Materials Technology for Large Lithium-ion Batteries

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OVERVIEW: Lithium-ion batteries are used in mobile phones, portable PCs and various other consumer devices and the expectation is that they will be used extensively in the future in applications such as hybrid electric cars and other vehicles as well as in energy storage systems installed at wind and other electricity generation facilities. The development of large lithium-ion batteries for these applications needs to achieve higher output, higher energy density, longer life, and lower cost. Hitachi has been working on research into innovative battery materials for many years with the aim of producing large lithium-ion batteries, including developing long-life manganese cathodes, carbon anodes, and electrolytes with low resistance, and designing electrode structures suitable for large batteries. It is Hitachi's hope that it will be able, through its lithium-ion battery business, to make progress on measures for helping protect the environment.

INTRODUCTION

HITACHI has been working on research and development of large lithium-ion batteries for electricity storage, automotive, and other applications since the early 1990s. It is participating in a number of development projects for large lithium-ion batteries organized by the New Energy and Industrial Technology Development Organization (NEDO) and has utilized some of the results of this research to lead the world in commercializing large lithium-ion batteries for HEVs (hybrid electric vehicles), hybrid railroad locomotives, and other uses. It aims to extend the applications for these batteries into fields such as smart grids and forms of green mobility that achieve even greater efficiency such as PHEVs (plug-in hybrid electric vehicles).

This article describes the development by Hitachi of battery materials technologies for large lithium-ion batteries and the outlook for this technology.

DEVELOPMENT OF LARGE LITHIUM-ION BATTERIES

High-performance rechargeable batteries are essential in vehicles such as PHEVs (which are expected to enter widespread use in the future), construction machinery, and trains as well as in energy storage systems used with wind, solar, and other forms of electricity generation. The lithium-ion batteries that have already been commercialized for use in HEVs have a high output but low energy density whereas the lithium-ion batteries used in EVs (electric vehicles) have high energy density but an output density that is considered inadequate (see Fig 1). In other words, it is necessary to combine the high output density of HEV batteries with the high energy density of EV batteries while also satisfying requirements such as long life and low cost. Accordingly, even higher performance is needed from the materials used in these batteries.

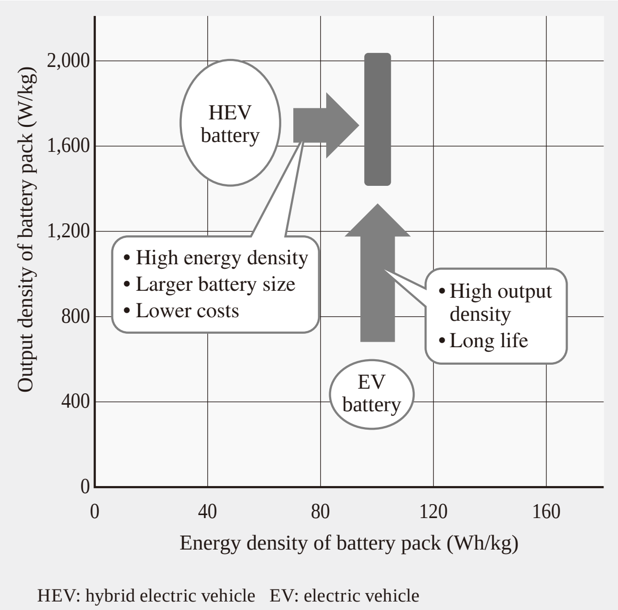

Fig. 1—Characteristics Required in Large Lithium-ion Batteries.
Large lithium-ion batteries need to combine the high output density of HEV batteries with the high energy density of EV batteries while also satisfying requirements such as long life and low cost.

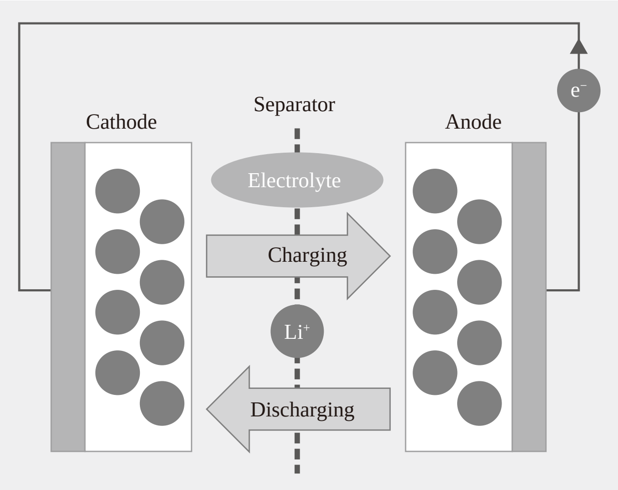

Fig. 2—Principle of Operation of Lithium-ion Battery.
A lithium-ion battery works by releasing electrons through the transfer of lithium ions between cathode and anode electrodes that sandwich a separator impregnated with electrolyte. The cathode and anode are made of materials that are able to intercalate and deintercalate lithium ions respectively.

BATTERY MATERIALS

The electrodes in lithium-ion batteries are made from metal oxide powder (for the cathode) and carbon powder (for the anode) which are mixed with a binder and coated as sheets of thin film on metal foil. A separator with micropores that allow the passage of lithium ions is placed between the cathode and anode and sets of electrodes formed by stacking and coiling. The basic structure of the lithium-ion battery is then completed by impregnating the electrode sets with an electrolyte of lithium salt dissolved in an organic solvent (see Fig. 2).

The cathode and anode can intercalate and deintercalate lithium ions respectively and charging and discharging is accomplished by this exchange of lithium ions between the two electrodes. Accordingly, achieving high output, high energy density, and long life in a lithium-ion battery requires developments such as improvements to the reversibility of the lithium ion intercalation and deintercalation reactions in the cathode and anode materials, reduction in the electrical resistance of the electrodes and electrolyte, and suppression of the side reactions that cause decomposition and lead to a loss of capacity.

Long-life Manganese Cathode

Most consumer lithium-ion batteries currently use cobalt, a scarce resource, as the main material in their cathodes. For the cathodes in its large lithium-ion batteries, however, Hitachi has directed its attention toward using manganese, an abundant material with scope for cost savings. Unfortunately, past cathodes based on manganese spinel have been subject to a phenomenon whereby the volume of the crystal shrinks when they deintercalate lithium ions during charging and expands again when the ions are intercalated during discharging. This repetitive change in volume with each charge/discharge cycle leads to degradation of the crystal structure and is one of the causes of capacity loss. Another cause of capacity loss when conventional manganese spinel cathodes are used is that acid present as an impurity in the electrolyte causes manganese to elute out of the cathode.

In response, Hitachi succeeded in improving the reversibility of charging and discharging by substituting some of the manganese with different elements. This had the effect of reducing the variation in cathode volume during the charging and discharging reaction by about 50% and stabilizing the crystal structure. Also, mixing in layered composite oxides with excellent acid-resistance reduced elution of manganese into the electrolyte by approximately 50% (see Fig. 3).

The result was that the loss of capacity associated with the charging and discharging cycle was halved compared to previous batteries that used manganese

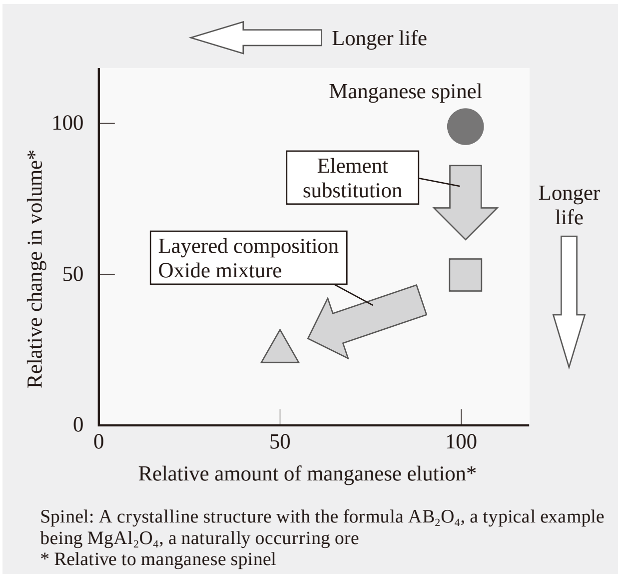

Fig. 3—Extending Life of Manganese-based Cathodes.
The crystal structure of the cathode was stabilized by substituting some of the manganese in the manganese spinel with different elements and elution of manganese was suppressed by mixing in layered composite oxides with excellent acid-resistance. The result of these improvements is a projected battery life of ten years or more.

spinel, achieving a projected battery life of ten years or more[(1)].

Also, because the required output characteristics are different for vehicles such as PHEVs, construction machinery, trains, and energy storage systems used with wind, solar, and other forms of electricity generation, Hitachi is working on tailoring cathode characteristics such as particle diameter and surface area ratio to suit each of these applications.

Carbon Anodes for Rapid Charging

Carbon is used as the anode material in lithium-ion batteries and because the lithium ions are intercalated and deintercalated into and out of the layers of carbon during charging and discharging, in principle metallic lithium should never form. When the battery is charged rapidly, however, the potential exists for metallic lithium to form on the anode surface if the rate at which lithium ions are absorbed into the carbon layers is too slow. Because metallic lithium is very reactive, the resulting problems include loss of reversibility due to side-reactions between the lithium and electrolyte. It can also, in some cases, result in the metallic lithium growing into dendritic shape creating the risk of an internal short circuit with the cathode[(2)].

To improve the rapid-charging characteristics of carbon anodes, it is important to increase the speed of movement of lithium ions at the surface of the carbon which is believed to be the rate-limiting factor. Because the lithium ions are intercalated from the infusion surfaces that are layered between the layers known as graphite edge surface, changes were made that sought to improve the quality of the carbon surface and increase the amount of infusion surface. Improvements made to the heat treatment, grinding, and other production processes succeeded in enlarging the area of lithium ion infusion surface by 1.4 times compared to the previous design which significantly enhanced the rapid charging characteristics (see Fig. 4).

In addition to successfully suppressing the precipitation of metallic lithium and improving the reversibility performance of the anode, this also enhances the safety of the lithium-ion battery.

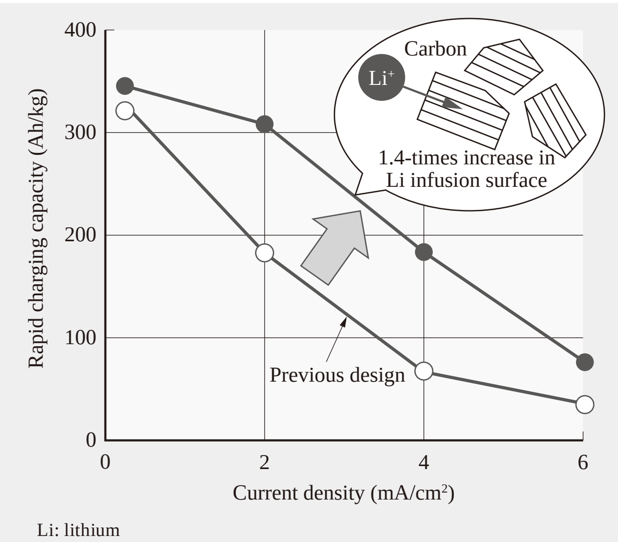

Fig. 4—Rapid Charging Capacity of Carbon Anode.
Improvements to heat treatment, grinding, and other production processes succeeded in enlarging the area of infusion surface through which lithium ions are intercalated and deintercalated by 1.4 times. This significantly enhanced the rapid charging characteristics.

Low-resistance Electrolyte

Compared to consumer lithium-ion batteries, large lithium-ion batteries need to be able to operate in a wide range of both low- and high- temperature environments. As automotive lithium-ion batteries used in HEVs, PHEVs, and other electric vehicles in particular require the ability to discharge at temperatures as low as –30°C, there is a need for electrolytes with lower electrical resistance.

The electrolyte solution used in lithium-ion batteries is a mixture of high-permittivity cyclic carbonate solvents and low-viscosity chain carbonate solvents. The reason for using this mixture is because it provides better ion conductivity and lower electrolyte resistance than using either on its own.

Cyclic carbonates form solvated ions that orient toward lithium ions. These act as the carriers during the charging and discharging reactions, but the amount of cyclic carbonate needs to be optimized because too little causes the carrier concentration to become too low and too much increases the electrolyte viscosity.

The results of studies of ion conductivity in different temperature ranges indicated that it reaches its maximum when the ratio of cyclic carbonates to lithium ions is around four (see Fig. 5). These results have been applied in the development of lithium-ion batteries with excellent low-temperature characteristics[(3)].

OPTIMIZATION OF ELECTRODE STRUCTURE

The electrodes for lithium-ion batteries are produced in sheet form by coating metallic foil (which acts as the electric collector and is made of aluminum

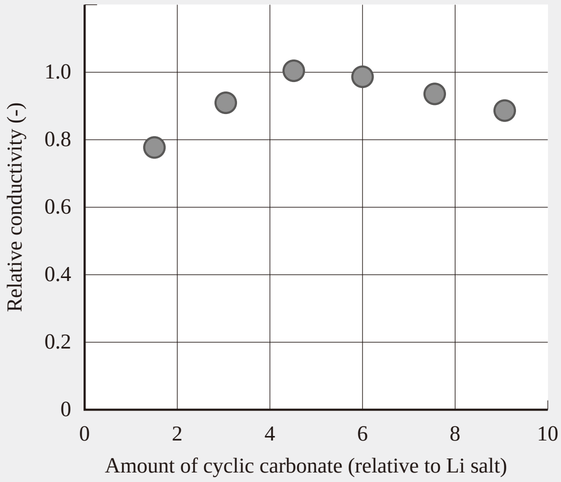

Fig. 5—Effect of Cyclic Carbonate Content on Electrolyte Conductivity.
Cyclic carbonates form solvated ions that orient toward lithium ions and act as the carriers during the charging and discharging reactions. Ion conductivity reaches its maximum when the ratio of cyclic carbonates to lithium ions is around four.

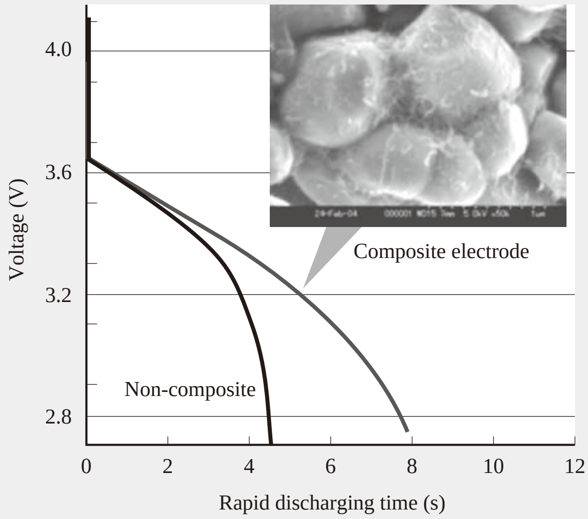

Fig. 6—Rapid Discharging Performance of Composite Electrode.
The electron microscope photograph shows a composite electrode produced by using a ball mill to mix carbon nanotubes into the cathode material. The photograph shows how the carbon nanotubes are uniformly distributed across the surface of the cathode particles. The rapid discharging performance approximately doubled compared to an electrode that does not contain any carbon nanotubes.

for the cathode and copper for the anode) with a thin film of composite made from a mixture of the cathode or anode material and additives such as conductivity promoters and binders. In addition to improvements to the cathode and anode materials as described above, optimization of the electrode composite, including the relative proportions of its constituents and how these are mixed together, and high-precision coating techniques are also essential to improving electrode performance.

Making the electrode resistance as low as possible is an important factor in developing lithium-ion batteries with high output density and the key to achieving this lies in the use and uniform distribution of conductivity promoters. Materials commonly used as conductivity promoters have included carbon black and graphite powder, while carbon nanotubes have attracted attention for its ability to form conductive networks with higher dimensionality. However, carbon nanotubes have a strong tendency to clump together making them difficult to distribute uniformly through the electrode. In response, a ball mill that subjects the particles to a strong shear stress is used when carbon nanotubes are mixed into the cathode material(4). This method distributes the carbon nanotubes across the cathode surface with a high degree of uniformity achieving an approximate doubling in rapid discharging characteristics (see Fig. 6). Because this high level of conductivity promoter dispersal means that only the minimum amount of additive is required to achieve the improvement in conductivity, it also contributes to improving the energy density of the lithium-ion battery.

CONCLUSIONS

This article has described the development by Hitachi of battery materials technologies for large lithium-ion batteries and the outlook for this technology.

Some of these technologies are already in use in products. In the future, it is anticipated that large lithium-ion batteries will be put to a wider range of uses in the environmental and energy sectors, including smart grids and PHEVs and other green mobility vehicles, and in more familiar settings such as backup power supplies for eco-housing fitted with solar panels, hospital medical equipment, elevators, and other systems. The major challenges in achieving this are working out how to improve output and energy density and achieve longer battery life, larger capacity, and lower cost.

Through its lithium-ion battery business, Hitachi aims to strengthen its involvement in protecting the environment and further develop its Social Innovation

Business, and it intends to continue developing high-performance battery materials and large lithium-ion batteries.

Some of the results described here were obtained as part of two ongoing research projects that Hitachi has been contracted to carry out by NEDO on the "Development of an Electric Energy Storage System for Grid-connection with New Energy Resources" and the "Development of High-performance Battery System for Next-generation Vehicles." Hitachi would like to take this opportunity to express its thanks.

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