

12

Energy Storage Technologies

12.1	Overview of Storage Technologies.....	12-1
12.2	Principal Forms of Stored Energy.....	12-3
12.3	Applications of Energy Storage.....	12-3
12.4	Specifying Energy Storage Devices.....	12-4
12.5	Specifying Fuels.....	12-6
12.6	Direct Electric Storage.....	12-7
	Ultracapacitors • Superconducting Magnetic Energy Storage	
12.7	Electrochemical Energy Storage.....	12-8
	Secondary Batteries • Lead–Acid • Lithium–Ion • Nickel–Cadmium • Nickel–Metal Hydride • Sodium–Sulfur • Zebra • Flow Batteries • Electrolytic Hydrogen	
12.8	Mechanical Energy Storage.....	12-13
	Pumped Hydro • Compressed Air • Flywheels	
12.9	Direct Thermal Storage.....	12-15
	Sensible Heat • Latent Heat	
12.10	Thermochemical Energy Storage.....	12-19
	Biomass Solids • Ethanol • Biodiesel • Syngas	
	References.....	12-21

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12.1 Overview of Storage Technologies

Energy storage will play a critical role in an efficient and renewable energy future; much more so than it does in today's fossil-based energy economy. There are two principal reasons that energy storage will grow in importance with increased development of renewable energy:

- Many important renewable energy sources are intermittent, and generate when weather dictates, rather than when energy demand dictates.
- Many transportation systems require energy to be carried with the vehicle.¹

¹This is almost always true for private transportation systems, and usually untrue for public transportation systems, which can rely on rails or overhead wires to transmit electric energy. However, some public transportation systems such as buses do not have fixed routes and also require portable energy storage.

Energy can be stored in many forms: as mechanical energy in rotating, compressed, or elevated substances; as thermal or electrical energy waiting to be released from chemical bonds; or as electrical charge ready to travel from positive to negative poles on demand.

Storage media that can take and release energy in the form of electricity have the most universal value, because electricity can efficiently be converted either to mechanical or heat energy, whereas other energy conversion processes are less efficient. Electricity is also the output of three of the most promising renewable energy technologies: wind turbines, solar thermal, and photovoltaics. Storing this electricity in a medium that naturally accepts electricity is favored, because converting the energy to another type usually has a substantial efficiency penalty.

Still, some applications can benefit from mechanical or thermal technologies. Examples are when the application already includes mechanical devices or heat engines that can take advantage of the compatible energy form; lower environmental impacts that are associated with mechanical and thermal technologies; or low cost resulting from simpler technologies or efficiencies of scale.

In this chapter, the technologies are grouped into five categories: direct electric, electrochemical, mechanical, direct thermal, and thermochemical. Table 12.1 is a summary of all of the technologies covered. Each is listed with indicators of appropriate applications that are further explained in Section 12.3.

TABLE 12.1 Overview of Energy Storage Technologies and Their Applications

	Utility Shaping	Power Quality	Distributed Grid	Automotive
		Direct electric		
Ultracapacitors		✓		✓
SMES		✓		
		Electrochemical		
Batteries				
Lead–acid	✓	✓	✓	
Lithium-ion	✓	✓	✓	✓
Nickel–cadmium	✓	✓		
Nickel–metal hydride				✓
Zebra				✓
Sodium–sulfur	✓	✓		
Flow Batteries				
Vanadium redox	✓			
Polysulfide bromide	✓			
Zinc bromide	✓			
Electrolytic hydrogen				✓
		Mechanical		
Pumped hydro	✓			
Compressed air	✓			
Flywheels		✓		✓
		Direct Thermal		
Sensible Heat				
Liquids			✓	
Solids			✓	
Latent Heat				
Phase change	✓		✓	
Hydration–dehydration	✓			
Chemical reaction	✓		✓	
		Thermochemical		
Biomass solids	✓		✓	
Ethanol	✓			✓
Biodiesel				✓
Syngas	✓			✓

All technologies are discussed in this chapter except hydrogen-based solutions.

12.2 Principal Forms of Stored Energy

The storage media discussed in this chapter can accept and deliver energy in three fundamental forms: electrical, mechanical, and thermal. Electrical and mechanical energy are both considered high-quality energy because they can be converted to either of the other two forms with fairly little energy loss (e.g., electricity can drive a motor with only about 5% energy loss, or a resistive heater with no energy loss).

The quality of thermal energy storage depends on its temperature. Usually, thermal energy is considered low quality because it cannot be easily converted to the other two forms. The theoretical maximum quantity of useful work W_{\max} (mechanical energy) extractable from a given quantity of heat Q is

$$W_{\max} = \frac{T_1 - T_2}{T_1} \times Q,$$

where T_1 is the absolute temperature of the heat and T_2 is the surrounding, ambient absolute temperature.

Any energy storage facility must be carefully chosen to accept and produce a form of energy consistent with either the energy source or the final application. Storage technologies that accept and/or produce heat should, as a rule, only be used with heat energy sources or with heat applications. Mechanical and electric technologies are more versatile, but in most cases electric technologies are favored over mechanical because electricity is more easily transmitted, because there is a larger array of useful applications, and because the construction cost is typically lower.

12.3 Applications of Energy Storage

In Table 12.1 above, each technology is classified by its relevance in one to four different, principal applications:

- *Utility shaping* is the use of very large capacity storage devices to answer electric demand, when a renewable resource is not producing sufficient generation. An example would be nighttime delivery of energy generated by a solar thermal plant during the prior day.
- *Power quality* is the use of very responsive storage devices (capable of large changes in output over very short timescales) to smooth power delivery during switching events, short outages, or plant run-up. Power-quality applications can be implemented at central generators, at switchgear locations, and at commercial and industrial customers' facilities. Uninterruptible power supplies (UPS) are an example of this category.
- *Distributed grid technologies* enable energy generation and storage at customer locations, rather than at a central (utility) facility. The distributed grid is an important, enabling concept for photovoltaic technologies that are effective at a small scale and can be installed on private homes and commercial buildings. When considered in the context of photovoltaics, the energy storage for the distributed grid is similar to the utility shaping application in that both are solutions to an intermittent, renewable resource, but distributed photovoltaic generation requires small capacities in the neighborhood of a few tens of MJ, while utility shaping requires capacities in the TJ range.² Renewable thermal resources (solar, geothermal) can also be implemented on a distributed scale, and require household-scale thermal storage tanks. For the purposes of this chapter, district-heating systems are also considered a distributed technology.

²Storage capacities in this chapter are given in units of MJ, GJ, and TJ: 1 MJ = 0.28 kWh, 1 GJ = 280 kWh, and 1 TJ = 280 MWh.

- *Automotive applications* include battery-electric vehicles (EVs), hybrid gasoline–electric vehicles, plug-in hybrid electric vehicles (PHEVs), and other applications that require mobile batteries larger than those used in today’s internal combustion engine cars. A deep penetration of automotive batteries also could become important in a distributed grid. Large fleets of EVs or PHEVs that are grid connected when parked would help enable renewable technologies, fulfilling utility shaping and distributed grid functions as well as their basic automotive function.

Additional energy storage applications exist, most notably portable electronics and industrial applications. However, the four applications described here make up the principal components that will interact in a significant way with the global energy grid.

12.4 Specifying Energy Storage Devices

Every energy storage technology, regardless of category, can be roughly characterized by a fairly small number of parameters. Self-discharge time, unit size, and efficiency serve to differentiate the various categories. Within a category, finer selections of storage technology can be made by paying attention to cycle life, specific energy, specific power, energy density, and power density.

Self-discharge time is the time required for a fully charged, noninterconnected storage device to reach a certain depth of discharge (DOD). DOD is typically described as a percentage of the storage device’s useful capacity, so that, for instance, 90% DOD means 10% of the device’s energy capacity remains. The relationship between self-discharge time and DOD is rarely linear, so self-discharge times must be measured and compared at a uniform DOD. Acceptable self-discharge times vary greatly, from a few minutes for some power-quality applications, to years for devices designed to shape annual power production.

Unit size describes the intrinsic scale of the technology, and is the least well-defined of the parameters listed here. If the unit size is small compared to the total required capacity of a project, complexity and supply shortages can increase the cost relative to technologies with a larger unit size. Some technologies have a fairly large unit size that prohibits small-scale energy storage.

Figure 12.1 maps all of the technologies discussed in this chapter, according to their unit size and 10% self-discharge time. The gamut of technologies available covers many orders of magnitude on each axis, illustrating the broad choice available. Utility shaping applications require a moderate self-discharge time and a large unit size; power-quality applications are much less sensitive to self-discharge time but require a moderate unit size. Distributed grid and automotive applications both require a moderate self-discharge time and a moderate unit size.

Efficiency is the ratio of energy output from the device, to the energy input. Like energy density and specific energy, the system boundary must be carefully considered when measuring efficiency. It is particularly important to pay attention to the form of energy required at the input and output interconnections, and to include the entire system necessary to attach to those interconnections. For instance, if the system is to be used for shaping a constant-velocity, utility wind farm, then presumably both the input and output will be AC electricity. When comparing a battery with a fuel cell in this scenario, it is necessary to include the efficiencies of an AC-to-DC rectifier for the battery, an AC-powered hydrogen generation system for the fuel cell system, and DC-to-AC converters associated with both systems.

Efficiency is related to self-discharge time. Technologies with a short self-discharge time will require constant charging to maintain a full charge; if discharge occurs much later than charge in a certain application, the apparent efficiency will be lower because a significant amount of energy is lost in maintaining the initial, full charge.

Cycle life is the number of consecutive charge–discharge cycles a storage installation can undergo while maintaining the installation’s other specifications within certain, limited ranges. Cycle-life specifications are made against a chosen DOD depending on the application of the storage device.

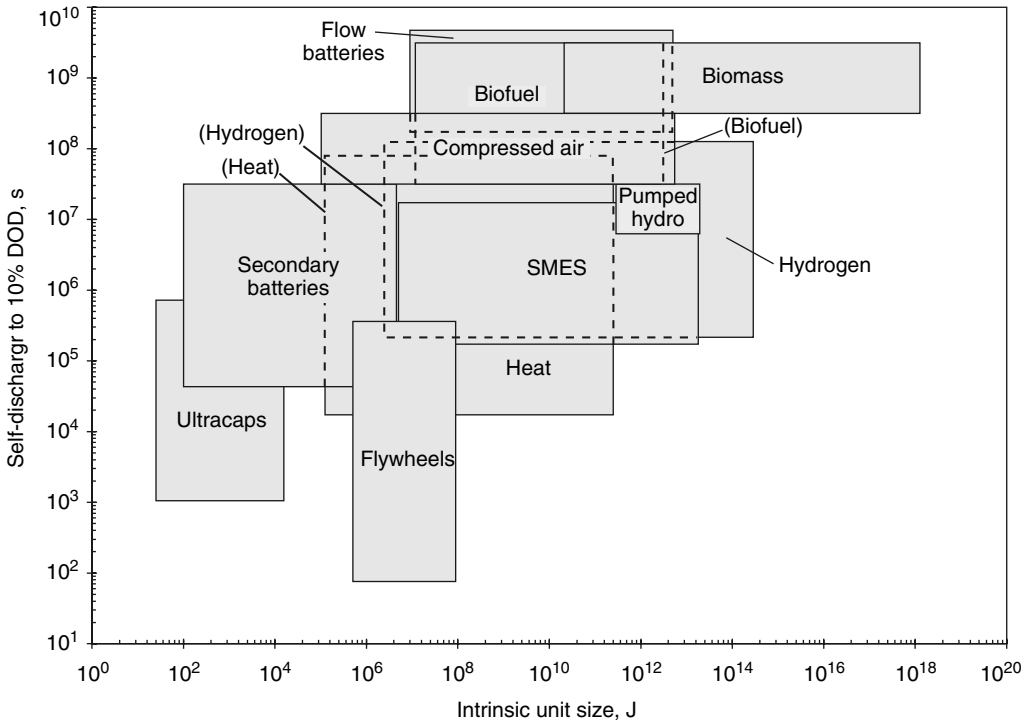


FIGURE 12.1 All storage technologies, mapped by self-discharge time and unit size. Not all hidden lines are shown. Larger self-discharge times are always more desirable, but more or less important depending on the application. Intrinsic unit size does not have a desirability proportional to its value, but rather must be matched to the application.

In some cases, for example pressurized hydrogen storage in automobiles, each cycle will significantly discharge the hydrogen canister and the appropriate DOD reference might be 80% or 90%. In other cases, for example a battery used in a hybrid electric vehicle, most discharge cycles may consume only 10% or 20% of the energy stored in the battery. For most storage technologies, cycle life is significantly larger for shallow discharges than deep discharges, and it is critical that cycle-life data be compared across a uniform DOD assumption.

Specific energy is a measure of how heavy the technology is. It is measured in units of energy per mass, and in this chapter this quantity will always be reported in MJ/kg. The higher the specific energy, the lighter the device. Automotive applications require high specific energies; for utility applications, specific energy is relatively unimportant, except where it impacts construction costs.

Energy density is a measure of how much space the technology occupies. It is measured in units of energy per volume, and in this chapter we will always report this quantity in MJ/L. The higher the energy density, the smaller the device. Again, this is most important for automotive applications, and rarely important in utility applications. Typical values for energy density associated with a few automotive-scale energy technologies are listed in [Table 12.2](#), together with cycle-life and efficiency data.

Energy-density and specific-energy estimates are dependent on the system definition. For example, it might be tempting to calculate the specific energy of a flow battery technology by dividing its capacity by the mass of the two electrolytes. But it is important to also include the mass of the electrolyte storage containers, and of the battery cell for a fair and comparable estimate of its specific energy. Therefore, the energy density and specific energy are dependent on the size of the specific device; large devices benefit from efficiency of scale with a higher energy density and specific energy. *Specific power* and *power density* are the power correlates to specific energy and energy density.

TABLE 12.2 Nominal Energy Density, Cycle Life and Efficiency of Automotive Storage Technologies

	Energy Density MJ/L	Cycle Life at 80% DOD ^a	Electric Efficiency %
Ultracapacitors	0.2	50,000	95
Li-ion batteries	1.8	2,000	85
NiMH batteries	0.6	1,000	80
H ₂ at 350 bar	3.0	n/a ^b	47
H ₂ at 700 bar	5.0	n/a	45
Air at 300 bar	<0.1	n/a	37
Flywheels	<0.1	20,000	80
Ethanol	23.4	n/a	n/a

Electric efficiencies are calculated for electric-to-electric conversion and momentary storage.

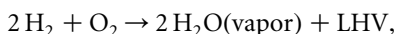
^aDepth of discharge.

^bNot applicable.

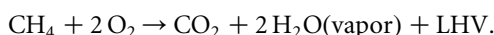
12.5 Specifying Fuels

A fuel is any (relatively) homogenous substance that can be combusted to produce heat. Though the energy contained in a fuel can always be extracted through combustion, other processes may be used to extract the energy (e.g., reaction in a fuel cell). A fuel may be gaseous, liquid, or solid. All energy storage technologies in the thermochemical category store energy in a fuel. In the electrochemical category, electrolytic hydrogen is a fuel.

A fuel's lower heating value (LHV) is the total quantity of sensible heat released during combustion of a designated quantity of fuel. For example, in the simplest combustion process, that of hydrogen,

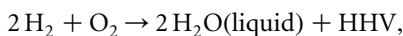


or for the slightly more complex combustion of methane,

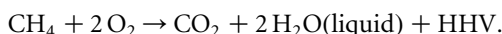


In this chapter, the quantity of fuel is always expressed as a mass, so that LHV is a special case of specific energy. Like specific energy, LHV is expressed in units of MJ/kg in this chapter.

Higher heating value (HHV) is the LHV, plus the latent heat contained in the water vapor resulting from combustion.³ For the examples of hydrogen and methane, this means



and



The latent heat in the water vapor can be substantial, especially for the hydrogen-rich fuels typical in renewable energy applications. Table 12.3 lists LHVs and HHVs of fuels discussed in this chapter; in the most extreme case of molecular hydrogen, the HHV is some 18% higher than the LHV. Recovery of the latent heat requires controlled condensation of the water vapor.

In this chapter, all heating values are reported as HHV rather than LHV. HHV is favored for two reasons: (1) its values allow easier checking of energy calculations with the principle of energy

³The concepts of sensible and latent heat are explained further in Section 12.9.

TABLE 12.3 Properties of Fuels

	Chemical Formula	Density g/L	LHV MJ/kg	HHV MJ/kg
Methanol	CH ₃ OH	794	19.9	22.7
Ethanol	C ₂ H ₅ OH	792	26.7	29.7
Methane	CH ₄	0.68	49.5	54.8
Hydrogen	H ₂	0.085	120	142
Dry syngas, airless process ^a	40H ₂ + 21CO + 10CH ₄ + 29CO ₂	0.89	11.2	12.6
Dry syngas, air process ^a	25H ₂ + 16CO + 5CH ₄ + 15CO ₂ + 39N ₂	0.99	6.23	7.01

^aChemical formulae and associated properties of syngas are representative; actual composition of syngas will vary widely according to manufacturing process.

Source: From All except syngas from U.S. Department of Energy, *Properties of Fuels*, Alternative Fuels Data Center 2004.

conservation, and (2) when examining technologies for future implementation, it is wise to keep an intention of developing methods for extracting as much of each energy source's value as possible.

12.6 Direct Electric Storage

12.6.1 Ultracapacitors

A capacitor stores energy in the electric field between two oppositely charged conductors. Typically, thin conducting plates are rolled or stacked into a compact configuration with a dielectric between them. The dielectric prevents arcing between the plates and allows the plates to hold more charge, increasing the maximum energy storage. The ultracapacitor—also known as supercapacitor, electrochemical capacitor, or electric double layer capacitor (EDLC)—differs from a traditional capacitor in that it employs a thin electrolyte, on the order of only a few angstroms, instead of a dielectric. This increases the energy density of the device. The electrolyte can be made of either an organic or an aqueous material. The aqueous design operates over a larger temperature range, but has a smaller energy density than the organic design. The electrodes are made of a porous carbon that increases the surface area of the electrodes and further increases energy density over a traditional capacitor.

Ultracapacitors' ability to effectively equalize voltage variations with quick discharges make them useful for power-quality management and for regulating voltage in automotive systems during regular driving conditions. Ultracapacitors can also work in tandem with batteries and fuel cells to relieve peak power needs (e.g., hard acceleration) for which batteries and fuel cells are not ideal. This could help extend the overall life and reduce lifetime cost of the batteries and fuel cells used in hybrid and electric vehicles. This storage technology also has the advantage of very high cycle life of greater than 500,000 cycles and a 10- to 12-year life span.¹ The limitations lie in the inability of ultracapacitors to maintain charge voltage over any significant time, losing up to 10% of their charge per day.

12.6.2 Superconducting Magnetic Energy Storage

An superconducting magnetic energy storage (SMES) system is well suited to storing and discharging energy at high rates (high power.) It stores energy in the magnetic field created by direct current in a coil of cryogenically cooled, superconducting material. If the coil were wound using a conventional wire such as copper, the magnetic energy would be dissipated as heat due to the wire's resistance to the flow of current. The advantage of a cryogenically cooled, superconducting material is that it reduces electrical resistance to almost zero. The SMES recharges quickly and can repeat the charge/discharge sequence thousands of times without any degradation of the magnet. A SMES system can achieve full power within 100 ms.² Theoretically, a coil of around 150–500 m radius would be able to support a load of 18,000 GJ at

1000 MW, depending on the peak field and ratio of the coil's height and diameter.³ Recharge time can be accelerated to meet specific requirements, depending on system capacity.

Because no conversion of energy to other forms is involved (e.g., mechanical or chemical), the energy is stored directly and round-trip efficiency can be very high.² SMES systems can store energy with a loss of only 0.1%; this loss is due principally to energy required by the cooling system.³ Mature, commercialized SMES is likely to operate at 97%–98% round-trip efficiency and is an excellent technology for providing reactive power on demand.

12.7 Electrochemical Energy Storage

12.7.1 Secondary Batteries

A secondary battery allows electrical energy to be converted into chemical energy, stored, and converted back to electrical energy. Batteries are made up of three basic parts: a negative electrode, positive electrode, and an electrolyte (Figure 12.2). The negative electrode gives up electrons to an external load, and the positive electrode accepts electrons from the load. The electrolyte provides the pathway for charge to transfer between the two electrodes. Chemical reactions between each electrode and the electrolyte remove electrons from the positive electrode and deposit them on the negative electrode. This can be written as an overall chemical reaction that represents the states of charging and discharging of a battery. The speed at which this chemical reaction takes place is related to the internal resistance that dictates the maximum power at which the batteries can be charged and discharged.

Some batteries suffer from the “memory effect” in which a battery exhibits a lower discharge voltage under a given load than is expected. This gives the appearance of lowered capacity but is actually a voltage depression. Such a voltage depression occurs when a battery is repeatedly discharged to a partial depth and recharged again. This builds an increased internal resistance at this partial depth of discharge and the battery appears as a result to only be dischargeable to the partial depth. The problem, if and when it occurs, can be remedied by deep discharging the cell a few times. Most batteries considered for modern renewable applications are free from this effect, however.

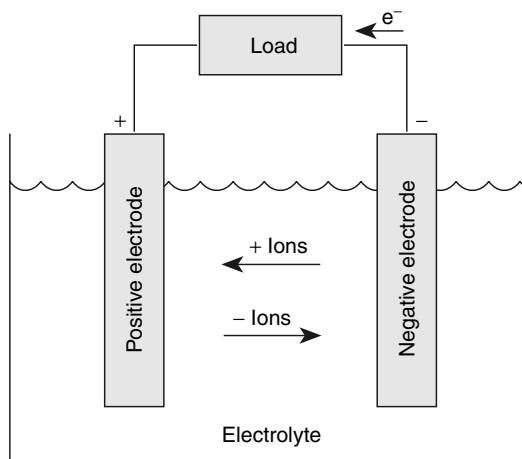
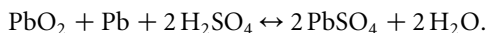


FIGURE 12.2 Schematic of a generalized secondary battery. Directions of electron and ion migration shown are for discharge, so that the positive electrode is the cathode and the negative electrode is the anode. During charge, electrons and ions move in the opposite directions and the positive electrode becomes the anode while the negative electrode becomes the cathode.

12.7.2 Lead–Acid

Lead–acid is one of the oldest and most mature battery technologies. In its basic form, the lead–acid battery consists of a lead (Pb) negative electrode, a lead dioxide (PbO₂) positive electrode and a separator to electrically isolate them. The electrolyte is dilute sulfuric acid (H₂SO₄), which provides the sulfate ions for the discharge reactions. The chemistry is represented by:



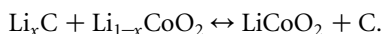
(In all battery chemistries listed in this chapter, left-to-right indicates battery discharge and right-to-left indicates charging.)

There are three main types of lead–acid batteries: the flooded cell, the sealed gel cell, and the sealed absorbed glass mat (AGM) lead–acid battery. The wet cell has a liquid electrolyte that must be replaced occasionally to replenish the hydrogen and oxygen that escape during the charge cycle. The sealed gel cell has a silica component added to the electrolyte to stiffen it. The AGM design uses a fiberglass-like separator to hold electrolyte in close proximity to the electrodes, thereby increasing efficiency. For both the gel and AGM configurations, there is a greatly reduced risk of hydrogen explosion and corrosion from disuse. These two types do require a lower charging rate, however. Both the gel cells and the AGM batteries are sealed and pressurized so that oxygen and hydrogen produced during the charge cycle are recombined into water.

The lead–acid battery is a low-cost and popular storage choice for power-quality applications. Its application for utility shaping, however, has been very limited due to its short cycle life. A typical installation survives a maximum of 1500 deep cycles.⁴ Yet, lead–acid batteries have been used in a few commercial and large-scale energy management applications. The largest one is a 140-GJ system in Chino, California, built in 1988. Lead–acid batteries have a specific energy of only 0.18 MJ/kg and would therefore not be a viable automobile option apart from providing the small amount of energy needed to start an engine. It also has a poor energy density at around 0.25 MJ/L. The advantages of the lead–acid battery technology are low cost and high power density.

12.7.3 Lithium-Ion

Lithium-ion and lithium polymer batteries, although primarily used in the portable electronics market, are likely to have future use in many other applications. The cathode in these batteries is a lithiated metal oxide (LiCoO₂, LiMO₂, etc.) and the anode is made of graphitic carbon with a layer structure. The electrolyte consists of lithium salts (such as LiPF₆) dissolved in organic carbonates; an example of Li-ion battery chemistry is

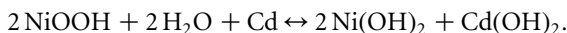


When the battery is charged, lithium atoms in the cathode become ions and migrate through the electrolyte toward the carbon anode where they combine with external electrons and are deposited between carbon layers as lithium atoms. This process is reversed during discharge. The lithium polymer variation replaces the electrolyte with a plastic film that does not conduct electricity but allows ions to pass through it. The 60°C operating temperature requires a heater, reducing overall efficiency slightly.

Lithium-ion batteries have a high energy density of about 0.72 MJ/L and have low internal resistance; they will achieve efficiencies in the 90% range and above. They have an energy density of around 0.72 MJ/kg. Their high energy efficiency and energy density make lithium-ion batteries excellent candidates for storage in all four applications considered here: utility shaping, power quality, distributed generation, and automotive.

12.7.4 Nickel–Cadmium

Nickel–cadmium (NiCd) batteries operate according to the chemistry:

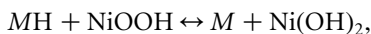


NiCd batteries are not common for large stationary applications. They have a specific energy of about 0.27 MJ/kg, an energy density of 0.41 MJ/L and an efficiency of about 75%. Alaska's Golden Valley Electric Association commissioned a 40-MW/290-GJ nickel–cadmium battery in 2003 to improve reliability and to supply power for essentials during outages.⁵ Resistance to cold and relatively low cost were among the deciding factors for choosing the NiCd chemistry.

Cadmium is a toxic heavy metal and there are concerns relating to the possible environmental hazards associated with the disposal of NiCd batteries. In November 2003, the European Commission adopted a proposal for a new battery directive that includes recycling targets of 75% for NiCd batteries. However, the possibility of a ban on rechargeable batteries made from nickel–cadmium still remains and hence the long-term viability and availability of NiCd batteries continues to be uncertain. NiCd batteries can also suffer from “memory effect,” where the batteries will only take full charge after a series of full discharges. Proper battery management procedures can help to mitigate this effect.

12.7.5 Nickel–Metal Hydride

The nickel–metal hydride (NiMH) battery operates according to the chemistry:

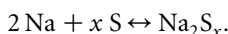


where M represents one of a large variety of metal alloys that serve to take up and release hydrogen. NiMH batteries were introduced as a higher energy density and more environmentally friendly version of the nickel–cadmium cell. Modern nickel–metal hydride batteries offer up to 40% higher energy density than nickel–cadmium. There is potential for yet higher energy density, but other battery technologies (lithium-ion, in particular) may fill the same market sooner.

Nickel–metal hydride is less durable than nickel–cadmium. Cycling under heavy load and storage at high temperature reduces the service life. Nickel–metal hydride suffers from a higher self-discharge rate than the nickel–cadmium chemistry. Nickel–metal hydride batteries have a specific energy of 0.29 MJ/kg, an energy density of about 0.54 MJ/L and an energy efficiency of about 70%. These batteries have been an important bridging technology in the portable electronics and hybrid automobile markets. Their future is uncertain because other battery chemistries promise higher energy storage potential and cycle life.

12.7.6 Sodium–Sulfur

A sodium–sulfur (NaS) battery consists of a liquid (molten) sulfur positive electrode and liquid (molten) sodium negative electrode, separated by a solid beta-alumina ceramic electrolyte (Figure 12.3). The chemistry is as follows:



When discharging, positive sodium ions pass through the electrolyte and combine with the sulfur to form sodium polysulfides. The variable x in the equation is equal to 5 during early discharging, but after free sulfur has been exhausted a more sodium-rich mixture of polysulfides with lower average values of x develops. This process is reversible as charging causes sodium polysulfides in the positive electrode to release sodium ions that migrate back through the electrolyte and recombine as elemental sodium. The battery operates at about 300°C. NaS batteries have a high energy density of around 0.65 MJ/L and a specific energy of up to 0.86 MJ/kg. These numbers would indicate an application in the automotive sector, but warm-up time and heat-related accident risk make its use there unlikely. The efficiency of this

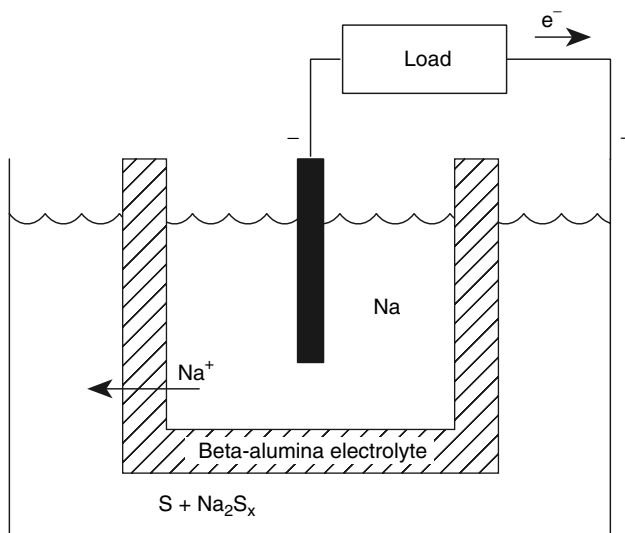
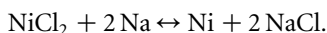


FIGURE 12.3 Sodium–sulfur battery showing discharge chemistry. The sodium (Na) and sulfur (S) electrodes are both in a liquid state and are separated by a solid, beta-alumina ceramic electrolyte that allows only sodium ions to pass. Charge is extracted from the electrolytes with metal contacts; the positive contact is the battery wall.

battery chemistry can be as high as 90% and would be suitable for bulk storage applications while simultaneously allowing effective power smoothing operations.⁶

12.7.7 Zebra

Zebra is the popular name for the sodium–nickel-chloride battery chemistry:



Zebra batteries are configured similarly to sodium–sulfur batteries (see Figure 12.3), and also operate at about 300°C. Zebra batteries boast a greater than 90% energy efficiency, a specific energy of up to 0.32 MJ/kg and an energy density of 0.49 MJ/L.⁷ Its tolerance for a wide range of operating temperature and high efficiency, coupled with a good energy density and specific energy, make its most probable application the automobile sector, and as of 2003 Switzerland’s MES-DEA is pursuing this application aggressively.⁸ Its high energy efficiency also makes it a good candidate for the utility sector.

12.7.8 Flow Batteries

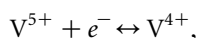
Most secondary batteries use electrodes both as an interface for gathering or depositing electrons, and as a storage site for the products or reactants associated with the battery’s chemistry. Consequently, both energy and power density are tied to the size and shape of the electrodes. Flow batteries store and release electrical energy by means of reversible electrochemical reactions in two liquid electrolytes. An electrochemical cell has two compartments—one for each electrolyte—physically separated by an ion exchange membrane. Electrolytes flow into and out of the cell through separate manifolds and undergo chemical reaction inside the cell, with ion or proton exchange through the membrane and electron exchange through the external electric circuit. The chemical energy in the electrolytes is turned into electrical energy and vice versa for charging. They all work in the same general way but vary in chemistry of electrolytes.⁹

There are some advantages to using the flow battery over a conventional secondary battery. The capacity of the system is scaleable by simply increasing the amount of solution. This leads to cheaper installation costs as the systems get larger. The battery can be fully discharged with no ill effects and has little loss of electrolyte over time. Because the electrolytes are stored separately and in large containers (with a low surface area to volume ratio), flow batteries show promise to have some of the lowest self-discharge rates of any energy storage technology available.

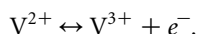
Poor energy densities and specific energies remand these battery types to utility-scale power shaping and smoothing, although they might be adaptable for distributed-generation use. There are three types of flow batteries that are closing in on commercialization: vanadium redox, polysulfide bromide, and zinc bromide.

12.7.8.1 Vanadium Redox

The vanadium redox flow battery (VRB) was pioneered at the University of New South Wales, Australia, and has shown potentials for long cycle life and energy efficiencies of over 80% in large installations.¹⁰ The VRB uses compounds of the element vanadium in both electrolyte tanks. The reaction chemistry at the positive electrode is:



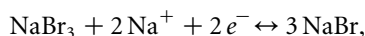
and at the negative electrode,



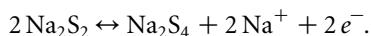
Using vanadium compounds on both sides of the ion-exchange membrane eliminates the possible problem of cross-contamination of the electrolytes and makes recycling easier.¹¹ As of 2005, two small, utility-scale VRB installations are operating, one 2.9-GJ unit on King Island, Australia and one 7.2-GJ unit in Castle Valley, Utah.

12.7.8.2 Polysulfide Bromide

The polysulfide bromide battery (PSB) utilizes two salt solution electrolytes, sodium bromide (NaBr) and sodium polysulfide (Na_2S_x). PSB electrolytes are separated in the battery cell by a polymer membrane that only passes positive sodium ions. The chemistry at the positive electrode is



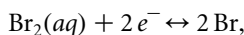
and at the negative electrode,



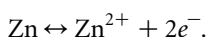
The PSB battery is being developed by Canada's VRB Power Systems, Inc.¹² This technology is expected to attain energy efficiencies of approximately 75%.¹³ Although the salt solutions themselves are only mildly toxic, a catastrophic failure by one of the tanks could release highly toxic bromine gas. Nevertheless, the Tennessee Valley Authority released a finding of no significant impact for a proposed 430-GJ facility and deemed it safe.¹⁴

12.7.8.3 Zinc Bromide

In each cell of a zinc bromide (ZnBr) battery, two different electrolytes flow past carbon-plastic composite electrodes in two compartments separated by a microporous membrane. Chemistry at the positive electrode follows the equation:



and at the negative electrode:



During discharge, Zn and Br combine into zinc bromide. During charge, metallic zinc is deposited as a thin-film on the negative electrode. Meanwhile, bromine evolves as a dilute solution on the other side of the membrane, reacting with other agents to make thick bromine oil that sinks to the bottom of the electrolytic tank. During discharge, a pump mixes the bromine oil with the rest of the electrolyte. The zinc bromide battery has an energy efficiency of nearly 80%.¹⁵

Exxon developed the ZnBr battery in the early 1970 s. Over the years, many GJ-scale ZnBr batteries have been built and tested. Meidisha demonstrated a 1-MW/14-GJ ZnBr battery in 1991 at Kyushu Electric Power Company. Some GJ-scale units are now available preassembled, complete with plumbing and power electronics.

12.7.9 Electrolytic Hydrogen

Diatomic, gaseous hydrogen (H_2) can be manufactured with the process of electrolysis; an electric current applied to water separates it into components O_2 and H_2 . The oxygen has no inherent energy value, but the HHV of the resulting hydrogen can contain up to 90% of the applied electric energy, depending on the technology.¹⁶ This hydrogen can then be stored and later combusted to provide heat or work, or to power a fuel cell.

The gaseous hydrogen is low density and must be compressed to provide useful storage. Compression to a storage pressure of 350 bar, the value usually assumed for automotive technologies, consumes up to 12% of the hydrogen's HHV if performed adiabatically, although the loss approaches a lower limit of 5% as the compression approaches an isothermal ideal.¹⁷ Alternatively, the hydrogen can be stored in liquid form, a process that costs about 40% of HHV using current technology, and that at best would consume about 25%. Liquid storage is not possible for automotive applications, because mandatory boil-off from the storage container cannot be safely released in closed spaces (i.e., garages).

Hydrogen can also be bonded into metal hydrides using an absorption process. The energy penalty of storage may be lower for this process, which requires pressurization to only 30 bar. However, the density of the metal hydride can be between 20 and 100 times the density of the hydrogen stored. Carbon nanotubes have also received attention as a potential hydrogen storage medium.¹⁸

12.8 Mechanical Energy Storage

12.8.1 Pumped Hydro

Pumped hydro is the oldest and largest of all of the commercially available energy storage technologies, with existing facilities up to 1000 MW in size. Conventional pumped hydro uses two water reservoirs, separated vertically. Energy is stored by moving water from the lower to the higher reservoir, and extracted by allowing the water to flow back to the lower reservoir. Energy is stored according to the fundamental physical principle of potential energy. To calculate the stored energy, E_s , in joules, use the formula:

$$E_s = Vdgh,$$

where V is the volume of water raised (m^3), d is the density of water (1000 kg/m^3), g is the acceleration of gravity (9.8 m/s^2), and h is the elevation difference between the reservoirs (m) often referred to as the *head*.

Though pumped hydro is by nature a mechanical energy storage technology, it is most commonly used for electric utility shaping. During off-peak hours electric pumps move water from the lower reservoir to the upper reservoir. When required, the water flow is reversed to generate electricity. Some high dam hydro plants have a storage capability and can be dispatched as pumped hydro storage. Underground pumped storage, using flooded mine shafts or other cavities, is also technically possible but probably prohibitively expensive. The open sea can also be used as the lower reservoir if a suitable upper reservoir

can be built at close proximity. A 30-MW seawater pumped hydro plant was first built in Yanbaru, Japan in 1999.

Pumped hydro is most practical at a large scale with discharge times ranging from several hours to a few days. There is over 90 GW of pumped storage in operation worldwide, which is about 3% of global electric generation capacity.¹⁹ Pumped storage plants are characterized by long construction times and high capital expenditure. Its main application is for utility shaping. Pumped hydro storage has the limitation of needing to be a very large capacity to be cost-effective, but can also be used as storage for a number of different generation sites.

Efficiency of these plants has greatly increased in the last 40 years. Pumped storage in the 1960s had efficiencies of 60% compared with 80% for new facilities. Innovations in variable speed motors have helped these plants operate at partial capacity, and greatly reduced equipment vibrations, increasing plant life.

12.8.2 Compressed Air

A relatively new energy storage concept that is implemented with otherwise mature technologies is compressed air energy storage (CAES). CAES facilities must be coupled with a combustion turbine, so are actually a hybrid storage/generation technology.

A conventional gas turbine consists of three basic components: a compressor, combustion chamber, and an expander. Power is generated when compressed air and fuel burned in the combustion chamber drive turbine blades in the expander. Approximately 60% of the mechanical power generated by the expander is consumed by the compressor supplying air to the combustion chamber.

A CAES facility performs the work of the compressor separately, stores the compressed air, and at a later time injects it into a simplified combustion turbine. The simplified turbine includes only the combustion chamber and the expansion turbine. Such a simplified turbine produces far more energy than a conventional turbine from the same fuel, because there is potential energy stored in the compressed air. The fraction of output energy beyond what would have been produced in a conventional turbine is attributable to the energy stored in compression.

The net efficiency of storage for a CAES plant is limited by the heat energy loss occurring at compression. The overall efficiency of energy storage is about 75%.²⁰

CAES compressors operate on grid electricity during off-peak times, and use the expansion turbine to supply peak electricity when needed. CAES facilities cannot operate without combustion because the exhaust air would exit at extremely low temperatures causing trouble with brittle materials and icing. If 100% renewable energy generation is sought, biofuel could be used to fuel the gas turbines. There might still be other emissions issues but the system could be fully carbon neutral.

The compressed air is stored in appropriate underground mines, caverns created inside salt rocks or possibly in aquifers. The first commercial CAES facility was a 290-MW unit built in Hundorf, Germany in 1978. The second commercial installation was a 110-MW unit built in McIntosh, Alabama in 1991. The third commercial CAES is a 2,700-MW plant under construction in Norton, Ohio. This nine-unit plant will compress air to about 100 bar in an existing limestone mine 2200 ft. (766 m) underground.²¹ The natural synergy with geological caverns and turbine prime movers dictate that these be on the utility scale.

12.8.3 Flywheels

Most modern flywheel energy storage systems consist of a massive rotating cylinder (comprised of a rim attached to a shaft) that is supported on a stator by magnetically levitated bearings that eliminate bearing wear and increase system life. To maintain efficiency, the flywheel system is operated in a low vacuum environment to reduce drag. The flywheel is connected to a motor/generator mounted onto the stator that, through some power electronics, interact with the utility grid.

The energy stored in a rotating flywheel, in joules, is given by

$$E = \frac{1}{2}I\omega^2$$

where I is the flywheel's moment of inertia (kg m^2), and ω is its angular velocity (s^{-2}). I is proportional to the flywheel's mass, so energy is proportional to mass and the square of speed. In order to maximize energy capacity, flywheel designers gravitate toward increasing the flywheel's maximum speed rather than increasing its moment of inertia. This approach also produces flywheels with the higher specific energy.

Some of the key features of flywheels are low maintenance, a cycle life of better than 10,000 cycles, a 20-year lifetime and environmentally friendly materials. Low-speed, high-mass flywheels (relying on I for energy storage) are typically made from steel, aluminum, or titanium; high-speed, low-mass flywheels (relying on ω for energy storage) are constructed from composites such as carbon fiber.

Flywheels can serve as a short-term ride-through before long-term storage comes online. Their low energy density and specific energy limit them to voltage regulation and UPS capabilities. Flywheels can have energy efficiencies in the upper 90% range depending on frictional losses.

12.9 Direct Thermal Storage

Direct thermal technologies, although they are storing a lower grade of energy (heat, rather than electrical or mechanical energy) can be useful for storing energy from systems that provide heat as a native output (e.g., solar thermal, geothermal), or for applications where the energy's commodity value is heat (e.g., space heating, drying).

Although thermal storage technologies can be characterized by specific energy and energy density like any other storage technology, they can also be characterized by an important, additional parameter: the delivery temperature range. Different end uses have more or less allowance for wide swings of the delivery temperature. Also, some applications require a high operating temperature that only some thermal storage media are capable of storing.

Thermal storage can be classified into two fundamental categories: sensible heat storage and latent heat storage. Applications that have less tolerance for temperature swings should utilize a latent heat technology.

Input to and output from heat energy storage is accomplished with heat exchangers. The discussion below focuses on the choice of heat storage materials; the methods of heat exchange will vary widely depending on properties of the storage material, especially its thermal conductivity. Materials with higher thermal conductivity will require a smaller surface area for heat exchange. For liquids, convection or pumping can reduce the need for a large heat exchanger. In some applications, the heat exchanger is simply the physical interface of the storage material with the application space (e.g., phase-change drywall, see below).

12.9.1 Sensible Heat

Sensible heat is the heat that is customarily and intuitively associated with a change in temperature of a massive substance. The heat energy, E_s , stored in such a substance is given by:

$$E_s = (T_2 - T_1)cM,$$

where c is the specific heat of the substance ($\text{J/kg } ^\circ\text{C}$) and M is the mass of the substance (kg); T_1 and T_2 are the initial and final temperatures, respectively ($^\circ\text{C}$). The specific heat c is a physical parameter measured in units of heat per temperature per mass: substances with the ability to absorb heat energy with a relatively small increase in temperature (e.g., water) have a high specific heat, whereas those that get hot with only a little heat input (e.g., lead) have a low specific heat. Sensible heat storage is best accomplished with materials having a high specific heat.

12.9.1.1 Liquids

Sensible heat storage in a liquid is, with very few exceptions, accomplished with water. Water is unique among chemicals in having an abnormally high specific heat of 4,186 J/kg K, and furthermore has a reasonably high density. Water is also cheap and safe. It is the preferred choice for most nonconcentrating solar thermal collectors.

Liquids other than water may need to be chosen if the delivery temperature must be higher than 100°C, or if the system temperature can fall below 0°C. Water can be raised to temperatures higher than 100°C, but the costs of storage systems capable of containing the associated high pressures are usually prohibitive. Water can be mixed with ethylene glycol or propylene glycol to increase the useful temperature range and prevent freezing.

When a larger temperature range than that afforded by water is required, mineral, synthetic, or silicone oils can be used instead. The tradeoffs for the increased temperature range are higher cost, lower specific heat, higher viscosity (making pumping more difficult), flammability, and, in some cases, toxicity.

For very high temperature ranges, salts are usually preferred that balance a low specific heat with a high density and relatively low cost. Sodium nitrate has received the most prominent testing for this purpose in the U.S. Department of Energy's Solar Two Project located in Barstow, California.

Liquid sensible heat storage systems are strongly characterized not just by the choice of heat-transfer fluid, but also by the system architecture. Two-tank systems store the cold and hot liquids in separate tanks (Figure 12.4). Thermocline systems use a single tank with cold fluid entering or leaving the bottom of the tank and hot fluid entering or leaving the top (Figure 12.5). Thermocline systems can be particularly low cost because they minimize the required tank volume, but require careful design to prevent mixing of the hot and cold fluid.

One particularly interesting application of the thermocline concept is nonconvecting, salinity-gradient solar ponds that employ the concept in reverse. Solar ponds are both an energy collection and energy storage technology. Salts are dissolved in the water to introduce a density gradient, with the densest (saltiest) water on the bottom and lightest (freshest) on top. Solar radiation striking the dark bottom of the pond heats the densest water, but convection of the heated water to the top cannot occur because the density gradient prevents it. Salinity-gradient ponds can generate and store hot water at temperatures approaching 95°C.²²

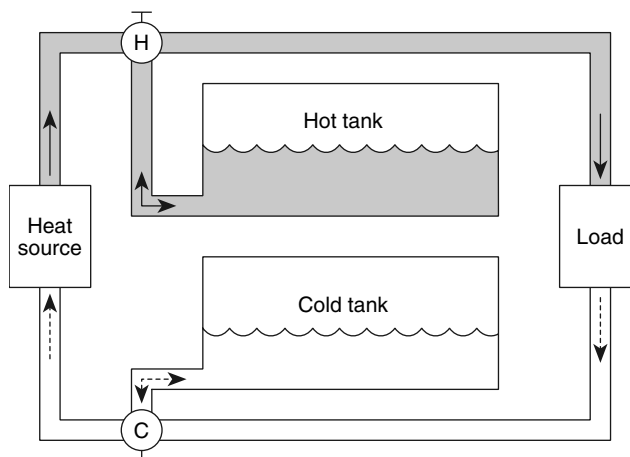


FIGURE 12.4 Two-tank thermal storage system; hot water is shown in gray and cold water is shown in white. When the heat source is producing more output than required for the load, valve H is turned to deposit hot liquid in the tank. When it is producing less than required for the load, the valve is turned to provide supplemental heat from the storage tank. Note that each tank must be large enough to hold the entire fluid capacity of the system.

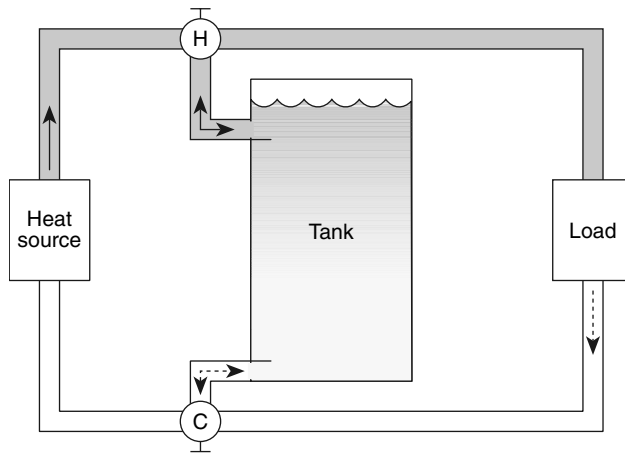


FIGURE 12.5 Thermocline storage tank. Thermocline storage tanks are tall and narrow to encourage the gravity-assisted separation of hot and cold fluid, and include design features (especially at the input/output connectors) to prevent mixing in the stored fluid.

12.9.1.2 Solids

Storage of sensible heat in solids is usually most effective when the solid is in the form of a bed of small units, rather than a single mass. The reason is that the surface-to-volume ratio increases with the number of units, so that heat transfer to and from the storage device is faster for a greater number of units. Energy can be stored or extracted from a thermal storage bed by passing a gas (such as air) through the bed. Thermal storage beds can be used to extract and store the latent heat of vaporization from water contained in flue gases.

Although less effective for heat transfer, monolithic solid storage has been successfully used in architectural applications and solar cookers.

12.9.2 Latent Heat

Latent heat is absorbed or liberated by a phase change or a chemical reaction and occurs at a constant temperature. A phase change means the conversion of a homogenous substance among its various solid, liquid, or gaseous phases. One very common example is boiling water on the stovetop: though a substantial amount of heat is absorbed by the water in the pot, the boiling water maintains a constant temperature of 100°C. The latent heat, E_s , stored through a phase change is:

$$E_s = lM,$$

where M is the mass of material undergoing a phase change (kg), and l is the latent heat of vaporization (for liquid–gas phase changes) or the latent heat of fusion (for solid–liquid phase changes), in J/kg; l is measured in units of energy per mass. Conservation of energy dictates that the amount of heat absorbed in a given phase change is equal to the amount of heat liberated in the reverse phase change.

Although the term *phase change* is used here to refer only to straightforward freezing and melting, many sources use the term *phase-change materials* or *PCMs* to refer to any substance storing latent heat (including those described in Section 12.9.2.2 and Section 12.9.2.3, as well.)

12.9.2.1 Phase Change

Practical energy storage systems based on a material phase change are limited to solid–solid and solid–liquid phase changes. Changes involving gaseous phases are of little interest due to the expense associated with containing a pressurized gas, and difficulty of transferring heat to and from a gas.

Solid–solid phase changes occur when a solid material reorganizes into a different molecular structure in response to temperature. One particularly interesting example is lithium sulfate (Li_2SO_4) which undergoes a change from a monoclinic structure to a face-centered cubic structure at 578°C , absorbing 214 J/g in the process, more than most solid–liquid phase changes.²³

Some common chemicals, their melting points and heats of fusion are listed in Table 12.4. Fatty acids and paraffins received particular attention in the 1990s as candidate materials for the heat storage component of phase-change drywall, a building material designed to absorb and release heat energy near room temperature for the purpose of indoor temperature stabilization.²⁴ In this application, solids in the drywall maintain the material's structural integrity even though the phase-change materials are transitioning between solid and liquid states.

12.9.2.2 Hydration–Dehydration

In this process, a salt or similar compound forms a crystalline lattice with water below a “melting-point” temperature, and at the melting point the crystal dissolves in its own water of hydration. Sodium sulfate (Na_2SO_4) is a good example, forming a lattice with ten molecules of water per molecule of sulfate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and absorbing 241 J/g at 32°C .²⁵

Hydration–dehydration reactions have not found significant application in renewable energy systems, although they, too, have been a candidate for phase-change drywall.

12.9.2.3 Chemical Reaction

A wide variety of reversible chemical reactions are available that release and absorb heat (see, for example, Hanneman, Vakil, and Wentorf²⁶). The principal feature of this category of latent heat storage technologies is the ability to operate at extremely high temperatures, in some cases over 900°C . Extremely high temperature applications have focused primarily on fossil and advanced nuclear applications; to date, none of these chemical methods of heat storage have been deployed in commercial renewable energy applications.

TABLE 12.4 Melting Points and Heats of Fusion for Solid–Liquid Phase Changes

	Melting Point $^\circ\text{C}$	Heat of Fusion J/g
Aluminum bromide	97	42
Aluminum iodide	191	81
Ammonium bisulfate	144	125
Ammonium nitrate	169	77
Ammonium thiocyanate	146	260
Anthracene	96	105
Arsenic tribromide	32	37
Beeswax	62	177
Boron hydride	99	267
Metaphosphoric acid	43	107
Naphthalene	80	149
Naphthol	95	163
Paraffin	74	230
Phosphoric acid	70	156
Potassium	63	63
Potassium thiocyanate	179	98
Sodium	98	114
Sodium hydroxide	318	167
Sulfur	110	56
Tallow	76	198
Water	0	335

Source: From Kreith, F. and Kreider J.F., *Principles of Solar Engineering*, Taylor & Francis, 1978. With permission

12.10 Thermochemical Energy Storage

This section provides an overview of biomass storage technologies from an energetic perspective only.

12.10.1 Biomass Solids

Plant matter is a storage medium for solar energy. The input mechanism is photosynthesis conversion of solar radiation into biomass. The output mechanism is combustion of the biomass to generate heat energy.

Biologists measure the efficiency of photosynthetic energy capture with the metric net primary productivity (NPP), which is usually reported as a yield in units similar to dry Mg/ha-yr (dry metric tons per hectare per year). However, to enable comparisons of biomass with other solar energy storage technologies, it is instructive to estimate a solar efficiency by multiplying the NPP by the biomass heating value (e.g., MJ/dry Mg) and then dividing the result by the average insolation at the crop's location (e.g., MJ/ha-yr). The solar efficiency is a unitless value describing the fraction of incident solar energy ultimately available as biomass heating value. Most energy crops capture between 0.2 and 2% of the incident solar energy in heating value of the biomass; Table 12.5 shows examples of solar efficiencies estimated for a number of test crops.

TABLE 12.5 Primary Productivity and Solar Efficiency of Biomass Crops

Location	Crop	Yield (dry Mg/ha-yr)	Average Insolation (W/m ²)	Solar Efficiency(%)
Alabama	Johnsongrass	5.9	186	0.19
Alabama	Switchgrass	8.2	186	0.26
Minnesota	Willow and hybrid poplar	8–11	159	0.30–0.41
Denmark	Phytoplankton	8.6	133	0.36
Sweden	Enthropic lake angiosperm	7.2	106	0.38
Texas	Switchgrass	8–20	212	0.22–0.56
California	<i>Euphorbia lathyris</i>	16.3–19.3	212	0.45–0.54
Mississippi	Water hyacinth	11.0–33.0	194	0.31–0.94
Texas	Sweet sorghum	22.2–40.0	239	0.55–0.99
Minnesota	Maize	24.0	169	0.79
West Indies	Tropical marine angiosperm	30.3	212	0.79
Israel	Maize	34.1	239	0.79
Georgia	Subtropical saltmarsh	32.1	194	0.92
Congo	Tree plantation	36.1	212	0.95
New Zealand	Temperate grassland	29.1	159	1.02
Marshall Islands	Green algae	39.0	212	1.02
New South Wales	Rice	35.0	186	1.04
Puerto Rico	<i>Panicum maximum</i>	48.9	212	1.28
Nova Scotia	Sublittoral seaweed	32.1	133	1.34
Colombia	Pangola grass	50.2	186	1.50
West Indies	Tropical forest, mixed ages	59.0	212	1.55
California	Algae, sewage pond	49.3–74.2	218	1.26–1.89
England	Coniferous forest, 0–21 years	34.1	106	1.79
Germany	Temperate reedswamp	46.0	133	1.92
Holland	Maize, rye, two harvests	37.0	106	1.94
Puerto Rico	<i>Pennisetum purpurcum</i>	84.5	212	2.21
Hawaii	Sugarcane	74.9	186	2.24
Java	Sugarcane	86.8	186	2.59
Puerto Rico	Napier grass	106	212	2.78
Thailand	Green algae	164	186	4.90

Source: From Klass, D. L., Biomass for Renewable Energy, Fuels, and Chemicals, Academic Press, San Diego, CA, 1998. With permission.

The principal method for extracting useful work or electricity from biomass solids is combustion. Therefore, the solar efficiencies listed in Table 12.5 need to be multiplied by the efficiency of any associated combustion process to yield a net solar efficiency. For example, if a boiler-based electric generator extracts 35% of the feedstock energy as electricity, and the generator is sited at a switchgrass plantation achieving 0.30% solar capture efficiency on a mass basis, the electric plant has a net solar efficiency of $0.30\% \times 35\% = 0.11\%$. Because biomass is a low-efficiency collector of solar energy, it is very land intensive compared to photovoltaic or solar thermal collectors that deliver energy at solar efficiencies over 20%. However, the capacity of land to store standing biomass over time is extremely high, with densities up to several hundred Mg/ha (and therefore several thousand GJ/ha), depending on the forest type. Standing biomass can serve as long-term storage, although multiple stores need to be used to accommodate fire risk. For short-term storage, woody biomass may be dried, and is frequently chipped or otherwise mechanically treated to create a fine and homogenous fuel suitable for burning in a wider variety of combustors.

12.10.2 Ethanol

Biomass is a more practical solar energy storage medium if it can be converted to liquid form. Liquids allow for more convenient transportation and combustion, and enable extraction on demand (through reciprocating engines) rather than through a less dispatchable, boiler- or turbine-based process. This latter property also enables its use in automobiles.

Biomass grown in crops or collected as residue from agricultural processes consists principally of cellulose, hemicellulose, and lignin. The sugary or starchy by-products of some crops such as sugarcane, sugar beet, sorghum, molasses, corn, and potatoes can be converted to ethanol through fermentation processes, and these processes are the principal source of ethanol today. Starch-based ethanol production is low efficiency, but does succeed in transferring about 16% of the biomass heating value to the ethanol fuel.²⁷

When viewed as a developing energy storage technology, ethanol derived from cellulose shows much more promise than the currently prevalent starch-based ethanol.²⁸ Cellulosic ethanol can be manufactured with two fundamentally different methods: either the biomass is broken down to sugars using a hydrolysis process, and then the sugars are subjected to fermentation; or the biomass is gasified (see below), and the ethanol is subsequently synthesized from this gas with a thermochemical process. Both processes show promise to be far cheaper than traditional ethanol manufacture via fermentation of starch crops, and will also improve energy balances. For example, it is estimated that dry sawdust can yield up to 224 L/Mg of ethanol, thus recovering about 26% of the higher heating value of the sawdust.²⁹ Because the ethanol will still need to be combusted in a heat engine, the gross, biomass-to-useful-work efficiency will be well below this. In comparison, direct combustion of the biomass to generate electricity makes much more effective use of the biomass as an energy storage medium. Therefore, the value of ethanol as an energy storage medium lies mostly in the convenience of its liquid (rather than solid) state.

12.10.3 Biodiesel

As starch-based ethanol is made from starchy by-products, most biodiesel is generated from oily by-products. Some of the most common sources are rapeseed oil, sunflower oil, and soybean oil. Biodiesel yields from crops like these range from about 300 to 1000 kg/ha-yr, but the crop as a whole produces about 20 Mg/ha-yr, meaning that the gross solar capture efficiency for biodiesel from crops ranges between 1/20 and 1/60 the solar capture efficiency of the crop itself. Because of this low solar-capture efficiency, biomass cannot be the principal energy storage medium for transportation needs.³⁰

Biodiesel can also be manufactured from waste vegetable or animal oils; however, in this case, the biodiesel is not functioning per se as a solar energy storage medium, so is not further treated in this work.

12.10.4 Syngas

Biomass can be converted to a gaseous state for storage, transportation, and combustion (or other chemical conversion).³¹ Gasification processes are grouped into three different classes: *pyrolysis* is the application of heat in anoxic conditions; *partial oxidation* is combustion occurring in an oxygen-starved environment; *reforming* is the application of heat in the presence of a catalyst. All three processes form syngas, a combination of methane, carbon monoxide, carbon dioxide and hydrogen. The relative abundances of the gaseous products can be controlled by adjusting heat, pressure, and feed rates. The HHV of the resulting gas can contain up to 78% of the original HHV of the feedstock, if the feedstock is dry.²⁹ Compositions and heating values of two example syngases are listed in Table 12.3.

The equivalent of up to 10% of the gas HHV will be lost when the gas is pressurized for transportation and storage. Even with this loss, gasification is a considerably more efficient method than ethanol manufacture for transferring stored solar energy to a nonsolid medium.

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