INTERCHAPTER U

Batteries

A representative sample of commercially available batteries.

A **battery** is a device that uses a chemical reaction to produce an electric current. Strictly speaking, a battery consists of two or more electrochemical cells that are connected together; however, the term battery is often applied to single electrochemical cells as well. Batteries are especially useful as electric power sources when mobility is a prime consideration. They are adaptable to a wide range of power requirements, from the production of very high currents over short periods to the production of stable voltages under low current drain for long periods.

Batteries are classed as **primary** if they are not rechargeable and as **secondary** (can be used a *second* and further times) if they are rechargeable. Examples of primary batteries are the alkaline batteries used in flashlights and the silver-zinc button batteries often used in wristwatches. Some examples of secondary batteries include the lead storage battery commonly used in cars and trucks, the rechargeable nickel-metal hydride batteries now used instead of alkaline batteries in many appliances, and the lithium ion batteries used in cellular telephones and handheld electronics.

U-1. The Lead Storage Battery Is Used in Vehicles

The 12-volt **lead storage battery** (Figure U.1) used in vehicles consists of six cells of the following type (each generating about two volts) arranged in series:

$$(-)\mathrm{Pb}(s)|\mathrm{PbSO_4}(s)|\mathrm{H_2SO_4}(aq)|\mathrm{PbO_2}(s),\mathrm{PbSO_4}(s)|\mathrm{Pb}(s)(+)$$

The minus and plus signs denote the electrode polarities during discharge (i.e., current drain), and the comma between $PbO_2(s)$ and $PbSO_4(s)$ denotes a heterogeneous mixture of the two solids. The battery electrolyte is a 10-M $H_2SO_4(aq)$ solution. The equations for the electrode reactions during discharge are

$$\mathrm{Pb}(s) + \mathrm{SO_4^{2-}}(aq) \rightarrow \mathrm{PbSO_4}(s) + 2\,\mathrm{e^-} \qquad \text{(oxidation)}$$

$$2\,\mathrm{e^-} + \mathrm{PbO_2}(s) + 4\,\mathrm{H^+}(aq) + \mathrm{SO_4^{2-}}(aq) \rightarrow \mathrm{PbSO_4}(s) + 2\,\mathrm{H_2O}(l) \qquad \text{(reduction)}$$

The equation for the overall cell reaction is obtained by adding together the equations for the two half reactions:

$$\mathrm{Pb}(s) + \mathrm{PbO_2}(s) + 2\,\mathrm{H_2SO_4}(aq) \underset{\text{recharge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2\,\mathrm{PbSO_4}(s) + 2\,\mathrm{H_2O}(l)$$

A good-quality lead storage automobile battery can provide a current of over 650 amperes for short periods and a power output of 7.8 kW, a very impressive power output for a portable battery.

According to the above overall equation, sulfuric acid is consumed and water is produced on discharge. Both of these effects dilute the $H_2SO_4(aq)$ electrolyte. The reaction quotient, Q, for the equation, given by

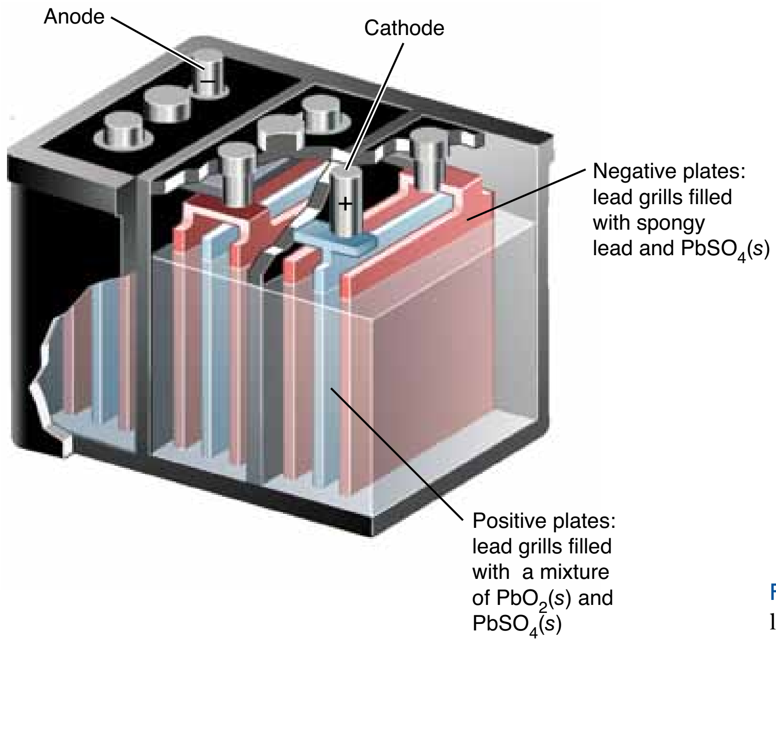

Figure U.1 Cutaway view of one-half of a 12-V lead storage battery.

$Q = 1/[H_2SO_4]$, increases upon discharge, and so the cell voltage, which is given by the Nernst equation

$$E_{cell} = E^{\circ}_{cell} - \left(\frac{RT}{nF}\right)\ln Q$$

decreases. On rapid recharge of a lead storage battery, appreciable amounts of $H_2(g)$ and $O_2(g)$ may be formed from the electrolysis of water at the $Pb(s)|PbSO_4(s)$ and $PbO_2(s)$, $PbSO_4(s)|Pb(s)$ electrodes, respectively. Thus, there is significant danger of an explosion on rapid recharge. For this reason, sparks and flames should not be brought near a lead storage battery, especially during recharging, and jumper cables should always be grounded to the chassis rather than connected to the negative terminal when jump-starting.

The most common cause of failure of lead storage batteries is the development of **dendrites**. These leaflike structures of lead metal (Figure U.2) form on rapid recharge and connect the anode and cathode within the cell, thus constituting an internal short circuit that kills the battery.

Figure U.2 Metallic dendrites formed during electrochemical deposition. Such dendrites occur in the rapid discharge of a lead storage battery and can lead to an internal short circuit.

U-2. NiCad and NiMH Batteries Are Rechargeable

Another type of rechargeable battery is the **nickel-cadmium (NiCad) battery**. The two half reactions occurring in a NiCad cell are

$$Cd(s) + 2\,OH^-(aq) \rightarrow Cd(OH)_2(s) + 2\,e^- \quad \text{(oxidation)}$$

$$2\,NiOOH(s) + 2\,H_2O(l) + 2\,e^- \rightarrow 2\,Ni(OH)_2(s) + 2\,OH^-(aq) \quad \text{(reduction)}$$

and the overall cell equation is

$$Cd(s) + 2\,NiOOH(s) + 2\,H_2O(l) \underset{\text{recharge}}{\overset{\text{discharge}}{\rightleftarrows}} Cd(OH)_2(s) + 2\,Ni(OH)_2(s)$$

A sealed NiCad battery is more chemically stable than a lead storage battery and can be left inactive for long periods. Each NiCad cell develops 1.2 V, so, for example, a 9.6-V NiCad battery contains eight NiCad cells in series. NiCad batteries suffer from "memory effects," which means that if they are not fully discharged and recharged for the first few cycles, their battery life can shorten. The NiCad battery concept was discovered by Thomas A. Edison, but Edison chose an $Fe(s)|Fe(OH)_2(s)$ electrode rather than the $Cd(s)|Cd(OH)_2(s)$ electrode because iron is much less expensive than cadmium. **Edison cells** have been used extensively in automobile batteries in Europe.

Today the NiCad battery is being replaced by the **nickel-metal hydride (NiMH) battery** due to concerns about the toxicity of cadmium. Moreover, NiMH batteries have a higher energy density and do not suffer from significant memory effects. In place of cadmium, the nickel-metal hydride battery uses a metal alloy hydride (abbreviated MH) anode, where M can stand for any of a number of metal alloys.

A single NiMH cell produces about 1.2 V. The cell half reactions are

$$MH(s) + OH^-(aq) \rightarrow M(s) + H_2O(l) + e^- \quad \text{(oxidation)}$$

$$NiOOH(s) + H_2O(l) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq) \quad \text{(reduction)}$$

and the overall cell reaction is

$$MH(s) + NiOOH(s) \underset{\text{recharge}}{\overset{\text{discharge}}{\rightleftarrows}} M(s) + 2\,Ni(OH)_2(s)$$

Figure U.3 Hybrid cars contain both a gasoline and an electric motor. NiMH batteries are charged while braking by spinning the electric motor in reverse, making it act as a generator. The stored energy is then used to supplement the gasoline engine when accelerating. In this way hybrid cars can achieve fuel efficiencies significantly greater than those of conventional vehicles.

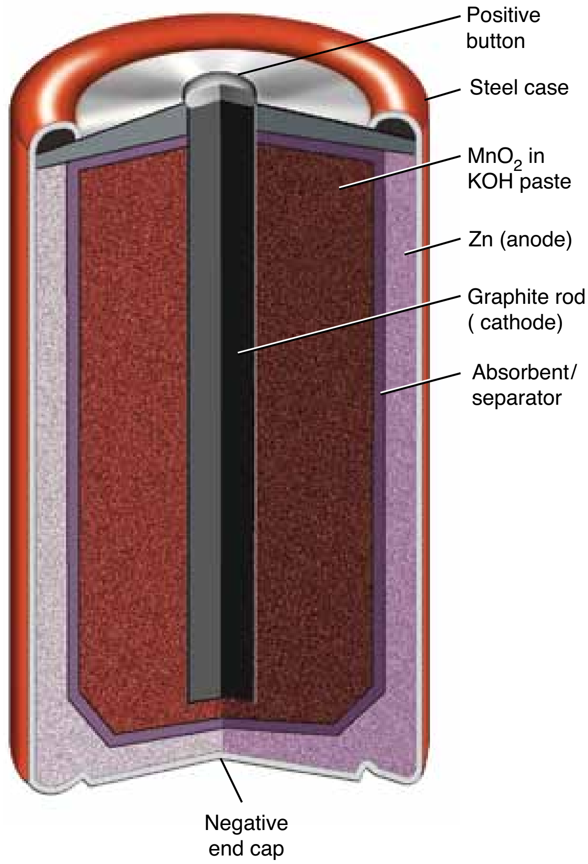

Figure U.4 A cutaway view of a typical alkaline manganese cell.

NiMH batteries are used extensively in cordless tools, rechargeable flashlights, and in hybrid cars that can charge a bank of onboard NiMH batteries while braking and then use the stored energy to supplement a gasoline engine when accelerating (Figure U.3).

U-3. Dry Cells and Alkaline Batteries Are Used in Flashlights and Toys

The **dry cell** and the **alkaline manganese cell**, both of which are widely used in flashlights, battery-powered toys, and similar devices, are closely related. Both contain a zinc metal negative electrode (anode) and an inert positive electrode (cathode), on which $MnO_2(s)$ is reduced to $Mn_2O_3(s)$. The positive electrode is a carbon rod in the dry cell. The name "dry cell" is used because the electrolyte in the cell is a paste composed of $MnO_2(s)$, $NH_4Cl(s)$, $ZnCl_2(s)$, carbon powder, water, and starch. An improvement on the dry cell is the alkaline manganese cell or "alkaline battery" (recall that alkaline means basic), which has twice the capacity, a steadier voltage under heavy current drain, and a higher available current than the dry cell. The alkaline manganese cell uses the same electrode materials as the dry cell, but the electrolyte is a basic paste of $KOH(aq)$ (Figure U.4). Its main disadvantage is that it costs roughly three times as much as the dry cell because of the more elaborate internal construction necessary to prevent leakage of the $KOH(aq)$. Both of these cells produce about 1.5 V. The equation describing the overall cell reaction occurring in the alkaline manganese cell is

$$Zn(s) + 2\,MnO_2(s) \rightarrow ZnO(s) + Mn_2O_3(s) \qquad \text{(basic)}$$

U-4. Button Batteries Are Used in Wristwatches and Medical Devices Where a Constant Voltage Is Required

Another type of primary battery is the **silver-zinc button battery** used in wristwatches, hearing aids, light meters, and other devices where a constant voltage

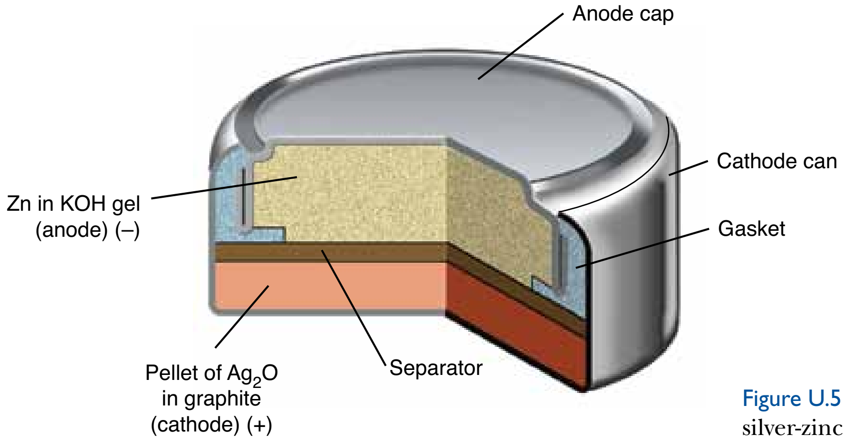

Figure U.5 A cutaway view of a typical silver-zinc button battery.

is of primary concern (Figure U.5). The silver-zinc button battery replaced the mercury battery in such applications because of environmental concerns over the disposal of mercury. The cell diagram of a silver-zinc button battery is

$$(-)\ Zn(s)|ZnO(s)|KOH(aq)|Ag_2O(s)|Ag(s)\ (+)$$

The advantages of this cell are its constant voltage (1.55 V) during discharge (because there is no change in the cell electrolyte composition during discharge); its capacity (i.e., total power output), which is about twice as great as the alkaline manganese cell; its very long shelf life; its small size; and its ability to supply large instantaneous currents. The main disadvantage is its high cost.

U-5. Lithium Ion Batteries Are Used in Portable Electronics

The most significant advance in battery technology is the primary **lithium battery** and the secondary **lithium ion battery**. Although work on a lithium battery was first started by G. N. Lewis (Chapter 7 Frontispiece) in 1912, it wasn't until recent decades that this battery has become commercially available because of safety problems in the containment of lithium. Because lithium is both the most potent reducing agent known and the metal with the lowest density, lithium batteries have the highest power-to-weight ratio of all batteries. A single lithium cell produces about 3.6 V. Primary lithium batteries also have the longest shelf lives of all batteries. For these reasons most modern medical implants and some wristwatches now employ primary lithium batteries, while cell phones, laptop computers, digital cameras, MP3 players, and similar devices generally use secondary (rechargeable) lithium ion batteries (Figure U.6).

Primary lithium cells use the direct oxidation of lithium metal at the anode, $Li(s)|Li^+(solv)$, where *solv* represents a solvent other than water (with which lithium reacts violently). A variety of cathode materials are used in the cells depending on the application, the most common of which is $MnO_2(s)|Mn(s)$.

Secondary lithium ion cells employ a cathode consisting of lithium in a solid such as $CoO_2(s)$ or $Mn_2O_4(s)$ and an anode consisting of lithium in graphite. The half-cell reactions and overall cell equation for a typical lithium ion secondary cell can be represented as

Figure U.6 Secondary lithium ion batteries are used to power cellular telephones.

$$\text{Li}(\textit{in graphite}) \rightarrow \text{Li}^+(\textit{solv}) + e^- \qquad \text{(oxidation)}$$

$$\text{Li}^+(\textit{solv}) + e^- \rightarrow \text{Li}(\textit{in CoO}_2) \qquad \text{(reduction)}$$

$$\text{Li}(\textit{in graphite}) \underset{\text{recharge}}{\overset{\text{discharge}}{\rightleftarrows}} \text{Li}(\textit{in CoO}_2) \qquad \text{(overall)}$$

where *solv* is an electrolyte consisting of a lithium salt such as $LiPF_6(s)$, $LiBF_4(s)$, or $LiClO_4(s)$, in a polar organic solvent. The voltage produced by the cell depends on the solid material used in the anode and cathode, but typical values are on the order of 3 to 4 volts.

One disadvantage of the secondary lithium ion battery is that it has a limited useful lifetime regardless of the number of charge/discharge cycles, starting from the time the battery is manufactured. Thus, lithium ion batteries all require eventual replacement (regardless of usage) and purchasers of new lithium ion batteries should always check the date of manufacture, which is typically stamped on the battery.

TERMS YOU SHOULD KNOW

battery *U1*
primary battery *U1*
secondary battery *U1*
lead storage battery *U1*
dendrites *U2*
nickel-cadmium (NiCad) battery *U2*
Edison cell *U2*
nickel-metal hydride (NiMH) battery *U2*
dry cell *U3*
alkaline manganese cell *U3*
silver-zinc button battery *U3*
lithium battery *U4*
lithium ion battery *U4*

QUESTIONS

U-1. What is the difference between a battery and a cell?

U-2. What is the difference between a primary and a secondary battery?

U-3. Why shouldn't lead-storage batteries be rapidly recharged?

U-4. List two advantages that nickel-metal hydride (NiMH) rechargeable batteries have over nickel-cadmium (NiCad) rechargeable batteries.

U-5. Why should used lithium batteries never be disposed of in a regular trash container?

U-6. The cell diagram for the Edison cell, used extensively in car and truck batteries in Europe, is

$$Fe(s)|Fe(OH)_2(s)|NaOH(aq)|NiOOH(s),Ni(OH)_2(s)|\text{steel}$$

where the steel electrode is nonreactive and the comma between $NiOOH(s)$ and $Ni(OH)_2(s)$ denotes a heterogeneous mixture of the two solids. Determine the equation for the cell reaction.

U-7. The cell diagram for the reaction occurring in silver-zinc button batteries is

$$Zn(s)|ZnO(s)|KOH(aq)|Ag_2O(s)|Ag(s)$$

Write the two half-reaction equations occurring in this cell and the overall cell reaction equation. Use the data in Appendix G to determine the value of E°_{cell} for the cell. Why are silver-zinc batteries used in applications where a constant voltage is required?

U-8. Standard alkaline manganese cells generate about 1.5 volts from the reaction described by

$$Zn(s) + MnO_2(s) + H_2O(l) \leftrightharpoons ZnO(s) + Mn(OH)_2(s) \qquad \text{(basic)}$$

(Recall that the word alkaline means basic.) Write the balanced half-reaction equations occurring in the alkaline manganese cell. Why does the voltage of an alkaline manganese cell remain fairly constant over the life of the cell?

U-9. Alkaline manganese cells all use the same reaction described by the equation in Question U-8. Explain why AAA- and D-sized cells both produce the same voltage if the quantity of chemicals in the D-sized cell is almost five times that of the AAA-sized cell. What advantage is there in using a D-sized cell over a AAA-sized cell in a toy or flashlight?

U-10. A standard 9-volt alkaline battery uses the same cell reaction as that described by the equation in Question U-8. How is it possible to generate 9 volts of electricity using these cells?