

Will Lithium-Ion Batteries Power the New Millennium?

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For many years, the nickel cadmium battery (NiCd) was the only battery available for portable devices such as wireless communications. In 1990, the nickel metal hydride (NiMH) and lithium-ion batteries emerged, offering higher capacities. Both chemistries fought nose to nose, each claiming better performance and smaller sizes.

Which chemistry will be the true winner and what system will pave the way in the new millennium? The favorite appears to be the lithium-ion family, especially for portables with a small form factor.

The lithium-ion battery is a low-maintenance battery; an advantage that no other chemistry can claim. There is no memory and no scheduled cycling is required to prolong the battery's life. In addition to a high energy density and a light weight, the self-discharge is less than half compared to the NiCd and NiMH, making the lithium-ion battery well suited for modern fuel-gauge applications.

On the negative side, the lithium-ion battery is fragile and requires a protection circuit to maintain safe operation. The load current is moderate and charging must be done according to strict standards. In addition, the lithium-ion battery is subject to aging, whether it is used or not.

History

Pioneering work for the lithium battery began in 1912 by G. N. Lewis, but it was not until the early 1970's when the first nonrechargeable lithium batteries became commercially available. Attempts to develop rechargeable lithium batteries followed in the 1980s, but failed due to safety problems.

Lithium is the lightest of all metals, has the greatest electrochemical potential and provides the largest energy content. Rechargeable batteries using lithium metal as the negative electrodes (anode) are capable of providing both high voltage and excellent capacity, resulting in an extraordinary high-energy density.

After much research on rechargeable lithium batteries during the 1980s, it was found that cycling alters the lithium electrode, thereby reducing its thermal stability and causing potential thermal run-away. If this occurs, the cell temperature quickly approaches the melting point of the lithium, which results in a violent reaction. A large quantity of rechargeable lithium batteries sent to Japan had to be recalled in 1991 after a battery in a cellular phone released hot gases and inflicted burns to a man's face.

Because of the inherent instability of lithium metal, especially during charging, research shifted to a nonmetallic lithium battery using lithium-ions. Although slightly lower in energy density than lithium metal, the lithium-ion is safe, provided certain precautions are met when charging and discharging. In 1991, Sony commercialized the first lithium-ion. Other manufacturers followed suite. Today, the lithium-ion is the fastest growing battery chemistry in the world.

Lithium-Ion Versions

There are several types of lithium-ion batteries that have emerged. Sony's original version used coke as negative electrode (anode). Since 1997, most lithium-ion batteries, including Sony's, shifted to graphite. This electrode provides a flatter discharge voltage curve than coke and offers a sharp knee bend, followed by a rapid voltage drop before the discharge cut-off (see Figure 1). As a result, the useful energy of the graphite system can be retrieved by discharging only to 3.0V of the cell, whereas Sony's coke version must be discharged to 2.5V to get the same performance.

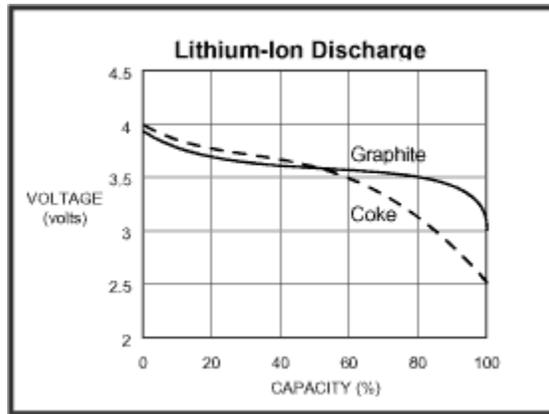


Figure 1. Discharge characteristics of lithium-ion with coke and graphite electrodes.

For the positive electrode (cathode), two distinct chemistries have emerged. They are cobalt and manganese, also known as spinel. Whereas the cobalt has been in use longer, spinel is inherently safer and more forgiving if abused. Protection circuits can be simplified or even eliminated. Small prismatic spinel packs for mobile phones may only include a thermal fuse and temperature sensor. In addition to the added safety, the raw material cost for manganese is lower than cobalt.

As a trade-off, the spinel offers a slightly lower energy density, suffers capacity loss at temperatures above 40 degrees C and ages quicker than cobalt. Figure 2 compares the advantages and disadvantages of the two chemistries.

	Cobalt	Manganese (Spinel)
Energy density (Wh/kg)	140 ¹	120 ¹
Safety	On overcharge, the cobalt electrode provides extra lithium, which can form into metallic lithium, causing a potential safety risk if not protected by a safety circuit.	On overcharge, the manganese electrode runs out of lithium, causing the cell only to get warm. Safety circuits can be eliminated for small one- and two-cell packs.
Temperature	Wide temperature range.	Capacity loss above 40 degrees C.
Aging	Short-term storage is possible, impedance increases with age and newer versions offer longer storage.	Slightly less aging than cobalt, impedance changes little over the life of the cell, and due to continuous improvements, the storage time is difficult to predict.
Life Expectancy	Minimum 300, 50 percent at 500 cycles.	May be shorter than cobalt.
Cost	Raw material is relatively high; protection circuit adds to costs.	Raw material is 30 percent lower than cobalt. Cost advantage on less circuitry.

Figure 2. Comparison of cobalt and manganese as positive electrodes.

¹ Based on present generation 18650 cells. The energy density tends to be lower for prismatic cells.

At present, the NEC Moli Energy Corporation is the only commercial producer of the spinel lithium-ion. While other manufacturers stated that the manganese system is not feasible because of low cycle count, the NEC Moli cells are known to perform as many as 1,000 cycles in a lab condition. Optimizing the cell design, such as carefully selecting materials, attains this performance.

Chemicals and additives help to balance the critical trade-offs between high energy density, long storage time, extended cycle life and safety. High energy densities can be achieved with relative ease. For example, adding more nickel in lieu of cobalt increases the ampere-per-hour rating and lowers the manufacturing cost, but makes the cell less safe. While a start-up company may focus on high energy density to gain quick market acceptance, the safety, cycle life and storage may be compromised. Reputable manufacturers, such as Sony, Panasonic, Sanyo and NEC Moli place high importance on safety.

Although lithium-ion cells have some environmental impact, they cause less harm when disposing than lead- or cadmium-based batteries. Among the lithium-ion battery family, the spinel is the friendliest.

Charging the Lithium-Ion Battery

The lithium-ion charger is a voltage-limiting device similar to that of the valve regulated lead-acid (VRLA) charger. The main differences of the lithium-ion charger are higher voltage per cell, tighter voltage tolerance, and the absence of trickle or float charge at full charge.

Whereas the VRLA offers some flexibility in terms of voltage cut-off, the manufacturers of lithium-ion cells are very strict about the voltage choice. When first introduced, the charge voltage limit of the graphite system was 4.10V per cell. Although higher voltages deliver increased energy density, cell oxidation severely limited the service life in the early graphite cells if charged above the 4.10V-per-cell threshold. This effect has now been solved with chemical additives and most new lithium-ion cells are now set to 4.20V. The tolerance on all lithium-ion batteries is a tight +/- 0.05V per cell.

The charge time of all lithium-ion batteries is about three hours at a 1C initial charge current. The battery remains cool during charge. Full charge is attained after the voltage reaches the upper voltage threshold and the current drops and levels off at about three percent of its nominal rating, or about 0.03C.

Increasing the charge current on a lithium-ion charger does not shorten the charge time by much. Although the voltage peak is reached quicker with a higher current, the topping charge will take longer. Figure 3 shows the voltage and current signature of a charger as the lithium-ion cell passes through stages one and two.

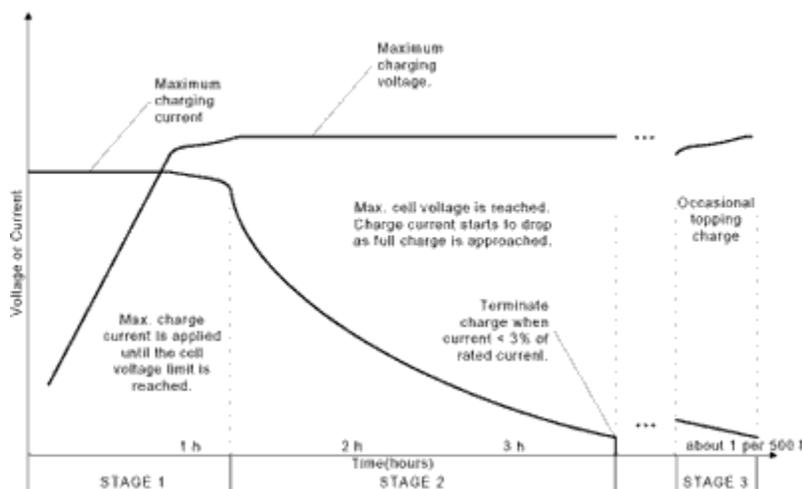


Figure 3. Charge stages of a lithium-ion battery.

Claims of fast charging a lithium-ion battery in one hour or less usually results in lower charge levels. Such a charger simply eliminates stage 2 and goes directly into "ready" once the voltage threshold is reached at the end of stage 1. The charge level at this point is about 70 percent. The topping charge typically takes twice as long as the initial charge.

No trickle charge is applied because the lithium-ion is unable to absorb overcharge. Trickle charge could cause plating of metallic lithium, a condition that renders the cell unstable. Instead, a brief topping charge is applied to compensate for the small amount of self-discharge the battery and its protective circuit consume. Depending on the charger and the self-discharge of the battery, a topping charge may be implemented once every 500 hours or 20 days. Typically, the charge kicks in when the open terminal voltage drops to 4.05V per cell and turns off when it reaches 4.20V per cell.

Protection Circuit

Commercial lithium-ion battery packs contain redundant protection devices to ensure safety under all circumstances. Typically, a field effect transistor opens if the charge voltage of any cell reaches 4.30V, and a fuse activates if the cell temperature approaches 90 degrees C. In addition, a pressure switch in each cell permanently interrupts the charge current if a safe pressure threshold is exceeded, and internal voltage control circuits cut off the battery at low and high voltage points. Exceptions are made to prismatic and cylindrical spinel packs containing one or two cells.

The lithium-ion is typically discharged to 3V per cell. The lowest "low-voltage" power cut-off is 2.5V per cell. During prolonged storage, however, a discharge below this voltage level is possible. Manufacturers recommend a "trickle" charge to gradually raise such a battery back up into the "acceptable" voltage window. Not all chargers are designed to apply a charge once a lithium-ion battery has dipped below 2.5V per cell.

Some batteries feature an ultra-low voltage cut-off that permanently disconnects the pack if a cell dips below 1.5V. This precaution is done to prohibit recharge if a battery has dwelled in an illegal voltage state. A deep discharge causes copper plating, which can lead to a short circuit in the cell.

Most manufactures do not sell the lithium-ion cells by themselves, but make them available in a battery pack, complete with a protection circuit. This precaution is understandable when considering the danger of explosion and fire if the battery is charged and discharged beyond its safe limits.

A major concern arises if static electricity or a faulty charger has managed to destroy the battery's protection circuit. Such damage often causes the solid-state switches to fuse to a permanent "on" position without the user's knowledge. A battery with a faulty protection circuit may function normally, but does not provide the required safety. If charged beyond the safe voltage limits with a poorly designed accessory charger, the battery may heat up, then bulge and, in some cases, vent with flame. Shorting such a battery can also be hazardous.

Analyzers for the Lithium-Ion Batteries

In the past, battery analyzers were used to restore batteries affected by "memory". With today's nickel-free batteries, memory is no longer a problem and the emphasis of an analyzer is shifting to battery performance verification, quality control and quick-test.

Conventional wisdom says that a new battery always performs flawlessly. Yet many users have learned that a battery fresh from the shrink-wrap does not always meet manufacturer's specifications. With a battery analyzer, all incoming batteries can be checked as part of a quality-control procedure. In addition, warranty claims can be made if the capacity drops below the specified level at the end of the warranty period.

A typical life of a lithium-ion is 300 to 500 discharge/charge cycles or two years from time of manufacturing. The loss of battery capacity occurs gradually and often without the knowledge of the user. Although fully charged, the battery eventually regresses to a point where it may hold less than half of its original capacity. The function of the battery analyzer is to identify these weak batteries and "weed" them out.

A battery analyzer can also be used to troubleshoot the cause of short runtimes. The charger may not provide a full charge or the portable device may draw more current than expected. Many of today's battery analyzers can simulate the load signature of a digital device and verify the runtime based on the available battery capacity.

Perhaps the most important feature of modern battery analyzers is its ability to read the internal battery resistance. As part of natural aging, the internal resistance of a lithium-ion battery gradually increases due to cell oxidation. The higher the resistance, the less energy the battery can deliver.

Cadex Electronics Inc. has developed the OhmTest, a proprietary pulse method to measure the internal battery resistance. Available with the C7000 battery analyzers, the OhmTest enables testing of a large volume of batteries in a matter of minutes, and a milliohm reading can be obtained in five seconds without discharging the battery. This technique is especially useful for organizations that need to verify the state-of-health of a batch of batteries before release.



Figure 4. The Cadex C7000 battery analyzer measures internal battery resistance. The milliohm readings can be read as part of a quick-battery test or can be included in the recondition program.

It should be noted that OhmTest does not provide definite conclusions as to the state-of-charge and state-of-health of a battery. The readings may vary widely and depend on the battery chemistry, cell size (mAh rating), type of cell, number of cells connected in series, protection circuit, and wiring and contact type. The state-of-charge at the time the reading is taken also plays a roll. A battery must have at least a 50 percent charge to obtain a meaningful milliohm reading. Solid terminal connection is essential because a poor contact will provide a high milliohm reading. Alligator connections and long battery leads are not suitable.

To utilize the OhmTest as a battery validation, it is essential to obtain a reference reading of a good battery with a known performance. Because each battery type may be different, a reference reading will be required for each model.

Conclusion

The lithium-ion receives good grades in performance and reliability. Supply shortages have eased and prices have become affordable. As a result, more portable equipment is being fitted with the lithium-ion battery.

The lithium-ion has found a strong market niche with portable devices demanding small form factors. The most popular uses are cellular phones and notebook computers. Because of the aging aspect, the lithium-ion is most suitable for applications with a hectic user pattern. Where the lithium-ion falls short is on high-current applications and operations that regularly need a full discharge. Typical applications for which the lithium-ion is less suited are power tools, heart defibrillators and mobile radios for public safety.

Another field where the lithium-ion has proven less favorable is in applications that require occasional battery use. On a laptop that is mostly powered by ac, for example, the lithium-ion battery ages in time and the full benefit of the battery cannot be realized. For these applications, other battery chemistries may serve better. High heat levels inside some laptops also cause the lithium-ion to fail prematurely. However, field tests have revealed that the lithium-ion is less affected by heat than the NiMH.

The lithium-polymer systems that are in early production states are struggling to meet and surpass the performance of the lithium-ion battery. High initial costs and limited supplies are the main drawbacks. Once mass-produced, the lithium-polymer is expected to be lower in cost than the lithium-ion because simpler packaging methods are possible.

On the positive, the lithium-polymer provides slightly higher energy densities and reduced weight. No standard form factor has been established for the lithium-polymer because this battery can be formed into virtually any shape and size. Someday, the battery may be part of the protective housing or serve as a soft carrying case.