"Anode'r' way" -- Why the anode yields better results

Find out how battery improvements occur with changes to the anode, including a longer battery life, and the elimination of thermal runaway.

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Prior to 1990, Nickel Cadmium (NiCd) and Lead Acid (PbA) technologies dominated the rechargeable battery market. During the 1990's, Nickel Metal Hydride (NiMH) and Lithium Ion (Li-Ion) rechargeable batteries emerged and today hold high volume positions in various markets alongside NiCd and PbA. Each with strengths and weaknesses, the collective issues of all rechargeable battery technologies revolve around life (cycle and calendar), safety, recharge time, power delivery, extreme temperature performance, and environmental friendliness.

A tremendous amount of activity is directed at developing battery technologies that address these issues. For all battery technologies, the ability to achieve high performance in each area of criteria are directly determined by how the battery is constructed; specifically, the types of electrodes and electrolytes used.

Battery Basics

All batteries produce energy from electrochemical reactions. Batteries are comprised of several components, but primarily consist of the following:

- A positive electrode (the cathode) and a negative electrode (the anode)
- An ionic electrolyte: a solution that contains and aids the movement of ions (charged particles) back and forth between the two electrodes
- A porous separator (ensures the two electrodes do not touch but allows ions to travel back and forth between the electrodes)

When a battery is charged, electrons travel from the positive electrode to the negative electrode. On discharge, these electrons return to the positive electrode releasing energy in the process.

Leading Rechargeable Battery Platforms

Nickel Metal Hydride (NiMH)

Using nickel as the cathode, much like nickel-cadium (NiCd) batteries, nickel metal hydride batteries use a hydrogen-absorbing alloy for the anode. A NiMH battery can have two to three times the capacity of an equivalent size NiCd. However, when compared to the lithium ion battery, the power level is lower and the self-discharge rate is higher. NiMH technology is gaining prominence within electric vehicle (EV) and hybrid electric vehicle (HEV) markets.

Strengths

- Specific energies range from 40 Whr/Kg to 100 Whr/Kg
- Contains only mild toxins and is more environmentally friendly
- Rapid charged in about 3 hours

Weaknesses

- Poor deep cycleability
- Dedicated usage in high current applications limits cycle life
- Poor shelf life (three years)
- High self discharge rates
- Intolerant to elevated temperature (performance and capacity degrade sharply above room temperature)
- Serious issues involving safety accompanying recharge (temperature and internal pressure of a NiMH cell rises sharply as the cell nears 100% state of charge, necessitating the inclusion of complex cell monitoring electronics and sophisticated charging algorithms in order to prevent thermal runaway[1])
- Limited supply of nickel (potentially rendering the technology economically infeasible)

Lithium Ion

In lithium ion batteries, the anode is made from carbon, the cathode is a metal oxide, and the electrolyte is a lithium salt in an organic solvent. The energy is released in these batteries through the movement of lithium ions. The current markets for lithium battery technology are focused on consumer electronics, such as cell phones and portable computers. In these types of applications, high energy and light weight are important. The same attributes are desired for EV, HEV, PHEV, power tool, and UPS markets. However, these applications are principally high power demand applications and/or pose other demands on usage, such as extremes of temperature, need for short recharge times, high proportional (to stored energy) current rates, and even longer extended lifetimes.

Strengths

- Best energy-to-weight ratio
- Stable, exhibiting low self discharge
- No-maintenance systems
- No memory effect
- 4C discharge rate and a C/2 to C/4 charge rate[2]
- 3 year life

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[1] Thermal runaway is a condition whereby a battery can enter into an uncontrollable reaction that produces high heat levels, fire and / or explosion.

[2] The letter C designates an electrical current rate that is in unitary proportion and absolute value to a batteries capacity in Ah. Thus, a 1Ah battery will discharge in 1 hour at a 1C rate at a current of 1A. Electric vehicles require currents for acceleration from 10C to 100C, and it would be highly desirable if an EV battery could be recharged in the time it takes to fill a common car's gasoline tank, i.e., a 6C to 10C rate (10 to 6 minute rate).

Weaknesses

- Intolerant of temperature extremes (intolerant of low temperatures in terms of recharge and of high temperatures in terms of safety)
- Cannot be recharged at low temperatures (below 0 to -10°C)
- Prone to thermal runaway at high temperatures (above 130°C for current batteries)

As previously mentioned, the electrolyte is a lithium salt dissolved in an organic solvent. Upon manufacturing a lithium ion battery and subjecting the battery to its first charge/discharge cycle, the electrolyte will partially break down at the anode, forming a passivating layer called the SEI – Solid Electrolyte Interphase. This layer serves to protect the electrode from further electrolyte breakdown, but it also imposes a resistance to the passage of electrolyte components (the lithium ions) needed to make the battery functional. Consequently, on the downside, the layer limits the discharge rates and seriously renders the battery un-chargeable at cold temperatures.

At cold temperatures the pores in the SEI are effectively closed. If charging a cell at severely low temperatures is attempted, lithium metal will plate on the surface of the SEI, resulting in two dangerous conditions, either of which can cause the battery to enter thermal runaway. The SEI layer, under normal operating temperatures, maintains a safety barrier between the reactive anode and the electrolyte. However, if the temperature of the battery rises above 120°C the SEI layer breaks down. In this situation the negative electrode (anode) can chemically react vigorously with the electrolyte. This uncontrollable reaction also causes the battery to enter thermal runaway.

Obviously, advancements must be made to the components in lithium ion batteries.

Improvements for the Cathode

The cathode material in a conventional lithium ion battery is typically made up of a metal oxide such as cobalt, manganese, or phosphate. Many next-generation lithium ion battery companies, such as Valence Technologies, Nonoexa, and A123Systems have created battery cells that alter the previous make-up of the cathode. By using an iron phosphate cathode material, the batteries contain all of the same strengths of conventional lithium ion batteries, and eliminate the threat of thermal runaway.

Improvements for the Anode

Another initiative is to improve the anode. Conventional lithium ion technology employs carbon as the active material in the batteries' anode. In a lithium battery environment, graphite (an allotrope of carbon) becomes very reactive with components of the battery's electrolyte system. Additionally, lithium-based materials can build-up on the anode, which can contribute to the overall instability of the battery. One company, Altairnano, has broken convention and focused their attentions on improving the anode. By removing the lithium ion/graphite interaction, Altairnano replaces the graphite of the anode with their own proprietary lithium titanate-based nanomaterials, and eliminates the threat of thermal runaway.

Better results with the anode

Like improvements to the cathode, improvements to the anode retain the strengths of conventional lithium ion batteries while eliminating the threat of thermal runaway. However, when retaining the cathode material from a common lithium ion battery and focusing on improvements to the anode (by replacing the graphite), the following benefits also occur:

- Longer life
- Higher power
- Faster charge
- Wider operating temperature range

Longer Life

During charge of conventional lithium-ion batteries, lithium ions deposit inside the anode and are then released on discharge. When the lithium ions enter or leave the anode, the graphite particles of the anode expand or shrink to accommodate the lithium ion's size. Over the life of the battery, this repeated expansion and shrinkage fatigues the graphite particles. As a consequence, the particles break apart, causing a loss in electrical contact between the resulting particles thereby reducing battery performance. Most battery materials suffer from this mechanical stress and strain; this particle fracturing reduces the life of the battery.

With an improved anode, such as using lithium titanate spinel oxide (LTO) materials to replace the graphite, the LTO material becomes a "zero strain" material. This means that the material essentially does not change shape upon the entry and exit of a lithium ion into and from the particle. This property results in a battery than can be charged and discharged significantly more often than conventional lithium ion batteries because of the absence of particle fatigue that plagues materials such as graphite. Conventional lithium ion batteries can be typically charged about 750 times before they are no longer useful (about 2 years), whereas, cells using LTO materials as the anode can achieve over 9,000 charge and discharge cycles (over 20+ years) while retaining up to 80% charge capacity.

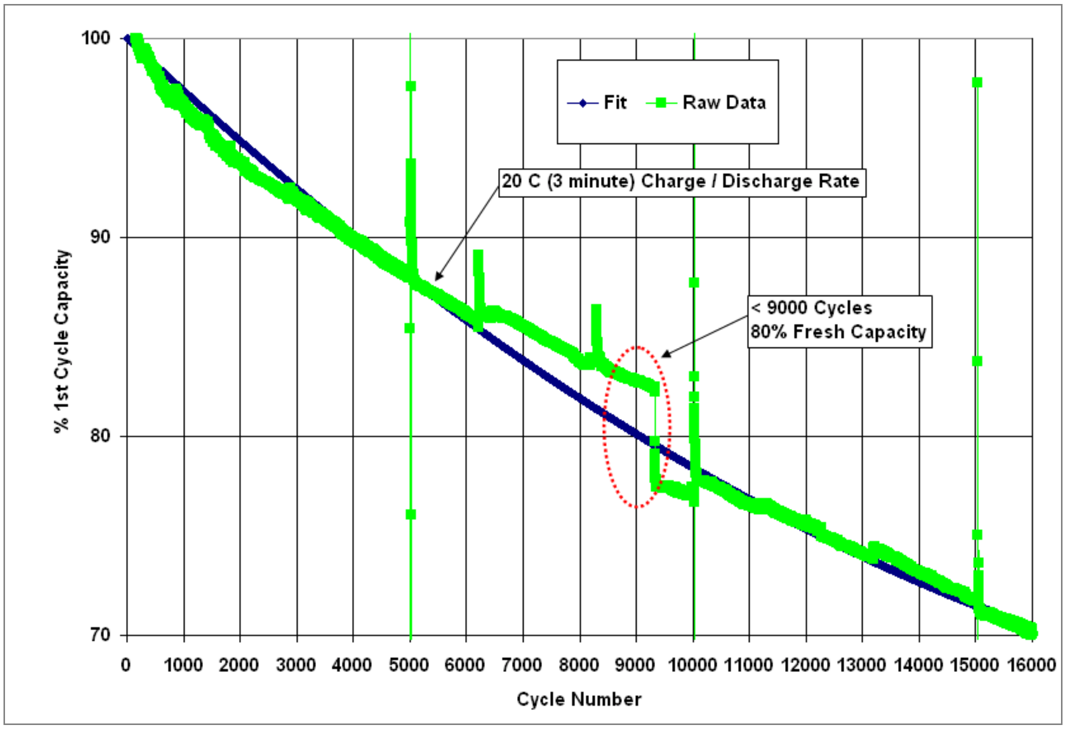

Figure 1: Three minute charge and discharge testing of LTO-based anode

Higher Power

An important attribute of any battery is their ability to deliver power quickly. With a conventional lithium ion battery, lithium ions deposit inside the graphite-based anode during charge. However, the rate at which lithium ions can be removed during discharge (the useful power-producing cycle of a battery) is limited by the graphite's electro-chemical properties, the size of the graphite particles, and the existence of the SEI layer. Therefore, power is restricted by the ion removal capability. Conventional lithium ion batteries result in power levels of 1000 watts per kilogram.

By removing the graphite from the anode and using LTO materials instead, the formation of an SEI layer is eliminated and particles are up to 100 times smaller than a typical graphite particle. Ions are able to be removed more quickly resulting in more power being generated with densities as high as 4000 watts per kilogram.

Faster Charge

If lithium ions are unable to enter graphite particles they may collect (plate) on the anode's surface as lithium metal. If this plating occurs, the battery severely degrades in performance and in extreme cases, causes thermal runaway. Therefore, the time to charge (charge rate) is restricted by the ion incorporation rate capability (measured in hours).

Through utilizing LTO materials instead of graphite as the anode, lithium metal plating does not occur. The electro-chemical properties of the LTO allow the lithium ions to incorporate at high rates, thereby reducing the time to charge. Cells using LTO materials as the anode can be fully charged in under 10 minutes (Figure 2 and 3). Rapid charge is important for electric vehicles – the ability to be charged in a few minutes versus hours is indispensable.

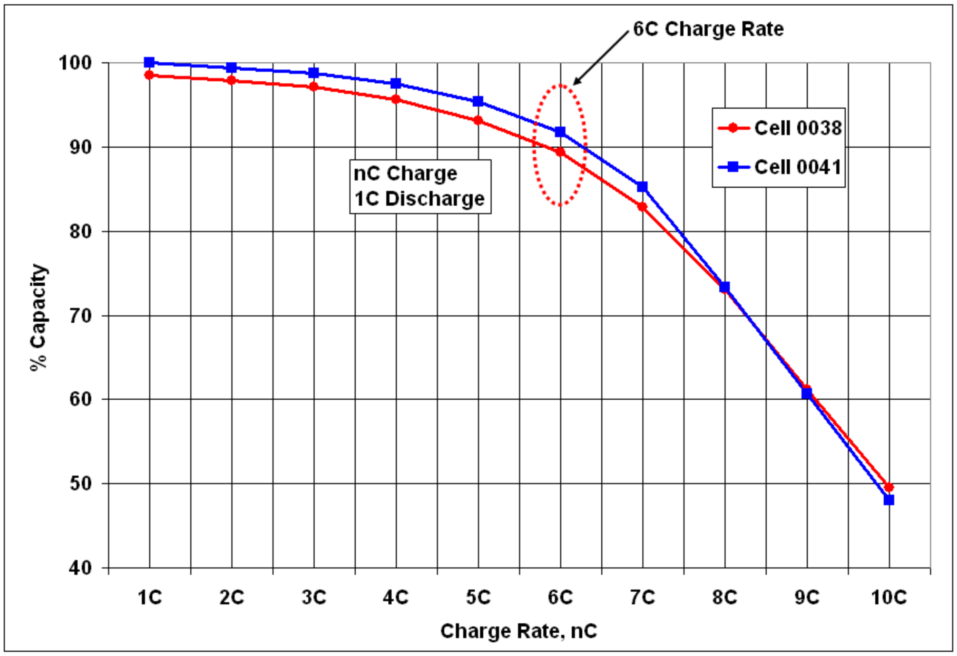

Figure 2: LTO anode-based cell charge rate

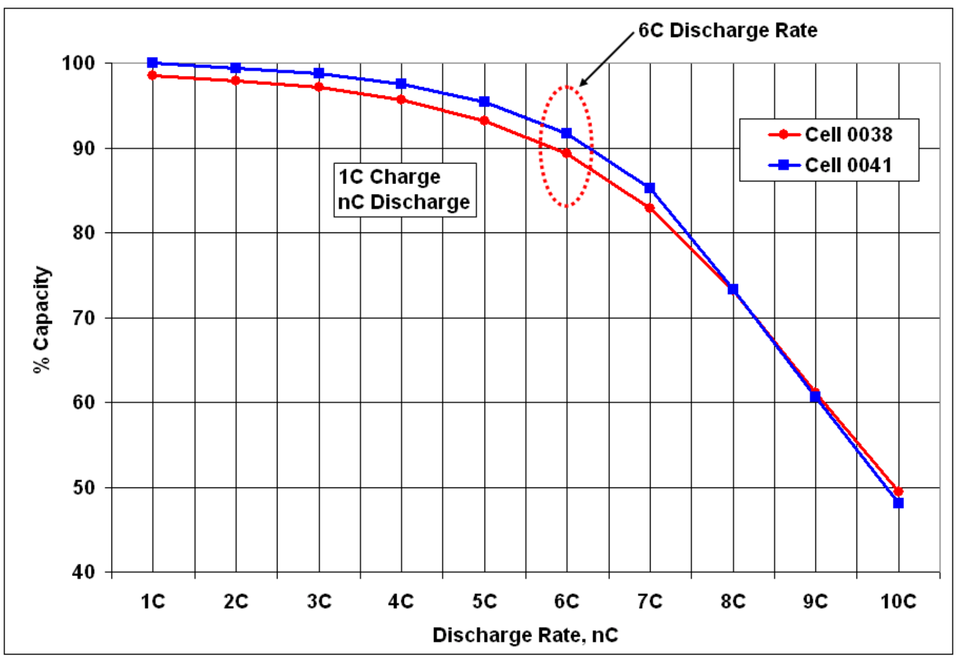

Figure 3: LTO anode-based cell discharge rate

Wider operating temperature range

Conventional lithium ion batteries are intolerant of temperature extremes. Below 0°C and above 50°C the batteries cannot be charged, and above 130°C (a temperature easily reached at the charge and discharge rates required for vehicle applications) they are unsafe due to the potential of thermal runaway.

LTO anode-based batteries can operate at temperatures as low as -50°C and as high as +75°C, all without unsafe characteristics. The ability to perform at wide operating temperatures is important in a variety of applications, such as electric vehicles required to operate in sub-zero conditions, and military operations in severe desert environments.

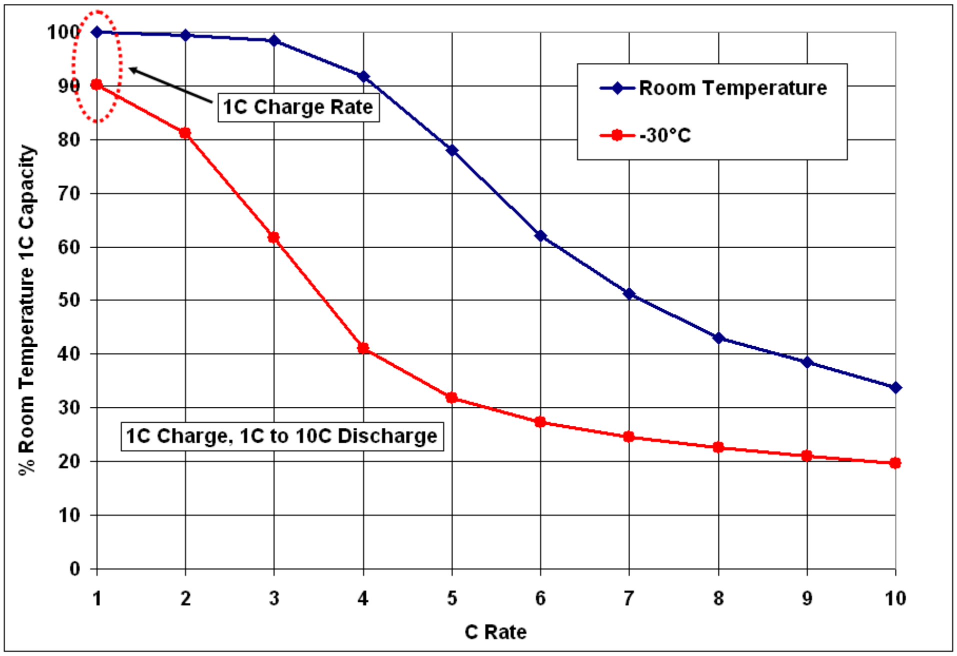

Figure 4: Comparison of room temperature and -30°C charge and discharge performance of LTO-based anode. In this case, the *charge* rate is held constant and the *discharge* rate is varied.

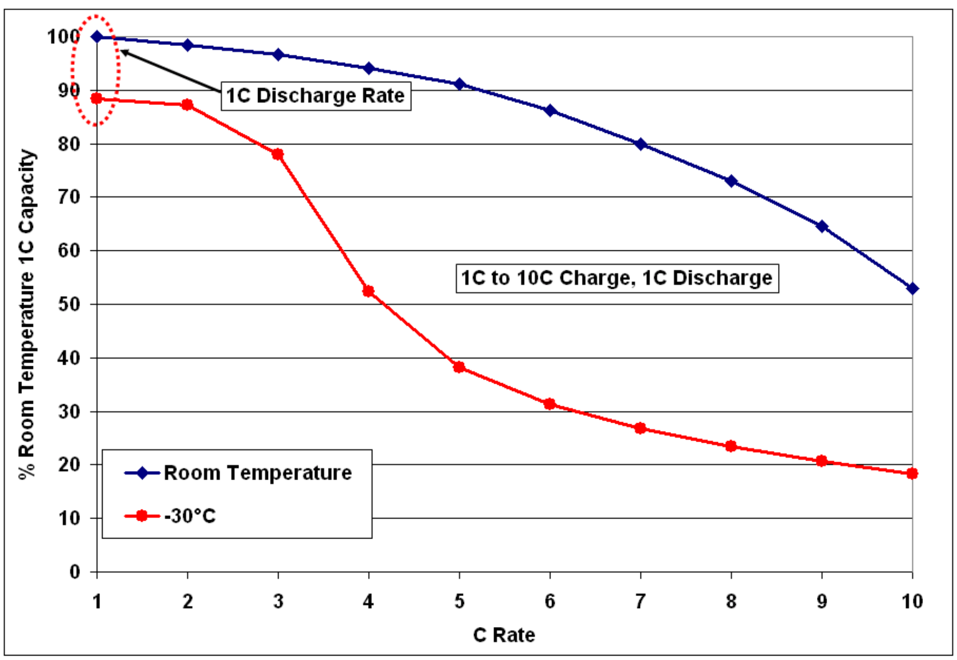

Figure 5: Same comparison as in Figure 4, although in this case, the *discharge* rate is held constant and the *charge* rate is varied.

Nickel Cadmium, PbA, NiMH and Li-Ion batteries have worked relatively well in today's products, but the technology to achieve high performance in battery life (cycle and calendar), safety, recharge time, power delivery, and extreme temperature performance is now readily available. Anode-focused batteries retain the same benefits of conventional lithium ion batteries while eliminating the weaknesses, such as thermal runaway. The future is bright for the rechargeable battery industry and the products that use them.

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