# Understanding Lithium-ion

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, cycling produced unwanted dendrites on the anode that could penetrate the separator and cause an electrical short. The cell temperature would rise quickly and approaches the melting point of lithium, causing thermal runaway, also known as “venting with flame.”

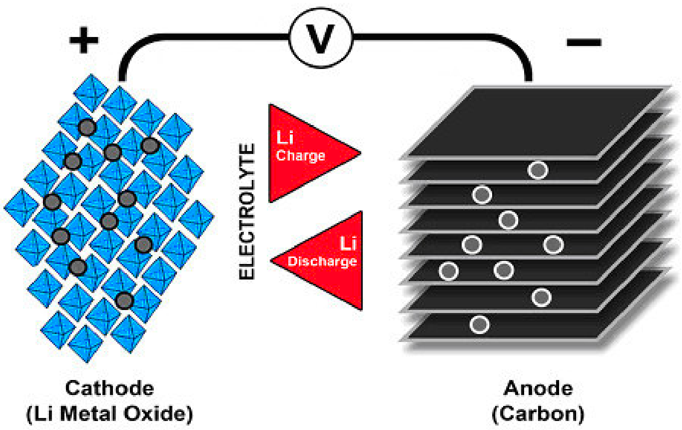
The inherent instability of lithium metal, especially during charging, shifted research to a non-metallic solution using lithium ions. Although lower in specific energy than lithium-metal, Li-ion is safe, provided cell manufacturers and battery packers follow safety measures in keeping voltage and currents to secure levels. 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 in the hope to make it safe.

In 1994, it cost more than $10 to manufacture Li-ion in the 18650* cylindrical cell delivering a capacity of 1,100mAh. 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 acceptable 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 to keep in shape. Self-discharge is less than half compared to nickel-based systems. This makes Li-ion well suited for fuel gauge applications. The nominal cell voltage of 3.6V can power cell phones and digital cameras directly, offering simplifications and cost reductions over multi-cell designs. The drawback has been the high price, but this leveling out, especially in the consumer market.

## Lithium Manganese Oxide (LiMn2O4) — LMO

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.

All materials in a battery possess a theoretical specific energy, and the key to high capacity and superior power delivery lies primarily in the cathode. For the last 10 years or so, the cathode has characterized the Li-ion battery. Common cathode material 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).

Sony's original lithium-ion battery used coke as the anode (coal product), and since 1997 most Li-ion batteries use graphite to attain a flatter discharge curve. 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 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, an enhancement in one area may compromise something else. Battery makers can, for example, optimize specific energy (capacity) for extended runtime, increase specific power for improved current loading, extend service life for better longevity, and enhance safety for strenuous environmental exposure, but, the drawback on higher capacity is reduced loading; optimization for high current handling lowers the specific energy, and making it a rugged cell for long life and improved safety increases battery size and adds to the cost due to a thicker separator. The separator is said to be the most expensive part of a battery.

Table 2 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. NMC stands for nickel-manganese-cobalt, a chemistry that is relatively new and can be tailored for high capacity or high current loading. 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 | Li-manganese | Li-phosphate | NMC [1] |
|---|---|---|---|---|
| **Voltage** | 3.60V | 3.70V | 3.30V | 3.60/3.70V |
| **Charge limit** | 4.20V | 4.20V | 3.60V | 4.20V |
| **Cycle life** [2] | 500 | 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 | 140Wh/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 | Average. Requires protection circuit and cell balancing of multi cell pack. Requirements for small formats with 1 or 2 cells can be relaxed | Very good, needs cell balancing and V protection | Good, needs cell balancing and voltage protection |
| **Thermal runaway** [3] | 150°C (302°F) | 250°C (482°F) | 270°C (518°F) | 210°C (410°F) |
| **Cost** | Raw material high | Material 30% less than cobalt | High | High |
| **In use since** | 1994 | 2002 | 1999 | 2003 |
| **Researchers, manufacturers** | Sony, Sanyo, FDK, Saft | NEC, Samsung, Hitachi | UT, QH, MIT A123, Valence | Sony, Sanyo, Nissan Motor |
| **Notes** | Very high specific energy, limited power; for cell phones, laptops | High power, average to high specific energy, power tools, medical, EVs | High power, average specific energy, higher self-discharge than other Li-ion | Very high specific energy, high power; tools, medical, EVs |

# Table 2: 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. |

* Standard of a cylindrical Li-ion cell developed in the mid 1990s; measures 18mm in diamter and 65mm in length; commonly used for laptops.

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

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