Lithium-based Batteries

Pioneer work with the lithium battery began in 1912 under G.N. Lewis, but it was not until the early 1970s that the first non-rechargeable lithium batteries became commercially available. Attempts to develop rechargeable lithium batteries followed in the 1980s but the endeavor failed because of instabilities in the metallic lithium used as anode material.

Lithium is the lightest of all metals, has the greatest electrochemical potential and provides the largest specific energy per weight. Rechargeable batteries with lithium metal on the anode (negative electrodes)* could provide extraordinarily high energy densities; however, it was discovered in the mid 1980s that cycling produced unwanted dendrites on the anode. These growth particles penetrate the separator and cause an electrical short. When this occurs, the cell temperature rises quickly and approaches the melting point of lithium, causing thermal runaway, also known as “venting with flame.” A large number of rechargeable metallic lithium batteries sent to Japan were recalled in 1991 after a battery in a mobile phone released flaming gases and inflicted burns to a man’s face.

The inherent instability of lithium metal, especially during charging, shifted research to a non-metallic solution using *lithium ions*. Although lower in specific energy than lithium-metal, Li-ion is safe, provided cell manufacturers and battery packers follow safety measures in keeping voltage and currents to secure levels. Read more about Protection Circuits. In 1991, Sony commercialized the first Li-ion battery, and today this chemistry has become the most promising and fastest growing on the market. Meanwhile, research continues to develop a safe metallic lithium battery.

The specific energy of Li-ion is twice that of NiCd, and the high nominal cell voltage of 3.60V as compared to 1.20V for nickel systems contributes to this gain. Improvements in the active materials of the electrode have the potential of further increases in energy density. The load characteristics are good, and the flat discharge curve offers effective utilization of the stored energy in a desirable voltage spectrum of 3.70 to 2.80V/cell. Nickel-based batteries also have a flat discharge curve that ranges from 1.25 to 1.0V/cell.

In 1994, the cost to manufacture Li-ion in the 18650** cylindrical cell with a capacity of 1,100mAh was more than $10. In 2001, the price dropped to $2 and the capacity rose to 1,900mAh. Today, high energy-dense 18650 cells deliver over 3,000mAh and the costs have dropped further. Cost reduction, increase in specific energy and the absence of toxic material paved the road to make Li-ion the universally accepted battery for portable application, first in the consumer industry and now increasingly also in heavy industry, including electric powertrains for vehicles.

In 2009, roughly 38 percent of all batteries by revenue were Li-ion. Li-ion is a low-maintenance battery, an advantage many other chemistries cannot claim. The battery has no memory and does not need exercising (deliberate full discharge) to keep in shape. Self-discharge is less than half that of nickel-based systems. This makes Li-ion well suited for fuel gauge applications. The nominal cell voltage of 3.60V can directly power cell phones and digital cameras, offering simplifications and cost reductions over multi-cell designs. The drawbacks are the need for protection circuits to prevent abuse, as well as high price.

Types of Lithium-ion Batteries

Similar to the lead- and nickel-based architecture, lithium-ion uses a cathode (positive electrode), an anode (negative electrode) and electrolyte as conductor. The cathode is a metal oxide and the anode consists of porous carbon. During discharge, the ions flow from the anode to the cathode through the electrolyte and separator; charge reverses the direction and the ions flow from the cathode to the anode. Figure 1 illustrates the process.

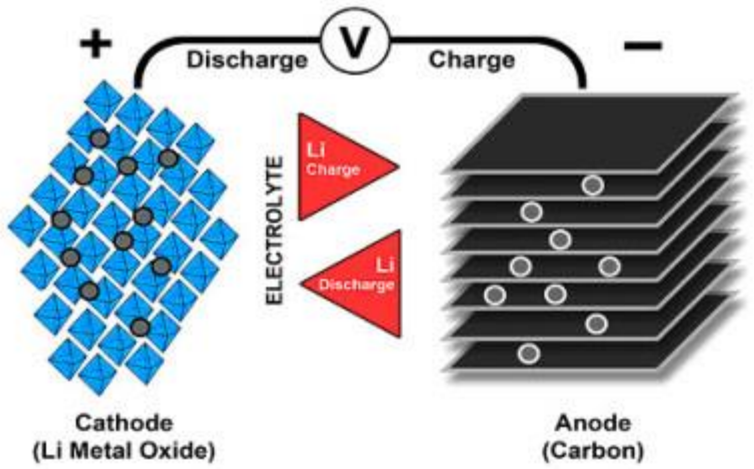

Figure 1: Ion flow in lithium-ion battery. When the cell charges and discharges, ions shuttle between cathode (positive electrode) and anode (negative electrode). On discharge, the anode undergoes oxidation, or loss of electrons, and the cathode sees a reduction, or a gain of electrons. Charge reverses the movement.

Li-ion batteries come in many varieties but all have one thing in common — the catchword “lithium-ion.” Although strikingly similar at first glance, these batteries vary in performance, and the choice of cathode materials gives them their unique personality.

Common cathode materials are *Lithium Cobalt Oxide* (or Lithium Cobaltate), *Lithium Manganese Oxide* (also known as spinel or Lithium Manganate), *Lithium Iron Phosphate,* as well as *Lithium Nickel Manganese Cobalt* (or NMC)*** and *Lithium Nickel Cobalt Aluminum Oxide* (or NCA). All these materials possess a theoretical specific energy with given limits. (Lithium-ion has a theoretically capacity of about 2,000kWh. This is more than 10 times the specific energy of a commercial Li-ion battery.)

Sony’s original lithium-ion battery used coke as the anode (coal product). Since 1997, most Li-ion manufacturers, including Sony, have shifted to *graphite* to attain a flatter discharge curve. Graphite is a form of carbon that is also used in the lead pencil. It stores lithium-ion well when the battery is charged and has long-term cycle stability. Among the carbon materials, graphite is the most commonly used, followed by hard and soft carbons. Other carbons, such as carbon nanotubes, have not yet found commercial use. Figure 2-8 illustrates the voltage discharge curve of a modern Li-ion with graphite anode and the early coke version.

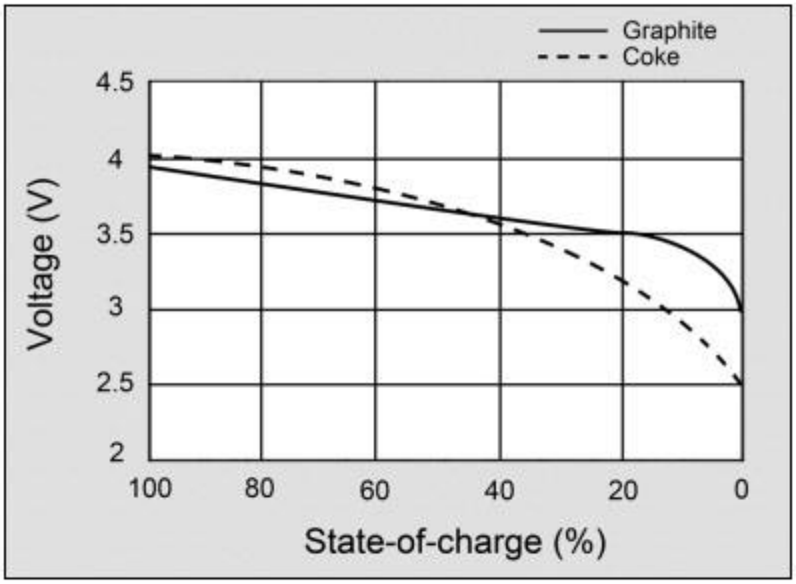

Figure 2: Voltage discharge curve of lithium-ion

A battery should have a flat voltage curve in the usable discharge range. The modern graphite anode does this better than the early coke version.

Courtesy of Cadex

Developments also occur on the anode and several additives are being tried, including silicon-based alloys. Silicon achieves a 20 to 30 percent increase in specific energy at the cost of lower load currents and reduced cycle life. Nano-structured *lithium-titanate* as an anode additive shows promising cycle life, good load capabilities, excellent low-temperature performance and superior safety, but the specific energy is low.

Mixing cathode and anode material allows manufacturers to strengthen intrinsic qualities; however, enhancing one attribute may compromise another. Battery makers can, for example, optimize the specific energy (capacity) to achieve extended runtime, increase the specific power for improved current loading, extend service life for better longevity, and enhance safety to endure environmental stresses. But there are drawbacks. A higher capacity reduces the current loading; optimizing current loading lowers the specific energy; and ruggedizing a cell for long life and improved safety increases battery size and adds to cost due to a thicker separator. The separator is said to be the most expensive part of a battery.

Manufacturers can attain a high specific energy and low cost relatively easily by adding nickel in lieu of cobalt, but this makes the cell less stable. While a start-up company may focus on high specific energy to gain quick market acceptance, safety and durability cannot be compromised. Reputable manufacturers place high integrity on safety and longevity.

Table 3 summarizes the characteristics of Li-ion with different cathode material. The table limits the chemistries to the four most commonly used lithium-ion systems and applies the short form to describe them. The batteries are *Li-cobalt, Li-manganese, Li-phosphate* and *NMC.* NMC stands for nickel-manganese-cobalt, a chemistry that is relatively new and can be tailored for applications needing either high capacity or high loading capabilities. Lithium-ion-polymer is not mentioned as this is not a unique chemistry and only differs in construction. Li-polymer can be made in various chemistries and the most widely used format is Li-cobalt.

Specifications	**Li-cobalt** $LiCoO_2$ (LCO)	**Li-manganese** $LiMn_2O_4$ (LMO)	**Li-phosphate** $LiFePO_4$ (LFP)	**NMC**[1] $LiNiMnCoO_2$
Voltage	3.60V	3.80V	3.30V	3.60/3.70V
Charge limit	4.20V	4.20V	3.60V	4.20V
Cycle life[2]	500–1,000	500–1,000	1,000–2,000	1,000–2,000
Operating temperature	Average	Average	Good	Good
Specific energy	150–190Wh/kg	100–135Wh/kg	90–120Wh/kg	140-180Wh/kg
Specific power	1C	10C, 40C pulse	35C continuous	10C
Safety	Average. Requires protection circuit and cell balancing of multi cell pack. Requirements for small formats with 1 or 2 cells can be relaxed		Very safe, needs cell balancing and V protection.	Safer than Li-cobalt. Needs cell balancing and protection.
Thermal. runaway[3]	150°C (302°F)	250°C (482°F)	270°C (518°F)	210°C (410°F)
Cost	Raw material high	Moli Energy, NEC, Hitachi, Samsung	High	High
In use since	1994	1996	1999	2003
Researchers, manufacturers	Sony, Sanyo, GS Yuasa, LG Chem Samsung Hitachi, Toshiba	Hitachi, Samsung, Sanyo, GS Yuasa, LG Chem, Toshiba Moli Energy, NEC	A123, Valence, GS Yuasa, BYD, JCI/Saft, Lishen	Sony, Sanyo, LG Chem, GS Yuasa, Hitachi Samsung
Notes	Very high specific energy, limited power; cell phones, laptops	High power, good to high specific energy; power tools, medical, EVs	High power, average specific energy, safest lithium-based battery	Very high specific energy, high power; tools, medical, EVs

Table 3: Characteristics of the four most commonly used lithium-ion batteries
Specific energy refers to capacity (energy storage); specific power denotes load capability.

[1] NMC, NCM, CMN, CNM, MNC and MCN are basically the same. The stoichiometry is usually Li[Ni(1/3)Co(1/3)Mn(1/3)]O2. The order of Ni, Mn and Co does not matter much.

[2] Application and environment govern cycle life; the numbers do not always apply correctly.

[3] A fully charged battery raises the thermal runaway temperature, a partial charge lowers it.

Never was the competition to find an ideal battery more intense than today. Manufacturers see new applications for automotive propulsion systems, as well as stationary and grid storage, also knows as load leveling. At time of writing, the battery industry speculates that the Li-manganese and/or NMC might be the winners for the electric powertrain.

Industry’s experience has mostly been in portable applications, and the long-term suitability of batteries for automotive use is still unknown. A clear assessment of the cycle life, performance and long-term operating cost will only be known after having gone through a few generations of batteries for vehicles with electric powertrains, and more is known about the customers’ behavior and climate conditions under which the batteries are exposed. Table 4 summarizes the advantages and limitations of Li-ion.

Advantages	High energy density Relatively low self-discharge; less than half that of NiCd and NiMH Low maintenance. No periodic discharge is needed; no memory.
Limitations	Requires protection circuit to limit voltage and current Subject to aging, even if not in use (aging occurs with all batteries and modern Li-ion systems have a similar life span to other chemistries) Transportation regulations when shipping in larger quantities

Table 4: Advantages and limitations of Li-ion batteries

* When consuming power, as in a diode, vacuum tube or a battery on charge, the anode is positive; when withdrawing power, as in a battery on discharge, the anode becomes negative.

** Standard of a cylindrical Li-ion cell developed in the mid 1990s; measures 18mm in diameter and 65mm in length; commonly used for laptops. Read more about Battery Formats.

*** Some Lithium Nickel Manganese Cobalt Oxide systems go by designation of NCM, CMN, CNM, MNC and MCN. The systems are basically the same.

Cycle Performance for Various Batteries

As part of ongoing research to examine performance degradation caused by cycling, Cadex tested a large volume of portable batteries for wireless communication devices. The population consists of nickel-cadmium, nickel-metal-hydride and lithium-ion. The batteries were prepared by applying an initial charge, followed by a regime of full discharge/charge cycles. The internal resistance was measured with *OhmTest*™ and the self-discharge was obtained from time to time by reading the capacity loss incurred during a 48-hour rest period. The tests were carried out on the *Cadex 7000 Series*battery analyzers.

Nickel-cadmium

In terms of life cycling, nickel-cadmium is the most enduring battery. Figure 1 illustrates the capacity, internal resistance and self-discharge of a 7.2V, 900mA pack with standard NiCd cells. Due to time constraints, the test was terminated after 2,300 cycles. The capacity remained steady; the internal resistance stayed low at 75mWand the self-discharge was stable. This battery receives a grade “A” rating for almost perfect performance.

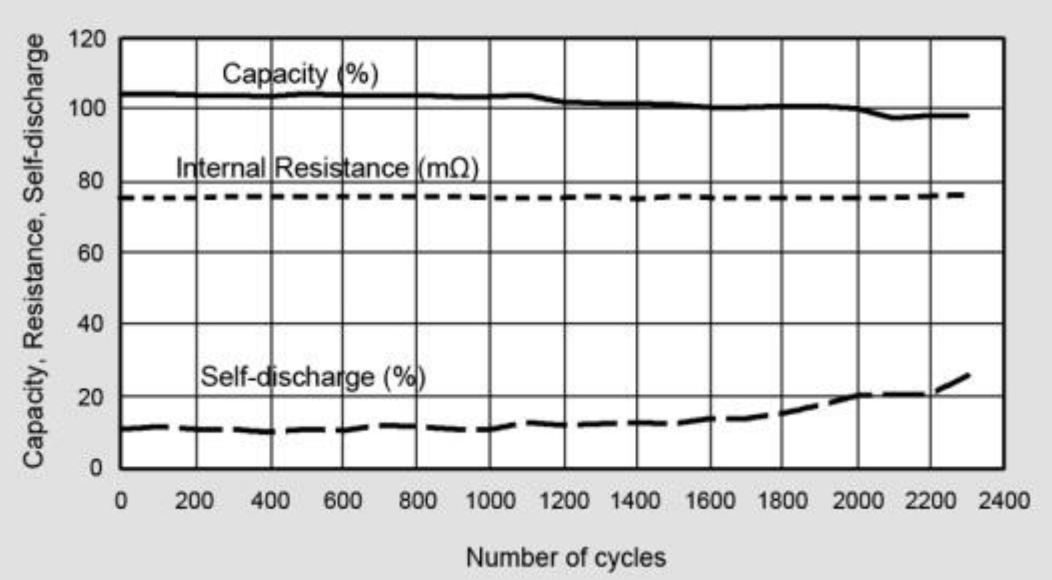

Figure 1: Performance of standard NiCd (7.2V, 900mAh)
This battery receives an “A” rating for a stable capacity, low internal resistance and moderate self-discharge over many cycles.

Courtesy of Cadex

The *ultra-high-capacity* nickel-cadmium offers up to 60 percent higher specific energy compared to the standard version, however, this comes at the expense of reduced cycle life. In Figure 2 we observe a steady drop of capacity during 2,000 cycles, a slight increase in internal resistance and a rise in self-discharge after 1,000 cycles.

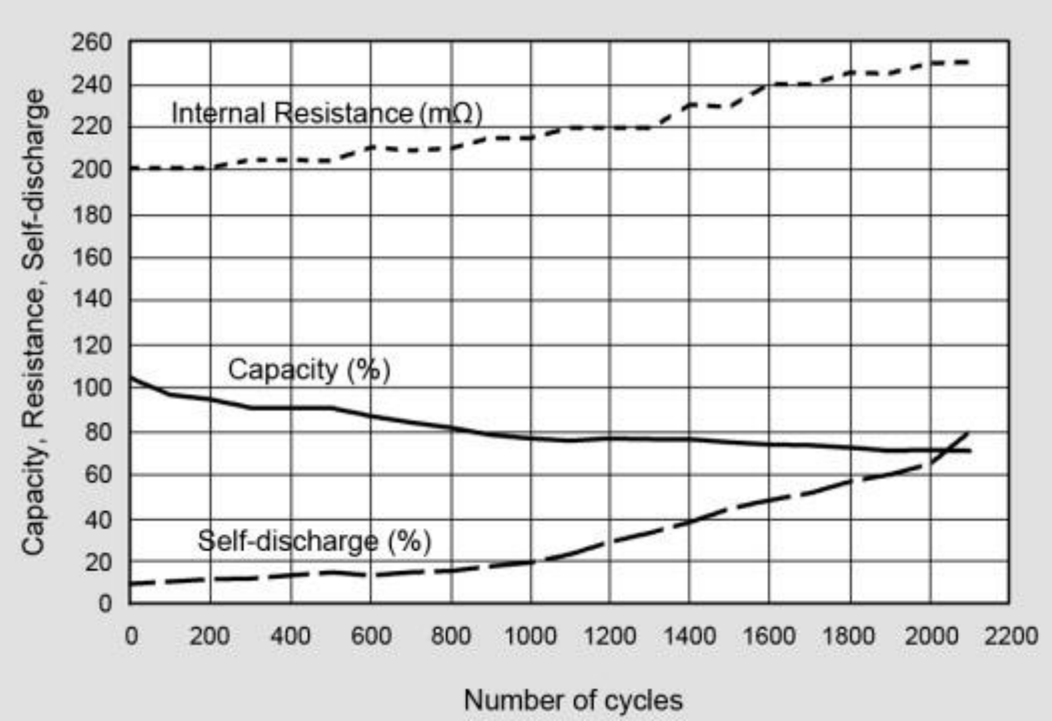

Figure 2: Performance of ultra-high-capacity NiCd (6V, 700mAh)
This battery offers higher specific energy than the standard version at the expense of reducedcycle life.

Courtesy of Cadex

Nickel-metal-hydride

Figure 3 examines NiMH, a battery that offers high specific energy at a reasonably low cost. We observe good performance at first but past the 300-cycle mark, the capacity starts to drift downwards rapidly. One can detect a swift increase in internal resistance and self-discharge after cycle count 700. NiMH has a higher specific energy than nickel-cadmium and does not contain toxic metals. The test battery was an older generation; new NiMH performs better.

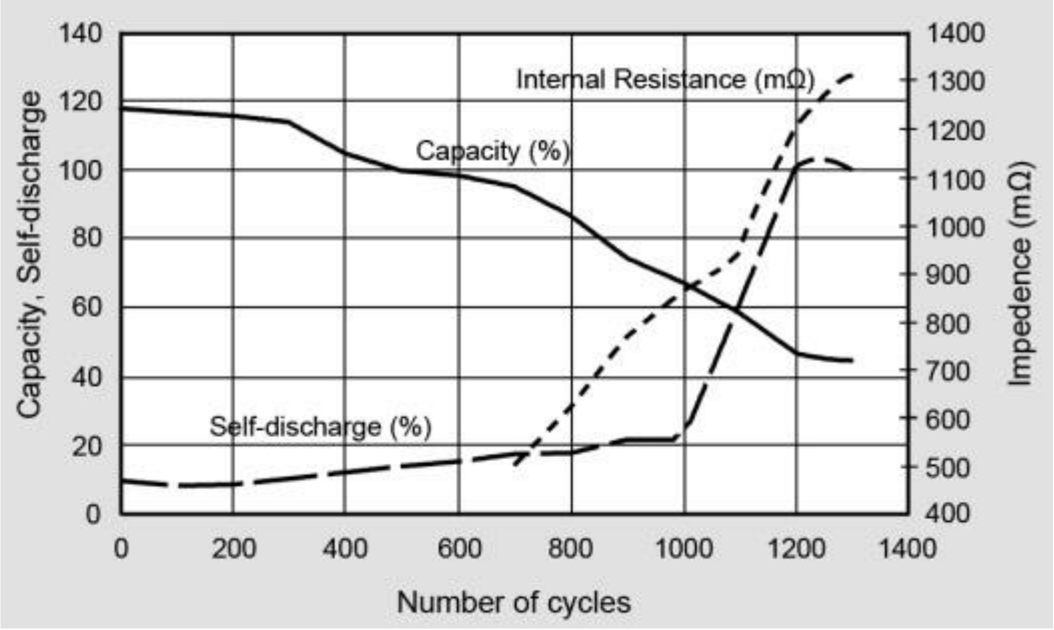

Figure 3: Performance of NiMH (6V, 950mAh)
This battery offers good performance at first but past 300 cycles, the capacity, internal resistance and self-discharge start to increase rapidly. Newer NiMH has better results.

Courtesy of Cadex

Lithium-ion

Figure 4 examines the capacity and internal resistance of lithium-ion. We observe a gentle and predictable capacity drop over 1,000 cycles while the internal resistance increases only slightly. Because of low readings, we omit self-discharge. Lithium-ion offers the highest specific energy among the above-mentioned chemistries, contains little or no toxic metals, but needs protection circuits to ensure safe operation. Li-ion is also more expensive to manufacture than the nickel-based equivalent.

Batteries tested in a laboratory environment tend to give better results than when used in the field; elements of stress in everyday use do not transfer well into the laboratory. Aging plays a minimal role in a lab because the batteries are cycled over a period of a few months rather than the expected service life of a few years. The temperature is often moderate and the batteries are charged with proper charge equipment, an advantage that the field cannot always claim.

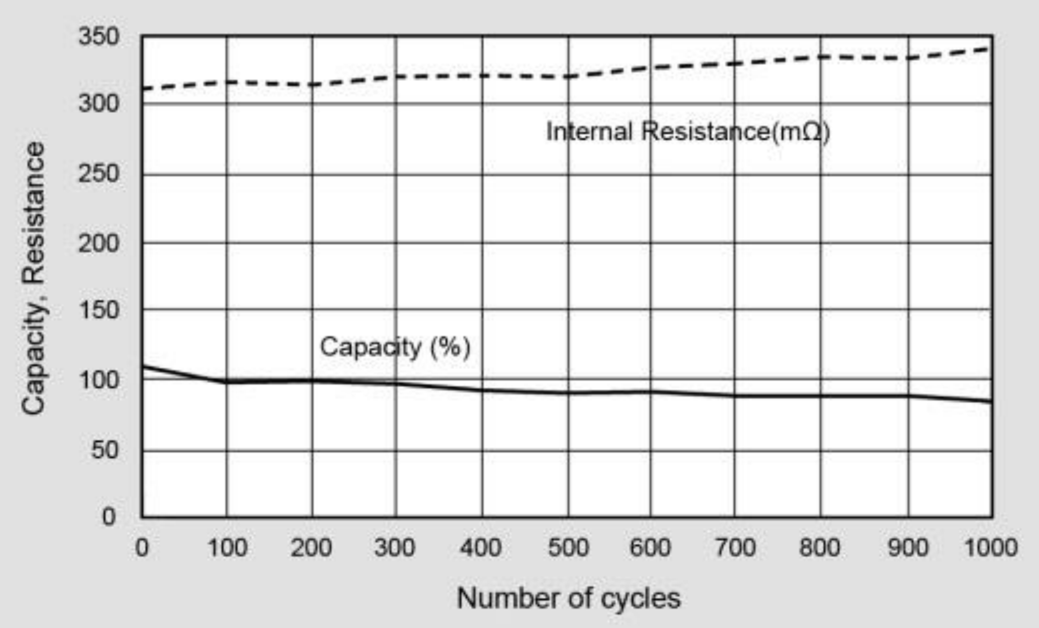

Figure 4: Performance of lithium-ion (3.6V, 500mA)
Lithium-ion offers good capacity and steady internal resistance over 1,000 cycles.
Self-discharge was omitted because of low readings

Courtesy of Cadex

The load signature of the discharge plays an important role when testing batteries, and our laboratory batteries were discharged with an even DC load. Cellular phones and other digital devices draw pulsed loads that stress the battery more than with DC. One could argue, however, that the lab tests apply a full discharge whereas the field user discharges the battery to about 80 percent. The degradation of a battery receiving a 100 percent discharge with a DC load may not be the same as an 80 percent discharge on a pulsed load, and we keep this possible discrepancy in mind when studying the results.

The tests were done with batteries from an earlier generation. Newer models show improved results, and this is especially apparent with NiMH. The internal resistance of the modern NiMH is similar to NiCd, so is the cycle life. The Li-ion battery tested was Li-cobalt for cellular phones. We excluded lead acid from the test because this battery is seldom used for portable applications. Lead acid is heavy and does not cycle well, especially on full discharges.

The outcome of battery tests depends very much on the application for which the battery is designed, and we distinguish between consumer and industrial use. With the advent of the electric powertrain, a new category of batteries is emerging. Built for safety and longevity, these batteries have a specific energy that is typically only one-half that of consumer batteries.