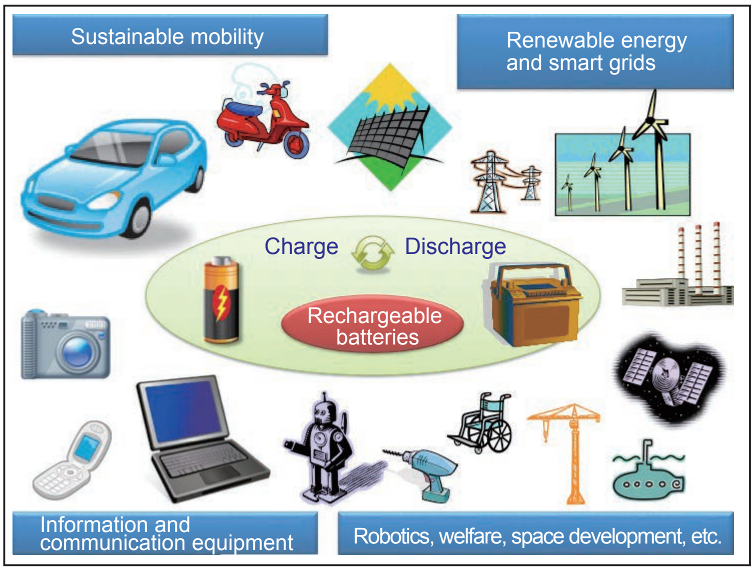
Lithium-Ion Battery Research at AIST

Research and Development of Lithium-Ion Batteries at AIST

From the nickel-metal hydride battery to the lithium-ion battery

A lithium-ion battery is a rechargeable battery used as a power source for the cordless operation of portable information and communication equipment such as mobile phones, laptops, and portable audio players. In addition, the practical application of large lithium-ion batteries is becoming increasingly common as a power source for hybrid, plug-in hybrid, and electric vehicles, which are expected to greatly reduce energy use compared with gasoline vehicles.

Japan was the first country in the world to develop a lithium-ion battery and began its commercial production in 1991. When mobile phones and laptops began to become popular in the 1990s, they were initially equipped with nickel-cadmium or nickel-metal hydride batteries as a power source. However, these batteries were replaced by the lithium-ion battery in the late 1990s and it has been used to the present day. This is because the lithium-ion battery is able to store much more electricity compared with other types of batteries of the same weight and volume and has thus been able to best meet the need for long-term operation. The rapid expansion of portable information and communication equipment has largely been made possible by the miniaturization of power sources through the development of the lithium-ion battery.



The expanding use of rechargeable batteries in society

The lithium-ion battery development project

Focused on the high potential of the lithium-ion battery, the predecessor of AIST, the Agency of Industrial Science and Technology of the former Ministry of International Trade and Industry, initiated a large-scale lithium-ion battery research and development project under the New Sunshine Program in 1992. The objective of this project was to develop a large-scale lithium-ion battery that could be used for electric vehicles and stationary rechargeable batteries for home use. The project was carried out with the participation of private companies, not only those within the battery industry but also those involved in chemical materials and in the use of these batteries, as well as research institutions and universities. Since lithium-ion batteries have a high energy density, the development of a large-scale battery that was both highly efficient and safe was a challenging goal, but the project was launched based on the judgment that it was a vital challenge for the future of the battery industry as well as for the automotive and energy industries.

The future of the lithium-ion battery

As a result of the technology development strategy pursued by the industrial sector and the government, which was decided much earlier in Japan than in the rest of the world, Japanese-made lithium-ion batteries have long held the largest share in the global market. However, the aggressive catching-up efforts of East Asian countries over the past several years have been posing a threat to Japan's leading share in the market of general-purpose lithium-ion batteries. Technological advancements of rechargeable batteries are characterized by so-called sporadic technological innovations based on new materials and new methods. Due to the demand for not only increases in the cruising range of electric vehicles but also for diversification of the vehicles themselves, and to the anticipated diversification of the use of rechargeable batteries, including their use in conjunction with electricity generated from renewable energy sources such as photovoltaic and wind power generation,

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the development of new technologies is becoming increasingly important. AIST is conducting research and development of new materials and new methods that can offer solutions to various issues surrounding rechargeable batteries so as to be able to propose pioneering industrial technologies. Moreover, to provide fundamental industrial technologies, AIST is striving to develop performance evaluation and safety evaluation technologies with the aim of establishing global standards and to elucidate the causes of deterioration of lithium-ion batteries. Through these efforts, AIST is hoping to contribute to enhanced international competitiveness of the battery, automotive, material, and other Japanese industries.

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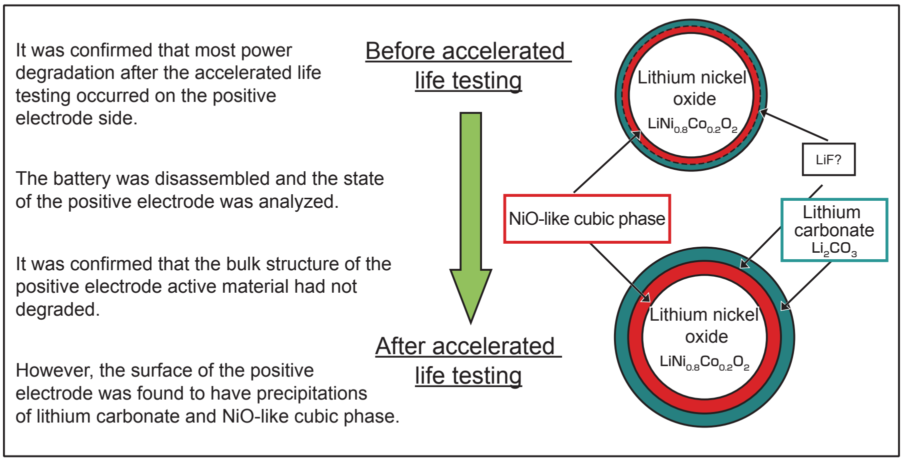
Challenges for Elucidation of the Degradation Mechanisms of Lithium-Ion Secondary Batteries for Vehicles

Requirements of rechargeable batteries for vehicles

In recent years, both hybrid and electric vehicles have become widely accepted in society as environment-friendly vehicles. Unlike conventional gasoline-powered vehicles, these vehicles are equipped with a high-capacity rechargeable battery and the adoption of high-energy-density lithium-ion secondary batteries has already begun. Since vehicles are required to have an operating life of more than 10 years, the rechargeable batteries used in them are also required to have a similar life and this is one of the various developmental issues of automotive rechargeable batteries that remain to be solved. In addition, along with the expansion of the market for automotive rechargeable batteries, global standardization activities at, for example, the International Organization for Standardization (ISO), the International Electrotechnical Commission (IEC), and the Society of Automotive Engineers (SAE) that aim to establish performance evaluation and safety evaluation methods for batteries are becoming widespread and the competition for leadership in the field of standardization is also intensifying. Responding to this situation, Japan is conducting international standardization activities within the fundamental technology development framework of a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO) called the Li-ion and Excellent Advanced Batteries Development (Li-EAD) Project.



It was confirmed that most power degradation after the accelerated life testing occurred on the positive electrode side.

The battery was disassembled and the state of the positive electrode was analyzed.

It was confirmed that the bulk structure of the positive electrode active material had not degraded.

However, the surface of the positive electrode was found to have precipitations of lithium carbonate and NiO-like cubic phase.

Comparison of a positive electrode material before and after an accelerated life test showing changes on the surface

Elucidation of degradation mechanisms

In the five-year Li-EAD Project, which began in FY 2007, AIST has been working from the material perspective with the Central Research Institute of Electric Power Industry (CRIEPI), the Japan Automobile Research Institute (JARI), and Tohoku University to develop a life evaluation method applicable to rechargeable batteries by accelerated life testing, as well as to elucidate the degradation mechanisms and develop methods to control degradation. Since rechargeable batteries for vehicles are required to be usable for more than 10 years, life estimation is vital in guaranteeing the quality of a product as well as in shortening the product

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development time, and accelerated life testing needs to be conducted.

Because of the characteristics of a lithium-ion secondary battery such as its capacity and power degrade sharply under high temperature and high state of charge (SOC) conditions, the testing conditions such as the temperature and the range of SOC conditions, under which common degradation mechanisms are applicable, must first be defined. To meet this objective, CRIEPI has been performing analyses without disassembling cells and AIST has been analyzing the interiors of batteries in detail by disassembling them and both institutes have been comparing the results before and after various tests to clarify the degradation mechanisms of battery characteristics.

The indexes that define the life of a rechargeable battery for vehicles are capacity and power. When developed cells provided by battery manufacturers and model cells developed by AIST were used in tests simulating the use in hybrid and plug-in hybrid vehicles, the results showed a general tendency whereby a decrease in the power level of the battery determined the life of the battery.

Analysis methods such as those employing quantum beams are being used to examine the surface structure and bulk structure of electrodes. The results are beginning to reveal that changes in the surface structure of the positive electrode cause a decrease in the power level. The changes observed on the surface of a positive electrode material after an accelerated life test are shown in the figure. Changes were observed in the crystal structure and the growth of coating materials near the surface of the positive electrode material after the test, leading to the finding that the change in the crystal structure in particular was related to the decrease in power.

Aiming to establish international standards and national validation system

AIST is also currently participating in projects for the development of performance evaluation methods for automotive rechargeable batteries and the development of safety evaluation methods for stationary lithium-ion secondary batteries. By applying the knowledge accumulated so far on analysis techniques and on lithium-ion secondary batteries in the development of these evaluation methods, AIST is pursuing research and development to contribute to projects for the establishment of international standards and a national validation system from the standpoint of technology development.

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Development of a Lithium-Ion Battery with a High-Capacity Silicon-Based Negative Electrode

Problems of lithium-ion batteries for electric vehicles

Significant progress has been made in the field of lithium-ion batteries since their commercialization in Japan in 1992. A national project entitled Research and Development of Dispersed-Type Battery Energy Storage Technology was launched in 1992 and continued for 10 years with the aim of developing large lithium-ion batteries that could be used in electric vehicles and as household rechargeable batteries. The outcome of the project was the world's first full-scale production of electric vehicles, which began in 2009. By around 2020, electric vehicles are expected to hold a 1 % share (about 700,000 vehicles) in global sales of automobiles. To make this a reality, increased cruising range, improved battery durability, further safety enhancements, reduced battery cost, and other advances are indispensable. Approximately 20 years have already passed since the commercialization of the current type of lithium-ion battery. To attain further improvements in its characteristics, a quantum leap in performance enhancement is required that breaks through the barriers of conventional thinking by means of innovations in materials technology.

Development of a high-capacity silicon-based negative electrode and enhancement of the thermal resistance and safety of batteries

A silicon-based negative electrode (1,500 mAh/g) with five times the capacity of a conventional graphite-based negative electrode was developed as a new high-

capacity negative electrode. Although the volume of a silicon-based material normally changes by more than double accompanying the charge and discharge of a lithium-ion battery, by developing polyimide-based binders and stainless steel foil substrates with high strength and superior heat resistance, its life has been prolonged (Fig. 1). A heat-resistant nonwoven fabric separator was also developed as the separator used to separate the positive and negative electrodes.

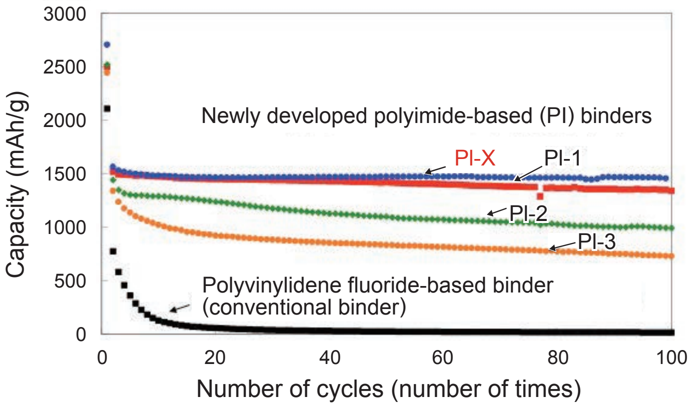

Fig. 1 Electric capacity of silicon-based negative electrodes and improvement in the cycle life

As for the positive electrode, an iron phosphate positive electrode with enhanced heat-resistance and output characteristics was developed. The results of performance verification showed that the newly developed battery can operate at temperatures from as low as -30 °C to as high as 120 °C, which was a huge improvement from the operational temperature range of between -5 °C and 45 °C of conventional batteries. Even at 80 °C, it showed stable operation during a 6-minute alternating rapid charge and discharge cycle (Fig. 2). As the next step, we made a 1 Ah-class laminated trial battery and conducted a nail penetration safety test. In the case of a conventional battery with a graphite-based negative electrode, the voltage dropped and the battery temperature rose to more than 90 °C due to a dead short circuit. However, the trial battery experienced only a momentary short circuit and the voltage immediately returned to its normal level, with a rise in temperature of less than 10 °C. This is because in the case of a graphite-based negative electrode, due to its high electrical conductivity, the electrical current becomes concentrated in the short-circuit area and begins to generate heat. In contrast, a silicon-based negative electrode has a function whereby the resistance is dramatically increased when a short-circuit area discharges electricity completely (lithium is released), and shuts down the electric current so as to control the rise in temperature. Hence, through the development of new materials, we were able to develop a new lithium-ion battery that has high capacity, superior heat resistance, and a higher level of safety.

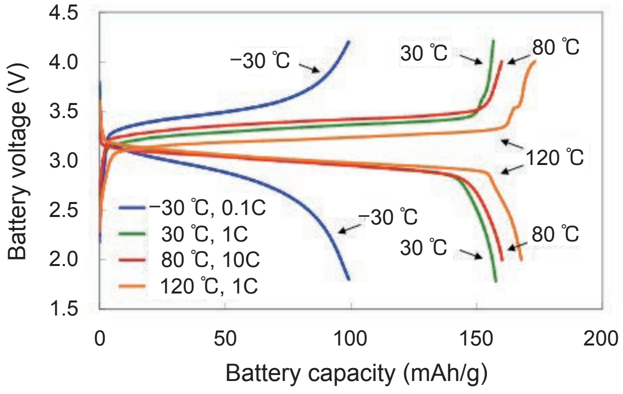

Fig. 2 Temperature characteristics of the new lithium-ion battery (with a silicon-based negative electrode and an iron phosphate positive electrode)

Future development

To create large batteries so as to expand their use to vehicles and industrial equipment, improvements are essential not only in battery characteristics and safety, but also in terms of a material composition that does not require the use of rare resources. Through collaborative research with the industrial sector, we are planning to further promote the development of new battery materials and to propose new designs for batteries that best suit their anticipated applications.

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Using Computational Science to Investigate the Interface between the Electrolyte and Electrode in a Lithium-Ion Secondary Battery

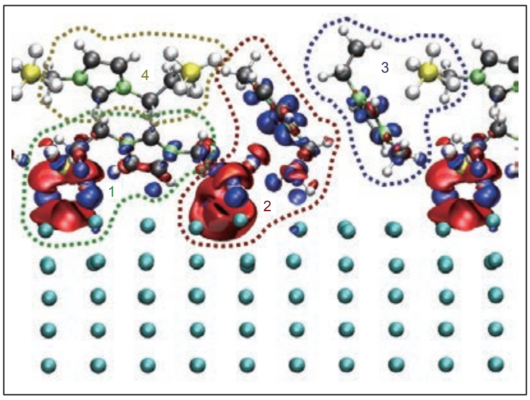
– First-principles calculations of the interface between an ionic liquid and metallic lithium –

Application of an ionic liquid as the electrolyte of a lithium battery

Ionic liquids are composed of positively and negatively charged molecules and have excellent properties such as high ionic conductivity, non-volatility, flame resistance, etc., and their application as an electrolyte for lithium-ion secondary batteries is desired. Ionic liquids are expected to be safer than flammable organic solvents, and the development of batteries with a higher energy density can be anticipated because they can prevent dendritic growth on metallic lithium negative electrodes, which are likely to be the next-generation high-capacity negative electrodes. The properties of bulk ionic liquids are beginning to be understood at the atomic level through studies using molecular dynamics simulations.[1] However, battery performance depends not only on the bulk electrolyte properties but also on the charge transfer properties at the interface between the electrode and the electrolyte,[2] and it is therefore essential to understand what takes place at the interface.

First-principles calculations based on the density functional theory

First-principles calculations can be effective in grasping the behavior of atoms and electrons at the interface between an ionic liquid and a lithium electrode.[3] High-accuracy computations based on the density functional theory were performed on a large supercell containing an interface between metallic lithium and an ionic liquid to understand the interactions between the positively and negatively charged molecules and the metal surface, the ionization and reduction of lithium, and the molecular species dependence. The figure shows an example of a calculated interfacial atomic arrangement between an ionic liquid composed of a cation, C_2mim^+ (1-Ethyl-3-methylimidazolium), and an anion, BF_4^-, and the metallic lithium, with interfacial electron transfer. Since an enormous amount of computations would be required for a first-principles calculation of a real liquid structure, the ionic liquid was represented by an $[C_2mim][BF_4]$ crystal and constructed as a layered structure on the surface of lithium in this calculation. In the figure, the interface lithium atoms were displaced due to the strong attraction of BF_4^-, nearby electrons were transferred to C_2mim^+, and unoccupied orbitals of C_2mim^+ close to the interface were partially occupied. This represents the main reaction between metallic lithium and an ionic liquid that progresses when they come into contact with each other and, reflecting the strong ionization tendency of lithium, the lithium atoms were ionized to the halfway level. When the same calculations were made for precious metals, a similar phenomenon did not occur. The reduction tendency of cationic molecules was also observed in experiments, and the stability of cationic molecules can be examined through the present kind of calculations.



Atomic arrangement and electron transfer at the interface between an ionic liquid ($[C_2mim][BF_4]$) and metallic lithium

Pairs composed of an C_2mim^+ cation (1-Ethyl-3-methylimidazolium) and a BF_4^- anion are circled by dotted lines. The areas in red are those where electron density decreased due to interface formation and the areas in blue are those where electron density increased.

Designing the optimized ionic liquid

On the other hand, we have found that rather simple first-principles calculations

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of the adsorption of only anion-cation molecular pair on the lithium surface also provide the results of electron transfer, atomic displacement, and adsorption energy, similar to the large-supercell calculation mentioned above. Thus we adopted such simple calculations of molecular-pair adsorption, and performed systematic investigations of the adsorption energy and the atomic and electronic structures for various pairs of molecular species placed on metallic lithium.[4] This should be effective to develop a design guideline for ionic liquids that express superior interfacial properties. In order to optimize the anionic molecular species for the fixed cation as C_2mim^+, we perfomed systematic calculations by varying the anionic molecule among amide-based FSA ($[(FSO_2)_2N]^-$), FTA ($[(FSO_2)(CF_3SO_2)N]^-$), and TFSA ($[(CF_3SO_2)_2N]^-$) and borate-based $CF_3BF_3^-$ and $C_2F_5BF_3^-$. The results showed a tendency that an ion pair with larger adsorption energy exhibited a lower experimental value of interfacial charge-transfer resistance between an ionic liquid and a lithium electrode. Our next plan is to extend and improve the design guideline for ionic liquids by making detailed comparisons between calculations and experiments for a larger variety of cationic and anionic molecules.

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Development of Rechargeable Batteries with Organic Substances
– Aiming for a rare-metal-free battery by replacing inorganic electrode materials with organic materials –

The need to reduce the use of rare metals in lithium-ion batteries

Presently, oxides of rare metals, represented by lithium cobalt oxide ($LiCoO_2$), are generally used for the positive electrode material in lithium-ion batteries, but reduction of their use and replacement with other materials are considered to be necessary in view of the restrictions on resources. In addition, since countries that produce lithium are also limited, replacement of lithium with other elements such as sodium and magnesium that are more universally distributed is also demanded.

The possibility of realizing an organic rechargeable battery

While there have been many attempts to reduce the use of rare metals through their replacement with other elements, we have been taking a different approach by focusing on reduction-oxidation (redox)-active organic materials as candidate materials to replace the rare-metal oxides used as positive electrode materials (Fig. 1). If the multielectron transfer reaction characteristic of organic materials can be employed in batteries, such materials will have a capacity density exceeding that of the present inorganic positive electrodes. Specifically, our research is centered on quinones and indigo derivatives. A quinone of the simplest structure, 1,4-benzoquinone, has a large theoretical capacity, but due to its high sublimability its application as an electrode material has been difficult. However, by introducing the peripheral substituents into the benzoquinone structure, we have succeeded in making use of its function as an electrode material (Fig. 2). For example, in the cases of a benzoquinone with methoxy groups[1] and a pentacene derivative with a polycyclic structure,[2] more than double the discharge capacity per weight has been attained compared with the current positive electrode material, $LiCoO_2$.

Meanwhile, we have discovered that indigo derivatives used in indigo dyeing etc. can also function as a positive electrode. While the capacity itself is insufficient, of particular note is a derivative with sulfo groups (indigo carmine) that has shown a life of more than 1,000 cycles of charge and discharge,[3] indicating that even organic substances that are believed to have inferior durability can reach a level comparable to that of inorganic materials presently in use.

We are also investigating the possibility of using these organic materials in a sodium secondary battery and a magnesium secondary battery, which are regarded as promising candidates for a post-lithium secondary battery. So far, several organic substances were found to function in sodium- and magnesium-based batteries as well. This high adaptability irrespective of cationic species is a feature that is not often seen in typical inorganic active materials, and is an indication of the usefulness of organic electrode materials as materials for post-lithium secondary batteries.

Expected future developments

We have discovered many organic materials that can function as positive electrode materials for lithium-ion batteries. Several organic materials appear to be promising as materials for post-lithium secondary batteries using sodium or magnesium. These organic materials show great possibilities as next-generation battery materials because they are free from resource restrictions, and their electrochemical properties can be controlled through molecular design.

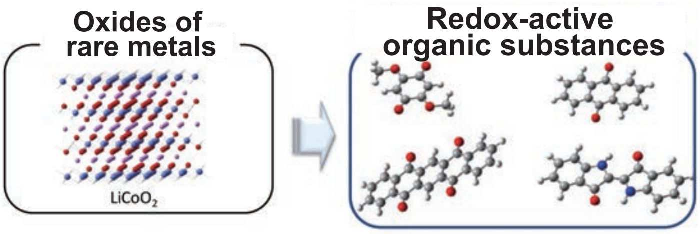

Fig. 1 Concept of this research to replace oxides of rare metals with organic substances

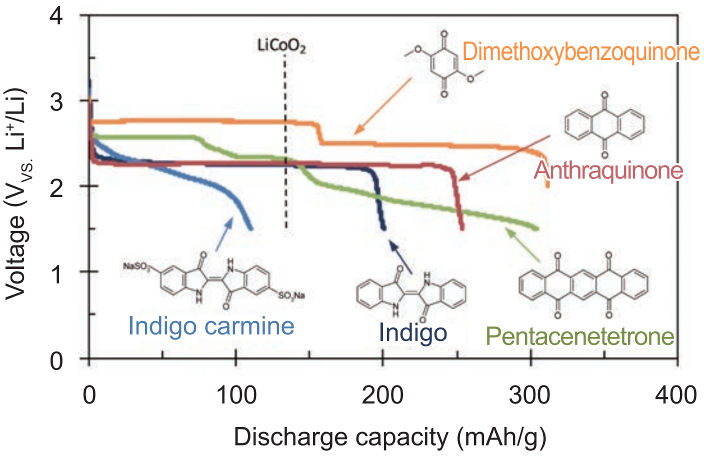

Fig. 2 Discharge curves of various organic positive electrode materials (dotted line: capacity of presently used $LiCoO_2$)

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Lithium Redox Flow Batteries

Utilization of renewable energy and electricity storage technology

The utilization of clean and safe natural energy such as solar and wind power is currently the focus of much attention. However, because large fluctuations exist in these natural energy sources, large-capacity electricity storage devices such as the sodium-sulfur battery (NaS battery) and the redox flow battery are necessary for their use. However, each of these batteries has disadvantages. The operating temperature of a NaS battery is as high as 300 °C, while in the case of a redox flow battery, since it uses aqueous solutions on the negative and positive electrode sides, the generated voltage is low, restricted by the hydrogen and oxygen evolution potentials. Given these circumstances, expectations are being placed on the development of a new electricity storage device.

Newly developed lithium redox flow secondary battery/fuel cell

We have developed a new type of lithium redox flow battery by applying a

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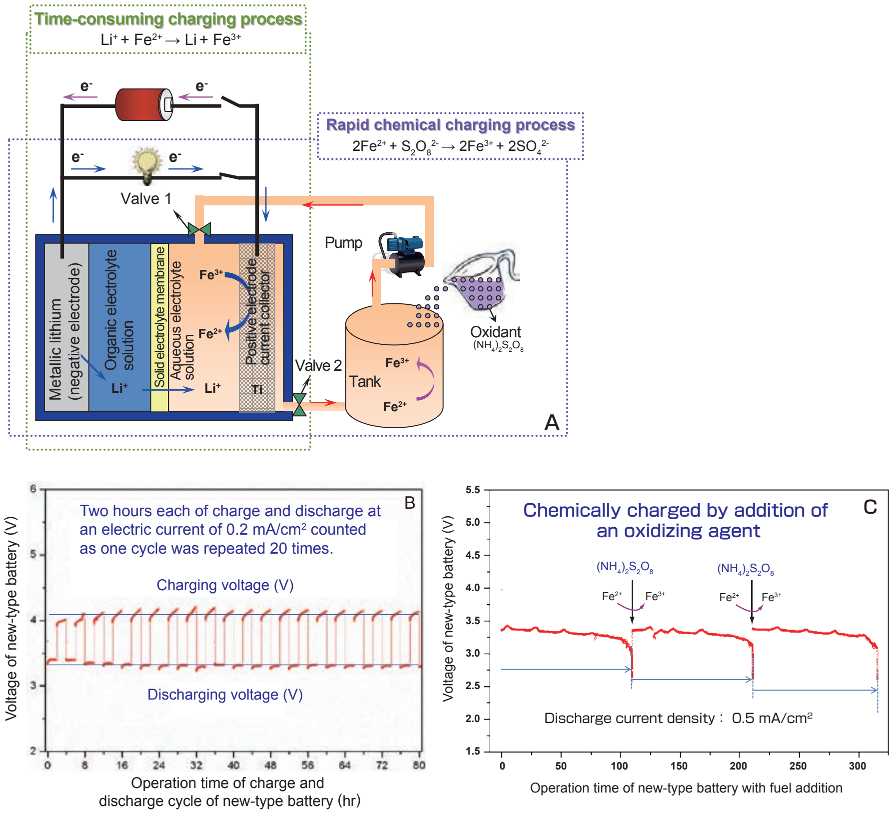

A:Schematic drawing of an electrically charging lithium redox flow secondary battery and a chemically charging lithium redox flow fuel cell
B:Characteristics of the charge and discharge cycles of a lithium redox flow secondary battery
C:Characteristics of the recovery cycle of a lithium redox flow fuel cell

hybrid electrolyte solution to the already developed new-type lithium-air battery, using metallic lithium as the negative electrode and an aqueous electrolyte solution containing a conventional redox ion pair (for example, Fe^{3+}/Fe^{2+}) as the positive electrode.[1] The configuration of this battery is shown in the figure (A), inside the green dotted frame. The use of metallic lithium as the negative electrode increases the voltage by approximately threefold compared with a conventional redox flow battery. Moreover, because no liquid active material is used on the negative electrode side, there is no need for an electrolyte solution storage tank on that side. As a result, space savings and improved energy density can be expected.

The figure (B) shows the charge and discharge cycle characteristics of the developed battery. When charging and discharging are repeated, the following reaction occurs: $Li + Fe^{3+} <=> Li^+ + Fe^{2+}$. During this process, the aqueous electrolyte solution that contains the Fe^{3+}/Fe^{2+} ion pair used on the positive electrode side is stored in a tank and then pumped back to the positive electrode side.

When the battery is completely discharged, Fe^{3+} is reduced to Fe^{2+}. A conventional redox flow battery cannot continue discharging unless the Fe^{2+} is converted back to Fe^{3+} through long hours of charging. However, in the case of this new-type battery, Fe^{2+} can be rapidly oxidized to Fe^{3+} without a long charging process by simply adding an oxidizing agent $(NH_4)_2S_2O_8$ (= fuel), allowing it to be used continuously (figure (C)). The added $(NH_4)_2S_2O_8$ seems to oxidize all Fe^{2+} to Fe^{3+} in a short period of time. What is more, since the chemical oxidation reaction and the electrical response of the electrode each occur in a separate space, the product of oxidation (in this case, Li_2SO_4) can be easily collected, and quick and easy recycling of lithium resources is expected.

Future developments

The new-type lithium redox flow battery is expected to be used not only in large-capacity stationary storage devices, but also as a mobile energy source in applications such as vehicles, for example. In this latter case, the battery would be used as a secondary battery when travelling for short distances and as a fuel cell requiring the addition of an oxidizing agent when travelling for long distances. We are planning to promote further research and development so that a stable and optimized new-type battery can be brought into practical use.

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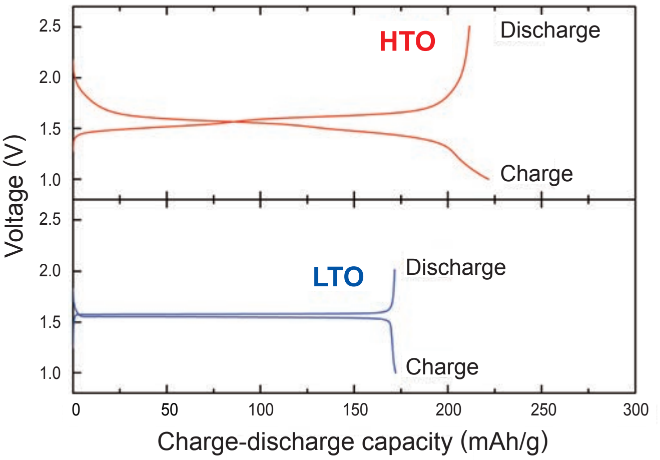
Development of a New Titanium Oxide Negative Electrode Material for Next-Generation Lithium-Ion Batteries

Present state of oxide-based negative electrode materials

The next-generation lithium-ion batteries, which are expected to be more widely used as large rechargeable batteries for stationary, automotive, and other applications, are assumed to be in use for longer than 10 years, so improvement of their life characteristics is vital. The most commonly used negative electrode materials for lithium-ion batteries at present are graphite-based carbon materials. However, batteries with a carbon material as the negative electrode have experienced problems, such as a dramatic decrease in capacity when used in high-temperature environments exceeding 60 °C. The cause of this is considered to be a side reaction on the electrode surface and in other areas that is triggered due to the low electric potential of the negative electrode. To improve the life of lithium-ion batteries, the negative electrode needs to be replaced by oxide-based materials with high potential.

Among possible oxides, due to the fact that lithium titanium oxide $Li_4Ti_5O_{12}$ (LTO) has an electric potential plateau at around 1.55 V against a lithium electrode and also has good charge-discharge cycle reversibility, it is now entering practical use as a negative electrode material in rechargeable batteries for vehicles. However, because of the characteristics of its crystal structure, the charge-discharge capacity of LTO has been limited to 175 mAh/g. Moreover, since it contains lithium as a constituent element, it has a drawback in terms of cost. Given this situation, there are strong expectations for the development of high-capacity, next-generation oxide-based negative electrode materials with high electric potential comparable to that of LTO.



Charge and discharge curves of the newly developed titanium oxide HTO and the conventional material, LTO (LT-017, Ishihara Sangyo Kaisha, Ltd.) (counter electrode: metallic lithium; current density: 50 mA/g)

Development of a new high-capacity titanium oxide, HTO

At AIST, we have been using a soft chemical synthesis method, one of low-temperature synthesis processes of inorganic materials, in the search for high-capacity titanium oxide materials. The advantage of this synthesis method is that the structural design of new materials can be easily performed by altering the chemical composition while the characteristics of the skeletal structure of the starting material remain unchanged. Using sodium titanium oxide ($Na_2Ti_3O_7$) as the starting material, we discovered that a new hydrogen titanium oxide, $H_2Ti_{12}O_{25}$ (HTO),[1] can be synthesized by first subjecting $Na_2Ti_3O_7$ to an acid treatment in order to synthesize a precursor substance, hydrogen titanium oxide ($H_2Ti_3O_7$), and then applying heat to dehydrate the precursor substance. The developed HTO has about the same level of voltage as the presently used LTO and can provide a high charge-discharge capacity of 225 mAh/g, which is higher than that of LTO (see figure).[2] Moreover, since hydrogen contained in HTO forms a skeletal structure by hydrogen bonding, it has a stable structure that is unaffected by the lithium insertion and extraction reactions occurring when the battery is charged and discharged.

Future developments

Together with Ishihara Sangyo Kaisha, Ltd., AIST is making efforts to develop a method for the industrial production of HTO and is searching for ways to further

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improve its capacity and output. HTO has the advantage of being inexpensive because it does not contain lithium as a constituent element. It is therefore expected to contribute to increased capacity, longer life, and lowering of the cost of large rechargeable batteries for various applications, including vehicles.

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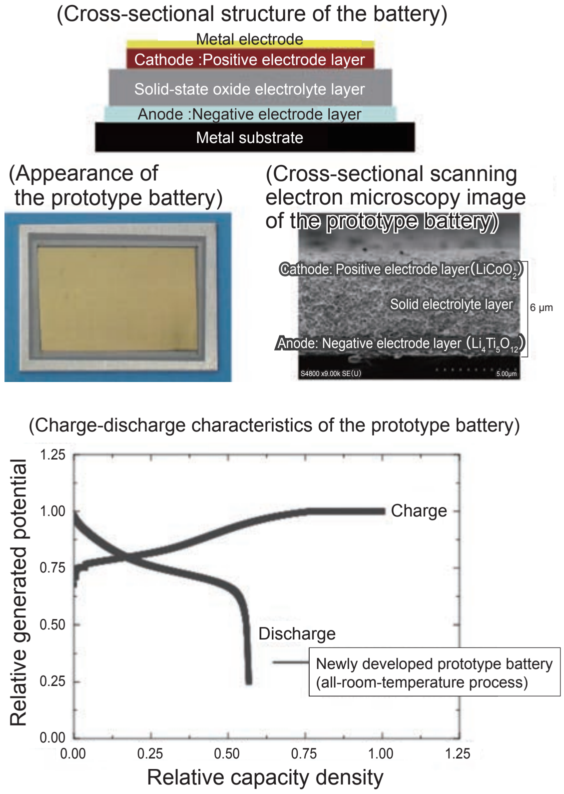
Challenging the Development of an All-Solid-State Thin-Film Lithium-Ion Battery by the Aerosol Deposition Method

Social background of the development

The all-solid-state lithium-ion battery, a type of next-generation rechargeable battery, uses a solid electrolyte that has neither combustibility nor fluidity. For this reason, many single batteries can be connected in series and stored in one container, simplifying the control system. This is expected to lead to the development of a high-energy-density battery pack, which is the key to improving the performance of plug-in hybrid vehicles and electric vehicles. However, because the electrolyte is solid, the ionic conductivity is much lower than that of a liquid electrolyte, the internal resistance is high, and the performance required for practical applications has not been achieved yet. The key to the development of an all-solid-state battery lies in the development of a solid electrolyte material with sufficiently high ionic conductivity, and in the development of a thin electrolyte layer while preserving the electric insulation to improve the ion transferability inside the battery. To make certain that ions are efficiently conducted to active materials inside the positive and negative electrode layers, it is also important to combine that the electrode layers and the solid electrolyte.



The all-solid-state thin-film lithium-ion battery fabricated by the AD method and its charge and discharge characteristics

Fabrication of an all-solid-state thin-film lithium-ion battery by the aerosol deposition method

To improve the performance of the battery, AIST is using the aerosol deposition (AD) method, AIST original method, to fabricate a thin-film solid electrolyte and combine the electrolyte with electrode materials. In the AD method, fine particles are spray-coated under reduced pressure, which, in principle, makes it possible to form a high-density solid-state thin-film electrolyte

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at room temperature and laminate it with cathode (positive electrode) and anode (negative electrode) layers. In our recent research, we have investigated various lithium oxides as materials for solid-state electrolytes and formed a solid-state electrolyte layer of between 3×10^{-6} and 5×10^{-6} S/cm ionic conductivity. Using common electrode materials such as $LiCoO_2$ or $LiMn_2O_4$ as a material for the cathode and $Li_4Ti_5O_{12}$ as a material for the anode, the electrolyte and cathode and anode were laminated into three layers by the AD method.

In the AD method, particles of the raw material are smashed onto a substrate at a very high pressure of more than 3 GPa. This is similar to powder compaction of raw material powder with a high pressing pressure. Due to this effect, each layer formed a very dense film structure, even though it was fabricated in a room-temperature process. In addition, since only a very limited surface area of the substrate and the underlying layer is subjected to high pressure, collision damage on the substrate and on the interfaces between the layers is minimized, and mutual diffusion due to heat was not observed. The thickness of each of the cathode layers, anode layers, and electrolyte layers was optimized and a prototype all-solid-state thin-film lithium-ion battery based on oxides was produced. The charge and discharge characteristics of this type of battery were confirmed for the first time in the world.

Future developments

The prototype all-solid-state thin-film lithium-ion battery is only at the initial stage of development and its performance is still far from practical applicability. Yet, the fact that an oxide-based all-solid-state thin-film lithium-ion battery fabricated by the AD method, a room-temperature process, actually functions shows that the AD method is a highly promising fabrication method for the realization of such a battery. We will persist in our search for a higher performing solid-state electrolyte material while continuing with the optimization of the fine structure of the thin film, so that a battery that exceeds the performance of the conventional lithium-ion battery can be brought into reality.

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Jun AKEDO

Ceramic Electrolyte Sheet for Next-Generation Rechargeable Batteries

Using an all-solid battery as a power source

With increasing demand for large-scale and high-capacity rechargeable batteries, the securing of additional safety is becoming a critical issue. All-solid-state lithium secondary batteries that do not use liquid electrolytes offer the possibility of increased voltage endurance and heat stability, and are therefore receiving considerable attention as a potential means of improving the safety of high-capacity batteries. The Advanced Manufacturing Research Institute is pursuing research and development of power supply technologies applicable to large equipment such as next-generation vehicles with a focus on ion-conductive ceramics, and is developing manufacturing technologies for various components necessary for improving the performance of all-solid batteries, etc.

Ceramic electrolyte sheet for large batteries

We are focusing on $Li_{1+x}T_{i2-x}Al_xP_3O_{12}$ (LTAP) ceramics with a sodium superionic conductor type crystal structure as candidate electrolyte materials that can be used over wide temperature ranges and are suitable for not only the all solid-state batteries but also for the lithium-air batteries. Generally, a lithium-ion conductive ceramic electrolyte is unstable when in contact with water, but LTAP is an exception to this with its high water resistance. It is therefore expected as a possible material for the lithium-air battery, which is referred to as the ultimate battery. LTAP is known to possess the physical property of high lithium-ion conductivity (about 10^{-3} S/cm) inside the bulk even at room temperature. However, there has been a problem in that the resistance at the grain boundary is high

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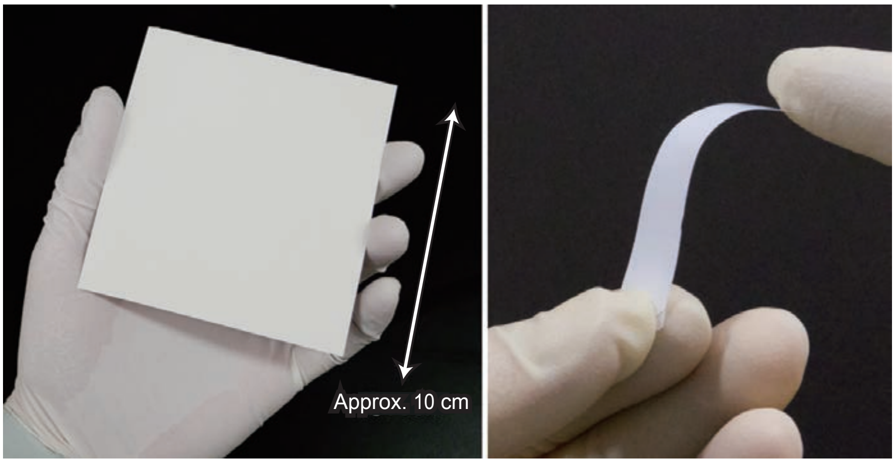
in the materials with a polycrystalline structure such as ceramics. When such materials were made into a polycrystalline sheet for a battery, the overall ionic conductivity decreased (about 10^{-4} S/cm at room temperature). In addition, the manufacture of a large and thin electrolyte sheet has been difficult.

We have developed a new manufacturing process in which the ceramic electrolyte sheets can be manufactured through the application of, for example, ceramic tape casting technology. With this, we achieved to fabricate large-sized thin ceramic electrolyte sheets that until now have been difficult to produce. Additionally, by optimizing the composition of starting materials and the sintering condition, the resistivity of grain boundary was drastically reduced and we succeeded in manufacturing a ceramic electrolyte sheet with a high overall conductivity at room temperature (10^{-3} S/cm, 27 °C, transport number: approx. 1). The developed ceramic electrolyte sheet has sufficient flexibility against bending stress and in the case of a sheet with a thickness of 80 μm, it demonstrated tolerance against bending with a curvature radius of approximately 5 cm, indicating the potential for further improvements in durability against vibration and other external forces.



The developed ceramic electrolyte sheet and a photograph showing that the sheet can be flexibly bent

Future developments

With the goal of developing a new safe and high-capacity ceramic battery, we are determined to establish a technique that can be used to easily manufacture thinner and larger-sized sheets. At the same time, we are planning to develop microstructural design technology for the surface of the electrolyte to realize rapid charge and discharge performance. We are also planning to conduct investigations in various areas including studies on technologies for achieving higher electrolyte-electrode interface performance and on the evaluation of material stability, to promote research and development aiming at a large all-solid lithium-ion battery module.

Functional Integration Group,
Advanced Manufacturing
Research Institute

Koichi HAMAMOTO

Establishment of Evaluation Technologies Applicable to Lithium-Ion Battery Materials

Introduction

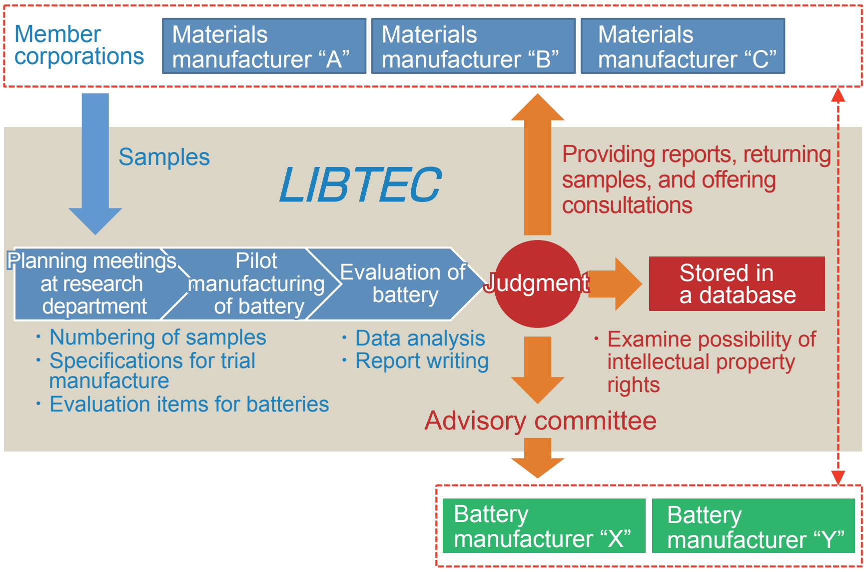
The light and compact-sized lithium-ion battery developed in Japan is a focus of widespread attention not only for its use in mobile information and communication devices such as cell phones, but also as a power source for electric vehicles and as a means for promoting the use of renewable energy. Japan has long held a dominant share of the global market for such batteries, but in recent years, companies throughout the world have been actively engaged in fierce international competition.

Lithium-ion battery material manufacturers in Japan have superior technologies, and each manufacturer has been developing a wide range of high-quality battery materials by applying its unique fundamental technologies. On the other hand, the manufacturers have encountered the problem that the practical characteristics of these materials when used in batteries were not being evaluated smoothly. Given this circumstance and from the perspective of strengthening international competitiveness, a framework that includes the development of evaluation technology and enables fast and accurate evaluation of new battery materials and the means to feed back these results into the development of battery materials has become indispensable.

Therefore, on April 2, 2010, the Lithium Ion Battery Technology and Evaluation Center (LIBTEC) was established under the auspices of the Ministry of Economy, Trade and Industry to evaluate materials developed by battery materials manufacturers, and began to conduct research and development at AIST Kansai.

Activities at LIBTEC

LIBTEC currently has a total of 19 corporate members, composed of 18 materials manufacturers and AIST. The goal of LIBTEC is to properly evaluate materials created by manufacturers for use in batteries, to develop coordination techniques and evaluation methods to reduce development times that will facilitate the provision of promising materials to battery manufacturers in a timely manner. At the present time, LIBTEC has adopted a concentrated research method with 43 personnel, comprising researchers sent from member corporations at the core as well as retirees from battery manufacturers providing directions in evaluation technologies. At LIBTEC, we are pursuing research on evaluation methods as well as research and analysis of electrode structures and processes that are fundamental technologies for these evaluation methods.



Materials evaluation process and flow of information at LIBTEC

In FY2010, LIBTEC selected standard model materials and the process of creating batteries using the materials and established an evaluation method based on them. Using this method, we evaluated materials created by the member corporations. We also formulated manufacturing and evaluation methods applicable to button type batteries and evaluated 35 types of battery materials.

In FY2011, we further advanced these technologies and methods and examined a standard battery manufacturing method for laminated type batteries. We also examined appropriate evaluation methods according to the battery application, such as for hybrid vehicles, electric vehicles, stationary use, etc. In addition, we are promoting research on the process of formulating electrode structures, which will be a fundamental technology, and research that will make possible the numerical evaluation of the structure of the conduction paths of electrons and ions by altering the material. We have also begun to investigate methods for evaluating single particles so that information on the characteristics of active materials can be obtained without the actual construction of a battery.

Web site of LIBTEC:
http://www.libtec.or.jp/_en/

Lithium Ion Battery Technology and Evaluation Center (LIBTEC)
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