Innovations

Leading the Charge for Better Batteries

The worldwide market for batteries in 2001 was estimated at $37.7 billion, according to *The Powers Review, Year 2000 Battery Industry Developments*, prepared by Donald M. MacArthur and George E. Blomgren, and in 1998 alone, more than three billion household and industrial batteries were sold in the United States, the top three markets being cell phones, notebook computers, and power tools. Each year, millions of batteries are disposed of, and therein lies one of the serious environmental issues confronting the electronics industry—some of these batteries contain substances such as lead and cadmium that under certain conditions can leach out of landfills into water causing serious environmental health problems. Inhaled cadmium, according to the Agency for Toxic Substances and Disease Registry (ATSDR), can cause lung damage and death, whereas long-term exposure can cause kidney disease. According to the Department of Health and Human Services, cadmium "may reasonably be anticipated to be a carcinogen." Lead, according to the ATSDR, can cause damage to the nervous system, kidneys, and reproductive system.

The battery industry and equipment manufacturers created the Rechargeable Battery Recycling Corporation in 1994 to recover used rechargeable batteries, but that addresses only part of the equation. The goal now is twofold: to make batteries last longer and to find more environmentally friendly substitutes for their harmful components.

One innovative approach is known as the zinc–air battery, which, rather than using potentially harmful reactants, relies on the oxygen existing in the air to create energy. The cell contains no significantly toxic compounds, and is neither highly reactive nor flammable. Frank Harris, vice president of marketing and licensing for AER Energy Resources in Smyrna, Georgia, which has designed a zinc–air battery, says, "It's important to be a realist about batteries. Batteries have metals in them, and because of that, you'll never have a battery that's truly 'green.' The goal is to make that metal as environmentally friendly as possible. For example, zinc [with no added mercury] is more benign than heavy metals used in some types of batteries."

One limitation of the zinc–air battery, however, is that constant contact with the ambient air can either dry up the zinc gel or flood it with water vapor, thus rendering the battery much less potent. AER has found a way around that problem with its proprietary "Diffusion Air Manager" to isolate the battery from air during storage. Built into a battery pack, as opposed to a single battery, the Air Manager turns on when the battery is in use, forcing air through an air inlet tube to start the chemical reaction, and the fan/tube combination minimizes the diffusion of air into and out of the battery when stored or not in use. According to Harris, the manager coupled with new cell design yields a longer-lasting battery with much higher energy density, or ratio of energy to weight or volume.

Nickel–Metal Hydride

One battery component of concern to the industry is cobalt, typically obtained as a by-product of manufacturing nickel. Cobalt can cause asthma and pneumonia, and the International Agency for Research on Cancer has labeled it a "possible human carcinogen." Cobalt is used in a battery electrode because of its propensity for picking up electrons. James Reilly, a guest scientist with Brookhaven National Laboratory's Department of Energy Sciences and Technology in Upton, New York, is part of a team working to find new alloys for use as electrodes—alloys that will last longer and that use more benign substances. Reilly's team was recently awarded a patent for a new electrode alloy that uses lanthanum, nickel, and tin as a replacement for cobalt.

"Nickel–metal hydride batteries are very nice batteries," says Reilly. "They have a much higher energy density than NiCads [nickel–cadmium batteries], and they're more benign. The downside to nickel–metal hydride batteries has been their cost—roughly twice that of NiCads, because cobalt is so expensive." Reilly's team discovered that tin, a much more environmentally benign substance, could be substituted for cobalt in the alloy. The new electrode formula includes one lanthanum atom to 5.157 atoms of the nickel–tin combination, and the resultant electrode has a very high energy storage capacity and does not decay over many charge/discharge cycles. "If you can manufacture the battery more cheaply," Reilly says, "it will be more widely used, displacing NiCads and benefiting the environment. At this point, it's up to the battery companies to adopt this technology or not."

Lithium Ion

Panasonic has been working on nickel–metal hydride (NiMH) batteries to replace NiCads, but the difficulty has been in developing batteries that can handle high-drain applications, such as power tools, as well as NiCads can. And although some NiMH batteries that can handle high drain are being developed, they're quite expensive. Kurt Kelty, director of business development for the Battery Research and Development Center of Panasonic Technologies, says that "absent regulatory enforcement, consumers and the companies that make the power tools and so on that they buy are going to stick with NiCads. They want to use the battery that best meets their needs from both a cost and a power perspective." Kelty says that the industry worldwide is in the process of shifting from NiCad batteries to lithium ion batteries. "Europe is seriously considering phasing out NiCad batteries," he says, "but the same trend is not yet apparent here." Today, lithium ion batteries dominate

Matt Ray/EHP

the market for use as power sources in cell phones and lap-top computers. Lithium is a more environmentally benign substance than many used in industry, and because lithium batteries last longer, they delay the entry of contaminants into the waste stream—which is not to say that lithium is without risk. If present as lithium sulfide, a common salt form, it will react vigorously with water to form sulfuric acid, and there was concern about early lithium batteries and potential for fire or explosion. In high doses, lithium is also a suspected kidney and liver toxicant.

Lithium metal is itself quite reactive, but as a lithium battery is discharged, the metallic lithium is converted into a nonreactive compound. According to the National Electrical Manufacturers Association (NEMA), spent lithium batteries pass the U.S. EPA tests to determine if a waste is hazardous. So NEMA says spent lithium batteries are safe for disposal in the municipal solid waste stream.

Lithium ion batteries have a high energy density, making them ideal power sources for many applications, but they use a lithium–cobalt oxide electrode. According to Jim McBreen, a researcher in the Energy Sciences and Technology Department at Brookhaven National Laboratory, even something as small as an AA battery uses about one-half ounce of cobalt in its electrode; something on the order of a battery for an electric vehicle would use substantially more. At a cost of around $60 per kilogram, "there just isn't enough cobalt production to sustain the manufacture of electric vehicle batteries," he says. "And that's one of the goals for lithium ion batteries."

As it happens, a lithium– manganese compound makes an admirable substitute, but, as McBreen explains, it's not that simple. "Manganese oxide is less toxic and far cheaper," he says. "The problem is that, with the electrolyte currently being used, manganese is very unstable, and the battery tends to lose its ability to recharge very quickly. And the phenomenon is even worse at high temperatures, like you'd find in an automotive engine."

The Brookhaven team's solution was to develop a different electrolyte, based on boron, that would provide virtually the same conductivity and would not cause the manganese electrode to break down. Boron, according to the ATSDR, is used in glass production, as well as cosmetics, fire retardants, photographic materials, and soaps (all in the form of borates). Although in large doses boron can irritate the throat and lungs as well as cause damage to the stomach, liver, kidney, and brain, in the amounts used in batteries it is relatively more benign than cobalt.

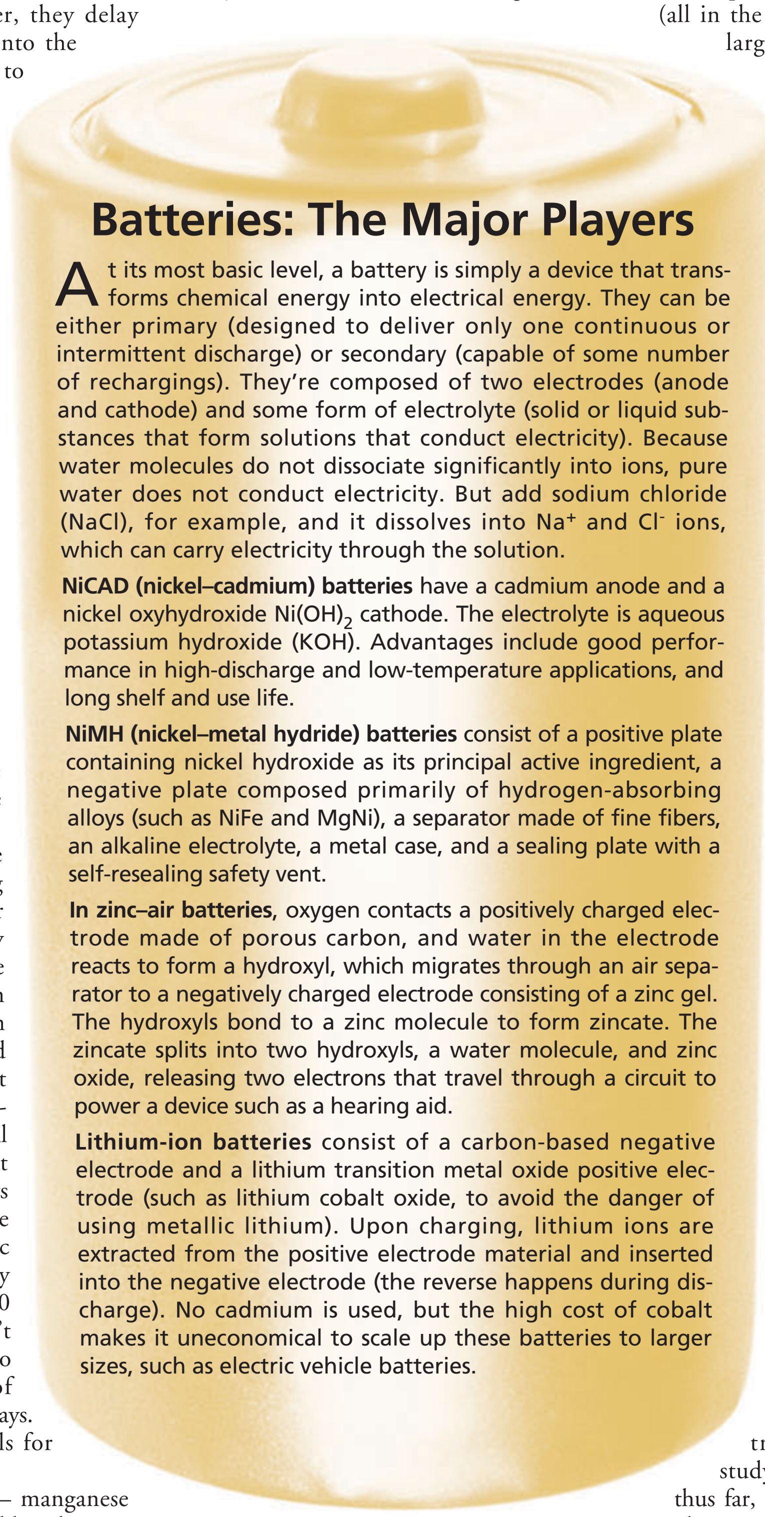
Bacterial Batteries

In the quest for batteries that are still more environmentally friendly, some researchers are even turning to the mud of the sea floor. Microbiologists at the University of Massachusetts at Amherst have tapped into the energy produced by a group of bacteria commonly found in ocean floor sediment to produce electricity.

These bacteria, of the family *Geobacteraceae*, break down the organic matter on the ocean floor to get the energy they need to live, and as they do, they release a stream of electrons that could be channeled into producing electricity. An anode buried in sea mud was connected with a copper wire to a cathode in the seawater, and as the bacteria stripped electrons from organic compounds in the mud, the electrons flowed from the anode to the cathode, producing an electric current. (As an added bonus, these bacteria have shown the ability to degrade toxic organic pollutants, such as benzene, by converting them into carbon dioxide and other benign wastes.) To date, the researchers envision the minimal current produced being useful for such applications as powering remote sensor stations, thus avoiding the necessity of long trips to change batteries. The study is still in its early stages, and thus far, power outputs are minimal, but it shows promise.

Carbon Nanotubes

Another team of researchers are going even farther down to search for new energy



Batteries: The Major Players

At its most basic level, a battery is simply a device that transforms chemical energy into electrical energy. They can be either primary (designed to deliver only one continuous or intermittent discharge) or secondary (capable of some number of rechargings). They're composed of two electrodes (anode and cathode) and some form of electrolyte (solid or liquid substances that form solutions that conduct electricity). Because water molecules do not dissociate significantly into ions, pure water does not conduct electricity. But add sodium chloride (NaCl), for example, and it dissolves into Na^+ and Cl^- ions, which can carry electricity through the solution.

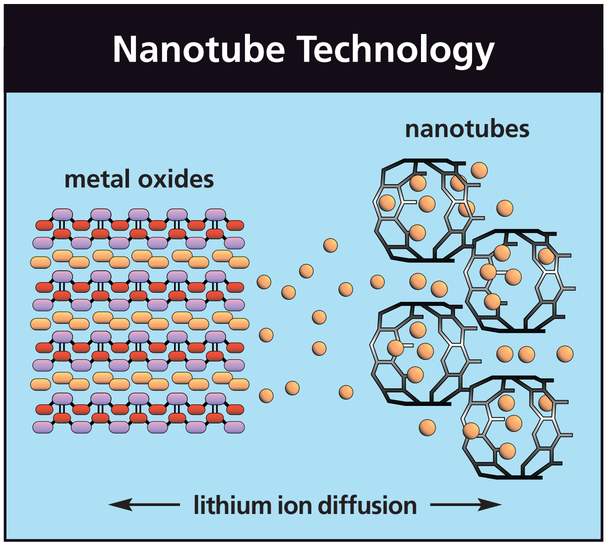
NiCAD (nickel–cadmium) batteries have a cadmium anode and a nickel oxyhydroxide $Ni(OH)_2$ cathode. The electrolyte is aqueous potassium hydroxide (KOH). Advantages include good performance in high-discharge and low-temperature applications, and long shelf and use life.

NiMH (nickel–metal hydride) batteries consist of a positive plate containing nickel hydroxide as its principal active ingredient, a negative plate composed primarily of hydrogen-absorbing alloys (such as NiFe and MgNi), a separator made of fine fibers, an alkaline electrolyte, a metal case, and a sealing plate with a self-resealing safety vent.

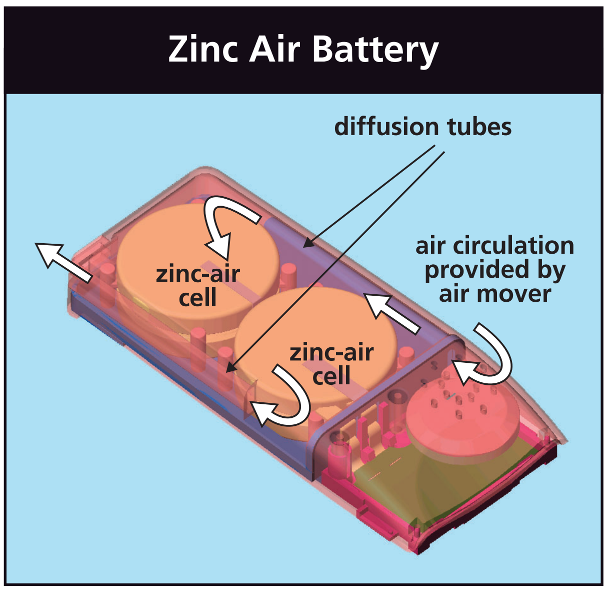
In zinc–air batteries, oxygen contacts a positively charged electrode made of porous carbon, and water in the electrode reacts to form a hydroxyl, which migrates through an air separator to a negatively charged electrode consisting of a zinc gel. The hydroxyls bond to a zinc molecule to form zincate. The zincate splits into two hydroxyls, a water molecule, and zinc oxide, releasing two electrons that travel through a circuit to power a device such as a hearing aid.

Lithium-ion batteries consist of a carbon-based negative electrode and a lithium transition metal oxide positive electrode (such as lithium cobalt oxide, to avoid the danger of using metallic lithium). Upon charging, lithium ions are extracted from the positive electrode material and inserted into the negative electrode (the reverse happens during discharge). No cadmium is used, but the high cost of cobalt makes it uneconomical to scale up these batteries to larger sizes, such as electric vehicle batteries.

Matt Ray/EHP



Filled up with energy. Nanotubes with an affinity for lithium ions may be the power storage solution of the future.



Pulling power out of thin air. One new technology uses a chemical reaction between zinc and the oxygen in air to create energy.

Top to bottom: J. Fischer, Matt Ray/EHP; Dave Rohm/AER Energy Resources, Inc., Matt Ray/EHP

sources, although in size rather than distance. Otto Zhou is director of the North Carolina Center for Nanoscale Materials at the University of North Carolina at Chapel Hill. Zhou and his team are looking into the submicroscopic world of nanotubes to find new ways to store energy in batteries.

Lithium ion batteries typically use graphite or some carbonaceous material as one of the electrodes. Reactions occurring at the electrodes create a flow of electrons that generate and store energy, but the atomic structure of the electrode materials limits the amount of energy that can be stored. With nanotubes, the horizon expands dramatically. In fact, says Zhou, "with graphite, we can store, reversibly, one charged lithium ion for every six carbon atoms, but we found that with nanotubes, we can store one charged lithium ion for every three carbons."

Zhou says there are a few ways to make carbon nanotubes. "You can take solid graphite, in a controlled environment, and add a tremendous amount of energy. That converts the graphite to atomic carbon, which you can then react with a catalyst, like nickel or cobalt, and 'direct' it into a tubular structure. Or you can start with a hydrocarbon, like carbon monoxide, and do the same thing."

What you end up with, he says, is a long, very thin cylinder—less than one nanometer in diameter with walls a single atom thick—that is closed at both ends. Zhou's team has found a way to, as he puts it, "chop off one end," leaving a very sturdy storage device that has an affinity for charged lithium ions. Discharging this battery means attracting the lithium ions out of the nanotube, where they give off their energy and are attracted to the other electrode. To recharge the battery, you merely add energy, forcing the ions back into the nanotube.

"We're not at the stage where we can produce a commercial product," Zhou says. "For one thing, it's very expensive to take carbon and create nanotubes. Our lab makes about half a gram daily, but to support a battery industry, you'd need to produce kilograms of nanotubes. Each battery, even the smallest, would require millions of these nanotubes. We're also looking at issues like the number of discharge–recharge cycles that are possible and the issue of voltage stability," he says.

"We have had interest from the industry, and we're talking with several companies about ways to produce batteries with this technology, but that's still a ways off. But if it can be made workable, you'll have batteries that are smaller and lighter, yet produce the same amount of power as much larger batteries do today, and you could have batteries that last a great deal longer. That's the name of the game."

These are all steps along the way, says Kelty. "The ultimate destination is a fuel cell that will safely power something like a laptop computer. You won't see fuel cells replacing batteries in all applications, but they're going to have a huge niche, and they'll be of tremendous benefit to the environment: no waste beyond some carbon dioxide, no toxic metals to worry about, and several times the power capability of a lithium ion battery. But that's still down the road, and in the meantime, these are all important steps for the industry and for the environment."

Lance Frazer

Suggested Reading

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