

# Development of Highly Reliable High-capacity Batteries for Mobile Devices and Small- to Medium-sized Batteries for Industrial Applications

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*OVERVIEW: As the functions of mobile handsets become more advanced, the power consumed by devices running applications such as mobile TV or Internet access is increasing. This creates a strong demand to improve the capacity of the batteries used in these devices. Maintaining battery safety while making these capacity improvements is also critical. Hitachi Maxell, Ltd. has spent many years devising innovative silicon-based anode and nickel-based cathode materials aimed at improving capacity, and developing ceramic separators for better safety and reliability. The company is working on commercializing prismatic lithium-ion batteries and developing small- to medium-sized laminated batteries for industrial applications based on its many years of experience with mobile batteries.*

## INTRODUCTION

THE progress that has taken place in the mobile handsets that underpin the recent spread of ubiquitous networks is truly spectacular. These devices are becoming essential tools for the information society and their uses have expanded beyond simple telephony to applications such as photography, music, mobile television, the Internet, and electronic transactions. However, the growing sophistication of these handsets is also leading to very strong demand for improvements in the performance of the batteries used to power them. The progressive improvements in the capacity of the prismatic batteries used in mobile phone handsets, for example, have increased their energy density from 350 Wh/L in 2002 to 500 Wh/L in 2009. Although developments in materials such as graphite anodes are a factor in this improvement, it is mainly due to structural enhancements such as higher filling of active materials and slim-profile designs for the other types of materials used in batteries. However, the potential for improvements in capacity achieved through structural enhancements is reaching its limit, creating a need for new active materials.

This article describes improvements in silicon anode materials and nickel-oxide cathode materials being undertaken by Hitachi Maxell, Ltd. and also a ceramic separator that is being developed to ensure safety (because capacity and safety are conflicting objectives in battery design)<sup>(1), (2)</sup>. It also describes a laminated battery that is being developed for industrial

applications where major progress is anticipated in the future.

## LITHIUM-ION BATTERIES

Lithium-ion batteries store or release energy by passing lithium ions back and forth through a microporous separator between the positive and negative electrodes (cathode and anode) that intercalate and deintercalate these ions respectively. Graphite is widely used as the anode and  $\text{LiCoO}_2$  (lithium cobalt oxide) as the cathode. Battery capacities have been improved by increasing the amount of this material that can be filled into the battery, but this approach is

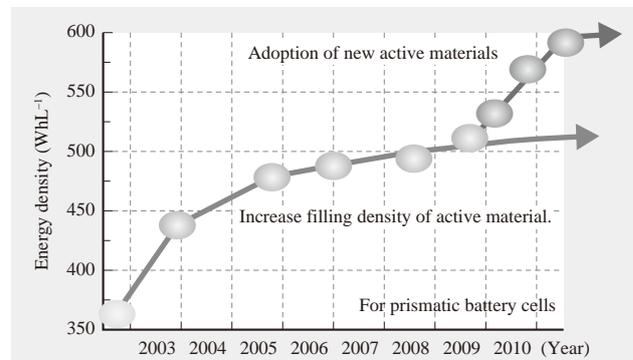


Fig. 1—Improvement in Energy Density of Prismatic Lithium-ion Cells for Mobile Applications.

Energy density improved from 350Wh/L in 2002 to 500 Wh/L in 2009. The adoption of new active materials will be needed to increase the energy density further.

reaching its limit and instead there is hope that new materials will provide a boost in performance (see Fig. 1).

### Silicon Anode

The theoretical capacity for graphite is 372 mAh/g. This compares to 4,190 mAh/g for Si (silicon) and 990 mAh/g for Sn (tin) which is why these alloy materials are seen as having the potential to provide much greater capacity. The barriers to achieving this are deterioration of the charge/discharge cycle when these materials are made into fine powder and a large irreversible capacity, and while an active program of research and development is underway, it has yet to lead to their widespread adoption.

Based on the knowledge that producing silicon particles with diameters in the nanometer range reduces the tendency to form fine powder in the charge/discharge cycle, a material called SiO (silicon monoxide) was selected to implement this idea using an industrial chemical. The structure of SiO consists of nano-particles of Si distributed in a matrix of amorphous SiO<sub>2</sub> (silicon dioxide) (see Fig. 2).

Although investigations into techniques for forming silicon materials into thin films that can be used as electrodes have been carried out, Hitachi Maxell has focused on SiO powder because it allows the use of an existing manufacturing process in which material in powder form is applied as a coating.

It is believed that when lithium enters the SiO during the initial charge, SiO<sub>2</sub> is transformed into amorphous Li<sub>4</sub>SiO<sub>4</sub> (lithium orthosilicate) which acts

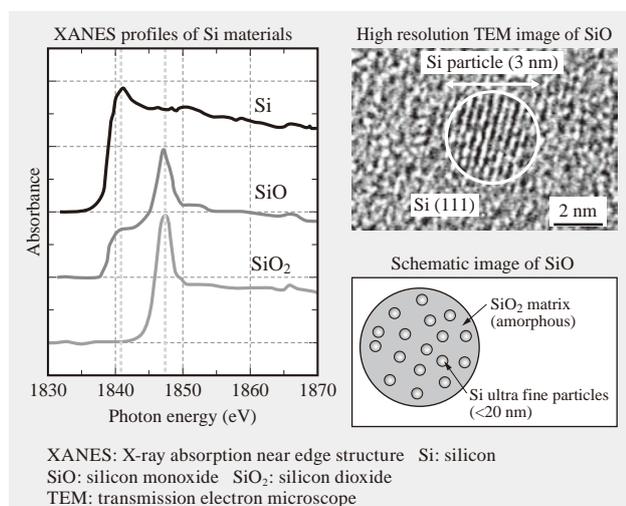


Fig. 2—Fine Structure of SiO Material.

The SiO material has a complex structure consisting of a mixture of Si nanoparticles and amorphous SiO<sub>2</sub>.

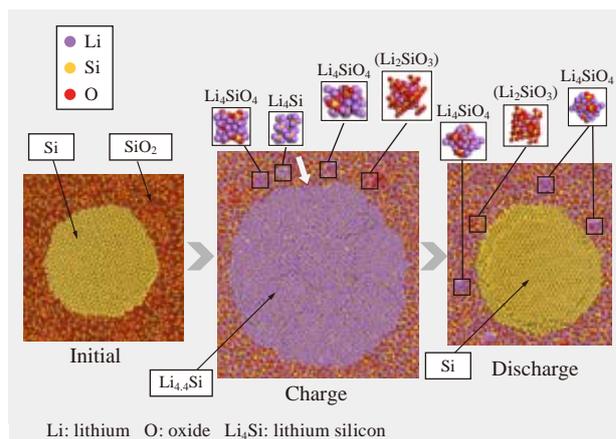


Fig. 3—Schematic Model of SiO Anode Charge-discharge Mechanism.

During initial charging, the SiO<sub>2</sub> changes to amorphous Li<sub>4</sub>SiO<sub>4</sub> (lithium orthosilicate) which acts as a conductor of lithium ions.

as a migration path for the lithium ions. Although the silicon nanoparticles expand in size as they intercalate the lithium, because they are already in the form of very small particles and are fixed in their location surrounded by the Li<sub>4</sub>SiO<sub>4</sub>, the extent of transformation into fine powder is reduced (see Fig. 3). However, there is no way to prevent the silicon from intercalating lithium and expanding in volume. It has been demonstrated, however, that forming voids in the electrode, increasing the adhesive strength of the binder, and strengthening the Cu (copper) current collector foil are effective countermeasures.

### High-capacity Lithium-nickel Oxide

Materials proposed as alternatives to the LiCoO<sub>2</sub> widely used as a cathode in lithium-ion batteries have included oxides with a spinel structure and Ni (nickel)-Co-Mn (manganese) based layered oxides. Recent attention has also focused on solid solutions [Li<sub>2</sub>MnO<sub>3</sub>-LiMO<sub>2</sub> (lithium-manganese oxide—lithium-metal oxide)] because of their high capacity. The aims of this research include mitigating the effects of cobalt price volatility, ensuring material stability, increasing capacity, and improving safety, but no material has yet been found that can satisfy all of these desired properties at the same time. The requirement for mobile applications is to be able to provide a high level of electrical storage at the operating voltage range (4.2–3.0 V). Fig. 4 shows the relationship between discharging capacity and cobalt content as indicated by “x” in LiCo<sub>x</sub>Ni<sub>1-x</sub>O<sub>2</sub> (lithium-cobalt-nickel oxide). A value of x = 0.1 achieved a capacity in excess of 200 mAh/g at the maximum voltage of 4.2 V while

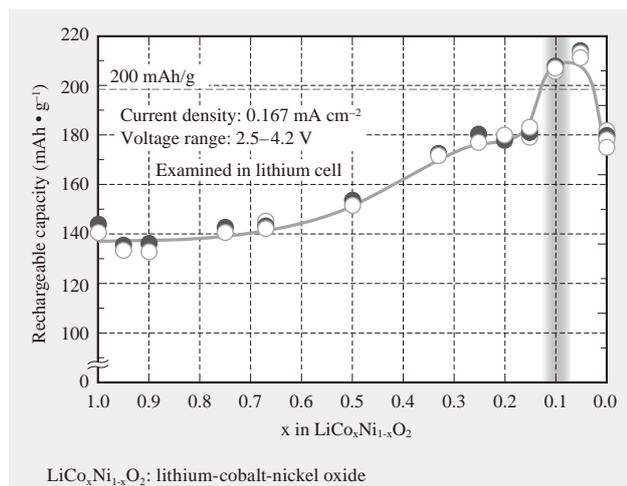


Fig. 4—Relationship between Recharging Capacity of  $\text{LiCo}_x\text{Ni}_{1-x}\text{O}_2$  and Co Ratio ( $x$ ). A capacity in excess of 200 mAh/g was achieved using  $\text{LiCo}_x\text{Ni}_{1-x}\text{O}_2$  with  $x = 0.1$  or 0.05.

also reducing the amount of cobalt used.

However, the charge/discharge cycle characteristics for this composition are inadequate and it is not sufficiently safe when used in prismatic batteries. This is due to the bond between nickel and oxygen being unstable and was mitigated by replacing some of the cobalt with manganese and magnesium. Fig. 5 shows the cycle characteristics of a material with Mn-Mg (magnesium) added. It is believed that this improvement came about because substituting 50% of the cobalt with manganese and magnesium stabilized the oxide bond.

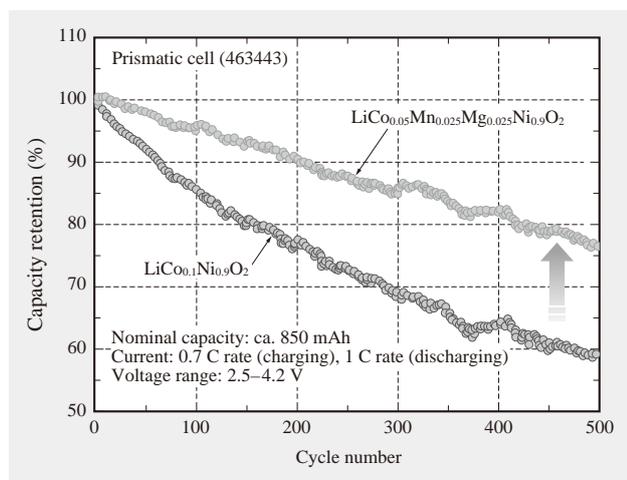


Fig. 5—Cycle Performance of  $\text{LiCo}_{0.05}\text{Mn}_{0.025}\text{Mg}_{0.025}\text{Ni}_{0.9}\text{O}_2$  and  $\text{LiCo}_{0.1}\text{Ni}_{0.9}\text{O}_2$ . A significant improvement in cycle characteristics was achieved when 50% of the Co (cobalt) was substituted with Mn (manganese) and Mg (magnesium).

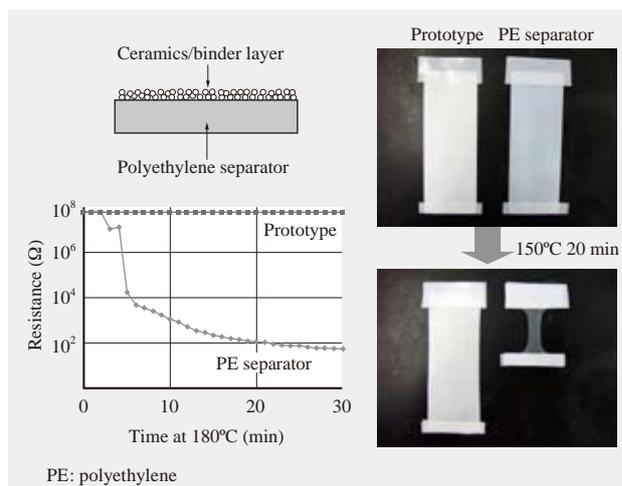


Fig. 6—Structure and Thermal Stability of Ceramic Separator.

Coating the polyethylene separator with a layer of ceramic/binder improved the thermal stability and reliability of the battery under adverse conditions.

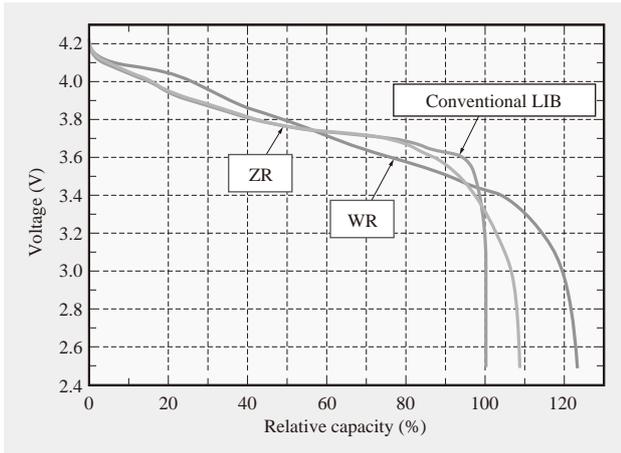
## Ceramic Separator

Microporous polyethylene is used as the separator in lithium-ion batteries. This takes advantage of polyethylene having a softening point of about 130°C to provide a shutdown function whereby the heat generated by the battery in abnormal situations such as a short circuit causes the micropores to become clogged, cutting of the current flow. For this function to work reliably, it is desirable that the material keep its shape in the temperature range between its softening and melting points. Coating a microporous polyolefin film with alumina-based ceramic particles to a thickness of 5 μm suppresses shrinkage at 150°C and succeeded in improving the safety of a prototype battery when it was forcibly subjected to an internal short circuit (see Fig. 6).

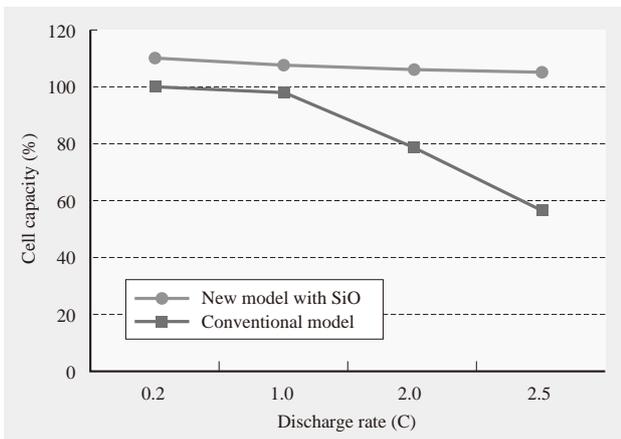
## LITHIUM-ION BATTERIES FOR VARIOUS APPLICATIONS

### Prismatic Batteries for Mobile Applications

Hitachi Maxell investigated improvements in materials as a way of increasing the capacity of the 494261 (4.9 mm thick with dimensions of 42 mm × 61 mm), a typical example of a prismatic battery for mobile applications. Fig. 7 shows the discharge characteristics of the battery. Compared to the 495-Wh/L capacity of the current graphite/ $\text{LiCoO}_2$  system, the capacity was improved to 530 Wh/L on the ZR model which has an SiO and graphite anode, and to 600 Wh/L on the WR model which has an SiO and graphite anode and a  $\text{LiCo}_{0.05}\text{Mn}_{0.025}\text{Mg}_{0.025}\text{Ni}_{0.9}\text{O}_2$



*Fig. 7—Discharge Characteristics of Lithium-ion Batteries with High Energy Density that Use Active Anode and Cathode Materials. The ZR series uses SiO anode material and the WR series uses SiO anode and nickel-oxide cathode material.*



*Fig. 8—Characteristics at High Discharge Rates of Lithium-ion Batteries with SiO Anode Material. At a discharge rate of 2.5 C, the prismatic cell with an SiO anode can discharge 100% of its capacity compared to only 60% for a conventional cell.*

(lithium-cobalt-manganese-magnesium-nickel oxide) cathode.

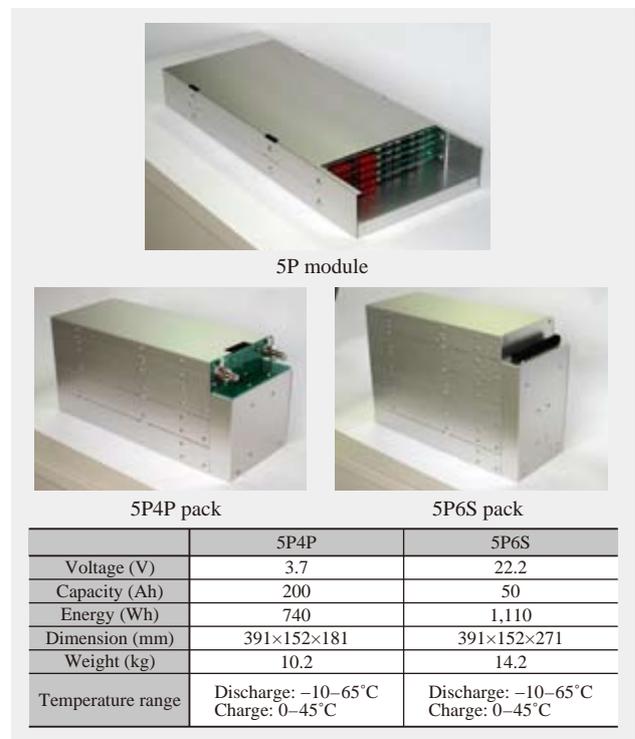
Fig. 8 shows the characteristics at high discharge rates which are one of the strong points of silicon-based anodes. This is believed to be due to the high rate of lithium dispersion in the Si and the surface SEI (solid electrolyte interface) layer which is different to a graphite anode. In addition to their characteristics at high discharge rates, silicon-based anodes also improve characteristics at low temperature.

Because silicon-based anodes have a superior potential to lithium, the cell voltage is reduced. Also, the capacity can be increased using a nickel oxide cathode if the cell is discharged down to a low 2.5 V.

However, the minimum discharge voltage for prismatic batteries used in mobile phones is 3.0 V or higher, so higher capacity in the actual operating range used in mobile phones was achieved by using appropriate compound electrodes for both the anode and cathode to increase the capacity for this application. In this way, it is necessary to design the battery so that its voltage, current, and other characteristics match the requirements of the target application.

### Laminated Batteries for Industrial Applications

Hitachi Maxell is applying the materials, processes, and other technologies it has been developing for batteries used in consumer products to commercialize cylindrical batteries for power tools. It is also developing a battery with a sealed laminated structure that has an even higher capacity (10 Ah). Because of the large amount of energy contained in a single 10-Ah battery, it is necessary to take a multi-dimensional approach to ensuring their safety in abnormal situations. By selecting an appropriate combination of active materials, separators, and other components, the batteries were able to pass tests of various different stress modes including overcharging, over-discharging, high ambient temperature, and nail



*Fig. 9—Battery Packs Made Using 10-Ah Laminated Package Cells. The 5P4P pack has a capacity of 200 Ah and the 5P6S pack has an energy storage capacity of about 1 kWh.*

penetration. The electrodes in the sealed laminated battery have a laminated structure which provides uniform reactivity and excellent heat dissipation characteristics. The batteries are targeted at use as battery units in large systems. Two examples of such large systems which were produced as prototypes are a large-capacity 200-Ah battery pack made up of four modules in parallel, each of which consists of five of these batteries in parallel, and a high-output, large-capacity pack (22.2 V, 50 Ah, 1 kWh) made up of six modules in series. Fig. 9 shows photographs of these battery packs together with their specifications. Even larger power supply systems can be configured by using a number of these packs together.

## CONCLUSIONS

This article has described work by Hitachi

Maxell, Ltd. on electrode material technologies and performance improvements in consumer batteries that use these technologies, and the new field of laminated industrial batteries.

Hitachi Maxell intends to utilize its experience in coating technologies built up over many years in the field of consumer batteries and work with other Hitachi Group companies to extend this into fields such as automotive and industrial batteries which are expected to undergo significant progress in the future.

## REFERENCES

- (1) M. Yamada et al., Proceedings of the 50th Battery Symposium, 2C12 (2009) in Japanese.
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