21.1 Electrochemical Cells

Connecting to Your World

On a summer evening, fireflies glow to attract their mates. In the ocean depths, anglerfish emit light to attract prey. Luminous shrimp, squid, jellyfish, and even bacteria also exist. These organisms, and others, are able to give off energy in the form of light as a result of redox reactions. In this section, you will discover that the transfer of electrons in a redox reaction produces energy.

Electrochemical Processes

As you have learned, chemical processes can either release energy or absorb energy. The energy can sometimes be in the form of electricity. Electrochemistry has many applications in the home as well as in industry. Flashlight and automobile batteries are familiar examples of devices used to generate electricity. The manufacture of sodium and aluminum metals and the silverplating of tableware involve the use of electricity. Biological systems also use electrochemistry to carry nerve impulses. In this chapter, you will learn about the relationship between redox reactions and electrochemistry.

A Spontaneous Redox Reaction When a strip of zinc metal is dipped into an aqueous solution of blue copper sulfate, the zinc becomes copper-plated, as shown in Figure 21.1. The net ionic equation involves only zinc and copper.

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

Guide for Reading

Key Concepts

- For any two metals in an activity series, which metal is more readily oxidized?
- What type of chemical reaction is involved in all electrochemical processes?
- How does a voltaic cell produce electrical energy?
- What current technologies use electrochemical processes to produce electrical energy?

Vocabulary

electrochemical process
electrochemical cell
voltaic cells
half-cell
salt bridge
electrode
anode
cathode
dry cell
battery
fuel cells

Reading Strategy

Building Vocabulary As you read the section, write a definition of each key term in your own words.

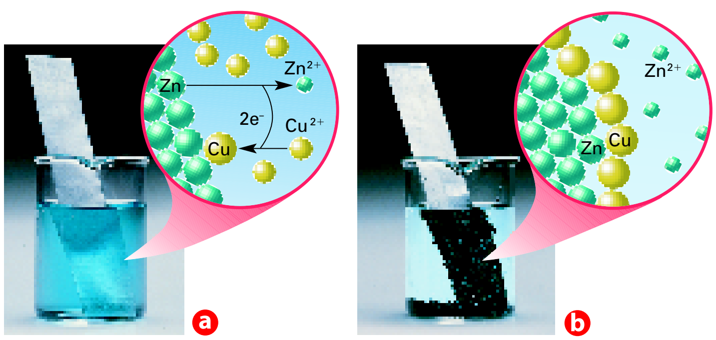

Figure 21.1 Zinc metal oxidizes spontaneously in a copper-ion solution. **a** A zinc strip is immersed in a solution of copper sulfate. **b** As the redox reaction proceeds, copper plates out onto the zinc, and the blue copper sulfate solution is replaced by a solution of zinc sulfate.
Classifying ***How can you classify this reaction?***

Section Resources

Print

- **Guided Reading and Study Workbook,** Section 21.1
- **Core Teaching Resources,** Section 21.1 Review
- **Transparencies,** T242–T245
- **Laboratory Manual,** Lab 47

Technology

- **Interactive Textbook with ChemASAP,** Assessment 21.1
- **GoOnline,** Section 21.1

21.1

1 FOCUS

Objectives

21.1.1 **Interpret** an activity series and **identify** the elements that are most easily oxidized and those that are least easily oxidized.

21.1.2 **Name** the type of reactions involved in electrochemical processes.

21.1.3 **Describe** how a voltaic cell produces electrical energy.

21.1.4 **Describe** current technologies that use electrochemical processes to produce energy.

Guide for Reading

Build Vocabulary L2

Word Parts Cathode comes from the Greek *kathodos* meaning way down. Anode also comes from the Greek *anodos* meaning way up. Thus the two words, cathode and anode, are opposites.

Reading Strategy L2

Outline Show students how to make an outline as they read this section. Have them use the red headings as their main entries and the blue headings as secondary entries. Ask them to include, under each heading, a sentence summarizing the important idea.

2 INSTRUCT

Connecting to Your World

Ask, **What have you learned that shows that energy can be released in the form of light?** *(When electrons drop from higher to lower energy levels in an atom they emit energy in the form of light.)*

Answers to...

Figure 21.1 It is a redox reaction. Zinc is oxidized, and copper is reduced.

Electrochemical Processes

Use Visuals L1

Figure 21.1 Ask, **What is the color of the copper sulfate solution in Figure 21.2a?** *(blue)* **Is the color different in Figure 21.1b?** *(It's still blue but lighter in color.)* **What is the significance of the lighter color?** *(Blue copper ions have been removed from the solution and changed into the copper atoms on the zinc.)*

TEACHER Demo

A Redox Reaction L2

Purpose Students observe a redox reaction.

Materials 200 mL 0.1*M* silver nitrate ($AgNO_3$) in a 250 mL beaker, glass stirring rod, strip of polished copper metal

Safety Wear gloves, apron, and safety goggles.

Procedure Put a glass stirring rod across the top of the beaker and suspend a polished copper strip from the rod so that the strip dips into the $AgNO_3$ solution. The metal surface will darken and appear "fuzzy" as silver metal is deposited. Over time, a layer of silver will form on the copper. Ask, **What is the significance of the blue color of the solution?** *(Blue copper(II) ions are being produced.)* Write on the board the net reaction for the electrochemical process:

$2Ag^+(aq) + Cu(s) \rightarrow 2Ag(s) + Cu^{2+}(aq)$

Point out that the reaction involves a transfer of electrons from copper atoms to silver ions. Ask, **What was oxidized? What was reduced?** *(Copper was oxidized; silver ions were reduced.)* Combine liquid wastes and add a 50% molar excess of NaCl. Filter or decant and dry the AgCl residue. Put in a plastic container and bury in an approved landfill. Flush the filtrate down the drain with excess water.

Expected Outcome Silver crystals form on the copper wire. The solution turns blue because of dissolved copper(II) ions.

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Table 21.1

Activity Series of Metals, with Half-Reactions for Oxidation Process

	Element	Oxidation half-reactions
Most active and most easily oxidized	Lithium	$Li(s) \longrightarrow Li^+(aq) + e^-$
↓ Decreasing activity	Potassium	$K(s) \longrightarrow K^+(aq) + e^-$
	Barium	$Ba(s) \longrightarrow Ba^{2+}(aq) + 2e^-$
	Calcium	$Ca(s) \longrightarrow Ca^{2+}(aq) + 2e^-$
	Sodium	$Na(s) \longrightarrow Na^+(aq) + e^-$
	Magnesium	$Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-$
	Aluminum	$Al(s) \longrightarrow Al^{3+}(aq) + 3e^-$
	Zinc	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$
	Iron	$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$
	Nickel	$Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^-$
	Tin	$Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^-$
	Lead	$Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-$
	Hydrogen*	$H_2(g) \longrightarrow 2H^+(aq) + 2e^-$
	Copper	$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$
	Mercury	$Hg(s) \longrightarrow Hg^{2+}(aq) + 2e^-$
Least active and least easily oxidized	Silver	$Ag(s) \longrightarrow Ag^+(aq) + e^-$
	Gold	$Au(s) \longrightarrow Au^{3+}(aq) + 3e^-$

*Hydrogen is included for reference purposes.

Electrons are transferred from zinc atoms to copper ions. This is a redox reaction that occurs spontaneously. As the reaction proceeds, zinc atoms lose electrons as they are oxidized to zinc ions. The zinc metal slowly dissolves. At the same time, copper ions in solution gain the electrons lost by the zinc. They are reduced to copper atoms and are deposited as metallic copper. As the copper ions in solution are gradually replaced by zinc ions, the blue color of the solution fades. Balanced half-reactions for this redox reaction can be written as follows.

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

Reduction: $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

If you look at the activity series of metals in Table 21.1, you will see that zinc is higher on the list than copper. **For any two metals in an activity series, the more active metal is the more readily oxidized.** As Figure 21.1 shows, zinc is more readily oxidized than copper because when dipped into a copper sulfate solution, zinc becomes plated with copper. In contrast, when a copper strip is dipped into a solution of zinc sulfate, the copper does not spontaneously become zinc-plated. This is because copper metal is not oxidized by zinc ions.

When a zinc strip is dipped into a copper sulfate solution, electrons are transferred from zinc metal to copper ions. This flow of electrons is an electric current. Thus the zinc-metal–copper-ion system is an example of the conversion of chemical energy into electrical energy.

Checkpoint ***Why doesn't a copper strip that is dipped in zinc sulfate solution become spontaneously zinc-plated?***

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Download a worksheet on **The Activity Series** for students to complete, and find additional teacher support from NSTA SciLinks.

Differentiated Instruction

Gifted and Talented L3

Challenge students to research the electrochemical nature of the nervous system. Students may want to focus on different aspects of the system and combine their findings into a visual display and/or oral report. Possible areas to be addressed include the role of sodium and potassium ions, how signals are transmitted across synapses, what an EEG measures, and the value of squid for nervous system research.

Redox Reactions and Electrochemistry An **electrochemical process** is any conversion between chemical energy and electrical energy. **All electrochemical processes involve redox reactions.** If a redox reaction is to be used as a source of electrical energy, the two half-reactions must be physically separated. In the case of the zinc-metal–copper-ion reaction, the electrons released by zinc must pass through an external circuit to reach the copper ions if useful electrical energy is to be produced. In that situation, the system serves as an electrochemical cell. Alternatively, an electric current can be used to produce a chemical change. That system, too, serves as an electrochemical cell. An **electrochemical cell** is any device that converts chemical energy into electrical energy or electrical energy into chemical energy. Redox reactions occur in all electrochemical cells.

Voltaic Cells

In 1800, the Italian physicist Alessandro Volta built the first electrochemical cell that could be used to generate a direct (DC) electric current. Figure 21.2 shows a photograph of Volta's illustration of one of his early cells. **Voltaic cells** (named after their inventor) are electrochemical cells used to convert chemical energy into electrical energy. **Electrical energy is produced in a voltaic cell by spontaneous redox reactions within the cell.** You use a voltaic cell every time you turn on a flashlight or a battery-powered calculator.

Constructing a Voltaic Cell A **half-cell** is one part of a voltaic cell in which either oxidation or reduction occurs. A typical half-cell consists of a piece of metal immersed in a solution of its ions. Figure 21.3 on the following page shows a voltaic cell that makes use of the zinc–copper reaction. In this cell, one half-cell is a zinc rod immersed in a solution of zinc sulfate. The other half-cell is a copper rod immersed in a solution of copper sulfate.

The half-cells are connected by a **salt bridge**—a tube containing a strong electrolyte, often potassium sulfate (K_2SO_4). Salt bridges usually are made of agar, a gelatinous substance. A porous plate may be used instead of a salt bridge. The porous plate allows ions to pass from one half-cell to the other but prevents the solutions from mixing completely. A wire carries the electrons in the external circuit from the zinc rod to the copper rod. A voltmeter or light bulb can be connected in the circuit. The driving force of such a voltaic cell is the spontaneous redox reaction between zinc metal and copper(II) ions in solution.

The zinc and copper rods in this voltaic cell are the electrodes. An **electrode** is a conductor in a circuit that carries electrons to or from a substance other than a metal. The reaction at the electrode determines whether the electrode is labeled as an anode or a cathode. The electrode at which oxidation occurs is called the **anode.** Because electrons are produced at the anode, it is labeled the negative electrode. The electrode at which reduction occurs is called the **cathode.** Electrons are consumed at the cathode. As a result, the cathode is labeled the positive electrode. Neither electrode is really charged, however. All parts of the voltaic cell remain balanced in terms of charge at all times. The moving electrons balance any charge that might build up as oxidation and reduction occur.

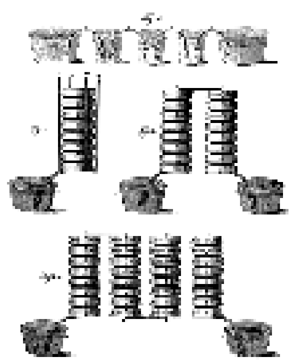

Figure 21.2 Volta built his electrochemical cell using piles of silver and zinc plates separated by cardboard soaked in salt water. He used his cell to obtain an electrical current.

Discuss L2

Explain that redox reactions make it possible for energy interconversion between electrical energy and chemical energy. Review oxidation and reduction half-cell reactions. Stress that the electrons must be balanced. Show how these reactions are combined to form the net ionic equation for an electrochemical process such as the one just demonstrated. The net equation summarizes the transfer of electrons from the species being oxidized to the species being reduced.

Voltaic Cells

Discuss L2

Remind students of the lemon battery they made in the Inquiry Activity. Explain that the lemon battery is an example of a voltaic cell. Use its parts to illustrate terms such as cathode, anode, salt bridge, and half-cell. Introduce the shorthand method for representing an electrochemical cell.

Relate L1

Italian physicist Alesandro Volta had already been experimenting with static electricity when, in 1780, his friend Luigi Galvani demonstrated that a current of electricity could be generated if two different metals were placed in contact with the muscle of a frog. Volta later showed that animal tissue was not necessary—current flowed with only the two dissimilar metals. A controversy arose between scientists who believed in animal-generated electricity and those who believed in metallic electricity. Volta settled the matter when, in 1801, he demonstrated his first voltaic cell for Napoleon. The unit of electrical potential, the volt, was named in Volta's honor.

Differentiated Instruction

Special Needs L1

Have students think about the half-reactions in Table 21.1 in terms of where the element is located in the periodic table. Remind them of what they learned in Chapter 6 about periodic trends in chemical properties. Point out that the elements on the left side of the periodic table are more easily oxidized (lose electrons) than the elements on the right side of the periodic table. Group 1A and 2A metals, listed at the top of the activity series, are some of the most reactive elements in nature. They readily form ions by giving up one or two electrons. Au, Ag, and Cu, represent some of the most stable elements in nature. They are not readily oxidized and so are listed at the bottom of the activity series.

Answers to...

Checkpoint Copper is not oxidized by zinc ions.

Use Visuals L1

Figure 21.3 Explain that voltaic cells can be used as sources of electrical energy because the two half-reactions are physically separated. The reaction in the illustration could take place in a single beaker, but it would not be possible to produce a stream of electrons. **At which electrode does oxidation (loss of electrons) take place?** *(Oxidation occurs at the anode (negative electrode).)* **Where does reduction (gain of electrons) take place?** *(Reduction occurs at the cathode (positive electrode).)* **What path do the electrons given up by zinc follow?** *(They go through the wire and the electric light to the copper electrode.)* **What happens to the electrons at the copper electrode?** *(They reduce copper ions to copper.)*

Relate L2

In discussing the need for a salt bridge in the Zn/Cu voltaic cell, explain that as zinc is oxidized at the anode, Zn^{2+} ions enter the solution. They have no negative ions to balance their charges, so a positive charge tends to build up around the anode. Similarly, at the cathode, Cu^{2+} ions are reduced to Cu and taken out of the solution leaving behind unbalanced negative ions. Thus a negative charge tends to develop around the cathode. The salt bridge allows negative ions, such as SO_4^{2-}, to be drawn to the anode compartment to balance the growing positive charge. Positive ions, such as K^+, are drawn from the salt bridge to balance the growing negative charge at the cathode.

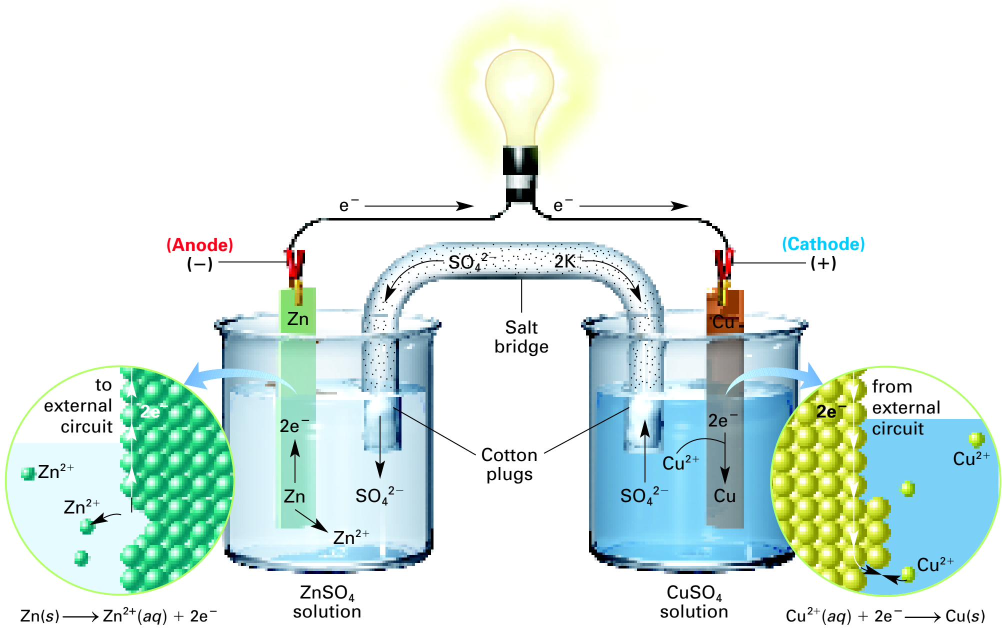

Figure 21.3 In this voltaic cell, the electrons generated from the oxidation of Zn to Zn^{2+} flow through the external circuit (the wire) into the copper strip. These electrons reduce the surrounding Cu^{2+} to Cu. To maintain neutrality in the electrolytes, anions flow through the salt bridge.

How a Voltaic Cell Works The electrochemical process that occurs in a zinc–copper voltaic cell can best be described in a number of steps. These steps actually occur at the same time.

1. Electrons are produced at the zinc rod according to the oxidation half-reaction.

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$$

Because it is oxidized, the zinc rod is the anode, or negative electrode.

2. The electrons leave the zinc anode and pass through the external circuit to the copper rod. (If a bulb is in the circuit, the electron flow will cause it to light. If a voltmeter is present, it will indicate a voltage.)
3. Electrons enter the copper rod and interact with copper ions in solution. There the following reduction half-reaction occurs.

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$

Because copper ions are reduced at the copper rod, the copper rod is the cathode, or positive electrode, in the voltaic cell.

4. To complete the circuit, both positive and negative ions move through the aqueous solutions via the salt bridge. The two half-reactions can be summed to show the overall cell reaction. Note that the electrons in the overall reaction must cancel.

$$\begin{array}{l} Zn(s) \longrightarrow Zn^{2+}(aq) + \cancel{2e^-} \\ Cu^{2+}(aq) + \cancel{2e^-} \longrightarrow Cu(s) \\ \hline Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s) \end{array}$$

When the zinc sulfate and copper(II) sulfate solutions in the voltaic half-cells are both 1.0*M*, the cell generates an electrical potential of 1.10 volts (V). If different metals are used for the electrodes or if different solution concentrations are used, the voltage will differ.

Differentiated Instruction

Less Proficient Readers L1

Students may have difficulty remembering that oxidation occurs at the anode of a voltaic cell and reduction occurs at the cathode. Tell them that consonants go together and vowels go together. Both cathode and reduction begin with a consonant and anode and oxidation begin with a vowel.

Representing Electrochemical Cells You can represent the zinc–copper voltaic cell by using the following shorthand form.

$$Zn(s)\,|\,ZnSO_4(aq)\,\|\,CuSO_4(aq)\,|\,Cu(s)$$

The single vertical lines indicate boundaries of phases that are in contact. The zinc rod ($Zn(s)$) and the zinc sulfate solution ($ZnSO_4(aq)$), for example, are separate phases in physical contact. The double vertical lines represent the salt bridge or porous partition that separates the anode compartment from the cathode compartment. The half-cell that undergoes oxidation (the anode) is written first, to the left of the double vertical lines.

Checkpoint ***Which half-cell is written first in the shorthand representation of an electrochemical cell?***

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Using Voltaic Cells as Energy Sources

Although the zinc-copper voltaic cell is of historical importance, it is no longer used commercially. **Current technologies that use electrochemical processes to produce electrical energy include dry cells, lead storage batteries, and fuel cells.**

Dry Cells When a compact, portable electrical energy source is required, a dry cell is usually chosen. A **dry cell** is a voltaic cell in which the electrolyte is a paste. A type of dry cell that is very familiar to you is the common flashlight battery, which, despite the name, is not a true battery. In such a dry cell, a zinc container is filled with a thick, moist electrolyte paste of manganese(IV) oxide (MnO_2), zinc chloride ($ZnCl_2$), ammonium chloride (NH_4Cl), and water (H_2O). As shown in Figure 21.4a, a graphite rod is embedded in the paste. The zinc container is the anode and the graphite rod is the cathode. The thick paste and its surrounding paper liner prevent the contents of the cell from freely mixing, so a salt bridge is not needed. The half-reactions for this cell are shown below.

Oxidation: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ (anode reaction)

Reduction: $2MnO_2(s) + 2NH_4^+(aq) + 2e^- \longrightarrow$
$Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$ (cathode reaction)

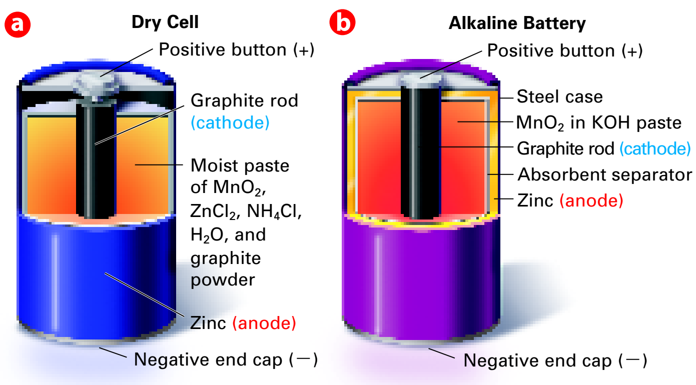


Figure 21.4 Both dry cells and alkaline batteries are single electrochemical cells that produce about 1.5 V. **a** The dry cell is inexpensive, has a short shelf life, and suffers from voltage drop when in use. **b** The alkaline battery costs more than the dry cell, has a longer shelf life, and does not suffer from voltage drop. **Inferring** ***What is oxidized in these cells and what is reduced?***

Using Voltaic Cells as Energy Sources

TEACHER Demo

Inside a Dry Cell L2

Purpose Students observe the construction of a dry cell and measure its voltage.

Materials dry cell, voltmeter, 2 wire leads, zinc electrode, carbon electrode, manganese dioxide/ammonium chloride paste (Prepare the paste by adding saturated ammonium chloride to powdered manganese dioxide until thick.)

Procedure Before class, cut through a dry cell with a hacksaw from the top down on the right side of the central carbon electrode. In class, have students identify the three parts of the cell. *(the central carbon electrode, the zinc container that serves as the other electrode, and the manganese dioxide/ammonium chloride paste.)* Construct a dry cell by placing a zinc electrode and a carbon electrode into a manganese dioxide/ammonium chloride paste. Connect the cell to a voltmeter and measure the potential.

Discuss L2

Explain to students that a dry cell is a voltaic cell in which the electrolyte is a paste. A common flashlight battery is an example of a dry cell. By itself, a dry cell does not provide a complete circuit, that is, electrons cannot flow from the anode to the cathode. When devices using dry cells are turned on, an external circuit is completed, allowing the flow of electrons from the anode to the cathode.

Use Visuals L1

Figure 21.4 Describe the difference between the common dry cell and the alkaline battery. *(In the alkaline dry cell, the electrolyte is a basic KOH paste.)*

Answers to...

Figure 21.4 In both the alkaline battery and the dry cell, zinc is oxidized and MnO_2 is reduced.

Checkpoint The half cell that undergoes oxidation is written first.

Use Visuals L1

Figure 21.5 Call attention to the grids, two containing Pb and two containing PbO_2. Ask, **What are the oxidation numbers of the metal lead (Pb) and the lead in lead(IV) oxide (PbO_2)?** *(oxidation number of elemental Pb is 0; oxidation number of Pb in PbO_2 is +4.)* **Which is the anode and which is the cathode?** *(Pb is the anode and PbO_2 is the cathode.)* **How do you know?** *(Pb can only lose electrons and be oxidized, and Pb^{4+} can gain electrons and be reduced.)* Write on the board the overall reaction for the battery when it is discharging. Call attention to the products ($PbSO_4$ and H_2O) and note that Pb is oxidized to form $PbSO_4$ and Pb^{4+} (in PbO_2) is reduced to also form $PbSO_4$. **What is the oxidation number of the lead in $PbSO_4$?** *(+2; Pb is oxidized to Pb^{2+} and Pb^{4+} is reduced to Pb^{2+}.)*

TEACHER Demo

Making a Lead Cell L2

Purpose Students observe a simple version of the lead storage battery.

Materials 2 strips of lead, wooden rod, 2 connecting wires, 250-mL beaker, dilute sulfuric acid (H_2SO_4), 6-V DC power supply, doorbell

Safety Sulfuric acid is corrosive. Wear safety goggles, gloves, and lab apron.

Procedure Attach two lead strips to a wooden rod so that the strips hang vertically in a 250-mL beaker. Place the strips 4 cm apart. Pour sufficient dilute sulfuric acid into the beaker to cover two-thirds of each strip. Connect a 6-V DC power supply to the strips with wires, and charge the battery for a few minutes. Then connect the cell to a doorbell.

Expected Outcome Students observe that after charging the battery, the bell rings. Discuss the half-cell reactions that occur. Ask students to write the shorthand notation for the electrochemical cell. *[Pb(s) I $PbSO_4$(s) II PbO_2(s) I $PbSO_4$(s)]*

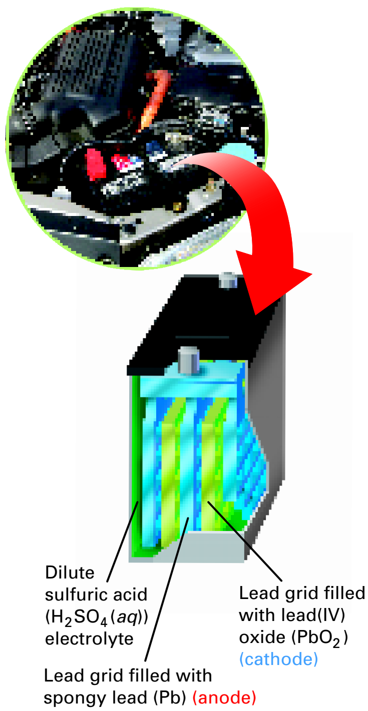
In an ordinary dry cell, the graphite rod serves only as a conductor and does not undergo reduction, even though it is the cathode. The manganese in MnO_2 is the species that is actually reduced. The electrical potential of this cell starts out at 1.5 V but decreases steadily during use to about 0.8 V. Dry cells of this type are not rechargeable because the cathode reaction is not reversable.

The alkaline battery, shown in Figure 21.4b on the previous page, is an improved dry cell used for the same purposes. In the alkaline battery, the reactions are similar to those in the common dry cell, but the electrolyte is a basic KOH paste. This change in design eliminates the buildup of ammonia gas and maintains the Zn electrode, which corrodes more slowly under alkaline conditions.

Checkpoint ***What electrolyte is used in an alkaline battery?***

Lead Storage Batteries People depend on lead storage batteries to start their cars. A **battery** is a group of cells connected together. A 12-V car battery consists of six voltaic cells connected together. Each cell produces about 2 V and consists of lead grids, as shown in Figure 21.5. One set of grids, the anode, is packed with spongy lead. The other set, the cathode, is packed with lead(IV) oxide (PbO_2). The electrolyte for both half-cells in a lead storage battery is concentrated sulfuric acid. Using the same electrolyte for both half-cells allows the cell to operate without a salt bridge or porous separator. The half-reactions are as follows.

Figure 21.5 One cell of a 12-V lead storage battery is illustrated here. Current is produced when lead at the anode and lead(IV) oxide at the cathode are both converted to lead sulfate. These processes decrease the sulfuric acid concentration in the battery. Reversing the reaction recharges the battery.



Oxidation: $Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$

Reduction: $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$

When a lead storage battery discharges, it produces the electrical energy needed to start a car. The overall spontaneous redox reaction that occurs is the sum of the oxidation and reduction half-reactions.

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$

This equation shows that lead sulfate forms during discharge. The sulfate slowly builds up on the plates, and the concentration of sulfuric acid decreases.

The reverse reaction occurs when a lead storage battery is recharged. This reaction occurs whenever the car's generator is working properly.

$$2PbSO_4(s) + 2H_2O(l) \longrightarrow Pb(s) + PbO_2(s) + 2H_2SO_4(aq)$$

This is not a spontaneous reaction. To make the reaction proceed as written, a direct current must pass through the cell in a direction opposite that of the current flow during discharge. In theory, a lead storage battery can be discharged and recharged indefinitely, but in practice its lifespan is limited. This is because small amounts of lead sulfate fall from the electrodes and collect on the bottom of the cell. Eventually, the electrodes lose so much lead sulfate that the recharging process is ineffective or the cell is shorted out. The battery must then be replaced. The processes that occur during the discharge and recharge of a lead-acid battery are summarized in Figure 21.6.

Facts and Figures

Car Battery

The forerunner of today's car battery was built by the French physicist Gaston Plant in 1859. Plant's first battery consisted of a single cell containing two sheets of lead separated by rubber strips and immersed in a 10% sulfuric acid solution. A year later he presented to Acadmie des Sciences a battery consisting of nine cells enclosed in box with outside terminals. Plant's invention was significant because it provided the first means of storing electricity.

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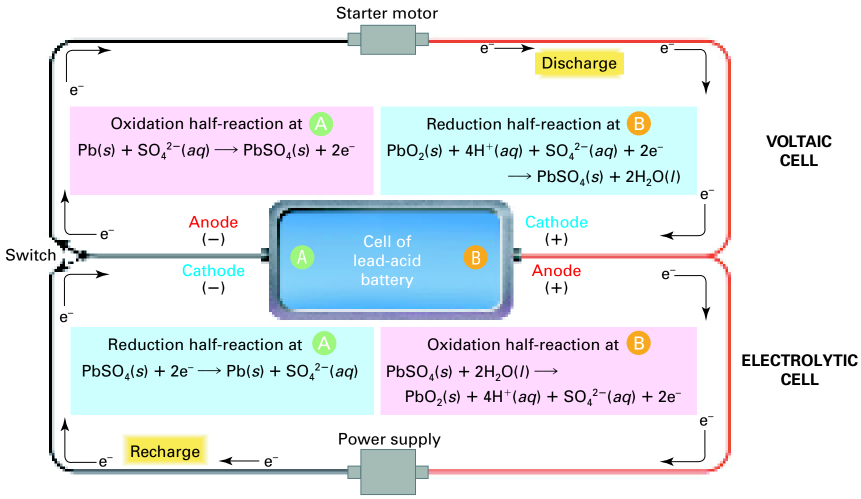


Figure 21.6 The lead-acid battery in an automobile acts as a voltaic cell (top) when it supplies current to start the engine. Some of the power from the running engine is used to recharge the battery which then acts as an electrolytic cell (bottom). You will learn more about electrolytic cells in Section 21.3.

Fuel Cells To overcome the disadvantages associated with lead storage batteries, cells with renewable electrodes have been developed. Such cells, called **fuel cells,** are voltaic cells in which a fuel substance undergoes oxidation and from which electrical energy is continuously obtained. Fuel cells do not have to be recharged. They can be designed to emit no air pollutants and to operate more quietly and more cost-effectively than a conventional electrical generator.

Perhaps the simplest fuel cell is the hydrogen–oxygen fuel cell, which is shown in Figure 21.7 on the following page. In this fuel cell, there are three compartments separated from one another by two electrodes made of porous carbon. Oxygen (the oxidizer) is fed into the cathode compartment. Hydrogen (the fuel) is fed into the anode compartment. The gases diffuse slowly through the electrodes. The electrolyte in the central compartment is a hot, concentrated solution of potassium hydroxide. Electrons from the oxidation half-reaction at the anode pass through an external circuit to enter the reduction half-reaction at the cathode.

Oxidation: $2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$ (anode)

Reduction: $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$ (cathode)

The overall reaction in the hydrogen–oxygen fuel cell is the oxidation of hydrogen to form water.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

Other fuels, such as methane (CH_4) and ammonia (NH_3), can be used in place of hydrogen. Other oxidizers, such as chlorine (Cl_2) and ozone (O_3), can be used in place of oxygen.

Discuss L2

Point out that fuel cells were developed for space travel where lightweight, reliable power systems are needed. Fuel cells differ from lead storage batteries in that they are not self-contained. Operation depends on a steady flow of fuel and oxygen into the cell—where combustion takes place—and the flow of the combustion product out of the cell. In the case of the hydrogen fuel cell, the product is pure water. Both the electricity generated and the water produced are consumed in space flights. Fuel cells convert 75% of the available energy into electricity, in contrast with a conventional electric power plant that converts from 35 to 40% of the energy of coal to electricity. Fuels other than hydrogen can also be used, for example, ammonia (NH_3), hydrazine (N_2H_4), and methane (CH_4). Students may be interested in the equations for the reactions that take place in these cells.

$4NH_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(g)$
$2N_2H_4(g) + 2O_2(g) \rightarrow 2N_2(g) + 4H_2O(g)$
$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

In each case, the products are gases and water vapor which are normally found in Earth's atmosphere.

Relate L2

Divide the class into groups of three or four students. Have them research the use of fuel cells in the space shuttle and by utility companies. Ask them to prepare posters showing different types of fuel cells and their applications. Where possible, have students include the half-cell and overall reactions for each fuel cell. Have them describe the advantages gained by using a fuel cells rather than more conventional sources of electrical energy.

Differentiated Instruction

Gifted and Talented L3

Electric cars are quiet and nonpolluting—no noisy engines spew noxious gases into the atmosphere. So why have car makers not built, promoted, and sold many electric vehicles? Have interested students research the current status of electric cars in the marketplace. Have them find out what obstacles stand in the way of mass usage of these cars. Students could choose to write a report or prepare an oral presentation. *(One obstacle that students may discover is the need for inexpensive, lightweight batteries for efficient storing of electrical energy to lengthen the distance of travel without recharging.)*

Answers to...

Checkpoint a basic KOH paste

3 ASSESS

Evaluate Understanding L2

Have students make a sketch of a tin/lead voltaic cell ($Sn|SnSO_4||PbSO_4|Pb$). Have them label the cathode and anode, and indicate the direction of electron flow. *(Tin is the anode; lead is the cathode. The electrons flow from tin to lead.)* Ask them to write the equations for the half-reactions.

[$Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$]

Reteach L1

Emphasize that a chemical reaction can produce a flow of electrons or a flow of electrons can cause a chemical reaction to occur. Note that reduction always occurs at the cathode, and oxidation always occurs at the anode. Discuss the half-reactions for the charging process in a lead cell and compare them to the half-reactions when the cell is producing electric current.

Writing Activity

In a zinc–copper voltaic cell, zinc is oxidized and copper ions are reduced.
Anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
A zinc rod serves as the anode; a copper rod serves as the cathode. The half-cells are connected by a salt bridge through which both positive and negative ions migrate. The overall reaction is as follows:
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

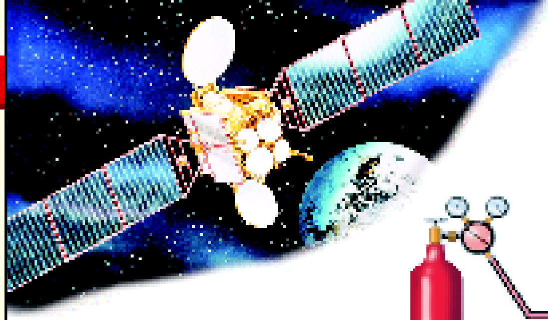
Interactive Textbook

If your class subscribes to the Interactive textbook, use it to review key concepts in Section 21.1

with ChemASAP

Answers to...

Figure 21.7 Water is the only product.



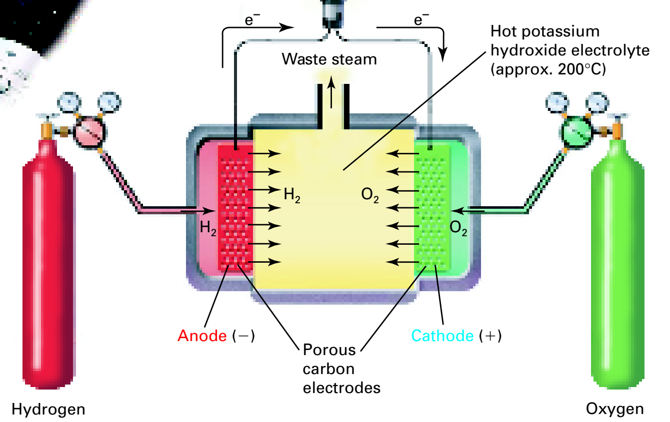


Figure 21.7 The hydrogen–oxygen fuel cell is a clean source of power. Such cells are often used in spacecraft. **Predicting** ***What waste products, if any, are produced?***

Since the 1960s, astronauts have used fuel cells as an energy source aboard spacecraft. Hydrogen–oxygen fuel cells with a mass of approximately 100 kg each were used in the Apollo spacecraft missions. Fuel cells are well suited for extended space missions because they offer a continuous energy source that releases no pollutants. On space shuttle missions, for example, astronauts drink the water produced by onboard hydrogen–oxygen fuel cells. Fuel cells are also used as auxiliary power sources for submarines and other military vehicles. At present, however, they are too expensive for general use.

21.1 Section Assessment

1. **Key Concept** If the relative activities of two metals are known, which metal is more easily oxidized?
2. **Key Concept** What type of reaction occurs during an electrochemical process?
3. **Key Concept** What is the source of electrical energy produced in a voltaic cell?
4. **Key Concept** What are three examples of technologies that use electrochemical processes to supply electrical energy?
5. Describe the structure of a dry cell. What substance is oxidized? What substance is reduced?
6. What is the electrolyte in a lead storage battery? Write the half-reactions for such a battery.
7. Write the overall reaction that takes place in a hydrogen–oxygen fuel cell. What product(s) are formed? Describe the half-reactions in this cell.
8. Predict the result when a strip of copper is dipped into a solution of iron(II) sulfate.

Writing Activity

Explanatory Paragraph Write a paragraph explaining how a zinc–copper voltaic cell works. Make sure to mention the half-reactions and the overall reaction in your explanation. (*Hint:* Use Figure 21.3 on page 666 as a reference.)

Interactive Textbook

Assessment 21.1 Test yourself on the concepts in Section 21.1.

with ChemASAP

Section 21.1 Assessment

1. the metal with the higher activity
2. a redox reaction
3. spontaneous redox reactions within the cell
4. fuel cells, lead storage batteries, and dry cells
5. A zinc container (anode) filled with electrolyte paste; the cathode is a graphite rod embedded in the paste. Zn is oxidized; MnO_2 is reduced.
6. 6. concentrated sulfuric acid;
Anode: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$
Cathode: $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$
7. $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$; water is the product. H_2 is oxidized at the anode; O_2 is reduced at the cathode
8. no reaction