NIMS NOW INTERNATIONAL

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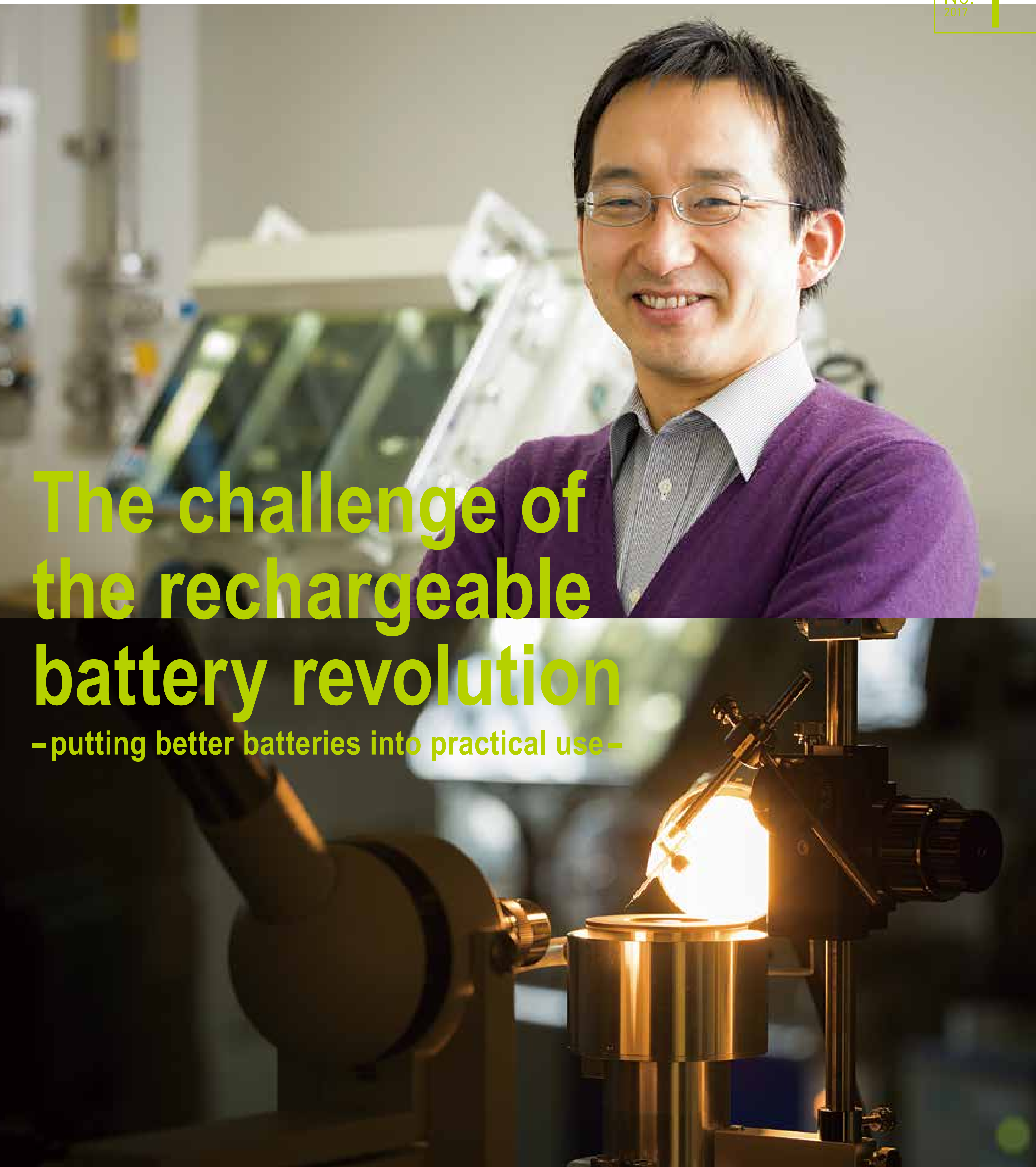

The challenge of the rechargeable battery revolution

–putting better batteries into practical use–

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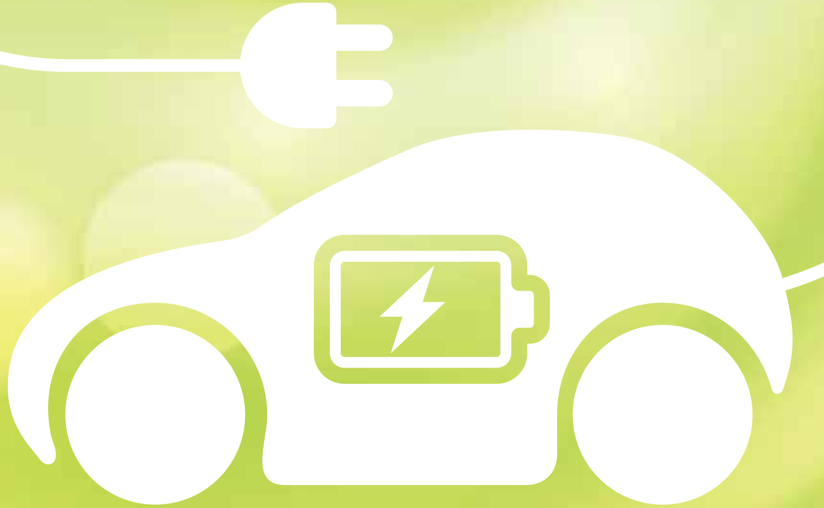
The rechargeable (secondary) battery, which store and carry electricity, has made it possible to use repeatedly through its charge/discharge cycle. The lithium ion battery—now playing a pivotal role in mobile devices and electric vehicles—was put into practical use as a result of major contribution from Japanese researchers. It is truly a groundbreaking invention.

It might be surprising to some people, but it is very difficult to store a large amount of electricity for a long time. It is because the performance of the battery is influenced by complex interactions among various factors such as the properties of battery materials and phenomena occurring at material interfaces, although battery itself has simple basic structure, consisting of a cathode, anode and electrolyte. Those interactions and phenomena are difficult to measure/observe as they occur at the nanoscale.

Despite the daunting challenge, NIMS has been leading Japan's effort to develop next-generation rechargeable batteries that have large capacity and long life. NIMS is steadily advancing research and development of such batteries by carrying out long-term experiments and employing computational science techniques, in order to achieve their practical application.

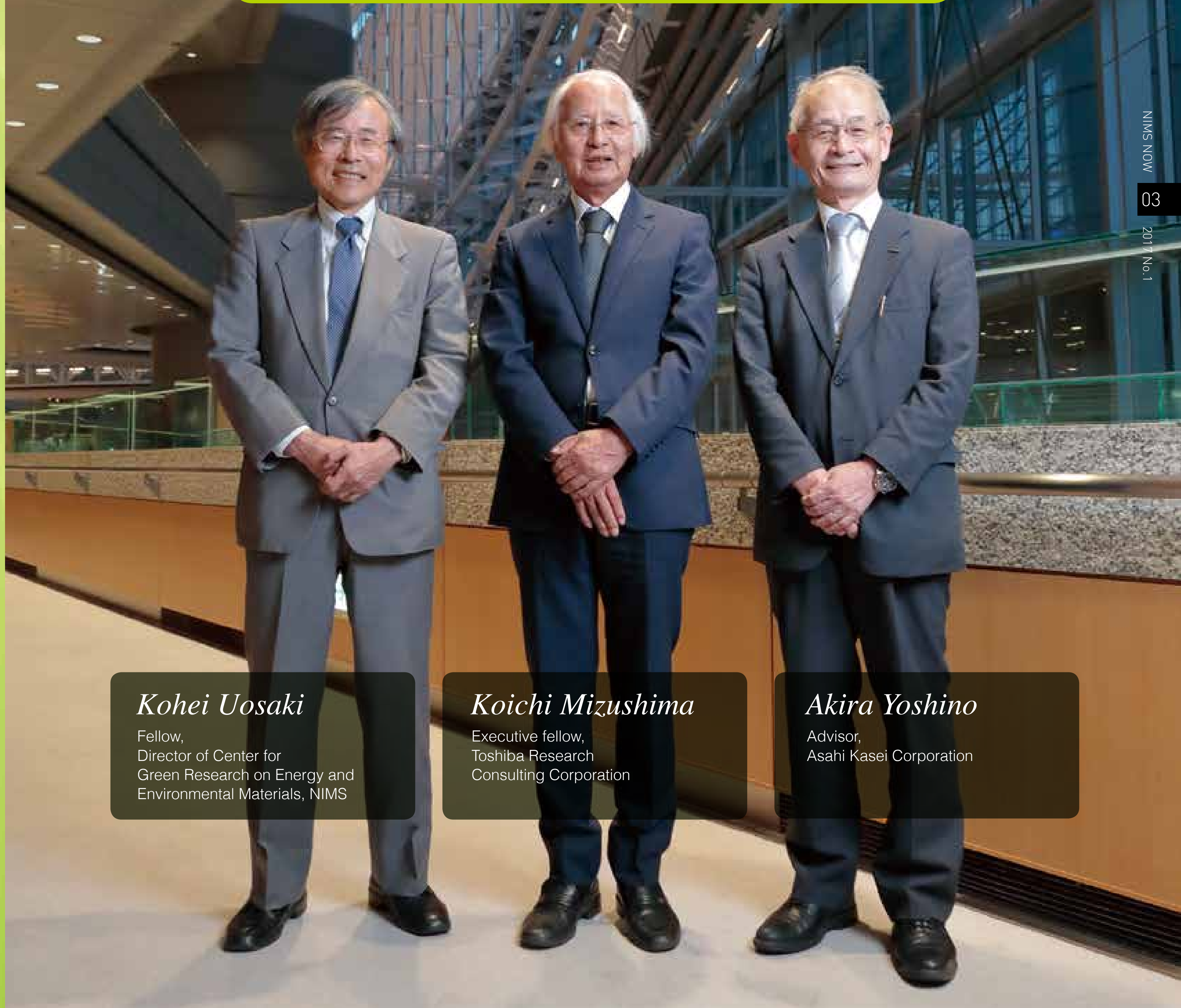
This NIMS NOW issue features the latest on R&D of rechargeable batteries.



Special tripartite talk

Out-of-the-box thinking led to the invention of lithium ion batteries

The NIMS Awards are bestowed upon researchers who have made a breakthrough in materials science. The 2016 awards were given to Koichi Mizushima, who discovered cathode materials for the lithium ion battery, and Akira Yoshino, who made a major contribution in the development of the battery. Mizushima, Yoshino and Kohei Uosaki, director of the NIMS Center for Green Research on Energy and Environmental Materials tell the story behind the birth of the lithium ion battery and discuss the future of rechargeable battery research.



Kohei Uosaki
Fellow,
Director of Center for Green Research on Energy and Environmental Materials, NIMS

Koichi Mizushima
Executive fellow,
Toshiba Research Consulting Corporation

Akira Yoshino
Advisor,
Asahi Kasei Corporation

Special tripartite talk

Professor Goodenough and I were both new to battery research, and that was the very reason we were able to create new things without being trapped in conventional thinking.

Koichi Mizushima

I believe that unique technologies can be created only through the discovery of novel materials and novel material functions.

Akira Yoshino

The battery changed the world

Uosaki Dr. Mizushima, you discovered the ideal cathode material for the lithium ion battery, lithium cobalt oxide ($LiCoO_2$), and Dr. Yoshino, you invented a prototype of lithium ion battery by combining a $LiCoO_2$ cathode with a polyacetylene anode. The advent of lithium ion batteries, which are compact but exhibit high energy/power density, had major impacts not only on industries but also on everyday living. Lithium ion batteries have made it possible to reduce the sizes of cellphones and laptop computers to the extent that people can carry them with ease, and are enabling electric vehicles to travel longer distances. Since the battery represents truly innovative materials technology, we presented the this year's NIMS Awards to you.

Mizushima Among the many materials and technologies I have studied, only the cathode material for lithium ion batteries made it to practical application. Most of the projects I carried out fell short of completion (smile). So, when I developed the cathode material, I was not sure whether it would be put into practical use. Dr. Yoshino played a crucial role in this regard. I am really honored by the award.

Yoshino I believe that unique technologies that have a global impact can be created only through the discovery of novel materials and novel material functions. The creation of lithium ion batteries is a very good example of that. I am greatly honored by the award presented by NIMS which is specialized in materials research.

Many complications before discovering the cathode material

Uosaki Dr. Mizushima, I know that you began the research leading to the development of lithium ion batteries in 1978.

Mizushima Yes. Before that, I was studying magnetism at the University of Tokyo, and one day, Professor Goodenough at the University of Oxford invited me to study batteries together.

Uosaki I believe he was also specializing in magnetism at that time.

Mizushima That is right. Despite the fact that he had studied magnetism for decades, he completely changed his research focus to batteries and energy.

We initially planned to search for new solid electrolyte materials. However, immediately after we began that endeavor, we heard news about the discovery of an intriguing electrode material that can be used as a cathode for lithium batteries. Since that news captivated our interest, we changed our plan and decided to search for electrode materials instead.

Uosaki I imagine that many battery researchers at that time were making vigorous efforts to find desirable electrode and electrolyte materials for the purpose of making rechargeable lithium batteries with a metal lithium anode.

Mizushima Sulfides were receiving particularly great attention as potential cathode materials. So, we conducted experiments to synthesize sulfides using a furnace of another lab. During the experiments, the furnace exploded and we made a big mess in that lab. While I felt sorry about the accident, I intended to continue the project. However, Professor Goodenough suddenly suggested that we study oxides as he heard at a research meeting that there are promising oxides as cathode materials. Because I handled oxides regularly when I studied magnetism, I was familiar with them. So, I gladly accepted the change of plan.

Since the lithium battery has a metal lithium anode, its cathode should be made of materials that accept lithium ions. However, to make the lithium battery rechargeable, it was necessary for the cathode material to be able not only to accept lithium ions but also to release them. I searched for materials with such properties, and finally found $LiCoO_2$. The material was capable of producing 4 volts, which was double the amount of voltage produced by conventional materials. I published this finding in 1980.

Uosaki That discovery made a breakthrough in the development of lithium batteries. Were you aware of that then?

Mizushima Well, my greater interest at that time was to find novel materials with unique magnetic or electrical conduction properties. Perhaps my college background as a physics major drives my interest in pursuing scientific discovery. My goal for that project was achieved when I found materials contributing to the development of rechargeable batteries, so I went back to magnetism research in Japan.

Finding the right combination of anode and cathode materials

Uosaki Dr. Yoshino, you also had been studying electrode materials in the 1970s.

Yoshino Around that time, electrically conductive plastics, polyacetylene, discovered by Professor Hideki Shirakawa were a hot topic among scientists. Like Dr. Mizushima, I was not particularly interested in applying these materials to batteries initially, but as I studied their functions in more detail, I realized that they can be used as anode materials. In those days, public expectations were high for the development of small, lightweight and high-voltage rechargeable batteries. Lithium, which ionizes easily, was considered to be an ideal material for that purpose, but its practical use had been challenging due to safety concerns. I knew that the use of metal lithium as an anode material had brought such concerns, so my idea was to use polyacetylene instead.

Uosaki To implement your idea, the cathode material needed to contain lithium.

Yoshino I carried out extensive material search without success. Then, I came across Dr. Mizushima's paper on $LiCoO_2$. In those days, it took several months for scientific journals published in Europe and the United States to arrive in Japan by ship. Even worse, the journals I received were left in a pile on my desk for a long time as I was very busy. I finally read Dr. Mizushima's paper about one year after it was published. When I read it, I wished I had read it sooner.

Uosaki Then, you created the prototype of a lithium ion battery consisting of a $LiCoO_2$ cathode, polyacetylene anode, and propylene carbonate electrolyte. Later, the prototype was put into practical use after the anode material was replaced with vapor grown carbon fibers (VGCFs) and many Dr. Yoshino's inventions were incorporated.

Lack of expertise acted favorably

Uosaki I think one important reason for the success in the development of lithium ion batteries is that research on cathode and anode materials were advanced at around the same time.

Special tripartite talk

NIMS is committed to searching for new battery materials. We want to boost the involvement of non-battery researchers, too, in such an effort.

Kohei Uosaki

Yoshino I think so, too. In addition to that, I believe that the success is also attributed to the fact that neither of Dr. Mizushima, Dr. Goodenough nor I was a battery expert. We were all new to battery research, and that was the very reason we were able to challenge new things without being trapped in conventional thinking.

Mizushima Battery experts at that time generally accepted the idea that materials that produce a high voltage cannot serve as electrodes. Accordingly, when I brought up the idea of $LiCoO_2$ cathodes, they simply rejected it. But only Dr. Yoshino expressed interest in the idea. This is another example that lack of expertise in batteries acted favorably for the invention.

Future challenges for the R&D of next-generation rechargeable batteries

Uosaki What are your prospects for rechargeable battery R&D, including that of lithium ion batteries?

Yoshino I expect that demand for lithium ion batteries for use in electric vehicles will increase. At the same time, it is also critical to enhance their performance given that some aspects of this technology, including electrode materials, are still incomplete. In addition, the development of next-generation batteries is an urgent issue. I personally believe that all-solid-state batteries are particularly promising.

Uosaki Rechargeable battery research teams at NIMS are also making full-fledged efforts in the development of all-solid-state batteries. Rechargeable batteries in their current forms employ flammable organic solvents as electrolytes. If non-flammable solid electrolytes can replace organic solvents, the batteries will become safer. However, all-solid-state batteries have some issues to be solved such as low rates of charging/discharging.

Mizushima Other issues include high electrical resistance at the interface between the electrode and electrolyte.

Uosaki Dr. Mizushima, you probably understand how difficult it is to overcome these issues as you once intended to study solid electrolytes suitable for all-solid-state batteries when you were at the University of Oxford. At NIMS, we are presently tackling the very issue you just mentioned—we are aiming to improve battery performance by dealing with the phenomenon occurring at the interface between the electrode and electrolyte. In relation to that, we are also organizing the NIMS Battery Research Platform (see P. 15) that will be available to researchers from research institutes, universities and private companies, for the purpose of promoting R&D of next-generation rechargeable batteries in Japan. NIMS is also committed to searching for new battery materials. We want to boost the involvement of researchers whose expertise is not in batteries in these initiatives.

Yoshino Private companies have their own specific needs regarding battery materials, but their capacities to develop batteries are limited if they work alone. I would like to see that these companies work jointly with research organizations such as NIMS and universities. Some research data, which has no importance to university and national institute researchers, may have great value to company researchers.

Mizushima It is difficult for private company researchers to carry out research projects that are not profitable in the short run or have no clear direction. I hope NIMS will tackle the types of research that companies cannot do.

Yoshino I would like to see NIMS develop materials with unique personalities, so to speak.

(by Shino Suzuki, PhotonCreate)

The NIMS Awards were presented and commemorative lectures were given during NIMS WEEK 2016 held in October 2016.
From left to right: Daisuke Fujita (NIMS executive vice president), Akira Yoshino, Koichi Mizushima and Kazuhito Hashimoto (NIMS president).

Basics of batteries

What are batteries?

There are three major categories of batteries: chemical, physical and biological. Among them, chemical batteries, which generate electrical energy through chemical reactions, are used most popularly in our everyday life. There are three types of chemical batteries: primary cells that can be used once, secondary cells that can be used many times (rechargeable), and fuel cells that generate electricity through reactions of hydrogen with oxygen. When people simply say “batteries,” they are usually referring to primary or secondary chemical cells.

What determines battery performance?

Different materials have different capabilities to release or accept electrons. The extent of these capabilities is expressed in terms of ionization tendencies. Materials having a high or low ionization tendency potentially serve as good anodes or cathodes, respectively. Great differences in ionization tendencies between the cathode and anode increase the flow of electrons and generate high voltages. The voltage of batteries also varies depending on the types of electrolytes used.

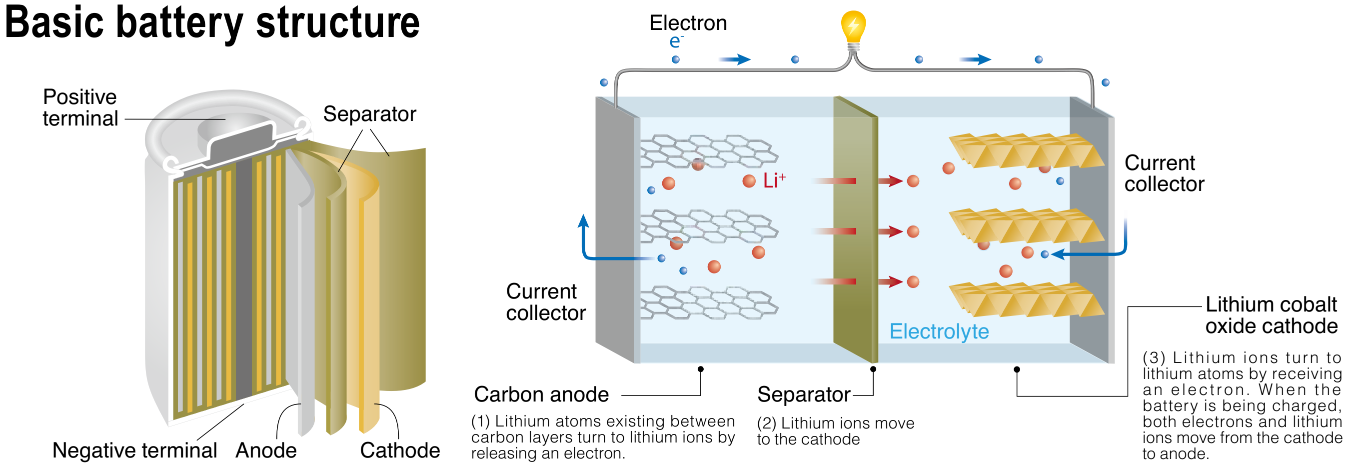
How do chemical batteries work?

Primary and secondary cells have the same basic structures; they both consist of a cathode, anode and electrolyte. A separator is added between the cathode and anode materials to prevent them from coming into contact and short-circuiting. When cathode and anode materials are connected by a conducting wire and immersed in an electrolyte solution, the anode material starts to dissolve and release ions. This reaction also releases electrons, which move along the wire and are accepted by the cathode material. The movement of electrons generate an electric current.

Revolutionary lithium ion batteries

Lithium has the highest ionization tendency among all metals and is light. Therefore, by using it as an anode material, batteries can be light and produce high voltages. However, its application in rechargeable batteries had been difficult due to the highly reactive nature of metal lithium, among other issues. At present, lithium ion batteries typically consist of a lithium cobalt oxide cathode, carbon anode and organic solvent electrolyte. These batteries can be charged/discharged repeatedly by allowing lithium ions to move back and forth between the cathode and anode materials. In addition, they are compact and lightweight, yet have large capacity and can produce high voltages.

Basic battery structure



History

1791 Luigi Galvani discovers the working principle of batteries based on experiments using frog legs

1800 Alessandro Volta invents the voltaic pile using copper and zinc discs

1836 John Daniell invents the Daniell cell that employs two types of electrolytes

1859 Gaston Planté invents the lead-acid battery, the first rechargeable battery, using two lead sheets

1866 Georges Leclanché invents the Leclanché cell—the prototype of the modern dry cell battery

1887 Sakizo Yai invents the dry cell battery, overcoming the issues of the wet cell battery

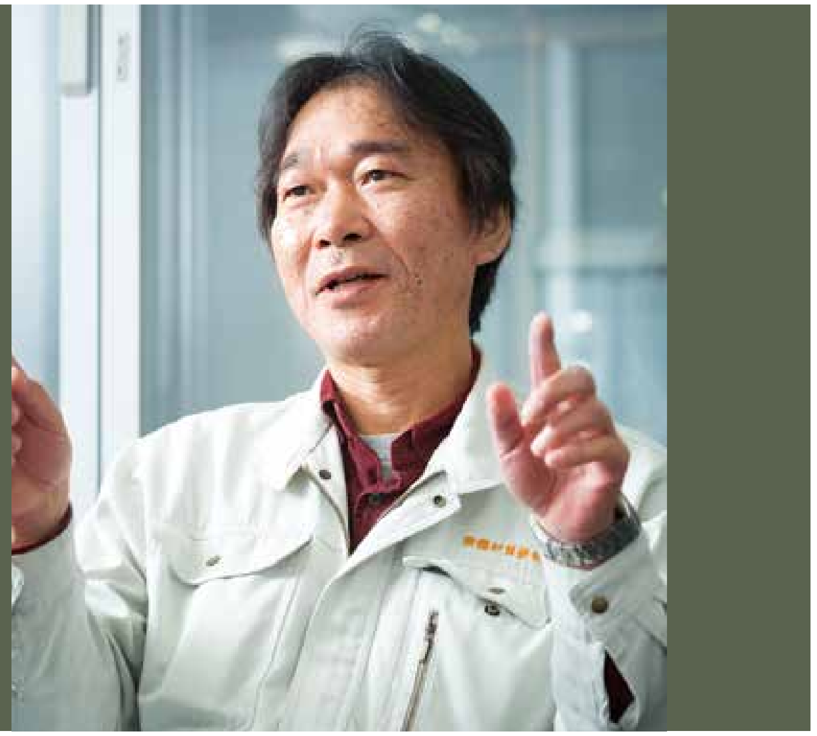
1979 John Goodenough and Koichi Mizushima discover a cathode material for the lithium ion battery

1983 Akira Yoshino discovers an anode material, which led to the prototyping of the lithium ion battery

1991 Sony releases the first commercial lithium ion battery

Safe and durable
All-solid-state batteries

Kazunori Takada
Deputy director-general,
Center for Green Research on
Energy and Environmental Materials



In efforts to promote sustainable society, demand is rising for large capacity, safe and long-lasting rechargeable batteries to be used in electric vehicles and smart grids. Among various types of next-generation batteries, all-solid-state batteries are most promising. We asked Kazunori Takada, who has been devoted to all-solid-state battery research for 30 years, about the current status of the development of the batteries and issues concerning their practical use.

Improving power performance by modifying interfaces between the electrode and electrolyte

Conventional lithium ion batteries employ organic solvent electrolytes. These electrolytes enable batteries to have high energy density. On the other hand, they are flammable and pose great safety concerns. Accordingly, energy densities of those batteries for vehicles are limited to 30 to 50% of their potential for safety reasons. Moreover, various side reactions occur between the electrode surfaces and liquid electrolyte, causing batteries to deteriorate and shortening their lifespan.

In consideration of these issues, expectations are rising for all-solid-state lithium ion batteries (hereinafter referred to as "all-solid-state batteries") as next-generation rechargeable batteries. Takada has been studying these batteries for 30 years.

All-solid-state batteries employ solid electrolytes, which renders the batteries non-flammable, free of side reactions, and thus resistant to deterioration. In other words, these batteries are very safe and durable (Fig. 1). However, there was a major issue to be resolved before achieving their practical use: low power performance attributed to solid electrolytes.

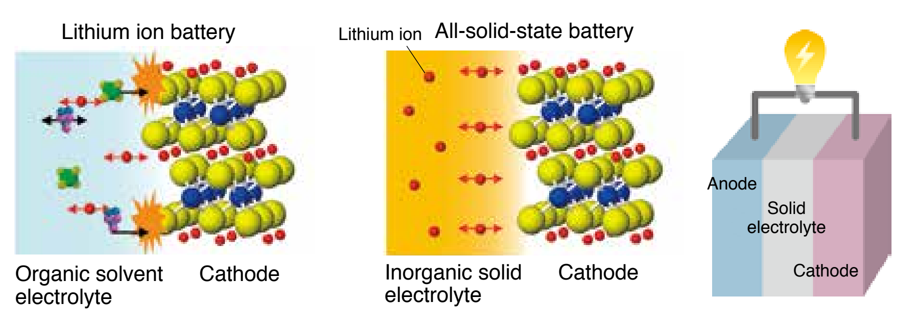
Takada began research on all-solid-state batteries when he started working at the Central Research Laboratory of Matsushita Electric Industrial Company in 1986. At that time, the main focus of the research was to improve the power performance of the batteries by finding solid electrolyte materials that are highly ion conductive. A sulfide was discovered in 1981 as a promising material with high lithium ion conductivity. However, the power performance of batteries employing that material was mysteriously low.

Cathodes of all-solid-state batteries are made of lithium cobalt oxide ($Li_{1-x}CoO_2$), which is a powerful oxidizing agent. In comparison, a sulfide solid electrolyte has only a weak force to retain lithium ions, so lithium ions, which are charge carriers, in the electrolyte move into the $Li_{1-x}CoO_2$ cathode. When this occurs, concentrations of lithium ions become very low in the interface (or space charge layer) of several nanometers thick between the cathode and electrolyte. Some experts in this field proposed that this phenomenon increases electrical resistance, resulting in depressed power performance of the batteries. The study of these phenomena is now called nanoionics.

Takada says, "My approach to solve that problem was to suppress the growth of the space charge layer by inserting a buffer layer material with more powerful lithium ion retaining force than sulfides between the cathode and electrolyte. This way, I thought that the interfacial resistance would decrease, lithium ions would flow more easily, and as a result, the power performance of the batteries would increase."

Takada developed a buffer layer of approximately 5 nanometers thick using lithium titanate, and inserted it to the interface in order to suppress the development of the space charge layer. Consequently, the power performance of all-solid-state batteries increased by two orders of magnitude, exceeding the power performance of commercially available lithium ion batteries (Fig. 2).

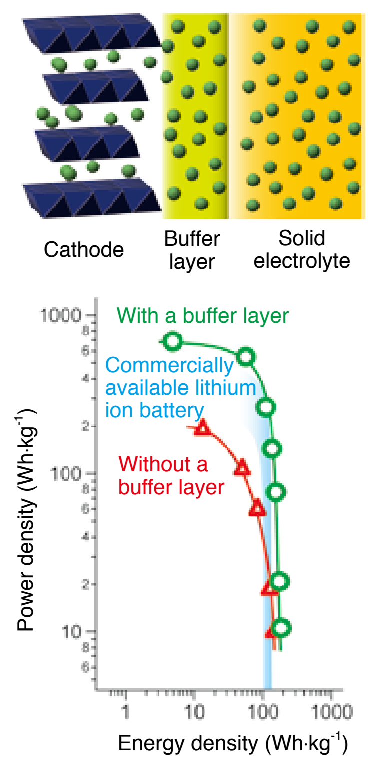
Figure 1. Characteristics of all-solid-state batteries



Use of an organic solvent as a lithium battery electrolyte causes side reactions involving anions and solvent molecules (decomposition of the electrolyte, dissolution of the active material, etc.) while allowing lithium ions to diffuse through the electrolyte.

Solid electrolyte allows only lithium ions to diffuse through it and causes no side reaction. Consequently, the battery does not deteriorate and can have a long life.

Figure 2. Conceptual image of inserting a buffer layer (top) and changes in power density in relation to energy density (bottom)



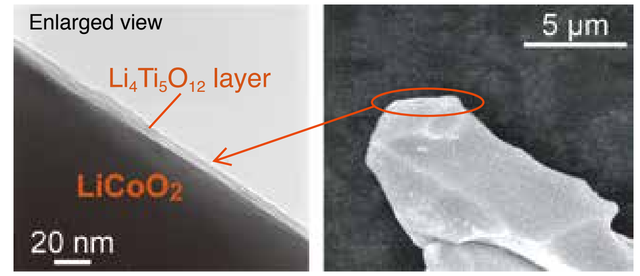


Figure 3. Electron microscopic image of $LiCoO_2$ particles forming a buffer layer. A $Li_4Ti_5O_{12}$ buffer layer, approx. 5 nanometers thick, was formed above the $LiCoO_2$ particles.

Takada also carried out joint studies with a research group led by Yoshitaka Tateyama, the leader of the Interface Computational Science Group. In July 2014, using computer simulations, they theoretically proved the existence of a space charge layer, in which lithium ion concentrations are very low, at the interface, and that the insertion of a buffer layer is effective in suppressing the formation of the lithium depleted layer. In light of these results, automobile manufacturers and other organizations are currently working to accomplish practical use of all-solid-state batteries that employ sulfide solid electrolytes.

Promoting research of sulfide- and oxide-based solid electrolytes

While sulfide solid electrolytes are superior materials, they also have some issues. Their production is costly as they need to be handled without exposure to air, and they may have environmental impact if sulfides leak out of damaged batteries. Taking account of these issues, Takada's current research effort is mainly focused on oxide solid electrolytes, which are stable in air and easy to handle, under the framework of ALCA-SPRING (ALCA: Advanced Low Carbon Technology Research and Development Program, SPRING: Specially Promoted Research for Innovative Next Generation Batteries) sponsored by the Japan Science and Technology Agency.

"The most challenging issue now is that there are no appropriate materials available that enable both electrodes and interfaces to be ion conductive, so it is difficult to increase the power performance of batteries. As such, we are taking two approaches: searching for materials with high ionic conductivity, and increasing the ionic conductivity of low conductive materials."

Takada has been making steady efforts in the search for materials with high ionic conductivity through continuous experiments. "Use of sintering at high temperature during the manufacturing of all-solid-state batteries will cause all elements of cathode, anode and electrolyte materials to mix together and ruin the products. To prevent this, we are looking for electrolyte materials with melting points as low as possible, such as borates."

On the other hand, solid electrolyte materials that have low ionic conductivity but excel in other aspects were discovered in the 1990s—there are three kinds of oxide crystal structures. All these materials have high ionic conductivity within their crystal structures, but they do not give batteries sufficient power performance due to high interfacial resistance and other factors. To increase the interfacial ionic conductivity of these materials, various methods have been tested. Such methods include a technique to increase the mobility of lithium ions through the crystal structure by substituting some of the elements composing the structure with other elements, thereby changing the size of the crystal, and a technique to change the concentration of lithium ions in the electrolyte.

Takada is also searching for new electrode materials in an effort to further increase the storage performance of batteries. "Most anodes are made of graphite, but we are currently studying silicon, which is capable of storing 10 times more electricity than graphite. Because silicon materials expand and shrink drastically in response to repeated charge and discharge, they deteriorate rapidly. So, we are attempting to minimize their deterioration and extend their life. There are still many problems to overcome, but as NIMS researchers, we will continue to strive in R&D activities in order to achieve practical use of all-solid-state batteries as soon as possible."

(by Kumi Yamada)

Next – generation Battery 2

The challenge of creating the ultimate rechargeable battery

The Li-air battery

Yoshimi Kubo

Team Leader, Lithium Air Battery Specially Promoted Research Team, GREEN, Center for Green Research on Energy and Environmental Materials

The current lithium ion rechargeable battery only allows electric vehicles to travel 100 to 150 km at a time, limiting its popularization. In order to extend the traveling distance to a level of conventional vehicles, it is indispensable to develop innovative batteries. Among batteries under development, the lithium-air battery (hereinafter referred to as the "Li-air") is especially promising as an ultimate rechargeable battery. To learn more about the battery, we interviewed Yoshimi Kubo, who has been carrying out research and development of the Li-air since FY2013 under the framework of the ALCA-SPRING program, with the goal of achieving its practical use as soon as possible.

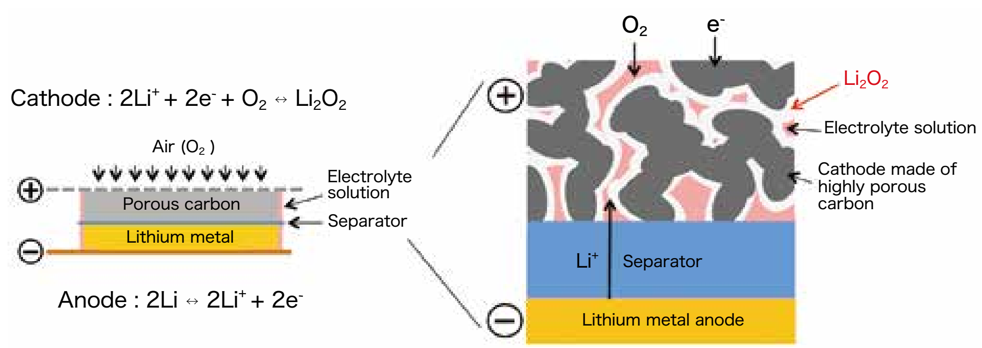
Super light with high energy density

The Li-air battery undergoes reduction of oxygen at the cathode and oxidation of lithium metal at the anode to produce current flow. Because the battery gains oxygen from the surrounding air and the anode is made of lightweight lithium metal, the battery as a whole is very light and its energy density is very high in theory. Due to these advantageous characteristics, the Li-air is said by some to be the ultimate rechargeable battery.

The Li-air has a simple structure, composed of a stack of many layers with each layer consisting of a cathode, anode and a separator between them. The cathode is made of a porous carbon material, and the pores are filled with an organic electrolyte solution (Fig. 1). When electric discharge takes place, lithium metal in the anode dissolves, leading to the deposition of solid lithium peroxide (Li_2O_2) on the cathode side. On the other hand, when electric charge takes place, Li_2O_2 on the cathode side dissolves, leading to the deposition of lithium metal on the anode side. The concept of the Li-air is to produce electrical energy through these redox reactions.

"Like Li-air batteries, fuel cells also produce electricity through chemical reactions between oxygen from the surrounding air and hydrogen. However, fuel cells contain an expensive platinum catalyst in order to completely break bonds between oxygen molecules. In contrast, Li-air batteries do not employ a platinum catalyst as it is unnecessary to break such bonds when producing Li_2O_2. For this reason, Li-air batteries are less expensive to produce than fuel cells," explains Kubo.

Figure 1. Basic structure of lithium air battery



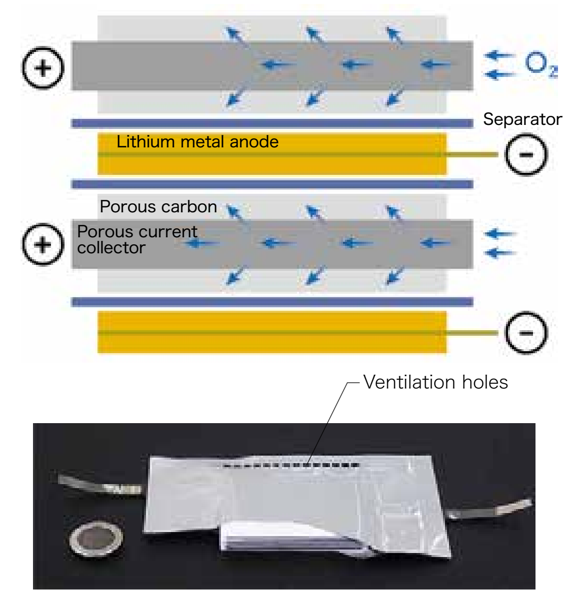
Biggest issue: voltage rises during charging

While Li-air batteries are a promising technology, there are many obstacles to overcome before achieving practical use. According to Kubo, there are three major issues: first, basic issues related to power generation efficiency, second, issues related to actual battery development, and third, figuring out how to extract oxygen from the surrounding air and incorporate it into the electrode.

The first issue concerns the fact that when the battery is being charged, its voltage increases, causing power generation efficiency to decrease. At present, the cause of the voltage rise has not been identified, and that is the major interest of researchers. "Some researchers have suggested that by-products of chemical reactions are causing the voltage increase, but that is mere speculation. We know so far that an increase in voltage can be suppressed to a certain degree by adding a substance that promotes chemical reactions, called a mediator, to an electrolyte solution. We expect that R&D of Li-air batteries will make rapid progress if the cause of the voltage increase is understood. Accordingly, we are presently observing chemical reactions occurring in Li-air batteries using, e.g. synchrotron X-ray diffraction."

Other basic research issues include exploration of appropriate carbon materials to be used as cathodes. During electric discharge, Li_2O_2 deposits on the surface of a porous carbon cathode. It is feasible to increase the amount of Li_2O_2 deposition by increasing the current density (electric current per unit area of electrode). This can be achieved by increasing the porosity of porous carbon, thereby increasing its specific surface area as much as possible. The problem to this approach is that if porous carbon has smaller pores that are filled with an electrolyte solution, these pores become occupied by Li_2O_2 deposition quickly, which in turn terminates discharge too soon. To address this problem, it is necessary to develop porous carbon with an optimum balance between specific surface area and pore size. Kubo is experimenting with various carbon materials such as carbon black, activated carbon, carbon nanotubes and graphene.

Figure 2. Schematic of passive parallel stack



Innovative solution triggered full-fledged research effort

The second major issue concerns actual battery development. Unlike lithium rechargeable batteries and all-solid-state batteries, the Li-air is viewed as an open system as it obtains oxygen externally. It was very challenging for Kubo to come up with a mechanism whereby external air (oxygen) can be incorporated into the battery. His solution took the shape of a "passive parallel stack" (Fig. 2).

In this structure, a material that incorporates air (porous current collector in Fig. 2) was set between upper and lower layers of porous carbon cathodes, and a separator and anode layers were added to the cathodes to form a unit of parallel layers. A pile of these units, called a stack, was packaged by laminating it with a film.

The laminate film has several holes that allow the surrounding air to flow inside. Because the porous current collector is highly permeable by air, the collector is expected to allow in- and outflow of the air required to generate power in a passive manner without active mechanisms such as a pump or fan. This simple stack structure is similar to the structure of the conventional lithium-ion rechargeable battery, thus is favorable for mass production at low cost.

"The idea of a passive parallel stack came to me about five years ago when I had just started Li-air battery research. I remember that moment vividly. Since calculations supported the initial estimation that the battery is capable of producing sufficient energy density, I decided to focus on the R&D of Li-air batteries in a full-fledged manner. Soon after that, the ALCA-SPRING program was kicked off, so I applied for the program without hesitation." Kubo recently demonstrated the effective mechanism of the passive parallel stack, and is planning to expand its capacity as a step toward its practical use.

Even if Kubo successfully finds solutions to the first two major issues, he still needs to tackle the third issue: extracting oxygen from the air containing various substances including water vapor. It will be challenging to exclude unwanted air components but oxygen from the air..

"My current R&D effort is focusing on the first and second issues, and I have yet to work on the third one. Before the ALCA-SPRING program ends in FY2023, I hope to find solutions to all three issues, and ensure the practical use of the Li-air by establishing the methods of expanding the battery's capacity and its mass production," says Kubo enthusiastically.

(by Kumi Yamada)

Computational Science

Computational approaches change the common sense of rechargeable batteries

Yoshitaka Tateyama

Group Leader,
Interface Computational Science Group,
Center for Green Research on
Energy and Environmental Materials

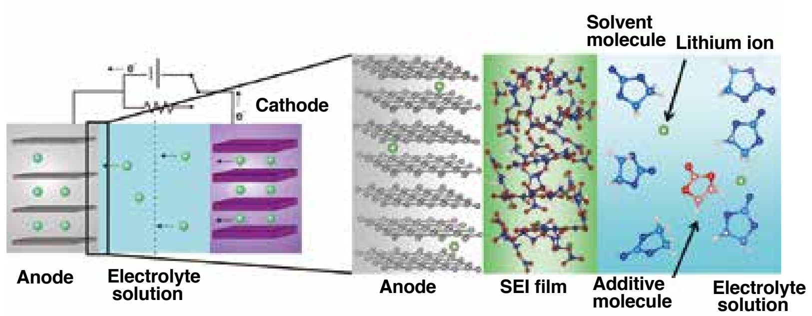
To improve the performance and reliability of rechargeable batteries, it is crucial to understand electrochemical reactions upon charging/discharging. However, it is difficult to observe these reactions at the atomic and molecular levels in real time. Yoshitaka Tateyama has been attempting to understand and visualize these reactions at high precision using computer simulations.

Solving long-standing mystery about lithium ion batteries

At first, Tateyama's research group tackled a long-standing mystery about lithium ion batteries (LIBs): the mechanism of an SEI (solid electrolyte interphase) film. LIB consists of cathode, anode and electrolyte, which are typically made of lithium cobalt oxide ($LiCoO_2$), graphite (carbon) and organic solvents, respectively. The use of organic solvent electrolyte is indispensible to achieve high voltage and high energy density of LIB, but the electrolyte molecules have a risk of decomposing at the anode interface and generating excessive heat. Therefore, present LIB technology uses intentional formation of the SEI film at the anode interface by initial charging in the factory. Of course, this formation slightly consumes the decomposed electrolyte molecules, but the resulting film prevents further decompositions of the electrolyte in the battery in operation (Fig. 1). Such role of the SEI film has been widely known for years, however, its actual microscopic mechanisms under operation were yet to be identified.

In 2011, Tateyama's group began studying the mechanism of SEI film formation at the interface between an anode and electrolyte using first-principles calculations*. "We first developed a free energy calculation program based on first-principles molecular dynamics, to accurately simulate chemical reaction dynamics under the temperatures at which the batteries operate. This is an important step because conventional first-principles calculations assume static situation at absolute zero temperature. In addition, we implemented large-scale multi-parallelization into the program for highly efficient use of supercomputers like the K computer. After these efforts were highly appreciated, Tateyama's group joined the Computational Materials Science Initiative (CMSI), launched under MEXT's High-Performance Computing Infrastructure (HPCI) program in 2013. This involvement allowed the group to carry out full-scale calculations of electrochemical reactions occurring in rechargeable batteries using the K computer.

Figure 1. SEI film in a lithium ion battery



(Left) Schematic image of a lithium ion battery
(Right) Schematic image of an SEI film formed at anode-electrolyte interface

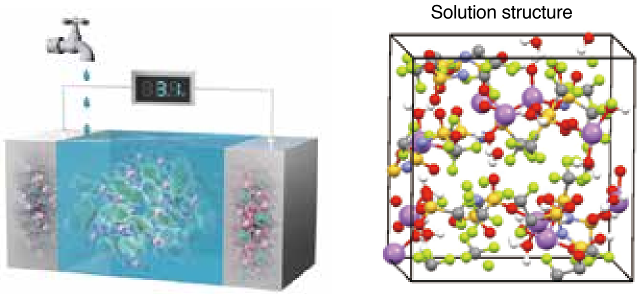
"The results of these calculations were not able to be explained by conventional theories," says Tateyama. Typical organic electrolyte is composed of ethylene carbonate (EC) and small amounts of additives such as vinylene carbonate (VC). It had been generally thought that the formation of an SEI film begins when VC undergoes reductive decomposition and oligomerization. However, the calculations led to a conclusion different from the conventional—an EC solvent undergoes reductive decomposition to make anion radicals, and VC inactivates these radicals. This conclusion was highly consistent with actual phenomena observed in batteries.

Tateyama's group then carried out further calculations to determine how the SEI film grows at the interface between the anode and electrolyte. "We initially expected that molecules will undergo reductive decomposition, and molecular fragments will slowly deposit on the anode surface, forming a film. However, the calculations indicated that the growth of the decomposed molecular fragments occur slightly away from the anode interface and the growth stops when the aggregate eventually attaches to the interface." These new mechanisms gained global attention, and are currently being verified through the experiments. Now, Tateyama's group addresses further search for ideal materials to improve the performance and the reliability of SEI films.

Challenge for understanding disordered and dynamic electrolytes

Recently, the experimental studies of superconcentrated electrolytes conducted by Professor Atsuo Yamada at the University of Tokyo also drew much attention. Viscous electrolyte solutions containing high concentrations of lithium salts generally block the transport of lithium ions and slow the rate of battery charging. For this reason, there have been few studies on such electrolytes so far. Then, Tateyama's group started the collaboration study with Professor Yamada, and investigated the mechanisms of electrochemical stability and rather fast ion transport observed in the studies by Yamada's group. The joint group performed analysis using the K computer and found that characteristic networks of lithium ions, anion molecules and solvent molecules are formed, and that such networking states not only suppress reductive decomposition of the solvent but also facilitate lithium ion transport. These results indicated that concentration of electrolyte solution is an important factor contributing to the performance of batteries.

Figure 2



(Left) Conceptual image of a lithium ion battery containing a hydrate-melt electrolyte involving a certain amount of water molecules.
(Right) Structure of a hydrate-melt electrolyte solution (H, white; Li, purple; C, gray; N, blue; O, red; F, green; S, yellow)

The joint research group also discovered that an aqueous solution called a hydrate-melt electrolyte, which exhibits lithium ion conductivity, can be applicable to conventional rechargeable batteries, and identified its mechanism (Fig. 2). "First-principles calculations using the K computer revealed that all water molecules in the electrolyte solution coordinate to lithium ions, and this unique state of water molecules plays a major role in preventing decomposition of the solvent even at high voltage." These discoveries suggest that flammable organic solvent electrolytes may be replaced with hydrate electrolytes that are easy to handle and non-flammable.

Unlike solid electrolytes, liquid electrolytes are disordered and dynamic, and therefore they are difficult subjects for highly precise calculations. To address this issue, Tateyama's group is further planning to integrate machine learning techniques for a more efficient material searching endeavor.

"Calculations using the K computer produced many results that could not be explained by conventional knowledge. As computational scientists, we will continue to use the K computer and its successor under development for the purpose of not only improving the performance of LIBs but also achieving practical use of next-generation rechargeable batteries, such as all-solid-state batteries and multi-valent ion batteries, as soon as possible." (by Kumi Yamada)

* In this article, first-principles calculations refers to techniques to calculate energy and atomic forces based on quantum mechanics.

Figure 3. The K computer

Characterization Technology

Single Particle Measurement – key to the enhancement of battery performance

Kei Nishikawa

Senior Researcher,
Interfacial Energy Conversion Group,
Center for Green Research on
Energy and Environmental Materials

Many aspects of electrochemical reactions occurring in batteries are not yet understood. To explore these aspects, Kei Nishikawa has been closely measuring and analyzing electrochemical reactions using a single particle measurement system.

In-situ observation of expanding silicon

The single particle measurement system allows electrochemical measurements from particles (several micrometers in diameter) of active materials* in lithium ion battery electrodes by positioning a needle probe so it makes contact with the particle. Nishikawa and Tokyo Metropolitan University researchers jointly adopted this system about four years ago.

The system is currently set up in a super-dry room at the NIMS Battery Research Platform, and is used by the abovementioned researchers and others for various measurements and observations.

One of the studies conducted using the system was measurement of the volume expansion of silicon when it was electrically charged. At present, anodes of lithium ion batteries are made of graphite, but use of silicon in place of graphite is under consideration to further increase the energy density of the batteries. The drawback of silicon, however, is that its volume is known to change drastically in response to charging/discharging. So, it is critical to understand and control the mechanism of that phenomenon in order to achieve practical application of silicon as a anode material.

To address this issue, Nishikawa's group took measurements from individual silicon particles one by one. By doing so, the group succeeded for the first time in the world in direct measurement of the volume expansion of silicon particles in response to electrical charging (Fig. 1). In this study, the group found that the actual rate of volume expansion was much greater than theoretically predicted.

Then, Nishikawa's group observed cross-sections of silicon particles that had been expanded due to electrical charging, and found that the charge reaction occurs unevenly across the particle. The group also found that the rates of volume expansion differ in relation to crystal orientations, and the different expansion rates cause gaps to occur between silicon particles. Then the gaps promote excessive expansion of the particles.

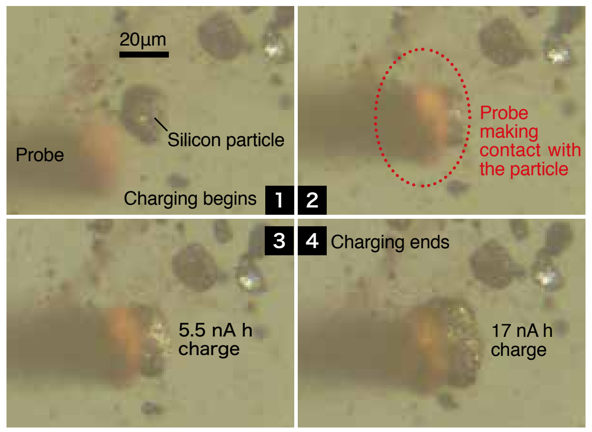


Figure 1. A microprobe was positioned so it makes contact with a single silicon particle, and electricity was applied to the particle. Then the particle's expansion rate was measured. In theory, the particle was expected to expand by about 400% in volume, but actual measurements demonstrated its expansion by up to about 800%, greatly exceeding the theoretical estimation.

Extending the technique to next-generation batteries

"In the past, we implemented the method of extracting individual particles of electrode materials from coin cells after cells were charged/discharged, and observing extracted particles one by one under an electron microscope. But this method does not allow us to keep track of the history of electrochemical reactions that took place in the particle. In comparison, the single particle measurement technique allows us to control and keep track of such history in detail, and therefore we can measure changes occurring in particles more accurately."

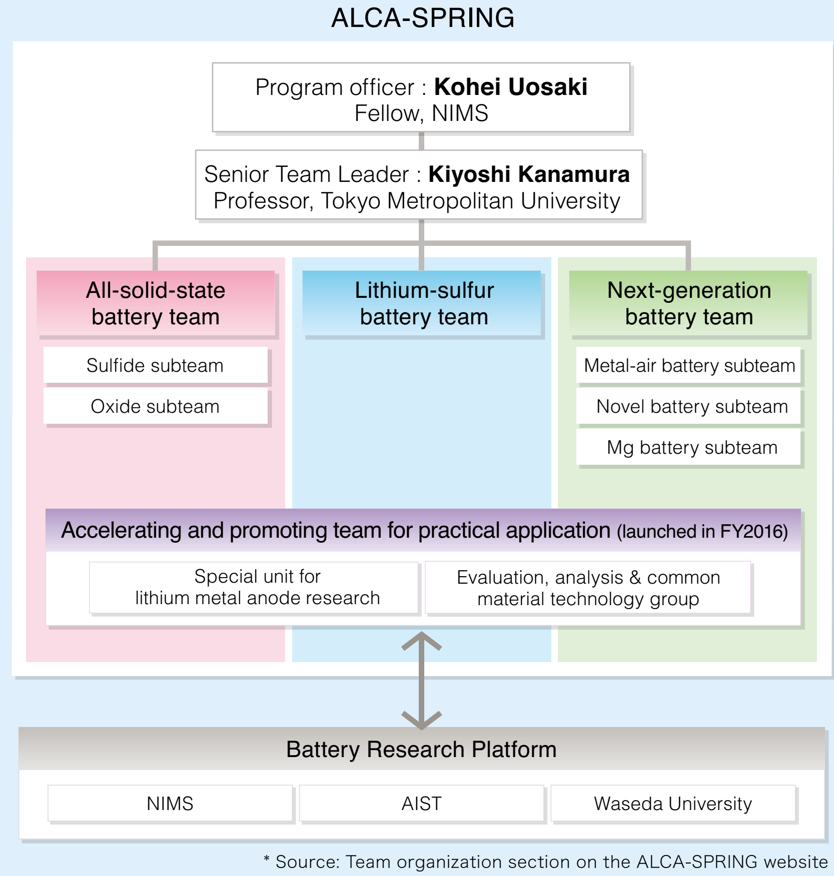
Nishikawa is also carrying out measurements of cathode materials in collaboration with Shinshu University. "Nickel and manganese in cathode materials are known to dissolve during charging/discharging and cause batteries to deteriorate. We are aiming to identify crystal structures that make these metals more resistant to dissolution by combining the single particle measurement technique with other observation techniques. These techniques are applicable to all-solid-state batteries, too. In the future, we plan to work with computational scientists to build up a measurement database, and thereby we would like to support efficient exploration of new electrode and electrolyte materials for the development of next-generation rechargeable batteries."

(by Kumi Yamada)

* Active materials in electrodes store electricity through electrochemical reactions.

What is ALCA-SPRING?

SPRING stands for "Specially Promoted Research for Innovative Next Generation Batteries," which is implemented under the "Advanced Low Carbon Technology Research and Development Program" or ALCA. Through the ALCA-SPRING framework, battery researchers aim to develop innovative rechargeable batteries that have high capacity and are compact and safe, to promote a low carbon society. As of January 2017, more than 80 research representatives from over 40 research organizations have joined the program. Research teams were organized by the categories of "all-solid-state batteries," "lithium-sulfur batteries" and "next-generation batteries." In addition, a "Accelerating and promoting team for practical application" was established in April 2016 to deal with issues common to all types of batteries. Moreover, ALCA-SPRING is planning to coordinate with the NIMS Battery Research Platform, a facility equipped with a collection of world-class instruments for rechargeable battery research, to further speed up R&D activities with an eye on practical use of new battery technologies.



* Source: Team organization section on the ALCA-SPRING website

What is the NIMS Battery Research Platform?

The platform is a state-of-the-art infrastructure for shared use in R&D of next-generation batteries, and is equipped with virtually all of the necessary tools to perform a full range of activities from prototyping small rechargeable batteries to analyzing/evaluating battery materials. All the facilities and instruments available are world class in terms of both quality and quantity, and are located in the NanoGREEN Building at the Namiki site.

Its 80 m² super-dry room provides an extremely dry environment (the dew-point temperature of incoming air is -90°C) indispensable for R&D of rechargeable batteries and enables prototyping of batteries and various measurements. The room is also equipped with a laser microscope, compact SEM, Raman spectroscope device, among others, to allow researchers to disassemble batteries and analyze/evaluate them all in one place. In this fashion, the platform serves as a one-stop facility for all steps of battery research and development.

The platform provides its resources to other organizations including ALCA-SPRING research teams, universities, national research institutes and private companies, to facilitate R&D of next-generation rechargeable batteries. Those interested in using the facility can submit an application on the NIMS battery Research Platform website:
http://www.nims.go.jp/brp/nims/

Super-dry room

High performance rechargeable batteries will ease Japan's electric power issues

Written by Akio Etori

Illustration by Joe Okada (vision track)

Improving the performance of rechargeable batteries is the key approach to solve electric power issues of the world. From this perspective, R&D of next-generation rechargeable batteries being carried out at NIMS is pivotal.

Many of us have thought for a long time that it would be nice to have means to store electric energy. That is why some of us even think wishfully about the realization of the room-temperature superconductor.

While rechargeable battery technology has made great progress over the last 30 years, many problems remain unsolved. For example, rechargeable batteries are still expensive, large and heavy, and deteriorate as they are used repeatedly.

Dr. Motoaki Saito, who is the president of PEZY Computing, presented interesting ideas to solve Japan's energy issues in his book. He predicts that in the future, electric vehicles may be perceived as transportable, large capacity batteries, rather than as mere automobiles.

Dr. Saito is well known globally as a Japanese leader in the development of supercomputers. In his book, he expects the following events—rapid advancement in supercomputer technology will bring major changes to all other technologies. Then, these changes will have profound impacts on the future of humankind and transform the world completely.

The evolution of supercomputers will enable the development of rechargeable batteries that perform at a much higher level than before. Signs of such developments can be seen already in various places. For example, a venture capital firm in Japan has apparently developed new technology for the conductive polymer battery, a type of next-generation lithium ion battery, using a supercomputer. This novel battery requires the use of inexpensive polymers as cathode materials, instead of valuable rare metals such as cobalt, nickel and manganese.

The new battery technology will permit major reductions in the price, weight and size of batteries, and make batteries safer and last longer. In addition, the development of such super high performance rechargeable batteries will enable smartphones and other mobile devices to be lighter, thinner, smaller and quickly rechargeable, and have a longer run time per charge.

Moreover, dramatic improvement in batteries for electric vehicles will greatly extend the vehicles' traveling distance per charge and lead to lower production cost. Consequently, the electric vehicles will become popular rapidly.

There are about 75 million cars being used in Japan, and about 5 million cars are sold every year.

Let's hypothetically replace all these cars with electric vehicles. Assuming that each vehicle is equipped with a rechargeable battery having a capacity of 24 kilowatt hours (equivalent to the battery in the Nissan Leaf), total battery capacity of 75 million vehicles amounts to 1.8 terawatt hours. If all of the batteries are recharged during nighttime every day, the cumulative amount of power stored in these batteries per year will be 657 terawatt hours. This amount equates to about two-thirds of Japan's annual power demand (1 petawatts), or is 2.2 times greater than the amount of power that can be generated by Japan's nuclear plants currently under suspension altogether.

Based on these estimations, if electric vehicles serve as transportable, large capacity batteries, they can provide electric power to places in need of that in times of emergency. The utilization of electric vehicles in this manner may also make Japan's power consumption rates more uniform in terms of fluctuation between day and night, and facilitate more stable power supply.

These ideas of Dr. Saito are applicable to a wide range of things from household rechargeable batteries to new power plants to be constructed. I expect that advancement in R&D of next-generation rechargeable batteries will provide new solutions to Japan's energy issues.

Akio Etori: Born in 1934. Science journalist. After graduating from College of Arts and Sciences, the University of Tokyo, he produced mainly science programs as a television producer and director at Nihon Educational Television (current TV Asahi) and TV Tokyo, after which he became the editor in chief of the science magazine Nikkei Science. Successively he held posts including director of Nikkei Science Inc., executive director of Mita Press Inc., visiting professor of the Research Center for Advanced Science and Technology, the University of Tokyo, and director of the Japan Science Foundation.

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