

Section 17.3

Batteries

Recent developments in electronics have revolutionized portable devices—you can now take radios, telephones, video recorders, and computers anywhere. These gadgets have created a need for portable electric power, most of which is supplied by batteries.

Batteries store energy in chemical form and deliver it when needed as electricity. Batteries are remarkable devices in their own right. They have no visible moving parts yet they manage to push electric currents through circuits. Batteries continue to improve from year to year, with designers always trying to increase energy capacity, reliability, and reusability while decreasing size, weight, and cost. Nonetheless, batteries remain the limiting factor in such technologies as electric vehicles and portable computers.

Questions To Think About: What happens when a battery runs down? Why are some batteries rechargeable while others are not? Why do some car batteries require maintenance periodically? Why do alkaline batteries last longer than carbon-zinc batteries? Why do nickel-cadmium rechargeable batteries lose their storage capacity with age?

Experiments To Think About: Batteries use electrochemical reactions to produce electric power. Electrochemical reactions are those that involve transfers of charge between atoms and molecules. Although nothing appears to be moving inside a battery, its atoms and molecules are exchanging electrons and converting some of their chemical potential energies into electric energy. As it operates, the battery produces electric power by converting various chemicals into new ones with less chemical potential energy.

While there is nothing to watch in a battery, there are electrochemical reactions that have visible results. Drop a small 9 volt battery into a glass of fresh water so that the water covers the two electric terminals. After a few moments, you will begin to see tiny bubbles of gas forming on those terminals or on the battery's case. The battery is causing an electrochemical reaction in the water—it is turning water molecules into oxygen and hydrogen gases. This reaction is opposite to a battery's because it consumes electric power by converting water into two gases with more chemical potential energy.

This electrolysis of water involves several different reaction pathways, all of which have the same outcome. In one pathway, the battery's positive terminal attracts and removes four electrons from a pair of water molecules (H_2O). As a result, the water molecules break up into one oxygen molecule (O_2) and four positive hydrogen ions (H^+). The hydrogen ions are attracted toward the battery's negative terminal, which gives them four electrons and converts them into two hydrogen molecules (H_2). So oxygen gas bubbles up around the positive terminal and hydrogen gas bubbles up around the negative terminal. Hydrogen gas is very flammable, so you should be careful not to make very much of it. Be sure to dry the battery carefully when you are done.

How a Battery Produces Electricity

A battery uses chemical potential energy to pump electrons from its positive terminal to its negative terminal. Since electrostatic forces push the electrons the other direction, the battery must do work on the electrons as it moves them. Each time the battery transfers an electron, it uses up a small portion of its chemical potential energy. After transferring a certain number of electrons, the battery runs out of chemical potential energy and must be recharged or discarded.

But a battery sitting on the shelf stops transferring electrons long before it runs out of chemical potential energy. With each transfer, the negative terminal

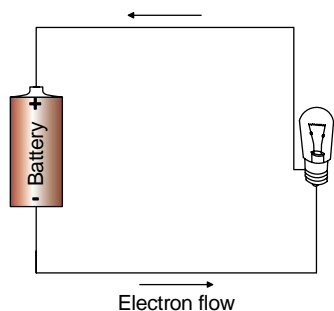


Fig. 17.3.1 - A simple circuit in which a battery provides power for a light bulb. The battery pumps electrons from its positive terminal to its negative terminal, giving each electron a certain amount of energy. These electrons flow through the light bulb on their way back to the battery's positive terminal. The electrons give up their energies in the bulb, which then produces light.

becomes more negatively charged and the positive terminal becomes more positively charged. The amount of separated charge on the terminals increases and so does the voltage rise across the battery—the battery must do more and more work to transfer each additional electron. Eventually, the electrostatic forces become so strong that the battery can't transfer any more electrons. The battery just sits on the shelf with negative charge on its negative terminal and positive charge on its positive terminal and it remains that way almost indefinitely.

However, when you install the battery in a flashlight and turn the flashlight on, an electric circuit connects the two terminals to one another (Fig. 17.3.1). Electrons flow from the negative terminal, through the light bulb, to the positive terminal and the amount of separated charge on the battery's terminals decreases. The battery begins to pump electrons again. The battery pumps electrons onto the negative terminal and the flashlight returns those electrons to the positive terminal. The electrons flow around and around this circuit, receiving energy from the battery and delivering that energy to the light bulb, until the battery's chemical potential energy is exhausted or you turn the flashlight off.

But how does a battery use its chemical potential energy to pump electrons from its positive terminal to its negative terminal? Many batteries are based on electron transfers from atoms of one element to those of another. These different atoms have different affinities for their outermost or valence electrons and many of the transfers result in releases of energy. When an atom that binds its valence electrons relatively strongly is missing some of them, it may extract electrons from another atom that binds them relatively weakly. Overall, the electrons move from one atom to the other and some potential energy is released. This process is the principal source of a battery's energy.

Choosing which atoms to use in a battery is by examining their properties. These properties depend in an orderly fashion on the numbers of protons and electrons the atoms have. One way to see this order is to arrange the atoms in a **periodic table** (Fig. 17.3.2). In this table, the atoms are arranged in horizontal rows according to their **atomic numbers**—the numbers of protons they contain. Since atoms are normally electrically neutral, their atomic numbers also indicate the numbers of electrons they contain. The atom with atomic number 1 is hydrogen (H), with atomic number 2 is helium (He), and so on.

Fig. 17.3.2 - The periodic table of elements. Elements are arranged according to their atomic numbers (indicated in the upper corner). As the electron count increases, various electronic shells are filled and completed. The table is structured by these shell closings. A major closing occurs on the right-hand column, so that elements in the left-hand columns are starting new shells. The number shown below each elemental symbol is that atom's Pauling electronegativity.

1 H 2.1																	2 He						
3 Li 1.0	4 Be 1.5											5 B 2.0	6 C 2.5	7 N 3.0	8 O 3.5	9 F 4.0	10 Ne						
11 Na 0.9	12 Mg 1.2																	13 Al 1.5	14 Si 1.8	15 P 2.1	16 S 2.5	17 Cl 3.0	18 Ar
19 K 0.8	20 Ca 1.0	21 Sc 1.3	22 Ti 1.5	23 V 1.6	24 Cr 1.6	25 Mn 1.5	26 Fe 1.8	27 Co 1.9	28 Ni 1.9	29 Cu 1.9	30 Zn 1.6	31 Ga 1.6	32 Ge 1.8	33 As 2.0	34 Se 2.4	35 Br 2.8	36 Kr						
37 Rb 0.8	38 Sr 1.0	39 Y 1.2	40 Zr 1.4	41 Nb 1.6	42 Mo 1.8	43 Tc 1.9	44 Ru 2.2	45 Rh 2.2	46 Pd 2.2	47 Ag 1.9	48 Cd 1.7	49 In 1.7	50 Sn 1.8	51 Sb 1.9	52 Te 2.1	53 I 2.5	54 Xe						
55 Cs 0.7	56 Ba 0.9	71 Lu 1.2	72 Hf 1.3	73 Ta 1.5	74 W 1.7	75 Re 1.9	76 Os 2.2	77 Ir 2.2	78 Pt 2.2	79 Au 2.4	80 Hg 1.9	81 Tl 1.8	82 Pb 1.9	83 Bi 1.9	84 Po 2.0	85 At 2.2	86 Rn						
87 Fr 0.7	88 Ra 0.9	103 Lr																					
			57 La 1.1	58 Ce 1.1	59 Pr 1.1	60 Nd 1.2	61 Pm 1.2	62 Sm 1.2	63 Eu 1.1	64 Gd 1.2	65 Tb 1.2	66 Dy 1.2	67 Ho 1.2	68 Er 1.2	69 Tm 1.2	70 Yb 1.1							
			89 Ac 1.0	90 Th 1.3	91 Pa 1.4	92 U 1.4	93 Np 1.4	94 Pu 1.4	95 Am 1.4	96 Cm 1.4	97 Bk 1.4	98 Cf 1.4	99 Es 1.4	100 Fm 1.4	101 Md 1.4	102 No 1.4							

The peculiar structure of the table comes from the way in which electrons fill the atomic orbitals surrounding the nucleus of each atom. Because of the Pauli exclusion principle, all electrons of a particular spin—either spin-up or spin-down—must be in different orbitals. The electrons fill the orbitals from the lowest energy orbitals on up until the atom has the right number of electrons. The electrons in the last few orbitals filled determine most of the chemical properties of the atom, particularly the atom's behavior in a battery. This filling process is quite complicated, but there are a few simple observations we can make.

Some atoms have just enough electrons to completely fill a major electronic shell. These atoms are extremely stable, unwilling to give up any electrons and uninterested in any additional electrons. These atoms are the **noble gases**, helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn), found in the rightmost vertical column of Fig. 17.3.2.

Some atoms have just one or two electrons more than are required to fill a major electronic shell and are relatively willing to give those electrons up. These atoms are the **alkali metals**, lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr), and the **alkaline earths**, beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra), found in the leftmost and second to leftmost vertical columns of Fig. 17.3.2.

Still other atoms have almost enough electrons to complete a major electronic shell and are relatively aggressive at attracting more. These atoms are found just to the left of the noble gases on the right side of Fig. 17.3.2. They include nitrogen (N), oxygen (O), sulfur (S), and the **halogens**, fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At).

The remaining atoms fall in between. While their major electronic shells are only partly complete, they tend to exchange electrons in order to complete minor electronic shells. The atoms in the long horizontal stretch between scandium (Sc) and zinc (Zn) are called the **transition metals** and differ from one another by how much of one minor shell they have completed. The atoms shown at the bottom of Fig 17.3.2 are called the **rare earths** and differ by how much of another minor shell they have completed.

Many of these atoms are important for batteries. The main issue for batteries is just how strongly the atoms attract electrons. This tendency to attract electrons is called **electronegativity** and is measured in various ways. One scheme developed by American chemist Linus Pauling (1901–1994) is called **Pauling electronegativity**. The more strongly an atom attracts electrons, the higher its Pauling electronegativity. Values range from 0.7 for cesium (Cs) atoms, which easily gives up electrons, to 4.0 for fluorine (F) atoms, which attracts electrons aggressively. Pauling electronegativities for the other atoms are shown in Fig. 17.3.2. Batteries generally work by transferring electrons from atoms with low Pauling electronegativities to ones with high Pauling electronegativities.

CHECK YOUR UNDERSTANDING #1: Charge Waiting

An automobile battery has two terminals, one labeled (+) and the other (-). When the battery is not in use, what is the electric charge on each of these terminals and on the battery overall?

Daniell's Cell

Unfortunately, real batteries aren't simple. For one thing, the atoms in a battery aren't isolated objects—they are usually contained in solids and liquids, a situation that affects the transfers of charges between them. Furthermore, since a battery uses the energy released during electron transfers to pump electrons from its

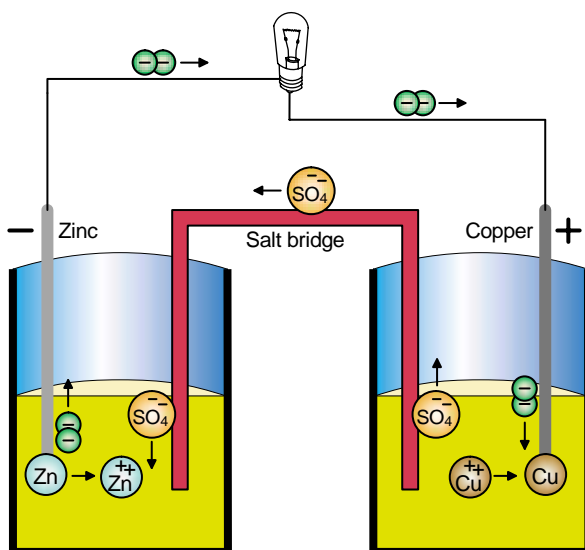


Fig. 17.3.3 - Daniell's cell is powered by a transfer of electrons from zinc atoms to copper ions. A copper ion (Cu^{2+}) picks up two electrons from the copper electrode and leaves the solution in the right container as a copper atom (Cu). To keep the solution electrically balanced, a sulfate ion (SO_4^{2-}) flows over the salt bridge to the left container. There the sulfate ion allows a zinc atom (Zn) to give up two electrons to the zinc electrode and enter the solution as a zinc ion (Zn^{2+}). The two electrons flow through wires and the light bulb to the copper electrode.

positive terminal to its negative terminal, the battery must carefully control electron transfers. Overall, a battery involves a number of interrelated processes. One way to see how all of these processes work together is to examine the operation of a *relatively* simple battery.

Daniell's cell (Fig. 17.3.3) is a simple battery that was invented in 1836 by English chemist John Frederick Daniell (1790–1845). **Cells** are the basic building blocks of batteries. Daniell's cell isn't a practical battery but it's one of the simplest cells to understand. It uses two metallic elements, copper and zinc. Because copper has a higher Pauling electronegativity than zinc, the cell releases energy by transferring electrons from zinc atoms to copper atoms.

Daniell's cell consists of two metal strips, each in its own container of salt solution. One of the metal strips is zinc and it sits in a water solution of zinc sulfate. This salt solution contains equal numbers of positively charged zinc ions (Zn^{2+}) and negatively charged sulfate ions (SO_4^{2-}), making it electrically neutral. The other metal strip is copper and it sits in a water solution of copper sulfate. This second salt solution contains equal numbers of copper ions (Cu^{2+}) and sulfate ions (SO_4^{2-}) and is also neutral.

When the two containers are isolated from one another, their contents don't appear to change. Their electrodes neither grow nor shrink and the solutions remain the same. But this constancy doesn't mean that nothing is happening in the containers. In fact, zinc and copper ions are constantly departing and arriving at the surfaces of the electrodes.

Zinc and copper ions are soluble because they polarize the water molecules, which then carry them around in solution. In contrast, zinc and copper atoms don't polarize the water molecules and are insoluble. Thus for an atom to leave an electrode, it must give up two electrons to the electrode and enter the water as an ion. Similarly, for an ion to return to an electrode, it must pick up two electrons from the electrode and leave the water as an atom.

In an isolated container, this exchange quickly reaches a **chemical equilibrium**, with equal numbers of ions leaving and returning to the electrode each second. If too many ions leave the electrode, the solution becomes positively charged and pushes ions back toward the electrode. If too few ions leave the electrode, the solution becomes negatively charged and pulls ions off the electrode. These balancing effects stabilize the chemical equilibrium. The containers remain electrically neutral.

But the two containers in Fig. 17.3.3 aren't isolated—a salt bridge connects them. This piece of damp cloth serves as a pathway for ions, allowing them to flow from one container to the other in response to electric fields. If the containers somehow develop a charge separation, ions will migrate over the bridge from one container to the other to balance the charge. Because it conducts an electric current through the movement of ions, the salt solution in the bridge is an *electrolyte*. So are the solutions in the two containers.

The electrodes, solutions, and salt bridge form an electrochemical cell, a Daniell's cell. This cell springs to life when wires and a light bulb connect its zinc and copper electrodes. Suddenly an electric current begins to flow through the circuit that has formed. This circuit includes the cell, the wires, and the light bulb. The cell pumps electrons from its copper electrode to its zinc electrode and these electrons return to the copper electrode by way of the light bulb. Chemical potential energy in the cell becomes thermal energy and light in the light bulb.

To see how the cell actually works, let's make our way around the circuit and watch the movements of atoms, ions, and electrons. We'll start at the copper electrode. Its surface is a busy place, with copper ions coming and going all the time. While the copper ions in the salt solution have relatively strong affinities for electrons, they are prevented from becoming atoms and returning to the electrode, on the average, because that would make the electrode positively charged and leave the salt solution negatively charged.

But suppose that some electrons suddenly arrive at the copper electrode through the wire attached to it. This delivery of negative charge upsets the chemical equilibrium in that container and allows some extra copper ions to return to the electrode. These ions pick up electrons and attach themselves to the electrode as atoms. The electrode now has more copper atoms than before and the salt solution has fewer copper ions.

The loss of copper ions from the salt solution leaves it with too many sulfate ions to be neutral. Here is where the salt bridge becomes useful. The extra sulfate ions migrate over this bridge and escape from the copper electrode's container. A proper balance between sulfate ions and copper ions is reached and the container returns to chemical equilibrium.

But the sulfate ions don't just disappear—they move into the zinc electrode's container and upset the chemical equilibrium there. The zinc electrode's surface is also busy with zinc ions coming and going all the time. While zinc atoms on the electrode have relatively weak affinities for two of their valence electrons, they are prevented from becoming ions and entering the solution, on the average, because that would make the solution positively charged and leave the electrode negatively charged.

When extra sulfate ions enter the zinc electrode's container via the salt bridge, they alter the balance of sulfate ions and zinc ions in the solution. Now extra zinc atoms can toss off their electrons and enter the solution as ions. The salt solution in the container quickly reaches the proper balance between sulfate ions and zinc ions. The electrode then has fewer zinc atoms than before and the salt solution has more zinc ions. But this change leaves the zinc electrode negatively charged. Electrons flow off the electrode through the wire attached to it and the container returns to chemical equilibrium.

The electrons that leave the zinc electrode pass through the light bulb and soon arrive at the copper electrode. There they start the whole process over again. Thus our initial supposition of electrons suddenly arriving at the copper electrode is reasonable, because the cell actually sends them there. Overall, each pair of electrons that arrives at the copper electrode causes (1) one copper ion to leave the copper sulfate solution as an atom, (2) one sulfate ion to migrate over the salt bridge, (3) one zinc atom to enter the zinc sulfate solution as an ion, and (4) a pair of electrons to leave the zinc electrode.

It seems that this complicated process has simply absorbed a pair of electrons through one wire and released another pair through a second wire. But the pair of electrons that leaves the zinc electrode has more energy than the pair that arrived at the copper electrode. The copper ion pulled the two arriving electrons toward it, doing work on them. The zinc atom pushed the two leaving electrons away from it, doing work on them, too. All of this work is conveyed via electric fields to the two electrons as they leave the zinc electrode so that they head out with extra energy. They deliver this energy to the light bulb, causing it to emit light, and then return to the copper electrode to participate in the next action.

You might have noticed that the electrons leaving the cell's zinc electrode don't seem to be the same ones that arrived at the cell's copper electrode. However electrons are indistinguishable particles so it really isn't possible to tell which one is which. In effect, the cell pumps electrons from the copper electrode to the zinc electrode. Since the zinc electrode becomes negatively charged, it becomes the negative terminal of a battery containing Daniell's cell. The copper electrode becomes the positive terminal.

The cell can't keep pumping electrons forever. Pumping each pair of electrons decreases the number of copper ions in the copper sulfate solution by one and decreases the number of zinc atoms in the zinc electrode by one. When either the copper ions or zinc atoms run out, the cell stops pumping. The cell is then completely dead.

But even before the last ions or atoms are used up, the cell will be relatively ineffective. The problem is that the amount of energy the cell gives to each electron, the cell's voltage, depends on the cell's condition. Each cell has a natural voltage but its condition can push its actual voltage either above or below that natural voltage. A fresh cell tends to exceed the natural voltage while a heavily used cell tends to fall below it.

The natural voltage is determined by the total amount of chemical potential energy released in transferring each electron from the positive terminal to the negative terminal. In Daniell's cell, chemical potential energy is released when one copper ion picks up two electrons and leaves its solution and when one zinc atom loses two electrons and enters its solution. This total energy is shared by the two electrons that are pumped in the processes, giving an overall energy-per-charge—a voltage—of 1.10 V. Daniell's cell has a natural voltage of 1.10 V.

When Daniell's cell is fresh, with lots of copper ions in the copper sulfate solution and relatively few zinc ions in the zinc sulfate solution, its voltage is roughly 1.20 V. With so many copper ions available to leave the concentrated copper sulfate solution and so many zinc ions available to enter the dilute zinc sulfate solution, random thermal motions in the fresh cell assist its operation and contribute an extra 0.10 V to the cell's voltage. As the fresh cell pumps electrons, it creates disorder and entropy at a particularly rapid rate and thermodynamic effects assist this entropy production by increasing the cell's voltage. The extra energy comes from thermal energy.

But a well-used cell has already accumulated so much disorder and entropy that thermodynamic effects no longer help it function. They even begin to hinder its operation and convert chemical potential energy into thermal energy.

The voltage of Daniell's cell diminishes with use. The concentration of copper ions in the copper sulfate solution decreases and the copper electrode has more and more trouble converting these scarce ions into copper atoms. The concentration of zinc ions in the zinc sulfate solution increases and the zinc electrode has more and more trouble sending zinc atoms into the solution as ions. When the concentrations of copper ions and zinc ions in their respective solutions are equal, the voltage of Daniell's cell reaches its natural voltage of 1.10 V. As the cell's chemical potential energy becomes more severely depleted, its voltage diminishes to 1.00 V, 0.90 V, or even less and the cell eventually becomes useless.

CHECK YOUR UNDERSTANDING #2: Is It Charged?

How could you tell how much chemical potential energy remains in Daniell's cell?

Lead-Acid Batteries

Although Daniell's cell is an interesting and simple cell, it isn't a practical battery. It's unable to pump large numbers of electrons each second, or equivalently, to handling large electric currents. If you try to send too many electrons through any battery, much of the battery's chemical potential energy will be consumed in transporting the current through the battery itself and less will be given to the electrons as they leave.

In effect, each battery has an **internal electric resistance**. If you try to send too much current through a battery, this internal resistance will convert the battery's own chemical potential energy into thermal energy. The battery will get warm and electrons will leave the negative electrode with relatively little energy. You may have noticed this effect when trying to operate a flashlight with old or damaged batteries. Their internal resistances are large, wasting most of their energy, and the light bulb glows only dimly.

Starting an automobile requires an enormous electric current, far more than Daniell's cell can provide. That's why automobiles use lead-acid batteries. The chemical cells in these batteries resemble Daniell's cell in some respects, but they use different electrodes and only a single container of liquid (Fig. 17.3.4).

The solution in a lead-acid cell contains sulfuric acid (H_2SO_4) in water. In water, sulfuric acid molecules dissociate into positively charged hydrogen ions (H^+) and negatively charged sulfate ions (SO_4^-). Since hydrogen ions carry only one positive charge and sulfate ions carry two negative charges, the electrically neutral solution contains twice as many hydrogen ions as sulfate ions.

The cell's negative electrode is a spongy form of lead metal, housed in a non-reactive lead-alloy lattice. The cell's positive electrode is lead dioxide, also housed in a protective lead-alloy lattice. The electrochemical process that pumps electrons from the lead dioxide electrode to the lead electrode is more complicated than in Daniell's cell, but it's still fairly simple to understand.

Let's start at the lead dioxide electrode. As before, we will assume that two electrons arrive at the lead dioxide electrode. They are picked up by a lead diox-

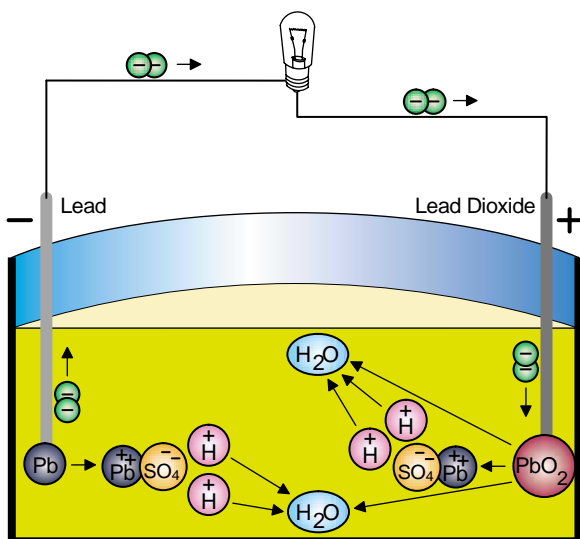


Fig. 17.3.4 - A lead-acid cell is powered by a complicated electrochemical reaction between lead, lead dioxide, and sulfuric acid, which creates lead sulfate and water. A lead dioxide molecule (PbO_2) picks up two electrons from the lead dioxide electrode and reacts with four hydrogen ions (H^+) in the solution to form a lead ion (Pb^{2+}) and two water molecules (H_2O). The number of positive charges in the solution decreases by 2, so a lead atom (Pb) can give up two electrons to the lead electrode to become a lead ion. The two electrons flow through the wires and light bulb to the lead dioxide electrode.

ide molecule, which reacts with four hydrogen ions and a sulfate ion to produce a lead sulfate molecule and two water molecules. The lead sulfate molecule consists of a positively charged lead ion and a negatively charged sulfate ion, but it's not soluble in water—the two ions bind together so strongly that water molecules can't separate them and carry them about in solution. The lead sulfate clings to the lead dioxide electrode as a solid.

Overall, the solution in the cell has lost four hydrogen ions and one sulfate ion. Because it has lost more positively charged ions than negatively charged ions, it can return to a proper balance by getting rid of one sulfate ion. So a lead atom on the lead electrode gives up two electrons and combines with a sulfate ion to form lead sulfate. This lead sulfate molecule is also insoluble and hangs onto the lead electrode. The solution is back to a proper balance, albeit with considerably fewer ions than before.

The two electrons that were released by the lead atom as it combined with a sulfate ion travel out through the wire, through the light bulb, and return to the lead dioxide electrode where they initiate the process again. Overall, each pair of electrons that arrives at the lead dioxide electrode causes (1) one lead dioxide molecule to react with four hydrogen ions and a sulfate ion to form a solid lead sulfate molecule and two water molecules, (2) one lead atom to become a lead ion and react with a sulfate ion to form a solid lead sulfate molecule, and (3) a pair of electrons to leave the lead electrode.

The pair of electrons leaving the lead electrode have considerably more energy than the pair that arrived at the lead dioxide electrode. Lead sulfate is a very stable chemical, with little remaining chemical potential energy. Lots of energy is released in the electrochemical reactions that form lead sulfate and the cell gives this energy to the electrons it pumps. Its natural voltage is 2.04 V.

Like all batteries, the lead acid cell's voltage depends on its freshness. As the hydrogen and sulfate ions in its solution are used up, its voltage decreases. Because of the way in which the cell is arranged, thermodynamic effects can't raise a fresh lead-acid cell's voltage above its natural voltage but they can decrease the voltage of a depleted cell. A fresh lead-acid cell has a voltage of about 2.03 V while a substantially discharged one has a voltage of about 2.00 V.

The solution in a lead-acid cell also becomes less dense as the cell's stored energy decreases. Sulfuric acid, the source of the hydrogen and sulfate ions, is more dense than water. You can use a density measuring tool called a *hydrometer* to measure the concentration of hydrogen and sulfate ions in the cell's solution and thus determine how fresh the cell is.

The lead-acid battery in an automobile has three other interesting features. First, it is a 12 V battery, not a 2 V one. Second, it seems to last for years before going dead. Third, it is able to deliver an enormous amount of current when you use it to start a car. What is going on?

A 12 V automobile battery actually contains 6 separate lead-acid cells connected in a series (Fig. 17.3.5). The electrons are pumped through each cell, one after the next, so that by the time they leave the sixth cell, they have considerably more energy than when they arrived at the first cell. Overall, the voltage rise from the battery's negative terminal to its positive terminal is 12 V. A few cars

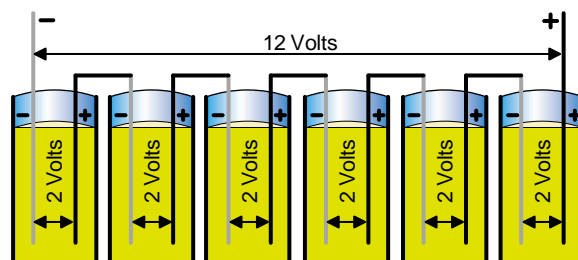


Fig. 17.3.5 - A car battery produces a 12 V voltage rise by sending current through a series of 6 separate lead-acid cells. Each cell contributes 2 V to the overall voltage.

and motorcycles use 6 V batteries that contain only 3 cells rather than 6.

The reason why an automobile battery lasts so long is that the car routinely recharges it. The car's electric system involves an electric generator that converts mechanical work from the engine into electric power. Some of this power is used to increase the battery's chemical potential energy. If everything is working well, an automobile's battery should be fully charged with energy almost all the time.

Recharging involves running the entire electrochemical process backward. Everything happens in reverse, driven by an outside source of electric power. Two electrons are pushed onto the lead electrode, where they bind with the lead ion in a lead sulfate molecule and convert it to a lead atom. The remaining sulfate ion then enters the solution in the cell. Two electrons are removed from the lead dioxide electrode, causing a lead sulfate molecule to react with water to produce a lead dioxide molecule, four hydrogen ions, and a sulfate ion. These ions also enter the solution in the cell.

As the recharging continues, the lead sulfate on the two electrodes is gradually converted into lead and lead dioxide. The concentration of hydrogen and sulfate ions in the solution slowly increases. Eventually the cell is back to its original condition, with concentrated sulfuric acid in the solution and very little lead sulfate on its electrodes.

Breaking up the stable lead sulfate molecules takes energy, energy supplied by the outside electric power source. Most of the energy supplied by that power source goes into returning the cell's chemicals to their original conditions. But a small amount of energy is lost to thermal energy. By acting to increase the randomness and entropy of the universe, thermodynamic effects ensure that some of the recharging energy is wasted. The faster you try to recharge the cell, the more severe the thermodynamic effects and the more energy is wasted. Overall, only about 75% to 85% of the electric power used to charge a lead-acid battery re-emerges from the battery during use.

What makes the lead-acid cell so easy to recharge is the solid nature of its electrodes—the lead atoms never leave. Because the electrodes retain their forms, the recharging process doesn't have to rebuild them. It just has to pull the sulfate ions out of the electrodes and put them back into the solution. In some other kinds of batteries, one of the electrodes actually disappears into solution as the battery discharges. Such batteries can't be recharged because the electrodes and their structures are gone and forgotten.

What allows a lead acid battery to deliver the enormous currents needed to start a car is the vast amount of surface area in each cell's electrodes. The spongy lead and lead dioxide contained in the electrodes aren't smooth. They have lots of nooks and crannies so that they provide plenty of surface area on which electrochemical reactions can occur. Moreover, in a real car battery each cell actually contains a dozen or more electrode plates. These plates are arranged as a multi-layered sandwich, with a negative (lead) plate next to a positive (lead dioxide) plate next to a negative plate and so on. A porous insulating material separates these individual plates so that they don't touch one another.

All of the negative plates in a cell are electrically connected so that they work together in parallel. All of the positive plates are, too. Overall, the cell has so much electrode surface area exposed to the sulfuric acid solution that it can pump enormous currents, even when the battery is cold and the thermal motions of its ions are diminished. Its internal resistance is extremely low and it wastes little of its chemical potential energy as thermal energy. A good automobile battery can handle more than 400 A of current while maintaining a 12 V voltage rise from its negative terminal to its positive terminal. The battery is then delivering 4800 W (12 V times 400 A) to the starter motor. No wonder the engine leaps into motion.

Of course, lead-acid batteries don't last forever. The charging and discharging cycles slowly damage the electrodes, which may eventually touch one another or fall to the bottom of the container. There is also the problem of electrolyzing water molecules in the solution, creating hydrogen and oxygen gases and depleting the liquid in the battery. This electrolysis usually occurs when charging the battery. Because of electrolysis, most lead-acid batteries need additional water periodically. "Maintenance-free" batteries include calcium in their electrodes. The calcium significantly reduces the electrolysis during charging and slows the loss of water.

CHECK YOUR UNDERSTANDING #3: Caustic Stuff

Which is more dangerous to your skin: the electrolyte in a fully charged lead-acid battery or that in a completely discharged battery?

Carbon-Zinc and Alkaline Batteries

However, liquid-filled batteries are impractical in many applications. Instead, most common household batteries are based on "dry cells." These cells may still contain water, but it's as a paste rather than a liquid. The most common dry cells, and the ones we'll examine, are carbon-zinc cells, alkaline cells, nickel-cadmium, and lithium cells.

There are actually two different types of carbon-zinc cells—one that contains ammonium chloride and one that contains zinc chloride. For many years, high purity chemicals were expensive and commercial carbon-zinc cells employed the ammonium chloride system. This system is so tolerant of impurities that ore grade chemicals right out of mines could be used to build batteries.

But these low-quality batteries didn't store much energy for their sizes and weights. They also tended to leak liquid electrolytes when their chemicals were used up, frequently damaging equipment. In recent years, purity control has improved so that most "heavy duty" batteries now use the zinc chloride system. This system packs more stored energy into the same size and weight as the ammonium chloride one and it's much less susceptible to leaking. However, higher purity chemicals are required to keep the electrochemical reactions proceeding properly. It's this zinc chloride system that we'll consider.

In the zinc chloride carbon-zinc cell (Fig. 17.3.6), a cylindrical carbon electrode is surrounded first by a layer of manganese dioxide (MnO_2) paste, then by a

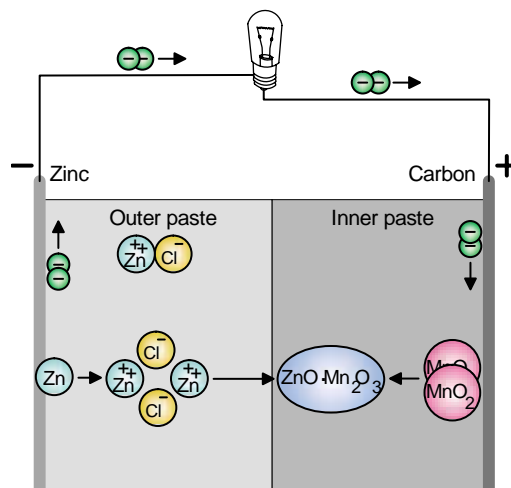


Fig. 17.3.6 - In a zinc chloride carbon-zinc battery, two manganese dioxide molecules (MnO_2) pick up two electrons from the carbon electrode and react with a zinc ions (Zn^{++}) to form a molecule of zinc/manganese oxide ($\text{ZnO}\cdot\text{Mn}_2\text{O}_3$). The number of positive charges in the pastes decreases by 2, so a zinc atom (Zn) can give up two electrons to the zinc electrode to become a zinc ion (Zn^{++}). The two electrons flow through the wires and light bulb to the carbon electrode.

layer of zinc chloride (ZnCl_2) paste, and then by a cup-shaped zinc electrode. The pastes contain water, so the zinc chloride dissociates into zinc ions (Zn^{++}) and chlorine ions (Cl^-).

The cell derives its energy from manganese dioxide's tendency to get rid of some of its oxygen atoms and in zinc's tendency to become ions. There are actually a number of different reactions that occur in the battery, but all of them pump electrons from the carbon electrode to the zinc electrode. We'll look at only one of the simpler reactions.

In this reaction, two manganese dioxide molecules (MnO_2) in the cell's inner paste pick up two electrons from the chemically inert carbon electrode. These molecules then react with a zinc ion (Zn^{++}) to form a complicated zinc/manganese oxide molecule ($\text{ZnO}\cdot\text{Mn}_2\text{O}_3$). With the loss of two positive charges from the pastes, it becomes possible for a zinc atom (Zn) to give up two electrons and become a zinc ion (Zn^{++}), dissolved in the pastes. The two electrons travel through the wires and light bulb to the carbon electrode, where they cause the process to repeat.

There is also another important reaction, not shown in Fig 17.3.6, in which the zinc and zinc chloride react with water to produce solid zinc oxychloride ($\text{ZnCl}_2\cdot 4\text{Zn}(\text{OH})_2\cdot\text{H}_2\text{O}$). This latter reaction is important because it uses up the water in the cell. When the cell finally runs out of chemical potential energy, it also runs out of water and is unlikely to leak in your flashlight.

The natural voltage of a carbon-zinc cell is about 1.5 V but it has a substantial internal resistance. It can't pump many electrons per second, particularly when it is cold, and thus is not very efficient in high current applications. Furthermore, it's not rechargeable. The zinc electrode slowly goes into solution in the pastes and can't be rebuilt by running current backward through the cell. Still, carbon-zinc batteries have been around for a long time and continue to be the cheapest batteries for many situations.

Alkaline batteries employ a somewhat more sophisticated electrochemical cell. Alkaline batteries look the same as carbon zinc batteries on the outside, but their electrochemistry is somewhat different (Fig. 17.3.7). To begin with, an alkaline battery is inside out, compared to a carbon-zinc battery. The alkaline battery's carbon and manganese dioxide positive electrode is on the outside and a powdered zinc electrode is at the center of the cell. The other main difference is that only one paste is used, consisting of potassium hydroxide (KOH) and water. The potassium hydroxide dissociates into potassium ions (K^+) and hydroxyl ions (OH^-). The large abundance of hydroxyl ions in the paste makes it alkaline.

The powdered zinc electrode at the center of the battery provides a large amount of surface area and increases the number of electrons this cell can pump

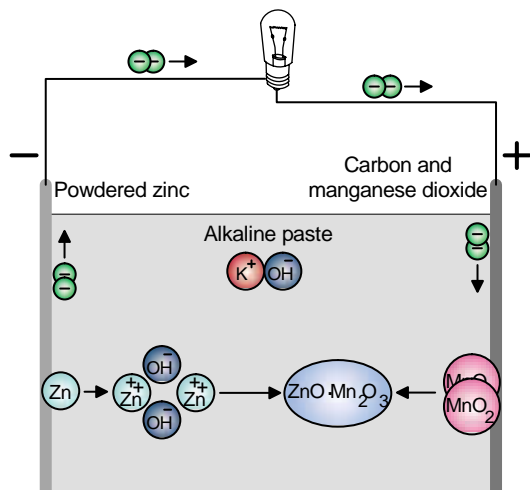


Fig. 17.3.7 - The electrochemical reactions in an alkaline battery are very similar to those in a zinc chloride carbon-zinc battery, except that the negative ions in the electrolyte paste are potassium ions (K^+), accompanied by hydroxyl ions (OH^-). The powdered zinc electrode at the center of the battery provides the large surface area needed for high-current applications.

□ Water drops rust iron through an electrochemical reaction with the air. Gaseous oxygen molecules at the edge of a water drop pick up electrons from the iron and react with water to form hydroxyl ions (OH^-). These ions in the water cause iron atoms near the center of the drop to give up two electrons and enter the drop as iron ions (Fe^{2+}). Iron hydroxide molecules form and settle on the surface as rust. The electrons flow through the iron to the edge of the drop, where they cause the process to repeat.

each second. Since the alkaline cell has a low internal resistance, it's very efficient at converting its chemical potential energy into usable electric energy. Like the zinc chloride carbon zinc battery, the alkaline battery uses up its water in a secondary reaction and rarely leaks as it ages.

Unfortunately, alkaline cells are very sensitive to contamination. The powdered zinc electrodes can corrode easily and the chemicals in the cell must be extremely pure. (For another example of electrochemical corrosion, see □.) One way to make the zinc electrode more corrosion resistant and also keep the powder electrically connected is to alloy it with a few tenths of a percent of mercury metal. The resulting alloy powder works better than pure zinc but mercury is toxic and a dangerous pollutant. For environmental reasons, it is gradually being phased out of alkaline batteries.

There are two special variations on the alkaline cell: the mercury oxide/zinc cell and silver oxide/zinc cell. Both of these cells are very similar to the standard alkaline cell shown in Fig. 17.3.7 except that the carbon and manganese dioxide (MnO_2) electrode is replaced by a mercuric oxide (HgO) electrode or silver oxide (Ag_2O) electrode.

Because oxygen has a very high electronegativity, the oxygen atoms in these oxide molecules have all but removed two electrons from the mercury or silver atom. However, mercury and silver also have relatively high electronegativities and seek out electrons. A mercuric oxide or silver oxide molecule can accept two electrons from the positive terminal of the battery and transfer its oxygen atom to a zinc ion (Zn^{2+}) to form zinc oxide (ZnO) and a mercury (Hg) or silver atom (Ag). The missing zinc ion is replaced when a zinc atom gives up two electrons to the zinc electrode.

The electrochemical reactions in mercury and silver oxide batteries are simple and convert solids into solids. The concentrations of ions in the cells' electrolytes don't change so thermodynamic effects don't alter the batteries' voltages with use. A mercury battery's natural voltage is 1.35 V while that of a silver oxide battery is 1.50 V. In contrast to carbon-zinc and alkaline batteries, which lose their voltage with age, mercury and silver oxide batteries maintain their natural voltages until they are essentially exhausted. This steady voltage makes them well suited to use in watches, hearing aids, and cardiac pacemakers.

While all of these dry cells have voltages of between 1.35 and 1.50 V, many of the batteries that are based on them have higher voltages. These high-voltage commercial batteries simply contain several individual cells connected in series. The common 9 V batteries used in many electronic devices actually contain six tiny carbon-zinc or alkaline cells, stacked on top of one another. Since these cells are small, they can't transfer as many electrons before running out of chemical potential energy. However, since all of the cells work together, they give each electron six times the energy of an individual cell. So these multi-cell batteries pump fewer electrons while giving each electron more energy.

CHECK YOUR UNDERSTANDING #4: Cheaper Isn't Always Better

A battery company decides to save money by halving the amount of powdered zinc it puts in its alkaline batteries. Before the change, one of its batteries could deliver a current of 1 A for 2 hours. How long will one of the new batteries be able to deliver a 1 A current?

Other Batteries

Two other important batteries are nickel-cadmium rechargeable batteries and lithium batteries. Nickel-cadmium batteries are based on the nickel atom's flexi-

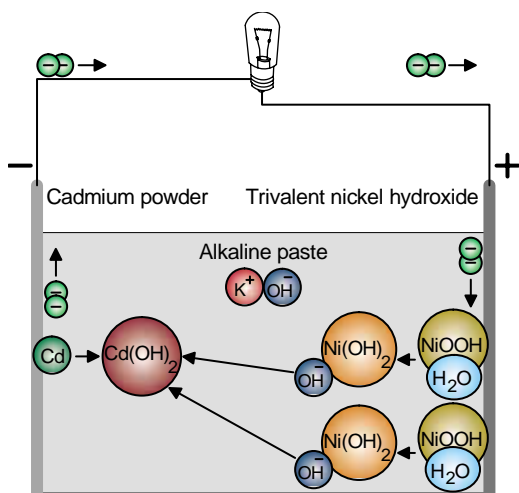


Fig. 17.3.8 - In a nickel-cadmium battery, trivalent nickel hydroxide (NiOOH) reacts with water (H_2O) and an electron to form divalent nickel hydroxide (Ni(OH)_2) and a hydroxyl ion (OH^-). When two new hydroxyl ions have formed, a cadmium atom (Cd) gives up two electrons to the cadmium electrode and reacts with the hydroxyl ions to form cadmium hydroxide (Cd(OH)_2).

bility in forming bonds with other atoms. It can form stable molecules when sharing either two or three of its electrons with other atoms. This flexibility is also found in a number of other atoms, including the manganese atoms that appeared in the carbon-zinc and alkaline cells.

A nickel atom can share three of its valence electrons by joining with an oxygen atom (O) and a hydroxyl radical (OH). It then forms trivalent nickel hydroxide (NiOOH). Here the nickel atom shares two electrons with the oxygen atom and one electron with the hydroxyl radical (OH). A nickel atom can also share two of its valence electrons by joining with two hydroxyl radicals (OH). It then forms divalent nickel hydroxide (Ni(OH)_2). The difference between these two nickel hydroxides is one hydrogen atom.

In a nickel-cadmium battery (Fig. 17.3.8), solid trivalent nickel hydroxide (NiOOH) picks up an electron from the battery's positive terminal and reacts with a water molecule (H_2O) to form solid divalent nickel hydroxide (Ni(OH)_2) and a hydroxyl ion (OH^-). When two of these reactions occur, they form two hydroxyl ions. The presence of two extra negative charges in the alkaline electrolyte causes a cadmium atom (Cd) to give up two electrons to the battery's negative terminal and form solid cadmium hydroxide (Cd(OH)_2). As usual, the two electrons flow out through the wires and light bulb, soon arriving at the positive nickel hydroxide electrode.

Oxygen atoms and hydroxyl radicals don't share electrons fairly with nickel or cadmium atoms. They pull the electrons so hard that they leave the nickel and cadmium atoms nearly ionic. But nickel has a higher electronegativity than cadmium. The nickel-cadmium battery's energy comes from a transfer of electrons from cadmium atoms to nickel atoms. As the battery pumps two electrons from its positive terminal to its negative terminal, a cadmium atom gives up two electrons and two nickel atoms get back one electron each. This electrochemical reaction releases enough chemical potential energy to give the cell a natural voltage of about 1.2 V.

What makes nickel-cadmium batteries interesting is that they can be recharged many times. If you push electrons onto the cadmium electrode and pull them off the trivalent nickel hydroxide electrode, you can make the electrochemical reactions run backward. The electrodes both remain solid during charging and discharging. As you use the battery, its positive electrode goes from trivalent nickel hydroxide to divalent nickel hydroxide and its negative electrode goes from cadmium metal to cadmium hydroxide. As you charge the battery, the re-

verse occurs. Since the electrodes remain solid, they keep their shapes and the battery can be charged and discharged many times before failing.

To give nickel cadmium batteries a low internal resistance and allow them to pump large currents, they are often built in a jelly-roll design. A long strip of insulating material is covered first with a thin layer of trivalent nickel hydroxide powder (the positive electrode), then with a thin porous separator soaked in a potassium hydroxide electrolyte, and then with a thin layer of cadmium metal powder (the negative electrode). This sandwich is rolled up around a cylindrical core to form a much larger cylinder. The cylinder is inserted into the battery housing, along with wires that attach the two electrodes to the battery's terminals and valves to prevent gases created by the cell during charging from bursting the sides of the battery.

However nickel-cadmium batteries aren't perfect. They produce only about 1.2 V, rather than the 1.5 V produced by carbon-zinc and alkaline batteries and some equipment doesn't operate well on this reduced voltage. Moreover, nickel-cadmium work best when their electrodes are finely divided powders. Unfortunately, these powders sometimes change their characteristics with use. If you only partially discharge a nickel cadmium battery and then recharge it, you can cause some of the cadmium metal/cadmium hydroxide powder particles to grow in size. If you repeat this partial discharge cycle several times, some of the particles can become quite large.

These large particles are associated with a phenomenon called "memory," where the battery suddenly loses electric efficiency when it's discharged past the point where it has usually been recharged. At that point, all of the small cadmium particles have been used up and only the less efficient large particles are left. Memory can usually be remedied by fully discharging the battery before recharging it. Presumably this deep cycling breaks up the large particles and improves the battery's overall efficiency.

The other drawback to nickel-cadmium batteries is cadmium's toxicity. Nickel-cadmium batteries should be returned for recycling rather than being discarded. In recent years, manufacturers have begun using materials other than cadmium for the negative electrodes in their rechargeable nickel batteries.

Lithium batteries derive their energy from lithium metal's extremely low electronegativity. It gives up an electron so easily that it reacts violently with many chemicals. It reacts strongly with water so lithium batteries use various organic solvents and lithium salts rather than water-based electrolytes.

The structure of a lithium battery is similar to those we've already examined. The negative electrode is lithium metal and the positive electrode is one of a number of salts or plastics that undergo electrochemical reactions with lithium atoms. Electrons cause those salts or plastics to release negatively charged ions that then react with the lithium metal to form lithium salts. During the latter reactions, the lithium atoms give up electrons to become lithium ions. Overall, electrons are pumped from the positive terminal to the negative terminal.

Lithium's high reactivity is accompanied by a large chemical potential energy. Lithium batteries have natural voltages of more than 2.50 V. Lithium is also one of the lightest elements, with a very light nucleus at the center of each atom, so lithium batteries pack a great deal of chemical potential energy into a very light package. They are thus ideal for watches and cameras, where reducing weight is important. (For an interesting alternative to normal batteries, see □.)

□ Spacecraft often use fuel cells, a peculiar type of battery in which the active chemicals at the positive and negative electrodes are gases. The most basic fuel cell uses electrolysis in reverse. Oxygen gas arrives at the cell's positive terminal and hydrogen gas at the negative terminal. Electrochemical reactions, assisted by platinum and other catalysts, convert these gases into water. In the process, electrons are pumped from the cell's positive terminal to its negative terminal.

CHECK YOUR UNDERSTANDING #5: Don't Go Away, We'll Be Right Back

Why is it so important for nickel-cadmium batteries that nickel hydroxide and cadmium hydroxide not be soluble in water?

