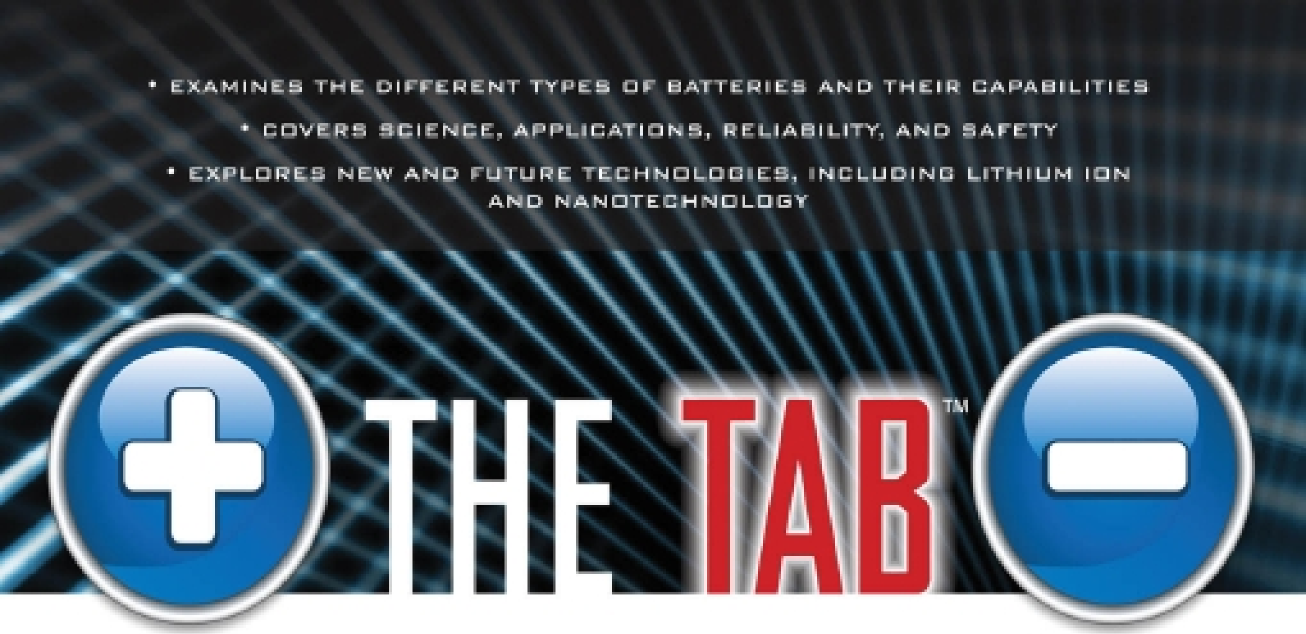

- EXAMINES THE DIFFERENT TYPES OF BATTERIES AND THEIR CAPABILITIES
- COVERS SCIENCE, APPLICATIONS, RELIABILITY, AND SAFETY
- EXPLORES NEW AND FUTURE TECHNOLOGIES, INCLUDING LITHIUM ION AND NANOTECHNOLOGY

THE TAB™ BATTERY BOOK

AN IN-DEPTH GUIDE TO CONSTRUCTION, DESIGN, AND USE

TAB™

MICHAEL ROOT

Foreword by Dr. Ralph J. Brodd

The TAB™
Battery Book

About the Author

Michael Root, PhD, is a battery electrochemist with over 20 years of battery research and development experience. He contributed to the development of battery technology for diverse applications like implantable medical devices and consumer electronics. His work may be found in patents, technical papers in peer-reviewed journals, and a book chapter on battery technology. Additionally, he wrote a number of articles for various general science publications.

The TAB™ Battery Book

An In-Depth Guide to Construction, Design, and Use

Michael Root

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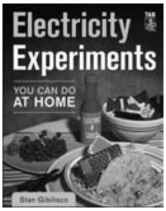

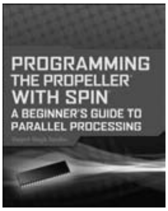

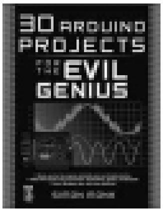

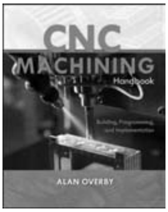

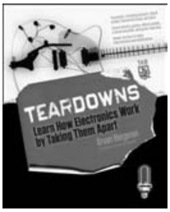

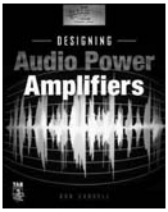

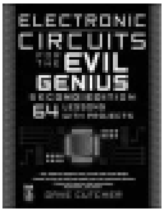

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Foreword

The TAB Battery Book enables the reader to understand in simple layperson terms the complex operations that occur inside a battery in order to generate electrical power on demand. The author offers simple, easily understandable explanations of the complex chemical processes that occur inside a battery. The book is written to provide the typical reader with a working relationship with the batteries he or she uses in everyday life.

The author starts at the very beginning with fundamental descriptions of the Volta pile and continues with the Leclanché 1.5-volt primary battery for flashlights and early portable radios. He goes on to describe the rechargeable lead acid 2.0-volt battery that is now common to most automobile operations. Today, new high-energy systems find wide application, especially the lithium-ion battery with the very high energy density needed to power mobile phones and portable computers, and readers will find that these systems are well covered.

Batteries are capable of very efficient direct energy conversion and can deliver about 95 percent of the contained energy to useful work, compared to an internal combustion car engine, which converts in the range of 25 percent of the energy stored in gasoline to useful energy in propelling the car. An electrical generation plant that converts coal to electricity operates at about 40 percent efficiency.

Batteries are an integral component of our daily lives, whether in mobile phones, portable computers, starting your car engine, or powering the satellite that brings radio communication signals down to earth. The various battery systems are discussed and explained in language that everyone can easily understand.

The reader should find this book to be a valuable resource.

Ralph J. Brodd
President of Broddarp of Nevada, Inc.

Introduction

The invention of the battery by Alessandro Volta over 200 years ago was one of those innovative leaps in technology that occur from time to time. Almost immediately after a letter from Volta describing his work was delivered to the Royal Society of London in 1800, the battery had a significant impact on science and technology.

Before the battery, electrical phenomena had to be studied using electrostatic sources. Electricity could be generated by friction (called triboelectric charging), such as rubbing together amber and wool, or harvested from natural sources, like lightning. The Leyden jar, a type of capacitor, was developed as a way to store electrical energy for later use.

The electrostatic energy produced from such sources could only be delivered in short bursts. This was not a practical way to deliver electrical energy. A more sustained source of electricity was needed.

The conversion of chemical energy to electrical energy accomplished what electrostatics could not. Assemble the right chemical substances in the right way and a controlled, sustained way of producing electricity can be available to almost anyone.

At first, batteries were used as a tool to study electricity and electrochemistry. The great English scientist Michael Faraday advanced our knowledge of electrochemical reactions. Faraday's mentor Humphry Davy discovered several new elements by electrochemical means using batteries as a power source.

It wasn't long before batteries were developed and commercialized to provide electricity for a number of different applications, like railway signals and telegraphs. As early as 1804, Charles Henry Wilkinson offered "different Galvanic Apparatus and Instruments" for sale on "moderate terms." A battery with fifty three-inch plates sold for five guineas. In the years before the invention of the electrical generator and construction of the electrical power distribution grid, battery installations provided electrical power. Some of the batteries developed in the nineteenth and early twentieth centuries we still use today—particularly lead acid, nickel-cadmium, and zinc-carbon batteries.

Many of the technologies we rely on today are enabled by batteries, including cellular phones, laptop computers, cars, and implantable pacemakers. The variety of battery types, sizes, shapes, and performance characteristics is vast. A complete description of any one of the batteries available today could fill a book on its own.

However, the intent here is to provide an overview of batteries from a number of different perspectives—how we use batteries, the historical foundations of today's battery technology, the scientific and engineering building blocks of batteries, different types of batteries (at least the more common ones), and some future directions of battery technologies. There should be something here for engineers, scientists, hobbyists, and students wanting to learn the basics of how batteries function and how to select the right battery for an application.

The idea for this book derives from a university professor I know who asked me to recommend a book to be used as supplemental course material for her course on electrochemical power sources. I had also been trying to think of ways to help provide information regarding battery technology to engineers who design batteries into their devices and those who procure batteries for the device design engineers. There are plenty of excellent reference books and specialized books aimed more at battery researchers and developers, but most of the more general battery books available are now out of print. So, *fiat liber*.

The book is divided into two sections: "Battery Basics" and "Battery Technologies." The former discusses some of the general battery chemistry and engineering. The latter is a rundown of the more common battery technologies. A glossary and selected battery resources are provided at the end. The structure of those chapters devoted to the more technical aspects of battery science and engineering start with some basic information and go into more detail as the chapter progresses.

There are many books regarding battery science and technology that have been written since the early 1800s. A few of the more recent books providing information you may find useful include the outstanding reference book *Handbook of Batteries* edited by David Linden and Thomas B. Reddy, *Modern Batteries* by Colin A. Vincent and Bruno Scrosati, *Understanding Batteries* by R.M. Dell and D.A.J. Rand, and *Industrial Applications of Batteries* edited by M. Broussley and G. Pistoia. Also, Henry Schlesinger's *The Battery,* published during the writing of this book, gives an engaging account of the development of battery technology and the applications that use them.

PART I

Battery Basics

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Chapter 1

Why We Need Batteries

Getting Unplugged: Portable Energy and Long-Term Energy Storage

We use electrical energy to power most of the devices, equipment, appliances, gadgets, and tools we use every day. This means we have two basic needs with respect to electrical energy: generation and storage.

The average home in the United States uses something over 30 kilowatt-hours of electricity each day. (Definitions of kilowatt- and watt-hours and other technical terms are found in later chapters.) That is about 36 percent of all the energy used by a typical U.S. household. Nearly all of this electricity is generated at large power plants by various means. From there, electricity is allowed to flow into high-voltage transmission lines that are really more like a transmission network connected to multiple power plants. Distribution lines convey the electricity from the high-voltage transmission lines by way of electrical substation transformers and through cables strung across or buried beneath much of the developed areas in countries throughout the world and into our homes and businesses. This energy is then readily available to us on demand by plugging the electric cords of our electrically powered devices and equipment into wall outlets—that is, if we are in a location that is served by the electrical grid distribution system.

The electricity in the distribution grid is generated by converting heat and kinetic energy into electrical energy. According to the U.S. Energy Information Administration, over 91 percent of the electricity generated in the U.S. in 2007 was derived from stored chemical energy, usually in the form of fossil fuels, or nuclear energy. These fuels are converted into heat. The heat, in turn, is converted into electrical energy. Other sources, like hydroelectric energy that utilizes the kinetic energy of fast flowing rivers and waterfalls moving by the force of gravity, make up the remainder at less than 6 percent of the total electricity generated.

Using the electricity that is distributed through the electrical grid requires stationary outlets connected to the electrical grid distribution system. This limits the use of devices and equipment to locations that are served by the electrical distribution grid. It also limits their portability to the length of the power cords that convey the electricity from the grid to the device or equipment.

In cases where connecting to the electric distribution grid through wall outlets is inconvenient, such as with devices that are intended to be mobile and not tied down by an electrical cord or not feasible because the location of the equipment is far from the electrical grid, other means of providing electrical energy become necessary. This is where batteries come into play.

There are two basic reasons to store energy: (1) the energy generated needs to be available for use at a later time, or (2) you want to carry energy with you. Examples of the former include storing energy generated by the wind or sun for use when the wind is not blowing or the sun is not shining. Examples of the latter are portable applications, like cell phones, pacemakers, and electric vehicles.

The Importance of Portable Energy

The need for portable energy is well depicted in an episode from the Looney Tunes Roadrunner animated series. These cartoons feature a hungry coyote, Wile E. Coyote, preying on a roadrunner in a desert in the American Southwest. The roadrunner is too clever and fast for the coyote to catch by simply running after it. So, the story lines of the cartoons largely consist of the coyote developing and implementing, or at least attempting to implement, inventive ways of capturing the roadrunner. Not only does he fail to catch it, there are usually unintended consequences wherein Wile E. Coyote is blown up, is crushed under a heavy object, or falls from a great height.

In one episode (“Highway Runnery,” Looney Tunes episode 34, 1965) the coyote mounts a sail on a skateboard. In one hand he holds a table-top fan to blow air into the sail and thereby propel him forward. In the other hand he holds a mallet to subdue the roadrunner. Stepping on the skateboard, he plugs the fan’s cord into a standard electrical outlet conveniently mounted on a nearby utility pole. The fan is switched on, the sail billows, and the skateboard with the coyote on board moves forward.

This arrangement works well at first. The coyote chases and gains on the roadrunner until the fan’s electrical cord becomes fully extended and is pulled from the outlet. With the electricity cut, the fan stops operating, the sail collapses, and the skateboard stops. Unfortunately for the coyote, this occurs after the skateboard has gone off the edge of a cliff. The coyote falls a long distance to the ground and the roadrunner escapes. Again.

If the fan were battery operated, the coyote would not have been limited by the length of the electrical cord, but rather by the energy contained within the battery. With the proper choice of batteries, and perhaps a few replacement batteries carried along with him, the coyote may have been more successful.

Chemical Energy Storage Compared

This book does not address the many ways of generating electrical energy, like converting the chemical energy of fossil fuels and other biological sources, the kinetic energy of waterfalls and wind, the energy of sunlight, the heat energy of geothermal sources, or the nuclear energy of highly radioactive isotopes.

A battery user might consider batteries to be a primary electrical generation source. However, it takes electrical energy to build batteries, including in most cases synthesizing the materials with proper levels of stored chemical energy.

Neither does this book examine methods of storing energy that are not chemical in nature, like the mechanical energy of flywheels.

That stated, batteries are not the only way to convert chemical energy into electrical energy. There are other ways, like capacitors and fuel cells. (In reality, capacitors rely on electrostatics rather than chemistry to store energy, but we will temporarily ignore this distinction, since a fair amount of chemistry is involved in most practical capacitors.)

Capacitors come in several varieties: electrolytic, solid state, and electric double-layer capacitors, which are also called supercapacitors or ultracapacitors. They can have a high power density, but a low energy density compared to batteries. (Power and energy densities are defined later in the book.) That makes them better suited for applications where short bursts of high power are needed, such as defibrillators or camera flash bulbs. Likewise, there are a number of different *fuel cell* technologies. Fuel cells generally have a higher energy density but lower power density than batteries. Both fuel cells and capacitors are useful under certain circumstances. For example, fuel cells are used in off-the-grid residential and commercial energy storage.

Even so, batteries are the most practical, versatile, and economical solution for portable energy applications, given the present state of capacitor and fuel cell technologies. That may change in the future as capacitors and fuel cells continue to improve. But not today. The battery is the technology behind the technology we use every day: cell phones, laptop computers, MP3 players, hearing aids, and pacemakers. They start our cars, and they power satellites and the Mars rovers.

In this book we will look at the diverse uses of batteries and the many different types of batteries developed and manufactured to meet our portable and off-grid energy needs.

Chapter 2

The Many Uses of Batteries

Every day we use devices that are unplugged from the electrical energy distribution grid. Cell phones, laptop computers, MP3 players, cameras, and calculators are unplugged because they are powered by batteries. Improvements in battery performance have enabled expansion of the power-hungry features supported by these devices as well as helping to reduce their size.

We can't list every single application that uses batteries—the numbers of applications and battery types are just too large. What follows is a brief survey of some of the applications, especially those that require some specialized batteries:

- Portable consumer devices: mobile power for an unplugged society, power tools
- Medical devices: life-sustaining and life-enhancing medical devices, including pacemakers, defibrillators, hearing aids, pain management devices, and drug pumps
- Electric vehicles, including hybrids
- Large-scale energy storage
- Space: satellites and Mars rovers
- Military batteries

Portable Consumer Devices

The type of battery for the devices we use every day depends on the power requirements of the device and how it is used. A *primary* cell or battery is designed to be used once and discarded after it is depleted. A device might use a *primary* battery because it only needs to be replaced occasionally and is conveniently replaced. A *secondary* or *rechargeable* battery, which can be recharged multiple times to replenish its store of energy, may be designed into the device if it is intended to be used frequently or requires very high power for extended periods of time. Other factors include the cost (always an important consideration for consumer batteries), size, and weight.

Low-rate applications, in other words those that require low power levels to operate, will only slowly discharge their batteries. Device designers can take advantage of the higher energy available from primary batteries, since they will not need to be replaced very often. The power loads for some of common low-power portable devices generally range from 0.01 to 0.1 watts (abbreviated W) for radios, calculators, clocks, and remote controls. Some are always on, like clocks, whereas others are only used occasionally, such as flashlights. Primary batteries are a good choice for these types of devices.

As the power load and frequency of use increases, rechargeable batteries become more attractive. Moderate power applications and those that only involve occasional use could go either way, and other factors may come into play. The power loads for compact disc players, electronic games, battery-operated toys, and flashlights are in the 0.1 to 1 W range, but the extra cost and added inconvenience associated with rechargeable batteries may not be justified and primary batteries are still a better option. Cellular phones pull from 0.5 W to over 1 W of power, but their small size and frequency of use make rechargeable batteries a better choice. Likewise for camcorders, high-power toys, and digital cameras that can consume over 1 W of power.

Higher-power devices that are used continuously, such as laptop computers (8 W to 45 W), require rechargeable batteries. Otherwise, the cost of frequently replacing primary batteries would be prohibitive. Not to forget the inconvenience of keeping enough batteries on hand and constantly exchanging new batteries for the depleted ones. High-power devices like power tools can require anywhere from 60 W for an orbital sander up to 1,800 W for electric saws and grinders. Such high power levels can be supported by nickel-cadmium (NiCd) and lithium ion cells.

Medical Devices

Implantable or wearable medical devices include hearing aids, pacemakers, implantable cardiac defibrillators, and neurostimulators.

Hearing aids are small devices that amplify the sounds picked up by a tiny microphone to enable the hearing-impaired to hear better. There are several types of hearing aid designs: behind the ear, in the ear, and completely in the canal.

Most hearing aids run on zinc-air cells because they have a high energy density. Depending on the hearing needs of the user and the type of hearing aid, batteries may last from a few days to over one month. Recently, hearing aids with rechargeable batteries have been introduced that use nickel–metal hydride (NiMH) or lithium metal rechargeable batteries.

Zinc-air cells can be used in hearing aids because they are exposed to the atmosphere. Implantable devices are placed inside the body and so the batteries must be hermetically sealed.

Pacemakers and implantable defibrillators are cardiac rhythm devices that apply a small electrical signal to heart tissue to stimulate the heart to beat. The devices are implanted in the chest with electrical leads extending from the device into the heart. If a patient's heart beats too slowly or tends to skip beats, the device will apply the electrical stimulus that gets the heart to beat at a normal rhythm. An implantable defibrillator operates as a pacemaker, but is also capable of delivering a high-power shock to a heart that is beating too fast or is fibrillating and cannot pump blood effectively.

The power requirement for cardiac pacing is rather low—in the tens of microwatts usually, depending on patient needs. Most pacemaker batteries today are lithium-iodine (Li/I_2) which has a high energy density, but only a low power output. Implantable defibrillators must also function as a low-power pacemaker all the time, but occasionally provide a high-power shock, on the order of watts, when needed. A combination of high energy and high power density is essential for defibrillator batteries.

Neurostimulators are much like pacemakers, except they apply electrical signals to nerve tissue. Devices are available for spinal chord stimulation to manage chronic pain, vagal nerve stimulation to control epilepsy and deep depression, and deep brain stimulation to help relieve symptoms of Parkinson's disease and other neurological disorders. While primary batteries have been used for these devices, the trend is toward using rechargeable batteries to extend the longevity of the device.

For implantable devices, the longer the battery lasts, fewer surgeries are required to replace the device, which in turn means lower risks of surgical complications, like infections.

Electric Vehicles

Scottish inventor Robert Anderson first built a battery-operated car in the 1830s. Battery-operated vehicles—cars, trucks, trains—became commonplace in the late nineteenth century and into the early twentieth century.

Battery-powered vehicles available today include electric wheelchairs, forklifts, and golf carts that use lead acid batteries. In some places of the world, electric bicycles are popular—about 24,000,000 electric bikes were sold in 2008 worldwide that use 250 to 500 watt-hour batteries. Bikes sold in China were primarily lead acid, whereas NiMH and Li ion bikes were sold elsewhere in the world.

Hybrid electric vehicles (HEVs) run on both battery power and gasoline. More than 515,000 HEVs were sold in 2008, and it is projected that 1,300,000 HEVs will be sold in 2015. NiMH batteries are used in HEVs today, but vehicles with Li ion batteries will become available soon.

Electric vehicles (EVs) are being developed using Li ion batteries, although nickel-zinc batteries are also under development. Peak power requirements for an EV run upward of 50 kilowatts.

Large-Scale Electrical Energy Storage

Large-scale electrical energy storage using lead acid batteries was implemented in the late nineteenth century because power stations at that time would sometimes shut down overnight. In his 1912 book *Storage Batteries,* Harry Morse wrote, "From the beginning of the nineteenth century until the early eighties was the era of the primary cell. Then came the dynamo and the motor, accompanied by improvements in our main prime source of power—the steam engine—and the storage cell has grown along with all of these in a somewhat subordinated place. It is a mere assistant to be called on for temporary aid in time of need, either to help over an ugly peak in the load on the prime source, or as insurance to be called in when the main source is disabled for a short time, and its aid is often quite invaluable under these conditions."

Today, batteries still have a role to play in energy management, such as load leveling and peak shaving, which store energy during times of the day when demand for power is low and utilize it when demand is high. In this way, electrical power generators can be designed for average power demands rather than oversized for the peak demand periods.

Large-battery electrical energy storage is used around the world for energy management, including lead acid installations in Germany, Spain, Puerto Rico, and California that can deliver between 4 megawatts for 1 hour (4 megawatt-hours) and 10 megawatts for 4 hours (40 megawatt-hours), as well as a NiCd batteries in Alaska used for emergency power delivering up to 40 megawatts for 7 minutes.

Batteries also support the energy storage needs for wind and solar generation facilities.

Space

Satellites require battery power when they enter Earth shadow and their solar panels do not function. The first rechargeable batteries used on satellites were NiCd. Starting in the 1980s, nickel-hydrogen (Ni/H_2) batteries started service, especially for geostationary satellites. More recently, Li ion batteries have started to be used because of their lighter weight.

It is expensive to replace or fix satellites in Earth orbit, so their batteries must have a long life and be highly reliable. The Hubble Space Telescope was released into a low earth orbit from the space shuttle Discovery on April 25, 1990. It has made a significant impact on astronomy with its telescope and scientific instrumentation. Contributing to the operation of Hubble are the three Ni/H_2 battery modules. The batteries were expected to last 7 years. They were still operational when they were replaced in May 2009, after 19 years of service.

The weight of a battery is an important consideration when the device they run needs to be placed into orbit with a rocket. The Ni/H_2 batteries are relatively heavy, and newer satellites are being fitted with lighter weight Li ion batteries.

Lithium ion batteries are also used on the two Mars Exploration Rovers. NASA planned on a 90-day mission. That was in 2004. The battery on Opportunity, one of the rovers, is still functioning despite the severe conditions on the planet surface.

Military

Like space batteries, military batteries need to be designed with long life and high reliability in mind. They could also experience a wide range of environmental conditions.

The energy demands of a modern fighting force is great. An infantry platoon (about 30 soldiers, give or take) during a 72-hour operation needs eight different battery types. They will use more than 2,500 batteries weighing 360 pounds at a cost of just over $10,000. Night vision, communications, and weapons all require portable battery power.

The 590 type military battery is a 24 V battery pack used for portable communication and surveillance equipment. Several different primary and secondary cell types are used, including lithium–manganese dioxide (Li/MnO_2) and lithium–sulfur dioxide (Li/SO_2) primary batteries and NiCd, NiMH, and lead acid secondary batteries.

A developing military battery application is wearable soldier power. The state of battery technology today requires soldiers to carry too many batteries that are too large for long missions. And future power and energy demands are increasing. The challenge is to provide more power and energy in a lighter-weight battery. A number of different technologies are in the development phase.

Batteries are also used to power and control advanced weapons and other equipment, including zinc–silver oxide and magnesium–silver chloride reserve batteries for torpedoes and Li ion batteries for the Global Hawk unmanned aircraft.

Chapter 3

The History of Batteries

We can mark the start of battery history on March 20, 1800. This is the date that Alessandro Volta, a professor of natural philosophy at the University of Pavia in Italy, wrote a letter to the Royal Society of London describing his research findings. The Royal Society of London (its full name was The Royal Society of London for the Promotion of Natural Knowledge) was one of the oldest and most prestigious scientific societies in Europe. If it was published in the Society's scientific journal, *Philosophical Transactions of the Royal Society,* it was sure to be widely read.

In his letter, titled "On the Electricity Excited by the Mere Contact of Conducting Substances of Different Kinds," Volta described an apparatus consisting of alternating disks of tin or zinc and either copper, brass, or silver. Zinc and silver were the preferred embodiments of the invention. One zinc and one silver disk were paired together. An absorbent material, paper or leather, for example, was moistened with an electrolyte solution, such as aqueous sodium chloride, and placed between each zinc and silver disk pair (Figure 3-1). Each elementary zinc-electrolyte-silver unit formed a single electrochemical cell. When stacked together, one on top of the other as shown in Figure 3-1, Volta created a battery made of individual cells connected in series.

It is relatively common for new advances in fundamental and applied science to follow the invention of a new tool. And so it was with the battery developed by Volta. The Voltaic pile, as it was called at the time for reasons that may be quickly figured out from Figure 3-1, opened up new areas of research into electrical current and electrochemistry.

For the first time in history, scientists could use a sustained source of electrical current. It would be another 70 years before French electrical engineer Zénobe-Théophile Gramme built the first practical electrical generator, or dynamo. The dynamo produced continuous, or direct, current by converting mechanical energy into electrical energy. It wasn't until later in the nineteenth century that electric power lines were installed to provide reliable electrical power.

Following the introduction of Volta's battery, there was a tremendous upsurge in scientists designing and performing experiments involving electrical phenomena that were difficult to carry out using only the Leyden jar. Many of our key concepts in

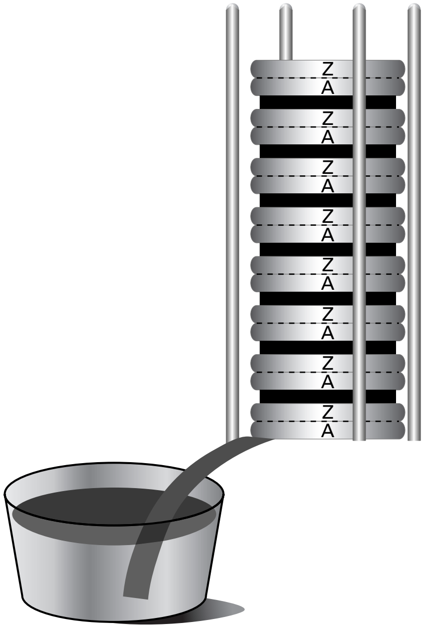

FIGURE 3-1 An illustration of the silver-zinc battery devised by Italian scientist Alessandro Volta. "A" stands for silver and "Z" for zinc.

electricity and electrochemistry came out of the first half of the nineteenth century because they were enabled by the Volta battery.

In the remainder of this chapter we will take a more in depth look at the discoveries and inventions leading up to Volta's battery and how battery technology started on the path that brings us to the batteries we use today.

Electrostatic Energy

Prior to Volta's battery, the study of electrical phenomena and use of electricity relied on static electricity, or electrostatics. Electrostatic energy was known to ancient civilizations. It was explored by the Greeks and Romans, and possibly even before that.

Electrostatic energy generation, which involves charge separation and release by electrical discharge, is ubiquitous in nature. Lightning is a familiar and powerful example.

The study of electrostatic energy dates back at least to the ancient Greeks. When they vigorously rubbed amber with wool, they found the amber would attract small bits of dust or lint. The words electron and electricity are derived from the ancient Greek word *elektron,* which means amber.

Generating static electricity by rubbing amber with wool is an example of triboelectric charging, which occurs as a result of friction when certain materials are brought into contact and then separated. Electrostatic energy in this case is formed

Lightning Electrical Energy

The form of lightning that occurs during thunderstorms is the result of electrostatic discharge and occurs in a number of complex steps. Numbers reported for the electrical characteristics of lightning vary widely, but they all indicate that lightning bolts discharge enormous amounts of power.

A potential difference of 20,000 volts to well more than 100,000,000 volts can develop between cloud and ground. There are a variety of different types of lightning. The type that discharges between clouds and ground, also called negative lightning, may have a peak current of 5,000 to 200,000 amperes with an average peak power of about 10^{12} watts.

Now, a lightning bolt lasts only about 0.03 seconds on average, so the energy delivered is lower than one might expect, somewhere in the neighborhood of 150 kilowatt-hours. If all of the energy dissipated by a lightening bolt could be captured, it would be enough energy to illuminate one 60-watt light bulb for about three months or supply the energy needs of a typical U.S. household for less than a week. However, the magnitude of the actual charge transferred is more like 20 to 90 coulombs, which is enough to run a flashlight for a few minutes.

when loosely held electrons are separated from one material and picked up by another when they are rubbed together. This process yields two objects possessing opposite charges—positive and negative—resulting from a deficit of electrons on one material and a surfeit of electrons on the other.

Dissipation of this pent-up energy occurs by recombination of the positive and negative charges. The process of combining negative charges deriving from excess electrons on one material with the positive charges from a shortage of electrons on another material is called electrostatic discharge.

Interest in electrical phenomena continued. Other materials were later found to do the same thing as amber and wool, including rubber and fur, glass and silk. Yet, the tools for the storage and controlled release of electrical energy were lacking.

Biological Electrical Energy

Electrical phenomena found in biological systems also involve separation of charge, but in these cases it is ions rather than electrons that carry the charge. Examples include nerve impulses that convey sensory information to the brain and the contraction of muscle tissue. Electric fish, like the well-known electric eel, have organs composed of modified muscle cells called electrocytes that build up an electrical potential. Electrocytes have a potential of about 0.15 volts when charged. Thousands of them are stacked in series to yield cumulative potentials up to about 650 volts for larger electric eels. Used for capturing prey and repelling predators, electric eels can discharge currents up to about 1 ampere.

Over 1,500 years after the ancient Greeks, German scientist and engineer Otto von Guericke developed an electrostatic generator in 1663 while seeking ways to study static electricity. He observed that he could generate electricity by rubbing his hand on the surface of rotating ball of sulfur about the size of a basketball.

Friction devices like that devised by von Guericke helped advance the study of static electricity. The Leyden jar helped further it along more when it came along in 1745. It was the first device, known today as a capacitor (also called a condenser at one time), which was able to store large amounts of electricity created by electrostatic generators.

The Leyden jar was invented by Dutch scientist and mathematician Pieter van Musschenbroek at the University of Leiden in the Netherlands and independently by German cleric and scientist Ewald Georg von Kleist. English physician and scientist William Watson made improvements that increased the amount of energy it could store. Introduction of the Leyden jar accelerated further advances in the understanding of electrostatics and electrical conduction throughout the remainder of the eighteenth century.

While the Leyden jar provided a means for storing electrical energy, the current it produced was short-lived. George Pearson reported his experiments on the electrolysis of water into hydrogen and oxygen gasses using a Leyden jar in 1797. Just a few years before Volta announced his battery, Pearson managed to generate just 8 cm^3 of gas after 16,836 cycles of charging and discharging the Leyden jar over the course of about 18 hours. No wonder he wrote it was impractical to perform these experiments over a longer period of time, "the expense of laborers being considerable." A more sustained source of electrical current was clearly needed to further advance the study of electrical phenomena.

Electrochemical Energy

Experimental observations eventually leading to the development of a chemical source of electrical current may have begun with Dutch naturalist Jan Swammerdam in 1678. He observed that muscle tissue contracted when touched with two different metals, like silver and copper. Similar experiments were made by other scientists continuing into the late eighteenth century. In related experiments, Swiss scientist Johann Sulzer experienced a metallic taste after contacting pieces of lead and silver and then placing them on his tongue in 1762.

Apparently none of these researchers recognized the electrical nature of these observations, though. It was Italian physician and physicist Luigi Galvani who made the connection in 1786. However, Galvani hypothesized that the source of the electrical phenomena was the animal muscle itself, which he called "animal electricity." He came to this conclusion even though he observed that known sources of electricity, such as the electrostatic discharge from lightning, also made the muscles twitch.

Volta disagreed, though. He correctly deduced that the source of electricity causing the muscle tissue to contract derived from the different metals used. He called it "metallic electricity." It was also known as contact theory at the time.

Volta did not quite get it completely right, though. He did not understand the electrochemical nature of the electricity that was produced. Rather, he thought the mere contact of dissimilar metals generated the electricity. Indeed, it was Volta's belief in "metallic electricity" that drove the design of his battery wherein the copper or silver and zinc were in direct contact. He included an extra disc of zinc at the positive end of his pile and an extra disc of copper or silver at the negative end (see Figure 3-1). These added discs were unnecessary for the function of the battery.

Even without a complete understanding of the actual electrochemical mechanisms involved, his work studying the electrical effects of combining dissimilar metals in the years leading up to the publication of his letter in 1800 presaged the electrochemical series for metals and lead to the development of the first battery.

Volta's contemporaries immediately recognized the importance of his invention. The battery provided a sustained source of current and it changed the course of research involving electrical phenomena. No longer were researchers limited to using only short bursts of electrical current from Leyden jars.

Ancient Battery?

There is some evidence that electrochemical power sources—batteries—were also in use in the Middle East perhaps as early as 2,000 years before Volta disclosed his battery to the Royal Society of London in 1800.

Austrian archeologist Wilhelm König first reported an intriguing hypothesis in 1938 following his study of artifacts found at Khujut Rabu'a in Iraq, not far from the city of Baghdad. He asserted that the iron and copper pieces along with a clay pot found there were parts of a 2,000-year-old battery. The relics have been variously attributed to the Parthians dating back to between 248 BC and 226 AD, or the Sassanians some time from 226 AD to 637 AD. Similar artifacts have since been found at other locations nearby.

There are skeptics, but if it was a battery it was assembled using a copper sheet rolled into a cylinder 1.5 inches diameter by 5 inches high—a little larger than two modern D-sized cells stacked end to end. The cylinder was capped on one end with a copper disc and sealed with asphalt. An iron rod was placed in the copper cylinder and the entire electrode assembly was put into a 6-inch-tall clay pot. The electrolyte solution may have been vinegar or even wine.

Whether it is a battery or not, it was not likely to provide much current, although a number of them connected together might provide sufficient current for useful purposes. Unfortunately, it is not known how the battery was used. Electroplating jewelry or use in religious ceremonies are a couple of suggestions. Neither is it known how the battery was connected to whatever it was used for. Multiple batteries could have been connected together to increase the current output, but no conductors were found with the other items.

Competing Theories

The Volta pile was a momentous innovation and resulted in new discoveries in the areas of electricity and electrochemistry, but it has been suggested that the further development of improved battery systems may have been temporarily impeded to some extent by Volta himself. His contact electricity theory—electricity generated when different metals are connected—as the operating principle behind his battery led some researchers down the wrong path.

There were some scientists, contemporaries of Volta, who were on the right track, though. They correlated both the electrical response of muscle tissue when touched by disparate metals and the current produced by Volta's battery with chemical reactions occurring at the metals.

The controversy between the competing theories of contact electricity and chemical action continued for years. Among them was English scientist William H. Wollaston, who took on Volta's theory. Wollaston forwarded the view that chemical action was involved in the operation of Volta's battery. "That the oxidation of the metal is the primary cause of the electric phenomena observed," he wrote in 1801.

Michael Faraday, the great English scientist who gave us so many of our concepts in electricity and electrochemistry, said, "I agree with those who believe that the supply of electricity is due to chemical powers."

Another famous English scientist, Sir Humphry Davy, recounted in 1806 his views on how the electricity produced by Volta's pile involves chemical action and not just conduction of electricity through metals. "Before the experiments of M. Volta on the electricity excited by the mere contact of metals were published, I had to a certain extent adopted this opinion; but the new facts immediately proved that another power must necessarily be concerned;" he stated.

Yet, defining the electrochemical theory behind the operation of the battery was to wait until Faraday, and others, formulated them years later.

Michael Faraday and the Terminology of Electrochemistry

Michael Faraday's contributions to electrochemistry cannot be overstated. In 1834 he proposed the terminology we use today in battery science: *electrode*, *anode*, *cathode*, *electrolyte*, *electrolysis*, *ion*, *anion*, and *cation*. An electrode is the site in a cell where the electrochemical reactions occur. Anodes and cathodes are types of electrodes. Electrons are removed at the anode and inserted at the cathode. An electrolyte is a solution containing dissolved chemical species with a net electrical charge called ions. Anions and cations are types of ions with either a negative or positive charge, respectively. Electrolysis is an electrochemical process.

Electroplating

Electroplating, sometimes more generally called electrodeposition, is the formation and deposition of materials by electrical means. Perhaps the most familiar example of electroplating involves the electrochemical reduction of metal ions dissolved in an electrolyte. The resulting metal, like gold or nickel, is deposited, or plated, on the cathode during the passage of electricity.

Some have suggested Parthian or Sassanian batteries found near Baghdad, Iraq, and possibly dating back as far as circa 250 BC were used for gilding jewelry with gold or silver by an electroplating process.

Many of the early discoveries using the Volta battery were foundational to the study of electrochemistry. About two months after Volta sent his letter, English chemist William Nicholson and surgeon Anthony Carlisle used a Volta pile to electrolyze water into hydrogen and oxygen, presumably without all of the exertion that Pearson needed to charge a Leyden jar. Scottish chemist William Cruickshank, German physicist Johann Wilhelm Ritter, and others used Volta batteries to study the electroplating of metals between 1800 and 1802.

Humphry Davy used a Volta battery with up to 2,000 anode and cathode plates in his work to isolate the elemental forms of alkali metals sodium and potassium, as well as alkaline earth metals magnesium, calcium, strontium, and barium.

Improvements in Battery Technology

In his 1800 letter to the Royal Society of London, Volta confidently described his invention as providing unlimited charge and perpetual electricity. This was an overstatement as we see it now, but presumably they had a different view at the end of the eighteenth century when they had to rely on Leyden jars for electrical energy storage.

Despite his claims, the battery invented by Volta needed substantial improvements to make it more efficient and practical. Then, as now, there were mounting demands to deliver batteries with more power and greater energy. Increasing the electrical output of batteries and making them more convenient to use were at the top of the list for battery developers in the early nineteenth century. And so it is in the early twenty-first century, for that matter.

Engineering Improvements to Volta's Battery

The work to develop new and improved batteries started quickly after Volta revealed his battery to the world. Many of the early efforts to improve the performance of Volta's battery were along the lines of engineering enhancements.

Volta's battery was open to the air. Even Volta realized that evaporation of water in the electrolyte limited how long the battery would operate, and thus how much

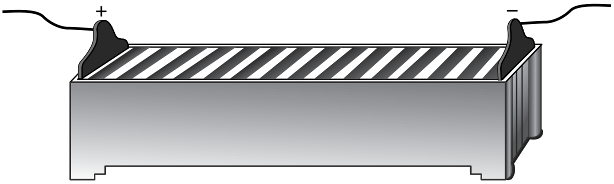

FIGURE 3-2 The Cruikshank trough battery

energy it could produce. It could be reactivated by replenishing the electrolyte, but sealing it in wax minimized the evaporation of water.

Another early improvement was offered by Scottish surgeon and scientist William Cruikshank. He took Volta's upright battery configuration and tipped it on its side. Pairs of copper and zinc electrode plates were inserted in slots cut into a trough (Figure 3-2). This particular configuration meant that more electrolyte could be used, which improved the performance.

Cruikshank's trough battery may have provided the inspiration for the battery symbol used in circuit diagrams (Figure 3-3).

The simplest way to increase the power and capacity of a battery is to make it larger. Increase the area of the battery electrodes or connect more cells together, and more power can be generated. Davy used a 2,000-cell Volta battery for his research. William H. Pepys built a 60-cell Cruikshank trough battery with 6-foot-square electrodes.

Charles H. Wilkinson added handles to the electrode plates of the trough battery to make it easier to remove them from the electrolyte. This helped solve another performance issue with these batteries, self-discharge, in which the battery electrodes deteriorate from parasitic chemical reactions. Removing the plates from the electrolyte solution extended their life.

Wollaston may have made the first contribution to a long history of battery size reductions. He significantly increased how much electricity the Volta battery could produce for a given volume. He did this by folding the copper cathode in a "U" shape around the zinc anode plate (Figure 3-4). Both sides of the zinc plate could now be utilized, doubling the electrode active area. This concept was improved by Münch and others (including Faraday) and this electrode configuration used today in certain battery designs.

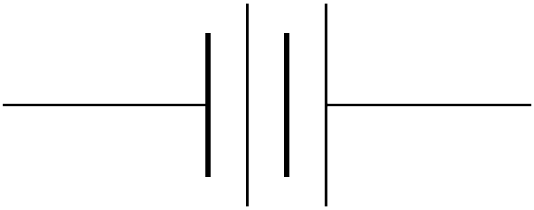

FIGURE 3-3 Electric circuit symbol for a battery

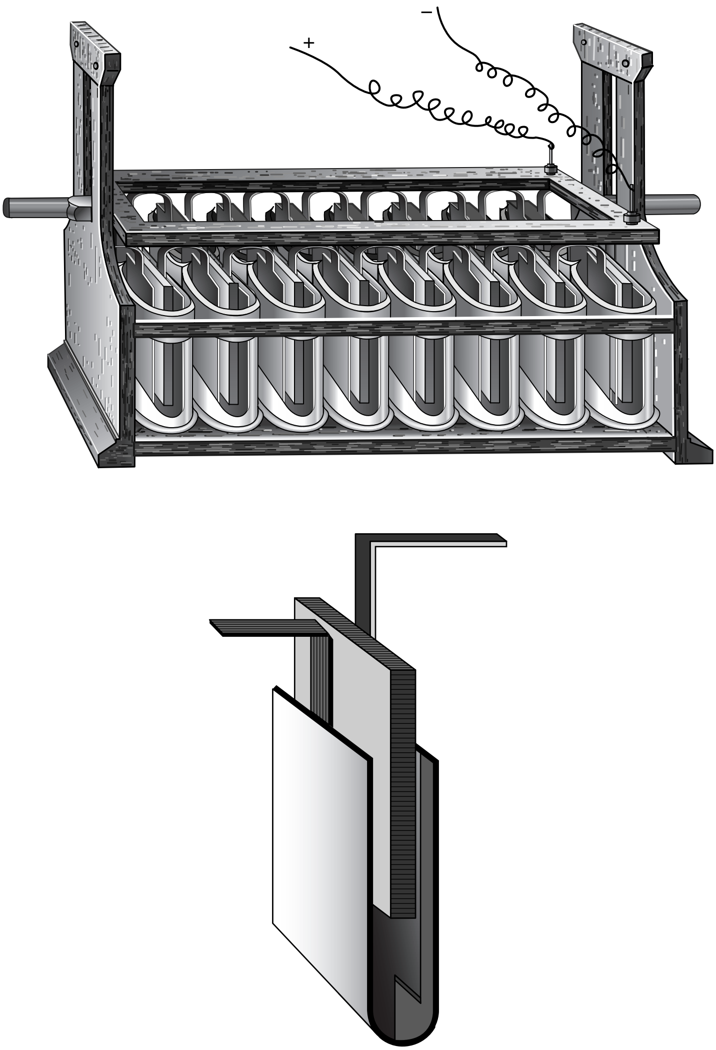

FIGURE 3-4 Wollaston battery design and the improved version from Münch that increased the surface area of the opposed electrode areas

Increasing the battery electrode area is one way to increase power and energy output of a battery. American chemist Robert Hare, in 1819, found a way to assemble battery electrodes with large surface areas without greatly increasing the space needed to accommodate large electrodes. He rolled the copper and zinc electrodes into a giant spiral rather than laying them out flat (Figure 3-5).

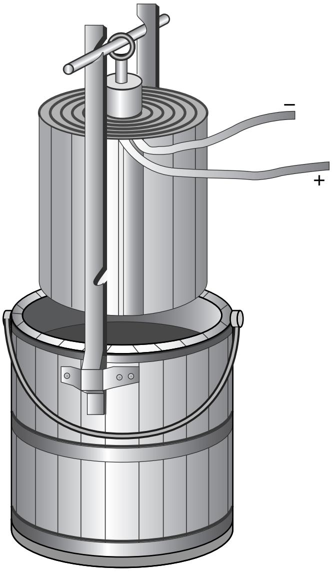

FIGURE 3-5 **The spiral-wound battery invented by American chemist Robert Hare allowed the large battery electrode areas to be assembled into a compact shape.**

This was the first spiral-wound battery. It is the same battery design concept that is used today and for the same reason—to increase electrode area while maintaining a compact package. As an example, lithium ion batteries used in laptop computers today are spiral-wound batteries.

Pepys used Hare's design to assemble a spiral-wound battery with copper and zinc electrodes that were 50 feet long and 2 feet wide.

Further Improvements to Volta's Battery

It wasn't long after Volta introduced his battery that other scientists built their own Volta batteries and started experimenting. Volta's findings were confirmed, and researchers examined a variety of characteristics that affected battery operation. In these investigations, many of the limitations of the battery were characterized.

One of the principal limiting factors of any battery system is *polarization.* This phenomenon results from several factors. (This will be covered in some detail in Chapter 6.) One source of polarization is the buildup or depletion of chemical compounds at the electrodes or in the electrolyte solution. These chemical compounds may be active participants in or the products of the electrochemical reactions. Whatever its cause, when polarization occurs it can diminish the power and energy a battery can produce, and so its performance declines.

The reduction of the water in the electrolyte at the copper (or silver) anode in the Volta battery yields hydrogen gas. The power produced diminishes after operating the battery for an extended period of time. As Faraday observed, "When the ordinary voltaic battery is brought into action, its very activity produces certain effects, which re-act upon it, and cause serious deterioration of its power. The battery becomes polarized."

The negative effect of polarization on battery performance led researchers to experiment with ways to reduce it. Interrupting battery discharge helped. Forced convection by stirring the electrolyte helped. As Faraday wrote, "agitation by a feather ... more than doubled the power of the battery." Others found that exposing Volta's battery electrodes to air or oxygen increased the battery output. This was the first realization of a practice that would come to be called air depolarization.

Mechanical methods were often used to reduce polarization; for instance, periodic removal of electrodes from the electrolyte, cleaning the electrodes, and moving the electrodes in the electrolyte to reduce polarization were popular ways to decrease the effects of polarization. Yet, maintaining a high level of power output for longer using these mechanical processes was labor intensive or required elaborate machinery.

Other researchers introduced improvements with different electrode materials. However, they relied on the same basic electrochemical processes as the Volta battery. The next advance in battery performance had to wait until new cathode materials were developed. These materials stored electrical energy in chemical form. This was a key distinction from the Volta battery, wherein the cathode merely served as a site for other electrochemical reactions to occur, like the formation of hydrogen from water.

Oxidizing Cathode Materials

Throughout much of the first half of the nineteenth century a variety of different cathodes, like platinum, carbon, and platinized carbon, along with various electrolyte solutions and battery designs, brought some performance improvements. Yet, the fundamental electrochemistry was the same as for Volta's battery.

Despite the relatively advanced state of electrochemical theory by the last part of the nineteenth century, it was believed that depolarizing materials (not surprisingly called *depolarizers*), which improved battery performance, acted to remove the hydrogen liberated at the cathode—even though the cell potential was well above the potential at which hydrogen could form. It was not understood that depolarizers were really acting directly as cathode materials.

The next phase in battery technology began when cathode materials that store electrochemical energy were integrated into cell designs. The use of oxidizing cathode materials was an important concept that brought battery technology to the next level of performance and utility. Cathode materials readily accept electrons from anode materials that tend to give them up. Rather than forming hydrogen at the cathode, the oxidizing cathode material took up the electrons supplied by the anode material.

Now, according to the theory of the time, such materials were called depolarizers because it was thought that their mode of action was to reduce the polarization resulting from hydrogen production and accumulation at the negative electrode. The direct role of cathode materials as the oxidizing reactants was unrecognized. Even today such materials are sometimes called depolarizers.

Even without knowledge of the exact mechanisms involved, the use of oxidizing materials led to an upsurge in new battery development.

There are several examples of different ways to incorporate oxidizing cathode materials. An early concept was to use soluble oxidants, a concept that is used for certain battery types even today. The challenge is to keep the electrolyte solution in contact with the anode separate from the soluble cathode material. Otherwise, direct reaction between the anode material and the soluble cathode material would result and limit the useful output of the battery.

The answer was to separate the two electrolyte solutions, creating what is naturally called a two-fluid cell. Of course, a means for providing for ion movement between the anode and cathode solutions was needed.

French scientist Antoine César Becquerel first investigated the two-fluid cell concept, reporting his results in 1829. He immersed a zinc electrode in zinc sulfate and a copper electrode in copper nitrate. Just as in the Volta battery, the anode reaction involved oxidation of the zinc electrode to form zinc ions: $Zn \rightarrow Zn^{2+} + 2e^-$. If the electrolyte is sufficiently acidic, the zinc ions are soluble. If not, zinc oxide or hydroxide would precipitate. For the cathode reaction, the presence of copper ions makes a big difference in the cathode reaction. Rather than forming hydrogen at the copper electrode, copper ions in the electrolyte solution are reduced and deposited on the copper electrode: $Cu^{2+} + 2e^- \rightarrow Cu$.

However, the utility of this concept was not fully realized until English chemist John Frederic Daniell described his version of this cell in 1836 using zinc and copper sulfate solutions. He gets the credit for it and his name attached to it. It proved to have a more constant current output compared to the Becquerel cell.

For a two-fluid cell to work, ion movement between the anode electrolyte and the cathode electrolyte must occur, which means there will be some mixing of the electrolyte solutions. This can reduce the operating time and performance of the cells, so keeping them separated without significantly impeding the movement of ions in the electrolyte solution between them can be difficult. In some designs, animal membranes were used, as were porous ceramic cups.

French inventor Gustave Trouvé introduced a dry-cell form of the Daniell cell where the two electrolyte solutions were soaked into the paper layers—one with zinc sulfate solution and the other with copper sulfate—which were inserted between the zinc and copper electrodes. (The term “dry cell” means the cell contained minimal amounts of electrolyte rather than a large excess of electrolyte as used in some cell designs.) The smaller amount of electrolyte available helped to lessen electrolyte solution mixing.

Another implementation of the Daniell cell had no separator at all. Called a gravity cell, it relied on the different densities of the two electrolyte solutions to minimize their mixing (Figure 3-6). The electrolyte solutions were carefully layered with a denser, saturated copper sulfate cathode solution on the bottom and the less dense zinc sulfate solution on top. The copper electrode was placed in the bottom of the cell in the copper sulfate solution, while the zinc electrode was positioned in the top of the cell in the zinc sulfate solution.

As the cell was discharged and copper plated on the negative electrode, copper ions were removed from the bottom electrolyte solution. To minimize polarization

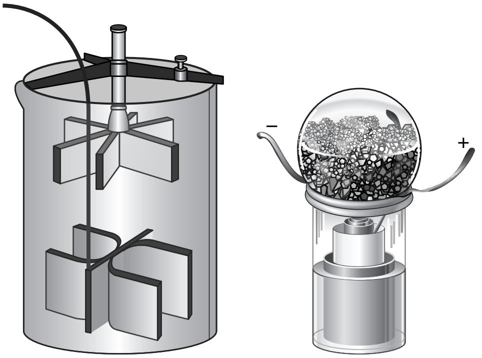

FIGURE 3-6 **Gravity cell designs for the Daniell cell. Anode and cathode electrolyte layers with different solution densities were carefully layered to minimize mixing. Left: This particular design used "crowfoot" electrodes to increase their surface areas, which in turn improved the power density of the battery. Right: The "balloon" battery included a large reservoir of copper sulfate crystals to replenish copper ions as they were depleted during battery operation.**

of the cell resulting from depletion of copper ions in the electrolyte, copper sulfate needed to be kept at a high concentration. For the type of cell commonly used in the United States at the time, a copper sulfate solution was periodically siphoned into the cell. In other designs copper sulfate crystals were added to the bottom of the cell. During operation of the cell, copper sulfate crystals would dissolve to replace the copper ions as they were consumed by the cathode reaction.

A number of contraptions were developed to maintain the saturation concentration of copper ions. One, called a balloon battery but looking more like a bubble gum machine (Figure 3-6), incorporated a flask containing two pounds of copper sulfate crystals that was then filled with water. The neck of the flask was fitted with a cork through which a glass tube was inserted. The entire flask assembly was upended such that the tube was immersed in the copper sulfate solution in the bottom of the cell.

Various designs of gravity cells were used for telegraph and railway installations in Germany, Russia, and the United States during the late nineteenth century. They were relatively easy to maintain and had a low operating cost. The batteries could generally operate for a year or longer without servicing, except under very heavy use situations wherein the copper sulfate needed to be replenished every four to six months. It cost about $30 per month to maintain up to 600 gravity cells.

We can probably mark the beginning of modern battery technology with the introduction of the Daniell cell. The voltage of an individual cell was about 1.1 V; if properly maintained, such a battery was long lived and provided somewhat constant power. For the first time, a relatively practical and efficient battery was available. As a result, it was quickly adopted as a power source for a number of commercial and industrial applications, like communications and electroplating.

Continued Development of New Active Electrode Materials

Another commercially successful battery was introduced by British scientist Sir William Robert Grove. In 1838 he developed a two-electrolyte cell using, again, amalgamated zinc in dilute sulfuric acid as the anode material but with a platinum electrode dipped in nitric acid as the cathode. The nitric acid served as the oxidizing cathode material. The battery had a higher potential than the Daniell cell, about 1.8 V to 1.9 V, and produced a high level of power. The platinum was later replaced with a less expensive carbon electrode by German chemist Robert Wilhelm Bunsen in 1841.

Despite its benefits as a high power output cell, the Grove-Bunsen cell had some serious drawbacks. One is that the cell required the use of concentrated nitric acid, which releases hazardous fumes. Further, during use it generated noxious nitrogen oxide gasses from the reduction reaction of the nitric acid. It was required to use this cell in a well-ventilated area.

The bichromate cell overcame some of the practical shortcomings of Grove-Bunsen cells. German physicist Johann Poggendorff is credited with substituting the nitric acid in the Grove-Bunsen cell with sodium or potassium bichromate (dichromate as we call it today), $Na_2Cr_2O_7$ or $K_2Cr_2O_7$, dissolved in sulfuric acid. The resulting zinc–chromic acid cell had an even higher potential—about 2.0 V at open circuit.

While it was a practical improvement over the Grove-Bunsen cell, it still required some maintenance, although less than previous batteries. In one example, bichromate cells at Paddington Station in London were used continuously in 1878. During that year the sulfuric acid was added ten times and dichromate added five times. The zinc plates lasted from 12 to 18 months.

A variety of other soluble oxidizing cathodes were investigated about that time, including chlorate and permanganate, along with a variety of different battery designs that improved their performance and ease of use. However, the next big innovation in battery technology was to involve the use of solid cathode materials, especially metal oxides.

Primary Batteries

Primary batteries are discharged once and must be replaced once the electrode materials become depleted.

Solid Cathode Materials

Most of the battery technologies in the first half of the nineteenth century involved liquid or dissolved cathode materials—particularly water, copper sulfate, nitric acid, and dichromate. There are a couple of liquid or soluble cathode battery types in use today, like lithium–thionyl chloride and lithium–sulfur dioxide, but modern battery technology overwhelmingly uses solid cathode materials, particularly metal oxides.

Solid cathode materials called depolarizers were explored from the start of battery research and development. (Remember, according to the electrochemical theory of the time, depolarizers are those substances that supposedly worked by reducing the effects of polarization at the electrode surface in Volta-type batteries.) As early as 1802, Volta reported that manganese dioxide improved the performance of his battery. A number of other researchers investigated various other compounds, like silver chloride, lead sulfate, and mercury sulfate. Others worked with metal oxides, like those of iron, nickel, copper, silver, lead, and manganese.

Two of the more familiar metal oxide cathode materials in use yet today are manganese dioxide and lead dioxide. Lead dioxide, PbO_2, is used in the batteries we use to start our cars. Manganese dioxide, MnO_2, is used in consumer alkaline batteries, like the AAA, AA, C, and D cells commonly used in portable electronics. It is also in certain lithium batteries, including watch battery coin cells and cylindrical photo flash batteries.

In 1843 Swiss scientist Auguste-Arthur de la Rive and English physicist Sir Charles Wheatstone independently developed electrochemical cells using lead dioxide (or lead peroxide as it was usually called then). The zinc–lead dioxide cell had some attractive characteristics. It had an open circuit potential of about 2.4 V with an operating voltage of about 2.2 V. Using an alkaline electrolyte solution, English physicist James Prescott Joule increased the cell potential to over 2.5 V. This cell tolerated heavy loads and could be recharged.

Zinc–lead dioxide batteries did see some limited use, such as powering electric streetcars in New York circa 1887. However, the real success of lead-based batteries came with the development of rechargeable lead acid batteries by Planté and Faure, as we will present later.

French chemist and engineer Georges Leclanche, in 1866 patented what was probably the most influential primary battery chemistry—the zinc–manganese dioxide (Zn/MnO_2) battery.

Now, Volta, de la Rive, and others tried manganese dioxide, but it was Leclanché who developed a battery that was commercially successful into the late twentieth century and is used today, such as 6-volt heavy duty lantern batteries.

Leclanché's first battery was a wet, or flooded, cell using an electrolyte composed of saturated ammonium chloride. He combined powdered manganese dioxide cathode material with a conductive carbon to form a cathode mixture. Most primary battery cathodes are made in a similar manner today. The cathode material was packed into a porous jar. The anode material was an amalgamated zinc rod.

There were a number of advantages to this type of battery. The ammonium chloride electrolyte did not react strongly with the zinc anode as did the acid containing electrolytes commonly used in Daniell-type cells. This helped prolong the life of the battery when not in use.

The potential of the battery was greater than the Daniell cell at about 1.5 V. As a result, Leclanché could claim that 24 of his cells could replace 40 Daniell cells. The current output was also greater when compared to a similarly sized Daniell cell.

The Leclanché cell performed better at low temperatures than the Daniell cell, which tended to freeze during the winter months. In an experiment to demonstrate this, a Leclanché battery was found to be capable of ringing an electric bell at temperatures at least down to –16°C. On the other hand, a saturated copper sulfate solution of the kind used in the Daniell cell froze at –5°C.

There was little maintenance necessary with Leclanché cells. At one French railway station, the same Leclanché batteries were in use for over nine years, from 1867 to 1876. The electrolyte was replenished once—the only expense incurred during that time.

For these reasons, the Leclanché cell supplanted the Daniell cell and was the most commonly used type for applications that required intermittent power, such as telegraphs and electric bells, by 1880.

The Dry Cell

The important uses of battery-generated electrical power throughout much of the nineteenth century generally involved stationary applications, like telegraph installations and railway signals. Wet cells containing a large amount of liquid electrolyte, like the Daniell and Leclanché cells, were adequate for these purposes. However, it would be even more convenient, especially for portable applications, if there was not a large amount of electrolyte solution that could be easily spilled.

Dry cells, batteries with sparing amounts of electrolyte (more like drier cells), had been considered occasionally since Volta's time. Although a dry form of the zinc–manganese dioxide cell was described by Leclanché in his patent, German scientist Carl Gassner is credited with developing the first commercially successful Leclanché dry cell in 1886.

Gassner's cell design cleverly conserved space by using zinc as the container as well as the anode material (Figure 3-7). Now batteries are starting to look like the batteries that are familiar to us today. This is the same basic design that has been used for Leclanché dry cells ever since.

The Leclanché dry cell, which is also called (although not very descriptively) a zinc-carbon or a zinc-chloride cell, was more convenient to handle without all of the extra liquid electrolyte.

The first battery of this type on the market was cylindrical—3 inches in diameter by 7 inches tall. Compare this to a Leclanché wet cell that was 4 inches square by over 6 inches high and contained one pint of electrolyte solution.

The Leclanché dry cell gained rapid and widespread popularity. By 1900, something on the order of 2 million Leclanché cells were manufactured annually in the United States alone. The number was over 40 million by 1910 and close to 2 billion in the 1950s. This battery system was one of the most important throughout the twentieth century.

The flexible design of the Leclanché dry cell meant that smaller batteries could be built. Smaller batteries are, of course, more practical for portable devices. One of the more enduring portable devices that uses smaller batteries is the flashlight. Invented

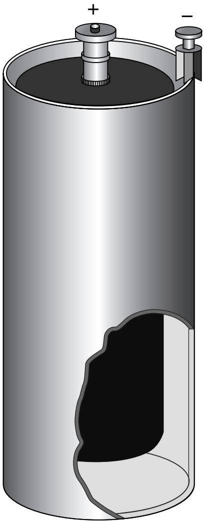

FIGURE 3-7 **The Gassner dry cell derived from the battery chemistry developed by Leclanché**

in the United States by novelty store owner Conrad Hubert in 1898, it was at first considered to be impractical. However, it soon gained acceptance and commercial success as an alternative to kerosene lamps and candles.

The success of the Leclanché dry cell, particularly the smaller, cylindrical types for applications like flashlights, at least partially encouraged the founding of new battery companies. The first commercial dry cell manufacturer in the United States was the National Carbon Company in 1896, later merging with Union Carbide, renamed to the Eveready Battery Company, and finally becoming Energizer. A close follower was the French Battery Company in 1906, which became Ray-O-Vac, later changed its name to Rayovac, and now is part of Spectrum Brands.

The first commercial radio broadcast was in 1920 by the Westinghouse Electric Company in Pittsburgh, Pennsylvania. At first, radio receivers were battery operated, but by the late 1920s they were largely powered by the electrical power grid.

The unqualified success of the Leclanché dry cell for a variety of applications drove further developments. Improvements to the Leclanché dry cell continued after its introduction. The capacity of the prevalent 6-inch dry cell improved from 10 ampere-hours to about 50 ampere-hours in the 1950s. This dramatic increase in performance came from improvements in battery quality through design modifications and using better materials, particularly higher-purity manganese dioxide.

One variation of the Leclanché dry cell replaced the zinc anode with a magnesium anode, which also served as the container. This battery was used primarily for military applications.

Alkaline Batteries

The next advance in primary battery technology came with the development of alkaline cells. Alkaline electrolytes were investigated intermittently from the early days of battery research. Yet, it wasn't until the zinc–copper oxide wet cell arrived on the scene, invented in 1881 by Felix de Lalande and Georges Chaperon, that an alkaline cell saw commercial success.

Zinc–copper oxide wet cells largely supplanted the Daniell and Leclanché wet cells that were used for applications, like railway and other signal installations and for telephone and telegraph communication circuits. Although the Lalande-Chaperon wet cell was useful for stationary applications, smaller zinc–copper oxide dry cells were not accepted as well for portable applications as the Leclanché dry cells.

During World War II, the military needed batteries for their equipment with high energy densities (that is, more electricity delivered per battery volume) and long storage life under a wide range of environmental conditions—from the cold winters in Northern Europe to the heat and humidity in the tropical South Pacific. In particular, Leclanché dry cell performance was negatively affected by the high temperature conditions.

American battery engineer Samuel Ruben developed the alkaline zinc-mercury oxide dry cell starting in 1942. This battery was capable of enduring harsh storage and operating conditions over prolonged periods of time. Ruben teamed with the Mallory Battery Co. to manufacture these batteries for the war effort.

This battery technology was important enough that the U.S. Signal Corps gave it a confidential classification. They were used in Walkie-Talkies, a portable radio transmitter carried like a backpack, and the handheld Handie-Talkies. Production reached over one million zinc-mercury oxide batteries per day by the end of the war.

Use of zinc-mercury oxide batteries continued after the war. Smaller batteries were developed for several applications.

One of the first postwar applications for zinc-mercury oxide batteries was hearing aids. The first portable, battery-operated radios developed in the 1930s led to the invention of the first portable hearing aid in 1937. The device used vacuum tubes and was the size of a lunch box. It was small enough to be carried around by the hearing aid user, but not very conveniently. With the introduction of smaller zinc-mercury oxide cells, and the development of electronic components to replace vacuum tubes, wearable hearing aids became available.

Another notable use of zinc-mercury oxide batteries was in early cardiac pacemakers, from 1958 until they were replaced by lithium batteries in the mid-1970s.

Alkaline electrolyte batteries—zinc-mercury oxide, zinc–silver oxide, and zinc-air—became a mainstay in many applications, including hearing aids, watches, and calculators. Some are still used today. However, it is the zinc–manganese dioxide alkaline cell that has had the largest impact in the consumer market.

Alkaline zinc–manganese dioxide wet cells were described in 1882, and dry cells, in 1912. However, it wasn't until 1949 that alkaline zinc–manganese dioxide dry cells were manufactured commercially by Ray-O-Vac. They were coin cells about the size of a dime and were called crown cells. They looked like they were made from crimped bottle caps. Multiple cells were used in hearing aids and portable radios.

Substantial commercial success of the alkaline zinc–manganese dioxide batteries took off in 1959 when Union Carbide Corporation produced them in the standard cylindrical shapes and sizes we are familiar with today.

Lithium Batteries

Development of lithium batteries started in the late 1950s and continues today in response to military and space applications requiring high power density, higher energy density, and lighter weight. This last requirement is particularly important for space vehicles because of the high cost per pound of launching them into orbit.

Lithium metal has a low density and a high potential, so it was a natural choice for anode material. Lithium batteries require nonaqueous, or aprotic, electrolytes, which are generally composed of organic solvents. So, finding suitable solvents and salts for electrolyte solutions was central to the development of lithium batteries. The nominal voltages of lithium cells can typically be somewhere between 1.5 V and 3.0 V, depending on the type of cathode material.

The extensive research and development effort led to the commercialization of a diverse selection of different types of lithium batteries during the 1970s. Some of these battery types are still manufactured today and will be described in more detail in Chapter 9.

One of the first lithium batteries launched commercially was the lithium–sulfur dioxide battery. The first patent for lithium–sulfur dioxide cells was awarded in 1969, and such cells were sold commercially by 1972. Lithium–sulfur dioxide batteries were largely replaced in many applications by lithium–thionyl chloride batteries starting in the late 1970s because of their higher energy density, longer shelf life, and ability to function well at elevated temperatures.

Sulfur dioxide and thionyl chloride are liquid cathode materials. Many more varieties of the solid-cathode lithium batteries were developed during the 1960s and 1970s. Among these were (and this is not an exhaustive list) copper oxide, copper sulfide, iron disulfide, silver chromate, vanadium pentoxide, manganese dioxide, and carbon monofluoride.

The last two systems are commonly used today in consumer, medical, and industrial applications. Lithium–carbon monofluoride batteries were first commercialized in Japan by the Matsushita Battery Industrial Company in 1973, while lithium–manganese dioxide batteries were introduced to the market in 1976.

Lithium-iodine batteries replaced zinc-mercury oxide batteries in pacemakers starting in the early 1970s. A pacemaker powered by a lithium-iodine battery was developed by Wilson Greatbatch and first implanted in 1972.

Secondary Batteries

The secondary, or rechargeable, battery was first reported by Ritter in 1805. They were called storage batteries or accumulators (as in, perhaps, electrical energy accumulators) at the time and were charged by primary batteries.

Successful implementation of a secondary battery did not occur until French physicist Gaston Planté started experiments that produced the first useful secondary battery in 1859. His battery consisted of two sheets of lead separated by rubber strips or a felt separator, wound into a spiral, and immersed in a 10 percent sulfuric acid solution (Figure 3-8). The electrodes were activated by repeated discharge and charge cycles using other batteries composed of, for example, three Daniell cells. This process forms the lead dioxide cathode material and lead sulfate at the surface of both cathode and anode.

The Planté battery was improved in 1879 by R.L. Metzger, then around 1881 by Camille A. Faure in France and, independently, by American scientist Charles F. Brush. The credit is generally given to Faure, though. They applied lead dioxide mixed with sulfuric acid as a paste on the lead electrode. Rather than relying solely on the discharge-charge formation process as with the Planté, the lead dioxide material was installed in the battery during manufacture.

This development resulted in one of the most commercially successful and widely used battery systems, even today. The Planté-Faure-Brush lead acid battery helped to make electric vehicles possible during the late nineteenth and early twentieth centuries. By 1900, nearly 40 percent of automobiles in the United States were powered by batteries. Over 33,000 electric cars were registered in the United States in 1912.

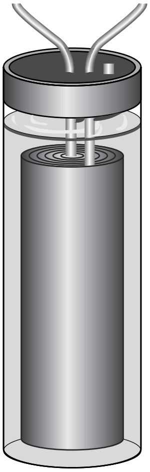

FIGURE 3-8 The Planté battery consisted of spiral-wound lead electrodes in sulfuric acid. This was the progenitor of the familiar lead acid battery used for car ignition and emergency lighting today.

The first gasoline cars were considered to be unreliable and noisy. However, as gasoline engines improved and batteries were used instead to start engines, thereby replacing the hand crank, the production of electric–powered vehicles declined.

A competitor to the lead acid battery in the early twentieth century was the alkaline nickel-iron secondary battery, which was launched commercially by Edison Storage Battery in 1910 following years of research and development. Thomas Edison was already familiar with batteries from his work with zinc–copper oxide and cadmium-copper cells. In 1898, Edison started investigating ways to replace the lead acid battery with a lighter, more reliable secondary battery. He was particularly interested in supplying secondary batteries for transportation applications like electric trucks and cars, mine locomotives, and yacht lighting.

At about the same time as Edison was working on his nickel-iron battery, a similar type of battery was patented by Waldemar Jungner of Sweden in 1899—the nickel-cadmium secondary battery. This type of battery gained increasing popularity starting around 1930 in Europe for bus and truck starting and lighting, train lighting, and mine lamps. Later in the century, smaller nickel-cadmium batteries were manufactured for portable applications like wireless telephones.

Two other commercially popular rechargeable batteries—especially nickel–metal hydride and lithium ion—were developed more recently.

Nickel–metal hydride batteries were commercialized around 1990. In this type of battery, the metal negative electrode reacts with hydrogen to form a metal hydride during charging. Battelle Memorial Institute disclosed the use of titanium and nickel negative electrode material in 1967. Later, improved alloys composed primarily of nickel, along with rare earth metals, especially lanthanum, resulted in the highly functional negative electrode material used in today's nickel–metal hydride batteries. The nickel oxyhydroxide positive electrode used in nickel–metal hydride batteries was developed by Japanese scientists in 1989.

Lithium ion also involved a convergence of a couple of different electrode technologies. New metal sulfide and metal oxide positive electrode materials were developed, including titanium disulfide and lithium cobalt oxide. Since then there have been many other rechargeable lithium ion positive electrode materials investigated. The graphite negative electrode material was initially investigated in the early 1980s. Lithium ion batteries were first produced commercially by Sony in 1991.

Nickel–metal hydride and lithium ion batteries will be covered in more detail in Chapter 9.

Battery Time Lines

Time lines marking the key developments in primary and secondary batteries are shown in Figures 3-9 and 3-10, respectively.

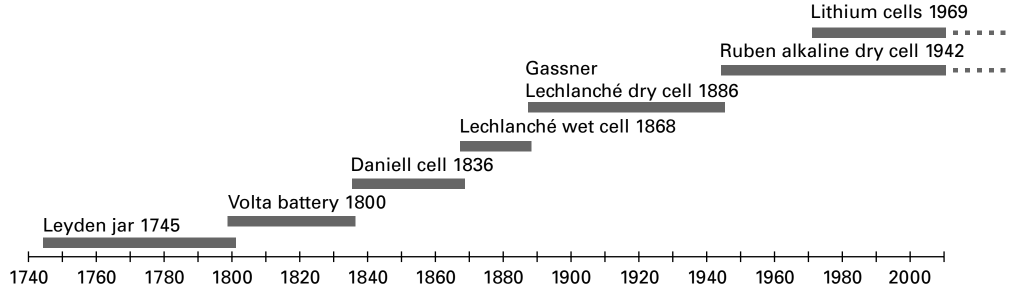

FIGURE 3-9 Primary battery milestones

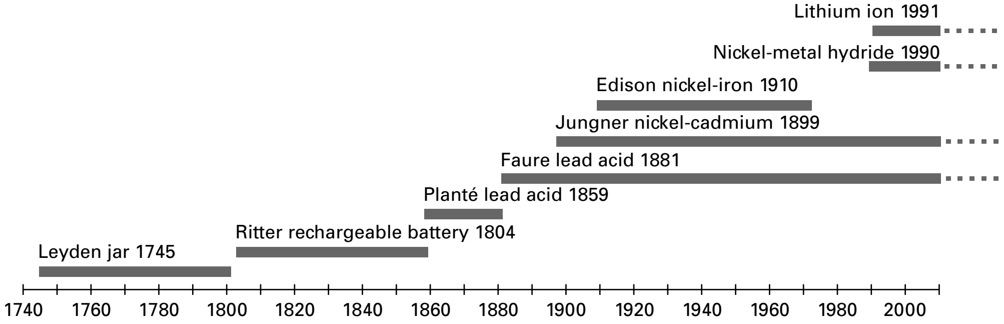

FIGURE 3-10 Secondary battery milestones

Chapter 4

Basic Physics and Chemistry

IMPORTANT CONCEPTS FROM THIS CHAPTER:

- Working with numbers and units of measure
- Matter, substances, and compounds
- Atoms, molecules, and ions
- Electrical charge
- Chemical reactions and energy

On the outside, batteries seem to be rather simple. No moving parts, and the only thing needed get them to work is to make the proper electrical connections. You can happily use batteries without ever knowing anything else about how they work. However, it just might help to get a deeper insight into the basic science and engineering of batteries, particularly if you design applications that use batteries, but also if you are an end user of batteries.

The electricity produced by batteries involves conversion of chemical energy into electrical energy through what are called electrochemical reactions. As a result, the underlying mechanisms of battery operation can be described by theories and concepts from physics and chemistry.

In this, and the next two chapters, some of the key concepts behind battery operation and design are introduced at a high level. Taken together, they present the same information that battery developers must understand to design a battery that functions efficiently, safely, and reliably. No difficult mathematical equations or quantum mechanics or complicated chemical reaction schemes are needed—just enough of some concepts from physics and chemistry to help impart a basic understanding of how batteries function.

This chapter includes descriptions of the building blocks of the chemical substances used in batteries: atoms, molecules, and ions. Following that is a discussion about the interactions that occur between them during chemical reactions. The next chapter will build on these essential concepts to describe in more detail those most relevant to battery operation, particularly electrochemical reactions.

What follows is not a comprehensive or an in-depth look at physics and chemistry. For more information, there are many good physics or chemistry books available.

Before we get into the concepts, we first need to understand some of the language of science: numbers and units of measure.

Writing Large and Small Numbers

Scientists and engineers measure quantities that are extremely small, extremely large, and everywhere in between. Battery scientists and engineers are no different. An example of a large number is the speed of light at about 300,000,000 meters per second in a vacuum. On the other hand, the weight of an *E. coli* cell is on the order of 0.000000000001 grams. Other quantities can be considerably larger or smaller or anywhere in between. It is rather unwieldy to work with numbers of this sort, so methods and abbreviations were devised to express more simply such wide-ranging numbers.

We use a base 10 number system in our everyday use of numbers. The number 1,200,000 (one million two hundred thousand) can be expressed as $1.2 \times 1{,}000{,}000$. One million, 1,000,000, equals $10 \times 10 \times 10 \times 10 \times 10 \times 10$, or 10^6 when written as a power of ten, also called exponential notation. So, 10^6 is shorthand for writing 1,000,000. Thus, 1,200,000 may be written as 1.2×10^6. Likewise, 0.0000012 can be written as 1.2×0.000001, or $1.2 \div 10 \div 10 \div 10 \div 10 \div 10 \div 10$ or 10^{-6} as a power of ten. The number 0.0000012 becomes 1.2×10^{-6}. This way of writing numbers, called scientific notation, greatly simplifies the expression of very large and very small numbers. The value for the speed of light in a vacuum can now be written as 3×10^8 meters per second rather than 300,000,000.

Another way to write numbers is a variation of scientific notation called engineering notation. Like scientific notation, it uses base 10 exponential notation. However, engineering notation uses the powers of ten in multiples of three (10^3, 10^6, 10^9, … and 10^{-3}, 10^{-6}, 10^{-9}, …). The speed of light in engineering notation is about 300×10^6 meters per second.

Yet another way to simplify writing some numbers is to use abbreviated prefixes to units of measure that symbolize a power of 10. These abbreviations are part of the International System of Units, or SI (which really stands for Système International—the French language version) and are given in Table 4-1.

There are certain advantages to engineering notation, but we will use scientific notation or the SI prefixes here, as they seem to be more commonly used.

TABLE 4-1 Selected SI Prefixes and Abbreviations for Common Powers of Ten

Number	Power of 10 (exponential notation)	Prefix	Abbreviation
0.000000000000000001	10^{-18}	atto	a
0.000000000000001	10^{-15}	femto	f
0.000000000001	10^{-12}	pico	p
0.000000001	10^{-9}	nano	n
0.000001	10^{-6}	micro	μ
0.001	10^{-3}	milli	m
0.01	10^{-2}	centi	c
1,000	10^{3}	kilo	k
1,000,000	10^{6}	mega	M
1,000,000,000	10^{9}	giga	G
1,000,000,000,000	10^{12}	tera	T

Units

Measurement units for physical quantities are standardized by the International Bureau of Weights of Measures. These units are part of the International System of Units, or SI (Système International) units. They are used worldwide, at least by scientists and engineers, but some of the units may be familiar to most of us as part of the metric system. The basic units are given in Table 4-2. (There is one other SI unit not included in Table 4-2, the candela, which is the unit of light intensity and is not necessary to include for our purposes.)

TABLE 4-2 Selected SI Units and Abbreviations

Basic Quantity	Name	Symbol for Unit
length	meter	m
mass	kilogram	kg
time	second	s
electric current	ampere	A
temperature	kelvin	K
amount of substance	mole	mol

TABLE 4-3 Units Derived from SI Units and Their Abbreviations

Quantity	Name	Symbol for Unit
area	square centimeter	cm^2
volume	cubic centimeter	cm^3
density	gram per cubic centimeter	$g\ cm^{-3}$
energy	joule	J
power	watt	W
electric charge	coulomb	C
electrical potential electromotive force voltage	volt	V
electrical resistance	ohm	Ω

One note about the mole. This unit represents a number of atoms. By international agreement, a mole is the number of atoms in 12 g of the carbon isotope carbon-12. This comes to 6.022×10^{23} carbon atoms per mole and is called the Avogadro constant after Italian scientist Amedeo Avogadro. A mole can refer to a number of atoms, ions, or molecules.

Other important units, like volume (cm^3), volts (V), and joules (J), can be calculated from the quantities in Table 4-2 along with the unit prefixes in Table 4-1. Units commonly used in this book that are derived from SI units are given in Table 4-3.

The units in Tables 4-2 and 4-3 can be used with the powers of 10 abbreviations for convenience. For example, 0.001 V can be abbreviated as 1 mV, 0.01 m is also written as 1 cm, 1 fA is 1×10^{-15} A, and so on.

Electrons

Electrons play a major role in our understanding of batteries. They are exchanged between chemical species (elements and compounds). We often say that electrons are both produced and consumed in the chemical reactions, but this is only from the perspective of the reacting chemicals. The electrons, of course, are there all along. They just become redistributed during battery use.

Now, electrons carry a negative charge and a surfeit or deficit of electrons creates an overall negative or positive electrical charge, respectively. Generally, nature does not like charge unbalance. Separation of oppositely charged species is relatively common in nature, but nature prefers electroneutrality, or electrical balance with the positive charges equaling the negative charges. Separation of oppositely charged species can happen; it just takes the right amount of energy to make it happen.

Atoms

For the level of physical and chemical understanding we need here, we can limit our discussion to *atoms* as the basic building blocks of matter, as well as the *electrons, protons,* and *neutrons* that form atoms.

Nobel laureate chemist Linus Pauling wrote in his 1955 *College Chemistry* textbook, "The properties of any kind of matter are most easily and clearly learned and understood when they are correlated with its structure, in terms of the molecules, atoms, and still smaller particles that compose it." Stated in a less elegant way, understanding chemical properties and chemical reactions is linked to knowledge of the differences between various atoms and the many ways they assemble themselves into molecules.

Of course, there is an amazingly large array of elementary and composite subatomic particles—quarks, bosons and many others—that are known. Describing the interactions between these subatomic particles may provide a more comprehensive picture of how the world works. However, continuing with the building block analogy, they are more akin to the shale, clay, and sand that compose the building block. The type of building block used and how the blocks are arranged are more suited to describing the architecture and other properties of the structure built from the blocks.

Atoms are made of three basic constituents: electrons, protons, and neutrons. One of the key characteristics of these three components is their electrical charge. There are two electrical charges: positive and negative. Objects with opposite electrical charges are attracted to each other. Protons have a positive charge, while electrons have a negative charge. As the name suggests, neutrons have no charge; they are electrically neutral.

Now, atoms consist of a nucleus formed by protons and neutrons that are bound together by nuclear forces. Electrons spend their time in the space surrounding the nucleus. The usual depiction of an atom shows one or more electrons orbiting a

Ancient Atoms

The first formulation of atomic theory dates back at least as far as the fifth century BC. That is when Greek philosophers Leucippus and Democritus speculated that atoms are indivisible, indestructible units that form all matter. Everything else is empty space—a vacuum. Of course, we now know that atoms are divisible and destructible, but this is such an amazing idea to come up with some 2,500 years ago.

Modern atomic theory, the one that is familiar to us today, was forwarded by English chemist and physicist John Dalton early in the nineteenth century. A key part of Dalton's theory states that not only is all matter composed of atoms but the atoms of each element have characteristics that are different from other elements.

Especially important for the study of chemistry, it provided a framework to understand the properties of chemical elements and molecules. Atomic weights are expressed with a unit termed daltons in recognition of Dalton's accomplishment.

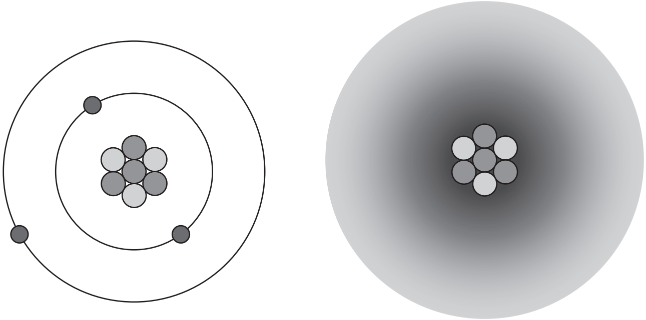

FIGURE 4-1 Different pictorial representations of a lithium atom with three protons, four neutrons, and three electrons

nucleus of protons and neutrons, like planets around the sun (see Figure 4-1). This representation is not scientifically accurate, but it easy to visualize, presumably because it is reminiscent of planetary motion around our sun that is so familiar.

A better way to imagine an atom is as a cloud surrounding a nucleus (Figure 4-1). The electrons are somewhere in a volume of space around the nucleus, rather than in distinct orbits. The cloud actually represents the probability of where the electrons may be found at any given time.

All atoms are composed of the same three particles: electrons, protons, and neutrons. Yet different types of atoms can have very different properties. How is this so? It is the numbers of neutrons and protons in an atomic nucleus that impart the distinct chemical identity of an atom, and thus its chemical and physical properties. Indeed, scientists use the number of protons in the nucleus, called the atomic number, as a way to identify a chemical *element.* Each chemical element has a different number of protons in its nucleus and its own atomic number representing that number. The familiar periodic table (Figure 4-2) is arranged to combine elements with certain similar properties in columns.

Electrical Charges in the Atom

Opposite electrical charges (negative and positive) are attracted to each other. Since opposite charges attract, then why don't the electrons encircling the nucleus crash into the protons? How electrons remain around the nucleus ultimately involves concepts described by quantum mechanics that overcome the electrostatic attraction between electron and proton.

On the other hand, like charges (negative and negative or positive and positive) repel each other. So then, why don't the protons in the nucleus fly apart? The answer is the presence of attractive nuclear forces strong enough to offset the tendency of protons to repel each other.

Decreasing electronegativity

Increasing electronegativity

hydrogen 1 H																	helium 2 He
lithium 3 Li	beryllium 4 Be											boron 5 B	carbon 6 C	nitrogen 7 N	oxygen 8 O	fluorine 9 F	neon 10 Ne
sodium 11 Na	magnesium 12 Mg											aluminum 13 Al	silicon 14 Si	phosphorus 15 P	sulfur 16 S	chlorine 17 Cl	argon 18 Ar
potassium 19 K	calcium 20 Ca	scandium 21 Sc	titanium 22 Ti	vanadium 23 V	chromium 24 Cr	manganese 25 Mn	iron 26 Fe	cobalt 27 Co	nickel 28 Ni	copper 29 Cu	zinc 30 Zn	gallium 31 Ga	germanium 32 Ge	arsenic 33 As	selenium 34 Se	bromine 35 Br	krypton 36 Kr
rubidium 37 Rb	strontium 38 Sr	yttrium 39 Y	zirconium 40 Zr	niobium 41 Nb	molybdenum 42 Mo	technetium 43 Tc	ruthenium 44 Ru	rhodium 45 Rh	palladium 46 Pd	silver 47 Ag	cadmium 48 Cd	indium 49 Rb	tin 50 Sn	antimony 51 Sb	tellurium 52 Te	iodine 53 I	xenon 54 Xe
cesium 55 Cs	barium 56 Ba	57 through 71	hafnium 72 Hf	tantalum 73 Ta	tungsten 74 W	rhenium 75 Re	osmium 76 Os	iridium 77 Ir	platinum 78 Pt	gold 79 Au	mercury 80 Hg	thallium 81 Tl	lead 82 Pb	bismuth 83 Bi	polonium 84 Po	astatine 85 At	radon 86 Rn
francium 87 Fr	radium 88 Ra	89 through 103	rutherfordium 104 Rf	dubnium 105 Db	seaborgium 106 Sg	bohrium 107 Bh	hassium 108 Hs	meitnerium 109 Mt	darmstadtium 110 Ds	roetgenium 111 Rg							

lanthanum 57 La	cerium 58 Ce	praseodymium 59 Pr	neodymium 60 Nd	promethium 61 Pm	samarium 62 Sm	europium 63 Eu	gadolinium 64 Gd	terbium 65 Tb	dysprosium 66 Dy	holmium 67 Ho	erbium 68 Er	thulium 69 Tm	ytterbium 70 Yb	lutetium 71 Lu
actinium 89 Ac	thorium 90 Th	protactinium 91 Pa	uranium 92 U	neptunium 93 Np	plutonium 94 Pu	americium 95 Am	curium 96 Cm	berkelium 97 Bk	californium 98 Cf	einsteinium 99 Es	fermium 100 Fm	mendelevium 101 Md	nobelium 102 No	lawrencium 103 Lr

FIGURE 4-2 The periodic table of the chemical elements with their atomic numbers

Each element also has a unique name and abbreviation to simplify writing chemical formulas. For example, hydrogen (elemental symbol H) is the lightest element, has one proton in its nucleus and has an atomic number of 1. Uranium (elemental symbol U) is the heaviest element found naturally (at least in any significant quantity) with 92 protons in its nucleus, and so it is assigned an atomic number of 92.

Then there are neutrons. They are not positively charged like protons and not negatively charged like electrons. Rather, they have no charge at all. The number of neutrons in the nucleus of an element can vary, at least within certain limits. They do not change the chemical identity of the element as the number of protons do, but rather they can change the properties of the element in other ways, including destabilizing the nucleus leading to nuclear fission and radioactive emissions. Atoms with the same number of protons (the same chemical element), but with different numbers of neutrons, are called isotopes.

Element Names

By the way, not all elemental symbols are simply abbreviations of the English versions of their names, like hydrogen, H, and uranium, U. Some of the elemental symbols derive from their Latin names. For example, the symbol for the element sodium is Na (Latin *natrium*), lead is Pb (Latin *plumbum*), and silver is Ag (Latin *argentum*).

Matter, Substances, and Their Properties

First, some basic definitions. Matter is anything that occupies space and has mass. That sure covers a lot of ground, but scientists organize matter into various categories based on its physical and chemical properties (Figure 4-3).

Matter can be found as a gas, liquid, or solid. A specific type of matter is called a *substance.* Oxygen is a substance. Water is a substance. Polyethylene is a substance.

Substances have physical and chemical properties that are characteristic of that substance. There are intensive and extensive physical properties. Extensive physical properties depend on the amount of a substance, like mass or volume. Intensive physical properties do not depend on the amount of a substance, like color or melting point. The density of a substance is an intensive physical property, although it may be calculated from two extensive physical properties—mass and volume.

Chemical properties describe the how matter changes from one substance to another through a chemical reaction.

Elements are simple forms of matter and, as mentioned earlier in this chapter, are identified by a particular atomic configuration. Different elements can chemically combine to form a pure substance called a *compound.* Compounds have different physical and chemical properties from their constituent elements. The elements in a given compound are found in specific proportions. Water, H_2O, is a compound composed of hydrogen and oxygen in the ratio two parts hydrogen to one part oxygen. This ratio is the same for every molecule in a glass of pure water.

Substances can be combined into *mixtures.* The composition of a mixture is variable, depending on how much of one substance is added relative to another. In a homogeneous mixture the substances are thoroughly blended such that the

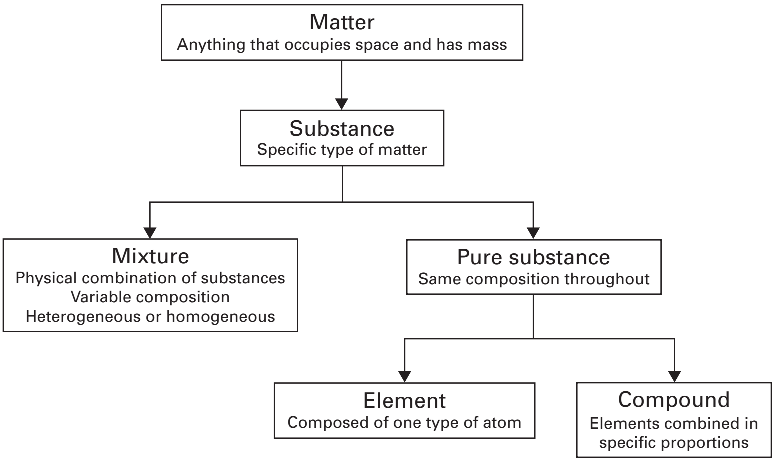

FIGURE 4-3 Categories of matter

mixture appears uniform throughout. A solution of sugar dissolved in water and the aqueous potassium hydroxide electrolyte solution in a nickel–metal hydride battery are homogeneous mixtures. The substances in a heterogeneous mixture remain physically separate, even if it is on a microscopic scale. Toothpaste and the manganese dioxide cathode mix of an alkaline battery are heterogeneous mixtures.

There are three empirical laws that summarize the combination of elements to form compounds.

The first is the law of conservation of mass: mass is neither created nor destroyed in chemical reactions. In other words, the total mass of all reactants involved in a chemical reaction equals the total mass of all products resulting from the reaction, at least at a macroscopic level. Albert Einstein expressed the relationship between mass and energy, $E = mc^2$, which says that energy changes occurring during a chemical reaction is accompanied by mass changes. However, the changes in mass are so small under normal circumstances that in a practical sense we can say that mass is conserved.

The law of definite proportions states that in a pure chemical compound, the different elements making up the compound are always found in definite proportions by mass. For a molecule like water, H_2O, there are two hydrogen atoms, weighing 1 g mol^{-1} (that is, 1 gram per mole) each, for every oxygen atom that weighs 16 g mol^{-1}. So, there is 1 g of hydrogen for every 8 g of oxygen, regardless of how much water there is. A small drop and a swimming full of water have the same proportion of hydrogen to oxygen by mass.

Another way atoms form compounds is explained by the law of multiple proportions. When two or more atoms of different elements react, the numbers of the atoms of each element in each molecular unit are whole numbers. For example, a carbon atom can bond with one oxygen atom to form carbon monoxide, CO. The ratio is 1 to 1 carbon to oxygen atoms. A carbon atom can also combine with two oxygen atoms to yield carbon dioxide, CO_2. Here, the ratio of carbon to oxygen atoms is 1 to 2.

Molecules, or chemical compounds, are denoted by chemical formulas consisting of the elemental symbols in the correct proportions. CH_3CH_2OH is the chemical formula for ethanol: two carbon, one oxygen, and six hydrogen atoms are part of every ethanol molecule. The formula is written in a way that illustrates, in a simple way, which atoms are directly connected. Three of the hydrogen atoms are bound to one of the carbon atoms (called a methyl group). Two more of the hydrogen atoms are bound to the other carbon atom (a methylene group). The sixth hydrogen atom is bound to the oxygen atom (a hydroxyl group). The two carbon atoms are also bound to each other, as are the oxygen atom and the carbon atom in the center of the molecule.

The formula for ethanol can also be written like so: C_2H_6O. This is the empirical formula for ethanol. Empirical formulas are a simple tally of the different atoms in a molecule. There may be a number of molecules that have the same empirical formula, though. Dimethyl ether has the same empirical formula as ethanol, but it is a very different molecule. The chemical formula for dimethyl ether, CH_3OCH_3, is more representative of the manner in which the atoms are connected.

Molecules and Bonding

Like blocks stacked to build a wall, atoms come together to form molecules. Most of the matter on Earth is composed of molecules, or compounds, rather than their constituent elements. The type of molecule that forms, and likewise the chemical and physical properties of the molecule, is dependent on the types of atoms involved, their proportions and energy.

When two or more atoms come together to form molecules (only one of several types of chemical reactions), there is a change in the structure of the electrons around the nuclei of the atoms. There are a number of different ways for these changes to manifest themselves, but we will concentrate on two: covalent and ionic.

For some reactions involving the combination of certain types of atoms, the electrons from each atom can be shared between the atoms. This type of bonding between atoms to form a molecule is called a *covalent* bond. An example of a covalent bond is the formation of a hydrogen molecule, H_2, from two hydrogen atoms. In this case, the electron from each hydrogen atom is shared equally between them.

For a molecule like water, H_2O, each hydrogen atom shares its electron with the oxygen atom and the oxygen atom shares a couple of its electrons with each hydrogen atom. In this case, however, the sharing is not equal and it depends on the electronegativity of the individual atoms sharing the bond. Electronegativity is a property of atoms that gauges their attraction to electrons. The more electronegative the atom, the better it is at attracting electrons. Generally, electronegativity tends to increase for elements in the periodic table (Figure 4-2) from left to right and from bottom to top. The trend in electronegativities gets a little more complicated in the middle of the periodic table, though.

Oxygen is somewhat more electronegative than hydrogen, meaning that it has a greater pull on electrons than the hydrogen atoms do. As a result, the electron density on each hydrogen atom is shifted somewhat in the direction of the oxygen atom.

Of course it's not just atoms that can combine to form molecules. Molecules can react with atoms or other molecules to form new molecules or ions. Molecules can consist of just two atoms like in hydrogen gas, H_2, or millions of atoms as in DNA molecules.

Ions

An *ion* forms when a neutral atom or molecule adds or loses one or more electrons, leading to negative or positively charges on the atom or molecule. *Anions* are negatively charged ions, and *cations* are positively charged ions. Ions can also form

Two in One

When two atoms of the same element are bonded together, it is called a diatomic molecule. Familiar examples of diatomic elements are nitrogen (N_2), oxygen (O_2), and chlorine (Cl_2).

when ions combine with neutral atoms or molecules, as in the case of hydrogen atom (H^+) associating with ammonia (NH_3) to form the ammonium ion (NH_4^+).

When an atom loses or gains electrons, whether part of a molecule or alone, its oxidation state changes. The *oxidation state* or *oxidation number* is the charge, positive or negative, an atom would have if it existed in isolation. It is a way to keep track of what element has what charge. A few rules govern oxidation states:

- The oxidation state of a free, uncombined atom is zero.
- The oxidation state is equal to the net charge on an ion consisting of a single atom, assuming all of the charge is localized at the atom (no partial charges).
- The sum of the oxidation states of all atoms in a neutral molecule is zero.
- The sum of the oxidation states of all atoms in an ion must be equal to the charge on the ion.

Atoms of the element barium can give up two electrons to form barium ions, Ba^{2+}, also written Ba(II). The oxidation state of the elemental form of barium is 0, and for the barium ion, it is +2. Bromine atoms can accept an electron to produce bromide ions, Br^-. The oxidation state of bromine is 0, and it is −1 for each bromide ion.

There are many ions composed of multiple atoms, such as sulfate, SO_4^{2-}. In this example, the oxidation state of each oxygen is −2, and it is +6 for the sulfur. The net charge on sulfate, then, is $6 + 4 \times (-2) = -2$.

Rather than sharing electrons as in covalent bonds, ionic bonds are more electrostatic in nature, wherein positively charged ions will associate with negatively charged ions. When oppositely charged ions come together and form a solid, the result is called an *ionic solid* or a *salt.* The proportion of ions in a salt depends on their charges. For sodium chloride (NaCl), one sodium ion, Na^+, with a +1 charge combines with one chloride ion, Cl^-, with a −1 charge. For a magnesium ion, Mg^{2+}, which has a charge of +2, the ratio is 2 Cl^- for every Mg^{2+} to yield $MgCl_2$.

Chemical Reactions

A chemical reaction is a process wherein atoms, molecules, or ions join together or split up or exchange electrons. The reacting atoms, molecules, or ions are called *reactants.* The new atoms, molecules, or ions that are formed as a result of a chemical reaction are called *products.*

Chemical equations are simple ways to convey the chemical changes from reactants to products. Reactants are collected on the left-hand side of the equation and the products on the right. An arrow (→) pointing to the right shows the direction of the reaction. For some reactions, a double arrow (⇆) is used to show that a reaction is occurring in both directions and is in equilibrium. That is, the rate of the forward reaction (from left to right) is equal to the rate of the backward reaction (from right to left).

The reaction of calcium carbonate, $CaCO_3$, with hydrochloric acid, HCl, yields calcium chloride, carbon dioxide, and water and is written this way:

$$CaCO_3 + 2\ HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

The number of each element is the same on both sides of the equation—one calcium, one carbon, three oxygen, two chlorine, and two hydrogen atoms. The only difference is how they are combined.

Note that we had to include two hydrochloric acid molecules to be sure the numbers of atoms are equal. This way the chemical equation is balanced. A balanced chemical equation is very important to accurately represent the chemical changes that are occurring in a reaction.

Of the different types of chemical reactions that occur, there are a few that are most relevant to understanding how batteries work.

In chemical reactions that form ions, there is a complete transfer of electrons from one atom to the other. The reactant that gives up electrons is called a *reductant,* and the reactant that takes up electrons is called an *oxidant.* This type of reaction is called an oxidation-reduction reaction, often contracted to redox reaction.

For example, a lithium atom, Li, will react with a fluorine atom, F, to form the ionic compound lithium fluoride (LiF). (Actually, under normal circumstances elemental fluorine exists as the diatomic molecule F_2, so the reaction equation is $2\ Li + F_2 \rightarrow 2\ LiF$.)

When an ionic compound, like sodium chloride (NaCl), is added to an appropriate solvent, like water, the ionic compound dissolves to form a homogeneous mixture called a *solution.* The ionic compound dissociates into its constituent ions. If water is the solvent, it is called an *aqueous* solution. If it is not water, it is called a *nonaqueous* solution.

Ionic solutions are key to most battery systems because of their use as electrolyte solutions.

Other chemical reactions that occur are combination reactions (the formation of a chemical bond between two or more elements or molecules), decomposition reactions (breaking apart a substance), and displacement reactions (exchange of one or more simple substances for others).

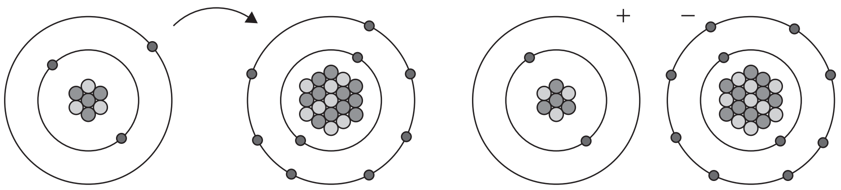

FIGURE 4-4 **Illustration of a redox reaction involving electron transfer from a Li atom to a F atom to form Li+ and F− ions**

Energy

A net amount of energy is either absorbed or released during a chemical reaction. Indeed, the change in energy that occurs is central to determining the tendency, or driving force, for a chemical reaction to proceed.

Energy represents the ability to perform work or transfer heat. Energy comes in a number of types: mechanical energy, radiant or light energy, heat or thermal energy, chemical energy, and electrical energy. It is the last three energy types that are most important in batteries. Chemical energy is converted into electrical energy during the discharge of a battery. The reverse occurs during charging of rechargeable batteries. Thermal energy comes into play as a result of the chemical reactions that occur during battery operation, and it is released when an electrical current is generated. The SI unit for energy is the joule (abbreviated J).

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Chapter 5

The Science of Batteries

IMPORTANT CONCEPTS FROM THIS CHAPTER:

- Battery active components: anode, cathode, and electrolyte
- Electrochemical cell potentials
- Electrochemical kinetics
- The theoretical capacity of battery materials

Anyone who stops at the battery display in stores that sell electronics will realize that batteries are available in a wide variety of shapes and sizes, not to mention other characteristics like voltage and capacity. Yet, all batteries have the same basic external features that the battery user interacts with: a positive terminal and a negative terminal.

The terminals are the electrical connection from the battery to the outside world. There are a wide variety of terminal designs. For example, if the battery is intended to be replaced by the user, terminals may be metal posts, as the lead posts on the top of car starter batteries, or even the battery container itself, as with common alkaline AA batteries.

The terminals are connected to an electrical conductor, such as metal wire, ribbon, clips, or springs, usually in a way that creates a low-resistance connection, like a weld joint, a solder joint, or a simple mechanical friction contact. When connected to a flashlight, a portable radio, or even a simple resistor, electrons spontaneously travel from the negative terminal to the positive terminal through the conductor (assuming the battery is sufficiently charged, of course).

This is all a casual battery user needs to know. However, if you want to get more out of the batteries you use or select the best battery for an application or, especially, design a battery that best meets the needs of your application, you need to know more about battery science and technology.

In this chapter, we first identify the active components of a battery. Next, we describe the basic reactions involved in battery electrochemistry, the cell potentials that are central to determining the battery voltage, the rates of electrochemical reactions, and the theoretical capacity of battery materials.

The Direction of Current

Current actually moves in the opposite direction as the electrons. So, the current moves from the positive to the negative terminal when a battery is in operation. It was American scientist Benjamin Franklin who defined the convention wherein current moves from positive to negative.

Like other scientists of his time, Franklin visualized electricity as a fluid. If a material had an excess amount of fluid, it had a plus or positive charge. A substance with a shortage of fluid possessed a minus or negative charge. It was a convenient theory that explained the observations from electrical experiments and played a large role in how scientists thought about electricity for a century. It wasn't until 1897 that the electron was discovered by Nobel prize winning English physicist J.J. Thomson.

Battery or Cell

Before we move on, there is one thing we should note about the use of the term "battery." In the strictest sense of the word, a battery is, as defined in *Webster's Collegiate Dictionary, Fifth Edition* (1940), "A group of two or more cells connected together, for furnishing electric current." The cell is the elementary unit for converting chemical energy into electrical energy. A battery is assembled by combining two or more cells together.

The words "battery" and "cell" are often used interchangeably to represent what is really an individual cell, though. We will generally follow the common usage of "battery" to describe the finished, packaged product, even if the battery is composed of only one cell. We will use the word "cell" when referring to an individual unit of a battery that consists of multiple cells and when discussing the electrochemistry of the active components of the battery.

The Basic Cell

All cells and batteries do the same thing: convert chemical energy into electrical energy. Each is composed of the same three active components: anode, cathode, and electrolyte. These are the only things that are needed to make a functional battery that converts chemical energy into electrical energy.

The active components of a cell are illustrated in Figure 5-1. The anode (the negative or reducing electrode) releases electrons to the external device circuit. The cathode (the positive or oxidizing electrode) accepts electrons from the external device circuit. The electrolyte is a medium containing mobile ions, with positive and negative charges (cations and anions, respectively). A complete, or closed, circuit is required to produce current and enable the cell to discharge and supply energy. The ions in the electrolyte solution serve to complete the electrical circuit within the cell.

The current may take different forms during battery discharge, but it always involves charge movement of some kind, from the flow of electrons between the

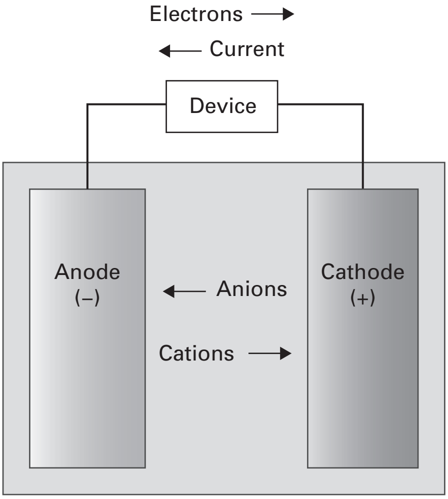


FIGURE 5-1 The basic components and operation of an electrochemical cell that is discharging spontaneously. Electrons flow through an external electrical conductor. The movement of ions in the electrolyte solution completes the circuit.

electrodes and passing through the external circuit to ions moving between the electrodes through the electrolyte and charge transfer at the electrodes.

We want the battery to operate upon connecting it to the external circuit, so the choice of electrode materials are limited to those that efficiently give up electrons for

The Origin of Electrochemistry Terms

It was English scientist Michael Faraday who developed many of the key terms we use in electrochemistry today. He wrote in 1834, "I propose using that of Electrode, and I mean thereby that substance, or rather surface, whether of air, water, metal or any other body, which bounds the extent of the decomposing matter in the direction of the electrical current." The word "electrode" is a contraction of the Greek words ήλεκτρον (electron) and όδος (a way), or a way for electrons.

Faraday arrived at the terms "anode" and "cathode" by imagining the direction of an electric current induced by the Earth's magnetic field. "Anode" comes from the Greek words άνα (upward) and όδος (a way), or the way in which the sun rises in the East. Then, "cathode" originates from κατα (downward) and όδος (a way), or the way in which the sun sets in the West.

He went on to fashion words like "electrolyte" and "ion." To differentiate between the differently charged ions, Faraday suggested, "calling those *anions* which go to the *anode* of the decomposing body; and those passing to the *cathode, cations.*"

The Real Electrodes

In the strictest sense of the terms as defined by Faraday, anode and cathode do not refer to the chemical materials that are undergoing the reactions, but rather the sites at which the electrochemical reactions occur. The anode or cathode is actually the location that accepts electrons from or releases electrons to the reactants. They are simply the carriers of the electrical current, typically called a current collector in the battery world. The anode and cathode are generally crafted from a relatively nonreactive material, like an inert metal or conductive carbon.

However, it is common in battery literature to speak of the anode and cathode as the reacting materials themselves. We will generally use anode or cathode to refer to the entire assembly—reacting material, other electrode constituents and the current collector. We will call the reactive components of the battery the anode material and the cathode material.

the anode material and those that readily accept electrons for the cathode material. The electrolyte typically is composed of a solvent containing one or more dissolved (and dissociated) salts, acids, or bases. Water is a common solvent for many battery systems, like lead acid car starter batteries or alkaline AA batteries. Organic solvents are used in battery systems like lithium and lithium ion batteries. Other electrolytes used, or at least under investigation in research laboratories, are solid ionic conductors or molten salts, including room-temperature molten salts called ionic liquids.

When the power switch of the device in Figure 5-1 is put in the "ON" or "1" position, the circuit is closed, the battery starts to discharge. Electrons move through the external circuit from the anode to the cathode. In the electrolyte anions (negatively charged ions) move from the cathode side of the cell toward the anode and cations (positively charged ions) move from the anode side of the cell toward the cathode.

There are a number of other components that make up a battery, of course. These components, which will be covered in more detail in Chapter 6 when we get into the specifics of battery design, serve to make the batteries safer to use or more efficient in terms of minimizing size or maximizing the electrical output you can get from a battery.

How those electrons come to flow and provide power to devices is the subject of the following sections. The delivery energy is all about the two *F*s: forces and flows. Thermodynamics describe the forces, while kinetics describe the flows. We build on and expand from the chemistry and physics presented in Chapter 4 to discuss some of the fundamental reactions that occur in batteries and how to harvest their energy for electrical power.

Battery Electrochemistry: Thermodynamics

In this section we discuss the forces, in the form of potentials and energy for the electrochemical reactions. There are a few thermodynamic and electrochemical concepts we must work through before we get into a deeper understanding of how batteries function and produce electricity. The first is electrochemical potential. The electrochemical potential, measured in units of volts and abbreviated as V, represents the energy of a system. Potential is an electrical force whose magnitude represents the propensity or tendency to undergo an electrochemical reaction.

The Electrochemical Cell

The electrons that flow between the positive and negative terminals are the end result of a series of complex chemical reactions that convert chemical energy into electrical energy. Since electrons are produced and consumed in these reactions, they are more specifically called *electrochemical* reactions. Electrochemistry is the study of chemical reactions that consume or produce electrons, or charge transfer between chemical substances, and the movement of charges like electrons and ions. Batteries are electrochemical power sources, meaning they supply energy by way of electrochemical reactions.

It takes two electrochemical reactions to make a battery operate—one that yields electrons and one that takes up electrons. We need to use some passive-active terminology to describe the characteristics of electrochemical reactions. These terms describe what a reactant is and what it becomes, what it does, and what is done to it.

A reaction that involves removing electrons from an atom or molecule is called an *oxidation* reaction. The valence state of the atom involved in the oxidation, and thus the overall charge on the atom or molecule that incorporates the atom involved in the reaction, is increased by one (+1) for every electron that is removed. The resulting atom or molecule is said to be oxidized. On the other hand, when electrons are added to an atom or molecule, it is called a reduction reaction and the overall charge on the atom or molecule is decreased by one (−1) for every electron added. The product atom or molecule is said to be reduced.

When an atom or molecule is oxidized, it is called a *reductant* because it is giving up electrons to an atom or molecule that is reduced. The atom or molecule that is reduced is called an *oxidant* because it is taking electrons from the atom or molecule that is oxidized.

Galvanic Cell

An electrochemical cell that discharges spontaneously when the electrodes are electrically connected is termed a *galvanic* cell. This is in honor of Italian scientist and physician Luigi Galvani, who in 1791 observed the movement of dissected frog leg muscles when contacted with dissimilar metals. He attributed this to an electric current generated by the animal itself, but fellow Italian Alessandro Volta later corrected Galvani by assigning the phenomena to the metals used, although he did not quite recognize the electrochemical nature of the electricity produced. The muscle tissue was acting as the electrolyte for the electrochemical reactions occurring at the metal surfaces. This is much like the staple of elementary school science fairs—the lemon battery wherein the lemon juice is the electrolyte for the zinc and copper metals electrodes.

For a battery to do its work, the oxidation and reduction reactions must occur spontaneously. When this happens, the battery is said to discharge. What this really means is that energy is released when the two materials are connected by an electronic conductor. This immediately limits the types of chemical compounds that can be used as active battery materials to those that can readily change their oxidation, or valence, state.

An example of a pair of electrochemical reactions is found in the Daniell cell:

$$\mathrm{Zn} + \mathrm{Cu}_{\mathrm{aq}}^{2+} \rightarrow \mathrm{Zn}_{\mathrm{aq}}^{2+} + \mathrm{Cu}$$

As it is written, this equation tells us that elemental zinc in the zero valence or oxidation state (as are all chemical elements) reacts with copper ions in the 2+ oxidation state, alternatively written as Cu^{2+}, Cu(II), or copper(II), to yield zinc ions in the 2+ oxidation state (Zn^{2+}, Zn(II), or zinc(II)) and elemental copper (Cu). For this to happen, the zinc (Zn) must lose two electrons while the copper ion picks up two electrons.

By the way, the subscript "aq" stands for aqueous, meaning this reaction is occurring in an aqueous, or water, solution. This means the copper ions are initially dissolved in solution before the reaction commences. Zinc ions end up dissolved in the solution as the transfer of electrons from zinc to copper ions occurs.

The reactions making up the Daniell cell with Zn and Cu^{2+} occur spontaneously and produce electricity. There are two ways to allow these reactions to proceed. One way is to simply put the reductant (zinc metal) into a solution containing the oxidant (copper ion). The spontaneous electrochemical reaction written in the preceding equation proceeds as electrons pass directly from the zinc to the copper ions in solution. The copper ions so reduced form copper metal that plates out onto the surface of the zinc metal.

Unfortunately, this reaction cannot be controlled very well and the electricity so generated cannot be utilized.

Another way to get energy out of this electrochemical reaction is to separate the active components, copper ions and zinc, so that they are not in direct contact yet there is a complete electrical circuit to allow current to flow. If done properly the electrical energy can be harnessed.

J. F. Daniell

The zinc–copper cell was introduced by English chemist John Frederick Daniell in 1836. Like some other eighteenth and nineteenth century scientists, he worked in more than one scientific discipline. Daniell was also a climate scientist. He studied the behavior of the atmosphere and published his research describing the importance of humidity for growing plants in greenhouses. He further related improvements to meteorological instruments and invented a dew point hygrometer for measuring atmospheric humidity. He became the first chemistry professor at King's College, London, in 1831 and invented a pyrometer for measuring heat. He won the Royal Society's highest honor, the Copley Medal, in 1837 for his work on the zinc–copper cell.

There are a couple of steps that must be taken to accomplish this. The first is to obtain two electrodes. These will be the sites where the electrochemical reactions occur. Zinc metal is one of the electrodes. For this example, we will make the other electrode out of a piece of copper metal.

Second, the electrodes must be immersed in an electrolyte solution. An electrolyte solution contains a salt, acid, or base of some kind, which when dissolved in a solvent like water, dissociates into ions—negatively charged ions called *anions* and positively charged ions called *cations.* ("Salt" is the generic term for any material that is composed of ions; it does not only refer to sodium chloride used to season food, but it could.) The solution—ions plus solvent—is commonly called the *electrolyte.* Rather than an electrical connection for electrons to pass directly between the copper ions and zinc, ions in the electrolyte solution convey electrical charge between the electrodes.

For the copper side of the reaction, we will use the salt copper sulfate, with the chemical formula $CuSO_4$, as the electrolyte. Remember the reaction involves copper ions, so we need copper ions in the electrolyte solution anyway. Copper sulfate dissociates into copper cations, Cu^{2+}, and sulfate anions, SO_4^{2-}, as it dissolves in water.

However, we cannot put copper ions into the same solution that is in contact with the zinc electrode. If we do, we will end up with the same situation we had before, when we put the zinc metal into a solution of copper ions, and we will be unable to capture the energy from the electrochemical reaction in the form of electricity. So, for the zinc electrode, we will use the salt zinc sulfate, $ZnSO_4$, as the electrolyte, since it also dissociates in water, but to yield zinc cations, Zn^{2+}, and sulfate anions.

Now, we need to maintain separation between the zinc metal and the copper ions while providing a path for ions to move between the two electrodes. We do this by incorporating a means to allow some of the ions in the electrolyte solution to pass through, but preventing the copper ions moving to the zinc electrode. They will do it anyway, but the idea is to slow them down so that we can get as much energy out of the electrochemical reactions as we can for as long as we can.

One way to accomplish this separation is to use a salt bridge. A *salt bridge* is simply a salt solution, often loaded into a tube, which provides the ionic connection between two containers, one with the zinc electrode and one with the copper electrode. This works well for laboratory experiments, but a more practical, or at least a more compact, way to do this is to include a porous barrier, or separator, in the electrochemical cell. It is porous enough to allow ions to pass through, but it reduces the rate of mixing of the two electrolyte solutions on either side of the barrier (Figure 5-2).

Not only that, if the separator does not conduct electrons (an electronic insulator) the anode and cathode materials can be placed against the separator to minimize the volume taken up by the entire cell. This is a key design feature in most batteries, but more on that in Chapter 6.

The next item to take care of is providing for an electrical conduction path to convey the electrons produced from the electrochemical reactions between the two electrodes outside of the electrochemical cell. Electrons must get from the zinc metal to the copper ions that are now in separate compartments of the electrochemical cell. The external electrical conduction path can connect through a device that utilizes electrical energy, like a light bulb.

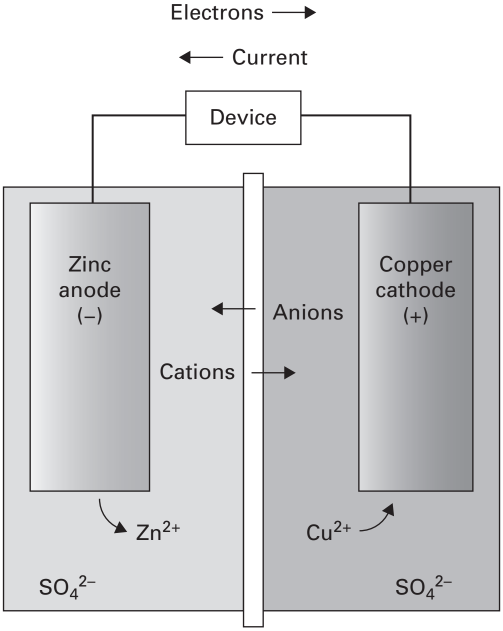


FIGURE 5-2 A conceptual Daniell cell is a zinc-copper electrochemical cell wherein the active components, zinc metal and copper ions, are separated.

Now the electrochemical reactions can be controlled and the energy produced from the electrochemical reactions can be used. When the external circuit is connected and the circuit is closed, zinc metal is oxidized to form electrons and zinc ions. Zinc ions dissolve in the electrolyte solution and the electrons are transferred to the electrical conductor connecting the electrodes. On the other side, copper ions in the electrolyte solution are reduced to copper metal by the electrons moving in the electrical conductor coming from the zinc side of the electrochemical reaction. The copper metal so produced is deposited on the copper metal electrode. Anions in the electrolyte solution, sulfate ions in this case, move toward the zinc electrode while cations move in the opposite direction (Figure 5-2).

This same basic sequence of events occurs in all batteries. The components might be different, but the processes are fundamentally the same—oxidation at the anode, reduction at the cathode, anions and cations move in the electrolyte, and electrons, and thus current, travel between the anode and cathode through an external electrical conductor.

Energy from Electrochemistry

We designed the conceptual Daniell cell in Figure 5-2 in such a way that the individual zinc and copper electrodes are electrochemically reversible. That is, each individual reaction, called a half-cell reaction because they each comprise one half of the electrochemical cell, can proceed in either direction. In such cases, the metal and the metal ion in solution can come to equilibrium (that is what the double arrows signify in the equations that follow) when there is no current moving between the two electrodes through the external portion of the circuit.

$Cu^{2+} + 2\ e^- \leftrightarrows Cu$

and

$Zn \leftrightarrows Zn^{2+} + 2\ e^-$

We can measure an electrical potential difference across the electrodes of cell. When the external circuit is open with no current moving between the electrodes and the electrodes are allowed to come to equilibrium, this potential is called the equilibrium potential, rest potential, or in battery terms, the open circuit voltage. The potential difference gauges the *electromotive force*, abbreviated emf, of the cell. The magnitude of the emf for a cell measures the propensity of the electrochemical cell reaction to proceed spontaneously. The greater the emf, the more energetically favorable the reaction is.

It also means that, thermodynamically, more electrical work, in units of joules (J), can be done with every charge-carrying unit of current, as measured in coulombs (C). The unit of emf is, then, the joule per coulomb, which is the definition of the volt.

Now, the potential depends on a number of factors, like the concentrations of the zinc and copper ions, the acidity (pH) of the electrolyte solution, and the temperature. Under standard conditions (25°C and the concentration of the ions in solution is 1 mol L^{-1}), the cell in Figure 5-2 has a potential of 1.10 V.

Naming Electrical Units

The volt is named after Alessandro Volta, the Italian scientist who furthered research into electricity after he introduced a battery capable of providing a sustained current. The joule gets its name from English physicist James Prescott Joule in honor of his work regarding the production of heat by electrical and mechanical means. The coulomb is named for French physicist Charles Coulomb, who contributed to the study of electricity and magnetism.

Gibbs and Chemical Thermodynamics

Gibbs free energy is named after J. Willard Gibbs, a chemist and physicist at Yale University who first applied thermodynamic relationships to chemical reactions. This forever changed the study of chemistry. No longer was chemistry simply an empirical science, but chemical reactivity was well characterized by thermodynamics and chemical reactions were predictable.

A Constant Named for Faraday

The Faraday constant is, of course, named after British scientist Michael Faraday. In 1833 he related that the quantity of product from an electrochemical reaction is equal to the amount of electricity used by the reaction.

The maximum work, or energy, that is theoretically achievable from the reaction of zinc metal and copper ions for the electrochemical cell in Figure 5-2 is defined in thermodynamic terms as the change in Gibbs free energy, abbreviated ΔG.

The value of ΔG (in J mol^{-1}) is the measure of the total possible chemical energy that can be converted into electrical energy for a specified amount of material and is given by the following equation:

$$\Delta G = -nFE$$

In this equation, n is the number of electrons transferred in the electrochemical reaction per mole of reactants, F represents a constant, the Faraday constant, which is the quantity of electrical charge in coulombs per mole of electrons (96,487 C mol^{-1}), and E is the emf of the electrochemical cell.

The maximum energy, or work that can be done, cannot be practically achieved, though. When the electrochemical cell is called on to do electrical work and provide energy to operate a device, like a cellular telephone, we will see later that there are a number of losses that occur that serve to reduce the maximum amount of energy that can be extracted from the cell.

Since the magnitude of the emf gives us the relative tendency of electrochemical reactions, according to the preceding equation relating emf and the Gibbs free energy, the value of $-\Delta G$ also gauges the propensity of the electrochemical reaction (or any chemical reaction for that matter) to proceed spontaneously. The more negative the ΔG for the total reaction is (alternatively, the more positive the emf is), the greater the energy that might be produced by the electrochemical reaction and the greater tendency to react spontaneously.

To build an efficient battery, the appropriate chemical materials must be paired for spontaneous electrochemical reactions to occur. Using the relationship between the Gibbs free energy and emf, we have the means to determine if electrochemical reactions are likely to produce energy. That is the subject of the next section.

Potentials of Electrochemical Reactions: Standard Conditions

When the terminals of a battery are connected and the battery is discharged, the quantity of energy available must be sufficient to meet the energy needs of whatever application the batteries are powering. This requirement limits the types of chemical compounds that can be used as active battery materials.

In other words, a battery produces energy only when certain combinations of anode and cathode materials are used. In particular, the electrochemical reactions for the anode and cathode material must proceed spontaneously (positive emf and negative Δ*G*) for the electrochemical reactions in a battery to produce energy. So, the proper choice of active materials that are in their proper oxidation states must be made such that the anode material, or negative electrode, gives up electrons and the cathode material, or positive electrode, accepts electrons.

Fortunately, values of potentials for many electrochemical reactions have been measured (or in some cases calculated) and tabulated for us so we can determine whether a certain combination of electrode materials has a chance of being useful in a practical battery. These potentials are presented in the form of half-cell reaction potentials.

A half-cell, as the name suggests, represents half of the complete electrochemical reaction. It is simply used as a way to conceptually separate the participants in electrochemical reactions so that they can be dealt with on an individual basis. The real electrochemical reactions in batteries are more complicated, but this does serve to illustrate the concept of cell emfs.

Table 5-1 collects the half-cell reduction potentials for selected elements from the most negative potentials to the most positive. (There are many more potentials for half-cell reactions, including those for more complex chemical systems, which can be found in various reference sources and chemistry textbooks.) Such collections of potentials are sometimes known as the electrochemical or electromotive series.

The half-cell reactions in Table 5-1 are given as reduction potentials. They could just as easily have been given as oxidation potentials, though. The reduction reaction for lithium ion, $Li^+ + e^- \leftrightarrows Li$ is written as the oxidation reaction for lithium by simply reversing the reaction: $Li \leftrightarrows Li^+ + e^-$. Changing the reaction from reduction to oxidation consequently changes the sign of the potential, so the reduction potential for Li^+ is –3.04 V and the oxidation potential for Li is +3.04 V.

The half-cell potentials in Table 5-1 are given for a standard set of conditions. Standard conditions just represent a set of conditions that were agreed upon by the scientific community. The first condition is that the reactions are in equilibrium. This is indicated by the double arrows, $\leftrightarrows$, in the half-cell equation. Equilibrium does not mean there is nothing happening. Both reduction and oxidation reactions occur simultaneously. Rather, it means the rate of the reduction reaction (the forward reaction progressing from left to right in the oxidation-reduction equation) is equal to the rate of oxidation (the reverse reaction going from right to left in the equation).

Since the potentials are dependent on temperature, reactant concentrations, pH and pressure (particularly for gaseous reactants), they are given under a set of standard conditions: 25°C, 1 atmosphere of pressure, and the concentration of ions 1 mol L^{-1}. The potential of half-cell reactions for the standard conditions is called the standard potential and is abbreviated E^0. The superscript *0* indicates the value of E^0 is for a reaction at equilibrium under a standard set of conditions. The corresponding standard Gibbs free energy is abbreviated ΔG^0.

TABLE 5-1 Potentials for Half-Cell Reactions at 25°C, 1 Atmosphere of Pressure, and the Concentration of Ions Given as 1 mol L^{-1} in Water

Electrochemical Reaction	Standard Reduction Potential, E^0
$Li^+ + e^- \leftrightarrows Li$	−3.04 V
$Rb^+ + e^- \leftrightarrows Rb$	−2.98 V
$K^+ + e^- \leftrightarrows K$	−2.93 V
$Cs^+ + e^- \leftrightarrows Cs$	−2.92 V
$Ba^{2+} + 2\ e^- \leftrightarrows Ba$	−2.91 V
$Sr^{2+} + 2\ e^- \leftrightarrows Sr$	−2.89 V
$Ca^{2+} + 2\ e^- \leftrightarrows Ca$	−2.87 V
$Na^+ + e^- \leftrightarrows Na$	−2.71 V
$Mg^{2+} + 2\ e^- \leftrightarrows Mg$	−2.37 V
$Be^{2+} + 2\ e^- \leftrightarrows Be$	−1.85 V
$Al^{3+} + 3\ e^- \leftrightarrows Al$	−1.66 V
$Ti^{2+} + 2\ e^- \leftrightarrows Ti$	−1.63 V
$Mn^{2+} + 2\ e^- \leftrightarrows Mn$	−1.19 V
$V^{2+} + 2\ e^- \leftrightarrows V$	−1.18 V
$Cr^{2+} + 2\ e^- \leftrightarrows Cr$	−0.91 V
$Zn^{2+} + 2\ e^- \leftrightarrows Zn$	−0.76 V
$Ga^{3+} + 3\ e^- \leftrightarrows Ga$	−0.56 V
$Fe^{2+} + 2\ e^- \leftrightarrows Fe$	−0.45 V
$Cd^{2+} + 2\ e^- \leftrightarrows Cd$	−0.40 V
$In^{3+} + 3\ e^- \leftrightarrows In$	−0.40 V
$Tl^+ + e^- \leftrightarrows Tl$	−0.34 V
$Co^{2+} + 2\ e^- \leftrightarrows Co$	−0.28 V
$Ni^{2+} + 2\ e^- \leftrightarrows Ni$	−0.26 V
$Mo^{2+} + 3\ e^- \leftrightarrows Mo$	−0.20 V
$Pb^{2+} + 2\ e^- \leftrightarrows Pb$	−0.13 V
$Fe^{3+} + 3\ e^- \leftrightarrows Fe$	−0.04 V
$2\ H^+ + 2e^- \leftrightarrows H_2$	0.00 V

TABLE 5-1 Potentials for Half-Cell Reactions at 25°C, 1 Atmosphere of Pressure, and the Concentration of Ions Given as 1 mol L^{-1} in Water (*continued*)

Electrochemical Reaction	Standard Reduction Potential, E^0
$Ge^{2+} + 2\ e^- \leftrightarrows Ge$	+0.24 V
$Cu^{2+} + 2\ e^- \leftrightarrows Cu$	+0.34 V
$Cu^{+} + e^- \leftrightarrows Cu$	+0.52 V
$I_2 + 2\ e^- \leftrightarrows 2\ I^-$	+0.54 V
$Ag^{+} + e^- \leftrightarrows Ag$	+0.80 V
$Hg^{2+} + 2\ e^- \leftrightarrows Hg$	+0.85 V
$Pd^{2+} + 2\ e^- \leftrightarrows Pd$	+0.95 V
$Br_2 + 2\ e^- \leftrightarrows 2\ Br^-$	+1.07 V
$Pt^{2+} + 2\ e^- \leftrightarrows Pt$	+1.12 V
$Cl_2 + 2\ e^- \leftrightarrows 2\ Cl^-$	+1.36 V
$Au^{3+} + 3\ e^- \leftrightarrows Au$	+1.50 V
$F_2 + 2\ e^- \leftrightarrows 2\ F^-$	+3.05 V

One important item to note in Table 5-1 is the hydrogen ion–hydrogen couple. The potential for this half-cell reaction is 0.00 V. This is no coincidence. It is not possible to measure a single electrode potential. The potential for any one electrode can only be measured against another electrode. As a result, all potentials are really a difference between the potentials for two individual electrochemical half-cell reactions. So, the half-cell potentials could be relative to any of the other half-cell potentials. However, to be sure everyone uses the same numbers, only one of the half-cell potentials must serve as a reference potential. The reduction of hydrogen ions to hydrogen was chosen to be the one, and its half-cell potential was set at 0.00 V. All the other potentials in Table 5-1 are referenced to the H^+/H_2 electrochemical couple, called the standard hydrogen electrode.

Of course, it takes two half-cell reactions to make an electrochemical cell, or a battery, operate—one that gives up electrons (oxidation) and one that takes up electrons (reduction). Let's take the electrochemical couples for the zinc-copper Daniell cell, $Zn + Cu_{aq}^{2+} \rightarrow Zn_{aq}^{2+} + Cu$, as our model electrochemical reaction once again.

The potential, or emf, for a complete electrochemical reaction can be calculated by adding the potentials for the individual half-cell reactions given in Table 5-1. Now, the half-cell reactions in Table 5-1 are written as reduction potentials. A complete electrochemical reaction has an oxidation step and a reduction step, so the direction of one of the half-cell reactions, the one that is being oxidized, must be reversed.

In our example it is the zinc-zinc ion couple. When we do this, the sign of the potential changes from positive to negative or from negative to positive. So for the $Zn \leftrightarrows Zn^{2+} + 2\ e^-$ half-cell, the oxidation potential is +0.76 V, compared with –0.76 V for the reduction potential given in Table 5-1.

Now we can calculate the equilibrium potential for a Daniell cell as follows:

$Cu^{2+} + 2\ e^- \rightarrow Cu$ $\quad E^0_{Cu^{2+}/Cu} = +0.34\ V$ (oxidation reaction)

$Zn \rightarrow Zn^{2+} + 2\ e^-$ $\quad E^0_{Zn/Zn^{2+}} = +0.76\ V$ (reduction reaction)

$Zn + Cu^{2+}_{aq} \rightarrow Zn^{2+}_{aq} + Cu$ $\quad E^0_{cell} = +1.10\ V$ (complete cell reaction)

The electrochemical potential, or emf, of the copper zinc electrochemical cell is 1.10 V, at least under standard conditions. (Of course, another way to do this is to subtract the Zn^{2+}/Zn reduction potential from the copper reduction potential like so: $E^o_{Cu^{2+}/Cu} - E^o_{Zn^{2+}/Zn} = +0.34\ V—(-0.76\ V) = 1.10\ V$.) The potential is positive, so ΔG is negative (remember $\Delta G = -nFE$) and thus the reaction occurs spontaneously as written. Now we can be assured that the cell in Figure 5-1 at least has the propensity to produce an electrical current and deliver energy when a device is connected between the electrodes.

The zinc–copper Daniell cell is a straightforward example. Each atom of zinc gives up two electrons and each copper ion takes up two electrons, so it was easy to balance the equation. The equation is balanced when the number of electrons produced equals the number of electrons consumed. Calculating overall cell potentials for reactions that are not quite so simple, like when the half-cell reactions involve different numbers of electrons, is only slightly more complicated.

Here are a few simple rules to follow for calculating cell potentials, from half-cell potentials such that the overall cell equation is balanced with an equal number of electrons produce and consumed.

1. Addition of an oxidation potential and a reduction potential for half-cell reactions involving the same number of electrons gives the potential, or emf, for the cell. Alternatively, subtraction of the reduction potentials (or oxidation potentials) for the half-cell reactions gives the overall cell potential.

   Take, for example, the half-cell reactions for a zinc-bromine (Zn/Br_2) battery:

   $Br_2 + 2\ e^- \rightarrow 2\ Br^-$ $\quad E^0_{Br2/Br^-} = +1.07\ V$

   $Zn^{2+} + 2\ e^- \rightarrow Zn$ $\quad E^0_{Zn^{2+}/Zn} = -0.76\ V$

   Or written as the anode reaction:

   $Zn \rightarrow Zn^{2+} + 2\ e^-$ $\quad E^0_{Zn/Zn^{2+}} = +0.76\ V$

   $Zn + Br_2 \rightarrow Zn^{2+} + 2\ Br^-$ $\quad E^0_{cell} = +1.07\ V - (-0.76\ V) = +1.83\ V$

   or

   $E^0_{cell} = +1.07\ V + 0.76\ V = +1.83\ V$

2. The value of the potential does not change when the half-cell reaction equation, reduction or oxidation, is multiplied through by any number.

   When aluminum is put into an acid solution (a solution that contains a relatively high concentration of hydrogen ions, H^+), Al spontaneously dissolves to form Al^{3+} and hydrogen gas, H_2. To calculate the cell potential for this reaction, we take the half-cell reactions, multiply through by the appropriate factors such that the number of electrons on the left side of the cell equation equals the number of electrons on the right side of the cell equation:

   $2\ H^+ + 2\ e^- \rightarrow H_2 \qquad E^0 = 0.00\ V$

   $Al^{3+} + 3\ e^- \rightarrow Al \qquad E^0 = -1.66\ V$

   Writing the Al/Al^{3+} as an anode reaction:

   $Al \rightarrow Al^{3+} + 3\ e^- \qquad E^0 = +1.66\ V$

   To make the number or electrons equal on both sides of the cell equation, the Al/Al^{3+} half cell reaction is multiplied by 2 and the H^+/H_2 half-cell reaction is multiplied by 3. The potentials for these reactions are not multiplied by these factors, though.

   For the aluminum half-cell reaction:

   $2 \times (Al \rightarrow Al^{3+} + 3\ e^-) \qquad E^0 = +1.66\ V$

   Or,

   $2\ Al \rightarrow 2\ Al^{3+} + 6\ e^- \qquad E^0 = +1.66\ V$

   For the hydrogen half-cell reaction:

   $3 \times (2\ H^+ + 2\ e^- \rightarrow H_2) \qquad E^0 = 0.00\ V$

   Or,

   $6\ H^+ + 6\ e^- \rightarrow 3\ H_2 \qquad E^0 = 0.00\ V$

   So, for the Al/H^+ cell reaction:

   $$\begin{array}{ll} 2\ Al \rightarrow 2\ Al^{3+} + 6\ e^- & E^0 = +1.66\ V \\ 6\ H^+ + 6\ e^- \rightarrow 3\ H_2 & E^0 = 0.00\ V \\ \hline 2\ Al + 6\ H^+ \rightarrow 2\ Al^{3+} + 3\ H_2 & E^0 = +1.66\ V - 0.00\ V = +1.66\ V \end{array}$$

3. Addition of an oxidation potential and a reduction potential for half-cell reactions can be used to calculate the potential for a different half-cell reaction. For example, say we want to calculate the half-cell potential for the reduction of iron(III) to iron(II):

   $Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad E^0 = -0.45\ V$

We have the potentials for the half-cell reactions for the reduction of each iron ion to iron metal in Table 5-1.

$Fe^{2+} + 2\ e^- \rightarrow Fe \qquad E^0_{Fe^{2+}/Fe} = -0.45\ V$

$Fe^{3+} + 3\ e^- \rightarrow Fe \qquad E^0_{Fe^{3+}/Fe} = -0.04\ V$

Subtracting the first half-cell reaction from the second gives the half-cell reaction for the reduction of Fe^{3+} to Fe^{2+} just shown. However, simply subtracting the reduction potentials gives –0.41 V, which is not the correct reduction potential for $Fe^{3+} + e^- \rightarrow Fe^{2+}$, 0.78 V.

The right way to calculate the Fe^{3+}/Fe^{2+} half-cell potential is to start with the equation for the Gibbs free energy: $-\Delta G^0 = nFE^0$, subtract the values for $-\Delta G^0$ for the reduction and oxidation reactions, and then convert the ΔG values back to the potential. Since F is a constant, we do not need to plug in the actual value for this calculation.

$Fe^{3+} + 3\ e^- \rightarrow Fe \qquad -\Delta G^0_{Fe^{3+}/Fe} = nFE^0 = 3F \times -0.04\ V$

$Fe^{2+} + 2\ e^- \rightarrow Fe \qquad -\Delta G^0_{Fe^{2+}/Fe} = nFE^0 = 2F \times -0.45\ V$

$-\Delta G^0_{Fe^{3+}/Fe^{2+}} = [(3 \times -0.04\ V) - (2 \times -0.45)] \times F = (-0.12\ V + 0.90\ V) \times F$

For the $Fe^{3+} + e^- \rightarrow Fe^{2+}$ half-cell reaction, then, the correct value for the potential is

$-\Delta G^0_{Fe^{3+}/Fe^{2+}} = (1 \times F)\ E^0$

$E^0_{Fe^{3+}/Fe^{2+}} = -\Delta G^0_{Fe^{3+}/Fe^{2+}}/(1 \times F) = +0.78\ V$

Potentials of Electrochemical Reactions: Nonstandard Conditions

The standard conditions in Table 5-1 are seldom experienced in real life and there are a number of reasons for an electrochemical cell to have a different open circuit potential from the cell potential calculated from the standard half-cell reaction values given in Table 5-1.

For one, the ambient temperature may not be 25°C. Cell potentials change with temperature, but we can calculate this change, dE/dT, using thermodynamics.

We saw the equation for the Gibbs free energy related to the cell potential. Another expression for the Gibbs free energy involving the enthalpy and entropy of an electrochemical reaction is the Gibbs-Helmholtz equation:

$$\Delta G = \Delta H - T\Delta S$$

where ΔH is the change in enthalpy and ΔS is the change in entropy for the electrochemical reaction. The change in ΔG with change in temperature (at constant pressure) is

$$\frac{d\Delta G}{dT} = -\Delta S$$

and for $\Delta G = -nFE$

$$\frac{\mathrm{d}\Delta G}{\mathrm{d}T} = -nF\,\frac{\mathrm{d}E}{\mathrm{d}T}$$

Combining the two, we get

$$\frac{\mathrm{d}E}{\mathrm{d}T} = \frac{\Delta S}{nF}$$

So, to calculate the potential of a reaction at a temperature other than 25°C (298 K), if one knows the value of ΔS, the formula is

$$E = E_{298} + (T - 298\mathrm{K})\frac{\Delta S}{nF}$$

Generally, the change in potential with temperature, $\mathrm{d}E/\mathrm{d}T$, is much less than a millivolt per °C.

Another example of nonstandard conditions resulting in a change in the half-cell potential is when the concentrations of the soluble ions in the half-cell reactions in Table 5-1 are not the standard concentration of 1 mol L^{-1}. Without going into the derivation and making a couple of assumptions, we can estimate the potential for any concentration of the ions when the cell is at equilibrium using the Nernst equation (named after Nobel prize winning German scientist Walther Nernst):

$$E = E^0 - \frac{RT}{nF}\ \ln\ \frac{(\text{concentration of products})}{(\text{concentration of reactants})}$$

In this equation, E is the measured potential, R is a constant called the gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature in degrees K on the Kelvin temperature scale (298 K for the standard temperature of 25°C), and the terms n and F have already been defined.

We just calculated the half-cell potential for the $\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}$ couple under standard conditions. This means the concentrations of Fe^{3+} and Fe^{2+} are at 1 mol L^{-1}. If we plug these numbers into the Nernst equation, we get

$$E_{\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}} = +0.78\ \mathrm{V} - 0.0257\ \mathrm{V} \times ln\ [(1\ \mathrm{mol\ L}^{-1}\ \mathrm{Fe}^{3+}) / (1\ \mathrm{mol\ L}^{-1}\ \mathrm{Fe}^{3+})] = +0.78\ \mathrm{V}$$

The answer is just the standard potential, E^0, which is what we expect for standard conditions.

If the concentrations of the Fe^{3+} and Fe^{2+} are not each at 1 mol L^{-1} (or if they are not equal regardless of the concentration), then we will measure a different cell potential. For example, if we halve the Fe^{3+} concentration (0.5 mol L^{-1}) while the Fe^{2+} concentration remains at 1 mol L^{-1} with all other conditions being the same, the cell potential becomes

$$E_{Fe^{3+}/Fe^{2+}} = +0.78 \text{ V} - 0.0257 \text{ V} \times ln\,[(0.5 \text{ mol L}^{-1}\ Fe^{3+}) / (1 \text{ mol L}^{-1}\ Fe^{2+})] = +0.80 \text{ V}$$

Table 5-1 half-cell reactions represent simple ionic species dissolved in a water solution. This is seldom the situation in batteries. Generally, a more complicated type of chemical species is involved. The measured potential for these compounds will be different than that found for the simple species in the Table 5-1. An example of this is silver chloride, AgCl, which has been used as a cathode material in combination with a magnesium anode in a type of reserve battery we will discuss later.

The silver ion in AgCl is Ag(I), just as it is in Table 5-1, but now the half-cell reaction includes chloride ion. The potentials are different for the two half-cell reactions even though they both involve silver (I).

The standard potential for the AgCl/Ag half-cell reaction is

$$AgCl + e^- \rightarrow Ag + Cl^- \quad E^o_{AgCl/Ag} = +0.22 \text{ V}$$

Compared to the Ag^+/Ag couple:

$$Ag^+ + e^- \rightarrow Ag \qquad E^o_{Ag^+/Ag} = +0.80 \text{ V}$$

The involvement of Cl^- in the electrochemical reaction changes the reduction potential of Ag(I).

Battery Electrochemistry: Kinetics

So far we investigated some of the thermodynamic aspects of battery electrochemistry, in particular half-cell electrode potentials and cell potentials. The cell potential, or electromotive force, tells us the likelihood of an electrochemical reaction proceeding spontaneously. However, our discussion so far applies only to electrochemical cells that are in equilibrium, that is, when there is no net current flowing in the electrochemical cell. If there is no net current, then there is no electrical energy delivered to the device.

For many applications we want our batteries to provide the energy in a reasonable amount of time. There are a number of factors that can limit how fast an electrochemical reaction can occur. That is where electrochemical kinetics comes in.

When we close the circuit by turning on the device powered by a battery, a current flows and a number of complex steps simultaneously take place. The oxidation reaction at the anode and the reduction reaction at the cathode are forced away from equilibrium through a net charge transfer of electrons and ions at the electrodes. Electrons move through the electron conductors both inside the battery and through the external circuit. Finally, ions in the electrolyte move between the electrodes by migration (the movement of ions under the influence of an electric field) and diffusion (the movement of ions as a result of a concentration difference). Each of these actions affects how fast and how much energy a battery will deliver. The effect of these three factors is central to understanding performance limitations of battery systems and will be discussed in more detail in Chapter 7. For now, we will stay with the electrochemistry of the active battery materials.

The rates of the electrode reactions are in large part dependent on the nature of the electrode materials themselves. Besides the battery voltage, this places an additional constraint during the selection of the active battery materials.

When the Zn-Cu Daniell cell is at equilibrium and no net current is flowing, the half-cell reactions are also at equilibrium. For the copper electrode, this means that the rate of the reduction (or cathodic) reaction

$$\mathrm{Cu_{aq}}^{2+} + 2\ \mathrm{e}^- \rightarrow \mathrm{Cu}$$

equals the rate of the oxidation (or anodic) reaction

$$\mathrm{Cu} \rightarrow \mathrm{Cu_{aq}}^{2+} + 2\ \mathrm{e}^-$$

The rates of electrochemical reactions are determined by measuring current, since electrons are produced or consumed. So, for the copper electrode at equilibrium (and the zinc electrode for that matter), the current of the cathodic reaction, i_c, is the same as the current of the anodic current, i_a:

$$i_c - i_a = 0$$

Under these conditions, the magnitude of the cathodic and anodic currents is called the exchange current, i_0:

$$i_c = i_a = i_0$$

The exchange current depends on the reaction kinetics of the particular electrode involved, so different chemical materials that react at different rates will exhibit different exchange currents.

When the circuit is closed and current is produced, the anodic and cathodic currents for each electrode are no longer equal. Rather, more Zn is oxidized than Zn^{2+} is reduced, producing a net anodic current at the anode. On the other hand, more Cu^{2+} is reduced than Cu is oxidized, so there is a net cathodic current at the cathode.

The kinetics of the electrochemical reactions occurring at each electrode is well described by the Butler-Volmer equation:

$$i = i_0 \left\{ \exp\left[-\frac{\alpha F}{RT}(E - E^0) \right] - \exp\left[\frac{(1-\alpha)F}{RT}(E - E^0) \right] \right\}$$

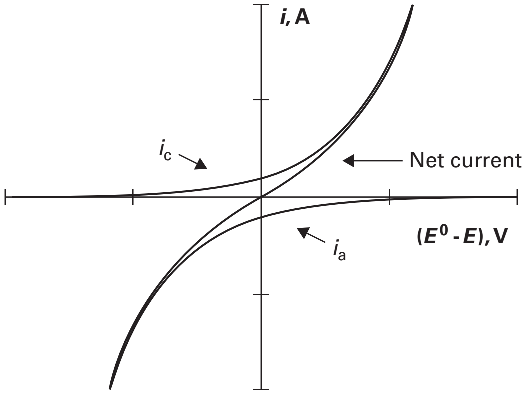


FIGURE 5-3 The net current ***i*** for an arbitrary electrode reaction as a function of the difference between the potential of the electrode while there is a net current and the standard electrode potential for the electrode. The contributions of the cathodic reaction current, i_c, and the anodic reaction current, i_a, to ***i*** are shown, as well.

In this equation, i is the net current, and E is the resulting electrode potential when there is a net current; i_0, E^0, F, R, and T have already been defined. The constant α is characteristic of the electrochemical reaction and generally lies between 0 and 1. If the value of α is unknown, it is usually assumed to be 0.5.

A plot current of i against $E - E^0$ calculated from the Butler-Volmer equation is shown in Figure 5-3.

So, the relative contributions of the cathodic and anodic currents for each electrode will depend on how facile the reactions are for each electrode material and how far the resulting electrode potentials are from their standard electrode potentials. Looked at from another angle, if the electrodes are connected and the battery is allowed to discharge resulting in a net current through the battery, the measured potential will be different from the standard potential measured when the cell was at equilibrium. The result is a less positive potential for the cathode and a less negative potential (more positive) anode potential, resulting in a lower overall cell voltage. This is one of the important factors that affect battery performance.

Capacity

The amount of active materials in a cell determines the capacity of the cell and is expressed as the total charge, or electricity, that the cell delivers. We can calculate the capacity for various electrode materials using Faraday's law, which states the quantity of electrical charge, the capacity, Q, is determined by the number of moles of the active material, M, and the number of electrons involved in the electrochemical reaction, n:

$$Q = nFM$$

where F is the familiar Faraday constant and equal to 96,487 C or 26.8 Ah for each electron involved in the electrochemical reaction.

Let's calculate the capacity of the Li/I_2 cell reaction. We will calculate the capacity for this cell on a weight and volume basis, so rather than multiply by the number of moles, we will divide the atomic or molecular weight for Li and I_2 in grams per mole to give us Ah g^{-1}. The capacity on a volume basis can then be determined by multiplying this number by the densities of Li and I_2.

The capacity on a mass basis for Li is

$$Q_{Li} = (1 \times 26.8 \text{ Ah}) / 6.94 \text{ g mol}^{-1} = 3.86 \text{ Ah g}^{-1}$$

Multiplying this number by the density of Li (0.534 g cm^{-3}) gives the capacity on a volume basis in Ah cm^{-3}.

$$Q_{Li} = 3.86 \text{ Ah g}^{-1} \times 0.534 \text{ g cm}^{-3} = 2.06 \text{ Ah cm}^{-3}$$

Likewise, for I_2 (molecular weight = 253.8 g mol^{-1}):

$$Q_{I2} = (2 \times 26.8 \text{ Ah}) / 253.8 \text{ g mol}^{-1} = 0.211 \text{ Ah g}^{-1}$$

or (I_2 density = 4.93 g cm^{-3})

$$Q_{I2} = 0.211 \text{ Ah g}^{-1} \times 4.93 \text{ g cm}^{-3} = 1.04 \text{ Ah cm}^{-3}$$

Now, for the capacities of the complete cell (or at least for the anode and cathode materials) per unit mass in g or volume in cm^3, add the mass or volume for 1 Ah capacity for both electrodes and take the inverse. The values come out to be

$$1 / (1 / Q_{Li} + 1 / Q_{I2}) = 1 / (0.258 \text{ g Ah}^{-1} + 4.74 \text{ g Ah}^{-1}) = 0.200 \text{ Ah g}^{-1}$$

More on the Faraday Constant and Faraday's Law

The units for the Faraday constant are actually 96.487 C per equivalent or 26.8 Ah per equivalent (abbreviated eq), where an equivalent, in this case, is an electron participating in the electrochemical reaction. The number of electrons in the reaction, *n*, has units of equivalents per mole. So, the capacity, Q, has the units of either coulombs or amp-hours, depending on the form of the Faraday constant used.

$$\frac{\text{equivalents}}{\text{mole}} \times \frac{\text{coulombs or amp-hours}}{\text{equivallent}} \times \text{moles} = \text{coulombs or amp-hours}$$

and

$$1 / (1 / Q_{Li} + 1 / Q_{I2}) = 1 / (0.485\ \text{cm}^3\ \text{Ah}^{-1} + 0.962\ \text{cm}^3\ \text{Ah}^{-1}) = 0.692\ \text{Ah cm}^{-3}$$

Now, these values represent the theoretical capacities and only calculate the maximum possible capacity available from the electrode materials by assuming complete utilization and that the reactants are the only components involved. This is not achieved with real batteries, of course. A battery will have a lower capacity per weight or volume because other components are needed to make a practical battery. Further, there are other factors of the battery design or use that act to reduce capacity.

In the chapters to come, we build on the concepts of cell potentials, current, and the capacity of electrochemical reactions to develop a realistic analysis of battery behavior.

Chapter 6

Battery Engineering Designs

IMPORTANT CONCEPTS IN THIS CHAPTER:

- Battery types: cylindrical, button, coin, and prismatic
- Electrode designs for energy and power
- Terminals, seals and vents
- Safety mechanisms
- Battery configurations

In his 1912 book *Storage Batteries: The Chemistry and Physics of the Lead Accumulator,* Harry Morse wrote, "Study of the storage battery calls for attention to two rather distinct viewpoints—one chemical, the other physical; and these will be found of nearly equal importance."

George Vinal agreed in *Storage Batteries, 3rd edition* (1940) but extended it further. Vinal wrote, "The storage battery is typically an electrochemical apparatus and as such must be discussed from three viewpoints. The first is chemical involving the nature and properties of the materials used in its construction and the reactions which occur during charging and discharging. The second is physical, and this includes a study of the electrical input and output, the factors which affect the capacity, and the theory of the transformation of chemical energy into electrical energy or vice versa. The third viewpoint is the practical one dealing with the engineering applications of storage batteries."

Vinal continued, "There is no sharp line of demarcation between the chemical, physical, and engineering aspects, but a full discussion of all is necessary to an adequate understanding of the nature and performance of storage batteries."

It is the cell chemistry—anode, cathode and electrolyte—that makes a battery work. However, the design and construction of a battery makes it more efficient or safer or more reliable or more convenient to use.

Battery design and construction requires the participation of different scientific and engineering disciplines. Chemists, materials scientists, mechanical engineers, and chemical engineers all contribute to the design, development, and manufacture of practical batteries.

In this chapter, we first present an overview of the wide variety of different battery types, shapes, and sizes. Next, we go inside the batteries to get a look at how they are constructed. Finally, we look at a couple of the mechanical features that are important to their function—terminal design, the seal, and vents.

Battery Shapes and Sizes

Batteries come in an astounding array of shapes and sizes. Add to that batteries that are custom built to dimensions specific to a particular application, and it becomes an overwhelming task to tabulate them all.

We can classify them into general categories based on their shapes, though. From a high level, batteries can be classified as round or prismatic.

Round cells are perhaps the most familiar to us because most of the batteries we use every day in applications like television remote controls, radios, flashlights, calculators, and watches. The No. 6 battery was a mainstay of school science projects for many years. Among the round cells, we can break them down further depending on their aspect ratio—the ratio of their height to their diameter (Figures 6-1 through 6-3).

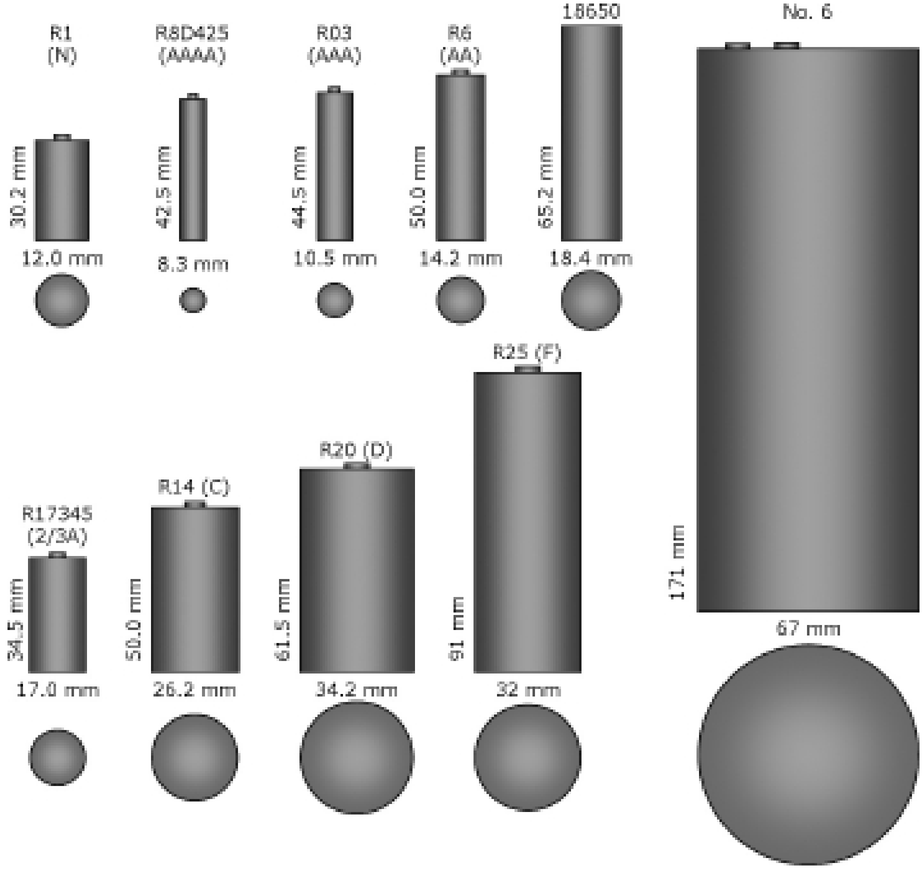


FIGURE 6-1 Common cylindrical cell sizes. The dotted circle is the outline of the cell diameter.

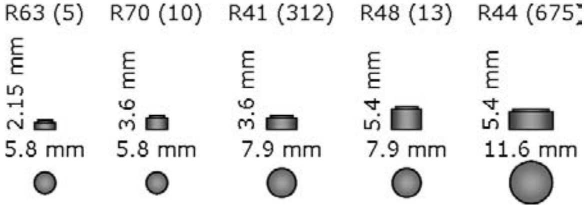


FIGURE 6-2 Common button cell sizes. The dotted circle is the outline of the cell diameter.

Cylindrical cells are taller than they are wide, with height-to-diameter ratios somewhere in the range of 0.9 to 8.0. One of the first cylindrical cells commercialized was the Columbia dry cell manufactured by the National Carbon Company starting in 1896. It was a Leclanché dry cell that was produced in five different sizes from 1½ inches in diameter by 4 inches in height up to a diameter of 3⅓ by 8 inches high, which was used as an ignition battery for starting gasoline engines. The popular Columbia No. 6 measured 2½ inches in diameter by 6 inches tall and was used for telephones and clocks. The smallest cylindrical cells measure just fractions of an inch—down to 2.9 mm (0.114 inches) in diameter by 11.8 mm (0.465 inches) tall.

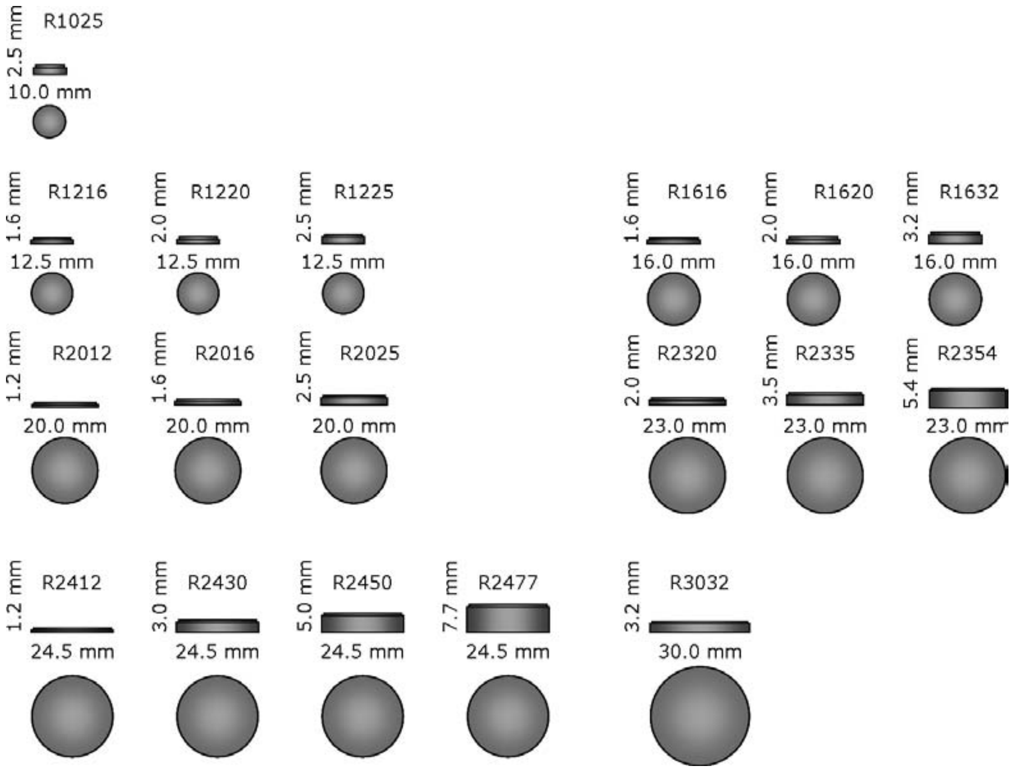


FIGURE 6-3 Common coin cell sizes. The dotted circle is the outline of the cell diameter.

Button cells are so called because they are shorter than their diameter. Height-to-diameter aspect ratios vary between 0.1 and 0.7. There are some cylindrical batteries that are made from button cells, like the 12 V A23 battery (28 mm diameter by 10 mm height) assembled by stacking eight alkaline zinc–manganese dioxide button cells.

Even more aptly named are *coin* cells, which have the smallest height to diameter ratios (although there is some overlap with button cells) between 0.05 and 0.31.

Prismatic batteries are, well, not round. We use prismatic batteries in our cell phones and to start our cars. The smallest are solid state thin film batteries, like the 5 mm long by 5 mm wide by 1 mm thick cells designed to be mounted on circuit boards and provide power for memory and clock chips, radio frequency identification (RFID) tags, and wireless sensors.

The largest are stationary battery installations used for electrical grid energy storage systems for load leveling or as backup for electrical power outages. One example is the emergency backup power system in Fairbanks, Alaska. It is a 2,000–square meter battery consisting of 13,760 large nickel-cadmium cells weighing a total of 1,300 tons. It can produce up to 40 MW of power for 7 minutes or 27 MW for 15 minutes.

Many batteries come in standard sizes with well-defined dimensions and have identification codes defined by the International Electrotechnical Commission (IEC) and the American National Standards Institute (ANSI). (More information on this is provided in Chapter 12.) Manufacturers generally have their own model numbers they use to identify their batteries, but at least for standard sizes they will also provide the IEC or ANSI standard size and chemistry designation.

Battery Components

All batteries need the same three active components to function—anode, cathode, and electrolyte. In our discussion here, the terms anode and cathode describe the role of the electrode during battery discharge. However, for rechargeable batteries, the electrodes reverse their roles during charging, so we will use the terms negative electrode (the anode during discharge) and positive electrode (the cathode during discharge) to describe the electrodes in a more general way.

Negative electrode materials are usually metals that are easily oxidized; that is, they easily surrender their electrons to form ions. These metals include the zinc in Leclanché zinc-carbon and alkaline zinc–manganese dioxide (Zn/MnO_2) cells, the lead in lead acid batteries, the cadmium in nickel-cadmium (NiCd) cells, and the lithium in lithium–carbon monofluoride cells. These batteries are built using zinc (Zn), lead (Pb), cadmium (Cd), and lithium (Li) metal.

Other negative electrode materials form substances that also readily yield their electrons, like the metal hydride in nickel–metal hydride cells or the carbon negative electrode material loaded with lithium ions in charged lithium ion cells.

The *positive electrode* materials are more often than not a metal oxide powder, like manganese dioxide (MnO_2), nickel oxyhydroxide (Ni(O)OH), silver oxide (Ag_2O), and lithium cobalt oxide ($LiCoO_2$). A variety of other materials are also used, though, including carbon monofluoride (CF_x), thionyl chloride ($SOCl_2$), iron disulfide (FeS_2), lithium iron phosphate ($LiFePO_4$), sulfur dioxide (SO_2), iodine (I_2), and oxygen (O_2).

The positive electrode materials that are solids (that leaves out $SOCl_2$, SO_2, and O_2) are usually in the form of a powder. Positive electrode materials are not very electrically conductive as a rule, so they must be mixed with an electronically conductive material like carbon powder, often graphite or carbon black or both, to get the electrons to the positive electrode materials. To hold the powders together, a binder is used. Binders are generally polymeric materials, such as polytetrafluoroethylene (PTFE or Teflon™) or polyvinylidene fluoride (PVDF).

For cells with an active positive electrode material that is not a solid, there is still a need to make good electrical contact with an electrode through which it can receive the electrons coming from the negative electrode. Zinc-air and lithium–thionyl chloride cells ($Li/SOCl_2$) have carbon electrodes at which O_2 or $SOCl_2$ can become reduced during discharge.

The third vital component that allows a battery to function is the electrolyte. Most batteries use a liquid electrolyte solution—either *aqueous* (water based) or *nonaqueous* (not water based).

Aqueous batteries have electrolytes made by dissolving into water a substance that dissociates into ions. Examples include bases, usually potassium hydroxide (KOH) in alkaline-type cells, or acids, like sulfuric acid (H_2SO_4) in lead acid batteries, or salts, like ammonium chloride (NH_4Cl) and zinc chloride ($ZnCl_2$) in Leclanché zinc-carbon cells.

Nonaqueous batteries use something other than water as the solvent for the electrolyte salts, usually one or more organic liquids. Organic electrolyte solutions are necessary to use in lithium and lithium ion cells because Li reacts violently with water.

A third type is the *solid state* electrolyte. Just like electrolytes that are based on liquid solvents, solid state electrolytes must be able to conduct ions between the positive and negative electrode materials. Because they are solids, ions cannot move as fast as they do in liquids, which limits the power output of the cell. So, solid state electrolyte batteries are generally only used for low-power applications. Examples include ionically conducting solids like LIPON (lithium phosphorus oxynitride) and lithium iodide (LiI). The latter forms in the Li/I_2 cells used in most of today's pacemakers.

It is important to pack the electrodes close together in a battery to maximize energy density. Yet, positive and negative electrodes cannot be so close that they touch each other. This is a short circuit that rapidly discharges the electrode materials without producing usable electrical energy. Battery designers use a component called a *separator* that allows them to efficiently package the electrodes without allowing them to make direct contact.

A battery separator has two functions: it must be an electrical insulator, but also allow ions to pass through. As an electrical insulator, it keeps the positive and negative electrodes from coming into contact when it is sandwiched between them. Insulating materials like paper or polymeric materials like polyethylene are good electrical insulators.

The separator must also allow ions in the electrolyte to pass through for the battery to function. So, a separator also needs to be porous such that the electrolyte soaks through and there is a channel for the ions to move between the electrodes.

Separator materials that have both electrical insulating and ionpermeable properties include paper, woven fibers mats, nonwoven fibers mats, and microporous polymer membranes.

The electrical current is carried from and to the negative and positive electrode materials by way of *current collectors.* These are usually metal grids or foils or ribbons and tabs that allow the current to move within a battery from the electrode materials to the battery terminals.

Battery terminals come in a number of designs and sizes, depending on the type of battery, how much current they are expected to carry, and if they are intended to be easily replaced by the end user.

The terminals of an off-the-shelf alkaline AA battery are incorporated into the case and an end cap. They make electrical contact with the device through a spring or with each other in a string of cells by a friction fit. Other batteries may have screw terminals to connect wires, posts to which wires can be welded or soldered, or metal ribbons for welding.

Electrode Design

The electrode design, along with the electrode materials themselves, helps to determine the output of the battery. Since most positive electrode materials are made from powders, the electrodes are porous (Figure 6-4). Electrolyte is imbibed throughout a porous electrode. This maximizes the area of active electrode material that is exposed to electrolyte and thus available to discharge compared to a solid electrode surface. More surface area means more power.

The thickness of a porous electrode limits how much power it can produce, though. A thick electrode has a higher resistance that limits its power output. Thin electrodes have low resistance and so can produce higher power.

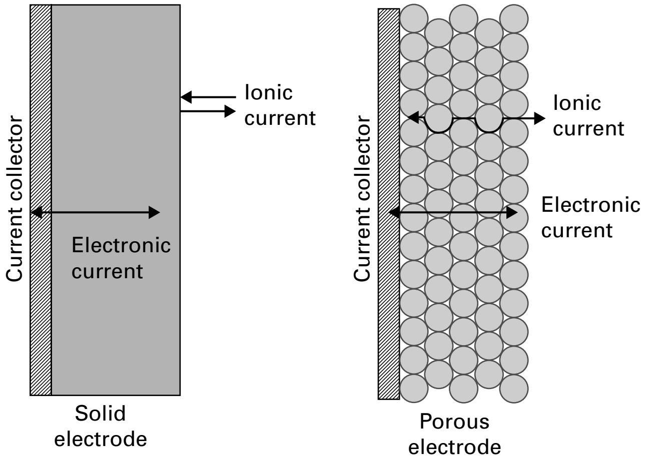


FIGURE 6-4 Porous electrode structure

On the other hand, thicker electrodes usually mean more active electrode for a given volume, since thinner electrodes require more inactive materials, like current collectors and separators. The energy vs. power trade-off is usually a consideration for battery designers as they define electrode thickness.

The electrodes in cylindrical cells are based on two different electrode designs: bobbin and spiral wound.

A *bobbin* cell is designed to optimize energy density, but it does so at moderate to low power loads or intermittent uses because the electrodes are thicker. The positive electrode materials for typical bobbin cell designs are made from an electrode powder mix (active material, conductive additive, binder) that is compressed into either a solid or hollow cylinder.

A Leclanché zinc-carbon bobbin cell may be made from a MnO_2 electrode mix that is compacted into a can. The can is made of zinc, which is also the negative electrode material, lined with a separator material.

An alkaline Zn/MnO_2 bobbin cell reverses this order. The positive electrode is formed by compressing the MnO_2 electrode mix into a hollow cylinder and pushing it into the battery can. The inside of the positive electrode cylinder is lined with a separator, and the negative electrode material as added to the center of the cylinder. The Zn is in the form of a powder in an alkaline electrolyte in the form of a gel (Figure 6-5).

A *spiral-wound* electrode is made by rolling up thin positive and negative electrodes with a separator between them. The tightly wound electrode roll is inserted into a battery can.

Button cells and coin cells generally have a single positive electrode pellet made from a compressed electrode mix (active material, conductive carbon, binder) that

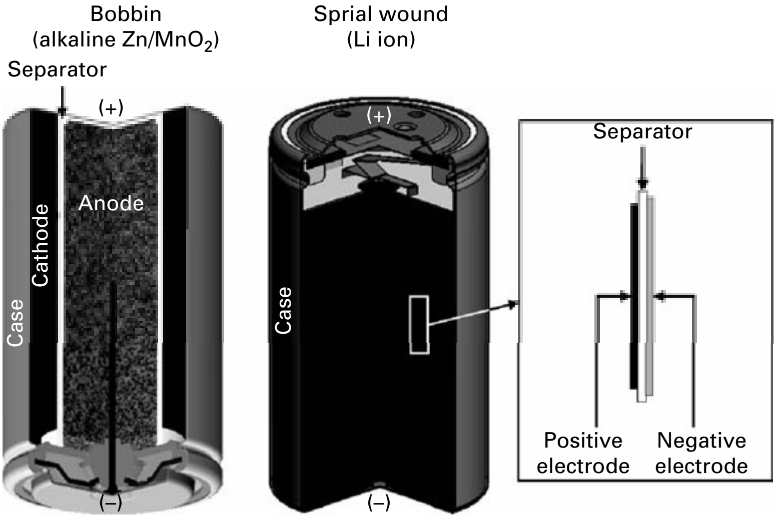


FIGURE 6-5 Bobbin and spiral-wound electrode designs in cylindrical cells. ©Spectrum Brands, Inc. Reprinted by permission.

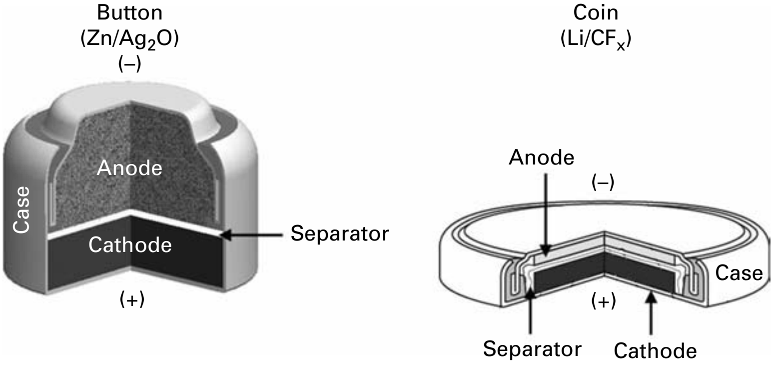


FIGURE 6-6 Button and coin cell electrode designs. ©Spectrum Brands, Inc. Reprinted by permission.

is pressed into a can half (Figure 6-6). The negative electrode material may be a Zn powder gel, as with Zn/Ag$_2$O or Zn/MnO$_2$ button cells, or a piece of Li metal, as in Li/MnO$_2$ and Li/CF$_x$ coin cells, placed in the other can half.

Prismatic cells may be wound, as in spiral-wound cylindrical cells, but are wound into a flattened form to fit the squared-off battery can. A prismatic cell may also be made from stacked electrode plates with alternating positive and negative electrode plates with a separator between them (Figure 6-7). Lead acid car starter batteries are made this way.

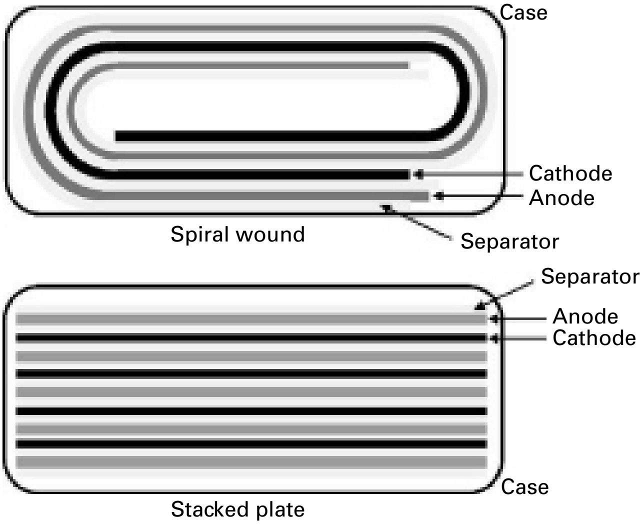


FIGURE 6-7 Prismatic electrode designs

Rather than using a metal can, prismatic battery electrodes may be sealed in plastic to form what is called a pouch cell (also, bag or envelope cell). Lithium ion polymer prismatic batteries are an example of a pouch cell.

Seal Design

The first commandment of batteries is "Thou shalt not leak." This means a sealing mechanism must be designed to keep the electrolyte and electrode materials contained.

There are a number of different ways to seal a battery. Cylindrical cells and coin cells may be sealed by crimping the battery can around an insulator used to keep the negative and positive terminals apart. The insulator may be a grommet (button and coin cells) or a plastic disk (cylindrical cells).

Other cells may be laser-welded if a stronger seal is needed. This is common for hermetically sealed cells. In this case, a special glass-to-metal seal is needed to keep positive and negative terminals separated.

Vent Design

A *vent* is a safety feature that is designed to release gasses and electrolyte in a controlled fashion. This is intended to prevent a catastrophic failure of the seal resulting in a violent release of internal pressure in the event of a problem, like an internal short circuit or a thermal runaway.

Vents may simply be areas of the cell case that are weakened by scoring or a burst panel in the case or incorporated into the seal. These types of vents can be activated one time only—the cell can no longer be used.

Other vent designs are reversible, like the rubber seal on NiMH batteries or valve-regulated lead acid (VRLA) battery vent mechanisms. These vents release pressure, but then reseal to enable continued use of the battery.

Other Safety Features

Other safety features are important especially for high-energy rechargeable battery systems to mitigate risks from electrical shock, chemical exposure, excessive heat, fire, or explosion. These hazards may result from battery failure, charger malfunction, or misuse or abuse—intentional or otherwise—by the end user.

Safety mechanisms activate and shut down battery discharge when the temperature, internal pressure, or current increase beyond a threshold level. These are among the more common safety mechanisms:

- A shut down separator is made of a polymeric material that melts when the temperature inside the battery increases to a high enough level, say from a short-circuit condition. The melted polymer seals the pores of the separator, inhibiting the movement of ions between the positive and negative electrodes, which stops or at least cuts back on the current the battery can produce.

- A positive thermal coefficient (PTC) switch is made from a conductive material, but the resistance of the PTC increases when heated. Under normal battery use conditions, the PTC allows the current to pass. If there is an external short circuit, the battery discharges rapidly, producing a large current. The excessive current heats the PTC, causing its resistance to increase, thereby curtailing the amount of current the battery can release.
- Other temperature switches including thermistors and thermal fuses.
- A pressure switch breaks a connection when the internal pressure builds beyond a threshold limit. This opens the circuit and stops the battery from discharging.
- Diodes block current in one direction to prevent current reversal and charging in the wrong direction.
- "Smart" battery systems involve microprocessors and circuits that monitor the condition of a battery (voltage, current, temperature, charge, and discharge capacity) and regulate the battery charge and discharge conditions.

Some of these safety features may also be included within battery packs, as well. Multiple, redundant safety mechanisms are often combined in a cell or battery pack to further reduce the risk of a catastrophic failure.

Batteries

A *battery* is built up by connecting two or more cells together. Batteries made from cells that are connected in series (Figure 6-8 (a)) have the same capacity as the individual cells, but the voltage is multiplied by the number of cells in the series string. The

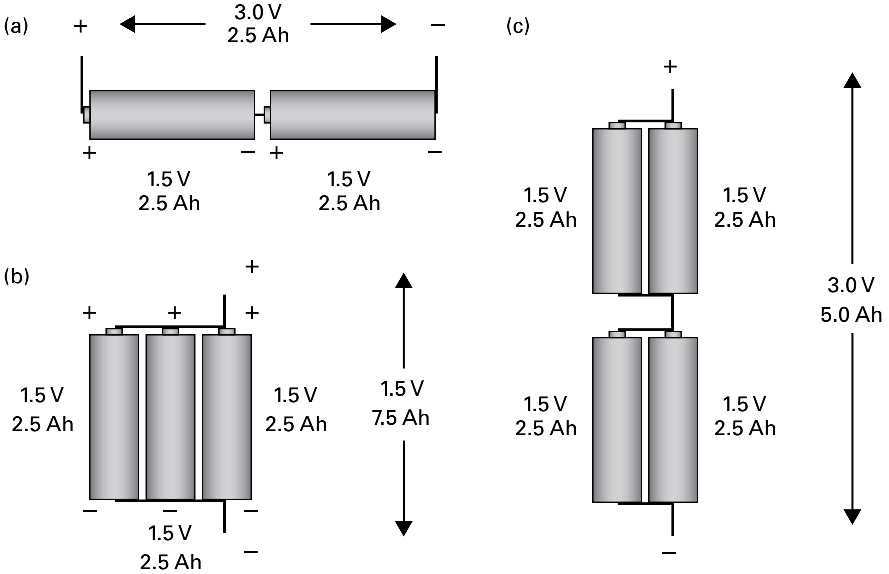


FIGURE 6-8 Batteries built up by connecting cells in (a) series, (b) parallel, and (c) series and parallel combinations

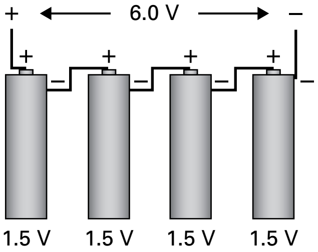


FIGURE 6-9 Parallel cell configuration for a 6 V lantern battery

positive terminal of one cell is connected to the negative terminal of the next, and so on. An example is a 6 V lantern battery made up of four 1.5 V Leclanché zinc-carbon cells in Figure 6-9: 1.5 V + 1.5 V + 1.5 V + 1.5 V = 6.0 V.

Batteries made from cells that are connected in parallel have the same voltage as the individual cells, but the capacity is multiplied by the number of cells (Figure 6-8 (b)). Take two CR123 Li/MnO_2 cells (International Electrotechnical Commission, or IEC, designation CR17345), each with a voltage of 3 V and a capacity of 1.5 Ah. Connect positive terminal to positive terminal and negative terminal to negative terminal and the result is a 3.0 V battery with a capacity of 3.0 Ah (Figure 6-10).

Series and parallel combinations of cells increase both the voltage based on the numbers of cells in the series strings and the capacity based on the number of series strings connected in parallel (Figure 6-8 (c)).

Charging battery packs (assemblies of multiple cells) presents a couple of other important items to consider. An imbalance between the cells in the battery pack occurs when the batteries are not closely matched with respect to characteristics that affect the extent of charging, such as internal resistance or total capacity.

For example, take a two-cell battery pack with the cells connected in series that we are going to charge with a constant current. If one of the cells has a lower capacity than its partner, it will become fully charged before the other one. If the charging is

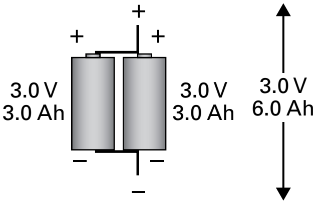


FIGURE 6-10 Series cell configuration for a two-cell battery

allowed to continue until the larger capacity cell is fully charged, the one with the lower capacity will become overcharged. The reduced performance of this cell as a result of overcharging will pull down the performance of the entire battery.

One way to avoid overcharging the lower-capacity cell is to simply stop charging the battery pack before the higher capacity cell is fully charged. This leaves the higher capacity cells undercharged meaning less than complete utilization of the usable energy in the battery.

However, if the cells were more closely matched in capacity, they could both get fully charged and the energy output optimized.

Chapter 7

Battery Performance

IMPORTANT CONCEPTS FROM THIS CHAPTER:

- Theoretical and practical energy from a battery
- Different ways to assess battery performance
- Factors that affect battery performance

Battery chemistry is often the focus of performance discussions, and certainly the electrode materials play a dominant role in determining battery performance characteristics. Yet, there is more to it than the reactivity of the electrode materials in the battery. The rate at which energy is released is modulated by practical factors associated with the battery design and selection of other materials used in the battery construction, including the type and amount of electrolyte. In this chapter, we look at the outputs of the battery as a complete system.

Terms and Units

As with any scientific and engineering topic, there are terms and units of measurement that are useful. They need to be understood for a full appreciation of the subject. Table 7-1 collects many of the terms and units used to describe battery characteristics. Their meanings and use are described in the text that follows.

Potential or Voltage

The electrochemical potential, or voltage (in volts, or V, in honor of Italian scientist and inventor of the battery Alessandro Volta), is the amount of work or energy (in joules, or J, after English physicist James Prescott Joule) that can be done by a unit of electrical charge (in coulombs, abbreviated C, and named for French scientist Charles-Augustin de Coulomb).

TABLE 7-1 Terms and Their Abbreviations Used to Gauge Battery Performance

Term	Characteristic Units	Unit Abbreviation
Electromotive force (emf) Potential Voltage	volt	V
Current	ampere or amp	A
Resistance	ohm	Ω or ohm
Capacity	ampere-hour or amp-hour coulomb	Ah C
Power	watt	W
Power density (weight basis)	watts per kilogram	W kg^{-1}
Power density (volume basis)	watts per cubic decimeter	W dm^{-3}
Energy	watt-hour joule	Wh J
Energy density (weight basis)	watt-hours per kilogram	Wh kg^{-1}
Energy density (volume basis)	watts-hours per cubic decimeter joules per cubic centimeter	Wh dm^{-3} J cm^{-3}

Note: Power and energy density units based on the volume of a cell are often calculated per liter (L). The liter is usually reserved as a liquid volume unit, so we use the cubic decimeter (dm^3) for volume-based power and energy densities. One cubic decimeter is equivalent to one liter.

Potential, Voltage, Tension

Potential is the term that conveys the proper meaning with respect to energy, as in potential energy, and is used by electrochemists and other scientists. Yet, voltage is commonly used as a synonym for potential and is now used widely, particularly in battery circles.

An outdated term (at least in English) for electrical potential is tension. For example, high-voltage power transmission lines, the large cables in the electrical power distribution grid, were once called high-tension power lines. They are capable of carrying hundreds of kilovolts, generally between 110 kV and 765 kV. Tension is a type of force, so the analogy is apt.

Tension does remain the French word for voltage.

Current

How fast the electrical charge (in coulombs per second) is delivered is called the electric current (in amperes or amps and abbreviated A, named for French physicist André-Marie Ampère). The electrical charge is carried through the external circuit by electrons. For a flashlight pulling a 320 mA current, the battery is supplying something on the order of 2×10^{18} (or 2,000,000,000,000,000,000) electrons; that is, that many electrons are traveling from the battery into the circuit, through the flashlight bulb and back to the battery every second. An electronic circuit component with a leakage, or parasitic, current of only 10 atto-amps draws about 62 electrons per second.

There is another and somewhat esoteric term for current used by the battery industry, called the “C rate.” It is sometimes maligned, but still widely used. The C rate is the discharge or charge current (in A) relative to the nominal or rated capacity of the battery (as defined by the manufacturer, usually at a typical discharge current). The baseline value is “C” or “1C” and is calculated as the current necessary to discharge or charge a battery to the rated capacity in one hour:

C or 1C rate = (rated capacity) / (1 hour)

where the C rate is in A and the rated capacity is in Ah.

The C rate is given as multiples or fractions of 1C, depending on whether the charge or discharge current used is greater or less than the 1C rate. For example, the 1C current for a 2.6 Ah lithium battery is 2.6 A (2.6 Ah / 1 h = 2.6 A). Say the manufacturer recommends charging the battery at C/2 or 0.5C, then the charging current is 2.6 A / 2 = 1.3 A. If the manufacturer states the maximum recommended discharge current is 1.5C, the current is 2.6 A × 1.5 = 3.9 A.

The International Electrotechnical Commission (IEC), an international standards organization, defined another term to express the relative charge or discharge current that is little more informative and, perhaps, a little more confusing:

$I_t = n\,\mathrm{C}_\mathrm{r}$ / (1 hour).

In this equation, I_t is the current in A that results in a charge or discharge lasting time t in hours, C is the capacity in Ah rated at a discharge rate, r, in hours, and n is the multiple or fraction of C_r. So, for a 2.6 Ah lithium ion battery rated at a 2-hour discharge rate, C_2 = 2.6 Ah. When this battery is discharged at a 5-hour rate, $I_\mathrm{t} = 0.2\mathrm{C}_2$ / (1 hour) or 0.2 × 2.6 Ah / (1 hour) = 0.13 A.

Resistance

Electrons, or current, traveling through a material experience a resistance against their movement. The current that a potential, or voltage, is capable of producing is limited by the resistance in the circuit according to Ohm’s law, named after the nineteenth-century German physicist, Georg Simon Ohm. According to Ohm’s law, the voltage difference between the two points is directly proportional to the current between those two points in a conducting medium and inversely proportional to the resistance of the conductor:

$$E = iR$$

where i is the current (A), E is the voltage difference (V), and R is the resistance (ohms).

The unit of resistance is the ohm. The unit may be written as ohm or Ω. A manufactured electrical component with a known resistance is a *resistor.*

The usual physical analogy that helps to visualize electric potential, current, and resistance is a tank of water suspended above the ground, like a municipal water tower (Figure 7-1). There is a pipe that drains the water from the tank. The pressure of the water, which is related to the height of the tank above ground level, forces the water through the pipe at a certain rate. We will assume the amount water flowing from the pipe is small relative to the volume of the water in the tank, so the water level does not change significantly. (The water pressure is also correlated with the amount of water in the tank, of course, but this violates the analogy with the electric potential. The electric potential does not depend on the amount of material.)

The diameter of the pipe provides a resistance against the flow of water from the tank. A larger diameter pipe offers less resistance and allows more water to flow than a smaller diameter pipe. A valve in the pipe is another resistance to water flow. The magnitude of resistance from the valve depends on whether it is open full, closed, or partially closed.

If the tank were built to a higher elevation (higher potential), the force of the water through the pipe would be greater and the rate of water flow through the pipe would increase. Assuming, of course, the resistance in the water pipe is small enough that the extra pipe length does not significantly impede the flow of water.

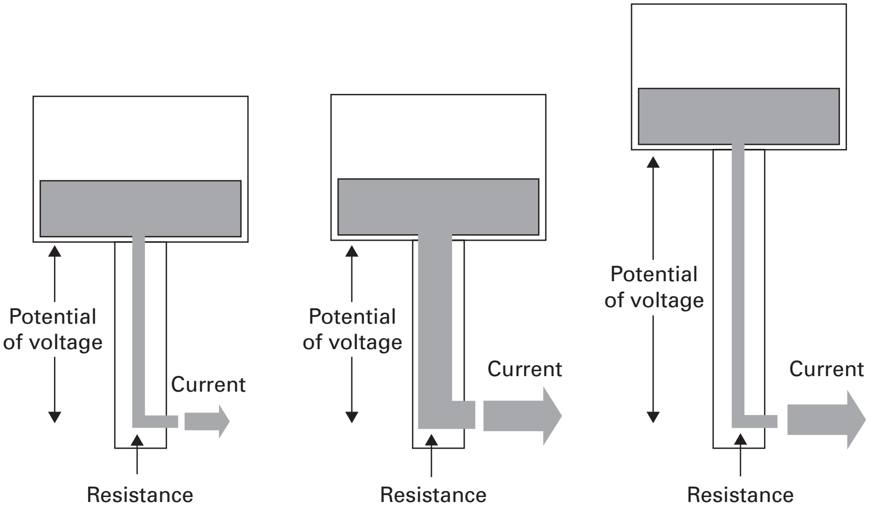


FIGURE 7-1 Water tank analogy for electric potential or voltage, hydraulic flow analogy for electric current and resistance

Just like Ohm's law, the rate at which the water flows (current) is proportional to the water pressure in the tank (electric potential or voltage) and inversely proportional to the resistance to flow through the pipe. This fluid dynamic version of Ohm's law describing the smooth, nonturbulent flow of fluid through a pipe is called the Hagen-Poiseuille equation, or just Poiseuille's law. It was independently developed by French scientist Jean-Louis-Marie Poiseuille and German engineer Gotthilf Hagen in the nineteenth century.

Capacity

The quantity of electricity delivered by a battery is its capacity and measured in units of ampere-hours or amp-hours (Ah). It quantifies how long a battery will last in hours at some discharge current in amps. This is an easy calculation to make when a battery is discharged at a constant current. The discharge current in amperes (A) is multiplied by discharge time in hours (h) to give capacity in ampere-hours:

capacity (Ah) = current (A) × time (h)

A battery that lasted 10 h when discharged with a constant current of 0.25 A delivered a capacity of 2.5 Ah. Alternatively, if you know the capacity of the battery and you want to know how long it will last, then divide the capacity in Ah by the discharge current in A. For example: A battery rated at 1.5 Ah when discharged at a constant current of 0.3 A is expected to provide 5 hours of use (1.5 Ah / 0.3 A = 5 h).

Many applications do not drain batteries using a constant current, though. How the battery is discharged will affect how long it lasts and the discharge voltage (Figure 7-2). The current is probably not constant throughout discharge for batteries discharged through a resistance or using a power load, so simply multiplying current by time will yield a wrong answer.

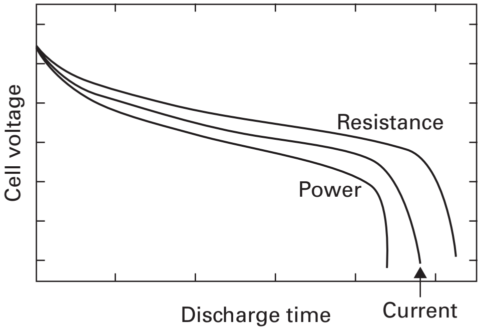


FIGURE 7-2 How different discharge loads affect battery discharge voltage

The capacity is calculated by integrating the current produced by a battery over the discharge time. In mathematical terms, it is written like this:

$$\text{capacity (Ah)} = \int_0^t i\,dt$$

We know from Ohm's law (see the preceding section) that:

$$i = E/R$$

Substituting this into the preceding equation for capacity gives:

$$\text{capacity (Ah)} = \frac{1}{R}\int_0^t E\,dt$$

Since the resistance R (in ohms) is constant, we can integrate the battery discharge voltage (which is the quantity normally measured) over time.

Graphically, the capacity is determined by measuring the area under a plot of discharge voltage against time, like what is shown in Figure 7-3 for a battery discharged with a resistor, divided by the resistance of the resistor.

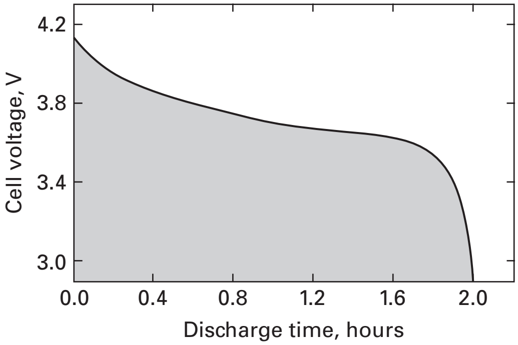


FIGURE 7-3 The capacity for a battery discharged with a resistor calculated using the area under the voltage vs. time curve

It is not very practical to exactly determine the discharge capacity by integration. We would need to be able to write a mathematical function that exactly describes how the current changes with time at each point in time. The next best thing is to approximate the integration by estimating the area under the curve using numerical integration methods.

Calculating the area of a rectangle is simple: height × width. We might use a single rectangle that is centered on the voltage midway through the discharge (Figure 7-4). We can now estimate the capacity by multiplying the height of this rectangle, (voltage E_0), divided by the resistance R to give the current i, by its width (time $t_1 - t_0$).

A single rectangle doesn't fit the curve very well, especially at the beginning and end of discharge. However, if we use many smaller rectangles with their midpoints centered on a voltage-time point on the curve rather than a single large one, the rectangles are a much better approximation for the curve (Figure 7-5). Hopefully by doing this the difference between the area of the rectangles and the curve is smaller, too. The accuracy of the discharge capacity estimate improves with the number of rectangles used.

The area of each rectangle is calculated individually, and they are all added together to give the estimated battery capacity. The shorthand mathematical formula for this is

$$\text{capacity (Ah)} \approx \sum_{j=0}^{n} i_j \times (t_{j+1} - t_j)$$

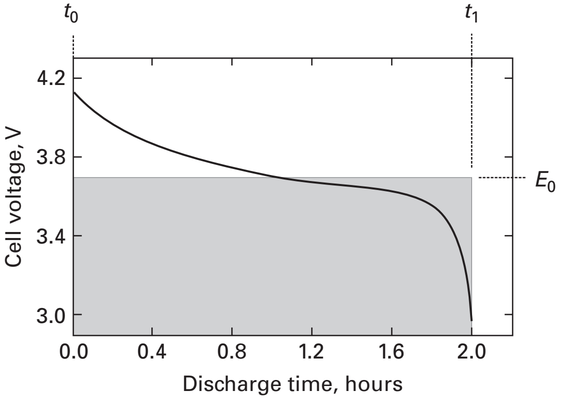


FIGURE 7-4 Estimating battery capacity using the rectangular numerical integration method using one rectangle

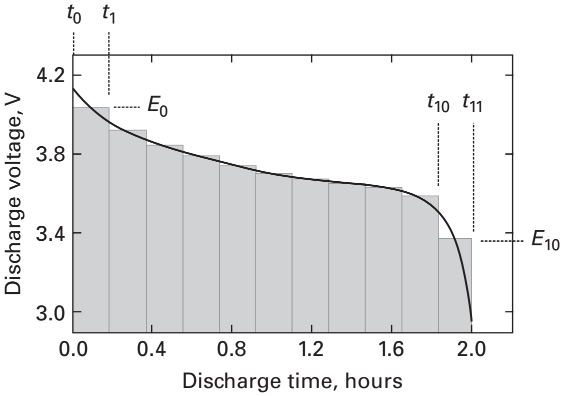


FIGURE 7-5 Estimating battery capacity using the rectangular numerical integration method using many rectangles

or, again using Ohm's law:

$$\text{capacity (Ah)} \approx \frac{1}{R}\sum_{\mathrm{j}=0}^{n} E_{\mathrm{j}} \times (t_{\mathrm{j}+1} - t_{\mathrm{j}})$$

The ≈ symbol means the calculation is an approximation, and the Σ symbol tells us to add all of the terms that follow it. The other symbols are: *i* is current (A), *t* is time (h), *E* is the potential or voltage (V), and *R* is resistance (ohms). The subscripts for *i* and *E* represent the rectangle number starting with 0, and those for *t* correspond to the time point for each increment starting with t_0. The dimensions of the first rectangle are E_0 high and $(t_1 - t_0)$ wide, the dimensions of the second rectangle are E_1 high and $(t_2 - t_1)$ wide, and so on.

We chose to use 11 rectangles in our example (that is, n = 10 for the preceding equations), so for the curve in Figure 7-5, the capacity calculation can be written out this way:

$$\text{capacity (Ah)} \approx [E_0/R \times (t_1 - t_0)] + [E_1/R \times (t_2 - t_1)] + [E_2/R \times (t_3 - t_2)] + \ldots + [E_{10}/R \times (t_{11} - t_{10})].$$

The accuracy of the approximation improves using smaller time increments (that is, more rectangles). There are other methods that could be used, such as the trapezoidal method, but the concept is basically the same.

Power

Electrical energy is the amount of work done to move coulombs of charge through volts potential difference. Electrical power is the how much energy is delivered per period of time. It can be calculated by multiplying the potential or voltage by the current:

$$P = iE$$

where P is the symbol for electrical power with units of watts (W), named in honor of Scottish inventor James Watt, or joules (J), i is the current (in A) and E is the potential or voltage (in V). Other ways to write an equation for electrical power can be done by substituting E from Ohm's law:

$$P = i^2R \text{ or } V^2/R$$

Just as there is a C rate that gives the charge or discharge current relative to the rated capacity of a battery, there is an analogous term for constant power discharge called the "E rate." The reference power load is "E" or "1E" and is computed as is the power (in W) required to discharge a battery to its nominal or rated delivered energy (in Wh) in one hour:

$$\text{E or 1E} = \text{(rated energy) / (1 hour)}$$

where E is in W and the rated energy is in Wh. The E rate is written as multiples or fractions of E, depending on whether the power used is greater or less than the 1E rate.

For our 2.6 Ah lithium ion cell, the rated delivered energy quoted by the manufacturer is 9.6 Wh, so the 1E power load is 9.6 W (9.6 Wh / 1 h = 9.6 W). To discharge this battery at an E/4 or 0.25E rate, the power load needed is 9.6 W / 4 = 2.4 W. The power required to discharge the battery at a 2E rate is 9.6 W × 2 = 19.2 W.

Energy

The energy delivered by a battery is measured in units of watt-hours (Wh). It quantifies how long a battery will last in hours at some discharge power load in watts. Just as it is for calculating capacity with the constant current case just described, the energy delivered by a battery is easy to calculate when it is discharged with a constant power load. The power in watts (W) is multiplied by discharge time in hours (h) to give energy in watt-hours:

$$\text{energy (Wh)} = \text{power (W)} \times \text{time (h)}$$

A battery that lasted 10 h when discharged with a power load of 0.25 W delivered an energy of 2.5 Wh. Looking at this from another angle, if you know the energy of the battery and you want to know how long it will last, then divide the energy in Wh by the power in W: A 9.6 Wh battery discharged at a constant power of 4.8 W will provide 2 hours of use (9.6 Wh / 4.8 W = 2 h).

Again, if the power load is not constant throughout discharge, the energy is determined using the equation

$$\text{energy (Wh)} = \int_0^t E i \, dt$$

The same numerical integration methods used to estimate the capacity can be used here to estimate the energy delivered. If the load is a constant current, then the discharge voltage–time curve is integrated and multiplied by the current.

We now have the terms we need to conveniently describe battery performance.

Practical Battery Performance

The practical, delivered capacity (in Ah) or energy (Wh) a battery can deliver depends on a number of different factors, including the identity of the electrode materials used, the amount of electrode materials in the battery, the design and construction of the battery, and how the battery is used.

The amount of active materials in a battery determines the maximum capacity it can deliver. It is expressed as the total charge, or electricity. While electrochemists usually count charges in coulombs (C), the battery world almost exclusively uses units of amp-hours (Ah) to gauge capacity.

As we saw in Chapter 5, we can calculate the maximum capacity for various electrode materials using Faraday's law, which states the quantity of electrical charge, or capacity, is determined by the number of moles of the active material and the number of electrons involved in the electrochemical reaction.

Let's find the theoretical capacity of a nickel-cadmium (NiCd) cell. The overall electrochemical cell reaction is (see Chapter 10):

Negative electrode reaction: $\mathrm{Cd} \leftrightarrows \mathrm{Cd}^{2+} + 2\ e^-$

Positive electrode reaction: $\mathrm{Ni(O)OH} + \mathrm{H_2O} + e^- \leftrightarrows \mathrm{Ni(OH)_2} + \mathrm{OH^-}$

Overall cell reaction: $\mathrm{Cd} + 2\ \mathrm{Ni(O)OH} + 2\ \mathrm{H_2O} \leftrightarrows \mathrm{Cd(OH)_2} + 2\ \mathrm{Ni(OH)_2}$

Using the equation describing Faraday's law and the atomic weight of Cd (112.4 g mol^{-1}), the capacity, Q_{Cd}, for the negative electrode (Cd) on a mass basis is

$$Q_{\mathrm{Cd}} = (2 \times 26.8\ \mathrm{Ah}) / 112.4\ \mathrm{g\ mol^{-1}} = 0.477\ \mathrm{Ah\ g^{-1}}$$

The equivalent calculation for the positive electrode (Ni(O)OH) is

$$Q_{\mathrm{Ni(O)OH}} = (1 \times 26.8\ \mathrm{Ah}) / 91.7\ \mathrm{g\ mol^{-1}} = 0.292\ \mathrm{Ah\ g^{-1}}$$

To get the total capacity of the negative and positive electrodes per unit mass in g, we add the mass that should provide 1 Ah of capacity for each electrode and take the inverse:

$1 / (1 / Q_{\mathrm{Cd}} + 1 / Q_{\mathrm{Ni(O)OH}}) = 1 / (2.10 \text{ g Ah}^{-1} + 3.42 \text{ g Ah}^{-1}) = 0.181 \text{ Ah g}^{-1}$

The theoretical energy on a mass basis is found by multiplying the mass-based capacity by the cell potential. The Cd/Ni(O)OH cell potential is 1.35 V, so the mass-based energy density is

$0.181 \text{ Ah g}^{-1} \times 1.35 \text{ V} = 0.244 \text{ Wh g}^{-1}$ or 244 Wh kg^{-1}

So, if we wanted to build a NiCd cell that delivers 1.1 Wh, we can calculate the weight of each active electrode material we need:

1.1 Wh / 1.35 V = 0.815 Ah

$0.815 \text{ Ah} / 0.477 \text{ Ah g}^{-1}$ Cd = 1.71 g Cd

and

$0.815 \text{ Ah} / 0.292 \text{ Ah g}^{-1}$ Ni(O)OH = 2.79 g Ni(O)OH.

The active material in our battery weighs a total of only 4.5 g (1.71 g Cd + 2.79 g Ni(O)OH).

The capacity and energy density values are the maximum possible theoretical capacities for electrode materials alone. When looking at actual battery data, though, the practical capacities and energies delivered will be much less, often less than half of the theoretical values.

Batteries usually have an excess of one electrode material over the other. For safety considerations, a lithium–carbon monofluoride cell might be designed to run out of lithium first so that little or none remaining after the battery is completely discharged and discarded. A lithium ion cell may contain an excess of carbon negative electrode material to protect against overdischarge reactions that could cause lithium metal deposits to form.

These cells are said to be either anode or cathode limited, depending on which of the electrodes contains less active material. The maximum theoretical capacity of the battery is then determined by the limiting electrode material.

An example might be a lithium–manganese dioxide cell that is anode limited. If allowed to completely discharge, the cell will be depleted when the Li runs out. We know this cell contains 0.13 g of Li. The electrochemical reaction involved in Li discharge involves one electron for each atom of Li:

$\mathrm{Li} \rightarrow \mathrm{Li}^+ + e^-$

We convert the number of grams of Li to the corresponding number of moles using the atomic weight of Li (6.94 g mol^{-1}) and calculate the maximum theoretical capacity so:

capacity (Ah) = $(1 \times 26.8 \text{ Ah}) \times (0.13 \text{ g} / 6.94 \text{ g mol}^{-1}) = 0.50$ Ah

The capacity of this cell will be 500 mAh regardless of how much MnO_2 is put into the cell. Battery designers must put in just enough extra MnO_2 to allow the Li to deplete first, but not so much that there is a lot of space in the cell taken up by a large excess of MnO_2 that will not be utilized.

Battery electrode materials do not function by themselves. There are other components that take away from the energy density of a battery. As we know from Chapter 5, an electrolyte is necessary for the electrochemical reactions in a battery to proceed. The electrolyte takes up space within the battery, so we already reduced the energy density just by adding in the electrolyte volume.

There are other inactive materials that must be included in a battery for it to work efficiently, conveniently, and safely. (See Chapter 6 for more detailed information on these inactive components.) Separators—the porous electrical insulators placed between anode and cathode—enable the anode and cathode materials to be packed closely together. This is an effective way to take minimize empty space in a battery, but still, they take up some of the battery volume.

The electrode materials may be mixed with materials that enhance conductivity, particularly conductive carbon powders in the positive electrode. This improves the power output and perhaps electrode utilization by reducing the internal resistance, but it does take away from the amount of active material that can be put into a battery. Electrodes formed from powders may also use an inert binder—usually a polymeric material—to maintain the physical integrity of the electrode.

Current collectors are used to convey electrons between the electrode materials and the battery terminals. Insulators and seals are necessary in a practical battery for safety, reliability, and good performance over a long period of time. Some batteries need a certain amount of empty space to help control gas pressure or for electrode materials to expand into during use.

Each of these inactive components is indispensable and key to getting the most energy out of a battery reliably and safely. However, the weight and volume they add end up decreasing the energy density the battery can deliver. The challenge for battery designers is to find ways to incorporate these components in an efficient way that maximizes the energy density of the battery.

The inactive components and battery design are just the start. When the battery discharges, there are other factors that come into play and reduce how much energy it can deliver.

When a battery is at open circuit, that is, not being discharged or charged, the cell potential measured across the terminals is the difference between the potential of the positive electrode (E_c) and the potential of the negative electrode (E_a):

$$V_{cell} = E_{cell} = E_c - E_a$$

where V_{cell} is the measured cell voltage measured at the terminals and E_{cell} is the equilibrium or rest potential.

When the terminals are connected to a load and a battery starts discharging and producing a current, the voltage decreases as a result of what is called polarization:

$$V_{cell} = E_{cell} - E_{polarization}$$

Here, $E_{\text{polarization}}$ is the voltage loss from all sources of polarization (there are several, as we will find out). The extent of the voltage drop is dependent on the current and other factors like temperature.

When a cell is being charged, polarization increases the voltage above the resting potential:

$$V_{\text{cell}} = E_{\text{cell}} + E_{\text{polarization}}$$

Polarization is usually broken down into three general components: ohmic, activation (or kinetic), and concentration (or mass transfer) polarizations:

$$E_{\text{polarization}} = E_{\text{ohmic}} + E_{\text{activation}} + E_{\text{concentration}}$$

Ohmic polarization is the change in voltage from the electronic and ionic, resistance of the battery. This is more like a true electrical resistance than the other polarizations. The voltage drop is proportional to the current (remember Ohm's law). It is alternatively called an *iR* (current times resistance) drop in recognition of this.

Energy is lost as heat as a result of ohmic polarization. This can lead to dangerous temperature increases within the battery if the current and the resistance are great enough, so battery designers work hard to minimize the ohmic resistance for batteries, especially if the battery will experience high current levels.

In many batteries, the electrolyte conductivity dominates the ohmic polarization, but there are contributions from all of the electrical connections as well (terminals, current collectors, weld joints, particle-to-particle contact in electrodes composed of compressed powders, and so on).

The activation polarization is the energy it takes to drive the charge transfer and associated chemical reactions that may occur during the electrode reactions. Activation polarization is sometimes called overpotential or overvoltage, but these terms are used less frequently today.

Concentration polarization occurs from mass transport limitations in the electrolyte or the electrode materials themselves. Mass transfer is the movement of molecules, atoms, or ions under the influence of a gradient of concentration, electric field, or density. So, mass transfer can be divided into three processes: diffusion, migration, and convection.

Diffusion is mass transfer that occurs when there is a gradient in the concentrations of chemical species. Molecules, atoms, and ions move from regions where they exist in a higher concentration to where they are in lower concentration. If allowed to continue unencumbered, the concentration will end up the same everywhere. Rates of diffusion can be on the order of 10 cm min^{-1} for gases, 0.05 cm min^{-1} in liquids, and about 1×10^{-5} cm min^{-1} in solids. Diffusion plays a large part in mass transfer polarization in batteries.

Migration is the movement of charged species like ions as a result a potential field gradient, meaning there is a potential difference between two points. Migration effects are reduced when there are high concentrations of ions dissolved in solution, though.

Convection is the movement of fluids as a consequence of a density gradient, including those caused by uneven temperature distributions. It can even result from diffusion in concentrated solutions, like most battery electrolytes.

Whatever the driving force for mass transfer, the chemical species involved in the electrochemical reactions can only move so fast. This is the maximum current, called the limiting current, at which the electrochemical reactions can be supported (Figure 7-6), even if the voltage is increased.

From another perspective, as a battery is discharged at currents approaching the limiting current, the battery voltage decreases (or increases during charging) as a result of concentration polarization. As the current is increased further, other, unwanted electrochemical reactions may occur, such as electrolyte breakdown to form gasses.

The relative contributions of the different polarization types are dependent on the current (Figure 7-7). Ohmic and concentration polarization are usually not very significant at low currents, so activation polarization tends to dominant. As the current is increased, ohmic polarization increases (Ohm's law, again) and takes over. At the highest current levels, concentration polarization becomes important because of the mass transfer limitations (limiting current).

The different processes involved in polarization also vary with the extent of battery discharge (Figure 7-8). Early on in the discharge and throughout most the discharge life of a battery, activation and ohmic polarization are the more significant contributions to the displacement from the open circuit voltage. As mentioned, the relative contributions are dependent on the current. Near the end of discharge, battery voltage starts to decrease rapidly as the battery electrode materials (and perhaps the electrolyte) become depleted. Ohmic polarization increases as a result, but also concentration polarization may become the most significant factor.

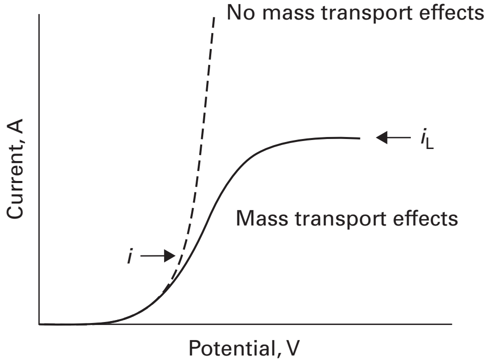


FIGURE 7-6 The net current i and the limiting current, i_L, for an arbitrary electrode reaction as a function of the difference between the potential of the electrode while there is a net current and the standard electrode potential for the electrode

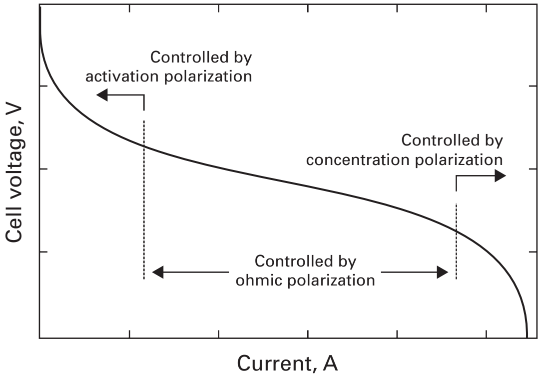


FIGURE 7-7 Contributions to polarization at different current levels

The manner in which a battery is discharged—resistance, constant current, or constant power—affects the voltage during discharge. In the case of a battery discharged using a constant current, the voltage behavior will respond as in Figure 7-2. If a battery is instead discharged using a resistor, the current decreases in response to the battery voltage decrease: $E = iR$. As the current decreases, so does polarization and the battery will last longer than one discharged using a constant current (Figure 7-2). Discharge a battery using constant power, $P = iE$, and the current increases as the voltage decreases. An increase in current increases the polarization and the battery will not last as long as the battery discharged using constant current.

The total polarization from all sources is frequently imagined simply as a single resistance, since polarization increases as the current increases, although it may not

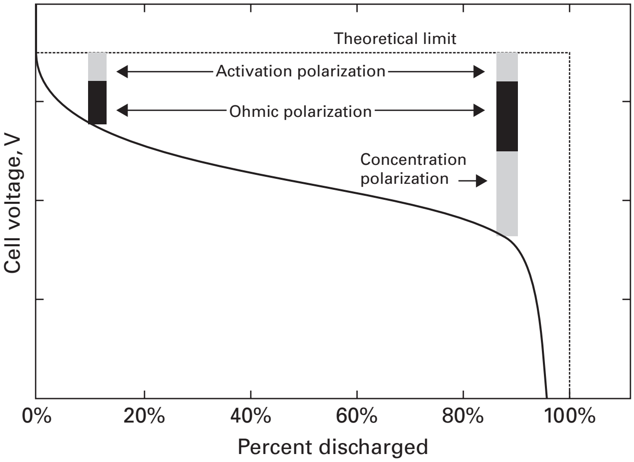


FIGURE 7-8 Contributions to polarization during battery discharge

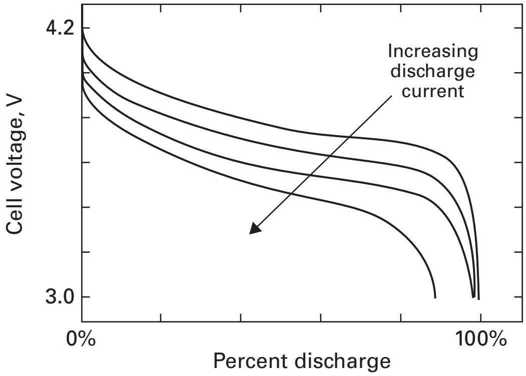


FIGURE 7-9 Discharge voltages as a function of discharge rates for a lithium ion cell

strictly follow Ohm's law because it is not an ideal resistor. A commonly used term in the battery industry for the total decrease in cell voltage during discharge, or increase during charge, is called the internal resistance or internal impedance. The internal resistance is an easy way to measure and think about voltage loss when there is a current.

The end result of polarization is a lower discharge voltage. As polarization increases, whatever the reason, the voltage is depressed and can reduce the battery discharge life because it will reach a minimum discharge voltage earlier (Figure 7-9). Likewise, polarization increases the charging voltage resulting in less capacity put into the battery when it attains its maximum charging voltage sooner.

Lowering the operating temperature also lowers the discharge voltage and constraining the energy a battery can deliver (Figure 7-10). Reaction rates and the

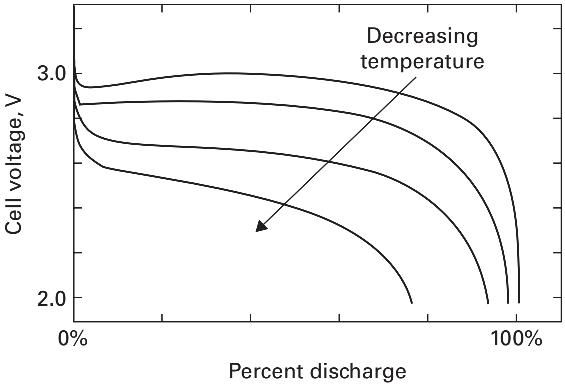


FIGURE 7-10 Battery discharge voltage curves with operating temperature

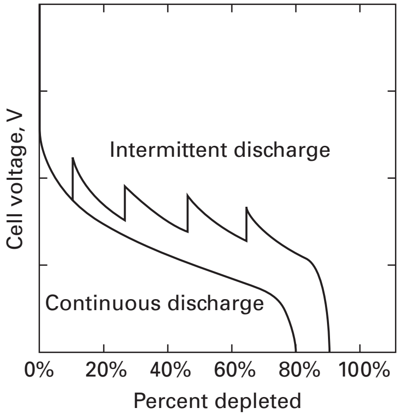


FIGURE 7-11 Comparison of continuous and intermittent discharge

movement of ions tend to slow as the temperature decreases. If the temperature is low enough, the electrolyte could freeze and effectively shut down cell performance.

Some battery designs, particularly those not designed to handle high currents, benefit from rest periods either at open circuit or a relatively low current. This, in effect, allows mass transfer to catch up and equalize the concentrations of the atoms, molecules, and ions involved in the electrochemical reactions of the battery. The net result is the battery voltage recovers and is able to discharge longer when the current is applied once again (Figure 7-11).

Other Battery Performance Behaviors

There are a couple of other factors that reduce battery output. These are generally related to the battery chemistry.

Discharge Voltage

The nature of the electrochemical reactions involved during battery discharge determines the voltage characteristics, at least at low levels of polarization. If an anode or cathode material forms a product that is in a different and distinct chemical substance, or phase, the battery voltage will remain relatively constant throughout discharge.

For example, in a zinc-mercury oxide battery, both the zinc (Zn) anode and the mercury oxide (HgO) cathode form different chemical phases during discharge. Zn dissolves into the electrolyte or precipitates as zinc oxide (ZnO):

$$Zn + 4\ OH^- \rightarrow Zn(OH)_4^{2-} + 2\ e^-$$

or

$$Zn + 2\ OH^- \rightarrow ZnO + H_2O + 2\ e^-$$

The HgO cathode forms mercury metal (Hg):

$$HgO + H_2O + 2\ e^- \rightarrow Hg + 2\ OH^-$$

The resulting discharge voltage is flat, as seen in Figure 7-12.

If the product of an electrochemical reaction is formed in the same phase as the starting material (a solid state solution), the discharge voltage will be characteristically sloped. An example is the discharge of alkaline zinc–manganese dioxide cells (Figure 7-12), at least for a large portion of the discharge.

Different chemical phases may form at different points during discharge with some electrode materials leading to a stepped discharge voltage curves. Divalent silver oxide, AgO, in some zinc-silver oxide cells discharges in two reaction steps,

$$2\ AgO + H_2O + 2\ e^- \rightarrow Ag_2O + 2\ OH^-$$

$$Ag_2O + H_2O + 2\ e^- \rightarrow 2\ Ag + 2\ OH^-$$

that result in two distinct discharge voltage levels during discharge (Figure 7-12).

Voltage delay generally occurs when an active electrode reacts with the electrolyte to form a partially passive layer. The passive layer increases the internal resistance of the battery leading to a voltage decrease (Figure 7-13). If the discharge current is sufficiently great enough, the passive layer will break down and the voltage recovers.

This behavior is usually a function of storage time as reaction products build up on the electrode surface or it may be a characteristic of the electrode chemistry, as for

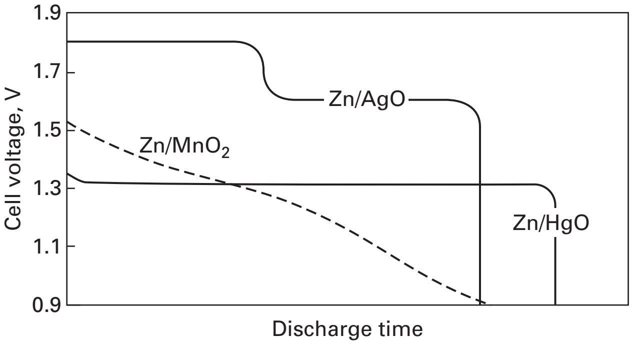


FIGURE 7-12 Different discharge voltage behavior for different battery electrochemical reaction types

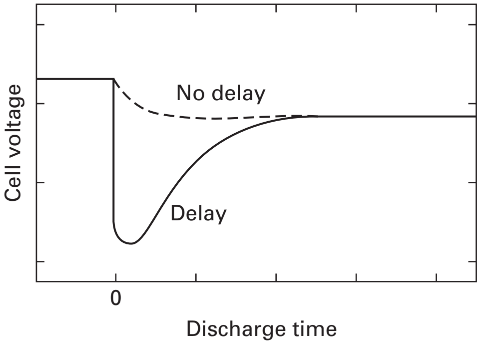


FIGURE 7-13 Battery voltage behavior in the presence or absence of a voltage delay

carbon monofluoride in Li/CF_x cells. Some batteries are designed to intentionally form a controlled passive layer to improve storage life. For instance, the chemical chromate may be added to magnesium–manganese dioxide (Mg/MnO_2) cells. Chromate reacts with Mg to form a magnesium oxide layer and stabilize it (that is, reduce self-discharge) during long periods of storage. This passive layer is easily removed when the battery is discharged, but results in a temporary dip in the battery voltage (Figure 7-13).

If the passive layer has a high enough resistance or the discharge current is too low, the passive layer may not be stripped off and the battery voltage will not recover.

Self-Discharge

Self-discharge is the term used for any loss in usable capacity that occurs over time as a result of parasitic chemical reactions. It may also be called charge retention sometimes, particularly for rechargeable batteries. It is sometimes quoted as a rate of capacity loss per some unit of time (month or year) or shelf life, the time it takes for the battery capacity to deteriorate to some minimum output level specified by the manufacturer. Self-discharge may not be a linear function with time. It may be faster at first, and then slow significantly with storage time.

The self-discharge reactions lead to loss of active material and increased internal resistance. The rate of self-discharge is dependent on the cell chemistry, cell design, the purity of the battery materials used, and the depth of discharge. Higher temperatures usually accelerate self-discharge.

Typical values for self-discharge rate and shelf life for some commonplace cell types at room temperature (about 21°C) are summarized in Table 7-2.

TABLE 7-2 Self-Discharge Rate and Shelf Life for Different Cell Types

Cell Type	Self-Discharge Rate
Leclanché zinc-carbon	5% to 10% per year
Alkaline zinc–manganese dioxide (Zn/MnO_2)	3% to 4% per year
Zinc-silver oxide (Zn/Ag_2O)	1% to 5% per year
Zinc-air	3% to 5% per year with tab on 20% to 60% per month with tab off
Lithium–thionyl chloride ($Li/SOCl_2$)	1% to 3% per year
Lithium–manganese dioxide (Li/MnO_2)	0.5% to 2% per year
Lithium–carbon monofluoride (Li/CF_x)	0.5% per year
Lead-acid	15% to 30% per month (SLI) 4% to 8% per month (VRLA)
Nickel-cadmium (NiCd)	5% to 25% per month
Nickel–metal hydride (NiMH)	12% to 25% per month
Lithium ion	2% to 5% per month

Measuring Battery Performance

The simplest way to evaluate battery performance in any particular use is an application test. Place the batteries, say R20 cells (Heavy Duty D size), in the test device, which for this example will be a flashlight. Turn the flashlight on and use a timer (clock or calendar) to measure how long it takes for the flashlight bulb to go dark. Write down this time in minutes and you have a record of battery performance in flashlight-minutes.

A flashlight is often used intermittently. It is turned on for a short period of time, then turned off and put away until it is needed again. So, you may also want evaluate performance of batteries under a protocol that represents this kind of use. For example, turn on the flashlight for four minutes every hour for eight hours a day. Somewhat tedious, but when the battery no longer lights the flashlight, record the total time the flashlight was on.

If the flashlight will be used outdoors in winter, you may want to know how long the flashlight will last in the cold. A continuous discharge test with the flashlight placed in a refrigerator set to 2°C (36°F) might be a good way to simulate winter use conditions. Place the flashlight in a refrigerator; allow some time for it to come to temperature of the refrigerator. Turn on the flashlight and check for when the light goes out.

These tests are repeated for the same type of battery from two other manufacturers, and the data might look something like what is in Table 7-3.

TABLE 7-3 Simulated Discharge Performance for R20 D-Size Heavy-Duty Batteries

Battery Manufacturer	Continuous Discharge Time, Flashlight-Minutes	Intermittent Discharge Time, Flashlight-Minutes	2°C Continuous Discharge Time, Flashlight-Minutes
A	415	640	330
B	380	595	300
C	425	645	340

Some battery designs, particularly those not designed to handle high currents, benefit from rest periods either at open circuit or a relatively low current. This, in effect, allows mass transfer to catch up and equalize the concentrations of the chemical species involved in the electrochemical reactions of the battery. The net result is the battery voltage recovers and is able to discharge longer when the current is applied once again (Figure 7-11).

Zinc-carbon batteries work best when used intermittently. Another thing to note is that these batteries do not last as long when discharged at a lower temperature. The battery reactions slowed as the temperature decreases.

There are differences among the batteries, and you probably have enough data to select the best battery for our flashlight application. You may choose the batteries from company C because they last the longest or those from company B if they are less expensive.

This is a simple example, but the most straightforward way to assess battery performance is to measure the capacity or energy under a set of conditions relevant to your application.

If you are evaluating a rechargeable battery, you may also calculate the coulombic efficiency. The coulombic efficiency is the ratio of the discharge capacity to the charge capacity, or the discharge energy to charge energy, for an individual charge-discharge cycle. If this ratio is one, then all of the capacity put into the battery when charging it is being recovered during discharge. Generally the coulombic ratio is slightly lower.

Losses may be the result of parasitic reactions that occur during charging, a higher internal resistance, or a charging rate that is just too fast for the battery to manage.

The battery testing we just performed is a straightforward way to test batteries, but the data is limited to the flashlight used, or could perhaps be extended to similar flashlights. What if you want to evaluate battery performance for different devices that use the batteries differently? Or you want more information about the battery discharge characteristics, like how the voltage changes over time.

The next simplest way to evaluate battery performance is to measure discharge capacity. This may be done by welding or soldering a resistor that is matched as closely as possible to your application load across the battery terminals. A $10 voltmeter can be used to monitor the battery voltage over time. Rather than watching the meter and writing down the discharge voltage with time, a computer interface might be set up using inexpensive software to take the measurements for you.

Battery manufacturers use sophisticated (and expensive) equipment to evaluate batteries. They have to test many, many batteries under a wide variety of conditions, so automated test equipment becomes important.

This equipment could be custom built using electrical test equipment and homemade software, or complete test systems can be purchased from equipment suppliers that manufacture dedicated battery test equipment. The ability to charge as well as discharge batteries is important for rechargeable battery manufacturers.

Battery test equipment may be used in controlled potential (potentiostatic), current (galvanostatic), or power modes to discharge batteries rather than resistors. The loads may be applied continuously, intermittently, or in short pulses.

Chapter 8

Battery Reliability and Safety

IMPORTANT CONCEPTS FROM THIS CHAPTER:

- Battery reliability: The probability of failure
- Battery safety: The consequences of failure

Reliability

Battery reliability is the probability that a battery will deliver energy and power in a specified manner under a defined set of conditions.

Battery performance—the ability of a battery to deliver defined power and energy levels—is not constant. How it performs depends on a number of factors. The environmental conditions under which a battery operates usually have a large effect on performance, particularly temperature and mechanical vibration or shock. For some batteries, pressure (high and low) and humidity may also affect their performance.

Batteries are designed and their materials are chosen to function under a range of conditions that are relevant to the intended applications. A lithium–manganese dioxide (Li/MnO$_2$) coin cell that runs a wristwatch will mostly operate at room temperature, or about 21°C (70°F).

That same Li/MnO$_2$ coin cell may instead be used to power a tire pressure sensor—devices mounted in an automobile wheel that measures the air pressure in the tire. Temperatures may range between –40°C (–40°F) and +120°C (+250°F), or even higher, in this application. Not to mention the severe shock and vibration it could experience on rough roads or hitting potholes.

So, battery manufacturers must either supply different batteries for different applications or design their batteries to reliably operate under as large of a range of conditions as possible.

Time is another factor. Some batteries may need to be stored unused for long periods of time, and then must function immediately when needed. Batteries typically lose some of their energy just sitting on a shelf for extended periods of time.

There are a number of ways a battery can fail to meet performance expectations, including self-discharge that decreases the energy output of a battery from parasitic chemical reactions depleting the active materials, or else increased internal resistance that reduces the power output of a battery.

Measuring Variability

Physical dimensions, discharge performance, internal resistance, and all of the other important characteristics of a single battery type vary somewhat from cell to cell and battery to battery. These variations are the cumulative result of all the variabilities associated with all of the individual cell components. Not only that, each of the many manufacturing process steps that are necessary to assemble the battery can have their own variability that affects the overall cell variability.

Battery manufacturers strive to minimize the sources of variability of cell components and manufacturing processes, but variability cannot be eliminated altogether. Raw material, component, and battery specifications are written with this fact in mind by including tolerances—an acceptable range of variability for each component part and for the battery itself.

Battery manufacturers also perform an assortment of quality assurance tests on incoming raw materials and purchased components, as well as the completed batteries during and after manufacturing to verify they meet specifications within the range of specified tolerances. There is variability in the equipment used to test batteries that may affect, however slightly, their measured performance outputs.

Batteries may be shipped to and stored in warehouses or other storage facilities following manufacture. They are shipped to the customer, who may store the batteries for unpredictable periods of time. During storage and while shipping, batteries may be exposed to different environmental conditions, especially high temperatures, which may measurably degrade performance. Finally, just the elapsed time between manufacture and use may also affect battery operation.

An end user who balances the purchase price against battery performance claims from the manufacturer expects the battery to meet specifications. So, measuring and understanding variability is important for manufacturers to evaluate battery quality during manufacturing and to predict the reliability of a battery to perform according to specifications under different use conditions.

For some attributes, like the physical dimensions or weight, a battery manufacturer can easily measure these and provide a specified range for these parameters for each battery type. They may even be standardized for some battery types and sizes. An alkaline zinc–manganese dioxide AA cell has the same dimensions as a nickel–metal hydride AA cell.

Battery performance reliability and failure predictions are not so easy. For some applications, this may involve predicting battery operational characteristics over many years using only short-term battery test data.

Calculating the probability of batteries meeting specifications, or stated another way the probability of some sort of battery failure occurring, is important for manufacturers so that they can establish appropriate expectations for the customer through performance claims or specifications. The customer, in turn, may require this information to help assess the performance characteristics and reliability of their equipment or device for their customers.

This kind of information is also used by the battery manufacturers to improve their batteries and reduce failure rates.

Another incentive is minimizing warranty costs paid to customers for underperforming batteries. If a battery manufacturer predicts the rate of failing to achieve the expected battery discharge capacity to be 0.1 percent, they can project the cost of paying out warranty claims on one battery out of every 1,000 batteries sold. This can then be used to help set pricing and factor into profit estimates. If their calculation is wrong and the failure rate is instead, say, 0.3 percent they would need to pay three times the original estimates in warranty claims.

For the reasons just stated, battery manufacturers devote considerable resources to measuring, monitoring, and evaluating battery quality and reliability during all stages of battery design, development, and manufacturing.

The variability of anything can be understood by looking at the distribution of a measured quantity. Like individuals are grouped together into a population and their characteristics measured.

Let's say we are a battery manufacturer and we want to understand the variability characteristics of our 18650 lithium ion cells. We know from past testing experience that our cells have a capacity of 2.2 Ah on average when discharged using a constant current of 1.1 A at room temperature (21°C) following a full charge per the recommended charging procedure.

The discharge time in hours is equal to the capacity in amp-hours divided by the current in amps, so the cells are expected to last 2 h when discharged under these conditions. We may not know all of the different uses of the battery, but we figured out that a 1.1 A discharge rate at 21°C reasonably simulates how our battery is utilized by the customer.

We remove a sample of 100 cells from a large manufacturing lot and test them as just described. These are only a sample, and we are hoping that what we find out about the performance characteristics of these batteries will accurately represent how the rest of them will perform in the users' hands.

The voltage curves might look like those of five of the cells shown in Figure 8-1. Not all of the cells complete discharge at the same time. Some last longer than two hours, and some less.

A graph of the different discharge times is shown in Figure 8-2. Discharge times range from 1.90 hours to 2.09 hours, but the mean, or average, discharge time is 2.00 hours.

Plotting the distribution of discharge times is more informative. We do this first by dividing the full range of discharge times into groups of equally spaced ranges of discharge times, or *bins* as they are commonly called. Your spreadsheet or statistics software probably provides a way to do this automatically.

For our example, we want to use time increments of 0.02 hours, so the bins are 1.88 to 1.90 hours, 1.90 to 1.92 hours, and so on up to 2.1 hours. Cells that completed discharge within a particular range of times are lumped together into a time bin and the number of cells within each bin is counted. A histogram of the number of

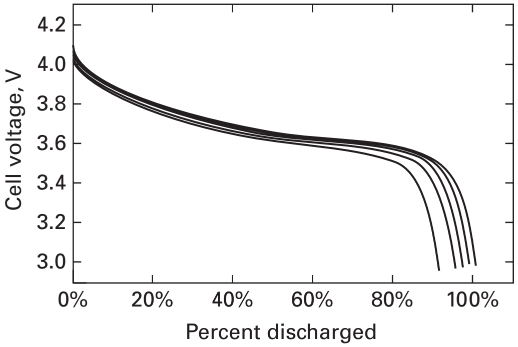


FIGURE 8-1 Discharge curves for five lithium ion 18650 cells with nominal capacities of 2.2 Ah charged per the manufacturer's recommended procedure, and then discharged with a 1.1 A constant current

batteries (or percent of the total number of batteries) within each bin is shown in Figure 8-3.

There are a number of different types of distributions, but many can be fit to what is called a "normal" distribution. A normal distribution curve depicts the probabilities of the individuals in a population will have a certain value. The peak of the curve occurs at the average value for all of the individuals. The curve drops off from the peak and tapers toward zero at each end (nicknamed the "tails" of the distribution).

Using a normal distribution like in Figure 8-3, we can also calculate various statistical parameters, like the standard deviation, which is a measure of the variability. (Refer to any book on statistics to get the mathematical formulation of standard deviation.) Here, the standard deviation for the discharge time is 0.03 hours. The mean and the standard deviation (abbreviated sd in Figure 8-3) are written like this: mean ± one standard deviation, or in this case 2.00 ± 0.03 hours.

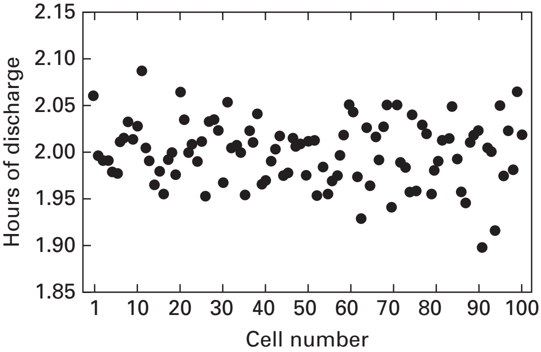


FIGURE 8-2 Variation in measured battery discharge times for 100 lithium ion 18650 cells with a nominal capacity of 2.2 Ah charged per the manufacturer's recommended procedure, and then discharged with a 1.1 A constant current

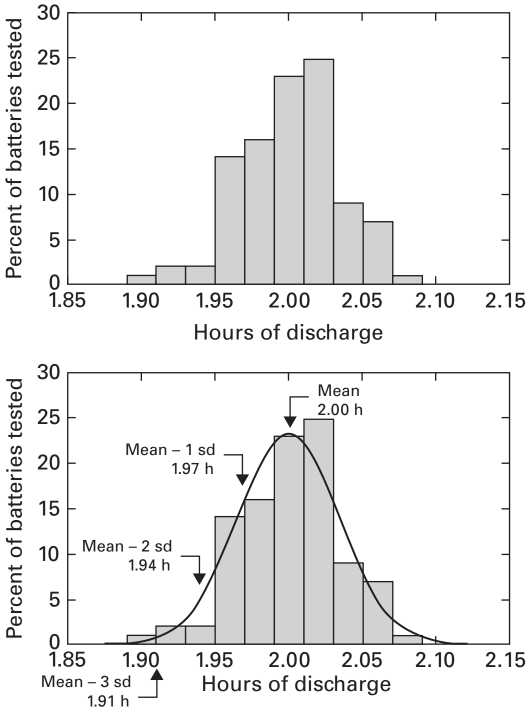


FIGURE 8-3 **Top: The distribution of measured battery discharge times for 100 lithium ion 18650 cells charged per the manufacturer's recommended procedure, and then discharged with a 1.1 A constant current. Bottom: The same distribution of discharge times with a superimposed normal distribution curve. The abbreviation "sd" stands for standard deviation.**

If these 100 test samples are sufficiently representative of the remainder of the batteries in the manufacturing lot, there is a 50 percent probability that any one battery will deliver a discharge time less than the mean value (2.00 hours in our example) under the same test conditions. The probability of one of our batteries having a discharge time within one standard deviation of the mean value, between 1.97 and 2.03 hours, is about 68 percent—a 34 percent probability of being greater than the mean discharge time and a 34 percent probability of being less than the mean discharge time.

We might really be interested only in the batteries that deliver less than the mean discharge time if we don't care that some cells may run longer than the average time. In this case, we can say there is an 84 percent probability a battery discharged under the same test conditions will deliver a discharge time equal to or greater than 1.97 hours (the mean minus one standard deviation). In other words, there is about a 16 percent probability a battery discharge time will be less than 1.97 hours, or a little more than 1 in 6 chance.

The probability of a battery with a discharge time less than two standard deviations from the mean, or 1.94 hours, is 2.3 percent, and less than three standard deviations (1.91 hours) is 0.13 percent.

So, let's say we want to offer a warranty and we budget for a warranty payout rate of 1 out of every 1,000 batteries. We can use the normal distribution curve to calculate the discharge time, 1.90 hours, below which there is a 0.1 percent probability that a battery will deliver less than 1.90 hours and fail to meet customer expectations. So, we might set our specification minimum at 1.90 hours when our battery is discharged with a constant current of 1.1 A at 21°C.

This is a simple example of how one can specify battery performance. It may not be that easy, though. The distribution may not be normal. Perhaps it is skewed to one side or the other. Or there could be more than one distribution superimposed. In addition, it may be difficult to compare the performance of a battery discharged in a controlled test environment to a battery used in an actual device.

Further, we have not considered any of the many other factors that contribute to early battery failures, rather just cell-to-cell variations in discharge performance under a strict and limited set of conditions. Outright battery failures may be more of a concern for users than missing the capacity specification by a few percent.

Assessing Reliability

We take a look at reliability and failures related to the battery in this section and not those where battery failure is externally induced. A faulty device may completely discharge a battery prematurely. An end user may misuse a battery by excessively charging a battery at a higher-than-recommended temperature or use it in the wrong application. Improper handling and misuse are said to be the most common causes of a battery failing to perform up to expectations. In each of these cases, battery performance will be adversely affected, but the battery is only an innocent bystander.

Remember that battery reliability is the probability that a battery will deliver defined energy and power levels under a specific set of conditions. The end of battery life can be defined in a number of ways, including

- The voltage, either without a load (open circuit voltage) or with a load (loaded or discharge voltage), falls below a specified limit at which a device can no longer properly operate.
- The internal resistance increases beyond a defined threshold value.
- The power output is too low.
- A decline in discharge capacity below a defined level with the number of charge and discharge cycles of a rechargeable battery.
- Venting of gas and electrolyte leakage as a result of excessive pressure buildup.

Any or all of these can be used by a battery manufacturer or end user to define the end of the useful service life for a battery. Some are related. For example, a high internal resistance results in a lower loaded voltage and reduced power output.

The usual figures of merit, or measure, that define battery life at the point of failure or normal depletion are time (minutes, years), capacity (Ah), energy (Wh), the number of charge and discharge cycles, or the number of high current pulses, depending on the battery type and target applications for the battery.

Here is an example: The end point limit is often a minimum voltage level for a particular load or range of loads and a set of environmental condition. For example, a PR70 zinc-air cell (10 size) discharged with a 3 kΩ resistor at 21°C and 50 percent relative humidity to a voltage limit of 0.9 V is expected to deliver 91 mAh.

For rechargeable cells, this limit might be the number of charge and discharge cycles before the discharge capacity decreases to 80 percent of the discharge capacity measured in the first cycle. Another example: An 18650 lithium ion cell with a nominal capacity of 2.40 Ah is charged to 4.2 V at 1.2 A and held at 4.2 V until the current drops to 0.12 A (constant current—constant voltage charging protocol—see Chapter 11) at 21°C. Following a 20-minute rest at open circuit, the cell is discharged with a constant 1.2 A current to 3.0 V.

The change in discharge capacity for this cell with the number of charge and discharge cycles is shown in Figure 8-4. This cell is expected to provide about 600 such charge and discharge cycles before the cell discharge capacity declines to 80 percent of the capacity delivered in the first cycle (2.40 Ah × 80% = 1.92 Ah).

Frequently, manufacturers will provide multiple values for battery life (as well as other functional characteristics like discharge voltage) for multiple sets of conditions.

The underlying causes for battery failure are many. They tend to vary across different cell chemistries, different construction types (cylindrical bobbin, spiral wound, prismatic, button, coin) and battery sizes. Different failure modes are more likely to occur at different times during the life of a battery, while some can occur at any time. They could have different probability distributions, and there may be multiple failure mechanisms operating simultaneously that confound the data and complicate analysis.

We can break down failures into four broad categories based on when they occur during the life of a battery—early failures, latent failures and random defects, premature end of life, and normal depletions. We will start with the last one first.

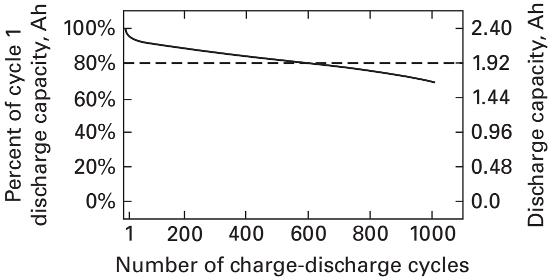


FIGURE 8-4 The change in discharge capacity with the number of charge and discharge cycles for a lithium ion cell. It takes about 600 cycles before the discharge capacity drops to 80 percent of the discharge capacity from the first cycle.

Normal Depletion

Normal depletion (or wear-out, as some call it) is not really a failure mode. All batteries have a finite service life—even rechargeable batteries. Eventually they will become depleted as the active materials are consumed or the internal resistance increases to a high enough level, or some other mechanism comes into play, and the battery is no longer able to supply sufficient power.

Primary batteries become depleted when the active materials are discharged with a load. Other parasitic chemical reactions, collectively called self-discharge, also decrease the amount of active material over time, but no useful energy can be captured from these reactions. Self-discharge results in the loss of performance as the active materials are consumed. The selection of battery chemistry and design, as well as environmental exposure (particularly temperature) influences the rate of self-discharge. Battery designers try hard to minimize self-discharge, of course.

The energy in secondary batteries is replenished with an external source of electricity that is converted into chemical energy. Even with recharging, secondary batteries eventually become unable to deliver an acceptable discharge capacity or power, often a result of their inability to accept a sufficient charge during recharging.

Secondary batteries also undergo self-discharge, usually at rates much greater than those of primary batteries. Some, but not all, of the capacity lost to self-discharge is recovered during charging.

Deterioration of performance is a function of time and the number of cycles, but also how the battery was stored, discharged, and charged, as well as the environmental conditions in which the battery is operating.

Performance requirements under a wide range of environmental conditions (especially temperature) are defined by battery manufacturers. They must first understand how their batteries will be used by customers, design appropriate tests to gauge battery performance under a set of conditions the battery will likely experience, implement enough testing to adequately characterize the outputs and limitations of their batteries, and then assign an expected battery life based on the test data or a model projection based on the test data. Of course, normal battery depletion is subject to cell-to-cell variability as discussed earlier in this chapter.

Early Failures

Early failures become evident soon after manufacturing and before, or at least not long after, a battery starts being used.

We won't count the failures at various steps during manufacturing and before completion of the battery. These failures may count against the manufacturing yields if the cause for the failure cannot be fixed and the battery must be scrapped. This, in turn, results in fewer batteries produced and a higher cost of manufacturing a completed battery. Such failures also may point to a quality issue that is the result of a design weakness, defective components, or an errant manufacturing process step.

Many early failures are exposed before the batteries leave the manufacturing facility. Battery manufacturers perform a variety of tests designed to find early failures and help assure the batteries will function as advertised. Testing may include electrical measurements like open circuit voltage, loaded voltage, and impedance or internal resistance., as well as physical characteristics like dimensions and weight. The seals may be tested for leaks. The entire cell may be inspected after assembly using X-ray imaging. Microcalorimetry is an instrumental method that measures very small amounts of heat released by a battery. The amount of heat released is related to the rate of self-discharge and the magnitude of an internal short circuit if one exists.

The rate of early failures starts at a relatively high level but rapidly decreases (see the top graph in Figure 8-5).

Some examples of early failure causes are

- **Human error** Handling errors or accidents; for instance, batteries may be stored under too severe conditions (such as high vibration or temperature levels), dropped from a height onto a hard surface, or inadvertently short-circuited by connecting the negative and positive terminals.
- **Design flaws** These are usually found with accelerated stress tests performed during battery development, though. (See the next section, "Accelerated Testing.")
- **Nonconforming or missing components** Component dimensions may be out of specification, or components made from the wrong material, resulting in chemical contamination, corrosion of metal parts, or mechanical weaknesses.

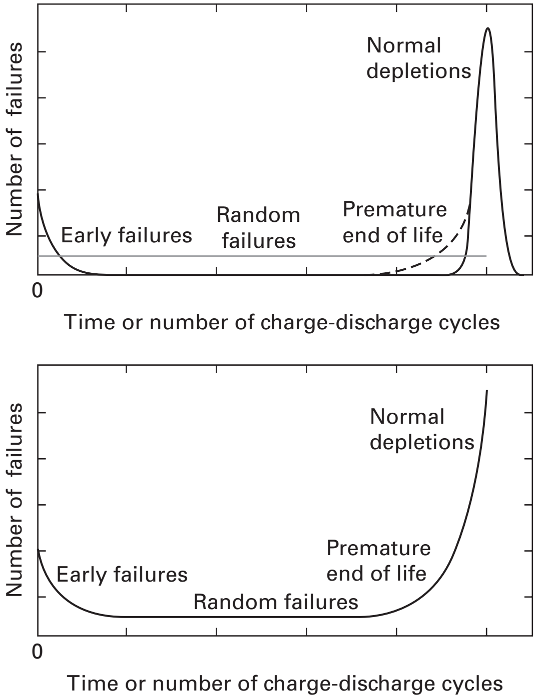


FIGURE 8-5 Top: Distributions of failure rates for different failure modes occurring throughout battery life—early failures, random defects, premature end of life, and normal depletion. Bottom: Combined failure rates for all failure modes.

Components may be damaged or incorrectly made. Burrs on metal edges can break through separators and insulators to make direct contact between electrodes, causing an internal short circuit and early battery depletion.

- **Contamination** Foreign materials unintentionally allowed to get into the battery during manufacture may contain certain chemicals that are incompatible with other battery materials or otherwise decrease performance. Foreign material like bits of metal can puncture separators and insulators, causing an internal short circuit and early battery depletion.

  Dendrites can form in some battery systems when a piece of metal finds its way to the surface of the cathode material. If the metal can be oxidized by the positive electrode material, it can dissolve in the electrolyte, and diffuse to the negative electrode. There it may be reduced back to the metal on the surface of the negative electrode material. The contaminating metal could increase the internal resistance if enough of the negative electrode material becomes blocked.

  The oxidation-dissolution-diffusion-plating reactions could persist until the contaminating metal is depleted. As the metal continues to plate on the negative electrode material, it may form dendrites or fingers of metal that grow toward the positive electrode. Eventually this process can create a direct connection between the negative and positive electrodes, causing an internal short circuit and early battery depletion (Figure 8-6).

  Other contaminants may result in other parasitic reactions that cause gassing, like iron in the zinc electrode of an alkaline zinc–manganese dioxide cell. If the internal gas pressure is high enough, it could cause the cell to swell or force a vent to open with an attendant loss of electrolyte.
- **Manufacturing variances** Processes may not be in control, and the resulting battery may have low quality or could have widely variable performance. If welded electrical connections are weak, the weld can break and create an open circuit. Weak seals can lead to electrolyte leakage and ingress of moisture, leading to a loss of battery performance.

Random Defects

These may occur at any time during battery life after manufacture. This type of failure can occur during storage on the shelf or while in use. Some of the same modes that cause early failures, like weld or seal failure and internal short circuits, can also occur at different times throughout battery life.

The rate of random defects is usually relatively constant, but low, throughout battery life (see the top graph in Figure 8-5).

Premature End of Life

Premature battery end of life is caused by slow but steady loss of active materials in the battery or the degradation of other components, like insulators or seals. These types of failures generally show up later in battery life, depending on how fast the materials deteriorate. The rates of deterioration, and thus battery failures, may vary enough that batteries could fail over an extended period of time.

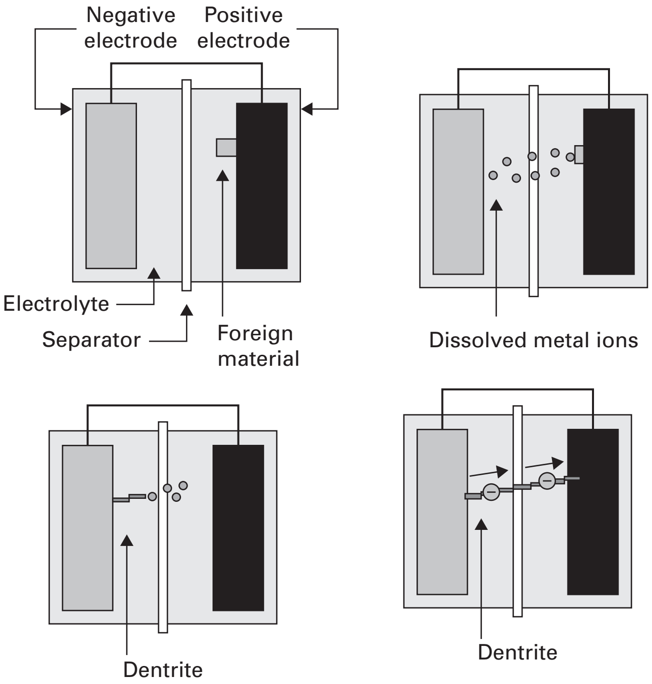


FIGURE 8-6 **Dendrite growth from a contaminating metal becoming oxidized at the positive electrode, dissolving in the electrolyte, diffusing to the negative electrode, becoming reduced and depositing on the negative electrode, growing as dendrites through the separator as the process continues, then forming a short-circuit path between negative and positive electrodes.**

Other reactions may lead to increased internal resistance, leaving the battery unable to support higher power demands. It may appear as though the battery were depleted even though there may be plenty of active material remaining in the battery for lower power discharge.

Regardless, the results are reduced battery capacity, compromised battery function, even an internal short-circuit condition, leading the batteries to prematurely reach end of life.

Examples of premature end of life causes are

- Excessive self-discharge and loss of active negative or positive electrode materials.
- Chemical breakdown of electrolyte, leading to gas buildup and drying out of the electrodes. The outcomes can include cell swelling and increased internal cell resistance.
- Electrolyte leakage from the cells through weakened seals or ruptured vents. Increased internal resistance from dried-out electrodes, ingress of moisture, and perhaps external corrosion of the metal battery case.

- Passivation or blockage of electrode surfaces from corrosion or deposition.
- Dendrites derived from foreign material (more details on this appear under "Early Failures"). Some lithium ion cells may form dendrites if they are discharged below the recommended discharge voltage limit.
- Lithium plating on negative electrode surfaces can occur in lithium ion cells when they are excessively charged. Similar to dendrites, the lithium may grow enough to directly contact the positive electrode and cause an internal short circuit that drains the battery.
- Other complications arise when considering batteries consisting of multiple cells connected together. The performance characteristics of the individual cells are not the same; rather, they have a distribution of performance characteristics. As a result, the entire battery can be limited by the weakest cell. It may have the least capacity or highest internal resistance or some other limiting performance characteristic.

  The cells with more capacity may not be completely discharged. This is a waste of battery capacity. Additionally, if the cells are connected in series and the battery is discharged beyond the capacity of the weakest battery, it can be driven by the higher-capacity cell or cells in the battery to a point where the polarity of the weak cell reverses. The negative electrode becomes positive and the positive electrode becomes negative. This situation can cause permanent damage to the cell that went into reversal and, thus, impact the overall battery performance.

  The ill effects of dissimilar cells in a battery can be minimized by closely matching, for example, the capacity and internal resistance of all the cells in the battery.

  However, even if the differences between cells in a rechargeable battery are small, they tend to become greater with the number of charge and discharge cycles.

A distribution of premature end of life failure rates may look like the top graph in Figure 8-5. There may be multiple failure modes that have their own distribution.

Putting It All Together

We may or may not care why a particular failure mechanism occurs, but we should care about the overall reliability of a battery over its entire useful life.

Combining all of the different failure rate distributions into a failure rate curve for the entire useful life of the battery may resemble the bottom graph in Figure 8-5. This type of curve is typical for battery failures and nicknamed a "bathtub curve" after its shape. Failure rates are typically higher at the beginning and end of battery life, but relatively constant throughout most the battery life. Even so, most batteries experience very low failure rates, often in the parts per hundred thousand range overall. This represents a very small fraction of a percent of the batteries manufactured.

Accelerated Testing

Manufacturers may have to predict long-term performance based on short-term testing. If a battery is intended to last ten years, it is unlikely the battery manufacturer has tested batteries for ten years before launching the product. They may get the data eventually, but generally a manufacturer will perform accelerated testing in a shorter period of time in a way that can be used to predict long-term behavior under real use conditions.

Failure modes that only occur at rates in the parts per ten thousand or lower may not appear during normal testing with, say, hundreds of batteries. The rates of occurrence are just too low. Highly accelerated life tests (HALT) are designed to apply high levels of environmental stress on a battery to force failures to occur. In this way, battery design, component, or material weaknesses will become apparent and the risks of failure under more normal conditions can be mitigated.

During HALT evaluations, a battery may be exposed to many hours of high temperatures, rapid temperature swings from very low to very high temperatures, mechanical shock, and vibration at high force levels or even combinations of these stresses.

For example, a weak weld joint may fail during HALT experiments, giving the manufacturer an opportunity to consider increasing the strength of the weld. An insulator might fail, causing an internal short circuit. The manufacturer can redesign the insulators, add more insulators, or change the insulation material, depending on how the battery failed.

Other types of accelerated testing attempt to predict the performance deterioration as a result of storage over a long period of time, operational lifetimes that may take years to discharge the battery, or a large number of charge and discharge cycles for rechargeable batteries.

For example, self-discharge during storage can be measured by placing groups of batteries at different temperatures (especially higher) for different lengths of time. At the end of their storage periods, they are discharged and the capacity or longevity is determined. From this data, the loss of capacity is used to calculate the self-discharge rate.

Unless there is a mechanical short-circuit condition within the battery, self-discharge reactions are chemical in nature. The rate of chemical reactions is often dependent on the temperature according to the equation

$$k = \mathrm{A} \exp(-E_a/RT)$$

where k is the rate of the chemical reaction, or loss of battery capacity in our case, A is a constant, E_a is the activation energy, R is the gas constant (8.314 J mol K^{-1}), and T is the temperature on the Kelvin temperature scale (K). This is the Arrhenius equation, named after Swedish chemist Svante Arrhenius.

A plot of $ln(k)$ against $1/T$ is linear for simple chemical reactions and yields a slope of $-E_a/R$. Performing these tests at different times and temperatures allows battery manufacturers to calculate the self-discharge rate under almost any set of conditions using the value activation energy.

This approach is widely used to determine the long-term behavior of batteries without waiting a long time to measure the data under normal operating conditions. It can get complicated if more than one chemical reaction is occurring, though.

Safety

The news reports are quite dramatic. Laptop computers catch fire. Battery factories catch fire. Trucks and planes transporting batteries catch fire. Here are just a few of the battery safety incidents that have been reported:

- A cell phone manufacturer issued a product advisory in 2007 regarding excessive heating of the battery brought about by a short circuit during charging.
- Laptop computer manufacturers recall millions of lithium ion batteries that power their devices out of concern that some may overheat or even catch fire.
- As of May 2010, the Federal Aviation Administration (FAA) logged over 100 aviation incidents around the world since 1991 that resulted in extreme heat, smoke, fire, or explosion from batteries and battery-powered devices. The incidents involved rechargeable batteries like lithium ion, nickel-cadmium, and lead acid as well as primary batteries like lithium–manganese dioxide and zinc–silver oxide. The incidents involved individual batteries on passenger aircraft and large shipments aboard cargo aircraft, alike.
- The Pipeline and Hazardous Materials Safety Administration (PHMSA) of the U.S. Department of Transportation (U.S. DOT) reported in 2009 that companies shipping used batteries may not be complying with transportation regulations and are causing serious safety problems. Noncompliance may have caused a November 2006 incident when a truck carrying used, rechargeable lead acid batteries caught fire and was completely destroyed. PHMSA also looked into two parcel delivery truck fires in April and July 2008 involving batteries on their way to be recycled.
- The U.S. Navy reported a battery fire in November 2008 aboard a battery-powered minisubmarine at a facility in Hawaii. The fire started during routine maintenance, which included battery charging.
- A September 2008 battery fire at a Connecticut battery manufacturer forced the evacuation of residents and students at three nearby schools within a four-square-mile radius of the facility.
- In March 2008, a large battery manufacturer in South Korea had a fire that affected the worldwide supply of lithium ion laptop batteries.
- A fire breaks out at a lithium ion battery manufacturing facility owned by a major Japanese battery manufacturer in September 2007.

There are others, but you get the idea.

Batteries are designed to release stored chemical energy in a controlled way to provide useful electrical energy. How effectively they do this is dependent on a variety of factors. The chemistry and the mechanical design of a battery are key to determining its ability to reliably deliver energy under a range of environmental conditions and over long periods of time.

Some batteries store substantial amounts of energy and are designed to deliver it quickly. An uncontrolled, rapid release of this energy, though, can result in heat, fire, and explosion.

Metal shrapnel from a battery explosion can cause bodily injury or damage to the device and surrounding structures. Toxic or corrosive liquids and noxious gasses may be released, as well.

Battery safety hazards may be classified as

- **Leaks** Electrolyte or gas seeps from a vent intended to release pressure, a burst safety vent, or a weakened seal. Excess gas can be generated within batteries as the result of normal battery electrode reactions or through a parasitic chemical reaction.
- **Ruptures** A more serious release of electrolyte, gas, or solid material occurs through burst vents, seals, or the battery case.
- **Overheating** This occurs when heat is produced by internal reactions, like direct contact between charged positive and negative electrode materials, or during rapid charging or discharging.
- **Explosion** Catastrophic and rapid destruction of the battery (sometimes called spontaneous disassembly by battery insiders) leads to rapid release of gas, shrapnel, and sometimes, fire. An explosion can be categorized as either a deflagration (lower-pressure explosion) or a detonation (higher-pressure explosion).

  Explosions usually occur when an internal or external short circuit, an external heat source, or a spark creates the conditions for an exothermic (heat-releasing) reaction to occur between the battery electrode materials.
- **Thermal runaway** The rate of chemical reactions usually increases exponentially with temperature. Heat deriving from internal reactions, like a rapid discharge from direct contact between charged electrode materials, external sources of heat, overcharging, or forced overdischarging, serves to increase the rate of the chemical reactions. As the chemical reactions proceed, more heat may be generated that, in turn, increases the rate of the chemical reactions even more.

  If the rate of heat generation is high enough, the rate of the chemical reactions will rapidly increase, generating even more heat that uncontrollably accelerates the chemical reactions. This is a thermal runaway and can end with an explosion.

These hazards could result from defects in the battery and abuse or misuse by the end user. Battery defects usually involve an internal short circuit, either from a foreign material breaching the separator, a torn separator or other insulator, dendrites growing from the negative electrode until it contacts the positive electrode, or the current-carrying components for both electrodes contacting each other.

Abuse leading to catastrophic failure of a battery can be deliberate or accidental and may include short-circuiting the negative and positive terminals; dropping, crushing, piercing, or otherwise breaching the battery container; or exposing the battery to extreme environmental conditions, like fire.

Consumer batteries carry cautionary messages like, “Warning: Battery may explode or cause injury if disassembled or exposed to fire.” Other batteries have additional precautions provided by the manufacturer.

Misuse may result from overcharging or overdischarging from combining old and new batteries in the same device or batteries with very different capacities. Batteries might be installed backward in a device.

There are a number of ways batteries could be abused or misused. A certain amount of abuse and misuse tolerance is designed into every battery, but there are limits to the safety mechanisms that can be built into batteries. Battery manufacturers do perform a suite of tests to evaluate the dependability of safety mechanisms, like the strength of the battery packaging, seals, vents, current interrupt devices, and insulators. Some of these safety features are covered in Chapter 6. These tests range from crushing a battery to puncturing it with a nail to creating an external low-resistance short circuit to putting it into a high-temperature oven to exposing it to fire. These tests give battery manufacturers an idea of failure outcomes and how much of a safety margin a particular battery has.

Still, the best approach is to handle batteries with care.

PART II

Battery Technologies

Chapter 9

Primary Batteries

IMPORTANT CONCEPTS FROM THIS CHAPTER:

- What is a primary battery
- What not to do with primary batteries
- Primary batteries with aqueous electrolytes
- Primary batteries with nonaqueous electrolytes

The primary batteries that are widely available to consumers can be categorized by the type of electrolyte—aqueous and nonaqueous.

Aqueous batteries contain electrolyte solutions that are water based. The electrolyte solution may be acidic, more or less neutral, or more often than not, alkaline or basic. Batteries with alkaline electrolytes are the most common type of aqueous battery available today for use in power-hungry portable devices.

Water is inexpensive and an excellent solvent for many different types of electrolyte ions. This corresponds to high ionic conductivity, which, along with the proper choice of the other active materials and the battery design, enables a battery to produce high current levels.

The use of water-based electrolytes does limit the types of materials that can be used, though. Lithium cannot be used because it will quickly and violently chemically react with the water of an aqueous electrolyte to form hydrogen gas. Most primary batteries with aqueous alkaline electrolytes use zinc as the anode material because of its high energy density. If the materials in the battery are chosen well and formulated carefully, it is quite stable in aqueous electrolyte solutions. You may recall from Chapter 3 that zinc also was the anode material of choice for the battery scientists of the early nineteenth century, as well.

Water readily reacts with compounds that possess high electrochemical potentials, so the types of electrode materials, particularly the anode materials, that can be used in aqueous electrolytes is limited. As a result, the voltage of aqueous electrolyte batteries typically comes in somewhere in the range of 1.4 V to 1.6 V for each cell (at least first before use), depending on the type of cathode material used.

Compounds that have higher electrochemical potentials can be used, though, by substituting water-based electrolytes with electrolyte solutions composed of nonaqueous solvents, usually, organic solvents.

Organic solvents for high-voltage battery electrolytes are chosen for their low chemical reactivity with electrode materials like lithium, as well as their ability to dissolve salts to form ion-conducting solutions. There is one nonaqueous cell type that uses an inorganic liquid as both electrolyte solvent and cathode material. Solid-state ionic conductors also work.

Batteries using nonaqueous solvents often use lithium as the anode material because of its high energy density. These types of batteries exhibit voltages somewhere in the neighborhood of 3 V for each cell.

The remainder of the chapter will give a rundown of the more common aqueous and nonaqueous batteries, their attributes, their performance characteristics. A few more specialized primary batteries are also discussed.

The information presented in this chapter is at a rather high level and centered on the general characteristics of the battery chemistries. The specific performance characteristics of each battery type, like the voltage behavior under different discharge loads or operating temperature range, can be dependent on a number of factors. These factors include how the battery active materials were made and formulated as well as the battery construction, like bobbin or spiral wound, certain battery components, and so on. More explicit details about battery performance attributes that best fit a particular application, such as the discharge capacity, the voltage under different loads, the voltage at different depths of discharge, and operating temperature ranges, should be investigated further. The first place to start is the manufacturers' data sheets. More on that in Chapter 12.

Batteries with Aqueous Electrolytes

Zinc is the most common anode material used in aqueous batteries because of its high energy density. It is mostly stable in aqueous electrolytes, but self-discharge—any of a number of parasitic chemical reactions that result in decreased battery life or reduced performance—can occur through corrosion of the zinc.

Zinc corrosion, like other corrosion reactions, proceeds when impurities come into contact with the zinc. This can occur when contaminants are occluded in the zinc or deposited on the zinc surface from the electrolyte. Contaminants in the electrolyte may originate from impurities in the electrolyte or come from other battery components. If the contaminant, a common one being iron, can act as a cathode in a galvanic couple with the zinc, then zinc corrosion ensues. Hydrogen gas will form at the iron surface by reduction of water in the electrolyte and zinc will dissolve as it corrodes.

If this happens at a fast enough rate for a long enough period of time, internal pressure builds within the cell, ultimately resulting in burst seals and electrolyte leakage. Gassing is difficult to completely avoid in aqueous batteries, but it can be mitigated and managed.

These reactions are generally very slow if the battery was designed and constructed correctly, but they still can limit shelf life and the discharge performance of the battery.

Zinc corrosion can be made better or worse, depending on the purity of the materials used in the battery. These self-discharge reactions occur more slowly as the temperature is lowered, so it was common practice to refrigerate Leclanché zinc-carbon batteries during storage. Lower temperatures also reduce the power output of batteries, though, so they needed to be warmed to the operating temperature before use. This practice is not necessary with the high-quality batteries manufactured using higher-purity materials today.

One way that was formerly used to stabilize the zinc against corrosion is to alloy it with mercury (Hg) to form an amalgam. Mercury works by increasing the electrochemical potential of hydrogen gas formation. The levels of Hg added to the Zn were generally somewhere between 2 percent and 15 percent Hg by weight of Zn.

Starting in the early 1990s battery manufacturers were required first by the European Union and then by the U.S. government to remove mercury from batteries like Leclanché and alkaline Zn/MnO_2. Mercury and its compounds are toxic and harmful to animals—human and otherwise. There were legitimate concerns about the detrimental effects of mercury released into the environment that could be leached from discarded cells in landfills. At one time batteries were the largest source of mercury in municipal solid waste.

A large part of that effort to remove mercury from batteries required higher-purity battery materials, including the zinc anode material and electrolyte, stronger seals, and improved manufacturing processes. This effort was successful, and today, most zinc-based batteries are free of added mercury. Until recently small button cells were exempted from the ban on Hg in batteries because, except for zinc–mercuric oxide cells, the amount of zinc in small button cells was below the minimum allowable levels. This has now changed, and battery manufacturers are now offering zinc-air button cells that have no added mercury.

The discharge reaction a zinc anode can be complicated, but, it may be written (at least early in the battery discharge reaction) as $Zn + 2\ H_2O + 2\ KOH \rightarrow K_2Zn(OH)_4$, where the potassium zincate, $K_2Zn(OH)_4$, may be dissolved in the electrolyte and dissociated into potassium ions, K^+, and zincate ions, $Zn(OH)_4^{2-}$. Depending on conditions, and particularly as the battery becomes fully depleted, zinc ions may precipitate as zinc oxide, ZnO.

Many of the aqueous batteries in this chapter use alkaline electrolytes. The usual formulation includes potassium hydroxide (KOH) somewhere in the range of 20 percent to 50 percent by weight in water. Anywhere from a few percent to saturation levels of zinc oxide (ZnO) is added to help stabilize the zinc anode. ZnO forms potassium zincate or $K_2Zn(OH)_4$ when dissolved in the KOH solution. The exact concentrations of KOH and ZnO are usually proprietary and not disclosed by the manufacturers.

If zinc was found to be a useful anode material with a particular cathode material and electrolyte system, it is probably safe to say that someone tried to substitute magnesium, Mg, or aluminum, Al, for the zinc. These metals hold the promise of higher energy density batteries than Zn-based cells. Notable examples include Mg/MnO_2 and

Al/MnO_2, Mg-air, and Al-air batteries. Mg and Al anodes have significant challenges that must be overcome, however, like excessive self-discharge or passivation.

Batteries using Mg or Al anodes have not achieved broad commercial success, but they are used in some special applications. Mg/MnO_2 has been used by the military in communications equipment. Mg anodes are also used in some reserve batteries and discussed further later in the chapter. Aluminum–silver oxide batteries are available for torpedo propulsion systems. This type of battery is also implemented as a reserve battery that must be activated with water or an electrolyte solution just prior to use.

Also a word about one of the most common cathode materials for aqueous batteries. There are three basic types of MnO_2. Although essentially the same chemical compound, there are some subtle differences in the molecular structures and chemical behaviors.

Manganese dioxide ore, called natural manganese dioxide or NMD, is mined in various locations around the world. Electrolytic manganese dioxide, or EMD, is formed by electrolysis from an electrolyte solution that contains manganese ions that were dissolved from manganese dioxide ore and purified. EMD has a higher energy density than NMD and is the type of MnO_2 used in alkaline Zn/MnO_2 batteries. Another type is called chemical manganese dioxide, or CMD, which is not quite as widely used as the other two MnO_2 materials.

NMD is a less expensive material to use, but may contain higher levels of impurities than the synthetic MnO_2 varieties. It is used only in Leclanché cells.

A brief description of some of the more common battery types follows. This is not a comprehensive list but rather touches on some of the more common and readily available cell types. The electrochemical reaction mechanisms are often complex and not always precisely known. The reaction equations given here are usually the simplified versions that may not fully reveal some of the intricate details of the true electrochemical reactions.

Leclanché Zinc-Carbon and Zinc-Chloride

In Chapter 3 we discussed the beginnings of the Leclanché cell. The dry cell version of the Leclanché cell was introduced by Carl Gassner in 1888, but Leclanché still gets his name attached to this battery type.

The Leclanché dry cell, alternatively called a zinc-carbon cell, was one of the most important battery types of the twentieth century. It was a popular battery for a variety of portable applications, like radios, toys, and flashlights, as well as stationary uses, like doorbells and telephones in the early part of the last century.

Although the high power demands of some electronics and toys have shifted the market to alkaline Zn/MnO_2 batteries, zinc-carbon cells are still widely used in developing countries because they are inexpensive.

Zinc-carbon batteries are manufactured as “General Purpose” or “Heavy Duty.” The latter may also be classified as “Industrial Heavy Duty,” “Extra Heavy Duty,” or “Super Heavy Duty.”

General-purpose batteries have changed relatively little since Gassner's dry cell. They are inexpensive and are best suited for applications that only require intermittent low power, rather than continuous use. The MnO_2 cathode material is usually a good-quality natural manganese dioxide ore mined from various sites, including Africa and Mexico.

Heavy-duty batteries are able to supply moderate continuous power to intermittent high power. These batteries may use synthetic MnO_2 manufactured by an electrolysis process (electrolytic manganese dioxide, or EMD) or by a chemical process (chemical manganese dioxide, or CMD). The electrolyte is an aqueous solution of ammonium chloride (NH_4Cl) and zinc chloride ($ZnCl_2$).

While they are most often used as individual cylindrical cells (D, C, AA, and AAA), other configurations are available, such as the 9 V prismatic battery. Four cylindrical Leclanché cells are connected in series and placed into the square can of 6 V lantern batteries used to operate large flashlights.

A flat zinc-carbon battery was used in Polaroid SX-70 instant cameras starting in the early 1970s. Four zinc-carbon cells were joined in series to produce a 6 V battery.

A cross section of a Leclanché Zn/MnO_2 cylindrical cell is shown in Figure 9-1. This type of battery is referred to as a bobbin cell. The most clever feature of Gassner's dry cell is the use of a zinc can to serve as both the container and the anode material. The zinc can replaced the glass jar used by Leclanché. This feature and the dry cell formulation rendered the Leclanché cell easier to transport and handle when compared to the wet cell version.

The can formed from a sheet of zinc is lined with a separator, usually a type of paper. The cathode mix is made of MnO_2 powder and a conductive carbon, like carbon black. The mix is compacted into the center of the can. A compressed graphite powder rod is pressed into the cathode mix and connected to the positive terminal end cap.

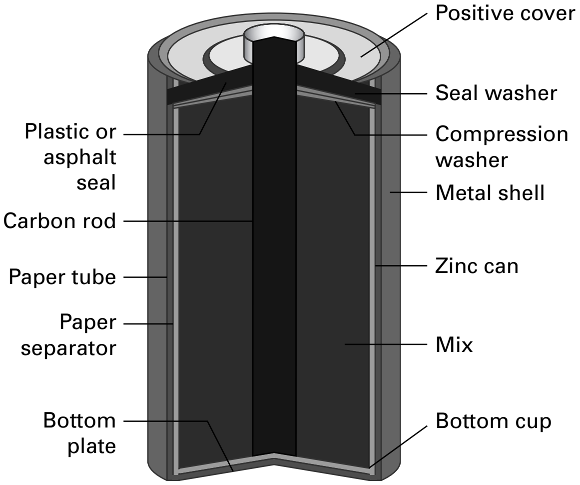


FIGURE 9-1 Cross section of a Leclanché or zinc-carbon cell. (Adapted from graphics provided by Spectrum Brands, Inc., and used with permission.)

The cell reactions (Table 9-1) are rather complicated and not always written consistently in the literature. They do depend on the electrolyte formulation and how the battery is discharged.

The voltage of the Leclanché Zn/MnO_2 cell decreases throughout discharge (Figure 9-2). The basic cell characteristics are given in Table 9-1.

Zinc-chloride batteries are similar to zinc-carbon batteries in most respects. The main difference is the use of an electrolyte composed of an aqueous solution of $ZnCl_2$ without, or at least without much, NH_4Cl.

Zinc-chloride cells are used for the heavy-duty varieties and can tolerate higher power loads than the zinc-carbon cells.

TABLE 9-1 Leclanché Zinc-Carbon Battery Attributes

Attribute	Description
Anode active material	Zinc (Zn) sheet formed into can that serves as both anode and container for the battery. Anode reaction: $Zn + 2\ Cl^- \rightarrow ZnCl_2 + 2\ e^-$
Cathode active material	Manganese dioxide (MnO_2) powder mixed with a conductive carbon powder and electrolyte. Compressed into the battery can. Cathode reaction: $MnO_2 + H_2O + e^- \rightarrow Mn(O)OH + OH^-$
Electrolyte	Solution of ammonium chloride (NH_4Cl) and zinc chloride ($ZnCl_2$) in H_2O.
Battery reactions	$Zn + 2\ MnO_2 + 2\ NH_4Cl \rightarrow + Zn(NH_3)_2Cl_2 + 2\ Mn(O)OH$ Or $Zn + 2\ MnO_2 + NH_4Cl + H_2O \rightarrow Zn(OH)Cl + 2\ Mn(O)OH + NH_3$
Nominal cell voltage	1.50 V
Discharge voltage profile	Sloped.
Energy density	Zinc-carbon 65 to 90 Wh kg^{-1} and 100 to 165 Wh dm^{-3} Zinc-chloride 84 to 195 Wh kg^{-1} and 100 to 180 Wh dm^{-3}
Commonly available sizes	Cylindrical D, C, AA, AAA. Prismatic 9 V, 6 V lantern

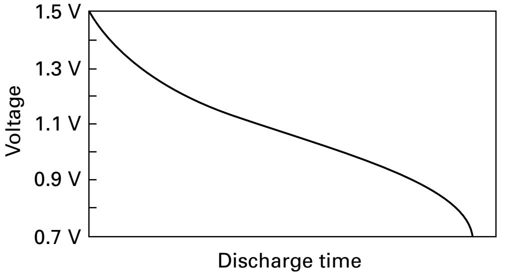


FIGURE 9-2 Discharge voltage for a Leclanché Zn/MnO_2 cell

Alkaline Zinc–Manganese Dioxide

In the U.S., Japan, and Europe, zinc-carbon batteries have been largely supplanted by alkaline zinc-manganese dioxide batteries. The anode and cathode materials are basically the same as in zinc-carbon batteries, but that is where the similarities end.

Alkaline Zn/MnO_2 cells have a higher energy density, higher power output, and longer shelf life than Leclanché zinc-carbon cells. These attributes make alkaline Zn/MnO_2 more suitable for many of today's electronic devices that require higher performance than what zinc-carbon brings.

A cross section of an alkaline Zn/MnO_2 cylindrical cell is shown in Figure 9-3. This type of battery is, like the zinc-carbon cell, a bobbin cell, but with a different design concept: something like an inside out zinc-carbon cell with the MnO_2 cathode on the outside of the cell and the zinc anode on the inside.

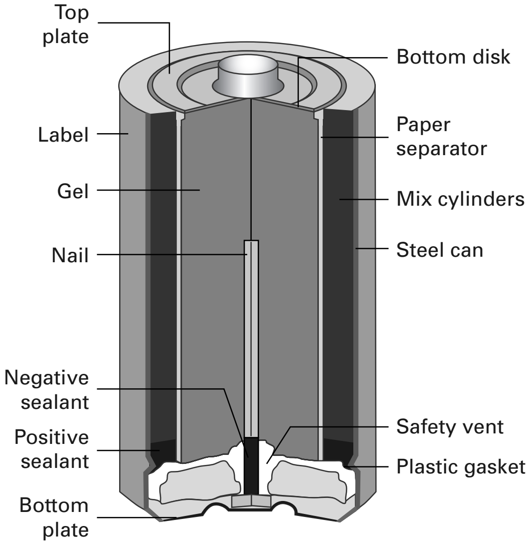


FIGURE 9-3 Cross section of a cylindrical alkaline Zn/MnO_2 cell. (Adapted from graphics provided by Spectrum Brands, Inc., and used with permission.)

The cathode mix is composed of electrolytic MnO_2 powder and one or more conductive carbons like graphite and acetylene black. A polymeric binder is often added to maintain cathode integrity after it is formed into the cylindrical shape.

The mix is compacted to form one or more hollow cylinders of densely packed cathode mix powder. The cathode cylinders are placed or stacked in the battery case or can such that they make good electrical contact with the walls of the battery can. Separator sheets—either overlayed strips or tubes—line the inside of the cathode cylinder.

The zinc used in alkaline Zn/MnO_2 cells is in the form of a powder, rather than the zinc container used in Leclanché zinc-carbon cells. Instead of the slightly acidic NH_4Cl-$ZnCl_2$ electrolytes of zinc-carbon cells, the electrolyte in alkaline cells is, well, an alkaline solution made of KOH and ZnO dissolved in H_2O. This electrolyte is mixed with the zinc powder and a gelling agent such as polyacrylic acid, sodium carboxymethyl cellulose, or a number of other materials that form gels and are stable in alkaline solutions. The resulting zinc anode gel is loaded into the center of the cell. Electrical contact between the zinc gel and the negative terminal of the cell is made by inserting a brass nail or foil into the zinc gel.

A plastic seal is used to isolate the negative cap, which is the negative contact, from the positive case. Although the entire battery case is positive because it is in contact with the cathode, a contact point, or nubbin, is formed at one end opposite to make the positive terminal. The negative terminal is simply a metal plate connected to the zinc by way of the brass nail or foil.

The plastic seal includes a vent that is intended to safely rupture if the internal pressure of the cell becomes too high. It is safer to have a battery that slowly leaks electrolyte than one that explodes.

Zn/MnO_2 button cells are also available. A cross section of this type of cell looks rather similar to that of the Zn/Ag_2O button cell shown in Figure 9-8.

The voltage of an alkaline Zn/MnO_2 cell decreases throughout discharge (Figure 9-4). The basic cell characteristics are given in Table 9-2.

Starting in 2004, a couple of manufacturers started to produce an alkaline Zn/MnO_2 cell that contains nickel oxyhydroxide, Ni(O)OH. The addition of Ni(O)OH to the MnO_2 cathode material raises the initial voltage to 1.7 V. The discharge voltage remains higher than standard alkaline Zn/MnO_2 cells during discharge, which means higher energy output.

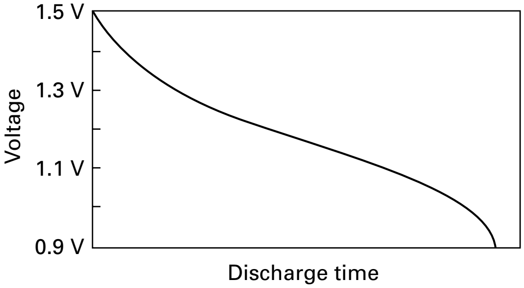


FIGURE 9-4 Discharge voltage for the alkaline Zn/MnO_2 cell

TABLE 9-2 Alkaline Zinc–Manganese Dioxide Cell Attributes

Attribute	Description
Anode	Zinc (Zn) metal powder mixed with gelled alkaline electrolyte solution. Anode reaction: $Zn + 4\ OH^- \rightarrow Zn(OH)_4^{2-} + 2\ e^-$ Or $Zn + 2\ OH^- \rightarrow ZnO + H_2O + 2\ e^-$
Cathode	Electrolytic manganese dioxide (EMD) powder mixed with one or more conductive carbon powders (e.g., graphite and acetylene black) and a binder. Cathode reaction: $MnO_2 + H_2O + e^- \rightarrow Mn(O)OH + OH^-$
Electrolyte composition	$KOH\text{-}ZnO\text{-}H_2O$. Contains gelling agent.
Battery discharge reaction	$Zn + 2\ MnO_2 + 2\ H_2O + 2\ KOH \rightarrow K_2Zn(OH)_4 + 2\ Mn(O)OH$ Or $Zn + 2\ MnO_2 + H_2O \rightarrow 2\ Mn(O)OH + ZnO$
Nominal cell voltage	1.50 V open circuit voltage.
Discharge voltage profile	Sloped.
Energy density	80 to 225 Wh kg^{-1} and 150 to 514 Wh dm^{-3}
Commonly available sizes	Cylindrical D, C, AA, AAA, AAAA. Button cells. Prismatic 9 V and 6 V lantern batteries.

Zinc-Air

Most batteries are designed to store all of the active materials needed to function as an electrochemical power source within the battery container. Zinc-air cells are different. The cathode active material is atmospheric oxygen, O_2, so only a thin cathode is necessary to provide a site at which the O_2 can react, or discharge.

Since the active cathode material is not contained inside the cell, more room is available for Zn anode material. A virtually limitless supply of oxygen from the air along with more space inside the cell to put more Zn gives zinc-air cells a very high energy density—the highest of commonly available batteries (see Table 9-3). A zinc-air cell may be thought of as half of a fuel cell, since the oxygen cathode is similar to some fuel cell cathodes.

TABLE 9-3 Zinc-Air Cell Attributes

Attribute	Description
Anode	Zinc (Zn) metal powder mixed with gelled alkaline electrolyte solution. Anode reaction: $Zn + 4\ OH^- \rightarrow Zn(OH)_4^{2-} + 2\ e^-$ Or $Zn + 2\ OH^- \rightarrow ZnO + H_2O + 2\ e^-$
Cathode	At mospheric oxygen (O_2). O_2 reacts at an electrode composed of activated carbon, catalyst, and polytetrafluoroethylene (PTFE, also known as Teflon). The cathode mix is coated or pressed onto a nickel screen to form a sheet. Separator and polytetrafluoroethylene membranes are laminated on either side the cathode sheet. Overall cathode reaction: $O_2 + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$
Electrolyte composition	KOH-ZnO-H_2O. Contains gelling agent.
Battery discharge reaction	$2\ Zn + O_2 + 4\ KOH + 2\ H_2O \rightarrow 2\ K_2Zn(OH)_4$ Or $2\ Zn + O_2 \rightarrow 2\ ZnO$
Nominal cell voltage	1.40 V open circuit voltage after exposure to air.
Discharge voltage profile	Flat.
Energy density	182 to 455 Wh kg^{-1} and 219 to 1,496 Wh dm^{-3}
Commonly available sizes	Button cells. Prismatic cells.

Oxygen from the air was found to improve battery performance early on in the research and development batteries, as long ago as 1800, although the electrochemical mechanism was not well understood. (Remember the theory of air depolarization from Chapter 3.)

Cells designed to use atmospheric O_2 as a cathode material were developed in the late nineteenth century, but they were not sufficiently practical until advances were made from the 1930s into the 1950s. Zinc-air wet cells (that is, containing large amounts of electrolyte) were used to provide power at installations isolated from the electrical power grid, such as railroad and buoy signals. Other applications included radios and telephones.

Zinc-air dry cells have been used since the early 1950s to power hearing aids. The first hearing aid cells were nearly 22 cm^3 in volume—over 2.5 times the size of a single AA battery.

Since then, the reduction in zinc-air cell sizes designed for hearing aids paralleled the reduction in the size of the hearing aids themselves as the electronics for these devices was improved. The largest zinc-air hearing aid battery today, the 675 cell, comes in at less than 0.6 cm³, or over 30 times smaller than the first zinc-air hearing aid batteries.

Other available sizes include an 8.4 V prismatic battery composed of multiple zinc-air button cells in a package that is the same size as the familiar 9 V battery. The zinc-air version is used in medical devices like external cardiac monitors.

The zinc anode is similar to that of an alkaline Zn/MnO_2 cell. Zinc powder is mixed with a gelling agent like polyacrylic acid and a $KOH\text{-}ZnO\text{-}H_2O$ electrolyte.

The cathode of a zinc-air cell is a complicated, multilayer assembly of different materials that is the result of decades of battery, as well as fuel cell, research and development efforts. It is not depleted during the discharge reaction but rather provides a site for the oxygen reduction reaction to occur.

A cross section of a zinc-air button cell is shown in Figure 9-5.

Although the reduction of oxygen is thermodynamically favorable in a zinc-air cell, the kinetics, or rate, of the reaction is relatively slow. A high–surface area electrode material, like activated carbon, is used to overcome the rate limitations of the oxygen reduction reaction and increase the power output. The high–surface area carbon material provides many reactions sites at which the oxygen can react. Electrically conductive carbons may be added to reduce the internal resistance of the cathode.

The reduction of O_2 occurs in two basic steps: $O_2 + H_2O + 2\ e^- \rightarrow HO_2^- + OH^-$, where HO_2^- is the hydrogen peroxide ion, and then $2\ HO_2^- \rightarrow 2\ OH^- + O_2$. The latter step tends to limit the oxygen discharge reaction, so a catalyst like manganese dioxide or some other metal compound is often used to facilitate the decomposition of peroxide.

An air cathode must strike a balance between a large area of contact with the air to allow contact with O_2 while maintaining contact with the electrolyte. This is done by incorporating a hydrophobic material, polytetrafluoroethylene (PTFE, also known as Teflon). Carefully adding the right amount of PTFE and properly dispersing it in

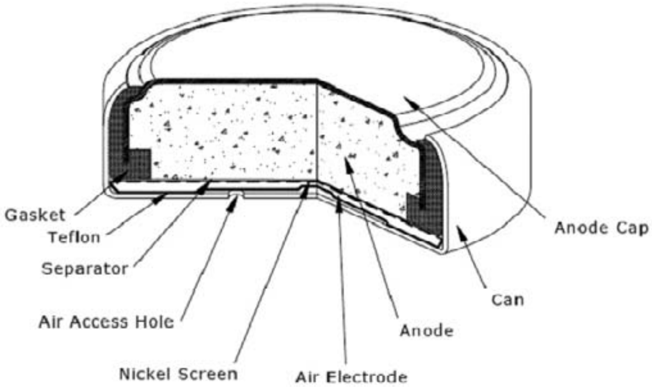


FIGURE 9-5 Cross section of a zinc-air cathode. ©Eveready Battery Company, Inc. Reprinted with permission.

the cathode is key. Too much PTFE and the electrolyte will not sufficiently wet the cathode, resulting in a loss of performance. Too little PTFE and the electrolyte could flood the cathode, thereby limiting the area available for O_2 to react, again with a concomitant loss of performance.

The cathode mix is pressed or coated onto a nickel screen, called a current collector, which conveys electrons to the cathode during battery discharge. The cathode is laminated on one side with a separator material that faces the zinc anode and a PTFE membrane that faces the air side of the electrode.

Two important factors to consider when designing or using zinc-air cells are air and water management.

Air is allowed to enter the cell through holes in the can close to where the cathode is placed. There must be a sufficient number of holes in the can, allowing enough air to enter the cell to feed the discharge reaction when the cell is in use. A means to evenly disperse air as it enters the cell, called an air diffusion layer, may be included in the cell next to the cathode.

Using O_2 from the air allows for high–energy density batteries, but it also presents a challenge as a result of being exposed to the atmosphere. Zinc-air batteries are more sensitive to environmental conditions, particularly humidity. The moisture in humid air is pulled into the electrolyte and can saturate the cathode. On the other hand, dry air may evaporate water from the electrolyte. Either situation results in loss of performance and battery life.

Another factor that can limit battery life is carbon dioxide, CO_2, in the air reacting with the alkaline electrolyte to form carbonates, which can reduce performance.

The holes are sealed with an adhesive tab or other sealing mechanism for shipping and storage after manufacturing to minimize exposure to the atmosphere. The open circuit voltage of the cell is less than 1.2 V while it is sealed. The seal is removed when the cell is needed, air enters the cell, and the open circuit voltage increases to about 1.4 V, usually within seconds. Sealing the holes of a cell between uses can extend its life.

The voltage of a zinc-air cell is relatively constant throughout discharge (Figure 9-6). The basic cell characteristics are given in Table 9-3.

Rechargeable zinc-air batteries have been under development for some time. Portable devices and especially electric vehicles, including electric scooters, cars, and

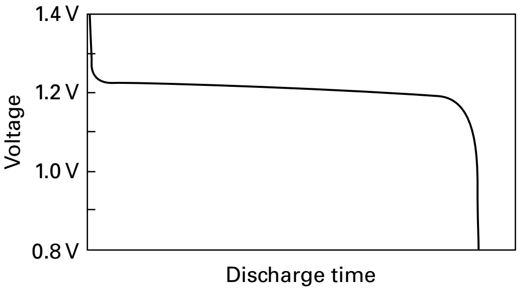


FIGURE 9-6 Discharge voltage for the zinc-air cell

buses, are the target applications for rechargeable zinc-air batteries. Recharging zinc-air cells electrically requires a bifunctional air electrode capable of utilizing O_2 during discharge and producing O_2 during charging. Another concept, mechanical recharging, involves replacing the depleted zinc with fresh metal rather than trying to recharge it electrically.

Aluminum air specialty batteries are sold, but other metal air batteries—magnesium, and more recently lithium—are not available at this time.

Zinc–Silver Oxide

Zinc–silver oxide cells have a high energy density, offer a stable voltage during discharge, and are capable of discharging at high rates. This type of battery is used in applications that need high energy and power in a small package, such as hearing aids. It is one of the battery chemistries that replaced zinc–mercuric oxide cells after the latter were taken off the market out of environmental concerns. More on that appears in the next section.

The first zinc–silver oxide cells similar to the types of cells manufactured today was patented in 1883. Further development in the 1940s and later eventually led to the first commercially available zinc-silver oxide cells in the early 1960s.

Zinc-silver oxide cells have been used in small electronic devices, including hearing aids, calculators, watches and cameras. Large size batteries have found use in military and space applications. For example, zinc–silver oxide reserve batteries are used by the military for high-power, short-term-use applications like ballistic missile guidance systems and torpedo motors. A reserve battery is assembled in the dry state—that is, without electrolyte. The electrolyte is added to activate the battery only when it is needed for use. This is done automatically when a missile or torpedo is triggered. Aluminum-silver oxide batteries are also available for torpedo propulsion systems.

The most commonly available zinc-silver oxide cells today use monovalent silver oxide, Ag_2O. There is another silver oxide—divalent silver oxide or AgO—that has been used in zinc-silver oxide cells, but more on that later.

The monovalent and divalent terms refer to the oxidation, or valence, state of the silver in silver oxide. Monovalent silver oxide, Ag_2O, is composed of Ag(I)—silver ion with one less electron than a silver atom. Two Ag(I) ions combine with an oxygen atom to yield monovalent silver oxide.

The voltage of a Zn/Ag_2O cell is relatively constant throughout discharge (Figure 9-7). The basic cell characteristics are given in Table 9-4.

A simplified cross section of a Zn/Ag_2O button cell is shown in Figure 9-8. Ag_2O powder is mixed with a conductive carbon, such as graphite, at the 1 percent to 5 percent level to reduce the internal resistance. A binder made from polytetrafluoroethylene, or PTFE, but better known as Teflon, is added to the mix to help hold the cathode together after it is compressed into a pellet.

MnO_2 may be used as an additive in the cathode mix, as well. This reduces costs by replacing some of the expensive silver oxide with a relatively inexpensive material. It also provides a progressively decreasing discharge voltage near the end of battery life.

TABLE 9-4 Zinc–Silver Oxide Cell Attributes

Attribute	Description
Anode	Zinc (Zn) metal powder mixed with gelled alkaline electrolyte solution. Anode reaction: $Zn + 4\ OH^- \rightarrow Zn(OH)_4^{2-} + 2\ e^-$ Or $Zn + 2\ OH^- \rightarrow ZnO + H_2O + 2\ e^-$
Cathode	Si lver oxide powder—monovalent silver oxideAg_2O—mixed with a carbon powder, like graphite, to improve conductivity. A polytetrafluoroethylene binder (PTFE, also known as Teflon) may be used to maintain cathode integrity. The cathode mix is compressed into a pellet. Cathode reaction: $Ag_2O + H_2O + 2\ e^- \rightarrow 2\ Ag + 2\ OH^-$
Electrolyte composition	$KOH\text{-}ZnO\text{-}H_2O$. Contains gelling agent.
Battery discharge reaction	$Zn + Ag_2O + 2\ KOH + H_2O \rightarrow K_2Zn(OH)_4 + 2\ Ag$ Or $Zn + Ag_2O \rightarrow ZnO + 2\ Ag$
Nominal cell voltage	1.60 V open circuit voltage.
Discharge voltage profile	Flat.
Energy density	130 to 285 Wh kg^{-1} and 250 to 575 Wh dm^{-3}
Commonly available sizes	A wide variety of button cell sizes.

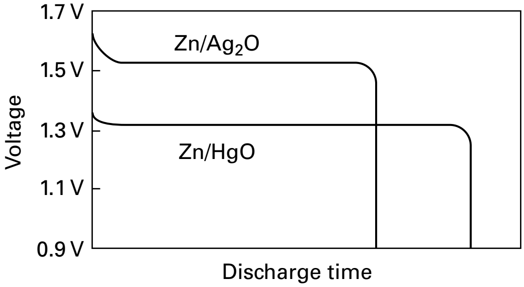


FIGURE 9-7 Discharge voltage for a Zn/Ag_2O cell compared with a Zn/HgO cell

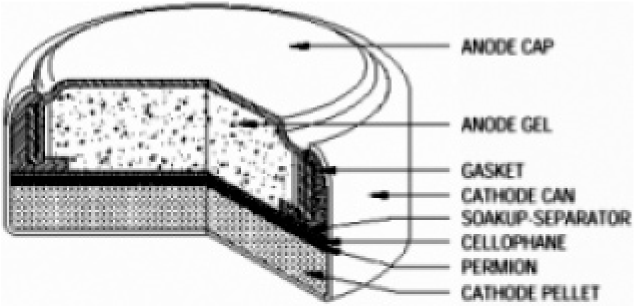


FIGURE 9-8 **Simplified cross section of a Zn/Ag_2O button cell. ©Eveready Battery Company, Inc. Reprinted with permission.**

Silver nickel oxide, $AgNiO_2$, has also been used as a conductive additive, but it has the added feature of being electrochemically active and so can be utilized during battery discharge.

The anode material is the familiar zinc powder in a gelled alkaline electrolyte. The electrolyte is the familiar alkaline formulation (KOH-ZnO-H_2O). NaOH can be used rather than KOH for applications that do not require high power.

One shortcoming of silver oxide cathode materials is their solubility in alkaline electrolyte. Small amounts of silver ions can dissolve into the electrolyte and diffuse to the zinc side of the battery. If this happens, the zinc reacts with the silver ion by reducing it to silver metal. The zinc is oxidized to zinc ions and dissolves in the electrolyte or may precipitate as zinc oxide, ZnO, depending on conditions. Either way, this process decreases the amount of zinc available for discharge.

Further, the silver metal is plated onto the surface of the zinc. This creates galvanic couple that causes the zinc to react further and form hydrogen gas, as well. If the silver continues to plate onto the zinc, these deposits, called dendrites, could continue to grow through the separator and cause an internal short circuit by creating an electrical connection between the anode and the cathode.

Separators that include barriers to silver ions are used to minimize their movement to the anode. Barrier materials include cellulose or synthetic polymer materials or laminated multiple layers of cellulose and polymer membranes. These materials allow the electrolyte to penetrate, but minimize the silver ions that pass through to the anode. Cellulose serves as a sacrificial barrier by reacting with silver ions to form silver metal.

Rechargeable zinc–silver oxide batteries have been developed for applications like electric vehicles.

As mentioned earlier in the chapter, there is another type of silver oxide that was used in zinc–silver oxide cells—divalent silver oxide. Divalent silver oxide, AgO, consists of a divalent silver ion, Ag(II), with two fewer electrons and an oxygen atom.

AgO is reduced in two steps: First the divalent silver oxide is reduced to monovalent silver oxide, $2\ AgO + H_2O + 2\ e^- \rightarrow Ag_2O + 2\ OH^-$. The second step is the reduction of the monovalent silver oxide to silver metal, $Ag_2O + H_2O + 2\ e^- \rightarrow 2\ Ag + 2\ OH^-$. These reduction steps can be seen in the discharge voltage curve in Figure 9-9.

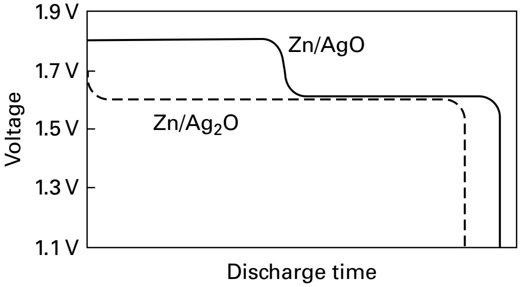


FIGURE 9-9 Discharge voltage for a Zn/AgO cell compared to a Zn/Ag_2O cell

Zn/AgO cells have a higher open circuit voltage, about 1.85 V, compared to about 1.60 V for Zn/Ag_2O cells. The divalent silver oxide also has a higher energy density—20 percent to 40 percent more than monovalent silver oxide.

However, AgO is not chemically stable in alkaline electrolyte solution and tends to decompose to Ag_2O and O_2. This can be cleverly overcome by reacting a small amount of the AgO at the surface of the particles to Ag_2O. As a result, the AgO is not in contact with the electrolyte and so does not react with it. Ag_2O is not electrically conductive, so another process step reduces some of the Ag_2O at the surface of the AgO to silver metal. The increased energy density of AgO is combined with the greater stability of Ag_2O and the electrical conductivity of Ag.

The downside is that the Ag will react with AgO over time during storage to form nonconductive Ag_2O, leading to an increased internal resistance and reduced performance.

Another process was subsequently developed wherein AgO is reacted with lead sulfide to form a layer of silver plumbate, $Ag_5Pb_2O_6$, on its surface. Silver plumbate is conductive and can be utilized during discharge. These batteries are no longer available because of concern over the consequences of releasing toxic lead compounds into the environment.

Zinc-Mercuric Oxide

The zinc-mercuric oxide (Zn/HgO) cell was patented by Charles Clarke in 1884. Zn/HgO cells were further developed by Samuel Ruben in the 1940s. They played an important role powering portable communication equipment during World War II and were a more practical alternative to the ubiquitous Leclanché cell. Their superior storage and performance characteristics were particularly valuable in tropical climates where high temperatures accelerate the performance loss of batteries.

Since that time, a wide variety of Zn/HgO button and cylindrical cell sizes were manufactured for use in many applications, including hearing aids, calculators, watches, and cameras, as well as a number of military and space applications. Some of the first commercially available pacemakers used Zn/HgO batteries.

The voltage throughout discharge is relatively constant (Figure 9-7), which makes these cells useful as a voltage reference. The basic cell characteristics are given in Table 9-5.

The cross section of a Zn/HgO button cell like those used in hearing aids looks similar to that for the Zn/Ag_2O cell pictured in Figure 9-8. A conductive carbon,

TABLE 9-5 Zinc-Mercury Oxide Cell Attributes

Attribute	Description
Anode	Zinc (Zn) metal powder (compressed or mixed with gelled alkaline electrolyte solution) or wound Zn foil. The Zn is amalgamated with Hg. Anode reaction: $Zn + 4\ OH^- \rightarrow Zn(OH)_4^{2-} + 2\ e^-$ Or $Zn + 2\ OH^- \rightarrow ZnO + H_2O + 2\ e^-$
Cathode	Mercuric oxide (HgO) powder mixed with a carbon powder, like graphite, to improve conductivity. Other additives like MnO_2 or Ag may be used to avoid Hg pooling during discharge. The cathode mix is compressed into a pellet for button cells. Cathode reaction: $HgO + H_2O + 2\ e^- \rightarrow Hg + 2\ OH^-$
Electrolyte composition	KOH-ZnO-H_2O. Might contain gelling agent.
Battery discharge reaction	$Zn + HgO + 2\ KOH + H_2O \rightarrow K_2Zn(OH)_4 + Hg$ Or $Zn + HgO \rightarrow ZnO + Hg$
Nominal cell voltage	1.35 V open circuit voltage. 1.40 V to 1.55 V open circuit voltage if MnO_2 is added to the cathode.
Discharge voltage profile	Flat.
Energy density	85 to 105 Wh kg^{-1} and 325 to 470 Wh dm^{-3}
Commonly available sizes	Zn/HgO cells are no longer available.

typically graphite, powder is mixed with HgO powder to improve its electrical conductivity. Usually 10 percent or less carbon is added. One feature of the HgO discharge reaction is the formation of mercury metal. Mercury is highly conductive, so it serves to maintain the low internal resistance of the cell. However, mercury is a liquid at normal operating temperatures. As HgO is reduced, the Hg forms droplets that can pool and negatively affect performance. Certain additives, predominantly manganese oxides or silver, are used to keep the Hg droplets from coalescing.

The zinc anode and electrolyte is reminiscent of other primary alkaline battery types. Amalgamated zinc powder was compressed into a porous pellet or simply mixed with the electrolyte and a gelling agent to yield a gelled anode mass. The alkaline electrolyte solution is the usual KOH-ZnO-H_2O solution. Other Zn/HgO cells have been manufactured use a wound Zn foil for the anode.

Cadmium (Cd) replaces Zn in some specialized batteries. Cd is more stable than zinc in alkaline electrolytes and can perform better over a wider temperature range. However, the voltage is lower—on the order of 0.9 V.

Cells containing mercuric oxide are no longer readily available because of concerns around the release of toxic mercury into the environment. Governmental regulatory agencies around the world have led to their removal from the market. In the U.S., the sales of mercuric oxide batteries are prohibited outright. Their disposal is regulated and manufacturers are responsible for collecting them.

Other cells are available for applications that previously used Zn/HgO cells, including alkaline Zn/MnO_2, Zn/Ag_2O, and Zn-air cells, discussed earlier in this chapter, and lithium batteries coming up later in this chapter.

Reserve Batteries

Reserve batteries are assembled without electrolyte. In the dry state, they can be reliably stored under a variety of adverse conditions that would compromise the performance of fully activated cells. When the battery is needed, they are activated by adding a solvent (usually water, which is why they are in the aqueous section of this chapter) or an electrolyte solution. Other reserve battery types include gas-activated and thermal (or heat-activated) batteries.

There are two general areas where this type of battery is used. A number of different types of reserve batteries are used by the military in applications such as torpedoes, missiles, artillery shells, and mines. Water-activated reserve batteries can also be used in marine emergency lighting for life jackets and beacons, as well as weather balloons. We will stick with the water-activated variety.

Water-activated reserve batteries were developed in the 1940s. They can be activated by adding or immersing in water or even seawater. The batteries typically last less than 24 hours following activation. The anode is usually magnesium metal (Mg). The cathode can be silver chloride (AgCl) or cuprous chloride (CuCl).

A summary description of these Mg water-activated reserve batteries is given in Table 9-6.

TABLE 9-6 Magnesium–Silver Chloride (Mg/AgCl) and Magnesium–Cuprous Chloride (Mg/CuCl) Water-Activated Reserve Cell Attributes

Attribute	Description
Anode	Magnesium (Mg) sheet.
	Anode reaction: $Mg \rightarrow Mg^{2+} + 2\ e^-$
Cathode	Silver chloride (AgCl) with Ag formed directly on the surface.
	Cathode reaction: $AgCl + e^- \rightarrow Ag + Cl^-$
	Or
	Cuprous chloride (CuCl) powder and a binder.
	Cathode reaction: $CuCl + e^- \rightarrow Cu + Cl^-$
Electrolyte composition	Seawater.
Battery discharge reaction	$Mg + 2\ AgCl \rightarrow MgCl_2 + 2\ Ag$
	Or
	$Mg + 2\ CuCl \rightarrow MgCl_2 + 2\ Cu$
Nominal cell voltage	1.5 V to 1.7 V
Discharge voltage profile	Flat.
Energy density	Mg-AgCl 100 to 150 Wh kg^{-1} and 180 to 300 Wh dm^{-3}
	Mg-CuCl 50 to 80 Wh kg^{-1} and 20 to 200 Wh dm^{-3}

Batteries with Nonaqueous Electrolytes

Certain organic or inorganic liquids as electrolyte solvents enable the use of anode materials with higher potentials, that is, anode materials with highly negative reduction potentials or highly positive oxidation potentials. (See Chapter 5 for more information on reduction and oxidation potentials.)

In addition, they must be able to dissolve sufficient amounts of an electrolyte salt. Otherwise, the ionic conductivity of the electrolyte solution may be too low and not support high-power operations.

Solid state electrolytes are also used in some Li battery systems, but they are low power because ionic motion in solids occurs more slowly than in liquids.

Common nonaqueous solvents are propylene carbonate (abbreviated PC, the full chemical name is 4-methyl-1,3-dioxolan-2-one), gamma-butyrolactone (abbreviated GBL, the full chemical name is dihydrofuran-2(3H)-one), and acetonitrile (abbreviated AN, the full chemical name is acetonitrile). A wide variety of others have been used, as well.

Sometimes two or more organic liquids are mixed to impart the desirable properties of both. One example is using a low-viscosity solvent like dimethoxyethane (abbreviated DME, the full chemical name is 1,2-dimethoxyethane) mixed with a viscous solvent like PC. The result strikes a balance between electrolyte conductivity and viscosity.

Lithium is a highly reactive metal. Put it in water and a violent reaction occurs that continues until the Li is exhausted, all the while producing hydrogen gas and intense heat. As a result, water must be assiduously eliminated from nonaqueous lithium batteries. Much effort is expended to minimize the moisture content in lithium cells, including rigorously drying battery constituents and assembling the cells in an extremely low-humidity environment.

In nonaqueous electrolytes, Li will still react with the solvents. However, rather than an aggressive and sustained reaction such as occurs with water, Li reacts with organic solvents in a more constrained fashion. Not only that, but the reaction tends to slow to an extremely low rate after a film of reaction products forms on the surface of the Li. This film protects the Li surface from further reaction with the solvents but allows ions to move within it, so the Li can still be utilized during discharge.

The anode material of choice in nonaqueous primary batteries is lithium (Li). It has the most negative reduction potential (Chapter 5), it is the lightest-weight metal there is, and it has a high energy density. When combined with a variety of cathode materials, most lithium cells have an initial open circuit voltage of about 1.8 V up to 3.9 V, give or take several tenths of a volt. Compare that to the 1.4 V to 1.6 V for most aqueous primary cells using zinc anode materials.

Lithium cells can be categorized by the physical form of cathode—liquid or solid. Many cathode materials have been investigated for use in primary lithium cells, and a few have achieved sustained commercial success. The more common cathode chemistries are briefly presented in the sections that follow. The electrochemical reactions are sometimes rather complicated with several different reaction steps. The simplified reaction schemes are written here.

Aqueous Lithium Batteries?

Despite the high reactivity, it is possible to make an aqueous lithium battery as long as an insoluble protective layer, or passivation layer, is carefully formed on the lithium surface to protect it from reacting with water. An example of such a layer is lithium hydroxide (LiOH). Like all Li passivation layers, it is electrically insulating, but permits ionic conduction to occur—a necessary process for the battery to function. This situation is similar to lithium passivation in lithium-iodine cells used in most pacemakers today. In these batteries a lithium iodide (LiI) layer is formed by the direct reaction of the lithium anode material with the iodine (I_2) cathode material. The LiI protects the Li from further reaction with the I_2 cathode material.

Lithium–Thionyl Chloride, Lithium–Sulfuryl Chloride and Lithium–Sulfur Dioxide

The batteries in this section are called liquid cathode systems because the cathode material is either a liquid or is dissolved in one. This means the electrolyte and the cathode are the same solution. It also means that the cathode material in the electrolyte solution is in direct contact with the lithium anode. If allowed to proceed, the direct reaction of cathode and anode would deplete the active compounds without producing any useful electricity.

As with other lithium battery systems, a passive layer is formed on the surface of the Li when exposed to the cathode solution. The direct anode-cathode reaction is self-limiting as the protective layer forms on the Li. The layer safeguards against further reaction with the cathode material. It is important that the passive layer be both electrically nonconductive and ionically conductive for the battery to discharge.

A side effect of passive layers on electrode surfaces is voltage delay. This behavior can negatively affect battery performance, at least temporarily. More on this in Chapter 7.

As with the air cathode in zinc-air cells (see the earlier section "Zinc-Air"), liquid cathode systems need an electrode to provide a site where they can pick up electrons during cell discharge. Again similar to a zinc-air cell, the cathode in liquid cathode cells is typically made of a highly porous carbon, like acetylene black, and a polytetrafluoroethylene (PTFE or Teflon) binder. A metal current collector, for example an aluminum screen, is used to make the electrical connection between the cathode and the positive terminal.

Cells with liquid or soluble cathode materials, like thionyl chloride and sulfur dioxide, were among the first lithium cells to be developed. Like many battery systems, the liquid cathode cells were developed first for military uses and later adapted for general consumer and OEM applications.

Lithium–thionyl chloride ($Li/SOCl_2$) cells have one of the highest voltages of all the lithium primary cells, 3.6 V to 3.9 V, and one of the highest energy densities. It is also one of the more readily available of the liquid cathode cells.

Thionyl chloride is an inorganic liquid, meaning it contains no carbon. It is both cathode material and electrolyte solvent in one. The electrolyte salt is usually lithium–aluminum chloride ($LiAlCl_4$), although lithium–gallium chloride ($LiGaCl_4$) is occasionally used.

The cathode discharge reaction results in sulfur (S) and particularly lithium chloride (LiCl) precipitating and ultimately building up in the porous carbon cathode. The cathode will eventually become obstructed and thereby limit the cell capacity. Sulfur dioxide (SO_2) gas also forms and leads to some pressure buildup as the cell discharges.

Bromine chloride (BrCl) is used as an additive to enhance performance by reducing the amount of cathode-clogging sulfur that forms during discharge. Cells containing BrCl as an additive are labeled BCX.

$Li/SOCl_2$ cells are manufactured in a wide variety of shapes and sizes, including bobbin and spiral-wound types (see Chapter 6). They are used in many applications—both high power and low power. They are used for military, space, remote monitoring like residential water meters, and medical applications, including implanted devices like a cardiac monitor, to name a few.

Li/$SOCl_2$ cell attributes are given in Table 9-7.

Lithium–sulfuryl chloride (Li/SO_2Cl_2) cells are very much like the Li/$SOCl_2$ cells (Table 9-8). Li/SO_2Cl_2 cells also have a high voltage, just over 3.9 V. Chlorine (Cl_2) is often added to the SO_2Cl_2 cathode-electrolyte solution to reduce voltage delay. Cells containing Cl_2 are tagged with the abbreviation CSC.

Sulfur dioxide (SO_2) is a gas at room temperature; its boiling point is –10°C. To make a practical cell system, SO_2 is dissolved in the organic solvent acetonitrile. Lithium bromide (LiBr) is the electrolyte salt.

The product of the SO_2 discharge reaction with Li is lithium dithionite ($Li_2S_2O_4$), which is insoluble and precipitates in the pores of the carbon cathode. If cells contain excess lithium (that is, it's cathode limited), enough $Li_2S_2O_4$ will form in the cathode that it eventually clogs the cathode pores and prevents the cell from discharging further.

Li/SO_2 cell attributes are given in Table 9-9.

A word or two of caution about the liquid cathode cells described in the preceding text. All lithium cells can present a danger if they are misused or abused or they are

TABLE 9-7 Lithium–Thionyl Chloride (Li/$SOCl_2$) Cell Attributes

Attribute	Description
Anode	Lithium (Li) foil or sheet. Anode reaction: $Li \rightarrow Li^+ + e^-$
Cathode	Th ionyl chloride ($SOCl_2$). $SOCl_2$ reacts at an electrode composed of acetylene black carbon and polytetrafluoroethylene (PTFE, also known as Teflon). BrCl may be added to the $SOCl_2$. Overall cathode reaction: $2\ SOCl_2 + 4\ e^- \rightarrow S + SO_2 + 4\ Cl^-$
Electrolyte composition	Lithium aluminum chloride ($LiAlCl_4$) in $SOCl_2$.
Battery discharge reaction	$4\ Li + 2\ SOCl_2 \rightarrow S + SO_2 + 4\ LiCl$
Nominal cell voltage	3.6 V to 3.9 V
Discharge voltage profile	Flat.
Energy density	240 to 750 Wh kg^{-1} and 630 to 1,270 Wh dm^{-3}
Commonly available sizes	Cylindrical cells. Prismatic cells.

TABLE 9-8 Lithium–Sulfuryl Chloride (Li/SO_2Cl_2) Cell Attributes

Attribute	Description
Anode	Lithium (Li) foil or sheet. Anode reaction: $Li \rightarrow Li^+ + e^-$
Cathode	Sulfuryl chloride (SO_2Cl_2). SO_2Cl_2 reacts at an electrode composed of acetylene black carbon and polytetrafluoroethylene (PTFE, also known as Teflon). Chlorine (Cl_2) may be added to the SO_2Cl_2. Overall cathode reaction: $SO_2Cl_2 + 2\ e^- \rightarrow SO_2 + 2\ Cl^-$
Electrolyte composition	Lithium aluminum chloride ($LiAlCl_4$) in SO_2Cl_2.
Battery discharge reaction	$2\ Li + SO_2Cl_2 \rightarrow SO_2 + 2\ LiCl$
Nominal cell voltage	3.91 V to 3.95 V
Discharge voltage profile	Flat.
Energy density	404 to 480 Wh kg^{-1} and 956 to 1,040 Wh dm^{-3}

TABLE 9-9 Lithium–Sulfur Dioxide (Li/SO_2) Cell Attributes

Attribute	Description
Anode	Lithium (Li) foil or sheet. Anode reaction: $Li \rightarrow Li^+ + e^-$
Cathode	Sulfur dioxide (SO_2) gas. SO_2 reacts at an electrode composed of acetylene black carbon and polytetrafluoroethylene (PTFE, also known as Teflon). The SO_2 is reduced to dithionite ($S_2O_4^{2-}$). Overall cathode reaction: $2\ SO_2 + 2\ e^- \rightarrow S_2O_4^{2-}$
Electrolyte composition	Lithium bromide (LiBr) in acetonitrile.
Battery discharge reaction	$2\ Li + 2\ SO_2 \rightarrow Li_2\ S_2O_4$
Nominal cell voltage	2.95 V
Discharge voltage profile	Flat.
Energy density	160 to 486 Wh kg^{-1} and 185 to 1,070 Wh dm^{-3}

intentionally opened. Electrolyte solutions containing organic solvents are flammable. Certain electrolyte salts are toxic or unstable. Lithium will violently react when exposed to water, forming hydrogen gas and heat.

Liquid cathode cells have other hazards. Li/SO_2 cells are under pressure because of the vapor pressure of SO_2. $SOCl_2$ and SO_2Cl_2 are highly toxic and corrosive. However, battery manufacturers take measures to make these cells safe to handle, safe to use under normal conditions, and mostly safe if misused or abused. Engineers design safety features into the cells themselves, battery packs if they are so configured, and the application using these batteries. More on battery safety features in Chapter 6.

Lithium–Manganese Dioxide

The remaining lithium cell cathode materials in this chapter are solids, of which lithium–manganese dioxide (Li/MnO_2) was one of the first to be used. Developed in the 1970s and successfully launched commercially in the late 1970s, it is one of the most commonly used lithium battery system used yet today, especially for devices that use batteries that can be replaced by the consumer.

Li/MnO_2 cells are made for low, medium, and high power for many diverse consumer, military, and electronics applications. They are available in a wide variety of sizes, from small coin cells to cylindrical cells to prismatic cells. Typical applications include wristwatches (low power) and digital cameras (high power). This versatile cell chemistry is also used for both low-and high-power functions in some implantable cardiac defibrillators. These are devices that are pacemakers requiring low power, but also are capable of correcting certain dangerous cardiac arrhythmias (rapid heartbeats or fibrillation) with high-power shocks to the heart.

The MnO_2 cathode material is not exactly the same MnO_2 used in alkaline Zn/MnO_2 cells described earlier in this chapter. The MnO_2 used in lithium cells starts out as the same basic material used in alkaline cells—EMD or in some cases maybe CMD. However, MnO_2 must be heat-treated at temperatures in the neighborhood of 300°C to 400°C to make it suitable for use in lithium cells. The heat treatment process removes water from the MnO_2 structure and changes its structural form. If this is not done properly, lithium cells made using the MnO_2 will tend to form gaseous by-products resulting in internal pressure buildup and cause the cell to leak in the more extreme cases.

MnO_2 is mixed with conductive carbon powders such as acetylene black or graphite and binder, typically polytetrafluoroethylene (PTFE or Teflon).

A cross section of a Li/MnO_2 coin cell is shown in Figure 9-10 and for a spiral-wound cell in Figure 9-11. Typical cell attributes are given in Table 9-10.

Lithium–Carbon Monofluoride

Reviewing the different types of battery chemistries, both aqueous and nonaqueous, throughout this chapter (and Chapter 10 for that matter), you might have noticed that most cathode chemistries are metal oxide compounds (for example MnO_2, AgO, and CuO) or even nonmetal oxides (SO_2, $SOCl_2$, SO_2Cl_2—the latter two are also known as oxychlorides) with metal sulfides thrown in, principally FeS_2. The reason for this

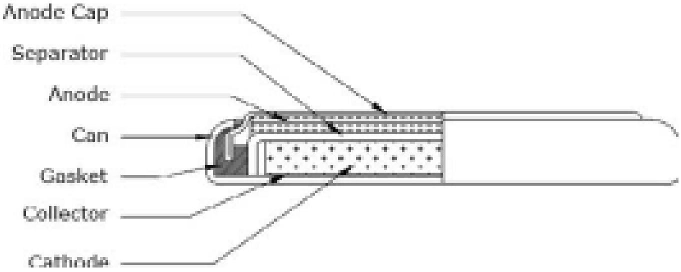


FIGURE 9-10 Cross section of a Li/MnO$_2$ coin cell. ©Eveready Battery Company, Inc. Reprinted with permission.

is that such compounds typically have high, positive electrochemical reduction potentials and are rather chemically stable.

However, there is another type of chemical compound that, at least theoretically, can yield high–energy density cells: fluoride compounds. A cell that pairs Li with

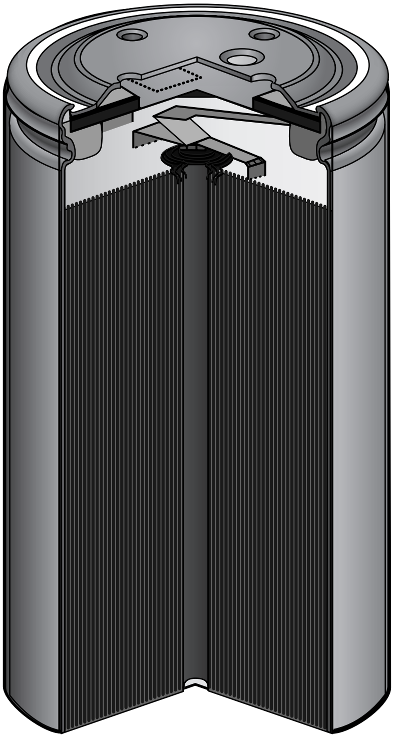


FIGURE 9-11 Cross section of a Li/MnO$_2$ spiral-wound cell. ©Spectrum Brands, Inc. Reprinted with permission.

TABLE 9-10 Lithium–Manganese Dioxide (Li/MnO_2) Cell Attributes

Attribute	Description
Anode	Lithium (Li) foil or sheet. Anode reaction: $Li \rightarrow Li^+ + e^-$
Cathode	Manganese dioxide (EMD) powder that is heat-treated and mixed with a carbon powder, like acetylene black or graphite, to improve conductivity, and a binder such as polytetrafluoroethylene (PTFE, also known under the brand name Teflon) Cathode reaction: $MnO_2 + Li^+ + e^- \rightarrow LiMnO_2$
Electrolyte composition	Lithium salt, such as lithium perchlorate ($LiClO_4$) or lithium trifluoromethane sulfonate (LiO_3SCF_3), dissolved in one or more organic solvents, like propylene carbonate and dimethoxyethane.
Battery discharge reaction	$Li + MnO_2 \rightarrow LiMnO_2$
Nominal cell voltage	3.0 V
Discharge voltage profile	Flat.
Energy density	100 to 500 Wh kg^{-1} and 240 to 770 Wh dm^{-3}
Commonly available sizes	Cylindrical cells. Coin cells. Prismatic 9 V.

elemental fluorine (F_2) would have an open circuit voltage of 5.9 V! Now, a Li/F_2 cell is not realistic, but using cathode materials made from fluorine can be. The voltage ends up lower than that of Li/ F_2, but they can still retain a relatively high energy density.

Carbon monofluoride (CF_x) is the best example of a practical fluoride cathode material. The CF_x used in batteries today is synthesized by the direct reaction of fluorine gas with a carbon starting material like petroleum coke or similar carbon. High temperatures, between 350°C and 600°C, are necessary to drive the reaction to completion. Fluorine gas is very hazardous and difficult to handle because of its reactivity, so there are few companies that have the capability or desire to manufacture it. It is also somewhat expensive because of the cost of F_2.

The carbon material used can be envisioned as flat sheets of carbon atoms connected together in a way that looks like a network of hexagons. These sheets, called graphene, are stacked one on another to build up a three-dimensional structure of graphene layers. This is the archetypal structure of graphite. In reality, graphite and many other carbon materials have varying degrees of structural disorder where the graphene layers are not so regularly stacked.

More on CF_x

The physical and chemical properties of CF_x are somewhat reminiscent of polytetrafluoroethylene (or PTFE), also known as Teflon. It is hydrophobic and can be used as a lubricant.

Li/CF_x cells were introduced commercially in the mid-1970s. Like Li/MnO_2 cells, Li/CF_x cells are available in a large range of shapes and sizes, from coin cells to spiral-wound cylindrical cells to prismatic cells. The cross section of Li/CF_x cells is similar to those of Li/MnO_2 (compare Figure 9-10 with Figure 9-12). Spiral-wound cylindrical Li/CF_x cells appear similar to Li/MnO_2 spiral-wound cells (Figure 9-11).

When reacted with F_2, most of the carbon atoms bind with one fluorine atom. Carbon atoms at the edges of graphene sheets may combine with more than one fluorine atom, though. The end result is CF_x, where x is the average number of fluorine atoms per carbon atom throughout the CF_x material. The value of x is generally between 0.9 to 1.2 for battery materials.

One challenge to designing Li/CF_x cells is the tendency of the CF_x cathode material to swell during discharge. While CF_x has a much greater theoretical energy density than MnO_2, battery designers generally need to accommodate CF_x swelling by including space within the battery in which it can expand. This tends to level the field and may help explain why Li/CF_x and Li/MnO_2 coin cells have similar energy densities.

One unique Li/CF_x cell size is a small cylindrical cell called a pin cell. These cells are about 4 mm in diameter and available in two lengths—26 mm and 36 mm. They were originally used in lighted fishing equipment in Japan.

Li/CF_x cell characteristics are summarized in Table 9-11.

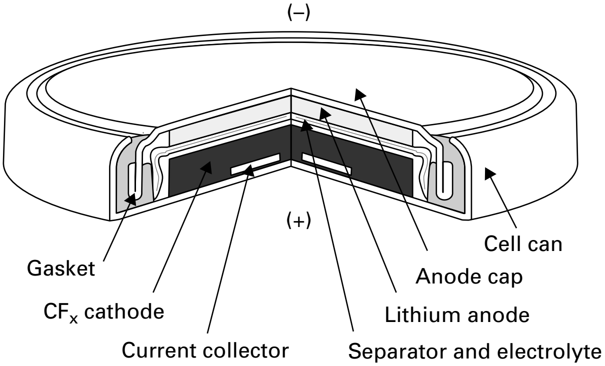


FIGURE 9-12 Cross section of a Li/CF_x coin cell. (Adapted from graphics supplied by Spectrum Brands, Inc., and used with permission.)

TABLE 9-11 Lithium–Carbon Monofluoride (Li/CF_x) Cell Attributes

Attribute	Description
Anode	Lithium (Li) foil or sheet. Anode reaction: $Li \rightarrow Li^+ + e^-$
Cathode	Carbon monofluoride (CF_x) powder mixed with a carbon powder, like acetylene black, to improve conductivity, and a binder. Cathode reaction: $CF + Li^+ + e^- \rightarrow C + LiF$
Electrolyte composition	Lithium salt, mainly lithium tetrafluoroborate ($LiBF_4$), dissolved in one or more organic solvents, like propylene carbonate or gamma-butyrolactone and dimethoxyethane.
Battery discharge reaction	$x\ Li + CF_x \rightarrow C + x\ LiF$
Nominal cell voltage	3.0 V
Discharge voltage profile	Flat.
Energy density	215 to 590 Wh kg^{-1} and 500 to 1,050 Wh dm^{-3}
Commonly available sizes	Cylindrical cells. Coin cells.

Lithium–Iron Disulfide

An alternative to metal oxide cathode materials is their corresponding sulfides—compounds formed by the combination of a metal with sulfur atoms rather than oxygen atoms. A notable example is iron disulfide (FeS_2).

Sulfide materials will have a lower voltage than their oxide counterparts, though. Li/FeS_2 cells have an initial voltage of about 1.8 V, which is of course lower than the voltage of the other popular 3 V lithium cells previously described. However, this can be an advantage if the cells are intended to be drop-in replacements for aqueous cells like alkaline Li/MnO_2. The advantage is that Li/FeS_2 cells can deliver a higher energy density at higher power levels than the alkaline Li/MnO_2 cells they replace.

Li/FeS_2 is available in a couple of cylindrical cell sizes. Cell attributes are in Table 9-12.

Lithium-Iodine

The lithium-iodine (Li/I_2) cell is among those that use a solid state electrolyte and is the most common one that is commercially available today. Its only application is to power pacemakers. Pacemakers are devices that are surgically implanted and are used to electrically stimulate heart tissue. The electrical stimulation initiates a heart beat in cardiac patients whose natural heart beats are too slow (in medical terms,

TABLE 9-12 Lithium–Iron Disulfide (Li/FeS_2) Cell Attributes

Attribute	Description
Anode	Lithium (Li) foil or sheet.
	Anode reaction: $Li \rightarrow Li^+ + e^-$
Cathode	Iron disulfide (FeS_2) powder, conductive carbon powder, and a binder.
	Cathode reaction: $FeS_2 + 4\ e^- \rightarrow Fe + 2\ S^{2-}$
Electrolyte composition	Li thium iodide (LiI) in a combination of organic solvents, like 1,2-dimethoxyethane and 1,3-dioxolane.
Battery discharge reaction	$4\ Li + FeS_2 \rightarrow 2\ Li_2S + Fe$
Nominal cell voltage	1.8 V
Discharge voltage profile	Flat to sloped.
Energy density	130 to 310 Wh kg^{-1} and 400 to 560 Wh dm^{-3}
Commonly available sizes	Cylindrical cells.

bradycardia). The power load is on the order of tens of milliwatts. Pacemakers are expected to have longevities of up to 10 or so years, depending on the specific therapy needs of the patient.

The first pacemaker powered by a Li/I_2 cell was implanted in 1972. For over 30 years, Li/I_2 cells have been the power source of choice for implantable pacemakers.

The I_2 cathode material is stabilized by combining it with a polymer material, typically poly-2-vinylpyridine (P2VP).

Direct reaction of the lithium anode with iodine cathode forms a solid electrolyte, lithium iodide (LiI), that serves as both an electrolyte and a separator. The movement of ions in the solid LiI is rather slow, so Li/I_2 cells are limited to the low rates required for pacemakers to function.

The thickness of the LiI electrolyte layer continues to grow during discharge, which, in turn, increases the internal resistance of the battery. While the discharge voltage remains relatively flat (at least compared to some cell chemistries) throughout most of the battery life, the voltage does tend to gradually decrease as the LiI layer increases in thickness (Figure 9-13). The voltage and internal resistance behavior provides a way to predict when battery depletion will occur. This is an important concern with life-sustaining implanted devices. The longevity of the battery must be accurately predicted so that the device then can be safely replaced prior to complete battery depletion and the failure of the device to provide therapy.

A cross section of a Li/I_2 prismatic pacemaker cell is shown in Figure 9-14.

Characteristics of Li/I_2 cells are given in Table 9-13.

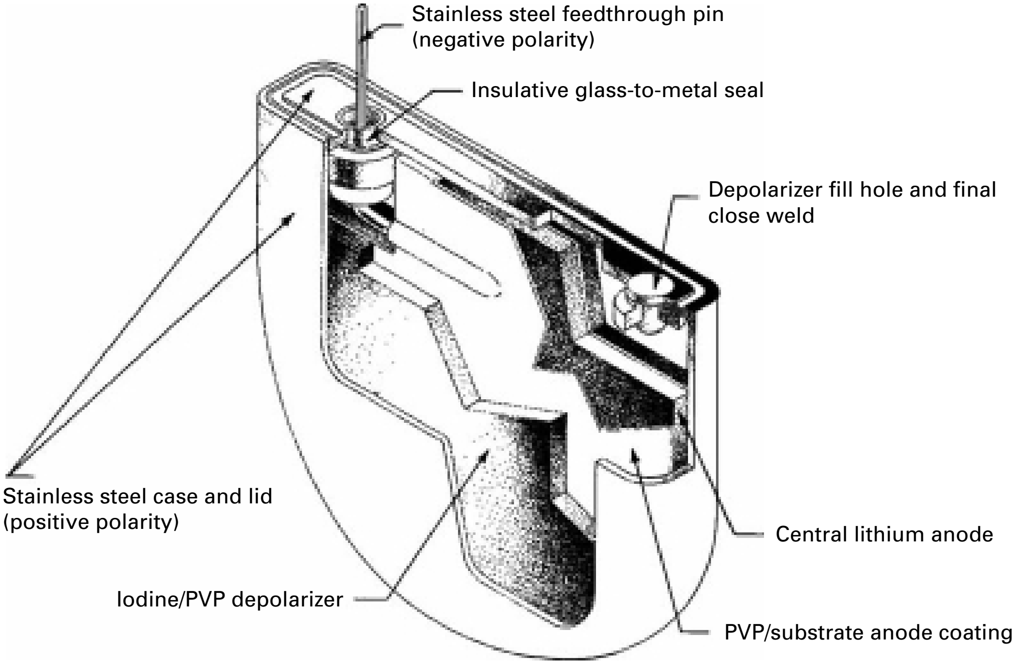


FIGURE 9-13 Discharge voltage and internal cell resistance for a Li/I_2 cell. ©Greatbatch, Inc. Reprinted with permission.

Lithium–Silver Vanadium Oxide

Implantable defibrillators work the same as pacemakers by stimulating heart tissue to maintain a proper heart beat rhythm. In addition, they can provide powerful shocks to the heart returning it to a normal rhythm if it is beating too fast (called tachycardia) or starts to fibrillate.

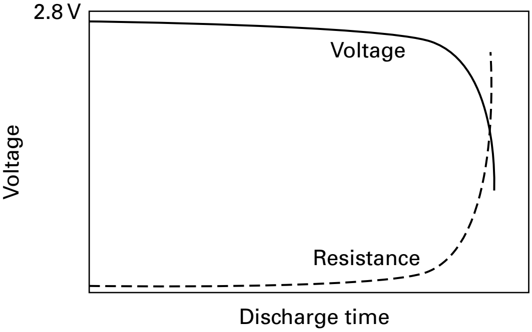


FIGURE 9-14 Cross section of a Li/I_2 prismatic pacemaker cell. (Adapted from graphics provided by Greatbatch, Inc., and used with permission.)

TABLE 9-13 Lithium-Iodine (Li/I_2) Cell Attributes

Attribute	Description
Anode	Lithium (Li) foil or sheet. Anode reaction: $Li \rightarrow Li^+ + e^-$
Cathode	Iodine (I_2) combined with poly-2-vinylpyridine (P2VP). Cathode reaction: $I_2 + 2\ e^- \rightarrow 2\ I^-$
Electrolyte composition	Solid state lithium iodide (LiI) formed *in situ*.
Battery discharge reaction	$2\ Li + I_2 \rightarrow 2\ LiI$
Nominal cell voltage	2.8 V
Discharge voltage profile	Flat.
Energy density	210 to 280 Wh kg^{-1} and 810 to 1,110 Wh dm^{-3}
Commonly available sizes	Prismatic cells.

Since they were first implanted in the mid-1980s, lithium–silver vanadium oxide ($Li/Ag_2V_4O_{11}$) has been the most common battery system used in implantable defibrillators. They provide a high energy density for the frequent and continuous low power drain needed for cardiac pacing and other device functions as well as high power density for infrequent shocks. More recently, they have been used in other devices, including pacemakers with functions that require power levels greater than lithium-iodine (Li/I_2) cells can supply.

A cross section of a $Li/Ag_2V_4O_{11}$ defibrillator cell is shown in Figure 9-15 and cell attributes are given in Table 9-14.

Silver and vanadium ions in $Ag_2V_4O_{11}$ are reduced sequentially at different points during discharge, resulting in a series of steps in the discharge voltage with the extent of discharge (Figure 9-16). The different voltage levels provide an indication of the battery state of charge, which means a prediction of remaining battery life is possible.

The first discharge step involves the reduction of the silver(I) ions to silver metal. Silver is a highly conductive metal, so the conductivity of the $Ag_2V_4O_{11}$ increases rapidly at the beginning stages of discharge.

One of the challenges with $Li/Ag_2V_4O_{11}$ cells is their tendency to exhibit an increase in the internal resistance during the middle of discharge life. The accepted mechanism is vanadium becomes slightly soluble, diffuses to the Li anode and deposits there. This only occurs in a certain depth of discharge range, but it does cause the internal resistance of the cell to rise. The internal resistance will decrease again if the cell is repeatedly discharged using high current pulses.

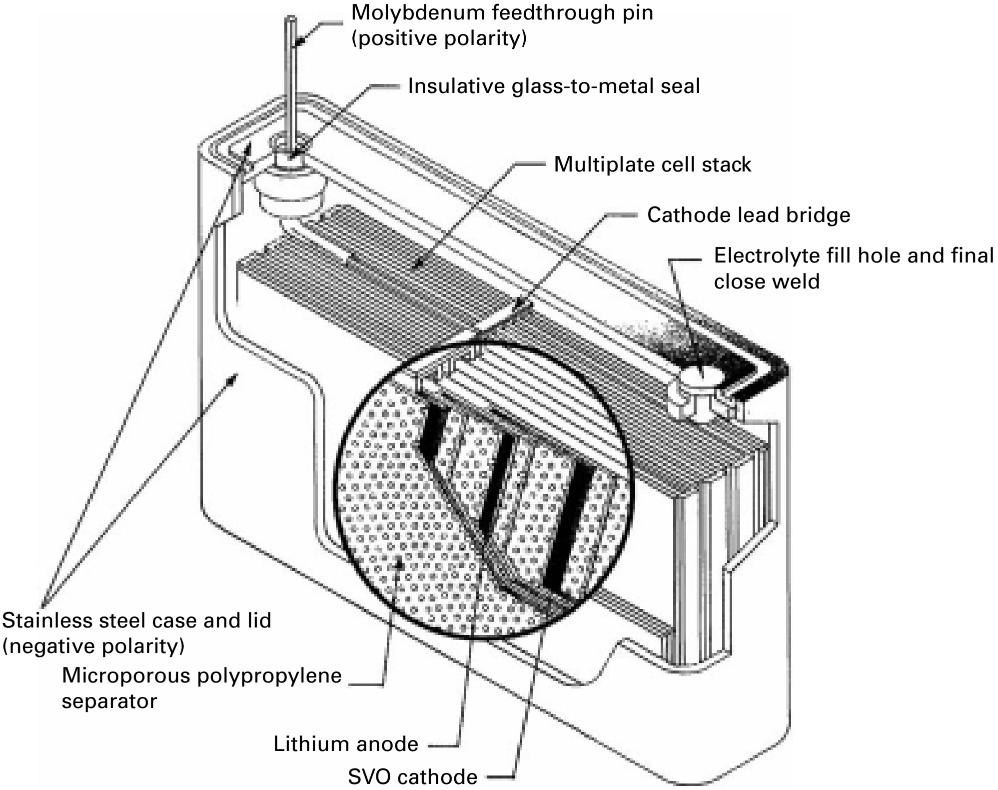


FIGURE 9-15 Cross section of a lithium–silver vanadium oxide (Li/$Ag_2V_4O_{11}$) cell for implantable defibrillators. ©Greatbatch, Inc. Reprinted with permission.

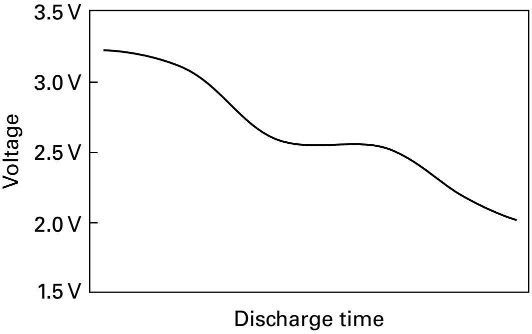


FIGURE 9-16 Discharge voltage behavior for a lithium–silver vanadium oxide (Li/$Ag_2V_4O_{11}$) cell

TABLE 9-14 Lithium–Silver Vanadium Oxide ($Li/Ag_2V_4O_{11}$) Cell Attributes

Attribute	Description
Anode	Lithium (Li) foil or sheet. Anode reaction: $Li \rightarrow Li^+ + e^-$
Cathode	Silver vanadium oxide ($Ag_2V_4O_{11}$) crystals combined with a conductive carbon and a binder, like polytetrafluoroethylene (PTFE, Teflon). Cathode reaction: $Ag_2V_4O_{11} + 7\ e^- \rightarrow 2\ Ag + V_4O_{11}^{7-}$
Electrolyte composition	Lithium hexafluoroarsenate ($LiAsF_6$) in mixed organic solvents, like propylene carbonate and 1,2-dimethoxyethane.
Battery discharge reaction	$7\ Li + Ag_2V_4O_{11} \rightarrow Li_7Ag_2V_4O_{11}$
Nominal cell voltage	3 V
Energy density	270 Wh kg^{-1} and 780 Wh dm^{-3}
Discharge voltage profile	Stepped.
Commonly available sizes	Prismatic cells.

New to implantable cardiac rhythm devices are lithium cells with two cathode materials—$Ag_2V_4O_{11}$ combined with CF_x. The CF_x material discharges at a higher voltage throughout most of the cell life. It is the CF_x, then, that is utilized when the devices only require low power (which is most of the time) for functions like cardiac pacing and sensing. For the infrequent, higher-power loads during radio frequency telemetry or defibrillation therapy, the $Ag_2V_4O_{11}$ is utilized instead.

Lithium–Copper Oxide

Like Li/FeS_2, the lithium–copper oxide (Li/CuO) cells were developed as an alternative to aqueous primary cells. Li/CuO cells have an initial voltage of 2.25 V, but rapidly drop to about 1.5 V or lower during use. These cells are better used for low-power applications. Copper oxide was marketed commercially in the 1970s through the 1980s, but they are no longer available.

Li/CuO characteristics are given in Table 9-15.

TABLE 9-15 Lithium–Copper Oxide (Li/CuO) Cell Attributes

Attribute	Description
Anode	Lithium (Li) foil or sheet.
	Anode reaction: $Li \rightarrow Li^+ + e^-$
Cathode	Copper oxide (CuO) powder, conductive carbon and binder.
	Cathode reaction: $CuO + 2\ e^- \rightarrow Cu + O^{2-}$
Electrolyte composition	Lithium perchlorate ($LiClO_4$) in 1,3-dioxolane organic solvent.
Battery discharge reaction	$2\ Li + CuO \rightarrow Li_2O + Cu$
Nominal cell voltage	1.5 V
Discharge voltage profile	Flat.
Energy density	80 to 290 Wh kg^{-1} and 450 to 650 Wh dm^{-3}

Chapter 10

Rechargeable or Secondary Batteries

IMPORTANT CONCEPTS FROM THIS CHAPTER:

- What is a secondary battery?
- Secondary batteries with nonaqueous electrolytes
- Secondary batteries with aqueous electrolytes

Secondary, or rechargeable, batteries produce power just like primary batteries by converting chemical energy into electrical energy. The difference is that rechargeable batteries can be forced the other way—externally supplied electrical energy can be converted back into chemical energy.

A primary battery is designed and built to be discharged only. Use it once and throw it away or recycle it. It is not intended to be recharged. Primary batteries have a wide range of uses, but there are many applications where is either inconvenient to use primary batteries or too costly or both.

Primary batteries generally work best for portable applications that require only low power, like wristwatches, or are used infrequently, like flashlights. Devices and equipment that require high power for extended periods of time, say laptop computers or golf carts, are better served with rechargeable batteries. This kind of usage would require frequent battery replacement if they could not be recharged.

On the other hand, recharging a battery puts energy back in so that it can discharged once again to produce power. For most rechargeable batteries under nominal conditions, this process can be repeated hundreds of times. Of course, a source of electrical power must be available to recharge the secondary batteries.

Secondary batteries are nearly as old as the primary battery. Just a few years after Alessandro Volta wrote about his battery invention, the first secondary battery was described by Wilhelm Ritter. In the decades before the invention of the dynamo and the electrical power grid distribution system, secondary batteries had to be recharged with other batteries. Raymond Louis Gaston Planté, who invented and worked

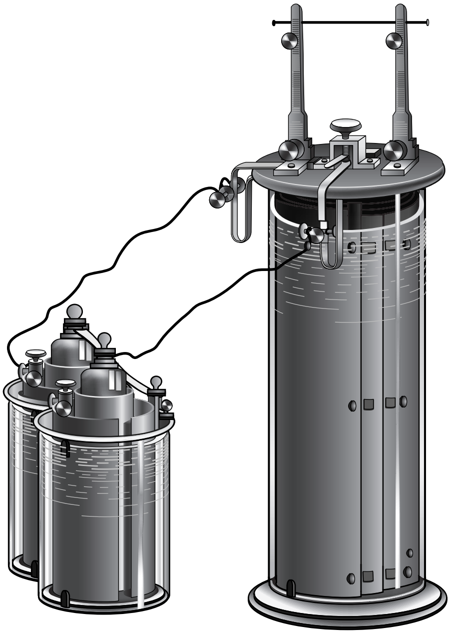


FIGURE 10-1 **The lead acid battery of Gaston Planté with two Bunsen cells used to charge the lead electrodes**

extensively on the lead acid battery system, charged his lead acid cells with two Bunsen cells (Figure 10-1). Three Daniell cells would do the job, as well.

Rechargeable batteries are almost always assembled in the discharged state. After manufacture they must be carefully charged and discharged under tightly managed conditions to condition the electrodes. Conditioning procedures are devised to improve cell stability and performance.

An important factor to consider with any battery system is self-discharge, or the loss of battery capacity from parasitic chemical reactions. Typically self-discharge is lower in primary batteries, from less than 1 percent loss of battery capacity per year to about 4 percent or so per year. Self-discharge in secondary cells can be many times that. It can also be a function of the state of charge of the battery. Lithium ion batteries have a lower rate of self-discharge when they are partially discharged. They prefer to be at about a 50 percent state of charge or lower.

Another factor is the energy density. The energy density obtained from a single discharge for a rechargeable battery is almost always lower than for a primary battery of the same size. Of course, this deficit is more than made up by recharging the secondary batteries hundreds to thousands of times.

The information in this chapter is presented more as an overview and highlights the general characteristics of secondary battery chemistries. The specific performance characteristics of each battery type, like the voltage behavior under different discharge loads or operating temperature range, depends on the chemistry and design of the battery. Further details about battery performance for a particular application, such as the discharge capacity, the voltage at different loads and depths of discharge, operating temperature ranges, and recommended charging methods, can be found in the manufacturers' data sheets (Chapter 12).

We stick with the different battery chemistries in this chapter; the methods used today to safely recharge different types of secondary batteries are discussed in Chapter 11. We also will use both of the terms "secondary" and "rechargeable" to describe the batteries in this chapter, because they are interchangeable, as are the words recharge and charge. We will leave the older terms accumulator and storage battery to history.

In addition, as part of our discussion about primary batteries in Chapter 9, we stated that the positive electrode is the cathode and the negative electrode is the anode. This is also true for a secondary battery, but only when it is being discharged. When it is being charged, the cathode and anode switch sides. However, the positive electrode is always the positive electrode and the negative electrode is always the negative electrode regardless whether the battery is being discharged or charged. So, we will use "positive" or "negative" to identify the electrode and drop the cathode and anode terms.

As with we did with primary batteries in Chapter 9, we separate rechargeable battery systems into two groups by the type of electrolyte they have: aqueous electrolytes that are based on water as the solvent and nonaqueous electrolytes based on solvents other than water.

Batteries with Aqueous Electrolytes

A common positive electrode material used in several different types of aqueous rechargeable cells is nickel oxyhydroxide, Ni(O)OH, also written NiOOH. Examples of batteries using Ni(O)OH are nickel-cadmium (NiCd or sometimes NiCad), nickel–metal hydride (NiMH), nickel-zinc (Zn/Ni(O)OH), nickel-iron (NiFe—the battery Thomas Edison developed and commercialized), and nickel-hydrogen (Ni/H_2). Some of these batteries—the ones that are more readily available—we discuss further in this chapter.

The nickel in Ni(O)OH is in the +3 oxidation state, Ni(III). It is discharged to the +2 oxidation state, Ni(II), forming nickel hydroxide, $Ni(OH)_2$. The charging reaction is just the reverse.

$$\mathrm{Ni(O)OH} + \mathrm{H_2O} + e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} \mathrm{Ni(OH)_2} + \mathrm{OH^-}$$

Most rechargeable cells are manufactured with the active materials in their discharged states. For nickel-based batteries, that is $Ni(OH)_2$.

The positive electrode material, $Ni(OH)_2$ is not very electrically conductive. Using high–surface area current collectors reduces the electrode resistance. The resistance of $Ni(OH)_2$ is further reduced by combining it with 1 percent to 10 percent cobalt oxide (CoO) or cobalt hydroxide ($Co(OH)_2$). CoO forms $Co(OH)_2$ when electrolyte is added to the battery assembly. $Co(OH)_2$ is then oxidized from the +2 oxidation state to the +3 oxidation state during the initial charging step used to condition the battery after manufacture. The resulting Co(O)OH that is deposited on the surface of the $Ni(OH)_2$ particles is electrically conductive, which reduces greatly the resistance of the positive electrode.

Some secondary cells use zinc (Zn) as the negative electrode material. Examples are alkaline zinc–manganese dioxide (Zn/MnO_2), nickel-zinc (NiZn), zinc–silver oxide (Zn/Ag_2O) and zinc-air.

The Ni- and Zn-based cell systems use an alkaline, or basic, electrolyte composed of potassium hydroxide (KOH) in water. Other components may be present as well, such as lithium hydroxide (LiOH) used in NiCd cells.

When a battery is forcibly charged beyond what the battery active materials can accept, called *overcharging,* the electrons are going to go somewhere. They will instead cause other unwanted electrochemical reactions to occur. These reactions do not add to the usable capacity of the battery but can be detrimental to battery performance. In more extreme cases, they may result in hazardous conditions, such as leakage, fire, or explosion.

The principal reactions that occur during overcharging of aqueous electrolyte batteries are the electrolytic oxidation and reduction of water.

Oxidation reaction at the positive electrode: $2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$

Reduction reaction at the negative electrode: $2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$

Overall reaction: $2\ H_2O \rightarrow 2\ H_2 + O_2$

These reactions lead to the generation of oxygen (O_2) at the positive electrode and hydrogen (H_2) at the negative—a potentially explosive mixture. Of course, the internal pressure of the cell increases with gas formation. These reactions also remove water from the electrolyte and so, if unchecked, could dry out the battery, thereby reducing its performance.

The best way to avoid harmful overcharge reactions is not to do it by using an appropriate charging method and carefully managing the charging process (see Chapter 11). A resealable vent or valve is sometimes part of a battery design that can relieve excessive gas pressures.

Battery designers also can take advantage of the certain electrochemical reactions to minimize the risks associated the overcharge reactions, as well.

During overcharging, the potential of the negative electrode drops low enough to reduce the O_2 generated at the positive electrode: $O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$. If it makes its way to the negative electrode, O_2 formed at the positive electrode will be reduced to H_2O. Oxygen gas pressure decreases and H_2O is recovered. This process, sometimes called recombination, is most effective if the rate of overcharging does not exceed the speed of O_2 diffusion to and reaction at the negative electrode. Different battery systems manage the recombination reaction differently. However, one feature that must be designed into the batteries is an excess of negative electrode material (otherwise called "cathode limited"). In this way the negative electrode is held at a low enough potential such that O_2 will be reduced. More information regarding recombination mechanisms, as well as other characteristics, specific to each battery type are discussed in the sections that follow.

Lead Acid

Harry Morse wrote in *Storage Batteries* (1912), "Into our present age of power, where we reckon by thousands and tens of thousands of kilowatts, there has come down from a previous era one single form of the galvanic cell which retains sufficient commercial importance to be worth consideration in connection with modern power plants and modern power operation. This is the lead-sulphuric acid accumulator."

In 2009 we marked 150 years since the first commercially viable lead acid battery was introduced by Robert Louis Gaston Planté. A number of improvements followed soon after by Camille Faure, Charles F. Brush, and others. The result was a battery that was to become one of the more successful battery systems.

The lead acid battery was first used in transportation. Such batteries were used for electric street cars starting in 1890 and electric automobiles beginning in 1895. More than fifty years following its invention, Morse asserted the lead acid battery "retains sufficient commercial importance." His statement is correct even today, over 150 years later and counting.

Indeed, lead acid remains the most popular rechargeable battery system, accounting for well over half of all rechargeable batteries in 2007. Hundreds of millions of lead acid batteries are manufactured each year for a number of diverse uses, including electric vehicles, like golf carts and electric wheelchairs, and stationary power, such as emergency lighting and uninterruptible power supplies (UPSs).

The lead acid battery may be anticipated to continue playing a key role in energy storage well into the future. Sales in the U.S. for all rechargeable battery types is projected to be $10.6 billion in 2012, about $6 billion of which will be lead acid batteries.

Lead (Pb), lead oxide (PbO_2), and sulfuric acid (H_2SO_4) are the negative electrode, positive electrode, and electrolyte of lead acid batteries, respectively. The negative electrode discharge reaction involves the oxidation of Pb metal to Pb ion in the +2 oxidation state (abbreviated Pb(II) or Pb^{2+}).

The Pb(II) so formed precipitates as $PbSO_4$ at the negative electrode by combining with sulfate ions from the electrolyte solution:

$$Pb + H_2SO_4 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} PbSO_4 + 2H^+ + 2e^-$$

The positive electrode proceeds by the reduction of PbO_2 with Pb in the +4 oxidation state, Pb(IV) or Pb^{4+}, to Pb(II), which precipitates as $PbSO_4$ at the positive electrode:

$$PbO_2 + 2\,e^- + H_2SO_4 + 2H^+ \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} PbSO_4 + 2\,H_2O$$

The overall battery reaction is

$$Pb + PbO_2 + 2\ H_2SO_4 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} 2\ PbSO_4 + 2\ H_2O$$

The discharge products of both the positive and negative electrodes are the same: $PbSO_4$. The charging reactions are just the reverse. $PbSO_4$ is reduced to form Pb at the negative electrode and $PbSO_4$ is oxidized to PbO_2 at the positive electrode.

Lead acid battery electrodes—both positive and negative—are manufactured in the discharged state, that is, as Pb(II). Following the basic method of Faure, lead oxide is mixed with H_2SO_4 to yield a paste. Various additives may be added, such as plastic fibers to strengthen the electrode plate and carbon black. Barium sulfate ($BaSO_4$) may be added to help $PbSO_4$ form in small, dispersed crystals rather than large crystals that are more difficult to charge. The electrodes are then conditioned by charging and discharging to form the Pb and PbO_2 at the negative and positive electrodes, respectively.

Alternatively, the Planté method may be used wherein the battery is constructed using Pb electrodes. The battery is then repeatedly charged and discharged in electrolyte to build up PbO_2 at the positive electrode.

Pb and PbO_2 electrode plates are alternated with an intervening separator (Figure 10-2). A number of different porous separator materials have been used, including cellulose polyvinylchloride (PVC) and polyethylene (PE).

The potential for each Pb/PbO_2 cell is nominally about 2.0 V. They are generally charged to less than 2.4 V per cell to minimize gas formation. The plates are connected in series within the battery case to boost the voltage. Common battery voltages are 6 V (three cells) and 12 V (six cells), but batteries with higher or lower voltages can be found. A higher-voltage battery be made by connecting carefully matched, multiple batteries in series.

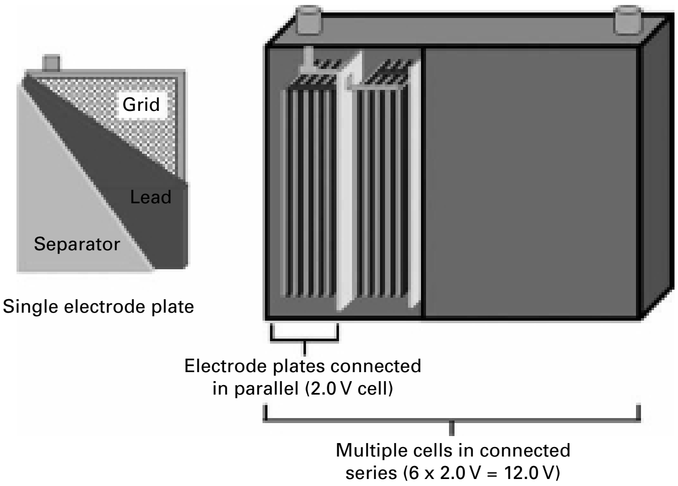


FIGURE 10-2 Cross section of a lead acid battery

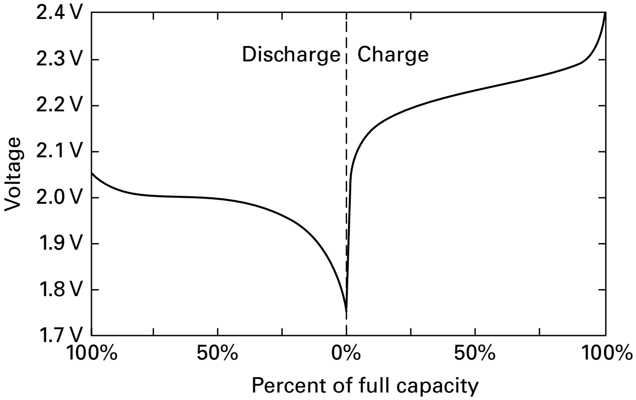


FIGURE 10-3 Discharge and charge voltage for a lead acid battery

A 12 V battery is usually charged to no more than 14.2 V, or about 2.4 V per cell. This voltage is a trade-off between charging the battery more completely with minimizing the overcharge reactions. Minimum discharge voltages can range from 1.8 V down to about 1.2 V per cell, depending on the battery type and the application requirements. Discharge and charge voltage characteristics are shown in Figure 10-3.

As with nearly all batteries, storing or operating them at elevated temperatures can decrease the usable capacity and often reduces the power output, as well. Deterioration of battery performance can also occur from the formation of excess $PbSO_4$, a process called *sulfation*. This can occur if the battery is overdischarged, if it remains for long periods of time in the discharged state, or if the electrolyte level is too low.

The electrolyte for conventional flooded electrolyte batteries is 30 percent to 40 percent by weight aqueous H_2SO_4. Since the H_2SO_4 is a participant in the electrode reactions, its concentration decreases as the battery is discharged. The H_2SO_4 concentration is about 15 percent by weight when the battery is fully discharged.

The change in the H_2SO_4 level during discharge is an important design consideration when specifying a starting concentration volume of electrolyte. The density of the electrolyte changes with the concentration of H_2SO_4, presenting another way to monitor the state of charge of a battery—the specific gravity of the electrolyte.

The three main uses for lead acid batteries are categorized as automobile SLI (starting, lighting, and ignition), traction (also called vehicle or motive power), and stationary power. Each has the same basic chemistry, but they are designed differently to meet the particular needs of the different applications.

The most familiar of these applications is starting car engines, but also boat and aircraft engines. When a car is started, the SLI battery is called on to produce high power to turn the starter motor and trigger the ignition system, but usually only for a couple of seconds until the car engine starts. Once the engine starts, the battery is charged using a float charge (see Chapter 11 for a description of charging methods).

Supplying high power for brief period of time is the most important function of SLI batteries, so they are rated by the current they provide under certain conditions. The cold cranking amperage (abbreviated CCA) is one of the more important ratings to consider for places like Minnesota in winter. The colder the temperature, the less power a battery can produce. The CCA of a battery is the current, in amps, that a battery can deliver at –18°C (0°F) for 30 seconds while maintaining a voltage of at least 7.2 V for a 12 V car battery, or at least 1.2 volts per cell. Typical CCA values for car batteries are in the range 350 A to 850 A. Larger batteries for trucks will have higher CCA values, and those for smaller motorcycle batteries will be lower.

The cranking amperage (CA), also called marine cranking amperage (MCA) when referring to the SLI batteries used to start boat engines, is similar to CCA, but measured at 0°C (32°). The CA of different car batteries can vary from 435 A to 1,000 A.

Another SLI battery rating, the reserve capacity, relates how long a fully charged battery will discharge at 25 A and 27°C (80°F) while maintaining a voltage of at least 10.5 V for a 12 V battery, or at least 1.75 V per cell. Car batteries generally have 62 min to 155 min of reserve capacity. Reserve capacity gauges the ability to run other car functions, like headlights, internal lighting, windshield wipers, defroster, heating fan, and radio, when the engine is not running.

SLI batteries are designed for high power, but not energy density. They are not designed to be fully depleted, such as what happens when the headlights are left on after turning off the car engine. Deep discharge reduces the useful life of SLI batteries.

There was a time when water had to be added periodically to SLI batteries. Electrolyte water lost to self-discharge and overcharge had to be replaced by the end user (or that user's auto mechanic). These batteries have been largely replaced with "maintenance-free" batteries. Improvements to battery designs and charging management reduced the amount of water loss, so it is no longer necessary to periodically check the battery electrolyte level and add water if needed.

Contrary to SLI lead acid batteries, traction (also called motive or vehicle) battery types must tolerate deep discharge while sustaining a higher energy density throughout hundreds of charge and discharge cycles. One way this may be accomplished is by using thicker electrode plates and denser lead pastes.

Two of the electrode design variations that are used for traction, or vehicle, batteries are flat pasted and tubular. Flat pasted electrodes are formed by applying the lead oxide–sulfuric acid paste, described previously, onto a conductive grid. Tubular electrodes are assembled from tubes made of a porous separator material that are filled with electrode material packed around a Pb rod.

Discharge voltage characteristics for flat pasted and tubular electrode batteries are shown in Figure 10-4.

The power output requirements of traction batteries depends on the particular application. Fork lift batteries must deliver higher power levels than wheelchair batteries.

Stationary battery applications include emergency power, for which batteries must remain operational even after long periods of inactivity in the charged state, and energy storage. The latter application includes electrical grid load leveling, as well as solar and wind energy storage. For this battery type, smaller size, lower weight,

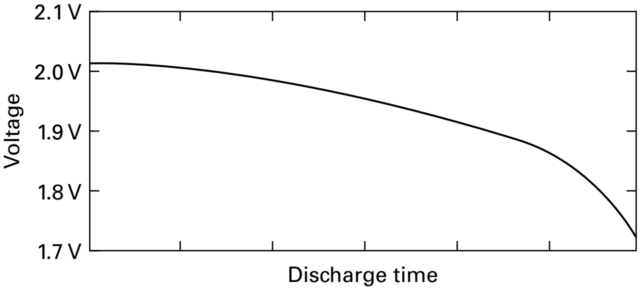


FIGURE 10-4 Discharge curves for lead acid batteries with either flat pasted or tubular electrodes

and higher power may not be quite as important as it is for SLI and traction batteries. Stationary batteries are constructed with thicker, denser electrode plates and flooded with electrolyte to reduce maintenance.

Valve-regulated lead acid (VRLA) batteries, sometimes called sealed lead acid (SLA) batteries are becoming more prevalent in certain applications, like standby power (UPS and emergency lighting) and electric vehicles. As the name suggests, VRLA batteries have a valve to relieve gas pressure if there is excessive gas formation from overcharging.

VRLA batteries contain less H_2SO_4 electrolyte than the flooded variety. An absorbed glass mat (AGM) separator that holds the electrolyte like a sponge or electrolyte gelled with fumed silica (SiO_2) serves to immobilize the electrolyte. This is an advantage for traction or vehicle batteries that may become involved in an accident—the H_2SO_4 electrolyte won't leak. A VRLA battery weighs less than a flooded battery because it has less heavy electrolyte and it can be positioned in any orientation without concerns that the electrolyte will spill out. This might seem familiar, since the Lechanché cell followed the same path, from wet to dry cell, for some of the same reasons (see Chapter 3).

Along with the usual flat plate, prismatic battery design, cylindrical VRLA batteries with spiral-wound electrodes are also available. Individual 2 V cells are manufactured in a D cylindrical cell size (IEC designation PBR20), for example.

During overcharge, O_2 can be reduced at the negative electrode to form water during the recombination process described earlier in the chapter. This recombination reaction is orders of magnitude more efficient for VRLA batteries because O_2 may more easily diffuse from the positive electrode to the negative in the gaseous state. This allows batteries to be sealed because the internal pressure does not build up under normal use. The rate of the recombination reaction is rather slow in flooded lead acid batteries because O_2 must diffuse from the positive electrode to the negative electrode through the electrolyte.

An overview of lead acid battery attributes is given in Table 10-1.

Charging methods and charge termination for lead acid batteries are discussed in Chapter 11.

TABLE 10-1 Overview of Lead Acid Battery Attributes

Attribute	Description
Negative active material	Lead (Pb) plates. Negative electrode reaction (discharge left to right, charge right to left): $Pb \rightleftarrows Pb^{2+} + 2\ e^-$
Positive active material	Lead dioxide (PbO_2). Positive electrode reaction (discharge left to right, charge right to left): $PbO_2 + 4\ H^+ + 2e^- \rightleftarrows Pb^{2+} + 2\ H_2O$
Electrolyte	30% to 40% sulfuric acid (H_2SO_4) in water. May include SiO_2 as a gelling agent in VRLA batteries.
Battery reactions (discharge left to right, charge right to left)	$Pb + PbO_2 + 2\ H_2SO_4 \rightleftarrows 2\ PbSO_4 + 2\ H_2O$
Nominal cell voltage	2.0 V
Discharge voltage profile	Flat to sloped, depending on battery type and discharge load.
Energy density	10 to 44 Wh kg^{-1} and 50 to 111 Wh dm^{-3}
Self-discharge	4% to 6% per month (traction). 20% to 30% per month (SLI). 2% to 3% per month (maintenance free).
Commonly available types	Prismatic 6 V, 12 V. Cylindrical 2 V.

Lead is a toxic metal, so there are strict regulations concerning the disposal of lead acid batteries. Lead acid batteries are classified as hazardous materials by the U.S. Department of Transportation. Thirty-eight states require lead acid battery recycling, and another five regulate disposal.

Today, over 96 percent of battery lead is recycled. New lead acid batteries contain 60 percent to 80 percent recycled lead and plastic.

Nickel-Cadmium

The nickel-cadmium (NiCd) cell was developed in the late nineteenth century by Waldemar Jungner of Sweden. The use of NiCd batteries for traction applications grew in the years before World War II. Today, sealed NiCd cylindrical batteries are used still in a number of portable devices. Larger, vented batteries are used to supply high power for traction, stationary, and aircraft engine starting applications.

The electrodes are assembled in their discharged state—$Ni(OH)_2$ and $Cd(OH)_2$ for the positive and negative electrodes, respectively. NiCd batteries are sometimes categorized by the form of the current collector used—pocket, sintered, fiber, or foam. The pocket plate design comes from Jungner. The active electrode materials are packed in channels formed from perforated steel.

Sintered nickel electrodes were subsequently developed to increase the contact area with the active electrode materials and, so, increase their power output. Fiber electrodes are a mat of sintered nickel plated fibers. Nickel metal foams have a very high porosity, about 90 percent open area. Sintered plate porosities are in the 80 percent to 85 percent range. Greater porosity means more active material can be loaded into the current collector electrodes thereby increasing energy density.

The negative electrode is made of cadmium hydroxide ($Cd(OH)_2$), up to 25 percent iron and small quantities of Ni and graphite. Cobalt oxide is added to the positive electrode material, $Ni(OH)_2$, which forms an electrically conductive coating of cobalt oxyhydroxide, $Co(O)OH$, on the surface of the $Ni(OH)_2$ particles during cell conditioning.

NiCd electrolytes are aqueous solutions of 20 percent to 32 percent potassium hydroxide (KOH) with up to 2 percent lithium hydroxide (LiOH).

The cylindrical cells used for many portable applications are constructed using spiral-wound electrodes similar to the analogous primary battery designs (Figure 10-5). Button cell sizes are also available. Typical voltage behaviors during discharge and charge are shown in Figure 10-6. An overview of NiCd characteristics is given in Table 10-2.

Charging methods and charge termination for NiCd batteries are discussed in Chapter 11.

Electrochemical reactions from the decomposition of water in the electrolyte solution will lead to excessive internal pressure if the battery is charged beyond the capacity of the active materials to accept the charge. This is mitigated in sealed NiCd batteries by including an excess of negative electrode material (or charge reserve), as illustrated in Figure 10-7. If the battery is overcharged, the excess $Cd(OH)_2$ in the negative electrode continues to form Cd, its normal charge reaction, rather than reducing water in the electrolyte solution to form hydrogen (H_2).

Oxygen (O_2) is formed at the positive electrode, though, by oxidizing water in the electrolyte solution:

$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^-$$

The O_2 so formed can diffuse to the negative electrode where it reacts with Cd to form (Figure 10-7):

$$2\,Cd + O_2 + 2\,H_2O \rightarrow 2\,Cd(OH)_2$$

Naturally, the charging current cannot exceed the rate of O_2 reduction or pressure will build within the cell.

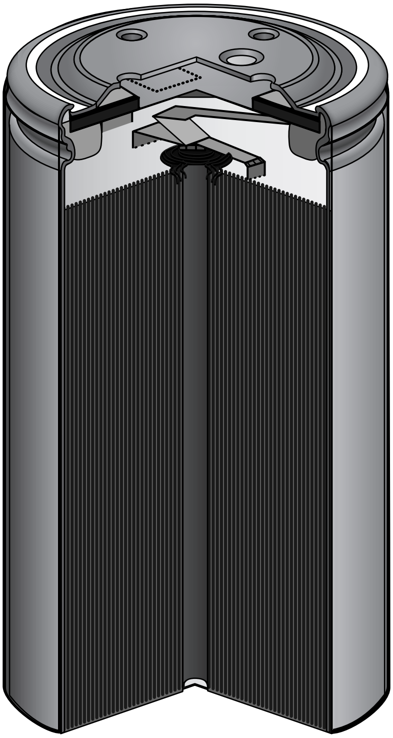


FIGURE 10-5 Cross section of a cylindrical nickel-cadmium spiral-wound cell. ©Spectrum Brands, Inc. Reprinted by permission.

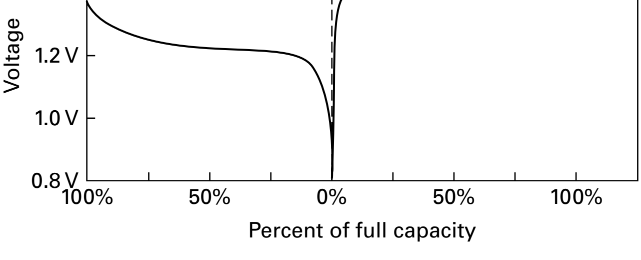


FIGURE 10-6 Voltage behavior for a nickel-cadmium cell during discharge and charge

TABLE 10-2 Overview of Nickel-Cadmium Cell Attributes

Negative active material	Cadmium (Cd). Contains iron, Ni, and graphite. Negative electrode reaction (discharge left to right, charge right to left): $Cd + 2\ OH^{--} \rightleftarrows Cd(OH)_2 + 2\ e^-$
Positive active material	Nickel oxyhydroxide (Ni(O)OH). Contains CoO and graphite. Positive electrode reaction (discharge left to right, charge right to left): $Ni(O)OH + H_2O + e^- \rightleftarrows Ni(OH)_2 + OH^-$
Electrolyte	20 % to 32% potassium hydroxide (KOH) and up to 2% lithium hydroxide (LiOH) in water.
Battery reactions (discharge left to right, charge right to left)	$Cd + 2\ Ni(O)OH + 2\ H_2O \rightleftarrows Cd(OH)_2 + 2\ Ni(OH)_2$
Nominal cell voltage	1.30 V
Discharge voltage profile	Flat.
Self-discharge	5% to 20% per month.
Energy density	18 to 75 Wh kg^{-1} and 30 to 220 Wh dm^{-3}
Commonly available types	Cylindrical cells in a variety of sizes from AAA to D, as well as fractional sizes. Button cells. Prismatic, including 9 V.

Just in case, NiCd cells are usually equipped with one-time or reversible venting systems to release excessive internal gas pressure.

Under certain conditions, some NiCd batteries can exhibit what is called the "memory effect." This occurs when a NiCd battery is repeatedly charged before the cell is completely discharged. Only a portion of the active materials are utilized during an incomplete discharge. The parts of the electrodes that are not discharged may become inactive. It's as though the cell forgets how much capacity it really has.

The memory effect is reversible, fortunately. The battery will recover its full capacity after a few discharge and charge conditioning cycles wherein the battery is completely discharged.

The market for NiCd is now shrinking. They are being replaced by nickel–metal hydride (NiMH) and lithium ion batteries, both described later in this chapter. One reason to consider alternatives is the presence of Cd in NiCd batteries. Cadmium is a toxic metal. Concerns regarding the release of cadmium in the environment from

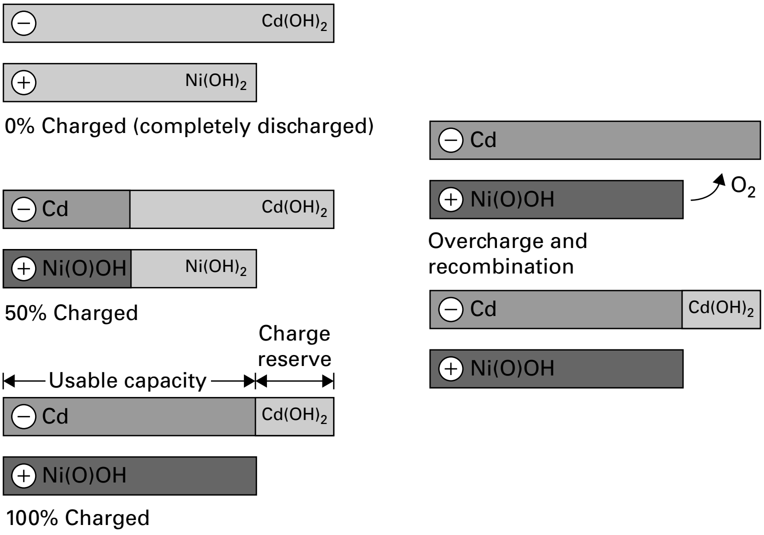


FIGURE 10-7 The oxygen recombination process in nickel-cadmium cells

disposal in landfills or by incineration at waste handling facilities is understandable. A handful of states in the U.S. now have compulsory recycling laws regulating the disposal of NiCd.

Nickel–Metal Hydride

Nickel–metal hydride (NiMH) cells use the same basic positive electrode nickel oxyhydroxide (Ni(O)OH) material as NiCd cells. The big difference is the negative electrode material, which for NiMH cells is a metal alloy that can reversibly absorb hydrogen and form a metal hydride upon reduction.

NiMH cells do not produce as much power as NiCd cells, and they are less tolerant of overcharging. They have a greater energy density, though, and do not contain toxic cadmium.

The positive electrode reaction is the same as for NiCd:

$$\mathrm{Ni(O)OH} + \mathrm{H_2O} + e^- \rightleftarrows \mathrm{Ni(OH)_2} + \mathrm{OH^-}$$

The negative electrode reaction is

$$\mathrm{MH} + \mathrm{OH^-} \rightleftarrows \mathrm{M} + \mathrm{H_2O} + e^-$$

where MH is the metal hydride and M is the metal alloy. Unlike in NiCd cells, there is no net loss of water. It is consumed at the positive electrode and produced at the negative electrode during discharge. This is reversed during charging.

A large number of metal alloys have been investigated as negative electrode materials. Most can be grouped into two categories: AB_5 and AB_2. The A and B represent different classes of metal in the alloy.

The more common alloy is AB_5. These alloys are based on an archetypal alloy composed of the rare earth metal lanthanum (La) and nickel (Ni): $LaNi_5$. Commercial batteries may use a lower-cost, naturally occurring mixture of La (the A in AB_5) with other lanthanide metals, primarily cerium (Ce), praseodymium (Pr), and neodymium (Nd). The combination of these metals is called a mischmetal, abbreviated Mm, which is based on the German word mischmetall, meaning mixed metal. A typical mischmetal might be 25 percent La, 50 percent Ce, 7 percent Pr, and 18 percent Nd. Other metals also can be present at low levels.

The Ni in the mischmetal AB_5 alloy (the B in AB_5) can be partially substituted with other metals to improve characteristics like increasing corrosion resistance, maintaining the structural integrity of the alloy over the course of hundreds of charge-discharge cycles, or as a stabilizer during manufacturing. Metals like cobalt (Co), manganese (Mn), and aluminum (Al) are commonly used for these purposes. Other metal elements may be added to further adjust the corrosion and cycle life properties.

AB_2 alloys are typified by $ZrNi_2$, made from zirconium (Zr) and Ni, but also contain elements like titanium (Ti), vanadium (V), and chromium (Cr), as well as a few other minor components.

Other alloy types have been investigated as well, but the predominant alloy used is AB_5. Regardless, we will simply use the letter M, as in MH, to broadly represent any and all of the alloys.

NiMH cells are manufactured as sealed cylindrical, button, and prismatic batteries in a wide variety of sizes. As in the sealed NiCd batteries, the electrodes in NiMH cylindrical cells are spirally wound, disks in button cells, and parallel plates in prismatic batteries.

The positive electrode is quite similar to those for other nickel-based batteries, like NiCd, described earlier in this chapter. The negative electrode is pressed on a perforated or expanded nickel sheet current collector. The alloy is mixed with a polymer like polytetrafluoroethylene (PTFE or Teflon). PTFE is hydrophobic, so it is not wetted by water, or an aqueous electrolyte. Now, an electrode must be in contact with the electrolyte for the battery to function properly. On the other hand, a dry electrode allows gas to escape during overcharge. The amount of PTFE added to the negative electrode material strikes a balance between these two competing requirements. There is not so much PTFE that electrolyte does not wet the electrode, and there is not so little that the electrode is flooded and gas, H_2 in this case, is impeded during overcharging. (See the discussion on NiMH overcharge reactions later in this chapter.)

Typical discharge and charge voltage behavior is shown in Figure 10-8. An overview of NiMH battery attributes is given in Table 10-3.

Charging methods and charge termination for NiMH batteries are discussed in Chapter 11.

The overcharge reactions for NiMH cells are somewhat different than for NiCd cells. As with NiCd cells, NiMH cells are cathode limited; that is, they have an excess

TABLE 10-3 Overview of Nickel–Metal Hydride Cell Attributes

Negative active material	Mischmetal hydride. Combined with polytetrafluoroethylene (PTFE or Teflon).
	Negative electrode reaction (discharge left to right, charge right to left):
	$MH + OH^- \rightleftarrows M + H_2O + e^-$
Positive active material	Nickel oxyhydroxide ($Ni(O)OH$). Contains CoO and graphite.
	Positive electrode reaction (discharge left to right, charge right to left):
	$Ni(O)OH + H_2O + e^- \rightleftarrows Ni(OH)_2 + OH^-$
Electrolyte	Potassium hydroxide (KOH) in water.Lithium hydroxide ($LiOH$) may be added.
Battery reactions (discharge left to right, charge right to left)	$MH + Ni(O)OH \rightleftarrows M + Ni(OH)_2$
Nominal cell voltage	1.20 V
Discharge voltage profile	Flat.
Self-discharge	15% to 25% per month.
Energy density	23 to 92 Wh kg^{-1} and 32 to 332 Wh dm^{-3}
Commonly available types	Cylindrical cells in a variety of sizes from AAA to D, as well as fractional sizes.
	Button cells.
	Prismatic, including 9 V.

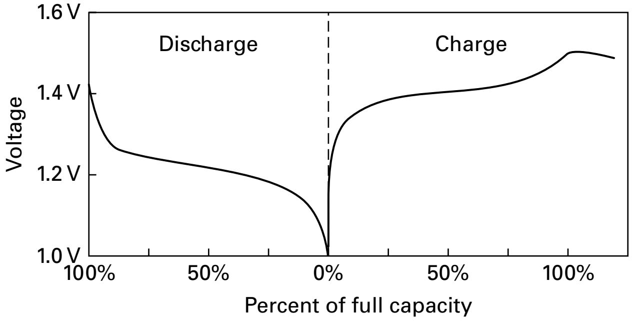


FIGURE 10-8 Discharge and charge voltage behavior for a nickel–metal hydride cell

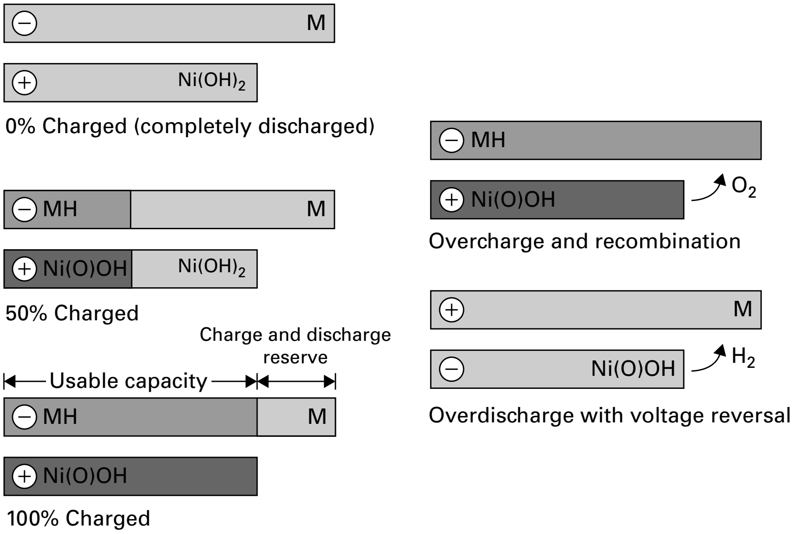


FIGURE 10-9 Oxygen recombination reactions during overcharge of nickel–metal hydride cells

of negative electrode material (Figure 10-9). When the battery is charged beyond the capacity of the positive electrode, O_2 forms at that electrode, which then diffuses to the negative electrode, where it reacts with the hydride to form water: $O_2 + 4\ MH \rightarrow 2\ H_2O + 4\ M$. So far, so good, because water is recovered. Excessive water loss reduces cell performance. Recall that water is removed during the oxygen recombination reaction in NiCd cells.

During overdischarge, when the cell is discharged beyond the capacity of the positive electrode, H_2 gas forms there. If the cell is discharged enough, the potential of the negative electrode may become more positive than the positive electrode. This is called *reversal*. When this occurs, H_2 can form. In this case, the H_2 diffuses to what was the negative electrode, but it is now the positive electrode because of voltage reversal and is oxidized to form water. Again, no loss of water occurs.

Alkaline Zinc–Manganese Dioxide

An alkaline zinc–manganese dioxide (Zn/MnO_2) battery designed and manufactured to be rechargeable was introduced in 1993. It filled a niche between single-use alkaline-zinc primary cells and other rechargeable cells, especially nickel-cadmium (NiCd) and nickel–metal hydride (NiMH).

This cell offers the advantages of an alkaline Zn/MnO_2 primary battery (greater initial capacity, higher voltage, lower self-discharge rate, longer shelf life, and lower cost), but it only can be recharged about 25 times—not the hundreds of deep discharge cycles achievable with NiCd and NiMH, and the capacity tends to decrease with each cycle. One can attain more or fewer useful cycles, depending on how the battery was used.

TABLE 10-4 Overview of Rechargeable Alkaline Zinc–Manganese Dioxide Cell Attributes

Attribute	Description
Negative active material	Zinc (Zn) metal powder mixed with gelled alkaline electrolyte solution. Anode reaction (discharge left to right, charge right to left): $Zn + 4\ OH^- \rightleftarrows Zn(OH)_4^{2-} + 2\ e^-$ Or $Zn + 2\ OH^- \rightleftarrows ZnO + H_2O + 2\ e^-$
Positive active material	Manganese dioxide (EMD) powder mixed with one or more conductive carbon powders (e.g., graphite and acetylene black) and a binder. Cathode reaction (discharge left to right, charge right to left): $MnO_2 + H_2O + e^- \rightleftarrows Mn(O)OH + OH^-$
Electrolyte composition	$KOH\text{-}ZnO\text{-}H_2O$. Contains gelling agent.
Battery reactions (discharge right to left, charge left to right)	$Zn + 2\ MnO_2 + 2\ H_2O + 2\ KOH \rightleftarrows K_2Zn(OH)_4 + 2\ Mn(O)OH$ Or $Zn + 2\ MnO_2 + H_2O \rightleftarrows 2\ Mn(O)OH + ZnO$
Noinal cell voltage	1.50 V open circuit voltage.
Discharge voltage profile	Sloped.
Energy density	80 Wh kg^{-1} and 220 Wh dm^{-3}
Commonly available types	Cylindrical cells in a variety of sizes from AAA to D.

Like their primary cell counterparts, rechargeable alkaline Zn/MnO_2 cells have a higher internal resistance than the corresponding NiCd and NiMH cells, so they do not produce as much power.

The rechargeable alkaline Zn/MnO_2 cell is assembled in its charged state. Off the shelf it is like an ordinary primary alkaline Zn/MnO_2 cell. It does not need to be charged before use like other rechargeable systems. It also is as environmentally benign as the primary cell version. Recycling or special disposal is not required, as with NiCd cells, so it can be discarded in the trash.

Batteries with Nonaqueous Electrolytes

The widespread acceptance the aqueous electrolyte rechargeable batteries over many decades, particularly lead acid and nickel-cadmium, clearly indicates the necessity of rechargeable batteries. As a result of this success, it is only natural to look for materials that can provide even higher energy densities. So, it was only a matter of time before rechargeable lithium battery systems were developed because of the large jump in energy density over aqueous systems.

Of the lithium rechargeable batteries available, lithium ion is by far the most successful nonaqueous secondary battery.

Lithium Ion

Of all the batteries developed and produced commercially, those originating from the works of Planté and Faure (lead acid), Leclanché (zinc-carbon) and Jungner (nickel-cadmium) have been the most successful and widely used. The newcomer to this group is lithium ion (Li ion). Li ion batteries provide the high power and energy needed to run higher-end (more expensive) electronic applications, like laptop computers, cell phones, cameras, and MP3 players. They are also starting to be used in space, military, and electric vehicle applications. The demand for Li ion batteries surpassed the combined demand for nickel-cadmium (NiCd) and nickel–metal hydride (NiMH) batteries several years ago.

Lithium primary batteries have higher energy densities than their aqueous counterparts, so it was a natural step to make Li batteries rechargeable such that their service life could be extended. Work to develop rechargeable Li metal batteries progressed from the 1970s into the 1980s. However, there are challenges with Li metal as a rechargeable battery negative electrode that limit its usefulness and reduce the practical energy densities that can be achieved (see the next section). As a result, battery developers turned to other negative electrode materials that retain the high energy density advantages of Li electrodes.

Lithium ion cells were developed to take advantage of the high energy density of Li cells, but make them rechargeable. The use of certain carbon materials as the negative electrode material has overcome some of the limitations and safety concerns that arise from recharging Li metal electrodes. Lithium is still involved, but in a different way, as we will see in the text that follows.

Lithium ion batteries were first sold commercially by Sony in 1991. Since then, Li ion technology development continues to accelerate, and it has seen a tremendous upsurge in use in portable devices like MP3 players, cameras, power tools, and, more recently, electric vehicles.

Indeed, the global market for Li ion batteries is estimated to be over $10 billion in 2010 with $3 billion of that in the U.S. alone. This corresponds to about 3.4 billion Li ion batteries used worldwide with a cumulative energy output of 20 GWh (20,000,000,000 Wh).

The market for Li ion batteries will increase, especially with new applications coming on line like electric vehicles and large-scale energy storage systems for wind and solar energy generation, as well as electrical grid energy storage. By 2018, the market is anticipated to be $32 billion, corresponding to almost 9 billion lithium ion batteries sold with a cumulative energy output of 75 GWh—the same electrical energy used by 6,800 average U.S. homes in a year.

The variety of different carbon materials is enormous, but most lithium ion negative electrodes are composed of either graphite, coke, or a “hard” carbon. There is another negative electrode material in commercially available batteries that is not a carbon-based, lithium titanate, that we will describe soon.

Graphite is the archetype for these carbon materials. It is composed of layers of carbon atoms linked together to create a network of carbon hexagons (Figure 10-10). These carbon atom networks form flat sheets that are stacked one on top of the other. Most carbons are not so highly ordered, though. The length, width, and height of the stacked carbon sheets vary among different carbon materials. In addition, the layers are not necessarily nicely stacked in an orderly fashion as drawn in Figure 10-10, but usually will have differing degrees of structural disorder, such as layers that are shifted or turned.

Some carbon materials can be made to be more highly ordered (more like graphite or graphitic) by heating them at high temperatures, usually above 2,000°C or so. This type of material has been called “soft” carbons, meaning they can be made more graphitic by heating. Coke is a type of soft carbon. Other carbon materials cannot be made more graphitic by heating at high temperatures. These are called “hard” carbons.

Lithium ion positive electrode materials in the batteries available today are metal oxide or phosphate compounds. Lithium ion electrode materials are prepared and built into cells in their discharged states. For the negative electrode, that is carbon. Positive electrode materials are synthesized containing lithium.

The four most common types of positive electrode materials are

- Lithium–cobalt oxide ($LiCoO_2$).
- Lithium–mixed metal oxide. Usually a combination of cobalt (Co) and nickel (Ni) and perhaps other metal ions. Examples include $LiNi_{0.8}Co_{0.2}O_2$, $LiNi_{0.8}Co_{0.15}Al_{0.5}O_2$, and $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$.
- Lithium–manganese oxide ($LiMn_2O_4$). Sometimes simply called spinel after the term used to describe its chemical structure.
- Lithium–iron phosphate ($LiFePO_4$).

Lithium ion cells work by a chemical mechanism called *intercalation* wherein lithium ions are inserted into the molecular structure of the electrode materials.

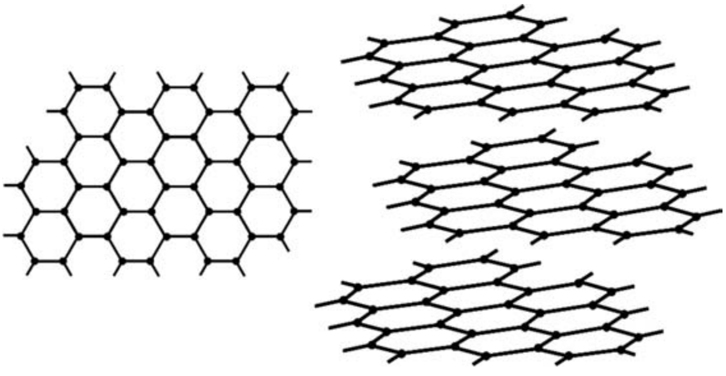


FIGURE 10-10 The chemical structure of graphite

When the negative electrode of a Li ion cell is electrochemically reduced during charging, lithium ions (Li^+) are inserted between the individual graphite layers (Figure 10-11):

$$C_6 + x\,Li^+ + x\,e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Li_xC_6$$

where C_6 is a single carbon hexagon unit in Figure 10-11 and x is the amount of Li intercalated per C_6 unit in carbon. The value for x is somewhere between 0 and 1. The electrode potentials of carbon electrochemically intercalated with Li^+ can get down to within tens of millivolts of the potential for lithium metal itself at the end of charging.

The reverse process occurs during discharge. The Li^+ exits, or deintercalates, from the carbon electrode material. The entire charge-discharge cycle leaves the structure of the graphite intact and available to repeat the intercalation-deintercalation process during charging and discharging of the battery (Figure 10-11).

The first positive electrode material used in commercially available cells was $LiCoO_2$. It forms a layered structure with Li^+ inserted between the layers of cobalt (Co) and oxygen (O) (see Figure 10-12). The intercalation and deintercalation reactions are reminiscent of those for carbon: Lithium ions exit $LiCoO_2$ during charging and they intercalate into CoO_2 during discharge.

$$LiCoO_2 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Li_{1-x}Co_2 + x\,Li^+ + x\,e^-$$

where x is the extent of reaction and lies somewhere between 0 and 1.

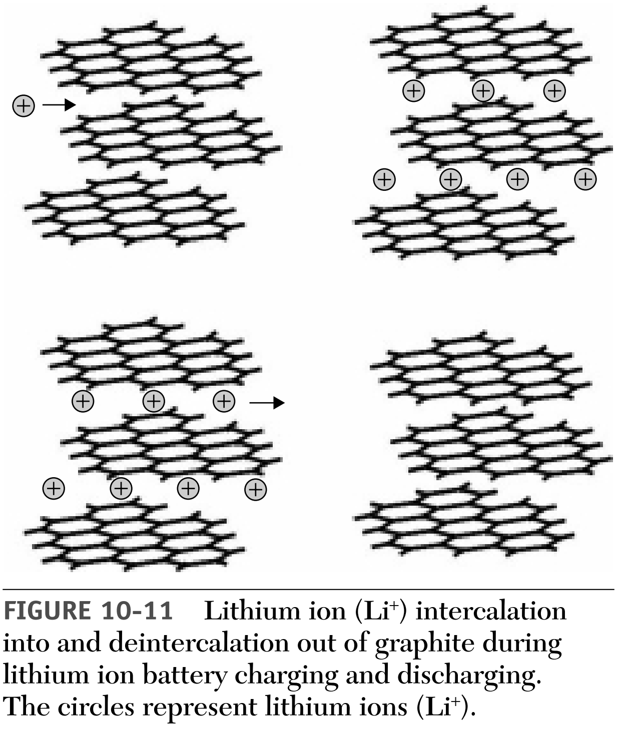


FIGURE 10-11 **Lithium ion (Li^+) intercalation into and deintercalation out of graphite during lithium ion battery charging and discharging. The circles represent lithium ions (Li^+).**

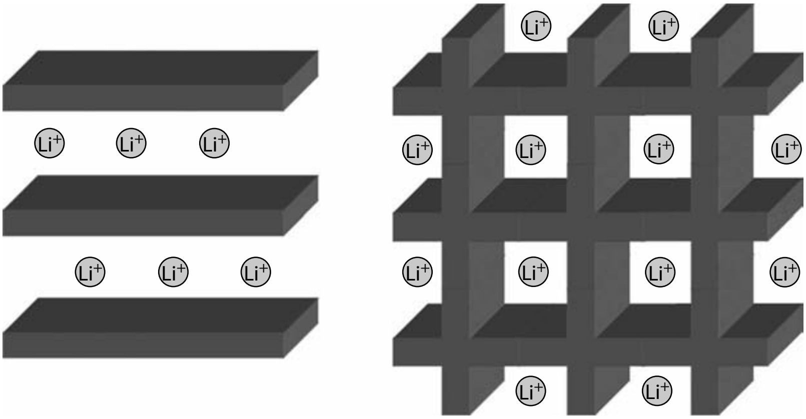


FIGURE 10-12 **Left: Layered structure for lithium–cobalt oxide ($LiCoO_2$). Right: Three-dimensional structure for lithium–manganese dioxide ($LiMn_2O_4$). The circles represent lithium ions (Li^+).**

Not all positive electrode materials have a layered structure, though. $LiMn_2O_4$ and $LiFePO_4$ have three-dimensional structures, and the lithium ions are inserted into the spaces between the rest of the atoms in the structure (Figure 10-12).

The overall cell reactions are (charge from left to right and discharge from right to left):

$$C_6 + LiCoO_2 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Li_xC_6 + Li_{1-x}CoO2.$$

The lithium ions alternate between intercalating into and deintercalating out of both electrode materials as the cell is cycled from charge to discharge. Envisioning that Li^+ is passed from one electrode to the other and then back again many times prompted some to call this a “rocking chair” or “shuttlecock” mechanism (Figure 10-13).

Another negative electrode material is now available—lithium titanate ($Li_4Ti_5O_{12}$). At first glance this lithium metal oxide looks more like a positive electrode material, but its potential is low enough to make it suitable as a negative electrode material. Even so, the nominal voltage $Li_4Ti_5O_{12}$ Li ion batteries are over 1 V lower than conventional Li ion batteries with carbon negative electrodes.

Lithium titanate batteries are being marketed for larger applications, particularly electric vehicles. They may be charged rapidly (less than 10 minutes), deliver 6,000 rapid charge-discharge cycles, and can be safer.

The positive electrode materials are typically combined with a conductive carbon powder and a polymer binder—polyvinylidene fluoride (PVDF) or a copolymer of PVDF and hexafluoropropylene (PVDF-HFP)—then coated on a thin aluminum foil current collector. The carbon negative electrode material uses the same binders and is coated on a thin copper foil current collector.

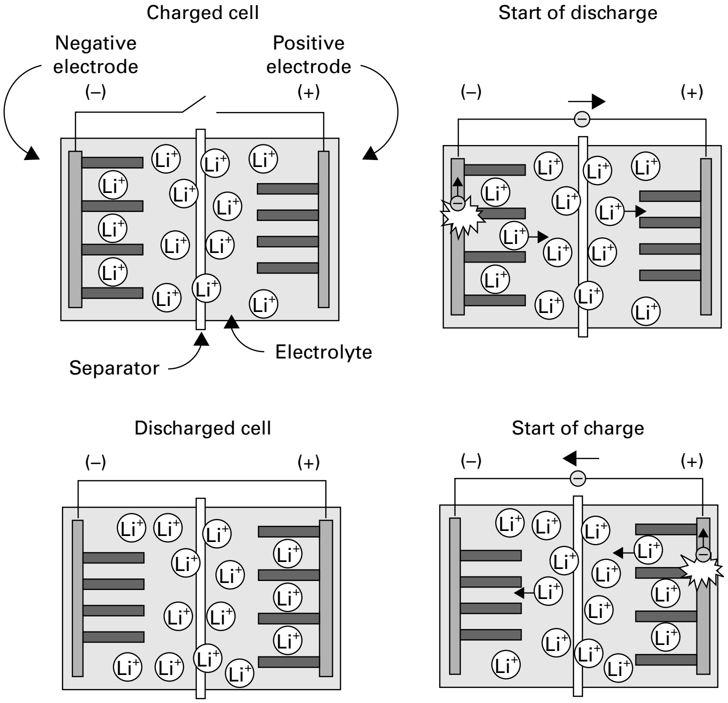


FIGURE 10-13 Discharge and charge processes in lithium ion cells

Cylindrical cells are made by winding the electrodes together with an interposed porous membrane separator. The electrolyte generally is a mixture of liquid organic solvents with a lithium salt like lithium hexafluorophosphate ($LiPF_6$).

Lithium ion polymer batteries use a polymer gel electrolyte composed of a polymer, like PVDF-HFP, infused with liquid organic solvents containing a dissolved lithium salt like $LiPF_6$. Lithium ion polymer batteries are generally prismatic cells and can be made very thin.

Typical discharge voltage behavior for lithium ion cells are shown in Figure 10-14 and typical cell attributes are given in Table 10-5.

Lithium Metal

Lithium primary cells (Chapter 9) have a high energy density, and combined with the right battery design and construction, they can produce high power. So, it was a natural step to develop rechargeable Li metal cells that retain the high energy and power outputs but can be charged many times.

A number of different positive electrode materials can be paired with Li. However, the challenge comes when charging a Li electrode. During charging, Li ions in the electrolyte solution are reduced and deposited, or plated, onto the negative electrode

TABLE 10-5 Overview of Attributes for Lithium Ion Cells

Attribute	Description
Negative active material	Carbon (graphite, coke or "hard" carbon) with polyvinylidene difluoride (PVDF) binder and coated on a thin copper foil. Lithium titanate ($Li_4Ti_5O_{12}$) also used for some batteries. Negative electrode reaction (charge from left to right, discharge from right to left): $C_6 + x\ Li^+ + x\ e^- \rightleftarrows Li_xC_6$
Positive active material	Lithium metal oxide or phosphate: $LiCoO_2$ $LiNi_{0.8}Co_{0.2}O_2$, $LiNi_{0.8}Co_{0.15}Al_{0.5}O_2$ and $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ $LiMn_2O_4$ $LiFePO_4$ Mixed with a conductive carbon and polyvinylidene difluoride (PVDF) binder, then coated on a thin aluminum foil. Positive electrode reaction (charge from left to right, discharge from right to left): $LiMO_2 \rightleftarrows Li_{1-x}MO_2 + x\ Li^+ + x\ e^-$ Or $LiFePO_4 \rightleftarrows Li_{1-x}FePO_4 + x\ Li^+ + x\ e^-$
Electrolyte composition	Lithium hexafluorophosphate dissolved in a mixture of organic solvents.
Battery reactions (discharge right to left, charge left to right)	$C_6 + LiMO_2 \rightleftarrows Li_xC_6 + Li_{1-x}MO_2$
Nominal cell voltage	3.6 V to 3.8 V
Discharge voltage profile	Sloped or flat.
Self-discharge	2% to 10% per month.
Energy density	84 to 210 Wh kg^{-1} and 168 to 555 Wh dm^{-3}
Commonly available types	Cylindrical cells. Prismatic cells. Coin cells.

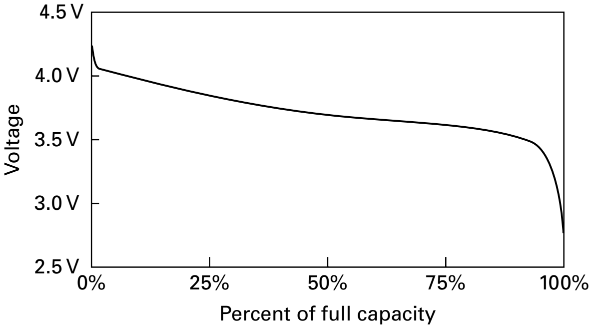


FIGURE 10-14 Discharge voltage characteristics for lithium ion cells

as Li metal. As it happens, Li has a propensity to form dendrites as it is deposited during the charging reaction (Figure 10-15). If this continues, they can grow through the separator and make contact with the positive electrode, resulting in a direct short-circuit path between the two electrodes.

On the subsequent discharge step, some of the dendritic Li metal deposits may break away from the rest of the electrode (Figure 10-15). This process produces a mass of small bits of Li metal that are electrically isolated from the negative electrode.

These bits of Li metal are no longer available to be discharged, so there is a net loss of active Li. A large excess of Li must be built into the cell to make up for the Li lost this way.

Not only that, but the finely divided Li is highly reactive. A problem, like an internal short circuit from Li dendrites connecting through to the positive electrode or exposure to very high temperatures, could be made worse because the presence of the small pieces of Li creates an increased risk for fire.

Even without the formation of dendrites, newly deposited Li reacts with the electrolyte to form a film on the surface of the electrode. This film helps to protect

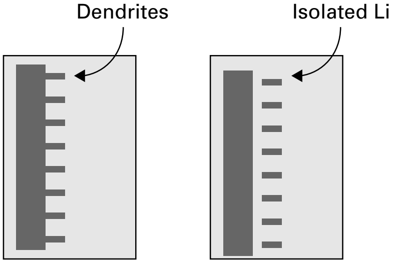


FIGURE 10-15 Charging a lithium metal rechargeable cell can result in dendritic deposits of Li metal at the negative electrode (left). Subsequent discharge can cause isolation of small bits of Li metal (right).

the Li from reacting further with the electrolyte, but it removes some of the active Li (and electrolyte) each time the cell is charged. This requires a large amount of extra Li—on the order of a three- to six-fold excess—to be built into the cell to account for the reactions with the electrolyte. The more excess Li, the more charge and discharge cycles a cell can achieve.

The rechargeable Li metal cells available today are coin cells designed for low-power applications, including memory backup for computers and mobile phones. They usually use a lithium-aluminum (LiAl) alloy, which further reduces the energy density from that of Li but provides greater thermal stability and is safer than Li.

Advantages include low self-discharge, about 2 percent per year, able to operate over a wide temperature range, –20°C to +60°C and resilient to being overdischarged to 0 V and overcharged.

Positive electrode materials used are molybdenum disulfide (MoS_2), titanium disulfide (TiS_2), manganese dioxide (MnO_2), vanadium pentoxide (V_2O_5), and niobium pentoxide (Nb_2O_5).

A larger, cylindrical rechargeable lithium–molybdenum disulfide (Li/MoS_2) cell was commercialized for use in cellular phones in the 1980s, but was discontinued in 1989 as a result of safety concerns. Li metal rechargeable cells have been largely supplanted by Li ion cells.

Comparing Rechargeable Batteries

There are a number of considerations that go into selection of a battery—energy or capacity, power, number of cycles, available sizes, recycling requirements, and cost.

Figure 10-16 compares the energy densities based on weight and volume for the most commonly available rechargeable battery systems. Lithium is a clear winner but tends to be more expensive.

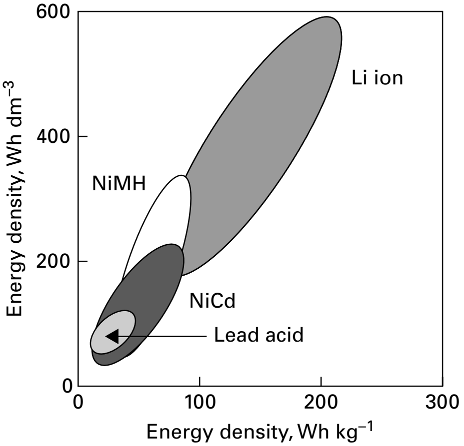


FIGURE 10-16 Comparison of energy densities by weight and volume for selected rechargeable batteries

Chapter 11

Charging Rechargeable Batteries

IMPORTANT CONCEPTS FROM THIS CHAPTER:

- Charging processes
- Charging considerations
- A rundown of different ways to charge batteries
- Charge termination

The thing about rechargeable batteries is they have to be recharged. To do that, engineers design battery chargers, those electrical devices that take electricity from the electrical power grid battery in addition to monitoring and managing the charging process. Charging can be done by another battery just as the early developers of rechargeable batteries had to do in the days before the electric generator was invented. The batteries that do the charging can be primary batteries that are discarded after use or recharged themselves if they are rechargeable.

Most battery chargers are the direct contact type—the batteries or the devices that house the batteries are in direct electrical contact with the charging circuit. Other types of energy transfer mechanisms are possible, as well. Notably, inductive charging where a magnetic field induces an electric current and is used when direct contact is not desired or not possible. Examples of the latter include certain implanted medical devices that use rechargeable batteries.

In Chapters 6 and 10 we looked at some of the materials and design features that are necessary to construct an efficient, safe rechargeable battery. In this chapter we will take a look at different ways to charge batteries. Not enough to be able to design charging circuits and chargers, but enough to understand what it takes to charge a battery. For end users, this chapter will help you understand what your charger is doing as it recharges your batteries.

Safe Charging

One note about safety. As we will see, chargers must be designed with ways to monitor the charging process and control the total amount and rate of electricity entering a battery during charging. Charging a battery is not something that should be improvised or done without the proper precautions. It is safest to use commercial charging stations designed specifically for your battery type.

Also, consult the manufacturers' information regarding their recommended methods for charging their batteries.

And another thing. Recharging primary batteries: Don't do it.

A primary battery is designed and constructed to be discharged only. Use it once and throw it away or recycle it as appropriate. It is not designed to be recharged, and there are some very good reasons not to do it.

Charging or recharging (the terms can be considered to be interchangeable under most circumstances) is the process of forcing an electric current into a battery. The direction of a charging current, from the negative electrode to the positive electrode, is the opposite direction of the current that is produced during discharge, which is from the positive electrode to the negative. (Recall that electrons travel in the opposite direction as the current, so they are conveyed from the positive to the negative electrode during charging.)

The ability of a battery to be recharged reflects its ability to accept a charging current. The charge acceptance of a battery is limited by a couple of factors: the chemistry (or active materials), other components in the battery, and its design or construction. The magnitude of the charging current plays an important role, as well. Even rechargeable batteries can fail to perform adequately if the rate of charging outpaces the ability of the battery to accept the charging current.

Many of the active materials used in primary batteries just cannot be charged. The discharge reaction is chemically irreversible. Sometimes, primary battery active materials can be recharged partially, but only under certain, well-controlled conditions. Attempts to recharge such batteries will result in other reactions occurring in the battery, including the decomposition of the electrolyte solution to form gas. Excessive gas pressure results in leakage or possibly explosion.

The design and components of the battery may also affect the ability of a battery to be recharged. For example, remember the different components of a battery from Chapter 6. Most batteries use a separator to keep the anode and cathode from directly contacting each other, which causes an internal short circuit. The separator is an electrical insulator, but porous so that ions in the electrolyte can move between the two electrodes.

Charging a primary battery can lead to plating of metal that may cause dendrites—literally, fingers of metal—to form and grow into and through the pores of a separator as the metal continues to deposit during charging. If this process continues, the dendrites can continue to get larger until they create a connection between the cathode and anode, which results in an internal short circuit. At best, this causes a loss in battery performance or leakage. At worst, explosion and fire in the most extreme circumstances.

That does not mean that it is impossible to charge some primary batteries, at least partially. However, it is risky to do so. Trying to get it right could lead to batteries that leak or even explode. You can even buy charging units that claim to recharge primary batteries. Well, maybe. If you really want a rechargeable battery, then use batteries that are designed to be recharged.

The Charging Process

A discharging battery is called a galvanic cell. The cell reactions will occur spontaneously when the terminals are connected to an external circuit and chemical energy is converted into electrical energy. The anode is the negative electrode and the cathode is the positive electrode.

Charging a battery is the reverse of discharge—electrical energy is converted into chemical energy. The discharge reactions of the cell are forced to proceed backward. This is an electrolytic cell.

For an electrolytic cell, the anode is the positive electrode and the cathode is the negative electrode. Which electrode we call the anode and which one is the cathode in a rechargeable cell all depends on what process is occurring—charge or discharge. The charge associated with the electrode remains the same, though. Sometimes it can be less confusing to just refer to the positive or negative electrode. Then it doesn't matter if the battery is discharging or charging; it is the same electrode. Many times the terms anode and cathode are used regardless of what the battery is doing. In this case, they refer to the anode and cathode of the battery during discharge, even if it is being charged at the time.

A couple of examples: For a lead acid battery (see Chapter 10), the lead sulfate ($PbSO_4$) that forms at both the negative and positive electrodes during discharge is converted back to lead (Pb) at the negative electrode and lead oxide (PbO_2) at the positive electrode:

$$Pb + PbO_2 + H_2SO_4 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} PbSO_4 + 2H_2O$$

(The double arrows indicate the reactions are reversible—they can proceed in either the forward or backward direction, although not necessarily with equal ease.)

In a lithium ion cell, lithium (Li) that was loaded into the positive electrode during discharge is removed. At the same time, Li is intercalated into the carbon negative electrode. The reactions may be simply written:

$$Li_{1-x}CoO_2 + Li_xC \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} LiCoO_2 + C$$

where x is the fractional amount of Li removed from $LiCoO_2$ that intercalates into the carbon electrode.

See Chapter 10 for more information on these and other rechargeable systems.

Charging Considerations

A charger must do two things to safely charge a battery—power conversion and charge control.

The charger must convert the voltage and current available from the electrical distribution grid (that is, the AC power that comes into our homes and businesses) to the voltage and current levels that are suitable to charge a battery. This function is not different from other electrical power supplies, except the load for a battery charger is an active power source itself.

Charge control circuitry manages the voltage and current levels applied to the battery, the total amount of electricity allowed to pass through the battery, how fast, and when.

Another factor to think about is what to call a full charge. In some cases, a battery intentionally may not be fully charged. This creates a safety margin used to reduce the likelihood of an overcharge condition. It might be important if the charging management system of the charger is variable or not very reliable. Naturally, the disadvantage is that a partially charged cell will deliver less energy compared to a fully charged cell.

The rate at which a battery is charged depends on the particular battery technology—chemistry and construction. The maximum charging rate of a battery can also depend on its state of charge. Battery materials are generally less able to charge at higher currents as the battery approaches a state of full charge.

Whatever the reason, if a current running through or the voltage applied to a battery is high enough, other electrochemical reactions can occur. These undesired side reactions can lead to degradation of the battery materials, loss of mechanical stability of the battery materials (such as loss of electrical contact within the electrodes), and the formation of gasses resulting from the decomposition of the electrolyte. Not only that, but excessive heat may be produced.

The unwanted electrochemical reactions can decrease battery performance characteristics in several ways, like diminished power and energy, and possibly render it unsafe to use. Further, performance can continue to decline over time and with each charge-discharge cycle.

A large increase in internal pressure from gas formation can lead to cell rupture, either through a vent designed to release pressure or, catastrophically, simply bursting open if the cell has no vent. Either way, the cell can leak, catch fire, or even explode in the most extreme circumstances. Even if the cell does not open, it can bulge from the internal gas pressure expanding the battery case.

The negative impacts on battery performance include a higher internal resistance, leading to decreased power output. It also results in lower charge acceptance, or stated another way, less energy can be put into the battery. Less energy in means less energy out.

Beyond the effects of increasing the internal pressure in a cell, reduction in the volume of electrolyte as a result of decomposition reactions can dry out the battery electrodes. This, too, increases the internal resistance of a cell.

The reactions may also reduce that amount of active battery materials available, either through chemical decomposition or by electrically isolating them within the cell. Less active material means less energy available from the cell.

Excessive heat affects the performance characteristics of a battery. Temperatures may rise to unacceptable levels during a fast battery charging process or may derive from the within the charger itself. As a result, heat management is an important consideration in battery charging. Higher temperatures accelerate unwanted chemical reactions that end in reduced performance characteristics through electrode degradation and electrolyte decomposition. Some chargers help control temperatures with cooling fans.

Charge termination is an important factor, since *overcharging* a battery—continuing to charge a battery beyond the point of fully charging the battery materials—can result in other reactions occurring regardless of the charging rate. In addition to the unwanted reactions simply reducing cell performance as already discussed, continued overcharging can eventually lead to internal short-circuit conditions or thermal runaway reactions in some cell systems, especially lithium ion cells. Thermal runaways are reactions that, once initiated, continue to accelerate and often end in fire or explosion.

Chargers are designed to manage the charging process in ways that minimize unwelcome side reactions as a result of current or voltage levels, overcharging, or heating. Proper selection of the charging rate, charging method, and charge termination, collectively called charge or battery management, is discussed in the remainder of this chapter. Charge management helps to sustain a high level of battery performance throughout many charge-discharge cycles while maintaining safety. A key to good charge management is monitoring battery conditions like current, voltage, temperature, and extent of charging.

Charge management circuits vary significantly. They can be simple circuit components like resistors and diodes, a dedicated integrated circuit specifically designed for the purpose, or a sophisticated microprocessor system with a battery "fuel gauge" indicating extent of charge and data communication capability. A highly developed charge management system can enable the use of more complicated fast charging methods or lowered risk in charging those battery types that are more sensitive to overcharging.

Additional safety features may be designed into rechargeable battery packs as well as the individual cells; these are covered in Chapter 6.

Charge Rate

Charging regimes are categorized by the time it takes to charge the batteries—slow charge, quick charge, and fast charge. Of course, there is a continuum of charging rates that could be used, but we will keep it simple here. Fast charging can be anywhere from a few minutes to a few hours. A quick charge takes 3 to 6 hours. Slow charging is anything longer than a quick charge, up to about 16 hours. How fast is fast can have different meanings for different applications, though.

The time it takes to charge a battery depends on the capability of the charger to produce a certain current and ability of the battery to accept it. Additionally, if the battery is not fully discharged, it will take less time to charge, as well.

Speeding up the time it takes to charge a battery is constrained by attempting to minimize negative effects to the battery, charger current output capability, and the safety mechanisms built into the system somewhere (battery, charger, or more usually both). A combination of fast, then slow charging rates is often used to maximize the amount of energy loaded into a battery. A fast charging step can rapidly charge some batteries most of the way to a full charge; then a slower charging step is applied to get to a full charge. Stringing two or more of these fast and slow charging steps works to fully charge the battery as quickly as possible while minimizing parasitic side reactions that could damage the battery, reduce its performance, and decrease its service life. More on this in the next section.

Charging Methods

Charging is usually controlled applying a constant voltage or a constant current or a combination of both. The more conventional methods of battery charging are discussed in the sections that follow. There is such a thing as an unregulated charger, but these have minimal safety controls and are not generally recommended.

Not every charging method can be used successfully for every kind of battery. Indeed, some methods could reduce battery performance or even cause an unsafe condition. More inventive charging methods may be necessary, like the pulse method used for rechargeable alkaline zinc–manganese dioxide cells presented in Chapter 10. Consult the battery manufacturers' data sheets for more information on appropriate charging methods for any particular battery type.

Some of the more common charging methods are described next.

Constant Potential or Constant Voltage Charging

The potential, or voltage, is regulated for constant potential (CP), or constant voltage (CV), charging. In other words, the voltage is maintained at a constant level throughout the charging process. A graph showing the charger voltage with the voltage and current response from the battery is given in Figure 11-1. This charging method is commonly used for lead acid batteries.

The charging voltage is set to a high enough voltage to charge the battery as quickly as possible, yet low enough to avoid or reduce unwanted reactions and battery heating. Or at least checked at tolerable and manageable levels.

Another factor to keep under control is the cell current. When a battery first starts charging at a constant voltage, the current can quickly rise to very high levels, but it declines from its initial peak with time (Figure 11-1).

If the charging voltage is high enough, though, the current can be too much for the battery to take, leading to excessive heating and parasitic electrochemical reactions, like gas production from electrolyte decomposition. As a result, the current

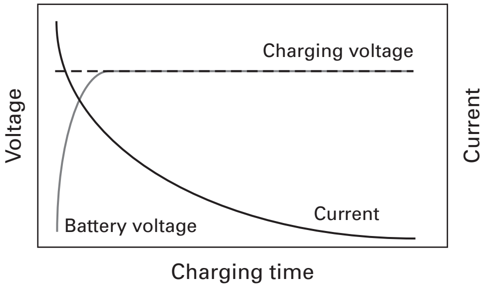


FIGURE 11-1 Constant voltage or constant potential charging with the battery voltage and current response

is usually limited or clamped (Figure 11-2). The current can be clamped either by the limitations of the charger power supply or by the charging circuit design. The current limit is a balance between minimizing the unwanted side effects while allowing the battery to charge in a reasonable amount of time.

In 2003, nickel–metal hydride (NiMH) cells and chargers that used constant voltage charging were manufactured and sold. This cell-charger combination, IC^3 from Rayovac (now Spectrum Brands), was developed to charge specially designed NiMH cells in 15 minutes. Prior to this, the fastest NiMH cell charging was in one hour using a particular type of charger. That was an advance itself, since typical NiMH chargers can take a number of hours to charge the cells.

NiMH cells will tend to form gas as the cells become fully charged. There is what is called a recombination reaction, discussed more fully in Chapter 10, that reduces the level of the gas that is formed. However, if the rate of gas production exceeds the rate of gas recombination, then pressure builds. For the typical NiMH cell design, the venting mechanism allows the pressure to be released.

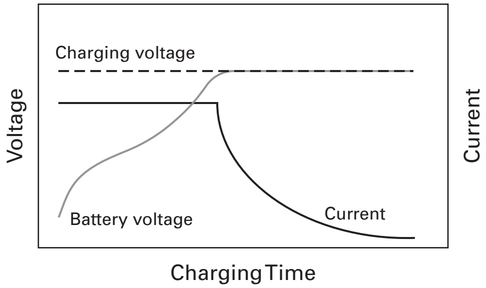


FIGURE 11-2 Constant voltage or constant potential charging including a current limit, with the battery voltage and current response

The 15-minute fast-charging NiMH cells used a different mechanism. These cells relied on a pressure switch (see Chapter 6) that was built into the cell to break the electrical connection between the charger and the battery electrodes. When sufficient gas pressure builds up, the pressure switch opens, thereby breaking electrical contact, and charging ceases. Once the recombination reaction reduced the pressure, the pressure switch closes, the electrical connection is reestablished, and charging is allowed to continue. In this way, the cell can be charged very quickly while managing the amount of gas produced.

Constant Current Charging

A common method used for a number of different battery systems is constant current (CC) charging. A graph showing the charger current with the voltage and current response from the battery is given in Figure 11-3.

Often a low charging current is used to avoid the parasitic reactions and excessive heating that can occur at higher currents, especially near the end of charging. A low charging current on the order of 0.1C (see the box in this section for a review of C-rate terminology) could take 16 hours to fully charge a battery.

A low-rate CC charging method is good for NiCd cells, which can endure overcharge for extended periods of time, at least at low currents. This is not a suitable method for recharging Li ion cells, as most are not very forgiving of being overcharged.

High charge currents, say between 0.5C and 1C or more, can be used as long as there is a reliable charge termination mechanism (see the next section) to stop charging before overcharging occurs. High-rate constant current is typically followed by a lower-rate method discussed in the following sections.

Two or more current levels may be used, starting with a high current to rapidly charge the battery, followed by successively lower current levels to safely bring the battery to a more full state of charge.

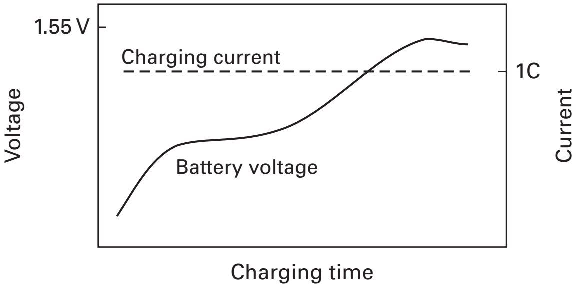


FIGURE 11-3 Constant current charging with the battery voltage response

C Rate Review

Remember from Chapter 7 that the C rate is whatever current it takes to discharge or charge a battery in one hour. That current will be different for each battery type or size. For example, a rechargeable battery rated at 2 Ah requires a current of 2 A to completely charge the battery in one hour. In this case, the C rate, or 1C, is 2 A. A 2C rate is 2 times the C rate, or 4 A for this battery. A C/2 or 0.5C rate is 1 A, a C/50 or 0.02C rate is 0.04 A, and so on.

Constant Current–Constant Potential or Voltage Charging

Most often used for Li ion charging, constant current–constant potential or voltage charging (CCCP or CCCV) is a two-step fast charge method (Figure 11-4).

The CCCV charger applies a specified maximum charging current. For most Li ion batteries today, the maximum recommended charging current is 0.5C. The battery is charged to about 80 percent of full charge during this step. When the voltage reaches the maximum battery charge voltage, usually 4.1 V or 4.2 V for each cell, the charger changes to constant voltage charging regulated at the maximum recommended charge voltage. During the constant voltage step, the current decreases with time as the battery continues to charge. Charging is terminated when the current drops below a defined level, say 0.2C.

Other Charging Modes

There are a handful of other charging methods; some are used to bring a battery to a full state of charge following a fast charge step. Others are used to maintain a full state of charge.

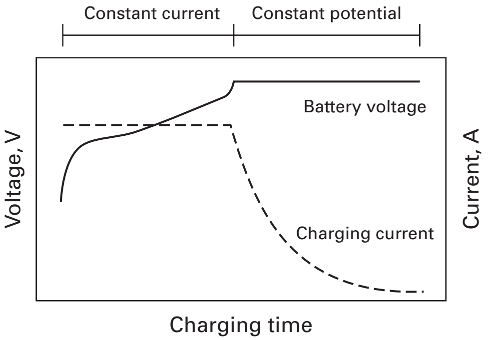


FIGURE 11-4 Constant current–constant potential charging with the battery voltage and current response

Float charging is a method where a constant potential is continually applied to a battery in order to maintain it at a full state of charge. It is primarily used for lead acid backup power supplies. The voltage is high enough to keep the battery charged, but not high enough to overcharge and curtail battery life.

Trickle charging is a low-rate constant current method used to keep batteries fully charged or fully charge a battery after a fast charge. Extended trickle charging is acceptable for certain battery types that are less sensitive to overcharging like NiCd and to some extent NiMH, but definitely not Li ion.

As the name suggests, during *taper* charging the charging voltage, or current, decreases over time. This method is sometimes used for sealed lead acid batteries.

High current pulses are applied to the battery with *pulsed* charging. Variables that define the charging efficiency include peak current amplitudes, pulse widths, and rest times between pulses. To maintain a constant average charging rate, the pulse widths can be adjusted within a constant time interval or changing rest interval times between for fixed pulse widths.

One variant of pulse charging is variously called *reverse, negative, burp,* or *reflex* pulse charging. In addition to charging pulses, small discharge (reverse or negative) pulses are applied. This method can have several beneficial effects that may overcome some of the negative side effects of applying a high current pulse. Reversing the current allows the battery to recover faster, possibly removes dendrites that might grow during charge, or even dislodges gas bubbles that may have formed during the high current pulses. This last one is where the burp charging term comes from.

Pulse charging is also used to maintain a battery at a full state of charge by intermittently applying a charging pulse either at a defined frequency or when the battery monitoring circuits detect the battery voltage has dropped.

Rechargeable alkaline Zn/MnO_2 cells are best charged using a pulse charging method. A transformer and rectifier circuit takes the AC voltage from a common electrical outlet (110 V, 60 Hz) and puts out a 120 Hz rectified voltage with a 4 V peak. The current is limited to prevent overcharging.

Charge termination methods typically used when charging NiCd and NiMH cells ($-\Delta V$, TCO, $\Delta T/\Delta t$—see the next section) are not satisfactory with rechargeable alkaline Zn/MnO_2 cells. Neither is trickle charging. A better approach is to measure the cell voltage using a pulse charging method when pulse signal amplitude is low.

As the battery gets close to becoming fully charged, the number of charging pulses decreases. The average charging current decreases as the number of pulses per unit time continues to decrease. This continues until the charging current decreases to a few milliamps and charging is stopped. The maximum cell voltage should be limited to about 1.65 V.

The cells should not be charged if the cell internal resistance is too high or the starting voltage is too low, indicating the battery may have been overdischarged. A well-designed charger can measure these values before charging commences.

The charging current and battery voltage for a rechargeable alkaline Zn/MnO_2 cell is shown in Figure 11-5.

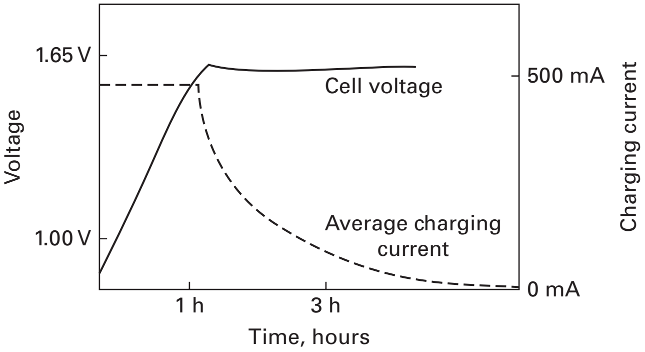


FIGURE 11-5 Current and battery voltage during charging of rechargeable alkaline Zn/MnO$_2$ cells

Battery Monitoring and Charge Termination

Fast chargers use high power in the form of constant current, constant potential, or voltage or pulses to quickly charge high-rate batteries. Reliable battery monitoring and charge termination mechanisms are necessary to prevent overcharge, thereby maintaining the useful lifetime of the battery.

Charging can be terminated based on elapsed charge time, maximum voltage (VCO for voltage cut off), a negative change in voltage (–ΔV), constant voltage (0ΔV), maximum temperature (TCO for temperature cut off), the increase in temperature over ambient (ΔT), and the rate of temperature increase with time (ΔT/Δt). Not all charge termination schemes are effective with every battery type or charging method.

Time-based charge termination simply stops charging after a defined time period. It is better suited for slower charging methods rather than fast charging and should only be used for batteries that can tolerate some limited overcharge, like NiCd and NiMH.

Charge termination methods based on voltage are shown in Figure 11-6.

The battery voltage during constant current charging increases as charging proceeds. It is relatively straightforward to implement charge termination once a battery reaches a predetermined maximum VCO.

The voltage of NiCd and NiMH batteries during charging decreases when approaching full charge. This occurs because the internal battery temperature increases at the end of charge. The internal resistance of the battery decreases as the temperature increases. When this occurs, the battery voltage stops increasing, even while charging continues, and then starts to decrease. This negative change in voltage (–ΔV) can be used then to detect when a battery is fully charged and terminate charging (Figure 11-6). A drop of 10 mV is typically used as a –ΔV limit.

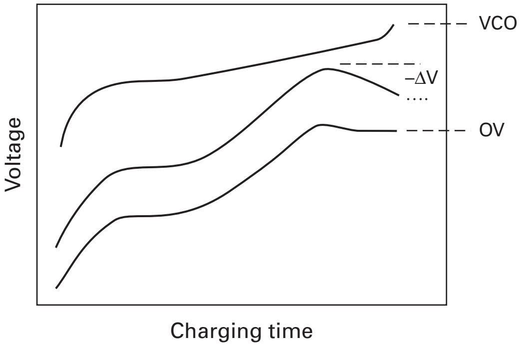


FIGURE 11-6 Charge termination methods based on battery voltage

The –ΔV method is less sensitive for NiMH batteries compared to NiCd batteries. Another method that is more effective for NiMH is a constant voltage 0ΔV end point (Figure 11-6). Charging is stopped when the battery levels off at the end of charge.

Temperature monitoring is also used to sense when a battery is fully charged. Charge termination methods based on temperature are presented in Figure 11-7. The TCO method stops charging when the battery reaches a specified temperature limit. The extent of battery charging using a TCO can vary, though, depending on the ambient temperature as well as other factors associated with the battery being charged.

A more sensitive method looks for the change in temperature from the start of charging. When the temperature changes by more than the ΔT limit, charging is discontinued (Figure 11-7).

Even better is measuring the rate of change in temperature with time (ΔT/Δt) to reduce the effect of ambient temperature in detecting the end of charge (Figure 11-7).

Multiple termination methods are often combined to further reduce the chances of overcharging.

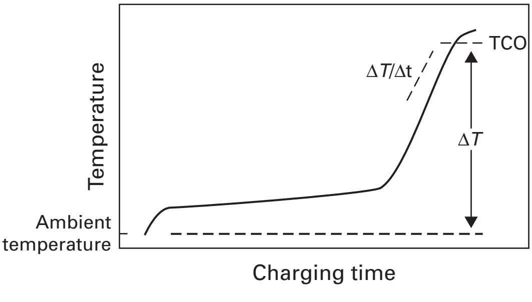


FIGURE 11-7 Charge termination methods based on battery temperature

Chapter 12

Selecting the Right Battery

IMPORTANT CONCEPTS FROM THIS CHAPTER:

- Battery standards
- Battery identification codes
- Data sheets from battery manufacturers
- What to consider when selecting the right battery

Battery Standards

The need to standardize batteries was recognized early in the twentieth century. Standard test methods were recommended by a committee of the American Electrochemical Society in 1912. It wasn't until after World War I in 1917 that battery manufacturers and government agencies started developing battery specifications for sizes and performance criteria, as well as tests that assess batteries against the performance criteria.

These standards were published by the National Bureau of Standards in 1919. A number of revisions followed over the years with new battery types added as they were introduced. Today, the American National Standards Institute (ANSI) and the International Electrotechnical Commission (IEC) are the principal organizations that publish battery standards, although standards have also been established by the military, governmental organizations worldwide, and trade groups, including the Japanese Industrial Standards (JIS).

Contemporary standards specify battery dimensions, terminal configurations, performance characteristics, and test methods—even nomenclature and definitions of terms (see Table 12-1). They provide a system by which some of the more prevalent batteries have a common set of dimensions and thus are interchangeable for the same battery type. Further, the standards create confidence in the stated performance outcomes if the test methods are well defined.

TABLE 12-1 Selected Battery Standards Documents Containing IEC, ANSI, and JIS Specifications

Publication Number	Title	Battery System
IEC 60086-1 IEC 60086-2	Primary Batteries - Part 1: General Primary Batteries - Part 2: Physical And Electrical Specifications	Zinc-carbon Lithium–carbon monofluoride Lithium–manganese dioxide Lithium–thionyl chloride Lithium–iron disulfide Lithium–copper oxide Zinc–manganese dioxide (alkaline) Zinc-air Zinc–silver oxide Zinc–nickel oxyhydroxide
IEC 60086-3	Primary Batteries - Part 3: Watch Batteries	
IEC 60095-1	Lead-Acid Starter Batteries - Part 1: General Requirements and Methods of Test	
IEC 60095-2	Lead-Acid Starter Batteries - Part 2: Dimensions of Batteries and Dimensions and Marking of Terminals	
IEC 60095-4	Lead-Acid Starter Batteries - Part 4: Dimensions of Batteries for Heavy Vehicles	
IEC 60050-482	International Electrotechnical Vocabulary - Part 482: Primary and Secondary Cells and Batteries	
IEC 60254-1	Lead-Acid Traction Batteries - Part 1: General Requirements and Methods of Tests	
ANSI C18.1 Part 1	American National Standard For Portable Primary Cells and Batteries with Aqueous Electrolyte - General and Specifications	
ANSI C18.2 Part 1	American National Standard for Portable Rechargeable Cells and Batteries - General and Specifications	
ANSI C18.3 Part 1	American National Standard for Portable Lithium Primary Cells and Batteries - General and Specifications	
JIS C 8511	Alkaline Primary Cells and Batteries	

Battery Identification Codes

Battery identification codes for a number of common battery types are given in this section. Not all batteries, though; for instance, a large number of lead acid battery sizes are excluded. Only those designed for portable, handheld applications appear.

This might be a little hard to follow, since there are a number of cell and battery characteristics to define, including chemistry, shape, size, number of cells in a battery, and tab or terminal type. Once the system is learned, you can identify a battery just by knowing the standard identification code.

Battery Chemistry Codes

A number of organizations have defined standard ways of identifying different battery chemistries, sizes, and shapes. Two of the more prominent standards organizations that define battery are the International Electrotechnical Commission (IEC) and the American National Standards Institute (ANSI).

Unfortunately, the nomenclature standards are not uniform; batteries are identified differently by different organizations. Battery manufacturers often provide charts that cross reference the different battery designations with their own model numbers and those of their competitors.

Once we go through some of the battery designations, you should be able to identify battery chemistry, shape, and size by the specific combination of codes, at least for some of the more common battery types.

Cell chemistries are given letter codes by both IEC and ANSI. Letter codes for different primary and secondary cell chemistries are given in Table 12-2 and Table 12-3, respectively. Refer to Chapters 9 and 10 for more information about the cell chemistries.

Battery Shape Codes

IEC, but not ANSI, also has letter designations for battery shapes (Table 12-4).

Battery Size Codes

So far we can identify the cell chemistry and shape by the first two or three letters of the designation given in Table 12-2 through Table 12-4. Using the IEC standards, for example, AP stands for a prismatic zinc-air cell. LR means an alkaline zinc–manganese dioxide cell.

The codes for cell size are next. Standard cell sizes are given a unique number that can be used to look up the specific dimensions. For example, the IEC code for a D cell is 20. The ANSI code number is 13. There are other IEC codes that specify flat and square cell dimensions.

TABLE 12-2 International Electrotechnical Commission (IEC) and American National Standards Institute (ANSI) Letter Codes for Primary Cell Chemistries

IEC	ANSI	Cell Chemistry
(none)	(none)	Zinc-carbon
(none)	C	Zinc-carbon industrial
(none)	CD	Zinc-carbon industrial heavy duty
(none)	D	Zinc-carbon heavy duty
(none)	F	Zinc-carbon general purpose
B	LB	Lithium–carbon monofluoride
C	LC	Lithium–manganese dioxide
E		Lithium–thionyl chloride
F	LF	Lithium–iron disulfide
G		Lithium–copper oxide
L	A	Zinc–manganese dioxide alkaline
L	AC	Zinc–manganese dioxide alkaline industrial
L	AP	Zinc–manganese dioxide alkaline photographic
P	Z	Zinc-air
P	ZD	Zinc-air heavy duty
S	SO	Zinc–silver oxide
S	SO	Zinc–silver oxide photographic
Z		Zinc–manganese dioxide + nickel oxyhydroxide

TABLE 12-3 International Electrotechnical Commission (IEC) and American National Standards Institute (ANSI) Letter Codes for Secondary (Rechargeable) Cell Chemistries

IEC	ANSI	Cell Chemistry
H	H	Nickel–metal hydride
K	K	Nickel-cadmium
PB	P	Lead acid
IC	I	Lithium ion (carbon–lithium cobalt oxide)
IM	I	Lithium ion (carbon–lithium manganese oxide)
IN	I	Lithium ion (carbon–lithium nickel oxide)

TABLE 12-4 International Electrotechnical Commission (IEC) Letter Codes for Cell Shapes

IEC	Shape
R	Cylindrical (round)
P	Prismatic (not round)
F	Flat
S	Square or rectangular

There is a wide variety of other cell sizes—over 50 button and coin cell sizes alone—so not all are listed in Table 12-5. Note that for some sizes, ANSI uses a separate number, depending on the cell chemistry. The common cell number designations for zinc-air (ZD) and zinc–silver oxide (SO) are given in the table. Consult the battery manufacturers' web sites for information about other cell sizes not listed here.

For the most common cylindrical cells, we can now identify the chemistry and size based on a cell's code. The ANSI codes are put together by size code, and then chemistry. The IEC codes are given as chemistry, then cell shape and finally size. So, looking at Tables 12-2 through 12-4, a Leclanché zinc-carbon heavy duty AA cell is coded as 15D by ANSI and the R6 by IEC. For an alkaline zinc–manganese dioxide AA cell, the ANSI code is 15A and LR6 for IEC.

So far we have worked through the codes for individual cells. What about multiple-cell batteries? ANSI and IEC also have codes for those, as well.

Remember from Chapter 6 that when connecting two cells in series to assemble a multiple-cell battery, the negative terminal of the first cell contacts the positive terminal of the second cell in the series. If more than two cells are required, this process is repeated by connecting the positive terminal of the next cell to the negative terminal of the previous one. The battery is connected to the device it is powering at the positive terminal of the first cell and the negative terminal of the last cell in the series.

Remember also that when cells are connected in series, the voltage of each cell is additive. A zinc–manganese dioxide cell has a nominal voltage of 1.5 V. Connect two of these cells in series and the voltage is 3.0 V.

To identify a battery, ANSI assigns it a different number with the same chemistry code letter. IEC adds a number before the cell code representing the quantity of cells in the battery. Let's take a 6 V heavy duty zinc-carbon lantern battery. It is assembled by connecting four heavy duty zinc-carbon F cells (IEC R25 or ANSI 60D) in series. The ANSI code is 908D, while the IEC code is 4R25. Another example is an alkaline zinc–manganese dioxide 9 V battery, assembled by connecting six LR61 cells (7.8 mm in diameter and 39 mm in height) in series (1.5 V per cell × 6 cells in series = 9.0 V). ANSI codes this cell as 1604A, and IEC as 6LR61.

TABLE 12-5 International Electrotechnical Commission (IEC) and American National Standards Institute (ANSI) Codes for Common Cylindrical Cell Sizes

IEC	ANSI	Common Cell Name	Diameter	Height	Available Cells (IEC, ANSI)
R63	7012ZD	5	5.8 mm	2.15 mm	Zinc-air (PR63, 7012ZD)
R70	7005ZD	10	5.8 mm	3.6 mm	Zinc-air (PR70, 7005ZD) Zinc–silver oxide (SR70)
R41	7002ZD 1135SO	312	7.9 mm	3.6 mm	Zinc-air (PR41, 7002ZD) Zinc–silver oxide (SR41, 1135SO)
R48	7000ZD 1137SO	13	7.9 mm	5.4 mm	Zinc-air (PR48, 7000ZD) Zinc–silver oxide (SR48, 1137SO)
R44	7003ZD 1131SO	675	11.6 mm	5.4 mm	Zinc-air (PR44, 7003ZD) Zinc–silver oxide (SR44, 1131SO)
R03	24	AAA	10.5 mm	44.5 mm	Zinc-carbon heavy duty (R03, 24D) Zinc–manganese dioxide alkaline (LR03, 24A) Nickel-cadmium (KR03) Nickel–metal hydride (HR03)
R1	910	N	12.0 mm	30.2 mm	Zinc-carbon heavy duty (R1, 910D) Zinc–manganese dioxide alkaline (LR1, 910A)
R6	15	AA	14.5 mm	50.5 mm	Zinc-carbon heavy duty (R6, 15D) Zinc–manganese dioxide alkaline (LR6, 15A) Nickel-cadmium (KR6) Nickel–metal hydride (HR6)
R14	14	C	26.2 mm	50.0 mm	Zinc-carbon heavy duty (R14, 14D) Zinc–manganese dioxide alkaline (LR14, 14A) Nickel-cadmium (KR14) Nickel–metal hydride (HR14)
R20	13	D	34.2 mm	61.5 mm	Zinc-carbon heavy duty (R20, 13D) Zinc–manganese dioxide alkaline (LR20, 13A) Nickel-cadmium (KR20) Nickel–metal hydride (HR20)
R25	60	F (4/3D)	32 mm	91 mm	Four zinc-carbon heavy duty cells (R25, 60D) or four zinc–manganese dioxide alkaline cells (LR25, 60A) are connected in series for a 6 V lantern battery

Another set of IEC codes are given for coin cells. These are numbers that represent the diameter and height of the cell preceded by the chemistry and the shape code letter, which is R, since coin cells are round.

A 1220 size coin cell has a diameter of 12 mm, which are the first two digits in the size code. This particular cell also has a height of 2 mm. The third and fourth digits in the size code represent the height in tenths of a mm, which in this case is 20. So according to the IEC, a BR2032 cell is for a lithium–carbon monofluoride cell that is 20 mm in diameter and 3.2 mm in height. ANSI calls it a 5004LB cell. The corresponding lithium–manganese dioxide cell is designated CR2032 by IEC and 5004LC by ANSI. The codes for some of the more common coin cell sizes are given in Table 12-6. Lithium–manganese dioxide and lithium–carbon monofluoride cells are available is some of these sizes.

TABLE 12-6 International Electrotechnical Commission (IEC) and American National Standards Institute (ANSI) Codes for Common Coin Cell Sizes

IEC	ANSI	Diameter	Height	Available Cells (IEC, ANSI)
R1025	5033	10.0 mm	2.5 mm	Lithium–manganese dioxide (CR1025, 5033LC)
R1216	5034	12.5 mm	1.6 mm	Lithium–manganese dioxide (CR1216, 5034LC)
R1220	5012	12.5 mm	2.0 mm	Lithium–manganese dioxide (CR1220, 5012LC) Lithium–carbon monofluoride (BR1220, 5012LB)
R1225	5020	12.5 mm	2.5 mm	Lithium–manganese dioxide (CR1225, 5020LC) Lithium–carbon monofluoride (BR1225, 5020LB)
R1616		16.0 mm	1.6 mm	Lithium–manganese dioxide (CR1616)
R1620	5009	16.0 mm	2.0 mm	Lithium–manganese dioxide (CR1620, 5009LC)
R1632		16.0 mm	3.2 mm	Lithium–manganese dioxide (CR1632) Lithium–carbon monofluoride (BR1632)
R2012		20.0 mm	1.2 mm	Lithium–manganese dioxide (CR2012)
R2016	5000	20.0 mm	1.6 mm	Lithium–manganese dioxide (CR2016, 5000LC)
R2025	5003	20.0 mm	2.5 mm	Lithium–manganese dioxide (CR2025, 5003LC)
R2032	5004	20.0 mm	3.2 mm	Lithium–manganese dioxide (CR2032, 5004LC) Lithium–carbon monofluoride (BR2032, 5004LB)
R2320		23.0 mm	2.0 mm	Lithium–manganese dioxide (CR2320)
R2325	5002	23.0 mm	2.5 mm	Lithium–carbon monofluoride (BR2035, 5002LB)
R2330		23.0 mm	3.0 mm	Lithium–manganese dioxide (CR2330) Lithium–carbon monofluoride (BR2330)
R2335		23.0 mm	3.5 mm	Lithium–carbon monofluoride (BR2335)
R2354		23.0 mm	5.4 mm	Lithium–manganese dioxide (CR2454)

TABLE 12-6 International Electrotechnical Commission (IEC) and American National Standards Institute (ANSI) Codes for Common Coin Cell Sizes (*continued*)

IEC	ANSI	Diameter	Height	Available Cells (IEC, ANSI)
R2412		24.5 mm	1.2 mm	Lithium–manganese dioxide (CR2412)
R2430	5011	24.5 mm	3.0 mm	Lithium–manganese dioxide (CR2430, 5011LC)
R2450	5029	24.5 mm	5.0 mm	Lithium–manganese dioxide (CR2450, 5029LC) Lithium–carbon monofluoride (BR2450, 5029LB)
R2477		24.5 mm	7.7 mm	Lithium–manganese dioxide (CR2477)
R3032		30.0 mm	3.2 mm	Lithium–carbon monofluoride (BR3032)

So far, so good. It all seems logical and orderly, if not somewhat overwhelming. It starts to get a little more complicated for other cell sizes. IEC codes the AAAA cell, which is a cylindrical cell that is 8.3 mm in diameter and 42.5 mm in height, as R8D425. (The ANSI code is 25A, by the way.) The letter R has its usual meaning from Table 12-4. The next number is the diameter, but 8.3 mm is not a “recommended” diameter according to the IEC. In such cases they use letter codes to identify the tenths of a millimeter (Table 12-7). Thus, 8.3 mm becomes 8D in the IEC code. The remaining three digits are the usual code for a cell that is 42.5 mm in height.

TABLE 12-7 The Diameter Tenths of a Millimeter Letter Code for “Nonrecommended” Cell Diameters

Tenths of a Millimeter Part of Cell Diameter	Letter Code
0.0 mm	A
0.1 mm	B
0.2 mm	C
0.3 mm	D
0.4 mm	E
0.5 mm	G
0.6 mm	H
0.7 mm	J
0.8 mm	K
0.9 mm	L

TABLE 12-8 International Electrotechnical Commission (IEC) and American National Standards Institute (ANSI) Codes for Cylindrical Cell and Battery Sizes

IEC	ANSI	Common Cell Name	Diameter or Width	Height	Available Cells (IEC, ANSI)
R11108	5008	1/3N	11.6 mm	10.8 mm	Lithium–manganese dioxide (CR11108, 5008LC)
R17345	5018	123 or 2/3A	17.0 mm	34.5 mm	Lithium–manganese dioxide (CR17345, 5018LC)
R18650			18.4 mm	65.0 mm	Lithium ion (ICR18650)
15H270	5046	CR2	15.6 mm	27.0 mm	Lithium–manganese dioxide (CR15H270, 5046LC)
P-2	5024	223 or 2 2/3A	35.0 mm	36.0 mm	Lithium–manganese dioxide 6 V battery (CR–P2, 5024LC)
	5047	CR-V3	28.9 mm	52.5 mm	Lithium–manganese dioxide 3 V battery (5047LC) Lithium–iron disulfide 3 V battery (5047LF)
R5	5032		34.0 mm	45.0 mm	Lithium–manganese dioxide 6 V battery (2CR5, 5032LC)
R11108	1406	2 1/3N	13.0 mm	25.2 mm	Lithium–manganese dioxide 6 V battery (2CR11108, 1406LC)

Other sizes you might run across are listed in Table 12-8. Some of their common names are, roughly, a fraction of another cell size.

There may be other codes tagged on to describe the type of battery terminal or other attributes of the battery.

Manufacturer Data Sheets

When selecting a battery, a great place to start is the manufacturer's data sheet. These are available from the manufacturers' web sites, but you may have to hunt a bit for them.

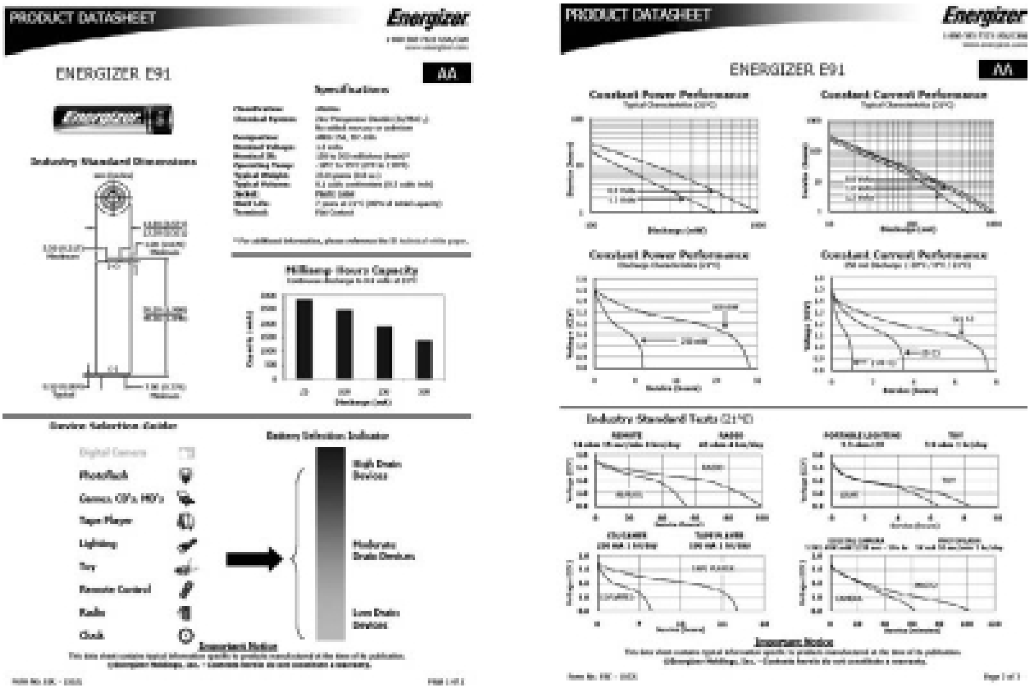
The amount of information included on data sheets varies widely from manufacturer to manufacturer. If the data sheet does not have the information you need, then the manufacturer may be able to supply it separately.

All manufacturers' data sheets (for example, see Figure 12-1) contain some of the more basic information about a battery, including the manufacturer's contact information, their model number, the cell chemistry, the common name if there is one, one or more standard size designations, and a drawing or photograph of the battery. The physical dimensions and weight, including dimensional tolerances, may be located on the drawing or in a table on the sheet.

A summary of the battery electrical outputs, especially the nominal voltage and discharge capacity, can be found in a table. There are usually graphs showing discharge characteristics—typically voltage against capacity or discharge time—under various conditions, like discharge load and temperature. Charging conditions and battery charging characteristics might be given for rechargeable batteries.

Some manufacturers also supply other data, such as the recommended operating temperature ranges and storage conditions, maximum discharge and charge current, maximum charge voltage, and minimum discharge voltage.

The discharge conditions or other attributes of the battery may not match your particular application. You might be able to estimate battery performance in your application if enough information is given on the data sheet. In some instances, you may just have to pick a battery and try it in your application.



PRODUCT DATASHEET

Energizer

ENERGIZER E91

AA

Specifications

Industry Standard Dimensions

Milliamp-Hours Capacity

Device Selection Guide

Battery Selection Indicator

Important Notice

PRODUCT DATASHEET

Energizer

ENERGIZER E91

AA

Constant Power Performance

Constant Current Performance

Constant Power Performance

Constant Current Performance

Industry Standard Tests (21°C)

Important Notice

FIGURE 12-1 Battery manufacturer data sheet. ©Energizer Battery Company, Inc. Reprinted with permission.

Putting It All Together

We've seen there is an abundance of battery sizes, shapes, and performance characteristics. Summarized next are many of the factors you should consider when selecting the right battery for your application. Some of these factors will be more important to you than others.

Considerations	Questions to Ask
Primary or secondary battery	Is charging an option?
(Chapters 9, 10, and 11)	Are the batteries easily replaced by the end user?
Size and shape	Are the batteries commercially available?
	Is a custom size or shape needed?
Voltage	Are you limited to a single cell?
	Is a battery pack available or can you assemble a battery?
	Flat, sloped, or stepped voltage behavior during discharge?
	Is time for the voltage to recover after pulsing important?
Energy or capacity	Individual cell energy or capacity?
	Single cell or battery?
Power	What is the peak power and the sustained power needed?
Storage temperature and shelf life	How long and under what sort of conditions before the battery will be used?
Operating temperatures	What are the ambient conditions the battery will be used in?
Self-discharge	What is the acceptable loss in battery energy over the time in storage and while in operation?
Cycle life	How many cycles are needed to achieve the required battery life under typical use conditions, especially charging rate, maximum charging voltage, depth of discharge, and ambient temperature?
Safety	Does the battery include appropriate safety features to minimize hazard risks under the expected use conditions?
Cost	What is an acceptable cost for the quantity of batteries needed over the expected life of the batteries?
Environmental	Does the battery need to be recycled?
	Is it safe to dispose in the regular waste stream?

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Chapter 13

The Future of Battery Technology

The number of diverse electronic device applications is driving the need for new battery technologies that run faster and longer. The push to increase energy density and power capability of batteries continues for electrical grid storage, electric vehicles, implantable medical devices, and handheld electronic devices like cell phones and portable computers. A number of new technologies designed to increase energy and power densities are at various stages of research and development. Here, we will touch on a few of the battery technologies that either are very small, are very large, or have a high energy density.

The ages of human history have been categorized according to the technology innovations that were developed and used during that time. There was the Stone Age from about the beginnings of early man through about 3000 BC, the Bronze Age from ca. 3000 BC to 1200 BC, and the Iron Age from 1200 BC through 500 AD. People who do such things may end up calling our time the Material Science Age because of the acceleration in materials technology development.

Small Batteries

Size is relative, but the technologies described in this section are directed toward small batteries and applications that require only low power in a small package, such as microelectromechanical systems (MEMS), sensors, "smart" cards, and RFID tags. Discrete cells can be made quite thin, down to about 0.01 mm thick and 1 mm^2 in area.

It may be more of a combination of technologies that drives the development of small batteries. They may be teamed with small energy sources that can generate or convert energy but need a place to put the energy as they generate it or if an application requires more power than the energy source can supply.

Low power generation could be done with a small solar energy photovoltaic cell. Another example is energy harvesting. Mechanical energy may be produced by vibrations or by the human body with voluntary motions like walking or involuntary movements such as the expansion and relaxation of the lungs, diaphragm, or chest during breathing or the rhythmic beating of the heart. Piezoelectric devices can turn

Moore's Law Does Not Apply

It's been observed by several writers that the rate of battery development in terms of energy density is slow compared with the rate of advances in density of integrated circuit components (that is, transistors and other electronic components) as characterized by Moore's Law. First published in 1965 by Intel cofounder Gordon E. Moore, then at Fairchild Semiconductor, Moore's Law states that the number of integrated circuit components per area of an integrated circuit roughly doubles every one and a half to two years.

Yet, comparing the density of integrated circuit components starting in 1959 to increases in battery energy and power or decreases in battery size is not a fair comparison. It could be argued that battery technology advances preceded IC development. Indeed, much of the battery technology we use today is based on technology developed starting in the late nineteenth century through the middle part of the twentieth century.

However, the difference is more fundamental. As explained by David Linden in "Handbook of Batteries," the energy produced by a battery is generated by the electrochemical reactions of the active materials in the battery. So, the total energy within a battery is ultimately constrained by how much active material is put into the battery. It is an extrinsic property, as scientists describe it, meaning it is dependent on the quantity of material in the battery.

That does not mean battery designers have run out of ideas and there are no further energy, power, and size improvements to be had. It is just that the improvements will not occur at the same rate as other technologies, like integrated circuit components, that operate by mechanisms that do not involve conversion or consumption of materials.

The Future of Energy Storage Materials?

The power source of the future, at least in the television series *Star Trek: The Next Generation,* is the rechargeable sarium krellide cell. These cells are used in the twenty-fourth century to run a number of different applications. They are manufactured in smaller sizes suitable for portable devices up to large installations aboard spacecraft.

According to *Star Trek: The Next Generation Technical Manual* by R. Sternbach and M. Okuda, sarium krellide stores up to 3.6×10^{11} Wh dm^{-3} of energy, nearly the same energy content of radioactive uranium-235 at 4.1×10^{11} Wh dm^{-3}. Compare that to an alkaline Zn/MnO_2 AA (LR6) from the twenty-first century that delivers about 3 Wh, or 3.7×10^2 Wh dm^{-3}, but only at low power (0.1 W).

The high energy density of sarium krellide makes it suitable for Type I and Type II phasers. These handheld energy beam weapons consume up to 10 kW of power. For Type I phasers, 2×10^9 Wh cells are used, and 1.25×10^{10} Wh cells are in Type II phasers. The cells must discharge through LiCu 521 crystals.

Another portable device run from a rechargeable sarium krellide cell is the tricorder, which is a scientific instrument used for sensing, data analysis, and data communications. The power requirements are more modest, about 15.5 W—a little more than the power used by a single compact fluorescent light bulb today.

these kinds of motion into an electrical current that charges a battery. Thermoelectric energy harvesting involves generating an electric current from a temperature gradient. Each of these methods could store their energy in small batteries that are wearable or embedded on a small circuit board installed in a portable device.

Thin-Film Batteries

Thin-film batteries have been around for some time—since the 1980s—but have only recently become available commercially. They are usually made by building up thin layers of battery electrode materials and other components (Figure 13-1) with vapor deposition techniques. The entire stack can be made as little as 10 μm to 15 μm thick with individual layers as thin as 1 μm. Thicker layers can be made by depositing multiple layers.

The active electrode materials are typically Li for the negative electrode and the familiar Li ion positive electrode material $LiCoO_2$ for the positive electrode, although other rechargeable materials can be used, like LiM_2O_4 and vanadium pentoxide (V_2O_5).

The electrolyte is a solid state Li^+ conductor. While solid state electrolytes have a high resistance, when the films are on the order of micrometers, the distance the Li^+ must travel is very short. This enables the cells to be charged and discharged rapidly.

Theoretical energy densities can get as high as 1,000 Wh dm^{-3}, but the energy densities of practical cells are more are on the order of 10 to 50 Wh dm^{-3}. All of the other components (electrode connections, protective packaging) add a significant amount of volume to the cell.

Thin-film cells have low self-discharge rates, a few percent of the cell capacity per year, that rival primary batteries and can be charged and discharged thousands of times. They also can be used in other processes that require temperatures higher than standard Li ion and Li ion polymer cells can withstand.

Nanotechnology

Nano-“anything” is a popular subject in the general science and technology mainstream media, and for good reason. Nanotechnology materials science and engineering operates on a very small scale and crosses over many different

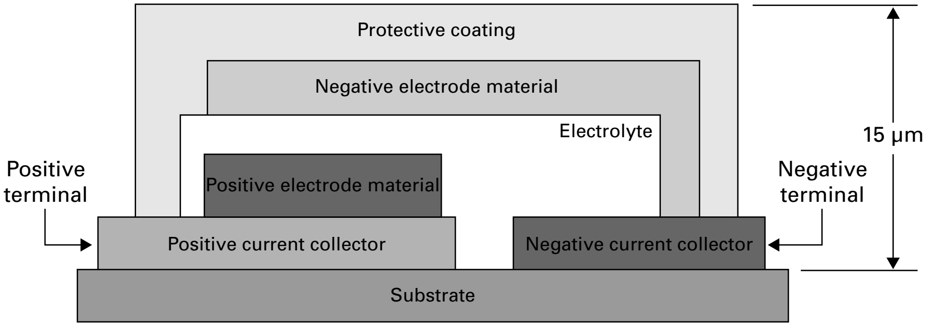

FIGURE 13-1 Cross section of a thin-film rechargeable lithium battery

scientific and engineering disciplines. The National Science Foundation in the U.S. defines nanotechnology in this way: "The systematic control of matter at the nanoscale has the potential to yield revolutionary technologies for electronics, medicine, aeronautics, the environment, manufacturing, and homeland security." Nanotechnology is having, and will continue to have, a huge impact in energy storage, as well. And battery technology is no exception.

Nano is the prefix for one billionth (0.000000001 or 1×10^{-9}) of something. With respect to nanotechnology it refers to size. A nanometer is one billionth of a meter (abbreviated nm). So, nanotechnology is working with materials, structures, and systems that are anywhere from 1 nm to 1,000 nm in size, although some argue the range should be 1 nm to 100 nm. This is small. A grain of coarse sand is about 1,000,000 nm (1 mm) across. The size of a typical Staphylococcus bacterium can be about 1,000 nm (1 µm) around. A cold virus comes in at about 20 nm in size.

It is more than working on a small scale. The properties of nanometer-sized materials and structures are different than those of larger, macroscopic materials. Quantum-level effects start to emerge and play a role in the optical, electrical, magnetic, thermal, chemical, and mechanical properties behavior of materials on the nanometer scale. For example, the electrical conductivity of ceramics and the hardness of metals and alloys can increase when made from nanomaterials.

Nanometer Electrode Materials

Even without enhanced physical and chemical properties, size effects can affect performance. The total surface area of all particles in a given volume of material increases as the particle size decreases. In Chapter 6 we described how porous electrodes increase the access of active electrode materials to electrolyte and increase the power output of a battery. So, we might expect that nanometer-sized particles of active electrode materials can enhance their performance even more.

The particle sizes for the positive electrode material powders in conventional batteries are in the tens of micrometers (remember, a micrometer is a millionth of a meter and abbreviated µm)—usually somewhere between 10 µm and 100 µm in diameter. Decreasing the particle sizes to the nanometer scale can increase their power output.

Lithium ion batteries today use carbon as the negative electrode material. Nanometer-sized carbon materials may be useful here, as well. Carbon nanotubes—a tubular form of graphite—are made of carbon atoms linked together in a way that forms tubes (Figure 13-2). Tubes with a single wall of linked carbon atoms range from 0.7 nm to 5 nm in diameter. Tubes with walls composed of multiple layers, called "multiwalled," can have diameters from 5 nm to 30 nm.

Carbon nanotubes have a high surface area because of their size, and this helps to increase the rate of Li^+ movement within them, which, in turn, could help to increase their power output capability.

Nanometer-sized particles also enable the use of other, higher–energy density materials. Most positive electrode materials used today, especially those that are rechargeable, work by a process called insertion or intercalation. This type of electrode mechanism involves an ion, usually hydrogen ion (H^+) for aqueous

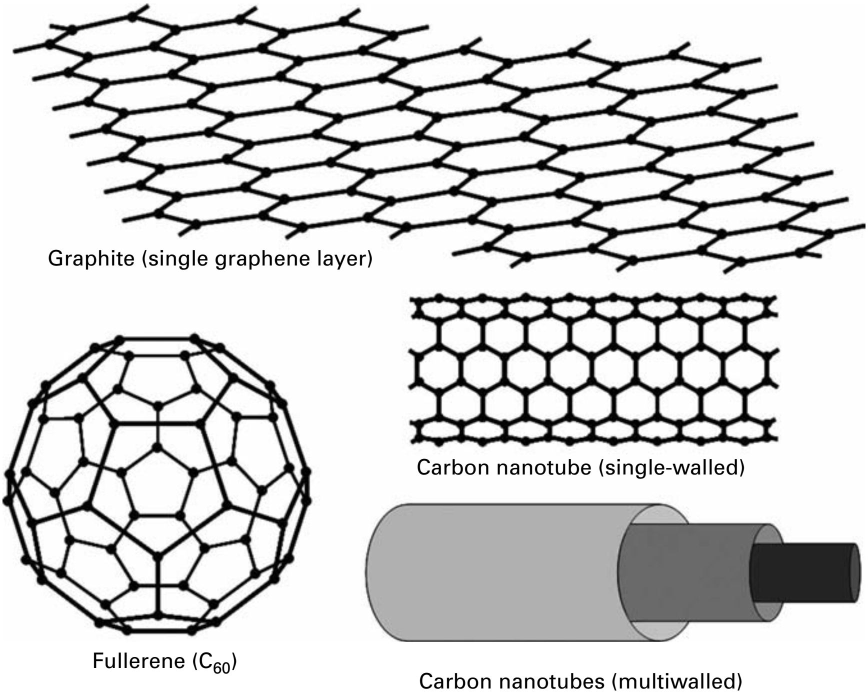

FIGURE 13-2 Structures of graphite, fullerene, and nanotubes

batteries, such as nickel-cadmium (NiCd), and lithium ion (Li^+) for nonaqueous batteries, like lithium ion, entering the structure of the positive electrode material during battery discharge. For a rechargeable battery, this reaction is reversible and the ion is removed during battery charging. At the end of the cycle, the molecular structure of the electrode material is not significantly changed.

Another electrochemical mechanism is called a conversion reaction where the electrode material is chemically converted to another compound. These reactions are not very efficient or reversible when the particle sizes are large, but become more so when nanometer-sized particles are used.

The ability to use materials that react in this manner opens up a large number of different types of materials for use as battery electrode materials.

Other materials, just in the research stage now, include metal oxides, sulfides, nitrides, and fluorides. They hold the promise of increasing energy densities severalfold over conventional battery electrode materials.

Nanometer Battery Structures

More recently, a new structural concept for small batteries expands from two-dimensional thin film cells into what are called 3-D (three-dimensional) batteries. The result is more electrode area and shorter distances for ions and electrons to travel.

These, in turn, serve to increase the power output of the battery and allow it to be charged faster.

Much of this is early-stage research, but there are several different electrode structure concepts that could lead to practical 3-D batteries (Figure 13-3).

The interdigitated cylinder array consists of negative and positive electrode materials in the form of nanometer-sized rods (Figure 13-3 A). A solid state electrolyte material is loaded between the rods. The interdigitated plate array is made of alternating negative and positive electrode nanometer-sized plates with electrolyte between them (Figure 13-3 B). A cylinder array of one electrode material in a block of the other electrode material is shown in Figure 13-3 C. Nanometer-sized holes made in the block are lined with an electrolyte material, and then the remainder of the hole volume is filled with the other electrode material.

The first three battery structure concepts might be constructed using known lithographic or deposition methods. The final concept, the self-assembled electrode network (Figure 13-3 D), must be made using a different method, called self-assembly. Self-assembly in this case involves adjusting the properties of nanometer-sized particles to get them to stick together in a chain. This can be done for one of the electrode materials, coating it with electrolyte material, and then filling the remaining gaps with the other electrode material (Figure 13-3 D).

Another negative electrode material that is generating interest is silicon metal. Silicon (Si) metal forms alloys with Li during charging that yield a negative electrode material for Li ion batteries with a much greater energy density than the carbon

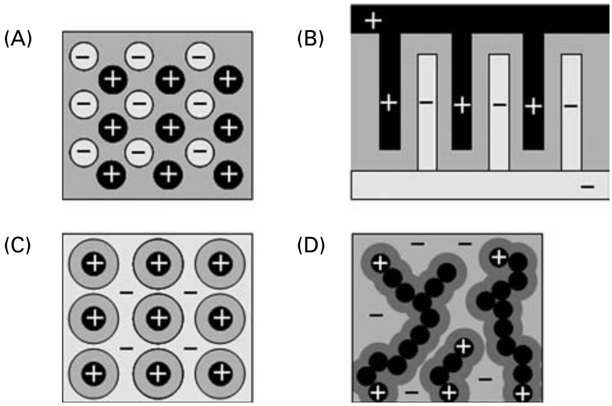

FIGURE 13-3 Nanometer-sized three-dimensional battery electrode architectures: (A) electrode cylinder array, (B) interdigitated electrode plate array, (C) cylinder electrode array in electrode block, (D) self-assembled electrode network

materials used now. However, the stresses associated with forming the Li-Si alloy cause it to expand to about four times its original volume. This weakens the mechanical integrity of the Si and causes it to crumble. The small bits that break away from the Si electrode material are no longer available to be utilized, which results in a loss of battery capacity.

Forming nanometer-sized wires out of Si overcomes the mechanical instability by allowing it to expand when combining with Li without falling apart.

Large Energy Storage Batteries

Large energy storage batteries are used for backup power, load leveling, load shaving, and intermediate storage for alternative energy sources, like solar and wind energy generation. Batteries that deliver in the tens of kilowatt-hours to tens of megawatt-hours have been built.

None of the battery technologies in this section is new, but they are the future of large-scale electrical energy storage. Some are also being developed for electric vehicles, as well.

Two battery technologies that could be used to support our electrical energy needs from the grid are flow batteries and high-temperature batteries. Large lead acid batteries are the most commonly used battery for electrical energy storage, and NiCd batteries are also in use. Li ion batteries are being studied for use in large electricity storage installations. These technologies were discussed previously, in Chapter 10.

Flow Batteries

Flow cells, also called redox flow cells and regenerative fuel cells, operate by discharging two electrolyte solutions (Figure 13-4). The positive electrode material is dissolved in one of the solutions, also called a catholyte during discharge. The other electrolyte can contain the dissolved negative electrode material (called an anolyte during discharge), or it may be deposited on the electrode surface. Each electrolyte solution is stored in a separate tank and pumped into the electrochemical cell stack, which houses the electrodes at which the catholyte is reduced and the anolyte is oxidized. The positive and negative electrodes in the electrode cell stack are separated by a microporous, ion-selective membrane that allows only one type of ion.

The sizes of the tanks determine the capacity of the battery, while the area of the electrodes in the electrode cell stack and the flow rate of the pump set the power output. The electrode materials can be regenerated, or recharged.

Zinc-Bromine Battery

The zinc-bromine (Zn/Br_2) flow battery was originally developed in the 1970s. The positive electrode material, bromine (Br_2), is carried in one of the electrolyte solutions,

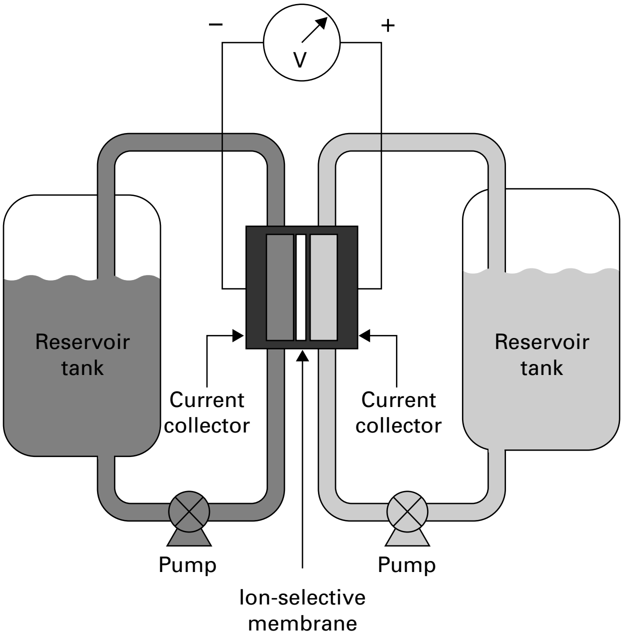

FIGURE 13-4 Flow cell

and zinc (Zn) is a deposit on the negative electrode. When the battery is discharged, zinc ion (Zn^{2+}) and bromide ion (Br^-) are formed:

negative electrode reaction $Zn \rightarrow Zn^{2+} + 2\ e^-$

positive electrode reaction $Br_2 + 2\ e^- \rightarrow 2\ Br^-$

overall battery discharge reaction $Zn + Br_2 \rightarrow ZnBr_2$

When the battery is charged, Zn is plated on the negative electrode and Br_2 is formed at the positive electrode.

Each Zn/Br_2 cell has a voltage of 1.85 V, and multiple cells are connected in series to increase the battery voltage. Energy density might not be quite as critical as it is for portable applications because weight and space limitations may not be as constraining, but a practical Zn/Br_2 can deliver up to about 40 Wh dm^{-3}.

Vanadium Redox Battery

In a vanadium redox battery, both positive and negative electrode materials are vanadium ions in different oxidation states dissolved in their respective sulfuric acid (H_2SO_4) electrolyte solutions. The battery reactions are negative electrode reaction $V^{2+} \rightarrow V^{3+} + e^-$

positive electrode reaction $V^{5+} + e^- \rightarrow V^{4+}$

---

overall battery discharge reaction $V^{2+} + V^{5+} \rightarrow V^{3+} + V^{4+}$

The voltage of each cell is 1.4 V. Energy densities are in the range 10 to 25 Wh dm^{-3}.

Polysulfide-Bromine Battery

The battery reactions in the polysulfide-bromine battery involve soluble species on both sides of the membrane:

negative electrode reaction $2\ Na_2S_2 \rightarrow Na_2S_4 + 2\ Na^+ + 2\ e^-$

positive electrode reaction $NaBr_3 + 2\ Na^+ + 2\ e^- \rightarrow 3\ NaBr$

---

overall battery discharge reaction $2\ Na_2S_2 + NaBr_3 \rightarrow 3\ NaBr + Na_2S_4$

$NaBr_3$ is called sodium tribromide, which forms when Br_2 and Br^- combine. The voltage of each cell is 1.5 V. The energy density is about 20 Wh dm^{-3}.

High-Temperature Batteries

The two more common high-temperature batteries are sodium-sulfur (Na/S) and sodium–nickel chloride (Na/$NiCl_2$). Sometimes they are collectively called sodium-beta batteries after the negative electrode and electrolyte materials. The electrolyte is beta-alumina, which is a ceramic that requires temperatures in the neighborhood of 300°C to become sufficiently conductive to sodium ions (Na^+). At these temperatures, the sodium (Na) metal is molten.

Sodium-Sulfur

The battery reactions in the Na/S battery are

negative electrode reaction $2\ Na \rightarrow 2\ Na^+ + 2\ e^-$

positive electrode reaction $S_x + 2\ e^- \rightarrow S_x^{2-}$

---

overall battery discharge reaction $2\ Na + S_x \rightarrow NaS_x$

The x signifies that sulfur is really in the form of a polysulfide, like S_5, where multiple sulfur atoms are linked together. The voltage of each cell is 2.1 V. Up to 170 Wh dm^{-3} can be achieved in practical batteries.

Sodium-Nickel Chloride (Zebra)

The sodium–nickel chloride, Na/$NiCl_2$ (nicknamed Zebra) battery uses nickel chloride ($NiCl_2$) positive electrode material in place of sulfur.

The battery reactions in the Na/S battery are

negative electrode reaction 2 Na → 2 Na^+ + 2 e^-

positive electrode reaction $NiCl_2$ + 2 e^- → Ni + 2 Cl^-

overall battery discharge reaction 2 Na + $NiCl_2$ → 2 NaCl + Ni

The battery voltage is 2.6 V, and the energy density is about 148 Wh dm^{-3} for a practical battery.

High-Energy Density Batteries

In Chapter 9 we looked at how to increase the energy density of a cell by utilizing oxygen (O_2) from the air as the cathode material in a zinc-air cell. Since the active cathode material is not stored in the cell, more room is available for the anode material. Add to that a practically unlimited supply of atmospheric oxygen and one can make a cell with a high energy density.

Now, change the negative electrode material from zinc to lithium and the energy density of the resulting cell may be increased several-fold on a weight basis. The theoretical energy density of lithium is about 11 kWh kg^{-1} compared to 1.35 kWh kg^{-1} for zinc. The lithium-air cell was first reported in 1996, but it is only recently that advances have been made that could lead to a practical lithium-air cell.

Lithium cannot be exposed to water or air without reacting, so the negative electrode material must be protected from exposure to moisture in the atmosphere. Further, some researchers use an aqueous electrolyte on the positive electrode side. Accommodating the functional needs of the positive electrode with those of the negative electrode can be done by shielding the Li using a nonaqueous electrolyte solution, a solid state electrolyte that conducts lithium ions (Li^+), like the ionically conducting glass LISICON, a polymer electrolyte, or an ionic liquid. Ionic liquids are organic salts that are molten at room temperature.

The battery reactions in the lithium-air cell are

negative electrode reaction: Li → Li^+ + e^-

positive electrode reaction: O_2 + 4 e^- → 4 O^{2-}

overall battery discharge reactions: 2 Li + O_2 → 2 Li_2O_2
4 Li + O_2 → 2 Li_2O

or, for aqueous electrolytes on the cathode side: 4 Li + O_2 + 2 H_2O → 4 LiOH.

The energy density for practical lithium-air cells is projected to be over 2 kWh kg^{-1}. A significant challenge to developing a practical lithium-air cell is protecting the lithium from atmospheric moisture. Some researchers are working to make lithium-air cells rechargeable. They have an additional difficulty to deal with: dendrite formation at the lithium electrode (see Chapter 10).

Going Forward

The development of energy storage materials and technology concepts is accelerating. Government and private sector funding is fueling this growth in recognition of the need for better ways to store energy and the commercial promise of energy storage technologies.

From alternative energy generation to smaller devices requiring more energy, there is a continuing need for new materials and new ways to assemble the materials into practical, efficient electrochemical power sources. And this is unlikely to change any time soon.

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Appendix

Battery Resources

A selection of different battery resources.

Standards Organizations

American National Standards Institute (ANSI): Organization for U.S. standards and compliance.
1819 L Street, NW
6th Floor
Washington, DC 20036 U.S.A.
Phone: 202.293.8020
Fax: 202.293.9287
E-mail: info@ansi.org
Web: www.ansi.org

International Electrotechnical Commission (IEC): International standards organization.
IEC Central Office
3, rue de Varembé
P.O. Box 131
CH - 1211 GENEVA 20 Switzerland
Phone: +41.22.919.02.11
Fax: +41.22.919.03.00
E-mail: inmail@iec.ch or info@iec.ch
Web: www.iec.ch

IEC Regional Centre for North America (IEC-ReCNA)
446 Main Street, 16th Floor
Worcester, MA 01608 U.S.A.
Phone: 508.755.5663
Fax: 508.755.5669

European Committee for Electrotechnical Standardization (CENELEC): European Community standards organization.
17, Avenue Marnix
B-1000 Brussels Belgium
Phone: +32.2.519.68.71
Fax: +32.2.519.69.19
Web: www.cenelec.eu

Japanese Standards Association (JSA): Standards group in Japan that develops Japanese Industrial Standards (JIS).
4-1-24 Akasaka Minato-ku
Tokyo 107-8440 Japan
Phone: +81.3.3583.8005
Fax: +81.3.3586.2014
Web: www.jsa.or.jp

Governmental Agencies and Nongovernmental Organizations

United Nations (UN): Battery transportation test standards.
UN Headquarters
First Avenue at 46th Street
New York, NY 10017 U.S.A.
Web: www.un.org

U.S. Department of Transportation (U.S. DOT): Oversees transportation systems in the United States through its agencies, including the Federal Aviation Administration (FAA) and the Pipeline and Hazardous Materials Safety Agency (PHMSA).
1200 New Jersey Ave, SE
Washington, DC 20590 U.S.A.
Phone: 202.366.4000
Web: www.dot.gov

U.S. Department of Transportation Federal Aviation Administration (FAA): Regulates and manages aviation in the United States.
800 Independence Avenue, SW
Washington, DC 20591 U.S.A.
Phone: 866.835.5322
Web: www.faa.gov

International Civil Aviation Organization (ICAO): A United Nations agency supporting civil aviation and providing guidance for transportation of batteries.
999 University Street
Montréal, Quebec H3C 5H7 Canada
Phone: 514.954.8219
Fax: 514.954.6077
E-mail: icaohq@icao.int
Web: www.icao.int

Pipeline and Hazardous Materials Safety Administration (PHMSA): Regulates the transportation of hazardous materials, including batteries.
East Building, 2nd Floor
1200 New Jersey Ave., SE
Washington, DC 20590 U.S.A.
Phone: 202.366.4433
Fax: 202.366.3666
Web: www.phmsa.dot.gov

U.S. Environmental Protection Agency (U.S. EPA): Development and enforcement of environmental regulations, including battery waste management.
Ariel Rios Building
1200 Pennsylvania Avenue, N.W.
Washington, DC 20460 U.S.A.
Phone: 202.272.0167
Web: www.epa.gov

U.S. Department of Energy (U.S. DOE): Oversight of energy security, technology innovation, and environmental responsibility.
1000 Independence Ave., SW
Washington, DC 20585 U.S.A.
Phone: 202.586.5000
Fax: 202.586.4403
E-mail: The.Secretary@hq.doe.gov
Web: www.energy.gov

U.S. Consumer Product Safety Commission (CPSC): Independent U.S. federal regulatory agency advocating for the safety of consumer products, including batteries.
4330 East West Highway
Bethesda, MD 20814 U.S.A.
Phone: 800.638.2772
301.504.7923
Fax: 301.504.0124
301.504.0025
Web: www.cpsc.gov

Industry Organizations

The Advanced Lead-Acid Battery Consortium (ALABC): Lead acid battery industry organization focusing on electric vehicles and hybrid electric vehicles.
Suite 100, 2525 Meridian Parkway
Durham, North Carolina, 27713 U.S.A.
Phone: 919.361.4647
Fax: 919.361.1957
Web: www.alabc.org

Association of Battery Recyclers (ABR): Group of lead acid battery recycling companies.
E-mail: info@batteryrecyclers.com
Web: americasbatteryrecyclers.org

Battery Association of Japan (BAJ): Industry group for battery and battery-powered device manufacturers in Japan.
Kikai Shinkokaikan Building
3-5-8, Shiba-koen Minato-ku
Tokyo 105-0011 Japan
Phone: +81.3.3434.0261
Fax: +81.3.3434.2691
Web: www.baj.or.jp

Battery Council International (BCI): Trade association for the lead acid battery industry.
401 North Michigan Ave, 24th Floor
Chicago, Illinois 60611-4267 U.S.A.
Phone: 312.644.6610
Fax: 312.527.6640
E-mail: info@batterycouncil.org
Web: www.batterycouncil.org

China Industrial Association of Power Sources (CIAPS): Battery industry association in China.
No. 18, Lizhuangzi Road
Nankai District
Tianjin 300381 China
or
P.O. Box 296
Tianjin 300381 China
Phone: +022.23959268
+022.23959269
+022.23959049
Fax: +022.23380938
E-mail: CIAPS@public.tpt.tj.cn
Web: www.cibf.org.cn
www.Chinabatteryonline.com

Electricity Storage Association (ESA): Trade association for energy storage technologies, including batteries.
1155 15th Street, NW
Suite 500
Washington, DC 20005 U.S.A.
E-mail: info@electricitystorage.org
Web: www.electricitystorage.org

European Portable Battery Association (EPBA): Trade organization for primary and rechargeable portable battery manufacturers, battery-powered equipment manufacturers, and battery distributors within the European Union.
Avenue Jules Bordet 142,
B-1140 Brussels Belgium
Phone: +32.2.761.1602
Fax: +32.2.761.1699
E-mail: epba@kelleneurope.com
Web: www.epbaeurope.net

Association of European Automotive and Industrial Battery Manufacturers (EUROBAT): Trade group for European automotive, industrial, and special battery industries.
Avenue Jules Bordet 142
B - 1140 Brussels Belgium
Phone: +32.2.761.1653
Fax: +32.2.761.1699
E-mail: eurobat@kelleneurope.com
Web: www.eurobat.org

International Air Transport Association (IATA): International trade organization representing airlines, including issues related to the transportation of batteries.
800 Place Victoria
PO Box 113
Montreal, Quebec H4Z 1M1 Canada
Phone: 514.874.0202
Fax: 514.874.9632
Web: www.iata.org

The National Alliance for Advanced Technology Batteries (NAATBatt): Industry group for corporations and organizations working on advanced batteries for use in transportation and large-scale energy storage applications.
122 South Michigan Avenue, Suite 1700
Chicago, Illinois 60603 U.S.A.
Phone: 312.588.0477
Web: naatbatt.org

National Electrical Manufacturers Association (NEMA): A trade association representing the electrical manufacturing industry. Develops technical standards and guidelines for batteries.
1300 North 17th Street
Suite 1752
Rosslyn, Virginia 22209
Phone: 703.841.3200
Fax: 703.841.5900
Web: www.nema.org

Portable Rechargeable Battery Association (PRBA): Trade association for battery manufacturers. Activities include working with governmental agencies on battery shipping issues.
1776 K Street
4th Floor
Washington, DC 20006 U.S.A.
Phone: 202.719.4978
E-mail: PRBAtt@gmail.com
Web: www.prba.org

RECHARGE: Promotes the rechargeable battery industry.
Avenue de Tervueren, 168 - Box 3
B-1150 Brussels Belgium
Phone: +32.2.777.05.67
Fax: +32.2.777.05.65
E-mail: recharge@rechargebatteries.org
Web: www.rechargebatteries.org

Rechargeable Battery Recycling Corporation (RBRC): Call2Recycle battery recycling program.
Call2Recycle
1000 Parkwood Circle
Suite 450
Atlanta, GA 30339 U.S.A.
or
Call2Recycle
PO Box 236
Station E
Toronto, Ontario M6H 4E2 Canada
Web: www.rbrc.org
www.call2recycle.org

Underwriters Laboratories (UL): Product safety certification and compliance, including batteries.
2600 N.W. Lake Rd.
Camas, WA 98607-8542 U.S.A.
Phone: 877.854.3577
Fax: 360.817.6278
E-mail: cec.us@us.ul.com
Web: www.ul.com

Scientific and Technical Societies

The Electrochemical Society (ECS): Professional society promoting the theory and practice of electrochemistry and solid state science.
65 South Main Street, Building D
Pennington, New Jersey 08534-2839 U.S.A.
Phone: 609.737.1902
Fax: 609.737.2743
E-mail: ecs@electrochem.org
Web: www.electrochem.org

IEEE: Professional association for engineering and technology.
3 Park Avenue, 17th Floor
New York, NY 10016-5997 U.S.A.
Phone: 212.419.7900
Fax: 212.752.4929
Web: www.ieee.org

International Society of Electrochemistry (ISE): Professional society advancing electrochemical science and technology.
Rue de Sébeillon 9b
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Glossary

activation polarization, activation overpotential, activation overvoltage The polarization (change in potential or voltage of a cell or battery) from charge transfer reactions.

active materials The materials in a battery that convert chemical energy into electrical energy through charge transfer (electrochemical) reactions. *See* anode, cathode, negative electrode, and positive electrode.

absorbed glass mat (AGM) A type of separator used in VRLA lead acid batteries.

alkaline electrolyte An aqueous electrolyte solution containing a strong base like potassium hydroxide (KOH).

alloy Two or more metals combined to form a single metal.

ampere or amp (A) A unit of electrical current. One ampere of current is produced when 1 volt is applied across 1 ohm of resistance.

ampere-hour or amp-hour (Ah) A quantity of electricity delivered over a period of time. When the current is constant, the current in amperes (A) is multiplied by discharge time in hours (h) to give capacity in ampere-hours (Ah).

anion A negatively charged ion.

anode The electrode where oxidation (release of electrons) occurs during the discharge of a battery.

battery A combination of two or more cells connected in series, parallel, or a combination of series and parallel. Also used to describe cells in a general way.

binder An electrode material additive, usually a polymer, used to maintain electrode integrity.

bobbin cell A cell with a cylindrical electrode (bobbin).

C rate The relative charge or discharge current (A) as a multiple or fraction of the capacity (Ah) of a cell or battery. For example, a 1C rate is the current required to deplete a battery in 1 hour.

capacity The quantity of electricity stored in or delivered by a battery. Units are amp-hours (Ah) or coulombs (C).

cathode Electrode where reduction (uptake of electrons) occurs during the discharge of a battery.

cation A positively charged ion.

cell An anode (electron source) and a cathode (electron acceptor) in an electrolyte (ion conduction path) capable of converting chemical energy into electrical energy through electrochemical reactions.

charge A quantity of electricity.

charge or charging Converting electrical energy into chemical energy by forcing current into a cell or battery.

closed circuit The state where a cell or battery is connected to an external electrical circuit and current is produced.

closed-circuit voltage (CCV) The potential or voltage measured across the terminals of a cell or battery when a current is produced.

cold cranking amps (CCA) The current produced by a lead acid battery at –18°C (0°F) for 30 seconds while maintaining a voltage of at least 1.2 volts per cell (7.2 V for a 12 V car battery).

concentration polarization, concentration overpotential, concentration overvoltage Polarization (change in potential or voltage of a cell or battery) from mass transport limitations in the electrolyte and the electrode materials.

convection The movement of fluids in response to a density gradient, including those caused by uneven temperature distributions.

coulomb A unit of electrical charge. The amount of electricity conveyed by a current of one ampere in one second.

cranking amperage (CA) The current produced by a lead acid battery at 0°C (32°F) for 30 seconds while maintaining a voltage of at least 1.2 volts per cell (7.2 V for a 12 V car battery). Also called marine cranking amperage (MCA) when referring to the SLI batteries used to start boat engines.

current The rate at which electrical charge is delivered.

current collector A conductive component contacting the active electrode materials. Used to convey current to and from the electrode materials.

current density (A cm^{-2} or A kg^{-1}) The current normalized to the area or weight of an electrode.

cycle A complete charge and discharge sequence.

cycle life The number of cycles to a defined performance level, like available cell or battery capacity.

depth of discharge (DOD) The fraction of capacity or energy removed from a fully charged cell or battery.

diffusion Mass transfer when there is a gradient in the concentrations of chemical species.

discharge Converting chemical energy into electricity through electrochemical reactions.

E rate The relative charge or discharge power (W) as a multiple or fraction of the energy (Wh) of a cell or battery. For example, 1E represents the power required to deplete a battery in 1 hour.

electrochemistry Chemical reactions involving the transfer of electrical charge.

electrode The site where an electrochemical reaction occurs.

electrolyte A source of mobile ions necessary to conduct current between the negative and positive electrodes within an electrochemical cell. May be a solution of dissolved ions, a gel containing ions, a solid containing mobile ions, or a molten salt.

electrolytic cell A cell where an external source of electricity is used to force nonspontaneous electrochemical reactions to proceed. A battery undergoing charging is an electrolytic cell.

electromotive force (emf) The propensity of the electrochemical cell reaction to proceed spontaneously. Measured as the open circuit potential difference (measured in volts) between two electrodes at equilibrium. The greater the emf, the more energetically favorable the reaction is.

electron A subatomic particle that carries a negative charge.

energy density The amount of energy related to the weight or volume of a cell or battery. Typical units are watt-hours per kilogram (Wh kg^{-1}) or watt-hours per cubic decimeter or liter (Wh dm^{-3} or Wh L^{-1}).

exchange current (A) Abbreviated i_0. The current for the forward and reverse electrochemical reactions at an electrode when a cell is at open circuit and the net current is zero.

float charging Charging a cell or battery at a very low rate with a potential or voltage that maintains a state of charge level.

galvanic cell An electrochemical cell that spontaneously (that is, thermodynamically favored) converts chemical energy into electrical energy through electrochemical reactions when the positive and negative electrodes are connected through an external circuit. A cell in its charged state is a galvanic cell.

half-cell A single, isolated negative or positive electrode.

internal resistance The total resistance (in ohms) of a cell or battery measured as the change in voltage (voltage drop) that occurs in response to a current, divided by the magnitude of the current.

ion An atom or molecule carrying a negative or positive charge.

joule (J) A unit of energy corresponding to delivering 1 watt of power for 1 second.

load General term for an external component through which a cell or battery discharges.

migration The movement of charged species as a result a potential field gradient, meaning a potential difference between two points.

mole A quantity of a substance with the same number of atoms, ions, or molecules as there are carbon atoms in 12 g of carbon. This works out to be 6.022×10^{23} (Avogadro's number).

molecule The combination of two or more atoms bound together with a chemical bond.

negative electrode The electrode of a cell or battery that produces electrons during discharge and accepts them during charging.

neutron A subatomic particle in the nucleus of atoms that carries no electrical charge.

ohm (or Ω) The unit of electrical resistance between two points in a conductor when a potential difference of 1 volt produces a current of 1 A.

ohmic polarization Polarization (change in potential or voltage of a cell or battery) resulting from the electrical and ionic resistance, or ohmic resistance, of the battery.

open circuit The state where a cell or battery is not connected to an external electrical circuit. No current is produced.

open circuit voltage The potential or voltage measured across the terminals of a cell or battery when no current is produced.

overcharge Excessively charging a cell or battery beyond a full charge.

overdischarge Excessively discharging a cell or battery beyond its capacity.

oxidant A substance that accepts electrons.

oxidation A chemical reaction involving the loss of electrons from a substance.

parallel An assembly of electrochemical cells that form a battery by connecting positive terminals together and negative terminals together. The capacity of cells connected in parallel is additive.

passivation Blocking the surface of an electrode, increasing its resistance.

polarity The sign of an electrical potential (negative or positive).

polarization The change in potential or voltage of a cell or battery from open circuit that occurs in response to current.

positive electrode The electrode of a cell that accepts electrons during discharge and gives up electrons during charging.

potential (V) The propensity for an electrochemical reaction to spontaneously occur between two electrodes of a cell and produce a current.

power (W) The rate at which energy is delivered.

power density (W dm^{-3} or W kg^{-1}) The power normalized to volume or weight of a cell or battery.

primary cell or battery A cell or battery designed to be discharged only and not recharged.

prismatic cell Not a round cell. Usually rectangular in shape.

proton A subatomic particle in the nucleus of atoms with a positive charge.

rechargeable cell or battery A cell or battery that is also designed to convert electrical energy provided from an external power source to chemical energy. Also called a secondary cell or battery. Formerly called a storage battery or an accumulator.

recombination The reduction of oxygen gas formed during charging at the negative electrode.

reductant A substance that gives up electrons.

reduction A chemical reaction involving the gain of electrons by a substance.

resistance The property of a conductor that determines the current produced by a potential difference across the conductor.

resistor An electrical circuit element with a defined resistance.

reversal (polarity reversal or voltage reversal) A change of the normal polarity of a cell or battery (positive or negative) to the opposite polarity (negative or positive).

secondary cell or battery A cell or battery that is also designed to convert electrical energy from an external power source to chemical energy. Also called a rechargeable cell or battery. Formerly called a storage battery or an accumulator.

self-discharge Loss of capacity in a cell as a result of parasitic chemical reactions.

separator An electrical insulator that keeps the positive and negative electrodes from coming into direct contact when placed together in a cell, yet also allows ions in the electrolyte to pass between the electrodes.

series An assembly of cells to form a battery by connecting the positive terminal of a cell to the negative terminal of the next. The voltage of cells connected in series is additive.

short circuit A condition when the terminals of a cell or battery are connected through a low resistance conductor rather than an external electrical circuit.

short-circuit current The current produced by a cell or battery when there is a short-circuit condition.

SLI battery A battery used for vehicle starting, lighting, and ignition.

spiral-wound cell A cell with thin electrodes and intervening separator that are tightly rolled together. The final electrode assembly may be cylindrical or flattened.

state of charge (SOC) The fraction of capacity or energy remaining in a cell or battery.

taper charge Charging a cell or battery with a gradually decreasing current.

terminals The site where a cell or battery is connected to an external circuit. There are a negative terminal and a positive terminal.

thermal runaway A reaction that produces sufficient heat to further accelerate the reaction. Usually occurs during abuse conditions, especially overcharge and overdischarge.

trickle charge Charging a cell or battery with a low current intended to just overcome capacity loss from self-discharge and maintain the cell or battery at a full state of charge.

valence state The number of extra or missing electrons on an atom.

volt (V) A unit of electrical potential difference and electromotive force (emf). It is equal to the electrical potential between two points that produces a current of 1 ampere in a conductor with a resistance of one ohm.

voltage (V) The potential difference between two electrodes of an electrochemical cell or the terminals of a cell or battery.

voltmeter A device that measures voltage.

valve-regulated lead acid (VRLA) A sealed lead acid battery that has a valve designed to release excessive internal gas pressure.

watt (W) A unit of electric power that provides one joule of energy in one second or a current of one ampere at one volt.

watt-hour (Wh) A unit of energy corresponding to delivering 1 watt of power for 1 hour.

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