Lithium-ion Batteries - Cathode and Anode Material

By Mark Bowler

The lithium-ion battery (LIB) is currently one of the most popular types of rechargeable battery and is utilized for numerous commercial applications. The battery's popularity is due to its slow loss of charge, comparatively high energy density, no memory effect and lower weight than comparative products. Initially used for consumer electronics, LIBs are of primary importance for their suitability for electric vehicle (EV) and hybrid electric vehicle (HEV) applications. Economic potential has seen intensive worldwide research resulting in lower production costs and in advances in the technology of safety, energy density and efficiency.

The U.S. Department of Transport reports that the national average distance driven by U.S. citizens per day is approximately 50 miles, falling well within the range of modern electric vehicles. The decreased running cost of electric vehicles, coupled with the range of ecologically proven benefits of battery driven vehicles has stimulated interest to the extent that demand continues to grow dramatically on a yearly basis.

Electrochemistry

The electrochemical reactions in a lithium-ion battery occur between the anode, cathode, and electrolyte. Both anode and cathode are constructed of materials which allow lithium to migrate in and out of the electrode. Lithium moves into the electrode in a process known as insertion and out of the electrode in the process of extraction. During the charging of a lithium-based battery, lithium is inserted into the anode and extracted from the cathode; the reverse process occurs when the battery discharges.

Materials used for components

The anode is generally constructed of graphite. One of three materials is usually used for the cathode: a layered oxide (such as lithium cobalt oxide), a polyanion (such as lithium iron phosphate), or a spinel (such as lithium manganese oxide).

The electrolyte usually consists of lithium ions suspended in organic carbonates, of which diethyl carbonate and ethylene carbonate are most often utilized. These non-aqueous electrolytes generally use non-coordinating anion salts such as lithium hexafluorophosphate (LiPF6), lithium hexafluoroarsenate monohydrate (LiAsF6), lithium perchlorate (LiClO4), lithium tetrafluoroborate (LiBF4), and lithium triflate (LiCF3SO3).

However, the choice of material of which the cathode and anode are constructed from has a major influence in the performance and characteristics of the battery. Voltage, charge time, capacity, safety and durability are all directly affected by the characteristics of differing electrodes. While most LIB's produced commercially have a carbon-based anode, a number of cathode chemistries exist. Much of the research into improving the efficiency if LIB's over the last twenty years has been based on finding and improving on cathode materials.

Cathodes

Manganese spinel ($LiMn^{2}O^{4}$)[1]

First developed for battery use in 1996, Lithium manganese spinel was identified as a suitable material due to the benefits it provided in durability and cost. One of the primary concerns for Li-ion battery development is the specification for cheaper, environmentally friendly cathode material with improved electrochemical qualities. Lithium manganese spinel is one of the leading contenders in this regard. For application as a cathode, manganese spinel needs development to improve its operating range, specific energy per weight and volume, and extending its cycling life.

Lithium manganese spinel is currently utilized in the Chevrolet Volt and the Nissan Leaf due to its increased power and safety over lithium cobalt oxide batteries used in consumer electronics. While spinel-based cathodes have high safety level, they have a shortcoming in not being able to store as much energy as many other cathode applications. The challenge of battery chemistry is in finding a suitable blend of the characteristics that the automotive industry requires in an electric car battery, namely high power, high energy density, durability and safety. Battery manufacturers have recently discovered that by mixing the high-energy battery-electrode chemistry from Argonne National Laboratory with manganese spinel, many of these objectives can be attained[2].

For future development, nanotechnology provides a means by which these improvements can be attained and for managing the structure of manganese spinel. Nano-structured lithium manganese spinel was created by Enerize technology, where the high density and conductivity of the proprietary Enerize manganese oxide was utilized as a starting material for spinel synthesis. During the synthesis process, gradual heat treatment of lithium manganese spinel adjusts the nanostructure of the final material. The resultant material shows an increase in conductivity and tap density, producing conductivity almost three times greater than lithium cobalt and double that of standard lithium manganese. Due to the increase in conductivity, this spinel can generate higher power density than lithium cobalt oxides.

Lithium iron phosphate (LFP)

The lithium iron phosphate battery makes use of lithium iron phosphate as a cathode material with potential for application in the EV and HEV field. Currently used in electric cars developed by Aptera[3] and QUICC, as well as for Killacycle's electric motorcycle, in 2007 Lithium Technology Corp. announced the development of cells large enough for use in hybrid vehicles[4]. The world's largest producer of Li-ion batteries, China's BYD Company, plans to make use of LFP batteries for its first commercial electric vehicle, originally planned for production in 2009.

LFP technology shows a significant safety advantage over Li ion batteries which utilize other cathode materials, due to LFP's increased chemical and thermal stability[5]. As phosphate creates stronger bonds with oxygen atoms than cobalt is able to achieve, oxygen is not easily released increasing safe operating temperatures and reducing fire hazard. Additionally, LFP has cost and environmental benefits as it contains no cobalt. LFP batteries also demonstrate a longer life cycle than that of standard Li ion batteries.

The main disadvantage of LFP technology is the relatively lower energy density and discharge rate in comparison to $LiCoO_2$ batteries. As both disadvantages can be overcome by increasing battery size, the challenge for developers is to reduce size and weight.

Lithium nickel manganese cobalt (NMC)

Nissan Motor Co. plans to incorporate a battery using a lithium nickel manganese cobalt oxide cathode[6] (NMC) in its electric vehicles by 2015. The company claims that this system will provide double the capacity of manganese spinel batteries currently used in their vehicles, by adding nickel and cobalt to manganese in the cathode. Sturdy enough of standard EV use, the battery is expected to be capable of 1 000 full charge cycles or more and will provide a single charge range of around 200 miles. Nissan claims that the expected cost of production will be similar to that of current Li-ion batteries due to the low content of cobalt in the product.

The potential of increased capacity of the NMC oxide materials has generated much international interest and Argonne Labs in the US, funded by the U.S. Dept. of

Energy, has done extensive development of mixed metal oxides resulting in patents covering cathode material containing NMC. General Motors have licensed Argonne patents and are working separately with the company to develop NMC to increase storage capacity for future batteries[7]. Relative proportions of the metals are being varied to increase the storage of lithium ions. Additionally, by activating some components, lithium is freed to increase movement between the electrodes. Freed lithium ions then move in and out of the active material, leaving inactive material as a stabilizing agent in the battery. Despite success with the material, both companies expect intensive innovation in engineering will be required before the technology can be incorporated in battery packs.

Lithium-air batteries (Li-air)[8]

Li-air batteries were first proposed as a viable source for EV power in the mid ‘70s, but a lack of technology saw insufficient development of it as an alternative. Advances in material technology have led to renewed interest in its development for both the industry and scientific field. IBM is currently involved in a research project to produce a Li-air battery capable of providing a vehicle with a range in excess of 500 miles per charge.

The battery operates on the principle of a reduction of oxygen at the cathode and the oxidation of lithium at the anode to induce a flow of current. Li-air technology is unique in this regard due to the use of atmospheric oxygen at the cathode, eliminating a traditional cathode structure. The lighter cathode, plus the fact that the available oxygen obviates the requirement to store it in the design, allows the battery a far higher energy density than most alternative technologies. This high energy density makes the battery a highly attractive solution, but research is still in its infancy and many engineering and science challenges need to be overcome before a commercial application can be considered. Some companies active in the field of Li-air research see the project as a 10 year program.

Anode Materials

Lithium titanate battery (LT)

Lithium titanate batteries charge considerably faster than comparable lithium-ion products, and are being touted in some quarters as a future solution for the EV and HEV industry. These batteries are currently produced by Altairnano in the USA and Toshiba in Japan for the EV market, Altairnano counting Lightning Car Company, Phoenix Motorcars and Proterra amongst its EV clients. Toshiba's Super Charge Ion Battery (SCiB) claims a 90% charge capacity within 10 minutes and is used by Schwinn for its Tailwind electric bike, and Mitsubishi in its MiEV ranges. Honda will also use the SCiB in its Fit EV, scheduled for release in mid-2012.

The battery incorporates lithium-titanate nanocrystals on the anode surface in the place of carbon. This effectively increases the anodes surface area from 3 m^2 to 100 square meters per gram. The resultant increase of the rate at which electrons enter and leave the anode provides higher currents and quicker recharging possible. Toshiba claims that their SCiB's long life cell is able to accommodate 6000 charging cycles, almost three times more than standard Li-ion batteries. This technologies main disadvantage is its lower voltage and capacity than many of its conventional lithium-ion competitors.

Nissan Leaf Battery

Lithium vanadium[9]

The high energy density of modern lithium vanadium phosphate batteries represents another promising battery solution for use in the automotive industry.

Displaying greater safety levels than that of cell phone and laptop batteries, and greater power than current electric vehicle batteries, the developers of these batteries claim the addition of vanadium makes these products the next generation in automotive EV solutions.

Major battery manufacturers, including America's Valence Technology Inc. and China's BYD Company Ltd. are among those engaged in further development of lithium vanadium technology. Japan's GS Yuasa Corporation (GSY) has a prototype lithium-vanadium phosphate battery which shows an increase of 20% in output over Li-ion battery capability. GSY claims that production costs are lower and safety rating higher than the Li-ion alternatives and expects the battery to be used in the HEV market. The company is well placed in the automotive market through joint ventures with Mitsubishi and Honda, and has Toyota Motor Corporation as one of its principal shareholders.

Subaru makes use of a lithium-vanadium battery in its prototype EV, the G4, and doubled the range of their previous EV to a range of 120 miles. The G4e battery is fully charged within 8 hours and reaches an 805 charge in a mere 15 minutes.

Author notes

Following a career as a military officer and political consultant in South Africa, Mark Bowler headed up companies in the construction, manufacturing and gold mining sectors. Today he spends his time in consultancy and research for a number of international clients in the commercial and industrial fields.

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