

Chapter 12

Energy Storage

Abstract In the beginning of the twenty-first century, our society mostly uses energy that has been accumulated for millennia: Fossil fuels have stored in their chemical compounds vast amounts of energy, which we now use for our primary energy needs, unfortunately, at a very high rate that cannot be sustained. When fossil-fuels are exhausted or when their use is curtailed because of environmental factors, such as the production of greenhouse gases, humans will have to rely more on alternative energy sources among which are nuclear, wind, and solar power. While the production of power by nuclear energy may be controlled, wind and solar power are intermittent or periodic sources, which may produce power when there is limited demand and may not produce power at all, when demand is high. For example, during the night hours of July 17th, when there is high demand for air-conditioning and electricity in the northern hemisphere, there is no Sun and the average wind power is significantly lower than average. If the society relies on alternative energy sources and stored energy is not available during this night, humans will experience a significant shortage of energy with the inconvenience this entails. As the human society moves more to the direction of alternative energy sources, the need for energy storage becomes apparent and more acute in order to satisfy the fluctuating energy demands. This chapter provides an exposition to the several energy storage methods that are currently used to smoothen the electric power demand and those that may become feasible and popular in the future. First, the electric energy demand patterns in a contemporary society that makes significant use of air-conditioning in the summer are explained. Secondly the various methods for energy storage, such as electromechanical, thermal—in both latent and sensible heat form—and chemical are explained with the devices/systems that make energy storage possible. The alternative method of storing “coolness” with materials that exhibit a temperature hysteresis in their melting/solidification processes is elucidated within the context of thermal storage methods. Finally, details are given on the possible switch to hydrogen as a clean energy storage medium, the long advocated “hydrogen economy” and the inherent

advantages of Fuel Cells as devices for the direct conversion of chemical energy to electricity.

12.1 The Demand for Electricity: The Need to Store Energy

It is apparent from our daily activities that the societal demand for electricity is not constant, but is subjected to diurnal, weekly and seasonal fluctuations: In general, electricity consumption is higher during the day and falls off during the night, when the majority of the population retires. On a given day, there are demand peaks that coincide with several daily activities of the population, such as the preparation of the daily meals, etc. In a typical week, there is higher demand during the working days and lower during Saturdays, when many of the offices and businesses close. The lowest demand is on Sundays, when most of the businesses close and most of the population does not work. In the United States and the OECD countries, the widespread use of air-conditioning has increased significantly the use of electricity during the hot summer season. This has resulted in a significant peak of electricity demand in the early afternoon hours, when ambient temperatures are higher and the need for air-conditioning is heightened. Figures 12.1 and 12.2 depict the hourly electric power demand during two typical winter and summer days in San Antonio, Texas. The figures include weekday days and weekends. The data were supplied by CPS Energy

One may draw the following conclusions from these two figures:

1. On a given working day, for both winter and summer, the peak daily electric power demand is approximately twice the minimum demand.
2. During the summer, the peak work-day demand is approximately three times more than the minimum demand on Sundays.
3. On a given day, the summer power demand is more than 60% higher than the winter demand on a similar day.
4. During the early hours of the morning, the electric power demand may almost double within a three-hour period (6:00–9:00 am). Similarly, in the late evening the electric power demand drops by almost 50% within a 4–6 h period.

Since electricity cannot be stored, all electric power demand must be met almost immediately on the supply side by the electric power plants, which are connected to the electricity grid. As a result of the frequent and wide fluctuations in the demand for power, the power plants must be able to meet satisfactorily the demand fluctuations and provide power to the consumers. For this reason, all the power plants do not operate continuously and, when they operate they often operate at reduced and not at full power. Several parameters that characterize the capability of a power plant to meet the electric power demand are:

Fig. 12.1 Typical electric power demand during the winter in San Antonio, Texas

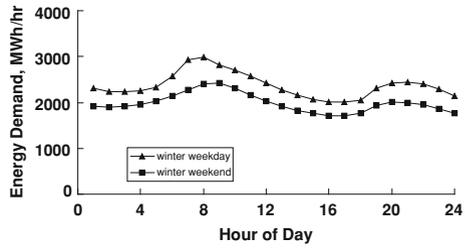


Fig. 12.2 Typical electric power demand during the summer in San Antonio, Texas

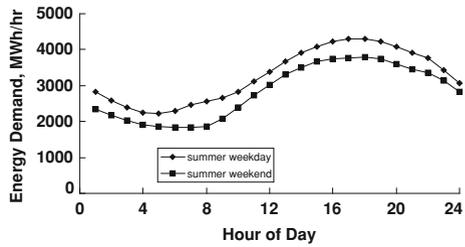
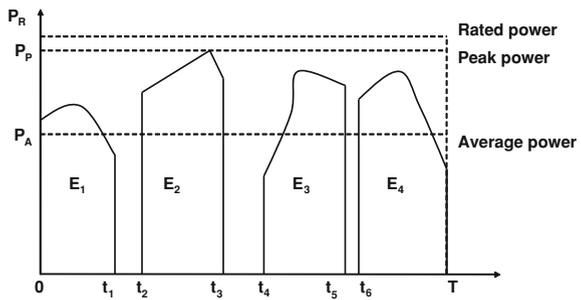


Fig. 12.3 Variable power parameters of a power plant



- The *rated power* is the nominal power a plant may produce.
- The *peak power* is close to the rated power and, depending on the type of the plant and the availability of cooling water, may be a few percentage points higher or lower than the rated power.
- The *average power*, an average usually taken over a period of a year.
- The *availability factor* is the fraction of time that the plant is on line and may contribute to the electric power demand, regardless of the level it contributes.
- The *power operating factor* or *plant capacity factor* is the ratio of the total electric energy generated to the total capacity to generate energy during a time period. This takes into account the fluctuations of the energy produced during a given period.

Figure 12.3 shows schematically these parameters for the operation of a hypothetical power plant during the time interval $[0, T]$, which is typically one year. The power plant is on line and produces power during the time intervals

$[0, t_1]$, $[t_2, t_3]$, $[t_4, t_5]$, and $[t_6, T]$ and is off-line (e.g. for maintenance or because power is not needed) during the time intervals $[t_1, t_2]$, $[t_3, t_4]$, and $[t_5, t_6]$. The rated, peak and average power are shown in the figure. The availability factor of the power plant, AF , is defined by the expression:

$$AF = \frac{t_1 + (t_3 - t_2) + (t_5 - t_4) + (T - t_6)}{T}. \quad (12.1)$$

The areas in the polygons and the symbols E_1 , E_2 , E_3 , and E_4 denote the total energy produced by the plant during the time intervals $[0, t_1]$, $[t_2, t_3]$, $[t_4, t_5]$, and $[t_6, T]$ respectively. The availability factor is a measure of the fraction of time the plant contributes to the production of electricity. The power operating factor (or capacity factor), POF , is a measure of the average power produced by the plant throughout a year and is defined in terms of the rated power, \dot{W}_{rat} , as:

$$POF = \frac{E_1 + E_2 + E_3 + E_4}{\dot{W}_{rat}T}. \quad (12.2)$$

It is apparent that the POF is different than, simply, the average power divided by the peak power or the rated power of the power plant. It is also apparent that the total energy produced by this power plant is significantly different than the total energy the plant *could have produced* if it operated continuously at its rated power during the time interval $[0, T]$.

The availability factor of the power plants depends significantly on their type and design: Large steam power plants operating with a steam cycle, such as nuclear and coal power plants may be damaged if they are started and stopped often (taken *out of line*) and must remain in operation for long periods of time. Some of these power plants may operate at reduced rather than peak power for long intervals. Smaller power plants, especially those operating with a gas Brayton cycle—the so-called gas turbines—may be taken in and out of line often, and are suitable to be used to meet the high frequency fluctuations of the electric power demand.

The availability of solar, wind, and wave power plants depends greatly on the availability of the respective resource: a solar unit does not produce any power during the night, a wind turbine is motionless when there is no wind and an engine powered by waves, does not produce any power during calm seas. A second factor that affects the availability of a power plant is the *operational cost* of the plant, which primarily depends on the cost of the fuel. Units that are expensive to produce electricity are taken off line more often, while units that produce power cheaper operate for as long as it is feasible. In terms of energy generated per kg of fuel (e.g. kWh/kg of fuel) nuclear fuel and coal are less expensive than other fuels. Thus, nuclear and large coal power plants are typically used in the production of electricity. Their availability is higher than the availability of gas power plants, which use a more expensive fuel in terms of kWh of electric energy produced per unit currency (\$) of fuel cost. The often quoted rate, \$/kWh or ¢/kWh (cents per

kWh), is one of the determining factors of the availability of a power plant. Based on these considerations, the power plants are divided in the following categories:

1. *Base-load plants*, which are large, very efficient units operating with Rankine cycles and, in general, utilize nuclear fuel or coal. These units operate almost continuously, except for periods of maintenance. During periods of lower demand (e.g. nights) their load is reduced in the range of 50–70% of rated power, but the plants are not taken off the system. Typical POF's for these plants are close to 75%.
2. *Intermediate or cycling plants*, which are usually older, less efficient steam units or gas-cycle units specifically designed to be taken in and off line relatively often, have a POF in the range 25–50% and typically come in line and supply power during the day-time.
3. *Peak power or peaking plants*, are designed to come on line and off line often, sometimes two or three times during a single day. They are usually Brayton cycle units operating with liquid or gaseous fuel, diesel or natural gas. Electric energy produced from peaking units is more expensive than that from nuclear or coal units. The peaking units produce a relatively small amount of electric energy at higher average cost, but they are very important because they enable the utility to meet the peak demand of its customers. Peaking units may be in operation for as little as two hours during a week and their POF is in the range of 5–15%.

The main objectives of the electricity production companies (utilities) are:

- a) To satisfy the demand, and
- b) To produce electric power at minimum cost.

Because peaking units produce electric energy more expensively, these corporations follow energy management methods that minimize the production of power from the more expensive peaking units. Among the methods presently used for the management of the power produced are the following:

1. Incorporate into the electric grid several geographic areas where peak demand occurs at different times.
2. Charge the consumer higher prices for peak power and supply the households with *smart meters*, which reveal the price charged to the consumer. Naturally, the majority of the consumers curtail their demand for power during periods when the price of energy is high, by conserving energy or switching off appliances that may be used at another time. For example, during a high-price interval, a home owner may raise the temperature of the air-conditioning thermostat or postpone the use of the dish-washer, the washing, and dryer machines for the late evening, when demand is less and the electricity price is lower.

3. Shifting the demand by 10–15 min, by delaying the starting of the operation of devices that consume significant amounts of power. This is achieved when the electric power production corporation remotely controls high powered units (e.g. air-conditioning units, industrial refrigeration units, etc.) and arranges for their staggered operation in a way that power demand is smoothed across the area supplied with electricity. When the shift is short (10–15 min) the effect of this practice to the consumer is almost imperceptible.
4. Use of units that have lower operational cost all the time as base load units and allow more costly units to run only when necessary.
5. Construct smaller, low capital cost units as peaking units, even though the fuel cost of these power plants is more expensive.
6. Use energy storage systems to produce power at low cost and use the power later, when demand peaks.

Since the 1990s energy storage systems are becoming more important in the modern society. The realization of the adverse effects of carbon dioxide accumulation in the atmosphere has put significant pressure on governments, corporations and individuals to “*become greener*” by using a higher percentage of non-polluting, renewable energy sources in their mix for power production. Among the most popular choices are wind power and solar energy. However, during a windless summer night, neither a solar nor a wind power plant is capable of providing the necessary energy to run the air-conditioning systems and other household appliances our society uses. Total or even highly increased reliance on these two sources would result in prolonged energy shortages that are unacceptable to the society. Therefore, a significantly increased solar and wind power capacity by constructing more solar and wind units by itself, would not solve any of today’s energy problems, unless it were accompanied by the construction of systems that store this energy for later use. With energy storage systems, some of the energy produced during a windy evening in the spring or during a sunny summer day may be stored to be used during the windless summer night. Thus, energy storage and energy storage systems are becoming very important in the increased utilization of the intermittent and periodic alternative energy sources, such as wind, solar, tidal and wave energy. The most frequently used systems for the storage of energy—electromechanical, thermal and chemical systems—will be presented in a systematic way in the next few sections. Hydrogen energy storage is essentially chemical, but will be treated in a separate section because of its enormous potential to store and supply very large quantities of energy and because of the transformational implications of hydrogen as the fuel of the future.

12.2 Electromechanical Storage

Electromechanical energy storage systems store energy as potential energy, kinetic energy, or electric energy. Chief among them are above and below ground water pumping, compressed air, mechanical springs, flywheels, superconducting coils, and ultra-capacitors.

12.2.1 Pumped Water

Water is abundant, inexpensive, easily transportable in pipelines and, among the fluids, has relatively high density. One cubic meter of water has a mass of approximately 1 ton. At a height of 360 m, the potential energy of this volume of water is 3.6 million J or 1 kWh. A natural or artificial lake or even a smaller artificial pond may store millions of cubic meters of water for very long periods of time. This makes the transformation of the potential energy of water an ideal medium for energy storage. Typical power plants with pumped-water energy storage units are located in valleys, close to high hills or mountains. If a natural lake does not exist, an artificial lake or pond is constructed, at or near the top of the hill or mountain. During periods of low demand, e.g. nights, the pumps transport the water to the lake or pond. This mass of water, which has significantly high potential energy may be used in the future, when peak power is demanded by the consumers. Oftentimes, the pump-motor systems that are used for the pumping of water may be reversed to operate as turbine-generator systems that produce the electric power. Thus, separate systems are not needed for the storage and the production of power. This reduces significantly the capital costs of energy storage and utilization. A schematic diagram of a typical pumped water system is shown in Fig. 12.4. Excess energy produced in the power plant is transmitted to the pumping/generating station. Water from a nearby river or lake is pumped via a simple pipeline to the artificial lake at a significantly higher elevation. The pumped water has high potential energy, which may be converted to electric power in the generating station by reversing the flow in the pipeline.

A $100 \times 100 \text{ m}^2$ artificial lake with an average depth of 5 m, may store 50,000 cubic meters of water. At an elevation of 800 m, the potential energy stored in such a lake is $4 \times 10^8 \text{ kJ}$ or 110,000 kWh. Typically, there will be minor energy losses during the transmission of the water. The most significant energy losses are at the hydraulic turbine, which is used in the generating station. Since typical turbine/generator efficiencies are in the range 70–72%, the energy that may be produced from such an artificial lake is closer to 77,000 kWh. However, these are not the only energy losses for the pumped water storage system: the pumping of the water is achieved by motor/pump systems, which have efficiencies also in the range of 70–72%. For the pumping of the 50,000 cubic meters of water to the higher elevation of the artificial lake, the energy consumption is approximately

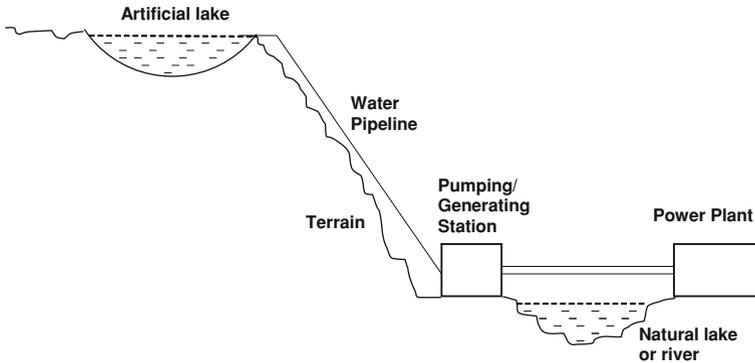


Fig. 12.4 Above ground pumped water system

110,000/0.7 or 157,000 kWh. Therefore, the electric energy recouped from this storage system is close to 50% of the energy used to produce it. Thus, the typical *storage efficiency* of the pumped water system is close to 50%, and of course this means that only half of the energy that is stored is finally recovered.

Despite the rather low storage efficiency, pumped water systems present a viable alternative to energy storage because:

- a) Pumped systems may store a significant amount of energy (millions of kWh) at relatively low capital cost, and
- b) The energy may be stored for long time periods.

Except for a small amount of water that may be lost to evaporation, there are no other losses. Oftentimes the evaporated water is recouped and even enhanced from rainfall water.

An alternative concept to storing water above ground is to store water in underground caverns. In underground storage, the pumping/generating station is located deep in a cavern and water flows to it from the surface gravitationally. When the power plant produces electric power in excess, the pumping station retrieves water from the cavern and stores it at the Earth's surface, close to the power plant. Underground energy storage has the same advantages and the same storage efficiency as the above ground storage. Some disadvantages of underground storage are:

- a) Underground caverns sometimes leak and a lot of stored water is lost in the ground fissures
- b) The storage capacity is limited to the size of the cavern
- c) Power must be transmitted from the power plant to the underground pumping station, and
- d) Access and maintenance of the underground pumping/generating equipment is difficult and more expensive.

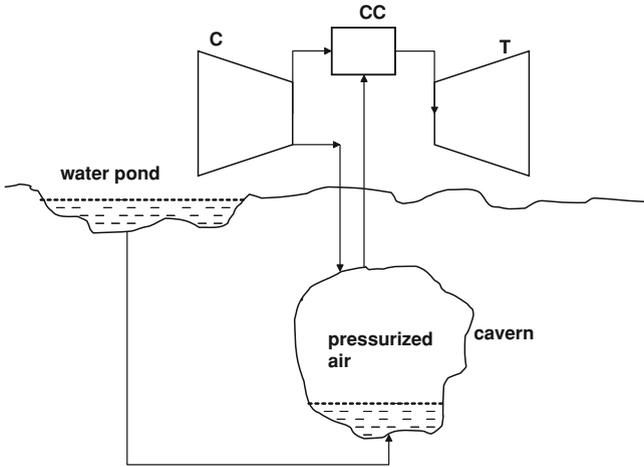


Fig. 12.5 Energy storage with compressed air

12.2.2 Compressed Air

The concept of compressed air storage working in conjunction with a Brayton power cycle and with a water reservoir as pressure regulator is demonstrated in Fig. 12.5. When there is no demand for its power, the gas turbine (T) simply supplies enough power to drive the compressor (C). In this mode of operation the function of the compressor is to pressurize and transport the air in the cavern. Any displaced water from the cavern is stored in the above-ground water pond. The displaced water helps maintain the higher pressure in the cavern, but is not essential for the energy storage. During hours of high power demand, the pressurized air is extracted from the cavern, is fed to the combustion chamber (CC) and finally to the turbine, thus augmenting the power produced by the Brayton cycle. A variation of this method of energy storage is to feed the compressed air directly to the turbine without heating in the combustion chamber.

The maximum amount of work that may be extracted from the combination of the pressurized air and water system may be obtained from the exergy of the air–water system. Writing the exergy of this system in terms of the volume of the cavern, V_c , the total exergy of the air–water system is:

$$E - E_0 = PV_c \left[\frac{c_v}{R} \left(1 - \frac{T_0}{T} \right) + \left(\frac{P_0}{P} - \frac{T_0}{T} \right) - \frac{T_0 c_p}{RT} \ln \frac{T}{T_0} + \frac{T_0}{T} \ln \frac{P}{P_0} \right] + V_c \rho_w g H, \tag{12.3}$$

where H is the average depth of the cavity, measured from the surface of the water reservoir; T , P , and ρ_a are the temperature, pressure, and density of the air respectively under the conditions prevailing in the cavity; T_0 , and P_0 are the

ambient temperature and pressure conditions, R is the gas constant; c_v is the specific heat of air at constant volume, which is 0.72 kJ/kgK and ρ_w the density of water. The last term in Eq. (12.3) represents the work that may be extracted when the water level is lowered to the level of the cavern with the use of hydraulic turbine at the cavity level.¹

Salt caverns, hard-rock caverns, aquifers, and artificial reservoirs have been suggested as reservoirs for air storage. An optimum storage medium would have the following characteristics:

- a) Low thermal conductivity to maintain the higher air temperature
- b) High permeability to charge and discharge with very low drop in pressure
- c) Absence of cracks and fissures to contain the air without significant air mass loss and
- d) High wall elasticity to avoid crack generation under frequent loading and unloading. Salt caverns and hard rock caverns have most of these characteristics and appear to be promising media for air storage.

Outside of possible losses in ground fissures, another disadvantage of compressed air storage is that the exergy per unit volume of compressed air is low. Hence, very large volumes and masses are required for the storage of significant amounts of energy. Air in the cavern typically assumes quickly a temperature that is close to the ambient temperature, T_o , and its exergy is given by the expression:

$$E - E_0 = PV_c \left[\frac{P_0}{P} - 1 + \ln \frac{P}{P_0} \right] + V_c \rho_w g H, \quad (12.4)$$

where the pressure P is not the original pressure of the hot air, P_T , but the pressure developed after the cooling process in the reservoir, $P = P_T^*(T_o/T)$. It is apparent that very large caverns are required for significant energy storage. In addition, there have been no extensive tests on crack formation and propagation under the cyclic loading of caverns at high pressures. Considerable research and testing must be done on this subject, before either salt caverns or hard-rock caverns are extensively used for energy storage.

Two compressed air energy storage (CAES) power plants have been built. The first one is a 290 MW unit in Huntorf, Germany, which was built in 1978; the second is the 110 MW unit of the Alabama Electric Corporation in McIntosh, Alabama, USA, which was commissioned in 1991. Both power plants use large underground caverns to store the compressed air. The two caverns of the Huntorf unit have a total capacity of $310,000 \text{ m}^3$ and operate between 43 and 70 bar pressure. These two power plants have demonstrated the technical soundness and reliability of CAES technology in storing and supplying significant power to the electric grid. However, the energy losses in the storage/production stages due to equipment efficiencies have been significant in both power plants. Because such

¹ During the storage mode, an exergy storage system is a closed system and for this reason, the expressions used for the exergy function are those pertinent to closed systems.

losses increase the cost of the electric power, there are no more CAES plants that are currently operational although there are a few in the planning stages.

12.2.3 Springs, Torsion Bars and Flywheels

All three are simple mechanical energy storage devices. The energy stored in a spring with constant, k , is proportional to the square of the displacement from the equilibrium position, x_0 :

$$E = \frac{1}{2}k(x - x_0)^2. \quad (12.5)$$

Typical values of spring constants for large steel springs are of the order of 1 MN/m. With typical displacements on the order of 0.2 m, the energy that may be stored in such springs is of the order of 20 kJ (0.0056 kWh), which is a very small number in term of typical electric power units. Therefore, even large steel springs cannot be used for the storage of significant amounts of electric energy.

Torsion rods are very similar. The energy stored in a cylindrical torsion rod of length L and radius R , with shear modulus G and angular displacement Ω from its equilibrium position Ω_0 is:

$$E = \frac{1}{2}(\pi R^2 L)G(\Omega - \Omega_0)^2. \quad (12.6)$$

Steel has a shear modulus $G = 81 \cdot 10^7 \text{ N/m}^2$. A 2 m long cylinder of steel with a radius 0.1 m and subjected to an angular displacement $\pi/12$ (15°) will store 1.7 MJ or 0.48 kWh. Even though this stored energy is higher than that in springs, it is very low in comparison to typical electric energy needs. As with the springs, the torsion bars are not good candidates for the storage of significant amounts of energy that would provide electric power. These two devices may store mechanical energy for long periods of time and may be used in highly specialized low energy applications, such as mechanical clocks and weight balancing devices.

The energy stored in a flywheel with mass m and radius R , which is rotating at n revolutions per second ($\omega = 2\pi n$) is:

$$E = \frac{4\pi^2}{2}mR^2n^2. \quad (12.7)$$

A metal flywheel with 100 kg of mass uniformly distributed at a radius of 1 m and $n = 10$ revolutions per second, stores 197.4 kJ (0.055 kWh) of energy. Flywheels, like the other mechanical energy storage devices, do not have the capability to store significantly higher amounts of energy than springs and torsion bars for the production of electricity. Flywheels are occasionally used with electric motors of elevators to store small amounts of mechanical energy during the descent of the elevator. Also, they are used with subway cars in some urban transportation systems. They store energy during braking and release it during the acceleration process. Flywheels have also been extensively used with reciprocating

engines, where they are attached to the crankshaft. During the power pulse, the flywheel absorbs some of the energy and releases it in the latter part of the stroke, when the power of the engine is reduced. Thus, the function of the flywheel is to make uniform the power delivered by the reciprocating engines and to smoothen their operation, but not to store significant amounts of energy.

The amount of stored energy is not significant enough for flywheels to be used extensively as energy storage devices in the power industry. Combinations of very large masses and rapid rotation would be required for the storage of significant quantities of energy. For example, a large flywheel of 3 m radius, which stores 100 kWh, while rotating at 20 revolutions per second, must have a mass of 5,066 kg. In addition, flywheels could not store energy for long periods of time: air friction and friction on their axis with its supports reduces the rotational speed, thus resulting in high losses of energy even in timescales of the order of minutes.

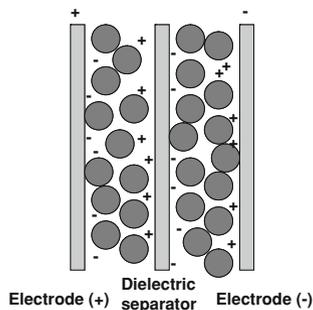
Because the flywheel material is subjected to high centrifugal forces, suitable materials for flywheel design must have high strength, high resistance to crack growth, and low cost. A type of steel, called the *maraging steel*, is suitable material for flywheels because of its high strength and density. Fiber reinforced composite materials are also suitable for use in flywheels, primarily because of their high-strength and relatively low cost. Because the material strength of the flywheel is one of the limiting factors in its design, the specific energy (energy stored per unit mass) is limited by the maximum strength of the material. The theoretical maximum specific energy is given by the expression [1]:

$$\left(\frac{E}{m}\right)_{\max} = 3.77 * 10^{-7} k_m \frac{\sigma}{\rho}, \quad (12.8)$$

where ρ is the density of the flywheel material, σ is the allowable stress and k_m is a dimensionless *mass efficiency factor*. Under optimum design conditions, the latter may reach the value 1.0 for isotropic materials (steel alloys) or 0.5 for anisotropic materials (composites).

The use of smaller flywheels has been advocated as an energy storage device in automobiles. A flywheel may absorb some of the engine power during braking and release it during the acceleration of the automobile. While this would improve the fuel consumption of a typical automobile, the weight of the flywheel and its mechanism would add significantly to the weight of the automobile. In addition, a fast rotating flywheel would reduce safety and reliability: gyroscopic forces on the axis of the flywheel are developed during turns and other changes in direction. Their effect would be to decrease the stability of the automobile, and this will increase the frequency of road accidents.

Fig. 12.6 The electrical double layer



12.2.4 Capacitors, Ultra capacitors, and Superconducting Coils

Capacitors and induction coils store electric or magnetic energy. When this energy is released it may be directly and almost instantaneously converted to electric energy at efficiencies close to 100%. Therefore, the storage of energy in capacitors or coils does not suffer from significant conversion penalties.

The electric energy stored in a capacitor is given by the expression:

$$E = \frac{1}{2} CV^2, \quad (12.9)$$

where C is the capacitance of the material, which depends greatly on the size of the capacitor, and V the applied voltage. Conventional capacitors are formed by two metal plates, or a sphere and a surrounding spherical shell. The two have equal and opposite charges. Dielectric materials inserted between the charged plates counteract the attractive forces; maintain the gap between the plates and cause different voltages and different amounts of energies to be stored. Optimizing the properties of these dielectric materials leads to higher energy densities for any given size of capacitor. The charge separation creates a voltage between the two plates, and the energy stored in the gap may be used in an external circuit that connects the two plates. This energy may be harnessed in an external circuit.

Conventional capacitors store very modest amounts of energy in a given volume, primarily because the dielectric material between the plates is bulky. Recently the *ultra capacitors* have been developed, which do not use as much volume for the dielectric material. The ultra capacitors utilize the concept of the double electric layer and use the polarization of an electrolytic solution to store energy electrostatically. The concept of the electric double layer is illustrated in Fig. 12.6, which depicts a typical ultra capacitor cell. Two porous plates, or collectors, are suspended within an electrolyte solution, with a voltage potential applied across the collectors. The applied electric potential on the positive electrode attracts the negative ions in the electrolyte, while the potential on the negative electrode attracts the positive ions. A dielectric separator between the two

electrodes prevents the charge from moving between the electrodes. Since the electric double layer is formed on a very thin liquid electrolyte layer of the order of molecular size, the separation distance between the two electrodes may be made extremely thin, on the order of nanometers. This allows the packing of several “plates” with much larger surface area into a very small size, resulting in extraordinarily high capacitances in packages of relatively low volume.

Although the ultra capacitors are electrochemical devices similar to the batteries, no chemical reactions are involved in their energy storage mechanism. Because of this, there is only a very small irreversibility associated with their operation and, thus, they may be charged and discharged hundreds of thousands of times, with no significant energy dissipation. In contrast with traditional capacitors, electric double-layer capacitors do not have a conventional dielectric. Rather than two separate plates, which are separated by an intervening substance, these capacitors may use as “plates” two layers of the same substrate. When their electrical properties are optimized, the electrical double layers that are formed cause the effective separation of the charges and significant storage of electric energy, despite their very thin size and small volume. This gives very high volumetric energy storage capacity for the ultra capacitors.

The material between the plates of an ultra capacitor is a porous material that is typically made of activated charcoal. This is a carbon powder that consists of fine particles with rough surfaces, which in bulk form a low-density volume of particles with inter-particle holes and passages that replicate the structure of a sponge. The overall surface area between the electrodes of these materials is many times greater than a traditional porous material, such as aluminum. The higher surface area allows a great deal more ions and radicals from the electrolyte, which are the charge carrying agents, to be stored in any given volume. This implies that electric double-layer capacitors using charcoal are limited to low potentials on the order of 2–3 V, a very low voltage for most practical applications. The electric double-layer capacitors, which would be used at higher voltages, must be made of matched capacitors of individual electric double-layer capacitors connected in series, in a way that is similar to the cells in higher-voltage batteries.

Activated charcoal is not an ideal material for ultra capacitors, because the charge-carrying ions and free radicals are often larger than the holes and passages allowed in the random packing of the charcoal particles. Recent research on improved materials has revealed other materials of higher usable surface areas. Carbon nanotubes, which are made of only carbon atoms arranged in long cylindrical matrices, have similar charge storage capability as charcoal, but are arranged in a more regular pattern that exposes a significantly higher surface area of carbon to the electrolyte and its charges. Other materials that are promising for energy storage and are under consideration are activated polypyrrole and even nanotube-impregnated common paper.

The two main advantages of the ultra capacitors are:

- a) They may store a high amount of energy per unit mass and
- b) They may be charged and discharged in fractions of a second.

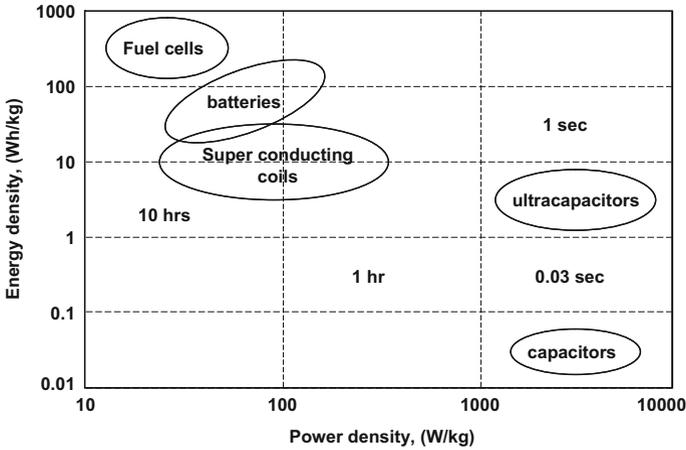


Fig. 12.7 Storage capacity of various electrochemical devices

In contrast, batteries need several minutes or hours to fully charge. Figure 12.7 shows a *Ragone chart* or “bubble chart” of the energy and power densities of ultra capacitors as compared to the other electrochemical energy storage devices. The energy and power densities are defined as the ratios of the total energy stored per unit mass of the device and the nominal power the device may produce per unit mass. It is apparent in this figure that, because of the short duration of charging and discharging, capacitors and ultra capacitors are ideal devices for storing small amounts of energy over short periods of time. When larger amounts of energy storage are required, and when the storage is to exceed a few seconds, the conventional batteries or fuel cells, which store energy in chemical form, are by far more suitable storage devices.

The energy stored in an electric coil or solenoid is given by the relationship:

$$E = \frac{1}{2} LI^2, \tag{12.10}$$

where I is the current flowing and L is the inductance of the coil. The latter is proportional to the radius of the coil, r , and to the square of the total number of turns of the coil. When made with the usual type of materials, a coil would exhibit significant ohmic energy losses (I^2R), because of the finite electric resistance, R , and would not be a good medium for energy storage. The discovery and recent use of superconducting materials at relatively high temperatures allows very high currents to pass through superconducting coils with minimum energy loss ($R \rightarrow 0$). Current density values on the order of 10^8 Amperes/m² and currents on the order of 10,000 Amperes in cables are routinely achieved with superconducting coils. With typical inductance values of 500 Henry (Henry = Volt*second/Ampere), Eq. (12.10) shows that a typical superconducting coil would store $2.5 \cdot 10^{10}$ J or approximately 7,000 kWh, which is a significant amount of energy. Therefore, coils made of superconducting

materials have been recommended as energy storage devices, because: a) they may store very high quantities of energy; b) the charging/storing time is very short and c) the released energy may be controlled very well. What prevents their more widespread use is that they are expensive to manufacture and operate.

12.3 Thermal Storage

Thermal storage may be accomplished for two purposes:

- a) To store energy in the form of sensible or latent heat for later use, and
- b) To store “coolness,” that is to produce materials at lower temperatures, which will be used at a later time for refrigeration or air-conditioning.

12.3.1 *Sensible and Latent Heat Storage*

During the *sensible heat storage*, the temperature of a material, which may be pressurized water, an organic fluid, or a solid (including solid beds), is raised for the energy stored to be extracted at a later time as heat. The material that stores heat is typically well insulated. Its energy is released by the convective flow of air in its interior, when this becomes desirable. Typical sensible energy storage units are space heaters that have been used in several European countries. These are made of packed bricks or other materials with high specific heat capacity. Electric resistance units and air channels run between the bricks. These units are supplied with electric power during the night and early morning hours from the base-load power plants, when the demand for electricity is very low. During the day, when there is high demand for electricity, the heating units gradually release their energy by circulating a controlled amount of air in their interior channels, thus, keeping the space temperature constant.

One may achieve better temperature control and heat flow with *latent heat storage*. This is accomplished with pressurized steam, another pressurized vapor, or a molten metal. Typically, the vapor is stored in a well-insulated, pressurized vessel. The energy stored in the vapor or the molten metal may be used for space heating, process heating or conversion to electric power. An advantage of the latent heat storage method is that, if the pressure of the storage material is kept constant, the energy released is at constant temperature. This is very important for some industrial processes as well as for power production, where constant temperatures are desired. All other factors being equal, stored latent heat is significantly higher than sensible stored heat. For example, 1 kg of vapor water—steam—at 1 atm may supply

approximately $2,550 \text{ kJ}^2$ at 100°C for space or process heating, while one kg of liquid water at the same temperature may only supply approximately 300 kJ for space heating. Thus, latent heat storage is ideal for storing large quantities of thermal energy for heating and for the production of electricity.

Latent heat storage has been proposed for transforming base-load power plants to peaking units, by storing very high amounts of energy in steam or a molten metal. When a steam power plant does not run at full load, some of the steam produced by the boiler or reactor may be diverted from the turbine and be stored at high pressure in “steam accumulators.” At high-demand periods, this steam may be fed to auxiliary turbines, where it produces additional power that is needed during the peak hours. Nuclear power plants must operate almost continuously and are essentially base-load units. Power plants operating with high-temperature cycles, such as HTAGR or HTGR power plants, which are depicted in Fig. 5.10, are excellent candidates for conversion to an intermediate or peaking unit by storing some or all of the heat produced during off-peak hours in a pool of molten salt at significantly high temperature. The stages of the production of electricity are as follows:

- a) During off-peak hours, all the heat produced by the reactor is transferred by the circulating helium to the pool of the salt, which melts and heats up. The pool temperature may rise to $650\text{--}700^\circ\text{C}$, or even higher if ceramic storage materials of very high melting points are used.
- b) The stored energy may be removed, either by circulating a molten metal of lower boiling point, such as lead, through the molten salt and then using a heat exchanger to produce steam at high pressure and temperature, or by circulating water through the molten salt and, thus, raise steam directly.
- c) The steam, which is produced during the day, is directed to a turbine and is used solely for the production of electricity. During this operation, the molten salt may cool to a lower temperature and, depending on the design of the unit, some or all of it may solidify. Because of the high temperatures that are achieved in the storage medium, the temperature of the steam may be in the range $550\text{--}600^\circ\text{C}$, which is in the higher range of temperatures achieved by modern fossil fuel plants. This implies that the steam component of this power plant would be as efficient as any modern fossil-fuel power plant.

A variation of this scheme would allow the HTAGR power plant to produce a small amount of base-load electric power continuously and store the rest. Such a power plant would continuously store a percentage of the produced heat in the molten salt pool and will produce additional steam and electric power during the periods of higher electricity demand.

Whether a system uses latent or sensible heat for the storage of thermal energy, the maximum amount of work that may be obtained from the system is given by its exergy. It must be recalled that a storage system is a closed system. When the specific properties of the system at its elevated temperature and pressure (T , P) are

² Upon condensation the steam will release $2,257 \text{ kJ/kg}$ and will become liquid water at 100°C .

denoted by u , v , and s and the properties of the same system at atmospheric conditions (T_0 , P_0) by u_0 , v_0 , and s_0 , the difference of the exergy between the state at the high temperature, T , and the dead state is:

$$W_{\max} = m(e - e_0) = m[u - u_0 + P_0(v - v_0) + T_0(s - s_0)]. \quad (12.11)$$

In the case of steam, or another material undergoing phase change, these properties may be obtained from the pertinent tables, such as steam tables. If the storage system is incompressible and there is no latent heat involved in the storage process, as in the heating of heavy oils or solid rocks, the maximum amount of work that may be produced is given approximately by the simpler expression, in terms of the specific heat capacity, c , as follows:

$$W_{\max} = m(e - e_0) = m \left[c(T - T_0) + cT_0 \ln \frac{T}{T_0} \right]. \quad (12.12)$$

12.3.2 Heat Losses in Thermal Storage Systems

The storage material (water, steam, molten salt, molten metal or solid rock) is at a temperature that is significantly higher than that of the environment. Because there is no material which is a perfect insulator, heat would be continuously lost from the thermal storage medium at a rate which is proportional to the storage temperature. Given enough time, and if the stored energy is not used, the energy dissipates in the environment and is eventually lost. For this reason, thermal storage is a good way to store thermal energy for short to intermediate periods of time. The following example illustrates the heat and temperature loss from a storage system:

Let us assume that sensible heat (e.g. superheated steam) is stored in a cylindrical vessel of diameter D and length L , that the storage material has density ρ , specific heat capacity c , and the ambient temperature is T_{amb} . The initial temperature of the vessel is T_0 and the temperature at a given instant is denoted as T . The rate of heat transfer from the cylindrical vessel depends on the overall heat transfer coefficient U . At a given time, the total rate of heat lost to the surroundings is:

$$\dot{Q} = U \left(2 \frac{\pi}{4} D^2 + \pi DL \right) (T - T_{amb}). \quad (12.13)$$

Assuming a uniform temperature in the vessel, the heat lost from the cylindrical vessel would reduce the temperature of the material by a rate, dT/dt , which is given by the following heat transfer equation:

$$\frac{1}{4} \pi D^2 L \rho c \frac{dT}{dt} = -\dot{Q} = -U \left(2 \frac{\pi}{4} D^2 + \pi DL \right) (T - T_{amb}) \quad (12.14)$$

Equation (12.14) is an ordinary differential equation with respect to the instantaneous (uniform) temperature of the storage tank, T . Under any conditions this equation may be solved numerically to yield the function $T(t)$. A good approximation to the solution may be derived by assuming that the properties of the storage medium, as well as the overall heat transfer coefficient, U , are constant. Under these conditions, the solution to this differential equation is:

$$\frac{T - T(0)}{T_{amb} - T(0)} = \exp(-t/\tau_{st}), \quad (12.15)$$

where τ_{st} is the characteristic thermal storage time, which is given by the coefficients of Eq. (12.14) as follows:

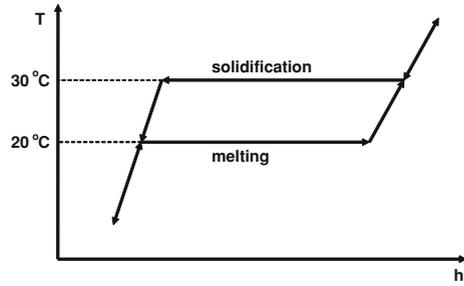
$$\tau_{st} = \frac{DL\rho c}{2(D + 2L)U}. \quad (12.16)$$

The last three equations demonstrate that the temperature of a sensible heat storage system drops exponentially and finally reaches the ambient temperature. A well insulated vessel (very low U) would have a significantly lower heat loss to the surroundings and would delay significantly the temperature drop. At any rate, Eq. (12.15) demonstrates that thermal storage systems may be best used for short to intermediate energy storage situations. In the long term, all the thermal energy is lost to the environment. Currently used insulation materials have high enough overall heat transfer coefficients, U , so that they may store significant quantities of heat for periods of 10–12 h without an appreciable temperature drop. The state of the art in insulation materials presently allows for the development of systems with diurnal cycles (e.g. storage of heat during the night and use during the day) but not for seasonal cycles (storage of heat during the spring/winter months to be used during the peak demand of the summer). The “coolness” storage system, which is described in the following section and operates on a diurnal cycle, is also feasible with commonly used insulation materials.

12.3.3 Storage of “Coolness” to Offset the Peak Power Demand

In the U.S.A. as well as many other OECD countries, the southern migration of the population and incessant need for air-conditioning has shifted the peak demand for electric power from the winter to the summer. This is demonstrated in Figs. 12.1 and 12.2, where it is apparent that the peak demand for electricity during the summer is 35% higher than the peak power demanded during the winter, for both weekends and weekdays. Although these figures were obtained from the San Antonio market, a southwestern city in the USA with very high cooling demand in the hotter months of the year, similar trends, with a lesser percentage difference between summer and

Fig. 12.8 The melting/solidification curve of a eutectic material



winter are observed in all the major cities of the United States and of most of the OECD countries, where summer air-conditioning is common.

Since the peak power demand is spent on cooling, it makes sense to store “coolness,” that is to produce materials at temperatures lower than the internal temperatures of buildings. “Coolness” or low temperature materials may be stored as latent heat/coolness, as sensible heat, or a combination of the two. As with the storage of heat materials, systems and materials working primarily with latent storage have an advantage because they would store significantly higher amounts of “coolness” per unit mass. A “coolness” storage material is cooled during periods of off-peak hours. The material receives heat from the hotter air of a building during peak electricity demand, cools this air in a heat exchanger and supplies the cooler air back to the building. The air-conditioning system uses electric power during off-peak hours and avoids the use of significant electric power during the peak afternoon hours.³ The coolness system has two significant advantages:

1. It shifts the electric power demand from peak hours to off-peak hours, when electricity is supplied by base load plants. This implies that utilities will not have to have available more power plants in order to meet the peak demand.
2. Because base-load and intermediate power plants are significantly more efficient than peaking units, the electric power used in air-conditioning is produced at higher overall plant efficiency. This implies that a lesser amount of energy resources is used for the satisfaction of the air-conditioning needs of the population.

A system for storing “coolness” during the summer months may also be used to store heat during the winter months. For this purpose, the materials used must store high quantities of energy at temperatures higher than the typical space temperature in winter (e.g. close to 80°F or 27°C). At the same time this material must also store high quantities of “coolness” at temperatures lower than the typical temperature in the summer (e.g. close to 74°F or 24°C). Excellent materials for cooling during the summer and heating during the winter are materials that exhibit a temperature hysteresis in their melting and solidification processes, by a few

³ A low amount of electric power is still needed for the circulation of air.

degrees. These materials melt at lower temperature than their solidification temperature as depicted in the temperature-enthalpy diagram, which is shown in Fig. 12.8. Ideally, such materials melt in the range 65–75°F and solidify in the range 80–90°F.

During the summer period the material stores “coolness:” The solidification of the salt occurs at 30°C, during off-peak hours and the temperature of the material may be dropped to values that are lower than the melting/solidification range. During the peak demand hours, the material melts and absorbs heat, which is stored as enthalpy, from the cooled space at 20°C. At this temperature the material cools the space air to the lower air-conditioning temperatures, thus keeping the temperature of the cooled space at the desired low levels. During the winter, the operation of the air-conditioning medium is reversed. When the material solidifies it supplies heat to the heated space at a temperature of 30°C, which is above the typical space temperature, thus, maintaining the space warmer. At off-peak hours the material absorbs most of its heat/enthalpy at 20°C during its melting process and then its temperature rises above 30°C.

The so-called *eutectic salts*, such as the sodium sulfite decahydrate or Glauber’s salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), exhibit this type of temperature hysteresis and are good materials for cooling and heating systems. Because of the finite temperature differences during the heat transfer processes, these materials operate better if their range of operating temperatures becomes wider than the 10°C, which are shown in Fig. 12.8. A wider use of heat storage based on eutectic salts or similar materials for cooling and heating purposes has the potential to shift significantly the peak electricity demand during the summer months and to reduce the peak heating requirements during the winter months. This will enable electricity production corporations to use their more efficient power plants for the satisfaction of the demand for electricity.

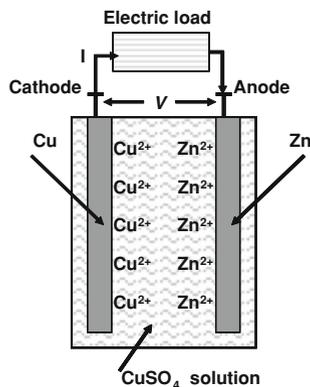
12.4 Chemical Storage: Batteries

12.4.1 The Electrochemical Cell

Most of the energy we use today for the production of electricity and propulsion is derived from chemical energy stored in fossil fuels: coal, oil, and natural gas consist of chemical compounds that have been formed millions of years ago and are now being used at an alarmingly fast rate. Chemical energy has very high energy density (in kJ/kg) and is easy to be used by combustion or direct conversion to electricity. For example, the chemical energy that may be released from the combustion of solid graphite ($-\Delta H^\circ$) is 32,770 kJ/kg. For octane this number is 49,010 kJ/kg; and for methane, 55,510 kJ/kg.

The energy density of most stable chemical bonds is significantly high and, hence, chemical storage is a very desirable method for energy storage. Apart from

Fig. 12.9 Electric power equal to $\dot{W} = VI$ is produced from the operation of the Daniel cell



having high storage density, an energy storage device with desirable properties must charge and discharge quickly, to provide not only large quantities of energy, but also high power when it is needed. Two very important parameters in chemical energy storage are:

- The characteristic time of storage, which is the time it takes for the chemical compounds to be formed (or formation time) and
- The characteristic time of discharge, in this case the combustion time.

The formation time of fossil fuels is on the order of hundreds of millennia and, hence, chemical storage in the form of fossil fuels is impractical, even though the discharge time, via a combustion process, is of the order of minutes or seconds.

Other chemical compounds, such as acids, bases, and metallic salts have shorter formation times and are frequently used in *electric accumulators*. These are energy storage devices that are commonly referred to as “batteries” or “electrochemical cells.” Common batteries consist of several individual cells in series. When electric power is desired, a chemical reaction, which is controlled by an external circuit, takes place inside the cells and, simultaneously, a voltage difference appears in the electrodes. The “Volta Cell” is the first electrochemical cell that was invented by Alessandro Volta in the late eighteenth century and comprises of copper and zinc electrodes with copper sulfate as the electrolyte. Its successor, the “Daniel Cell” was invented in 1836 and makes use of a semipermeable porous medium that prevents the deposition of copper on the zinc anode. Figure 12.9 depicts the operation of the Daniel cell: The cell is made with solid copper and zinc *electrodes*, which are called the *cathode* and the *anode*. The electrodes are surrounded by water solution of copper sulfate (CuSO_4) and zinc sulfate respectively. These solutions constitute the *electrolyte*. A porous material, originally made of clay, separates the two types of the electrolyte, allows the SO_4^{2-} ions to pass through its pores, but inhibits the passage of the Cu^{2+} and Zn^{2+} ions and, thus, effectively keeps them in the vicinity of their respective electrodes. At the anode, a

solid zinc atom deposits two electrons and enters the solution as a positive ion according to the reaction:



At the cathode, a copper ion (Cu^{2+}) absorbs two electrons and is converted to a solid copper atom, which is deposited on the cathode:



Therefore, the overall reaction that takes place in this electrochemical cell is:



The anode of the Daniel Cell has a surplus of electrons and, hence, a negative charge, while the cathode has a deficiency of electrons, and a positive charge. This creates a potential difference (voltage) between the anode and the cathode, which may be utilized in an outside circuit for the production of electric power: $\dot{W} = VI$. At the same time, the cathode has a surplus of sulfuric ions (SO_4^{2-}) and the cathode has a deficiency of SO_4^{2-} . These ions move through the electrolyte and the porous material from the anode to the cathode and maintain the electric current in the electrolyte. The released electrons travel from the anode to the cathode (by convention, “current” flows in the opposite direction to the electrons) and deliver electric power to the circuit.

The reactions stop and the cell stops producing power and voltage difference when all the zinc material in the anode has eroded and has been converted to ions. At this point the cell may be *regenerated* or *recharged* if an external voltage is supplied to the electrodes with the positive pole connected to the cathode and the negative to the anode of the cell. During the recharge process, energy is supplied to the cell and the reactions described by Eqs. (12.17) and (12.18) are reversed: Zn comes out of the electrolyte solution and forms the cathodic material; Cu enters the electrolyte solution as Cu^{2+} ions; the sulfate ions, SO_4^{2-} , move from the cathode to the anode; and the electrons move in the outside circuit from the cathode to the anode. The recharging time of a Daniel cell and other similar cells is typically on the order of hours. This makes such cells cumbersome to use with applications that require rapid charging and discharging.

In contrast to common uses of chemical energy in fossil fuels, which is by combustion and thermal energy release, electrochemical cells convert the energy stored in the chemical bonds directly into electricity, without producing heat or thermal energy as an intermediate stage of the energy conversion process. Because of this, electrochemical cells are not subjected to the Carnot limitations, which are described in [Chap. 3](#). The total chemical energy that may be converted to electric energy is equal to the exergy of the electrode materials. According to (Eq. 3.34),

the exergy is equal to the change of the Gibbs free energy at atmospheric conditions, $-\Delta G^o$, of the overall chemical reaction in the cell. In the absence of thermodynamic irreversibilities this energy is converted to electric work (voltage times electric charge transferred). If one kmol of a substance reacts (e.g. 1kmol of Zn in the Cu–Zn cell) the charge transferred would be equal to ζF , where F is the *Faraday constant* (=96,500,000 Coulomb/kmol) and ζ is the valence number of the reaction, or the number of electrons transferred per reacting atom or ion. Hence, the electromotive force of the cell during a reversible operation, or the maximum voltage the cell may produce is given as follows:

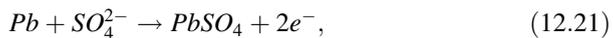
$$-\Delta G^o = \zeta F V_{max} \Rightarrow V_{max} = \frac{-\Delta G^o}{\zeta F}. \quad (12.20)$$

In the Zn–Cu reaction of Eq. (12.19) $\Delta G^o = 216,160$ kJ/kmol and $\zeta = 2$. Hence, the maximum voltage the Zn–Cu cell may produce is approximately, 1.1 V. This is a typical value for most electrochemical cells. Several electrochemical cells must be connected in series to develop the voltage of 10–20 V, which is needed in many applications. In practice, internal irreversibilities related to the passage of ions in the electrolyte and external irreversibilities caused by the flowing current, would reduce the voltage that is actually developed in a cell typically by 10–25% from the maximum value given by Eq. (12.20).

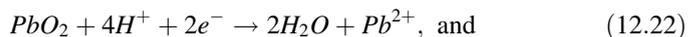
12.4.2 Commonly Used Battery Types

One of the most common types of cells for batteries is the lead cell, which is invariably used in the automotive industry. The lead cell consists of an anode, made of solid lead (Pb); a cathode made of solid lead oxide (PbO₂); and an electrolyte between the two electrodes, typically made of a sulfuric acid solution (H₂SO₄). The acid in the electrolyte solution separates into hydrogen (H⁺) and sulfuric (SO₄²⁻) ions. The chemical activity in the electrolyte causes chemical reactions to occur at the surface of the electrodes, which release or absorb electrons. This in turn causes the erosion of the material of the two electrodes and its dissolution in the electrolyte as described by the following reactions:

A. Anode:



B. Cathode:



C. Electrolyte:

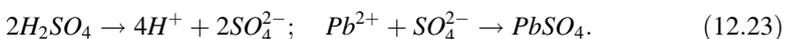


Table 12.1 Voltage, charge capacity and energy density for several types of Li-ion cells

Cathode	Voltage (V)	Capacity (A-h/kg)	Energy density(kJ/kg)
LiCoO ₂	3.7	140	1,865
LiMnO ₂	4.0	100	1,440
LiFePO ₄	3.3	120	1,426
Li ₂ FePO ₄ F	3.6	115	1,490

It is apparent from these reactions that the lead in the anode and the lead oxide in the cathode are eroded by the hydrogen cations and the sulfuric anions, which are formed by the ionization of the sulfuric acid. The excess of electrons in the anode and the consumption of electrons in the cathode results in the polarity and the development of the voltage difference of the cell. The overall reaction that occurs in the entire cell may be obtained from the sum of Eqs. (12.21) through (12.23) as follows:



The Gibbs free energy change of the last expression, ΔG° , would determine the maximum voltage developed from this cell according to Eq. (12.20).

More recently, the lithium batteries have been developed for use in electronic devices and several light vehicles. The term “lithium battery,” or “Li-ion battery” refers to different types of batteries comprising several types of cathodes, anodes and electrolytes. The most common type of lithium batteries for consumer applications uses metallic lithium as anode and manganese dioxide as cathode, with a lithium salt dissolved in an organic solvent. Another type of Li-ion battery is the lithium-thionyl chloride cell, a liquid solution of thionyl chloride (SOCl₂) and lithium tetrachloroaluminate (LiAlCl₄) acts as the cathode and electrolyte respectively. A porous carbon material serves as the cathode of the cell. This type of batteries are well suited to be used in very low-current applications, where reliability and long life is necessary, such as wireless alarm systems. Because of their complexity, lithium-thionyl chloride cells are used only in specialized industrial applications, or are installed into devices where no consumer replacement may be performed and, generally, they are not sold in the consumer market.

Table 12.1 shows several types of Li-ion cells, the typical voltage they produce, in Volts, the electric charge capacity they have, in Ampere-hours per kg of weight and the total energy that may be stored in such cells, in kJ/kg. It is apparent that Li-ion batteries may store a significant amount of energy per unit weight and for this reason they have been recommended as an alternative to gasoline-powered vehicles. However, the recoverable energy density (kJ/kg) stored in fossil fuels, such as gasoline is approximately thirty times more than the energy density of the Li-ion cells. When taking under consideration the finite conversion efficiencies of the components, an electric vehicle must carry approximately 1 ton of battery weight if it were to have the same range as a vehicle with an 18-gallon gasoline tank. In

addition, the recharge time for conventional batteries and Li-ion batteries is on the order of hours, which implies that a quick recharge, similar to a tank filling at a gas station, is impossible.

As any car operator knows, a battery has a finite life: after several months and a few thousand charge-recharge cycles (currently on the order of 1,000) batteries do not recharge and must be chemically regenerated. In an economy heavily dependent on batteries for energy storage, the extensive transportation and chemical regeneration of batteries that contain large quantities of heavy metals will cause significant environmental and public health problems. Almost all the solid battery types, including lithium batteries, contain to a small or large degree heavy metals (Pb, Ni, Co, Mn, Cd, etc.) which have been proven to be harmful to humans. Since the useful life of a solid battery is finite, the battery must be replaced or refurbished after approximately 1,000 full charge–discharge cycles. Let us assume that our economic system uses these solid batteries for the storage of significant amounts of energy, which is produced from renewable sources, in households. This type of economic system will necessitate the use of the equivalent of 20–25 car batteries in every household in the USA, which will be typically charged and discharged every day. These batteries will need to be replaced and regenerated every 24–48 months. Hence, every household must have the equivalent of six to ten batteries per year sent to a central facility for refurbishment or replacement. The sheer volume of this battery traffic is simply very high for the society to sustain. The environmental and public health problems that will be created from the use and transportation of such a storage system are prohibitive. A contemporary society simply cannot rely solely on metal oxide batteries for energy storage without risking significant environmental damage and future public health problems. Even if the life-cycle of the solid batteries improves by a factor of two, a rather unlikely number if the cost of batteries is to be kept at affordable levels, the environmental risk by misplaced or discarded batteries during their transportation would still be enormous.

Another disadvantage of all batteries is the imperfect electrical insulation of the battery cells, which causes a *current drift* or a very weak internal current, even when the poles of the battery are not connected to an external circuit. A car battery that is not operated and charged for a few weeks is completely discharged and becomes a “dead” battery. The drift is continuous and results in the gradual loss of energy. The current types of batteries are not good energy storage systems for long periods of time.

Even though since the 1990s there has been significant progress in the manufacturing of durable, reliable and high capacity Li-ion batteries, it is apparent that at present they are not ready to replace the gasoline tanks of the vehicles. For this replacement to happen, a significant amount of research and several technological advances must first occur that will: a) improve the battery energy density; b) reduce the recharge time; c) lengthen significantly the life cycles of batteries; and d) eliminate the current drift.

12.5 Hydrogen Storage: The Hydrogen Economy

Hydrogen has been advocated as an environmentally friendly and physically powerful energy storage medium. The advantages for the use of hydrogen as an energy storage medium may be summarized as follows:

1. It is the lightest element and the specific chemical energy stored in hydrogen (142,700 kJ/kg at ambient conditions vs. 49,500 kJ/kg for octane) is higher than that of most other materials. On a volumetric basis, as a compressed gas hydrogen may store many more times the energy stored in compressed air: At 20 bar pressure, 1 m³ of H₂ stores 229 MJ of energy in chemical form, while 1 m³ of air at the same pressure would store merely 6.0 MJ of energy as exergy of compressed air. At 700 bar pressure, 1 m³ of hydrogen will store 8,010 MJ and the compressed air only 459 MJ.
2. It is a stable molecular compound and does not change form if stored. This implies that it may be used after a long time.
3. It combines readily with oxygen to form water, which is harmless.
4. It is abundant on the surface of the Earth and it may be relatively easily and economically produced by the electrolysis of water.
5. It is not harmful to the environment if released and does not pose any health threat to humans.
6. It may be readily used in fuel cells (Sect. 12.6) with high conversion efficiencies.
7. It has been used for a long time as an industrial material and as propulsion fuel in the space shuttle and several types of rockets. There is significant expertise in storing and handling it.

Hydrogen has also several disadvantages as an energy storage medium: At first it is flammable and explosive, and, hence, it must be kept in special containers and be transported under well-controlled conditions. Because of its high specific energy content and its high diffusivity, hydrogen forms a powerfully explosive mixture with air. For this reason, hydrogen containers or pipelines must be well-designed to avoid significant leakage and mixing with air. Secondly, since hydrogen is the lightest element, its density is very low under atmospheric conditions (0.08 kg/m³ vs. 1.2 kg/m³ for air). High pressures or very large containers must be used for the storage of a significant mass of this gas. Thirdly, because the hydrogen molecule is very light, hydrogen may diffuse through the matrix of several metals including steel. When hydrogen diffuses through metal matrices it causes *hydrogen embrittlement* and *decarburization*.

Hydrogen embrittlement (or hydrogen grooving) occurs when hydrogen atoms diffuse through the metal matrix and accumulate in very small cracks. The accumulation of the gas in these, so called “voids” of the metal matrix creates high internal pressure, lower ductility and lower strength for the metal. Cracks in the metal matrix may easily propagate and open under relatively low internal

pressure to release the stored hydrogen. Decarburization of steel is another consequence of the hydrogen diffusion: hydrogen atoms combine with the carbon in the grain boundaries and voids of the steel matrix to produce methane. This gas does not diffuse through the metal matrix. It accumulates in cracks and induces a significantly higher local internal pressure, which causes the cracks to propagate and the metal to break. A similar process occurs with copper alloys that contain oxygen: The diffusing hydrogen combines with oxygen and forms water (steam) which accumulates in the metal matrix and induces a higher pressure. Oftentimes, this process is called steam embrittlement and leads to a significant reduction of the strength of a copper container.

Despite the disadvantages of hydrogen as an energy storage medium, the high energy storage capacity of this chemical in combination with its abundance on the surface of the Earth and the relative easy way to produce it by electrolysis, make this gas a very viable energy storage medium. Improved materials and metal coatings in combination with improved methods of storage and transportation will evolve in the future. These would enable the extensive use of hydrogen as an energy storage medium. Several scientists have suggested that the widespread use of hydrogen as energy fuel will transform the economy of the planet into the *hydrogen economy*.

The term hydrogen economy was coined in the 1970s. In the context of the hydrogen economy, hydrogen is not a primary energy source but an energy carrier, similar to what electricity is in the beginning of the twenty-first century. Under the hydrogen economy concept, hydrogen will be generated by the electrolysis of water using the energy harnessed by the abundant solar or wind power, or by a chemical method using the heat generated by nuclear power plants. Assuming that the current problems of hydrogen storage and transportation are solved and suitable materials for the storage of hydrogen become readily available, the hydrogen produced will be chemically stable and may be easily stored and transported. The use of the stored and transported hydrogen would virtually eliminate the emission of carbon dioxide and, therefore, will become a method to alleviate the greenhouse effect and global warming. A hydrogen economy may become a panacea for developing countries without fossil fuels: since renewable energy sources, such as wind and solar, are widely and uniformly distributed on the planet, all countries will be capable to achieve energy independence and avoid expensive fossil fuel imports, by using a combination of renewable energy and hydrogen.

Whether a hydrogen economy will evolve in the near or far future would depend greatly on the technological advances related to the storage and transportation of hydrogen as well as on the technological progress that will be made in other methods for energy storage. Proponents of a world-scale hydrogen economy argue that hydrogen is the cleanest source of energy known to end-users, particularly in transportation applications, where it does not release particulate matter and greenhouse gases. Critics of the transition to a hydrogen economy contend that the cost of switching to a national or a global hydrogen distribution system may be prohibitive and an intermediate step may become economically more viable: for example, synthetic fuels from locally-produced hydrogen and atmospheric CO₂,

such as ethanol and methanol, might accomplish the same goals of a hydrogen economy at significantly lower investment. Since the CO₂ input will be from the atmosphere, this scheme will not contribute to the growth of the GHG emissions.

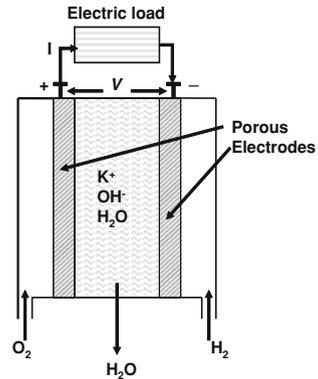
At the end of the first decade of the twenty-first century one may see small but persuasive signs that point to a future transition to a hydrogen economy:

- a) Several European communities from Iceland to Greece have adopted public buses that make use of hydrogen fuel cells.
- b) Several hospitals in the OECD countries have installed combined units that accomplish the electrolysis of water and storage of hydrogen to be used with fuel cell units for emergency power locally. These systems are advantageous for emergency use because of their low maintenance requirement and non pollutant emissions. Such devices may be located at any place, as opposed to internal combustion driven generators, which must have adequate exhaust space.
- c) Countries such as Portugal, Iceland, Norway, Denmark, Germany, Japan, and Canada as well as several states in the U.S.A., such as California, Oregon, Minnesota, and Texas have started investing in hydrogen distribution network systems. Even though these systems have proven to be initially costly, technological breakthroughs and improved methods of hydrogen transport may become lucrative in a future society dominated by hydrogen.
- d) Hydrogen, fuel-cell pilot programs have started in all of the OECD countries as well as in Russia, China, India, and the many of the countries of the Middle East.

The concept of a hydrogen economy has become a futuristic concept that has drawn a great deal of criticism and debate, primarily stemming from the expense of the hydrogen fuel cells and the expense of a hydrogen distribution infrastructure. Our society is dominated at present by fossil fuels to the point that it is almost impossible to think of a mode of transportation outside the framework of liquid fossil fuels, such as gasoline and diesel. However, one must not forget that both of these fuels were entirely novel and very little used until the end of the nineteenth century. Hydrogen is to the humans of 2011, what gasoline was to the humans of 1880. During the twentieth century, a century that is characterized by the widespread use, the extensive exploration and the rapid depletion of fossil fuels, a planet-wide infrastructure was developed for the mining, transportation and distribution of liquid fossil fuels. The petrol/gasoline station, which is ubiquitous in the modern society, was not always present in almost every corner of urban developments. To the citizen of 1880s, today's infrastructure for the transportation and distribution of liquid fossil fuels would have appeared prohibitively expensive and out of reach. A future with an extensive hydrogen infrastructure appears the same way to the citizens of the early twenty-first century.

It is an undisputable fact that gasoline and diesel will be exhausted at some point in the near or far future. There will be a point in the future of the humanity, when the use of liquid fossil fuels will be significantly curtailed and will finally

Fig. 12.10 Schematic diagram of the hydrogen–oxygen fuel cell



cease. Another fuel will inevitably take the place of the currently used liquid fossil fuels, and hydrogen is a good candidate to become this fuel. This inevitable evolution will be followed by considerable private and public investment in the production, transportation, and distribution of hydrogen. The hydrogen filling station may become in the future as ubiquitous as the gasoline/petrol station is in the beginning of the twenty-first century. The difference between the two fuels is that hydrogen may be continuously produced by renewable or other reliable and environmentally friendly sources of energy in all the countries and all human communities. As a result, the hydrogen distribution station and the hydrogen economy is sustainable and will last for a much longer period of time than the liquid fossil fuels.

12.6 Fuel Cells

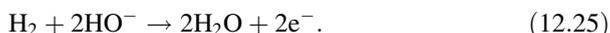
Fuel cells are an integral part of the transition to a hydrogen economy, because they offer a direct conversion of chemical energy to electric energy that is both convenient and has very high efficiency. Fuel cells are similar to batteries, but are open thermodynamic systems, which may operate continuously. They are continuously supplied with fluid fuels and oxidants, their electrodes are not part of the reaction process and, hence, do not need to be regenerated or recharged. Although fuel cells were invented almost one century before the internal combustion engine, in 1802 by Sir Humphrey Davy, and were used for the operation of a tractor as early as 1839 by Sir William Grove, they have not been widely used in practical operations. This, despite the distinct thermodynamic and environmental advantages they present for the conversion of energy.

A schematic diagram of a fuel cell operating with hydrogen as the fuel and oxygen as the oxidant is shown in Fig. 12.10. Hydrogen is supplied to the cell on the side of the cathode, and oxygen is supplied on the side of the anode. The two

Table 12.2 Several types of fuel cells and corresponding maximum voltage at 298 K

Fuel	Reaction	$-\Delta G^\circ$ (kJ/kmol)	V_{max} (V)
H ₂	H ₂ +1/2O ₂ →H ₂ O	236,100	1.22
CO	CO+1/2O ₂ →CO ₂	275,100	1.43
CH ₄	CH ₄ +2O ₂ →CO ₂ +2H ₂ O	831,650	1.08
CH ₃ OH	CH ₃ OH+3/2O ₂ →CO ₂ +2H ₂ O	718,000	1.24
C ₂ H ₅ OH	C ₂ H ₅ OH+3O ₂ →2CO ₂ +3H ₂ O	1,357,700	1.17

electrodes are composed of a porous material and enclose a strong basic solution of potassium hydroxide (KOH), which is dissociated into K⁺ and OH⁻ ions. Hydrogen diffuses into the pores of the cathode, combines with the hydroxyl ions (OH⁻), forms water and releases two electrons according to the reaction:



On the side of the anode, oxygen also diffuses into the pores and combines with water molecules and electrons to form hydroxyl ions (OH⁻):



Overall, the water forming reaction from oxygen and hydrogen takes place in the fuel cell with the potassium ions being the catalyst. As in the case of the batteries, the anode has a deficiency of electrons and, hence, a positive electric charge, while the cathode has a surplus of electrons and a negative charge. The potential difference created between the anode and the cathode induces an electric current to pass through an external circuit. Hydrogen and oxygen may be continuously supplied to their respective chambers, from where they are diffusing in the pores of the cathode and the anode respectively. The water produced may also be continuously removed from the fuel cell. In practice, instead of water, a weak solution of potassium hydroxide (KOH) is removed from the cell. In order to restore the chemical balance, a hydrogen–oxygen fuel cell must be supplied periodically with a concentrated solution of KOH.

In general, fuel cells are supplied with a fuel and an oxidant, which is normally air at atmospheric pressure. Several types of fuels, other than hydrogen, have been proposed to be used. Table 12.2 lists some of these fuels; the corresponding overall oxidation reactions; the Gibbs free energy of these reactions; and the electromotive force or maximum voltage that may be obtained according to Eq. (12.20). It is apparent from this table that all these practical fuel cells produce a maximum voltage of the order of 1 V. Therefore, several fuel cells in series would be required to produce a significant voltage difference and this is one of the main disadvantages of fuel cell systems: Operating too many fuel cells in series or having very high currents would increase significantly the electrical losses (irreversibilities) of the fuel cell systems.

12.6.1 High-Temperature Fuel Cells

Higher values of the produced voltage with fuel cells are achieved by having several fuel cells in series, or “stacks.” Typically, fuel cells are in stacks of 20–30 units, which provide operational voltages close to 30 V. The fuel cells are joined by the *interconnect*, which is either a metallic or ceramic layer that connects the individual cells. The function of the interconnect is to connect each fuel cell in series, so that the voltage each cell generates may be added. Because the interconnect is exposed to both the oxidizing and the reducing side of the cell at high temperatures, it must be an extremely stable material. Ceramic materials as well as metals have been used as interconnect materials.

One of the ways to increase the voltage of an individual fuel cell is to operate the cell at a temperature higher than the ambient: ΔG° is a strong function of temperature and there are several reactions, for which the maximum voltage at elevated temperatures is significantly higher than the voltage at ambient conditions. An added advantage of such fuel cells is that the rates of all chemical reactions are faster at elevated temperatures. This implies that the power produced by the high-temperature cells may be significantly higher than the power produced by the same cells at ambient temperature. High-temperature fuel cells have been put in service where the operating temperature is in the range of 600–1,000°C and the maximum voltage is in the range of 3–7 V. Examples of such high-temperature fuel cells are the Solid Oxide Fuel Cells (SOFCs).

Because of the high temperatures, SOFCs do not use water as the electrolyte, but a dense layer of ceramic that conducts oxygen and fuel ions. Both cathode and anode must be good electric conductors and of high porosity to allow the diffusion of ions. The lanthanum-strontium-manganite (LSM) is one of the cathode materials that are frequently used for high temperature fuel cells and the yttria stabilized zirconia mixed with nickel metal for high conductivity is an anode material that is commonly used. The oxidation reaction that occurs between the fuel and the oxygen ions produces both water and electricity. If the fuel is hydrogen, water is the only product of the reaction. However, if the fuel is a hydrocarbon a high-temperature fuel cell may be used for the production of hydrogen.

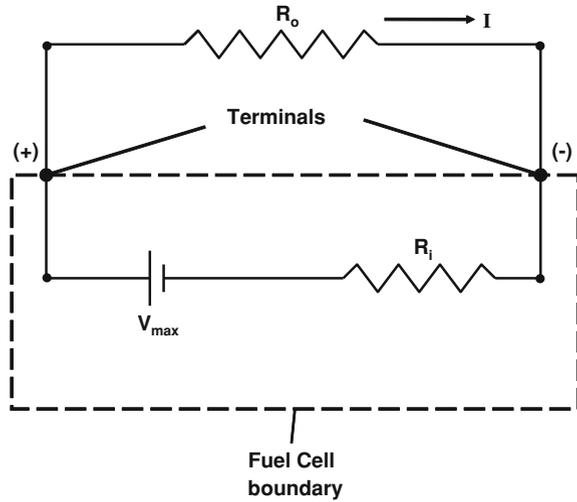
While the high operating temperatures of SOFCs allow the kinetics of oxygen ion transport to be sufficiently fast for the good performance of the cell and the production of sufficient power, when the operating temperature approaches the lower limit for the SOFCs operation, which is around 600°C, the electrolyte begins to exhibit large ionic transport resistance. This lowers the voltage generated and adversely affects the overall performance of the high temperature fuel cells [2].

12.6.2 Thermodynamic Losses and Fuel Cell Efficiency

Similar to the other electrochemical cells, fuel cells are direct energy conversion devices (DEC) and are not subject to the Carnot limitations of heat engines. In principle, the entire chemical energy of a fuel cell, $-\Delta G^o$, may be converted to electric energy ($-\Delta G^o = VI$) in a fuel cell that operates reversibly. In practice, thermodynamic losses occur, fuel cells do not operate reversibly, a fraction of the chemical energy is converted to heat and, as a result, the actual voltage obtained is lower than the maximum voltage given by Eq. (12.20). The following are the most common irreversibilities that result in power losses in fuel cells:

1. *Polarization losses*: Polarization or over-potential losses are due to the imperfections of the materials, of the microstructure, and of the design of the fuel cell. Polarization occurs from the ohmic resistance of oxygen ions as they are transported through the electrolyte; the electrochemical activation barriers at the anode and the cathode (this is almost absent in high-temperature fuel cells, where activation rates are high); and the concentration polarization, which is due to the very slow diffusion of ions through the porous anode and cathode.
2. *Ohmic polarization losses*: Ohmic losses emanate from the ionic conductivity through the electrolyte, which is a material property of the electrolyte and the ions involved. Ionic conductivity may be enhanced by: a) operating at higher temperatures, which decreases significantly the ohmic losses; b) doping methods that optimize the crystal structure of the electrolyte and control concentrations of material defects in the electrolyte matrix; and c) decrease of the thickness of the electrolyte layer.
3. *Concentration polarization losses*: These losses are the result of the finite fuel and oxidant diffusion processes that govern the movement of gases in the overall electrochemical reaction. Since the rate of mass transport of gases is subject to the Fick's diffusion law, the maximum rate of gas diffusion, which is directly related to the maximum current density that may be obtained, is achieved when the concentration of the fuel in the electrochemically active area is zero. The measure of the concentration polarization is the potential difference between two modes of operation of the fuel cell: a) when the current is flowing and b) when the external circuit is open and current is not flowing at all.
4. *Activation polarization losses*: These losses are the result of the reaction kinetics involved with the overall electrochemical reactions. Each chemical reaction has an activation barrier, which must be overcome for the reaction to proceed and the voltage to be developed. This barrier leads to additional polarization. The activation barrier is the result of the many electrochemical reaction steps, where the rate limiting step is responsible for the polarization. Good design and optimization of the microstructure of the electrolyte and the electrodes of the fuel cell may reduce significantly the activation polarization losses. This is in general accomplished by increasing the *triple phase boundary length (tpbl)*, which is the electrochemically active part of a fuel cell.

Fig. 12.11 The electric circuit diagram of a fuel cell



All the irreversibilities associated with the operation of a fuel cell may be lumped together in the concept of the *internal resistance* of the cell.⁴ The internal resistance is the cause of energy dissipation that would have been produced by the cell under ideal conditions. Figure 12.11 shows the electric circuit model of the fuel cell with the internal resistance R_i . While the cell produces its full electromotive force or maximum voltage, V_{\max} , because of the internal losses, $R_i I$, the voltage available to the external circuit, V , and which produces the power delivered is lower:

$$V = V_{\max} - IR_i \quad (12.27)$$

The power produced by the fuel cell is the power that is available to the circuit outside the cell:

$$\dot{W} = VI = V_{\max}I - I^2R_i. \quad (12.28)$$

Under the normal operation of fuel cells and batteries an amount of power equal to I^2R_i is dissipated inside the cell as heat and should be removed. As with all the power producing devices, fuel cells produce their own waste heat. It must be noted, however, that this is not a consequence of the Carnot limitations of thermo-mechanical conversion devices, but of the electrical and chemical irreversibilities outlined above.

⁴ The same concept may be applied to the operation of the Daniel cells and all electrochemical devices.

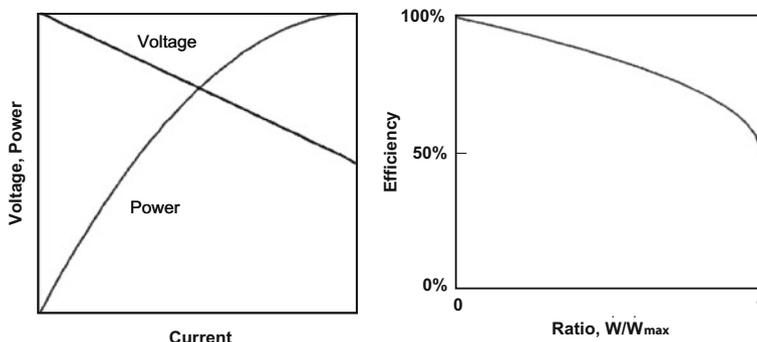


Fig. 12.12 Voltage, power and efficiency of a fuel cell or battery

Another source of irreversibilities in the operation of fuel cells stems from the fact that fuel cells and batteries produce direct voltage and direct current. The same applies to other direct energy conversion devices, such as photovoltaic solar cells. Most of the electric appliances and equipment used in households and industry are designed to use alternating current. If the power produced by the fuel cells is to be used for the supply of electricity to residential communities, the power must be converted or “inverted” to alternating current. Industrial inverters, which are placed at the point of power production, are commonly used for this purpose. A small amount of power, typically 10–20%, is lost in the inverter. This loss of power is expressed by the efficiency of the inverter, which is defined as the ratio of the electric power output to the electric power input. As with all devices, the lost power in the inverter is dissipated as heat and must be removed.

There are several figures of merit or efficiencies that describe the operation of fuel cells, as well as that of other electrochemical cells. These figures of merit are expressed in terms of the voltage or the current obtained from the cell or in terms of the total electric energy produced in the fuel cell. The following three different measures of the ability of a fuel cell to produce voltage, current and power, and which are often called efficiencies of fuel cells, have been commonly used:

$$\eta_V = \frac{V}{V_{\max}}, \quad \eta_I = \frac{I}{I_{\max}} \quad \text{and} \quad \eta = \frac{VI}{-\dot{n}\Delta H^o} = \frac{\dot{W}}{-\dot{n}\Delta H^o}, \quad (12.29)$$

where \dot{n} is the rate of moles of the fuel that is fed to the fuel cell. The first two figures of merit are often called *voltage efficiency* and *current efficiency* of the fuel cell. The last expression is the *energetic efficiency* of the cell or, simply, the *efficiency* of the fuel cell. This figure of merit is the ratio of the instantaneous electric power produced to the chemical power delivered to the cell. Figure 12.12 shows the external voltage and power as a function of the current as well as the efficiency of the fuel cell as a function of the power produced. A glance at Eqs. (12.28) and (12.29) and this figure proves that the external voltage and the

efficiency of the fuel cell decrease significantly with the current and power produced. Actually, at maximum power, the voltage at the electrodes is $V = 0.5V_{max}$ and the efficiency of the fuel cell is 50%. This is achieved when $R_i = R_e$. The maximum efficiency of the fuel cell is reached when the current approaches zero and the power produced also approaches zero. Therefore, in fuel cells as well as in batteries there is a trade-off between achieving maximum power and high energetic efficiency. For this reason, practical fuel cells operate at conditions below maximum power, conditions that make their efficiencies higher than 50%.

It is observed in Eq. (12.29) that the enthalpy difference of the underlying reaction is used in the expression for the energetic efficiency, instead of the Gibbs free energy ($-\Delta G^o$), which is more relevant to chemical reactions. The reason is historical and stems from the fact that common fuels, such as methane, hydrogen, or ethyl alcohol, have been routinely used for the production of heat. When these fuels are burned in a conventional way for the production of power, the maximum energy (heat) produced is $-\Delta H^o$, not $-\Delta G^o$. Hence, the former quantity has been traditionally used with these fuels and was extended to the determination of the efficiencies of fuel cells. Since the maximum electric energy that may be produced by a fuel cell is equal to $(-\Delta G^o)$, and given the relationship between ΔG^o and ΔH^o , the maximum power efficiency of a fuel cell is given by the expression:

$$\eta_{max} = \frac{-\Delta G^o}{-\Delta H^o} = 1 - T \frac{\Delta S^o}{\Delta H^o}, \quad (12.30)$$

where ΔS^o is the entropy change of the overall reaction.⁵

It must be noted that the entropy change of several fuel-oxidant reactions is negative, especially the entropy change of the combustion of liquid fuels. This implies that $\eta_{max} > 1$. For example, the combustion reactions of methanol (CH_3OH) and ethanol ($\text{C}_2\text{H}_5\text{OH}$) to form carbon dioxide and water at 298 K and 1 atm have $\Delta G^o = -689,420$ and $-1,299,640$ kJ/kmol respectively. The enthalpy change of these combustion reactions, ΔH^o , is $-676,270$ and $-1,234,810$ kJ/kmol respectively. The maximum theoretical efficiencies of fuel cells that would operate with methanol and ethanol would be $\eta_{max} = 1.02$ and 1.05 . Of course, the maximum efficiencies are achieved at extremely low values of the flowing current and of the power produced.

Although efficiencies higher than 1 (100%) are uncommon in engineering applications, they are not impossible and do not by any means violate any physical laws. Most of the efficiencies, as well as other figures of merit, such as coefficients of performance for heat pumps and refrigerators, have been defined by engineering convention, not by natural laws. Although these figures of merit have been defined so that, in most cases, their numerical values are in the range between 0 and 100%,

⁵ Most of the fuel cells operate at atmospheric pressure and for this reason the relevant properties ΔH^o and ΔG^o , which may be readily found in thermodynamic or chemical tables, are used here. In the rare case when the fuel cell operates at a different pressure, the relevant properties would be ΔH and ΔG , evaluated at the temperatures and pressures of the pertinent reactions.

in practice they may take any numerical value. Of all such figures of merit, it is only the Carnot efficiency, which stems from the second law of thermodynamics that is always constrained to be less than 100%. As it may be concluded from Eq. (12.30), all fuels that react with oxygen and have a negative entropy of reaction, would also yield $\eta_{max} > 1$ when they are used in fuel cells.

Problems

1. A small, 40 MW peak-power gas turbine operates every day from 10:00 am to 6:00 pm during the months of May, June, July and August. The gas turbine is shut down the rest of the time. Determine the availability factor and the capacity factor of this power plant.
2. A 1,000 MW nuclear power plant operates at full power during the day and at 80% from 11:00 pm to 6:00 am every day of the year. The plant is recharged with fuel and maintained every 18 months. During re-charging and maintenance, the plant does not produce any power for 20 days. Determine the availability factor and the capacity factor of this power plant.
3. A large, 800 MW nuclear power plant produces electricity at full capacity during the day. 40% of its electric capacity during the night is diverted to pump water from a river to a mountainous lake at 740 m higher elevation. The pumped water is used for the production of additional power during the daytime. The same conduits are used for the return of the water and the pump-motor assemblies double as turbine-generator pairs when the flow is reversed. It is estimated that the frictional and other losses during the pumping/returning operation are 15% of the head (that is equivalent to 111 m). The efficiency of the turbomachinery is 70% when they operate in the pump-motor mode and 75% when they operate in turbine-generator mode. What is the peak power this combination of nuclear/hydroelectric power plant produces and how much energy is lost annually by the storage-generation part of this power plant?
4. A 120 m³ air vessel has been designed to store pressurized air. A compressor fills this vessel with 420 K, 100 atm air. During the storage period, the temperature of the air drops to 370 K. Determine:
 - a) The mass of air stored in the vessel.
 - b) The total exergy of the air when the filling process stops.
 - c) The final pressure of the air and the total exergy of the air.
 - d) The exergy loss during the storage period.
5. A 9,000 m³ underground cavern has been constructed for the storage of pressurized air at 25 bar. An above-ground water reservoir maintains the pressure of the air constant during the filling and emptying processes. The temperature during the filling process is 178°C. What is the total mass of the stored air and what is the maximum amount of work this air–water system may produce? During the storage time, the temperature of the air drops to 83°C. As a result, the volume of the air shrinks and water seeps into the cavern to maintain the constant

- pressure of 25 bar, without producing any work. What is the maximum amount of work the air–water system may produce at this state?
6. A $10,000 \text{ m}^3$ underground cavern has been proposed for the storage of pressurized air at 32 bar. An above-ground water reservoir maintains the pressure of the air constant at 32 bar during the filling and emptying processes. If the temperature during the filling process is 155°C , what is the total mass of the stored air and what is the maximum amount of energy this air–water system may produce? After a few months of operation, it is discovered that fissures develop in the cavern and that air leaks at an average rate of 1.2 kg/s . How much air mass is leaked during a 12 h storage period and how much volume does this correspond to? If the temperature of the air also drops to 37°C during the storage period, what is the maximum total energy that may be recovered from this storage facility?
 7. A steel torsion bar is to be used for the storage of energy. The bar is cylindrical ($R = 5 \text{ cm}$) and has a length of 1.2 m. What is the energy stored in the bar when it is rotated by 15° ? What are the friction forces at the grips of two ends of the bar that would maintain this shear?
 8. A flywheel is constructed with thin spokes and resembles a bicycle wheel. Assuming that the mass of the flywheel is 500 kg and that all the mass is concentrated at a radius of 2 m, what would be the rpm of the flywheel if it is to provide 0.1 MW power for 1 min?
 9. Rock has often been suggested as a medium for the thermal storage of energy. A cylindrical piece of rock with diameter 10 m and height 20 m is used for the storage of thermal energy. The rock is insulated and has an average heat transfer coefficient, $U = 0.28 \text{ kW/m}^2 \text{ K}$. The density of the rock material is $2,650 \text{ kg/m}^3$ and its specific heat capacity is 0.72 kJ/kgK . The temperature of the rock is raised to 500°C and the ambient temperature is 25°C . Determine:
 - a) The total energy stored in the rock in MWh.
 - b) The temperature of the rock 12 h after the heating process stops.
 - c) The heat that has escaped from the rock during this 12 h period.
 - d) The loss of exergy of the rock during this 12 h period.
 10. The power demand during a typical summer day in San Antonio, Texas is depicted in Fig. 12.2. This power demand is typical of urban environments in the OECD countries during the hot summer season. 60% of the demand between the hours noon to 10:00 pm is due to air-conditioning. In order to reduce peak power demand it is suggested that eutectic salts be used in conjunction with air conditioners to provide “coolness.” The eutectic salts will be frozen from midnight to 10:00 am and will provide cooling from noon to 10:00 pm. Draw a diagram of a typical power demand during a typical summer day if 20% of the consumers in San Antonio adopt this air-conditioning method. What is the percent reduction of the peak power?
 11. The Gibbs free energy change of the Pb-PbO_2 reaction with sulfuric acid is $\Delta G^\circ = 286,160 \text{ kJ/kmol}$. Determine what is the maximum voltage an electrochemical cell based on this reaction will produce.

12. The combustion of methane produces $\Delta H^\circ = 800,320$ kJ/kmol of heat, which is typically used in a Rankine or Brayton cycle for the production of electricity. If the overall efficiency of the thermal cycle is 43%, what is the mass flow rate of methane that would power a 10 MW small power plant? If the same quantity of methane were to be used in a system of fuel cells with 70% efficiency, what is the power these fuel cells would produce?
13. A steel vessel of 0.5 m^3 may be used for the storage of pressurized air or pressurized hydrogen. The maximum pressure for air is 100 bar, and the maximum pressure for hydrogen 70 bar. What is the maximum electric work that may be obtained from the storage of the two substances? What is the ratio of the two and what do you conclude about the suitability of the two gases for energy storage?
14. Under normal operation, a hydrogen–oxygen fuel cell produces a current of 3.6 A and a voltage of 0.86 V. What is the internal resistance of this fuel cell? What is the energetic efficiency of this fuel cell?
15. A hydrogen–oxygen fuel cell is designed to produce 3.2 MW of electric power for a small town. The efficiency of the fuel cell is 72% and the efficiency of the inverter is 88%. For the rated power of 3.2 MW calculate:
 - a) The flow rates (kmol/s) of hydrogen and oxygen consumed by the fuel cell.
 - b) The waste heat generated in the fuel cell.
 - c) The waste heat from the inverter.

Suggest ways to remove the waste heat from the fuel cell and the inverter.

References

1. EL-Wakil MM (1984) Power Plant Technology, McGraw-Hill, Newyork
2. Tester JW, Drake EM, Driscoll MJ, Golay MW, Peters WA (2005) Sustainable Energy: Choosing among options, MIT Press, Cambridge