

Lithium Ion Battery

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The market of lithium ion battery (LIB) is growing year by year in small electronic equipment, cars and industrial applications, and the further expansion in future is expected. We have developed and commercialized the LIB related materials such as high-performance carbon cathode based on the technologies of various organic and inorganic materials. In October 2012, the development group of our Tsukuba Research Laboratory and the LIB equipment development group of Shin-Kobe Electric Machinery Co., Ltd. were consolidated for the fusion of technologies of material and device. In this paper, our LIB and LIB material technology for industrial use is outlined.

1 Trend of the Lithium Ion Battery Market

The LIB market got underway with applications to consumer products represented by cellular phones and personal computers (PC), followed by cars and then industrial use. Currently however, LIB used in consumer electronics products must offer even higher energy density due to the emergence of new devices such as smartphones and tablet computers. In response, silicon anode active material looks set to replace carbon anode active material for LIB. Moreover, technology¹⁾ to apply ceramic coating to the surface of a separator or electrode is being practically applied to further enhance safety.

In the LIB field for car applications, car-grade battery cells tailored for individual vehicles such as HEV and EV has been developed, the full-scale practical application of which is already underway. In response to the high LIB power output requirement for HEV, battery cells with power density of 4500 W/kg have been developed. Various innovations are being attempted to reduce the internal resistance of a battery. Since LIB for EV requires a high-energy output to extend driving distance, a battery cell with power density of around 130 Wh/kg has been put into practical use. Technologies to control the battery cell condition and cell temperature are also important because LIBs for car applications are used in battery modules comprising many cells.

In contrast, LIB for industrial use has now reached the stage of performing wide-range verification tests for output variation control for photovoltaic power generation system and wind power generators, back-up power supply while striving to reduce power consumption during peak demand at factories, buildings, etc., back-up power supply during power outages and partly employed for practical use. Performance requirements for LIB for industrial use vary significantly depending on the intended applications but the extended service life, high-level safety and reliability are common baseline performances, which development activity is thus continuing to achieve.

As case examples of LIB for industrial use, we introduce products and technologies developed/manufactured by our group company, Shin-Kobe Electric Machinery Co., Ltd., in the following:

2 LIB for Industrial Use

2.1 Large-Capacity, High Output Power and Long Service Life: CH75

This battery cell comprises a 75 Ah large-capacity cell that can be built into a large-scale electric energy storage system using relatively few cells with reliable performance and low operating cost. Even though CH75 is a large-capacity cell, it can maintain continuous discharge at 3 CA (225 A) and meet the required discharge current of a battery for 30 minutes or less while reducing power consumption during peak demand at factories, etc. Also CH75 can expect a service life to endure up to 4,000 repeated charge-discharge cycles (25 °C, at a 75% depth of discharge). To achieve such high output power and extended service life, we employed a newly Mn-rich cathode active material, reduced the electrode and electrolyte resistance and stabilized the SEI layer formed on the anode surface.

Notwithstanding its high-energy storage capacity, CH75 maintains a high level of safety and satisfies JIS (Japanese Industrial Standards) C8715-2, etc. Photos showing the external appearance of a cell and a module comprising 6 cells are shown in **Figure 1**.

2.2 Large-Capacity, Long Service Life, Float Charging: KL200F

KL200FL is a type of 210 Ah large-capacity float charging cell co-developed by Shin-Kobe Electric Machinery Co., Ltd. and NTT FACILITIES, INC. KL200F is used in a battery system to supply back-up power in emergencies for communication equipment and data centers. The distinctive feature of the cell is a type using non-flammable electrolyte by replacing flammable organic electrolytes to achieve high-level safety as we anticipate numerous cells will be installed in data centers and other facilities



Figure 1 CH75 Cell and Module



Figure 2 KL200FL Cell and 48 V Battery System

inside urban buildings. To make electrolyte non-flammable, phosphazene flame retardant is used in combination with a new electrolyte composition³⁾. Also, an expected service life of a decade or more has been achieved by improving the Mn cathode active material and employing the aforementioned new electrolyte composition⁴⁾. Photos showing the external appearances of a battery cell and a 48 V Battery System for Back-up Power Supply using this cell are shown in **Figure 2**.

Our technologies developed for LIB for industrial use are introduced as mentioned above; as for LIB service life for use in large-scale electric energy storage systems, a lifetime of 10 to 20 years, almost equivalent to installed facilities, is desired. Hence, we are engaged in developing technologies to secure intrinsic safety and extended battery life by using non-flammable electrolyte or non-combustible ionic solution.

3 Toward the Expanded Application of LIB in Future

The market size of LIB for consumer products, cars and industrial use is expected to continue growing in future. The LIB market for cars in particular has been soaring in recent years, while the market size for industrial use is also expected to reach around 4.5 billion yen annually. To maintain the expansion of the LIB market for cars, a huge breakthrough in terms of improving electric energy density and cost reduction is required. NEDO announced electric energy density of 250 Wh/kg and product cost of about 20 yen/kg as its development targets for 2020 or so. Furthermore, NEDO set an energy density of 500 Wh/kg and a product cost of about 10 yen/kg as targets for around 2030 in anticipation of the post-LIB age.

Since the expansion of the LIB market for industrial use in our business domain is expected to trail the market growth of LIB for cars, we foresee that proven LIB technologies backed by experience in consumer products and car markets can be provided for industrial applications at lower cost. Accordingly, we must be engaged in developing new LIB technologies for industrial use while constantly monitoring leading technologies. We must also validate various large-scale electric energy storage systems considered promising in a future energy plan, at an early stage and accumulate such technologies as required for practical use.

Conversely, LIB usage varies significantly depending on the intended use, such as the output variation control for photovoltaic power generation systems, back-up power supply during reduced power consumption at factories during times of peak demand. Therefore we need buildings and proposals for optimum electric energy storage systems from a cost perspective and with long-term reliability in mind by adopting a performance-sharing approach supported by an LIB/lead-acid battery hybrid energy storage system where LIB provides a quick charge/discharge rate and a lead-acid battery one that is slow. In addition to LIB improvements for industrial use, the development of technology offering optimum solutions established by combining our lead-acid battery, lithium ion capacitor and condenser is expected and will become increasingly important in future.

4 Overview of LIB Materials

LIB was first commercialized in 1991 and its market size is expected to reach 1 trillion yen in 2020 thanks to soaring demand for compact mobile equipment such as mobile phones and PCs, the market for environmentally friendly HEVs and EVs and that for industrial applications prompted by the introduction of a renewable energy policy after the Great East Japan Earthquake. Conversely, given the need for a breakthrough in battery performance including even higher energy density, extended service life, enhanced safety or further product cost reduction, the development of new technologies, including new battery materials, is considered crucial. The major common challenges for us to develop main LIB materials are indicated in the following:

- Cathode material: Higher capacity, Improved electronic conductivity, Accommodation of a swift charge/discharge rate, and others
- Anode material: Higher capacity, Improved cycle life performance characteristics, and others
- Separator: Safety improvement (balancing heat resistance and shutdown mechanism), and others
- Electrolyte: Non-flammable, Non-combustible, Lithium ion conductivity, Permeability, and others
- Binder resin: Electrolyte resistance, High adhesion, and others

Many materials are under development to meet wide-ranging performance requirements with potential LIB applications and usages. To date, we have been involved in R&D and production of mainly high-performance carbon anode LIB materials utilizing our material-related proprietary technologies, including various synthetic technologies involving organic/inorganic materials and process technology. Here, we introduce LIB material and other material technologies which we have developed in-house as case examples.

5 Our Proprietary LIB Materials and Material Technologies

5.1 Anode Material

Since LIB was commercialized in 1991, there has been sustained demand for high-energy density and improvement of the high current property required in the high-performance environment. While carbon material remains the mainstream material, metal anode materials such as silicon (Si) and tin (Sn), which can stoichiometrically allow higher battery capacity, and hybrid materials, have already been practically applied on a partial scale. However, some pending technical issues remain to be solved, including (charge/discharge) cycling characteristics, hence continued effort to boost the conventional performance of carbon anode materials⁷⁾ is required. Currently we are continuing efforts to develop and commercially produce graphite anode materials selected within our carbon anode material group, and supply them to our clients thanks to the advantageous feature of graphite anode material, where graphite anode material shows a rated capacity close to the theoretical capacity of graphite (372 Ah/Kg), a slight decrease in discharge capacity under high current discharge conditions, superior fast charge/discharge performance, a slight decrease in discharge capacity at high electrode density and the ability to materialize a higher-capacity battery. In addition, in response to the needs for a next-generation material which can offer battery capacity exceeding the theoretical value of carbon, we are in the process of validating the commercialization of next-generation metal anode material with more than twice the capacity of carbon and superior fast charge/discharge performance. We will continue this R&D activity toward commercialization of products to achieve even higher performance targets.

5.2 Binder Resin

In the resin binder field, a critical building block to construct electrodes, we newly developed solvent-based acrylic binder resins with superior anti-swelling property, thanks to electrolytes and good adhesion⁹⁾. Since this solvent-based acrylic binder resin shows high adhesion, with even small amounts of resin sufficient to fully activate the active material with a high specific surface area, and a slight decrease in discharge capacity at higher electrode density, it is effective to construct a high-capacity battery. In recent years, we have seen increasing demand for water-dispersible binders (hereinafter referred to as “waterborne”), which gives advantages from the point of adverse impact to environment and availability of resources, as a binder resin used for constructing anode material. Also, dimensional change (expansion and contraction) of next-generation metal anode material such as Si during charge-discharge cycles is relatively significant compared to carbon anode material, meaning additional performance improvements in binders will be required to retain the electrode structure. Accordingly we have been engaged in developing waterborne acrylic binder resins capable of meeting these performance requirements and have established the following elemental technologies:

- (a) Improve the modulus of elasticity at elevated temperatures by controlling the cross-linked structure and improving battery cycle life performance.
- (b) Achieve the target of high adhesive strength by screening monomers.
- (c) Realize high adhesion strength between layers of active material and current collector and balance with low (contact) resistance during the construction of electrodes by controlling optimum dispersibility and the degree of binder coverage.

We will continue our efforts to enhance performance by incorporating waterborne acrylic binder resin developed based on these elemental technologies toward next-generation LIBs.

5.3 LIB Safety-Enhancing Additive/Metal Impurity Trapping Material: Imogolite

Amid a continuing trend for upscale higher-capacity LIB, demand is also soaring for environmentally friendly cars and expanding industrial applications. In response to the increased significance of safety improvement, the progress of our approaches to enhance material safety, such as the development of flame retardant and the implementation of a short-circuit protection mechanism alongside system-related measures such as an excessive charge/discharge protection circuit and protection element is remarkable⁶⁾. We are in the process of developing and commercializing imogolite, a material to trap metal impurities that is effective in preventing LIB short circuits. Photos showing its external appearance are shown in **Figure 3**. Imogolite is an aluminum silicate of a monolayer nanotube with a high specific surface area and featuring many hydroxyl groups bound to inner/outer peripheral surfaces. Moreover, its superior capability to absorb Mn, Fe, Co, Ni and Cu to other adsorption materials such as zeolite and activated carbon has also been confirmed. To validate the principle of enhanced LIB safety based on such findings,

electrolyte added with minimal short-circuit suppression effect using Cu (foreign object) was assessed. Consequently, the degree of reduction in the open-circuit voltage of the cell using cathode material with an imogolite layer was improved. It was also confirmed that said short-circuit suppression effect achieved via an imogolite layer was better than with a ceramic or chelating agent/ceramic layer. Henceforth, we anticipate enhanced safety for next-generation large size/high-capacity LIBs by matching imogolite with LIB component materials (cathode/anode materials, separator and electrolyte).



Figure 3 Appearance of Imogolite

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Organizational Integration of LIB Next-Generation Material Development Group and Device Development Group of the Hitachi Chemical Group Companies

In future, we expect performance and other requirements against LIB component materials (cathode/anode materials, separator, electrolyte), including aforementioned materials, with high-level safety and reliability, advantages in terms of environmental compatibility and resource availability, a flexible manufacturing process, high performance and economically superior as well as excellent electrochemical performance will be further intensified. To date, we have been engaged in the business of high-performance carbon anode material. Henceforth, we intend to fully exploit our proprietary organic/inorganic material technology, promote new materials following current technical trends and wish to contribute to the development of next-generation high-performance LIBs.

The LIB Device Group, Shin-Kobe Electric Machinery Co., Ltd. and our LIB Material Development Group merged and formed an organization to promote battery technology in an integrated manner as of October 1, 2012. Henceforth, we will accelerate competitive product development activities by integrating material technology and LIB device technology and wish to make continuing contributions to energy industry.

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