Pearson

19.7: Batteries: Using Chemistry to Generate Electricity

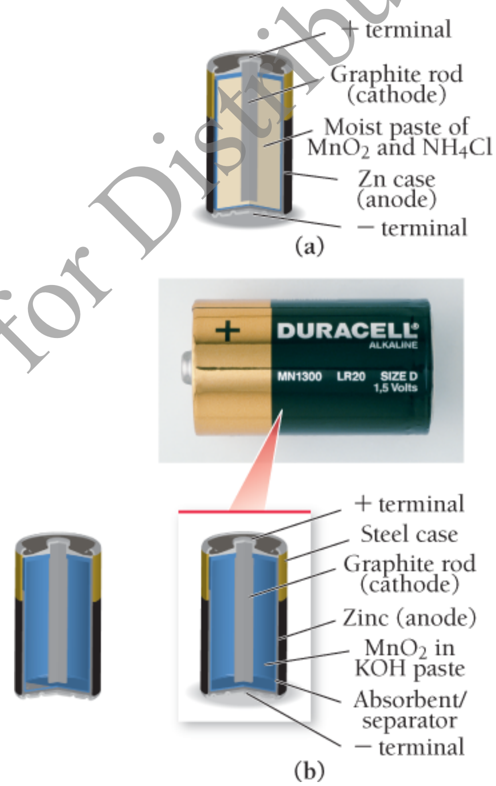
We have seen that we can combine the electron-losing tendency of one substance with the electron-gaining tendency of another to create electrical current in a voltaic cell. Batteries are voltaic cells conveniently packaged to act as portable sources of electricity. The oxidation and reduction reactions depend on the particular type of battery. In this section, we examine several different types.

Dry-Cell Batteries

Common batteries, such as the kind you find in a flashlight, are called **dry-cell batteries** because they do not contain large amounts of liquid water. There are several familiar types of dry-cell batteries. The most inexpensive are composed of a zinc case that acts as the anode (Figure 19.13(a)). The zinc is oxidized according to the reaction:

Figure 19.13 **Dry-Cell Battery**

(**a**) In a common dry-cell battery, the zinc case acts as the anode and a graphite rod immersed in a moist, slightly acidic paste of MnO_2 and NH_4Cl acts as the cathode. (**b**) The longer-lived alkaline batteries employ a graphite cathode immersed in a paste of MnO_2 and a base.



Oxidation (Anode): $Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-$

The cathode is a carbon rod immersed in a moist paste of MnO_2 that also contains NH_4Cl. The MnO_2 is reduced to Mn_2O_3 according to the reaction:

Reduction (Cathode): $2\,MnO_2(s) + 2\,NH_4^+(aq) + 2\,e^- \rightarrow Mn_2O_3(s) + 2\,NH_3(g) + H_2O(l)$

Reduction (Cathode): $2\ MnO_2(s) + 2\ NH_4^+(aq) + 2\ e^- \rightarrow Mn_2O_3(s) + 2\ NH_3(g) + H_2O(l)$

These two half-reactions produce a voltage of about 1.5 V. Two or more of these batteries can be connected in series (cathode-to-anode connection) to produce higher voltages.

The more common **alkaline batteries** (Figure 19.13(b)) employ slightly different half-reactions in a basic medium (therefore the name alkaline). In an alkaline battery, the zinc is oxidized in a basic environment:

$$\begin{array}{ll} \textbf{Oxidation (Anode):} & Zn(s) + \cancel{2\ OH^-}(aq) \longrightarrow Zn(OH)_2(s) + \cancel{2\ e^-} \\ \textbf{Reduction (Cathode):} & 2\ MnO_2(s) + 2\ H_2O(l) + \cancel{2\ e^-} \longrightarrow 2\ MnO(OH)(s) + \cancel{2\ OH^-}(aq) \\ \hline \textbf{Overall reaction:} & Zn(s) + 2\ MnO_2(s) + 2\ H_2O(l) \longrightarrow Zn(OH)_2(s) + 2\ MnO(OH)(s) \end{array}$$

Alkaline batteries have a longer working life and a longer shelf life than their nonalkaline counterparts.

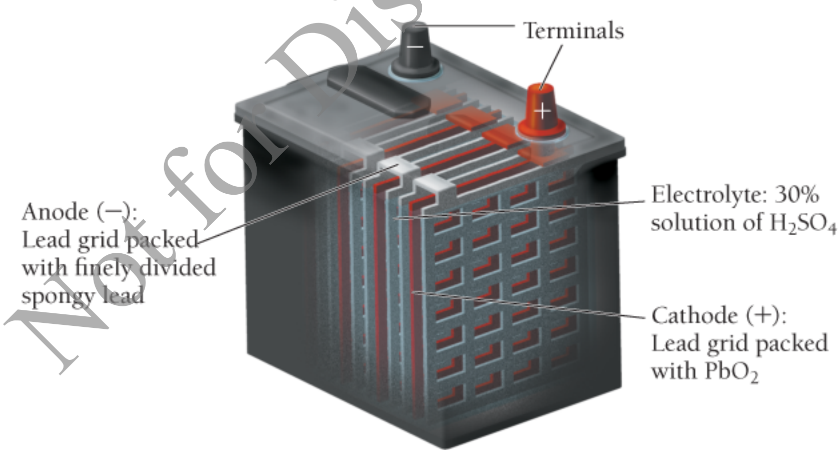
Lead–Acid Storage Batteries

The batteries in most automobiles are **lead–acid storage batteries**. These batteries consist of six electrochemical cells wired in series (Figure 19.14). Each cell produces 2 V, for a total of 12 V. Each cell contains a porous lead anode where oxidation occurs and a lead(IV) oxide cathode where reduction occurs according to the reactions:

$$\begin{array}{ll} \textbf{Oxidation (Anode):} & Pb(s) + HSO_4^-(aq) \longrightarrow PbSO_4(s) + \cancel{H^+(aq)} + \cancel{2\ e^-} \\ \textbf{Reduction (Cathode):} & PbO_2(s) + HSO_4^-(aq) + 2\ \cancel{3}\ H^+(aq) + \cancel{2\ e^-} \longrightarrow PbSO_4(s) + 2\ H_2O(l) \\ \hline \textbf{Overall reaction:} & Pb(s) + PbO_2(s) + 2\ HSO_4^-(aq) + 2\ \cancel{H^+}(aq) \longrightarrow 2\ PbSO_4(s) + 2\ H_2O(l) \end{array}$$

Figure 19.14 Lead–Acid Storage Battery

A lead–acid storage battery consists of six cells wired in series. Each cell contains a porous lead anode and a lead oxide cathode, both immersed in sulfuric acid.



Both the anode and the cathode are immersed in sulfuric acid (H_2SO_4). As electrical current is drawn from the battery, both electrodes become coated with $PbSO_4(s)$. If the battery is run for a long time without recharging, too much $PbSO_4(s)$ builds up on the surface of the electrodes and the battery goes dead. The lead–acid storage battery can be recharged by an electrical current (which must come from an external source such as an alternator in a car). The current causes the preceding reaction to occur in reverse, converting the $PbSO_4(s)$ back to $Pb(s)$ and $PbO_2(s)$.

Other Rechargeable Batteries

The ubiquity of electronic products such as laptops, tablets, cell phones, and digital cameras, as well as the growth in popularity of hybrid electric vehicles, drives the need for efficient, long-lasting, rechargeable batteries. Common types include the **nickel–cadmium (NiCad) battery**, the **nickel–metal hydride (NiMH) battery**, and the **lithium ion battery**.

The Nickel–Cadmium (NiCad) Battery

Nickel–cadmium batteries consist of an anode composed of solid cadmium and a cathode composed of NiO(OH)(*s*). The electrolyte is usually KOH(*aq*). During operation, the cadmium is oxidized and the NiO(OH) is reduced according to these equations:

$$\begin{aligned} &\textbf{\textit{Oxidation (Anode)}}: \ \mathrm{Cd}\,(s) + 2\,\mathrm{OH^-}\,(aq) \rightarrow \mathrm{Cd(OH)_2}\,(s) + 2\,\mathrm{e^-} \\ &\textbf{\textit{Reduction (Cathode)}}: \ 2\,\mathrm{NiO\,(OH)}\,(s) + 2\,\mathrm{H_2O}\,(l) + 2\,\mathrm{e^-} \rightarrow 2\,\mathrm{Ni(OH)_2}\,(s) + 2\,\mathrm{OH^-}\,(aq) \end{aligned}$$

The overall reaction produces about 1.30 V. As current is drawn from the NiCad battery, solid cadmium hydroxide accumulates on the anode and solid nickel(II) hydroxide accumulates on the cathode. However, by running current in the opposite direction, the reactants can be regenerated from the products. A common problem in recharging NiCad and other rechargeable batteries is knowing when to stop. Once all of the products of the reaction are converted back to reactants, the charging process should ideally terminate—otherwise the electrical current will drive other, usually unwanted, reactions such as the electrolysis of water to form hydrogen and oxygen gas. These reactions typically damage the battery and may sometimes even cause an explosion. Consequently, most commercial battery chargers have sensors that measure when the charging is complete. These sensors rely on the small changes in voltage or increases in temperature that occur once the products have all been converted back to reactants.

Several types of batteries, including NiCad, NiMH, and lithium ion batteries, are recharged by chargers that use household current.

The Nickel–Metal Hydride (NiMH) Battery

Although NiCad batteries were the standard rechargeable battery for many years, they are being replaced by other types of rechargeable batteries, in part because of the toxicity of cadmium and the resulting disposal problems. One of these replacements is the nickel–metal hydride or NiMH battery. The NiMH battery employs the same cathode reaction as the NiCad battery but a different anode reaction. In the anode of a NiMH battery, hydrogen atoms held in a metal alloy are oxidized. If we let M represent the metal alloy, we can write the half-reactions as follows:

$$\begin{aligned} &\textbf{\textit{Oxidation (Anode)}}: \ \mathrm{M \cdot H}\,(s) + \mathrm{OH^-}\,(aq) \rightarrow \mathrm{M}\,(s) + \mathrm{H_2O}\,(l) + \mathrm{e^-} \\ &\textbf{\textit{Reduction (Cathode)}}: \ \mathrm{NiO\,(OH)}\,(s) + \mathrm{H_2O}\,(l) + \mathrm{e^-} \rightarrow \mathrm{Ni(OH)_2}\,(s) + \mathrm{OH^-}\,(aq) \end{aligned}$$

In addition to being more environmentally friendly than NiCad batteries, NiMH batteries also have a greater energy density (energy content per unit battery mass), as we can see in Table 19.2. In some cases, a NiMH battery can carry twice the energy of a NiCad battery of the same mass, making NiMH batteries the most common choice for hybrid electric vehicles.

Table 19.2 **Energy Density and Overcharge Tolerance of Several Rechargeable Batteries**

Battery Type	Energy Density (W•h/kg)	Overcharge Tolerance
NiCad	45–80	Moderate

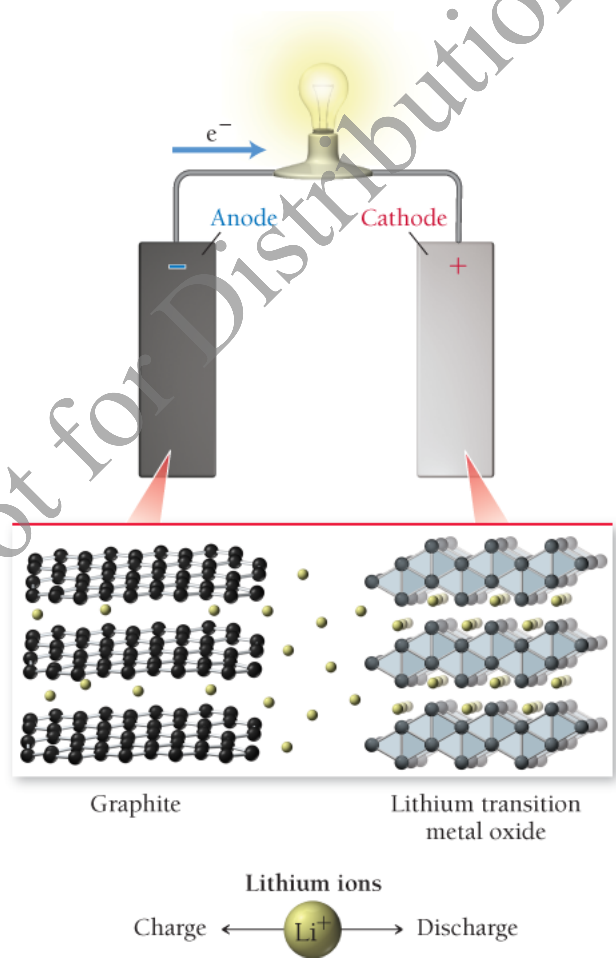
NiMH	60–120	Low
Li ion	110–160	Low
Pb storage	30–50	High

The Lithium Ion Battery

The newest and most expensive common type of rechargeable battery is the lithium ion battery. Since lithium is the least dense metal $\left(0.53\ \mathrm{g/cm^3}\right)$, lithium batteries have high-energy densities (see Table 19.2). The lithium battery works differently than the other batteries we have examined so far, and the details of its operation are beyond the scope of our current discussion. Briefly, we can describe the operation of the lithium battery as being due primarily to the motion of lithium ions from the anode to the cathode. The anode is composed of graphite into which lithium ions are incorporated between layers of carbon atoms. Upon discharge, the lithium ions spontaneously migrate to the cathode, which consists of a lithium transition metal oxide such as $\mathrm{LiCoO_2}$ or $\mathrm{LiMn_2O_4}$. The transition metal is reduced during this process. Upon recharging, the transition metal is oxidized, forcing the lithium to migrate back into the graphite (Figure 19.15). The flow of lithium ions from the anode to the cathode causes a corresponding flow of electrons in the external circuit. Lithium ion batteries are commonly used in applications where light weight and high-energy density are important. These include cell phones, laptop computers, and digital cameras.

Figure 19.15 Lithium Ion Battery

In the lithium ion battery, the spontaneous flow of lithium ions from the graphite anode to the lithium transition metal oxide cathode causes a corresponding flow of electrons in the external circuit.



Fuel Cells

Fuel cells are like batteries; the key difference is that a battery is self-contained, while in a fuel cell the reactants

Fuel cells are like batteries; the key difference is that a battery is self-contained, while in a fuel cell the reactants need to be constantly replenished from an external source. With use, normal batteries lose their ability to generate voltage because the reactants become depleted as electrical current is drawn from the battery. In a **fuel cell**, the reactants—the fuel provided from an external source—constantly flow through the battery, generating electrical current as they undergo a redox reaction. Fuel cells may one day replace—or at least work in combination with—centralized power grid electricity. In addition, vehicles powered by fuel cells may one day usurp vehicles powered by internal combustion engines.

The most common fuel cell is the hydrogen–oxygen fuel cell. In this cell, hydrogen gas flows past the anode (a screen coated with platinum catalyst) and undergoes oxidation:

$$\boldsymbol{Oxidation\ (Anode):}\ 2\ \mathrm{H_2}\,(g) + 4\ \mathrm{OH^-}\,(aq) \rightarrow 4\ \mathrm{H_2O}\,(l) + 4\ \mathrm{e^-}$$

Oxygen gas flows past the cathode (a similar screen) and undergoes reduction:

$$\boldsymbol{Reduction\ (Cathode):}\ \mathrm{O_2}\,(g) + 2\ \mathrm{H_2O}\,(l) + 4\ \mathrm{e^-} \rightarrow 4\ \mathrm{OH^-}\,(aq)$$

The half-reactions sum to the following overall reaction:

$$\boldsymbol{Overall\ reaction:}\ 2\ \mathrm{H_2}\,(g) + \mathrm{O_2}\,(g) \rightarrow 2\ \mathrm{H_2O}\,(l)$$

Notice that the only product is water. In the space shuttle program, hydrogen–oxygen fuel cells consume hydrogen to provide electricity, and astronauts drink the water that is produced by the reaction. In order for hydrogen-powered fuel cells to become more widely used, a more readily available source of hydrogen must be developed.