The Past, Present and Future of Batteries and Microbatteries

We are all familiar with batteries. A battery is a device that provides electricity. It does this through a chemical reaction between the battery components.

Batteries come in two very basic types: primary (also known as “single use”; they are used once and thrown away when they die) and “secondary” (also known as “rechargeable”; they can be recharged and re-used many times).

Today, within the two basic types of batteries there are many battery chemistries (that is, different materials used to make the battery components). Each chemistry produces different results and, therefore, may be used in different applications.

For example, primary batteries like carbon zinc (also called zinc carbon) are inexpensive and may be used for very low power applications like flashlights and some toys. Single use alkaline chemistries last longer than carbon zinc but are a little more expensive and commonly used in things like calculators, smoke detectors and other consumer goods.

Secondary batteries include lead acid chemistries, which are used primarily in automobiles. Lithium ion chemistries are also rechargeable but are used mostly in portable devices (like cell phones and laptops).

The differences lie in the materials that are used to make the battery components. A brief explanation of these components follows.

How Batteries Work

Batteries provide electrical power through a chemical reaction that happens in a pile of stacked materials (a "voltaic pile"). The main materials are called:

♦ a “cathode”, which is the positive pole of the battery,
♦ an “anode”, which is the negative pole of the battery, and
♦ an “electrolyte”, which conducts ions between the anode and cathode.

An internal chemical reaction causes electrons to flow out of the anode where they are used to power electronic devices (see figure 1). Specifically how that reaction occurs is described in the following paragraph.
When a battery is used electrons and positive ions are produced at the anode by the oxidation half reaction.

The anode then "pumps" these electrons into the external circuit. The electrons move through the external circuit, where they do useful work, and they then enter into the cathode. At the same time positive ions move through the internal circuit of the battery (through the electrolyte) from the anode to the cathode. At the cathode the electrons from the external circuit and positive ions from the internal circuit meet and combine in the reduction half reaction (see figure 2). This completes the current flow loop. The anode is labeled as the negative pole of the battery and the cathode is labeled as the positive pole of the battery. By convention current is the flow of positive charges, so current flow is in the opposite direction from electron flow. Current flows from the cathode (+) to the anode (-).

The materials used to make the cathodes, electrolytes and anodes vary depending on whether the battery is to be a primary or secondary device, and what the end use of the battery will be. For example, an anode may be made of zinc powder, a cathode of manganese dioxide and a potassium hydroxide electrolyte could make a single use alkaline cell. However, if you used a cadmium anode, a nickel oxyhydroxide cathode and an aqueous potassium hydroxide electrolyte, you could have a rechargeable nickel cadmium (or, NiCad) cell. The following table shows just a few of the different chemicals used in different battery chemistries.

<table>
<thead>
<tr>
<th>Battery</th>
<th>Type</th>
<th>Cathode Chemistry</th>
<th>Anode Chemistry</th>
<th>Electrolyte Chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline</td>
<td>Primary</td>
<td>Manganese dioxide</td>
<td>Zinc</td>
<td>Potassium hydroxide</td>
</tr>
<tr>
<td>Carbon zinc</td>
<td>Primary</td>
<td>Manganese dioxide</td>
<td>Zinc</td>
<td>Ammonium chloride</td>
</tr>
<tr>
<td>Lead acid</td>
<td>Secondary</td>
<td>Lead dioxide</td>
<td>Lead</td>
<td>Sulfuric acid</td>
</tr>
<tr>
<td>Lithium</td>
<td>Primary</td>
<td>Several varieties</td>
<td>Lithium</td>
<td>Organic</td>
</tr>
<tr>
<td>Lithium ion</td>
<td>Secondary</td>
<td>Carbon dioxide or manganese dioxide</td>
<td>Carbon</td>
<td>Nonaqueous material</td>
</tr>
<tr>
<td>Mercury</td>
<td>Primary</td>
<td>Mercuric oxide</td>
<td>Zinc</td>
<td>Potassium hydroxide</td>
</tr>
<tr>
<td>Nickel cadmium (NiCad)</td>
<td>Secondary</td>
<td>Nickel oxyhydroxide</td>
<td>Cadmium</td>
<td>Potassium hydroxide</td>
</tr>
<tr>
<td>Nickel metal hydride (NiMH)</td>
<td>Secondary</td>
<td>Nickel oxyhydroxide</td>
<td>Nickel alloy</td>
<td>Potassium hydroxide</td>
</tr>
<tr>
<td>Zinc air</td>
<td>Primary</td>
<td>Oxygen</td>
<td>Zinc powder</td>
<td>Potassium hydroxide</td>
</tr>
</tbody>
</table>

There are many more chemistries in use. Each chemistry produces a battery with varying characteristics and each has a different level of importance, depending on the application. For example, a camera battery may not need to last long, but should be fairly powerful and rechargeable. However, in a smoke detector you may not need a lot of power, but the battery should have a long life.

The most important characteristics of batteries tend to be (but are certainly not limited to) the following:

- Cost
- Recharge (whether it is a primary or secondary battery)
- Voltage (the pressure that forces electricity to flow; measured in volts [V])
- Capacity (the amount of energy in the battery; expressed in amp-hours [Ah]; that is, the total current (amps) the battery can provide multiplied by the time (h) that the battery can continue to produce the current.)
Energy density (the amount of energy in the battery; expressed in watt hours (Wh) per either unit weight or unit volume)

Cycle life (the number of times one can use and recharge the battery [each charge and discharge equals one cycle])

Shelf life (the length of time the battery can be stored before it is considered unusable; this has to do with the self-discharge rate [that is, the rate at which the battery discharges itself (current leakage through the internal circuit of the battery) while not in use])

Service life (the length of time the battery can provide service in a given application)

We all know that batteries come in different sizes and different chemistries for different applications. To illustrate, consider the following:

- A smoke detector may use a single use alkaline 9V battery, will not need a lot of power but will need a relatively long life.
- A digital camera may use a 7.2V specialized rechargeable lithium ion device and use more power more quickly than the smoke detector.
- A flashlight will need two “D” cells, bringing a total of 3.0V in a carbon zinc chemistry.
- An automobile will likely use a 12V, large, lead acid unit with a comparatively large amount of power.

However, they all use the same methodology (i.e., a chemical reaction) to create portable power, they each have their specific design for their application(s) and they can pretty much all be traced back to their origins which date back a little over 200 years.

**A Brief History of Batteries**

Although there is evidence to suggest that batteries (in one form or another) may have been around for thousands of years, almost everyone agrees that the first real battery was invented by Alessandro Volta (his name is where we get the term “volt”) in 1800. During the 19th century, there were several advances in battery chemistries, notably:

- John Daniell, who made some major improvements on Volta’s battery, particularly during the 1830s;
- Gaston Plante, who invented the lead-acid battery in 1859, which is still used in automobiles;
- Georges Leclanche, who patented the first wet cell battery in 1866; these were widely used in telegraph equipment; and
- Carl Gassner, who is widely recognized as the inventor of the dry cell battery in 1888.

Batteries began to be standardized (in terms of size, testing and performance) early on. One of the standard references in the field, “Handbook of Batteries”, states that testing of dry cells began being standardized in 1912, which eventually led to standardization of other factors. The International Electrotechnical Commission (IEC) and the American National Standards Institute (ANSI) published standards for battery sizes and safety (see IEC 60086 and ANSI C18). While there are dozens of defined sizes with varying characteristics, over time 6 general dimensions
became very commonplace: D, C, AA, AAA, 9V and button cells (which have a wide range of sizes).

In the United States, three major battery companies emerged during the latter part of the 19th century and through the 20th century: Energizer, Duracell and Rayovac:

**Energizer**

The National Carbon Company introduced the first battery for home use in the late 19th century. The "Columbia" device was used to power another relatively new invention: the telephone.

By 1914, it had acquired American Ever Ready, a leading battery company. In 1917, the company merged with Union Carbide and soon introduced the enormously popular Eveready battery brand. Eveready was the first to offer alkaline batteries to consumers in the late 1950s and continued to cement its reputation as the premier battery company in the world. Duracell and Rayovac made strides against the leader, but Eveready never lost its position in the industry.

Ralston Purina purchased the company in 1984 and today the Energizer brand has replaced the old Eveready name, but maintained the leadership position. In April 2000, Ralston Purina spun off Energizer as its own company. In 2003, Energizer bought the Schick-Wilkinson Sword shaving product business. Today, Energizer trades on the New York Stock Exchange and reported over $3 billion in sales in 2006.

**Duracell**

Phillip Rogers Mallory, the owner of the PR Mallory Company, teamed with Samuel Ruben in the 1920s to create innovative battery products. In 1964, the Mallory Battery Company, as it came to be known during World War II, introduced the Duracell brand – the first highly successful alkaline battery. The company continued to produce standard batteries under the Mallory label for some time while also selling the more expensive, but longer lasting Duracell alkaline type.

In 1980, five years after Mallory’s death, the company changed its name to Duracell International. It continued to improve its product line by incorporating features like the “Power Check” element (which gives the user an idea of how much power was left in the cell) and expiration dates. In 1996, Duracell merged with Gillette.

Today, Duracell is the second largest battery company in the world. Its parent company announced Duracell’s sales hit $2.02 billion in 2003.

**Rayovac**

Rayovac Corporation was founded in 1906 as the French Battery Company, changing its name in the mid-1930s to Rayovac. It has been described as a “sleepy”, family-run business for its first 90 or so years of existence. But, then the Thomas H. Lee Partners bought it and brought in David A. Jones.

Jones engineered an IPO on the New York Stock Exchange in 1997 and the company made several acquisitions, most notably Remington in 2003. After several other acquisitions, the corporation changed its name to Spectrum Brands and today trades on the NYSE under the
symbol SPC. Its sales in 2006 were over $2.5 billion.

Of course, there are other battery companies out there. Panasonic, Kodak and Sony all have their own battery line for use in their products. There are many smaller companies as well, specializing in niche markets and specialized uses.

**Microbatteries**

With the advent of the integrated circuit, the consumer electronics industry began to take shape and, in the latter part of the 20th century, exploded into a huge market. The use of smaller and multi-functional portable devices drove the need for smaller, more powerful batteries, and continues to do so today.

In the early 1990s, Oak Ridge National Laboratory (ORNL), in Oak Ridge, Tennessee, began development of a thin film based lithium battery. In other words, some of the same techniques used to manufacture integrated circuits were used to create a battery. The result was a flat battery that was thinner than plastic wrap. By placing the device in a semiconductor package, ORNL created a battery-on-a-chip. To date, ORNL has been awarded (by our count) 16 patents relating to this technological endeavor.

**Manufacturing Microbatteries**

Microbatteries are often manufactured using the same techniques as semiconductors. The manufacturer builds the battery by depositing materials one layer at a time:

1) Start with a silicon wafer; this is a flat disc made of (you guessed it) silicon, which is commonly used in manufacturing integrated circuits.

2) Add current collectors. These will serve as the connectors for the positive and negative poles of the battery.

3) Deposit cathode materials

4) Deposit electrolyte materials.
5) Deposit anode materials (note: the material proportions in these diagrams are NOT to scale).

6) Seal the device.

7) Install the device in an integrated circuit package.

Although there are additional steps for other components, fundamentally, this is all there is to it.

There are a number of methods which could be used to put the layers of materials onto the silicon, including things like sputtering, electrodeposition, sol-gels, etc. The expense, precision and performance levels among these methods vary.

**Microbattery Companies**

ORNL licensed its patents to six companies. Dozens of others (each with their own take on the idea) joined in the market niche. These companies are targeting a myriad of applications, including chip memory backup, wireless remote sensors, RFID tags, “smart” cards, low-power wireless remote controls, MEMs and NEMs, etc. One third party market research company estimated the market value of microbatteries for these applications to grow to over $3 billion by 2012 (according to NanoMarkets).

The key to unlocking this market is two-fold – price and performance. There are a few applications where companies have been successful (military, for example) but not nearly enough to push the market door wide open.

**The Landscape Today**

There continues to be a tremendous amount of research conducted in microbattery technology. We are aware of close to 50 companies and research institutions that are working in this area in the US; there are many more outside the country.

One of the leading battery experts in the world is Isidor Buchmann, of Cadex Electronics. He is the author of “Batteries in a Portable World” and he pointed out something that should be considered when looking at the state of the industry today:
Think about the improvements the computer has seen over the past 50 or so years; from the size of an entire room to a laptop. There have been several breakthroughs in technology that have spurred these improvements.

Then consider the automobile battery; it’s essentially the same size and weight as it was in our grandparents’ time. There has been no such radical changes in technology to benefit the battery.

As such, researchers are technologically limited in what they can do. There are limited numbers of electrons in various materials. Other materials may be discovered, which may improve cost or performance, but until the basic idea of the storage and transfer of electrons changes, there will be only so much that battery researchers can do.

The Future of Batteries

So, what will replace batteries in the future? There have been a lot of technologies suggested, including some that incorporate things like mud, bugs and garbage. Certainly fuel cells represent a promising technology, with the promise of powering a device like a laptop computer for days. In fact, we believe they will eventually replace some batteries.

Fuel cells are similar to batteries in that they use a chemical reaction to create electricity. However, a fuel cell uses a fuel (i.e., hydrogen, natural gas, etc.) to create the electricity. Today, the biggest barrier to the advent of the fuel cell continues to be cost and the need to supply fuel.

Still, it must be remembered that the future replacement technology, whatever it is, will replace a very well-known and trusted device. Whatever replaces batteries must meet several criteria in order to be accepted in the marketplace:

• It will have to be economical; consumers are used to spending a certain amount on batteries to power their devices. The market is mature, established and conditioned. Pricing will need to be competitive with established technologies.

• It will have to be technologically benign; for example, with fuel cell technology, the consumer must add fuel to a fuel cell to make it work. How will the consumer feel about the extra effort? The effort must be “worth” the result. The same is true with batteries: if any extra effort is required on the part of the consumer, it had better be easy to do and worth the benefit.

• It will have to have some major advantage; we’re talking about replacing a trusted technology that people have long grown comfortable with. They won't change products without the promise of a major performance and/or economic advantage.

For the immediate and foreseeable future, batteries will remain the dominant small, portable power technology.

More Information . . .

The most comprehensive source on batteries and battery chemistries that we have found is the *Handbook of Batteries*, published by McGraw Hill and edited by David Linden and Thomas B. Reddy.
Another, less comprehensive work is R.M. Dell and D.A.J. Rand’s *Understanding Batteries*, published by the Royal Society of Chemistry in the UK. It’s not written as simply as the title suggests, but it contains valuable information nonetheless.

One of the most popular books on rechargeable batteries is Isidor Buchmann’s *Batteries in a Portable World*, which is published by Cadex Electronics, Inc. Buchmann also provides this very informative data at www.batteryuniversity.com.

There are also some very well-written and easy-to-understand discussions on batteries on the websites of the three largest battery manufacturers in the United States:

www.energizer.com
www.duracell.com
www.rayovac.com