

## "Resources, Energy, Environment and Social Infrastructure" field

#### **Achievement: Development of lithium ion batteries**

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# Summary

The lithium ion battery is a type of secondary battery capable of charge/discharge that has become the backbone of today's mobile society by powering smartphones and laptop PCs. It is also being adopted in electric vehicles that are becoming increasingly widespread, serving to reduce emissions of environment-impacting substances. In the early 1980s, Dr. Yoshino put forth the concept of the lithium ion battery and demonstrated its charge/discharge capability. At the time, research on batteries using lithium metal anodes was more predominant, with a strong focus on cathode materials and non-aqueous electrolyte solutions. Dr. Yoshino proposed and demonstrated a viable secondary battery using lithium cobalt oxide for the cathode and a carbon-based material for the anode, which he combined with his original separator and current collector technology. The resulting battery attained high voltage, high energy density and a long-life. Lithium ion batteries have since continued to improve through constant refinements in materials and manufacturing methods, and their application is anticipated to grow into the future.

## Lithium ion battery: the key player in the mobile revolution

There are two types of batteries: primary and secondary. A primary battery is only capable of a single discharge, whereupon its life is finished. Notable examples include the zinc carbon battery and the alkaline battery often found in remote-controllers and flash lights. A secondary battery, in contrast, can be recharged for repeated use.

The lithium ion battery, developed by Dr. Yoshino in the 1980s, is a type of secondary battery. The secondary batteries in use at the time were the lead acid battery and the nickel cadmium battery, with the nickel metal hydride battery still under development. The lithium ion battery had an advantage over such batteries, in that it was smaller, lighter, had higher capacity and a longer life. Once it was adopted for practical use in 1991 as a battery for compact video cameras, it rapidly saw widespread use in laptop PCs and smartphones, becoming the driving force in today's mobile revolution

During the discharge of a secondary battery, reduction occurs at the cathode and oxidation at the anode, thereby causing electric current to flow from the cathode to the anode. Similarly, during a recharge, electric current is externally applied in the opposite direction, causing a reverse reaction. The battery contains an electrolyte solution, which conducts electricity between the cathode and the anode. The lithium ion battery is a secondary battery that uses lithium ion metallic oxide, such as lithium cobalt oxide (LiCoO2) for the cathode, carbon-based materials for the anode, and an organic solvent for its electrolyte solution. Operating on the principle that lithium ions traverse the cathode-anode gap during the charge/discharge cycle, the battery is able to produce a high voltage of approximately 3.9V.

Secondary batteries prior to the lithium ion battery used a water-based solvent for their electrolyte solution, and could therefore only generate an electromotive force below 1-2V, the threshold for the electrolysis of water. A Lithium ion battery, in contrast, can generate a higher electromotive force due to its use of an organic solvent with high-voltage electrolytes. This offers the advantage of being able to power devices that require high voltage with a single battery. Furthermore, the amount of energy that can be stored in a battery (charging capacity) is dependent on the discharge voltage and the discharge amount (current x time), so that a stronger electromotive force translates into greater battery capacity.

# It all began with Dr. Shirakawa's discovery of polyacetylene

Upon graduating from Kyoto University in 1972 with a Master's degree in Engineering, Dr. Yoshino joined Asahi Chemical Industry Co. (now known as Asahi Kasei Corporation). In 1981, he began researching polyacetylene at the company's laboratory. Polyacetylene is a substance discovered in 1967 by Dr. Hideki Shirakawa (currently Professor Emeritus, University of Tsukuba), who at the time was an assistant researcher at the Tokyo Institute of Technology. Polyacetylene has the ability to conduct electricity despite being an organic substance.

Primary batteries that used lithium for the anode were already in use in the 1970s, and by the 1980s, many researchers were pursuing developmental research on a secondary battery with a lithium anode. At the time, there was a strong momentum in the development of what we now call mobile devices, which created a need for a small, lightweight and high-capacity secondary battery. The fact that lithium is the most oxidizable of the elements made it ideal as an anode material, and it also has the highest electric quantity per unit weight among the metallic elements. For these reasons, it was anticipated that if a secondary battery with a lithium anode capable of high voltage and high energy density could be realized, it could meet the needs of the times. Lithium, however, was not without its problems, for it is a highly flammable metal, and is prone to short-circuit with the cathode when dendrites form on the lithium anode over multiple charge/discharge cycles.

Dr. Yoshino, who was researching polyacetylene, considered using it as an anode material instead of lithium, but soon reached a deadlock because he could not find a suitable cathode material. At the time, the phenomenon of lithium ions traversing layered materials, such as titanium disulfide (TiS2), was already common knowledge. Such layered materials were thus being considered for use as a cathode material to be paired with a lithium anode. But using polyacetylene as the anode was not enough for the battery to function, because there would be no supply of lithium ions, which was the most essential component.

Just around that time, Dr. Yoshino came across a paper reporting on a new cathode material called LiCoO<sub>2</sub>,. This material could supply the much-needed lithium ions, making it the ideal counterpart to a polyacetylene anode. Without hesitation, Dr. Yoshino conducted experiments using this combination and confirmed that it successfully functioned as a secondary battery. This took place in 1983. "I feel that this was a moment of discovery", says Dr. Yoshino recalling that moment.

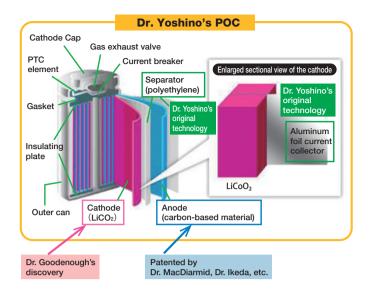
After this breakthrough, Dr. Yoshino led a research team to refine the battery. The team sought carbon-based materials better suited for the anode, and in 1985, filed a patent on the design of the lithium ion battery as we know it today, composed of a LiCoO<sub>2</sub> cathode and a carbon-based anode. The patent was granted in 1995.

## The importance of proving the concept behind a system

The realization of the lithium ion battery by Dr. Yoshino would not have been possible without the research and development efforts of many researchers and engineers who came before him.

LiCoO<sub>2</sub>, the substance Dr. Yoshino used for the cathode, was discovered in 1979 by Dr. John B. Goodenough of the University of Texas and Dr. Koichi Mizushima of the University of Tokyo, who was visiting Dr. Goodenough's laboratory on an exchange program. Dr. Goodenough not only discovered this substance but also made distinguished achievements in the basic field of solid-state chemistry, for which he was awarded the 2001 Japan Prize.

Meanwhile, Dr. Yoshino had initially used polyacetylene for the anode but later switched to carbon-based materials. Because lithium ions traverse the cathode-anode gap, the anode must be able to absorb and release lithium ions. There had also been preceding studies on this topic. Graphite's ability to absorb lithium ions was reported in 1975, and from



By combining existing technologies with his own, Dr. Yoshino proposed and demonstrated that the lithium ion battery system, in which "charge/discharge is achieved by the traversal of lithium ions through the cathode-anode gap," is capable of delivering the performance necessary for practical application.

1980 to 1981, patents were filed by Dr. Alan MacDiarmid of the University of Pennsylvania for the polyacetylene anode, and by Dr. Hironosuke Ikeda of Sanyo Electric Co. for the graphite anode. Furthermore, there was a proposal in 1980 of a battery with a lithium-inserted tungsten oxide (LixWO<sub>2</sub>) anode and a TiS<sub>2</sub> cathode that permits the traversal of lithium ions.

A secondary battery is a complex system. Even if one develops cathode and anode materials of excellent quality, if the combination cannot achieve the performance and safety necessary for practical use and the capability to charge/discharge repeatedly, one cannot claim to have developed a secondary battery. Dr. Yoshino was able to realize the lithium ion battery system by discovering the right cathode-anode combination and developing an original elemental technology. One of his original technologies is the very thin polyethylene-based porous membrane which he used as a separator between the battery's cathode and anode. Lithium ions can normally traverse the membrane pores, but in case of abnormal overheating, the membrane melts and closes off the pores, thereby halting the function of the battery. Dr. Yoshino demonstrated through reliability tests that a polyethylene membrane of a specific structure and composition could indeed prevent an overheated battery from exploding. His other original technology is the use of aluminum foil as a current collector which draws electricity from the cathode. The various improvements he made on the current collector achieved a necessary level of performance including high voltage and high capacity.

Dr. Yoshino's greatest achievement is the establishment of the POC (proof of concept) for the lithium ion battery, in which he demonstrated that the traversal of lithium ions through the cathode-anode gap enables the battery to be charged/discharged (see diagram). The performance of lithium ion batteries has improved in the ensuing years through refinements in materials and manufacturing methods. Besides mobile devices, they are now being used in electric vehicles, serving to significantly reduce emissions of environment-impacting substances. Furthermore, it is anticipated that "downcycling", or the recycling of retired lithium ion batteries from electric vehicles into electricity storage for solar power and the like, will become increasingly prevalent. The lithium ion battery that Dr. Yoshino brought into the world has not only made our lives dramatically more convenient, but is also playing a crucial role in resolving the resource, energy and environmental issues we face.