cathode/ anode)	CELLS: Producer	Capacity (Ah)	Voltage (V)	Energy density Wh/kg	Energy density (Wh/L)	Battery Packs: Energy (kWh)	Range (km)	EV Model
LFP:								
(a) LFP/C	A123	20	3.3	131	247	21	130	Chevrolet spark EV (2012)
(b) LFP	BYD	--	3.3	120	220	61	300	BYD e6 (2010)
NCA:								
(a) NCA/C	Panasonic	3.2	3.6	236	673	60-100	330-500	Tesla S (2012)
(b) NCA/Si-C NCA/SiO-C	Panasonic	3.4	3.6	236	673	60-100	300-500	Tesla X (2015)
(c) NCA/ Si-C	Panasonic	4.75	3.6	260	683	75-100	350-500	Tesla 3 (2017)
NMC:								
(a) NMC/C	Panasonic/Sanyo	25	3.7	130	215	24	190	VW eGolf (2015)
(b) NMC/LTO	Toshiba	20	2.3	89	200	20	130	Honda Fit EV (2013)
(c) NMC/C	Li-Tec	52	3.65	152	316	17	145	Smart Fortwo EV (2013)
(d) NMC/C	SK Innovation	38	3.7	--	--	27	145	KIA Soul EV (2014)
(e) NMC/C	LG Chem	56	3.65	186	393	60	383	Chevrolet Bolt (2016)
(f) NMC/C	LG Chem	59	3.7	241	466	41	400	Renault Zoe (2017)
Blended chemistry:								
(a) NMC/LMO-C	Li energy Japan	50	3.7	109	218	16	160	Mitsubishi i-MIEV (2008)
(b) NMC/LMO-C	Samsung SDI	63	3.65	172	312	24	140	Fiat 500e (2013)
(c) NMC/LMO-C	LG Chem	16	3.7	--	--	35.5	160	Ford Focus EV (2012)
(d) NMC/LMO-C	LG Chem	36	3.75	157	275	26	150	Renault Zoe (2012)
(e) LMO-NCA/C	AESC	33	3.75	155	309	24	135	Nissan Leaf (2010)
(f) LMO-NCA/C	AESC	40	3.75	167	375	30	172	Nissan Leaf (2015)

Notes: C: graphite; LTO: $Li_4Ti_5O_{12}$; Si: silicon; LFP: $LiFePO_4$; LMO: $LiMn_2O_4$; NCA: $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$; NMC: $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$.

Among the major Li-ion battery technologies, LMO, NCA, NMC and LFP, the cathode materials have advantages as well as disadvantages. The maximum-specific capacities, up to 200 mAh per gm, can be achieved with layered structures (NCA, NMC), but they get affected by structural and/or chemical vulnerabilities during constant cycling, that are associated with chemical composition and the state-of charge. Therefore, the automotive industry has preferred Ni-rich NMC battery chemistries (such as NMC-622, NMC-811, and NCA) for use among these technologies, to reach the best performance and affordable costs in the future (Fig. 4.8).

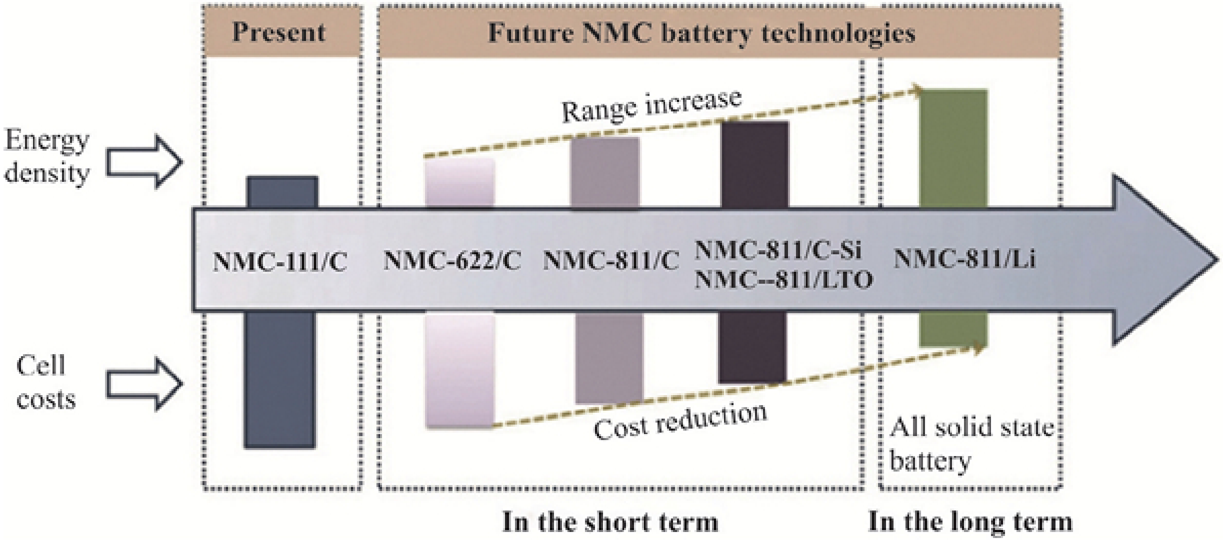


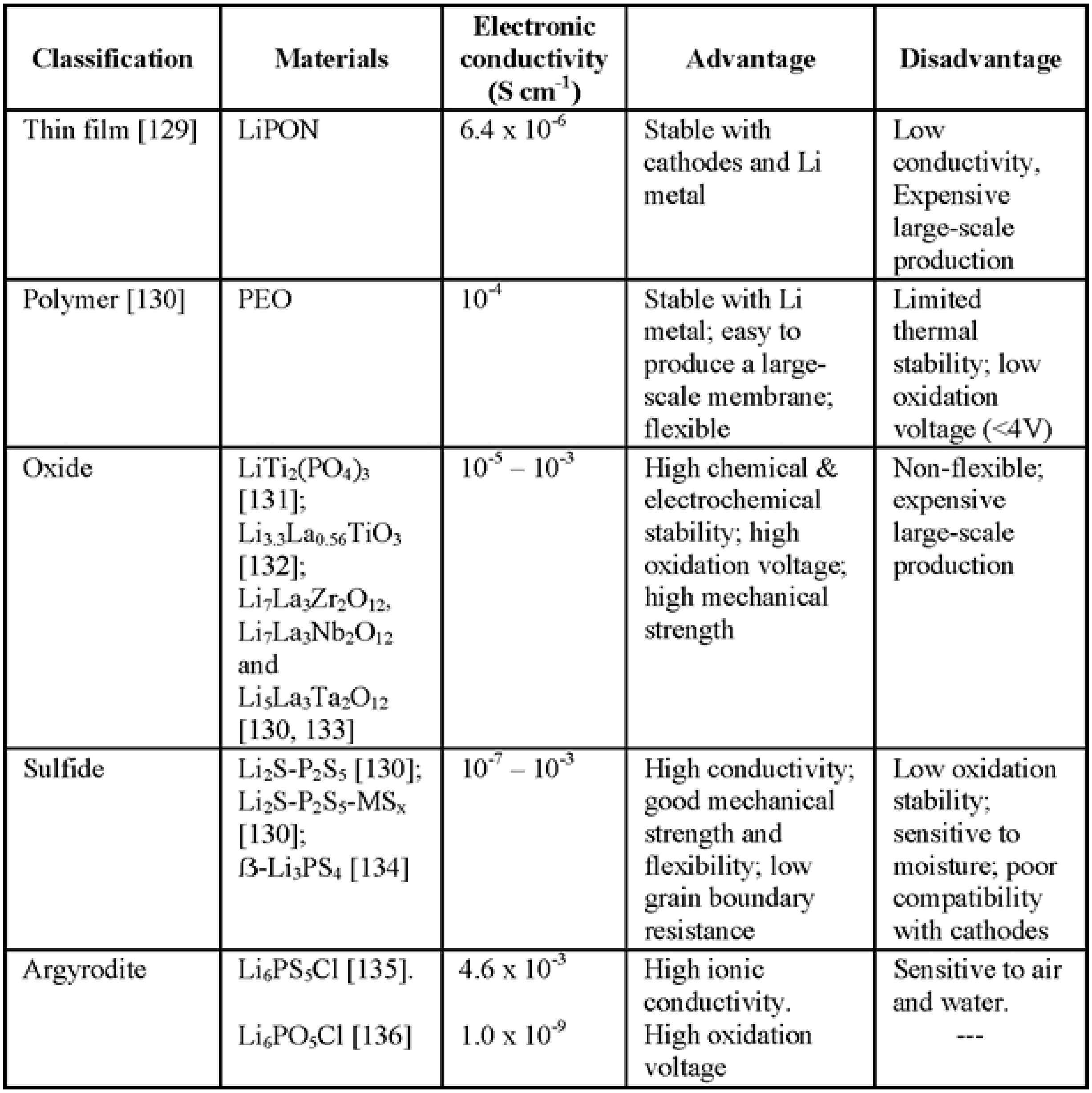
Figure 4.8: Roadmap of the present and future NMC-based battery technologies [100]

Solid State Battery chemistry for Next-Generation EVs

The limitations of conventional LIBs in terms of energy densities and material resources have led to the development of new types of battery chemistry for the coming EVs with long range. Currently, solid-state batteries (SSBs), lithium-sulfur and lithium-air batteries are most appealing due to their high specific energy and low costs, and are favored.

As conventional LIBs usually use organic liquid electrolytes, they suffer from complex reactions at the solid/liquid interface and thermal instability. Solid-state batteries are therefore superior options owing to their nonflammable solid electrolytes (SEs) and higher thermal stability [128]. Table 4.6 gives a summary of properties of common solid-state electrolyte materials [100].

Table 4.6: Properties of common solid-state electrolyte materials [100].



Classification	Materials	Electronic conductivity (S cm^{-1})	Advantage	Disadvantage
Thin film [129]	LiPON	6.4 x 10^{-6}	Stable with cathodes and Li metal	Low conductivity, Expensive large-scale production
Polymer [130]	PEO	10^{-4}	Stable with Li metal; easy to produce a large-scale membrane; flexible	Limited thermal stability; low oxidation voltage (<4V)
Oxide	$LiTi_2(PO_4)_3$ [131]; $Li_{3.3}La_{0.56}TiO_3$ [132]; $Li_7La_3Zr_2O_{12}$, $Li_7La_3Nb_2O_{12}$ and $Li_5La_3Ta_2O_{12}$ [130, 133]	10^{-5} – 10^{-3}	High chemical & electrochemical stability; high oxidation voltage; high mechanical strength	Non-flexible; expensive large-scale production
Sulfide	Li_2S-P_2S_5 [130]; Li_2S-P_2S_5-MS_x [130]; ß-Li_3PS_4 [134]	10^{-7} – 10^{-3}	High conductivity; good mechanical strength and flexibility; low grain boundary resistance	Low oxidation stability; sensitive to moisture; poor compatibility with cathodes
Argyrodite	Li_6PS_5Cl [135]. Li_6PO_5Cl [136]	4.6 x 10^{-3} 1.0 x 10^{-9}	High ionic conductivity. High oxidation voltage	Sensitive to air and water. ---

Currently, the main inorganic solid electrolytes for all-solid-state lithium-ion batteries are oxides and sulfides because of their high ionic conductivity.

SSBs are characterized by a long cycle life, high-energy density and less materials on packing and circuits to observe the state-of charge. They are safe too. Further, the core solid electrolytes have some extra benefits for battery applications. The solid nature of the electrolyte facilitates the piling of cells in a single package devoid of ionic short circuits. Such a battery arrangement successfully reduces the ‘dead volume’ between single cells, resulting in more compact space and higher specific energy for the battery packages. This is beneficial for application in automotive sector, as shown in Fig. 4.9 [100].

Regardless of these positive features, the electrochemical performance of all-solid-state batteries is still poorer than that of commercial lithium-ion batteries and serious challenges need to be addressed [129].

As of now, several conventional cathode materials in LIBs are similar (in working) to Li metal anodes for SSB applications. Zhang et al. reported a LiFePO4/Li solid-state battery using a composite electrolyte as the solid-state-electrolyte [130]. Although all-SS batteries provide a great possibility for application in EVs, more intensive studies are still needed on the entire SSB systems, especially related to electrode materials, SEs, electrode/electrolyte interface and cell configuration design, for their practical application at the industrial level.

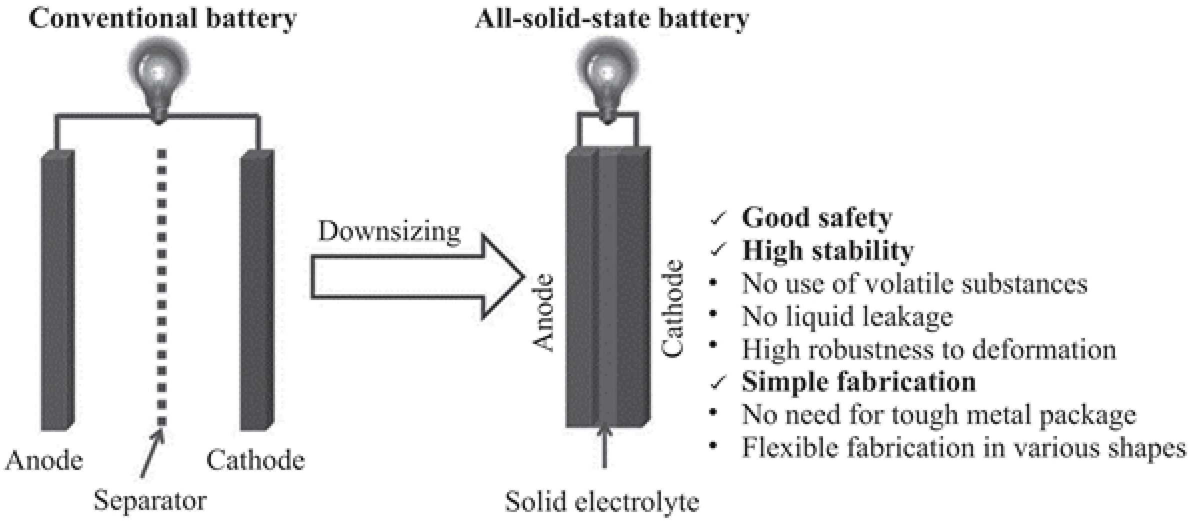


Figure 4.9: Schematic illustration of the conventional battery and all-solid-state battery [100]

Status: The top battery manufacturers in 2017, A123 Systems, AES, LG Chem, Panasonic, Samsung SDI and Toshiba (Technavio ranking) and several other big players such as Axion, and Chinese giant, BYD are ramping up capital expenditure with a view to triple the capacity by 2020 [111]. Most of this growth is expected to be in Asia, particularly China [131]. More than 140 EV battery manufacturers exist in China and want to capture major share of the EV battery market [122].

Government pledges to shift to electric vehicles are adding further push to the scale-up of the Li-ion battery industry. China, India, France, and the UK, among others, announced timelines for the elimination of sales of vehicles with internal combustion engines. California was said to be opting for EVs [132]. The UK government recently announced that from 2035, all new diesel and petrol car sales (including hybrids) would be banned (https://energypost.eu/uk-to-phase-out-petrol-diesel-hybrid-car-sales-by-2035-heres-how/).

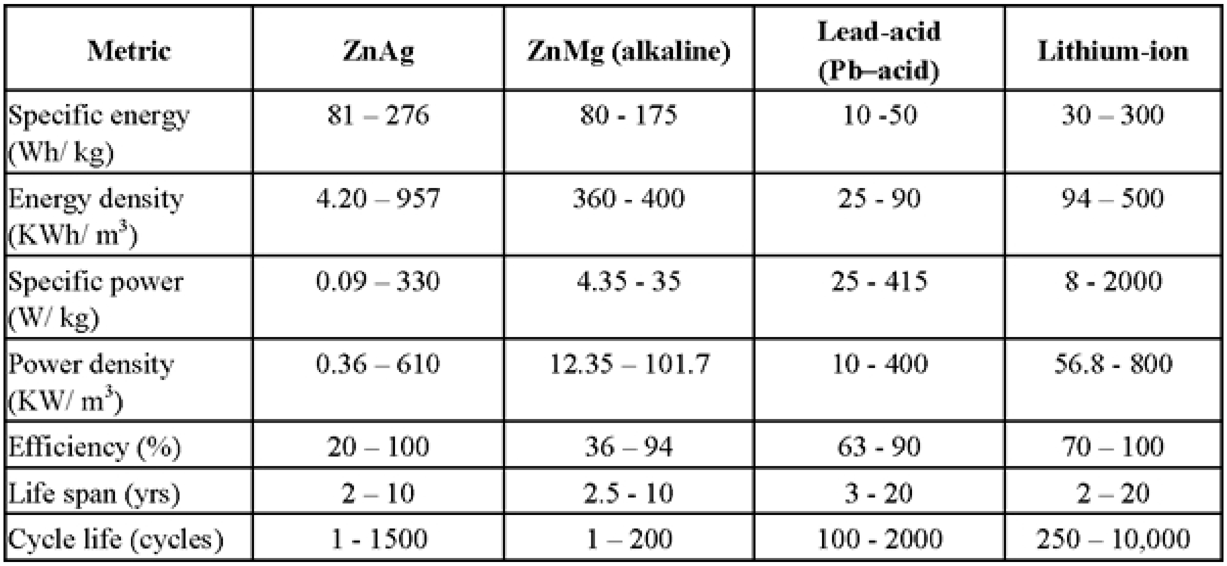
Metal-air batteries for EVs: The aluminum/air battery system can generate adequate energy and power to accelerate and drive for similar distances as performed by the gasoline-powered cars. The cost of aluminum anode material can be as low as US$ 1.1/kg so long as the used product is recycled. The overall fuel efficiency during the cycle in electric vehicles (EVs) fitted with Al-air battery is around 15% presently, which can be projected to 20%, comparable to that of internal combustion engine vehicles, 13%. The design battery energy density is currently 1300 Wh/kg and projected to 2000 Wh/kg. The cost of battery system is US$ 30/kW at present that may slightly decrease in future. The life-cycle analysis of Al/air EVs was compared to Pb-acid and NiMH EVs. Only the Al/air EVs can be projected to have a travel range comparable to IC s. The analysis of Yang and Knickle [133] shows Al/air EVs are the most promising candidates compared to ICEs in terms of travel range, purchase price, fuel cost, and life-cycle cost.

Zhang et al. (2019) explain that Zn-air batteries are particularly promising by virtue of their large theoretical energy density (1353 Wh/ kg excluding oxygen), lower cost (currently <\$100 kW^{-1} h^{-1} and has potential to come down to <\$10 kW^{-1} h^{-1}) and intrinsic safety. They are the ones probably having technical and economical viability that can offer a layout for fast-charging EVs in the future [134].

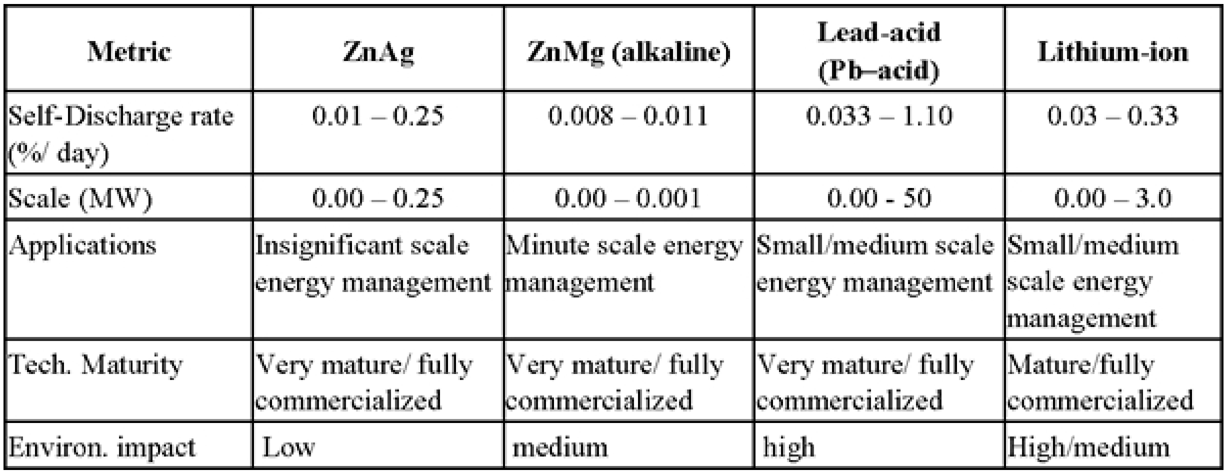
4.4.4 Comparison

The battery systems discussed so far are compared in Tables 4.7 and 4.8 [1].

Table 4.7: Comparison among ZnAg, ZnMn (alkaline), Pb-acid, and Li-ion battery systems; For each metric, the range is given. (Source: [1])

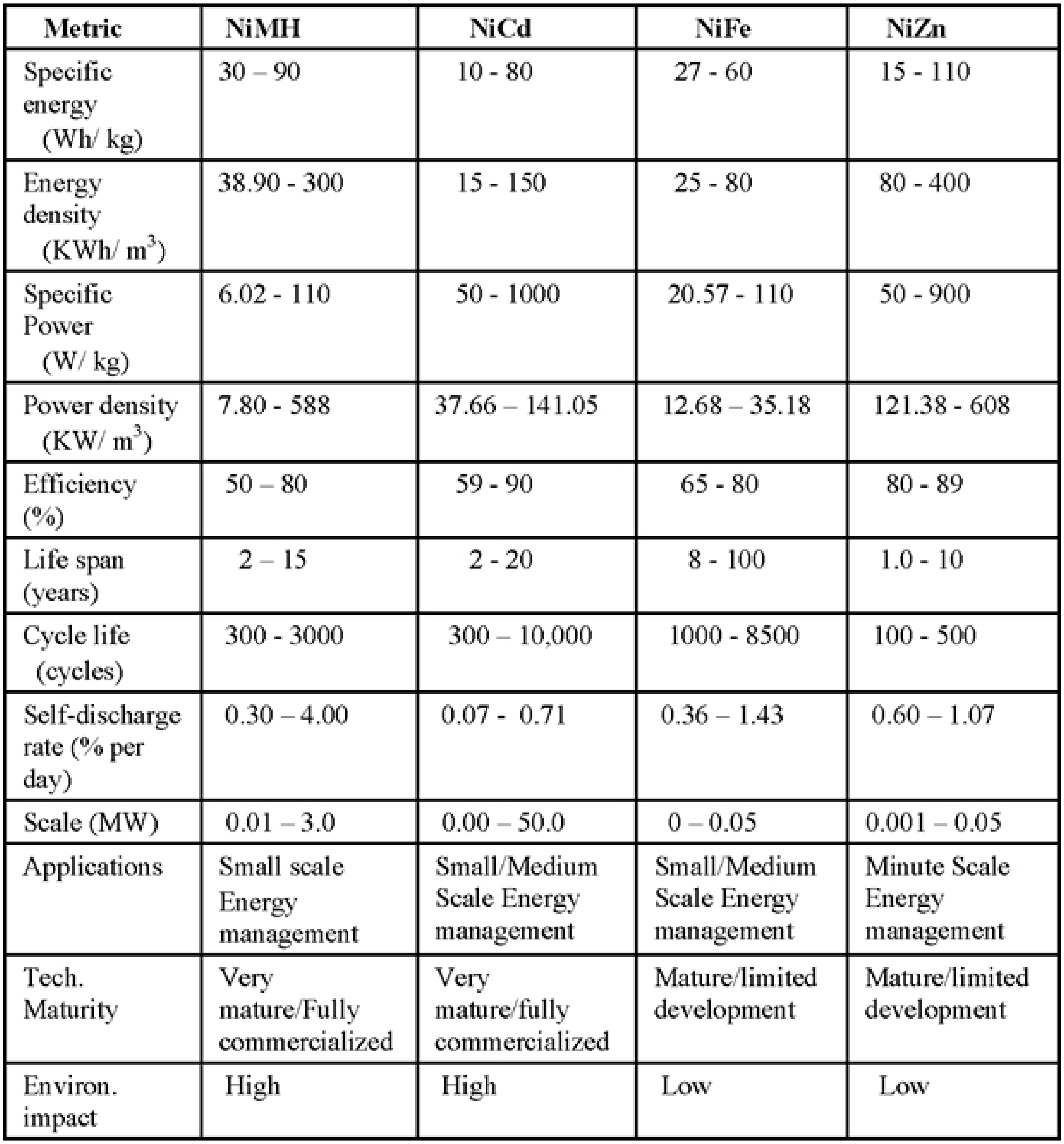


Metric	ZnAg	ZnMg (alkaline)	Lead-acid (Pb–acid)	Lithium-ion
Specific energy (Wh/ kg)	81 – 276	80 - 175	10 -50	30 – 300
Energy density (KWh/ m^3)	4.20 – 957	360 - 400	25 - 90	94 – 500
Specific power (W/ kg)	0.09 – 330	4.35 - 35	25 - 415	8 - 2000
Power density (KW/ m^3)	0.36 – 610	12.35 – 101.7	10 - 400	56.8 - 800
Efficiency (%)	20 – 100	36 – 94	63 - 90	70 – 100
Life span (yrs)	2 – 10	2.5 - 10	3 - 20	2 – 20
Cycle life (cycles)	1 - 1500	1 – 200	100 - 2000	250 – 10,000



Metric	ZnAg	ZnMg (alkaline)	Lead-acid (Pb–acid)	Lithium-ion
Self-Discharge rate (%/ day)	0.01 – 0.25	0.008 – 0.011	0.033 – 1.10	0.03 – 0.33
Scale (MW)	0.00 – 0.25	0.00 – 0.001	0.00 - 50	0.00 – 3.0
Applications	Insignificant scale energy management	Minute scale energy management	Small/medium scale energy management	Small/medium scale energy management
Tech. Maturity	Very mature/ fully commercialized	Very mature/ fully commercialized	Very mature/ fully commercialized	Mature/fully commercialized
Environ. impact	Low	medium	high	High/medium

Table 4.8: Comparison among NiMH, NiCd, NiFe and NiZn battery systems; (Source: [1])



Metric	NiMH	NiCd	NiFe	NiZn
Specific energy (Wh/ kg)	30 – 90	10 - 80	27 - 60	15 - 110
Energy density (KWh/ m^3)	38.90 - 300	15 - 150	25 - 80	80 - 400
Specific Power (W/ kg)	6.02 - 110	50 - 1000	20.57 - 110	50 - 900
Power density (KW/ m^3)	7.80 - 588	37.66 – 141.05	12.68 – 35.18	121.38 - 608
Efficiency (%)	50 – 80	59 - 90	65 - 80	80 - 89
Life span (years)	2 – 15	2 - 20	8 - 100	1.0 - 10
Cycle life (cycles)	300 - 3000	300 – 10,000	1000 - 8500	100 - 500
Self-discharge rate (% per day)	0.30 – 4.00	0.07 - 0.71	0.36 – 1.43	0.60 – 1.07
Scale (MW)	0.01 – 3.0	0.00 – 50.0	0 – 0.05	0.001 – 0.05
Applications	Small scale Energy management	Small/Medium Scale Energy management	Small/Medium Scale Energy management	Minute Scale Energy management
Tech. Maturity	Very mature/Fully commercialized	Very mature/fully commercialized	Mature/limited development	Mature/limited development
Environ. impact	High	High	Low	Low

4.5 High Temperature Batteries

Recently, new approaches to develop battery technologies have been seen outside the conventional battery chemistry. These include high-temperature batteries that use molten salts and liquid metals.

Sodium-Sulfur and Sodium-nickel-chloride batteries are high-temperature batteries that use liquid/molten salts as electrolytes. The electrolytes also function as electrodes, and are separated by a solid membrane separator. This is entirely a different approach and battery chemistry.

These batteries consist of molten sodium anode material and a solid ceramic electrolyte. Depending on the cathode solid reactant, they are divided into sodium-sulfur (NaS) and sodium-nickel-chloride (NaNiCl or ZEBRA) [135].

4.5.1 Sodium-sulfur Battery (NaS)

NaS battery cell contains a molten sodium anode, a solid electrolyte of β-alumina (β"-Al_2O_3), and molten sulfur. Sodium ions, which are positive charges move across the solid ceramic electrolyte into molten sulfur; there through an electrochemical reaction, a current is produced (Fig. 4–10). Sodium and sulfur are ever kept in a molten state, keeping temperatures between 300° and 360°C to enable ion transfer [136].

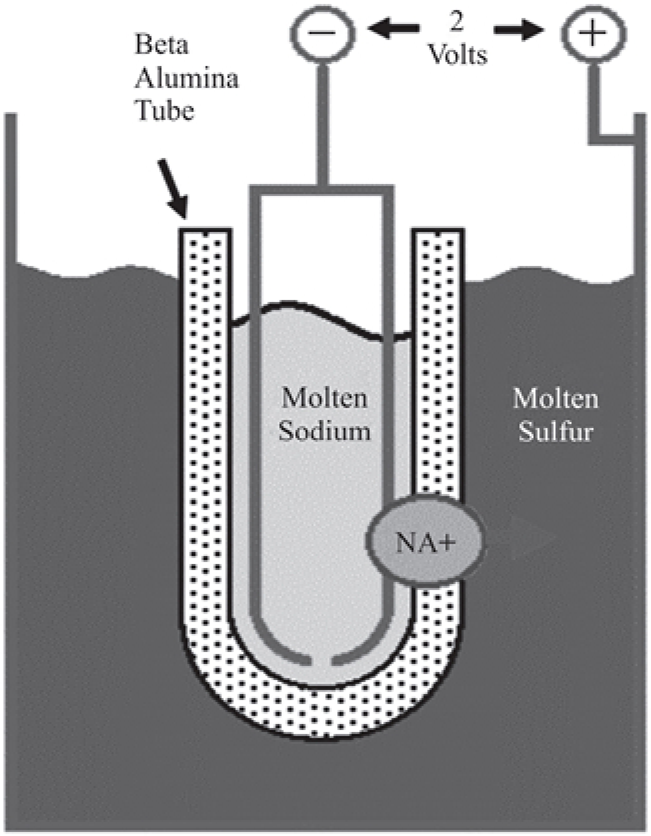


Figure 4.10: Schematic of NaS cell (source: [136]).

The chemical reactions at the negative electrode:

$$2\text{Na} \leftrightarrow 2\text{Na}^{+} + 2\text{e}^{-}$$

at the positive electrode:

$$\text{S} + 2\text{e}^{-} \leftrightarrow \text{S}^{2-}$$

During discharge, Na^{+} drifts from Na to S and create polysulfides, and creation of Na_2S_3 at 1.78 V is presumed as the discharge limit. The typical voltage at the C/3 rate is 1.9 V.

In the charging phase, the reactions that give rise to Na_2S_3 are reversed; and towards the end, there is a striking increase in resistance because sulfur is insulating in nature. Therefore, charging must be terminated before recovering Na fully, and the ensuing discharges produce about 8590% of the theoretical capacity [137].

In practice, in the high-temperature NaS cells, the movement of sodium and sulfide ions produce density gradients of sulfide anions and sodium cations in the melt, and the size of the density gradients is determined by the number of transference numbers of the sodium ions and to a slighter extent of the sulfur anion.

The sodium ions are presumed to be the main current transferring species due to (a) their larger ion size of 1.02 Å relative to 0.37 Å for sulfur, and (b) the diffusivity of the single ions that tend to neutralize the drift of species by migration [138].

The NaS batteries use harmful materials that include metallic sodium, which is flammable when coming in contact with water. Hence, in the fabrication of NaS batteries, series-parallel arrays of NaS cells are enclosed in airtight, double-walled stainless-steel cases. Each cell is hermetically sealed and surrounded with sand both to tie up the cells and to diminish fire. Other safety facets include bonded electrical separation and a battery controlling system that observes cell block voltages and temperature. Battery constituents, namely, sodium, sulfur and betaalumina ceramic electrolyte, and sulfur polysulfide are disposed of by routine industrial processes or recycled at the end of the NaS battery life [80].

NaS batteries provide high-energy density of 150 to 345 kWh/m^3, cycle efficiency of 89 to 92%, and high cycle life ranging from 1500 to 5000 cycles. Also, they are much smaller and lightweight than NiCd, NiMH and Pb-acid battery types. Therefore, they are an attractive option for large-scale stationary electrical storage applications [73,139, 140].

The Japanese manufacturer NGK projects its NaS battery to have a cycle life of 4500 cycles for rated discharge capacity of 6 MWh per installation MW. With that cycle life, NaS batteries are projected to have a calendar life of 15 years [80]. Other distinct advantages are good power density, independent of external temperature and moderate cost.

The high cycle life, up to 5000–6000 cycles is mainly due to the liquid state-of reactants and products. The aging process resulting from morphological changes of the electrodes does not function here.

An essential criterion for the Na electrode is high purity, that is, devoid of other metals and Na compounds. Impurities tend to aggregate at the interface with the electrolyte, thereby sinking the electrode-active area or even triggering its failure. The sulfur electrode is permeated into a layer of carbon or graphite felt. The carbon fibers make certain that electronic conductivity is good, since sulfur is an insulator for both electrons and ions. Na polysulfides, incidentally are good ionic conductors [137].

The electronic conductivity of solid electrolyte, β''-Al_2O_3 (β alumins Solid Electrolyte, BASE) is insignificant; and the electrolyte is resistant to molten Na and S. The idealized composition of BASE is $Na_2O \bullet 5.33Al_2O_3$. It is rather difficult to prepare pure e''-Al_2O_3; hence, it must be stabilized with Mg or Li-ions which substitute for Al ions. The ionic conductivity of BASE is ~0.5 $\Omega^{-}1$ cm^{-1} at 350°C for the multicrystalline type. β''-Al_2O_3 is somewhat sensitive to moisture, which leads to weakening of its mechanical properties. Therefore, some β-Al_2O_3 is enclosed in the mixture, in spite of its lower conductivity, as it is less hygroscopic. The conductivity value of ~0.2 Ω^{-1} cm^{-1} is satisfactory for practical electrolytes [137].

The disadvantages of NaS technology are mainly (a) the corrosive nature of the manufacturing materials, and (b) the need for continuous heat input to maintain the electrolyte's molten state, which is confirmed at 300 - 350°C. This constant heat input increases the danger of probable reaction between electrode materials and the accompanying risk of fire [141].

Other types of NaS batteries

NaS battery types can be categorized by their operating temperatures: high-temperature (HT) (300 - 350°C), intermediate temperature (IT) (150–200°C), and room temperature (RT) (25 - 60°C) NaS batteries. The main components of HT and IT NaS cells are the solid ceramic electrolyte (β''-alumina, BASE), sodium and sulfur electrodes in the liquid state (melting point of Na, $T_m N_a$ = 98°C and melting point of sulfur, $T_m S$ = 118°C) and a container. The cell structure can be represented as Na(l)|e''-Al_2O_3|Na_2S_x (l) + S(l)|C, where C represents carbonaceous material that is used as current collector. In the room temperature NaS system, metallic sodium is used and hence, BASE can be substituted by inexpensive glass fiber, a good economic incentive for using RT NaS technology [142].

Applications: NaS batteries are a commercial energy storage technology. These can be installed at power generating facilities, substations, and renewable energy power generation facilities. NaS batteries have potential for grid services' applications due to its long discharge period (roughly 6 hours). Like several other storage methods, NaS is capable of rapid and defined response to grid requirements such as lessening of power quality actions and response to AGC signals for area regulation.

Japan is particularly active in the production of NaS batteries for stationary applications. Very large energy storage systems, as high as 57 MWh, can be built with NaS modules.

NGK Insulators of Japan offer 2 types of units: the plug-and-play style system, comprising 4 container subunits in one such unit. (One subunit includes 6 NaS modules, each module rated at 33kW/200kWh). The second, package type unit, has a rated output of 1,200kW/8,640kWh, made up of 40 NaS modules, each rated at 30kW/216kWh. The system is designed to perform 4,500 cycles in the estimated lifespan of 15 years, i.e, making 300 per year [143, 137]. In the NGK Insulator's energy storage installations, standard units normally contain 5 50kW NaS modules that include a control unit, heater, heater controller, and sensors to measure voltage and current. Numerous, parallel standard units are used to build multi-megawatt systems [80].

Installations: The largest single installation is the 34-MW Rokkasho wind-stabilization project in Northern Japan operational since August 1, 2008. By 2015, about 316 MW of NaS capacity has been installed at 221 sites around the world, representing 1896 MWh.

In the United States, American Electric Power (AEP), PG&E, and Xcel Energy are providers who have installed

11 MW at 5 locations, 6 MW, and 1MW, respectively.

A large utility-scale electricity storage is a 4 MW NaS battery system deployed to deliver improved reliability and power quality for the city of Presidio in Texas. It was energized early in 2010 to arrange for speedy back-up for wind capacity in the local ERCOT grid. NaS batteries are extensively used in other places for analogous roles [95].

NGK's system deployed in 2008 at Xcel in Lucerne, MN, holds 20 50kW modules with 7.2MWh of storage capacity and a charge/discharge capacity of 1 MW (Figure 4.11a). Batteries get charged when wind turbines operate and deliver additional power when the turbines are not operating.

NGK also deployed NaS battery systems in Abu Dhabi (UAE) in January 2019 across 10 locations. They are 15 systems overall, adding up to a total of 108MW/648MWh, with each system able to store energy for 6 hours. The 15 systems include 12 4 MW systems and 3 20 MW systems (Fig. 4.11b).

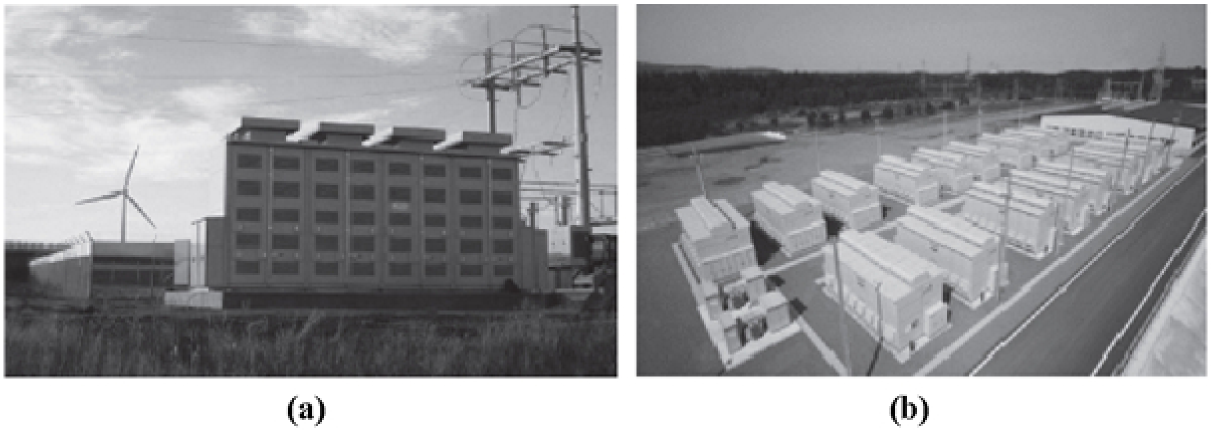

(a) (b)

Figure 4.11(a): Xcel NaS battery system integrated into Wind turbine in Lucerne, MN, USA in 2008 [source: Sandia 2015]. **(b)** 108MW/648 MWh NaS battery energy storage with 15 systems installed in Abu Dhabi, UAE in January 2019 [Image source: NGK Insulators, Japan]

4.5.2 Sodium-nickel-chloride (Na-$NiCl_2$) Battery

This technology displays a few advantages relative to NaS systems. These include safer operation, no corrosion, lower average temperature of 250 to 350°C, high cell voltage of 2.58 V, and the capacity to endure restricted overcharge and discharge [144, 145].

Sodium-nickel-chloride batteries, like the NaS battery, rely on the oxidation and reduction of sodium at the anode and use a BASE separator, but they rely on the oxidation and reduction of nickel metal at the cathode. Specifically, the cathode reaction is supported in a metal halide molten salt electrolyte, traditionally NaCl and $AlCl_3$, which combine to form $NaAlCl_4$ (sodium tetrachloroaluminate). As such, these batteries are also referred to as sodium metal halide batteries or molten salt batteries, or even just salt batteries. The overall electrochemical reaction of this system is [135c]:

$$NiCl_2(s) + 2Na\ (l) \leftrightarrow 2\ NaCl + Ni(s), \qquad \text{Cell} \sim 2.58\ \text{V at } 300\ °\text{C}$$

Cells are hermetically sealed and packaged into modules about 20 kWh each [80]. During regular discharge, Ni and NaCl are produced. The battery voltage, 2.58 V, is higher than that of NaS, 2.06–1.78 V [137].

Other differences between them: Liquid Na is placed in the outer part of the cell, whereas in NaS cells, it is in the central part. Na is not originally included in the cell assembly, but produced *in situ* during charge, as the cell is assembled during discharge. The positive electrode being solid, would create problems because the solid-solid interface with the electrolyte would allow only low currents. Therefore, a second electrolyte, $NaAlCl_4$, a liquid at the battery-operating temperatures, is added. Tolerance to overcharge and over-discharge is exceptional because the reversible reactions occur in these settings. On the overcharge, the liquid electrolyte, $NaAlCl_4$ further chlorinated the Ni matrix, and on overdischarge, excess Na reacts with the liquid electrolyte. This property of the cell has practical consequence: several cells can be feasibly connected in series without parallel connections, as cell imbalances are leveled out by the above mentioned cell reactions [137]. As the initial research was performed in South Africa for EV applications, the acronym ZEBRA (zero emission battery research activity) is often used for this battery.

Another advantage of this battery, with respect to the NaS system, is its enhanced safety. The Zebra system is specifically intended for EV applications, where features such as safety, easiness in construction, cyclability, and low corrosion, are desired [137]. Also, Na-$NiCl_2$ batteries have high-energy per kg metrics, on par with today’s lithium-ion packs.

The safety of Na-$NiCl_2$ cells is subject to their structural reliability. If the cell is broken or cracked, the high cell temperature causes a potential safety issue. Their high working temperature range is also an encouraging aspect of this chemistry because such temperatures allow chemistry somewhat insensitive to the wide array of ambient conditions experienced in transportation. As a result, these batteries are adept of functioning across the entire ambient temperature range, -40°C to +50°C, seen in ground-based transportation.

However, 2 most important issues prevent implementing this chemistry in many transportation applications: (1) consumption of a substantial amount of power to sustain the high cell temperature, which is mostly challenging for vehicles that may not stay plugged-in during parking; in this situation, the battery continues to use energy to keep the temperatures resulting in a fully discharged battery over time, and (ii) the limited power to energy ratio. The high-temperature liquid sodium electrode requires a unique separator, which possess adequate structural strength to endure pressure loading from the liquid sodium in the vehicle's high vibration situation. The high operating temperature combined with the needed structural strength necessitates the design of a thick separator fabricated with aluminum oxide. The separator thickness seems to be the principal hurdle to achieve higher power-to-energy ratios for this battery [146].

MES-DEA of Switzerland released a 21 kW-hr battery pack (Model # Z5–278-ML3P-76) for transportation applications having the following standards: specific power, 170 W/kg; specific energy, 120 W-hr/kg; power density, 250 W/L; and energy density, 175 W-hr/L [taken from ref. 146].

Figures 4.12a,b show 2 FIAMM-developed containerized systems deployed at utility sites [80].

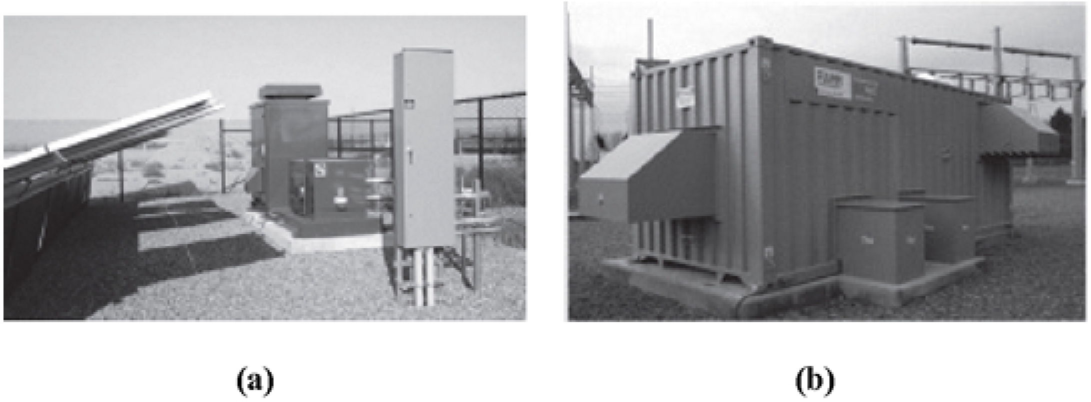

(a) (b)

Figure 4.12(a): Containerized 25 kW/50 kWh FIAMM Battery Unit (large housing) on Concrete Pad, Next to S&C Pure Wave CES (small green housing); **(b)** FIAMM 222 kWh System Site at the Duke Energy Rankin Substation. Source: [80]

FZSoNick employed Na-$NiCl_2$ systems to provide back-up power for telecom, community transport, and isolated (out-of-the way) site applications. So far, FZSoNick installed roughly 100 MWh of energy storage with about 2 MAh of back-up storage capacity, mostly concentrated on standby for telecommunications. They have deployed more than 14 MWh of additional storage for use in ‘Energy Storage Systems’ that allow renewables integration, microgrid applications, and grid services (e.g., grid balancing, voltage regulation) [FZSoNick Battery Applications, @ https://www.fzsonick.com/applications]. These batteries have found their most significant application as a large-scale system in the back-up energy market in North America, South America (Fig. 4–12c), Europe, and to a lesser degree, Asia. In the United States, Na-$NiCl_2$ batteries provide stand-alone back-up power for telecom data centers at 17 sites for 2 major cell phone providers. In Mexico, Zambia, and the Philippines, Na-$NiCl_2$ batteries provide back-up power for telecom systems. For larger-scale energy storage systems, Na-$NiCl_2$ batteries are used in the Maldives Islands (1.2 MWh), Ollagüe, Chile

(560 kWh), Tilos, Greece (2.88 MWh), and French Guiana (4.5 MWh) to support integration of renewables such as solar PV (Fig. 4.12c), and wind power. FZSoNick is also engaged with Terna S.p.A., using a 4.5 MWh system to facilitate electricity transmission in Sicily and Sardinia [135c].

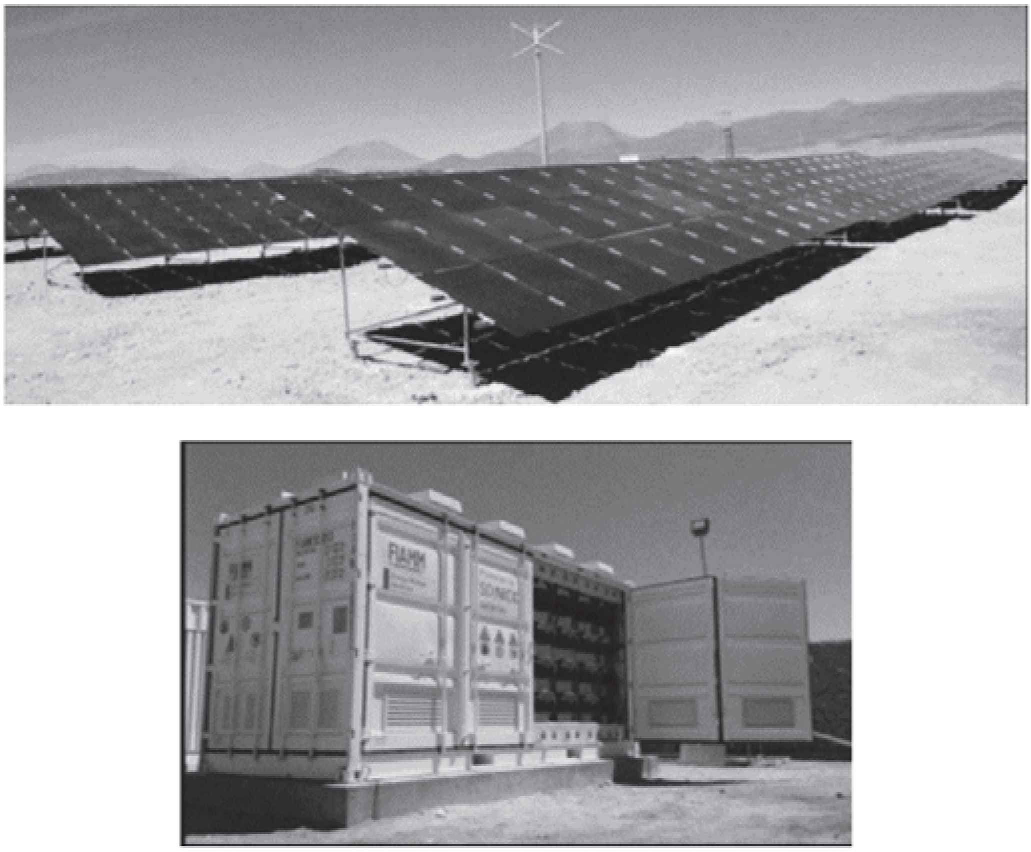


Figure 4.12c: An FZSoNick Na-$NiCl_2$ battery system supporting the integration of renewable remote photovoltaic energy in South America. Reprinted with permission of FZSoNick (Source 135c])

Currently, over 300 installed energy storage sites with ZEBRA and NaS technologies are working globally [147] offering encouraging, cost-viable technologies for large-scale electrical energy storage. Battery modules of megawatt power are usual for these battery systems since large unit cells reduce the economic concerns by realizing low unit costs [148]. The driving force for the realization of room temperature and intermediate temperature NaS is the anticipated gains in energy density from the reduced temperatures alongside improved safety [149, 150]. The same fundamental principle was effected in ZEBRA batteries besides introduction of a planar cell structure [142].

4.6 Metal-air Batteries (MABs)

Metal-air batteries are a technology with potential to take care of the global energy needs in the future [151a]. Metal-air batteries are grouped on the basis of the electrolyte: first is a cell system that uses an aqueous electrolyte such as typical Zn-air battery, and the second is a watersensitive system using organic electrolyte such as a typical Li-air battery.

At present, metal-air batteries are assumed to be potentially the most feasible energy system to substitute the developed Li-ion battery and even hydrogen fuel cell that has virtually got to theoretical performance limits. However, hydrogen FC is faced with tough challenges ranging from difficult hydrogen production/storage/transportation to complicated cell design [151b, 152–154].

In the molten battery chemistry explained earlier, if the second electrode is replaced with an air electrode, the new battery chemistry operates on hydroxyl ion exchange to produce energy. These metal - air battery chemistries have attracted significant attention recently as they can operate in an open-air atmosphere.

MAB is an electrochemical cell and uses a metal for the anode and ambient air as cathode along with a liquid electrolyte typically aqueous or aprotic. During discharging of this cell, a reduction reaction occurs in the ambient air cathode while the metal anode is oxidized. Metal-air batteries combine the design features of both conventional batteries and fuel cells (Wikipedia). Due to the open battery structure of metal-air batteries, the oxygen reagent can be directly received from the surrounding air, thus contributing to their high theoretical energy densities [155].

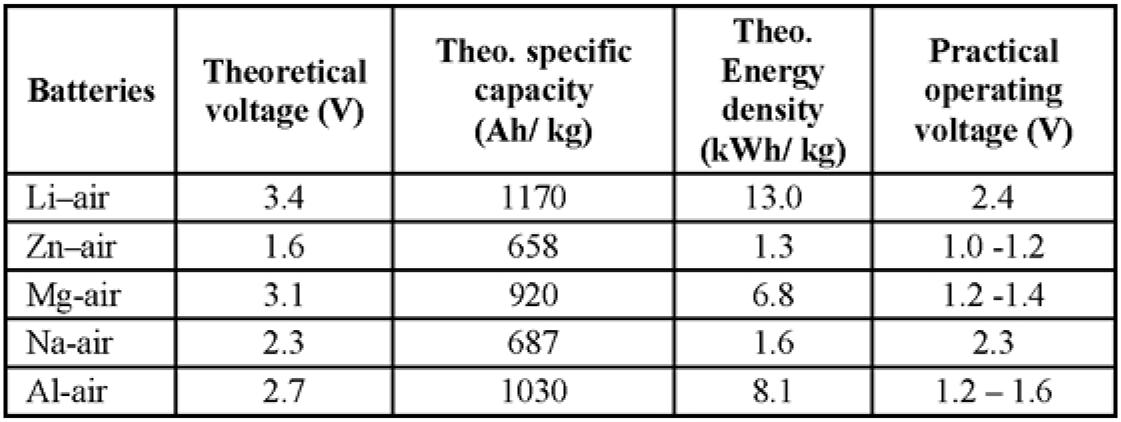
Among the new energy storage systems, metal-air batteries have gained great interest because of their high-energy density and capacity, low cost (depending on the metal anode), insignificant dependence of their capacity on operating load and temperature, and constant discharge voltage [156–160]. Different kinds of metal-air batteries, such as lithium-air, zinc-air, magnesium-air, sodium-air, and aluminum-air batteries have been widely investigated [161–165].

Metal-air batteries demonstrate high theoretical energy densities ranging 2 to ten-folds higher than that of state-of-the-art LIBs [166]. This feature makes them the leading energy storage solution for various portable electronics, and widely viewed as the most viable option for electric vehicles (EVs) and grid-scale energy storage [167–170].

It is to be noted, despite the great commercial success, the current Li-I technology is still suffering from insufficient energy density (limited to be <350 Wh/kg based on the intercalation chemistry) [171], relatively high cost (currently ~$150/ kWh) and potential safety risk.

Table 4.9 summarizes the voltage, theoretical specific capacity and energy density of typical metal-air batteries [172].

Table 4.9: Features of metal-air batteries [172]



Batteries	Theoretical voltage (V)	Theo. specific capacity (Ah/ kg)	Theo. Energy density (kWh/ kg)	Practical operating voltage (V)
Li–air	3.4	1170	13.0	2.4
Zn–air	1.6	658	1.3	1.0 -1.2
Mg-air	3.1	920	6.8	1.2 -1.4
Na-air	2.3	687	1.6	2.3
Al-air	2.7	1030	8.1	1.2 – 1.6

The Li-air battery exhibits a maximum energy density of13 kWh/kg, which far exceeds the energy density of other rechargeable battery technologies [173, 174]. Even so, rechargeable Li-air battery s have many issues to be resolved such as the blocking of porous carbon cathodes by discharge products, insecurity of lithium in moist settings [175], poor comprehension of catalytic mechanism [176], low electrochemical efficiency due to high charging over potentials [177], and creation of extra product (such as lithium alkyl-carbonates and Li_2 CO_3) during cycling [178]. These issues adversely impact the reversible charging and cycle life [179]. Additionally, using non-aqueous electrolytes in Li-air batteries escalate the cost and cause safety concerns associated with the flammable organic solvents [172].

MABs having aqueous electrolytes also face substantial challenges. Aqueous Zn-air batteries struggle with the complications of precipitation of zinc, Zn anode dendrite formation, uneven zinc suspension, incomplete oxygen solubility in electrolytes, and higher charge over potentials [180].

The Mg-air and Al-air batteries are in their early stages but have earned much appeal due to their many valuable advantages, such as high-energy density, high theoretical voltage, safety, and richness of raw materials. But then, these battery chemistries are subjected to several complications such as corrosion of Mg and Al metals, high self-discharge rate, inactive discharge kinetics, lack of recharge capacity, and short shelf lifespan [181]. Even though some Al-air batteries with non-aqueous electrolytes such as ionic liquids have been reported to be rechargeable, they may be prohibitively expensive [182]. Therefore, more research needs to be focused to overcome numerous scientific and technical challenges before these promising energy storage devices are put into use.

4.6.1 Aluminum-air Batteries

Among the MABs, Al-air batteries hold abundant potential for future wide-ranging energy applications because they have a high theoretical specific capacity of 2.98 Ah/g (next only to that of lithium and much higher than those of magnesium, 2.20 Ah/g and zinc, 0.82 Ah/g [183–185] and inexpensive. Aluminum is a cheap, plentifully available and environmentally-sound metal with high reprocessing capability [186]. This battery is characterized by a high theoretical voltage, 2.7 V, and energy density, 8.1 kWh/kg, much bettering that of state-of-the-art lithium-ion batteries [187, 188].

Figure 4–13 represents a schematic of a primary Al-air battery. It consists of an aluminum anode, air cathode, and an electrolyte, normally comprising sodium hydroxide, potassium hydroxide or sodium chloride solutions [188]. The electrochemical reactions happening at the electrodes are [185]:

$$\text{At anode:}\quad Al \rightarrow Al^{3+} + 3e^{-}$$

$$\text{At cathode:}\quad O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$$

$$\text{Overall reaction:}\quad 4Al + 3O_2 + 6H_2O \rightarrow 4\ Al(OH)_3$$

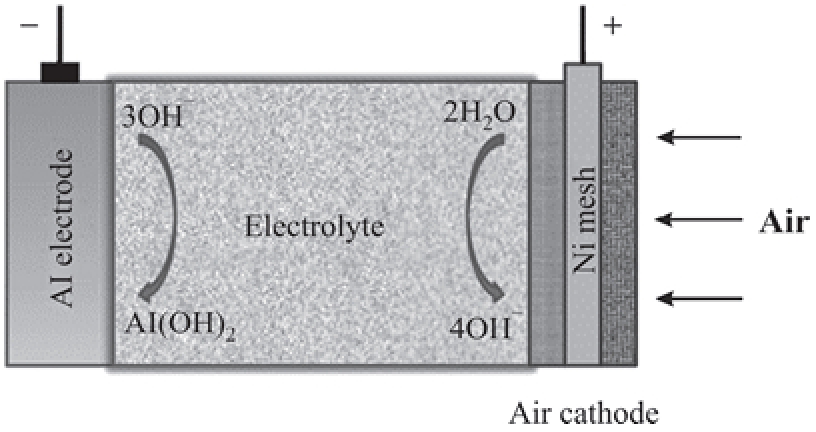


Figure 4.13: Representation of an Al-air battery structure using a 3-layer air electrode [172]

The aluminum metal anode was first proposed by Zaromb in 1962 [194, 195] in an aluminum/oxygen system regarded as a high-energy density system. In the years followed, various applications for Al-air battery energy storage systems were investigated [191–199], such as powering electric vehicles (EVs), military communications, unmanned underwater vehicles (UUVs), and unmanned aerial vehicle (UAVs). In 2016, an Al-air battery weighing 100 kg was fabricated which displayed the capability of extending the range of an electric vehicle to over 3000 km. Many research groups have been working to enhance the capacity and lifetime of Al-air battery systems, though many technical issues yet to overcome remain. Recently, Liua et al. [172] reviewed the basics, problems and recent progress in Al-air battery technology right from aluminum anode, air cathode and electro-catalysts to electrolytes and inhibitors in great detail. The alloying of aluminum with transition metals had shown the decrease in Al self-corrosion and enhanced battery performance. Several studies of electro-catalytic materials for oxygen reduction/evolution including Pt and Pt alloys, nonprecious metal catalysts, and carbonaceous materials at the air cathode are underlined. The application of aqueous and non-aqueous electrolytes is discussed to decide on the electrolyte, while exploring the addition of inhibitors to the electrolyte to enhance electrochemical performance. Also, the challenges and future research directions are proposed for the further development of Al-air batteries.

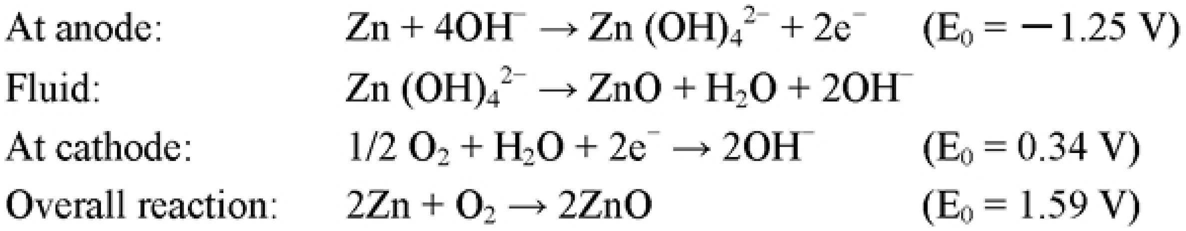
To deal with the corrosion in Al-air battery, Hopkins and his team at MIT investigated the following. A thin membrane barrier was placed between the battery electrodes and the 2 sides of the membrane were filled with a liquid electrolyte while the battery was working. When the battery was placed standby, oil was pumped into the side nearby to the Al electrode, which protects the Al surface from the electrolyte on the other side of the membrane. When aluminum is dipped in water, drive back oil from the surface. So, when the battery was reactivated and electrolyte pushed back into the cell, the electrolyte easily replaced the oil from the Al surface, which returned the battery’s power. The energy loss was cut to just 0.02% per month, more than a thousand-fold improvement. This ensued in an Al-air prototype with a greater shelf lifetime than that of traditional Al-air batteries. When the battery was continually operated and then put on standby for one to 2 days, this new design lasted 24 days, while the conventional design persisted for only 3 days. It was noticed that even after oil and a pumping system were incorporated in scaled-up primary Al-air battery packs, they were still lighter by 5 times and compact by twice than rechargeable lithium-ion battery packs used in electric vehicles [199a].

4.6.2 Zinc-air Batteries

Zn-air batteries are predominantly favorable due to their substantial theoretical energy density (1353 Wh/ kg excluding oxygen), low cost (currently < \$100 kW^{-1} h^{-1}, and possibly <\$10 kW^{-1} h^{-1}) and intrinsic safety [200–202a]. They are technically and economically viable and are well suited for fast-charging EVs in the coming years [203]. As such, electrically rechargeable zinc-air batteries have gained significant attention in the past few years. Besides their high-energy density, there are other desirable features - availability of abundant raw materials, environmental friendliness, and safety.

A standard Zn-air battery contains a porous air cathode and a Zn metal anode set apart by a membrane and filled the space with a concentrated alkaline electrolyte. In the discharge phase, oxygen from the surroundings infuses the porous cathode and gets reduced on the surface of electrocatalyst; in the intervening time, the Zn metal anode is oxidized to soluble zincate ($Zn\ (OH)_4^{2-}$) ions. If an appropriate bifunctional oxygen electrocatalyst is present, the above process can be reversed; that is, oxygen develops at the cathode which gets released back to the surroundings, and metallic Zn is plated at the anode. During experiments, oxygen is directly fed, instead of air, to the cathode. The batteries, therefore, should be called $Zn\text{-}O_2$ batteries [203].

The chemical reactions at the electrodes are (ref: Wikipedia):



At anode: $Zn + 4OH^- \rightarrow Zn\,(OH)_4^{2-} + 2e^-$ ($E_0 = -1.25$ V)

Fluid: $Zn\,(OH)_4^{2-} \rightarrow ZnO + H_2O + 2OH^-$

At cathode: $1/2\ O_2 + H_2O + 2e^- \rightarrow 2OH^-$ ($E_0 = 0.34$ V)

Overall reaction: $2Zn + O_2 \rightarrow 2ZnO$ ($E_0 = 1.59$ V)

Sealed battery cases cannot be used for Zinc-air batteries since air must enter. It is believed, the oxygen in one liter of air is needed for every ampere-hour (Ah) of capacity used.

In 2012, NantEnergy (formerly Fluidic Energy) produced for the first time commercial rechargeable Zn-air batteries, which were later in 2017, stated to have limited energy density, ~35 W h/kg [202b].

In spite of an early entry, these are yet to reach their total potential. The reason for this is two-fold: (a) both the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) at the cathode consist of multiple proton-coupled electron transfers and are extremely lethargic and leads to a small current density and large electrode polarization; and (b) the corrosion and the dendrite evolution of Zn metal in recharge end up in poor cyclability of most of the existing Zn anodes [204, 200, 201, 205].

To address these challenges, there have been tremendous research efforts on the development of efficient oxygen electrocatalysts [206–209a] though considerably less attention has been paid to the Zn side [210- 212]. Recent 2021 review by Yuan Qin et al [209b] sum up the most recently suggested plans for the production of designer carbon-based electrocatalysts and the maximization of their electrocatalytic performances in air electrodes. They also significantly emphasize the analysis of the innate active sites and their electrocatalytic mechanisms when used as flexible Zn-air battery catalysts. The results of this review can help the design of more valued carbon-based air electrodes and their consistent flexible Zn-air batteries for use in wornout electronic devices.

Fu et al. [201] have discussed their reaction mechanism, different battery configurations, and an in- depth analysis of the major issues that affect individual cellular components, along with respective strategies to alleviate these issues to enhance battery performance. Additionally, battery-testing techniques and the best practices to be adopted are explained while offering suggestions for future research to prolong the lifespan of electrically rechargeable zinc-air batteries.

Gu et al. [202a] have focused on the main challenges of the electrically rechargeable zinc-air batteries in alkaline electrolytes and the latest progress from materials to technologies toward overcoming these technical barriers. Offering an overview of the design and working mechanism of the battery, the authors have classified limitations such as dendritic growth at the anode, lack of higher performance bifunctional catalysts at the air electrode, and electrolyte-related problems. Further, the latest progress to solve these technical problems based on nano/ micromaterials is discussed along with future perspective.

Some recent publications on aspects of Zn-air batteries are worth perusing [210a-210d].

4.6.3 Iron-air Batteries

Iron-air flow battery is known since the 1970s. Recent interest is due to the enticements to produce inexpensive, environmentally-acceptable and strong rechargeable batteries. With an anticipated open-circuit voltage (V_{OC}) of 1.28 V, the specific charge capacity of <300 Ah/kg and stated charge efficiency of 96%, voltage efficiency of 40% and energy efficiency of 35%, the iron-air battery system could be well appropriate for a widerange of applications, including automobiles. However, several issues still need to be fixed that include (a) efficient bifunctional oxygen electrodes at reasonable cost, (b) low-priced iron electrodes to reduce corrosion and hydrogen growth, (c) novel cell structures using additive industrial technologies and (d) scientific models to advance battery performance. McKerracher et al [163] studied the thermodynamics and kinetics aspects of the iron-air battery, the operational variables and cell components, thereby highlighting current challenges and assessing recent developments.

4.6.4 Magnesium-air Batteries

Rechargeable Mg-air batteries are a favorable substitute for Li-air cells because of the safety it offers, low-cost due to plentiful resources, and high theoretical volumetric density (3832 Ah/ L for Mg anode against 2062 Ah/ L for Li). Investigations about this highly reversible battery are scanty. The major issues hampering the rapid progress of secondary Mg-air cells are ascribed to the reduced thermodynamic and kinetic properties because of the creation of an insulating film of MgO or MgO_2 as the primary discharge product on air-breathing cathode. This coating contributes to the growth of a large over-potential and an extraordinary polarization.

Recent significant studies, first-principle calculation and experimental, on rechargeable Mg-air batteries have tried overcoming the major limitations in organic electrolytes. Li et al. [164] have performed a general and crisp survey of the important advances so far made in secondary Mg-air batteries, and in-depth illustrations of related reaction mechanisms. The review is meant to generate a new area for influencing the nanostructures to control the best reaction pathway in novel cell arrangement and to comprehend the future Mg-air battery with improved energy density and cycling ability.

Overall, MABs are attractive not only as compact power sources for portable electronics and electric vehicles but also as compelling energy transfer stations or energy storage devices to manage power from renewable energy sources (wind turbines and solar photovoltaic panels), electric grids and end-users [213].

4.7 Flow Batteries

All electrochemical energy storage systems convert chemical energy in the electro-active materials to electrical energy when discharging, and the reverse occurs when charging. In conventional batteries, the conversion and storage occur in closed cells. However, in a flow battery, the electroactive materials are stored typically on the outside in an electrolyte and are led into the device only during the process. Battery structures in which all the electro-active materials are dispersed into a liquid electrolyte are called redox (for reduction/oxidation) flow batteries (RFBs). In RFBs, the energy storage material is conveyed by an energy converter, unlike in conventional batteries. This requires the energy storage material to be in a flowable form. The RFB has a structure similar to that of a fuel cell, and the charging and discharging processes can occur in the same cell. Thus, with RFBs the conversion and storage of energy are separated [214] and has the distinctive feature that energy and power can be scaled separately.

The power is defined by the cell size and the number of cells and the energy is determined by the amount of the energy storage medium (i.e. electrolyte) in the reservoirs. Hence, flow battery can be optimized for either energy and/or power delivery. This permits redox-flow batteries to be better adapted in certain applications than other technologies. Redox flow batteries are, therefore, electrochemical devices that use electrochemical reactions between 2 redox couples to reversibly conduct the conversion between chemical energy and electrical energy.

It is also critical to investigate efficient and reliable electrical energy storage systems (EES), which can improve the stability of new renewable energy sources and make them easier to couple with traditional energy sources. The electrochemical energy storage devices such as batteries, fuel cells/flow batteries, and capacitors are among the leading EES technologies for the future because of their scalability and versatility. Among them, particularly redox-flow batteries very well suited for this purpose because, in terms of cost, system flexibility, quick response and safety concerns for large-scale applications, they show great advantages over other types of batteries such as Pb-acid and Li-ion batteries.

Figure 4.14 is the schematic of a typical redox-flow battery functioning. Energy conversion occurs in an electrochemical cell that is split into 2 half-cells. An ion-permeable membrane or separator divides the 2 half-cells to ensure that the liquids in the half-cells do not mix much. The separator also makes sure a charge balance between positive and negative half-cells, without negative and positive active materials coming into direct contact with each other. However, as the separators are not flawless, some passes over the active materials occur all the time leading to the self-discharge effect [215].

Since the electrodes should not partake in the energy conversion process and create further side reactions (e.g. undesirable gas formation), carbon electrodes are used in most redox-flow batteries. The cell voltage varies between 0.5 and 1.6V in aqueous systems. During the charge, ions are oxidized at the positive electrode (releasing electrons) and reduced at the negative electrode (accepting electrons). This means that the electrons travel from the active material of the positive electrode to the active material of the negative electrode. During discharge, reverse occurs and energy is let free. The active materials used are redox pairs, i.e., chemical compounds, which absorb and release electrons.

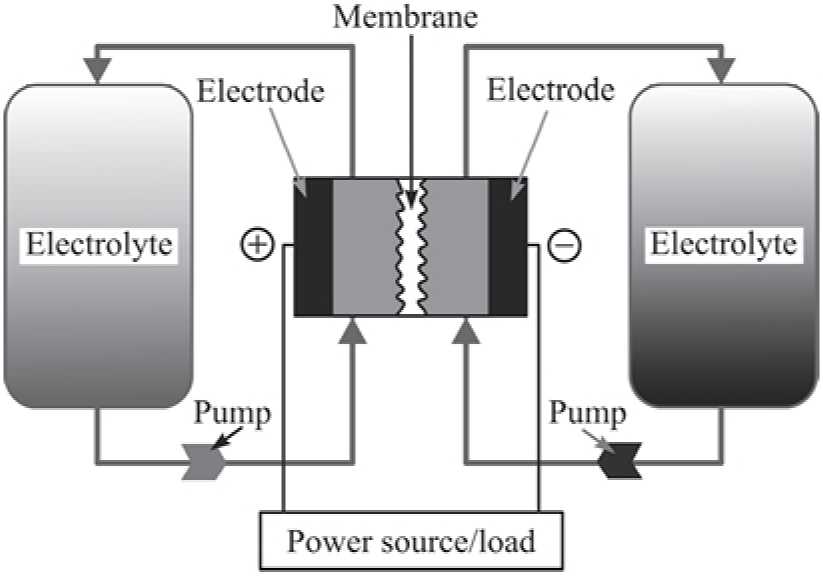
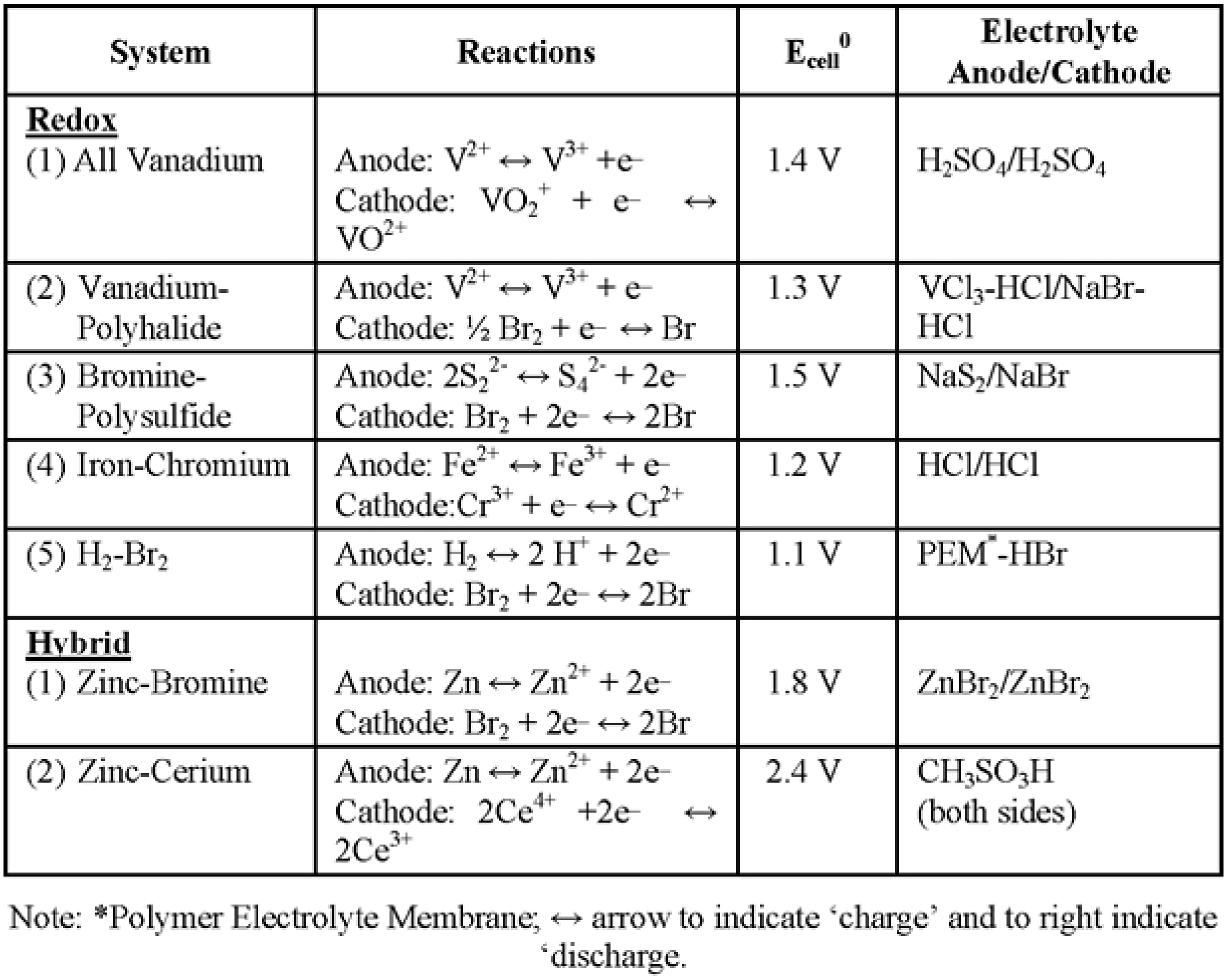


Figure 4.14: Working principle of Redox flow battery (Source [215])

In certain redox-flow batteries a gas is used that is not an electrolyte (e.g. H/Br-RFB), just like hydrogen as the energy storage medium. Similar to all other aqueous batteries, aqueous energy storage media from redoxflow batteries are sensitive to water limitations. In case of too high voltages or more specifically, too high or too low half-cell potentials, the water split into hydrogen and oxygen. Hydrogen production, though insignificant, is an adverse side effect causing a charge carrier inequality between positive and negative half-cells that leads to a steady capacity loss. Due to the flow-ability of the storage medium, the side products that would typically stay in the half-cell can be removed from the cell and kept separately. This allows the capacity to increase compared to the achievability with conventional batteries [215].

Over the past 30 years, several redox couples have been investigated [216]: all vanadium, iron-chromium, zinc-bromine, bromine-polysulfide, zinc-cerium, etc. as shown in Table 4.10.

Table 4.10: Characteristics of some Flow battery systems. Source: [217]



System	Reactions	E_{cell}^0	Electrolyte Anode/Cathode
Redox (1) All Vanadium	Anode: $V^{2+} \leftrightarrow V^{3+} + e^-$ Cathode: $VO_2^+ + e^- \leftrightarrow VO^{2+}$	1.4 V	H_2SO_4/H_2SO_4
(2) Vanadium-Polyhalide	Anode: $V^{2+} \leftrightarrow V^{3+} + e^-$ Cathode: $½ Br_2 + e^- \leftrightarrow Br$	1.3 V	VCl_3-HCl/NaBr-HCl
(3) Bromine-Polysulfide	Anode: $2S_2^{2-} \leftrightarrow S_4^{2-} + 2e^-$ Cathode: $Br_2 + 2e^- \leftrightarrow 2Br$	1.5 V	NaS_2/NaBr
(4) Iron-Chromium	Anode: $Fe^{2+} \leftrightarrow Fe^{3+} + e^-$ Cathode: $Cr^{3+} + e^- \leftrightarrow Cr^{2+}$	1.2 V	HCl/HCl
(5) H_2-Br_2	Anode: $H_2 \leftrightarrow 2 H^+ + 2e^-$ Cathode: $Br_2 + 2e^- \leftrightarrow 2Br$	1.1 V	PEM*-HBr
Hybrid (1) Zinc-Bromine	Anode: $Zn \leftrightarrow Zn^{2+} + 2e^-$ Cathode: $Br_2 + 2e^- \leftrightarrow 2Br$	1.8 V	$ZnBr_2/ZnBr_2$
(2) Zinc-Cerium	Anode: $Zn \leftrightarrow Zn^{2+} + 2e^-$ Cathode: $2Ce^{4+} + 2e^- \leftrightarrow 2Ce^{3+}$	2.4 V	CH_3SO_3H (both sides)

Note: *Polymer Electrolyte Membrane; ↔ arrow to indicate 'charge' and to right indicate 'discharge.

Battery systems that store one or more electro-active components on the inside are called hybrid flow batteries. The zinc-bromine and zinccerium batteries are examples. The energy densities of hybrid flow batteries, as in traditional batteries, are restricted by the quantity of electro-active materials stored in batteries; moreover, they have limited increase in gains.

Of all, vanadium redox-flow battery (VRFB) has the best chance to be widely adopted because of its simple structure and competitive cost and contains no toxic materials [e.g. 218]. Vanadium redox-flow batteries serve as large-scale stationary electricity storage systems with many potential applications in a deregulated and decentralized network.

4.7.1 Vanadium Redox-Flow Battery (VRFB)

Vanadium redox-flow batteries are the most developed and the most close to commercialization [29, 220].

Operating Mechanism: Fig. 4.15a shows the schematic of a vanadium redox-flow battery. It has 2 chambers, a positive chamber and a negative chamber, separated by an ion-exchange membrane. The electrolytes containing active species of vanadium in different valence states, VO_2^+/VO^{2+} in the positive electrolyte and V^{2+}/V^{3+} in the negative electrolyte, circulate through the 2 chambers. During discharge, VO_2^+ is reduced to VO^{2+} at the positive electrode, and V^{2+} is oxidized to V^{3+} at the negative electrode, as shown in the reaction equations below. The reactions proceed in the opposite direction during charging. The active species are normally break in a strong acid, and the protons move across the ion-exchange membrane to stabilize the charge. The vanadium redoxflow battery produces a typical voltage of 1.25 V [218–222].

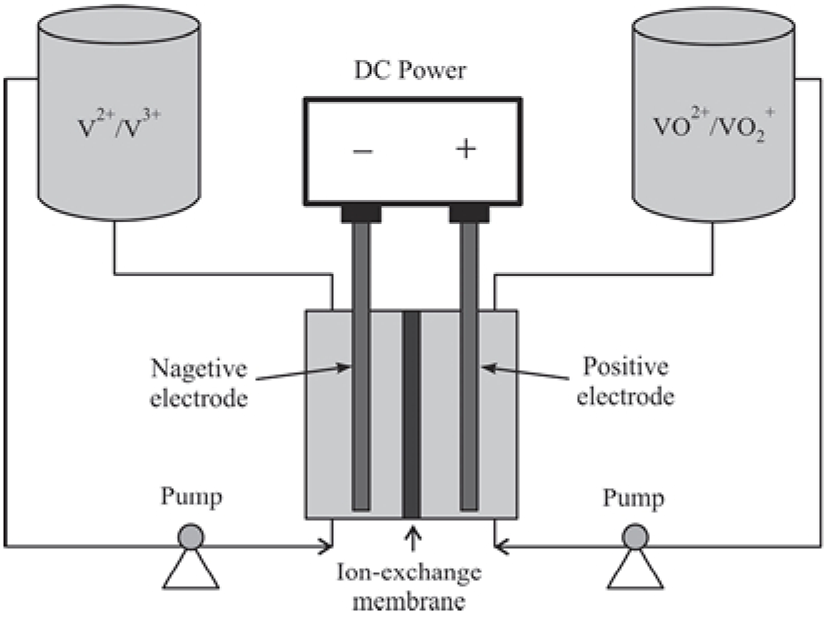


Figure 4.15a: Schematic representation of a VRB (Source: [222]) open access.

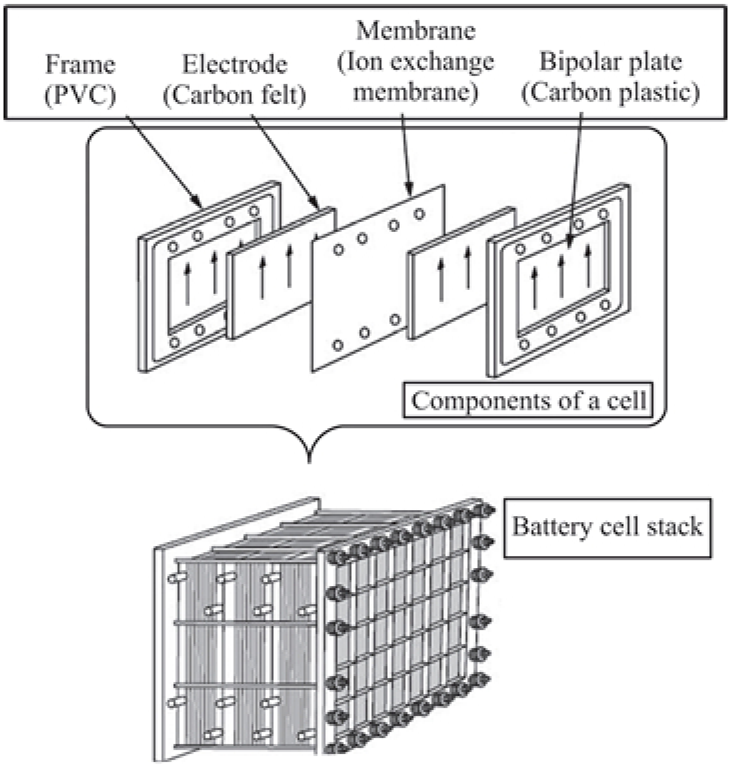


Figure 4.15b: Construction of a Vanadium redox cell Stack. (Source: [80])

At positive electrode:

$$VO^{2+} + H_2O - e^- \rightarrow VO_2^+ + 2\,H^+ \qquad (E^0 = 0.99V \text{ vs SHE})$$

At negative electrode:

$$V^{3+} + e^- \rightarrow V^{2+} \qquad (E^0 = -0.26V \text{ vs SHE})$$

Overall reaction:

$$V^{2+} + VO^{2+} + 2H + \leftrightarrow VO^{2+} + V^{3+} + H_2O$$

At a given temperature, if pH and quantity of vanadium species are known, the cell voltage can be evaluated using the Nernst equation:

$$E = 1.26\ V - RT/F \ln ([VO^{2+}] \times [V^{3+}]) / ([VO^{2+}] \times [H^{+}]^{2} \times [V^{2+}])$$

Here, R, T, and F are the universal gas constant, absolute temperature and the Faraday constant, respectively.

The crossover of vanadium ions through the membrane may occur, resulting in self-discharge with the unwanted mixing of vanadium species on both sides of the cell [223]:

At the negative electrode:

$$V^{2+} + VO^{2+} + 2\,H^{+} \rightarrow 2V^{3+} + H_2O$$

$$2V^{2+} + VO^{2+} + 4H^{+} \rightarrow 3V^{3+} + 2H_2O$$

$$V^{3+} + VO^{2+} \rightarrow 2VO^{2+}$$

At the positive electrode:

$$V^{2+} + 2VO^{2+} + 2\,H^{+} \rightarrow 3VO^{2+} + H_2O$$

$$V^{3+} + VO^{2+} \rightarrow 2VO^{2+}$$

$$V^{2+} + VO^{2+} + 2\,H^{+} \rightarrow 2V^{3+} + H_2O$$

Reactions such as hydrogen generation from water decomposition and CO_2 release due to oxidation of carbon-based electrode may happen during battery functioning [224].

The battery performance is normally determined by 3 kinds of efficiencies: coulombic efficiency (CE), voltage efficiency (VE) and energy efficiency (EE). These are expressed as the following:

CE = ratio of discharge capacity to charge capacity × 100%;

VE = ratio of average discharge voltage to average charge voltage × 100%; and

EE = Product of CE and VE

The CE decreases due to move over of vanadium ions during cell operation and side reactions. The VE depends on the operation current density, membrane's ionic conductivity, electrode materials, flow-rate and mass transport of electrolyte. As current density rises, the VE reduces owing to the increase in polarization [225].

VRF batteries have V^{3+}/V^{2+} redox reactions on the negative side and VO_2^+/VO^{2+} on the positive side. Such a battery uses the same metal ions on both sides. Hence, the crossover of metal ions through the membrane does not result in pollution of the electrolyte. In contrast, for RFBs with different metal ions such as Fe^{3+}/Fe^{2+} and Cr^{3+}/Cr^{2+} in an iron-chromium flow battery, the cross-pollution through ion penetration may cause permanent performance loss. More on the latter is covered in the following pages.

Development path: The VRFB was invented and established by Maria Skyllas-Kazacos and coworkers at the University of New South Wales in the 1980s.They conducted investigations into vanadium ions as active materials for redox-flow batteries and found the possibility of using 4 different oxidation states on carbon electrodes in fundamental electrochemical investigations [226, 227] and later as battery experiments [228]. This group studied several aspects: (a) developing efficient manufacturing processes from inexpensive and abundantly available raw materials for the active material, (b) electrochemical and chemical basics, (c) increasing the energy density by using concentrated solutions and stabilizing agents and inexpensive separators, (d) membrane modification techniques, (e) increasing power density through electrode treatment processes and so on. Also developed an inexpensive conducting plastic bipolar electrode substrate that could be welded to the cell flow frame that reduced the cost of the Stack. This research led to the development of a 1 kW power battery in 1991[228, 229]. In 1995, UNSW group installed 15kWh battery in a Solar Demonstration House in Thailand and tested a 200kW/800kWh battery at Kashima Kita, Japan.

The energy density is limited by the concentration of the pentavalent VO_2, which incline to react with each other, forming larger molecules. These in turn coalesce as solids and can damage the system.

The reaction depends on the temperature and quantity of VO^{2+} (state of charge), but also on the proton concentration. While increasing the acid concentration enhances the stability of VO^{2+}, it diminishes the solubility of the V(II), V(III) and V(IV) sulfates.

Therefore, vanadium and total sulfate concentrations are fixed at around 1.8 and 4.2 mol/L respectively to accomplish adequate operating temperatures. If the state of charge and temperature are high, the inclination to form solids in the positive half-cell increases; and so, the electrolyte temperature is restricted to around 40°C. To cut down the threat of precipitation of the other species at low temperatures, a minimum of 10°C is normally suggested. Otherwise, the SOC limits can be attuned to operate temperatures outside this range [215].

The life of a vanadium redox battery is decided by a number of its components. The cell stack is perhaps the component with limited life, a useful life estimated around 10 years, which is difficult to approve due to lack of operational data. The tanks, plumbing, structure, power electronics, and controls have a longer useful life. The electrolytes and the active materials they contain do not degrade with time [80].

VRFB is capable of attaining a total output starting from zero outputs within a few milliseconds, if the stacks are already prepared with reactants. The actual controlling factor for starting battery discharge is the control and infrastructure apparatus. For short-time discharges needed for voltage support, the electrolyte in the stacks can react without running the pumps at all. The cell stack can deliver 3 times the rated power output if the state of charge is between 50% and 80% [230].

Progress in VRFB's chemistry: The classic VRFB has undergone several further developments. First, the V/Br-RFB called Gen 2 was developed by Skyllas-Kazacos et al. [231]. Using the fast redox pair Br_2 /Br-, it was aimed to achieve a higher energy density, improved temperature stability, and perhaps higher energy efficiency.

Pacific North West National Laboratory developed Gen 3. A mixture of hydrochloric acid and sulfuric acid was used as solvent for vanadium ions [232] , which improved temperature stability and energy density up to 50Wh/L. A handicap is the in-house formation of chlorine gas in the battery, which has a greater insistence on the materials' stability.

Gen 4 are the vanadium/oxygen cells, in which vanadium ions are oxidized by oxygen from the air during discharge, thus generating energy. The process is reversed in the charging process. In theory, the energy density of up to 150Wh/L energy can be achieved [233].

Like all other redox-flow batteries, VRFBs also have a battery management, which ensures optimum and safe conditions for battery operation. Often a heat management system is integrated to avoid too high or too low temperatures [215].

Advantages and Disadvantages: Today, the vanadium redox-flow battery is best studied and most installed redox-flow battery. The VRFB uses vanadium as an active material in 3 different oxidation states; the redox pair VO^{2+}/VO^{2+} at the positive electrode and the redox pair V^{2+}/V^{3+} at the negative electrode. If the same ions are used in the positive and negative electrolytes, it allows rather high concentrations of active material [215].

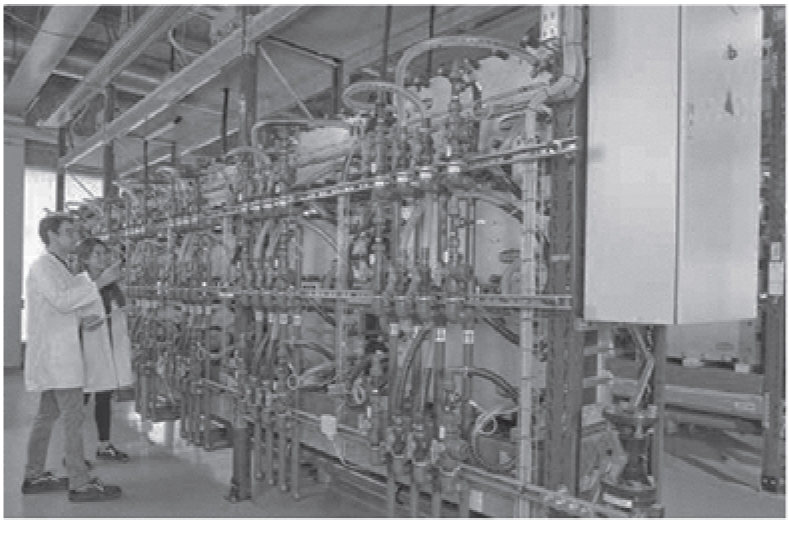


Figure 4.16a: Stacks of 2MW/20MWh vanadium redox-flow battery at Fraunhofer ICT; (Source: [143e])

Vanadium redox-flow batteries have high energy efficiency, short response time, long cycle life, and independently tunable power rating and energy capacity [220; 234], similar to other redox batteries. The active species in positive and negative electrolytes are only vanadium in different valence states. Hence, vanadium redox-flow batteries do not suffer from cross-mixing of positive and negative electrolytes [221].

The cycle life of VRFB is not contingent on the depth of discharge. Battery’s cycle life is rated at 10,000 cycles. Sumitomo Electric Industries, Ltd., did some speeded testing and produced a battery system for cycle testing, consisting of one 20-kW stack, which sustained for more than 13,000 cycles in about 2 years [80].

Vanadium is a relatively abundant metal that is enriched as a byproduct during the burning of fossil fuels, and mainly used as an alloying element in the production of steel. Vanadium ions in solution, can achieve high cycle lifetimes, as no complex phase transitions and new phase developments are essential. Another advantage is the recycling of the batteries is simple.

As the liquid electrolyte contains a high content of vanadium, it can easily be recombined into process chains and the current value reclaimed [215].

One disadvantage of VRB is the low volumetric energy storage capacity, limited by the solubility of the active species in the electrolyte. Also, the system requires the use of expensive ion-exchange membrane, which costs more than 40% of the overall battery cost [235a].

Current Applications/Installations: Today’s VRFB range from a few KW/KWh to several hundred MW/MWh. Power utilities and industrial customers can use VRFBs in numerous storage applications such as improved power quality, UPS, peak shaving, better security of supply and integration with intermittent renewable energy sources

[235b]. Several companies sell VRFBs today in different size classes.

Several large-scale demonstrations have been built world-over including Australia, Thailand, Japan, USA, and China [221; 236, 237]. A 260 kW system was installed at Dalian Institute of Chemical Physics and Rongke Power in 2010 in China. They are also building a 5 MW system at a 30–50 MW wind farm for output power stabilization [219]. Rongke Power has installed a 200 MW/800 MWh VRFB system at Dalian, China, declaring it as the world's largest unit. This system is expected to provide peak demand, improve grid stability and offer black start capacity. Prudent Energy installed a VRB-energy storage system of 600 kW/3600 kWh consisting of 200kW modules providing6 hours of electrochemical energy storage at Gills Onions, Oxnard, CA.

According to Andy Colthorpe [238], around 70 MW and 250MWh of RFBs (in medium to large-scale projects) have been deployed so far by virtue of their fast response times and long cycle life along with ease of recyclability of the components, and are likely to gradually increase their adoption in the place of Li-ion batteries in the future.

Figure 4.16b: Prudent Energy installed 600kW/3,600-kWh VRB-energy storage system at Gills Onions, Oxnard, CA.

Further research: Studies have been conducted on these aspects critical to the performance of VFB: (a) low-cost and strong ion-exchange membranes with high proton conductivity, and good selectivity [235]; (b) three-dimensional electrodes having large surface area, good chemical steadiness in strong acid, and extraordinary catalytic activity [239]; (c) additives or other methods to stabilize the active vanadium species in high concentration electrolytes [234]; (d) designs with minimal pumping and shunt current losses; and large-scale power and system management and grid integration and so on [240]. Generally, the main hurdles for large-scale energy storage to reach commercial viability are (a) round trip storage efficiency, (b) cost for energy storage expressed as \$/kWh, and (c) cost for the power capacity expressed as \$/kW [240].

4.7.2 Iron-Chromium Redox-flow Battery (Fe-Cr RFB)

The vanadium redox-flow battery is estimated to have a high system cost of $325/kWh [241]. To easily commercialize a flow battery, it is essential to develop a low-cost redox-active material. So, wide-ranging efforts have been focused on developing inexpensive redox-active materials [242–249].The non-aqueous RFB has a potential to achieve high cell voltage and high energy density [250–254], but it is still in its infancy.

The iron-chromium redox-flow battery benefits from the soluble redox couples of, Fe(II)/Fe(III) as the positive electrolyte, and Cr(II)/ Cr(III) as the negative electrolyte in the acid supporting medium. An ion-exchange membrane separates them [250, 255]. The Fe-Cr RFB charge and discharge through the electrochemical reactions:

At positive electrode:

$$Fe^{3+} + e^{-} \leftrightarrow Fe^{2+} \qquad (E^0 = +0.77V \text{ vs SHE})$$

At negative electrode:

$$Cr^{2+} \leftrightarrow Cr^{3+} + e^{-} \qquad (E^0 = -0.41V \text{ vs SHE})$$

Overall reaction: $Fe3^{+} + Cr^{2+} \leftrightarrow Fe^{2+} + Cr^{3+}$ ($E^0 = 1.18V$)

Extensive studies on ICRFB regard to several issues (electrodes, hydrogen evolution, membrane etc.) have been conducted over the last few decades [256–263].

The cheap and plentiful chromium and iron as the redox-active materials help facilitate a cost-effective energy storage system [250, 255, 261]. For instance, a 250 kW/1 MWh Fe-Cr redox-flow battery energy storage system has been demonstrated in California, US [265].

The Fe-Cr RFB is typically a flow-through cell structure, shown in Fig. 4.17, in which the electrolyte is directly driven through the porous electrode [266]. The cell structure is simple and easy to produce. However, a clear drawback of this structure lies in the difference between the flow resistance and ohmic resistance. A thinner electrode decreases the ohmic resistance, but increases the flow resistance substantially because the cross-sectional area is decreased for electrolyte flow. It has been reported that, at the same flow-rate, the pump loss increases threefold when the electrode thickness is reduced from 2.5 mm to 1.25 mm [267]. To avoid high flow resistance and pump loss, customary graphite-felt electrodes are designed to be fairly thick, typically 3.0–6.0 mm [267–269] leading to high ohmic resistance of 3–5 ohm/ cm^2 [270, 271]. Consequently, the conventional Fe-Cr RFBs are restricted to a moderate operating current density of 40 mA/cm^2, and an energy efficiency of 70% at room temperature [270]. At a higher temperature of 65 ∘C also, the current density is limited to 80 mA/ cm^2 with an energy efficiency of around 80%. This results in huge, costly cell stacks with a likely cost of $116/kWh, accounting for 60% of the capital cost of the battery system [264, 256].

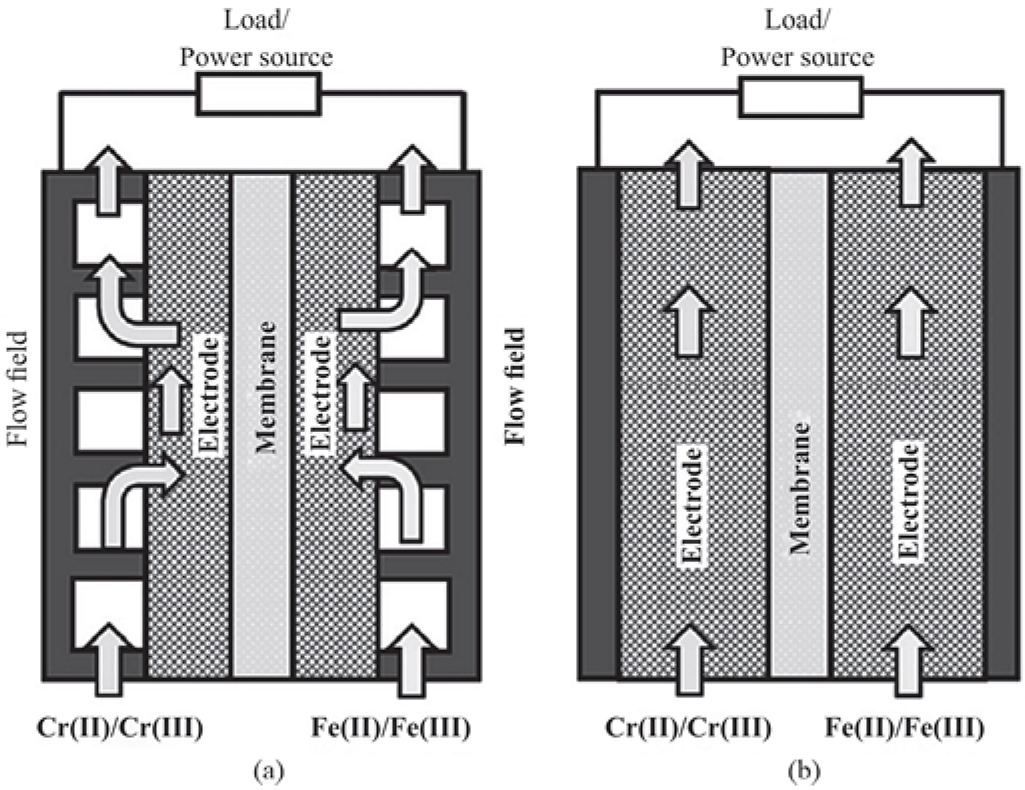


Figure 4.17: Schematic of (a) flow-through cell structure, and (b) flow-field cell structure of Fe-Cr RFB, (Source [276])

Recently, a flow-field cell structure with a thin electrode has been applied to all: V, H_2 /Fe and H_2 /Br_2 RFB systems. This novel cell structure, which is drastically different from conventional flow-through cell structure, dramatically improves battery performance because of reduced ohmic resistance [248, 272–275]. In the flow-through cell structure the electrolyte is dispersed through indiscriminate pores of the electrode, whereas in the flow-field cell structure, well-defined flow channels close to the electrode dispense the electrolyte across the total electrode area. So, in the flow-field structure, the electrolyte transfer is in the in-plane direction and is unrelated to the porous electrode. Thus, the pump loss is less sensitive to the electrode thickness compared to the flow-through cell structure. As a result, the flow-field cell structure allows a thinner electrode [269, 273]. It has been reported that the pump loss for the flow-field cell having a 1.0 mm thick electrode is only 47% of that for the flow-through cell structure having a 3.0 mm thick electrode at the same flow-rate [275]. The carbon paper, another type of carbon, which has better stiffness, lesser contact resistance and compact thickness compared to the graphite-felt, make a reasonable electrode material for the flow-field cell structure [269].

Zeng et al. [276] have shown that the high ohmic resistance of conventional Fe-Cr RFB critically limits the battery performance and to enhance performance, they developed a flow-field structure Fe-Cr RFB (Fig. 4–14b). The energy efficiency at 25°C, is presently 76.3% with a current density of 120 mA/cm^2, while at 65 ∘C, the energy efficiency stretches to 79.6% with a current density of 200 mA/cm^2.

Comparative Performance & Cost evaluation: The RFBs using soluble redox couples, such as all vanadium ions and iron and chromium ions, have unique advantages including scalability, intrinsic safety, and long cycle life, which are major factors for commercialization. Hence, they are becoming increasingly recognized for large-scale energy storage of renewables such as wind and solar, which are intermittent and inconsistent. This debate on these 2 RFBs is to determine which of the 2 is more appropriate and economical for large-scale energy storage. As part of this concern, Zeng et al. [264] conducted a comprehensive comparative study based on their charge-discharge performance, cycle performance, and capital cost. It is found that (a) both types of batteries have similar energy efficiencies at large current densities (energy efficiency of 80.3% for VRFB and 78.4% Fe-CrFB can be realized at 120 mA/cm^2, which remain stable during the cycle test); (b) the capacity decay rate is higher for Fe-Cr RFB (1.2%) compared to that of VRFB (0.3%); and (c) the capital costs of Fe-Cr RFB are much less when functioned at high power densities or at large capacities. For the base case of the 1 MW- 8 h energy storage system, the VRFB electrolyte costs $122/kWh representing 53% of the total capital cost, whereas Fe-Cr RFB electrolyte costs around $17/kWh, only about 9% of its capital cost.

Both iron and chromium are inexpensive active materials and offer a vast potential for the Fe-CrRFB to cost less. This analysis further indicates that the cost of the Fe-CrRFB can be significantly lowered if the current density is increased or if the discharge duration is lengthened. These are still at demonstration stage only and yet to reach commercial level.

4.7.3 Hybrid Redox-flow Batteries

There are flow batteries in which solids are deposited and dissolved at one or both electrodes, unlike in vanadium redox-flow battery. A typical representative is the zinc/bromine redox-flow battery, patented in 1885 by Charles Bradley [277]. Such batteries are called hybrid redox-flow batteries. Zinc-Cerium and redox-flow lithium are 2 other examples. Unlike in redox-flow batteries, power and energy are not individually expansive, as the quantity of likely deposition of solids is restricted by the cell geometry [215].

Hybrid redox-flow batteries have 2 electrolyte circuits like conventional RFBs, but a large amount of active material leads to a thicker layer of solids in the half-cell, and thus resulting in blockage of the fluidic system or dendrites’ uneven growth. These can be open to short circuits via the separator. Like in all other batteries, the power density drops with an increase in the layer thickness of the half-cells. Due to this reason, the space for the deposition and thus the layer thickness is adjusted with reference to the power density, and commonly takes to storage times of 4 to 8 hours [215].

For instance, zinc-bromine and zinc-cerium systems make use metal stripping/plating reactions (Zn^{2+}/Zn, and -0.76 V vs. SHE) on an electrode inside the cell, and normal soluble flowing electrolyte on the other side. Likewise, redox-flow Li batteries in non-aqueous electrolytes are investigated to use the low redox potential of Li^+/Li couple (-3.04 V vs. SHE). During charge, zinc or lithium from the electrolyte is deposited, and during discharge, Zn^{2+} or Li^+ dissolves into the solution again. In consequence, the energy storage ability is limited by the free space inside the cell obliging the metal deposits [225, 235].

Electrochemistry of Zn/Br battery*:* Zinc is the electro-active kind at the negative electrode, which has long been used in primary cells as the negative electrode. Zn is commonly available and relatively inexpensive metal and is electropositive with a standard reduction potential $E° =$ -0.76 V vs SHE as given above.

At the negative electrode, the reaction is the reversible dissolution/plating of zinc:

$$Zn_{(s)} \leftrightarrow Zn^{2+}{}_{(aq)} + 2e^-$$

At the positive electrode, bromine is reversibly reduced to bromide (with a standard reduction potential of +1.087 V vs SHE):

$$Br_{2(aq)} + 2e^{-} \rightarrow 2Br^{-}_{(aq)}$$

Overall cell reaction:

$$Zn_{(s)} + Br_{2(aq)} \leftrightarrow 2Br_{(aq)} + Zn^{2+}{}_{(aq)}$$

The measured voltage is around 1.67 V per cell (a little less than the predicted value from the standard reduction potentials). The 2 electrode chambers of each cell are separated by a microporous or ion-exchange membrane. The membrane helps to stop bromine getting to the positive electrode, where it reacts with the zinc triggering the battery to selfdischarge. To lessen self-discharge and to moderate the bromine vapor pressure, organic complexing agents are supplemented to the positive electrolyte. These react reversibly with bromine to produce an oily red liquid decreasing the Br_2 content in the electrolyte (Wikipedia).

The active materials, Zn and Br are cheap and the energy density is high, about 70–80 Wh/litre, which are the advantages of Zn/Br flow batteries. The demerits are the use of bromine and its moderately short cycle life with several thousand charge and discharge cycles [215].

Plain bromine is produced at the positive electrode during charging of the battery. To reduce the risk potential and self-discharge, organic complexing agents are added to the energy storage medium to hold the bromine and to prevent it from fleeing [215]. The complexing agent is reasonably costly, adding to the battery price. The used redox pair Br/Br-has an extraordinary reaction speed and is perfect for batteries from the point of electrochemistry.

Application status: Exxon and General Electric companies in the U.S. initiated commercialization efforts in the 1970s that directed to stack concepts, materials and fabrication methods that are still appropriate. In the 1980s, these efforts resumed mainly by ZBB Corp. Australia, and modular multi-megawatt battery systems were produced. Then, they stopped working a few years ago. In the same period, these batteries were tried using various electric vehicles and buses, primarily by the Australian companies, SEA and Powercell.

Actually, they are in an early phase of field installation and demonstration trials. With insufficient field data, the vendors declare estimated lifetime of 20 years, long cycle life, and operating efficiencies (ac-to-ac) of roughly 65%. Module capacities ranging from 5 kW to 1000 kW in varying sizes, and with variable energy storage periods from 2 to six hours, depending on the service necessities and need are available. Small projects consist of 5kW/ 2-hour systems are being set up in rural Australia as an alternative to erecting new power lines. Electric utilities in the U.S. undertook early studies of 0.5 - 1.0 MW systems for grid support and reliability [80]. RedFlow produce a range of zinc bromide flow battery modules capable of daily deep discharge and charge; they can be integrated with intermittent energy supply sources.

ZnBr are sturdier than lithium-ion type, and the expected energy output for smaller modules goes up to 44 MWh. Large-scale battery systems contain 60 ZBM-3 batteries that deliver continuous 240 kW and peak 300 kW at 400–800 volts, and supply power of 660 kWh. Today, only one company is selling Zn/Br-RFBs [215].

Second-type *hybrid redox* **-***flow batteries* use gas like Cl_2, O_2 and H_2 for the reaction medium or employ gas evolution reaction at the cathode or anode (see Fig. 4–18a).

For instance, oxygen reduction reaction, such as $O_2 + 4\,H^+ + 4e^- \rightleftarrows 2H_2O$ with high positive voltage can be used as the cathode. The cell capacity is then determined only by the analyte capacity.

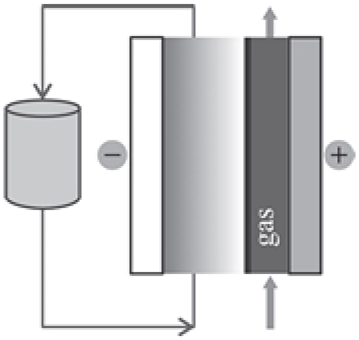


Figure 4.18a: Configurations of a hybrid redox-flow battery with gas supply at one electrode [225],

The oxygen reduction reaction in non-aqueous electrolytes with the presence of lithium ions can proceed differently:

$$O_2 + 2Li^+ + 2e^- \rightleftarrows Li_2O_2.$$

Moreover, oxygen reduction and oxidation during discharge and charge can be catalyzed chemically with redox mediators. By the way, the electrocatalyst usage for oxygen reduction and oxidation, as in a conventional redox system can be circumvented. It may be seen that the formation and deposition of Li_2O_2 proceed at a porous matrix, which can be held statically in a gas diffusion tank over charging/discharging. Such a concept decouple energy and power for flow batteries [225].

Regarding aqueous electrolytes, oxygen and hydrogen evolution reactions by the electrolysis of water happen during charging at positive and negative electrode potentials, respectively. The hydrogen generation reaction is detected as a parasitic side reaction at the negative electrode for some flow battery systems. Such behavior is used to store electricity as well as to generate hydrogen simultaneously, as revealed in a vanadium-cerium flow battery [225].

$$2V^{2+} + 2H^{+} \rightarrow H_2 + 2V^{3+}$$

Hydrogen generated can then be used to produce electricity in fuel cells.

A typical RFB energy storage system integrated into solar power generation is shown in Fig. 4.18b.

Figure 4.18b: Solar power generation plant combined with storage facility with RFBs. Credit: [238].

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CHAPTER 5

Electrical/Electromagnetic Energy Storage

5.1 Capacitors

Electricity is a hugely adaptable form of energy, but unfortunately it is relatively difficult to store in an urgency. Batteries are known for storing large amounts of energy in a relatively small space, but they are heavy, slow to charge, limited lifespan, often made of toxic materials and moreover, expensive.

The device, ‘Capacitor’ is better in that respect, charge almost instantly but store only tiny amounts of power. A typical capacitor can be charged and discharged instantly, almost any number of times, and both the positive and negative charges in a capacitor are produced entirely by static electricity.

In a capacitor, there is no chemistry involved to store energy. A capacitor comprises 2 metal plates with a *dielectric material,* an electrical insulator, sandwiched between them. As in the case of battery, a capacitor can be charged by adding electrical energy, and discharged releasing the energy from the capacitor.

A capacitor can be charged by connecting it in an electric circuit. When the power runs in the circuit on switching, an electric charge steadily accumulates on the plates, with one plate gaining a positive charge and the other plate gaining an equal negative charge. If the power is cut off, the capacitor retains its charge although some charge leak away slowly over time. The dielectric allows a capacitor of a certain size to store more charge at the same voltage, allowing the capacitor more efficient than a charge-storing device.

If the capacitor is connected to a circuit containing a bulb or an electric motor, charge will flow from the capacitor through the motor or lamp until it is exhausted and no charge remains on the plates.

In addition to storing electric charge, the capacitors perform different functions in electrical circuits. For instance, (a) as timing devices because it takes ‘expectable’ amount of time to charge the capacitors, (b) as electrical filters , which are circuits that permit only certain signals to flow, (c) for voltage smoothing in circuits, (d) for tuning in radios and TVs, and (e) for numerous other functions.

Capacitors have many advantages over batteries: they are light-weight, do not contain harmful chemicals or toxic metals, and they can be charged and discharged millions of times without draining out. But the main drawback is that their basic design prevents them from storing as much as the amount of electrical energy as the batteries store [1].

What is the capacitance? The amount of electrical energy a capacitor can store depends on its ‘capacitance’; higher the capacitance, higher the electricity the capacitor can store. The capacitance of a capacitor can be increased in 3 ways: (i) increasing the size of the plates; (ii) to position the plates closer; and (iii) to choose an excellent insulator as dielectric.

There are several kinds of materials used as dielectrics in capacitors. A large variable capacitor used to tune transistor radios has air between its plates. The capacitors included in most electronic circuits are sealed ones containing dielectrics made of ceramics such as mica, glass, oil-soaked paper, or plastic materials such as Mylar.

Capacitance measurement: The size of a capacitor (capacitance) is measured in units called *farad*(F), named after its discoverer Michael Faraday. One farad is an enormous amount of capacitance; in practice, most of the capacitors have capacitance, just fractions of a farad, typically microfarad (μF), or nanofarad (nF) or picofarad (pF). Super capacitors store far bigger charges, rated in thousands of farad, which will be seen in the following pages.

The capacitor can store more energy if the plates are as big as possible, and as closer as possible, with a good insulator between them. The capacitance (C) and charge (Q), are related to a simple equation,

$C = Q/V$, where V is the voltage.

A flat metal plate with the maximum possible charge stored on it will be at a certain voltage. If a second identical plate is brought close to it, much more charge can be kept on the first plate for the same voltage. This happens because the first plate generates an electric field all over it that produces an equal and opposite charge on the second plate. Hence, the second plate lessens the voltage of the first plate. So, more charge can be kept on the first plate without producing a spark. This can be repeated until the original voltage is reached.

As more charge (Q) can be stored for precisely the same voltage (V), the equation C = Q/V reveals that the capacitance of the capacitor is increased by adding a second plate, and this is essentially why capacitors have 2 plates.

How to increase the capacitance? It's obvious that bigger plates enable to store more charge. So increasing the area of the plates also increases the capacitance. Moving the plates closer also increases the capacitance because the smaller the distance between the plates, the more influence they have on each other. Being nearer, the second plate diminishes the voltage of the first plate much more, and that in turn enhances the capacitance.

The dielectric by reducing the electric field between the plates (that is, by reducing the voltage of each plate) increases the capacitance of a capacitor. That is, more charge can be stored on the plates at the same voltage. In the capacitor, the electric field goes from the positive plate to the negative plate; hence, the polar molecules of the dielectric align in the reverse, and reduce the field.

To increase the capacitance, the dielectric material needs to be changed. Air is a good dielectric, but there are other better materials. Compared to air, glass is at least five-fold more impressive, but it is weighty and tough to press into small volumes. However, the initial capacitors, for instance, Leyden jars, using ordinary glass as the dielectric functioned so well.

Waxed paper dielectric is superior by about fourfold to air. Its positive features like (a) low cost, (b) easy to make thin, (c) simple to produce large portions and to roll, make it an exceptional and practical dielectric material. The exceptional dielectric materials are made of polar molecules (those with more positive electric charge on one side and more negative charge on the other), which normally increases the capacitance. Water, made of truly tiny polar molecules, would make an excellent dielectric, roughly 80 times better compared to air. But, it is not a favored dielectric material because it leaks and dries out and undergoes a phase change with temperature variations.

A metric called ‘relative permittivity’ indicates how good an insulator becomes a good or bad dielectric. Vacuum is given a relative permittivity of one as it is a poorest dielectric. Other dielectrics are measured relative to the vacuum. Air’s permittivity is roughly the same.

Relative permittivity of certain insulators used or useful as dielectrics are the following: water - 80, alcohol - 25, glass - 6.5, salt - 6.0, mica -4.0, paper - 3.0, rubber - 2.5, polystyrene - 2.0, air - 1.0, and vacuum -1.0. Water and alcohol, which have polar molecules, have the highest relative permittivity values and hence make good dielectrics.

The parallel plate condenser used at National Bureau of Standards, USA, to measure the speed of light in 1907 is shown in Figure 5–1. It is an adjustable parallel plate capacitor that Edward Bennett Rosa and Noah Earnest Dorsey of the National Bureau of Standards (NBS) used to measure the speed of light in 1907. The precise distance between the plates could be adjusted (and measured) with a micrometer screw [1].

The capacitors are classified into 3 types: (a) the classic capacitor, which is the best elementary electrostatic capacitor with a dry separator; has low capacitance, size varies from a few pico-farads (pf) to a few microfarads (µF); and mainly employed to tune radio frequencies and filtering; (b) the *electrolytic capacitor* that uses a moist separator provides higher capacitance than the electrostatic capacitor and is rated in microfarads (µF), a million times larger than a picofarad. Similar to a battery, the electrostatic capacity has a positive and negative that must be observed, and these are used for filtering, buffering and signal coupling; (c) the *supercapacitor*, having high capacitance (in farads), very much higher, nearly thousands of times higher, compared to electrolytic capacitor.

The supercapacitor is used for energy-storage that experiences repeated charge and discharge cycles at high current and short duration.The supercapacitor, also known as ultracapacitor or double-layer capacitor, differs from a regular capacitor with high capacitance [2].

Figure 5.1: Photo of the adjustable parallel plate capacitor used to measure the speed of light in 1907. (Courtesy of National Institute of Standards and Technology Digital Collections, Gaithersburg, MD.) [1]

5.2 Super Capacitors (SCs)

Supercapacitors are electro-chemical devices capable of storing and supplying high-power electricity quickly and for a large number of cycles (up to millions of cycles) with no decline in performance.

It is an electrical energy-storage device [3] and looks very much like a battery. The supercapacitor consists of 2 carbon electrodes immersed in an organic electrolyte with a separator between them (Figure 5–2). The electrodes are fabricated from a high surface area porous material having pore diameters in the nanometer (nm) range. The surface area of the electrode materials used in a supercapacitor, around 500–2000 m^2 /gm, is much greater than that used in battery electrodes [4].

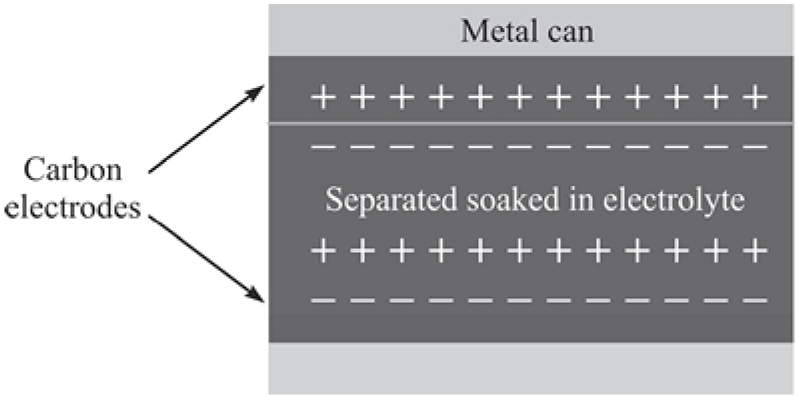


Figure 5.2 Schematic of a Supercapacitor. Source: [5]

During charging, the charged ions in the electrolyte drift toward the electrodes of opposite polarity because of the electric field between them generated by the applied voltage. Thus, 2 separate charged layers are produced.

The charge is stored in the micropores at or near the solid electrodeelectrolyte interface. The energy stored in the capacitor is expressed as $\frac{1}{2} CV^2$ where C is its capacitance and V is the voltage across the capacitor.

The capacitor’s rated voltage depends on the electrolyte. The charge Q carried by the capacitor is the product of capacitance and voltage, expressed in coulomb. The charge and energy stored in the supercapacitor are also calculated similarly. But, the capacitance estimation of the electrochemical capacitor is more complicated as it depends on complex reactions occurring in the micropores of the electrodes.

With regard to ideal double-layer capacitor, the charge is transmitted into the double-layer and no Faradaic reactions happen among the solid material, ions, and electrolyte. Hence, the capacitance, (dQ/dV), is a constant and feebly reliant on voltage [4]. Though akin to a battery, the double-layer capacitor is influenced by electrostatic action.

Devoid of chemical action, the effect is simply reversible and the characteristic cycle life is a hundred thousand cycles, much higher than that of rechargeable batteries. It typically stores 10 to 100 times more energy per unit volume or mass than electrolytic capacitors, and can accept and deliver charge much faster than batteries. Though energy density is low (< 15Wh/ kg), the power density is high (4000 W/kg) and the capacitance of the order of thousands of farad is possible. Despite high-power density, the cell voltage is restricted to roughly 2.3 V to prevent the electrolysis of the electrolyte with the subsequent emission of gas [5]. They are characterized by a low leakage current and are appropriate for several applications requiring a voltage in the 1.8V - 2.5V range. The lifespan of a supercapacitor is generally 10 to 20 years, and a decrease in the capacity may happen, after about 8 to 10 years of operation, from 100% to 80% [6].

The conventional solid dielectric is not used in the supercapacitor, but electrostatic double-layer capacitance and electro-chemical pseudocapacitance, both of which contribute to the capacitor’s total capacitance is used, with some changes [7,8]: (a) *Electrostatic doublelayer capacitors* use carbon electrodes or end-products having much greater electrostatic double-layer capacitance than electro-chemical pseudocapacitance, realizing the separation of charge in a Helmholtz doublelayer at the interface of conductive electrode surface and electrolyte. The separation of charge is much smaller than in a conventional capacitor, about 0.3 to 0.8 nm; (b) *Electrochemical pseudocapacitors* make use of metal oxide or conducting polymer electrodes having a large electrochemical pseudocapacitance in addition to double-layer capacitance. Pseudo-capacitance is realized by Faradaic electron charge-transfer with redox reactions by intercalation or electrosorption [7, 8]. The supercapacitors can also be produced using a double-layer (carbon) material for electrode and a battery-like material for the other electrode. Such designs are frequently mentioned as *hybrid capacitors* [9–11]. So far, in most of the hybrid capacitors fabricated, metal oxides (such as lead or nickel oxide) are used as the battery-like material in the positive electrode and lithiated graphite in the negative electrode. These devices retain significantly higher energy density than carbon/carbon double-layer capacitors [4].

5.3 Battery Vs Supercapacitor

Supercapacitors function strictly like rechargeable batteries in storing or delivering electric charge, but their mechanisms of charge storage are different, in most cases. Thus, supercapacitors are not alternatives for batteries but somewhat *complementary* to them for charge storage or supply. They can provide rapid charge or discharge rates than many batteries of similar volume, but their energy density is less than the batteries by 3 to 4 times. Their high-power and power densities allow them to be used along with batteries in fascinating complementary ways in hybrid systems.

The charging of a capacitor differs very much from the charging of a battery; in a capacitor, there is an *inherent* increase in voltage on charge or decrease in voltage on discharge as the charge per cm^2 is increased or decreased, where as a perfect battery has a consistent or steady voltage during discharge or recharge except when the state of charge tends to 0 or 100%.

Applications: Supercapacitors are more appropriate in applications demanding several rapid charge/discharge cycles rather than for extended compact energy-storage, or in cars and buses, trains, cranes and lifts, where they offer services such as regenerative braking, short-term energy-storage, or blowup-mode power delivery. Smaller systems serve as power reserve for ‘static random-access memory (SRAM)’ [7]. These units also function as cold-start help diesel locomotives, reserve power for computer systems in emergencies, static power-system load leveling or linking for short time power outages, energy supply for primary heating of catalytic converter units, and storage of energy from windmills [12].

For *high voltage* applications such as electric vehicles, a series chain of capacitors is needed to avert going over the operational voltage of individual capacitors, which lessens the effective capacity of the chain. For a series chain of N capacitors of similar value, the capacity is evaluated using $C = c/N$ where C is the capacitance of the chain and c, the capacitance of the individual capacitors. Simultaneously, the internal resistance of the chain is increased to R, which is the product of ‘r’ and N, where r is the internal resistance of the capacitor. With more capacitors added to the chain, R increases. The increase in internal resistance slows down the charge-discharge rate and escalates the losses.

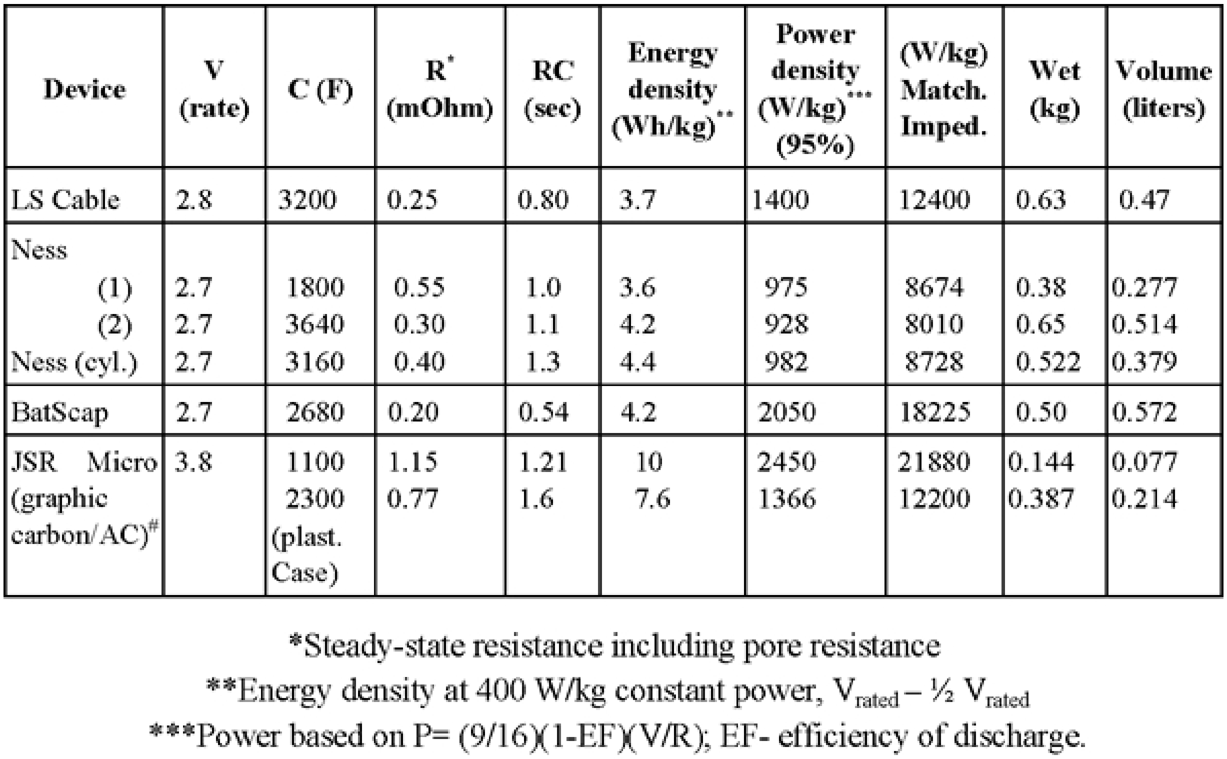
Capacitances can be accomplished higher by parallel connection of capacitors. Then, the capacitance of an assembly of N parallel capacitors is C = N x c. At the same time the resistance of the assembly is decreased and is stated as R = r/N.

Typical capacitors for automotive applications range from 10 to 200 F, 100V.

A number of new supercapacitor devices are tested in the laboratory at the University of California-Davis [13–15a, b]. These are carbon/carbon devices acquired from Skeleton Technologies of Estonia and Yunasko of Ukraine; and hybrid devices obtained from Yunasko and JSR Micro of Japan. The carbon/carbon device from Skeleton Technologies has high-power ability with no loss in energy density. This device has the highest energy density (9 Wh/kg) of all carbon/carbon devices examined. This is because of improved carbon and an increase in the rated voltage from 2.7V to 3.4V consequent to the use of an upgraded organic electrolyte. The characteristics of the various supercapacitors tested at University of California, Davis are given in Table 5.1.

Table 5.1: Characteristics of various available supercapacitors [4, 15b]

Device	**V (rate)**	**C (F)**	**R* (mOhm)**	**RC (sec)**	**Energy density (Wh/kg)****	**Power density (W/kg)*** (95%)**	**(W/kg) Match. Imped.**	**Wet (kg)**	**Volume (liters)**
Maxwell									
(1)	2.7	2885	0.375	1.1	4.2	994	8836	0.55	0.414
(2)	2.7	605	0.90	0.55	2.35	1139	9597	0.20	0.211
Vinatech									
(1)	2.7	336	3.5	1.2	4.5	1085	9656	0.054	0.057
(2)	3.0	342	6.6	2.25	5.6	710	6321	0.054	0.057
Ioxus									
(1)	2.7	3000	0.45	1.4	4.0	828	7364	0.55	0.49
(2)	2.7	2000	0.54	1.1	4.0	923	8210	0.37	0.346
Skeleton Technol.									
(1)	3.4	3200	0.47	1.5	9.0	1730	15400	0.40	0.284
(2)	3.4	850	0.8	0.68	6.9	2796	24879	0.145	0.097
Yunasco									
(1)$^{\#}$	2.7	510	0.9	0.46	5.0	2919	25962	0.078	0.055
(2)$^{\#}$	2.75	480	0.25	0.12	4.45	10241	91115	0.060	0.044
(3)$^{\#}$	2.75	1275	0.11	0.13	4,55	8791	78125	0.22	0.15
(4)$^{\#}$	2.7	7200	1.4	10	26	1230	10947	0.119	0.65
(5)$^{\#}$	2.7	5200	1.5	7.8	30	3395	30200	0.068	0.038



Device	V (rate)	C (F)	R* (mOhm)	RC (sec)	Energy density (Wh/kg)**	Power density (W/kg)*** (95%)	(W/kg) Match. Imped.	Wet (kg)	Volume (liters)
LS Cable	2.8	3200	0.25	0.80	3.7	1400	12400	0.63	0.47
Ness									
(1)	2.7	1800	0.55	1.0	3.6	975	8674	0.38	0.277
(2)	2.7	3640	0.30	1.1	4.2	928	8010	0.65	0.514
Ness (cyl.)	2.7	3160	0.40	1.3	4.4	982	8728	0.522	0.379
BatScap	2.7	2680	0.20	0.54	4.2	2050	18225	0.50	0.572
JSR Micro (graphic carbon/AC)#	3.8	1100 2300 (plast. Case)	1.15 0.77	1.21 1.6	10 7.6	2450 1366	21880 12200	0.144 0.387	0.077 0.214

*Steady-state resistance including pore resistance

**Energy density at 400 W/kg constant power, $V_{rated} - ½\ V_{rated}$

***Power based on P= (9/16)(1-EF)(V/R); EF- efficiency of discharge.

All devices except those with # are packaged in metal/plastic containers. Those with # are laminated pouched packaged.

Except the supercapacitors from Skeleton Technologies and Yunasko, all the others shown in the Table are available in the market. Many of the carbon/carbon devices commercially available have energy density of 4 to 5 Wh/kg and power capability of 1000 W/kg for 95% efficient pulses. Due to the high-power ability of the hybrid devices, their improved energy density can be entirely made use of particularly in hybrid vehicles, where the device needs to be sized by the energy-storage constraint [4, 15b].

Intense R & D studies on supercapacitors energy-storage have been in progress over the last few years. The incorporation of a short-term electrical energy-storage device akin to a supercapacitor in an induction generator has been investigated to use it for smoothing the fast wind-induced power fluctuations [15c].

5.4 Superconducting Magnets

The superconducting magnetic energy-storage (SMES) technology uses ‘superconducting’ property of materials. A superconductor has zero electrical resistance and when current flows through it, there is neither heat nor energy loss.

The best materials are metal alloys that must be cooled to close to the absolute zero before they become superconducting. Once reached that state, a superconducting coil can be charged with an electric current, which in turn generates a strong magnetic field in which energy is stored. This energy will remain as long as the low temperature is maintained.

SMES systems, therefore, store energy in the magnetic field created by allowing a direct current pass through a spiral of superconducting material that is cooled cryogenically below its superconducting critical temperature (T_C). The coil, when discharged, can deliver the stored energy back to the network. This system is capable of releasing megawatts of power (the stored energy within the magnet) within a fraction of a cycle to replace a sudden loss in line power.

SMES system is based on 3 distinct concepts not relevant to other energy-storage methods: (i) electric current flow through some materials with no resistive losses; (ii) magnetic fields are generated by an electric current; (iii) the magnetic field is energy that can be put in storage. These 3 basic ideas are used competently to store energy in a superconducting coil [16].

The characteristics of a typical SMES system are

Specific power: ~10–100 000 kW/kg

Charge/discharge efficiency (round trip efficiency): 95%

Energy density: less than 40 kJ/L

Self-discharge rate: 0% at 4°K; 100% at 140°K

Specific energy: 1–10 W h/kg (4–40 kJ/kg)

Cycle durability: Unlimited cycles

A typical SMES system consists of 4 main sub-systems (Fig. 5–3):

(a) Superconducting coil kept in a vacuum in a thermally insulated vessel, normally a helium vessel; (b) the refrigeration system alongside a vacuum pump continuously working to maintain the temperature below Tc; (c) the power-conditioning system (PCS) including an inverter/rectifier to transform ac-to-dc and/or convert dc-to-ac. In the inverter/rectifier, about 2–3% energy loss occurs in each direction. The power-conditioning system in the SMES loses the least amount of electricity in the energy-storage process compared to other methods of storing energy; (d) the control system to continuously monitor the essential factors such as temperature, pressure, current, coil strain, regulating the operation of the cryogenic system accordingly.

Besides these 4 main sub-systems, a SMES system has a protection arrangement to prevent damage in the superconductor in the event of a sudden quench [17].

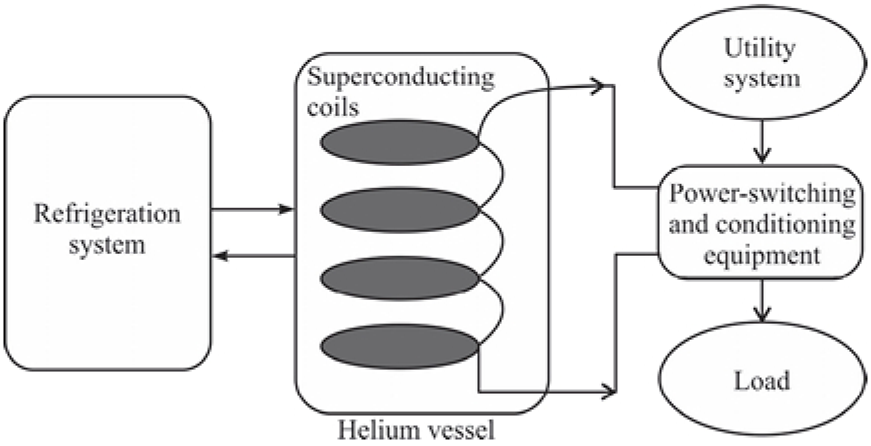


Figure 5.3: Components of a SMES system [18]

The amount of energy that can be stored in a SMES system is represented as $E = \frac{1}{2} L I^2$.

Here L is the inductance of the coil and I is the electric current flowing through the coil. The equation shows that the energy stored would be higher/more if the inductance and the current flowing through the coil are high.

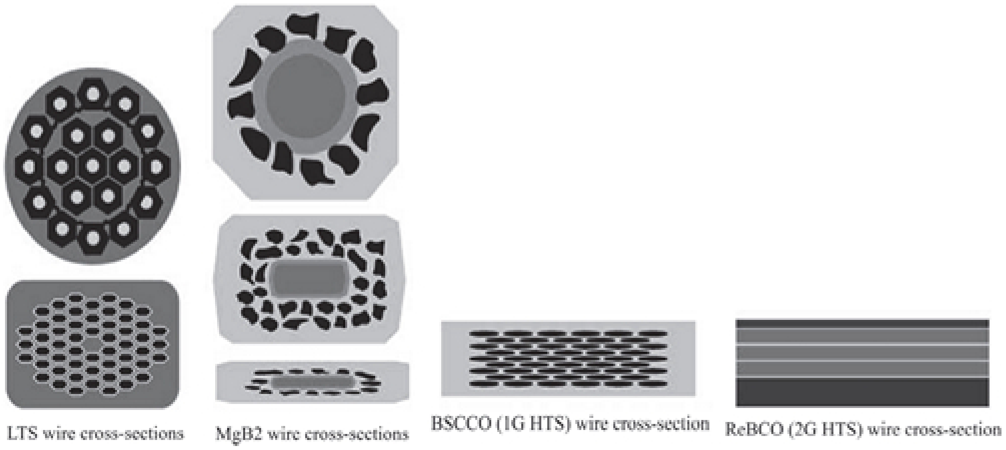
Operation: A source voltage is fed into the superconducting coil. Whenever the voltage from the source is AC, it must be converted to DC. Most renewable energy sources do supply DC voltage.

The design of the device will limit the maximum energy stored. The power-conditioning system decides on when to provide power for charging, or when to draw energy from the SMES to provide power. When energy is needed, currents induced on the coils are superimposed on the load as specified by the control system. DC-to-AC current conversion can also be done when required.

During energy-storage in the superconductor coil, the refrigeration system keeps the coil at a temperature below T_C needed to have no resistive loss. It means that the current stored will flow in the coil until the moment of usage. The PCS uses solid-state electronics [18]. The subsystems are briefly explained.

Superconducting coils: The superconducting coil consists of multiple windings of superconducting wire or tape. Several superconducting materials are prepared into thin wires and placed in a matrix of Cu, Al, or Ag alloys for better strength and quench safety (acts as sink for the current in case the temperature exceeds T_C when the material is no more superconducting). Each superconducting material is defined by its critical temperature T_C, critical magnetic field B_C and critical current density j_C. These 3 parameters are directly dependent, with lower working temperatures enabling higher current densities and magnetic fields to be achieved.

The materials are classified, depending on the critical temperatures, into low temperature (LTS), medium temperature (MTS) and high temperature (HTS) superconducting materials. LTS have a critical temperature below 20° K, and the most normally used materials are NbTi, Nb3Sn and Nb3Al, having transition temperatures in the range 10° - 18°K [21]. Figures 5–4a,b,c,d represent cross sections of different types of superconducting wires [19].



(a) LTS section (b) MgB_2 section (c) 1G HTS section (d) 2G HTS section

Figure 5.4(Source of the figures: [19])

Magnesium diboride (MgB2) with T_C = 39° K, considered a medium temperature superconductor is used at the optimal temperature of 20° K.

Rare-earth Barium copper oxide (ReBCO) compounds with Yttrium, Gadolinium, Samarium or Neodymium, having T_c of over 90° K [20], and Bismuth Strontium Calcium Copper Oxide (BSCCO 2212 with T_C = 95° K, and BSCCO 2223 with T_C =108° K [23] are HTS materials in use.

Depending on their behavior in the magnetic field in the Tc region, HTS superconductors can either be 1stgeneration superconductor (BSCCO-abrupt change to resisting magnetic fields below T_C, cannot withstand high magnetic fields in the superconducting region) or 2ndgeneration superconductor (ReBCO demonstrate a region of mixed behavior around T_C, can withstand much higher magnetic fields without quenching) [21]. They can be produced “either as wires (e.g. all low temperature superconductors, MgB_2 and BSCCO) or multi-layer tapes of structural layers sandwiching a layer of powdered superconductor (e.g. ReBCO materials)” [22].

Currently, the most commonly used superconductors in SMES are LTS (NbTi and Nb_3Sn), with applications of up to 100 MJ [160b]. They require temperatures lower than liquid He temperature (4.2° K), which is expensive. Also, they have a much lower maximum current density and magnetic field compared to other superconductors such as BSCCO or YBCO at the same temperature [19].

If the superconducting coil can be operated close to room temperature by using MTS and HTS, the cost of SMES can be lowered because liquid nitrogen, which boils at 77°K can be used, which is cheaper than liquid He. Further, MTS and HTS have potential to sustain higher fields and current densities at higher temperatures.

MgB_2 coils operating at 20°K have shown encouraging results with magnetic fields of 2 to 5 T and current densities of up to $200A/mm^2$ [24, 25]. MgB_2 wires though currently expensive, are expected to decrease by 2020–2025 [19]. However, the main issues in using this material in SMES applications are the increase of the current density to a level similar to NbTi and producing lengthy wire with economic viability. Silicon carbide fibers coated in MgB_2 have demonstrated the prospect of enduring high magnetic fields of up to 55T, which discloses the possibilities for the application of coated superconducting wires in these systems [26].

Layered rare-earth metal oxypnictides (i.e. LnOFeAs, with a T_c, 26° K) and the combination with other rare-earth elements exceeding 50° K are the superconducting materials, which are of recent interest [27].

Coil designs: The common shapes of superconducting coils are solenoid or toroidal as shown in Fig. 5–5. The solenoid consists of linearly stacked pancake coils, and in the toroidal design the superconducting coil is wound around a toroid-shaped supporting structure. The main advantage of the solenoid design is that it can store higher energy. However, a stray magnetic field is developed in such a system that can be detrimental to the surroundings. Similar stray field is found in modular toroidal coils, comprising equally spaced pancake coils fixed together in a toroidal shape. Nonetheless, if the wire is consistently wound in a helical toroid, the coil can have the stray magnetic field within the structure. A toroidal coil design cost lesser capital budget for uses larger than 100 MJs [19]. Various design changes of pancake coil modules can increase the amount of energy that can be stored keeping the amount of superconducting material as low as possible.

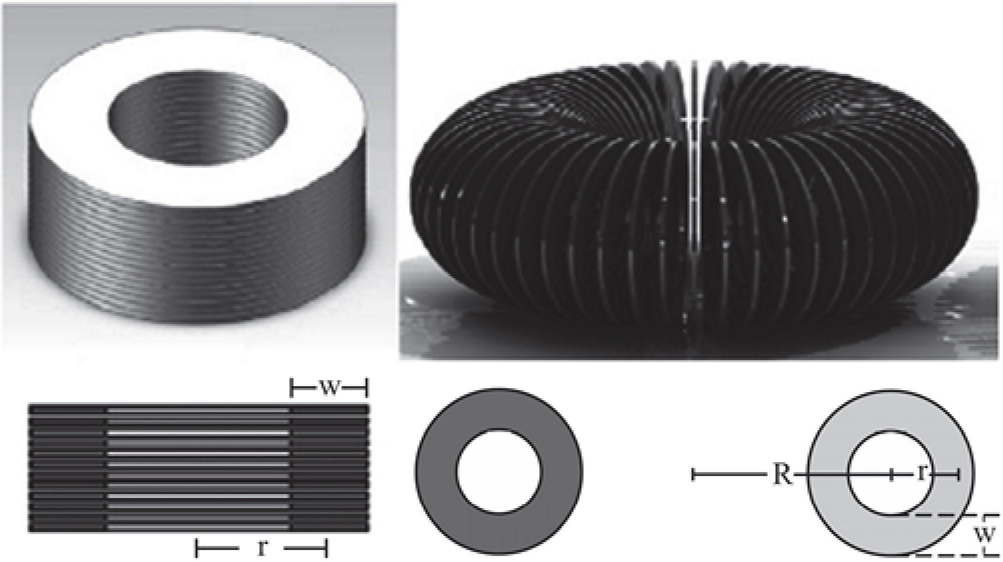


Figure 5.5: solenoid and toroidal configurations. Source: [28]

Certain solenoid designs with a large single-direction length can be compacted by splitting the structure, subject to the space accessible, into several smaller solenoids; and can be placed either vertically or horizontally to form polygons, reducing the storage loss to roughly 5% [29].

In modular toroidal SMES, if a few modular coils are built in a D-shape rather than circular and inserted between the other circular coils, there would be 18% increase in the energy-storage capacity, and at the same time, the cost and complexity would rise [30]. By using the same D-shape windings, the size of toroidal coils can be lessened by linking 2 semi toroidal concentric coils [34]. For large-scale applications, configurations such as Tilted Toroidal Coils [31], Force-Balanced Coils [32], and Stress Balanced Coils [33] are tried, which have shown promising results. Other interesting coil types are the N side polygons displaying excellent stray field containment. They are however extremely difficult to manufacture, especially using ceramic superconductors [34].

Refrigeration system: The refrigeration system is an important unit that maintains the superconducting coil at a temperature below Tc. For situations where LTS coils are used, working temperatures of 4.2^{o} K and below can be maintained by placing the coil in liquid helium. The entire system is then encased in a vacuum vessel and insulated using a radiation shield. Despite the relatively low cost of LTS coils, the operating costs are higher due to high cost of liquid He and a higher energy input necessary for maintaining the cryogen at such low temperatures. Other cryogen such as liquid H_2, liquid Ne and liquid nitrogen are used for applications at around 20° K, $27\circ$ K and 77° K, respectively.

The cryo-free conduction coolers that are lighter, more compact and can operate at a wider range of temperatures can also be used [35]. These systems can be Gifford-

McMahon (GM) or GM with Joule-Thomson circuit (GMJT), Sterling cycle (ST) or ST pulse tube (STPT).

In majority of SMES demonstrations using HTS coils, combinations of single or double stage GM cryo-coolers are employed, along with a series of heat dissipation disks and tubes interposed between coils. These disks and tubes are normally made of high thermal conductivity materials such as copper [36a, 37].

Power conditioning and control system: The power-conditioning and control design of SMES system is shown in Fig. 5.6. The circuit outline comprises 2 sections: SMES main circuit and control circuit. The converter set in the SMES main circuit includes 2 models: voltage source converter and current source converter, through which SMES engage with the power grid. The system assumes loop control to get a steady compensation effect. As shown in the figure, 3 variables (voltage of load system, voltage of power-system, and current of main bus) are assumed as feedbacks to the control circuit. In addition, fault control by sensors is made available to ensure that the HTS coil work in the superconducting state [38a].

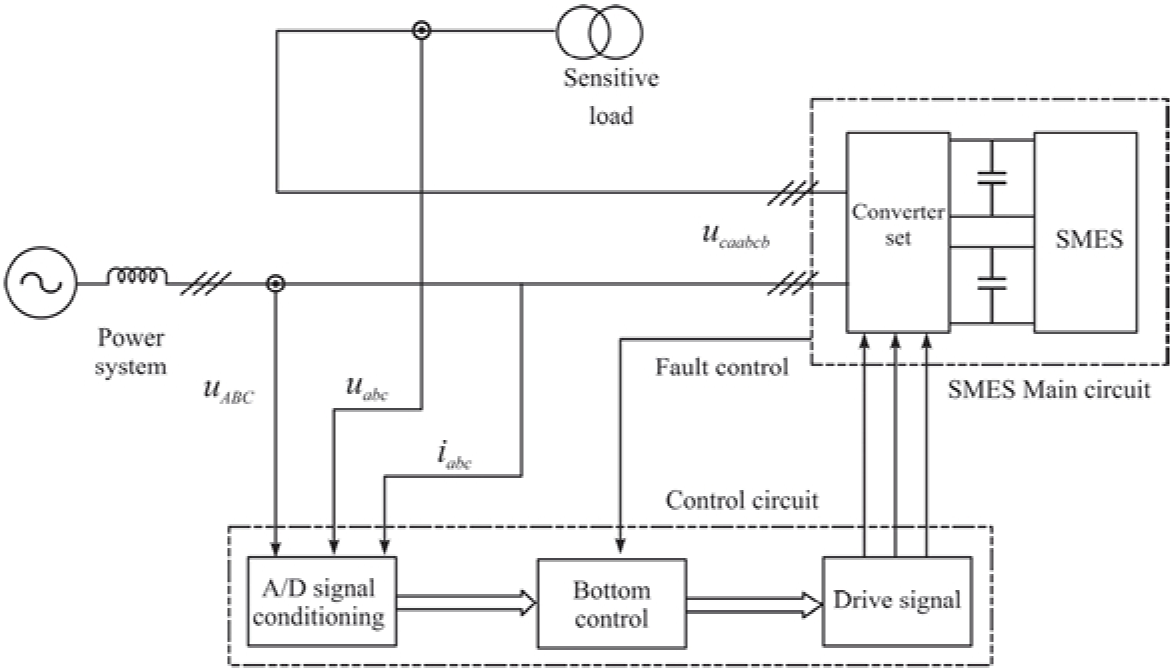


Figure 5.6: Control and power circuit layout of SMES system [38a]

Limitations on the amount of stored energy: There are limits on the amount of energy that can be stored in a SMES system. Due to the formation of a high magnetic field, the structure of the coil is subject to multidirectional stresses like longitudinal, radial and hoop; at a certain high stress level, the entire structure can collapse, much before the limits on the current or magnetic field are reached. This aspect poses one of the major issues for this technology: the inevitability of strong infrastructure for supporting the superconducting magnet, which escalates the capital costs and restrict the possible installation sites.

Applications: SMES systems have a number of applications in power systems. Most of the studies, however, are implemented through computer simulations or in laboratories because of high cost and large investment, though there are some practical applications with small capacities [38b].

Most of the commercial uses are centered on the more mature LTS technology. As technology is capable of rapid discharge or absorb energy, it is applicable principally in power networks for improving power quality [39, 40], low frequency damping, controlling system stability, UPS, and as flexible AC transmission systems (FACTS).

SMES systems can be used in *distributed power generation* for the following applications: (a) voltage stabilization to quickly regulate voltage sags, surges or drops; (b) frequency regulation by damping frequency variations by modulating the real/reactive power; (c) power quality improvement by quickly injecting or absorbing real power in the grid in case of sudden fluctuations; (d) renewable energy sources such as wind, solar and hydroelectric stabilization: SMES systems may be directly coupled to wind or solar PV or hydroelectric plants to enormously improve the voltage stability by taking excessive power when generated in excess, or by pumping into the grid if the voltage is dropping suddenly [19, 33, 41, 42, 44b,c,d]; (e) UPS: providing protection in case of power outage for sensitive loads; (f) EV charging stations and Vehicle to Grid (V2G) operation; (g) certain configurations of SMES can be used for storing vast amounts of energy which can be used for peak shaving, contingency or during periods of decreased generation capacity (less windy/sunny days). Given the current technology status, this may not be economically viable [19].

5.4.1 Renewable Energy Sources Coupled with SMES

The intermittence nature of the wind or solar power makes the successful integration of the distributed generation (DG) schemes, and integration of SMES significantly improves operating stability of the entire system [43, 44a]. For example, Fig. 5.7 shows a schematic for the coupled solar photovoltaic and SMES systems. The PV generation system and the SMES system are linked by a common bus that is attached to the utility grid [44a].

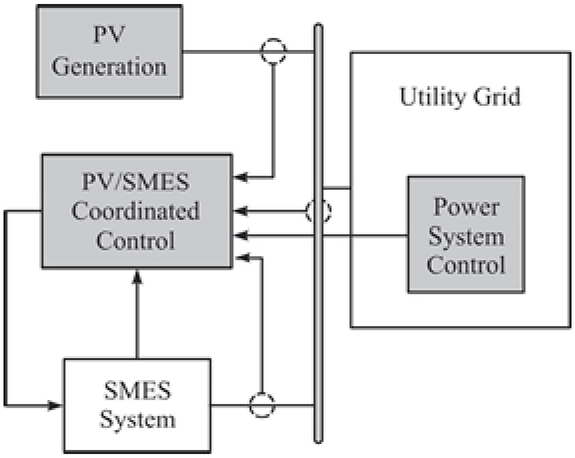


Figure 5.7: Diagram for solar PV/SMES system [38a]

The following results are obtained with/without the modulation by PV/SMES system. Fig. 5.8 shows the power generated by the SMES system can smooth out solar PV power fluctuations very well, resulting that the combined PV/SMES output is transmitted free of oscillations. The power generated from PV installations can be completely used and PV penetration can be significantly increased without having side effects to the power-system.

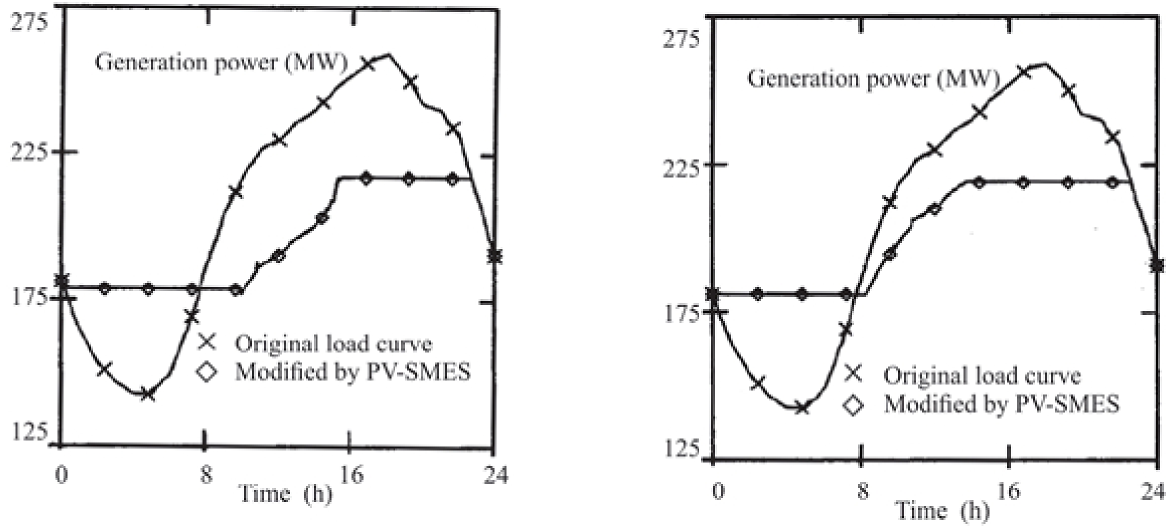


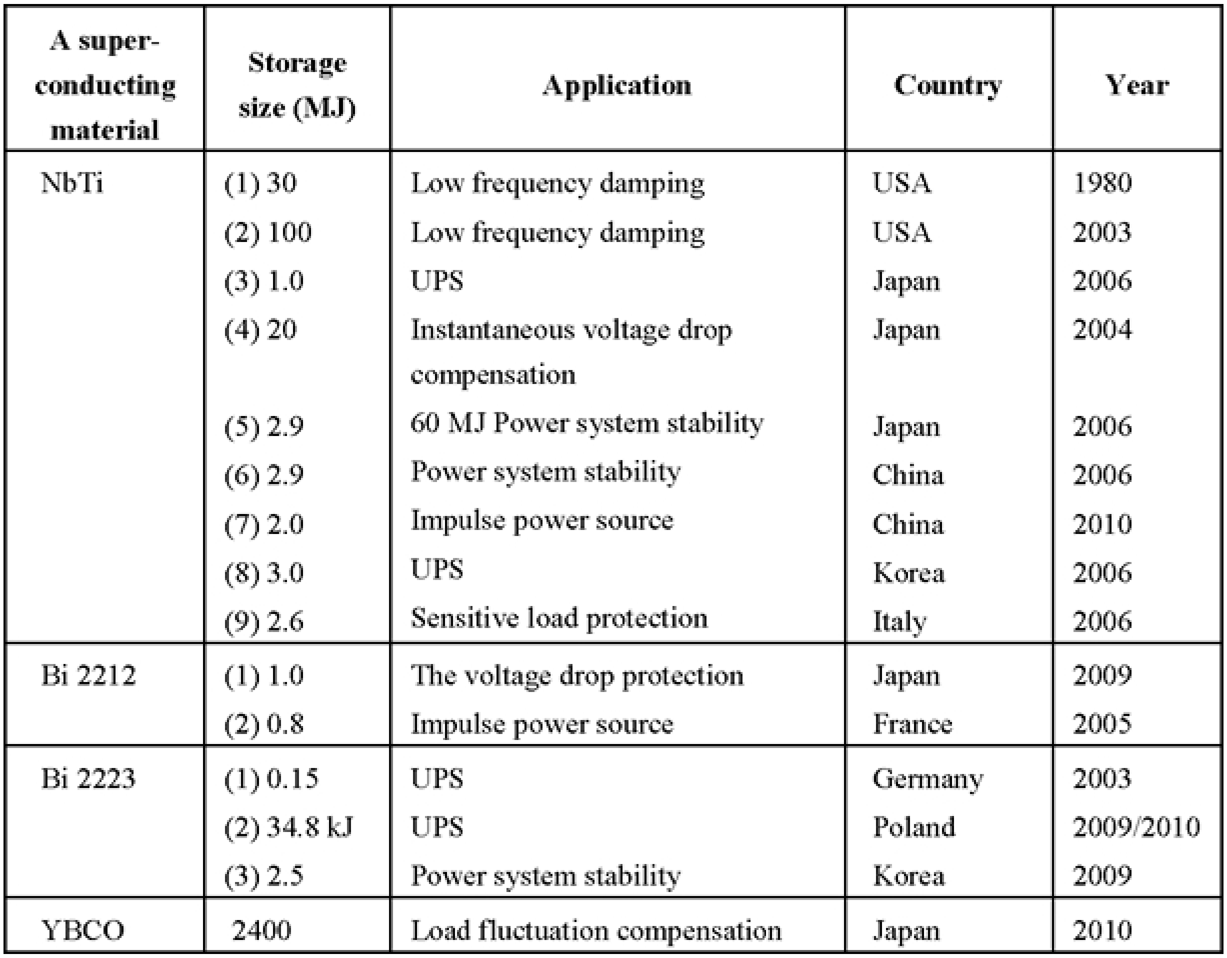
Figure 5.8: System daily load curve with (without) coordinated PV/SMES: (left) operation on a sunny day; (right) operation on a cloudy day [38a, 44a]

Hybrid Energy Storage Systems: The main advantages of SMES are (a) high-power density, (b) low response time and (c) high efficiency, but its energy density is low and the costs are high. Networking this system with energy-storage systems having high energy densities such as batteries, CAES or PHS ensues a hybrid system that can apply to a wider range of situations, including demand-side energy management including power quality control, peak shaving and voltage stability [45]. Further, the cost can be significantly decreased [33]. Significant ideas have emerged around this hybrid storage system concept for use in transportation, with SMES being tried for storing the regenerative braking energy and discharging it to provide boosts [46].

Challenges: There are only a few installations; therefore, available knowledge of system needs and operational capabilities of SMES systems is limited [47]. Its long-term reliability and operation are still unproven. Further, SMES systems necessitate constant refrigeration, which requires energy and upkeep, again raising apprehension with long-term reliability. Also, SMES needs to be constantly discharge and charge as there are standby losses because of the cooling necessity [48]. These issues need consideration when employing a SMES system.

Some installed SMES systems worldwide for different applications are given in Table 5.2.

Table 5.2: SMES projects installed around the world [19, 38a]



A super-conducting material	Storage size (MJ)	Application	Country	Year
NbTi	(1) 30	Low frequency damping	USA	1980
	(2) 100	Low frequency damping	USA	2003
	(3) 1.0	UPS	Japan	2006
	(4) 20	Instantaneous voltage drop compensation	Japan	2004
	(5) 2.9	60 MJ Power system stability	Japan	2006
	(6) 2.9	Power system stability	China	2006
	(7) 2.0	Impulse power source	China	2010
	(8) 3.0	UPS	Korea	2006
	(9) 2.6	Sensitive load protection	Italy	2006
Bi 2212	(1) 1.0	The voltage drop protection	Japan	2009
	(2) 0.8	Impulse power source	France	2005
Bi 2223	(1) 0.15	UPS	Germany	2003
	(2) 34.8 kJ	UPS	Poland	2009/2010
	(3) 2.5	Power system stability	Korea	2009
YBCO	2400	Load fluctuation compensation	Japan	2010

Most of these projects have used LTS. There are several other ongoing projects using MTS and HTS; one of them being the MgB_2 toroidal system of capacity, 48GJ, proposed for shielding power instability at a rating of 200

MW for up to 4 minutes [49]. The inexpensive MgB_2 superconductor enables such a high energy capacity, and as the whole coil is immersed in a liquid H_2 tank, it becomes a hybrid energy-storage system.

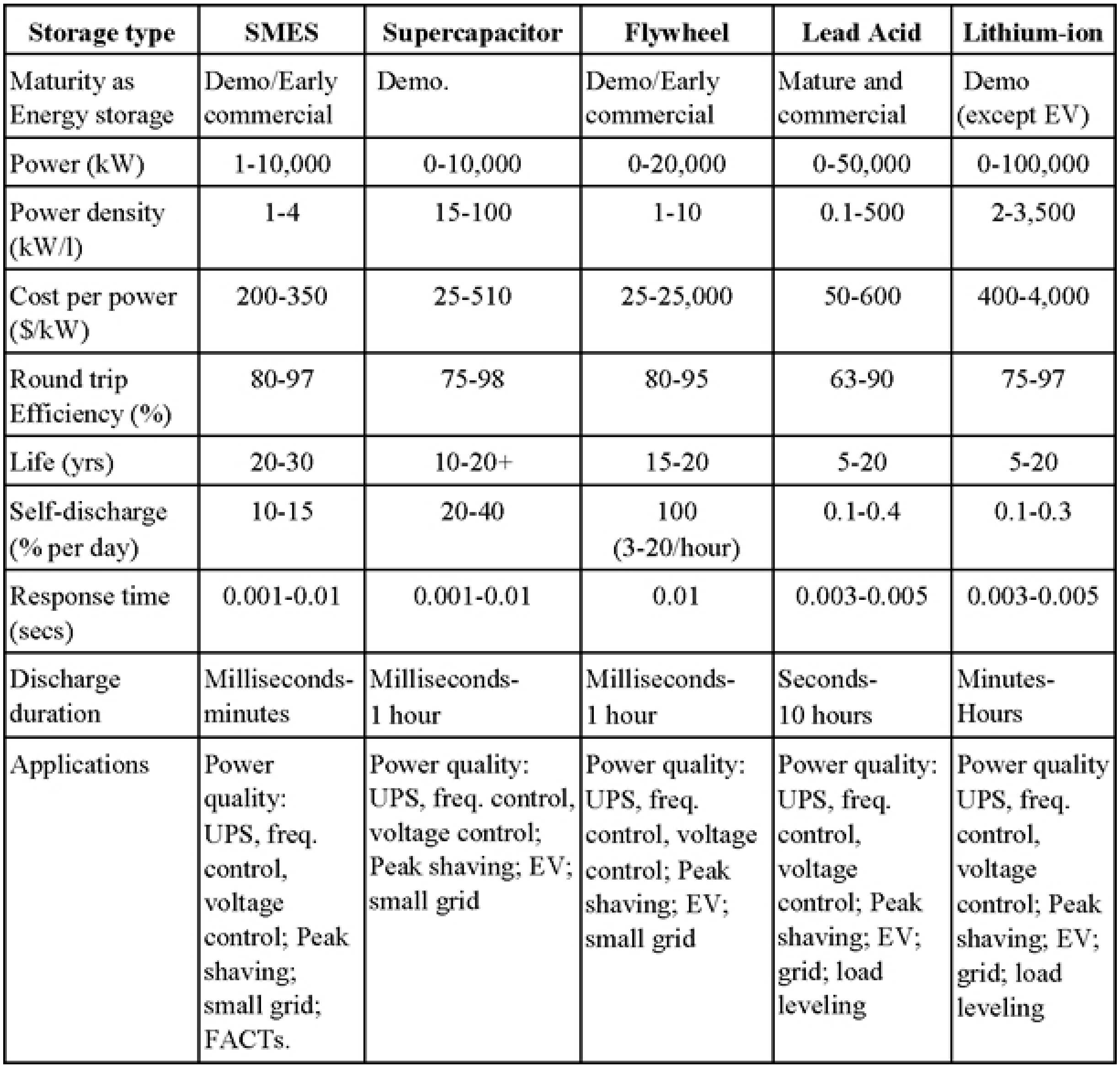
SMES technology has the largest market potential in the area of providing backup for utility transmission voltage against abrupt disturbances because these systems can be favoured with respect to low price and high capability. In 2000, the Wisconsin Public Service Corporation set up 6 D-SMES units of 3MJ/3MW supplied by American Superconductor Corporation, to solve voltage instability trouble while additionally increasing the power grid capacity [50a]. Almost all the SMES systems have been used for power management and power quality applications. Therefore, SMES is the type of energy-storage technology that will be used by utility companies, distribution network operators and industry because they require and use such services that SMES can offer.

Significant research and development has been done to reduce the cost of the systems and to develop materials, which are less cryogenically sensitive [15c, 50 b].

5.5 Comparison

Table 5.3 gives a summary of the characteristics of SMES along with other competing energy-storage technologies [52]. Supercapacitors have high efficiency, high-power capability and long cycle life similar to SMES and directly compete in the market. But, they have low energy density and a high cost per installed energy. Supercapacitors and SMES suit mostly similar applications, while the former are also used in electric vehicles. Flywheels have a fast charge and a long life with low maintenance. However, they have low energy density, require a vacuum chamber and high safety requirements and suffer from high self-discharge. Flywheels are not yet fully commercialized, and the first large-scale grid storage flywheel appeared in 2011. They are suitably established as UPS, and used for frequency control. Lead acid and Li-ion batteries are in no way the challengers to SMES; they are rather more appropriate for energy management. However, SMES, having a broad range of promising applications and the potential for GWh, may establish as energy management facility by 2040 [51, 52].

Table 5.3: Comparison of SMES with other competing energy-storage technologies [52]



Storage type	SMES	Supercapacitor	Flywheel	Lead Acid	Lithium-ion
Maturity as Energy storage	Demo/Early commercial	Demo.	Demo/Early commercial	Mature and commercial	Demo (except EV)
Power (kW)	1-10,000	0-10,000	0-20,000	0-50,000	0-100,000
Power density (kW/l)	1-4	15-100	1-10	0.1-500	2-3,500
Cost per power ($/kW)	200-350	25-510	25-25,000	50-600	400-4,000
Round trip Efficiency (%)	80-97	75-98	80-95	63-90	75-97
Life (yrs)	20-30	10-20+	15-20	5-20	5-20
Self-discharge (% per day)	10-15	20-40	100 (3-20/hour)	0.1-0.4	0.1-0.3
Response time (secs)	0.001-0.01	0.001-0.01	0.01	0.003-0.005	0.003-0.005
Discharge duration	Milliseconds-minutes	Milliseconds-1 hour	Milliseconds-1 hour	Seconds-10 hours	Minutes-Hours
Applications	Power quality: UPS, freq. control, voltage control; Peak shaving; small grid; FACTs.	Power quality: UPS, freq. control, voltage control; Peak shaving; EV; small grid	Power quality: UPS, freq. control, voltage control; Peak shaving; EV; small grid	Power quality: UPS, freq. control, voltage control; Peak shaving; EV; grid; load leveling	Power quality UPS, freq. control, voltage control; Peak shaving; EV; grid; load leveling

In summary, compared to other energy storages, SMES has better performance as the coil transferring current functions at cryogenic temperature with effectually no resistive losses. SMES can increase the power-system stability and advanced power quality via active and reactive power compensation because of its extraordinary conversion efficiency and quick reaction speed. The major advantages of the SMES are (a) high energy-storage efficiency, (b) rapid energy charge (in a few milliseconds) and discharge ability, and (c) independent controlling capability of active and reactive power. Its development and commercial applications are not yet realized, but the viability of applications would be witnessed in near future along with the development of HTS technology [38a].

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CHAPTER 6

Chemical Energy Storage *(Hydrogen and SNG)*

6.1 Hydrogen Production

The concerns about global warming and climate change, which are attributed to anthropogenic carbon dioxide emissions resulting from the use of fossil fuels, have compelled for a rapid shift away from fossil fuels. Renewable energy sources, such as wind, solar, biomass, hydropower, and geothermal energy are the alternatives recognized so far [1]. In this context, hydrogen assumes importance. Hydrogen is a versatile light gas and an important and potential element in the context of energy storage medium.

As early as 1973, hydrogen was proposed as a promising candidate for a secondary source of energy [2]. As a prospective energy carrier in the future, hydrogen could play a significant role in low-carbon future: (a) offsetting electricity as a zero-carbon energy carrier that can be easily stored and transported, (b) facilitating a more secure energy system with reduced dependence on fossil fuels, and (c) having the adaptability to operate across the important transport, industry, electricity and heating sectors which account for two-thirds of global CO_2 emissions [4–8g].

Almost all hydrogen on earth is found in compounds, mainly in combination with oxygen as water or in combination with carbon as organic substances.

The current global hydrogen production has been estimated at7 x 10^{18} J/annum, corresponding to about 630 billion Nm^3/a, which is about 2% of the world's total energy consumption [8h].

There are many processes for hydrogen production from both conventional and alternative energy resources, such as natural gas, coal, biomass, solar, wind and nuclear. Several reviews of the process descriptions along with the technical and economic aspects of different production methods are found in the literature [e.g. 9a-d].

Presently, the technologies that dominate hydrogen production are based on extraction from fossil fuels that include reforming of natural gas (~48% of the global production) [10], gasification of coal and petroleum coke (18%) [11, 12], as well as partial oxidation (POX) and reforming of heavy oil (30%) [13, 14]. Biomass is also a source of hydrogen. Wood, farm crops and its byproducts, animal waste, organic waste and so on are all sources of biomass [15]. By pyrolysis or gasification of biomass, hydrogen can be produced. These are matured technologies operating on the ground for a long time.

Water electrolysis is another popular hydrogen production technology in vogue for several decades. The water-electrolysis produces pure hydrogen for use in electronics, pharmaceutical, food and other industries. This technology is well-suited for integration with renewable energy sources, which have been recently showing phenomenal growth globally. Hydrogen production through water-electrolysis has become popular and is acquiring interest in Europe and many regions of the world because it enables higher renewable penetration on their power grid. Hydrogen is an attractive storage medium for additional renewable energy and can be used, once stored, for several applications.

Hydrogen can be burned in thermal power plants to generate electricity again. A major attraction of hydrogen is its compatibility with fuel cells and their high-energy efficiencies in converting chemical hydrogen with air (or oxygen) to electricity. In both cases, the only combustion product is water.

Hydrogen is a clean fuel and can replace unsustainable fossil fuels in a future energy economy, given that its use emits almost nothing other than water. Further, hydrogen has a high-energy density making it an efficient way of storing energy. It may also be used (a) as a fuel in automobiles instead of petroleum or natural gas, (b) for supplementing the natural gas grid for increased efficiency, and (c) for producing green fertilizers and other chemicals. However, several problems need to be addressed to make it possible; for instance, improving the efficiency of its production and finding an economical method for storing it for automotive applications and so on.

6.1.1 Hydrogen Production Methods

Hydrogen production methods are several involving chemical, electrochemical, catalytic, thermal and biological processes.

(a) Fossil fuel-based hydrogen production

Nearly 95% of the hydrogen is produced today from carbonaceous raw material, primarily fossil type. Most of this hydrogen is used as a chemical feedstock for petrochemical, food, electronics and metallurgical processing industries. Only a small part of it is used for energy.

Coal, oil, natural gas, methanol and other fossil fuels have been traditional feedstocks. In fossil fuels, hydrogen is a major element and some of them have high hydrogen to oxygen ratios, making them highly suitable for reforming processes.

Hydrogen is produced from natural gas (predominantly methane) by gasification or steam reforming processes. The dominant method is endothermic catalytic steam reforming (Fig. 6–1), which combines the fuel with steam and catalytically reacts them together at high-temperatures (>500°C) in a two-stage process. Steam-methane reforming (SMR) normally happens at 850°C, and at pressures from 2.5 to 5 MPa using a catalyst , which is iron or nickel or ruthenium [16]:

The reaction for methane:

$$CH_4 + H_2O \leftrightarrow 3\ H_2 + CO \qquad -206\ \text{kJ/mol}$$

$$CH_4 + 2\ H_2O \leftrightarrow 4\ H_2 + CO_2 \qquad -165\ \text{kJ/mol}$$

The number of moles is increased during the conversion; so, high-temperatures and low pressures are by and large, advantageous for this process. Pressures of up to 5 MPa are preferred to conserve compression energy for large quantities of synthesis gas generated. To increase the hydrogen output and to prevent carbon growth due to the Boudouard reaction, the carbon monoxide, CO is catalytically converted in an exothermic water-gas-shift reaction with steam:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad +43.3\ kJ/mol$$

The water-gas-shift reaction is usually performed in industrial processes in 2 steps, the first at 350–450°C using an iron-oxide catalyst, and the second at lower temperatures, 150–250°C using a Cu-Zn or Al catalyst. As a result, one gets more H_2 and a lower CO content, which can be reduced to 0.5–2% of the dry gas. The feedgas (natural gas) are desulphurized to protect the catalyst inside the reformer tubes, which are heated externally by flaming some of the feed gas (Fig. 6.1). Radiation and convection are the processes of heat transfer. Flue gas moves through the furnace at a temperature greater than 1300°C and is used as waste heat to generate steam and to preheat the feedgas [16].

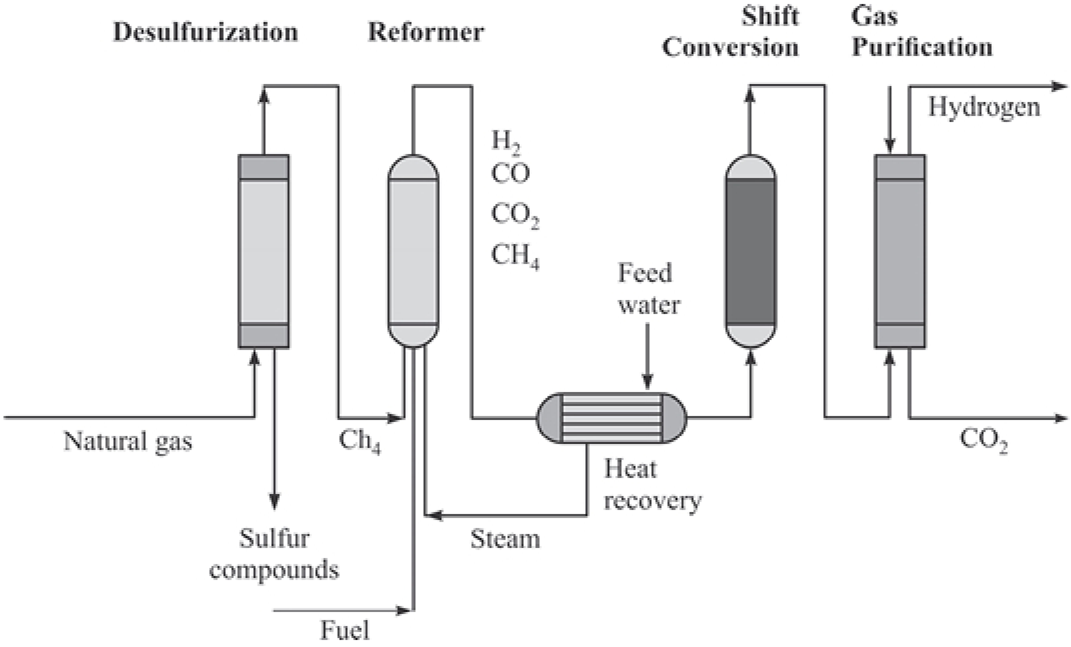


Figure 6.1: Processing scheme of methane-steam reforming [16].

Hydrogen is then separated from the mixture of pollutants using pressure swing adsorption (PSA). Another efficient method for cleaning the H2 product gas is using a methanator developed by AECL , which converts the still available CO to methane, reducing concentrations to a level, below the parts per billion (ppb) [16].

A drawback of steam reforming is that it is endothermic requiring heat, which means energy is consumed.

Steam reforming of natural gas is a well-proven industrial-scale technology both technically and commercially and the most cost-competitive. This technology is mainly used in the petrochemical and fertilizer industries for the production of ‘on-purpose’ hydrogen.

Several large steam reformer units are operating, and the one at the Fortum refinery in Porvoo, Finland is one of the largest on-line steam reforming H_2 plants operating since 2007, with a capacity of 180,000 Nm^3/h or 16.2 t/h of H_2 , corresponding to a stored power of 645 MW (based on HHV). Besides natural gas, this plant can also convert refinery off-gas or liquid propane. Commercial large-scale steam-methane reforming units produce H_2 at an efficiency of about 75% and a CO_2 intensity of 9.5 kg per kg of H_2 produced. Recent steam-methane reformers use many catalysts instead of one, at different temperatures to augment the H_2 output. Given the heat losses and thermodynamic constraint, a total efficiency of around 80% is achieved. Catalytic autothermal reforming is best for fuel cell systems because of its plain design, moderate operating temperatures, workable load and high-efficiency [16].

More compact and higher efficiency advanced reforming methods operate using micro-porous ceramic membranes at lower temperatures around 550°C. The membrane modules made of palladium-based alloy and a nickel-based catalyst can drive the steam reforming reaction, the shift reaction and H_2 separation all together i.e., without shift converter and pressure swing adsorption stages. Tokyo Gas Company, Japan, demonstrated such a system at a hydrogen-fuel station in Tokyo [16]. The system's working, efficiency and long-term trustworthiness was confirmed with the generation of >99.99% pure hydrogen at the rate of 3.6 kg/hour for more than 3000 hrs establishing an efficiency (for hydrogen generation) of roughly 68% (LHV).

Another type of reformer is the *partial oxidation (POX) reformer*, which reacts the methane with oxygen at high-temperatures, 1200–1450°C and pressures, 3 to 7.5 Mpa to produce hydrogen:

$$CH_4 + O_2 \leftrightarrow CO_2 + 2\,H_2$$

To remove the heat generated, downstream equipment is required. The oxygen required is provided by an air separation plant. There is no need for a catalyst. These temperatures and pressures are needed to ensure high conversion rates. In comparison to steam reforming, the hydrogen yield is smaller; that is, larger reactors for the shift reaction are required if the objective is to produce H_2 , which may result in high costs. The quality of H_2 produced is comparatively low.

Reforming hydrocarbons produce CO_2 emissions, contributing to pollution. So, if the hydrogen produced is meant to generate electricity using fuel cells, purification of gas is essential, mainly to keep carbon monoxide levels less than 20 ppm [17]

(b) Water Electrolysis for H_2 production

The water-electrolysis has been known for around 200 years [18, 19]. Currently, this method produces small quantities, about 4% of global hydrogen generation [20. 21]. Water electrolysis, of all available methods, has the advantage of generating exceedingly pure hydrogen (>99.9%), perfect for a few better-quality processes such as the fabrication of electronic components [22]. Water electrolysis is frequently limited to small-scale applications and to particular cases such as marine, spacecraft, electronic, food industries and medical applications. In these situations, large-scale hydrogen generating systems are either economically not practicable or not existing.

There are 2 types of room-temperature water-electrolysis, characterized by their electrolyte (acidic or alkaline) type: (a) Alkaline electrolysis and (b) Proton Exchange Membrane (PEM) electrolysis.

Both the technologies have the ability to deliver (i) on-site and on demand hydrogen (load following), (ii) pressurized hydrogen without a compressor, and (iii) 99.999% pure, dry and carbon-free hydrogen.

Alkaline electrolysis is a mature technology for large systems and most commonly used in the industry. PEM water-electrolysis [23–26] although offers several advantages, such as high-energy efficiency, excessive hydrogen production rate and compact design, their application is rather troubled by the high cost of catalysts and membranes [27–29]. PEM electrolysis is more flexible and can be used for small decentralized solutions. The conversion efficiency for both AE and PEM electrolysers is about 65%~70% (lower heating value). The water demand is in practice, 1.0 L/Nm^3 and the water should be as clean as possible to prevent deposition and electrode corrosion.

Large-scale electrolysers have been built that are capable of handling inputs of 100MW for hydrogen generation and the hydrogen produced is around 99.8% pure. The conversion efficiency is 90%.

High-temperature ceramic electrolysers are currently under development and could represent an efficient alternative to PEM and alkaline systems, with efficiencies up to 90%. At a limited scale, waterelectrolysis operates satisfactorily; the method is better maintainable if power used is obtained from renewable energy sources - wind, solar or hydro. In an ideal energy system requiring generation, conversion, storage, and usage in inaccessible areas, water-electrolysis may be largely appropriate. When abundant solar or wind energy is available, extra energy may be used to produce hydrogen using water-electrolysis and stored. And the stored hydrogen can be consumed in fuel cells for electricity generation or can serve as a fuel for heating. Thus, the electricity produced by the renewable energy can be used to generate hydrogen or directly pumped into the power grid.

(i) Alkaline Water Electrolysis

Henry Cavendish for the first time in 1766 observed hydrogen’s ability to combine with oxygen. In 1800, the first electrolyzer emerged when Nicolson and Carlisle pressed a static charge into water. For over 2 centuries, many researchers improve on these fundamental discoveries [30].

Alkaline water-electrolysis is one of the easiest methods for hydrogen production. The challenges for widespread use of water-electrolysis are to reduce energy consumption, cost and maintenance and to increase reliability, durability and safety.

The principle of this process is simple. Oxygen and hydrogen are separated from the water when the direct current is applied to the water. The electrolyte in this system is an aqueous solution of potassium hydroxide or sodium hydroxide (KOH or NaOH) and their concentrations vary as a function of the operating temperature. The concentrations generally range between 25 wt% and 30 wt% for temperature range 70°C -100°C, and pressure range 1–30 bars. The schematic of an alkaline electrolysis process is shown in Fig. 6.2.

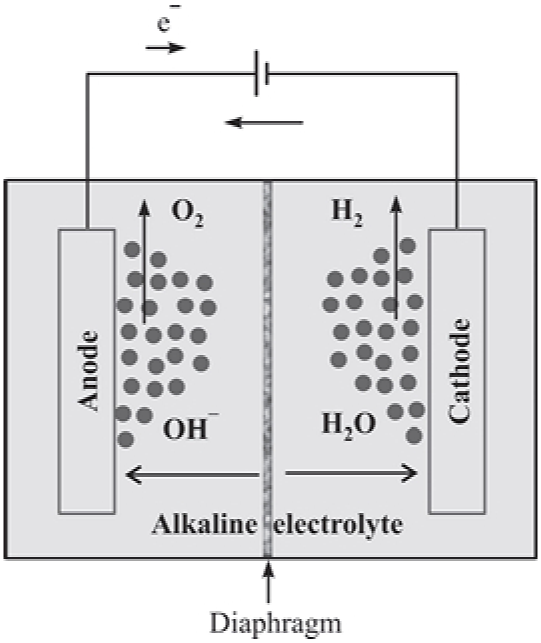


Figure 6.2: Schematic of Alkaline electrolysis [31].

When an appropriate voltage is pressed across the 2 electrodes, water molecules at the cathode pull electrons to produce OH^- ions and H_2 molecules. OH^- ions pass through the 30% KOH electrolyte toward the anode; there they combine and release their extra electrons creating H_2O, electrons, and O_2 as shown in the figure.

The chemical reactions are represented as the following:

At the cathode: $2H_2O$ (liq) + $2e^-$ → H_2 (gas) + $2OH^-$ (aq.)

At the anode: $2OH^-$(aq.) → ½ O_2 (gas) + H_2O (liq) + $2e^-$

Owing to the diffusion and migration activity of this species, and with the aim to separate the different gases formed at the cathode and anode, a diaphragm is commonly placed in the alkaline systems, mainly for safety concerns.

A diaphragm is a micro-porous substance, with less than 1 μm pore size, letting the passage of water and hydroxyl ions between the anode and the cathode and separating gases. The diaphragm is expected to have high infiltration to water, high corrosion resistance in a strong alkaline medium, and large ionic conductivity to achieve high cell efficiency. Actually, the excess voltage over the designed value, during working is for 2 reasons: (i) the over-potentials from HER (hydrogen evolution reaction) and OER (oxygen evolution reaction), and (ii) the ohmic loss in the electrolyte, including the resistance arising from ionic transfer in the diaphragm. This ohmic loss due to the presence of the diaphragm explains why lesser current densities can be used in alkaline electrolysis compared to PEM electrolysis [31]. The electrolyte remains in the system due to a clever and pump-free closed-loop recirculation system.

The most common diaphragm in alkaline electrolysis was made of porous white asbestos [$Mg_3Si_2O_5$ $(OH)_4$]. But its toxicity leads to asbestosis and lung cancer, it is no more used.

Several kinds of diagrams have been studied such as composite materials based on ceramic or micro-porous materials: reinforced micro-porous PES membranes, glass reinforced polyphenylene sulfide compounds, titanium oxide and potassium titanate (K_2TiO_3) fibers and polytetrafluoroethylene, PTFE (as felt and as woven) [32]. NiO has shown to be a good material and a few fabrication methods have been developed for controlling its thickness or porous structure. Highly favorable results are achieved with a hydrocarbon-based polymeric membrane in a zero-gap (i.e., zero distance between electrodes and electrolyte) alkaline electrolysis cell with 4-M NaOH applied to both electrodes. A current density of 1 A/cm^2 at 2.12 V with constant performance observed during a 10-day durability test [31]. ‘Zirfon Perl’ from Agfa is another polymeric membrane available [33]. Using an ion-conducting membrane represents a new direction in the development of advanced alkaline electrolysers [22]. It allows for a zero-gap design with an inter-electrode distance of less than 100 µm, in which the membrane is sandwiched between 2 porous electrodes.

For electrodes, Ni-treated steel plates were used because Ni is an inexpensive material. Metals such as cobalt, iron, and vanadium were added to the electrodes as supplements. Cobalt is an additive to the anode; and iron and vanadium are supplemented to the cathode where they could reactivate the electrode (cathode). It was not the metal incorporated in an alloy that reactivated the cathode but the ions of iron or vanadium in solution. The deactivation of the cathode was attributed as a formation of nickel hydride, which iron and vanadium could overturn [32].

The hydrogen produced is 99% pure. Further purification processes enable us to reach the higher purity rates required for hydrogen-fuel cells. The efficiency of hydrogen production is roughly 80%.

They are more successful if operated at low current densities, 0.3 A/cm^2. The current density in commercial alkaline electrolysers varies from 100 to 400 mA/cm^2. The drawback is high corrosive nature of the liquid electrolyte used in high-temperatures, resulting in a short life-time [32]

The alkaline electrolysis system has a number of technological disadvantages: low current density, restricted capability to operate at low loads, and incapacity to function at high-pressure. The latter 2 limitations are because of the transfer of gases, possibly through the membrane. This will increase as the hydrogen pressure grows at the cathode and load decreased; as a result, the oxygen generation rate decreases and the hydrogen-content in the oxygen stream can rise to risky levels (hydrogen lower explosion limit is greater than 4%) [33].

(ii) PEM Water Electrolysis

The schematic of a PEM electrolyzer is shown in Fig. 6.3[34]. A PEM electrolyzer uses an ionically conductive solid polymer, for example, nafion, less than 0.2 mm thick as the separator. When the voltage source is connected across the 2 electrodes, oxygen in the water molecules, which is negatively charged their electron at the anode to create protons, electrons, and O_2 at the anode. The H+ ions pass through the proton-conducting polymer toward the cathode, where they become neutral H atoms by taking electrons; then they combine to make H_2 at the cathode. Iridium (Ir) is used as a catalyst for water oxidation or oxygen generation, which can resist corrosive environs because of high over-potential on the anode. Water is fed to the anode by a titanium flow field, and a small porous titanium mesh positioned between the anode-catalyst-layer and water channel serves as the diffusion layer. The cathode structure is identical to PEM fuel cell having a Pt-based catalyst and a graphite flow field to deliver hydrogen. A carbon paper is located between cathode catalyst and the flow field to function as diffusion layer [34]. The whole combination -electrolyte and 2 electrodes - are packed between 2 bipolar plates. The bipolar plate helps (a) to transfer water to the plates, (b) to push away product gases from the cell, (c) to conduct electricity, and (d) to circulate coolant to regulate the process [30]. PEM electrolysis is a scalable method for producing H_2, and is also a promising solution for energy storage when coupled with renewable energy sources.

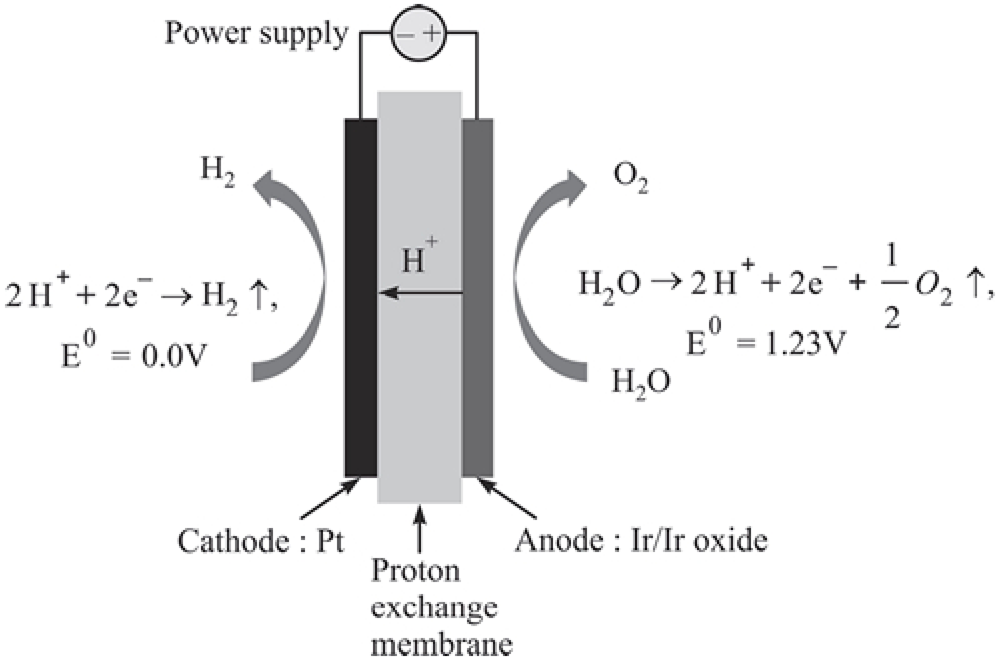


Figure 6.3: Schematic of a PEM electrolyzer [34, Open access].

The acidic environment limits the catalysts for the oxygen-evolving reaction (OER) and hydrogen-evolving reaction (HER) to noble metals. The PEM that must prevent the H_2/O_2 mixing is expensive, and hence the electrolyzer cost will significantly increase. In addition, the stability of the membrane is so small that PEM electrolysers turn out to be costly for general applications [35, 36]. Cronin's group [37,38] developed a new technique to divide the conventional PEM water-electrolysis process into 2 steps using the polyoxometalate $H_3PMo_{12}O_{40}$ as a buffer for redox equivalents [37, 38]. By separately generating O_2 and H_2, the gas handling becomes easy, demands on the membrane become less, and the cost possibly reduces [39]. Cronin et al. though undoubtedly provided a remarkable idea for future water-electrolysis technology, their results only focus on PEM water-electrolysis and cannot be used in alkaline waterelectrolysis.

One of the major benefits of PEM electrolysis is its ability to operate at high current densities with high-efficiency, leading to reduced operating costs. The polymer electrolyte allows to operate with a thin membrane, around 100–200 µm, while permitting high pressures and electrochemical compression of the hydrogen amount produced. The electrolyte cells are stacked into units of up to 15 to 20 Nm^3/h hydrogen production.

The active surface of the cells can stretch to an extent of 600 cm^2 and a maximum of 100 cells are contained in a stack. Increasing active surface per cell and its current density while maintaining the output above 83% efficiency are essential to reach the capability of power consumption above 1 MW [40]. However, the catalyst and membrane material and the fabrication process for PEM electrolyzer need to be significantly improved for cost-viability so as to apply extensively in renewable energy systems [41].

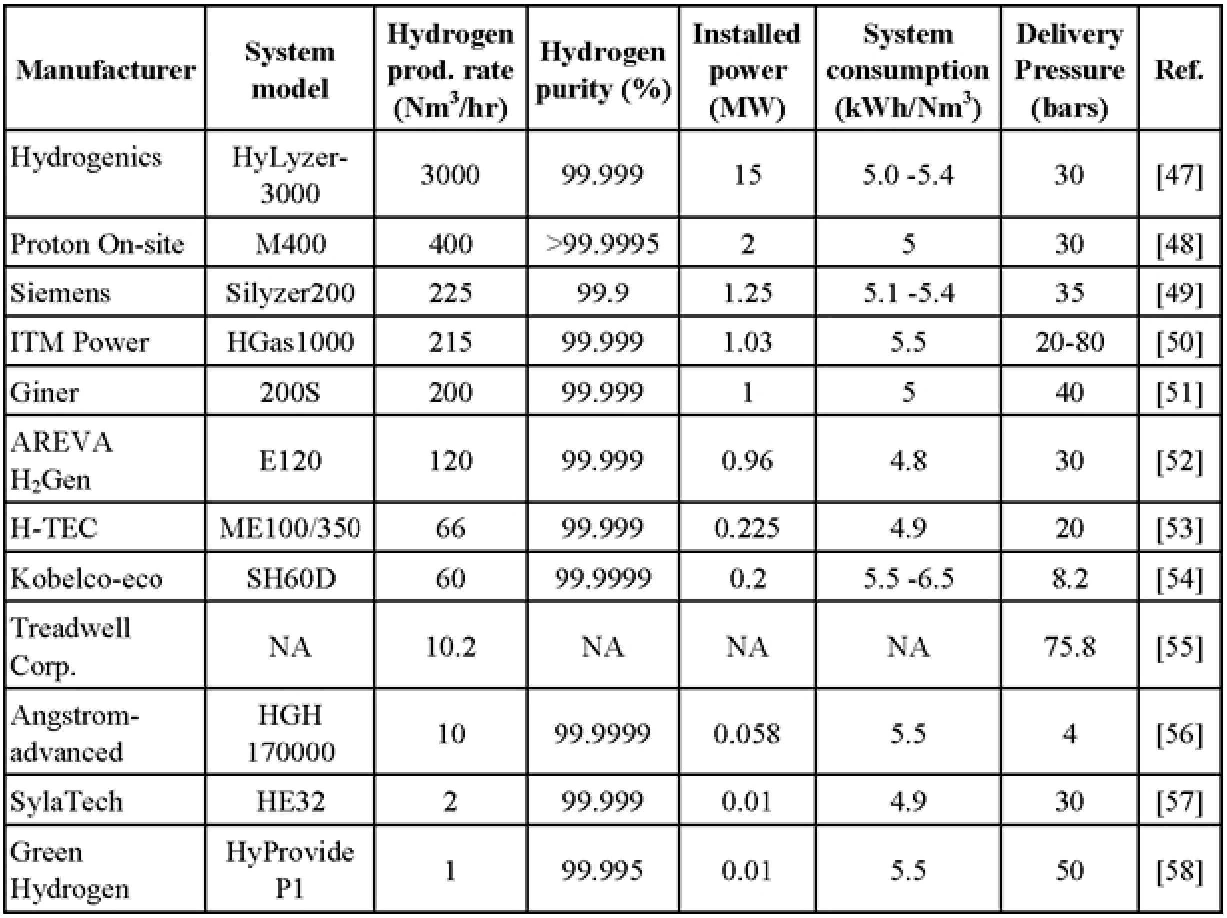
The recently-developed anode-catalyst in traditional PEM electrolysis is iridium oxide (I_rO_x) or mixed oxide with ruthenium [42, 43]. Typical catalysts have I_rO_x loading from 1 to 3 mg/cm^2 for marketable electrodes [44]. This amount of catalyst loading is high enough to bear the cost goals for energy markets in the long-run [43, 45, 46]. Given the current electrolysis technology status, the scaling of catalyst development from laboratory to the megawatt level remains challenging in terms of catalyst cost and stability [45].

The alkaline anion-exchange membrane (AEM) system is a low-cost polymer membrane electrolyzer system because the low-cost materials are involved. Recent research has revealed that the alkaline membrane electrolysers can perform like PEM electrolyzer, showing a cell voltage of 1.8 V at 1.0 A cm^{-2} having a copper cobalt oxide anode-catalyst and Ni cathode at 25 °C [18].

Maric and Yu [34] discussed several on-going studies on longer-term electrolysis operation ranging from hundreds to thousands of hours and listed the commercially available PEM electrolysis systems from 12 major manufacturers worldwide. Table 6.1 shows the list of manufacturers and the systems they produce with their characteristics (Open access).

Several electrolyzer single cells can be coupled in series to make the cell stack, the core part of an electrolyzer system where both hydrogen and oxygen are formed. Certain amount of cooling is needed to cool down the process and produce gas. A water treatment unit is set up to produce demineralized water from the delivered tap water. A cleansing system washes hydrogen to deliver high purity gas meeting the specifications. A power system is incorporated to supply the power needed for the reaction (converting the grid delivered AC into DC used for the process). And a control panel enables the operator to oversee the whole unit. Installation of the unit can be done inside a building or outside.

Table 6.1: List of manufacturers of PEM electrolysers [34, open access].



Manufacturer	System model	Hydrogen prod. rate (Nm^3/hr)	Hydrogen purity (%)	Installed power (MW)	System consumption (kWh/Nm^3)	Delivery Pressure (bars)	Ref.
Hydrogenics	HyLyzer-3000	3000	99.999	15	5.0 -5.4	30	[47]
Proton On-site	M400	400	>99.9995	2	5	30	[48]
Siemens	Silyzer200	225	99.9	1.25	5.1 -5.4	35	[49]
ITM Power	HGas1000	215	99.999	1.03	5.5	20-80	[50]
Giner	200S	200	99.999	1	5	40	[51]
AREVA H_2Gen	E120	120	99.999	0.96	4.8	30	[52]
H-TEC	ME100/350	66	99.999	0.225	4.9	20	[53]
Kobelco-eco	SH60D	60	99.9999	0.2	5.5 -6.5	8.2	[54]
Treadwell Corp.	NA	10.2	NA	NA	NA	75.8	[55]
Angstrom-advanced	HGH 170000	10	99.9999	0.058	5.5	4	[56]
SylaTech	HE32	2	99.999	0.01	4.9	30	[57]
Green Hydrogen	HyProvide P1	1	99.995	0.01	5.5	50	[58]

(c) High Temperature Water Electrolysis

Current research interest is the development of high-temperature electrolysers based on solid oxide ionic conductor technology, used for solid oxide fuel cells (SOFCs). Electrolysis at high-temperature consumes less electricity and achieves high operational efficiencies in the solid oxide electrolyzer. The foremost advantage is that a significant part of the needed energy for the electrolysis process is supplied as heat, which is much cheaper than supplying electrical energy. Moreover, the high-temperature helps the conduction of the electrolyte, and to speed up the reaction kinetics, reducing the energy loss due to the polarization of the electrode. Thus, higher efficiency of the electrolysis can be obtained at high-temperature than at low/ordinary temperatures. The normal high-temperature electrolyzer can obtain an electrical efficiency of 92% compared to 85% at low-temperature. The process can also provide waste heat recovery [59].

A typical high-temperature system uses oxygen-ion-conducting ceramics, yttria-stabilised zirconia (YSZ) as electrolytes and nickel zirconia cermet (ceramic-metal) as cathode and the strontium-doped lanthanum manganite as anode [60, 61]. Zirconia stabilized MgO or CaO are also used as electrolytes. The water is heated to 200°C to provide steam in the cathode. The electrolysis cell functions in the temperature range, 800–1000°C ensuring the conduction of the solid electrolyte. Then, the water vapor splits into hydrogen gas and oxygen ions. The oxygen ions are transferred via the ceramic solid electrolyte to the anode, where they form gaseous oxygen through oxidation [59].

(d) Hydrogen Production from Biomass

Hydrogen's share in the energy sector is increasing mainly because of the application of fuel cell systems and increased demand for emission-less fuels.

Biomass includes agricultural crop residues, forest waste and residues, special crops grown specifically for energy use (such as switchgrass or willow trees), organic municipal solid waste, and animal wastes. The amount of hydrogen in biomass is around 6 to 7 wt%.

The gasification of biomass, a thermo-chemical process, produces hydrogen and other products. It is a mature technology and feasible.

The pyrolysis of biomass, also a thermo-chemical process, is similar to the gasification process but occurs in the absence of oxygen (or air).

How Gasification and Pyrolysis work?

Gasification is a process that converts organic or carbonaceous materials, e.g., biomass, at high-temperatures (>700°C) in the presence of a controlled amount of oxygen into CO, CO_2, hydrogen and other hydrocarbons. For more technical details of the process refer to a book by the author [61].

The biomass undergoes partial oxidation in a reactor resulting in gas and charcoal production. The charcoal is finally reduced to form H_2, CO, CO_2, and CH_4. This conversion process can be stated as the following:

Biomass + heat + steam → H_2 + CO + CO_2 + CH_4 + some hydrocarbons + char.

The hydrogen-content in the gas mixture depends on the fuel/feedstock, the availability of steam and oxygen, and the process temperatures.

The methane (CH_4) and other hydrocarbons produced can be steam reformed for more hydrogen production:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

The CO then reacts with water to form CO_2 and more hydrogen via a water-gas-shift reaction.

$$CO + H_2O \rightarrow CO_2 + H_2 \text{ (+ small amount of heat)}$$

Adsorbers or special membranes are used to separate hydrogen from this gas stream.

Biomass has highly variable composition and complexity with *cellulose* as one major component.

Pyrolysis is similar to gasification of biomass, but occurs in the *absence* of oxygen at temperatures, 400°-550°C. In general, unlike coal, biomass does not easily gasify and generates other hydrocarbon substances in the gas mixture that leaves the gasifier. This is particularly true when oxygen is not used. Therefore, these hydrocarbons must be reformed using a catalyst to produce a clean syngas mixture of H_2, CO, and CO_2. Then, a shift reaction with steam changes CO into CO_2, similar to the gasification process. The produced hydrogen is then separated and cleansed [62]. The technical details of gasification and pyrolysis processes of biomass, the types of reactors and byproducts produced in each process and their treatment are discussed in the book by this author [61].

Issues: One of the major issues in biomass gasification is to deal with tar formation that occurs during the process , which is not favorable for hydrogen production through steam reforming. Three methods are presently available to decrease the tar formation: (i) appropriate design of gasifier, (ii) proper control and operation and (iii) choosing suitable additives/catalysts. The use of additives such as dolomite, olivine and char inside the gasifier also helps tar reduction [63]. When dolomite is used, total elimination of tar can be achieved [64]. Some of the widely used catalysts are dolomite, Ni-based catalysts and alkaline metal oxides. Process modifications by two-stage gasification and secondary air injection in the gasifier are also useful for tar reduction [65].

In Pyrolysis, the byproducts are tar and oils that remain in liquid form at room-temperature and solid residues mainly consisting of char, carbon and other inert materials. The oily products can also be processed to produce hydrogen [66, 61]. The water-soluble fraction of pyrolysis oil can be separated and used for hydrogen production. It has been established that by using Ni-based catalyst, the production of hydrogen can reach as high as 90%. Using a steam reforming and water-gas-shift reaction in addition, the amount of hydrogen can be significantly improved.

The pyrolysis process and its efficiency depend on the particle size of feedstocks. Most of the pyrolysis technologies can only process small particles, the order of 2 mm, to facilitate rapid heat transfer through the particle. Thus, the feedstock requires size-reduction before being pyrolyzed.

In their analysis, Ni et al. [65] discussed different approaches and several experimental studies on the production of hydrogen from several types of biomass. A Report by the National Renewable Energy Laboratory (Milne et al.), “Hydrogen from Biomass -State of the Art and Research challenges” covers largely thermo-chemical studies for generating hydrogen from whole biomass and stable intermediate products from biomass [67]. This report prepared for IEA thoroughly analyses all studies related to the thermal gasification of biomass and provides all relevant references.

Benefits of the technology: Biomass feedstocks are abundantly available and easy to use. Biomass recycles CO_2. That is, plants consume CO_2 from the atmosphere as part of their natural growth process, off-setting the CO_2 released from producing hydrogen through biomass gasification, resulting in low net greenhouse gas emissions. Biomass is thus a major renewable and sustainable energy source to replace fossil-fuel.

The pyrolysis and gasification methods for hydrogen production are economically viable and will become competitive with the conventional method of hydrogen production by natural gas reforming method.

These technologies can be profitably operated on a small-scale, especially in remote locations because the cost of hydrogen transportation and storage can be reduced and the availability of hydrogen to endconsumers be improved. Further advances in these technologies help biomass play an important role in the development of sustainable hydrogen economy.

Key Challenges: The main issue is the costs associated with capital equipment and biomass feedstocks. They need to be reduced. Some suggestions to lessen costs include (a) switching the currently used cryogenic process to segregate oxygen from air when oxygen is used in the gasifier with new membrane technology, (b) to evolve new membrane technologies to separate and purify hydrogen from the outlet gas stream like in coal gasification, (c) intensifying the process by reducing operational steps. And to lower costs of biomass feedstock, improved agricultural practices and breeding efforts should be implemented.

Biomass gasification is a mature technology. The experiences from commercial demonstrations will determine its potential as a viable method for cost-competitive hydrogen production [62].

However, biomass conversion looks less appropriate if devoted to hydrogen generation only, but as well be used for producing heat and electricity, thus supporting the reduction of CO_2 emissions. Besides, biomass can be transformed into a range of value-added chemicals and liquid fuels like methanol, without problems.

(e) Hydrogen production by solar conversion

Renewables are the most preferred energy sources for hydrogen production because they are diverse, abundant, and sustainable. The most exciting possibilities, with huge potential are solar conversion techniques. These are 2 types: photolysis and thermolysis. Currently, these techniques are mostly at the laboratory demonstration level and require more development and field experience for commercialization.

I. ***Photolysis.*** It is a chemical process used to break down molecules into smaller entities through the absorption of light. Photobiological photolysis uses microorganisms such as green algae and sunlight to divide water into oxygen and hydrogen ions, and these hydrogen ions combine directly or indirectly to release as hydrogen gas. And no carbon-based molecules are required in the process. More research efforts must optimize the processes within the organisms, and several engineering issues to be sorted to find large photo-biological systems for hydrogen generation.

1. *Photo-electrochemical* (PEC) photolysis, in simple terms, involves the disassociation of water into hydrogen and oxygen directly at the surface of a semiconductor immersed in an electrolyte through the irradiation by solar light. This is something like electrolysis without the electrolyzer because the photovoltaic semiconductor material acts as a catalyst to produce hydrogen directly at the semiconductor-water interface.

   That is, both the generation of electricity from solar energy and the water-splitting reaction to form hydrogen can be unified into a single activity in which light absorption generates electron-hole pairs that electrochemically divide water molecules. The efficiency of this combined photochemical method is approximately 8 to12% [18]. A major problem here is finding a semiconductor that has the right photoelectrochemical properties, while at the same time robust enough to withstand the severe chemical and physical environment. It must also be economically feasible.

   In the actual process, solar photons are absorbed directly into an absorber material (a semiconductor with an appropriate bandgap), without fully turning into heat. The absorber can transform part of the light energy to electricity (as in the case of a solar PV cell) or use it fully for the splitting of water to oxygen and hydrogen. Fujishima and Honda [68] demonstrated for the first time, the generation of hydrogen and oxygen in a photo-electrochemical (PEC) cell using a TiO_2

photoanode that was irradiated with near ultraviolet light. The electrons created at the anode traveled to a platinum (Pt) cathode, where hydrogen was developed. Thus, the intermittent solar energy can be converted into an inherently more storable form of chemical energy.

PEC solar water-splitting is a powerful, but complex process. For this process to be efficient and sustainable, several important conditions must be satisfied simultaneously: (a) the semiconductor must produce adequate voltage when irradiated with solar radiation to break water, (b) the semiconductor band width must be small enough to absorb a considerable portion of the solar spectrum, (c) the band edge potentials at the surfaces must overlap the hydrogen and oxygen redox potentials, (d) the system must demonstrate long-range strength against corrosion in aqueous electrolytes, and (e) the charge transfer from the semiconductor surface to the solution must be simple to reduce energy losses due to kinetic over-potential and selective for the HER and OER.

There is no cost-effective material system that satisfies all of these technical requirements. Research and development to find materials with bulk and interfacial features that meet the above criteria, and advances in material science and interfacial electrochemistry are much needed [69].

Three options for arranging photo-electrodes in PECs are available: (a) n-type semiconductor as photo-anode and a metal as the cathode; (b) p-type semiconductor as photo-cathode and metal as the anode; (c) n-type semiconductor as photo-anode and a p-type semiconductor as photo-cathode [65].

The fundamental processes in a PEC device with a two-electrode system containing a single absorber photo-anode are shown schematically in Fig. 6.4a. The incident solar photons generate electrons and holes with an efficiency, η_{eh}. These photo-generated charge carriers then separate and travel through the semiconductor in opposite directions; the charge transport efficiency is $\eta_{transport}$. The holes drive the OER at the surface of the semiconductor electrode. At the same time, the electrons are driven to the rear ohmic contact and then to the surface of the counter electrode to drive the HER. The combined efficiency of the charge transfer at the solid-liquid interface for both electrons and holes is $\eta_{interface}$. The minimum thermodynamic voltage for splitting water (ΔE^0) is 1.23 V as shown.

A more extensive illustration of the PEC water-splitting system is shown in Fig. 6.4b. Apart from the thermodynamic requisite, there are over-potentials (OP) allied with driving the kinetics of the hydrogen evolution reaction (OP_{HER}) and oxygen evolution reaction (OP_{OER}) at the solid- liquid interface. It is necessary to minimize these overpotentials for the device to operate with high-efficiency. Hence, the development of efficient catalysts for each half-reaction is vital in making highly efficient water-splitting devices.

Oxide semiconductors, such as TiO_2, are robust in aqueous environments and have wide band gaps and require higher-energy photons for excitation. Several approaches were studied that involve (a) altering the band gap of a material by changing the semiconductor’s composition, or (b) using other stable, non-oxide semiconductors such as GaAs, InGaAs, MoS_2, WSe_2 and $MoSe_2$ as n-type electrode, or (c) using illuminated organic dyes [70] to generate electricity at oxide electrodes. The use of dye-sensitised photocells, also called Gratzel cells [71, 72] that can accumulate energy from low energy photons and inject higher-energy electrons into the semiconductor can be used to match the solar spectrum and semiconductor band widths

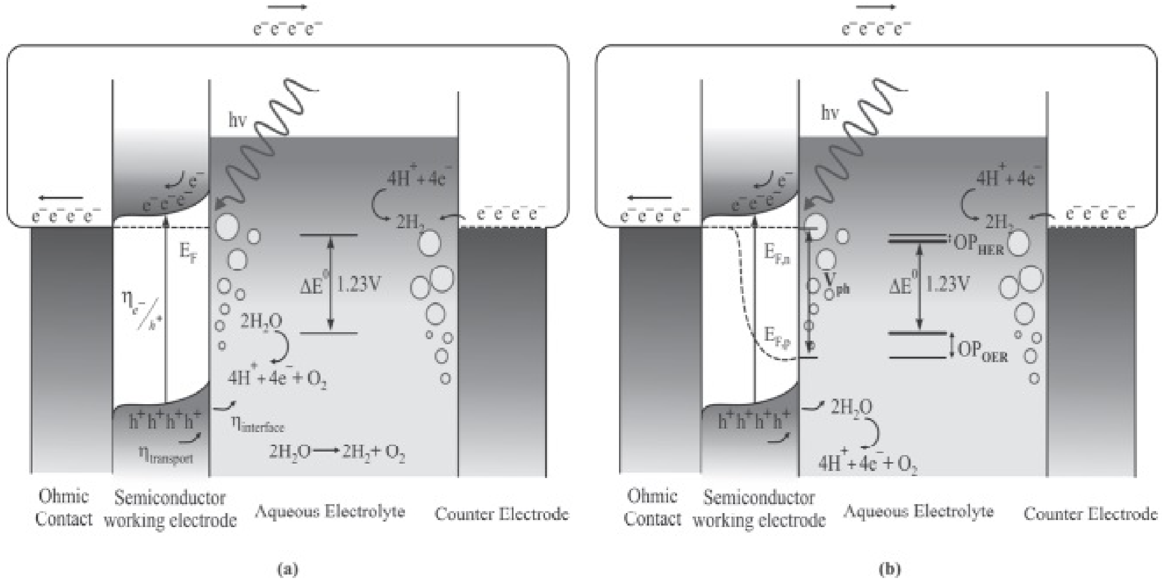


Figure 6.4: Band structure of an n-type photo-anode, (a) showing various processes of photon irradiation, electron-hole pair formation, charge transport, and interfacial reactions, (b) showing the energetic requirements associated with the minimum thermodynamic energy to split water, catalytic over-potentials for the HER and OER half-reactions, and photovoltage [69]’.

There are also entropic losses associated with the photo-generated electrons and holes [73, 74, 69]. The actual driving force for watersplitting, the photovoltage (V_{ph}), is always less than the band gap of the semiconductor due to losses that result from factors such as spontaneous emission, incomplete light trapping, and non-radiative recombination [73]. Issues such as non-ideal band structure alignment can also reduce available photovoltage. V_{ph} is normally the voltage difference between the quasi-Fermi levels of electrons ($E_{F,n}$) and holes ($E_{F,p}$) under illumination. But, the correctness of this practice, principally in the area of semiconductor-liquid interface, remains a matter of serious debate. A more traditional necessity for unaided water-splitting is, the photovoltage (compensated for over-potential losses) must allow the quasi-Fermi levels under light to connect the OER and HER redox potentials [69].

Tandem cell designs: The tandem cell structure depends on dyes , which respond over a wide solar spectral range. E.g., the dye, gallium indium phosphide ($GAInP_2$) has a band gap of 1.8–1.9 eV that satisfies the band gap energy norms of a solar cell; but to achieve the band edge overlaps criteria, its band edges, 0.2 to 0.4 V, are too negative to realize. This issue can be fixed by chemical amendments of the semiconductor electrode surface, which shifts the band edges to correct energetic places , which catalyze the interfacial charge transfer. By the adsorption of organic and inorganic molecules such as metallated porphyrins and transition metals at p-type $GaInP_2$, the band edges of the semiconductor can be moved to positive or negative values [70]. Khaselev and Turner [75] demonstrated a double junction $GInP_2$/GaAs PEC system and produced hydrogen achieving solar-to-hydrogen (STH) conversion efficiency of 12.4 %, emphasizing the great potential for PEC technology. Further, it has excellent corrosion stability, though relatively costly.

Lab. Demonstrations: Ager et al. [76], in their review of laboratory demonstrations of PEC solar water-splitting cells, found the reported STH conversion efficiencies ranging from <1% to 18%. These experiments were grouped based on factors such as (i) the number of PV junctions employed, (ii) PV junction type (solid-solid or solidliquid) and (iii) the ability of the structures to produce *separated* reaction products. PEC systems that have 2 PV junctions but contain a semiconductor-liquid junction have the reported efficiencies of 12.4% [75] whereas those that do not contain a semiconductor-liquid junction have 18% efficiency. The solar cells in these systems were based on III-V semiconductors. Several demonstrations using inexpensive semiconductors reported >10% STH efficiency. The major challenge is the device stability, as evidenced by lifetimes of less than 24 hours in all except in a few demonstrations. In the absence of a globally accepted protocol for evaluating and certifying STH efficiencies and lifetimes, Ager et al. recommended a protocol similar to that used by the PV sector so that future demonstrations of solar PEC watersplitting could be compared on equal grounds.

Theoretical studies using various assumptions predicted that the maximum attainable efficiency using a tandem PEC water-splitting device was 23–32% [77–80].

Rothschild and Dotan [74] also examined the efficiency of solar watersplitting systems and proposed power management and light management structures that facilitate boosting of the efficiency of PV-PEC tandem cells with *marginal* changes in system components. As a result, the add-on costs would be minimum, and the competitiveness of PV-PEC tandem cells is likely to improve.

Several books [69, 81–83], review articles [71, 84, 85] and numerous papers are published on this technology which may be consulted for details.

2. *Photovoltaic Electrolysis (PV-Electrolysis)* is a mature and probably more efficient technology for hydrogen production compared to the earlier PEC method.

   In a PV-Electrolysis system (PV-E), a photovoltaic module delivers electricity to a separate electrolyzer to produce hydrogen. PV-electrolysis systems have demonstrated remarkable potential to achieve higher STH efficiencies [86–90]. The highest STH efficiency achieved to date, 24.4%, was demonstrated by a PV-electrolysis system using GaInP/GaAs/Ge multi-junction solar cells and PEM eletrolyser[89].

   Jia et al. [86] reported a photovoltaic-electrolysis system with the highest STH efficiency for any water-splitting technology to date. The PV-electrolysis system comprises 2 PEM electrolysers and an InGaP/GaAs/GaInNAsSb triple-junction solar cell; the solar cell produces a voltage adequate enough to drive the 2 electrolysers requiring no extra energy input. The solar radiation is so adjusted that the maximum power point (P_m) of the solar is well in-step with the operating capacity of the electrolysers to augment the system efficiency. The system showed a 48-hour average STH efficiency of 30%. This performance displays the prospects of PV-electrolysis systems for solar energy storage with cost-viability. The PEM electrolyzer is selected to combine with PV-panels in most of the studies, because of its flexibility to handle strong fluctuating current from the PV cell/module [91–93].

A schematic of this PV-Electrolysis system is shown in Fig. 6.5. The solar cell was a triple-junction solar cell with an active area of 0.316 cm^2. The 3 sub cells of the solar cell were fabricated with InGaP, GaAs and GaInNAs(Sb) semiconductor compounds having bandgap (E_g), of 1.895 eV, 1.414 eV, and 0.965 eV, respectively [94]. To maintain a temperature of ~25°C for the cell, it was mounted on a water-cooled stage. White light from a xenon arc lamp was used to simulate concentrated AM 1.5 solar light on to the Cell. The 2 PEM electrolysers consisted of Nafion membranes layered with 0.5 mg/cm^2 thick Pt black catalyst at the cathode and 2 mg/cm^2 thick iridium black catalyst at the anode, and were connected in series with the solar cell. Water was pumped into the anode section of the first electrolyzer, with no input flow to the cathode of the electrolyzer. The water and O_2 discharge from the first electrolyzer’s anode section flowed into the second electrolyzer’s anode section. Similarly, the H_2 from the cathode side of the first electrolyzer streamed into the second electrolyzer’s cathode side. The resulting hydrogen and oxygen from the second electrolyzer were collected and measured, and the water, not reacted, was returned to a water reservoir and recycled through the system. The electrolysers were maintained at ~80 °C, consistent with standard operational conditions for industrial water electrolysers [87, 88]. The system worked nonstop for 48 hours, reaching an average STH efficiency of 30%.

The STH efficiency of the PV-electrolysis system measured over a 48 h continuous operation is shown in Fig. 6.6. The right y-axis shows the current passing through the 2 electrolysers and the left y-axis shows the corresponding STH efficiency. The inset show up a smaller *y*-axis range for better precision.

The laboratory-scale PV-electrolysis system described here was constructed from components that could be scaled up to larger PV-electrolysis installations. Optimizing the design of PV-electrolysis system would be crucial for developing cost-effective large-scale systems. The components used in this system like the 3-junction solar cell made of III-V compounds and the metal catalysts are expensive; however, the high STH efficiency (30%) realized indicates that this method may have the prospects to generate low-cost hydrogen provided cost-effective materials and fabrication techniques are developed. Techno-economic studies of big-size solar hydrogen generating systems suggest that realizing high STH efficiency is perhaps the primary factor in reducing the cost of H_2, possibly much more significant than reducing the cost of the photovoltaic module or catalyst materials [95, 96].

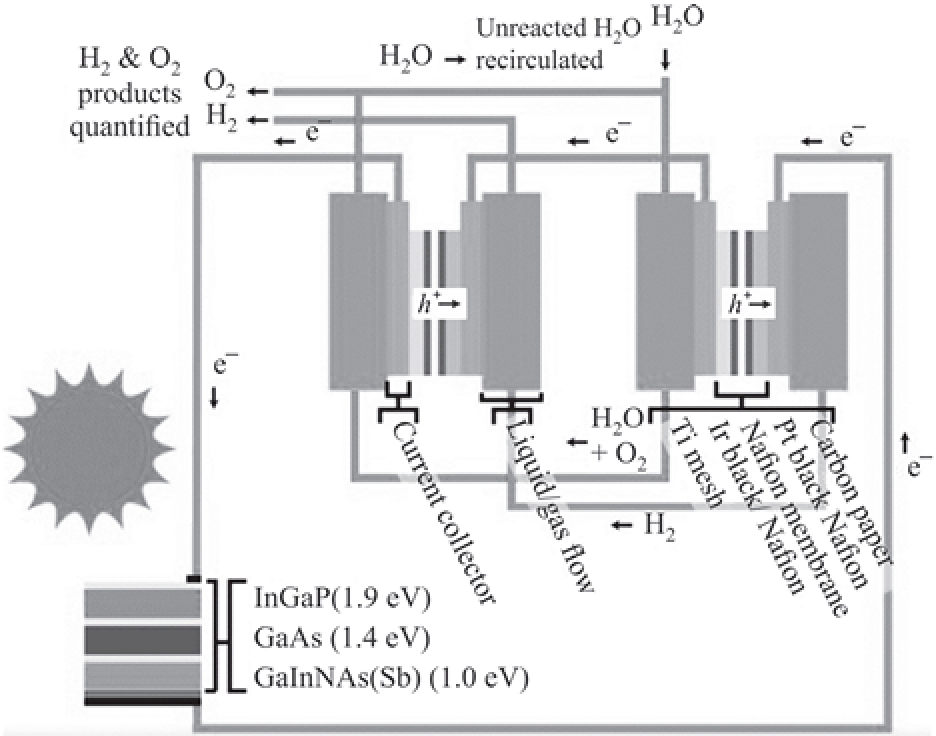


Figure 6.5: Schematic of the PV-electrolysis system consisting of a triplejunction solar cell and 2 PEM electrolysers connected in series [86].

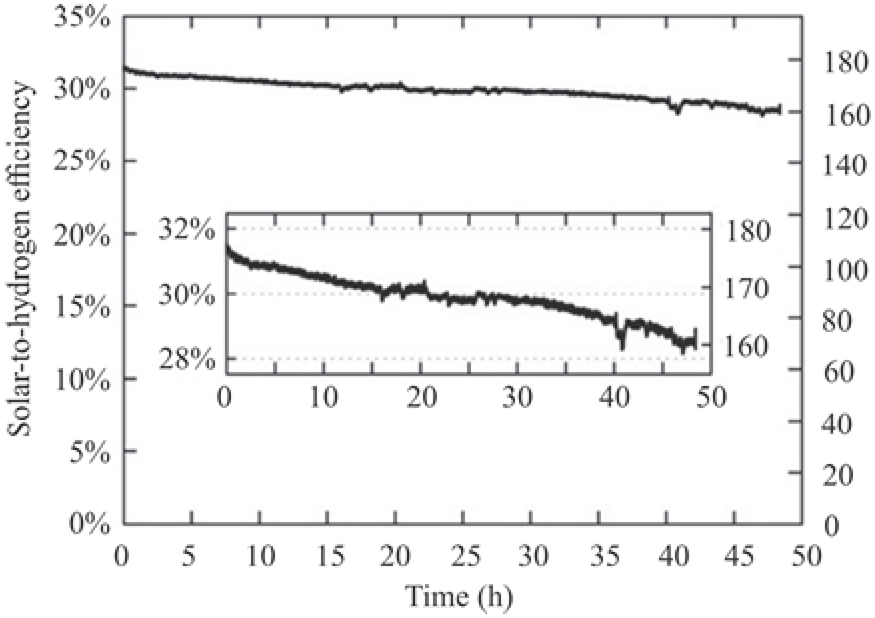


Figure 6.6: The STH efficiency of the PV-electrolysis system measured over 48 hr continuous operation [86].

Some of the attractive features of this technology are (a) PV-E components are commercially available, (b) these components are developed separately, (c) PV cells/modules and electrolysers can be used for commercial purposes other than hydrogen production, (d) current STH efficiency demonstrated (30%) is much higher than that recorded for PEC technology, (e) any PV cell/module with good stable efficiency can be used, unlike in PEC [96b].

Peharz et al. also presented an integrated system combining highly efficient III-V solar cells in an optical concentrator system with a PEM electrolyzer to produce hydrogen and oxygen by solar water-splitting. The measured STH conversion efficiency of the prototype system with an area of 96 cm^2 was 18% outdoor. The integrated design and the high concentration factor of 500 not only allowed material savings but facilitated high system efficiencies [90]. Numerous publications on solar PV-electrolysis technology are available in the literature.

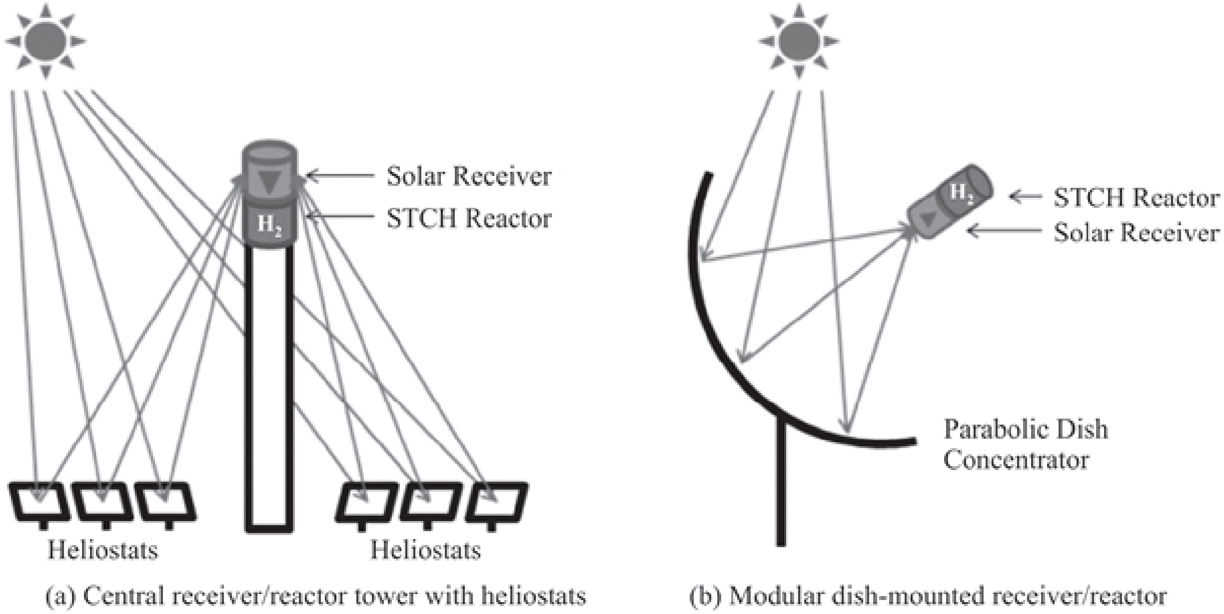
Proton Energy Systems of the US has set up several Electrolysis-based hydrogen *fueling demonstrations* throughout the U.S. (e.g. Figure. 6.7). These stations typically comprise 13 kg H_2/day capacity from electrolysis, the hydrogen generating at 215–430 psi (ie. 15–30 bar). The hydrogen is then packed down to about 10,000 psi for supplying to the vehicle.

Figure 6.7: Electrolysis-Based Hydrogen Fueling Station [Source: 87].

II. Thermolysis using CSP or Waste-heat from nuclear reactor

The heat produced from concentrated solar power (CSP) (Figure 6.8) or waste heat from nuclear power reactors is used to drive a thermo-chemical reaction that can produce hydrogen, or to drive electrolysis at high-temperatures for more efficient water decomposition. The chemicals used in the process are reused within each cycle, thus creating a closed-loop that consumes only water and produces hydrogen and oxygen.

A high-flux solar furnace reactor is used at NREL, U.S. to concentrate solar energy and generate temperatures between 1,000 and 2,000° C, essential for thermo-chemical reaction cycles to generate hydrogen. This is a novel approach - using high-temperatures, high-flux, and solar-induced thermo-chemical processes - for producing environmental-safe hydrogen. Extreme reaction rates at higher temperatures produce rapid reaction rates that considerably improve generation rates and more than compensate for the intermittent kind of solar energy source.



(a) Central receiver/reactor tower with heliostats (b) Modular dish-mounted receiver/reactor

Figure 6.8: Schematic of 2 approaches for focusing sunlight on a thermochemical reactor to produce temperatures up to 2,000°C: (a) a field of heliostat mirrors concentrate sunlight onto a central reactor tower; (b) parabolic dish concentrator focus sunlight onto an attached STCH reactor. The heat generated is used to drive thermo-chemical reactions [101]

Solar- and nuclear-driven high-temperature thermo-chemical watersplitting cycles produce hydrogen with near-zero greenhouse gas emissions.

In thermolysis, heat at 500^-2000^C alone is used to decompose water into hydrogen and oxygen [97]. Several solar thermo-chemical watersplitting cycles have been examined for hydrogen generation, each with diverse sets of working conditions, manufacturing challenges, and hydrogen production projections [98].Over 300 water-splitting cycles are reported in the literature. It is believed that overall efficiencies close to 50% can be achieved using these processes [99].

However, all cycles, have issues related to design, and none of them has matured to the commercial level. Several studies have systematically examined thermo-chemical cycles; out of them, the sulfur family, namely, sulfur-iodine, hybrid sulfur, sulfur-bromine hybrid, have been recognized as the most promising candidates with great potentiality and higher efficiency and less of complexity (in terms of number of reactions and separations) [US DOE, Nuclear Hydrogen R&D Plan, Washington DC, 2004]. All 3 have in common the thermal decomposition of sulfuric acid at high-temperatures [16].

The simplest single-step thermal dissociation of water is presented as [99]:

$$H_2O + \text{heat} \rightarrow H_2 + \frac{1}{2} O_2$$

One major disadvantage of this process is the necessity of an effective technique to separate H_2 and O_2 to avoid the formation of an explosive mixture. Semipermeable membranes based on ZrO_2 and other high-temperature materials are used. Another way to achieve separation is by quenching the product gas mixture to lower temperatures, and then using palladium membranes for effective hydrogen separation [100].

The water, as we know, decomposes at 2500°C, but stable materials at this temperature and maintainable heat sources are hardly obtainable. Therefore, chemical reagents have been suggested to lesser the temperature [102]. These attempts have significantly reduced the operating temperature to lower than 2500°C, but typically require higher pressures. It is believed that scaling-up the processes may *improve* thermal efficiency. A better understanding of the relationship between capital cost, thermodynamic losses, and process thermal efficiency may lead to reduced hydrogen production costs [99]. However, several issues must be solved through research, development and demonstration of commercially viable thermo-chemical cycles: (1) improving the efficiency and durability of reactant materials for thermo-chemical cycling, (2) developing efficient and robust reactor designs compatible with high-temperatures and heat cycling, and (3) lowering the costs of the concentrating mirror systems.

Two-step thermo-chemical cycles for H_2 production: Materials are available which can function as active redox pairs in a double-step watersplitting process. In the initial step, metal oxide is reduced by supplying oxygen. The reduced compound reacts with water, in the second step, pulling out its oxygen as the hydrogen is set free. Two-reaction processes have high potential for achieving high efficiencies economically.

Several couples of materials such as Fe_3O_4/FeO, Mn_3O_4/MnO, ZnO/Zn, CoO_3/Co-O, and Ce_2O_3/CeO_2 were investigated. Water splitting was executed at temperatures less than 650°C, and a high-temperature requiring reduction step was done at around 2000°C. Solar heat/power generating systems were used for supplying primary energy. This method is advantageous because it produces pure hydrogen. A major drawback is that the activity decreases over frequent oxidation/reduction cycles. The general reactions are represented as the following:

$$\begin{aligned} &1^{st}\text{ step: } M_xO_y \rightarrow M_xO_{y-\delta} + \delta/2\ O_2 \\ &2^{nd}\text{ step: } M_xO_{y-\delta} + \delta\ H_2O \rightarrow M_xO_y + \delta\ H_2 \end{aligned}$$

Two-step metal oxide cycles have been experimentally proved in laboratory-scale. They are being studied at the PSI, Switzerland using solar-concentrated heat input and at INET, China employing nuclear heat input. Research focus is mainly on finding new metal oxides with a comparatively low decomposition temperature. Many examples of two-step metal oxide cycles were discussed highlighting the prospects as well as the issues to be addressed in the IAEA Report of 2013 [16].

Two examples of thermo-chemical water-splitting cycles are illustrated here: (1) the ‘direct’ two-step cerium oxide thermal cycle shown in Fig. 6.9, and (2) the ‘hybrid’ copper chloride cycle. The direct cycles are less complex with fewer steps, but they require higher operating temperatures than the more complicated hybrid cycles. A hybrid cycle combines the benefits of thermo-chemical and electrolytic reactions. Here, the low-temperature reaction, while thermodynamically unfavorable, is forced electrochemically.

1. Cerium oxide two-step cycle

Ce(IV) oxide, ceria, is a prominent metal oxide for water-splitting process due to its favorable features such as high melting point [184b], high oxygen exchange capacities, rapid oxygen-ion transport, large oxidation rates, and phase transition irreversibility between oxidized oxide and non-stoichiometric partially reduced oxides is absent [104].

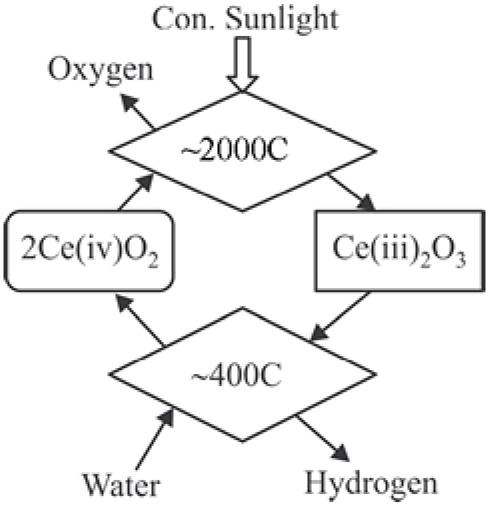


Figure 6.9: An illustration of a two-step ‘direct’ cerium oxide thermo-chemical cycle. Redrawn from [101].

The stoichiometric cycle of CeO_2/Ce_2O_3 was first proved successfully as a system for thermo-chemical cycles by Abanades and Flamant [105]. The thermo-chemicalcycle for H_2 production based on $CeO_2/$ Ce_2O_3 oxides is schematically shown in Fig. 6.9.

The process consists of 2 chemical steps:

(a) Reduction, $2Ce\ (IV)O_2 \rightarrow Ce(III)_2O_3 + ½\ O_2$;

(b) Oxidation, $Ce_2O_3 + H_2O \rightarrow 2CeO_2 + H_2$.

Net reaction, $H_2O \rightarrow ½\ O_2 + H_2$

The thermal reduction of Ce(IV) to Ce(III) (endothermic phase) is made in a solar reactor having a precise inert atmosphere. The possibility of this first step and the operating conditions has been established: $T = 2000^{o}C$, $P = 100–200$ mbar.

The hydrogen generation phase, ie, water-splitting with Ce(III) oxide, is performed in a fixed bed reactor and the reaction is perfect with fast kinetics in the temperature range from 400 to 600 °C. The recovered Ce(IV) oxide is then recycled in which water is the material input and heat is the energy input. The outputs are hydrogen and oxygen, which are obtained in different steps evading high-temperature energy-intense gasphase separation. The produced H_2 is pure and is not contaminated with CO and CO_2. So, the hydrogen from this process is ready for use directly in fuel cells. The results have shown that the cerium oxide two-step thermo-chemical cycle is a promising process for pure hydrogen production.

However, the stoichiometric reduction of cerium (the above experiment) requires high-temperatures (2000 °C). But, at 1500 °C, cerium oxide presents non-stoichiometric partially reduced forms [106], which are realized promising by several researchers to perform two-step water-splitting as well. Ceria redox reactions are expressed as [107]:

$$\text{Reduction phase: } CeO_2 \leftrightarrow CeO_{2-\delta} + \delta/2\ O_2 \qquad (T > 1200\ °C)$$

$$\text{Oxidation phase: } CeO_{2-\delta} + \delta\ H_2O \leftrightarrow CeO_2 + \delta\ H_2 \qquad (T \sim 800\text{–}1000\ °C)$$

An ideal solar reactor is necessary that withstands high-temperatures, minimizing thermal losses and favors mass and heat transfer. Solar reactors that are illuminated directly are normally used at 1 kW to 500 kW power; unitary sizes beyond that power level are hard to be suitably equipped with a single see-through window and the corresponding efficient cavity to reduce thermal emission losses. This arrangement is beneficial when working at temperatures > 500 °C. Transparent/ see-through windows are essential to allow direct absorption of the photons by the reactants, while at the same time, not allowing them to connect with outside atmosphere. The scaling-up of direct particle reactors is difficult and particularly windows of sizes above 1 m^2 are strongly restricted. Therefore, at high power levels, indirect designs comprising an intermediary surface for heat exchange are preferred.

Arribas et al. [107] developed a fixed-bed solar reactor design and experimental setup that facilitates the analysis of different materials for solar thermo-chemical cycles using simulated radiation. This facility is flexible, modular and easy to operate and maintain. They chose to study ‘ceria’ as the ‘benchmark’ to explore a working method in the solar simulator test bed that was developed. Ceria has favorable properties and its cyclability was proved earlier in a laboratory-scale solar reactor with a radiative power input of 4 kW by Marxer et al. at ETH Zurich [108].

In the study by Arribas et al, the sample was directly irradiated to consider radiation effects; and redox reactions occurred continuously in the sample, without intermediate charges/discharges so that consecutive cycling was reproduced. The experimental approach (radiation changes, measurements, flux conditions and cycling procedures) established in this study is considered suitable for further study on materials including ceria to be capable of solar-driven processes. This requires them to be analysed at the low-kW scale in ‘high-flux solar simulators as best equivalents earlier to complete on-sun tests.

2. Copper chloride ‘hybrid’ thermocycle

The copper-chlorine cycle (Cu-Cl cycle) is a four-step *hybrid* thermochemical cycle for the production of hydrogen. The Cu-Cl cycle employs both thermo-chemical and electrolysis steps. It has a maximum temperature requirement of about 530°C, which is much lower operating temperature compared to other thermo-chemical cycles.

The Cu-Cl cycle consists of 4 chemical reactions for water-splitting, whose overall reaction splits water into hydrogen and oxygen. All other chemical substances are recycled. This cycle can be associated with nuclear installations or heat sources, such as solar and industrial waste heat to potentially achieve higher efficiencies with lower environmental impact and cost of hydrogen production compared to any other conventional technology. The 4 reactions in the Cu-Cl cycle are as follows [109, 110]:

1. $2\ Cu + 2\ HCl(g) \rightarrow 2\ Cu\text{-}Cl(l) + H_2(g)$, (430–475 °C), thermal reaction
2. $2\ CuCl_2 + H_2O(g) \rightarrow Cu_2OCl_2 + 2\ HCl(g)$, (400 °C), hydrolysis
3. $2\ Cu_2OCl_2 \rightarrow 4\ Cu\text{-}Cl + O_2(g)$, (500 °C), thermal decomposition
4. $2\ Cu\text{-}Cl \rightarrow CuCl_2(aq) + Cu$, (30° -70°C), electrolysis

Overall reaction: $2\ H_2O \rightarrow 2\ H_2 + O_2$

Atomic Energy of Canada Limited (AECL) has experimentally shown a Cu-Cl electrolyzer, producing hydrogen electrolytically at the cathode, and Cu(I) oxidizing to Cu(II) at the anode, thus combining above reactions to exclude the intermediate production, and consequent transferring of solid copper [110].

This demonstration was made possible by using the right type of membrane for the electrolysis. Approximately 50% of the heat required to drive this reaction can be captured from the reaction itself. The rest can be low-grade waste heat, which improves cycle and power plant efficiencies. Recent research has focused on a cogeneration scheme using the waste heat from nuclear reactors, specifically the CANDU supercritical water reactor [112].

6.2 Hydrogen Storage Technologies

Hydrogen storage is key for advancing hydrogen and fuel cell technologies for use in stationary and portable power and in the transportation sector. Hydrogen has the highest mass-energy density among fuels; but, its low ambient temperature density leads to a low volume-energy density. As a result, advanced storage methods that have prospects for higher volume-energy density need to be developed. Compressing or storing in a concentrated state, or alternately cooling and storing as a liquid are tried and tested over long periods. These are called '*physically-based technologies.*' There have been attempts to store hydrogen in the solid-state within certain alloys that will absorb it in large quantities. Hydrogen and carbon form covalent bonds and behave like alloys or inter-metallic compounds at ambient temperature. The chemical storage of hydrogen with other elements can be achieved with reasonable volumetric energy densities. However, the main issue is the *reversibility* of the chemical arrangement and the hydrogen discharge from the host material. The reversibility condition *eliminates* all covalent C-H compounds because on heating these compounds to above 800 °C, hydrogen is only released, alternately if the carbon is oxidized [17]. These technologies can be grouped together as '*materials-based storage technologies*.' These can include solids, liquids or surfaces. This may eventually offer the best storage method for automotive applications although the weight of the storage system is currently a major problem. These are shown in Fig. 6.10.

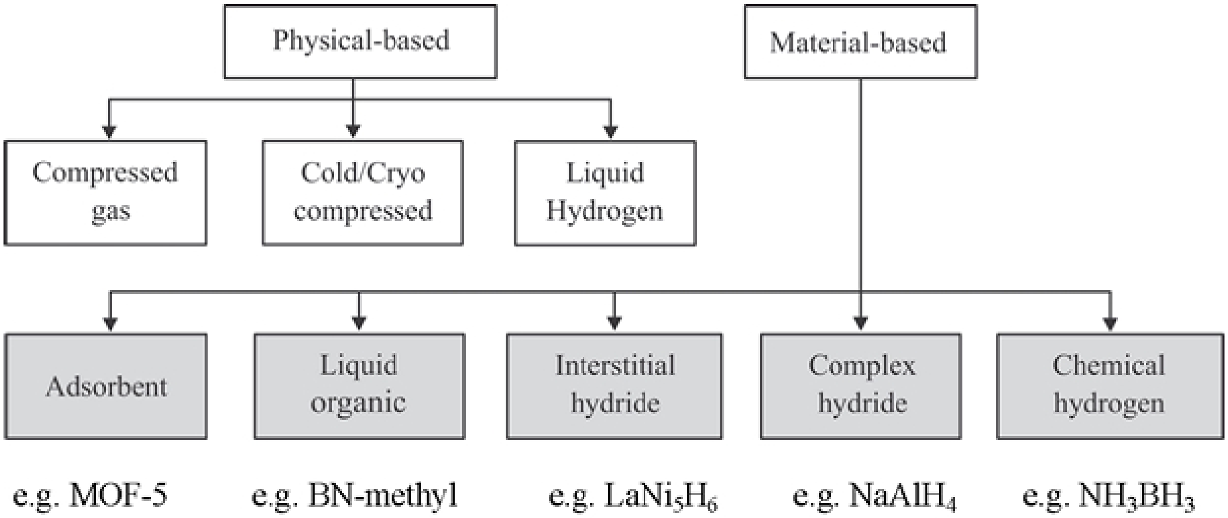


Figure 6.10: Hydrogen storage methods. Redrawn from [101].

The methods avaiable today for *reversible hydrogen-storage* , which offer a high volumetric and gravimetric density are (a) conventional storage using high-pressure gas cylinders or in the form of liquid hydrogen; (b) the physi-sorption of hydrogen on materials having a high specific surface area (e.g. carbon nanotubes, nanofibres, fullerenes, activated charcoals, other forms of nanoporous carbon); (c) new inorganic nanoporous materials; (d) hydrogen intercalation in metals and complex hydrides; (e) inorganic and organic liquids and solids, and such others [17].

6.2.1 Hydrogen Gas Storage

At ambient temperature and pressure of 100 bar, the density of hydrogen gas is only 7.5 kg/m^3. Hydrogen storage requires the reduction of an enormous volume of gas to reach the highest volumetric density, using as little additional material and energy as possible. The storage of hydrogen as a gas uses high pressures, typically tank pressure of 350–700 bar (5,000–10,000 psi).

High density hydrogen-storage is a challenge for static and portable applications and much greater challenge for transport applications. Steel tanks are a suitable method for storage in stationary systems, as weight and size are not significant. But for transportation, these tanks are unsuitable due to their additional weight and inadequate volume to store the gas. The issue of compression of hydrogen to these pressures (350 to 700 bar) is an important concern due to the associated energy costs and the need for specialized compressors.

The compression work depends on the thermodynamic compression process. The ideal isothermal compression cannot be realized. The adiabatic compression equation describes more closely the thermodynamic compression process for ideal gases [113a] as given here.

$$W = [\gamma/(\gamma - 1)]\ p_0\ V_0\ [(p_1/p_0)^{(\gamma - 1)/\gamma} - 1]$$

Here, W - specific compression work (J/kg)

p_0 - initial pressure (Pa)

p_1 - final pressure (Pa)

V_0 - initial specific volume (m^3/kg)

γ - ratio of specific heats (C_p/C_v), adiabatic coefficient

The compression work depends on the gas. The compression of hydrogen is compared with helium and methane in Figure 6.10a. The adiabatic coefficient, γ and V_0 for these 3 gases are

H_2: $\gamma = 1.41$, $V_0 = 11.11\ m^3/kg$

He: $\gamma = 1.66$, $V_0 = 5.56\ m^3/kg$

CH_4: $\gamma = 1.31$, $V_0 = 1.39\ m^3/kg$

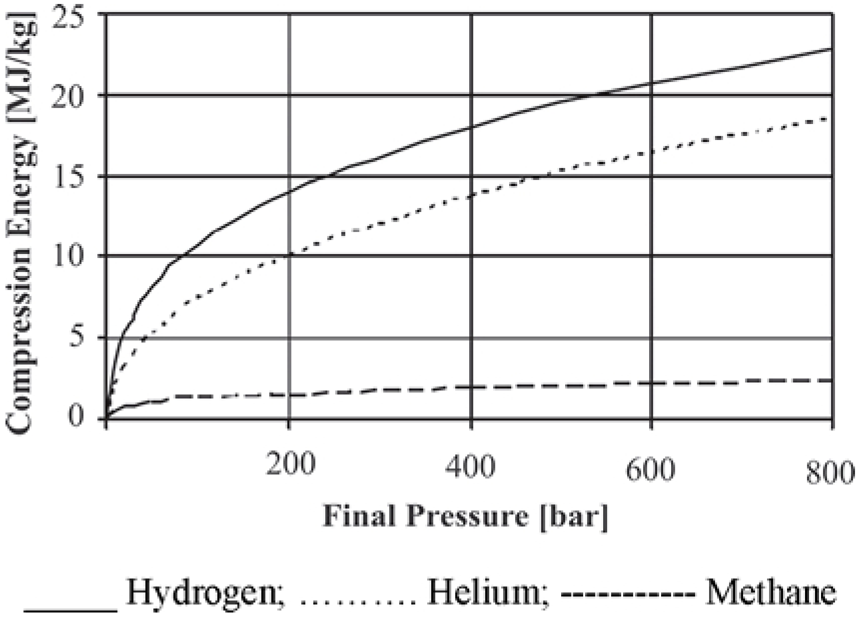


Figure 6.10a: Adiabatic compression work for hydrogen, helium and methane [113a].

Ideal isothermal compression, which is impossible to realize, follows a simple equation:

$$W = p_0\, V_0 \ln(p_1/p_0)$$

In the ideal isothermal case, the temperature would remain constant, while under adiabatic conditions, the temperature significantly rises. Moreover, the magnitude of the compression work depends on the gas.

The multi-stage compressors with intercoolers operate somewhere between the 2 limiting cases of isothermal and adiabatic compression. Hydrogen passes compression heat to the cooler walls more readily, which makes the process more nearly isothermal. Data show that the energy required for a 5-stage compression of 1,000-kg hydrogen per hour from ambient pressure to 200 bar is about 7.2% of its HHV. That is, for a final pressure of 200 bar, the actual energy requirements for multi-stage compression would amount to about 8% of the HHV energy content of hydrogen. But, there are losses in the electrical power supply system, which are not considered here. To obtain one unit of hydrogen HHV at 200 bar, at least 1.08 units of energy must be spent in compression. And it rises to 1.12 for compression to 800 bar, if the automobile industry adapts the newly proposed tank pressure standard of 700 bar [113b].

6.2.2 Liquid Hydrogen-Storage

Cryogenic storage of hydrogen as a liquid is not direct, requiring a reduction in temperature to 22° K (-252.8^{o}C), and even then, the density is still modest at 71 kg/m^{3} [17]. Moreover, the liquefaction of hydrogen is highly energy-intensive besides severe boiling losses. The energy consumed for cooling hydrogen to liquid state was estimated to be 30% of the LHV of hydrogen, which is countless [113].Hydrogen liquefaction involves several processes. Cooling is achieved by 2 processes: multistage compression and expansion combined with counter-flow heat exchange and recovery of energy by expansion turbines. Mostly, for cooling from room-temperature to 73 ∘ K, a three-stage vapor compression propane refrigeration system is used; then, a multi-stage nitrogen expansion to reach 77^{o}K, and a many-time helium compression-expansion to get liquid hydrogen at 20.3oK and atmospheric pressure [113b].

Figure 6.10b illustrates the Energy consumption Vs plant capacity; for the current hydrogen liquefaction plants. It is clear, the small capacity plants consume more electrical energy than the large capacity liquefaction units. The energy requirements decrease as the plant capacity increases. From the figure, it can be seen that for existing plants of 10 and 1,000 kg liquid H_2/h capacity, at least 100 and 40 MJ/kg liquid H_2 are required respectively for liquefaction.

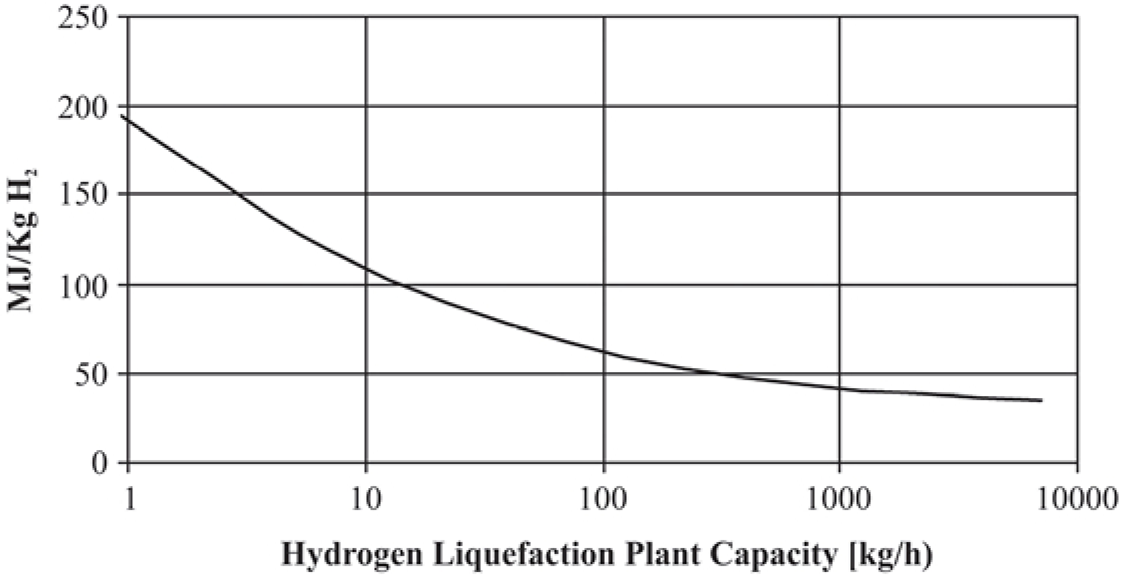


Figure 6.10b: Typical energy requirements for the liquefaction of hydrogen Vs plant capacity [113b]

In addition, some hydrogen gas may boil-off from the liquid H_2 system because of unavoidable heat leaks. The loss rate depends on the size of the storage system and the loss must be allowed for safety reasons. However, this estimated loss of 3 to 4% per day would be significant for the systems used in vehicles [113c]. This gas may be used when the vehicle is moving, but must be vented during the parking. For example, if parked at an airport for 14 days, the loss of hydrogen could be 50 to 60% [113b].

Storing and driving distance: Storing enough fuel for driving comparable distances to petrol or diesel-powered cars is a challenge. The energy content of 1.0 kg hydrogen is approximately equivalent to that of ~4 liters of petrol. So, a tank of about 60 liter capacity needs an equivalent storage volume for 15 kg hydrogen. An 800 bar pressure storage tank would thus need to have a volume of 375 liters for hydrogen, *i.e.*, six times that of a petrol tank because H_2 gas density is 40 kg/m^3.

Fuel cell-powered vehicles require enough H_2 to allow a driving range of more than 300 miles. Light-duty hydrogen-fuel cell electric vehicles (FCEVs) have this feature are now in use, but compressed gas storage onboard by means of large-volume, high-pressure composite tanks are required. On a volume basis, liquid hydrogen has a density of 8MJ/L as against 32MJ/L for gasoline. So, on-board hydrogen-storage capacity of 5 to 13 kg hydrogen must meet the driving range of 300 miles for all lightduty vehicles [113].

US DOE Strategic approaches: To get over these problems, FCTO (Fuel cell technology office of the U.S. Department of Energy) pursues 2 strategic approaches, looking for short-term and long-term answers. The *short-term* plan centers on storing compressed gas by advanced pressure containers made of fiber-reinforced composites; these are capable of reaching 700 bar pressure with affordable cost. The *long-term* strategy emphasizes (a) cryo-compressed hydrogen storing using enlarged hydrogen density and insulated pressure containers, and (b) hydrogen storing based on materials that include sorbents, chemical hydrogenstorage materials and metal hydrides. The USDOE has developed a comprehensive set of hydrogen-storage system targets for light-duty vehicles to enable widespread commercialization of FCEVs [114, 115], which need to be met in all developmental studies.

DOE expected (i) a minimum hydrogen-storage capacity of 6.5 wt% and 65 g/L hydrogen available, at the decomposition temperature, 60 to 120°C for commercial viability, and (ii) low-temperature hydrogen desorption and low pressure of hydrogen absorption and nonthermal transformation between substrates and products of decomposition [116].

***Short-term hydrogen-storage solutions*:** First generation FCEVs make use of 700 bar Type-IV composite overwrapped pressure vessels (COPVs) to store hydrogen. A typical COPV shown in Figure 6.11 has a plastic inside layer overwrapped by carbon-fiber composite material to offer strength. The carbon-fiber composite overwrapped vessels are significantly lower weight than all metal pressure vessels. However, the cost of storing hydrogen in FCEVs increases, due to the high cost of the carbon-fiber composite material. The cost of high-strength carbon-fiber comes almost equally from the cost of the precursor fiber and its conversion to carbon-fiber. To reduce the cost of carbon-fiber, evolving cheaper precursor fibers and cost reduction approaches for conversion processes are debated. A number of cost saving efforts for compressed hydrogen-storage methods are undertaken, including developing other inexpensive and high-performance fiber and resin materials, composite additives for better functioning, and substitute pressure vessel engineering processes and finding other materials for BOP components.

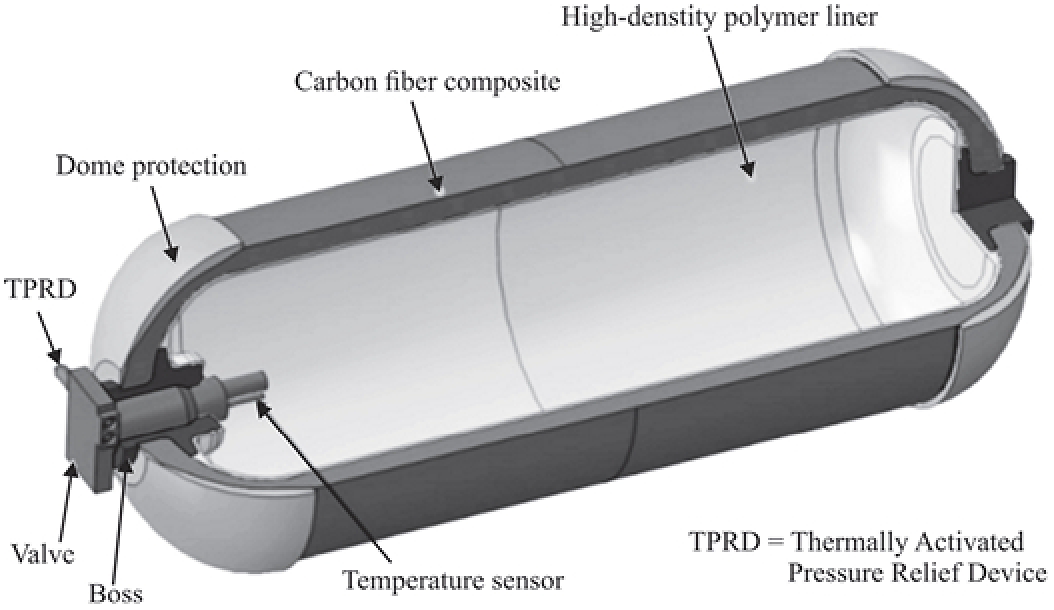


Figure 6.11: A schematic of a Type-IV Composite Overwrapped Pressure Vessel (COPV) designed for H_2 storage on-board FCEVs (Credit: Process Modeling Group, Nuclear Engineering Division, Argonne National Lab.) [Taken from 114].

Long-term hydrogen-storage strategies

Longer-term research focuses on developing advanced hydrogen-storage technologies that can meet the challenging performance levels required for FCEVs while pursuing 2 key approaches mentioned above.

(a) The higher hydrogen densities can be obtained by lowering temperatures. Cold and cryo-compressed hydrogen methods facilitate to store the same amount of hydrogen in smaller volumes at the same pressure, or in the same volume at lesser pressures. Research is essential (i) to develop and appraise insulated systems that reduce heat leakage into the vessels to store hydrogen for lengthy periods without a provision for venting, and (ii) to better understand material behavior when subjected to these temperatures and pressures.

(b) It is also possible to compactly store hydrogen in materials at low pressures. As mentioned earlier, (i) atomic hydrogen binds with elements to form compounds or solid solutions, and (ii) molecular hydrogen adsorbs onto the porous solid surfaces creating prospects for higher storage densities at considerably lesser pressures. Two kinds of metal hydrides are presently studied as rechargeable storage materials: (i) inter-metallic (or interstitial) hydrides: here the interstitial spaces within metal alloys are filled with hydrogen (for e.g. $LaNi_5H_6$), and (ii) complex hydrides: here hydrogen forms covalent bonding with a metal to result in a multi-element anion that joins with another metal through ionic interactions, e.g. $NaAlH_4$. In chemical-hydrides, hydrogen normally bonds to other elements either covalently, e.g., NH_3BH_3 or through ionic interfaces, e.g., CaH_2. Hydrogen is obtained from these materials by way of non-equilibrium processes; and the residual materials are removed and reprocessed chemically off-board to revive the original material containing hydrogen [114].

6.2.3 Hydrogen Storage in Solids

(a) Hydrogen adsorbents

Hydrogen sorbents are high-surface area, micro-porous solids where the diatomic hydrogen molecule adsorbs onto the surface through weak van der Waals interactions. These interactions suggest that low temperatures are needed to obtain a significant amount of hydrogen gas adsorbed. Porous materials such as high-surface area-activated carbons, carbon nanotubes, carbon structures such as graphitic nanofibers, carbon aerogels,carbon nanorods, zeolites, metal-organic frameworks (MOF) and polymers of intrinsic porosity (PIMs) are widely studied.

(i) Carbon structures

Studies by Zhou et al. [117] showed that activated carbons and activated carbon fibers could take up and store 5 wt% hydrogen at low-temperature (77^{o}K) and high-pressure (30 to 60 bar). In an other investigation, 7 wt% of hydrogen was observed at 77°K and a pressure of 20 bar for ordered porous carbon with surface area of 3200 m^2/g, prepared by template [118]. Hydrogen storage in carbon nanotubes was first reported by Dillon et al [119] that led to research on carbonaceous materials worldwide. It is possible for hydrogen to physically adsorb on activated carbon and get ‘packed’ on the surface and within the carbon structure more densely than if it was compressed. The greatest results observed with carbon nanotubes were hydrogen-storage density corresponding to about 10% of the nanotube weight [120]. The possibility of improving the hydrogen-storage capacity by activating carbon nanotubes and/or by using a catalyst was studied by many research groups. Studies reveal that for all micro-porous carbon materials the hydrogen-storage capacity is proportional to the specific surface area or the pore volume of the micropores at roomtemperature and at 77°K [121–123]. Therefore, many factors are involved in the synthesis processes and any variation can affect the quality of the carbon nanotubes produced, the specific surface area and thus the hydrogen-storage capacity. The experimental results on hydrogen-storage in carbon nanomaterials differ over several orders of magnitude, between 0.2 and 10 wt% [124, 125]. The experiments to date claiming high values could not independently be reproduced in different laboratories. Although they have good reversibility and fast kinetics, carbon nanostructures cannot store the amount of hydrogen required for automotive applications [126] as of now.

(ii) Metal organic frameworks (MOFs)

MOFs are emerging ones and perhaps the most intensively-researched hydrogen adsorbents [113, 127–130; 140–143]. MOFs have the potential as hydrogen-storage media in fuel cell vehicles. Microporous crystalline MOFs are formed by the self-assembly of inorganic metal clusters and organic linkers [129]. Most MOFs have a three-dimensional porous framework with uniform pores that provides an ordered network of channels. The many possible variations of the self-assembly allow MOFs to exhibit a wide range of properties, some of which (e.g., surface area) are unmatched by other materials [140, 144]. This design flexibility helps the tuning of MOF properties, but also complicates the identification of optimal compositions, because there are several parameters to be fixed. For the first time, Li et al reported the use of MOFs as a medium for hydrogen-storage [145]. Studies on MOF-5 have shown that it has a hydrogen-storage capacity of 4.5 wt% at the temperature, 77°K and pressure, 0.8 bar, whereas 1 wt% capacity at room-temperature and a pressure of 20 bar. The maximum hydrogen uptake of MOF-5 was observed to be 1.32 wt% at 1 bar, 77°K by Roswell et al. [146]. The adsorption capacity of MOF-5 was low at room-temperature < 0.2 wt% even at high-pressure up to 67 bar [147].

It was observed that the MOF-5 synthesized in the totally moisture-and air-free environment revealed a high gravimetric hydrogen-storage capacity of 7 wt% [148]. The low density of MOFs affects their total volumetric hydrogen-storage capacity [149]. Some MOFs are expected to degrade due to the presence of impurities in the hydrogen-fuel stream unlike lower capacity adsorbents such as zeolites and carbons. Some adsorbents including MOF-5 have low thermal conductivities and can limit the performance of adsorption-based hydrogen-storage systems. The addition of 10 wt% ENG to MOF-5 and compaction to 0.5 g/cm^3 increased the thermal conductivity by a factor of 5 [127].

Recent studies have shown that in addition to the surface area, the pore geometry and pore volume are also important in determining the hydrogen-storage capacity. These porous materials possess better kinetics and show superb cyclability as the materials do not undergo any changes during adsorption or desorption. But the major issue is the requirement of cryogenic temperatures.

(b) Metal hydrides (Interstitial hydrides)

Metal hydrides are known as a prospective efficient, low-risk option for high-density hydrogen-storage since the late 1970s. Since the early 1990s, interstial metal hydrides are known as base materials for Ni-metal hydride rechargeable batteries. For hydrogen-storage, metal hydride systems were developed during the 2010s [132a, b] for stationary applications such as emergency usage or backup power.

Most of the metals and alloys react reversibly with hydrogen to form hydrides. These hydrides offer hydrogen-storage facility under moderate temperature and pressure, and are safe compared to the gaseous and liquid hydrogen-storage methods. Metal hydrides have higher hydrogen-storage density (e.g. 6.5 H atoms/cm^3 for MgH_2) compared to gaseous hydrogen (0.99 H atoms/cm^3) or liquid hydrogen (4.2 H atoms /cm^3). Hence, metal hydride storage may be volume-efficient path for on-board vehicle applications.

Metal hydride cartridges, however, are weighty [132c]. A small metal hydride vessel containing around 2-g hydrogen weighs 230 g [113c]. So, a hydride storage unit of about 200 kg weight must hold 2-kg hydrogen. This is equivalent to only about 8 liters of gasoline; hence, this type of hydrogen packing is unfeasible for applications in automobiles, particularly for long driving distances.

Metal hydride is a concerted single-phase compound between a host metal and hydrogen. Several hydrides employed for storing hydrogen are metallic [150], and transition metals including the rare-earth and actinide series are used to prepare them. Acting as a metal, hydrogen forms a metallic bond. They are characterized by high thermal and electrical conductivities and are breakable. Metals such as Li, Be, Na, Mg, B and Al also form a range of metal-hydrogen compounds because of their lightweight and the number of hydrogen atoms per metal atom. Metal hydrides, e.g. MgH_2, FeTi, and $LaNi_5$ are some of the commonly studied materials [113]. Magnesium based materials have shown high hydrogen capacity and excellent cyclic stability, but their use is restricted due to the demand for high-temperature and poor sorption and desorption kinetics. $LaNi_5$ is another extensively studied material. This inter-metallic compound shows better hydrogen-storage characteristics in terms of kinetics and temperature needs compared to MgH_2. But the amount of hydrogen stored is significantly low. At moderate temperature, the hydrogen-storage capacity goes up to 1.4 wt%. Considerable research efforts have taken place on these materials as seen from the numerous publications in the literature.

(c) Complex hydrides

Complex hydrides have high hydrogen capacities [151]. These materials have a crystal lattice structure consisting of complex anions as hydrogen is covalently bound to the central atoms. In general, complex hydrides have the formula $A_xMe_yH_z$. These compounds have position A preferentially occupied by elements of the first and second groups of the periodic table, and Me is in general occupied by boron or aluminum. Elements lighter than Mg such as sodium, lithium and beryllium also form solid compounds with hydrogen. The hydrogen-content can reach up to 18 wt% for $LiBH_4$. Complex hydrides usage for storing hydrogen is challenging because of both kinetic and thermodynamic restrictions [152, 153]. A lot of interest has been generated in low weight complex hydrides such as alanates $[AlH_4]^-$, amides $[NH_2]^-$, imides, and borohydrides $[BH_4]^-$. The alanates and borates are of low weight and have the capacity for connecting the large number of hydrogen atoms per metal atom. Hence, they are the most interested ones. Borates are known to be stable and decompose only at high-temperatures. Alanates have high-storage capacities and hence are significant; however, upon dehydriding, they decompose in 2 stages.

Sodium alanates are complex hydrides of aluminum and sodium. Sodium tetrahydroaluminate ($NaAlH_4$) and trisodium hexahydroaluminate (Na_3AlH_6) have been studied for a long time. Sodium aluminium hydride, NaAlH has a theoretical reversible hydrogen-storage capacity of 5.6 wt%, and is low-cost and available in bulk. Therefore, it could be a possible candidate for use as a practical on-board hydrogen-storage material. Despite possessing good hydrogen storage capacity, complex Al hydrides, because of their irreversibility and poor kinetics, are unknown as rechargeable hydrogen carriers. But, by using proper transition or rare-earth metals as catalysts, the complex hydrides can be made reversible. By doping with appropriate titanium compounds, Bogdanovic and Schwickardi [154] proved that the dehydriding of aluminum hydrides could be kinetically enhanced and maintain reversibility under moderate conditions in the solid-state. Many others have also investigated how to enhance the hydriding properties of $NaAlH_4$ by doping with titanium and zirconium with mixed results. To improve the kinetics, the effects of mechanical ball-milling on the microstructural characteristics of $NaAlH_4$ in the presence of catalyst are investigated. The milled $NaAlH_4$ or Na_3AlH_6 exhibited great improvement in the kinetics of absorption and desorption [155].

These complex hydrides release hydrogen through a series of decomposition reactions as shown below:

$$NaAlH_4 \leftrightarrow \tfrac{1}{3}\, Na_3AlH_6 + (2/3)\ Al + H_2$$

$$Na_3AlH_6 \leftrightarrow 3NaH + Al + (3/2)\ H_2$$

Theoretically, $NaAlH_4$ and Na_3AlH_6 contain 7.4 wt% and 5.9 wt% of hydrogen, respectively, which are regarded large. But, the release of hydrogen does not occur in a single-step reaction. To begin with, $NaAlH_4$ decomposes gradually developing molecular hydrogen and forming an intermediate compound, Na_3AlH_6 and metallic Al. The transitional phase then decomposes to NaH with extra Al metal formation and hydrogen evolution. The reversibility of these 2 reactions is critical for practical applications.

These and several other aspects are dealt in detail by Sakintunaa et al. in their review [156]. Several other alanates, e.g. $LiAlH_4$, $LiBH_4$ are also well investigated for hydrogen-storage applications.

In conclusion, due to continued research, there have been some encouraging results - improved kinetics and lower decomposition temperatures for metal hydrides. Hence, there is a high potential to develop better metal hydride materials with high reversible hydrogen capacity at ambient temperatures. However, more material study is needed to find appropriate materials that satisfy the requirements for technical applications. Additionally, technological improvements in vehicle design and system integration and the cost-viability are vital. These factors determine the on-board applicability of the selected material.

The realization of hydrogen economy using hydrogen stored solid fuel technology will depend on the progress of these aspects.

(d) Chemical hydrides

Chemical hydrogen-storage technologies involve 2 reactions: (a) the release of hydrogen through a chemical reaction and (b) restoring hydrogen through an ‘off-board’ chemical reaction. These reactions mean, heating chemical-hydrides to release hydrogen and/or reacting chemical-hydrides with water or alcohols. As these reactions are not easily reversible on-board a vehicle, the residue fuel and/or byproducts are taken out from the vehicle and renewed off-board. Many compounds currently being investigated for chemical hydrogen-storage were not synthesized, and so material safety data (MSD) are not available. Chemical hydrides create unusual risks such as toxic byproducts, water and air reactivity, pyrophoricity, possibility for runaway reactions with gas formation, roomtemperature gas emissions and instability, and so on [157]. Chemical hydride storage, in essence, is an alternative method for producing hydrogen via a chemical reaction involving the hydrides, water, and alcohols.

Reacting with water: Hydrogen gas can also be produced exothermically by combining solid chemical-hydrides, like alkali metal hydrides and complex binary hydride compounds. These compounds do not occur in nature, and using pure metals and hydrogen, these are synthesized.

For instance, consider the synthesis of calcium hydride, CaH_2 [113b]. It is produced by reacting pure calcium metal with pure hydrogen at a temperature of 480°C. This is energy-intensive because energy is required both to extract calcium from limestone (calcium carbonate) and hydrogen from water by electrolysis. These are described by the following endothermic processes [113b]:

$$CaCO_3 \rightarrow Ca + CO_2 + 1/2\ O_2\ (\Delta H = +\ 808\ \text{kJ/mol}$$

$$H_2O \rightarrow H_2 + 1/2\ O_2 \qquad (\Delta H = +\ 286\ \text{kJ/mol})$$

Some energy is recovered when calcium and hydrogen are combined at 480°C by an exothermic process:

$$Ca + H_2 \rightarrow CaH_2 \qquad (\Delta H = -\ 192\ \text{kJ/mol})$$

The above 3 equations combine into the virtual net reaction

$$CaCO_3 + H_2O \rightarrow CaH_2 + CO_2 + O_2 \qquad (\Delta H = +902\ kJ/mol)$$

Similar reactions occur for the production of NaH and LiH from NaCl or LiCl respectively.

Then, the material is cooled to room-temperature in hydrogen presence, granulated and packed in airtight containers.

During its use, CaH_2 strongly react with water releasing heat and hydrogen.

$$CaH_2 + 2\ H_2O \rightarrow Ca\ (OH)_2 + 2\ H_2 \qquad (\Delta H = -224\ kJ/mol)$$

The hydride reacting with water produces twice the hydrogen confined in the hydride itself, because the water is reduced simultaneously as the hydride is oxidized to hydroxide. The generated heat needs to be removed by cooling and are normally lost in the majority of cases.

Alkali metal hydrides are high-density energy movers with energy content comparable to firewood or lignite. However, the energy losses in producing the alkali metals and then the hydrides are high, their use is limited to a few applications [113b].

Examine 3 more hydrides, lithium hydride, lithium aluminum hydride, and sodium borohydride reacting with water. These are represented as the following:

$$LiH + H_2O \rightarrow LiOH + H_2 \qquad (\Delta H = -312\ kJ/mol\ LiH)$$

$$LiAlH_4 + 4\ H_2O \rightarrow LiOH + Al(OH)_3 + 4\ H_2 \qquad (\Delta H = -727\ kJ/mol\ LiH)$$

$$NaBH_4 + H_2O \rightarrow NaOH + H_3BO_3 + 4H_2$$

These compounds are light-weight compared to reversible metal hydrides and discharge more hydrogen because hydrogen is liberated from the water reactant. The main concerns with the chemical-hydrides are heat generation and the cost.

Between the first 2 reactions given above, the second one ($LiAlH_4$ reaction) is less exothermic than LiH, and generates 182 kJ of heat per mole of H_2 released. This means, that subject to the system design and power, several kilowatts of heat could be produced. This aspect needs consideration when looking at the overall system design.

They are currently prepared in small quantities with greater than 95% purity because of the purity demand for experimental/application . Hence, they are expensive.

The remaining waste solution, the byproduct from the chemical reaction, can be recycled to reduce the costs linked with the manufacturing of fresh chemical hydride powder [158].

Hydrolysis reactions: Some chemical-hydrides react with water producing hydrogen via hydrolysis reactions [e.g. 159–165]. One of the most widely studied reactions is sodium borohydride, $NaBH_4$, because this hydride offers a safe and low-cost path to generate hydrogen. It can be synthesized by the reaction of sodium trimethyloxyborohydride or sodium tetramethyl-borohydride with diborane (B_2H_6), or by the direct synthesis of sodium, boron, and hydrogen at temperatures, 823–973∘K and a 3–15 MPa hydrogen atmosphere. $NaBH_4$ is a sodium chloride-type crystalline material and freely reacts with water [161], while spontaneous hydrolysis can be sunken in alkaline solutions. The solution can efficiently liberate hydrogen at room-temperature in the presence of catalysts [e.g. 159–163, 165] via the following reaction:

$$NaBH4 + 2H2O \rightarrow NaBO2 + 4H2$$

An inert stabilizing liquid that shields the hydride from contact with moisture and that makes the hydride pumpable is commonly used to activate the reaction. When the slurry is mixed with water, the resulting reaction generates high purity hydrogen. These reactions can be carefully controlled in an aqueous medium using an electrocatalyst (such as Pt, Au, Pd, Ru) and through pH. Despite high hydrogen capacity and fast kinetics, this reaction demands water and fuel to be carried separately on-board, and the sodium borohydride to be rejuvenated off-board. Therefore, $NaBH_4$ is an excellent choice for a one-time application as the reaction is not reversible and leads to borate waste materials. Several issues such as cost, life-cycle impact, and regeneration process for converting the spent borate back to $NaBH_4$ and energy supplies need further studies. The schematic of a chemical hydride reaction system is shown in Fig. 6.12 [158].

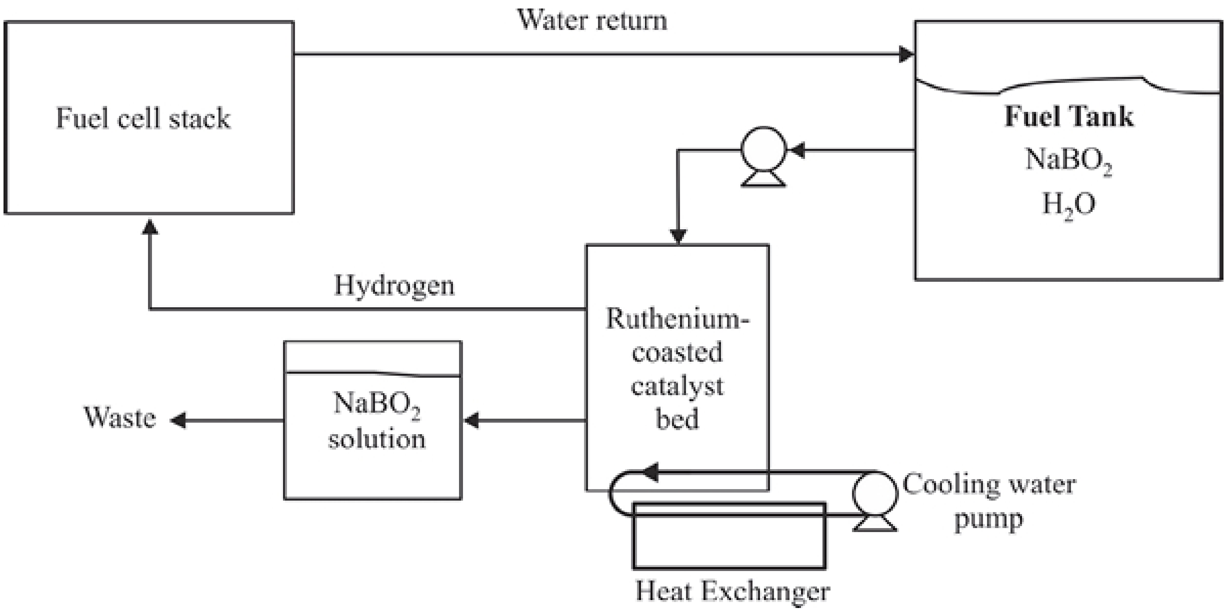


Figure 6.12: Schematic of $NaBH_4$ hydrolysis reaction [158].

Another attractive candidate for chemical hydrogen-storage applications is ammonia-borane, NH_3BH_3, which has a hydrogen capacity of 19.6 wt %, exceeding that of gasoline. The combination of ammonium salts with borohydrides gives high yields of NH3BH3. The direct reaction of ammonia gas with BH_3.THF, diborane, or $BH_3.SMe_2$ also yield NH_3BH_3 effectively [167].Several studies have been conducted to enhance the kinetics of hydrogen release from this compound from both solid and solution approaches [168–174].

NH3BH3 → NH2BH2 +H2 → NHBH + H2

This reaction occurs at a temperature below 120 °C and gives out 6.1 wt % hydrogen. Hydrogen release kinetics and selectivity are enhanced by the addition of ammonia-borane nanosized particles in a mesoporous frame.

Another approach for hydrogen generation from NH_3BH_3 is its reaction with water or alcohol, the so-called hydrolysis or alcoholysis. While NH_3BH_3 is relatively stable in neutral water and alcohol, the hydrolysis of NH_3BH_3 proceeds rapidly in an acidic solution. Metal catalysts are also used to control the hydrolysis or alcoholysis rates [170, 172–174]. Hydrogen gets released from the hydrolysis or alcoholysis of NH_3BH_3 by the following reactions

$$NH_3BH_3 + 2H_2\,O \rightarrow NH_4BO_2 + 3H_2$$

$$5NH_3BH_3 + 22CH_3OH \rightarrow [NH_4B(OCH_3)_4]_5\ .2CH_3OH + 15H_2$$

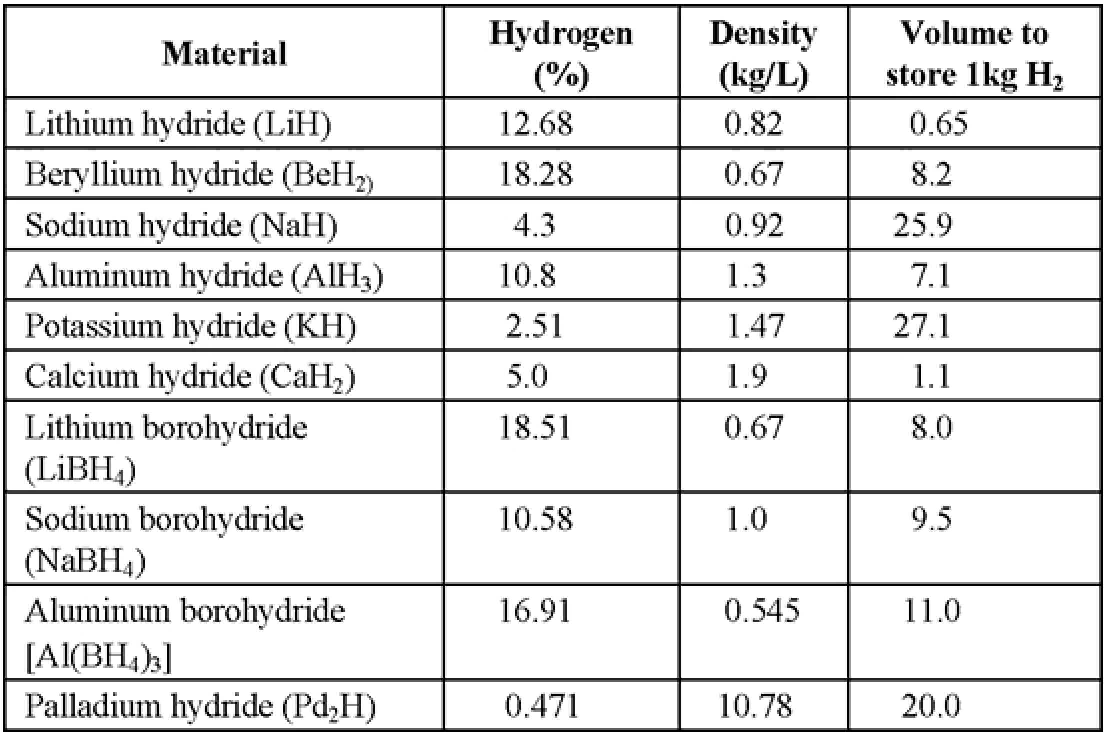
The reaction rate significantly depends on the metal catalysts or precatalysts used. Pt-based catalysts show the highest activities, and the above first reaction can be completed within 2 min using Pt/ $NH_3BH_3 = 0.018$. TEM observations of the catalysts post-reaction indicate that higher catalytic activities, smaller and more dispersed are the Pt nanoparticles. For practical use, low-cost non-noble metal (Ni or Co) catalysts, which exhibited high activities are preferred [167].

Several approaches have been investigated for hydrogen generation from several boron- and nitrogen-based chemical hydrogen-storage materials at reasonable temperatures and rates, and these developments were reviewed in detail by Umegaki et al. [167]. Table 6.2 shows characteristics of a few chemical hydride hydrogen-storage materials [158].

Research on materials-based hydrogen-storage technologies is advancing fast and publications are surging with interesting findings. However, the main issue with the development efforts is to prepare cost-affordable materials with high hydrogen density by volume and mass. These materials shall possess rapid charge/discharge rates within the fuel cell operative ranges of temperature and pressure.

Further, they may be able to endure adequate charge/discharge cycles to last the life-time of the FCEV. In addition to developing such hydrogenstorage materials, comprehending the functioning of the materials in the total system is critical. System design is also required to explain (a) the packing of the material, (b) flow of hydrogen into and through the system, and (c) how heat accompanying the charge and discharge of hydrogen go into and out of the systems, though at the same time, sustaining safety necessities. These technologies must help the commercialization of lightduty hydrogen-fuel cell electric vehicles (FCEVs).

Table 6.2: Some characteristics of a few chemical hydride storage materials (Source [158])



Material	Hydrogen (%)	Density (kg/L)	Volume to store 1kg H_2
Lithium hydride (LiH)	12.68	0.82	0.65
Beryllium hydride (BeH_2)	18.28	0.67	8.2
Sodium hydride (NaH)	4.3	0.92	25.9
Aluminum hydride (AlH_3)	10.8	1.3	7.1
Potassium hydride (KH)	2.51	1.47	27.1
Calcium hydride (CaH_2)	5.0	1.9	1.1
Lithium borohydride ($LiBH_4$)	18.51	0.67	8.0
Sodium borohydride ($NaBH_4$)	10.58	1.0	9.5
Aluminum borohydride [$Al(BH_4)_3$]	16.91	0.545	11.0
Palladium hydride (Pd_2H)	0.471	10.78	20.0

6.3 Hydrogen Fuel Cells

Fuel cells are devices that convert chemical energy (energy stored in molecular bonds) to electrical energy; it’s an electrochemical energy conversion device. Fuel cells provide the enabling technology that allows hydrogen to serve as the storage and transport agent. Fig. 6.13 illustrates the working of fuel cells and electrolysers (fuels running in reverse). Hydrogen and oxygen are united into water in a fuel cell, and in the course of chemical conversion, electricity is generated. In the electrolyzer, on the other hand, an electrical current is passed through water (electrolysis) and is the converse of the electricity-generating process occurring in a fuel cell.

Hydrogen fuel cells offer tremendous opportunity for storing and transporting energy enabling several applications for home, business, motor vehicle and large-scale energy projects. Hydrogen and fuel cells can contribute in many ways spanning the whole energy system [175 a-g].

In using hydrogen-fuel cells, the aspects to consider are operating efficiency, operating temperature range, and the material used for the electrolyte (the catalyst that separates hydrogen) and fuel oxidant (that transfers the oxygen atoms).

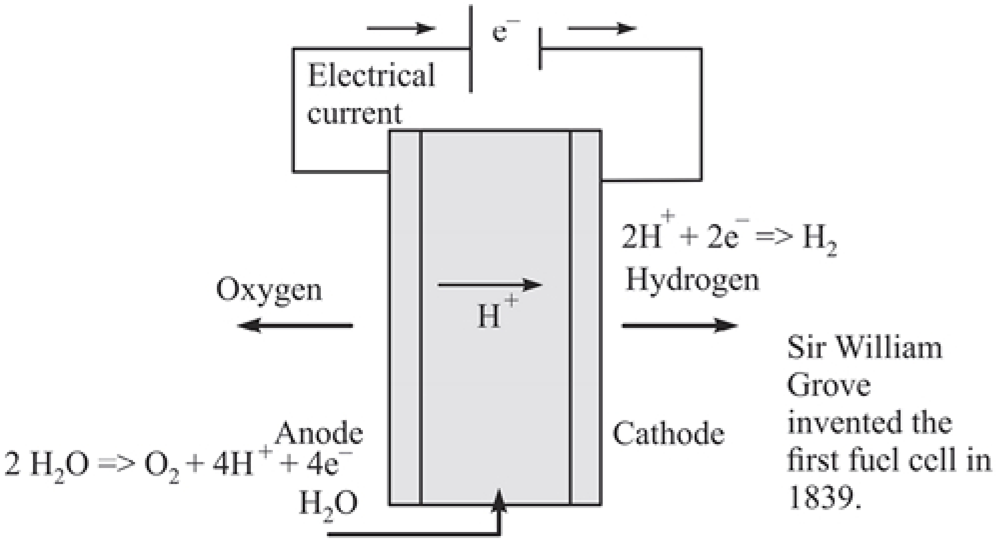


Figure 6.13: Working principle of a fuel cell [175].

Comparison with battery systems and thermal engines: FCs are analogous to batteries in terms of their electrochemical features and the method for generating electricity; but differ from battery technologies in not requiring recharging. Also, FCs are similar to thermal engines by their capability to generate electricity constantly consuming fuel, whereas they differ from engines by their quiet operation [176c, d]. FCs operate free of emissions and efficiently compared to batteries and engines. Though some form of thermodynamic processes is associated with FCs, they are unlike thermal engines as they are not limited by the Carnot efficiency [176e, f, g]. These features are of interest in modern energy planning, generation, and development, in the context of achieving decarbonized and sustainable energy future.

FCs are classified by the kind and the level of purity of the fuel and oxidant and the operating temperature. The chemical reactions between the fuel (i.e., hydrogen) and oxidant (i.e., oxygen) vary in different kinds of FC systems.

Five types of FC technologies are operating: proton-exchange FC, alkaline FC, phosphoric acid FC, molten carbonate FC, and solid oxide FC [178a-181e] which are briefly described below.

Proton exchange membrane (PEM) fuel cell technology is used in many applications, especially for electric vehicles, because it operates at normal ambient temperatures and offers high electrical efficiency. PEM also stands for polymer electrolyte membrane. They are also called polymer membrane fuel cells, or just membrane fuel cells. In the beginning, during the 1960s, they were known as Solid Polymer Electrolyte (SPE) fuel cells. This technology has become attractive due to its simplicity, viability, quick startup and load following capability, modularity and versatility.

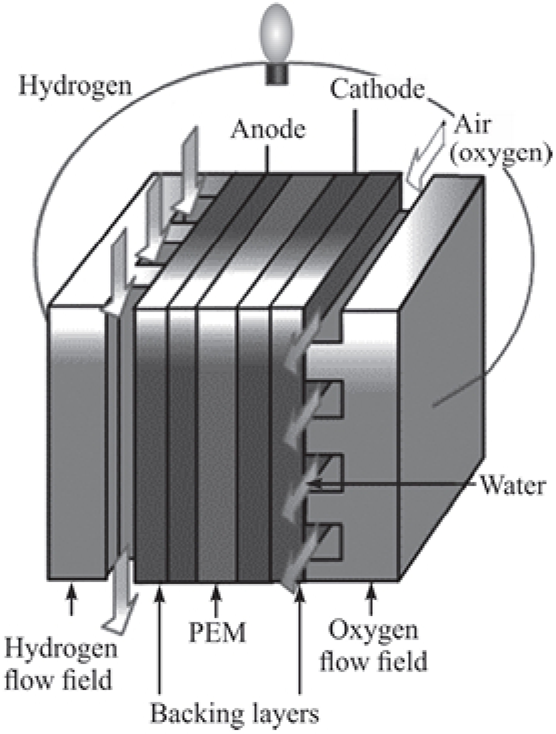


Figure 6.14a: Schematic of PEM fuel cell [176].

A PEM fuel cell consists of 4 basic elements as shown in Fig. 6.14a: (a) the anode (negative electrode) conducts the electrons that are freed from the hydrogen molecules. It is etched with channels that disperse hydrogen gas equally over the surface of the catalyst; (b) channels are etched into the cathode (positive) that dispenses the oxygen molecules onto the catalyst surface. It also moves the electrons from the external circuit back to the catalyst, enabling them to recombine with the hydrogen ions and oxygen to become water; (c) a specially treated material, proton-exchange membrane is the electrolyte, which conducts only positive ions and block electrons. It is a polymer, and the appearance of the electrolyte varies depending upon the manufacturer; the most prevalent membrane, Nafion, produced by DuPont uses perfluoro sulfonylfluoride ethyl-propyl-vinyl ether (PSEPVE). Similar materials have been developed and marketed either as a commercial or development product by other manufacturers. Nafion is more substantial and available in several thicknesses, 50, 89, 125, 178, 250 μm. The main characteristics of the FC membrane are proton conductivity, water transference, gas infusion, physical strength and dimensional steadiness. All these properties are directly correlated to the membrane-water content. Hence, the membrane must be hydrated to function properly and remain steady; (d) the catalyst is a distinct material that enables the reaction of oxygen and hydrogen. It is typically made of platinum nanoparticles of size, 4 nm or smaller, very thinly covered onto carbon paper or cloth. To deposit a catalyst layer on the porous substrate or the membrane, several techniques are employed: spreading, painting, spraying, sputtering, screen printing, decaying, electro-deposition, evaporative deposition, and impregnation reduction.

The catalyst is rough and porous so that the maximum surface area of the platinum can be exposed to hydrogen or oxygen. The platinum-coated

side of the catalyst faces the PEM. The catalyst is an expensive part of the PEM fuel cell.

The chemical reactions are

Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Anode: $2H_2 \rightarrow 4H^+ + 4e^-$

Overall: $2H_2 + O_2 \rightarrow 2H_2O$

The membrane is the core of the fuel cell. Pressurized hydrogen enters the fuel cell on the anode side and is pushed through the catalyst by its pressure. The H_2 molecule that contacts with the platinum on the catalyst, break into 2 H+ ions and 2 electrons (e^-). The electrons travel through the anode and go through the external circuit having a load and come back to the cathode side of the FC. In the interim, oxygen is being forced through the catalyst on the cathode side of the FC forming 2 oxygen atoms. These atoms, each has a strong negative charge. This negative charge attracts the 2 H+ ions through the membrane, and they combine with an oxygen atom and 2 of the electrons from the external circuit to form a water molecule. All these reaction occurs in a ‘cell stack.’ The stack is embedded in a module including fuel, water and air management, coolant control hardware and software. This module is then integrated into a complete system for use in different applications.

A single cell supplies a voltage of about 0.7 volts, adequate for lighting a bulb. The cells are stacked in series and the operating voltage increases depending on the number of stacked cells.

Water management is key for the PEM fuel cell to operate effectively. Despite water being a product of the fuel cell reaction, and is passed out of the cell during its operation, it is essential to humidify both the fuel and air entering the fuel cell. This extra water retains the PEM hydrated. The humidity of the gases must be cautiously organized. Otherwise, less water prevents the membrane from conducting the H+ ions well, resulting in the drop in the cell current. The air flow past the cathode needs to be suitably adjusted to carry all the water produced at the cathode out of the fuel cell, to avoid the flooding of the cathode. The performance of the cell is affected when enough oxygen is unable to force the excess liquid water to reach the cathode catalyst sites [177].

Efficiency estimation: The amount of electrical energy (W_{elec}) generated in a fuel cell corresponds to the Gibb’s free energy (ΔG) of the overall chemical reaction of the Cell given above.

$$W_{elec} = -\Delta G$$

The theoretical potential (E) of the Cell is, $E = - \Delta G/nF$.

Here, n is number of electrons involved in the above reaction and F is the Faraday constant. Since the quantities (ΔG, n, and F) are known, the theoretical potential of hydrogen/oxygen fuel cell at $25 \circ C$ and at atmospheric pressure can be calculated, which turns about to be 1.23 volts.

If the total Gibbs free energy can be assumed to be altered into electrical energy, the theoretical efficiency (η)

of the FC is the ratio of the Gibbs free energy and hydrogen higher heating value,

$$\eta = \Delta G/\Delta H = 237.34/286.02 = 83\%$$

Actual cell potentials are always smaller than the theoretical ones due to voltage losses caused by several factors, such as (i) kinetics of the electrochemical reactions, (ii) internal electrical and ionic resistance, (iii) stray currents, (iv) mass transport limitations, and (v) crossover of reactants.

The fuel cell efficiency, defined as a ratio of the electricity produced and hydrogen consumed, is directly proportional to its potential:

$$\eta = V/1.482$$

Here, 1.482 is the thermoneutral potential corresponding to hydrogen's HHV.

If the efficiency is expressed in terms of the lower heating value (LHV), then

$$\eta = V/1.254$$

Normally, there is a loss of hydrogen during the diffusion of H_2 through the membrane, or while linking with oxygen that dispersed through the membrane or because of internal currents. So, intake of hydrogen would be higher than that corresponding to current produced; as a result, the fuel cell efficiency would be slightly lesser [177a].

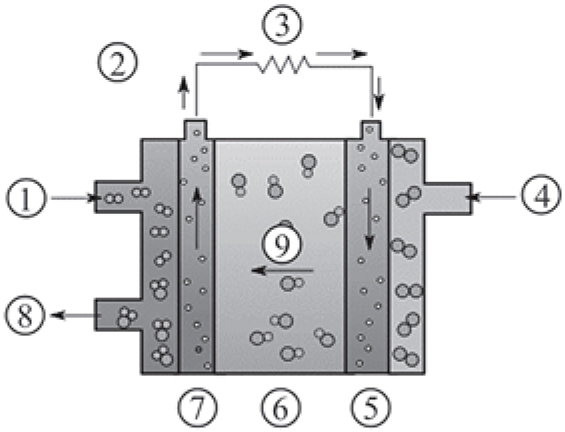
Uses: The high-energy content of hydrogen and high-efficiency of the fuel cells (around 55%) enable this technology to be used in several applications such as transport (cars, buses, forklifts, etc), and portable and backup power source to produce electricity when the electricity grid fails [176].

Advantages: (a) Fuel cells convert chemical potential energy directly into electrical energy, thus avoiding the ‘thermal bottleneck’. Hence, they are intrinsically more efficient than combustion engines; (b) direct emissions from a fuel cell vehicle are just water and some heat, enormous progress over IC engines which emit greenhouse gases; (c) Fuel cells have no moving parts, thus much more reliable than traditional engines; (d) H_2 can be produced in an environmental-friendly manner, compared to damaging processes of oil extraction and refining.

The PEM fuel cell is one of the 5 distinct types of fuel cells. The others are the following:

Alkaline Fuel Cell (AFC): Alkaline fuel cells consume hydrogen and pure oxygen, to produce potable water, heat, and electricity. A schematic of an Alkali Fuel cell is shown in Fig. 6.14b. The electrolyte is a porus matrix soaked in an aqueous solution of potassium hydroxide. As aqueous alkaline solutions do not reject CO_2, KOH can convert into potassium carbonate ‘poisoning’ the fuel cell. As a result, alkaline fuel cells normally operate on pure oxygen or purified air. The cell design includes a 'scrubber' to clean carbon dioxide. The generation and storage needs of pure oxygen increase the costs of oxygen-operated AFCs. The electrodes consist of a double layer structure, an active electrocatalyst layer and a hydrophobic layer. The active layer is made of an organic mixture that is ground and then rolled at room-temperature into a crosslinked selfsupporting sheet. The hydrophobic structure averts the leaking of electrolyte into the reactant gas flow channels and make sure the flow of the gases to the reaction site. Then, the 2 layers are hard pressed onto a conducting metal mesh and sintered.

AFC operates at temperatures of 90–100°C. The efficiency is about 70% and cell output has a range, 300 W - 5 kW.



1. Hydrogen, 2. Electron flow, 3.Load, 4.Oxygen, 5. Cathode, 6. Electrolyte, 7.Anode, 8.Water, 9. Hydroxide ions

Figure 6.14b: Schematic of an Alkaline Fuel cell (Wikipedia).

The electrochemical reactions that occur are

$$\text{Anode: } H_2 + 2(OH)^- \rightarrow 2H_2O + 2e^-$$

$$\text{Cathode: } \tfrac{1}{2}\,O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$$

$$\text{Overall cell: } H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O$$

AFCs are used in military and space projects, and for more than 25 years, NASA has used this technology. A faster cathode reaction in the alkaline electrolyte, resulting in high-performance is the main benefit of AFC. The disadvantage is the necessity of pure hydrogen and expensive carbon dioxide removal from the fuel and air streams.

Phosphoric Acid Fuel Cell (PAFC): PAFCs are the first generation of commercial modern fuel cells that were developed for terrestrial applications. PAFCs use phosphoric acid (H_3PO_4) in highly concentrated form (> 95%) as its electrolyte and porous carbon electrodes containing the platinum catalyst as shown in Fig.6.14c. CO_2 containing air is used as the oxidant and pure hydrogen or a hydrogen-rich gas acts as the primary fuel for power generation. A porous SiC matrix is often used to immobilize the electrolyte by capillary action. Since the electrolyte is acidic, there is high corrosive environment and the internal parts of the cells must be able to withstand.

The chemical reactions at the anode and cathode are

Anode: $H_2 \rightarrow 2H^- + 2e^-$

Cathode: $\frac{1}{2} O_2 + 2H^- + 2e^- \rightarrow H_2O$

Overall cell: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

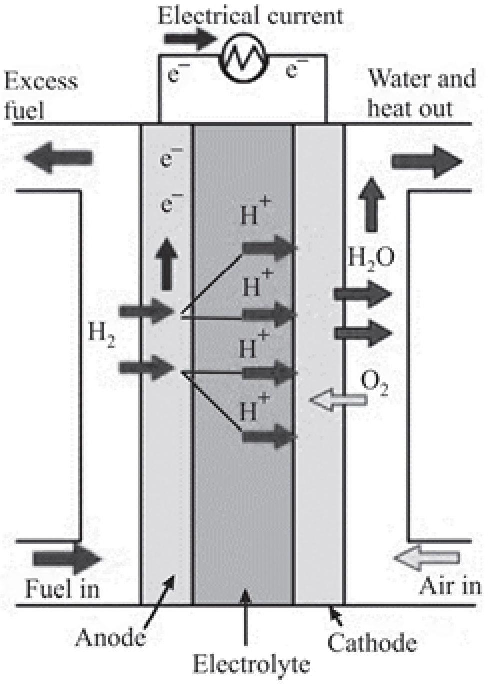


Figure 6.14c: Schematic of a Phosphoric acid fuel cell. Source: [176a]

It operates at temperatures of 175–200°C. Existing PAF cells have up to 200 kW; and 11 MW units have been tested. PAFC applications include electric utility and transportation.

The advantages are that the efficiency reaches up to 85% when used in cogeneration of electricity and heat as compared to 40–50% generating electricity alone. *Impure* hydrogen as fuel can be used. PAFCs tolerate a CO concentration of about 1.5%, which broadens the choice of fuels they can use. Hydrogen produced by steam reforming of organic fuels such as natural gas or methane, and alcohols such as methanol or ethanol, are often used as the anodic reactants. If gasoline is used, the sulfur must be removed.

The main disadvantages are that it requires an expensive platinum catalyst, has low current and power, and requires a large size and weight.

Molten Carbonate Fuel Cell (MCFC): MCFCs are high-temperature fuel cells, typically operating at 600° - 1000°C. Through their high-temperature operation, they can improve reaction kinetics, which implies that they can achieve a high rate of electrode reactions without the need for platinum catalysts [180f]. These are also capable of ‘internal reforming’ whereby they convert other fuels to hydrogen directly because they operate at sufficiently high-temperatures to avoid an external reformer to generate hydrogen. These features help reduce cost compared with alkaline FC, phosphoric acid FC, and proton-exchange membrane FC, which are low-temperature technologies. Another benefit of the MCFCs is that they are not as much vulnerable to CO poisoning as low-temperature technologies [180g]; it is also promising to efficiently deal with the reaction heat for generating more electrical energy [180f].

These cells use an electrolyte composed of a molten carbonate salt mixture (lithium carbonate and potassium carbonate) suspended in a ceramic matrix solid electrolyte, which is chemically inert and porous. To increase the pore size delivery and functioning of the electrolyte, a small amount of sodium carbonate and carbonate of earth-alkaline metals is supplemented to the mixture. The electrodes are inexpensive nickel-based ones and can be constructed as a stack of bipolar plates. The system must include a system for recycling carbon dioxide in the gaseous phase that includes a water separation process. The schematic of a MCFC is shown in Fig. 6.14d [176b].

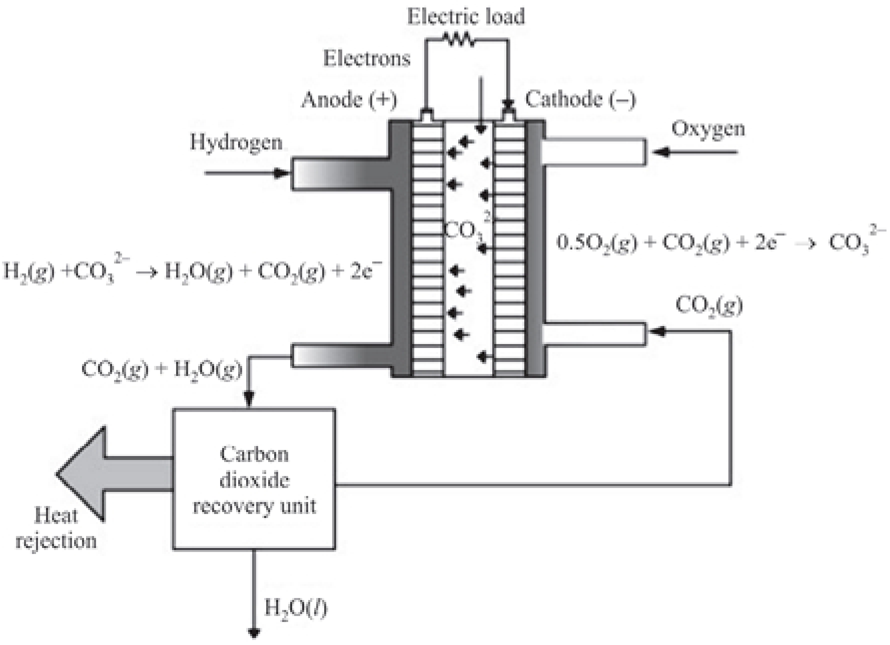


Figure 6.14d: Schematic of Molten carbonate Fuel cell. Source: [176b]

The reactions are

$$\text{Anode: } H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$$

$$\text{Cathode: } \tfrac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$$

$$\text{Overall cell: } H_2O + \tfrac{1}{2}O_2 \rightarrow H_2O$$

(CO_2 is consumed at cathode and produced at anode)

The efficiency ranges from 60 to 80%. Units with output up to 2 MW have been constructed and designs exist for units up to 100 MW. MCFCs are mainly used for electric utilities.

MCFC’s high-efficiency, fuel flexibility, low emissions and its ability to use various catalysts such as inexpensive Ni are the advantages. These cells allow the recovery of waste heat for use in the generation of steam, hot water, hot air, and so on. High-temperature MCFCs are mostly appropriate for stationary cogeneration of heat and electricity and distributed energy supply.

The disadvantages are (i) the high-temperature enhances corrosion and breakdown of the cell components, (ii) low power density, and (iii) short life-time. Research efforts to resolve these issues and to achieve lessening of operating, maintenance and stack replacement costs, and to explore less expensive manufacturing technologies are on-going.

Solid Oxide Fuel Cell (SOFC)

Solid oxide fuel cells use a solid oxide electrolyte unlik others. The solid oxide electrolyte enables negative oxygen ions move from the cathode to the anode. So, on the anode side, the electrochemical oxidation of the hydrogen, carbon monoxide or other organic intermediates by oxygen ions happens. The proton-conducting SOFCs (PC-SOFC), which are recently fabricated transport protons instead of oxygen ions through the electrolyte with the advantage of being able to operate at lower temperatures than traditional SOFCs. A schematic of a SOFC is shown in Fig. 6.14e.

The electrochemical reactions are

Anode: $H_2 + O^{2-} \rightarrow H_2O + 2e^-$

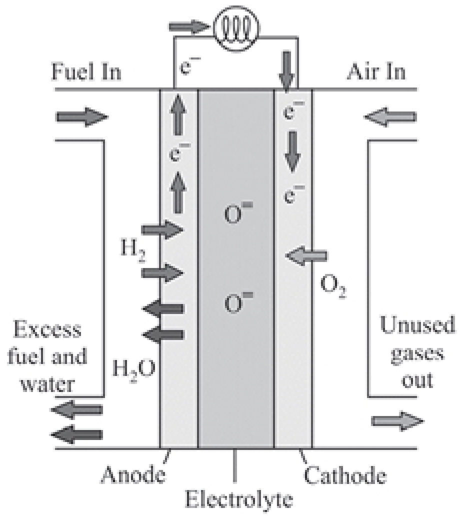


Figure 6.14e: Schematic of SOFC (Wikipedia).

Cathode: $\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$

Overall cell: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

SOFC is a fuel-flexible device, and, besides pure hydrogen, it can use carbon monoxide, biogas, and higher hydrocarbons such as methanol, ethanol, and so on as fuels. Also, it can tolerate some amount of fossil-fuel impurities such as ammonia and chlorides.

In SOFCs, the main properties for an electrode material according to [177c] are (a) best catalytic activity; (b) higher electrical conductivity; (c) effective thermal expansion steadiness; (c) must be compatible with electrolyte at operating temperature; (d) stability at higher temperatures; (e) fuel flexibility; and (f) low coking resistance and low-cost [177c].

A large variety of electrode materials are being used in SOFCs. Besides composites consisting of metal and electrolyte components can be used for gaining good electronic as well as ionic conductivity. The electrode materials are the most crucial part of the fuel cell and to function effectively, the cell should have electrode with good electronic conductivity and electrolyte with good ionic conductivity [177c].

SOFCs operate in the temperature range, 600–1000°C where (a) expensive platinum catalyst is not needed unlike in lower temperature fuel cells like PEMFCs, and (b) not at risk to carbon monoxide catalyst poisoning. SOFC’s efficiency is about 60%, and the output of the cells is about 100 kW.

SOFCs are in effect multilayer assemblies, consisting of a solid dense electrolyte packed between 2 porous electrodes. A supporting element provides mechanical resistance to the cell, which is most commonly the thick anode; the typical electrolyte is *yttria-doped zirconia* ionic conductor. The single cells are joined through metallic plates, which also collect current. More research, however, is needed to improve the lifespan and reliability of the single device. Most of the studies are currently devoted to reducing the operating temperature (around 800°C) using most performant materials such as proton conductors and ceria-based anionic conductors, reduce the number of critical elements and improve the resistance of interconnectors and sealant [177b].

SOFC types: SOFCs are designed as tubular and planar. Both types comprise one or several single cells per stacking unit, i.e., on a single tube or in a single multilayer. As the application requires, the dimensions of tubular SOFCs vary from needle-like to lengths of about 1.5–2 m for quick startup times and large gross power, respectively. The planar SOFC design is the most common due to its advanced performance. This design leads to 2 different stacks comprising metallic or ceramic connecting material as well as with cells having thick (electrolyte-supported, 1st generation cells) or thin (electrode-supported, 2nd generation cells) membranes, their thickness generally in the range of 150–250 μm and 520 μm, respectively.

The technologically significant planar cells vary in size from 10 × 10 cm^2 to 25 × 25 cm^2 or equivalent areas in round or rectangular shape. The current general trend of decreasing the operating temperature from ~1000°C to 500–800°C favors cell designs having thin electrolytes, small ohmic resistance and thus higher power density; that means, moving from the 1st to the 2nd generation of cells, shown in Fig. 6.14f. Many developers have preferred electrode-supported cells, the best choice for realizing SOFCs operating at reduced temperature.

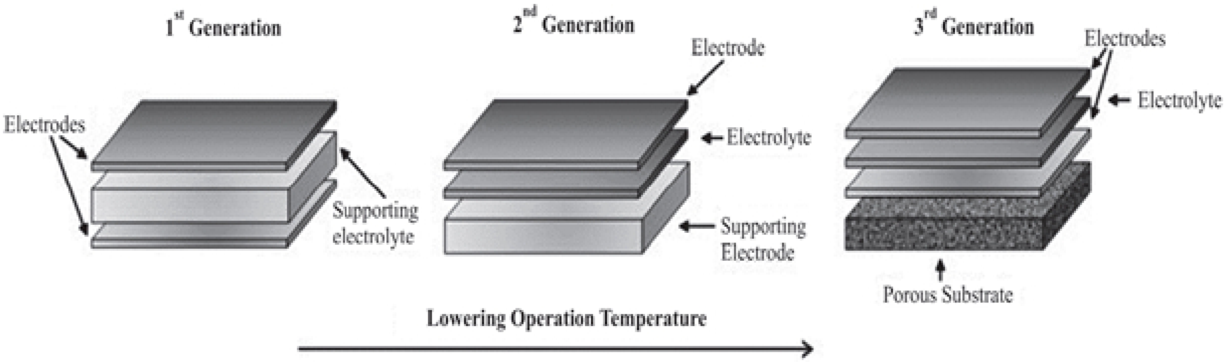


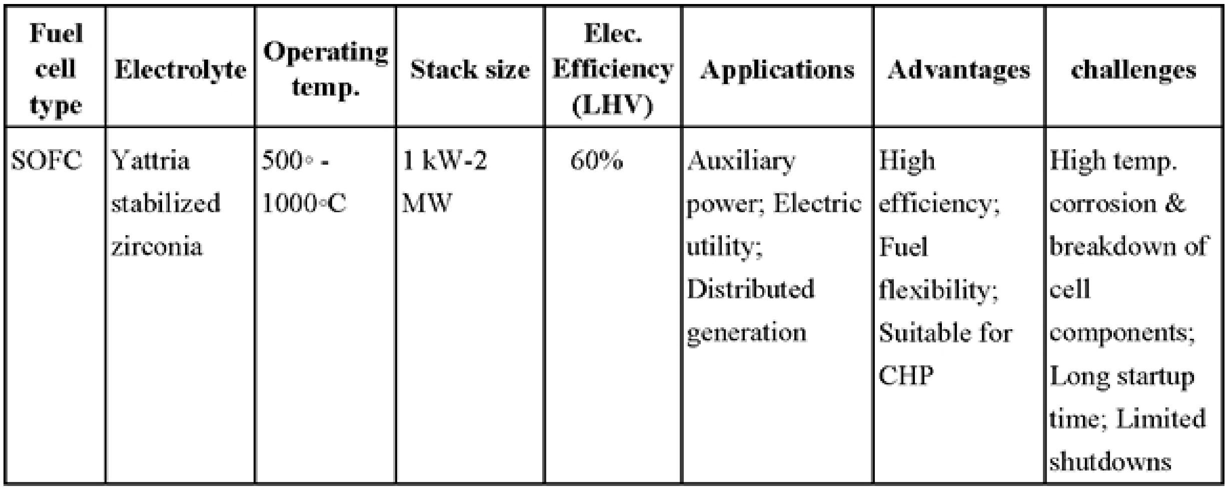
Figure 6.14f: Schematic representation of the SOFC generation designs. Source: [177b]

The second generation of cells could be supported on the anode or cathode side. Although the cathode-supported structure showed better structural stability and allows inexpensive cathode material, the anodesupported design is favored due to easier production. Recently, more attention is focused on the 3rd generation SOFCs (Fig. 6.14f) wherein the mechanical strength is provided by the electrode side, not essentially by the electrode substrate. The substrate in all of these is porous to permit gas passage to and from the anode. The substrate materials used normally are metals or alloys, or simply refractory ceramics. Ferritic stainless steel is one of the most considered materials because its coefficient of expansion is similar to the cell ceramic materials (YSZ, GDC, electrolyte, or anode functional layer). It’s cheaper than YSZ or GDC ceramics, cathodic and anodic materials, thus enabling savings in the total cell cost. Nevertheless, in metal-supported cells (MS-SOFC), severe cation interdiffusion occur among different components during manufacturing and corrode intensely at high operating temperature (≥800°C). Therefore, the manufacturing processes need to be changed. More details are given in several publications [for e.g. 177b].

In general, the main advantages of SOFCs are its high-efficiency, fuel flexibility, ability to use various catalysts and reduced corrosion. The waste heat can be recycled to make extra electricity [178]. The characteristics of these 5 types of fuel cells are compared in the following Table 6.3.

Table 6.3: Comparison of the characteristics of the fuel cells (USDOE-OEE & RE).

Fuel cell type	Electrolyte	Operating temp.	Stack size	Elec. Efficiency (LHV)	Applications	Advantages	challenges
PEM	Perflouro sulfonic acid	< 120◦C	<1-100 kW	60% direct H_2, 40% reformed fuel	Backup power, Portable power; Distributed generation; Transportation; Specialty vehicles	Solid electrolyte reduces corrosion & Electrolyte management; Low temp operation; Quick startup and load following.	Expensive catalysts; Sensitive to fuel impurities
AFC	Aqueous KOH soaked in a porous matrix or alkaline polymer membrane	< 100◦C	1 –100 kW	60%	Military; Space; Backup power; Transportation	A wide range of stable materials allow low-cost components; Low temp.; & Quick startup.	Sensitive to CO_2 in fuel and air; Electrolyte management; Electrolyte conductivity (membrane)
PAFC	Phosphoric acid soaked in porous matrix or imbibed in a polymer membrane	150◦ - 200◦C	5-400 kW, 100 kW module (liquid PAFC), <10 kW (polymer membrane)	40%	Distributed generation	Suitable for CHP; Better tolerance for fuel impurities	Expensive catalysts; Long startup time; sulfur sensitivity
MCFC	Molten Li, Na and/or K carbonates soaked in a porous matrix	600◦ - 700◦C	300 kW-3 MW, 300 kW module	50%	Electric utility; Distributed generation	High efficiency; Fuel flexibility; Suitable for CHP; Hybrid/ gas turbine cycle	High temp. corrosion & breakdown of cell components; Long startup time; Low power density



Fuel cell type	Electrolyte	Operating temp.	Stack size	Elec. Efficiency (LHV)	Applications	Advantages	challenges
SOFC	Yattria stabilized zirconia	500◦ - 1000◦C	1 kW-2 MW	60%	Auxiliary power; Electric utility; Distributed generation	High efficiency; Fuel flexibility; Suitable for CHP	High temp. corrosion & breakdown of cell components; Long startup time; Limited shutdowns

[Source: USDOE (2016): Comparison of Fuel cell technologies, DOE- Office of Energy efficiency & Renewable energy, April 2016 @ https://www.energy.gov/sites/default/files/2016/06/f32/fcto_fuel _cells_comparison _chart_apr2016.pdf]

However, recently, Akinyele et al [181f] compiled data from different sources, where each metric in Table 6.3 has a range of values.

Power Generation: The generated and stored hydrogen can be converted back into electricity in a number of ways. It can be combusted like natural gas, but the combustion temperature is higher than that for natural gas. However, most gas turbines, piston engines and gas-fired boilers can easily be reformed and used for hydrogen-fuel. The only byproduct results in this method is water. As an alternative, hydrogen can offer as the fuel for a fuel cell system most efficiently [179].

Hydrogen from Renewables for Fuel cell power generation

We have seen that hydrogen can be produced by water-electrolysis, steam reforming, and so on, which can be used in fuel cells. Hydrogen from industrial waste, hydrogen from propane, or methane generated at the waste-water treatment units can also be used in fuel cells. Eventually, hydrogen obtained from renewable resources such as solar, wind, or biomass energy would provide a sustainable and clean source of *hydrogen for fuel cell power generation* [178]. A schematic of a hydrogen energy storage system designed to store power from wind and solar power plants is shown in Figure 6.15 [180]. The figure is self-explanatory.

For a future hydrogen energy economy, this process offers one of the most favorable solutions with a feasible 60% efficiency in a simple fuel cell system, and possibly 70%-75% with a hybrid system.

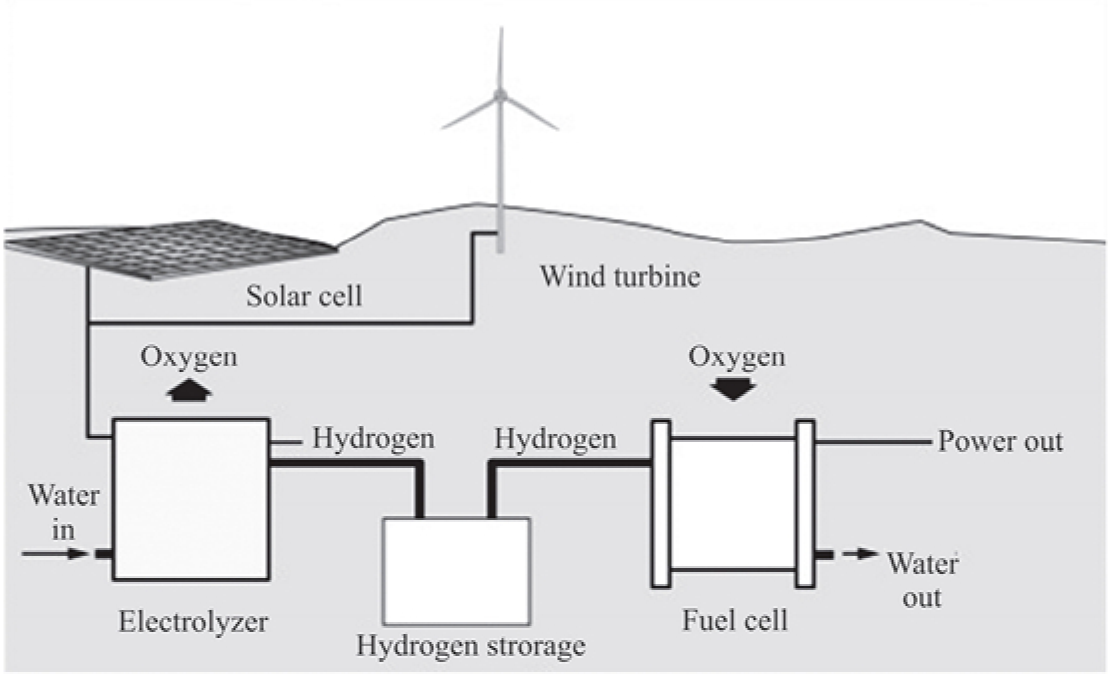


Figure 6.15: Schematic of hydrogen-storage system to store power from wind/solar plants [179].

Performance Characteristics: Hydrogen can be used as an energy storage medium within an electricity system. But, hydrogen-burned conventional power plants cannot be brought into service as quickly as some of the storage systems that act fast, as discussed earlier. Therefore, it should be regarded as a system for energy arbitrage, or storing extra or off-peak renewable power rather than supporting grid. The stored energy is then pumped into the grid as demand rises or renewable output decreases.

The main problem today of hydrogen-storage is the round-trip efficiency. With an electrolyzer operating at 90% efficiency and a power plant converting it back into electricity with around 60% efficiency, the best round-trip efficiency that can be anticipated is 54%. This is much lower than other storage systems described earlier. Such low efficiency may be acceptable in a renewable energy storage system such as a windhydrogen-storage unit where the wind energy must otherwise be shed. It is improbable to regard as amply efficient for generation from off-peak grid power in most situations [179].

Costs: Hydrogen energy storage as an electrical energy storage medium is not tested so far; so, no representative costs are available for systems. However, hydrogen energy storage should be able to compete with the high-storage capacity technologies such as PHS, CAES or large battery storage systems to become practical [179].

Transportation applications

PEM fuel cells are largely used in fuel cell electric vehicles (FCEVs) because they are capable of offering high-efficiency, high power density, and cold-start capabilities. A 60 kW capacity fuel cell typically suits European cars. Though FCEVs have high capital and operating costs, they have the potential for considerable cost reduction as manufacturing volumes rise, and finally to turn into cheaper alternatives. FCEVs have zero emissions at the point of use and are low-carbon at the production stage if made from renewable-powered electrolysis.

FCEVs though currently expensive, several studies suggest that cost reductions from mass-production could see their life-time cost matching with vehicles powered by other fuels by 2030[181].

There are 3 key challenges to be addressed, (a) cost (less than $50/kW of engine power), (b) durability (at least 5,000 hours) and (c) rapid startup (less than 30 seconds) for use in cars, buses and trucks.

While much work needs to be done to optimize the fuel cell system, hydrogen-fuel cell vehicles are on the road now. The gasoline internal combustion engine is nearly 120 years old, but still being improved! In March 1998, Chicago became the first city in the world to put pollution-free, hydrogen-fuel cell-powered buses in their public transit system [177]. Significant early deployment of fuel cell buses happened with 7 million km of operational experience so far in Europe with 83 operating fuel cell buses. North America has 44 buses in use. London city and California state have experience with fuel cell buses, 18,000 hours and >20,000 hours, respectively. Japan, South Korea and China are other countries planned to introduce fuel cell buses. Every major automobile manufacturer in the world is developing fuel cell vehicles. For instance, major car makers, Toyota, Hyundai and Honda now offer FCEV passenger vehicles, and other prominent manufacturers like Audi, Mercedes-Benz and others are likely to follow. FCEVs are offered in only a few countries because of infrastructure requirements, yet, around 3000 FCEVs are sold to date [181]. The International Energy Agency concludes that FCEV sales could reach 8 million by 2030 in developed nations, and 150 million sales and a 25% share of road transport by 2050 [182].

6.4 Power to Gas Technology (P2G)

It is explained already that for a reliable energy grid and stable security of supply, the availability of and demand for power must constantly be in equilibrium. Actually, this does not just happen automatically. The production must be ramped up when demand is greater than supply. As renewable power largely relies on natural factors, it cannot be controlled as easily as fossil-fuel-based sources. Geothermal power is the only form of renewable energy that is completely immune to fluctuations. Thus, surplus renewable (green) energy is wasted when supply exceeds demand.

Energy storage is thus seen as the solution for using full renewable energy sources. That is, even in times when renewable energy is not/less available (i.e. no wind or sun), the electricity demand can be met. Several methods have been discussed so far for storing renewable power.

Another approach is P2G technology, a technology that converts energy, mainly electricity through electrolysis into hydrogen and oxygen and then into methane through a chemical reaction called methanation. The resulting product is a ‘synthetic natural gas’ or ‘substitute natural gas (SNG)’, also known as e-gas. SNG has similar properties as natural gas and can be used, stored and transported. The whole process works as an efficient energy storage system. If the electrolysis is powered by fluctuating wind or solar energy, and the methanation uses carbon capture, the resulting gas is a carbon-neutral energy source.

SNG can be generated via the established conversion process, ‘Biogas-to-SNG’. The other approach, ‘BioSyngas-to-SNG’ is at the demonstration stage. SNG production from wind power, ‘Wind-to-SNG’ is a new concept [183].

Electricity from renewable energy sources (e.g. wind power, solar power) is used for electrolytic generation of hydrogen, as already explained. This is converted to methane with CO_2 (e.g. coming from biogas) or with CO/CO_2 compounds (e.g. available in the product gas of the thermo-chemical conversion of biomass) in a synthesis reactor in the wind-to-SNG concept. Currently, available natural gas infrastructure can be used to efficiently store the renewable produced methane and made available for use when required.

(a) Biogas-to SNG

In anaerobic digestion of biomass, raw biogas containing mainly CH_4 (50 -70 vol %) and CO_2 (30–50 vol %) are produced. The gas also contains steam, nitrogen, oxygen and small amounts of H_2S and NH_3, depending on the type of pre-desulphurisation. The raw biogas is treated to biomethane by removing water, the minor constituents and the CO_2, until it reaches the quality required for feeding (substitute gas quality) for the maximum concentration of the gas components and combustion properties. CO_2 is removed via pressure swing adsorption or using various scrubber systems. The treated gas is used to generate heat for the fermenter in a burner or in a gas motor for combined electricity/heat generation.

Biogas can be generated from many kinds of biomass, such as the organic content of municipal solid waste and industrial waste, sludge from wastewater treatment, farm waste, energy crops and manure.

Biogas thus produced is contaminated and needs to be purified and improved to around 97% methane; then the gas can be injected into a natural gas grid or used in transport vehicles.

Biomethane can also be produced synthetically, for example, by gasification of biomass followed by methanation. It is then called SNG (Synthetic natural gas or Substitute natural gas).

(b) BioSyngas-to SNG

If solid biomass like energy crops, forest and agricultural residues (lignocellulosic biomass) is gasified (not combusted) at high-temperatures (>700 C), a combustible gas is produced which can be used for various purposes. Its composition depends on the gasification method, the process conditions and the materials used. Ideally, the gas is not diluted with inert nitrogen (gasification with air). The main constituents in the combustible gas include H_2, CO, CO_2, H_2O, and CH_4 depending on the gasification temperature. Also, present are impurities such as sulfur compounds, ammonia, tars and dust loads which must be removed from the gas [184 a, b].

ZSW has developed ‘Absorption Enhanced Reforming (AER) process’ to produce SNG through biomass gasification. This process has ideal properties for down stream methanation due to its high hydrogen-content of > 60 vol %. In this reaction, CO and CO_2 are converted to methane via the hydrogen present in the gas as per the reaction given below. The first 2 are ‘methanation reactions’, and the third one is CO-Shift reaction [183].

$$3H_2 + CO \rightarrow CH_4 + H_2O\ (g) \qquad \Delta H_R = -206\ kj/mol$$

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O\ (g) \qquad \Delta H_R = -165\ kj/mol$$

$$H_2O\ (g) + CO \rightarrow H_2 + CO_2 \qquad \Delta H_g = -\ 41\ kj/mol$$

This requires a defined $H_2/CO/CO_2$ ratio, as long as no gas conditioning/gas separation is required. Due to its configurable stoichiometry [185], its components and CH_4 are there now. Hence, the product gas is appropriate for producing SNG since further processing is not necessary after quantitative conversion and separation of reaction water. The synthesis gases from gasification require adjustment of hydrogen-content; if otherwise used, removal of downstream CO_2 is necessary.

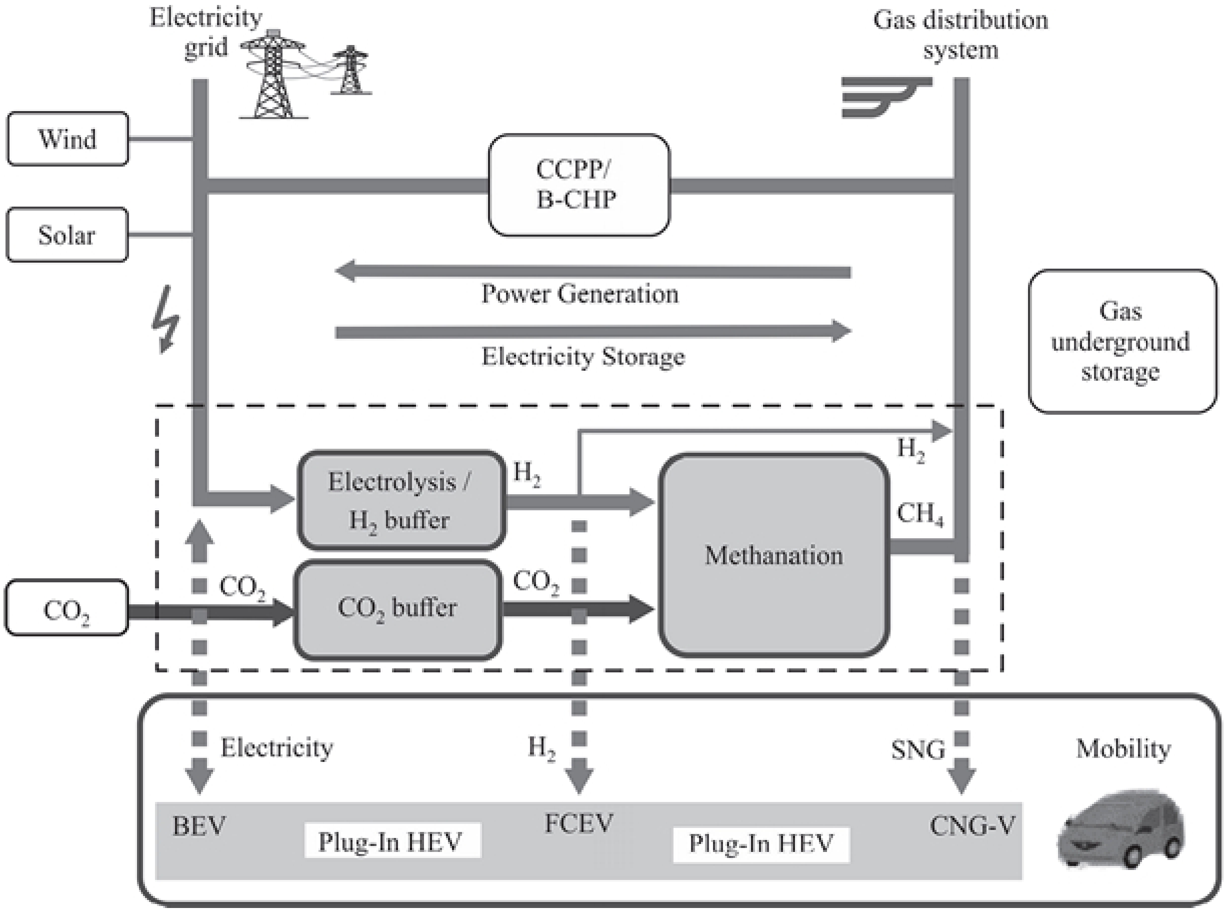
(c) Wind-to-SNG

The basic principle of the wind-to-SNG idea is bidirectional linking of the existing electricity grid and the gas grid, to establish a new method for managing loads and generation. This enables us to accommodate large quantities of fluctuating power from renewable energy sources into the energy system. This linkage currently exists as far as the generation of electricity from natural gas (gas-to-power), but not the reverse (power-togas). This idea (power-to-gas) arises from storing electricity that cannot be pumped into the grid to avoid grid instability, or economically available electricity (for instance, power generated when a large amount of wind power exist) in the form of substitute natural gas (Figure 6.16).

In this method, the electrolysis is used to convert the excess electricity from fluctuating renewable sources into hydrogen (and oxygen), and then by synthesizing with CO_2 (and/or CO) into substitute natural gas (SNG). The energy efficiency for this process is > 60 % (kWh_{SNG}/kWh_{el}).

A wind-to-SNG system can thus temporarily store the produced SNG in the natural gas grid. When the wind power becomes less or when the electric power demand is higher, the electrolysis level can be lessened by orderly reduction or deactivation of the electrolysis. Adequate generation of electricity even during periods of absence of wind or low-level wind can be made sure by combining a wind-to-SNG system with a gas or combined heat-power plant to avoid conversion to electricity at the site of the wind-to-SNG system.

This system can be easily integrated into the existing energy system. The natural gas grid with its high-storage and transport capacity is relatively helpful to use. A high voltage DC transmission is limited to outputs < 7 GW, but gas pipelines can stretch up to a capacity of 70 GW. The seasonal high wind power production can be stored or transported extended distances using high-energy transmission levels. As the renewable energy volumes increase in the electricity grid, more of the high-efficiency (up to 60%) gas power stations (that convert into electricity) are needed to be able to react quickly to load fluctuations. Unlike nuclear power plants and coal-fired power plants, gas power stations can be regulated fast and with no problems. In addition to converting SNG into electric power, it can be used as fuel or for heating. Using SNG as fuel is of particular interest in the context of the intended increase in renewable fuels in transport area to reduce carbon emissions.



[CCPP: Combined Cycle Power Plant; B-CHP: Block-Type Combined Heat and ower Station; BEV: Battery Electric Vehicle; FCEV: Fuel Cell Electric Vehicle; NG-V: Compressed Natural Gas Vehicle; Plug-In HEV: Plug-In Hybrid Electric hicle; especially, Plug-In Electric Drive Motor Vehicles/Range-Extended Electric Vehicle]

Figure 6.16: Wind-to SNG concept for bidirectional coupling of the electricity and gas grids with a link to the mobility consumption sector. Source: [183].

Fig. 6.16 shows how energy carriers H_2 and SNG are produced and used to run BEV, FCEV, CNG-V, and plug-in hybrid vehicles (plug-in HEV). Hydrogen from electrolysis of wind-to-SNG systems can be distributed via H_2 grids and be made available for mobility. Hydrogen can also be provided via decentralized generation at petrol stations by reforming SNG using the existing infrastructure, without requiring a large-scale distribution infrastructure for hydrogen [183].

All forms of SNG share one advantage, they can easily be phased into global gas supplies depending on availability and can slowly replace the natural gas.SNG is a potential fuel for the future and plays a crucial role in the energy transition. It would enable several energy-intense industries more efficient and sustainable, and at the same time, help to reduce their carbon footprint.

Another desirable feature is that this fuel is flexible and can be easily stored and transported. So it can double as energy storage, safeguarding the security of supply in the future world that would be powered by renewable energy sources [186]. Further, this method offers 2 more advantages over the other tested-forms of energy storage: the methanation process can employ carbon capture and the resulting gas can be fed directly into the natural gas grid, where energy is transported with less energy loss than through the power grid.

Studies at ZSW have established the suitability of the wind-to-SNG concept for energy storage and grid control. Compared to Fischer-Tropsch or methanol synthesis, SNG can be produced in decentralized applications with much less complexity, distributed via the natural gas grid, stored and used when needed.

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CHAPTER 7

Thermal Energy Storage

7.1 Introduction

Thermal energy storage (TES) technologies facilitate to reserve energy produced in the form of heat or cold in a storage medium for use at a different time for heating or cooling or power generation. Depending on the scale of the storage, heat can be stored for hours, days, months or seasons.TES systems are used particularly in industrial processes and in large buildings.

There are three well-known methods for TES at temperatures from -40 °C to > 400 °C:

(a) Sensible heat, (b) Latent heat associated with ‘phase change materials (PCMs)’, and (c) thermo-chemical heat storage associated with chemical reactions. They are grouped by their technical use [1, 2]. As the temperature of a material increases, its energy content also increases. The energy released by the material as its temperature is reduced or absorbed as its temperature is increased is called sensible heat which can be ‘sensed.’ Hot water tanks are one example of sensible heat storage systems, and are found in almost every home, and require adequate thermal ‘insulation.’

Materials are also chracterised by ‘heat of fusion’ which is the heat required to convert from solid to liquid state, and heat of vaporization, the heat required to change from liquid state to gaseous state. These are heat requirements for phase changes to occur. With these phase changes, latent heat is associated which cannot be sensed. Several materials are identified in which the state of the medium changes. These are called ‘phase change materials (PCM)’. In buildings, latent heat storage systems can store and release heat with small temperature fluctuations; they have low self-discharge. Thermo reversible chemical reactions are utilized for thermochemical heat storage. Heat is required to dissociate a chemical product and so chemical heat accompanies the reversible chemical reactions. This heat would be fully recovered when synthesis reaction takes place.

In essence, thermal energy storage consist of three main stages: charging, storing, and discharging. The storage medium depends on the nature of TES and the proposed application. For example, in *sensible heat* storage, water is the medium due to its high specific heat at ambient temperatures. Water, being a liquid, is easier to transport thermally and allows for better heat transfer rates. Several PCMs and other materials have been identified and investigated. Aquifer TES based on sensible heat have been examined in depth in addition to the feasibility of solar ponds and water thermal energy storage.

Using a set of technical, environmental and economic criteria, TES is evaluated. The technical criteria include storage capacity, size, cost, lifetime, efficiency, resource use, commercial viability, and safety. Environmental criteria include the system design, emissions, material, and operational practices in addition to a number of practices in the entire life span of the storage system. Economic norms take into account hourly thermal loads for the peak day, appraisal of the electrical load profiles of a conventional system against the TES system, and the magnitude of the storage system (3, 4).

Consider the case of solar thermal power plants, the energy is produced during the day when the sun shines. The excess energy generated during peaktime of sunshine is generally stored in the TES facilities, usually molten salt or other materials. This stored heat energy is used when there is no sun, or to generate steam to drive a turbine to produce electricity. TES is becoming particularly important for electricity storage in combination with concentrating solar power (CSP) plants (see Fig. 6.8 in the previous chapter) where solar heat absorbed can be stored for electricity production when sunlight is not available. Thus, the thermal energy storage is an effective means at capturing and storing energy for a short-term to be used at a later time.

Additionally, TES systems make available better environmental working by increasing overall efficiency, reducing GHG emissions and costs. Efficient TES systems utilise a range of materials - liquids and solids - having different thermo-physical properties to realize enhanced storage efficiencies.

As mentioned, TES systems are closely linked to solar energy systems. Solar radiation being intermittent and uneven makes a perfect integration with TES systems, which enable the solar thermal technology to become highly consistent and effective for numerous applications.

The main types of thermal energy storage of solar energy are shown in Fig. 7.1.

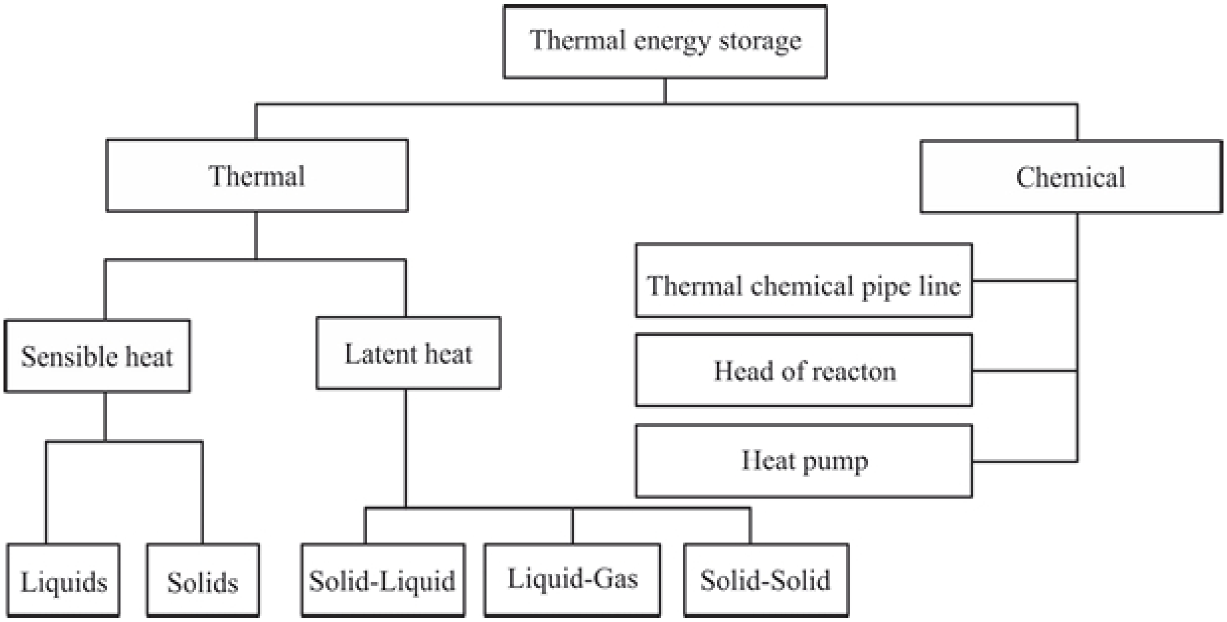


Figure 7.1: Main types of thermal energy storage for solar energy[1].

An energy storage system can be described in terms of the following definitions [1]:

(a) Capacity: the energy stored; determined by the storage process, the medium, and the extent of the system;

(b) Power: the rapidity of discharging or charging of the energy stored in the system;

(c) Efficiency: ratio of the energy offered to the customer to the energy required to charge the storage system. Also explains the energy loss during the storage time and the charging/ discharging cycle;

(d) Storage period: time of the energy storage - hours, days, weeks, or months for seasonal storage;

(e) Charge and discharge time: time needed to charge/discharge the system;

(f) Cost: generally refers to capacity (per kWh) or power (per kW) of the storage system and subject to the capital and operational costs of the storage system and its lifespan (the number of cycles).

High-energy storage density, high power capacity for charging and discharging, good heat transfer between heat transfer fluid (HTF) and storage medium, chemical stability of storage material, compatibility between HTF, heat exchanger and/or storage medium; low thermal losses, and easy control are desirable properties of any storage system.

7.2 Sensible Heat Storage (SHS)

Sensible thermal storage consists of a storage material, a tank (to contain the storage medium) and inlet/outlet devices. Tanks must prevent thermal energy losses, and a thermal gradient across storage medium is desirable. There are different sensible heat storage solids and liquids. Solids are normally preferred in packed beds, but a fluid needed to exchange heat. If a liquid is used as the fluid, heat capacity of the solid in the bed is significant, and the system is referred to as dual storage system. Packed beds prefer thermal stratification and has advantages, for example, the use of inexpensive solids such as rock, sand or concrete for packed beds.

The SHS systems are classified based on several factors such as direct or indirect storage with and without filler material, the number of storage volumes, phase change in the heat transfer fluid (HTF), as well as direct and indirect contact of HTF with storage medium.

Direct storage systems are simple in design and utilize a single medium for both the HTF and the storage. An additional solid filler material which is inexpensive compared to the HTF may be used to ensure stratification within the storage volume. *Indirect storage systems* utilize different media for HTF and storage; that is, the HTF transfers heat to a secondary fluid that serves as storage medium. Indirect storage systems require sufficient heat transfer rates from the HTF to the storage medium. The direct and indirect systems are referred to as ‘active systems.’[5].

There is ‘passive heat storage’ also. Here, storage medium is fixed and heat transfer fluid passes through storage medium only during charging and discharging. Some examples are presented in the later pages.

Sensible heat storage basically is the simplest method, storing thermal energy by heating or cooling a liquid or solid storage medium (e.g., water, sand, molten salts, or rocks). The most prevalent heat storage medium commercially used is water and it has several applications in the residential and industrial sectors. Sensible heat stored underground using both liquid and solid media is another source available for typically large-scale applications. The main advantages of sensible heat storage systems are risk-free and low cost.

SHS system utilizes the heat capacity and the change in temperature of the storage medium during the process of charging and discharging. These storage materials do not undergo any change in phase over the temperature range of operation in the storage process. The amount of heat stored depends on the specific heat of the medium, the temperature change, and the amount of storage material [6].

$$Q_s = mc_p(t_f - t_i) = \rho\ v\ c_p\ (t_f - t_i).$$

Here, Q_S is the quantity of heat stored in Joules; m is the mass of heat storage medium in kg; c_p is the specific heat [J/(kg.K)]; t_i and t_f are the initial and the final temperatures in $\circ$C; v is the volume and ρ is the density of the storage medium expressed in kg/L.

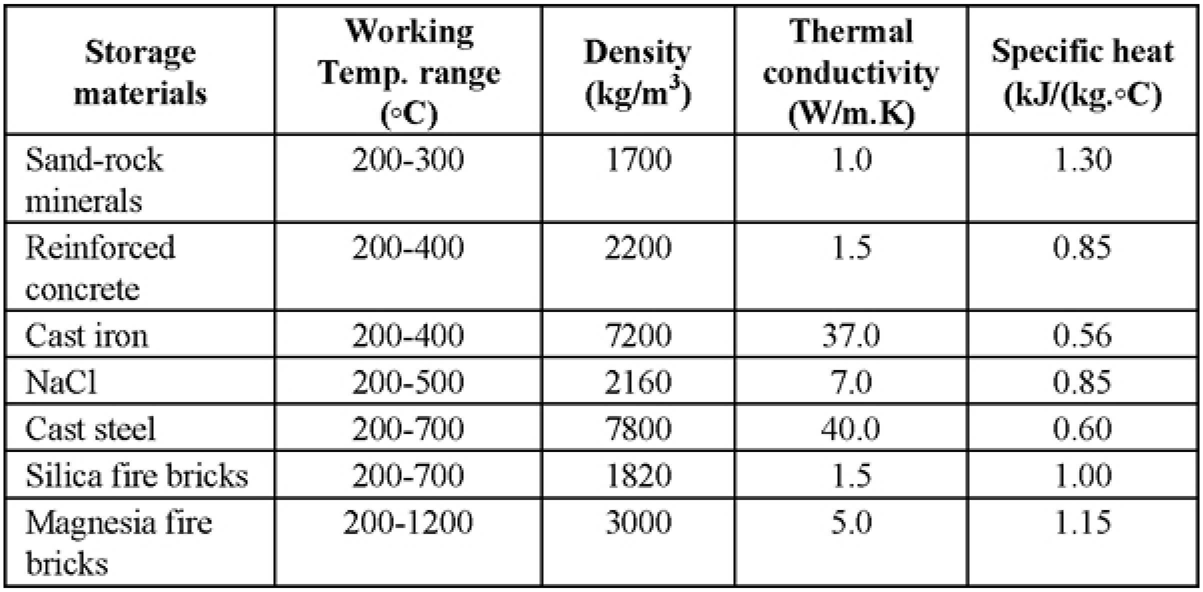
The material for use in a thermal energy storage system must be inexpensive and have good thermal capacity (m c_p).The rate at which the heat can be released and extracted which is a function of the thermal diffusivity is also important.

The mostly used materials for SHS are sand, rock, concrete, granite, aluminum, cast iron, water, engine oil, ethanol, propane, butane, octane, isotunaol, and isopentanol, so on. Water is the best at ordinary temperatures because it is low-priced and its specific heat is high. Above 100°C, generally, oils, molten salts, and liquid metals are utilised. For air heating, rock bed type storage materials are used.

The most commonly used solid thermal storage materials and their characteristics are shown in Table 7.1 [7, 8]. These inexpensive materials have working temperatures from 200 to 1200°C and have excellent thermal conductivities. Concrete and castable ceramics are extensively studied due to their low cost and good thermal conductivities. The only disadvantage is that their low heat capacities can make the storage unit unusually large.

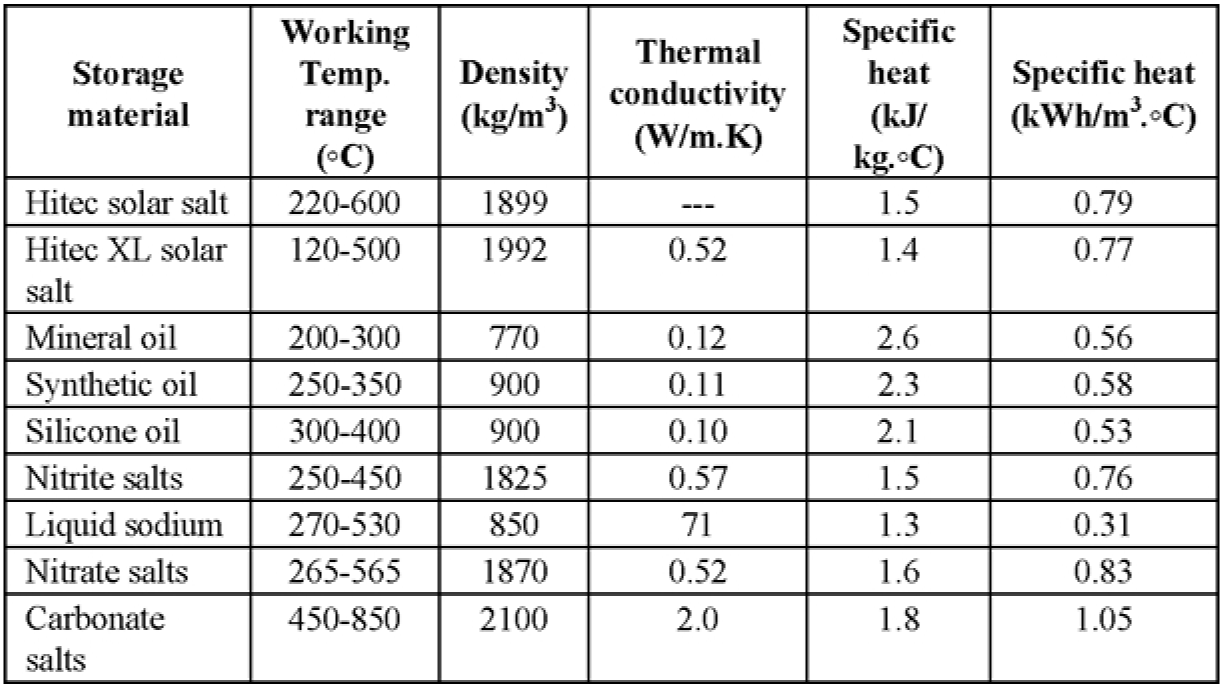
There are also *liquid-state* thermal energy storage materials that include oils, inorganic molten salts and liquid sodium, shown in Table 7.2 [4]. Liquids offer the advantage of a possible use as both storage medium and HTF. The storage approach using liquids can be realized as a single tank or a two tank structure. The high vapour pressure of the oils [9] is likey to cause serious safety problem to the airtight container. For high-temperature storage systems, molten *alkali metals*, such as sodium (T_m = 98 °C) and sodium-potassium, could be used. Experience with these metals exists since the times of nuclear reactor operations. Their major advantages are the high thermal stability and the high thermal conductivity. Liquid sodium has a thermal conductivity as high as 71.0 W/ (m.K); however, due to its highly unstable chemical reactivity, extra safety measures are required which pushes the cost high.

Table 7.1: Solid type Sensible heat materials. Source: [7, 8]



Storage materials	Working Temp. range (◦C)	Density (kg/m^3)	Thermal conductivity (W/m.K)	Specific heat (kJ/(kg.◦C)
Sand-rock minerals	200-300	1700	1.0	1.30
Reinforced concrete	200-400	2200	1.5	0.85
Cast iron	200-400	7200	37.0	0.56
NaCl	200-500	2160	7.0	0.85
Cast steel	200-700	7800	40.0	0.60
Silica fire bricks	200-700	1820	1.5	1.00
Magnesia fire bricks	200-1200	3000	5.0	1.15

Table 7.2: Liquid-state Sensible heat materials. Source: [4]



Storage material	Working Temp. range (◦C)	Density (kg/m^3)	Thermal conductivity (W/m.K)	Specific heat (kJ/ kg.◦C)	Specific heat (kWh/m^3.◦C)
Hitec solar salt	220-600	1899	---	1.5	0.79
Hitec XL solar salt	120-500	1992	0.52	1.4	0.77
Mineral oil	200-300	770	0.12	2.6	0.56
Synthetic oil	250-350	900	0.11	2.3	0.58
Silicone oil	300-400	900	0.10	2.1	0.53
Nitrite salts	250-450	1825	0.57	1.5	0.76
Liquid sodium	270-530	850	71	1.3	0.31
Nitrate salts	265-565	1870	0.52	1.6	0.83
Carbonate salts	450-850	2100	2.0	1.8	1.05

For temperatures above 100°C, *molten salts* are observed as the ideal liquid-state materials for use in solar power plant [4, 7, 9, 10] because of their excellent thermal stability under high temperatures, low vapour pressure, low viscosity, high thermal conductivities, non-flammability and nontoxicity.

They are liquid at atmospheric pressure, provide an efficient, low cost medium to store thermal energy, and their operating temperatures are compatible with the current high pressure and high-temperature steam turbines. In addition, molten salts are used in the chemical and metals industries as heat-transport fluid, so experience with non-solar applications also exist [11, 12].The low vapor pressure helps in storage designs without having pressurized vessels. In the application of salts, the lower temperature limit set by the melting temperature need to be considered.

The main trouble with molten salts is their freezing during operation; this has to be avoided in the piping, the heat exchanger and in the storage tanks using auxiliary heating systems. Other issues with molten salt storage are the high costs of the storage material media, the threat of corrosion and problems in managing hygroscopic salts. The upper temperature limit (maximum temperature) is decided by the thermal stability of the salts. Salt mixtures, compared to single salts, have the benefit of lower melting temperatures. The salt mixtures possess similar thermal stability limits as the single salts constituting the mixtures. Therefore, salt mixtures such as eutectics, can have an extensive temperature range compared to individual salts [5]. Zhao and Wu [9] published a group of innovative ternary salt mixtures with ultra-low melting temperatures of 76°C, 78°C and 80°C enabling easier melting of the system. These salt mixtures comprising KNO_3, $LiNO_3$ and Ca $(NO_3)_2$ exhibited much lower viscosities (more than 80%) compared to synthetic oils and commercial molten salts. Besides, these salt mixtures demonstrated good chemical stability under high temperatures, around 500°C'. Recently Wang et al [13] also reported such eutectic salts with melting temperatures below 10(X' that include a novel quaternary eutectic salt with its melting temperature as low as 99°C [14].

Solar thermal power plants prefer to use the fluids such as alkali nitrate salt mixtures and to some extent alkali nitrite salts for storage, and the typical mixture used is a non-eutectic salt mixture of 60 wt% sodium nitrate and 40 wt% potassium nitrate. This mixture is usually called *solar salt*. This mixture has a melting temperature of 222 °C and the thermal stability limit is approximately 550 °C [5].

ENEA, an Italian research laboratory established the technical viability of using molten salts in a parabolic trough solar field with salt mixtures that freeze at 220°C [4].

7.2.1 Normal Temperature Storage Systems (<100°C)

The working principles of three storage systems for temperatures, <100°C), namely, Water-tank thermal energy Storage, Packed-bed and Underground thermal energy storage are briefly described here.

(a) Water tank thermal energy storage

Water is the most common material used in a sensible heat storage system. Hot-water tank is a well-known technology for thermal energy storage [15] and is cost-effective. Hot-water tanks save energy in water heating systems via solar energy and co-generation (i.e., heat and power) energy supply systems. The efficiency of the water tank storage can be enhanced by ensuring optimal water stratification in the tank and an effective thermal insulation. Schematic of a typical water tank system is shown in Figure 7.2.

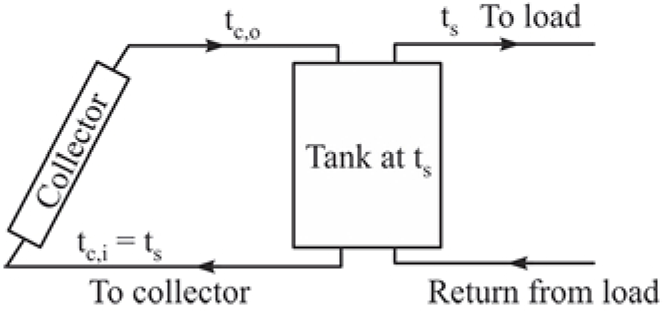


Figure 7.2: Schematic of a typical Water tank heat storage, redrawn [16].

The energy storage capacity of the storage system at uniform temperature (i.e., fully mixed and not stratified) operating over a finite temperature difference is given by

$$Q_s = m\ c_p\ \Delta t_{s,}$$

Here Q_S is the total heat capacity for a cycle operating through the temperature range Δt_S, and ‘m’ and ‘c_p’ are the mass and the specific heat respectively of water.

The temperature range of operation of such a system is restricted to the lowest for most applications by the process necessities. The upper limit may be influenced by the process, vapor pressure of the liquid, or the heat loss by the collector.

An energy balance on the no stratified tank is [1],

$$m.c_{p}.\ (dt_s/d\tau)= Q_u - Q_L - U_sA_s\ (t_f - t_a)$$

Here, Q_u and Q_L are rates of adding or deletion of energy from the collector and to the load;

U_s is the heat loss coefficient of storage tank;

A_s is the storage tank surface area; and

t_f is the final temperature, t_a is the ambient temperature for the tank in ∘C, and τ is the time.

By integrating the above equation over time one can determine the long-term performance of the storage system and the solar process. Using simple Euler integration (i.e., rewriting the temperature derivative as $(t_S - t_i)/\Delta\tau$ and solving for the tank temperature at the end of a time increment),

$$t_s = t_i + (\Delta\tau / m\, c_p)\, [Q_u - Q_L - U_s\, A_s\, (t_i - t_a)].$$

This expression can be used to predict water storage temperature as a function of time from which other temperature-dependent quantities can be estimated [1].

A more complex system with tank storage, a solar combisystem was discussed by Heier et al. and other researchers [17a, 17b]. The combistore is charged with solar collectors and a second heating source, like a biofuel or gas boiler, and heat is extracted to two different types of heat sinks: domestic hot water and space heating.

Water has become a good storage media suitable for low temperature solar cooling applications because of its high specific heat, wide availability, chemical stability, and low cost (e.g., single stage absorption chillers and desiccant systems). However, for use at high temperature applications, requires increase of system pressure due to its low boiling point.

(b) Packed-bed thermal energy storing

The heat capacity of a bed comprising loosely packed particulate material is utilised by packed-bed system to store energy. A fluid, generally air, is dispersed through the bed to add or to take out energy. A range of solids are used, but rock and pebble are the commonly used materials. The flow is maintained through the bed in one direction during addition of heat (usually downward) and in the opposite direction during removal of heat. Unlike in water storage systems, the heat cannot be added and removed simultaneously in packed-bed storage. A foremost benefit of a packed-bed storage system is its high grade of stratification. The pebbles near the entry get heated, but then at the exit, temperature of the pebbles is unchanged; the temperature of the exiting air remains very close to the initial bed temperature. With time, a temperature front passes through the bed and the temperature becomes uniform in a fully charged bed. A packed bed in a solar heating system does not normally operate with constant inlet temperature. The fluctuating solar radiation, the ambient temperature, the collector inlet temperature, load requirements, and other time-dependent factors decide the collector outlet temperature that is variable.

Several theoretical and experimental studies on the heating and cooling of packed-bed thermal storage were published from as early as 1929 [e.g. 18–20].

(c) Underground thermal energy storage

This is another widely used method where heat transfer fluids are pumped through array of pipes laid in the ground. These pipes may be inserted as vertical U-tubes in evenly spaced wells (boreholes) in the storage area or as horizontal pipes hidden in dugouts. The charging and discharging rates are influenced by the area covering the entire piping and the rates of heat transfer through the earth close to the pipes. If the storage medium is porous, energy transfer take place by evaporation and condensation and by the water flow through the medium in which both heat and mass transfer are involved. These storage systems are generally non-insulated, though the ground surface is insulated. Boreholes (or ground heat exchangers) are regularly employed in combination with heat pumps to extract the low-temperature heat from the soil [1].

Aquifer storage is closely linked to ground storage, as water is the principal storage medium flowing at low rates in the ground. This needs a permeable layer of soil (like pebbles or sand) bounded by two parallel layers of impermeable clay material. Under these promising conditions, two springs separated by some distance can be drilled; and hot water can be injected in summer and removed in winter. The minerals dissolved in the water and precipitating on tubes and heat exchangers can create problems. The built-aquifers are in sizes of 10000 m^3 and the ground pits are filled with pebbles and water and sealed by plastic sheets [21]). Most applications of aquifier storage utilize the storage of winter cold for the cooling of large office buildings and industrial processes in the summer.

Paksoy et al. have reviewed the state-of-the-art of aquifer storage for heating and cooling of buildings [22], and conclude that borehole storage is more applicable than aquifier storage because the ground conditions required are critical, though the latter has in comparison more advantages.

7.2.2 High Temperature Storage Systems

Solar power plants of *direct storage* concept and *indirect storage* concept are described [4, 5].

1. The two tanks *direct system* consists of a hot tank to store HTF to use it at the time of need, and a cold tank into which the cooled HTF is pumped where it remains to be heated again. Fig. 7.3 shows the schematic of the plant Solar Tres located near Seville in Spain. The plant utilises molten salts of $NaNO_3$ and KNO_3 as HTF. The two tanks solar systems have advantages

such as (a) individually storing of cold and heat storage materials; (b) prospect of raising the solar field output temperature to 450/500°C (in trough plants), which enables increase in the Rankine cycle efficiency of the steam turbine to the 40% range; this is higher than that achieved in conventional plants[23]; (c) low risk; and (d) the HTF temperature rise in the collector field can be increased reducing the physical size of the thermal storage system [23, 24]. The disadvantages are (a) the high cost of HTF, storage materials and heat exchangers; (b) using two tanks instead of one, raising the cost; (c) somewhat small temperature variance between the hot and the cold fluid in the storage unit; (d) danger of freezing of storage fluid because of its relatively high freezing point, which is likely to increase the operation costs; (e) rise in losses in the solar field because of the high temperatures of both tanks; and (f) the lowest cost of the system design though the operation does not necessarily result in the lowest cost of electricity (usually at night) [25].

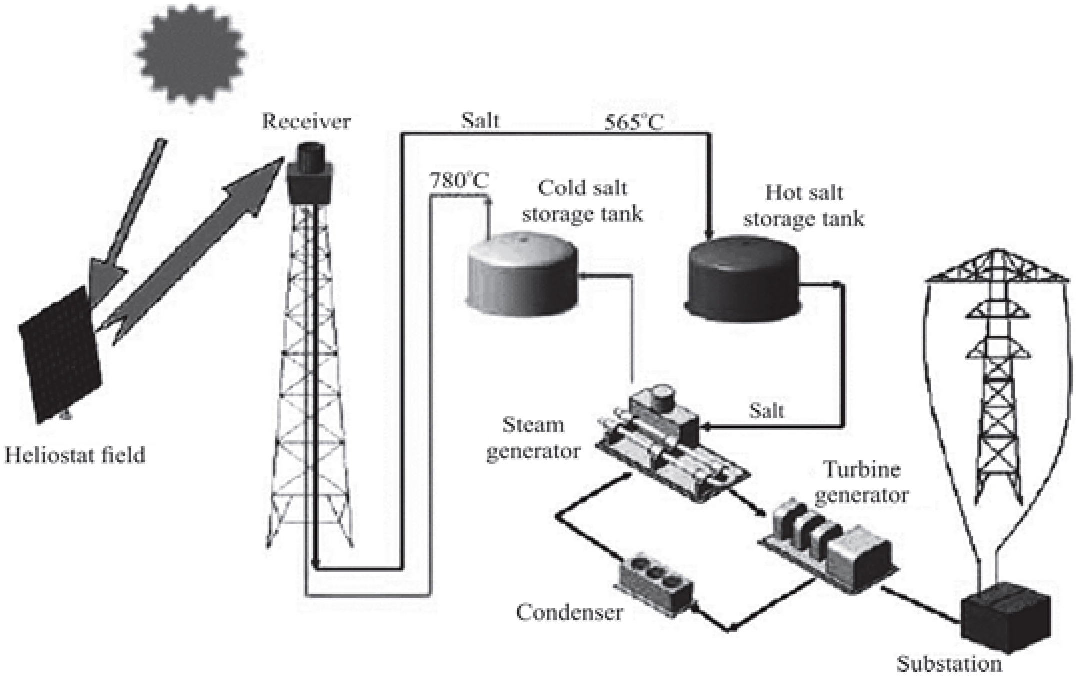


Figure 7.3: Schematic of Plant Solar Tres, with direct two-tanks [26].

2. *Indirect storage systems*: There are two types - the two tanks indirect system and the single tank indirect system (also called thermocline system). In the recently developed two tanks indirect system, the HTF circulating in the solar field is different from the thermal energy storage medium.

   The two tanks indirect system comprises two tanks for storing the energy, not directly with HTF, but using a second heat fluid (generally oil), which is heated by HTF and drove through the heat exchanger. The heat given out by HTF is taken up by a storage medium, usually molten salts in the oil-to-salt heat exchanger (Fig.7.4a). In the course of thermal storage charge cycle, a fraction of the oil from the collector field is sent to the oil-to-salt heat exchanger; the oil then cools from the small entry temperature of 391°C to an exit temperature of around 298°C. The cold storage tank delivers nitrate salt in a counter current prearrangement via the heat exchanger. The salt gets heated from an entry temperature of 291 ∘C to an exit temperature of 384°C, and then stored in the hot storage tank. Through the discharge cycle, the flow paths of oil and salt are overturned in the oil-to-salt heat exchanger. The heat is then transmitted from the salt to the oil to make available the thermal energy for the steam generator.

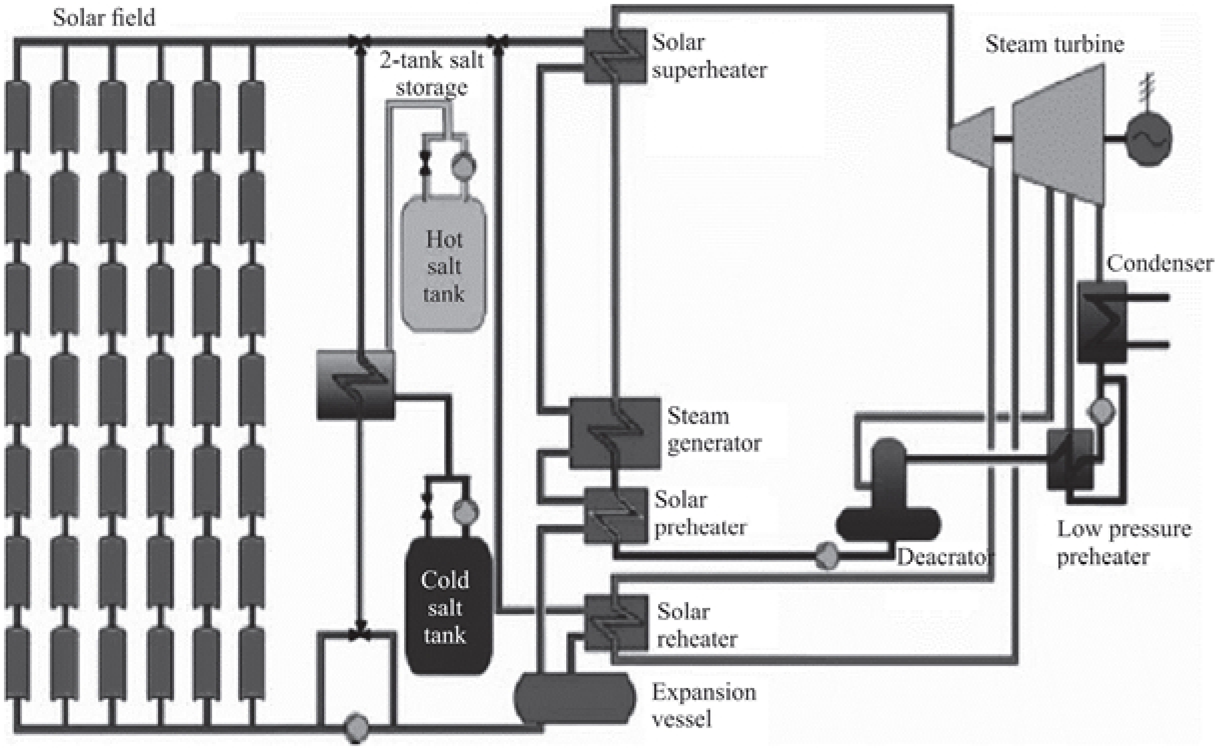


Figure 7.4a: Schematic of a parabolic trough power plant, with two tanks indirect thermal storage system [8].

The benefits and drawbacks of the two tanks indirect systems are analogous to the direct systems: cold and hot HTF is independently stored; and the storage material flows are confined to hot and cold tanks and not through the parabolic troughs.

Another *indirect storage* system is the single tank system, storing both hot and cold fluids in the same tank. It is possible for this system to reduce the cost of a direct two-tank storage system. The hot and cold fluids in this setup are divided due to the stratification, and the region separating the hot and cold fluids is called the thermocline. The thermocline storage system, the hot fluid would be on top and the cold fluid at the bottom. The HTF delivered from the solar field travels through a heat exchanger, raising the temperature of the storage fluid media which is stored in a single tank. Commonly a filler material is used to help the thermocline effect. The studies reveal that these filler material functions as the principal thermal storage medium, but choice of other storage and filler material can change this [4].

The U.S. Sandia National Laboratories recognized quartzite rock and silica sands as prospective filler materials [2, 7] and both materials could withstand the molten-salt environment relatively well with no significant deterioration.

The advantage is that the single tank thermocline system is a low-cost system because of the use of only one tank and low-cost filler materials such as quartzite rock and sand. The thermocline system is about 35% cheaper than the two-tank storage systems as per Brosseau et al. [27]. The drawbacks are many: (a) relatively high freezing points of most molten salts (it is necessary to maintain a minimum system temperature to avoid freezing and salt dissociation); (b) difficulty in separating the hot and cold HTF; (c) increased losses in the solar field due to high outlet temperatures; (d) for maintaining the thermal stratification, controlled charging and discharging is required; similarly, appropriate methods or devices to avoid mixing; (e) design of storage system is complex; (f) thermodynamically, an inefficient power plant [28].

7.3 Latent Heat Storage (LHS)

Phase change materials (PCMs) in which the state-of the medium changes with varying temperature store or give out a large amount of heat when rearranging their phase configurations during melting/solidification or gasification/ liquefaction methods. Also, the phase-transition enthalpy of PCMs are commonly much higher (100–200 times) than sensible heat; hence, latent heat storage possesses much higher storage density than the SHS [14]. In LHS, as the energy-storage density increases, the volume is reduced (Figure 7.4b). The heat is mainly stored in the phase-change process at a constant temperature and is directly related to the latent heat of the substance. Effective storing of thermal energy can be achieved using PCMs with the extra advantages of having high-energy-storage density and isothermal nature of the storage process. The chief advantage of using latent heat storage over SHS is their ability to store heat at nearly comparable temperature range. To begin with, these materials function like SHS materials; that is, the temperature rises linearly with the system enthalpy; later, heat is absorbed or given out at the same temperature with a change in phase [1]. The main disadvantage of LHS is its

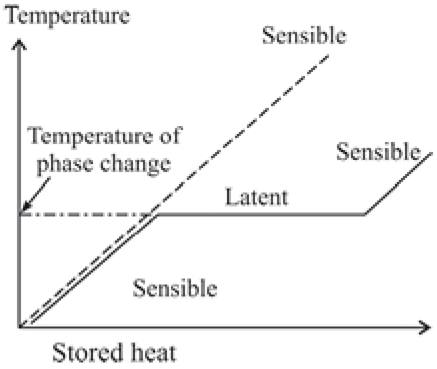


Figure 7.4b Latent heat thermal storage [30].

low thermal conductivities requiring heat transfer enhancement technologies [29].

Therefore, LHS is centered on the absorption or release of heat during the phase-change of the storage material, solid to-liquid or liquid-to-gas or the other way around.

The storage ability Q_S (in Joules) of the LHS system having a PCM medium is expressed as [1],

$$Q_s = m\ \{c_{ps}\ (t_m - t_i) + f.\Delta q + c_{pl}\ (t_f - t_m)\}$$

Here, t_m is melting-temperature in ∘C; m is the mass of PCM medium, in kg; c_{ps}, the average specific heat of the solid phase between t_i and t_m, in kJ/(kg.K); c_{pl}, average specific heat of the liquid phase between t_m and t_f, in J/(kg.K); f, melt fraction; Δq, latent heat of fusion, in J/kg.

For example, Glauber's salt ($Na_2SO_4.10H_2O$) has c_{ps}~1950 J/(kg.°C), c_{pl}~3550 J/(kg.°C), and Δq = 2.43 x 10^5 J/kg at 34^{o}C.

PCM materials: These materials are normally grouped into three classes, organic, inorganic and eutectic mixtures:

(a) *Organic materials*: these are paraffin- or non-paraffin-compounds. They used for heating and cooling in buildings because their melting points are low, around 20–32°C and are chemically stable, noncorrosive and nontoxic with heat capacity. However, they are flammable. Non-paraffin organic PCMs are the most plentiful of the PCM group having highly diverse properties. Several esters, fatty acids, alcohols, and glycols appropriate for energy-storage are recognized [31]. These organic materials possess high heat of fusion, inflammability, low thermal conductivity, low flash points, and instability at high temperatures.

(b) *Inorganic materials*: These are metallic alloys and salt compositions (hydrates), with the latter mostly used in solar thermal applications. They are rather inexpensive and offer high heat capacity and better thermal conductivity, though they are corrosive and cool quickly. Handling is a problem because at lower temperatures, they freeze and at high temperatures, they are difficult to handle. Metallic alloys include low melting point metals and their alloys which are barely used in heat storage applications because of their low melting enthalpy per unit weight. Salt hydrates have been extensively studied due to their high latent heat of fusion per unit volume, a relatively high thermal conductivity (almost double that of paraffin), low corrosiveness, and compatibility with plastics. The disadvantages are dissimilar melting and super-cooling, which can be tackled by adding thickening agents or mechanical stirring or encapsulating the PCM to reduce separation. The spontaneity of salt hydrates and lower number of water moles during the discharge process are other issues under study.

(c) *Eutectic mixtures of three types*: organic-organic, organic-inorganic, and inorganic-inorganic, which are used in building applications. Two or more low melting materials with comparable melting and freezing points and nearly melt and freeze without segregation are combined to obtain these mixtures. Additionally, these materials have high thermal conductivities and densities. The weight percentage of each component materials can be changed to achieve deviations in the melting point of the eutectic mixture obtained. This facility makes them promising even if they are less diffused than the other groups. However, they have low latent and specific heat capacities.

For solar power generation, mostly inorganic materials are used due to their melting points in the range 115–897°C and latent heat ranges from 124 to 560 kJ/kg. The selection of PCM largely depends on the correct melting enthalpy and temperature, availability and cost. While paraffin is attractive from the viewpoint of latent heat of fusion to meet high melting point requirements, fatty acids and metallic are preferable. Common types of materials under use as PCMs are given in Table 7.3 along with the typical range of melting enthalpy and melting temperatures.

Table 7.3: Typical materials used in latent heat thermal storage (LHS).

Material	**Melting temperature ($^\circ$C)**	**Melting enthalpy (Mj/m^3)**
Water-salt solutions	-100 to 0	200–300
Water	0	330
Clathrates	-50 to 0	200–300
Paraffins	-20 to 100	150–250
Salt hydrates	-20 to 80	200–600
Sugar alcohols	20 to 450	200–450
Nitrates	120–300	200–700

Hydroxides	150–400	500–700
Chlorides	350–750	550–800
Carbonates	400–800	600–1000
Fluorides	700–900	> 1000

Source: L.F. Cabeza et al [32].

Only a few of several materials studied have been commercialized as PCMs because there are several issues such as phase separation, subcooling, corrosion, long-term stability and low-heat conductivity require further investigations.

As already shown in Fig.7.1, the phase-change happens in three ways: solid-solid, liquid-gas, and solid-liquid. In the first case, heat is stored by changing between contrasting kinds of crystallization types. For liquid-gas systems, latent heat is high, but problems arise in controlling storage because of the high variations in volume during the phase-change. The most dominant are the solid-liquid PCMs because these have a restricted volume variation during latent heat exchange, generally below 10%, and a high melting latent heat. The melting courses comprise energy densities of 100 kWh/m^3 (for e.g., ice) compared to a usual 25 kWh/m^3 for SHS. PCMs can be used from daily energy-storage to seasonal energy-storage employing a range of methods and materials.

Measurement techniques: Currently, the latent heat of fusion and melting-temperature of PCMs is measured by two methods: (i) differential thermal analysis (DTA) and (ii) differential scanning calorimeter (DSC) [4]. In both the techniques, the sample and reference materials are heated at a constant rate. The temperature difference resulted between them is related to the difference in heat flow among the two materials; this is presented by the DSC curve. The material, alumina (Al_2O_3) is used for reference. The latent heat of fusion is estimated using the area under the peak of the curve, and the melting-temperature is assessed by the tangent at the point of greatest slope on the face portion of the peak.

7.4 Chemical Heat Storage

The technology using the heat of chemical reactions has the prospect of achieving higher energy efficient processes than other TES technologies [4]. The main advantage of using chemical reactions as storage systems is the potentially high-energy density.

The energy is stored in chemical compounds A and B that are produced by an endothermic reaction; the energy is recovered later by an exothermal reaction between the compounds. At high enough temperatures, the compounds A and B are structurally separated.

$$AB \leftrightarrow A + B \quad (\text{enthalpy of reaction} = \Delta H_r)$$

The heat-stored and released is the same as the enthalpy of reaction, ΔH_r. The enthalpy of reaction is normally far higher than the enthalpy of transition in LHS or the SHS over a practical temperature range. Therefore, the storage density based on solid mass or volume is considerably larger for thermo-chemical storage materials than that of latent heat or sensible heat storage materials [33, 34]. Many of the thermochemical energy-storage concepts are in the nascent stage of progress, unlike sensible and latent heat systems, except ‘low-temperature sorption systems’ [5].

The sorption process can be regarded as a chemical reaction system dependent on weaker chemical bonds, in contrast to covalent bonds come in other systems. In a sorption heat storage system, the sorbent gets heated in the charging process, desorbing the vapor from the sorbent. During discharging, vapor at a lower temperature is adsorbed (using solid sorbent) or absorbed (thru a liquid sorbent) and heat is given out at an elevated temperature.

Two most relevant chemical processes for thermal storage reactions are (i) metal oxide/metal (SnO_X/Sn) and (ii)ammonia [4].

(i) According to Foster [202c], the reaction (SnOx/Sn) is technically feasible as seen in the reactions below:

$$SnO_2 + 2CH_4 + \text{heat} \rightarrow Sn + 2CO + 4H_2 \qquad (1)$$

$$Sn + 2H_2O \rightarrow SnO_2 + 2H_2 + \text{heat} \qquad (2)$$

The first reaction occurs at 980°K and SnO_2 is reduced with methane, CH_4. At these temperatures, SnO_2 is solid (dust) and floats on the top of liquid Sn in a solar reactor. This significantly simplifies the concept and fabrication of the solar reactor.

Adding of CH_4 produces the SnOx dissociation, and the liquid Sn is stored in a tank. In cloudy times or nights, Sn is passed through the heat exchanger. Water vapor is added to the tank containing cold Sn, allowing the second reaction shown above to occur. Thus, SnO_2 can be recovered to start over the process.

The kinetic behavior of the reactions is the essential point of this device [31]. Even though the solar energy can enable the reaction feasible, technically the process is not fully developed.

(ii) Ammonia is a pungent smelling gas, used in several applications, mainly in the production of fertilizers and cleaning agents. The ammonia production is one of the world’s largest chemical industries, annually producing higher than 125 million tons. In the modern ammonia plant, the exothermic reaction heat from ammonia synthesis converters is usually altered to superheated steam appropriate for electricity production in conventional Rankine cycle systems [36]. The liquid ammonia (NH_3), as it absorbs solar thermal energy, is dissociated in an energy-storage (endothermic) chemical reactor [3741]. If needed, the reaction products, hydrogen and nitrogen, react in an exothermic reactor to re-synthesis ammonia [42].

$$2NH_3 + \text{heat} \rightarrow N_2 + 3H_2\text{, and}$$
$$N_2 + 3H_2 \rightarrow 2NH_3 + \text{heat}$$

The thermal decomposition of a few metal oxides for energy-storage has been considered [43]. These reactions may have a benefit because the produced oxygen can be used in other applications or rejected. The atmospheric oxygen can be used in the reverse reactions. A few examples:

(a) *Decomposition of potassium oxide*

$$4KO_2 \rightarrow 2K_2O + 3O_2$$

This reaction occurs over temperatures between 300 and 800 ∘C by way of a heat of decomposition of 2.1 MJ/kg;

(b) *Decomposition of lead oxide,*

$2PbO_2 \rightarrow 2PbO + O_2$

This thermal decomposition occurs over temperatures of 300 to 350 $\circ$C with a heat of decomposition of 0.26 MJ/kg.

Several practical problems arise in using these reactions, which need to be investigated.

(c) *Thermal decomposition of calcium hydroxide* (otherwise called caustic lime or slack lime) for energy-storage has been extensively studied by Fujii et al. [44].

$Ca\ (OH)_2 \rightarrow CaO + H_2O.$

The onward reaction proceeds at temperatures above ~450 $\circ$C; by adding zinc or aluminum, the rates of reaction can be improved. The product CaO is stored isolating from water. The reverse exothermic reaction also follows easily.

(d) *Photochemical decomposition* reaction of nitrosyl chloride:

$NOCl + \text{photons} \rightarrow NO + Cl.$

The resulting atomic chlorine forms chlorine gas, releasing a considerable part of the energy added to the NOCl during decomposition.

The overall reaction is

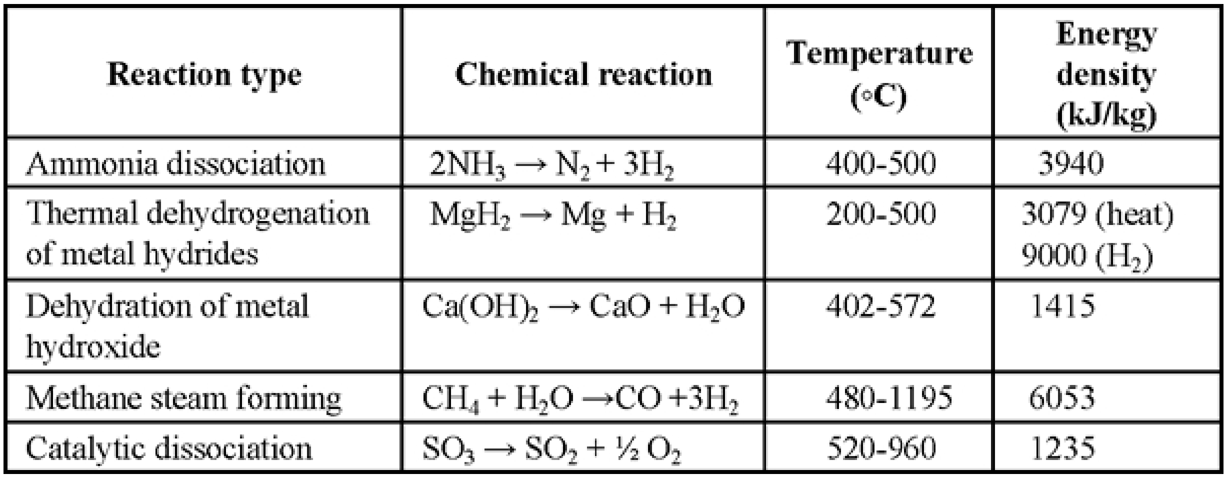
$2NOCl + \text{photons} \rightarrow 2NO + Cl_2.$

The reverse reaction can be executed to recuperate part of the energy from photons entering the reaction.

Thermo-chemical reactions like adsorption can be used for storing heat and cold and to regulate humidity. The extraordinary storage capability of sorption processes also permits transference of thermal energy.

Some of the most remarkable chemical reactions for thermal energy-storage are listed in Table 7.4 [45]. The sorption storage can only function at temperatures below ~350 ∘C, but the temperatures of chemical reactions can reach much higher.

Table 7.4: A few chemical reactions used for thermal storage [45].



Reaction type	Chemical reaction	Temperature (∘C)	Energy density (kJ/kg)
Ammonia dissociation	$2NH_3 \rightarrow N_2 + 3H_2$	400-500	3940
Thermal dehydrogenation of metal hydrides	$MgH_2 \rightarrow Mg + H_2$	200-500	3079 (heat) 9000 (H_2)
Dehydration of metal hydroxide	$Ca(OH)_2 \rightarrow CaO + H_2O$	402-572	1415
Methane steam forming	$CH_4 + H_2O \rightarrow CO + 3H_2$	480-1195	6053
Catalytic dissociation	$SO_3 \rightarrow SO_2 + \frac{1}{2} O_2$	520-960	1235

7.5 Conclusions

Sensible heat storage is appropriate to domestic systems, industry and district heating. Water is the most popular and commercial heat storage medium for several residential and industrial applications. Underground storage of sensible heat in both liquid and solid media is used for typically large-scale applications. Solid sensible heat storage has recently been studied and tested the performance; the concrete and castable ceramics turn out to be the most promising materials. The low-cost of the solid material needs to be adjusted with the enlarged cost of the required heat exchanger. However, SHS systems offer a storage capacity limited by the specific heat of the storage medium.

Latent heat storage is a promising technology, as it brings higher storage density and nearly constant temperature. Several materials have been analysed and identified; the focus has been mostly on commercial PCM materials such as paraffin. PCMs with a wide temperature range such as salt hydrates and specialized PCMs suitable for specific building applications require more attention.

The chemical storage technology is also promising, but is even less developed than the LHS for CSP heat storage. Some studies have claimed that ammonia and the SnOx/Sn reactions may be the most suitable, but much more studies are still needed. Adsorption, the thermo-chemical reaction, can be used to mount up and discharge heat and cold when required and to regulate humidity in many kinds of applications via different chemical reactants. The most important challenge with thermochemical materials is to find the appropriate reversible chemical reaction for the energy source used [32,46a-c].

TES systems based on sensible heat are commercially available, while no commercial high-temperature PCM technology is offered. PCM-based and TCS storage systems are mostly under development and demonstration [1, 4].

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CHAPTER 8

Applications of Energy Storage

8.1 Introduction

Energy storage systems have been used for a multiplicity of applications covering different groups of users and grid operators [1]. The importance of energy-storage technologies is seen in the services they provide. These technologies can be used all through the electricity grid, in heating and cooling systems, in dispersed systems and off-grid instances. They can also arrange for infrastructure support services through supply, transmission and distribution, and demand-side of an energy system. Largely speaking, they are valuable functional tools for grid operators in systems with supply and/or demand-side instability. The supply-side becomes worrying in situations where increased introduction of intermittent renewable energies occurs [2]. Energy storage systems like PHS, flywheels and thermal storage are used in specific applications, whereas Battery energy-storage systems (BESS) are widely employed.

The applications are categorized broadly in 2 ways: (a) applications for utilities and grid operators, and (b) applications for customers. Figure 8–2 illustrates potential applications and appropriate storage technologies within each segment of the *value chain*.

8.2 Applications for Utilities and Grid Operators [1]

1. Seasonal Storage

It is the ability to store energy for days, weeks, or months enabling redelivery for a longer-period supply interruption or seasonal variability on both the supply and demand sides of the energy system (e.g. heat storage in the summer time for use during the winter period via thermal energy-storage systems concealed below the earth).

2. Energy Arbitrage

Energy arbitrage refers to extensive purchase and sale of electricity simultaneously, practiced by grid operators. In places sometimes, there is a substantial difference in locational marginal price (LMP) of electricity; then, the energy arbitrage can be used to balance costs. Electricity is bought and stored when the LMP is low and resell when the LMP increases. This practice is also referred to as ‘storage trade’. Some losses occur during charging and discharging. Load following, which is ramping up electricity supply as demand increases in the morning and ramping down as demand reduces in the evening, is considered a subset of energy arbitrage.

3. Flexible Peaking Resource (or Resource Adequacy)

Peak demand on the grid happens for a few hours in a day. Further to the main power generation that ensures the ‘base load’ of electricity, utilities and grid operators hold onto peaking resources as reserves, which are set to deliver fast additional power into the grid (see Fig. 8.1).

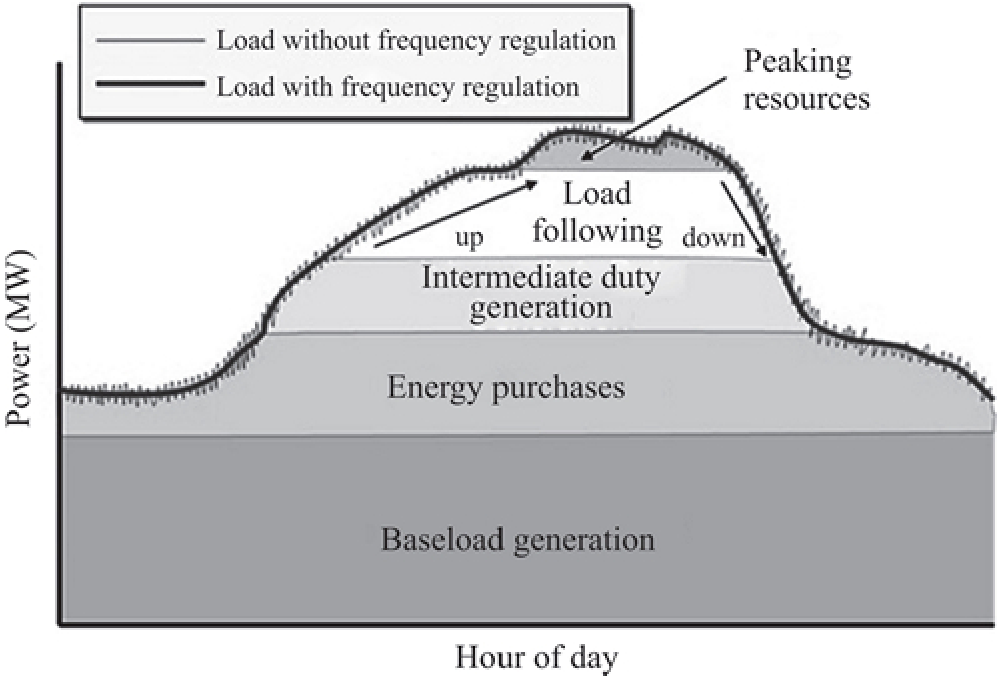
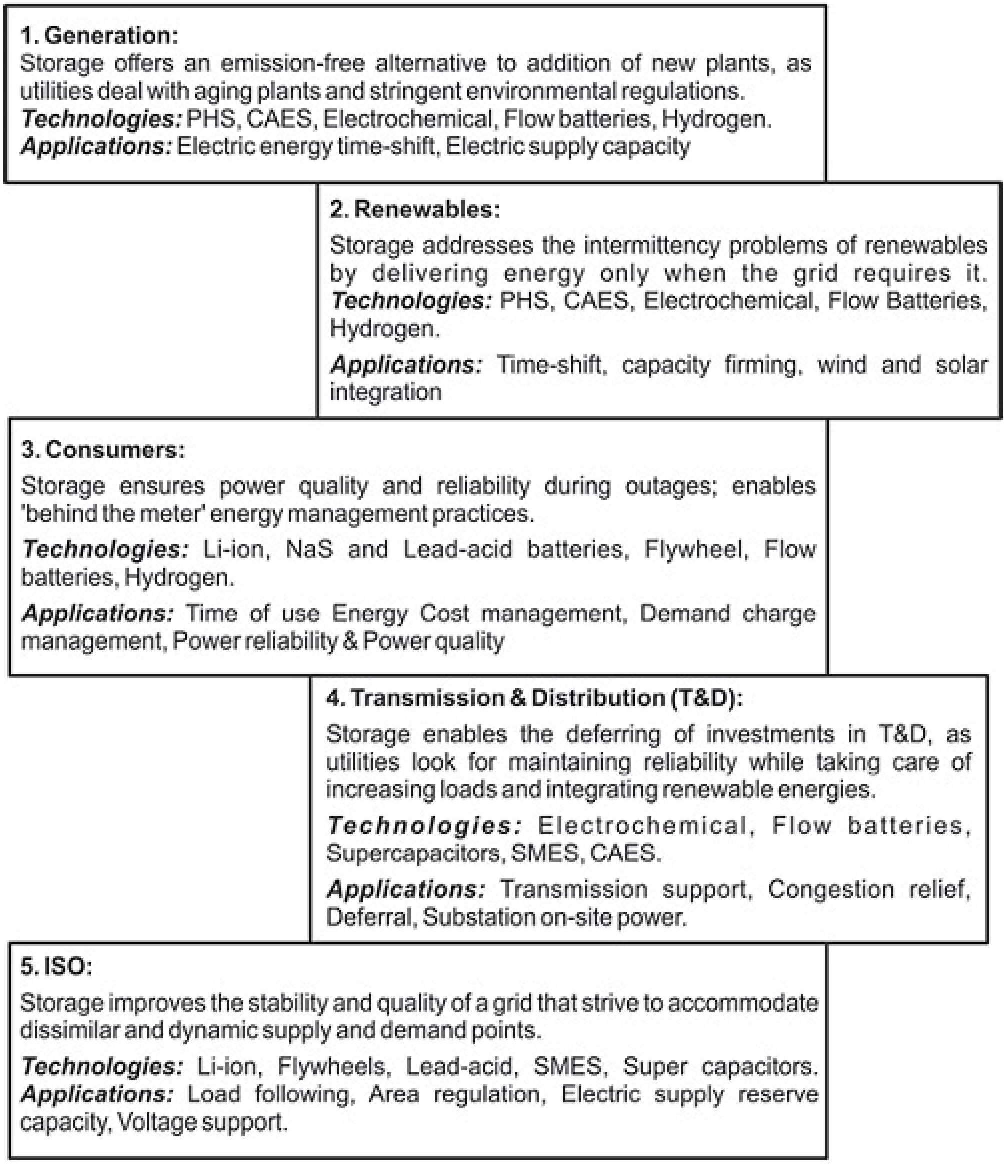


Figure 8.1: Electric Resource Stack' and hourly system load for one day [Source: E&I consulting]

Usually, gas-operated thermal plants serve as peaker supply resources. Many different types of electricity storage are becoming popular as peaker resources because of their extremely fast response times; e.g., lithium-ion batteries that respond in milliseconds and pumped hydropower storage are extensively used as peaker resources.



1. Generation:
Storage offers an emission-free alternative to addition of new plants, as utilities deal with aging plants and stringent environmental regulations.
Technologies: PHS, CAES, Electrochemical, Flow batteries, Hydrogen.
Applications: Electric energy time-shift, Electric supply capacity

2. Renewables:
Storage addresses the intermittency problems of renewables by delivering energy only when the grid requires it.
Technologies: PHS, CAES, Electrochemical, Flow Batteries, Hydrogen.
Applications: Time-shift, capacity firming, wind and solar integration

3. Consumers:
Storage ensures power quality and reliability during outages; enables 'behind the meter' energy management practices.
Technologies: Li-ion, NaS and Lead-acid batteries, Flywheel, Flow batteries, Hydrogen.
Applications: Time of use Energy Cost management, Demand charge management, Power reliability & Power quality

4. Transmission & Distribution (T&D):
Storage enables the deferring of investments in T&D, as utilities look for maintaining reliability while taking care of increasing loads and integrating renewable energies.
Technologies: Electrochemical, Flow batteries, Supercapacitors, SMES, CAES.
Applications: Transmission support, Congestion relief, Deferral, Substation on-site power.

5. ISO:
Storage improves the stability and quality of a grid that strive to accommodate dissimilar and dynamic supply and demand points.
Technologies: Li-ion, Flywheels, Lead-acid, SMES, Super capacitors.
Applications: Load following, Area regulation, Electric supply reserve capacity, Voltage support.

Figure 8.2: Energy Storage across the power-sector; Source: [3].

4. Frequency Regulation

The electrical grid transmits power from generators to end-users at a fixed AC frequency. It is 60 Hz for North and South America regions, and 50 Hz for Europe and Asia. This frequency is stable when power generation equals power usage. If demand/usage exceeds generation, the frequency falls causing brownouts or total crash of power grid. When power generated surpasses the demands from the grid, the frequency increases causing damage to the grid and connected devices.

The frequency regulation comprises controlling supply and demand on a *second-by-second* basis to retain the AC current within the mandatory tolerance limits. By pumping more of intermittent renewables into the electrical grid, the changes in supply and frequency fluctuations become increasingly recurrent and severe.

The power generating resources are usually increased or decreased to make available frequency regulating services, and is the maximum-value ancillary service to the grid. Energy storage is extensively used now in the place of fossil-fuel-fired plants because their flexibility and quick response times facilitate them well-suited.

5. Load Following

Load following brings about system fluctuations on a time-frame varying from 15 minutes to 24 hours (one day); this can be regulated via manual or automatic generation control.

It is another constant electricity balancing mechanism for operation under normal conditions, subsequent to the frequency regulation.

6. Spinning and Non-spinning Reserve

The electrical utilities are expected to retain the power even if one generator goes off. The entire system must maintain frequency and power flow within small variations even with the failure of even the largest generator of the system. Normally, all generating resouces in the system are purposely run with a small proportion of reserve capacity, increasing inefficiency, added costs and waste. As an alternative, fast-responding energy-storage systems like capacitors, flywheels and batteries can be used for this purpose, letting generators to run with their nearly rated power. This reserve capacity is categorized depending on response time as *spinning* (response time < 15 mts) and *non-spinning* (>15 minutes). More rapid response times are much important to the system. Reserve capacity is referred to as ‘frequency containment reserve’ in some areas.

7. Voltage Support

It is essential for the grid operators to ensure a certain level of voltage and voltage stability in addition to frequency regulation. This involves managing reactance across the entire grid, for which an additional service known as ‘voltage support’ is used. Earlier, generating resources that produce reactive power would have to be added to or take away from the grid. But the major issue with this procedure is that reactive power can only be transmitted over short distances. Energy storage, particularly distributed energy-storage, can be made by an attractive option for voltage support by locating it extremely close to end-users.

8. Black Start

Imagine an extraordinary situation where the total grid system and all other ancillary mechanisms have broken down; then, ‘black start’ capabilities allow electricity supply resources to resume without drawing electricity from the grid. Energy storage systems are perfectly suitable for ‘black start’ applications because they can function as backup and independently to reactivate the other grid systems.

9. T and D Infrastructure Investment Deferral

With increased demand for electricity, grid operators must upgrade existing transmission and distribution (T&D) equipment or add extra. However, using energy-storage facility can delay or even avoid the need for the extra improvements or equipment. Such an energy-storage facility is preferable for 2 reasons: (a) saving the costs of the proposed extra equipment, and (b) the energy-storage system can be used for other valuecreation uses.

10. Transmission Congestion Relief

Electricity transmission pathways, like other forms of transport, experience bottle neck at certain times of the day. In such peak times, grid operators charge utilities higher prices to use the corridors. The installation of energy-storage systems downstream of the congested transmission segments facilitates electricity to be stored during peak times and released at the drop of the congestion levels, thus eliminating higher prices.

8.3 Applications for Consumer (that is, ‘Behind-the-meter’) [1]

1. Usage Time and Bill Management

The electricity prices vary subject to the time (or demand) of the day; so, using energy-storage for later use can lessen the costs of the power.

Energy is drawn from the grid when demand and prices are low (normally at night) and stored; then draw from the storage system and use during peak times when prices are higher (normally during the day).

2. Increased Self-Consumption or Self-sufficiency from Solar Plus Storage

Storage combined with solar generation installed by the consumer can be used for storing excess solar power generated during the day to reduce reliance on the grid. Thermal storage (using water tanks) and battery energy-storage are highly preferred technologies for this application.

Solar plus storage is particularly useful in areas where utility rate schemes are unfavorable to distributed solar or for micro-grid energy-storage systems, with restricted grid connectivity.

3. Demand Charge Reduction

In several countries consumers in industrial and business sectors pay for both the electricity consumed and for the maximum power they draw. This charge called ‘Demand Charge’ can reach close to 50% of their total power costs sometimes. If the maximum power drawn from the grid can be reduced, it is possible to save the costs significantly. A strong demand charge management has been practiced for decades. However, the energy-storage concept is more advantageous in this situation. Like in the time-of-use management, energy can be stored during times of low-demand and withdrawn when demand is high, decreasing the drawing of power from the grid. Demand charge management and reduced dependence on the grid is a most important value-generator for the commercial and industrial sectors.

4. Backup Power/UPS

In times of power breakdown, electricity storage becomes convenient to carry on operations without disruptions. This facility is specifically significant in the wake of natural disasters like cyclones and wildfires. The properly deployed energy-storage systems are essential to the continued operation of critical sectors such as hospitals and emergency services.

5. **Variable Supply Resource Integration**

   Solar and wind are intermittent power generating sources. To change and optimize the output from these variable sources, the energy-storage system is used. Also, the energy-storage system facilitates mitigating rapid and seasonal output changes and bridging both temporal and geographic gaps between supply and demand for increasing quality of supply and value.

6. **The Usage of Waste Heat**

   Energy storage is used for the temporal and terrestrial decoupling of heat supply. Examples are CHP facilities and thermal power plants. Also, for purposes such as heating/cooling buildings, industrial process heat requirements and so on, hitherto wasted heat is used.

7. **Combined Heat and Power (CHP)**

   Electricity and thermal energy-storage can be used in combined heat and power facilities to link temporal gaps between electricity and thermal energy demand.

8.4 Integrating Renewable Energy to Grid

Many countries have taken to renewable-energy generation on a large-scale for their electricity supply in the process of decarbonizing energy sector for combating global warming. Solar and wind are the 2 main variable energy sources in the deployment. Introducing large production volumes of variable energy technologies involve changes to power system planning and operations.

Grid integration involves developing methods for efficient delivering of variable renewable-energy (RE) to the grid. The integration methods must maximize the cost-effectiveness of mixing REs into the power system and help maintain or increase system stability and reliability. However, there are several issues to be addressed before the grid integration is considered. The issues relate to (a) new renewable-energy generation, (b) new transmission, (c) increased power system flexibility and (d) design for a high renewable-energy future [4].

(a) New renewable-energy generation

Sustained investment in new renewable-energy generation can be secured by *supporting targets and incentives with grid integration concerns.* Long-term renewable-energy targets may create conditions that can push for innovative policies and system operations, which promote clean energy. Incentives such as rewarding wind and solar generators who use technologies that contribute to grid stability encourage investment in REs and mitigate negative impacts of grid integration.

As the share of the renewable-energy connected to the grid increases, the impact of increased variability and uncertainty on system operations need to be assessed and managed. It is also essential to ensure that policy and regulatory planning provide adequate certainty and revenue sources to encourage investment in renewable-energy sources.

There are several approaches for estimating the capacity value of renewable-energy and techniques that enable utilities and power operators use these energy sources to meet the power demand reliably.

Integrating *distributed* solar photovoltaic (PV) power offers unique benefits as well as tasks compared to the utility-scale solar and wind energy incorporation. Substantial growth in solar PV in localized areas may create problems such as voltage disturbances and reverse power flow in low-voltage distribution systems. However, investigations have revealed that beneficial effects such as reduced line losses and avoiding generation costs result from distributed PV. Modernizing integrating standards, processes, and circulation planning practices that clearly reveal the features of distributed PV can help realize the above benefits while delaying or even avoiding the need for grid strengthening.

Role of enabling technologies: Deploying variable renewable-energy sources, solar and wind, is one primary reason for evincing interest in energy-storage. The intermittent energy produced by them should be ‘smoothed’ or shifted to times when the wind is not blowing or the sun is not shining. However, the actual role of renewables in the grid is much more, which include their lower costs and benefits or the potential usage of energy-storage or other enabling technologies [5].

Currently, a large variation in daily electricity demand is taken care of by the continuous cycling of generators. Further, frequency regulation and incident reserves are delivered by partly loaded generators and receptive load. These flexible generators are mostly hydroelectric plants, combustion turbines, a few combined-cycle plants, and sometimes large thermal generators.

To understand the impact of renewables on the grid, they may be considered a source of demand reduction with unique temporal characteristics; that is, instead of seeing wind or PV as generating sources, they can be thought of a reduction in load with conventional generators meeting the ‘residual load’ of normal demand minus the electricity produced by renewable sources. The advantages of the utility are (i) reduced usage of fuel and accompanying emissions, and (ii) slightly reduced necessity for a total system capacity that is small for the wind but substantial for solar considering its coincidence with load. There are also other significant impacts that change the operation of the system and the costs: (a) higher necessity for frequency regulation, because wind can increase the near-term inconsistency of the net load, (b) the increase in the ramping rate, or the speed at which load-following units must increase and decrease output, (c) the uncertainty in the wind resource and resulting net load, and (d) the rise in the total ramping range (the change between the least and extreme demand in a day) and the related decline in minimum load, which can push base load generators to decrease output; and in severe cases, drive the units to cycle off in times of high wind output. Together, the enlarged variability of the net load needs a greater flexibility and operating reserves in the system, having extra ramping capability to encounter both the expected and unexpected variability. The usage of these flexible resources requires changes in the operation of the remaining system. This involves additional costs, usually called integration costs [205e].

(b) New transmission

RE generation sources are often remotely located from the existing transmission network. So, grid expansion and upgrades are needed to get access to these energy-resources. Transmission upgrades and expansion provide large non-utility customers access to low-cost renewable-energy. By increasing the renewable supply through transmission, some benefits can be achieved, such as reduced costs, grid reliability advantages, and declines in GHG emissions by all customers. Improving and escalating this transmission network would also remove congestion difficulties and could reduce costs for non-PPA consumers.

Investments for large-scale transmission expansion can be boosted by appropriately designing policies, rules, and procedures. These measures not only improve the usage of renewable energies but also potentially hold off the need for network refurbishment.

(c) Increased power system flexibility

According to IEA, the flexibility of a power system refers to ‘the extent to which a power system can modify electricity production or consumption in response to variability, expected or otherwise’. Another explanation is “the modification of generation injection and/or consumption patterns in reaction to an external signal (price signal or activation) to provide a service within the energy system” [6]. So, flexibility can denote the ability to alter power supply/demand of the system in total or an individual power plant or a factory [6].

Operational flexibility is an important feature of electric power systems and is crucial for the transition from the fossil-fuel based power systems to power systems that can efficiently accept a high number of variable RE sources. Sufficient operational flexibility is a necessity for the effective grid integration of large shares of fluctuating power from variable RE sources, especially wind and solar PV.

System operating procedures and market-place practices, largely the execution of real-time forecasting, quicker planning, and auxiliary services, are some of the inexpensive options for providing substantial flexibility without extensive financial inputs into fresh physical infrastructure.

One more vital established flexibility option is operational management among balancing areas; this allows sharing of resources through reserve allocation, organized programming, and/or united operation. (Balancing area means the collection of generation, transmission, and loads within the metered boundaries of the balancing authority that maintains balance between electricity supply and demand within this boundary). Other sources of flexibility include flexible conventional generation and transmission networks. Moreover, demand response and storage are emerging as tools for increasing flexibility at high penetrations of renewable energies [4].

Choices for accomplishing flexibility differ depending on the regulatory setting. For vertically integrated utilities, prescribed or policy instruments make available the primary base for furthering the approval of flexibility measures. In contrast, moderately or entirely reorganized power markets encourage flexibility via inducements and market-oriented mechanisms, such as sub-hourly dispatch, auxiliary services markets, and price-sensitive demand.

(d) Preparation for large renewable future

Estimating long-range demand and assessing options for expanding capacity and transmission is important in any power system. The introduction of considerable number of renewables pushes *the power system planning* to focus even more on assessing choices for enlarging flexibility through the power system.

Studies on grid integration benefit to organize the flexibility necessities and to convince stakeholders and operators that the power system can function consistently at enhanced renewable-energy volumes. Further, these studies (a) simulate the power system operation under several settings, (b) recognize possible limitations to dependability, and (c) estimates the finances required to lessen the limitations. Serious grid incorporation studies are centered on investor involvement, next to a broad set of *foundational data* [4]. The grid integration studies commonly comprise fabrication cost simulations to model unit assurance and economic dispatch; but defining the *total costs (that is, system-wide) of integrating solar and wind power* is most interesting. The over-all costs and importance of renewable-energy-resources to the power system are determined by the complex interfaces among these generators and a system's loads, assets, thermal producers, and transmission networks. Additionally, grid integration studies (i) highlight the difficulties and prospects that wind and solar integration could create to a power system, (ii) help clear grid integration *untruths and misperceptions* that impede large-scale installations, and (iii) create base for first preference of grid integration investments.

8.5 Smart Grid [7, 8]

'Grid' is referred to the electrical power-transmission network consisting of transmission lines, transformers, substations and so on. It is over a century old in European countries. In India, grid management started operating on a regional basis from 1961, and individual state grids were interconnected to form 5 regional grids covering entire country. These grids are the Northern, Eastern, Western, North Eastern and Southern Grids.

After nearly a century, the grid is beginning to transform into somewhat much ‘smarter.’ ‘Sensors’ are deployed at the point of power generation, along transmission lines, on electricity meters, even on individual appliances, which give an overview of generation and consumption in real-time. In addition, computers, controls and automation, digital signals are used to automatically trigger necessary actions requiring almost no human involvement.

Smart Grid is, therefore, an electrical grid with automation, communication and IT systems that monitors and adjusts, based on information received from suppliers and consumers of electricity in realtime. Smart grids correlate the requirements and abilities of all power generators, grid operators, consumers and power market investors to enable the total system function with maximum efficiency, system dependability, resilience and steadiness while keeping costs and environmental impacts down [9]. Smart grids comprise the entire electricity system, including transmission and distribution networks, producers, grid storage systems and consumers. The different areas of application for different smart-grid technologies through the network are shown in Fig. 8.3. Smart grids vary significantly in their design and layout.

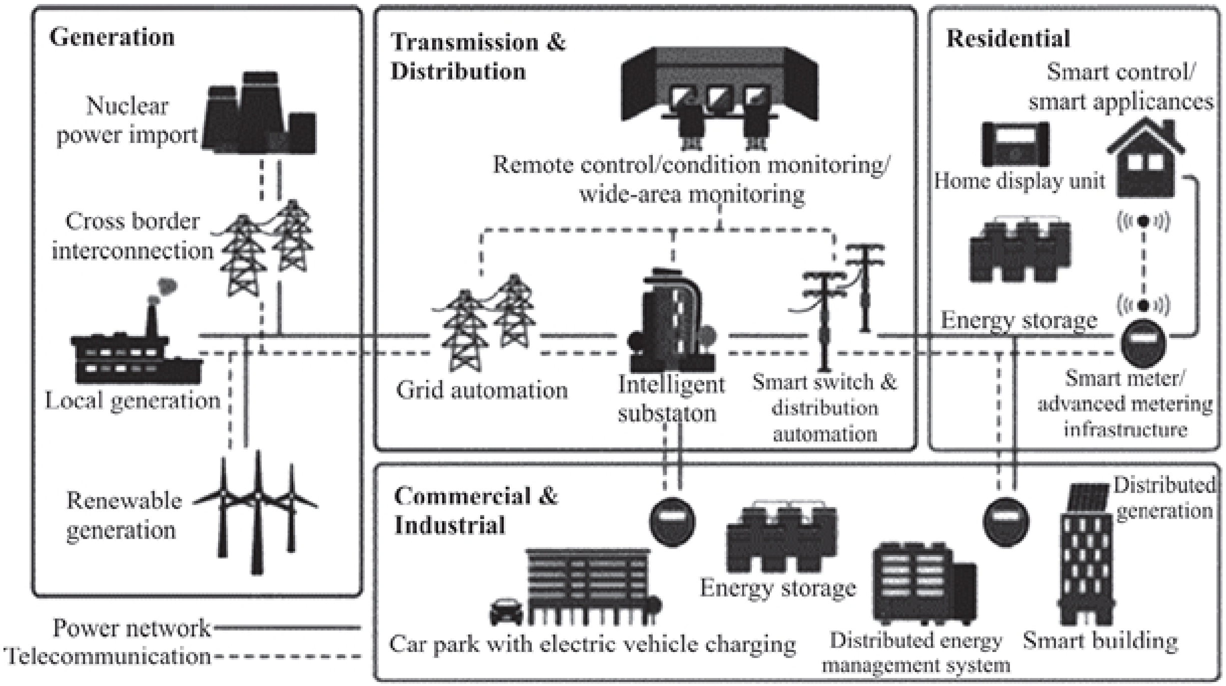


Figure 8.3: Schematic of Smart Grid [11].

Smart grids can be accomplished by effecting efficient T&D systems, system operations, consumer addition and renewables incorporation. Smart grid solutions facilitate monitoring, determining and regulating power flows in real-time that can help to discover losses; thus, leads to initiate technical and administrative actions to end the losses.

The benefits associated with the Smart Grid are (a) highly effective transmission of electricity, (b) faster reinstatement of electricity after power disorders, (c) decreased operating and running costs for utilities resulting in lesser power costs for consumers, (d) reduced peak demand that helps lower electricity charges, (e) much more integration of extensive renewable-energy systems, (f) enhanced the integration of customer-owner power producing systems also comprising renewable energy systems, and (g) better security [10].

Role of Energy-storage Technologies

We have seen that for appropriately operating the *electrical grid*, the supply and demand need to be flawlessly balanced always. Otherwise, the fluctuations to grid-wide voltage and frequency can produce power breakdowns, failures and even damage or rescind electrical apparatus.

If sources with a continuous output, for example, fossil-fuel-fired thermal plants and nuclear power plants supply greater part of the electricity, it is relatively simple to control power supply levels. As more renewable generation sources are plugged into the grid, their intermittent nature increases new challenges. For instance, a passing cloud shadow over the solar panels or a transient decrease in wind, result in a sharp fall in power supply.

If supply and demand alter too often, it is highly challenging to maintain the grid stability. It is a common observation that demand constantly fluctuates depending on time-of day, month of the year and consumption of the end-user. When clouds cover the sun or when a large number of air conditioning units turn on a hot day, stored energy is needed to pick up the slack at almost instantly.

Most of the world’s stored energy, about 95%, is in pumped hydropower (PHS), the world’s water-battery. Although this is highly suited for injecting a surge of power into the grid to meet peak demand, the suitable geographical conditions are not available in every region for this technology to operate. More importantly, the rapid fluctuations of the modern grid require energy-storage systems with more flexibility and faster response times.

Recent experiences have revealed that *battery energy-storage systems* are perfectly appropriate for *smart-grid* objectives. When wind or solar electricity production surges on windy days or peak sunshine periods, battery energy-storage systems charge by using additional power. If sudden fall in supply or surge in demand occurs, power is added back to the grid for prompt smoothing of the fluctuations. The smart digital technology that links these networks allow these processes automatic.

What are the benefits of combining energy-storage with smart grids?

It’s recognized that *smart* digital technology combined with *energy-storage* together function very well to improve grid flexibility and strength and bring out definite advantages.

Smart grids provide multitudes of benefits to grid operators and power utilities. Power is transmitted with added efficiency, systems resume rapidly after brownouts and blackouts, peak demand is dropped and the costs of operations and supervision are lowered. In addition, energy systems with varying output, such as renewable sources can be better integrated. In the recent developments, several households installed with solar PV panels plus battery storage employed smart technology to function as ‘virtual-power plants’. As a result, the users benefit from better flexibility, few outages and reduced electricity bills.

With residential energy-storage systems in place, the residents are virtually fully self-sufficient and able to sell electricity to the grid and make profit. The costs of energy-storage technology have fallen significantly allowing the residential and wide-scale *installation* to become economically achievable.

Smart Grids in Developing Economies

Most of the development and investment of smart grids has come from developed countries, mainly in Europe and North America, and the interest in developing countries is relatively new. Smart grid development is associated closely to the economic development of countries. Most smart-grid development has been focused in countries with high renewable-energy targets, as they begin facing problems with their power supply stability due to intermittent nature of generating source. In most developing countries, achieving universal energy access is the priority compared to the development of renewable-energy generation [12]. However, recently, RE generation sources in developing countries, especially in emerging economies such as China, India, Brazil, and Mexico are increasingly deployed. As a result, applying smart-grid technology is increasingly being explored [9]. In the world's least economically developed nations, there exists little experience with smartgrid technology.

Smart grid technology presents many advantages for improving grid performance and increasing energy access in these countries. Most of these countries still have largely weak grid networks, giving them the opportunity to move fast technically and going straight for a smart-grid network in their plans of infrastructure expansion. If the country is expanding its renewable-energy capacity, it is advantageous to invest in smart grids because they facilitate increased flexibility and grid responsiveness [13, 14].

While there are opportunities which smart grids present to these countries, there are challenges too.

(a) *Opportunities*: (i) can right away install smart-grid technologies when constructing their T&D network;

(ii) prospects for state-of-the-art energy services such as linking costs to the mobile communication network, setting up local charging stations, or installing mini/micro grids for rural electrification; and (iii) well-meaning facility to reduce losses including power theft losses in the power network.

(b) *Challenges*: (i) Utilities in developing countries are often capital-constrained, limiting their ability to invest in smart-grid projects despite their economic viability; (ii) Upper cap on the utility tariffs needs to be affordable for the users who make it difficult to retrieve O&M for the system; (iii) Lack of detailed data, for example, the systems operation and consumer demographic; (iv) Regulatory and institutional issues such as regional standards, harmonizing of different power networks, and limited innovation for ensuring data privacy [14].

Smart Meters

Smart meters provide the Smart Grid interface between the consumer and the energy supplier. Smart meters replace the old mechanical meters and operate digitally, and allow for automated and complex transfers of information between home and the energy providers.

Power generation companies now have facility to determine the power demand in different areas and determine time periods of maximum electricity consumption or minimum consumption in that locality.

It is easy to integrate a smart meter into a desktop or a television set. The data received by the meter from the energy provider and displayed on these devices help the consumer organize the electricity consumption. These devices also help the consumer track and determine the power consumed by each appliance in the household.

Smart Mini Grid

The mini-grid is a network, which involves “small-scale electricity generation from 10 kW to 10 MW, and the distribution of electricity to a limited number of customers via a distribution grid that can operate isolated from national electricity transmission networks and supply relatively concentrated settlements with electricity at grid quality-level” [15a]. In the context of energy accessibility, the term refers to a system akin to a mini-grid (or micro-grid), but operating at a reduced size and production capacity (1–10 kW) [15a]. In other than energy access situations, micro-grid is occasionally referred to a system comprising loads and distributed energy-resources, which *can connect and disconnect from the main utility grid* [15b].

A Smart Mini-Grid (SMG) is described as a smart electrical power distribution network, having an operating capacity of11 KV or less, and the electricity demand is efficiently and intelligently managed by different kinds of Distributed Energy Resources (DERs). Distributed energy is a system in which electricity is produced by a large number of small to medium-sized power plants such as solar PV, micro-hydro, wind, biomass, and small conventional generators such as diesel gensets along with each other through smart control techniques [16] rather than by one or more large capacity plants. Currently, there is a need to focus on distributed small-scale generation of power particularly from renewable-energy sources as their generation volumes have been rapidly rising. Even though DERs require extra infrastructure and budget to link them to the grid, they (a) require no costly transmission system and (b) lesson T&D losses.

The prospect of distributed generation can be better recognized by taking a system approach in which generation and associated loads are a subsystem or a 'micro-grid.' That is, a micro-grid is an assembly of interrelated loads and DERs within fixed electrical boundaries that functions as a distinct manageable unit concerning the grid. A micro-grid can choose to connect and disconnect from the grid to operate in either mode.

Nonetheless, to deal with these crucial issues, Smart Mini-Grid is more suitable because it can optimally and logically manage the load and distributed generation resources. This methodology allows extreme use of the RE resources with a lower installed renewable-energy capacity; also, lesser batteries can be ensured by organizing the energy demand with the electricity generation. Further, generation from fossil fuels can be reduced by managing energy loads more efficiently, and the power quality can be improved [17].

8.6 Smart House

The smart home is a new concept visualizing the energy’s role in the lives of people and the altering connection between power utilities and users. The smart home signifies the merging of energy-efficient and well-regulated appliances with real-time access to energy usage data. The integration of smart devices and grid facilitates users to foresightedly manage energy use conveniently, cost effectively, and without hurting the environment. The power users would be happy with smart homes because they provide more efficient and cost-effective demand response programs enabling them to get the energy when required.

The smart home functions along with the smart meter and the smartgrid, and is the central unit of end-user interaction with the utility [18]. However, smart home is still at conceptual and modular experimental level and a smart home functioning is yet to be realised.

8.7 Power Electronics in DER Systems

Several structures for grouping DERs have been proposed mainly to identify critical areas that need R & D efforts to make it possible for a reliable operation within and off the utility grid [19–25]. Extensive adoption of DERs is dependent mostly on the status of power electronics that enable effective linking to the grid. Highly reliable power electronics technology is in place, and so it has become safe and economically viable to set up co-generation equipment even at the domestic level. More advanced power electronics enable successful participation of DERs by supportive actions to the grid such as reactive supply ancillary service and power quality [26, 27].

DER systems are classified as (a) nonrenewable generation units such as IC engine-, microturbine-, and fuel cell systems, (b) renewable generation units such as solar PV, wind energy, wave energy and small hydrosystems, (c) energy-storage units such as flywheel storage and battery storage, and (d) controllable loads for grid ancillary services such as plug-in electric vehicles (PEV) and power electronic loads. Several DERs need precise power electronics proficiency to transform the generated power into suitable power for directly linking to the utility grid and/or for use for consumer uses. Several functions of traditional power devices can be performed with a single power electronic device, and the advances in digital technology have added additional features to power electronic couplings [28]. The requirements of the power electronics couplings for one application under each of the above mentioned 4 classifications are discussed here.

(a) Fuel cell systems

These are electrochemical devices that generate electricity without any intermediate power conversion stage. Their energy density is nearly 10 times that of a battery. Fuel cells produce DC power and thus require power conditioning systems to couple them to the grid. Fig. 8.4 shows the simplest configuration of a fuel cell system coupled to the grid.

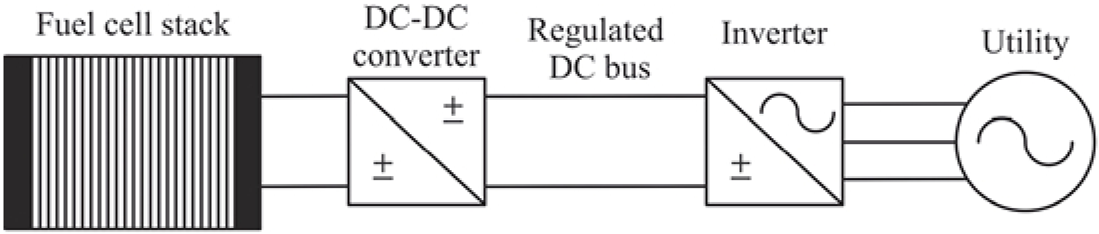


Figure 8.4: Representation of a Power electronic coupling for Fuel cell system [29] .

In case, separation or high ratio of voltage change is necessary, a transformer is included in the system. The foremost disadvantage of this system is, with the inclusion of a line frequency transformer next to the inverter, the system becomes massive and costly [29].

(b1) Solar PV system

Solar photovoltaic systems can be organized in quite a few schemes. Every design comprises a simple power electronic interface to convert the DC power output from the solar arrays to AC for direct linking to the power grid and/or for consumer use. Fig. 8.5 shows one typical configuration with a centralized inverter included.

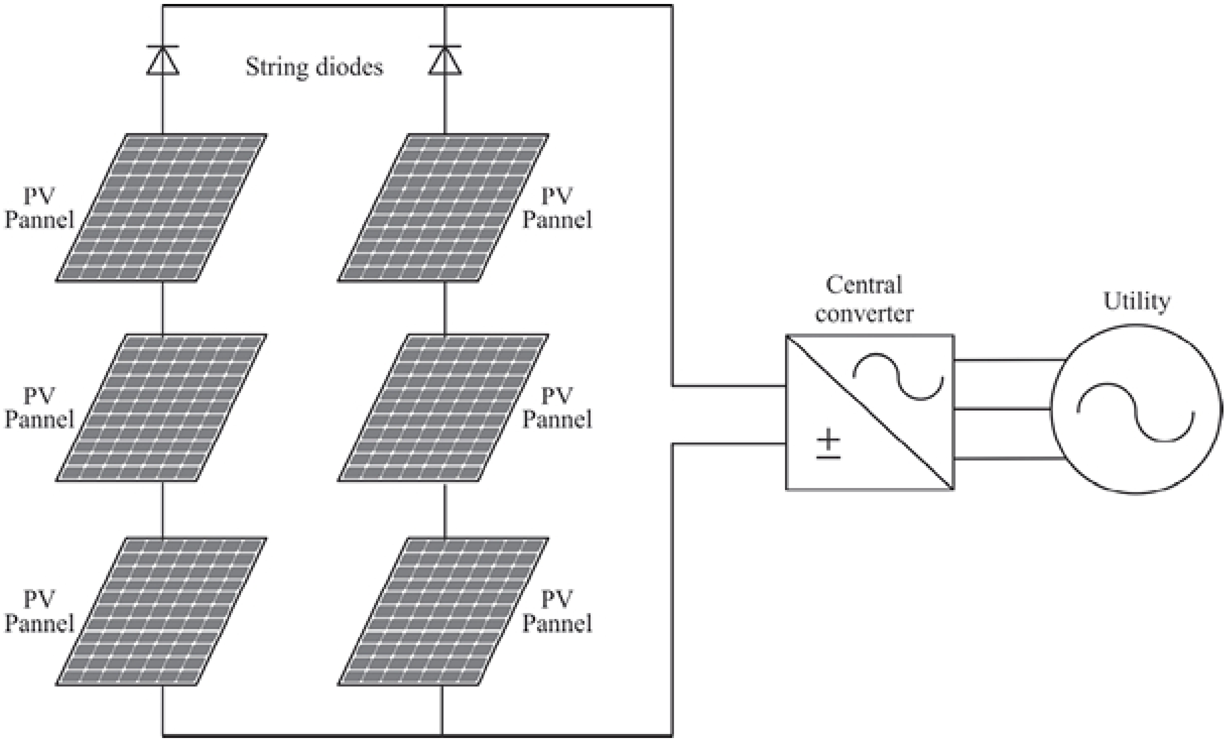


Figure 8.5: Schematic of a typical PV configuration with a centralized power electronic coupling [28].

Photovoltaic modules are coupled in series and/or in parallel methods which are then joined to a centralized DC/AC converter. String-array PV systems are also in use; in this scheme, chains of PV panels are connected into a single string and linked to the grid with one inverter for every string. Also in operation, PV strings having both DC/DC converter and inverter, with the prospect of maximum power point tracking (MPPT) for boosting the power generation of the PV system [29, 30]

(b2) Wind Energy Systems

Like solar PV, wind energy systems are becoming increasingly important in renewable electricity generation.

Fig. 8.6 illustrates a wind energy conversion system with its components [31].

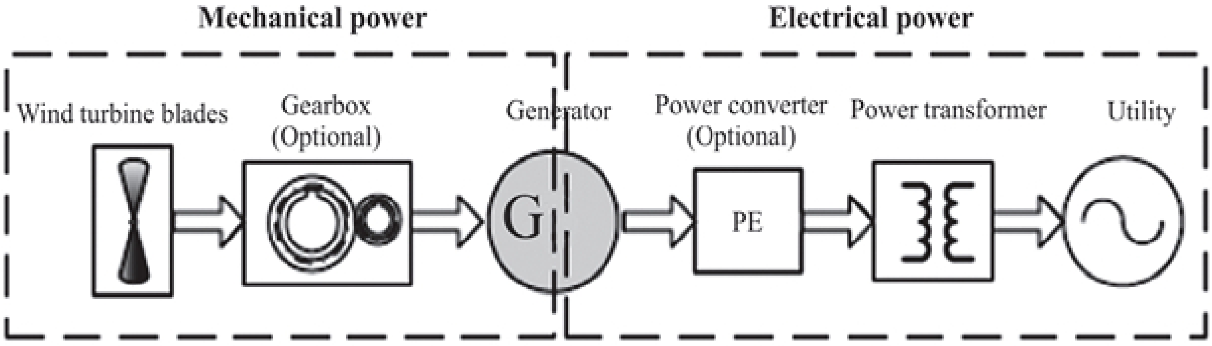


Figure 8.6: Schematic representation of a generalized wind energy system [31]

These systems are connected to the electricity grid in 3 different ways: (a) with short power electronics, (b) with power electronics to some degree, and (c) with complete power electronics. The first category systems (without power electronics) use induction generators, which require a reactive power advantage to operate. This reactive power is delivered either by the grid, or capacitor arrays or power electronics created reactive current addition. Systems using partly rated power electronics use wound-rotor induction device. Systems having complete power electronic converter use a conventional or permanent magnet synchronous generator or induction generator [32].

This structure permits the wind turbine to function in a variable-speed mode enabling the capture of more wind energy and regulate the torque to smooth it during unusual operation.

High frequency direct AC-AC conversion is also suggested for integrating wind energy conversion systems to the grid [33]. Also, matrix converters are presented for wind energy systems for both partly rated and complete power converters for variable-speed mode of functioning [34].

(c) Battery energy-storage systems

Lead-acid or flow batteries are employed to connect BESS to the power grid. Currently, the most widely used electrical energy-storage systems are lead-acid batteries. The battery energy-storage system in its simplest configuration is presented in Fig. 8.7. A DC-AC converter is the coupling power electronics. The main disadvantage of this system configuration is the system becomes huge and costly due to the positioning of a line frequency transformer at the output of the inverter [35]. In some designs, hf transformers are used in DC-DC converters for galvanic isolation. Galvanic isolation is a principle of isolating functional sections of electrical systems for preventing current flow.

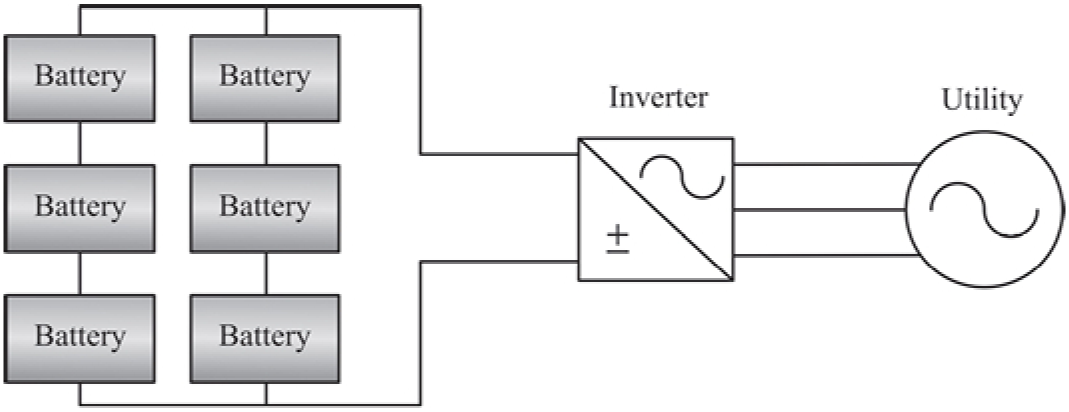


Figure 8.7: Battery energy-storage system configuration with power electronic coupling [28].

Topologies without including transformers have also been described [36]. BESS are regularly used together with other forms of variable energy sources like wind or solar PV (a) to counter balance the daily and seasonal intermittent nature of the primary source, (b) to level out load variations, (c) to damp out utility transients, and (d) for islanding operation. [Islanding is an unsafe condition in which a distributed generator, e.g, a solar system, continues to supply power to the grid while the electric utility is down]. One such system (hybrid) where BESS joined with a wind energy system is shown in Fig. 8.8.

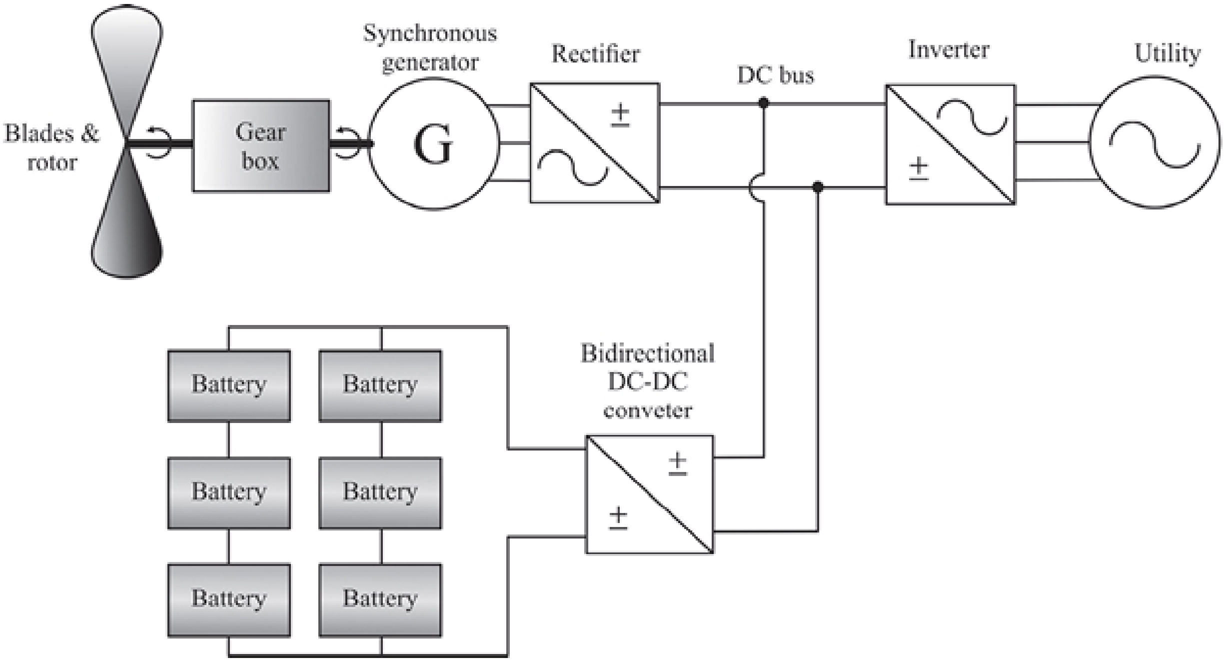


Figure 8.8: Hybrid system with BESS and wind energy system with power electronic couplings [28].

(d) Plug in Vehicles are classified into electric vehicles, hybrid electric vehicles, plug-in hybrid vehicles and plug-in fuel cell vehicles. The battery onboard of these vehicles is charged drawing power from the electrical utility or any other energy source using a power electronic coupling. In plug-in vehicles, batteries are charged when the vehicles are parked. This can be facilitated via a utility-connected AC-DC converter to acquire DC power from the grid as shown in Fig. 8.9.

Further, the vehicle batteries can be directly charged from a solar energy source with a DC-DC converter or from a wind energy source using AC-DC or DC-DC converter depending on power obtainable from the wind resource. It is stated that if plug-in hybrid vehicles substitute about 50% of the vehicles on the road by 2050, an increase of 8% electricity generation only would be needed [37].

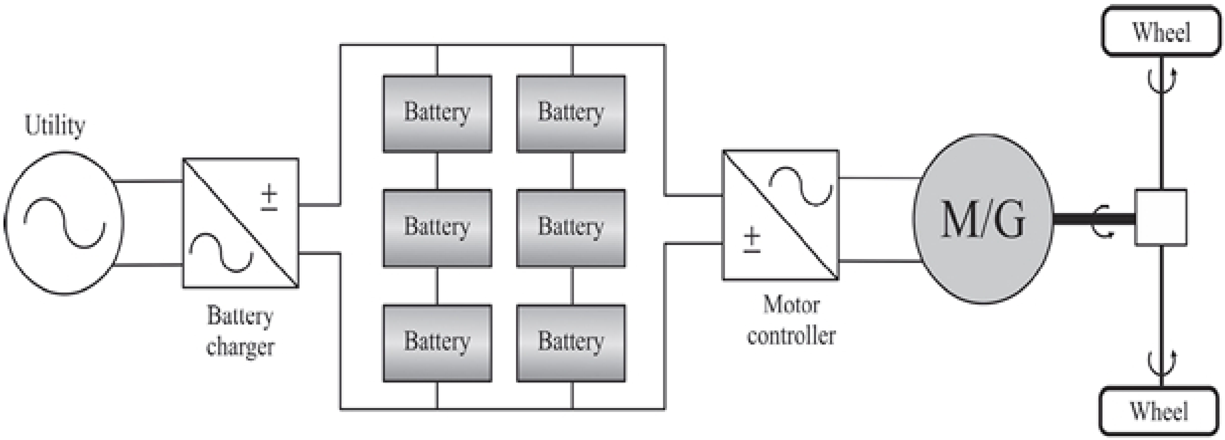


Figure 8.9: Schematic of a typical electric vehicle configuration with power electronics coupling [28].

In summary, different DER systems require different power electronic couplings for making it compatible to the utility. NREL in the U.S. proposed a generalized representation (Fig. 8.10) of a coupling between different DER systems using several modular blocks of power electronics [37]. This generalized coupling is one possible answer for “a standardized, highly integrated, modularized power electronic coupling with the idea to make ‘plug and play’ for DER systems” [37]. Each module in the Figure can be designed to put up different DER systems.

The distinctive advantages of using power electronic couplings are (i) ability for variable-speed operation letting optimization of fuel usage, (ii) possible for Maximum power point tracking (MPPT) for PV and wind energy systems, (iii) Flexibility to incorporate energy-storage systems in the converter DC link to deliver quality power and additional services such as reactive support by generating units and loads, (iv) Dispatching competencies with energy-storage systems and (v) enhanced efficiency.

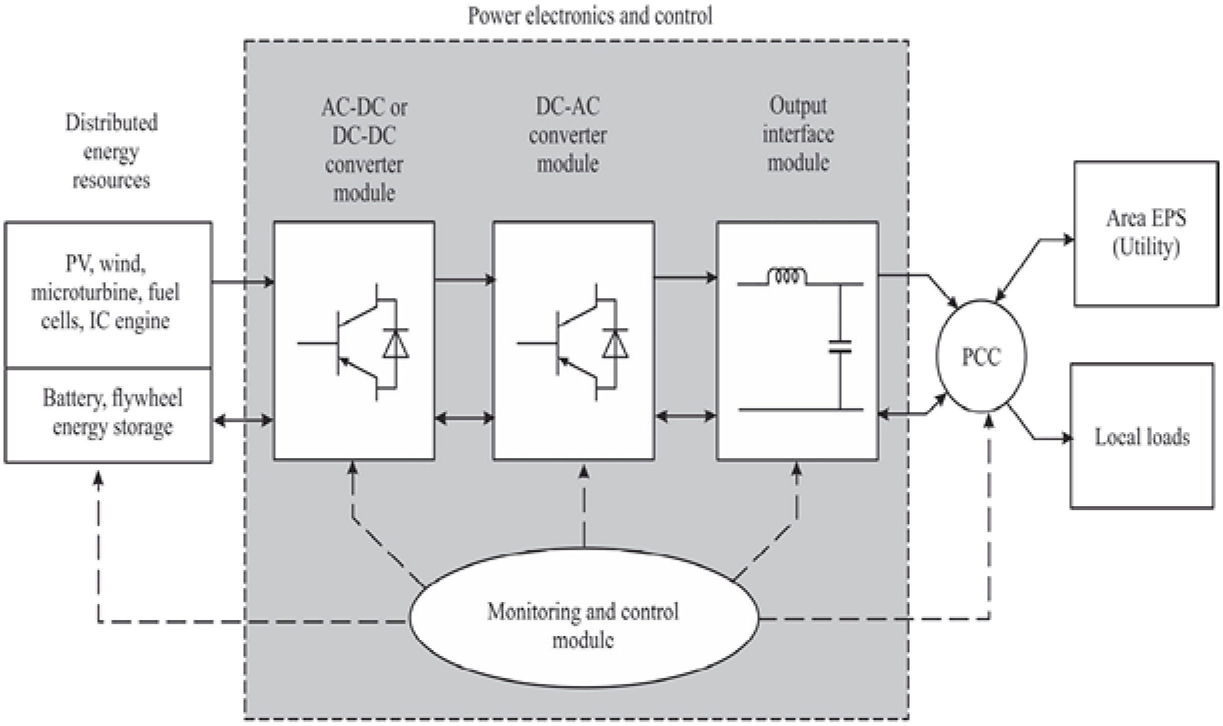


Figure 8.10: Generalized power electronics interface for DER systems proposed by NREL [37]

The future power grid will witness DER systems providing ancillary services and loads become part of such support system to the grid.

This depends on intense R & D, with particular focus on cost reduction of the most suitable power electronic coupling technology for each application, high volume production, improved reliability (with a meantime of at least 10 years) of power electronics converters, scalability and modularity [28].

8.8 Virtual Power Plant

A virtual-power plant is an innovative concept that works distantly to pool several independent energy-resources from divergent locations into a system that affords consistent power all through the day. These plants use software-based technology dependent on the smart-grid. They use planning, arrangement, and bidding of distributed energy sources (DERs) to create a system that provides the reliable power.

So far, all the countries have depended on power from centralized coal-fired or gas-fired thermal plants with power flowing from the utility to the consumer, i.e, in one direction. Recently, minor and major independent power producers began generating both onshore and offshore wind power, solar energy, bioenergy, and hydropower, allowing the power flow to become bi-directional.

But the amount of renewable-energy produced is highly weatherdependent resulting in unreliable energy supply as its use increases. Here comes the new concept of energy service (VPP) as a way to sustain supply stability. This means, for e.g, the scattered DERs and storage batteries can be distantly controlled by IoT equipment and function as if they were one power plant.

Thus, the ‘virtual-power plant’ can be regarded as a result of increasingly DERs making their way to the grid. The DER has created several challenges, including network congestion. The utilities and grid operators must deal with supply variability by turning to conventional resources to cope with sudden drops of solar supply in case of no sunshine, creating a spike in demand. It is argued that this balancing of supply can be done with less expensive, less polluting, virtual-power plants based on clean power. As ‘virtual’ plants are capable of providing power all through the day, they can substitute fossil-fuel-fired plants. VPP is expected to promote the introduction and expansion of renewable-energy and contribute to a decarbonized society. But there are certain issues such as vulnerability to cyber attack, affecting local voltage and so on. If these are solved, they can provide ancillary services to respond to imbalances created by intermittent resources, or by collapse of large power generating plants. Also, they can deliver automatic demand response avoiding the necessity for prior planning and can instantly react to (a) price indications, (b) fluctuating commercial and residential loads, or (c) collecting other distributed energy-resources. In addition, they can deliver load shedding, capacity relief, and frequency regulation [38–40]. Fig.8.11a shows the different elements that constitute a VPP.

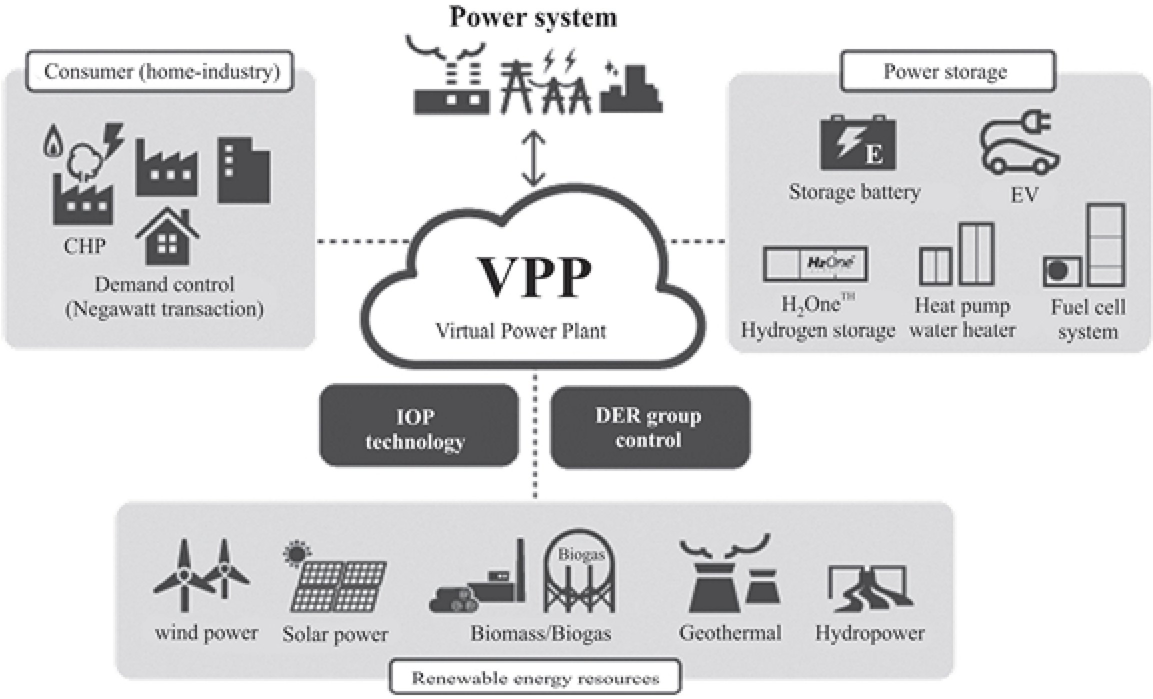


Figure 8.11a: Elements of Virtual power plant [40].

Virtual power plants Vs micro-grid: Similar to virtual-power plants, the micro-grid aggregate and optimize distributed energy-resources. However, micro-grid have a much defined network boundary and a specific area that benefits their operators. Also, they can cut off from the main grid to act as independent or isolated units of power supply. Instead, virtual-power plants often extend over a broader area and are adequately flexible to enlarge or diminish the area of operation, contingent on market conditions. VPPs serve the main grid, while micro-grid rarely provide services to the main grid.

Plants in action: The Australian Energy Market Commission was one of the early regulatory bodies to implement the idea of virtual-power plants by allowing them to compete in the country’s extensive electricity market freely. This example is sure to inspire others to aggregate solar and battery storage in homes and businesses. The battery systems allow the customers to store and take the benefit of more rooftop solar and get lower power costs. And the battery systems provide backup power in the event of an outage. In the U.S., Michigan’s Consumers Energy proposed using virtual-power plants to reduce energy demand 22% by 2040, a necessity as it started closing fossil-fuel generation plants [38]. In Germany, the virtual-power plant was the first and biggest of its kind in Europe; it has more than 1300 wind farms in its system, in addition to 100 solar energy producers, 8 hydropower plants and 12 biomass power plants (Fig. 8–10b). The total capacity of this VP plant goes above 10,000 MW, similar to that of 10 nuclear reactors. It amounts to more than twice of the capacity of Neurath coal power plant, Germany’s largest power plant. With the change in weather, significant uncertainty could happen to supply many types of renewable-energy. So, numerous weather forecasts from most important meteorological establishments are pooled and coupled with a statistical model developed by Statkraft. Distinct advice on uncommon weather occurrences, such as the impact of storms, is included. To comprehend the weather and energy markets, the digital platform scrutinizes and evaluates more than 50,000 pertinent data points per minute [39].

Virtual power plants are gaining ground while achieving cost-savings and environmental benefits for the grid, consumers, and utilities. They help utilities and grid operators in saving the huge costs of setting up power plants and by avoiding the use of expensive, polluting peaker plants. Importantly, they bring more renewable-energy to the grid, helping utilities integrate it all through the day [38].

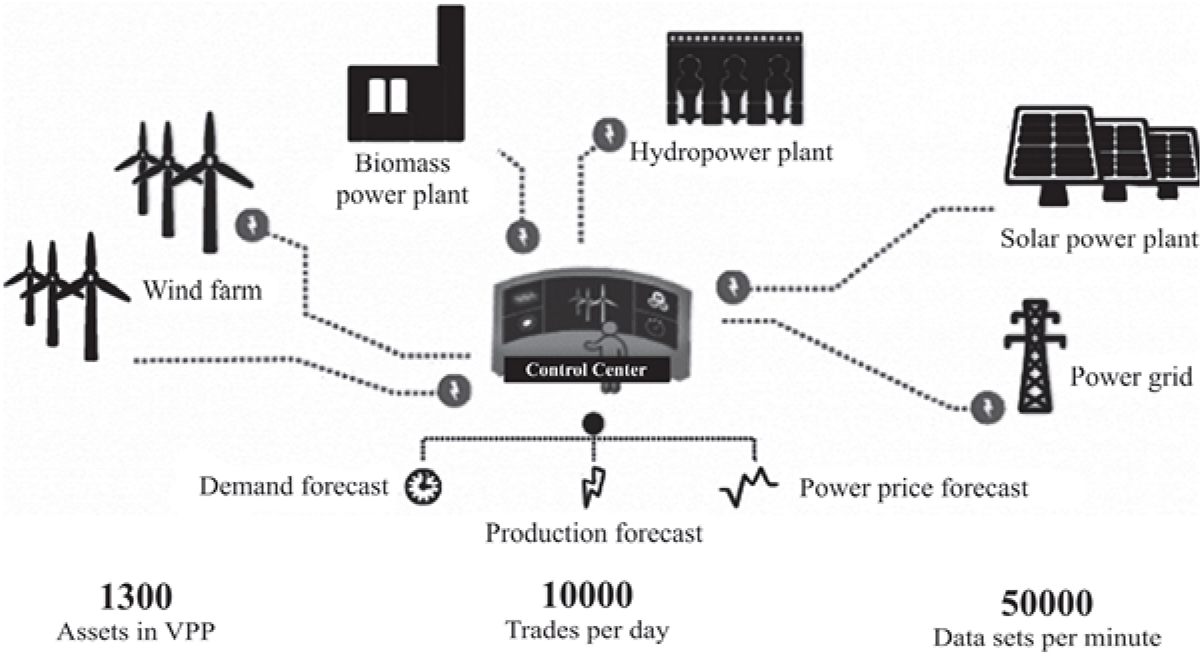


Figure 8.11b: Representation of Germany’s Virtual power plant, the Europe’s first and the biggest [39].

Negawatt trading: The range of VPP know-hows extends even further. VPP can generate and support innovative services, if used together with energy management systems at end-user locations. For instance, the nonconsumed power due to the provision of incentives on the demand-side can be regarded to have the equivalent value as the generated power, and is measured as a ‘Negawatt’. Negawatt represents a watt of energy that has not been used through energy conservation or the use of energy-efficient products, and Negawatt trading is ‘consolidating the electricity saving of consumers and trade as electricity demand adjustment.’

VPP can encourage recognition of megawatts and achieve them. In a market, totally understood, it would be possible to buy electricity generated from the different power sources that include low-cost production by users. With the advancement of time, the new energy supply market develops, and VPP will assume the role of handling and using extensively distributed power sources. The prospects of plentiful small-scale production facilities broadly distributed in offices, factories and homes, and even electric cars, are enormous. In the years to follow, the role of VPP will be crucial in realizing a decarbonized society [41].

8.9 Battery SCADA System

SCADA (Supervisory Control and data Acquisition) is a program using a specific software for process control and data collection in real-time from far away and secluded locations to help regulate equipment and settings. SCADA is applicable in several situations: power plants, industrial units, oil and gas refining units, communications, transportation, and waste treatment plants. By their use at the control station, it is possible to display the data collected from all the sensors and controllers, to visualize the progress of the process and to control. This enables an operator to monitor and oversee the process as well as to respond appropriately to any disturbance or emergency. The SCADA systems may also respond automatically to any changes that occur in the supervised system. The systems may well be applied, for example, in diverse optimization tasks, in the modeling and simulation of phenomena happening in many fields of electrical engineering, in monitoring the operation of modern electricity supply systems and in systems intended for the identification of equipment's condition being part of the generation and supply systems [42]. Battery SCADA system demonstrates battery aggregation technology for power grid operation contribution.

Battery Aggregation Technology

Grid-connected Battery Energy Storage system (BESS) comprises one or several battery strings, coupled in 2 ways: (a) in parallel to one principal inverter, or (b) each battery string having an inverter for itself. The second way of coupling has many advantages over the first one: the battery inverters' losses consist of a permanent share which is power-independent and a flexible share which is power-dependent; the permanent share of the inverter losses would be large compared to the throughput power if the inverter functions with only a few percentage of its rated power. As a result, high efficiency losses would occur. For example, if the BESS had to provide frequency-response reserve (FRR), the BESS is operated at around 10–20 % of its rated power. Further, non-uniform aging of the battery string would result in a quick breakdown of the whole BESS because the fastest aging battery string restricts the total life of the system. The second method, each battery string with its own inverter would be manageable to optimize power flows allowing minimal losses and homogeneous aging. In addition, the failure of the principal inverter would end up with a breakdown of the total BESS. In terms of price per kilowatt, a central/principal inverter could have an economic advantage, but the technical benefits of the decentralized concept most likely prevail over the lower costs of a central inverter choice in most cases and must prefer.

In both the methods, each battery string is coupled to the inverter via DC cables. Regarding earthing, either positive or negative pole of a battery string or the center of the battery string can be earthed or the battery can be insulated from the ground (called IT system, isolationterra). If a pole or the center point is earthed, one of the 2 systems, TN-(terra-neutral) or TT- (terra-terra) system can be chosen. The main variation of these systems is that the TN-system earths separately the conductive parts such as cabinets, casings, etc. Both systems are susceptible even to a single fault leading to an instant blackout.

In an IT system, however, a single fault may not result in abrupt shutdown and provides time for reaction. This is a benefit, particularly, if large BESS accessibility is essential. Otherwise, the necessity for an insulation monitoring device arises to determine a single fault. If the voltage of a battery string exceeds 1500 V DC, a high voltage regulation is required, which considerably increases the costs of BESS. Using inverters in the range of 500 - 1000 kW seems to be a good compromise between modularity and costs. Regarding heating, ventilation and air conditioning (HVAC), one must consider each battery technology’s specific properties.

When lithium-ion batteries are used, the battery rooms are cooled ordinarily using split air conditioning. The air conditioning need not essentially be sized to the total thermal losses at nominal power of the battery storage system. For instance, lead-acid-batteries have a high thermal capacity; therefore, HVAC could be sized for them as required to the typical losses during the intended BESS application. The coulombic efficiency of Li-ion batteries is almost one, which means that almost no side reactions occur during charge and discharge times; therefore, the cooling requirement is equal to the ohmic losses of the batteries at their internal resistance.

The lead-acid batteries, apart from ohmic losses, generate a lot of extra heat in charging due to side reactions. This heat, absorbed by the large thermal capacity of Pb-acid batteries initially, requires to be constantly dissipated by air conditioning.

Sodium-nickel-chloride batteries run at a high temperature of around 300°C (572°F). So, the large temperature difference from ambient temperature facilitates easy cooling by ventilation giving excess heat to the surroundings. But, they need auxiliary heating if the internal temperature becomes too low, that is if placed in cold setting. BESS can be stored in a house or in containers. Containers usage is economical and more modular in majority situations. For example, in the future, each battery string of BESS could be set up in a single container along with related air conditioning and inverter, whereas one central container could house the grid link, central electrical equipment (e.g. MV switchgear) and BESS-SCADA system. However, in freezing environments or if larger BESS are planned, it can be beneficial to use buildings because the idea of a modular container may be highly costly. But, the building needs to be specially planned to house a distributed load of 2,000 kg/m^2. It is necessary in the case of lead-acid-batteries, mounted cell-by-cell on a one-story-rack; and Li-ion batteries installed module-wise in racks with heights of more than 2 m [43].

Safety issues: Hydrogen generation probably is the highest risk in taking care of lead-acid batteries. Sufficient ventilation and air circulation are essential and ensures that hydrogen cannot accumulate in corners, beneath the ceiling or in hollow spaces. Sufficient standards are available which can be applied in the planning. More challenging in the planning is the most feared hazard, the thermal run-away with Li-ion batteries. Burning of these-batteries cannot be extinguished because they provide their own oxygen for the fire. Hence, detailed observation of battery characteristics such as voltage, current, temperature, and so on and out-of-work observation and regulation in terms of a fail-safe battery-management-system (BMS) is central for safe functioning of BESS including Li-ion-batteries. Besides, there are no suitable standards to refer at present. The 3 most critical safety happenings to examine are overcharging, over temperature and mechanical misuse. The first two, overcharging and over temperature happen due to extremely high currents and may be avoided by proper monitoring and regulation. These functions can be achieved by the BMS, inverter control unit and battery SCADA system. Even if one of these flops, the BESS must be closed [43].

A BESS-SCADA system needs to coordinate the data from the BMS, the power conversion systems (PCS) that consist of inverters plus inverter controller, and external requests to ensure a safe and reliable control of the BESS for an economically viable operation. The system comprises the SCADA unit, the energy management system (BMS), the PCS and extra constituents such as a state-of-the-art EMS, a database server or hardware for monitoring. The BMS monitors all pertinent measurements and ensure the operation of the batteries well within the permitted values of voltage, current and temperature. Even if one of these permitted values surpasses by the failure of any SCADA component, the BMS need to turn off the batteries by opening the contactors. The PCS functions to regulate the inverters and keep up a safe operation. The main SCADA unit collects external power needs (according to the BESS operator's demands) or estimate its own power demand from measured signals (in case of FRR) and dispatch the power from each battery string. This dispatch is the work of EMS, which computes the power of each battery string. If the EMS reforms the power dispatch allowing minimal losses, aging etc., more complex algorithms are wanted necessitating a lot of computing power. Therefore, it is preferable to execute such modern EMS separately, for instance, a workstation to eliminate the main SCADA unit from these calculations. Such separate arrangement is advantageous because any breakdown of the EMS-computer would not result in the shutdown of the complete BESS. Also, in this case, the main SCADA unit can assume the control of dispatch by a simple algorithm (e.g. the distribution of power is equal among the existing battery strings). Faced with the failure of any SCADA total system's components (main SCADA unit, BMS or PCS), the others can still switch off the system safely. In addition, a database must be arranged to store all significant information during the operation. A visualization GUI presents all recorded information and the present state of the BESS in an attractive way [43].

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CHAPTER 9

Maturity and Status of Energy Storage Systems

9.1 Maturity

Technology maturity for each storage technology is assessed based on (a) technology readiness level (TRL), which is a type of measurement method to assess the maturity level of a particular technology and (b) stage of market development. The stage of market development is evaluated based on R&D, demonstration, introduction, growth, and maturity [1]. The energy capacity of an energy-storage system is expressed in MWh, and the power (or maximum output at a given time) is expressed in MW or MWe.

Comparison of different storage technologies is not an easy exercise as so many factors are involved as seen above. The maturity of the technologies also makes the comparison difficult. Some types of energy storage, e.g. thermo-chemical are still in the research stage while some other technologies are mature and already have several working plants, e.g., PHS. Therefore, a useful and accurate comparison is difficult to do without first performing more in-depth research [3]. This can be deduced when looking at Figure 9.1, where some large-scale energy-storage technologies are presented with respect to the maturity of the technology Vs the capital requirement and technology risk (i.e. the probability that the technology will succeed in relation to the capital requirements) is presented [2]. Fig. 9–1 is redrawn based on the figure presented by the IEA [2] and complemented with other studies [13 - 15, 17, 18], data from the U.S. Department of Energy [16] and some assumptions. It is not to be taken as an absolutely precise representation but rather as an overview of the existing situation currently [3].

Fig. 9.1 only represents some examples of large-scale storage technologies (i.e. Li-ion batteries for use in portable electronics are excluded). Achieving progress in the maturity of technology depends on how much the institutions are willing to invest in R&D of the less mature technologies. IEA’s analysis of technological maturity of different energy-storage technologies (2014) is presented in Fig. 9.2. When comparing these 2 figures, it can be recognized that several additional technologies have reached their commercialization stage since 2014.

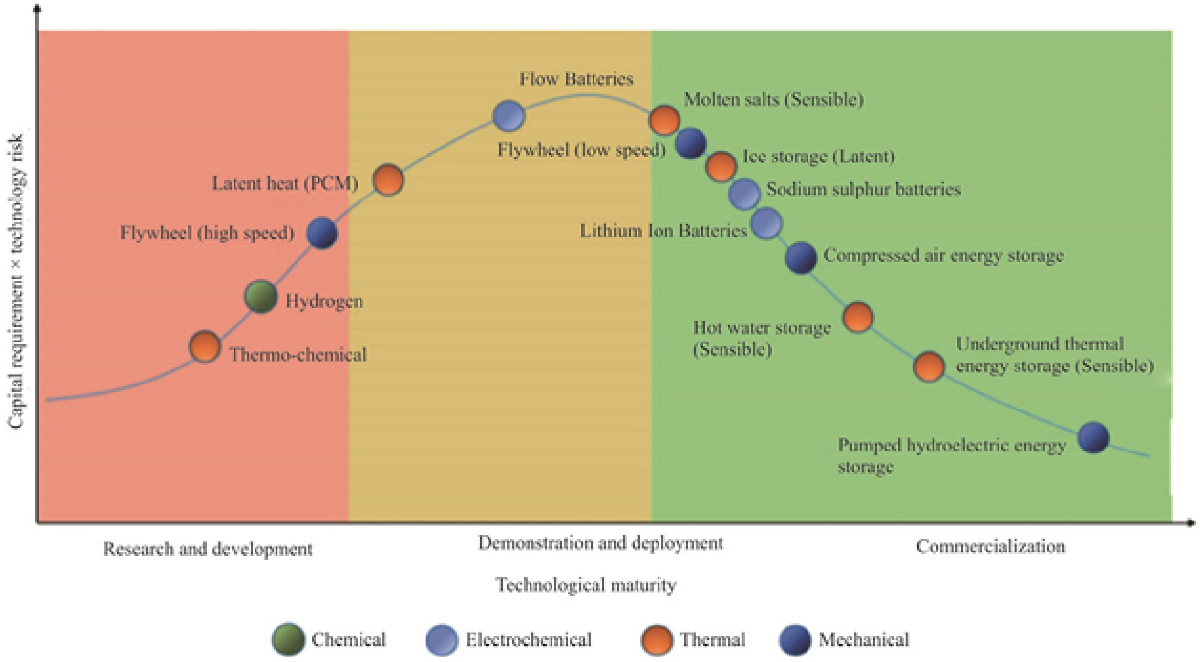


Figure 9.1: Technological maturity overview [3] (This maturity figure is redrawn from a figure published by the IEA [2]. It is complemented with

assumptions based on data from the U.S. Department of Energy and with discussions with studies from the Energy Technology department at the Royal Institute of Technology.)

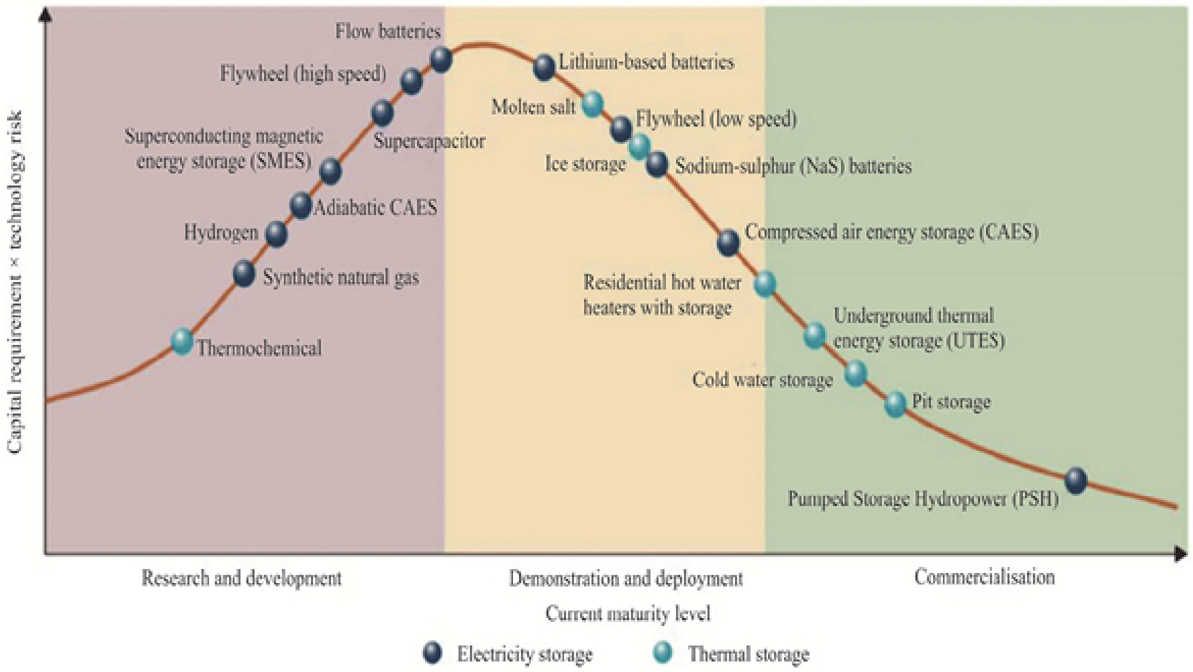
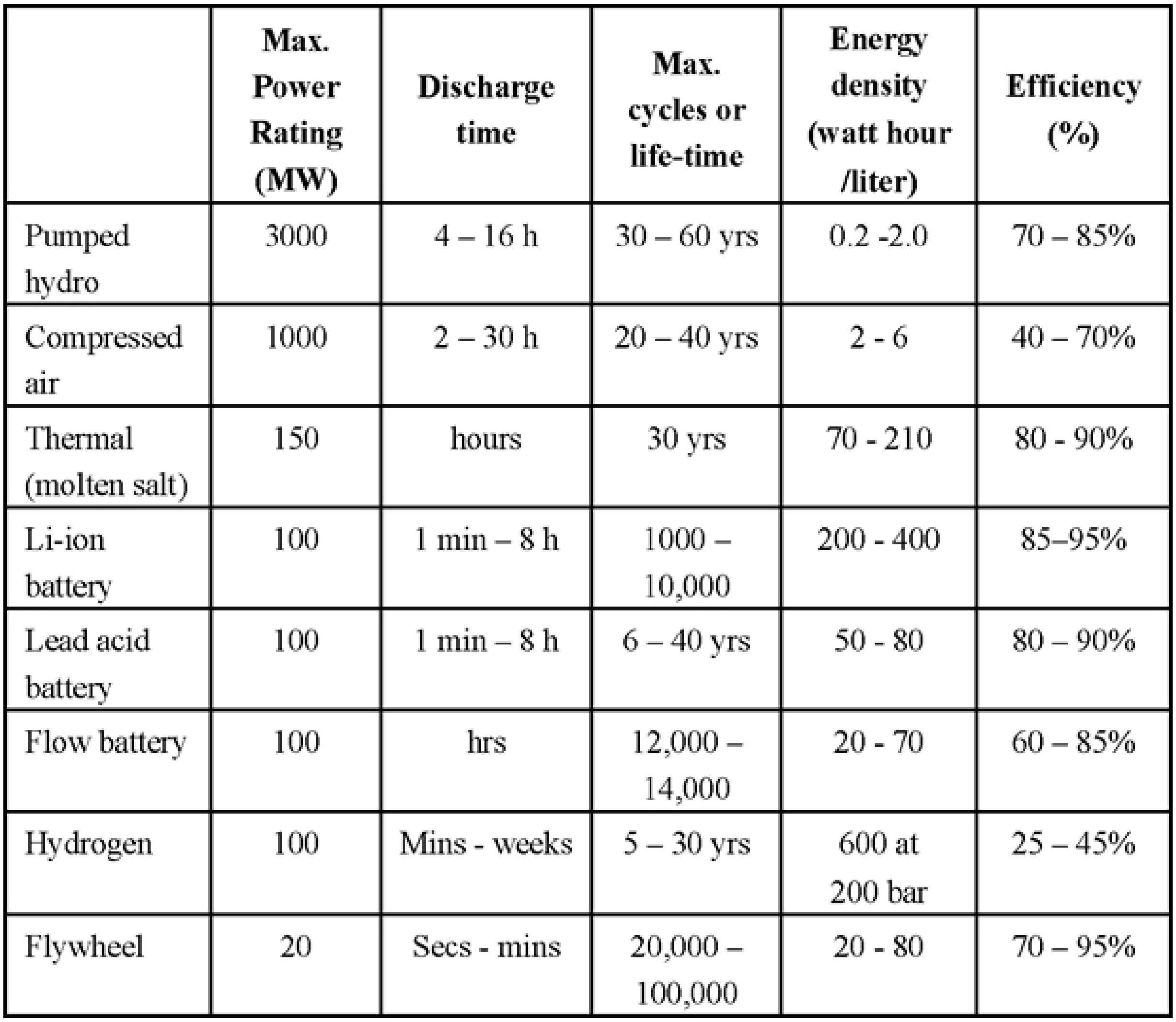


Figure 9.2: Technology maturity overview presented by IEA, 2014 [2].

Several storage systems can store large amounts of energy and become an alternative to PHS. Hydrogen storage is one such technology due to its high storage capacity and low energy cost. It also requires a similar initial investment as PHS. However, hydrogen is highly flammable and is stored at high pressure, which leads to risks not present in the PHS. As seen in Figure 9–1, hydrogen storage technology is still under development and might take time before it could be an actual alternative to PHS.

Technologies that provide currently large storage capacities, at least 20 MW is given in Table 9.1. It excludes superconducting magnetic energy-storage and supercapacitors (with power ratings of less than 1 MW).

Table 9.1: Characteristics of selected energy-storage systems (source: The World Energy Council, 2016)



	Max. Power Rating (MW)	Discharge time	Max. cycles or life-time	Energy density (watt hour /liter)	Efficiency (%)
Pumped hydro	3000	4 – 16 h	30 – 60 yrs	0.2 -2.0	70 – 85%
Compressed air	1000	2 – 30 h	20 – 40 yrs	2 - 6	40 – 70%
Thermal (molten salt)	150	hours	30 yrs	70 - 210	80 - 90%
Li-ion battery	100	1 min – 8 h	1000 – 10,000	200 - 400	85–95%
Lead acid battery	100	1 min – 8 h	6 – 40 yrs	50 - 80	80 – 90%
Flow battery	100	hrs	12,000 – 14,000	20 - 70	60 – 85%
Hydrogen	100	Mins - weeks	5 – 30 yrs	600 at 200 bar	25 – 45%
Flywheel	20	Secs - mins	20,000 – 100,000	20 - 80	70 – 95%

Electrochemical storages are also increasing in size and could compete with PHS. There are already large EES facilities operational, mainly in Japan, the U.S. and South Korea, capable of storing several MWh of energy. In Japan, the largest Na/S power plant currently operational is 50 MW/300 MWh [17] and in Korea, one Li-ion storage facility, 48 MW/12 MWh has recently become operational [20]. These are examples of the largest operational electrochemical storage plants at present in the world. In addition, there are also several hundred more, still of considerable sizes, currently in operation [16] while many even larger are planned, such as the 100 MW/400 MWh Alamitos Energy Storage Array contracted in California, USA [21]. This indicates that EES technologies have matured to the commercial stage. Batteries can also be used in flat landscapes where PHS is not an option and requires a smaller area for storing a considerable amount of energy.

9.2 Status

Energy storage was all set to boom in 2020. The utility scale storage projects were growing around the world, and especially in the U.S. and Australia, the variable wind/solar, and storage together looked like ready to start its grid balancing functions.

Solar-plus-storage will continue to have a synergetic relationship. The large-scale execution of solar PV finally will result in the extensive implementation of storage. This development leads to more prospects to install solar. Energy storage is useful in several situations; but storage technology performance is much linked to solar because prospects for fast growth of energy-storage lay in the solar sector. To achieve a target of 20% of solar in total power generation by 2030, storage technology will play a primary role in delivering electricity in the absence of the sun [4].

According to a study in California, solar projects with 4 hours of storage are expected to have a 99.8% ‘effective load carrying capacity’ in 2022, as compared to only 6.2% for a project with no storage facility. This shows that a solar-plus-storage project is much more beneficial in terms of grid stability than just a solar project. Adding storage to a solar power generation project will also make it harder for other technologies to compete that are usually taken as more reliable, including gas plants (especially peaker plants that run infrequently). Further, adding storage to solar also helps mitigate limitation. Normally, the daily peak in solar production does not typically coincide with the peak in demand. So, when supply exceeds demand, the production is curtailed. By adding storage, the energy that would otherwise not be produced and sold can be stored and used later in the day when demand is high and solar production is unavailable. This feature can increase the value of solar projects [5].

The number of systems combining renewable energy with energy-storage in the U.S. more than doubled from 2016 to 2019 according to U.S. Energy Information Administration (EIA). There were 19 sites pairing solar or wind with batteries in 2016, which soared to 53 sites by 2019, and by 2023, another 56 projects will be in place. Enormous opportunity for further growth exists: only 2% of solar capacity and 1% of wind are integrated with battery storage; even though roughly 25% of battery storage capacity is set-up in a hybrid, co-located project.

The best 3 uses of utility-scale batteries for renewable energy plants are (i) storing excess wind and solar, (ii) providing frequency regulation and (iii) peak shaving. According to IHS, a market research firm, the global energy-storage market had grown exponentially to an annual installation size of 6 GW in 2017 from an initial size of 0.34 GW installed in 2012 and 2013 and projected to over 40 GW by 2022 [6].

According to the projection in 2017 by Bloomberg New Energy Finanace [6], the global energy-storage market would double 6 times between 2016 and 2030, rising to 125 GW/305 GWh (Figure 9–3), similar to the surprising expansion in the solar industry that happened from 2000 to 2015. In this extraordinary growth, the share of photovoltaics of total generation doubled 7 times in terms of percentage. Eight countries were projected to lead the market, with 70% of capacity to be installed in the U.S., China, Japan, India, Germany, U.K, Australia, and South Korea. Energy storage, both utility-scale (i.e., front-of-the-meter) and behind-the-meter, would be a crucial source of flexibility throughout this period and would be essential to integrating increasing levels of renewable energy [6].

At the end of this decade, 2030, North America (with 41.1 GWh), China (32.6 GWh), Europe (31.2 GWh), Japan (2.3 GWh) and South Korea (1.2 GWh) is projected to be the leading markets for stationary energy-storage [6].

With China excluded, Japan and South Korea become a major part of the rest of the Asian market. A significant portion of the projected extensive growth is hybrid structures of 4-hour duration coupled to utilities, and commercial, industrial and residential renewable sources (usually solar photovoltaics).

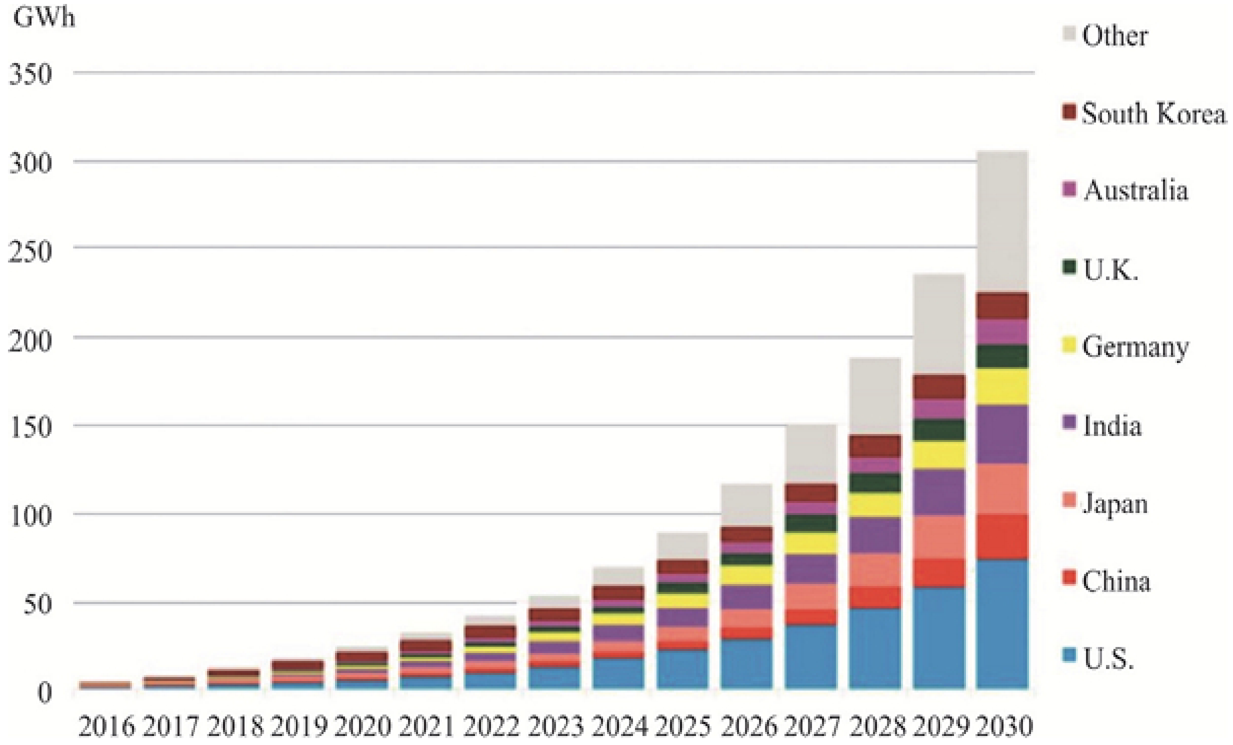


Figure 9.3: Global Energy Storage Market Forecast (Source: Bloomberg New Energy Finance [6])

9.3 Systems in Operation

A few chosen systems in operation are described.

9.3.1 Lu del Norte 141 MW Facility in Chile to Provide Anciliiary Grid Services

The 141 MW Luz del Norte solar project is the “world’s first” utility-scale solar facility licensed to provide ancillary grid services including automatic generation control (AGC) in Chile. The First Solar designed the power plant. Chile’s independent system operator (ISO) Coordinator Electrico Nacional recently added this facility located in the Atacama Region to its portfolio of large-scale power generators.

Commissioned in 2016, it is used to manage the frequency of the country’s electricity system, helping ensure the grid’s reliability and stability. First Solar along with NREL, USA, examined the power plant's ability to provide AGC, primary frequency control, ramp rate control and voltage regulation and found that the PV power plant performed better than fast gas turbine technologies.

The 141 MW Luz del Norte facility is helping to maintain grid reliability and stability in Chile. Image: First Solar.

In the wake of several utility companies and ISOs worldwide addressing the challenge of decarbonizing their grids, Luz del Norte facility signifies how the potential of large-scale solar can be achieved. By providing both clean electricity and no-carbon grid services, the facility establishes the importance of financing large-scale solar power generation [7].

9.3.2 250MW/250MWh Gateway Energy Storage Project in California, USA

The 250MW/250MWh Gateway Energy Storage project in San Diego County, California operated by LS Power using Lithium-ion cells supplied by LG Chem was brought on-line in August 2020, just in time to help prevent blackouts during the historic heatwave in the State. It is the largest and beats the earlier record held by the 150MW/193MWh Hornsdale Power Reserve in South Australia, which uses batteries supplied by Elon Musk's Tesla.

This project will improve grid reliability and reduce customers' energy costs, according to LS Power.

The 2020 heatwave in California and the consequent increased power demand for air conditioning threatened to bring down the state's overloaded grids, especially after the sun set when the solar electricity ceases. Due to this disaster, the grid link operator California ISO must introduce regular blackouts with the threat of more outages.

An aerial view of the Gateway Energy Storage Project in California, Photo credit: LS Power

230 MW of battery cells only was energized by early August 2020, and the total project was due to be completely built and started by August end. The energy

capacity of the facility would be enlarged to 750MWh of storage by summer 2021, and later to 1GWh.

Battery storage projects of this kind not only improve electric reliability and reduce costs for consumers but also help the state meet its climate objectives.

9.3.3 Council owned Battery storage at Fideoak Mill in Taunton, UK

The UKs largest council-owned battery storage site, the 30 MW Fideoak Mill site, are now fully operational and able to participate in delivering multiple revenue-generating services.

In June 2020, 25 MW battery storage was installed and started providing grid balancing services to national grid. In August 2020, another 5 MW was added taking the total capacity to 30 MW.

It uses Kiwi Power’s proprietary hardware Fruit, which was installed on all 22 battery units at the site. These allow the batteries to provide balancing services to National Grid to help keep the power network stable and safe, and participate in any of the UK’s 15 flexibility markets. The battery devices were offered by BYD Europe BV.Over the next 2 years, the 4 coal-fired UK power stations are due to close and the gap will be filled by renewables.

30 MW battery project, the largest owned by a local council authority in the UK. Image: Kiwi Power.

This will put increasing pressure on the grid and to keep the grid safe and balanced, the need for battery storage will increase dramatically [8].

9.3.4 Grid-scale Battery Storage Systems in Australia

Victoria's 2 grid-scale battery storage systems integrated with solar farms are up and running, ready to shore up the grid as temperatures rise and demand for electricity soars. Some details are provided for each System [9].

(a) Gannawarra Energy Storage System, Victoria, Australia

Gannawarra Energy Storage System (GESS) is a 25MW/50MWh battery that is integrated with Victoria's first large-scale 50 MW solar farm. GESS was developed and structured by Edify and financed by ARENA and DELWP stop Tesla was the battery provider. Energy Australia is the long-term operator of GESS.

It is one of the largest co-located ‘solar farm and battery systems’ in the world.

Commissioned in 2018, the GESS was planned to:

(a) keep up its linking point power factor at unity during charging and discharging, and control power factor in association with solar farm such that it helps to maintain network voltages during failings;

(b) deliver uninterrupted operation in the frequency range 49.5 - 50.5Hz and simultaneously provide support during control after a generation or load exigency has happened and contingency markets have improved and the system frequency settled;

(c) use control system settings that can provide for automatic rises or falls in active power for frequency changes outside the usual frequency range of operation, as well as protecting power system oscillations are sufficiently checked.

Arial view of Gannawarra, Victoria's first big battery site. Source: [9]

GESS functioned on average one cycle per day since early March 2019 to August 2019 (6-month period), for an overall charge energy of 9,271 MWh, and discharge energy of 7,991 MWh.

For the next 6-month period (Sept. 2019 to Feb. 2020), the charge energy and discharge energy values were 10,522, and 9,022 MWh, respectively. The cycle rate was marginal over the earlier and winter times, but the activity was increased subsequent to the registration for regulation FCAS in June and consequent months leading into summer.

The round-trip efficiency for the system averaged 86.2% for the first 6-month period and 85.7% for the next 6-month period, fluctuating in a range, 82 to 88% approximately. This round-trip efficiency calculation was made at the facility revenue meter based on observed aggregate energy bought and sold into the market. It was inclusive of balance of system losses and unadjusted for MLF.

The availability of the storage system was high throughout the reporting period, greater than 97.8%, inverter block availability recorded in all months, except March 2019. The March value did not represent actual availability because errors in the SCADA data collection subsequent to a software update for a couple of days in March occurred, which were not adjusted.

The System performed well from a revenue perspective too. The facility recorded no safety or environmental incidents in the entire year of performance study. This is expected due to the facility and the workplace health and safety policies adopted on site.

(b) Ballarat battery Energy Storage System, Victoria, Australia

The Ballarat Energy Storage System is a 30MW/30MWh system using Lithium-ion battery technology and Fluence's proprietary hardware and software controls. The battery was supplied by Fluence. The system was installed at Ballarat Terminal Station (BATS) and connected to the transmission network. The system operations by Energy Australia started in December 2018 [10].

The project was designed (1) to improve network stability and lessen the bottleneck on Victoria's transmission grid through direct grid connection and partaking in both Australia's National Electricity Market's (NEM) exigency, and regulation Frequency Control Ancillary Services (FCAS) markets; and (2) to supplement a peak power resource to manage price instability and steadiness risks in periods of high demand, by furnishing a reliable energy source to the Australian Energy Market Operator (AEMO).

Source: ARENA [9]

For the first 12 months of operation, the System (a) delivered 7,312 MWh in the Energy and FCAS markets, (b) realized $6.07million in returns, with revenue reaching predictions in Energy markets and more than predictions in FCAS markets, and (c) ensured a total availability of 86.36%.

The operating parameters are Rated power: 30.38 MW; Usable energy: 30.38 MWh; and Round trip efficiency: 87.17% [10].

9.3.5 Tehachapi Energy Storage Project (TSP) at the Monolith Substation of Southern California Edison (SCE) in Tehachapi, CA, USA

Source: Wikipedia (from https://www.sandia.gov/ess-ssl/publications/SAND2015–5242.pdf)

It is a lithium-ion battery-based grid energy-storage system. At the time of installation in 2014, this system was the largest lithium-ion battery system in North America and one of the largest in the world. This energy-storage project can supply 32 MWh of power at a maximum rate of 8 MW. This energy is adequate to power around 1,600 to 2,400 homes for a period of 4 hours.

It is the first battery energy-storage system integrated with SCE’s systemwide Supervisory Control and Data Acquisition (SCADA) system providing high-level visibility and control to grid operators.

TSP is a modern energy-storage harbinger with substantial activities establishing the feasibility of utility-scale energy-storage using lithium-ion technology. Though initially proposed as a R&D project, TSP remains functioning today as a distribution-level resource for

Southern California Edison. The system was tested for the 13 operational uses listed below:

(a) *Transmission*: Voltage support, decreased losses, diminished congestion, increased system reliability, delayed transmission investment, optimized renewable-related transmission;

(b) *System*: System capacity/Resource adequacy, renewable integration (firming & shaping), output shifting

(c) *ISO market*: Frequency regulation, spin and non-spin reserves, deliver ramp rate, energy price arbitrage

For 2020, SCE reported that TSP operated in the extensive energy market with revenue exceeding operating and maintenance costs.

9.3.6 Grid-scale Battery Storage System in India

India's first grid-scale battery-based energy-storage system, 10 MW/10MWh, owned by AES Corp. and Mitsubishi Corp., and operated by Tata Power Delhi Distribution Ltd. (Tata Power-DDL) was launched in February 2019 at Rohini, Delhi.

The project (shown in Figure) is located at a substation operated by Tata Power-DDL. The facility is ready to be upscaled to 20 MWh at any time [Indo-German Energy Forum]. As South Asia's largest grid-scale energy-storage system, it is expected to play a key role in enhancing the flexibility and reliability of India's power grid.

(Source: https://www.powermag.com/india-installs-its-first-grid-scale-battery storagesystem/)

The System is designed to provide grid stabilization, better peak-load management, add system flexibility, enhance reliability, and protect critical facilities for 2 million consumers served by Tata Power-DDL. Fluence, a supplier of energy-storage technology jointly owned by AES and Siemens, supplied its Advancion technology for the project. Fluence has more than a decade of experience deploying and operating grid-scale battery-based energy-storage projects, with over 730 MW deployed or contracted around the world.

Indian officials hope the project paves the way for wider adoption of grid-scale energy-storage across the country. Grid-scale energy-storage will facilitate ancillary market services, power quality management, effective renewable integration and peak-load management of Indian grids, according to Tata Power.

9.4 Examples of BES Systems Operating World-wide [11, 12]

It’s clearly established that the rapid increase of intermittent renewable wind and solar world-wide has led to a strong incentive to develop large-scale energy-storage for electricity.

The scope of development of electricity storage will decide the extent of displacement of dispatchable sources by renewable sources, accepting excess power at appropriate times and linking intermittency intervals. Also exist, large scale difficulties, particularly power and energy capacity, and the need for the availability of stored electricity over days and weeks rather than minutes and hours.

Storage systems for electricity include battery, flywheel, compressed air, and pumped hydrostorage, which have different limits in the total amount of energy they can store. Electricity storage systems are also designed to provide ancillary services to a transmission system, including frequency control, which is the main function of grid-scale batteries today.

Cost projections: World Energy Council (January 2016) anticipated a considerable reduction in cost for most of the energy-storage technologies as from 2015 through 2030. Battery energy-storage technologies displayed the maximum cost reduction, and then by sensible thermal storage, latent thermal storage and supercapacitors. BESS showed a cost range of €100–700/MWh in 2015 and is estimated to lessen to €50–190/MWh in 2030, over 70% decrease in the upper cost limit in the next 15 years. Then, follows sodium-sulfur, lead-acid and lithium-ion battery technologies. The WEC report models storage associated with wind and solar plants, evaluating the ensuing levelized cost of storage (LCOS) in specific plants. The analysis finds that the load factor and the median discharge time at rated power mainly contributes to the LCOS though the cycle frequency is a minor factor. The solar-energy-storage case considered was daily storage with six-hour discharge time at rated power, and for the wind-related storage considered was for two-day storage with 24 hours discharge at rated power. In the first one, the most economical storage technology had LCOS of €50–200/MWh. In the latter one, levelized costs were higher and susceptible to the number of discharge cycles per year, and few technologies looked attractive [Ref: World Energy Council (2016): Estorage: Shifting from cost to value Wind and solar applications, January 2016 @ https://www.worldenergy.org/assets/downloads/Resources-E-storage-report-2016.02.04.pdf]

Battery Energy-storage Requirements

It is established that the battery should have high energy density, high power, long life (large charge-discharge cycles), high round-trip efficiency, safety, and reasonable cost to be considered for energy-storage. Discharge duration and charge rate are other attributes. Several concessions are allowed among these criteria, comparing the limitations of BESS with dispatchable generation sources.

Another aspect, ‘energy return on energy invested (EROI)’ that intensely related to ‘service life’ of a battery and how its round-trip efficiency sustains over that period. The PCS together with inverter to connect to a normal AC system enhances about 15% to the basic battery cost.

Several MW-scale projects have revealed that batteries are highly appropriate to smoothing the variability of power from wind and solar systems over periods extending from minutes to even hours, for their short-time integration into the grid. It is also established that batteries can react more swiftly and consistently than conventional resources like spinning reserves and peaking plants. Therefore, large battery arrangements are the preferred stabilization technology for integrating transient renewables to the grid. This, being a function of power, the demand for it is much lower than for energy-storage.

At household level, behind-the-meter, battery storage is being promoted. There is clear compatibility between solar PV and batteries as both generate DC.

In Germany, solar PV has an average 10.7% capacity factor, and 41% of new solar PV systems in 2015 were arranged with back-up battery storage, contrary to 14% in the previous year.

KfW Development Bank organizes low-interest government loans and payback support up to 25% of the total investment costs; hence, the bank suggests that sufficient PV electricity be used for onsite intake and storage so that not exceeding half of the output goes to the transmission network. By doing this, 1.7 to 2.5 times the usual solar capacity can be accepted by the grid without causing overloading.

The IRENA (2017) estimates that the world needs 150 GW of battery storage to meet IRENA's desired target of 45% of power generated from renewable sources by 2030.

Some Installations [8]

(a) Lithium-ion, NaS, and VRF battery systems

Over one-third of the 1.5 GW 'battery storage' in 2015 was lithium-ion batteries, and 22% was sodium-sulfur batteries. In Germany, installed utility-scale battery storage increased from about 120 MW in 2016 to about 225 MW in 2017.

**In 2015 lithium-ion batteries accounted for 86% of deployed ESS power capacity. An estimated 1,653 MW of new ESS capacity was announced globally in 2015. Li-ion batteries are the most popular technology for distributed energy-storage systems, which have a 95% round-trip DC efficiency, falling to 85% when the current is converted to AC for the grid. Depending on use, they have a 10–20 year lifespan.

**A large BESS is a 40 MW/20 MWh Toshiba Li-ion system at the Nishi-Sendai substation owned by Tohoku Electric Power Company in Japan, commissioned early in 2015, and San Diego Gas & Electric has a 30 MW/120 MWh lithium-ion BESS in Escondido, California.

The 2 largest grid storage batteries in the U.S. used lithium-ion batteries, each with a capacity of 31.5 MW, one at Grand Ridge Power plant in Illinois and the other at Beech Ridge, West Virginia.

Tesla erected a 52 MWh lithium-ion battery storage facility on Kauai, Hawaii in 2017, to time-shift the output from a 13 MW solar farm to the evening. The objective was to avoid the use of fossil fuels on the island.

In Ontario, Canada, battery storage with 13 MW/53 MWh capacity was established by 2016 with batteries from the Swiss battery manufacturer Leclanche .The storage unit was intended to provide mainly voltage and reactive power control and other fast grid services. There are many wind and solar power generating plants in and around Ontario, resulting in wide variations in the power supply.

In South Australia, a 100 MW/129 MWh Li-ion system of Tesla was deployed next to Neoen’s Hornsdale wind farm of 309 MWe near Jamestown. The state government uses about 70 MW of the capacity to make available for grid stability and system security, and frequency control ancillary services (FCAS) via a Tesla's Autobidder platform in timerange of 6 seconds to 5 minutes. The remaining 30 MW having 3 hours of storage is used as load shifting by Neoen for the nearby wind farm. The system has shown effectively a quick response for FCAS, delivering up to 8 MW for about 4 seconds before slower contracted FCAS interrupt at the falling frequency below 49.8 Hz.

Nord GmbH & Co. KG, an energy-storage company has been handling some largest hybrid batteries in Braderup (Schleswig-Holstein, Germany) from July 2014. The hybrid storage system comprises a lithium-ion battery storage (2 MW/ 2 MWh) and a vanadium flow battery storage (330 kW/ 1 MWh). The system is connected to the local community wind park of 18 MW capacity. Sony made the Li-ion modules, and Vanadis Power GmbH manufactured the flow batteries.

Several kinds of Li-ion batteries are available: some having high energy density and fast charging applicable to EVs, and others such as lithium iron phosphate (LFP), which are heavier, less energy-dense but with extended cycle-life.

**The costs of Lithium-ion battery fell by two-thirds between 2000 and 2015, to about $700/kWh, mainly by the high demand in the vehicle market. A further drop of 50%

of cost is projected by 2025. However, power conversion system (PCS) costs have not fallen at the same rate and added about 15% to battery cost in 2015 for non-vehicle applications.

**In Germany, STEAG has planned to set-up 90 MW battery storage system at its Lunen coal-fired plant site. The first of the six 15 MW lithium-ion units was energized in June 2016. The batteries must answer automated calls within 30 seconds and be able to feed-in for a minimum of 30 minutes to be eligible for a commercial operation.

**RWE has set-up a 7.8 MW/7 MWh lithium-ion battery system at its Herdecke power station site near Dortmund. Here the utility operates a pumped hydrostorage plant since 2018.

**A 10 MW/10.8 MWh Li-ion battery storage system was started in 2015 at Feldheim, Brandenburg. The system comprises 3360 lithium-ion modules from LG Chem of South Korea. This battery storage system stores power produced by a local 72 MW wind farm, installed to stabilize the grid of TSO 50 Hz Transmission. The unit also partakes in the weekly tendering for primary control reserve.

** Eneco and Mitsubishi (as EnspireME), a utility of Netherlands installed a 48 MW/50 MWh Li-ion battery in Jardelund, Germany. The battery was to deliver primary reserve to the grid and improve grid stability in the area where many wind turbines were located and troubled with grid congestion issues.

**In Spain, Acciona installed a wind power plant with BESS in May 2017. Samsung supplied 2 Li-ion battery systems to the plant, 1 MW/390 kWh and the other 0.7 MW/700 kWh. These are connected to the 3 MW wind turbine and on to the power grid. Both systems appear to have a frequency response as part of their task.

**In May 2016, Fortum of Finland arranged with French battery supplier Saft for the delivery of a MW-scale lithium-ion battery energy-storage system for its Suomenoja power plant. It would have a nominal output of 2 MW and capable of storing 1 MWh of electricity. This would be offered to the TSO for frequency regulation and output smoothing. It would be akin to the system operating in the Aube region of France, linking 2 wind farms of 18 MW total capacity.

**In the UK, 475 MW of battery storage was in service since August 2019. Out of these 11 projects ranged from 10 to 87 MW, most with improved frequency response deals.

Renewables Energy Company (RES), using Li-ion battery energy-storage system, provides 55 MW of dynamic frequency response to national grid. RES already has installed more than 100 MW/60 MWh of battery storage systems mostly in North America.

**EDF’s Pivot Power (UK) intended a 2 GW storage facility for a network of grid-scale batteries for ancillary grid services and for charging electric vehicles. In March 2020, Finland’s Wartsila was given a contract to supply two 50 MW lithiumi-ion batteries to this facility. Downing LLP deliveries one-third of 50 MW battery at Southampton.

**In Northern Ireland, AES (USA) completed a 10 MW/5 MWh energy-storage facility at its Kilroot power station in Carrickfergus. The system comprises over 53,000 Li-ion batteries organized in 136 separate nodes with a control system that responds to changes in the grid in less than a second. It was the biggest modern energy-storage system in the UK and Ireland, and the only such system at transmission scale.

**On the Orkney Islands of UK, a 2 MW/500 kWh Li-ion battery storage system is operating. This Kirkwall power station uses Mitsubishi batteries and store power from wind turbines. The project is for demonstrating power supply stabilization in the islands.

**In Somerset, Cranborne Energy Storage has a 250 kW/500 kWh Tesla Powerpack Li-ion storage system integrated with a 500 kW solar PV set-up. The Tesla Industrial Powerpack unit is 50 kW/210 kWh, with 88% round-trip efficiency. The powerpacks can be configured to provide power and energy capacity to the grid as a standalone asset, offering a frequency regulation, voltage control, and spinning reserve services.

**Statoil has commissioned a 1 MWh lithium-ion battery system, Batwind, for onshore storage for the 30 MW offshore Hywind project at Peterhead, Scotland. It was intended to store excess generation, reduce balancing costs, and let the project regulate its own power supply and seize peak prices through arbitrage.

**In August 2015, GE was contracted to build a 30 MW/20 MWh lithium-ion battery storage system for Coachella Energy Storage Partners (CESP) in California. The 33 MW facility completed by ZGlobal in November 2016 offers grid flexibility and improved dependability on the Imperial Irrigation District network by providing solar enlargement, frequency regulation, power balancing and black start capability for a nearby gas turbine.

SDG&E's 30 MW battery storage facility in Escondido, California. (Photo: San Diego Gas & Electric)

**San Diego Gas & Electric (SDG&E) got a 30 MW/120 MWh lithium-ion BESS in Escondido, installed by AES Energy Storage. This system delivers evening peak demand, and partially substitutes for the Aliso Canyon gas storage, discarded due to a massive leak. (It was used for peak-load gas generation.)

**Vistra has entered into a 10-year resource adequacy agreement in July 2020 with PG&E Company for a new 100 MW/400 MWh lithium-ion battery to complement the 300-MW/1200-MWh battery already under construction at its Moss Landing Power Plant site. Vistra’s total contract of battery energy-storage in California stands at 436.25 MW/ 1,745 MWh, with distribution, Moss Landing- Phase I (300-MW/1,200 MWh), Moss Landing - Phase II (100 MW/400 MWh), and Oakland (36.25 MW/ 145 MWh) (ref: https://investor.vistracorp.com/investor-relations/news/press-release-details/2020/Vistra-Announces-Next-Phase-of-Battery-Energy Storage Systems-at-its Moss Landing-Facility/default.aspx).

**In July 2020, PG&E and Tesla Inc. began construction of a 182.5 MW lithium-ion battery energy-storage system at PG&E's electric substation in Moss Landing in Monterey County. This unit expects to be operational in 2021(https://www.pge.com/en/about/newsroom /newsdetails/index.page? title=20200729_pge_tesla_break_ground_on_landmark_battery_energy_storage_system).

**Southern California Edison (SCE) started installing a 100 MW/400 MWh battery system comprising 80,000 Li-ion batteries in containers to be commissioned in 2021; (2) SCE proposed another project, a 20 MW/80 MWh storage for AltaGas Pomona Energy at its San Gabriel natural gas-fired plant; (3) SCE’s Tehachapi 8 MW/32 MWh lithium-ion battery storage project in conjunction with a 4500 MWe wind farm is a large project using 10,872 modules of 56 cells each from LG Chem, which can supply 8 MW over 4 hours; (4) For SCE’s Mira Loma substation, Tesla contracted in 2016 to supply a 20 MW/80 MWh lithium-ion battery storage system to help meet daily peak demand.

**The 98 MW Laurel Mountain wind farm in West Virginia employs a multi-use 32 MW/8 MWh grid-connected BESS. The lithium-ion batteries were made by A123 Systems, and the plant was responsible for frequency regulation and grid stability in the PJM market as well as arbitrage. It was considered the largest lithium-ion BESS world-wide at the time of deployment in 2011.

**EDF Renewable Energy commissioned a battery energy-storage project with 40 MW flexible capacity on the PJM grid network in Illinois in Dec 2015. This facility was to be operated in the regulation and capacity markets. BYD

America supplied Li-ion batteries consisting of 11 containerized units totaling 20 MW and power electronics.

**Texas Waves energy-storage projects installed by E.ON in early 2018 consists of two 9.9 MW short duration lithium auxiliary services to the Electric Reliability Council of Texas market and respond to power demand changes more rapidly, enhancing system reliability and efficiency.

**272 Tesla Powerpacks (Li-ion storage system) was used by SolarCity for its 13 MW/52 MWh solar PV project in Kauai Island, Hawaii, to take care of evening peak demand. Kauai Island Utility Cooperative (KIUC) along with AES commissioned a 28 MW solar farm and 20 MW/100 MWh battery system.

**Toshiba delivered a large BESS to Hamilton, Ohio, consisting of 6 MW/2 MWh lithium-ion batteries. This system is expected to have a lifetime of over 10 thousand charge-discharge cycles.

**Powin Energy and Hecate Energy built 2 projects totaling 12.8 MW/52.8 MWh in Ontario, for the IESO. Powin’s Stack 140 battery array of 2 MWh will comprise the systems, at Kitchener (20 arrays) and Stratford (6 arrays).

**Sodium-sulfur batteries (NaS)* are in use for over 25 years and are well proven, though costly. Since they operate at about 300°C, some power intake is necessary even when unused.

PG&E’s 2 MW/14 MWh NaS battery energy-storage system has a cycle-life of about 4500 cycles, and round-trip efficiency was 75% in an 18-month trial. The trials of PG&E showed that they need to be co-located with the wind or solar farms if they were to be used for energy arbitrage, generally far away to the main load center. But, to use for frequency regulation, preferable to locate close to the urban or industrial load centers. Since the frequency regulation is far better than arbitrage, utilities normally avoid distant locations for their assets. The study revealed that batteries were still far from cost-effective, even assuming a 20 year battery life. Operational control proved extremely complex.

**A large utility-scale 4 MW NaS battery storage system was installed in Texas to offer upgraded reliability and power quality for the Presidio city. Energized early in 2010, the system affords rapid standby for wind capacity in the local ERCOT grid. Sodium-sulfur batteries are extensively used for similar roles.

**In Anchorage, Alaska, a 2 MW/0.5 MWh battery system is accompanied by a flywheel to assist use of wind power.

** Chuckwalla solar farm in Nevada will have a rated capacity of 200 MW solar and 180 MW/720 MWh storage. Considered the largest, it will be developed, built and operated by EDF Renewables and expected to reach commercial operation by the end of 2023 (PV Magazine, Aug, 2020).

**The US unit of German developer and EPC provider juli has entered a PPA with Colorado Springs Utilities for a 175 MW solar project coupled with a 25 MW battery storage system.

The Pike Solar and Storage project will be located in El Paso County, Colorado, and slated for completion in 2023. Connected to both the solar array and the electric grid, the battery will have a discharge duration of 4 hours (100MWh).

**Ontario's ISO has contracted a 2 MW zinc-iron redox flow battery from ViZn Energy Systems.

In China:

**NDRC of China has announced to install several 100 MW capacity vanadium redox flow battery (VRF) by 2020 end. Further, the following systems would be installed: (a) 10 MW/100 MWh supercritical compressed air energy-storage system, (b) 10 MW/1000 MJ grade flywheel energy-storage array unit, (c) 100 MW lithium-ion battery energy-storage systems, and (d) a new type of large-capacity molten salt storage device.

**Canada-based VRB Energy stated (Energy Storage news, March 16, 2021) that a solar PV power plant would be incorporated with a 100MW/500MWh (five-hour duration) battery, which was under construction in Xiangyang in China.

**Rongke Power announced a 200 MW/800 MWh Vanadium RFB storage at Dalian, China to provide peak demand, improve grid stability, lesson restriction from adjacent wind farms, and provide a black start capacity. The first phase of 100MW/400MWh was initially listed for completion during 2020, but so far it was not declared. [Black Start is the practice used to restore power when a total or partial shutdown of the national electricity transmission system happens.]

**VRB Energy planned to develop several flow cell battery projects in China: In Qinghai province, 2 MW/10 MWh for connecting to the wind; In Hubei province, 10

MW/50 MWh system to integrate into solar PV, expected to increase to 100 MW/500 MWh; In Lianlong province, 200 MW/800 MWh system for linking to renewables; In Jiangsu 200 MW/1000 MWh unit for offshore wind integration.

In Japan:

**Hepco in Japan installed in 2015, a 15MW/60 MWh system with VRF batteries supplied by Sumitomo.

**Sumitomo would deliver to Hokkaido Electric Power a grid-scale VR flow battery energy-storage system of 17MW/51 MWh capable of 3-hour storage for a wind farm in northern Japan. This is due on-line in 2022. Sumitomo has already set-up a 60 MWh VRFB in the same region in 2015.

In Australia:

**Near Lakeland in Australia, a 10.4 MW solar PV plant would be linked to 1.4 MW/5.3 MW of lithium-ion BESS as edge of grid set-up; it operates in island mode during evening peak time. It would use the Conergy Hybrid Energy Storage Solution plant, and the project would lessen the necessity for upgrading the grid.

**In South Australia a 330 MWe solar PV plant is proposed by the Lyon Group, backed up by a 100 MW/400 MWh BESS.

Near the Olympic Dam mine in the north of the state, 120 MW solar PV plus 100 MW/200 MWh BESS Kingfisher project is proposed.

**A large battery system, 120MW/140 MWh is planned in South Australia along with the Cultana 280 MWe solar PV project to serve Arrium’s Whyalla steelworks.

**In Victoria, at Gannawarra near Kerang, a 25 MW/50 MWh Tesla Powerpack battery was integrated with a 50 MWe solar farm and operating sinc 2018.

**In northwest Australia, a 35 MW/11.4 MWh Kokam lithium-ion battery alongside a 178 MWe gas-fired plant has been operating since September 2017 on a private grid serving mines. It enables frequency control and stabilizing the small grid. An addition of 60 MWe of solar capacity has been proposed for which a second battery storage system is expected.

**GE started developing a 1.2 MW lithium-ion battery to function in several units with wind power generation plant, in its Reservoir project.

**Neoen planned a 20 MW/34 MWh battery addition to a 196 MWe wind power generating farm at Stawell in Victoria.

In Rwanda, Germany’s Tesvolt supplied 2.68 MWh of battery storage made of Samsung Li-ion cells in 4.8 kWh modules to provide back-up power for agricultural irrigation, off-grid. The supplier claims 6000 full charge cycles with 100% depth of discharge over a service life of 30 years.

In Brazil, the mining company Vale and Siemens and MicroPower Comerc joined to put up a 5MW/10MWh lithium-ion battery storage system at a huge port facility in Rio de Janeiro. This system comprising Tesla Megapacks charge when power demand is low and discharge in periods of peak demand.

***In Jordon,* Albadyia Power Generation Plant has a 3MW/12.6 MWh capacity storage unit that uses 60 Tesla

Power packs containing Li-ion batteries, integrated with 23MWp of solar PV system. The plant, installed in 2019, aimed to improve the grid by power peak shaving and power shifting; further, expected to smooth the power generation variations to increase grid stability and help the grid at peak-load time in the night. Also, it boosts the accessible energy during the daytime. In the MENA region, it is the first operated commercial utility-scale PV plus energy-storage system for these purposes.

(b) Other battery storage systems

**Eos Energy Storage (USA) optimized its Znyth aqueous *zinc battery* for utility grid support, delivering nonstop discharge for 4 to 6 hours. It includes 4 kWh units constituting 250 kW/1 MWh subsystems and a 1 MW/4 MWh complete system.

**Duke Energy has tried a *hybrid ultra capacity battery storage* system close to a 1.2 MW solar farm in North Carolina. The 100 kW/300 kWh battery storage uses aqueous hybrid ion chemistry with salt water electrolyte using synthetic cotton separator. The fast-response ultracapacitors help smooth the load fluctuations.

**The inexpensive *Lead acid batteries* with up to 1MW arrays are extensively used to stabilize wind power generation at small-scale utility. Some can provide up to 4000 discharge cycles, and can be completely recycled after their effective life. These are much cheaper than lithium-ion batteries.

**The Ecoult Ultra Battery connects a valve-regulated lead-acid battery and an ultracapacitor in a single cell, providing an extraordinary partial-state-of-charge operation efficiently and a long life.

S&C Electric installed a 250 kW/1000 kWh Ultra Battery system comprising 1280 Ecoult batteries at Albuquerque, New Mexico in 2011 to function in association with a 500 kW solar PV system, mainly meant for voltage regulation.

**The largest lead-acid battery storage system in Australia is 3 MW/1.5 MWh system located on King Island.

**Stanford University developed an aluminium-ion battery (Al-air), affirming low flammability and high-charge storage capability over 7500 cycles and low cost. This battery comprises an aluminum anode, graphite cathode and salt electrolyte, but generates small voltage only.

***Domestic-scale BESS*

Tesla reported in May 2015, a battery storage system of 7 or 10 kWh using lithium-ion batteries for storing electricity generated from renewables at the domestic level. It will deliver 2 kW and works at 350450 volts. Though this is domestic-scale, it will have grid implications if used at large-scale.

Powervault, UK supplies assorted batteries for household use, mainly with solar PV but also aiming savings with smart meters. Its 4 kWh lead-acid battery is the most popular product, although the batteries need replacing every 5 years.

LG Chem offered a range of both low and high voltage batteries in North America in April 2017. The range extends from 48-volt batteries at 3.3, 6.5, and 9.8 kWh energy to 400-volt batteries with 7.0 and 9.8 kWh energy.

Domestic-level lithium-ion storage units are subject to fire limitations, which prohibit them fixing to the walls of the house.

(c) Compressed air energy-storage

**Duke Energy and 3 other companies are developing a 1200 MW CAES in Utah, auxiliary to a large 2100 MW wind farm and other renewable energy sources. This project called Intermountain Energy Storage Project, uses salt caverns. It is intended to have a 48-hour discharge duration to link intermittency gaps, hence apparently over 50 GWh. The system is also projected to store surplus solar power supplied from Southern California. The plan is to construct in 4 stages, each 300-MW.

**A 550 GWh/year CAES project was planned by Gaelectric Energy Storage at Larne, Northern Ireland.

**The Gill Ranch CAES project in the U.S. is presently modified to be a compressed gas energy-storage (CGES) unit using natural gas instead of air. The gas is stored at pressure of about 2500 psi and a temperature, 38°C. To expand pipeline pressure to 900 psi, preheating is essential to avoid water and hydrate formation.

**Toronto Hydro along with Hydrostor work on a pilot project using compressed air in bladders at 55 m below the water surface in Lake Ontario to generate 0.66 MW over one hour.

(d) Cryogenic storage

Highview Power, UK put up a 350 kW pilot plant in Slough and a demonstration plant near Manchester of cryogenic storage facility. Based on this experience, the Company announced a 50 MW/250 MWh cryogenic-energy-storage facility, the first on a commercial level, at an abandoned thermal power plant location. This is “a clean large-scale energy-storage facility that can help the UK achieve its goal of decarbonizing industry, power, heat, and transport.” [https://www.powerengineeringint.com/emissions-environment/uk-announces-first-commercial-cryogenic-energy-storage facility/].

Energy can be stored for weeks, instead of hours or days like in batteries, at a projected levelized cost of £110/MWh ($142/MWh) for a 10-hour, 200 MW/2 GWh system.

(e) Thermal energy-storage

Gemasolar of Spain 20 MWe has installed a CSP plant using molten salt with 63% capacity factor. The Company asserts the plant as the first near base-load CSP plant in the world.

The 200 MWe Andasol plant in Spain also uses molten salt heat storage.

A molten salt reactor (MSR) developer, *Moltex* offered a molten salt heat storage concept (GridReserve) to add-on to intermittent renewable energy sources. Moltex developed a 1000 MWe Stable salt reactor working nonstop, deflecting heat at 600°C when demand was low to *nitrate salt* storage similar to that in solar CSP plants. During times of high demand, power output can be doubled to 2000 MWe using the stored heat for close to 8 hours. It is declared that the heat store enhances only £3/MWh to the levelized cost of electricity (LCOE).

** In South Australia, the *1414 Company* developed a heat storage using *molten silicon medium.* This method can stock 500 kWh in a cubeshaped container of molten silicon (70-cm side), which is about 36 times the Tesla’s Powerwall in almost the same space. The melting point of silicon is 1414°C. It discharges through a heat-exchanger such as a

Stirling engine or a turbine and recycles the heat. A 10 MWh unit would approximately cost Australian $ 700,000.

**Ice is another form of energy-storage. *Ice Energy* has requests from Southern California Edison to deliver 25.6 MW of thermal energy-storage using its Ice Bear system, connected to large air conditioning units. This method makes ice at night when power demand is low, providing cooling during the day alternative to air conditioning compressors, thus decreasing peak demand.

(f) Hydrogen storage & fuel cells

**Siemens has installed a 6 MW hydrogen storage plant in Germany applying *proton exchange membrane (PEM)* technology to turn excess wind power into hydrogen. This hydrogen can be used in fuel cells or add to natural gas supply. The hydrogen storage plant located in Mainz is the largest PEM system in the world.

**Hydrogenics joined with German utility E.ON in Ontario to set-up a 2 MW PEM facility that began functioning from August 2014, splitting water into hydrogen through electrolysis. The efficiency of the entire process, electrolysis to fuel cells to electricity is around 50%.

**San Diego Gas & Electric and Israeli GenCell are jointly working to install 30 GenCell G5rx utility back-up fuel cells at its substations. These are hydrogen-based alkaline fuel cells providing 5 kW output. They are manufactured in Israel, and used internally by Israel Electric Corporation.

(g) Flywheels

Flywheel energy-storage systems store kinetic energy and have an effective cycle-life of tens of thousands of recharging cycles.

**ISO of Ontario ordered for a 2 MW flywheel storage system from NRStor Inc., Canada.

**Hawaiian Electric Co is setting up 80 kW/320 kWh flywheel system obtained from Amber Kinetics for its Oahu grid. This one module has the potential of several. Usually flywheels that store kinetic energy and all set to transform into electricity, are employed for frequency control rather than energy-storage; they supply energy over a short period and each can provide up to 150 kWh. Amber Kinetics asserts they are capable of four-hour discharge.

**Stornetic of Germany fabricates DuraStor units having capacities from tens of kilowatts up to about a megawatt. The uses are many and vary from regenerative braking for trains to providing subsidiary services to wind farms.

**The major use of flywheels is in ‘diesel rotary uninterrupted power supply (DRUPS)’ set-ups, with 7 to 11 second ride-through synchronous function in the startup of an integrated diesel generator subsequent to the breakdown of main supply. This provides enough time, for example 30 sec, for normal diesel standby to start.

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Glossary

A

AC: Alternating current; household current is AC.

AC Batteries: the combination of batteries, a battery management system and inverter-charger in a single unit, allowing AC coupling to a power system.

AC Coupled System: a PV inverter coupled with a hybrid inverter, or combination inverter-charger, to manage battery storage.

Acid: chemical substance in a battery that promotes electro chemical reaction

Active power: The portion of electricity that establishes and sustains the electric and magnetic fields of AC equipment.

Advanced Adiabatic CAES (AA-CAES): a traditional CAES integrating with a thermal-energy-storage subsystem, which has no fuel combustion in the expansion mode. Here, the heat generated during compression is removed and stored separately, and used again during the expansion before running through the turbine. This process may increase the roundtrip efficiency.

Advanced inverter: An electronic device that transforms variable direct current (DC) to AC and that delivers functions like reactive power control and voltage and frequency ride-through responses to improve the stability, reliability, and efficiency of the distribution system.

Absorbed Glass Mat (AGM) Batteries: They use an Absorbed Glass Matt (AGM) process, superior to traditional flooded technology. Fine, highly porous, micro-fiber glass separators (boron-silicate mat) absorbs the electrolyte, increasing efficiency by lowering internal resistance, which in turn boost capacity.

Ampere-hour: A unit of charge represented as Ah. For example, drawing a current of one ampere (1A) from a battery for one hour (1h) equates in one ampere-hour (1Ah).

Ancillary Grid Services: Non-electrical energy services that generation resources provide to maintain a reliable grid system; they are spinning and non-spinning reserve, frequency regulation, ramping up or down, voltage control, black start capability and other services defined by a grid operator or utility control operator.

Anode: Electrode on which oxidation occurs; releases electrons on discharge

Application: A combination of end uses and benefits that an energy storage system may capture when positioned at a specific location and managed in a particular way.

Area control error: The instantaneous difference between a Balancing Authority’s net actual and scheduled interchange, taking into account the effects of Frequency Bias and correction for meter error.

Automatic Generation Control (AGC): A regulatory mechanism that provides for automatically adjusting generation within a balancing area from a centralized location to maintain a specified frequency and/or scheduled interchange.

B

Back-up Power: Electric energy supplied by an electric provider during an unscheduled outage of the distribution system. Energy-storage is a best bet.

Balancing authority: The responsible entity that integrates resource plans ahead of time, maintains load-interchange-generation balance within a Balancing Authority Area, and supports Interconnection frequency in real time.

Balancing (authority) area: The collection of generation, transmission, and loads within the metered boundaries of the balancing authority that maintains balance between electricity supply and demand within this boundary.

Base load: The minimum amount of electric power delivered or required over a given period at a constant rate.

Base load generating plants: Normally coal or nuclear generating units, that are usually devoted and dispatched at constant or near-constant levels with minimum cycling.

Battery: Electrochemical cells composed of the anode (negative electrode), cathode (positive electrode), separator and electrolyte as catalyst, and connected in series or parallel

Battery Cycle: Charge followed by a discharge and recharge. No standard exists as to level of charge and discharge to constitute a cycle.

Battery Energy Storage Systems (BESS): Devices that enable energy from renewables, like solar and wind, to be stored and then released when customers need power most. Intelligent battery software uses algorithms to coordinate energy production and computerised control systems are used to decide when to keep the energy to provide reserves or release it to the grid.

Battery Management System (BMS): An electronic system that manages a rechargeable battery (cell or battery pack) by protecting it from operating outside its safe operating area, monitoring its state, calculating secondary data and reporting that data, controlling its environment, authenticating it and/ or balancing it.

Black-start: A generating unit which has the ability to be started without support from the System with the capability to energize a bus, meeting the restoration plan needs for real and reactive power capability, frequency and voltage control.

C

Capacity: (a) The maximum generation of a power plant, measured in a kilowatt (kW), megawatt (MW), or gigawatt (GW); also be referred to as peak capacity. Also, (b) Electrical charge of battery in ampere-hours (Ah), and is the health indicator of a battery

Capacity (energy storage): The capacity of a storage system is defined as the amount of energy that it can deliver in discharge; typically specified in amp-hours or in watt-hours.

Capacity factor: A measure of how much energy is produced by a plant compared with its maximum output, and measured as a percentage.

Capacity credit: The contribution of a power plant to reliably meeting demand.

Capacitor: device consisting of two conductive surfaces separated by an insulator. Passes AC; indefinite resistance for DC; voltage lags behind the current (opposite of a coil).

Carbon fiber composite: Carbon fibers are combined with other materials to form a composite. For e.g, when permeated with a plastic resin and baked, it forms carbon-fiber-reinforced polymer which has a very high strength-to-weight ratio and is extremely rigid although somewhat brittle. Carbon fibers are also composited with other materials, such as graphite, to form reinforced carbon-carbon composites, which have a very high heat tolerance.

Carbon Nano Tubes (CNTs): cylinder-shaped allotropic forms of carbon, most widely produced by chemical vapor deposition, and typically measured in nanometers; possess astonishing chemical, electronic, mechanical, and optical properties.

Cathode: Electrode in an electrochemical cell in which reduction takes place by absorbing electrons. During discharge, the cathode is positive; reverse on charge

Charge/Discharge Cycle: The operational profile of an energy storage device that defines how much of the time it must be used to store electrical energy versus how much time it is available to supply electrical energy or other services. This could also be referred to as the “duty cycle”.

Chemical energy: the energy stored in the bonds of atoms and molecules.

Chemical heat storage: *also called thermochemical heat storage, these* systems use thermochemical materials to store and release heat in a reversible endothermic/exothermic reaction process.

Climate change: Refers to long-term shifts in temperatures and weather patterns that may be natural; since mid-1800s, human activities, primarily due to the burning of fossil fuels which produces heat-trapping gases, have been the main driver of climate change.

Combined Heat and Power (CHP): Electricity and thermal energy-storage can be used in combined heat and power facilities to link temporal gaps between electricity and thermal energy demand.

Complex hydrides: Materials that have a crystal lattice structure consisting of complex anions as hydrogen is covalently bound to the central atoms.

Compressed Air Energy Storage (CAES): a power-to-power energy-storage option, which converts electricity to mechanical energy and stores it in the subsurface; uses electricity in the off-peak times to compress air at high pressures and store it in large underground caverns or depleted wells. The compressed air can also be stored aboveground using high-pressure pipes and/ or vessels. When electricity is needed, the compressed air can be released and directed through turbines to generate power.

Contingency: The unexpected failure or outage of a system component, such as a generator, transmission line, circuit breaker, switch or other electrical element.

Contingency reserves: Reserves used to respond to an unexpected failure or outage of a system component, such as a generator, transmission line, circuit breaker, switch or other electrical element

Coulomb: Unit of electric charge. One coulomb equals one ampere per second.

Coulombic Efficiency: also faradaic efficiency or current efficiency: describes the charge efficiency by which electrons are transferred in a batteries

C-rate: Unit by which charge and discharge times are scaled. At one coulomb, the battery charges and discharges at a current that is at par with the marked Ah

Cranking battery: *see* Start battery

Cryogenic energy storage: *see* Liquid-air energy storage

Curtailment: A reduction in the output of a generator from what it could otherwise produce given available resources.

Cycle life: Number of cycles a battery can deliver (End of battery life for portable devices is commonly set to 80%)

D

DC: Direct current; current flows in one direction. A battery delivers a DC current.

DC Coupled System: system to charge batteries using PV modules and charge controllers, and an inverter to supply AC power.

Deep cycle battery: Designed to discharge by as much as 80% of their capacity (depth of discharge) over thousands of charging and discharging cycles; used to store electricity in autonomous power systems (e.g., solar energy system) for emergency back-up and in EVs.

Demand charge: Consumers in industrial and business sectors pay for both the electricity consumed and for the maximum power they draw; this charge called ‘demand charge’ reaches about 50%of total power costs. Instead of drawing from the grid, energy-storage can be used to save the costs significantly.

Depth of Discharge (DoD): 100% is full discharge; 80% commonly used for specification.

Demand Response: the variation in the power intake of a consumer to better match the demand for power with the supply.

Demand Side Management (DSM): Demand-side management and demand response allow consumers to partake in load control based on price indications.

Dielectric: an electric insulating material

Dispatchability: Operational control during the times when a storage resource is employed to generate, supply or charge electrical power.

Distribution system operator: An entity responsible for operating, maintaining, and developing the distribution system and its interconnections with other systems.

Duration: A measure of how long a storage device can discharge, or supply electrical energy; may be measured in a range from milliseconds to hours.

Dynamic transfer: Facility for the real-time monitoring, telemetering, computer software, hardware, communications, engineering, energy accounting (including inadvertent interchange), and administration required to electronically move all or a portion of the real energy services associated with a generator or load out of one Balancing Authority Area into another.

E

Economic dispatch: Allocating demand to individual generating units on line to effect the most economical production of power.

Effective Load-Carrying Capacity (ELCC): It is the amount by which the system's loads can increase when the generator is added to the system while maintaining the same system reliability.

Electrochemical Impedance Spectroscopy (EIS): Also known as impedance spectroscopy, used to test electrochemical characteristics of a battery. EIS injects AC signals at different frequencies and analyzes the response.

Electrical energy: a type of kinetic energy caused by moving charged particles such as electrons, and the speed of the charges decide the amount of energy they carry.

Electric energy storage: Technologies capable of storing electricity generated at one time, for use at a later time

Electrode: Conductor or plate in a cell in which an electrochemical reaction occurs

Electrolyte: Non-metallic electricity conductor (typically liquid) placed between positive and negative electrodes of a battery. Ion movement enables current flow.

Energy arbitrage: Refers to extensive purchase and sale of electricity simultaneously, practiced by grid operators. Electricity is bought and stored when the ‘locational minimum price (LMP)’ is low and resell when the LMP increases. This practice is also referred to as ‘storage trade’.

Energy density: Also known as volumetric energy density, specifies the amount of energy a cell can hold in volume (Wh/1).

Energy imbalance service: A market service that provides for the management of unscheduled deviations in individual generator output or load consumption.

Energy Management System (EMS): a system of computer-aided tools used by electric utility grid operators to monitor, control, and optimize the performance of the generation or transmission system. Also, it can be used in small scale systems like micro grids.

Energy Return on Energy Investment (EROI): the amount of energy spent to produce a certain amount of net energy. EROI is an important factor in energy service and electricity pricing. It decreases when energy becomes rarer and more difficult to extract or produce.

Energy Storage (ES): Storing energy that is interconnected to the electric distribution, transmission or electric user site to supply electric energy. Energy storage technologies include batteries and fuel cell storage systems and flywheels and compressed air, pumped hydro, thermal storage etc. Energy-storage allows for improved management of energy supply and demand.

Energy Time Shift: The differential value derived by using energy during off-peak periods to charge an energy storage device that can be discharged during a peak or other period of higher prices.

End Use: A specific, targeted operational use for a resource on the ground that may result in one or more benefits.

Eutectic mixture: Two or more low melting materials with comparable melting and freezing points and nearly melt and freeze without segregation are combined to obtain these mixtures which have high thermal conductivities and densities.

F

Fault: An event occurring on an electric system such as a short circuit, a broken wire, or an intermittent connection.

Fault ride through: The capability of electrical devices, especially wind generators, to be able to operate through periods of lower grid voltage.

Flexibility (operational): Capability of a power system to respond to changes in electricity demand and supply. Operational flexibility is crucial for the transition from the fossil-fuel based power systems to power systems that can efficiently accept a high number of variable Resources.

Flexible generation: Ability of the generation units to change its output (ramp) rapidly, start and stop with short notice, and achieve a low minimum turn-down level.

Flywheel Energy Storage (FES): a mechanical battery where it does not create electricity but simply converts and stores energy as kinetic energy until it is required for use. As electricity can be created from the spinning flywheel within seconds, it makes an ideal choice to help regulate supply in the electrical grid. Suitable mostly to short-term energy storage applications requiring instant power delivery for meeting frequent load fluctuations as well as in power conditioning sectors.

Forced outage: Removal from service availability of a generating unit, transmission line, or other facility for emergency reasons, or the condition in which the equipment is unavailable due to unanticipated failure.

Forecast error: The difference between actual and predicted time-series values of wind and solar resource data.

Frequency Control Ancillary Services (FCAS): a process used by the energy market operator to maintain the frequency of the system within the normal operating band around 50 cycles per second. FCAS provides a fast injection of energy, or fast reduction of energy, to manage supply and demand.

Frequency response: The ability of generation (and responsive demand) to increase output (or reduce consumption) in response to a decline in system frequency, and decrease output (or increase consumption) in response to an increase in system frequency.

Frequency regulation: controlling supply and demand on a *second-by-second* basis to retain the AC current/ frequency within the mandatory tolerance limits. By pumping more of intermittent renewables into the grid, the changes in supply and frequency fluctuations become increasingly recurrent and severe.

Fuel cells: These are electrochemical devices that generate electricity without any intermediate power conversion stage. Their energy density is nearly10 times that of a battery. They produce DC power and thus require power conditioning systems to couple them to the grid.

Fuel gauge: State of charge (SOC) indicator to estimate the charge level of a battery

G

Gasification: a process that converts organic or fossil-based carbonaceous materials at high temperatures (>700°C), without combustion, with a controlled amount of oxygen and/or steam into carbon monoxide, hydrogen, and carbon dioxide; this industrial gas mixture is called syngas.

Gel-type battery: This contains a jellified electrolyte and do not leak. Completely maintenance-free, non-spill and good lead-acid battery. This battery possesses greater resistance to extreme temperatures, shock, and vibration.

Generation-Sited Storage: An energy storage that are co-located with large-scale generation (vs. distributed generation); includes molten salt or other media (co-located with CSP), and storage co-located with natural gas combustion turbines.

Generator trip: A generator failure caused by electrical or mechanical malfunction that causes a emergency condition on a power system. Generator trips occur very quickly, usually within a few cycles.

Global warming: the long-term heating of Earth's climate system observed since the pre-industrial period due to human activities, primarily fossil fuel burning, which increases greenhouse gas levels in Earth's atmosphere.

Governor response: The instant proportional increase or decrease in real power output by generating units, and the natural real power dampening response provided by load, to stabilize system frequency when deviations occur.

Gravitational energy: it is the potential energy stored in an object positioned above the Earth and is released (as kinetic) when the object falls.

Grid/electric: It is the electrical power-transmission network consisting of transmission lines, transformers, substations and so on.

Grid congestion: Situation that occurs when actual or planned flows of electricity over a line or an equipment are constrained below desired levels.

Grid integration of renewable energy: The kind of operation that enables efficient and cost-effective use of renewable energy (or connecting to the grid) while maintaining the stability and reliability of electricity delivery (or power system).

Ground heat exchanger: an underground heat exchanger that can capture heat from and/or dissipate heat to the ground. They use the Earth's near constant subterranean temperature to warm or cool air or other fluids for residential, agricultural or industrial uses.

Graphical User Interface (GUI): It is a system of interactive visual components for computer software. A GUI displays objects that convey information, and represent actions that can be taken by the user. The objects change color, size, or visibility when the user interacts with them.

H

Heat Transfer Fluid (HTF): A gas or liquid that involves in heat transfer by serving as an intermediary in cooling on one side of a process, transporting and storing thermal energy, and heating on another side of a process.

Hybrid Generation Storage System: An energy system that usually consists of two or more renewable energy sources to provide increased system efficiency and balance in the energy system.

Hybrid Inverter Systems: An inverter that operates on grid, off-grid, hybrid operation (both on-grid and off- grid), and for backup.

Hybrid supercapacitors: They have higher operating voltage (3.8 V max) and much higher capacitance and energy density (up to 10 times) than traditional supercapacitors. They also have much lower self-discharge and standby current.

Hydrogen fuel cells: fuel cells which use the chemical energy of hydrogen to cleanly and efficiently produce electricity, and the only products are electricity, water, and heat.

Hydrogen production: a set of industrial methods for generating hydrogen gas. As of today, ~95% of hydrogen is produced from fossil fuels by steam reforming of natural gas and other light hydrocarbons, partial oxidation of heavier hydrocarbons, and coal gasification. Water electrolysis/ water splitting using renewable, nuclear, geothermal and other energy is also used.

Hydrogen storage: a technology which has high storage capacity and low energy cost; requires a similar initial investment as PHS. Hydrogen is highly flammable and is stored at high pressure, which leads to risks.

Hydrolysis: It is a common form of a chemical reaction where water is mostly used to break down the chemical bonds that exists in a particular substance.

I

Independent System Operator (ISO): A transmission operator, or reliability coordinator, who directs the operation of the electric system in real time.

Inertial response: Inertial response is the immediate response to a power disturbance based on a supply-demand imbalance; this response is typically provided by synchronous machines.

Interconnection: An independent electricity system network that operates at a particular frequency, and consists of one or more balancing area authorities that balance demand and generation within certain geographic areas of the interconnection.

Interruptible load or interruptible demand: Demand that the end-use customer makes available to its Load-Serving Entity via contract or agreement for curtailment.

Imaginary impedance (also known as complex impedance): characterizes the electrical resistance of reactive components as a function of frequency.

Internal resistance: Electrical resistance of a battery pack in milli-ohms.

Impedance: Combination of capacitive, inductive and ohmic resistance which is frequency dependent.

Iron-chromium RFB: consists of the soluble redox couples of Fe(II)/Fe(III) as the positive electrolyte, and Cr(II)/ Cr(III) as the negative electrolyte in the acid supporting medium. An ion-exchange membrane separates them.

Isothermal CAES: the process involves continuous removal of heat from the air during compression cycle and similarly continuous addition of heat during expansion stage to maintain the typical isothermal process; technologically an exciting task.

L

Latent Heat Storage: the absorption or release of heat during the phasechange of the storage material, solid to-liquid or liquid-to-gas or the other way around.

Lead-acid-battery: earliest rechargeable battery; used as starter battery, UPS.

Levelised Cost of Storage (LCOS): The cost of kWh or MWh electricity discharged from a storage system when accounting for all cost incurred and energy produced throughout the lifetime of the system.

Line capacities: The maximum and minimum voltage, current, frequency, real and reactive power flows on individual equipment under steady state, short-circuit and transient conditions, as permitted or assigned by the equipment owner.

Lithium-ion battery: Rechargeable battery with lithium-metal oxide (metal is cobalt or manganese or nickel or other metals) as cathode and graphitic carbon as anode; the electrolyte is normally a non-aqueous organic liquid containing dissolved lithium salts; a separator is placed to prevent short-circuit between the electrodes.

Liquid Air Energy Storage (LAES): similar to CAES facility; here the heat lost to the atmosphere during air compression is stored in a phase change material. Excess electricity is used to cool ambient air to -196^{o} C where it liquefies and the liquid is stored in an insulated low-pressure container. When more electricity is needed on the grid, the liquid-air is converted back to the gaseous state by exposing it to ambient temperature and expanding in the turbine to produce electricity.

Load: An end-use device or customer that receives power from the electric system.

Load following: It is a constant electricity balancing mechanism for operation under normal conditions, subsequent to the frequency regulation. Load following is slower than regulation, and thus do not require automatic generation control.

Load forecast: Guessing of future demand. For normal operations, daily and weekly forecasts of hour-by-hour demand are used to develop generation plans that ensure adequate quantities are available when needed.

Load Serving Entity (LSE): Organization that supplies energy and transmission to meet the electricity demand of its end-users. A utility is an example of an LSE.

Load shedding: The reduction of system demands by systematically and in a predetermined sequence interrupting the load flow to major customers and/or distribution circuits, normally in response to system or area capacity shortages or voltage control considerations.

Load following: Ramping up electricity supply as demand increases in the morning and ramping down as demand reduces in the evening; it is considered a subset of energy arbitrage.

Locational Marginal Price (LMP): The market-clearing price for electricity at the location the energy is delivered or received.

Loss of Load Expectation (LOLE): The loss of load expectation is the sum of the LOLPs (loss of load probabilities) during a planning period, typically one year. LOLE gives the expected number of periods in which a loss-of-load event occurs.

Loss of Load Probability (LOLP): The probability of a loss-of-load event in which the demand is greater than available generating capacity during a given period.

M

Metal Air Battery (MAB): an electrochemical cell using a metal for the anode and ambient air as cathode along with a liquid electrolyte typically aqueous or aprotic. During discharging of this cell, a reduction reaction occurs in the ambient air cathode while the metal anode is oxidized. They combine the design features of both conventional batteries and fuel cells (Li-air, Mg-air, Zn-air, Na-air, Al-air are widely studied).

Metal hydrides: a class of materials containing metal or metalloid bonded to hydrogen and are single-phase compounds. These are classified by the nature of the chemical bond (ionic, metallic, or covalent) between hydrogen and metal.

Metal Organic Frameworks (MOFs): organic-inorganic hybrid crystalline porous materials that consist of a regular array of positively charged metal ions surrounded by organic 'linker' molecules. The metal ions form nodes that bind the arms of the linkers together to form a repeating, cage-like structure. Because of this hollow structure, MOFs have an extraordinarily large internal surface area.

Methanation: the conversion of carbon monoxide and carbon dioxide to methane through hydrogenation. It is an exothermic reaction which occurs at about 300–350°C.

Micro-grid: An assembly of interrelated loads and DERs within fixed electrical boundaries that functions as a distinct manageable unit concerning the grid. A micro-grid can choose to connect and disconnect from the grid to operate in either mode.

Minimum run (turn-down) level: The minimum output that can be provided by a generator. Different generators have different minimum run levels based in part on fuel source, plant design, and common use.

Molten salts: Salts are perceived as the ideal liquid-state materials for use in solar power plant because of their excellent thermal stability under high temperatures, and so on. They are liquid at atmospheric pressure, provide an efficient, low cost medium to store thermal energy; examples, alkali nitrate and alkali nitrite salts.

N

Negative market pricing: Takes place when the marginal price is negative. Happens when the generation quantity exceeds demand due to a variety of operational constraints.

Negawatt: Represents a watt of energy that has not been used through energy conservation or the use of energy-efficient products, and Negawatt trading is ‘consolidating the electricity saving of consumers and trade as electricity demand adjustment’.

Net load (net demand): Demand that must be met by other generation sources if all wind and solar power is consumed.

Nickel-cadmium battery: This contains a nickel hydroxide positive electrode plate, a cadmium hydroxide-negative electrode plate, a separator, and an alkaline electrolyte; normally sealed into a metal case with a sealing plate fitted with a self-sealing safety valve; can withstand significant mechanical and electrical abuse; have long life (up to 20 years or more depending on the type), excellent cycle life and are generally maintenance-free.

Nickel Iron (NiFe) Battery: consists of nickel (III) oxide-hydroxide plates as positive electrode and iron plates as negative electrode, with potassium hydroxide electrolyte. They are robustly built, have extended cycle life and the utmost durability. Thomas Edison patented and marketed this battery in 1901 in the US and, proposed this battery as energy provider for electric vehicles.

Nickel-Metal-Hydride (NiMH) Battery: the negative electrode is mainly composed of hydrogen-absorbing alloy, usually alloys of lanthanum and rare earths; nickel hydroxide remains the positive electrode. The rest is similar to the Ni-Cd with a separator made of fine fibers, an alkaline electrolyte, a metal case and a sealing plate provided with a self-resealing safety vent. Environmentally friendly, safer than Li-based cells in case of an accident or abuse due to the use of more benign active chemicals.

Nickel Zinc (NiZn) battery: Comprises nickel oxide as the positive electrode and zinc metal as the negative electrode, and KOH as electrolyte. Shows a higher energy density than Ni-Cd batteries, by about 25%. Comparatively these have a higher energy-to-mass ratio and power-to-mass ratio.

Non-Generator Resources (NGRs): Grid resources, other than electrical generation units, such as energy storage devices and demand response.

Non-spinning reserve: (a) The generating reserve not connected to the system but capable of serving demand within a specified time, (b) Interruptible load that can be removed from the system in a specified time.

Nuclear energy: the energy stored in the atom's nucleus, the core of the atom, which is huge. This energy can be released by nuclear fission or fusion, and is used to produce electricity.

O

Operational Mode Programming: The energy storage controller software programming that controls the charging, discharging, and bypass of the energy storage system.

Operating reserves: Electricity generating capacity available to a system operator to provide for regulation (i.e., response to random movements during normal conditions), load forecasting error, forced and scheduled equipment outages, local area protection, and other types of reserves.

P

Packed bed TES: a bed comprising loosely packed particulate material; the heat capacity of the bed is utilised to store energy. A fluid (air) is dispersed through the bed to add or to take out energy. Rock and pebble are the commonly used materials. Flow is maintained through the bed in one direction during addition of heat and in the opposite direction during removal of heat.

Peaking resources: Reserves that utilities and grid operators hold on, which are set to deliver fast additional power into the grid. For example, different types of electricity storage are becoming popular as peaker resources because of their extremely fast response times; e.g., Li-ion batteries that respond in milliseconds and PHS are extensively used as peaking resources.

Peaking Capacity: Capacity (in MW) associated with a conventional generation unit used specifically to meet demand during high load periods.

Peak load: (a) The highest hourly demand within a Balancing Area occurring within a given period (e.g., day, month, season, or year); (b) The highest instantaneous demand within the Balancing Area.

Peaking plants: Power generating plants operated to meet the peak or maximum load on the system. [cost of energy from such plants is usually higher than from baseload plants].

Peak Shaving: Reducing the amount of energy used during peak periods of demand; this may be accomplished through conservation or by shifting consumption patterns to off-peak periods.

Phase Change Materials (PCMs): Heat of fusion and heat of vaporization are heat supplies for phase changes to occur in a material. With these phase changes, latent heat is associated which cannot be sensed. Materials in which the state of the medium changes are ‘phase change materials (PCM)’

Photolysis: Also called photodissociation, is a chemical reaction in which an inorganic or an organic chemical is broken down by photons and is the interaction of one or more photons with one target molecule.

Photo-electrochemical (PEC) Photolysis: the disassociation of water into hydrogen and oxygen directly at the surface of a semiconductor immersed in an electrolyte through the irradiation by solar light.

Photovoltaic Electrolysis System (PVE): Here, a photovoltaic module delivers electricity to a separate electrolyzer to produce hydrogen. PV electrolysis systems have demonstrated remarkable potential to achieve higher solar-to-hydrogen (STH) efficiencies.

Plug-in Electric Vehicles (PEV): An electric vehicle with rechargeable battery packs that can be charged from the electric distribution system.

Plug-in Hybrid Electric Vehicle (PHEV): An electric vehicle with a battery that can be recharged by plugging it in the electric distribution system or be charged with its on-board engine-generator.

Power Conditioning System (PCS): The general class of devices that use power electronics technologies to convert electric power from one form to another; for example, converting between DC and AC, and/or providing specific operational interface functionalities required by the subsystems being interfaced by the PCS.

Power Quality (electric): A measure of the electric system’s ability to deliver steady energy within a prescribed voltage level, frequency, and waveform.

Power Reliability: The electric system’s ability to deliver uninterrupted service.

Production cost simulations: These optimize the scheduling of load and generation resources to meet expected demand over various timeframes with consideration of cost and constraints (system, physical, operational). This mainly helps to evaluate the impacts of variable renewable power on the operational costs of a system.

Protective Functions: Protective functions (or relays) monitor voltage or current transducers and operate in response to electrical quantities, according to ANSI device numbers, either to close or to open contacts.

Pouch cell: Packaged into a flexible, heat-sealable foil pouch similar to wrapping food products.

Power: Voltage x current (in watts, W or in horsepower; 1hp = 746W)

Pumped Hydro Storage (PHS): utilizes gravity as well as the power of water. Water from a reservoir is pumped during off-peak times (when power is cheaper) to another reservoir at a higher altitude. When the demand for electricity arises, water is made to flow from the high altitude reservoir into the low reservoir through a hydroelectric turbine to generate electricity.

Pyrolysis: It is the thermal decomposition of materials at elevated temperatures in an inert atmosphere (in the absence of oxygen). It involves a change of chemical composition.

R

Radiant energy: it is electromagnetic energy that includes visible light, X-rays, gamma rays, and radio waves.

Ragone chart: Battery performance charts showing specific energy Vs specific power.

Ramp: Increase or decrease in output of electricity supply to follow changes in net demand.

Ramp rate: The change in output of a generating unit per unit time, often measured in MW per minute.

Ramping reserve: Emerging type of reserve that could be used during failures and occasions that are not instantaneous but occur over long time frames (e.g., wind ramps, forecast errors).

Rated power capacity: the maximum rate of discharge that the system can accomplish beginning from a fully charged condition.

Reactive Power (RP): The portion of electricity that establishes and sustains the electric and magnetic fields of ac equipment. RP is provided by generators, synchronous condensers, or electrostatic equipment such as capacitors and directly influences electric system voltage (expressed in kilovars or megavars).

Redox Flow Battery (RFB): Battery structures in which all the electroactive materials are dispersed into a liquid electrolyte are called redox (for reduction/oxidation) flow batteries. With RFBs the conversion and storage of energy are separated.

Regional Transmission Organization (RTO): An independent entity responsible for maintaining system balance, reliability, and electricity market operation on the bulk system. Similar names for this function are Independent System Operator (United States) and Transmission System Operator (Europe).

Regulating reserves (secondary frequency reserves): Respond to random movements and maintain area control error during normal conditions in a time frame that is faster than economic dispatch. Requires automatic control by the system operator.

Renewable Energy Zone (REZ): Region with high-quality RE resources designated as a focus for coordinated expansion of generation and transmission. Used to support expansion of wind and solar power in areas that offer higher capacity values by providing, in advance, adequate grid infrastructure to meet projected generation.

Renewable Energy Integration: focuses on incorporating renewable energy, distributed generation, energy storage, thermally activated technologies, and demand response into the electric distribution and transmission system.

Reserve sharing: Two or more Balancing Authorities that collectively maintain, allocate, and supply operating reserves required for each Balancing Authority’s use in recovering from contingencies within the group.

Resistance: Restriction to current flow; high resistance generates voltage drop and heat.

Round Trip Efficiency: The ratio of energy put in to energy (in MWh) retrieved from storage; also called AC/AC efficiency, expressed in percentage (%). The higher the round-trip efficiency, the less energy is lost in the storage process.

S

Scheduling: Procedure of ensuring that a generator is committed and available when needed. It also can refer to the scheduling of imports into and exports out of a balancing area.

Self-discharge: the decay in the charge of the battery either through internal chemical reactions, or energy lost without out-performing work

Semiconductor (n- and p-types): Material that has an electrical conductivity value falling between that of a conductor, like copper, and an insulator like glass is a semiconductor. Its resistivity falls as its temperature rises in contrast to metals. If doped with pentavalent material, it becomes n-type semiconductor, and if doped with trivalent material, it becomes p-type semiconductor.

Sensible heat: Energy released by a material as its temperature is reduced or absorbed as its temperature is increased is sensible heat.

Sensible heat storage: basically storing thermal energy by heating or cooling a liquid or solid storage medium (e.g., water, sand, molten salts, or rocks).

Separator: Isolates cathode and anode in a battery; acts as catalyst to promote ion movement from cathode to anode on charge and on discharge.

Smart Grid: an electrical grid with automation, communication and IT systems that monitors and adjusts, based on information received from suppliers and consumers of electricity in real time. Battery energy-storage systems are perfectly appropriate for smart-grid objectives.

Smart Home: homes that provide more efficient and cost-effective demand response programs enabling them to get the energy when required. It functions along with the smart meter and the smart grid, and is the central unit of end-user interaction with the utility. It is still at conceptual and modular experimental level.

Smart Meters: Meters that provide the Smart Grid, interface between the consumer and the energy supplier. They operate digitally, and allow for automated and complex transfers of information between home and the energy providers.

Smart Mini Grid: a network which involves “small-scale electricity generation from 10 kW to 10 MW, and the distribution of electricity to a limited number of customers via a distribution grid that can operate isolated from national electricity transmission networks and supply relatively concentrated settlements with electricity at grid quality-level”.

SMBus: System management Bus is a two-wire interface based on I2C; communicates with the battery and device by accepting control parameters and providing battery status, such as state-of-charge, manufacturer information, cycle count and error messages.

Sodium Sulfur (NaS) Battery: This is a high temperature battery utilizing molten salts as electrolytes. NaS battery cell contains a molten sodium anode, a solid electrolyte of β-alumina (β''-Al2O3) and molten sulfur. The electrolyte acts as anode.

Sodium nickel chloride (Na-NiCl$_2$) battery: Also, a high temperature battery; like NaS battery, this battery rely on the oxidation and reduction of sodium at the anode, and on the oxidation and reduction of nickel metal at the cathode; and use a BASE separator. Has enhanced safety and intended for EV applications.

Solar-plus-storage: Storage combined with solar generation installed by the consumer can be used for storing excess solar power generated during the day to reduce reliance on the grid.

Solar thermal plant: the unit which produces energy during the sun-shine time. The excess energy generated during peak time of sunshine is stored in the TES facility, and used when there is no sun, or to generate steam to drive a turbine to produce electricity

Sorption heat storage system: the sorbent gets heated in the charging process, desorbing the vapor from the sorbent. During discharging, vapor at a lower temperature is adsorbed (using solid sorbent) or absorbed (thru a liquid sorbent) and heat is given out at an elevated temperature.

Spinning and Non-spinning Reserve: The entire Power system must maintain frequency and power flow within small variations even with the failure of one of the generators of the system. Instead of running with a small amount of reserve capacity with added cost, fast-responding energy storage systems like capacitors, flywheels and batteries can be used allowing generators to run with their nearly rated power. This reserve capacity is classified depending on response time as *spinning* (response time < 15 minutes) and *non-spinning* (>15 minutes).

Stage of Market development: It is evaluated based on R&D, demonstration, introduction, growth, and maturity of a technology.

Start Battery: Also known as Cranking battery, specifically designed to produce a large burst of current in a short period, which is particularly useful in engine starting applications. Can deliver a very large current in a short time, discharging by about 2 to 5%.

State of Charge (SOC): Indicates charge level of a battery; normally measured in percent.

State of Function (SOF): Reflects battery readiness that verifies capacity, current delivery, voltage, SOC, self-discharge and more; expressed in %.

State of Health (SOH): Reflects battery performance that verifies capacity, current delivery, voltage and self-discharge; measured in %.

Steam reforming: or steam methane reforming (SMR) is a process in which methane from natural gas is heated, with steam, usually with a catalyst, to produce a mixture of carbon monoxide and hydrogen used in organic synthesis and as a fuel; SMR is the most widely used process for the generation of hydrogen.

Storage duration: the period that the storage system can discharge at its rated power capacity before run down its energy capacity.

Sub-hourly energy markets: Electricity markets that operate unit commitment and economic dispatch on time steps of five or fifteen minutes.

Sulfation: Formation of lead sulfate crystal in a lead acid battery that inhibits current flow; storage at low state of charge causes this.

Super-capacitor: electro-chemical devices capable of storing and supplying high-power electricity quickly and for a large number of cycles (up to millions of cycles) with no decline in performance.

Superconductor: Material having zero electrical resistance and when current flows through it, there is neither heat nor energy loss.

Superconducting coil: It consists of multiple windings of superconducting wire or tape. Several superconducting materials are prepared into thin wires and placed in a matrix of Cu, Al, or Ag alloys for better strength and quench safety.

Superconducting Magnet Energy Storage (SMES): Superconducting coil can be charged with an electric current, which in turn generates a strong magnetic field in which energy is stored. This energy will remain as long as the low temperature (Tc) is maintained. The coil, when discharged, can deliver the stored energy back to the network, and is capable of releasing megawatts of power.

Supercritical-CAES (SC-CAES): a kind of new CAES system that incorporates the benefits in both AA-CAES and LAES systems such as high energy density, high thermal efficiency, and environmental safety.

Supervisory Control and Data Acquisition (SCADA): A program using a specific software for process control and data collection in real-time from far away and secluded locations to help regulate equipment and settings.

Supplemental reserve: Generation and responsive load that is offline but can be fully responsive online within a short period of time to replace spinning reserve that has been activated in response to a contingency or other power system requirement.

System: A combination of generation, transmission, and distribution components.

System operator: An individual at a Control Center of a Balancing Authority, Transmission Operator, or Reliability Coordinator, who operates or directs the operation of the Bulk Electric System in Real-time.

System stability studies: Analysis and simulation of the grid under a range of dynamic events to evaluate (a) frequency stability after a major imbalance of generation and load, (b) voltage stability after a disturbance, (c) transient stability to maintain generator synchronism after a disturbance and (d) small-signal stability to maintain steady-state conditions of voltage, current, and power magnitudes after a small disturbance.

T

Technology Readiness Level (TRL): a measurement method to assess the maturity level of a particular technology and the stage of market development.

Thermal decomposition (Adsorption): a chemical reaction where heat is a reactant; these reactions are endothermic, requiring thermal energy to break the chemical bonds in the molecule.

Thermal energy: the energy given by a hot (or heated) substance via the process of conduction or convection or radiation. Thermal energy provided by concentrated solar radiation can be converted into electrical energy.

Thermal Energy Storage: An energy storage system that stores heat or cold energy for use at a later time. Examples include molten salt to store and later convert excess heat to electricity, or cold thermal storage may create ice or chilled water in tanks to displace air-conditioning load.

Time shifting: The ability to store something for consumption at a more convenient time. It is ideal for solar PV, but not yet reached a stage where solar energy is widely time shifted via a programmable unit

Transmission operator: The entity responsible for the operation and reliability of its ‘local’ transmission system.

Transmission congestion relief: Electricity transmission lines experience bottle neck at certain times of the day. Installation of energy-storage systems downstream of the congested transmission segments facilitates electricity to be stored during peak times and released at the drop of the congestion levels, thus eliminating charging higher prices.

Transmission constraint: A limitation on one or more transmission elements that may be reached during normal or contingency system operations.

Transmission network: A system of structures, wires, insulators and associated hardware that carry electric energy from one point to another in an electric power system. Lines are operated at relatively high voltages varying from 69 kV up to 765 kV, and are capable of transmitting large quantities of electricity over long distances.

Transmission planner: The unit that develops a long-term plan for the reliability/ adequacy of the interconnected bulk electric transmission systems within its portion of the Planning Authority Area.

Turn-down capability: The minimum stable generation level that can be achieved by a generating unit.

U

Unintentional islanding: A situation in which distributed generation continues to supply power after the utility power source has disconnected.

Unit: A single generator that may be part of a multiple-generator power plant.

Unit commitment: The process of starting up a generator so that the plant is synchronized to the grid.

V

Vanadium Flow Battery (VFB): Also called vanadium redox flow battery (VRFB), it is a type of rechargeable flow battery employing vanadium ions as charge carriers. The battery uses vanadium's ability to exist in solution in four different oxidation states to make a battery with a single electroactive element.

Variability: The changes in power demand and/or the output of a generator due to underlying fluctuations in resource or load.

Variable Energy Resources (VER): Some renewable energy technologies such as wind and solar whose output may vary over time exhibiting intermittency.

Vehicle-to-Grid: The use of batteries that power plug-in electric vehicles (PEVs) as energy storage capable of providing electrical services to the grid.

Virtual Power Plant (VPP): an innovative concept that works distantly to pool several independent energy-resources from divergent locations into a system that affords consistent power all through the day. They use software-based technology dependent on the smart-grid, and is a way to sustain supply stability.

Voltage: The difference in electrical potential between any two conductors or between a conductor and ground.

Electric energy potential per unit charge.

Voltage regulator: A device designed to maintain voltage levels within acceptable limits.

Voltage Support: Services provided by generating units or other equipment such as shunt capacitors, static VAR compensators, or synchronous condensers that are required to maintain established grid voltage criteria.

W

Water electrolysis: Also known as electrochemical water splitting, is the process of using electricity to decompose water into oxygen and hydrogen by a process called electrolysis.

Water Gas Shift Reaction (WGSR): describes the reaction of carbon monoxide and water vapor to form carbon dioxide and hydrogen; it is an endothermic reaction.

Watt hour (Wh): Unit of electrical energy equivalent to a power consumption of one watt for one hour (1 Wh = 3600 Joules)

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