$$\text{Electrochemical Cells}\begin{cases}\text{Expendable}\\ \text{Nonexpendable}\begin{cases}\text{Rechargeable}\\ \text{Refuelable}\end{cases}\end{cases}$$

Although fuel cells date back to 1839 when Sir William Groves demonstrated his "gaseous voltaic battery," until recently they still remained in their technological infancy.

NASA revived fuel cell research: both *Gemini* and *Apollo* used fuel cells, and so does the space shuttle. The most important applications of fuel cells in the near future are as power sources for buses and automobiles, as central utility power plants, as dispersed (including residential) power suppliers, and as power sources for cell phones and other small electronic devices.

9.2 Electrochemical Cells

The purpose of electrochemical cells is to provide a flow of electrons in an external circuit where useful work can be done. To this end, the cells must consist of a source and a sink of electrons.

The reactions used in electrochemical cells are called **reduction-oxidation (redox)** reactions, because the buzz word for releasing electrons is **oxidation** and for capturing electrons is **reduction**.

Numerous old scientific terms are confusing or at least not self-explanatory. The terms **reduction** and **oxidation** require explanation.

The word *oxygen* stems from *oxús* = acid or sharp, and means generator of acids, a name that appears in de Morveau and Lavoisier's "Nomenclature Chimique" in 1787, when chemists were under the wrong impression that oxygen was an essential element in acids. Actually, it is hydrogen that is essential. When an acid is dissolved in water, some of its hydrogen atoms lose their electron—the water becomes *acid*; the hydrogen is *oxidized*. By extension any reaction that involves the loss of electrons is called **oxidation**. The reverse reaction—gaining electrons—is called **reduction**.

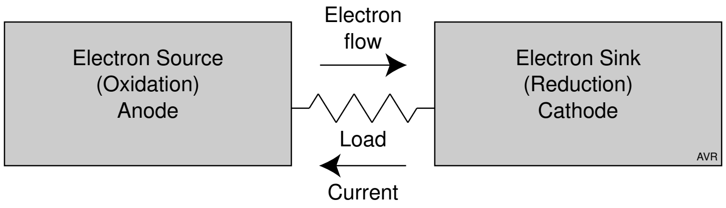

Figure 9.1 An electrochemical cell must consist of a source and a sink of electrons.

9.2

In electrochemical cells, the full reaction is broken down into two **half-cell reactions** or **half-reactions** that occur in physically separate regions of the device. These regions are interconnected by an **electrolyte** that conducts ions but not electrons. The latter, having been released by the oxidizing half-reaction, can move to the reduction side only via an external circuit. This establishes the external current that is the purpose of the cell. The *conventional* direction of this external current is from the reduction to the oxidizing side—the current exits the device from the reduction side which thus becomes the **cathode** of the cell, and enters the device at the oxidizing side which becomes the **anode**. As in any source of electricity, the cathode is the positive electrode and the anode the negative one, exactly the opposite of what happens in sinks of electricity (**loads**). See the Introduction to Chapter 6 for a discussion of the words "anode" and "cathode."

As an example of an electrochemical cell, consider a membrane capable of acting as an electrolyte. Put hydrogen in contact with one side of this membrane. At ambient conditions, most of the gas will be in the form of H_2 molecules; however, a small amount will **dissociate**:

$$\mathrm{H_2} \rightarrow 2\mathrm{H}, \tag{1}$$

and some of the resulting H will **oxidize** (ionize)—that is, lose an electron:

$$\mathrm{H} \rightarrow \mathrm{H^+} + \mathrm{e^-}. \tag{2}$$

Since the membrane does not conduct electrons, these will remain on its surface while the ions will **diffuse** across it and arrive at the other side. Because the ions carry a positive charge, the hydrogen side becomes negative owing to the excess electrons that remain on it and the opposite side becomes positive owing to the positive ions that arrived there. The resulting electric field causes some of the ions to drift back to the hydrogen side. A **dynamic equilibrium** is established when the diffusion exactly equals the returning drift. It is easy to calculate the potential developed (Chapter 7, Section 7.1).

Now sprinkle a conducting powder on both sides of the membrane so as to create two porous electron-conducting layers, i.e., two **electrodes**. Interconnect the electrodes externally through a load resistance, R_L. Ions cannot flow through this external connection, but electrons can and, when they do, they flow from the hydrogen side where they are abundant to the opposite side establishing an electric current as indicated in Figure 9.2. The reaction of interest that occurs at the hydrogen electrode is

<u>Anode reaction:</u>

$$2\ \mathrm{H_2} \rightarrow 4\ \mathrm{H^+} + 4\ e^-. \tag{3}$$

The difficulty with this picture is that it contradicts the first law of thermodynamics in that it causes an I^2R_L amount of heat to be generated in the load, while, at the cathode, the incoming electrons will combined with the H^+ that diffused through the membrane regenerating the hydrogen atom, H, and, eventually recreating the H_2 gas used as "fuel." We would generate heat without using any fuel.

The external circuit creates a *path* for the electrons, but cannot by itself force a current to circulate, just as a pipe with one end dipped into a lake cannot cause water to flow up inside it. For the water to flow, the open end of the pipe must be lower than the level of the lake. Similarly, to have an external current, it is necessary to lower the (thermodynamic) potential on the cathode side. This can conveniently be done by introducing oxygen so that, combined with the electrons and the H^+, water is formed:

Cathode reaction: $$4\ e^- + 4\ H^+ + O_2 \rightarrow 2\ H_2O. \tag{4}$$

This reaction is strongly exothermal—that is, it releases energy (although, in this case, not mostly as heat, as in case of the combustion of hydrogen, but mainly as electricity.) This is, of course the energy that powers the fuel cell.

The electrochemical cell just described is shown in Figure 9.2.

Under STP conditions, the degree of hydrogen dissociation at the anode is small. It can be increased somewhat by altering physical conditions (for example, increasing the temperature,). Remember the Le Chatelier's principle. It also can be increased by the action of catalysts.

The overall cell reaction is:

$$2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (g). \tag{5}$$

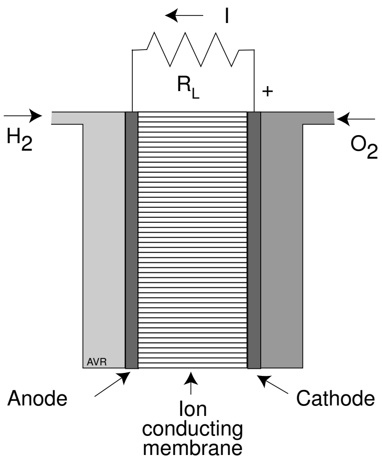

Figure 9.2 The simplest electrochemical cell.

9.4

The electrochemical cell invented by Alessandro Volta (1745–1827) in 1800 was the first device capable of generating sustained electrical currents. It consisted of zinc disks separated from silver (or copper) disks by a sheet of paper soaked in salt. A battery or pile was formed by stacking the cells so that there was a direct contact between the copper electrode of one with the zinc electrode of the next—the cells were all in series.

A “Volta” cell can be made by dipping a zinc and a copper electrode into a dilute (say, 10%) sulfuric acid solution. The zinc will oxidize:

$$\mathrm{Zn} \rightarrow \mathrm{Zn}^{++} + 2\ \mathrm{e}^-, \tag{6}$$

providing electrons for the external current. Zinc ions are soluble in water. The sulfuric acid, being a strong acid,[†] will mostly dissociate into ions:

$$\mathrm{H_2SO_4} \rightarrow 2\ \mathrm{H}^+ + \mathrm{SO_4^{--}}. \tag{7}$$

The zinc ions combine with the sulfate ions forming zinc sulfate. The protons, in the form of hydronium, $H^+(H_2O)_x$, migrate through the electrolyte to the copper where they are reduced to hydrogen (by combining with the electrons arriving via the external circuit) and evolve as gas bubbles. This type of cell is of little practical use because soon the copper electrode is covered with adhering hydrogen bubbles that severely limit the current delivered. The so called “dry cells” use some scheme to avoid the formation of the insulating gas layer at the cathode. The chemical used to absorb the hydrogen is called a **depolarizer**. One of the consumables is in general a metal that can be easily oxidized, zinc being a common choice. Note that the copper in Volta’s cell remains unchanged, not undergoing any chemical reaction.

Inexpensive batteries were, until recently, of the **Leclanché** type in which the anode is made of zinc and the cathode of a graphite rod surrounded by pulverized manganese dioxide mixed with carbon (to increase the conductivity). The MnO_2 combines with the liberated hydrogen and keeps it from coating the cathode. The electrolyte is ammonium chloride. More modern batteries use an alkaline electrolyte (**alkaline batteries**).

Perfectly pure zinc is consumed only when a current is drawn. The presence of impurities causes corrosion of the electrode even when the cell is inactive (the impurities form numerous microscopic electrochemical cells within the mass of the metal). To insure a long shelf life the zinc is alloyed with mercury (**amalgamated**). Leclanché cells have been mostly replaced by alkaline ones.

[†] The strength of an acid is a measure of the degree of its dissociation when in aqueous solution. Hydrochloric acid dissociates completely into H^+ and Cl^-; it is a very strong acid. Sulfuric acid is weaker, but is still a strong acid. Surprisingly, hydrofluoric acid, in spite of its corrosiveness, is a weak acid: when in water solution at room temperature, the concentration of H^+ is less than 3% of the concentration of neutral HF molecules.

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