SCH4U-C

10

Electrochemistry

Introduction

During the 1960s, hydrogen fuel cells were first introduced by NASA to power the onboard electrical systems in their *Gemini* and *Apollo* space capsules. A useful by-product of the hydrogen fuel cell reaction is pure H_2O. Modern versions of these fuel cells still provided power, as well as drinking water, for space-shuttle missions as recently as the 2010 flights. Since their use in the space program, many companies have attempted to transfer hydrogen fuel cell technology to the automobile—with very limited success. Will the cars of the future run on hydrogen or is hydrogen a lot of hype?
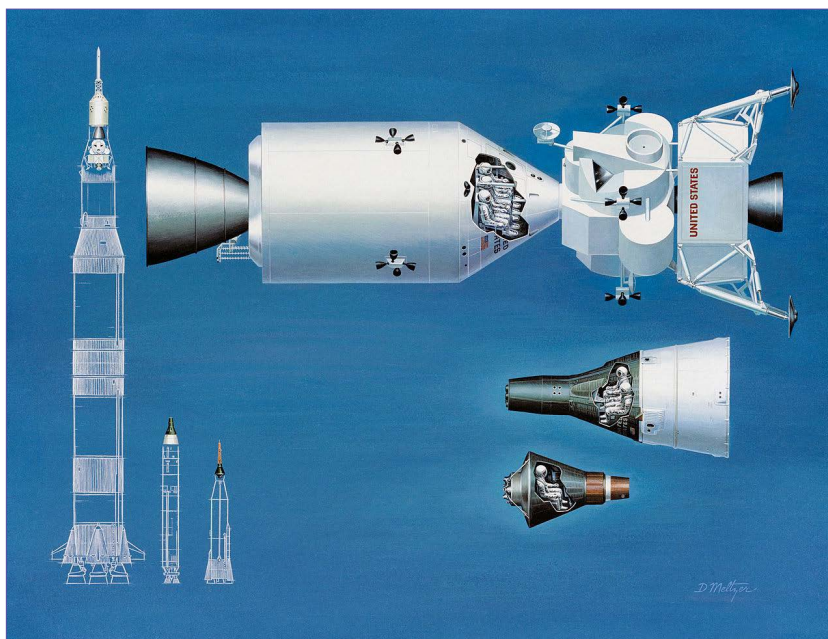

Figure 10.1: The one-person Mercury capsule, the two-person Gemini capsule, and the three-person Apollo capsule are shown side by side.

Source: http://commons.wikimedia.org/wiki/File:NASA_spacecraft_comparison.jpg

Fuel cells are a technology that produces electrical energy resulting from redox reactions. In this lesson, you will learn about current and future potential applications of the hydrogen fuel cell. You will also learn about some surprising similarities between fuel cells and the standard AA batteries that you use to power portable electronic devices. For instance, both are examples of galvanic cells.

Planning Your Study

You may find this time grid helpful in planning when and how you will work through this lesson.

| Suggested Timing for This Lesson (Hours)	
Introduction to Galvanic Cells	1½
Cell Reactions and Voltages	1
Applications of Galvanic Cells	1
Key Questions	1

What You Will Learn

After completing this lesson, you will be able to

- describe the operation of a galvanic cell

- predict the half-reactions and overall cell potential of a given galvanic cell

- describe the operation of a typical alkaline battery

- compare fuel cells with alkaline batteries

- identify the factors that cause and contribute to the corrosion of metals

- apply the principles of galvanic cells to a corroding metal

Introduction to Galvanic Cells

The use of fuel cells in the space program involves some sophisticated engineering. However, the basic chemistry of how a fuel cell works is relatively simple. In fact, it's not that different from how a common AA-sized battery works. Fuel cells and batteries are both examples of galvanic cells. A galvanic cell is a device that spontaneously converts stored chemical energy into electrical energy, when the battery is connected to some load like a light bulb. This energy change occurs because of redox reactions.

Before discussing how galvanic cells work, you'll review some key redox concepts. In Lesson 9, you learned that a redox reaction might occur when a metal is placed into a solution containing ions. Whether or not a reaction occurs depends on the strength of the metal and ion as the reducing agent and oxidizing agent. Zinc, for example, is a good reducing agent, while Cu^{2+} ions are good oxidizing agents. The following chemical reaction occurs spontaneously when a strip of zinc is placed in a Cu^{2+} solution:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$$
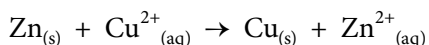
In this reaction, two electrons from a zinc atom are transferred to a copper ion that is in contact with the zinc, allowing the copper ion to take electrons from the zinc metal. As a result, copper ions are reduced to copper metal, while zinc atoms are oxidized to form zinc ions, which dissolve in solution. If there are enough copper ions present, the entire zinc strip dissolves. If either the copper ion, in solution, or the zinc metal strip was totally consumed, then this reaction would cease.

In this reaction, there is a net flow of electrons to the copper ions. Moving electrons have energy. You can tap into the energy of these electrons by applying a simple chemistry trick. As you will see, this trick involves physically separating the zinc strip and copper ions, while maintaining the electrical connection between them. The next three diagrams show how this is done. First, a strip of zinc is placed in a solution of its own ions, in this case, zinc nitrate. Meanwhile, a strip of copper is also placed in a solution of its own ions, in this case, copper nitrate. No reactions are observed in Figure 10.2 since, at this time, there is no connection between the two.
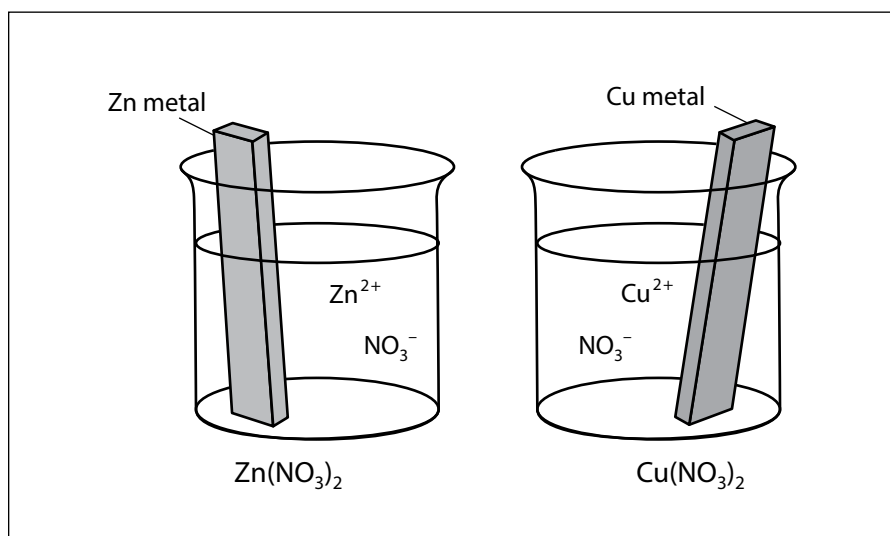
Figure 10.2: Making a galvanic cell begins with two half-cells. In this case, they are in two separate glass beakers. Each beaker contains a metal strip immersed in a solution containing ions of the same metal. This configuration is referred to as a Zn/Cu cell. The Zn/Cu simply refers to the metal strips (electrodes) being used.

Next, the two metal strips are linked with a conducting wire (Figure 10.3). The wire serves as a pathway for electrons to travel from one metal to the other. A voltmeter placed in this path shows that the voltage across the two metal strips is zero. This means that there is no electron flow between the metals. A galvanic cell with no electron flow behaves like a "dead" battery.
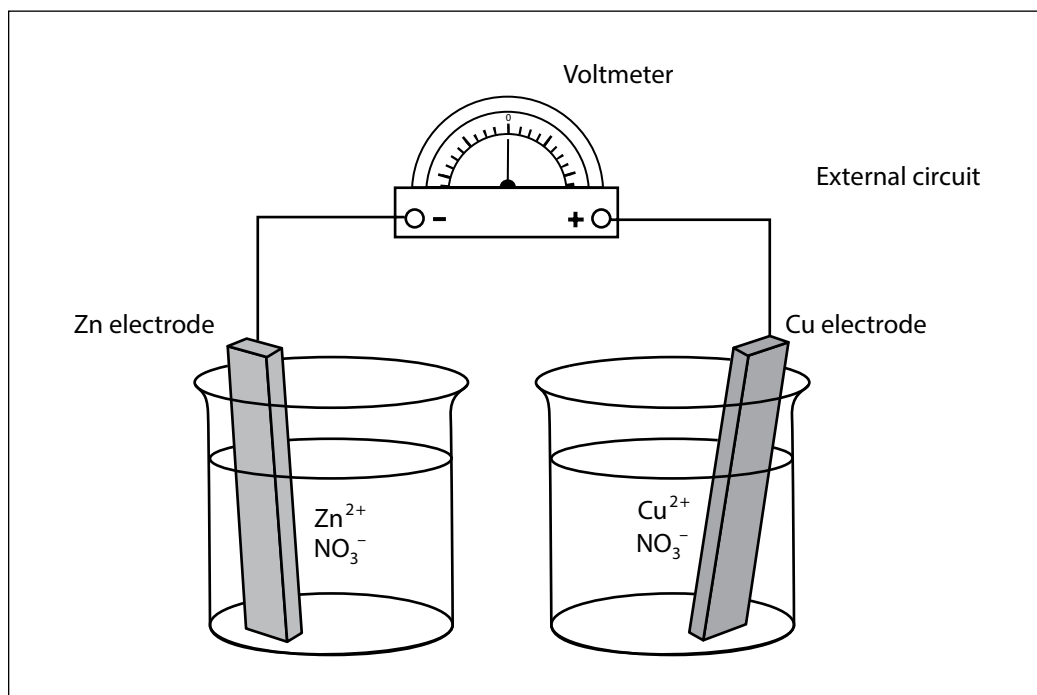

Figure 10.3: The external circuit, composed of the wire and voltmeter, provides an electron path.

In order for charges to flow, the circuit must be one continuous path. Since there is no continuous loop, the circuit shown in Figure 10.3 is incomplete. There is a gap between the two solutions.

This can be corrected by "connecting" the solutions with a tube containing a solution of potassium nitrate. The U-shaped tube is called a salt bridge because it contains a neutral, dissolved ionic solid (also called a salt). The U-shaped tube has cotton plugs at each end. These plugs prevent the salt solution from pouring out, but are porous enough to allow ions and water to pass through it. Once this connection is made, the voltmeter immediately moves to a reading of positive electrical potential, indicating that current is flowing within this cell. Figure 10.4 illustrates the basic structure of any galvanic cell.
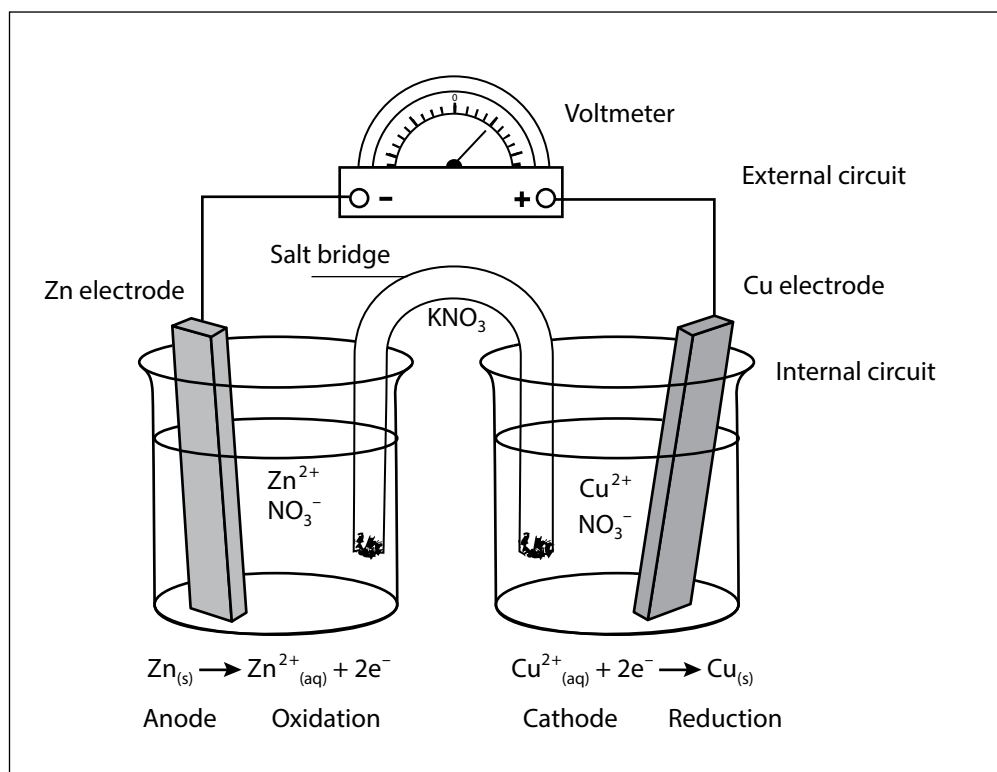

Figure 10.4: An operating galvanic cell consists of two half-cells connected by a salt bridge and a wire. Each half-cell contains an electrode and a conducting solution. IMPORTANT NOTE: Oxidation always occurs at the anode, while reduction occurs at the cathode. Electrons flow through the wire from anode to cathode.

Components of a Galvanic Cell

Each beaker and its contents are called a half-cell. The galvanic cell in the above example is made up of a zinc half-cell and a copper half-cell. The metal strips that come into contact with the solutions are called electrodes. The electrode where oxidation occurs (in this case, zinc) is called the anode. The electrode where reduction occurs is called the cathode. An oxidation reaction occurs at the surface of the anode. A reduction reaction occurs at the surface of the cathode. Figure 10.4 shows the oxidation half-reaction and the reduction half-reaction occurring at the surfaces of the anode and cathode respectively.

Note that electrons are being produced at the anode where the zinc metal is losing its electrons. Electrons are are being consumed at the cathode side as the copper ions, in the solution, take these electrons. The cathode is defined as having a positive charge, while the anode is defined as having a negative charge. These correspond to the positive and negative terminals on a battery.

Purpose of the Salt Bridge

A galvanic cell cannot function without a salt bridge. The salt bridge is necessary for maintaining the electrical neutrality of both solutions. Take a closer look at how this works (Figure 10.5). As the zinc electrode is oxidized, it becomes surrounded by positively charged zinc ions. If the electrode's environment becomes too positive, it prevents the negatively charged electrons from leaving the strip and the electron flow stops. Matching charges or "like charges" repel each other. The positive zinc ions push against each other, causing the zinc ions to move (diffuse) into the neutral salt solution. To prevent the buildup of a positive charge in the salt solution, negatively charged nitrate ions from the salt bridge spontaneously migrate into the zinc half-cell. Study the diagram to observe the movement of the ions in the solution and salt bridge.

Similarly, the reduction of copper ions in the cathode half-cell removes positive ions from its beaker. This leaves an excess of nitrate ions in the copper nitrate solution. Any accumulation of negative charge around the surface of the electrode would repel incoming electrons, preventing them from reaching the copper electrode. In addition to negatively charged nitrate ions, the salt bridge has potassium ions (K^+). Positive potassium ions spontaneously flow into the cathode half-cell to offset any buildup of negative charge.
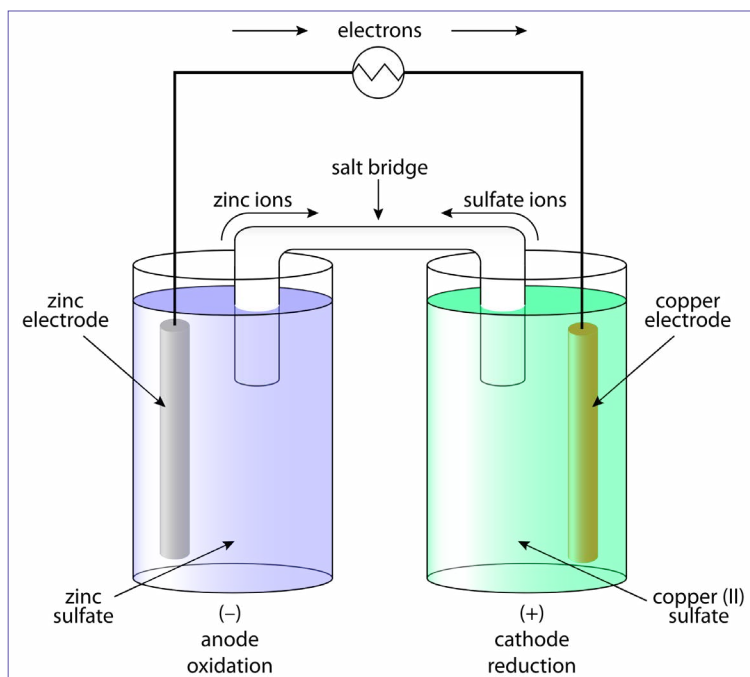
Figure 10.5: In an operating galvanic cell, electrons flow through the conducting wire, while ions flow through the solution and salt bridge. Study the diagram to observe the movement of the ions in the solution and salt bridge.

Source: http://commons.wikimedia.org/wiki/File:Galvanic_cell_labeled.svg

The continuous flow of electrons and ions completes the circuit, allowing the cell to convert stored chemical energy into electrical energy. You may be wondering at what point the reaction will grind to a halt. Eventually, the copper half-cell reaches its limit when it converts all (or nearly all) of its Cu^{2+} ions into $Cu_{(s)}$, creating a shortage of Cu^{2+}. Another limit that can be reached is that all of the solutions can become saturated with Zn^{2+}, making it impossible to create any new Zn^{2+} ions.

Now view a video called [Lemon Battery](). The video teaches you how to build lemon galvanic cells, connect them in a circuit, and measure the circuit's cell potential. Most galvanic cells do not produce a high voltage, which is why most personal electronics require two or more cells to be connected in one circuit. After watching the video, you will be prepared to answer a Support Question about the lemon battery.

Support Questions

**Be sure to try the Support Questions on your own before looking at
the suggested answers provided.**

11. What mass changes are expected as the Zn/Cu cell operates? (**Hint:** Look back at Figure 10.5. Study the half-reactions occurring at each electrode. Describe what will be happening to each electrode strip.)

12. What will happen if two zinc half-cells are connected? Why?

13. Why is the operation of the Zn/Cu cell dependent on the concentration of the solutions used? (**Hint:** One of the ions in the solution is being consumed.)

14. **This question is based on the video you watched earlier in this lesson.** Four pennies and four nails can be inserted into four lemon slices with wires connecting the four cells into one circuit. The circuit will generate enough electrical energy to power a small LED light bulb. What similarities and differences does this "lemon-cell" battery have with the galvanic cell in Figure 10.5?

Cell Reactions and Voltages

As you know, a galvanic cell is composed of two half-cells joined by a wire and a salt bridge. The electrons flow through the wire with a certain amount of force. This amount of force, called voltage, is similar to pressure. The cell reaction that exerts this chemical force is composed of two half-cell reactions.

All redox reactions involve the transfer of electrons. You saw earlier how the Zn/Cu cell could be set up as a galvanic cell. The two half-reactions occurring in that cell were:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$$

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$$
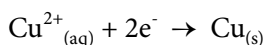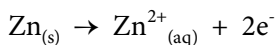
Together, these two half-reactions create a chemical driving force which moves the electrons through the wire of the cell from the Zn electrode to the Cu electrode. The driving force of this cell (a battery) is called the electrical potential or voltage of the cell, given the symbol E. Under standard conditions (explained later), this cell generates a voltage, $E = +1.10$ volts. Any redox reaction that occurs spontaneously will have a cell voltage greater than zero. Any redox reaction that has an associated voltage less than zero (negative) does not tend to occur naturally (spontaneously). An example of a reaction that would *not* occur spontaneously is

$$2Ag_{(s)} + 2H+_{(aq)} \rightarrow H_{2(g)} + 2Ag+_{(aq)} \text{ here } E = -0.80 \text{ V}$$
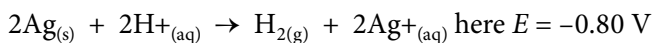
How that voltage is determined will be described later. This negative voltage is telling us two things:

1. That this reaction does not occur spontaneously.

2. Since the driving force for that reaction is negative, the reverse reaction actually will occur naturally (spontaneously). $H_{2(g)} + 2Ag^+_{(aq)} \rightarrow 2Ag_{(s)} + 2H^+_{(aq)}$

Cell Reactions

Each operating galvanic cell consists of two half-cell reactions and an overall cell reaction. The half-cell reactions can be written, and then added, as follows:

Anode half-reaction: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ (oxidation)

Cathode half-cell reaction: $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ (reduction)

Overall cell reaction (sum): $Cu^{2+}_{(aq)} + Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

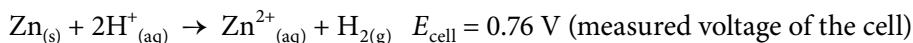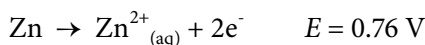# Half-cell Potentials and the $E°$ Table

Scientists wanted to be able to assign a voltage to every known half-reaction. We call these half-cell potentials. Table 10.1 lists just a few of these half-reactions and their associated voltages.

To obtain these, a half-reaction such as

$Zn \rightarrow Zn^{2+}_{(aq)} + 2e^-$
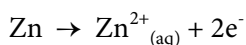
is paired with the half-reaction $2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$ in a special half-cell called the hydrogen half-cell, shown in Figure 10.6. The exact configuration of the whole cell is not important here. The voltage of the whole cell was measured to be 0.76 V. Of course this positive voltage reminds us that this redox reaction is spontaneous and this cell is really a small battery.

A standard was established where the voltage associated with the hydrogen half-reaction was assigned a zero value. The result is the following:

$Zn \rightarrow Zn^{2+}_{(aq)} + 2e^-$ $E = 0.76$ V

$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$ $E = 0.00$ V (assigned value)   If we now add the half-reactions

$Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)}$ $E_{cell} = 0.76$ V (measured voltage of the cell)

By matching other half-reactions with the hydrogen half-cell, we can generate the data found in Table 10.1.
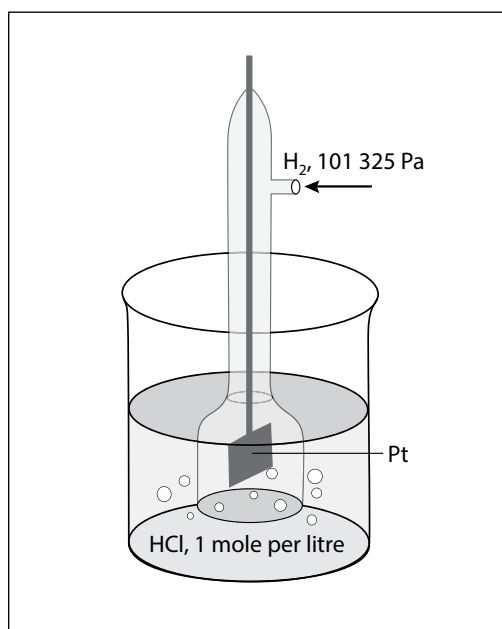
Figure 10.6: The standard hydrogen electrode

It consists of a platinum conductor immersed in a solution of hydrochloric acid, HCl, through which hydrogen gas bubbles. Hydrochloric acid is used because it is a good source of hydrogen ions. Platinum is used because it is non-reactive and merely serves as a passive conductor of electrons. At the electrode surface, two reactions can happen:

Either

hydrogen ions are reduced: $2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$

or

hydrogen gas is oxidized: $H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^-$

The half-cell potential for either process was arbitrarily set at 0.00 volts. Hydrogen may be oxidized or reduced, depending on the cell to which the hydrogen half-cell is attached.

Table 10.1 Standard Electrode Potentials in Aqueous Solution at 25°C

Cathode (Reduction) Half-Reaction	Standard Potential $E^°$ (volts)
$Li^+_{(aq)} + e^- \rightarrow Li_{(s)}$	−3.04
$K^+_{(aq)} + e^- \rightarrow K_{(s)}$	−2.92
$Ca^{2+}_{(aq)} + 2e^- \rightarrow Ca_{(s)}$	−2.76
$Na^+_{(aq)} + e^- \rightarrow Na_{(s)}$	−2.71
$Mg^{2+}_{(aq)} + 2e^- \rightarrow Mg_{(s)}$	−2.38
$Al^{3+}_{(aq)} + 3e^- \rightarrow Al_{(s)}$	−1.66
$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$	−0.83
$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$	−0.76
$Cr^{3+}_{(aq)} + 3e^- \rightarrow Cr_{(s)}$	−0.74
$Fe^{2+}_{(aq)} + 2e^- \rightarrow Fe_{(s)}$	−0.41
$Cd^{2+}_{(aq)} + 2e^- \rightarrow Cd_{(s)}$	−0.40
$Co^{2+}_{(aq)} + 2e^- \rightarrow Co_{(s)}$	−0.28
$Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)}$	−0.23
$Sn^{2+}_{(aq)} + 2e^- \rightarrow Sn_{(s)}$	−0.14
$Pb^{2+}_{(aq)} + 2e^- \rightarrow Pb_{(s)}$	−0.13
$Fe^{3+}_{(aq)} + 3e^- \rightarrow Fe_{(s)}$	−0.04
$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$	0.00
$Sn^{4+}_{(aq)} + 2e^- \rightarrow Sn^{2+}_{(aq)}$	0.15
$Cu^{2+}_{(aq)} + e^- \rightarrow Cu^+_{(aq)}$	0.16
$ClO_4^-{}_{(aq)} + H_2O_{(l)} + 2e^- \rightarrow ClO_3^-{}_{(aq)} + 2OH^-_{(aq)}$	0.17
$AgCl_{(s)} + e^- \rightarrow Ag_{(s)} + Cl^-_{(aq)}$	0.22
$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$	0.34
$ClO_3^-{}_{(aq)} + H_2O_{(l)} + 2e^- \rightarrow ClO_2^-{}_{(aq)} + 2OH^-_{(aq)}$	0.35
$IO^-_{(aq)} + H_2O_{(l)} + 2e^- \rightarrow I^-_{(aq)} + 2OH^-_{(aq)}$	0.49
$Cu^+_{(aq)} + e^- \rightarrow Cu_{(s)}$	0.52
$I_{2(s)} + 2e^- \rightarrow 2I^-_{(aq)}$	0.54
$ClO_2^-{}_{(aq)} + H_2O_{(l)} + 2e^- \rightarrow ClO^-_{(aq)} + 2OH^-_{(aq)}$	0.59
$Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)}$	0.77
$Hg_2^{2+}{}_{(aq)} + 2e^- \rightarrow 2Hg_{(l)}$	0.80
$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$	0.80
$Hg^{2+}_{(aq)} + 2e^- \rightarrow Hg_{(l)}$	0.85
$ClO^-_{(aq)} + H_2O_{(l)} + 2e^- \rightarrow Cl^-_{(aq)} + 2OH^-_{(aq)}$	0.90
$2Hg^{2+}_{(aq)} + 2e^- \rightarrow Hg_2^{2+}{}_{(aq)}$	0.90
$NO_3^-{}_{(aq)} + 4H^+_{(aq)} + 3e^- \rightarrow NO_{(g)} + 2H_2O_{(l)}$	0.96
$Br_{2(l)} + 2e^- \rightarrow 2Br^-_{(aq)}$	1.07

$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)}$	1.23
$Cr_2O_7{}^{2-}_{(aq)} + 14H^+_{(aq)} + 6e^- \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$	1.33
$Cl_{2(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}$	1.36
$Ce^{4+}_{(aq)} + e^- \rightarrow Ce^{3+}_{(aq)}$	1.44
$MnO_4{}^-_{(aq)} + 8H^+_{(aq)} + 5e^- \rightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}$	1.49
$H_2O_{2(aq)} + 2H^+_{(aq)} + 2e^- \rightarrow 2H_2O_{(l)}$	1.78
$Co^{3+}_{(aq)} + e^- \rightarrow Co^{2+}_{(aq)}$	1.82
$S_2O_8{}^{2-}_{(aq)} + 2e^- \rightarrow 2SO_4{}^{2-}_{(aq)}$	2.01
$O_{3(g)} + 2H^+_{(aq)} + 2e^- \rightarrow O_{2(g)} + H_2O_{(l)}$	2.07
$F_{2(g)} + 2e^- \rightarrow 2F^-_{(aq)}$	2.87

The voltages in Table 10.1 are said to be for "standard conditions." This means that they would have been derived at a temperature of 25°C (standard temperature) with solution ion concentrations of 1.00 mol/L. If gases are involved, their pressure is 101.3 kPa (standard pressure for gases). Therefore, the Table 10.1 half-cell potentials are termed "standard half-cell potentials" and are given the symbol $E°$. The symbol, "°" denotes standard conditions.

In our work with cell voltages, we will make the assumption that conditions are "standard." Determining the voltage for non-standard conditions is beyond the scope of this course.

Calculating Cell Potentials

If you examine Table 10.1, you will notice that all of the half-reactions are reduction half-reactions.

$Br_{2(l)} + 2e^- \rightarrow 2Br^-_{(aq)}$ $E° = 1.06$ V (a reduction)

We can easily write an oxidation reaction from this by simply reversing the reduction and changing the sign of the voltage.

$2Br^-_{(aq)} \rightarrow Br_{2(l)} + 2e^-$ $E° = -1.06$ V (the corresponding oxidation)
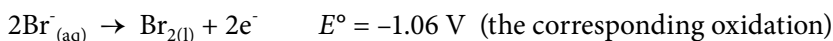
Example

Determine the overall cell voltage of the following redox reaction and decide if that reaction will be spontaneous or not.

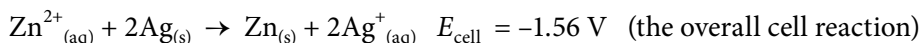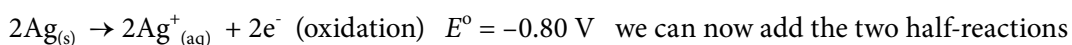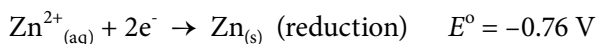$Zn^{2+}_{(aq)} + 2Ag_{(s)} \rightarrow Zn_{(s)} + 2Ag^+_{(aq)}$
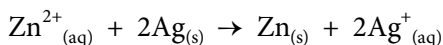
Solution

Metals exist as either positive ions or as the neutral metal atom. Metals never form negative ions. Here we see the zinc ion being reduced to the zinc metal and the silver metal being oxidized to the silver ion. The two half-reactions are:

$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$ (reduction)

$2Ag_{(s)} \rightarrow 2Ag^+_{(aq)} + 2e^-$ (oxidation)
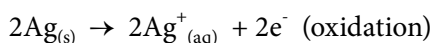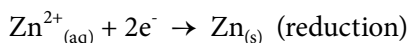
The standard half-cell potentials for these half-reactions can be found by consulting Table 10.1

The zinc reduction half-reaction is shown on the table to have $E° = -0.76$ V. The oxidation half-reaction is shown on the table, but in reverse so we change the sign from the table, making $E°$ for the silver half-reaction to be $E° = -0.80$ V. Even though we have doubled the silver half-reaction to make electrons lost equal electrons gained, this has no effect on the voltage for that reaction. The cell potential is only affected by temperature and concentration of ions in the solution. Doubling the equation has not changed those conditions.

Now we have all of the information required for our redox reaction:

$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$ (reduction) $E° = -0.76$ V

$2Ag_{(s)} \rightarrow 2Ag^+_{(aq)} + 2e^-$ (oxidation) $E° = -0.80$ V   we can now add the two half-reactions

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$Zn^{2+}_{(aq)} + 2Ag_{(s)} \rightarrow Zn_{(s)} + 2Ag^+_{(aq)}$ $E_{cell} = -1.56$ V   (the overall cell reaction)

This redox reaction has a negative voltage, meaning that this process will not occur spontaneously. This reaction would not occur in a galvanic cell. If that overall reaction was reversed, we would have a spontaneous reaction with a positive driving force, and that (reversed) reaction could occur in a galvanic cell (it could form a battery).

Example

Decide if the following redox reaction would be spontaneous:

$Co^{2+}_{(aq)} + Zn_{(s)} \rightarrow Co_{(s)} + Zn^{2+}_{(aq)}$
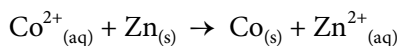
Solution

The two half-reactions and their voltages from Table 10.1 are:

$Co^{2+}_{(aq)} + 2e^- \rightarrow Co_{(s)}$ (reduction) $E° = -0.28$ V

$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ (oxidation) $E° = +0.76$ V   adding the two reactions now

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$Co^{2+}_{(aq)} + Zn_{(s)} \rightarrow Co_{(s)} + Zn^{2+}_{(aq)}$ $E_{cell} = +0.48$ V
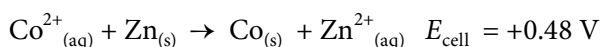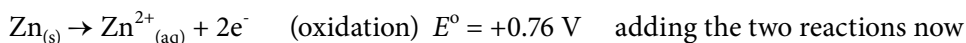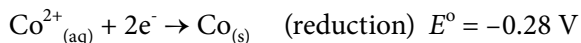
This redox process will be spontaneous and could occur in a galvanic cell, so theoretically could be used to construct a battery.

Support Questions

15. a) Predict the cell potential of the following redox reactions. Indicate whether the given reaction will be spontaneous or not, and explain why. Write the two half-reactions. Balance electrons lost and gained. Add to produce the accurate overall cell reaction.

i) $Ag^+_{(aq)} + Al_{(s)} \rightarrow Ag_{(s)} + Al^{3+}_{(aq)}$

ii) $Cu_{(s)} + Na^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Na_{(s)}$

b) Explain why reaction i) could be used in a galvanic cell. Identify the half reaction that would be occurring at the anode and at the cathode.

16. Think about how you might assemble a high-voltage galvanic cell. What is the most important factor involved in determining the overall cell potential?

17. What determines the total amount of electrical potential that a galvanic cell can generate?

18. What is the voltage of a "dead" galvanic cell? Explain.

19. Consider the following standard reduction half-cell potentials. What would the overall cell potentials be if the zinc half-cell reaction was paired with each of the following? Write the two half-reactions. Balance electrons lost and gained. Add and produce the accurate overall reaction with the associated cell voltage. (**Hint:** Would the zinc half-cell reaction need to be a reduction or an oxidation reaction?)

a) $Ag^+ + e^- \rightarrow Ag_{(s)}$ $E° = 0.80$ V

b) $Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$ $E° = +0.34$ V

c) $Zn^{2+} + 2e^- \rightarrow Zn_{(s)}$ $E° = -0.76$ V

Applications of Galvanic Cells

In the nineteenth century, some of the early uses for galvanic cells included powering stationary light bulbs, small electric motors, and even telegraph systems. You'll agree that the galvanic cell in Figure 10.5 is not a practical power source for personal electronics because it is wet and bulky.

Common Batteries

The batteries that you buy to power personal electronic equipment are made of a type of galvanic cell that uses an ion-rich paste instead of a liquid, and is sometimes called a dry cell (Figure 10.7). A common type of dry-cell battery, called an alkaline battery, has been designed to be small and reliable, and to have a long shelf life. Take a closer look, now, at the inside of an alkaline battery to see how the principles of the galvanic cell apply. This type of battery contains an alkaline electrolyte of potassium hydroxide, which is how it got its name.
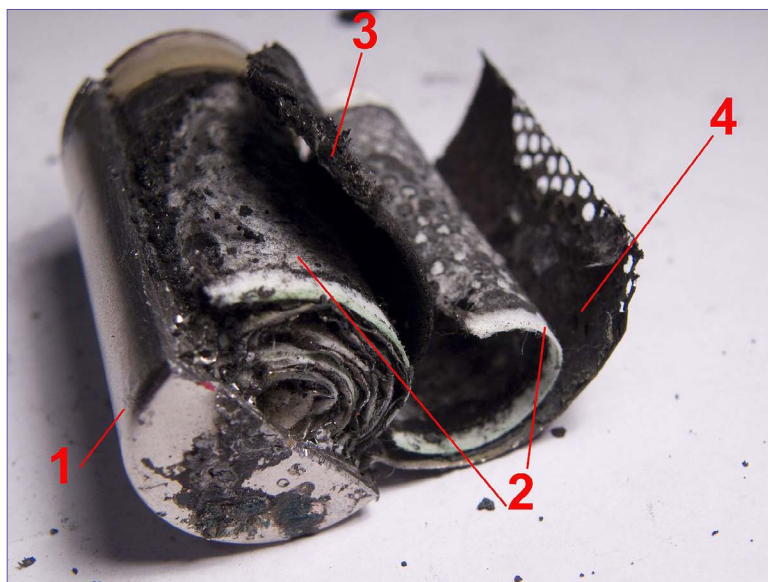

Figure 10.7: Disassembled alkaline AA battery. 1) outer metal casing (also negative terminal); 2) separator (between electrodes); 3) positive electrode; 4) negative electrode with current collector (metal grid, connected to metal casing).

Source: http://commons.wikimedia.org/wiki/File:Nicd_disassembled.jpg

The simplest type of alkaline battery has two separate inner and outer compartments or half-cells (the anode and the cathode). The chemicals in these compartments are prevented from mixing by a porous fabric called a separator. Consider how electrons flow in a flashlight. When a flashlight is turned on, electrons generated by the anode half-cell pass through the anode current collector to the negative cap. This is marked as the negative terminal of the battery. Electrons move from the negative cap through a wire, to a light bulb. There, some of the energy of the moving electrons is used to light the bulb. From the bulb, these electrons are conducted

through the wire to the positive terminal of the battery. Then, the electrons continue to the cathode half-cell to complete the circuit. This process happens continually, while the flashlight is on.

When the flashlight is off, no electron flow occurs, but the two chemicals in the battery will slowly react with each other (through the porous separator) until they have degraded each other. An increase in heat speeds up most electrochemical reactions, including the reaction that degrades batteries. That's why a battery can have a shelf life ranging from several months to several years, depending on factors such as the temperature at which it is stored.

Corrosion

Each year, Canadians spend millions of dollars trying to prevent corrosion—a chemical reaction involving the deterioration of metals. Rusting is the act of corroding (oxidizing) iron or steel. Steel is manufactured from iron. A rusting patch on a piece of steel is essentially a galvanic cell in which both the anode and the cathode are on the same object, such as the metal body of a car (Figure 10.8).
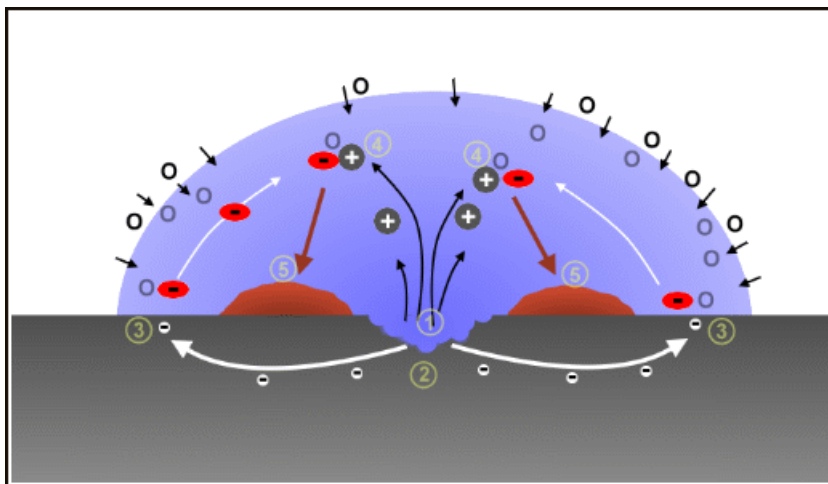
Figure 10.8: Cross section of steel rusting inside a water drop, in five steps. 1) Fe^{2+} ions enter water from the anode site; 2) Anode loses electrons that flow outward; 3) Electrons enter the water at the cathode sites that encircle the anode; 4) Electrons react with oxygen and water to form hydroxide ions; 5) Hydroxide ions form iron oxide on surface of the steel.

Source: http://commons.wikimedia.org/wiki/File:Rosten_schematisch.png

Oxidation of iron occurs at the anode. This anode (seen in Figure 10.8) can be a spot in the steel containing a reactive impurity, a scratch, or a dent. The anode half-reaction for rusting is:

Anode half-reaction: $Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^-$

The cathode can be found anywhere along the surface of the metal, provided it is in electrical contact with the anode. The electrons are conducted through the car's metal body to the cathode. There, several reduction reactions can occur. One possibility is that electrons are used to reduce water, in order to form hydroxide ions:

Cathode half-reaction: $\frac{1}{2}O_{2(g)} + H_2O_{(l)} + 2e^- \rightarrow 2OH^-_{(aq)}$
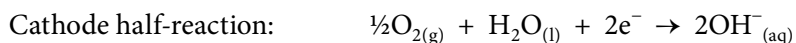
Note that both oxygen and water are required for the cathode half-reaction to occur. This explains why cars rust more quickly in humid or wet climates than in dry ones. Iron ions then migrate through any water on the metal surface and combine with hydroxide to form an insoluble reddish-brown crust, which we call rust. Rust isn't a pure substance. Its composition varies, depending on how it is formed.

Does Salt Cause Rust?

Many people think that salt causes rust. This is a popular misconception. Notice that salt (NaCl) doesn't appear in either of the half-reactions required for the corrosion of steel. The only chemicals that cause corrosion are water and oxygen. However, once corrosion starts, salt helps it to occur more quickly. The ions released by salt as it dissolves improve the electrical conductivity of the corrosion cell. If the conductivity is better, then the cell reactions occur at a faster rate. Therefore, the use of road salt in the winter clearly contributes to the rusting of cars, but doesn't cause it.

Preventing Corrosion

There are a variety of strategies that limit the damage caused by metal corrosion. Two of them are discussed below.

Protective Coatings

The simplest way of providing more protection from corrosion is to isolate a metal from its environment. Metal can be isolated by painting it or applying a clear, anti-rust coating. If oxygen and water can't get at the metal, then it won't corrode. In order to be effective, protective coatings must cover the entire surface of the metal. Any exposed metal could be a potential corrosion site. For example, a stone chipping a car's paint or a minor collision creating holes in the paint can expose the steel to water and oxygen.
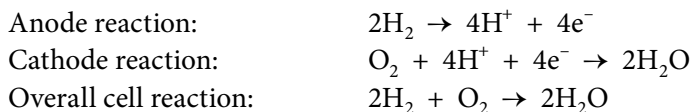
Cathodic Protection

Cathodic protection works by making the metal you wish to protect the cathode (that is, the site where reduction occurs). This can be done by continually supplying the protected metal with electrons, so that it doesn't lose its own electrons. One way to do this is to attach another more reactive metal to the steel. Zinc, for example, oxidizes more readily than the iron in steel. We know this because zinc is below iron on the standard reduction potentials table. The oxidation potential for zinc is higher than iron. Compare the standard potential values in Table 10.1 for these two elements. Since zinc oxidizes more readily than iron, it loses its electrons first. These electrons flow into iron, preventing it from losing its electrons. Corrosion protection remains, as long the reactive metal is present. A metal that is intentionally corroded to protect another metal is called a sacrificial anode.

A zinc coating provides additional corrosion protection. As zinc corrodes, zinc ions react with air to form zinc compounds, like zinc carbonate. These adhere tightly to the metal beneath them, forming a tough protective coating that prevents further corrosion from occurring. Steel that is coated with zinc is called galvanized steel. When zinc corrodes, it forms zinc oxide, which becomes zinc hydroxide. Zinc hydroxide reacts with carbon dioxide in the atmosphere to yield a dull grey layer of zinc carbonate, which protects the underlying zinc.

Fuel Cells

Galvanic cells, like disposable alkaline batteries, contain a finite number of chemicals. Once these chemicals run out, the battery is "dead." Fuel cells, such as NASA's hydrogen fuel cells, which you read about in the introduction, are also galvanic cells. However, fuel cells differ from typical galvanic cells in one respect. In a fuel cell, the fuels (anode and cathode chemicals) are continuously pumped into the cell. Likewise, the products of the chemical reaction are continuously removed. In this way, a fuel cell can supply an indefinite amount of electrical energy, as long as the supply of anode and cathode chemicals is maintained. The hydrogen fuel cell used on NASA's space shuttle generates electricity by oxidizing hydrogen (Figure 10.9). As the cell operates, hydrogen gas is pumped into the anode compartment, while oxygen is pumped into the cathode compartment. The reactions involved in the operation of this cell are:
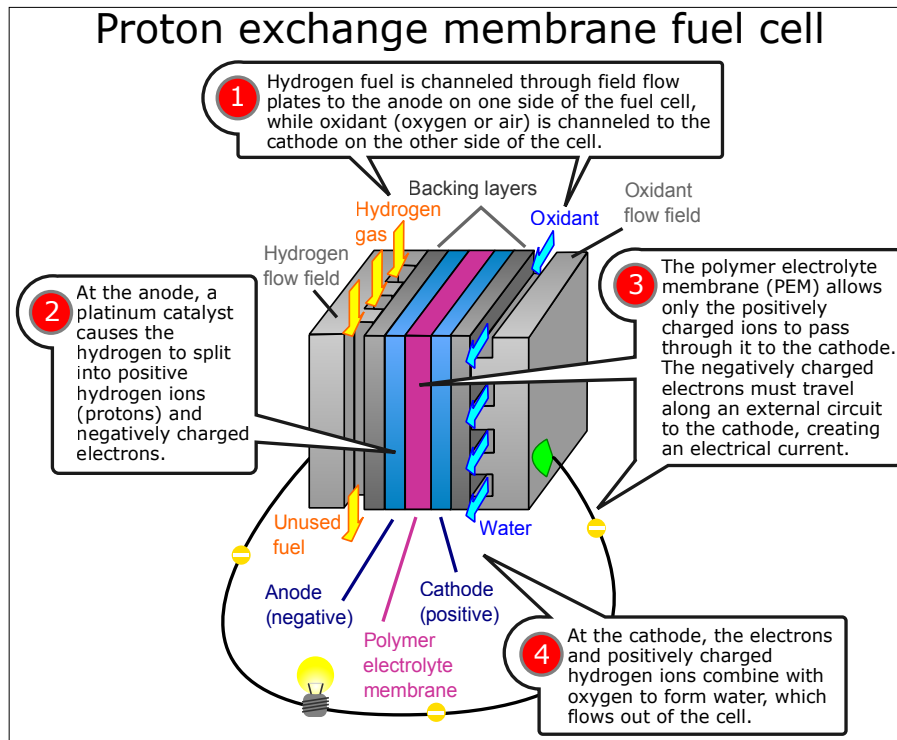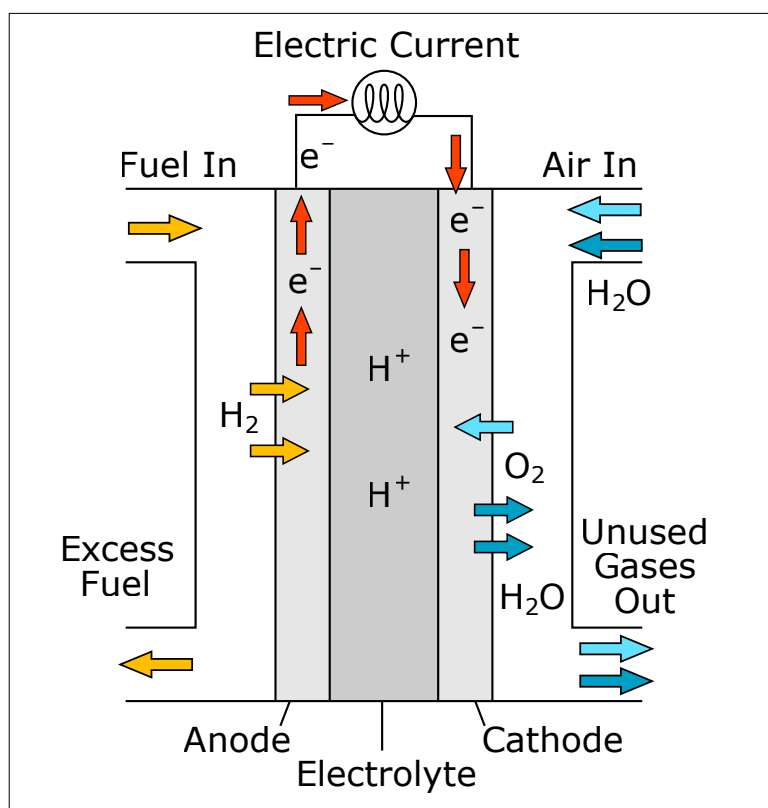
Anode reaction: $\qquad 2H_2 \rightarrow 4H^+ + 4e^-$
Cathode reaction: $\qquad O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
Overall cell reaction: $\qquad 2H_2 + O_2 \rightarrow 2H_2O$

Figure 10.9: Fuel cell operation

The main environmental benefit of a hydrogen fuel cell is that its only waste product is warm water. Many researchers have attempted to transfer this technology to the automobile. A car powered by hydrogen fuel cells would generate no pollution. Does this sound too good to be true? Perhaps it is. If you had a car based on these cells, the first question you'd ask is, "Where do I get hydrogen?" Hydrogen is the most abundant element in the universe. However, H_2 is never found in the form of an element on earth, and there are no underground "hydrogen pockets" to be tapped. Instead, hydrogen is trapped in compounds like water and the hydrocarbons you studied in the previous unit. In order to make hydrogen gas, these compounds must be broken down.

Hydrogen can be extracted from H_2O by passing electricity through water. As you learned in Unit 1, breaking bonds requires energy—in this case, electricity. So, energy has to be used to produce hydrogen. To be non-polluting, this energy should come from a renewable "green" energy source, such as hydroelectric dams, geothermal energy, wind farms, or solar energy. However, a significant portion of Ontario's electricity comes from polluting resources such as fossil fuels and nuclear energy.

When pollution-tainted electricity is used to generate hydrogen, the environmental benefits of hydrogen as a fuel disappear. This is because a significant portion of Ontario's electricity contributes to greenhouse gases and smog (from burning fossil fuels) and difficult-to-store nuclear waste (from aging nuclear reactors). Therefore, any hydrogen produced in this province is only as environmentally clean as the energy source used to generate it. One other difficulty in using hydrogen (or anything that is a gas at room temperature) is that its molecules are very far apart. In order for it to be a useful fuel, you must compress hydrogen so that a great number of gas molecules are concentrated in a relatively small gas tank or canister. Pressurized gases are difficult to safely store and handle. Even NASA, with its expertise in pressurized gas fuels, has experienced accidents and fatalities related to high-pressure explosions.

Support Questions

20. These are the half-cell reactions in the silver oxide "button cell," a battery used in watches and other tiny electronics. Which half-reaction is oxidation, and which is reduction?

$$Ag_2O_{(s)} + H_2O_{(l)} + 2e^- \rightarrow 2Ag_{(s)} + 2OH^-_{(aq)}$$

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$$

a) Identify the anode and cathode in this cell. (**Hint:** Which type of half-reaction always occurs at the anode of any cell?)

b) What is the overall cell reaction? (**Hint:** How is the overall reaction obtained when the two half-reactions are known? Check that electrons lost equal electrons gained.)

c) What reactant makes this cell more expensive than standard alkaline cells?

d) Name two properties that this battery should have if it is to be used in watches.

21. Oils are often used as car lubricants because they adhere well to metal, reduce friction, and flow slowly. Consider the other qualities of the various oils you studied in Lesson 6, as well as what you have learned about corrosion in Lesson 10, when answering this question: Why is the undercarriage of a car often sprayed with an undercoat of oil, prior to winter?

22. Why does a galvanized coating protect steel, even if the coating is lightly scratched or punctured? (**Hint:** Review cathodic protection.)

23. Is hydrogen an environmentally "clean" fuel? Explain. (**Hint:** Look at the overall reaction occurring in the fuel cell. This is identical to burning hydrogen gas. Also, consider how the hydrogen gas is created, to use as a fuel.)

24. Gasoline is a liquid at room temperature, while hydrogen is a gas. What practical complications would this difference in state create for the driver wanting to "fill up" her new hydrogen fuel-cell car at the "hydrogen pump"? (For the purpose of this question, assume that hydrogen is readily available.)

Key Questions

Now work on your Key Questions in the <u>online submission tool</u>. You may continue to work at this task over several sessions, but be sure to save your work each time. When you have answered all the unit's Key Questions, submit your work to the ILC.

38. The following figure shows a diagram of an Al/Fe galvanic cell. Use the diagram to answer the questions that follow it.
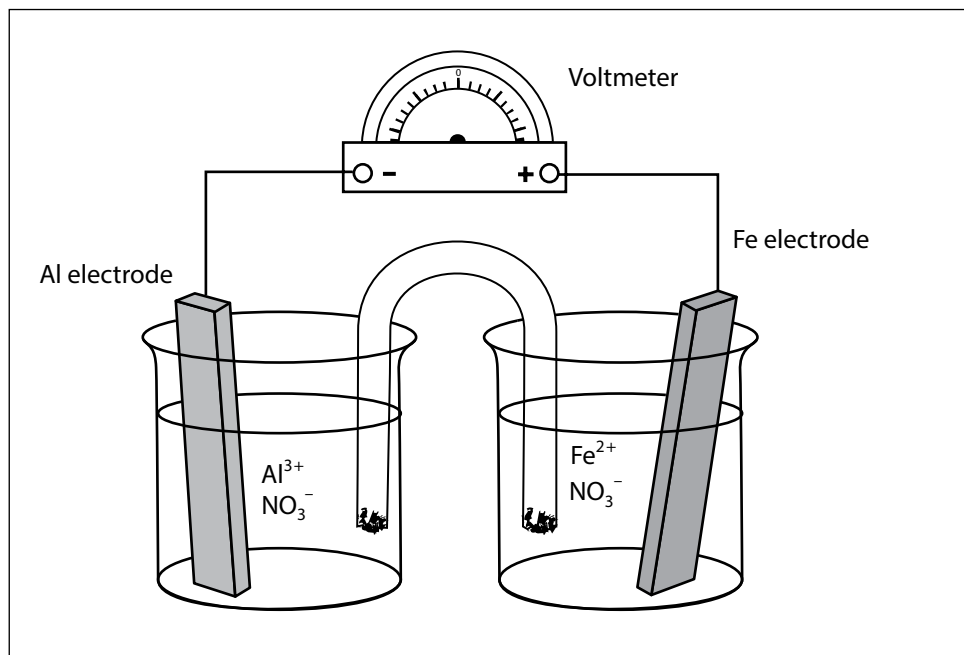
   a) Predict the anode half-cell reaction, the cathode half-cell reaction, and the overall cell reaction that occurs as this cell operates. **(4 marks)**

   b) Predict the overall cell potential. **(2 marks)**

   c) Describe the direction of ion and electron flow in the diagram. **(3 marks)**

39. What is the half-reaction for the reduction of oxygen that occurs with the corrosion of iron? Using this reaction, explain why corrosion occurs more slowly in dry climates. **(2 marks)**

40. Which provides better protection against corrosion: painting a metal or galvanizing a metal? Justify your prediction. **(4 marks)**

41. **a)** Research and write one paragraph describing two advantages of using hydrogen to fuel cars. **(4 marks)**

   b) Research and write one paragraph about two technical or logistical problems we face in trying to fuel cars with hydrogen. **(4 marks)**

Now go on to Lesson 11. Send your answers to the Key Questions to the ILC when you have completed Unit 3 (Lessons 9 to 12).