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Research Center for Energy and Environmental Materials (GREEN)

Energy revolution

Energy revolution

Global warming, caused by excessive greenhouse gas emissions, is becoming increasingly serious, compelling countries around the world to fundamentally alter their energy policies. Japan has shown great resolve on this issue by declaring its commitment to achieve carbon neutrality by 2050.

Humans produce, store, transport and consume energy to sustain their livelihoods and activities. Significantly reducing the amount of greenhouse gases emitted as a result of energy utilization will require a radical shift from heavy dependence on fossil fuels to power generation using renewable resources, such as sunlight and wind.

The NIMS Research Center for Energy and Environmental Materials (GREEN) has been tackling this issue by focusing its R&D on battery materials and hydrogen-related materials.
The public now widely recognizes the importance of photovoltaic power generation using highly efficient solar cells and of high-capacity rechargeable batteries for energy storage.
In addition to these technologies,
GREEN has been working tirelessly to make hydrogen both a practical CO_2 emission-free fuel and an energy storage and transportation medium for electricity generated from renewable resources in combination with a power-to-gas process.

GREEN will continue to deliver innovative energy-related materials with the goal of promoting sustainable energy utilization.

Data : **Research Center for Energy and Environmental Materials (GREEN)**

Director : Yoshitaka Tateyama  Number of permanent researchers: 34

Battery and Cell Materials Field

- Solid-State Battery Group
- Battery Interface Control Group
- Battery Materials Analysis Group
- Photovoltaic Materials Group
- Interface Electrochemistry Group
- Rechargeable Battery Materials Group
- Automated Electrochemical Experiments Team

Hydrogen Technology Materials Field

- Magnetic Refrigeration System Group
- Superconducting System Group
- Hydrogen Related Materials Group
- Hydrogen Production Catalyst Materials Group
- Advanced Superconducting Wire Group
- ☐ Battery Research Platform
- ☐ Center for Advanced Battery Collaboration

Cover Story

Newly developed electrocatalyst in action during water electrolysis

During water electrolysis*—a clean hydrogen production process free of CO_2 emissions—oxygen and hydrogen are simultaneously produced through separate chemical reactions taking place on the surfaces of two different electrodes. Improving water electrolysis efficiency will require higher-performance materials for both the oxygen- and hydrogen-producing electrodes. Most efforts to accelerate oxygen evolution reactions involve the use of electrocatalysts composed primarily of expensive and scarce platinum group elements. Taking an unconventional approach, Ken Sakaushi succeeded in developing an electrocatalyst composed entirely of relatively cheap and abundant chemical elements: manganese, iron, nickel, zinc and silver (the L-shaped material on the left side of the cover photo). Under specific conditions, this material can exhibit electrochemical properties superior to those of ruthenium oxide—the most electrochemically active material known among existing oxygen evolution reaction electrocatalysts (see the related article on p. 15).

* Water electrolysis is the splitting of water into oxygen and hydrogen using electricity.

The electrocatalytic material shown in the cover photo can be seen here as the solid material in the second vial from the right. Different metallic elements dissolved in ethanol (shown as solutions of different colors on the left side of the photo) were mixed in equal ratios to prepare the orange solution at extreme right. This solution was applied to a substrate surface which was then fired in a furnace to form the electrocatalytic material.

Key Projects

Overview of research projects being carried out at the Research Center for Energy and Environmental Materials (GREEN)

Basic research on energy conversion and storage materials

Project leader

Yoshitaka Tateyama

Battery materials: maximizing the utilization of renewable energy

More than 30 years have passed since the first lithium ion batteries appeared on the market. No battery has been commercialized since that exceeds their energy densities or cycle lives. Recent rapid growth in demand for electric vehicles has made the development of safer, higher-capacity, more durable rechargeable batteries imperative. GREEN has been engaged in research and development of next-generation rechargeable batteries, including advanced lithium ion batteries. Solid-state batteries composed entirely of ion-conducting solid materials are particularly promising. A major hurdle preventing their practical use is poor ionic conductivity at the interfaces between different solid materials. We have been working to overcome this issue by analyzing phenomena occurring at the interfaces, optimizing connections between different solid components, searching for higher-performance battery materials and through other efforts. In addition, we have been researching and developing rechargeable batteries with liquid electrolytes. These include lithium–oxygen batteries with extremely high specific energies (i.e., high energy capacity to weight ratios) and batteries developed through strategic utilization of abundant chemical elements. We aim to put these innovative batteries into practical use.

Lithium–oxygen batteries being subjected to electrochemical measurements

Magnesium button cell (see the related article on p. 15)

As part of our renewable energy generation technology R&D, we have been researching and developing perovskite solar cells that can be formed on the surfaces of flexible substrates. We are working to improve their power conversion efficiencies and durability by designing high-performance materials, optimizing their structures and using them in tandem with crystalline silicon solar cells. We are also attempting to remove toxic lead from perovskite materials. In addition, we are actively promoting collaboration between the industrial, academic and public sectors with the goal of putting renewable energy generation technologies into practical use. As part of this effort, we have been participating in the activities of the solid-state battery materials open platform (MOP)—a basic research collaboration framework for private companies in the battery industry—and several national rechargeable battery-related projects. Moreover, GREEN manages the Center for Advanced Battery Collaboration where collaborative JST-funded R&D projects are underway. GREEN also operates the NIMS Battery Research Platform, a state-of-the-art shared use facility equipped with virtually all of the resources needed to perform next-generation rechargeable battery R&D. We will leverage GREEN's resources to spearhead Japan's efforts to develop innovative rechargeable batteries and cultivate capable human resources.

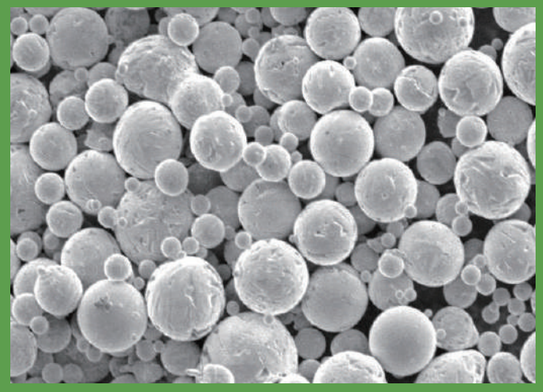
See Research 1 on **p. 6**
See Research 2 on **p. 8**
See Research3 on **p. 10**

Hydrogen-related materials crucial to promoting the hydrogen economy

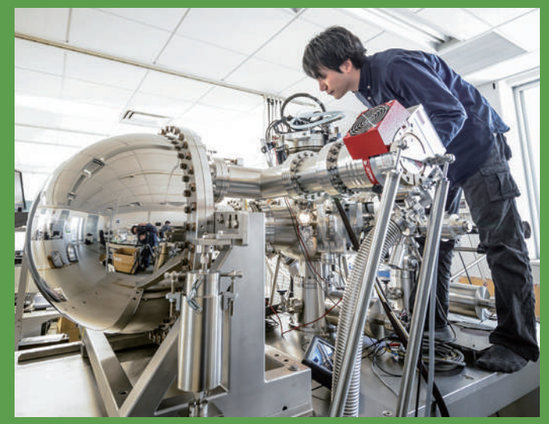
Developing a hydrogen infrastructure is an urgent part of efforts to popularize the use of hydrogen as a green energy source. GREEN has been researching and developing hydrogen production technologies through a number of projects, including the search for high-performance electrocatalytic materials capable of accelerating water electrolysis—the splitting of water to extract hydrogen from it using electricity—and the development of catalytic materials capable of isolating high-purity hydrogen from a mixture of methane (CH_4) and carbon dioxide (CO_2)—the two main components of natural gas. We have succeeded in constructing lab-scale hydrogen production systems using these catalysts and demonstrating their ability to extract hydrogen. We plan to enlarge these systems to increase their hydrogen production capacities.

Hydrogen gas can be liquefied by cooling it to a temperature of -253℃. This is a vital process in making hydrogen storage and transportation significantly more efficient. We have been seeking to improve the performance of the magnetic refrigeration system NIMS developed to liquefy hydrogen. This effort began during NIMS' fourth medium-to-long-term (MTLT) plan implementation period and has continued into the current fifth MTLT period. To achieve this goal, we have been researching and developing new component materials, superconducting magnets capable of generating stronger magnetic fields and coating techniques to protect heat absorbing/releasing magnetic refrigeration materials from hydrogen diffusion. In addition, we are developing a superconducting wire fabrication process, which could be useful in developing electric aircraft fueled by liquid hydrogen. Through these and other efforts, GREEN has been developing the materials and technologies needed to bring a hydrogen economy into existence.

See Research 4 on **p. 12**



Rooted Ni#Y_2O_3 catalyst for use in high-purity hydrogen production



Hard x-ray photoemission spectroscopy (HAXPES) instrument capable of non-destructively analyzing bulk materials as thick as approximately 50 nm

Analyzing complex physiochemical phenomena using advanced measurements, theoretical calculations and automated experimental systems

Batteries are densely packed with diverse materials. While they are being charged and discharged, complex physiochemical phenomena (e.g., chemical reactions between active materials, changes in crystalline structures and localized stress) take place at different scales within them. Advanced measurement techniques, theoretical calculations and data science are effective tools in understanding these phenomena and designing high-performance, durable batteries. GREEN has been developing sophisticated in-situ electrochemical measurement techniques to enable measurements to be taken from a battery while it is being charged and discharged and even during the synthesis of battery materials. GREEN is also developing theoretical calculation techniques to ascertain the electronic, ionic and molecular dynamics at the various interfaces within battery materials and AI-based data-driven techniques to analyze data generated by these calculations. In addition, we are actively incorporating robotic automation technologies into our laboratories and are employing AI to expedite searches for materials with desirable characteristics. We have already adopted fully automated systems capable of performing all of the steps in lithium ion and lithium–oxygen battery production, from electrolyte formulation to battery cell assembly, in search of high-performance electrolyte materials for these batteries. In addition, we are aiming to establish a high-throughput materials search process with a feedback loop in which AI is used to analyze electrochemical data and predict battery materials with desirable properties. We are also developing theories to explain the complex electrochemical phenomena we have observed using these techniques.

RESEARCH 1

Development of extremely safe solid-state oxide batteries

Tsuyoshi Ohnishi
Leader,
Battery Interface Control Group

The tightly sealed container Ohnishi is holding contains a thin-film solid-state battery sample in an argon gas atmosphere. He is evaluating its ionic conductivity and other properties by connecting it to electrodes and repeatedly charging and discharging it.

Solid-state batteries are composed entirely of solid materials. Their practical use as safer, larger-capacity electric vehicle (EV) batteries has been eagerly anticipated. Tsuyoshi Ohnishi has been using his expertise in thin film deposition to identify the reasons for these batteries' power output limitations. He is also developing solid-state batteries using bulk materials to increase their energy capacities.

Growing expectations for safer, more durable solid-state batteries

EVs are rapidly becoming more popular amid increased public interest in reducing CO_2 emissions. EV rechargeable batteries need to be lightweight, high-capacity, durable and very safe.

Among the types of rechargeable batteries commercially available today, lithium ion batteries have the highest energy density*. However, EVs equipped with lithium ion batteries can travel no more than 500 km per charge. In addition, these batteries contain flammable electrolyte solutions, posing safety concerns. They are also susceptible to capacity loss caused by repeated charge-discharge cycles—another major issue. Solid-state batteries have the potential to resolve these issues.

A solid-state battery is similar in overall structure to a lithium ion battery. The two differ in that a lithium ion battery contains a liquid electrolyte while a solid-state battery features a solid one (see the schematic diagram on p. 8). Solid-state batteries are incombustible and can theoretically have higher energy densities than commercially available lithium ion batteries. Moreover, liquid electrolytes contain many different substances, including some that are not directly involved in battery reactions. They migrate back and forth between the electrodes, inducing performance degrading side reactions which also impact batteries' service lives. By contrast, only lithium ions travel within solid electrolytes, potentially curing these issues.

Solid-state batteries are already available commercially. However, they only have limited applications and are inadequate for use in EVs due to inferior performance attributed to poor lithium ion conductivity at the interface particularly between the solid electrode and the cathode. Tsuyoshi Ohnishi has been working to resolve this issue using his original thin film deposition techniques.

Identifying factors that limit lithium ion flow using thin films

Solid-state batteries fall under two major categories based on their composition: sulfide and oxide types. Solid-state sulfide batteries entered practical use before their oxide counterparts. However, these batteries risk releasing poisonous hydrogen sulfide when they react with atmospheric moisture, necessitating countermeasures. By contrast, oxides are stable in the air, and their use will make solid-state batteries even safer.

Solid oxide electrolytes have a shortcoming, however. Most are made of hard materials, making it difficult for them to be brought into tight contact with a cathode. This causes poor lithium ion conductivity at the interface.

"Lithium ion conductivity had been believed to be greatly influenced by the crystalline orientations of battery materials," Ohnishi said. "I therefore decided to thoroughly investigate the causes of resistance to lithium ion flow by fabricating thin-film solid-state batteries—stacks of thin film cathode, electrolyte and anode layers—and evaluating their charge-discharge properties. I wanted to use the techniques I've developed for precisely controlling the chemical compositions and crystalline orientations of thin films to fabricate battery samples with cathodes with different crystalline orientations and determine how these differences influence ionic conductivity."

Ohnishi used pulsed laser deposition (PLD) to create lithium cobalt oxide ($LiCoO_2$) thin film cathodes. In PLD, the surface of a solid raw material is irradiated with pulsed ultraviolet laser radiation to vaporize it. The vaporized raw material is then deposited on the surface of a substrate, forming a thin film. Ohnishi has been utilizing PLD as his principal technique since he was a college student.

In addition, Ohnishi fabricated a solid oxide electrolyte made of lithium phosphate (Li_3PO_4) and a metallic lithium anode in the form of high-quality thin films. The electrolyte was created using radio frequency sputtering while the anode was formed using vacuum thermal deposition. These cathodes, electrolytes and anodes were then integrated to form thin-film solid-state batteries. Ohnishi then evaluated the charge-discharge properties of these battery samples with different cathode thin film crystalline orientations.

"Based on these evaluations, I was able to identify cathode thin film crystalline orientations favorable to higher ionic conductivity and succeeded in increasing the power output of thin-film solid-state batteries (Figure 1)," Ohnishi said. "In addition, I gained a better understanding of how thin film crystalline quality (e.g., the presence/absence of defects) may impact battery performance."

These insights on electrode-electrolyte interfaces (e.g., how film deposition conditions, such as substrate temperatures and durations, influence interfacial ionic conductivity) are expected to provide valuable clues leading to the fabrication of larger-capacity solid-state batteries using bulk materials and to the design of bulk material sintering processes.

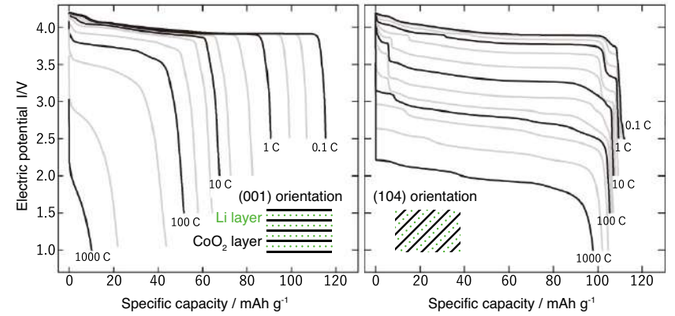


Figure 1. Graphs showing the charge-discharge properties of thin-film solid-state batteries composed of a $LiCoO_2$ thin film cathode, a Li_3PO_4 solid oxide thin film electrolyte and a metallic Li thin film anode. The graph on the left represents a $LiCoO_2$ thin film cathode with the (001) crystalline orientation while the graph on the right represents the cathode with the (104) orientation. Ohnishi succeeded in increasing the power output of the battery by precisely controlling the crystalline orientation of its cathode.

Applying insights on thin film battery fabrication to bulk-type battery development

Ohnishi's years of R&D efforts have been mainly focused on thin-film solid-state batteries. More recently, he has begun researching bulk-type solid-state batteries equipped with solid oxide electrolytes.

"I succeeded in fabricating large-area thin-film solid-state batteries with interfaces highly conductive to ions. However, the energy capacities of these batteries were small," Ohnishi said. "In an attempt to overcome this issue, I increased the thickness of the cathode by affixing powder material with the same composition as the cathode layer on the solid electrolyte plate. This addition increased battery capacity to a certain extent, although the improvement was still far too small to satisfy practical battery capacity requirements. I therefore shifted gears and have since been developing larger-capacity bulk-type solid-state batteries by leveraging my experience in thin-film solid-state battery fabrication."

Sintering processes are key to fabricating larger-capacity bulk-type solid-state batteries. As described above, the hardness of solid oxide electrolytes makes it difficult for them to be brought into tight contact with a cathode material. Solid electrolytes and electrodes are commonly sintered together as a combined unit at high temperatures (approximately 1,000°C) to increase their interfacial ionic conductivity. However, high-temperature sintering also causes chemical reactions to take place at the electrolyte-electrode interfaces that result in the formation of a layer with poor ion conductivity, hampering efforts to improve battery performance.

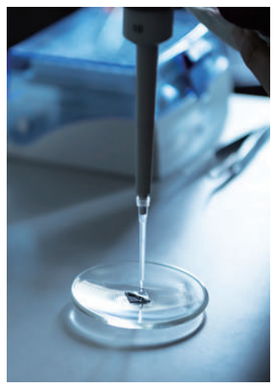
To address this issue, Ohnishi affixed a layer of powder cathode material to the surface of a solid electrolyte with a sintering additive using a technique he developed in his thin-film solid-state battery R&D. This technique allowed the combined cathode and electrolyte to be sintered at temperatures as low as approximately 700°C.

Ohnishi reported that powder cathode material incorporation and lower temperature sintering actually enabled the resulting cathode-electrolyte unit to exhibit higher interfacial ionic conductivity. During this fabrication process, he used a sintering additive he formulated which turned out to be a key ingredient in this success (Figure 2).

"Sintering additives are normally used to densify sintered products and make them more stable," Ohnishi said. "I used the additive in an unusual way by applying it to the layer of powder cathode material adhered to the surface of the solid electrolyte. I was very surprised that this treatment led to such unexpectedly good results. The performance of solid-state batteries still has room for improvement, as it can be influenced by various sintering conditions (e.g., the amount of powder cathode material incorporated, the types and amounts of sintering additives applied, sintering temperatures and durations and the type of gas atmosphere used). I'll continue to work to find optimal sintering conditions."

Ohnishi has been researching and developing solid-state oxide batteries using his expertise in thin film deposition with the goal of producing practical battery products as soon as possible.

*Energy density is the amount of energy stored in a battery per unit volume or per unit mass.



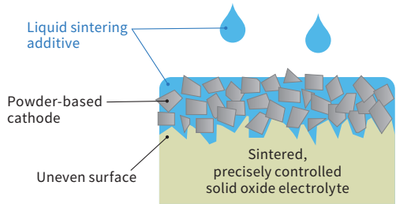


Figure 2. Ohnishi also fabricated a bulk-type solid-state battery. A solid oxide electrolyte with an uneven upper surface was first prepared. A powder material was then layered over the uneven surface to form a cathode. A sintering additive was then applied to the cathode and the cathode-electrolyte structure was sintered at approximately 700°C. An anode material (either a metallic Li thin film (foil) or a Si thin film) and a current collector were then attached to the sintered structure to create the bulk-type solid-state battery. By precisely controlling crystalline orientations and other features of this bulk-type solid-state battery, Ohnishi was able to achieve performance equivalent to that of the thin-film solid-state battery he had previously developed.

Kuwata (left) and Gen Hasegawa (a postdoctoral researcher at NIMS) successfully imaged lithium ion diffusion within solid electrolytes using the TOF-SIMS (time-of-flight secondary ion mass spectrometry) instrument shown in this photo. This instrument is available at the Battery Research Platform, a state-of-the-art facility run by NIMS.

RESEARCH 2

Enabling observation of fast-moving lithium ions within solid-state batteries

Naoaki Kuwata

Principal Researcher, Battery Interface Control Group

Poor lithium ion conductivity has been the most critical issue in the development of solid-state batteries. Efforts are being made to identify its causes through observational research. Naoaki Kuwata succeeded for the first time in the world in imaging the movement of lithium ions within solid electrolytes. We asked him how he achieved it.

Freezing lithium ions: key to imaging them

Solid-state rechargeable batteries (Figure 1) are a potentially very safe and durable technology whose practical use is being vigorously pursued. NIMS has been working to improve lithium ion conductivity in these batteries by developing high-performance battery materials (see p. 6). As part of this effort, Naoaki Kuwata has been investigating lithium ion diffusion mechanisms using cutting-edge observational techniques.

"A solid-state battery is composed of electrodes and a solid electrolyte. The solid electrolyte contains various interfaces, including grain boundaries, that had been thought to obstruct the movement of lithium ions. However, no method had been available to identify specific bottlenecks. I therefore decided to develop techniques to image the interfacial movement of lithium ions within solid electrolytes in the hope of gaining insight into how the performance of solid-state batteries can be improved."

Secondary ion mass spectrometry (SIMS) is a technique used to precisely analyze the chemical composition of a solid material specimen. This is achieved by sputtering the surface of a solid material specimen with a focused primary ion beam and collecting and measuring the mass of ejected secondary ions. SIMS imaging of moving lithium ions within solid-state batteries had been considered impossible due to the rapidity of their movement despite the poor ion conductivity of these batteries.

To overcome this problem, Kuwata employed cryo-SIMS, in which a material specimen is cooled to a temperature of approximately -100°C to freeze the movement of ions and other particles while they are subjected to SIMS measurement. Lithium ions are first immobilized by cooling the specimen and are then allowed to move by raising its temperature. This process is repeated to allow the ions to move slightly each time they are measured so that their movement can be tracked. Kuwata envisioned using cryo-SIMS to image the distribution of lithium ions within solid electrolyte specimens in terms of their diffusion coefficient.

Kuwata and Gen Hasegawa, a postdoctoral researcher at NIMS, began constructing a SIMS instrument capable of taking measurements under cryogenic conditions in 2019.

Tracking the movement of specific lithium ions

Even if the overall movement of lithium ions can be imaged, this information would be of little help in identifying the factors that obstruct ionic movement without determining the diffusion pathways and speed of individual lithium ions. To track specific lithium ions, Kuwata came up with the idea of "marking" certain ions using isotopes—the same chemical elements but with different numbers of neutrons.

"Lithium ions exist in two stable isotopes in nature: ^{7}Li and ^{6}Li," Kuwata said. "They normally exist in a ratio of 92% ^{7}Li to 8% ^{6}Li, making ^{6}Li very rare in solid electrolytes. Based on this assumption, I planned to intentionally introduce ^{6}Li ions into a solid electrolyte specimen using an ion exchange technique and track their movement. High-precision mass spectrometry using SIMS is capable of distinguishing even between these different isotopes. I had actually read research papers reporting the SIMS measurement of different oxygen and sodium isotopes and thought that SIMS would also be applicable to measuring lithium isotopes."

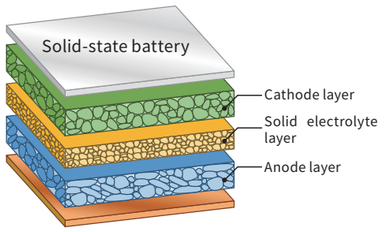


Figure 1. Schematic diagram of a solid-state battery

An unexpected bottleneck identified within solid electrolytes

Among the different types of interfaces existing in solid-state batteries, Kuwata's group decided to focus on interfaces within solid electrolytes. The group selected lithium lanthanum titanium oxide (LLTO) as a model solid electrolyte specimen due to the fact that its lithium ion conductivity is among the highest of all known solid electrolyte materials.

After about four and half years of struggle, Kuwata's group finally succeeded in imaging and quantifying the movement of lithium ions within solid electrolytes for the first time in the world. These results—including an unexpected discovery—were published in December 2023.

"The LLTO specimens we observed were polycrystalline, meaning they were composed of numerous minute crystalline grains and their boundaries," Kuwata said. "Grain boundaries—where crystalline defects or structural irregularities are prone to occur—had been expected to be more conductive to lithium ions than the grains themselves. However, our cryo-SIMS observation found that diffusing lithium ions traveled approximately 10,000 times more slowly when crossing grain boundaries than when travelling through the grains. These results ran contrary to the conventional wisdom and were very surprising to us (Figure 2)." Kuwata noted that these outcomes are specific to LLTO specimens and ionic movement at grain boundaries differs depending on the materials used.

"I'd like to continue to use SIMS observation on other materials to help improve the lithium ion conductivity of various solid electrolyte materials by suggesting material-specific strategies, such as optimizing crystalline structures and coating crystalline grains," Kuwata said.

New projects: high-precision simulations and in-situ observations

Kuwata is currently developing mathematical models needed to simulate lithium ion migration within LLTO and other polycrystalline specimens on a computer. The accuracy of solid-state battery simulation models has previously been evaluated based solely on their ability to reproduce batteries' charge-discharge properties. Kuwata's recent success in measuring the diffusion coefficient of lithium ions within LLTO crystalline grains and their boundaries has made it possible to compare physical phenomena actually observed within batteries and mathematical model outputs. This comparison is expected to be helpful in improving the accuracy of solid-state battery simulation models.

In addition, Kuwata plans to image lithium ion movement at the interface between a cathode and a solid electrolyte.

"We are developing an operando SIMS instrument," Kuwata said. "This instrument is designed to be capable of real-time, in-situ observation of lithium ion movement within a solid-state battery while it is being charged and discharged. Although this instrument has lower spatial resolution than the cryo-SIMS instrument, it will be capable of room-temperature measurements. The lower resolution won't pose a problem in observing ionic movement at a cathode-solid electrolyte interface because the required resolution isn't as high as that needed to observe ionic movement within a solid electrolyte. I'm considering combining the use of operando SIMS observation within operating batteries with cryo-SIMS high-resolution observation under cryogenic conditions. This could be a very effective approach to closely analyzing lithium ion movement within solid-state batteries."

Hasegawa placing an LLTO specimen in a cryo-holder to cool it to a temperature below -100°C, enabling SIMS observation of virtually immobilized lithium ions within the specimen.

Kuwata will continue to observe and image ionic movement, including interfacial movement, in various battery materials in the hope of making breakthrough discoveries leading to the development of practical solid-state batteries.

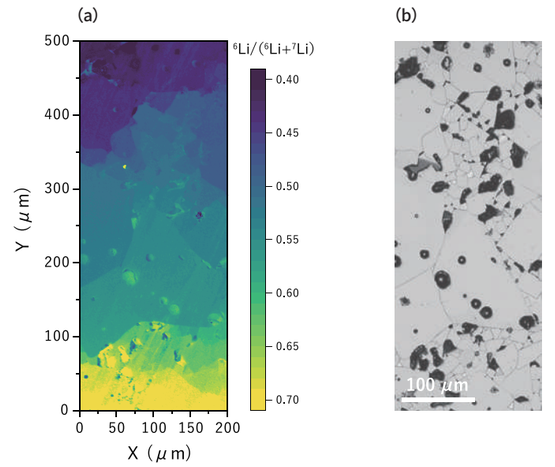


Figure 2. (a) Cryo-SIMS image of an LLTO solid electrolyte specimen into which ^{6}Li ions were introduced from the bottom edge. The ratio of ^{6}Li to the total amount of lithium of both isotopes was color mapped. As a result of upward ^{6}Li diffusion, high concentrations of ^{6}Li can be seen in the lower areas (represented by yellow) while low concentrations of ^{6}Li can be seen in the upper areas (represented by purple). This image visualized lithium ion diffusion pathways within the LLTO specimen. (b) Laser microscope image of the corresponding LLTO microstructure.

These images revealed that ^{6}Li concentrations are uniform within crystalline grains but change greatly at the grain boundaries, indicating that the grain boundaries obstruct the movement of lithium ions.

RESEARCH 3

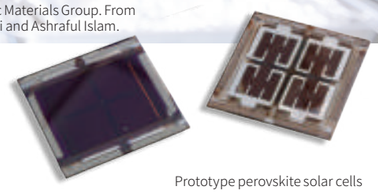
Overcoming issues hampering the development of practical perovskite solar cells

Yasuhiro Shirai

Leader,
Photovoltaic Materials Group

Shirai and his permanent researcher colleagues in the Photovoltaic Materials Group. From left to right: Dhruba B. Khadka, Masatoshi Yanagida, Yasuhiro Shirai and Ashraful Islam.

Perovskite solar cells can be formed on flexible surfaces using simple processes—a significant advantage. Research is being actively pursued to expedite the development of practical perovskite solar cells. In February 2024, the NIMS Photovoltaic Materials Group led by Yasuhiro Shirai succeeded in developing the most durable and power conversion-efficient perovskite solar cell device ever. We asked Shirai about his group's current R&D activities.



Prototype perovskite solar cells

Shortcomings of perovskite solar cells

Solar cells convert sunlight into electricity. Their household use is becoming more popular and public interest in solar cells with higher power conversion efficiency is growing.

Crystalline silicon solar cells are currently the most widely used. Perovskite solar cells, which use perovskite-structured materials to absorb light (Figure 1), have some advantages over their crystalline silicon counterparts: they can be simply painted or printed over substrate surfaces at temperatures of around 100°C. In addition, they can be formed on the surfaces of plastic films to create flexible, lightweight solar cells. Moreover, their power conversion efficiency has improved significantly, making them almost as efficient as crystalline silicon solar cells.

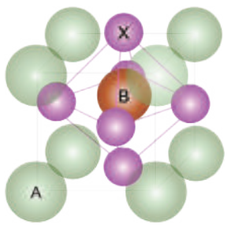


Figure 1. Perovskite crystalline structure

This crystalline structure consists of three chemical elements: the A-site element (e.g., Cs and Rb), the B-site element (e.g., Pb and Sn) and the X-site element (either I, Br or Cl).

Despite these advantages and improvements, practical use of perovskite solar cells has yet to be achieved due mainly to their inferior durability. They are susceptible to oxygen and water penetration, causing crystalline defects to develop that significantly degrade their power conversion efficiency. In addition, solar cell surfaces become hot during the summer, reaching temperatures as high as 80°C. The combined effects of heat and sunlight cause various parts of perovskite solar cells to deteriorate, shortening their service lives.

The Photovoltaic Materials Group led by Yasuhiro Shirai has been pursuing R&D to extend the service lives of perovskite solar cells.

Nanostructures provide protection from oxygen, water and heat

A perovskite solar cell is composed basically of a sunlight-absorbing perovskite layer sandwiched between an upper electron transport layer and a lower hole transport layer (Figure 2). When the semiconducting perovskite layer is placed in sunlight, it generates electrons and holes which are transferred to the electrodes via these respective layers.

"We're developing perovskite solar cells with improved power conversion efficiency by integrating several high-performance materials we previously developed," Shirai said. "A major issue with perovskite solar cells is their susceptibility to oxygen and water infiltration from the interface between the perovskite and electron transport layers. It was therefore vital to find ways of allowing electrons to be smoothly transferred from the perovskite layer to the electron transport layer while protecting the perovskite layer from oxygen and water. A potential solution we pursued was the use of 2D perovskite nanostructures."

A 2D perovskite is composed of a stack of alternating perovskite and organic compound thin layers (Figure 2). These structures can be obtained by incorporating organic amine compounds into a layered perovskite structure to separate it into individual layers.

"2D perovskite structures had been known to be very stable in the presence of oxygen and water," Shirai said. "However, the organic amine layers within 2D perovskite act as insulators and impede the flow of electrons. To overcome this problem, we distributed only small amounts of 2D perovskite nanostructures over the surface of the perovskite layer. The goal here was to prevent the 2D perovskite nanostructures from obstructing electron flow while still allowing them to protect the perovskite layer from oxygen, water and heat. This strategy turned out to work very well."

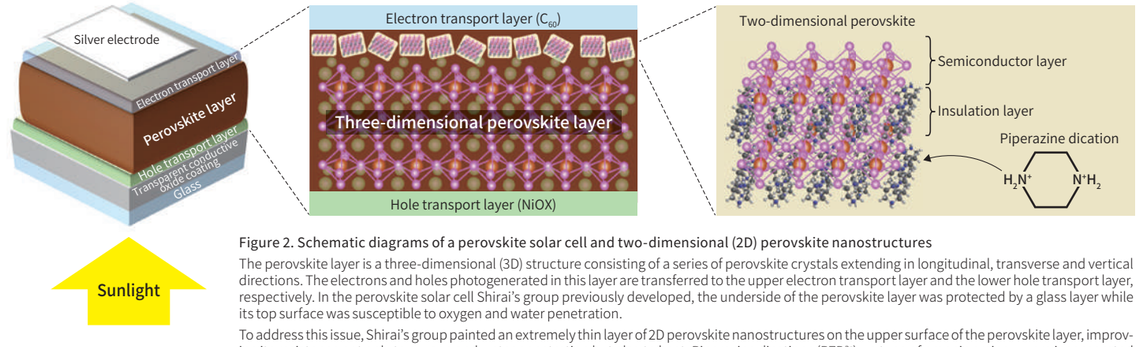


Figure 2. Schematic diagrams of a perovskite solar cell and two-dimensional (2D) perovskite nanostructures

The perovskite layer is a three-dimensional (3D) structure consisting of a series of perovskite crystals extending in longitudinal, transverse and vertical directions. The electrons and holes photogenerated in this layer are transferred to the upper electron transport layer and the lower hole transport layer, respectively. In the perovskite solar cell Shirai's group previously developed, the underside of the perovskite layer was protected by a glass layer while its top surface was susceptible to oxygen and water penetration.

To address this issue, Shirai's group painted an extremely thin layer of 2D perovskite nanostructures on the upper surface of the perovskite layer, improving its resistance not only to oxygen and water penetration but also to heat. Piperazine dications (PZD^{2+})—a type of organic amine—were incorporated into the 2D perovskite nanostructures.

Shirai's group developed a technique to distribute 2D perovskite nanostructures over the surface of the perovskite layer. The group then used this technique to fabricate a 1 cm x 1 cm solar cell exhibiting greater than 20% power conversion efficiency for 1,000 continuous hours at 60°C—a temperature to which operating solar cells are commonly exposed.

Shirai explained how his group was able to develop the most durable perovskite solar cell ever.

"We were able to identify an organic amine compound which can be used to produce optimally sized 2D perovskite nanostructures. 2D perovskite productivity, component layer thickness and size vary depending on the type of organic amine used. We spent more than a year screening approximately 50 types of organic amine compounds. After a period of trial and error, we finally identified an optimal organic amine compound. We've just begun compiling the data we've generated into a database in preparation for a data-driven analyses."

Substituting lead with tin in perovskite solar cells

Another major issue with perovskite solar cells is their toxic lead content. Lead must be removed from them before they can be used to power sensors for collecting large amounts of systematic data—a promising application due to the fact that they are easy to produce and can be printed on flexible surfaces.

"When we attempted to substitute lead within perovskite crystals with a non-toxic chemical element, the realistic candidates based on chemical properties and size were tin—a group 14 element like lead—and bismuth, which is adjacent to lead on the periodic table," Shirai said. "Encouraged by international efforts to discover additives capable of preventing tin from oxidizing, we chose tin despite its susceptibility to oxidation and instability."

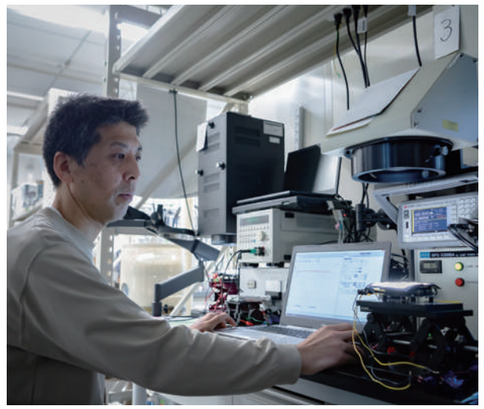
This global engagement helped enable Shirai's group to succeed in developing an original additive effective for this purpose. Using this additive, his group was able to develop a lead-free, tin-substituted perovskite soler cell. In addition, this solar cell was certified by international standards testing organizations* in June 2023—a great feat.

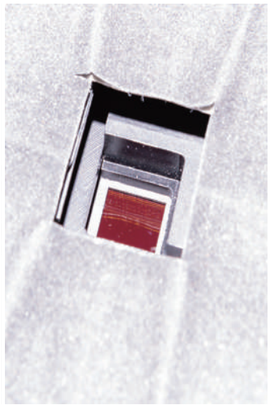
"To get the cetification, We needed to fabricate a stable device capable of producing consistent results. None of the tin-incorporated perovskite solar cell devices previously developed passed certification testing due to their instability. The fact that we have overcome this hurdle enables us to now focus on R&D aimed at putting our product into practical use. We will further improve its durability by identifying more effective additives and through other efforts."

In addition to these projects, Shirai's group is collaborating with private companies to develop multi-junction solar cells, including tandem solar cells in which a crystalline silicon solar cell is paired with a perovskite solar cell. This pairing is intended to exploit a broader range of wavelengths of light for power conversion as crystalline silicon and perovskite absorb different wavelengths. Successful development could potentially lead to a power conversion efficiency of 35% or higher.

Shirai and his colleagues are determined to put the high-performance solar cells they have long dreamt of into practical use by making steady progress on overcoming challenging issues.

*The international standards testing organizations were the National Renewable Energy Laboratory (NREL) in the US, the Fraunhofer Institute for Solar Energy Systems ISE in Germany and the National Institute of Advanced Industrial Science and Technology (AIST) in Japan.





Shirai measuring the power conversion efficiency of the 1 cm x 1 cm (the size required for international standards testing) solar cell device his group fabricated while exposing it to artificial sunlight. "The solar cell we developed in the past was able to maintain a power conversion efficiency greater than 20% for 1,000 continuous hours as long as it was kept at room temperature (25°C)," Shirai said. "The newly developed solar cell into which 2D perovskite nanostructures were incorporated succeeded in maintaining the same power conversion efficiency for the same duration even at a higher temperature of 60°C."

In front of the AMR system for liquefying hydrogen, with Tsuyoshi Shirai (right), a Technical Staff involved in the construction of the equipment.

RESEARCH 4

Updates on NIMS' magnetic refrigeration technology for hydrogen liquefaction

Koji Kamiya
Leader,
Magnetic Refrigeration System Group

Kyohei Natsume
Principal Researcher,
Magnetic Refrigeration System Group

Urgent efforts are underway to develop technologies able to liquefy hydrogen to make its transportation and storage more efficient and economical. NIMS successfully developed and demonstrated a magnetic refrigeration system capable of liquefying hydrogen in 2021. We asked the leaders of this effort, Koji Kamiya and Kyohei Natsume, to tell us how they achieved it and about the new challenges they have been taking on since.

Magnetic refrigeration technology vital to bringing a hydrogen economy into existence

Hydrogen combustion emits no CO_2, making it a potential source of clean energy. In combination with a power-to-gas process, hydrogen could also serve as an effective energy storage medium, enabling international transportation of surplus electricity generated from solar energy.

Liquefaction is an effective way of reducing the volume of hydrogen gas, allowing it to be efficiently transported and stored. Hydrogen needs to be cooled to an extremely low temperature of 20 K (-253°C) before it liquefies. This has already been achieved using existing vapor compression refrigeration systems[*1]. However, the large compressors and other equipment they require consume considerable amounts of energy, limiting their liquefaction efficiency (i.e., the ratio of the amount of energy stored in liquid hydrogen to the energy required for the liquefaction process) to 25%. NIMS has been researching magnetic refrigeration with the goal of developing a significantly more efficient hydrogen liquefaction system. This effort has been featured in previous NIMS NOW issues[*2] in addition to this article.

Magnetic refrigeration is a cooling technology based on the magnetocaloric effect that involves the use of magnetic materials and magnets. In absence of an external magnetic field, the electron spins within a magnetic material are randomly orientated. When the magnetic material is adiabatically magnetized by placing a magnet close to it, the electron spins within it align with the direction of the external magnetic field , causing it to release heat. When the magnetic field is removed (i.e., demagnetization), the electron spins within the material revert to random orientations, causing it to absorb heat. By repeatedly magnetizing and demagnetizing a magnetic material and allowing it to dissipate heat while magnetized , it can be progressively cooled. Unlike vapor compression refrigeration, magnetic refrigeration does not require energy-consumptive compressors. Because of this advantage, its theoretical liquefaction efficiency could reach 50%. Public interest in the hydrogen economy is growing and projects are underway in many places, including the US, to develop magnetic refrigeration technologies capable of hydrogen liquefaction.

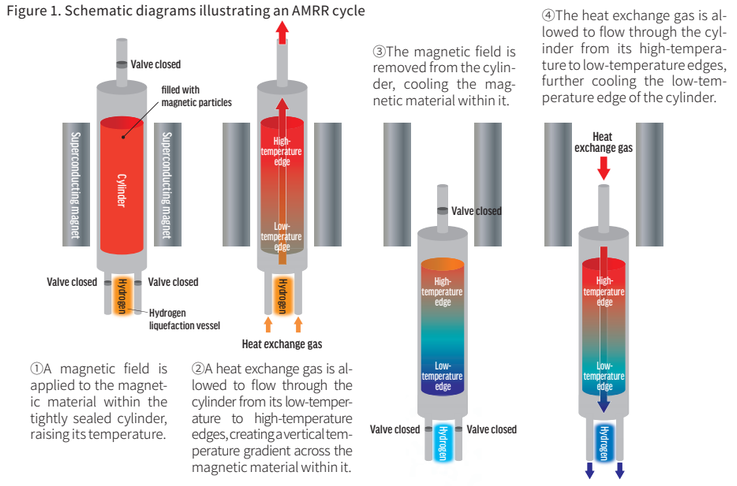
NIMS' magnetic refrigeration system liquifies hydrogen for the first time ever

A major issue with magnetic refrigeration is its ability to cool hydrogen only within a narrow temperature range. This is in sharp contrast to vapor compression refrigeration, which can cool hydrogen from room temperature all the way down to 20 K.

"NIMS succeeded in liquefying hydrogen using magnetic refrigeration for the first time in the world in 2007," said Kamiya who leads magnetic refrigeration R&D at NIMS. "We achieved this using Carnot magnetic refrigeration (CMR). Due to its mechanical nature, this technology can cool hydrogen only by 5 K (5°C). To address this issue, Takenori Numazawa—my predecessor and now a NIMS special researcher—began researching active magnetic regenerative refrigeration (AMRR) in 2018."

The AMRR system Numazawa developed consisted of a hydrogen liquefaction vessel in contact with a tightly sealed cylinder containing a magnetic material. A heat exchange gas (refrigerant) flows through the cylinder each time the magnetic material releases and absorbs heat, allowing the gas to transport heat out of the cylinder and creating a temperature gradient across the cylinder so that the edge adjacent to the vessel becomes cold. This cold vessel is then used to cool the hydrogen gas

Figure 1. Schematic diagrams illustrating an AMRR cycle



①A magnetic field is applied to the magnetic material within the tightly sealed cylinder, raising its temperature.

②A heat exchange gas is allowed to flow through the cylinder from its low-temperature to high-temperature edges, creating a vertical temperature gradient across the magnetic material within it.

③The magnetic field is removed from the cylinder, cooling the magnetic material within it.

④The heat exchange gas is allowed to flow through the cylinder from its high-temperature to low-temperature edges, further cooling the low-temperature edge of the cylinder.

within it (Figure 1). This NIMS' AMRR R&D project was granted funding from the Japan Science and Technology Agency (JST)'s Mirai Program starting in 2018. The goal of this project was to develop an AMRR system capable of cooling hydrogen from 77 K (-196°C) to 20 K. Vapor compression refrigeration was used to prepare 77 K-hydrogen during this project.

In 2018, Numazawa succeeded in developing an AMRR system able to cool hydrogen from 34 K (-239°C) to 22 K (-251°C). Extending the system's cooling temperature range down to 20 K necessitated further modifications of the system and the use of higher-performance magnetic materials.

Creative modifications enable NIMS to make another first-ever achievement

Kamiya's group took over the AMRR R&D project from Numazawa, and Kamiya and Natsume have since been leading it.

"Our basic strategy for expanding the cooling temperature range of the AMRR system was to chill a helium heat exchange gas to generate low temperatures that could then be transferred to hydrogen gas—a secondary cooling mechanism in addition to the primary, magnetocaloric effect-based cooling," Natsume said. "To achieve this, we sandwiched the hydrogen liquefaction vessel between two tightly sealed cylinders containing magnetic materials capable of absorbing and releasing heat (Figure 2). We then positioned two stationary superconducting magnets on either side of the vessel-cylinder unit. As the unit repeatedly moves up and down between the magnetic field-generating superconducting magnets, the magnetic materials within the cylinders are repeatedly magnetized and demagnetized. Smoothly and completely demagnetizing a magnetic material after it has been magnetized generally requires that it be moved a considerable distance away from the superconducting magnets. To reduce this distance to the extent possible, we installed auxiliary magnets on either side of each superconducting magnet to cancel out the magnetic fields generated by the superconducting magnets as needed. This arrangement reduced the distance the vessel-cylinder unit needed to be moved by 67%."

"We also gave careful thought to incorporating heat exchangers into the system to control the temperatures of the heat exchange gases," Kamiya said. "There were commercially available heat exchangers, but they were all designed to work with heat exchange gases that flow in only one direction. Because we designed the heat exchange gas flow direction in our system to be switchable, we ended up designing original heat exchangers compatible with this arrangement."

Kamiya's group also made other improvements and innovations. The group created tiny patterns on the metallic walls of the hydrogen liquefaction vessel to more efficiently transfer cold temperatures from the heat exchange gas to the hydrogen gas within the vessel. The group also developed an original liquid level sensor capable of measuring the amount of liquid hydrogen produced within the very narrow hydrogen liquefaction vessel.

After making these modifications, Kamiya and his colleagues finally succeeded in achieving hydrogen liquefaction using an AMRR system for the first time ever in 2021.

New challenges: expanding the system's cooling temperature range and increasing its liquid hydrogen production capacity

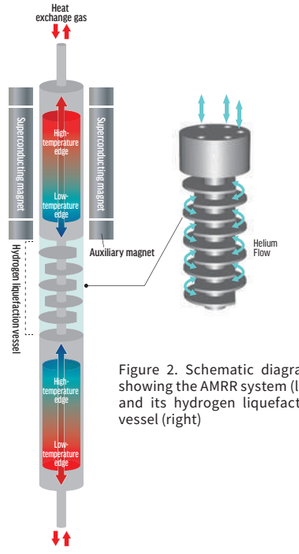


Figure 2. Schematic diagrams showing the AMRR system (left) and its hydrogen liquefaction vessel (right)

The AMRR system Kamiya's group developed is currently able to cool hydrogen from 34 K to 20 K. The group aims to expand its cooling range to 77 K to 20 K.

"Achieving this will require not only improving the current system but also developing new magnetic materials suitable for magnetic refrigeration," Natsume said. "We recently evaluated more than 20 candidate materials with known physical properties and ultimately selected $HoAl_2$ due to its broad cooling temperature range. However, we still need to optimize its properties. There are significant differences between different magnetic materials in terms of the temperature ranges in which they produce magnetocaloric effects and the extent of the temperature changes produced. In addition, the shapes of magnetic materials influence their physical properties. We plan to collaborate with a materials development team to optimize the $HoAl_2$ magnetic material. In the meantime, our group is currently carrying out hydrogen liquefaction experiments using $HoAl_2$."

The group is also developing a larger AMRR system with a significantly increased liquid hydrogen production capacity. Kamiya is passionate about making the hydrogen economy a reality by putting magnetic refrigeration into practical use.

*1 Vapor compression refrigeration can be used to liquefy hydrogen gas. This process involves adiabatically compressing a refrigerant (e.g., nitrogen or helium gas) to increase its pressure and then cooling it through a series of heat exchangers. The compressed and cooled gas is then expanded, causing a drop in temperature and further cooling. This cycle is repeated to cool the hydrogen gas until it reaches a temperature low enough for it to condense into a liquid state.

*2 NIMS NOW: Revolutionary H2 Liquefaction, vol. 19, no. 4
NIMS NOW: 2021→2022: Transition to new challenges, vol. 22, no. 2

Leaders of the future

We highlight research project carried out by four young researchers as part of NIMS' efforts to develop next-generation energy materials.

Calpa Marcela

Calpa Marcela
Researcher,
Solid State Battery
Materials Group

Challenge to improve battery performance in a state-of-the-art environment

I joined NIMS in 2021 after obtaining my doctorate, and have since been exploring battery electrode materials. In particular, I am focusing on "lithium-rich" materials as cathode material candidates. Since these materials contain large amounts of lithium—the element responsible for battery charge and discharge—they are expected to enable increases in battery capacity. The drawback, however, is that while high voltages are required to charge these batteries (high input voltages), the voltages that can be achieved during discharge are significantly lower (low output voltages). This phenomenon, known as "voltage hysteresis," leads to energy loss. To find a way of overcoming this problem, we used Li_2RuO_3 as a model material and investigated changes in its crystalline structure during charge and discharge.

A high-energy X-ray diffractometer (photo) played a particularly important role in this process. Using a measurement cell originally developed by Kei Kubota (below), it is possible to make measurements in real time with high x-ray intensity and precision compared to conventional methods. In fact, changes in crystalline structure were clearly detected during this analysis, and results that overturned the commonly accepted theory about the cause of voltage hysteresis were obtained*. This is truly a state-of-the-art research environment for materials development. Taking advantage of this favorable environment, I aim to design superior materials for energy storage, by elucidating the relationship between the structure of the materials and their physical and chemical properties.

*Related information: Press Release 2023.12.15
https://www.nims.go.jp/eng/news/press/2023/12/202312150.html

Kei Kubota

Kei Kubota
Senior Researcher,
Battery Materials
Analysis Group

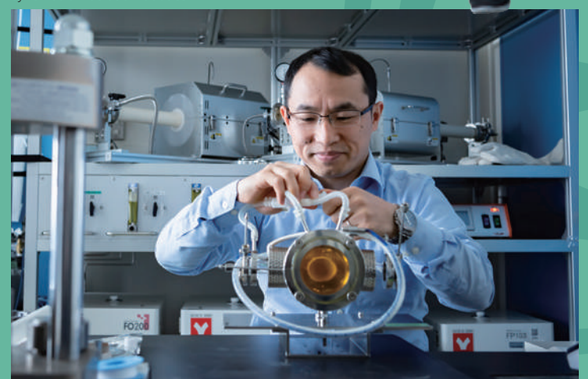
Creation of new materials based on in-depth investigation of underlying mechanisms

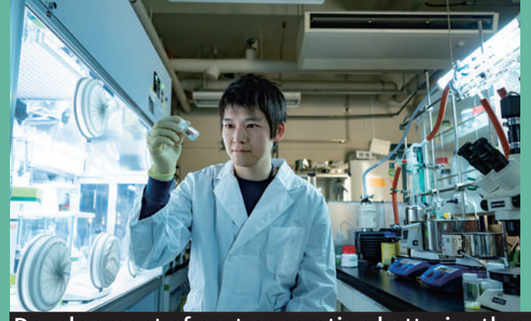
I have been synthesizing novel ceramics suitable for use as cathode and solid electrolyte materials to develop higher-performance lithium-ion and sodium-ion batteries. I leverage my expertise in materials synthesis in these activities primarily by thoroughly analyzing factors that may be hampering improved battery performance (e.g., issues with existing battery materials and their underlying causes). I then synthesize battery materials based on the analysis results. In addition, I actively develop new analytical methods using synchrotron and neutron facilities in addition to the equipment available in our laboratories.

There is a great deal of interest in extending the battery life of sodium-ion batteries by employing multi-element cathode materials. In pursuit of this, I performed a neutron analysis on these cathode materials and succeeded in elucidating their charge-discharge mechanisms. The disordered arrangement of transition metals in the cathode materials had previously been believed to significantly influence battery life. To verify this, I synthesized and analyzed new, long-life multi-element cathode materials with ordered arrangements of transition metals. This finding revealed that the extended battery life is actually caused by electron configuration varied by electrochemically inactive elements of the cathode material.

In another project, I am developing a technique to measure the synthesis process of cathode materials in real time. No one has ever achieved this due to the many hurdles involved. For example, it is necessary to prevent a specimen holder from affecting the chemical reactions taking place within the specimen during synthesis at high temperatures. I am eager to develop techniques that would enable us to accurately reproduce real material synthesis conditions and precisely measure the synthesis reactions of material specimens under these conditions. Also, as a member of NIMS—Japan's sole public research institute specializing in materials—I have a sense of mission about creating new, high-performance materials. My R&D continues to be motivated by these commitments and ambitions.

Synthetic reactors for real-time measurements at synchrotron radiation facilities





Toshihiko Mandai

Toshihiko Mandai
Senior Researcher,
Rechargeable Battery
Materials Group

Development of next-generation batteries through strategic utilization of chemical elements

Depletion of lithium (Li) resources is becoming a real threat. One objective of the Element Strategy Initiative is to develop batteries made only from chemical elements that are abundant on Earth. To achieve this, I have been developing new electrolyte and electrode materials. Earlier in my career, my research focus was structural chemistry. This enabled me to gain a broad understanding of the structures and associated characteristics of coordination complexes and liquid electrolytes, as well as material synthesis techniques. I' m now able to leverage this knowledge and skill in materials design and development. I can also quickly revise my molecular designs based on the results of molecular property evaluations. I consider these to be my unique strengths.

My research has been focused on magnesium (Mg) batteries incorporating Mg metal as anode materials. In collaboration with computational scientists, we succeeded in developing an Mg battery electrolyte with the highest performance ever recorded, showing a reaction efficiency of 99.5% on the anode side. This electrolyte has been adopted as the standard for use in national battery development projects. In addition, we tackled Mg metal anodes' susceptibility to deactivation when exposed to air and succeeded in preventing this by forming an artificial zinc coating on their surfaces.* This groundbreaking achievement may enable the manufacture of Mg metal batteries using existing lithium ion battery production lines.

While engaging in these R&D projects, I am always mindful of the need to develop the materials and techniques that are truly vital to creating high-performance batteries. In keeping with this basic principle, I plan to perform operando measurements in operating batteries to understand phenomena occurring within them in collaboration with my research partners. The findings from these measurements are expected to be useful in optimizing my materials design.

*This subject was covered in the May 16, 2023 NIMS press release:
https://www.nims.go.jp/eng/news/press/2023/05/202305160.html

The round holes in the Mg foil shown in this NIMS NOW cover photo (vol. 23, no. 5) were cut by Mandai. He used the round pieces of foil as a component in a prototype Mg battery (for details, please see NIMS NOW vol. 23, no. 5, p. 2).

Ken Sakaushi

Ken Sakaushi
Principal Researcher,
Interface Electrochemistry Group

Speeding up water electrolysis with the aid of Artificial Intelligence (AI)

Green hydrogen production free of CO_2 emissions may be achieved using efficient water electrolyzers which split water into hydrogen and oxygen using electricity. However, the current efficiency of water electrolysis is inadequate, and increasing it necessitates the use of expensive, scarce platinum group elements as main electrocatalyst components. To address this issue, scientists around the world, including myself, have been racing to discover electrocatalytic materials composed entirely of relatively abundant chemical elements. I am currently developing an artificial intelligence (AI)-based technique capable of expediting the process of identifying electrocatalytic materials with desirable characteristics in collaboration with Ryo Tamura, a data science expert. Using this technique, we actually discovered new platinum group-free electrocatalytic materials as electrochemically active as existing platinum group-based electrocatalytic materials (see the cover and the photo on p. 2) in just a single month. For reference, if the same comprehensive search were carried out manually, it is estimated that it would have taken almost six years. Using the evolution-capable AI we developed dramatically accelerated our materials search efforts.

We first manually selected 11 relatively abundant chemical elements and prepared a list of approximately 3,000 candidate electrocatalytic materials composed of five of them. We then randomly chose 10 of the candidate materials, actually synthesized them and evaluated their electrochemical properties. A pre-evolved AI (i.e., the first AI) was used to study the evaluation results and the trained AI winnowed the approximately 3,000 candidate materials down to a small number of the most promising ones. We again synthesized the materials predicted to be promising, evaluated their electrochemical properties and had the AI study the results. This process was repeated until we had amassed a substantial amount of data. We then upgraded the first AI' s algorithm to allow it to evolve into a second AI with improved prediction accuracy in a manner similar to the gradual evolutionary processes through which mammals acquired the abilities to perform more complex tasks. This AI-based technique reduced the number of materials we needed to manually synthesize and evaluate to only 2% of the approximately 3,000 candidate materials. We plan to apply this AI-based technique to screening various other materials in addition to electrocatalytic materials.

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