Battery University

Weird and Wonderful Batteries

Considering the importance which the battery holds in modern life, improvements have been slow in coming when compared to the advancements made in microelectronics. Let us not point the finger at laid-back scientists and engineers but realize the complexity encountered. As long as the battery relies on the electrochemical process, limitations will continue. These are low energy storage, slow charging, short service life and high cost per watt.

Each battery system offers distinct advantages but none provides a fully satisfactory solution. For many years, nickel-based batteries delivered reasonably good service, but this chemistry is being superseded with lithium-ion offering higher specific energy (capacity), lower self-discharge and no maintenance. Lead acid with its many warts and blemishes still holds a solid position and will continue to keep its lead as starter and deep-cycle battery. No other system can meet the price and robustness on bulk power.

Never has there been so much activity in battery research and the electric vehicle (EV) is the catalyst for this frenzy. Expectations are high and the media is quick to announce a new battery that promises long runtime, good durability and is environmental friendly. Indeed, some systems show good potential, but most are years away from becoming commercially viable. Many disappear without a trace of the passing.

Typical failings of new battery concepts are weak load capabilities and short cycle life. Even a lemon can be made into a battery. Just poke a copper coin and galvanized nail into the innards. The power is low, and 500 lemons can light a flashlight bulb. Using seawater as an electrolyte has also been tried. The sea would produce an endless supply of electricity, but the retrieved energy is only good to light a flashlight. Corrosion of the plates limits the useful service life and renders the seawater battery impracticable.

With the interest in battery developments at an all-time high, it is only fitting that we review old and up-and-coming systems. The chemistries listed below are placed in roughly the sequence of development. Many older batteries are being revised to offer longer lives, extended runtimes and better pricing.

Nickel-iron

After inventing nickel-cadmium in 1899, Sweden’s Waldemar Jungner tried to use iron instead of cadmium to save money, but poor charge efficiency and gassing prompted him to abandon the project without securing a patent. In 1901, Thomas Edison continued the development as an alternative to lead acid for the electric vehicles, claiming superior performance. He lost out when gasoline-powered cars took over and was deeply disappointed when the auto industry chose lead acid as the starter battery.

The nickel-iron battery (NiFe) uses an oxide-hydroxide cathode and an iron anode with potassium hydroxide electrolyte to produce a nominal cell voltage of 1.2V. NiFe is resilient to overcharge and over-discharge and can last for more than 20 years in standby applications. Resistance to vibrations and high temperatures made NiFe the preferred battery for mining in Europe, and during World War II powered the German V-1 flying bomb and the V-2 rockets. Other applications are railroad signaling, forklifts, and stationary applications. NiFe has a low specific energy of about 50Wh/kg, has poor low-temperature performance and exhibits high self-discharge of 20 to 40 percent a month. These disadvantages together with high manufacturing cost prompted the industry to stay faithful to lead acid.

Nickel-zinc

Nickel-zinc (NiZn) batteries are similar to nickel-cadmium in that they use an alkaline electrolyte and a nickel electrode, but differ in voltage; NiZn provides 1.6V/cell rather than 1.2V, which NiCd delivers. Nickel-zinc was first developed in the 1920s but it suffered from short cycle life caused by dendrite growth and electrical shorting. Improvements in the electrolyte reduced this problem. Low cost, high power output and good temperature operating range make this chemistry attractive, and NiZn is being revived for commercial uses. NiZn charges at a constant current to 1.9V/cell, but cannot take trickle charge. The specific energy is similar to other nickel-based systems. NiZn is good for 200–300 full cycles, has no heavy toxic materials and can be recycled. The battery is also available in AA cells.

Nickel-hydrogen

When research for nickel-metal-hydride began in 1967, problems with metal instabilities shifted the development towards the *nickel-hydrogen*battery (NiH). NiH uses a steel canister to store the hydrogen gases at a pressure of 1,200psi (8,270kPa). The cell includes solid nickel electrodes, hydrogen electrodes, gas screens and electrolyte that are encapsulated in the pressurized vessel.

NiH has a nominal cell voltage of 1.25V and the specific energy is 40–75Wh/kg. The advantages are long service life even with full discharge cycles, good calendar life due to low corrosion, minimal self-discharge, and a remarkable temperature performance of –28°C to 54°C (–20°F to 130°F). These attributes make NiH ideal for satellite use. Scientists are developing NiH batteries for terrestrial use and hope to supply markets for energy storage systems and the electric vehicle. The negatives are low specific energy and high cost. A single cell for a satellite costs thousands of dollars.

Zinc-air

Zinc-air batteries generate electrical power by an oxidation process of zinc and oxygen from the air. The cell can produce 1.65V, but 1.4V and lower achieves a longer lifetime. Removing a sealing tab activates the battery by enabling airflow and the battery reaches full operating voltage within five seconds. Once turned on, the battery cannot be stopped. Inhibiting airflow by adding a tape only slows degeneration.

Zinc-air batteries have similarities to the proton exchange membrane fuel cell (PEMFC) by using oxygen in the air as fuel for the positive electrode. Air can, to a certain extent, control the rate of the reaction. Zinc-air is considered a primary battery; however, there are recharging versions for high-power applications. Recharging occurs by replacing the spent zinc electrodes, which can be in the form of a zinc electrolyte paste. A different type of zinc-air battery uses zinc pellets. Rechargeable zinc-air batteries have been tried on electric vehicles and discontinued.

At 300–400Wh/kg, zinc-air has a high specific energy, manufacturing cost is moderate, but the specific power (current handling) is low. In a sealed state, the self-discharge is two percent per year. Zinc-air is sensitive to extreme temperatures and high humidity. Pollution also affects performance; high ambient carbon dioxide reduces the performance by increasing the internal resistance. Typical applications are hearing aids and safety lamps at construction sites.

Silver-zinc

The silver-zinc battery served as an important power source in defense, aerospace, high-end TV cameras and other professional equipment that needed long runtime. High cost, short service life and the advent of Li-ion caused silver-zing to lose favor.

Rapid degradation of the zinc electrode and separator were the primary cause of failure in the original design. During cycling, the buildup of zinc dendrites pierced the separator and caused electrical shorts. Furthermore, the separator degraded by itself sitting in the potassium hydroxide electrolyte. This limits the shelf-life to about two years. Improvements in the zinc electrode and separator promise a longer service life and a 40 percent higher specific energy than Li-ion. Silver-zinc is safe, has no toxic metals and can be recycled, but the use of silver makes the battery expensive to manufacture.

Sodium-sulfur

Sodium batteries, also known as *molten salt* or *thermal battery*, come in primary and secondary versions. The battery uses molten salts as an electrolyte and operates at a temperature of 400–700°C (752–1,292°F). Newer designs run at a lower 245–350°C (473–662°F) temperature.

Conceived by the Germans during World War II and used in their V-2 rockets, the electrolyte of the molten salt batteries is inactive when cold and can be stored for more than 50 years. Once activated with a heat source, the battery can provide a high power burst for a fraction of a second or deliver energy over several hours. High power is made possible with good ionic conductivity of the molten salt. Primary sodium batteries are almost exclusively used for the military as a “one-shot” engagement in guided missiles; however, the interest lies in the rechargeable version.

The modern rechargeable sodium-sulfur is known as *sodium-nickel-chloride* battery or ZEBRA, so-called after the *Zeolite Battery Research Africa* project. The battery has a nominal cell voltage of 2.58 volts and a specific energy of 90–120Wh/kg, a level comparable with Li-manganese and Li-phosphate. The service life is about eight years and 3,000 cycles. It can be fast-charged, is non-toxic and the raw materials are abundant and at low-cost. ZEBRA batteries come in large sizes of 10kWh or higher. Typical applications are forklifts, railways, ships, submarines and electric cars in continuous use such as taxis and delivery vans. A growing market for sodium-based batteries is load leveling, also known as grid storage.

The ZEBRA battery must be heated to 270–350°C (518–662°F). Even with special insulation, heating consumes 14 percent of the battery’s energy per day, which results in the equivalent of an 18 percent self-discharge. A ZEBRA battery should be either on charge or in use. It takes 3–4 days to cool down; reheating requires about two days depending on the SoC at time of shutdown. Common failures are electrical shorts due to corrosion and dendrite growth, which increases self-discharge.

Experimental Rechargeable Batteries

Experimental batteries live in laboratories and connect to the outside world through glowing reports, mostly to entice investors. It is our hope that these developments will one day mature into a battery that does more than talking on cell phone; the goal is to achieve environmental benefit for automotive transportation. There are no immediate candidates that could disrupt present battery chemistries, but the potential is there. Below are the most promising experimental batteries worth mentioning.

Lithium-metal (Li-metal)

Most lithium-metal batteries are non-rechargeable. Moli Energy of Vancouver was first to mass-produce a rechargeable Li-metal battery for mobile phones, but occasional shorts from lithium dendrites caused thermal runaway conditions and the batteries were recalled in 1989. Li-metal has a high specific energy. In 2010, a trial Li-metal-polymer with a capacity of 300Wh/kg was tested in an experimental electric vehicle (this compares to 80Wh/kg for the Nissan Leaf), but safety remains a major issue.

Lithium-air (Li-air)

Li-air batteries borrow the idea from zinc-air and the fuel cell in that they breathe air. The battery uses a catalytic air cathode that supplies oxygen, as well as a lithium anode and electrolyte. Scientists anticipate an energy storage potential that is 5 to 10 times larger than that of Li-ion but say it will take one to two decades before the technology can be commercialized. Depending on materials used, Li-ion-air will produce voltages in between 1.7 and 3.2V/cell. IBM, Excellatron, Liox Power, Lithion-Yardney, Poly Plus, Rayovac and others are developing the technology. The theoretical specific energy of lithium-air is 13kWh/kg; aluminum-air has similar qualities, with an 8kWh/kg theoretical specific energy.

Lithium-sulfur (Li-S)

By virtue of the low atomic weight of lithium and the moderate weight of sulfur, lithium-sulfur batteries offer a very high specific energy of 550Wh/kg, about three times that of Li-ion, and a specific power potential of 2,500Wh/kg. During discharge, the lithium dissolves from the anode surface, and reverses itself when charging by plating itself back onto the anode. Li-S has good cold temperature discharge characteristics and can be recharged at –60°C (–76°F). The challenges are limited cycle life of only 40 to 50 charges/discharges and instabilities at high temperature. Since 2007, Stanford engineers get promising results experimenting nanowire. Li-S has a cell voltage of 2.10V and is environmentally friendly. Sulfur as the main ingredient is abundantly available.

Silicon-carbon Nanocomposite Anodes for Li-ion

Unlike carbon as the typical anode material in the regular lithium-ion battery, researchers have developed silicon-carbon nanocomposite. This promotes the access of lithium ions to achieve stable performance and a capacity gain of five times that of regular Li-ion. Manufacturing is said to be simple and low-cost, and the battery is safe; however, the cycle life is limited due to structural problems when inserting and extracting lithium-ion at high volume.

Summary

During the last five years or so, no new battery emerged that could be called a major breakthrough. This is not surprising when considering that few other products have requirements as stringent as the battery. A battery must have high energy storage capability, provide a long service life, be safe to use, and require little maintenance. In addition, the battery must work at hot and cold temperatures, deliver high power on demand, charge quickly, and cost little. As we expand the use of the battery in transportation, it becomes apparent that this electrochemical power source is best suited for portable use. For motive applications such as trains, ocean going ships and aircraft, the battery lacks capacity, endurance and reliability. The dividing line, in my opinion, will be the electric vehicle.

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Comments

On August 17, 2011 at 3:41pm

BWMichael wrote:

Wow. I never knew there were so many different chemistries of batteries.

Im guessing that is because most of these chemistries are not available for retail sale at the supermarket or local battery experts

On September 1, 2011 at 8:35pm

linly wrote:

Wow, there is so much knowledge about battery. When can we use a battery with super high capacity and small size?

On September 21, 2011 at 12:08pm

Jan van Staveren wrote:

It’s a pity that (as usual) power and energy are mixed up in thia article

On September 22, 2011 at 3:13am

John Gowing wrote:

Have you seen the millimetre turbine project at MIT? Although not strictly a battery in the chemical sense it is (may / will be) a competitor to batteries in small portable power applications. Anticipated 10 - 50 Watts from a micro gas turbine generator, in a similar volume to a laptop battery, including fuel supply.
Still in early stages of development, but a fascinating project nonetheless
http://thefutureofthings.com/articles/49/engine-on-a-chip.html

On October 31, 2011 at 10:08am

John Hardy wrote:

I would add the tin anode Li ion battery. This uses tin encapsulated in nanotubes see for example Kamali and Fray:http://www.ipme.ru/e-journals/RAMS/no_12711/kamali.pdf. Morgan are involved: http://www.enterprise.cam.ac.uk/news/2011/6/university-researchers-partner-morgan-amt-develop-/

On November 14, 2011 at 1:01pm

Bob Beatty wrote:

How about adding some information on the emerging LiFePO4 technology. Not as high energy density as LiPo batteries, but few of the nasty side effects. Non toxic, relatively cheap materials, flatter discharge curve, etc. etc.

Downside is slightly lower energy density.

This is showing up in mainstream market as a much longer life replacement for SLA batteries in bikes, carts, etc.

On December 16, 2011 at 8:03pm

T.Sampath Kumar wrote:

Have you given up on rechargeable Zn/MnO2 systems?

On December 18, 2011 at 5:15am

Tom Tercek wrote:

What about the so called “precharged” NIMH batteries with low self discharge. How are these different from the normal NIMH type.
What is the chemistry difference?
What are the pros and cons or these?

On June 11, 2012 at 6:46pm

The Same Chemistry-Thicker separators wrote:

The precharged NIMH batteries have just been precharged and ready to use. Most of them are low self discharge, which means that the separators are usually thicker, to greatly slow the escape of electrons, so that you can use most of the battery before losing too much energy to self discharge. There are a few rare ones that are precharged, but not actually low self discharge. The pros of LSD type NIMH are the same chemistry as the regular ones, but have that different design of the separator. The drawbacks are slightly lower capacity since the design difference does take up more room inside the battery. There were some 3100MAH regular NIMH available in AAs, but high self discharge rates make these batteries impractical, except for the highest drain devices, like a portable TV that uses AAs. The same problem with early failure led to Energizer abandoning the higher capacity 2500MAH AA cells.

On June 11, 2012 at 7:13pm

Bob Beatty wrote:

“There are a few rare ones that are precharged, but not actually low self discharge”...

Absolutely NOT true. Almost ALL of the low self-discharge NiMH batteries are pre-charged at the factory. That is precisely because their self-discharge is so low that it allows a pre-charged battery to be sold.

On November 1, 2012 at 12:08pm

Nice to Know wrote:

Well, that is nice to know. Of course, Rayovac does not want to endanger their C and D alkaline line, so the ones they are offering are only the 3000MAH variety. I am currently using the Accupower Evolutions, but the one major drawback with these LSD cells are the sometimes lack of cell matching, and trouble with uniform capacity retention among individual cells across a whole set. I have bought a new set just under a year ago, and cell number 4 just mysteriously lost some part of its capacity, becoming mismatched, while the others were fine. I need more than the Centura brand only giving 8000MAH, and the only other good options are the green Maha Powerex that are 12000MAH, but not low self discharge, or the insanely expensive Imedions that are LSD type. (9500MAH) I am positive that these Imedions will have a better uniform capacity retention amongst their individual cells, as long as you sometimes use a hobby charger to even them up. The Powerex charger does not do a good job of forming, so for the 1st charge, I use the silver Rayovac charger for the AA,AAA sizes, and a pack charger for the C and D sizes.

On February 13, 2013 at 4:33pm

goatboy wrote:

crossing several lessons: load-leveling, grid storage, weird & wonderful: Is there a no-brainer approach to storage batteries? I am thinking low-tech like aluminum cans and sheet steel with a salt-water electrolyte in a bucket. If the materials are readily available and cheap, you can afford to sacrifice efficiency and life-span with regular low-risk service (material replacement) and quantity/size (like the attic/basement/crawl-space) and use a lap-top program to monitor the recharge from the solar/wind source…why so much focus on high-tech?

On March 24, 2016 at 7:49am

andy Lam wrote:

Much research is being done on crystal cells. Inventor pioneers include John Hutchison, Marcus Reid, Fausto Heikkinen, and Thomas Townsend Brown who are and have experimented with geochemical mixtures that have produced interesting and curious results out of mainstream research. I think more attention should be given on these unorthodox quests.

On April 29, 2019 at 8:31pm

sls4ak wrote:

Aluminum Air batteries, with better recycling has merit for grid management, or perhaps not. The load leveling link is broken

On October 4, 2019 at 5:33am

Radhakrishna Kurup wrote:

What about lithium titanate batteries?

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