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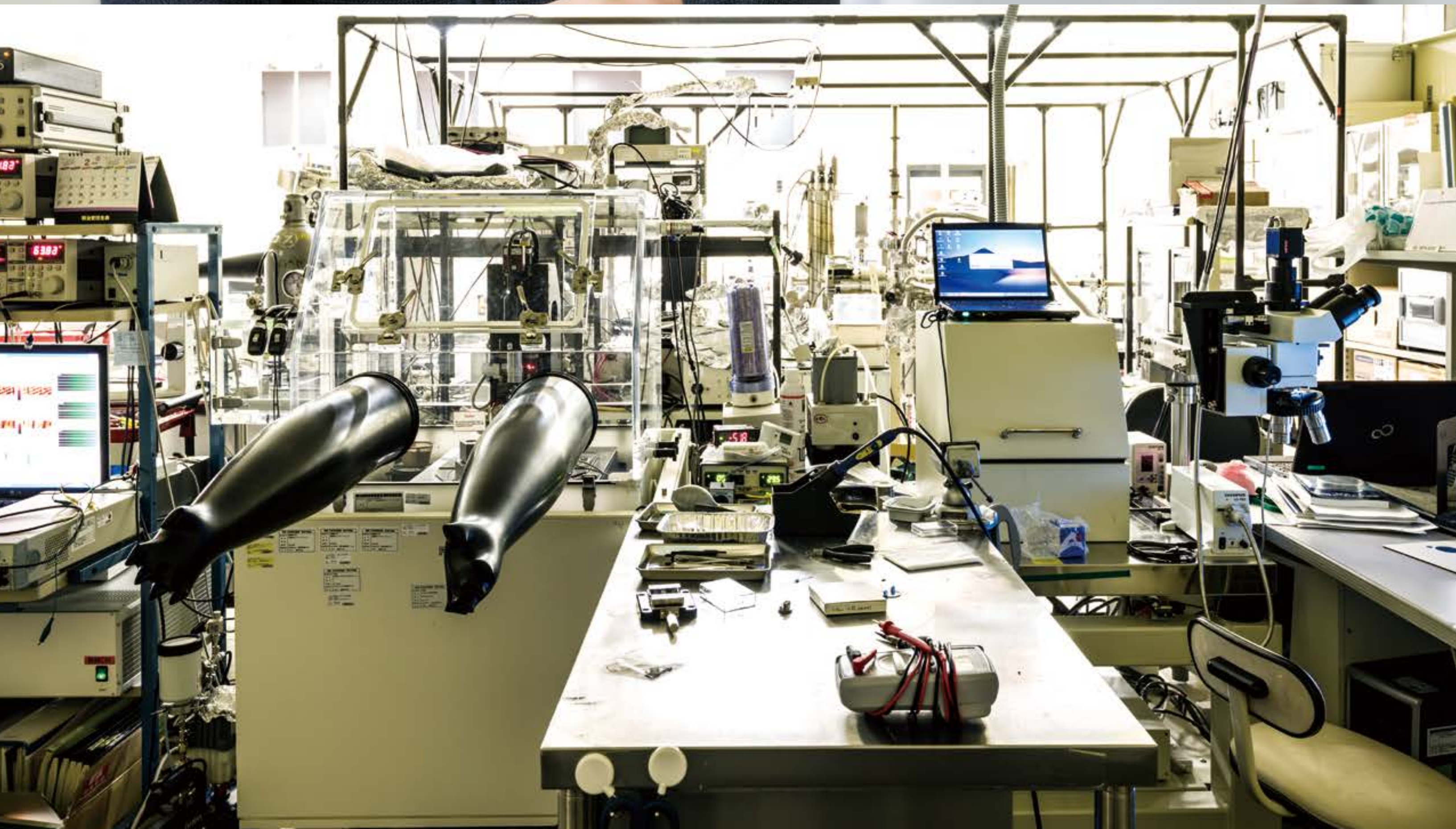
Research Center for Advanced Measurement and Characterization

Under Real-operation Conditions

Operando techniques for observation of materials in actual operational conditions



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Measurement of the distribution of electrical potential within a section of a perovskite solar cell. The section of the solar cell—which was extracted while preserving its functionality as a photovoltaic cell—is maintained in an operational state by connecting it to an electrode and irradiating it with light during measurement (see p. 10 for details).

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Techniques have been developed to optimize observational conditions using ultrahigh vacuums, extremely low temperatures and the processing of samples into thin films to enable the measurement and analysis of materials at high resolutions using electron microscopy and other microscopic methods with the goal of achieving atomic-level observation.

However, do these observational conditions match the real-world environments in which the materials being studied are expected to be used?
These materials may be used in the ambient atmosphere or in the presence of other gases or liquids.
They may be exposed to low or high temperatures or strong magnetic fields.
The performance of materials may be influenced by chemical reactions induced by certain environments, and some phenomena occurring in devices can only be detected when electric currents are applied to them.

More materials scientists today focus on observing and analyzing phenomena in realistic environments.
To more efficiently utilize energy, it is vital to increase the power output of rechargeable batteries by overcoming their current limitations and to rapidly develop high-performance materials by fully exploiting their intrinsic properties. These goals can be effectively achieved only after determining the performance of materials under real-operation conditions.

Operando measurement techniques—which are used to measure materials while they are in actual operation—are attracting a great deal of attention.
At the NIMS Research Center for Advanced Measurement and Characterization, researchers have been investigating internal battery states in relation to the charge and discharge processes and observing atomic movement during catalytic reactions. These researchers made creative modifications to measurement equipment and specimen preparation processes which ultimately enabled breakthroughs.
This NIMS NOW issue will highlight these evolving operando measurement techniques.

Special Talk

What to Observe?

"Operando measurement" techniques are used to observe materials at the atomic and molecular level in actual operational conditions. The need for these techniques has been increasing in recent years. Two experts in this area discussed the importance of operando measurements: Daisuke Fujita, Director of the Research Center for Advanced Measurement and Characterization, NIMS, and Takeshi Fukuma, Director of the Nano Life Science Institute (NanoLSI), Kanazawa University.

NIMS leads the world in microscopic measurement technology

Fujita: The development of innovative materials today requires control of material structures at the nanometer level. This necessitates the use of high-performance measuring equipment with nanometer resolution to measure and observe material structures. We have been developing advanced measuring equipment by increasing the resolution and sensitivity of transmission electron microscopes (TEMs), scanning probe microscopes (SPMs) and other microscopic devices.

Fukuma: The performance of TEMs and SPMs has improved rapidly over the past decade or so. These instruments are now indispensable in materials development. You spent many years developing measurement technology using SPMs.

Fujita: I have been working on that project for more than 20 years, including the time I worked for the National Research Institute for Metals (NRIM), the predecessor of NIMS. At NRIM, we initially started with

Takeshi Fukuma

Director, Nano Life Science Institute (WPI-NanoLSI), Kanazawa University

Advancing measurement and characterization technologies to a whole new level

R&D of measurement technology using scanning tunneling microscopes (STMs)—a type of SPM—and atomic force microscopes (AFMs). Around 2001, when I was still focusing on these projects, nanotechnology began to become very popular in the United States. Since then, research efforts have intensified to develop materials with novel functions by controlling material structures at the nano level. Inspired by this movement, NIMS decided to create a research center specialized in the development of measurement and characterization technologies. As a result, the Advanced Nano Characterization Center was established in 2006 and later reorganized into the current Research Center for Advanced Measurement and Characterization (RCAMC). RCAMC carries out materials R&D using not only NIMS-based measuring equipment but also the equipment of larger research facilities, such as the J-PARC Center, to complement our R&D activities.

Fukuma: I began researching AFM measurement technology in around 2000. By that time, you and my other predecessors had steadily built the foundation for the development of measurement technology in Japan. Nanotechnology then became very popular and attracted a great deal of attention. Its popularity was rather impressive.

I remember that major NIMS achievements include the development of the world's first technology to visualize atomic columns of different elements in crystals, which was published in 2007.

Fujita: That is the technology called "STEM-EELS," which is a combination of a scanning transmission electron microscope (STEM) with electron energy loss spectroscopy (EELS). When the atomic-column resolution STEM-EELS was published in the Nature, it drew global attention. NIMS has also developed various other technologies, including a technology to visualize magnetic structures of materials at the world's highest resolution.

Daisuke Fujita

Director, Research Center for Advanced Measurement and Characterization
Operation Director, Promotion Office for Microstructural Characterization Platform

Desire to observe functions of materials and biological phenomena in real-operation conditions

Fujita: Our earlier expectation was to develop devices with resolution adequate to observe atoms and molecules. However, as measurement technology advanced to a certain level, we realized that this level of achievement was unsatisfactory. More recent materials research requires measurement of materials in actual operational conditions (i.e., operando measurements) to enable accurate evaluation of material performance. RCAMC is striving to develop measurement technology that meets these needs.

Fukuma: The measurement of materials at atomic resolutions using existing TEMs and SPMs is often performed in ideal "ultrahigh vacuum" conditions. The results of such measurements are therefore inappropriate for use as material performance evaluation under actual operational conditions.

Fujita: That is exactly right. For many years, my main research focus had been to determine the properties of target materials using measurement technology under extreme conditions characterized by extremely high vacuum, vary low temperatures, and high magnetic fields.

However, Japan has recently been promoting the development of innovative materials, such as next-generation rechargeable batteries, solar cells and fuel cells, in line with the government's "super smart society" policy. The use of operando measurement techniques is critical for achieving a detailed understanding of the various mechanisms associated with these materials.

Fukuma: Many existing battery products were developed based on assumptions rather than concrete knowledge of the precise means by which they operate. I believe that the era of the blindly approach to battery development is nearing an end.

Era of the blindly approach to the product development is nearing an end

—Takeshi Fukuma

Fujita: I think so, too. In the case of lithium ion batteries, for example, the reason for the deterioration of the electrode materials is not clearly understood. It is vital to identify the mechanisms of its deterioration before we can develop new electrode materials. The use of operando measurement techniques is essential for this type of research. Similarly, replacement of the platinum catalyst currently used in fuel cells with a less expensive catalyst will require detailed observation of catalytic reactions using operando techniques.

I imagine that more researchers in the life sciences are also becoming interested in taking measurements in actual biological systems.

Fukuma: Certainly. The Human Genome Project—a major life science project—was completed in 2003. However, we later realized that the complete mapping of the human genome does not enable us to fully understand the mechanisms of various biological phenomena. In this "post-genome" era, demand has rapidly grown for measurement of the functions of biological molecules—including proteins—in liquid at the nano level.

The phrase "operando measurements" is mainly used in the material and device field. In the life sciences, "in vivo measurements"—measurements taken directly within living organisms and cells—is the most conceptually comparable phrase.

Similar to your early career, my initial professional focus was developing measurement technology using AFMs and other devices. I was not a life sciences researcher at all. However, because I developed an AFM that enabled high-resolution measurement of specimens in a liquid, I was gradually introduced to life sciences research starting in 2005.

Fujita: Kanazawa University's NanoLSI, of which you serve as a director, was selected by the WPI Program as a high-quality research institute in October 2017. Many researchers at the university use STMs and AFMs in their research.

I am very pleased by the WPI's selection of NanoLSI, a research center that takes full advantage of advanced measurement technology. It seems to me that this selection is very positive news for the future of Japan. European countries and the United States have been making huge national-level investments in the development of measurement technology based on the strong conviction that advances in measurement technology will expedite innovative scientific discoveries. I really hope that a similar recognition takes place in Japan.

Operando measurements further define "flowchart arrows"

Fujita: What do you think is the role of "in vivo measurement" in the life sciences?

Fukuma: Let me answer the question using cancer cells as an example. Research on the relationship between specific genes and the symptoms they are responsible for has made considerable progress. These relationships can often be described in the form of flowcharts. However, it is unclear what sorts of actions/processes are exactly represented by the arrows in these flowcharts. Because of the uncertainty associated with the arrows, it is difficult to change their directions, even when such modification seems appropriate. It is vital to precisely define these arrows in preparation of means to prevent cancer cells from growing and developing resistance to drugs. For this purpose, in vivo measurement of cancer cells in a liquid using an AFM is crucial.

Fujita: As implied by the proverb "seeing is believing," you sometimes gain a lot of information about materials by observing them in detail with your own eyes. Advanced microscopic observation sometimes even leads to the formulation of a new theory that upsets a long-lasting theory. This has actually happened in the materials field.

Fukuma: I also have seen a similar instance in the life sciences. Professor Toshio Ando of NanoLSI studies motor protein motions, on which opinions had been divided. He developed a high-speed AFM for the first time in the world and used it to observe the protein in action in a liquid. His observational results eventually resolved all arguments.

Advanced observation even leads to the formulation of a new theory that upsets a long-lasting theory

—Daisuke Fujita

Fujita: Operando measurements have also produced many materials science discoveries. Research at NIMS has yielded many intriguing results at the atomic level. For example, research is underway to observe a platinum catalyst in action within a fuel cell in the presence of oxygen using a TEM with a modified specimen holder (see p. 8). In other battery research, electric potential is being measured in extracted battery materials while they are being charged and discharged (see p. 10).

Establishing Japanese-made measurement technology as an international standard

Fujita: While we strive to improve measurement technology, we also need to establish common evaluation methods for the technology and ensure global technological compatibility. To this end, we must take a proactive approach to ensure that Japanese-made measurement technology becomes the international standard.

Fukuma: You have been leading this effort for more than decades.

Fujita: Yes. I have been involved in international standardization activities since about 1985 when I started full-scale work on measurement technology R&D. I currently serve as Chair of the domestic council committee, which operates under the ISO (International Organization for Standardization) Technical Committee for Surface Chemical Analysis (TC201).

Fukuma: It is very important for Japan to gain control over international standardization, as this will give Japan a competitive edge over other countries in the acquisition of global market share. Japan has failed to gain control over international standardization in many previous instances and has subsequently lost market share to overseas companies. It is unfortunate that Japan has been unable to profit substantially from its vast investments in research projects. Under the WPI program, I aim to formulate an effective strategy to gain control over international standardization.

Fujita: For Japan to successfully lead international standardization, all of the relevant organizations must work together. NIMS hopes to play a leading role in organizing collaboration. NIMS has been providing state-of-the-art measurement technology to its collaborators—major research institutions and universities around the country—under the Nanotechnology Platform Japan Program sponsored by MEXT (Ministry of Education, Culture, Sports, Science and Technology). I would be delighted if Kanazawa University were to utilize the program.

Fukuma: Thank you very much for your invitation. Although research at Kanazawa University is focused on the highly specialized Bio-AFM (biological research using AFMs) field, the techniques we developed are applicable not only to life sciences but also materials measurement and evaluation. I look forward to opportunities to work with NIMS.

(by Kumi Yamada)

Observation of catalytic reactions in fuel cells using a transmission electron microscope

Measurement by transmission electron microscopes (TEMs) is normally performed in a vacuum condition to achieve atomic-scale spatial resolution. Senior Researcher Ayako Hashimoto has developed a system to measure material-related phenomena in actual operational conditions, such as the air environment and high temperatures. She is now using the system to study catalytic reaction mechanisms in fuel cells.

Ayako Hashimoto
Senior Researcher
In-situ Characterization Technique Development Group
Research Center for Advanced Measurement and Characterization

Observing specimens in actual conditions

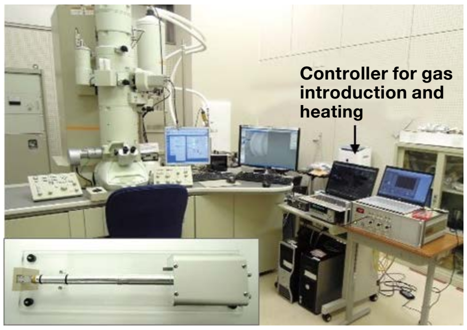
Transmission electron microscopes (TEMs) measure a material's internal structure by irradiating a specimen with an electron beam and measuring the beam transmitted through the specimen to make an image. The conventional observation has been to place specimens in high vacuum conditions to prevent the electron beams from being scattered by oxygen and nitrogen molecules in the air, reducing the TEM's resolving power. However, appropriate evaluation of the performance of materials requires measurement of phenomena occurring in actual operational conditions.

To achieve this, Hashimoto has been researching and developing TEM systems to achieve operando measurements.

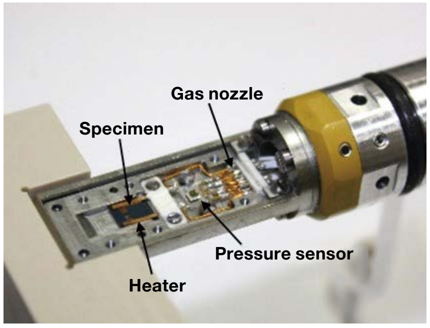
Combining the advantages of two measurement methods

Two TEM methods for measuring air-exposed specimens are already available for practical use. One method uses a modified TEM and the other uses a specimen holder. "Each of these methods has advantages and disadvantages," Hashimoto commented. "I decided to develop a new system combining the advantages of both."

The "differential pumping method" uses a modified TEM. Two plates, each with a single tiny hole, are installed above and below a specimen, creating space around it. Air or other gases can be introduced into the specimen-containing space. Gases that leak out of the holes are pumped out of the TEM, maintaining a higher pressure in the specimen-containing space than in the external space. Electron beams targeting the specimen also pass through these holes.



The TEM system
The complete TEM system assembly being used for observational study and the newly developed specimen holder (lower left)



Specimen holder
Front part of the newly developed specimen holder

Among the methods that use a specimen holder, the "window method" is a popular option. This method involves the use of thin films permeable to electron beams but not gases. These films are installed above and below a specimen, creating a space between them near the specimen in the holder. This arrangement allows the specimen space to be filled with a gas while the outer space can remain a vacuum. This specimen holder is used in the usual way using an unmodified TEM.

"Implementation of the differential pumping method is very expensive because major modifications need to be made to a TEM, including the addition of plates with a hole and a vacuum pump to a microscope body," Hashimoto said. "By contrast, methods that use a specimen holder cost much less to implement. However, the window method, which uses a specimen holder, reduces the resolving power of the TEM because electron beams pass through both the specimen and the window films."

Taking these advantages and disadvantages into account, Hashimoto developed a new TEM system which combined the use of a specimen holder with the differential pumping method. She explained the operation of the system.

"I place a specimen in a space between two plates, each with a tiny hole, within the specimen holder. Pressure in the space between the plates remains higher than in the outer space due to the differential pumping effect. In addition, the amount of gas to be intro-

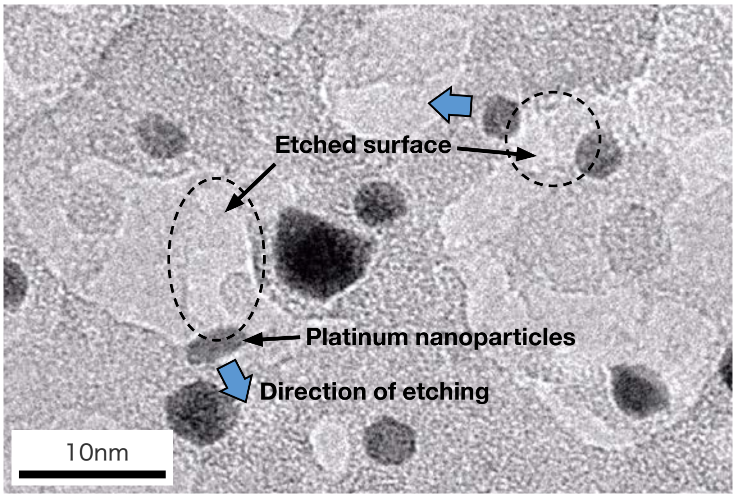


Figure 1. Graphite flakes being etched by platinum nanoparticles in the presence of 0.5 Pa air at 600°C. Etched graphene surfaces appear brighter.

duced into the specimen holder can be adjusted in response to gas pressure change detected by a minute sensor installed in the vicinity of the specimen."

In addition to these inventive modifications, Hashimoto also installed a heater in the specimen holder to allow high temperature measurements. These arrangements have enabled her to perform high-resolution operando measurements of a specimen while it is exposed to a certain type of gas and being heated.

"The greatest development challenge was significantly reducing the size of the specimen holder. The holder had to be less than 3 mm in thickness in order for it to fit between paired objective lenses about 3 mm apart. We used the MEMS microfabrication technology to install a gas nozzle, heater and wiring system within the specimen holder. It took us three years from the initial planning to complete the product. I was really happy when I saw clear images produced by the TEM system," said Hashimoto.

Heating of specimen in gas environments

Hashimoto successfully observed platinum-catalyzed reactions in action in fuel cell electrodes through operando measurements using the TEM specimen holder system capable of subjecting a specimen to various types of gases and heat.

More specifically, she measured a specimen—graphite, which is composed of carbon, on which platinum nanoparticles were deposited—while it was heated in the presence of air as a model of fuel cell electrodes. She succeeded in observing the surface of the carbon material being etched by platinum nanoparticles (Figure 1).

"During this measurement, I observed platinum nanoparticles catalyzing the oxidation of carbon molecules and oxidized molecules vaporizing into the air," Hashimoto said. "I also confirmed that higher temperatures cause catalytic activity and etching rates to increase. In future studies, I intend to investigate the effects of temperature, gas type, gaseous pressure and other factors in an effort to understand the mechanisms of platinum-catalyzed reactions and the mechanisms of carbon degradation. I hope that these studies will lead to optimization of fuel cell catalysts and facilitate the search for innovative catalysts capable of replacing current platinum catalysts."

According to Hashimoto, her operando measurement results may facilitate the development of techniques for producing graphene nanoribbons (GNRs), which are ribbon-like graphene strips with high electrical conductivity. GNRs are known to possess either metallic or semiconductor properties depending on their edge structures. Because interest in using GNRs in electronic devices has been growing in recent years, it is important to establish a GNR production method.

"Earlier experiments did not allow me to determine the relationship between catalytic etching actions and graphene's crystalline structures, because the surface of the specimen was covered with amorphous carbons," Hashimoto said. "So we recently synthesized "clean" graphene by means of chemical vapor deposition (CVD) and produced platinum nanoparticles using sputter deposition. We then made operando measurements of the interaction between the graphene and the nanoparticles. As a result, we found that the etching of graphene by platinum nanoparticles proceeds along graphene crystal structures (Figure 2)."

In 2017, Hashimoto joined a research project entitled, "Science and the creation of innovative catalysts," funded by the Japan Science and Technology Agency (JST)'s PRESTO (Precursory Research for Embryonic Science and Technology) program. In this project, she is undertaking the new challenge of conducting operando measurements of catalytic reactions occurring during the conversion of methane into methanol by leveraging know-how obtained from the experience in developing specimen holders. She is now applying operando techniques to a wider range of material-related phenomena. "I will continue supporting the creation of innovative catalysts by performing operando measurements," said Hashimoto.

(by Kumi Yamada)

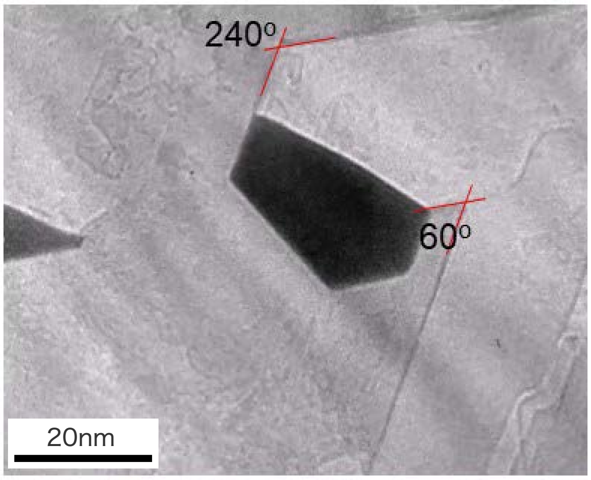


Figure 2. CVD graphene being etched in the presence of 0.3 Pa oxygen at 700°C Photo: Hajime Akimoto (University of Tsukuba)

A. Hashimoto, M. Takeguchi, 18th International Microscopy Congress, September, 2014, Prague, Czechoslovakia, proceeding IT-6-P, 1815.

Research Highlight 2

Investigation of battery under running condition using a scanning probe microscope

Research & development of various types of next-generation rechargeable batteries and solar cells are being carried out in an effort to improve their performance. A detailed understanding of their working principles must be achieved by analyzing critical events occurring within them under actual operational conditions. Senior Researcher Nobuyuki Ishida has been developing operando measurement techniques using scanning probe microscope for R&D of all-solid-state lithium ion batteries and perovskite solar cells.

Nobuyuki Ishida
Senior Researcher
Surface Characterization Group
Research Center for Advanced Measurement and Characterization

Searching for the fundamental problem of all-solid-state batteries

Global R&D efforts are underway to develop next-generation rechargeable batteries. Among these batteries, the possibility of bringing all-solid-state lithium ion batteries (hereinafter referred to as "all-solid-state batteries") into practical use in the near future is very promising. NIMS has been committed to all-solid-state battery R&D for many years.

Currently prevalent lithium ion rechargeable batteries contain inflammable liquid electrolytes. By contrast, all-solid-state batteries contain solid electrolytes and are thus expected to be safer. However, all-solid-state batteries have a major issue that must be resolved: use of a solid electrolyte significantly decreases the flow of lithium ions across the interface between the cathode and the electrolyte, reducing the power density of the battery.

"The reduced lithium ion flow—or increased ionic resistivity—at the interface is presumably caused by the formation of a "space charge layer" from which lithium ions are virtually absent," Ishida explained. "This hypothesis can be effectively verified by first observing the process of space charge layer formation and measuring changes in lithium ion concentration in this layer during the charge and discharge processes. It should then be possible to determine the correlation between ionic resistivity and these measurements." To carry out this study, Ishida had to establish a technique that would allow him to take the necessary measurements from a battery in operation.

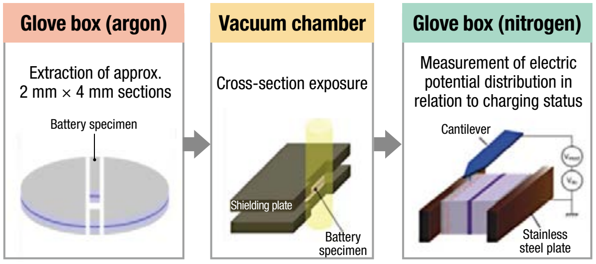
Enabling measurement of the distribution of electric potential while maintaining operational capacity

Ishida attempted to develop a technique compatible with a Kelvin probe force microscope (KPFM), a type of scanning probe microscope. The KPFM probe is capable of tracing the surface of a specimen and collecting data on electric potential from the surface. The current spatial and electric potential resolutions of the probe are several tens of nanometers (nm) and several tens of millivolts (mV), respectively.

Electric potential distribution measurements can be used to determine the electronic and ionic states of a given material and are therefore a very effective means of evaluating battery materials. This method has been used in research on lithium ion rechargeable batteries, although its application had been limited to the surfaces of electrode materials.

"No previously available method permitted evaluation of the interior electric potential of a battery while maintaining its operational capacity," Ishida said. "I first had to develop a specimen preparation technique."

An all-solid-state battery is composed of



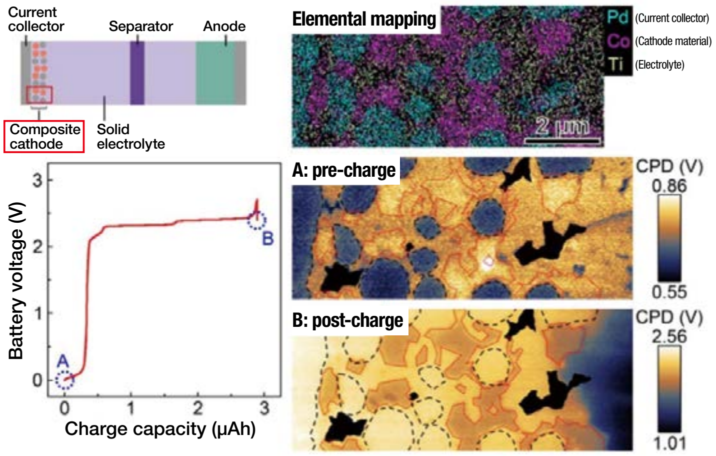


Figure 1. An all-solid-state lithium ion battery is composed of cathode, solid electrolyte and anode layers. Ishida carried out all of the specimen preparation steps—extraction of a battery section, exposure of the cross-section and measurement of its electric potential using a KPFM—either in inert gases or in a vacuum. The illustrations to the right show the distribution of electric potential actually measured across a composite cathode (with which a solid electrolyte and current collector were integrated to increase lithium ion mobility) of the all-solid-state battery before and after it was charged. CPD (contact potential difference) values indicate differences in work function between the probe and specimen. These results revealed that the area of low lithium ion concentration in the specimen increases when the specimen is charged and that charging conditions are unevenly distributed across the specimen.

cathode, solid electrolyte and anode layers stacked together. Measurement of electric potential at the interface between the cathode and electrolyte layers requires an exposed cross-section of the layered structure. Accordingly, small sections of the battery need to be cut out for use as specimens for microscopic measurements. However, these specimens cannot be prepared in ambient conditions because exposure to the air will cause them to react with oxygen and moisture, leading to deterioration of their battery performance.

To prevent this, Ishida performed all of his specimen preparations (i.e., cutting battery materials into small sections) and measurements (i.e., electric potential measurement using a KPFM) either in inert gases or in a vacuum.

In December 2016, Ishida succeeded in measuring and visualizing changes in electric potential distribution in the vicinity of the interface between the cathode material and the electrolyte at a resolution of 50 nm or higher. As a result, he discovered that the area of low lithium ion concentration in the electrolyte within the cathode extended when the specimen was charged. He also found uneven distribution of charging conditions across the specimen (Figure 1).

"In this recent study, I measured the electric potential distribution of the specimen before and after it was charged and visualized the difference between the two measurements," said Ishida. "In future studies, I hope to measure changes in electric potential distribution in real time during the charge/discharge processes by further improving KPFM measurement techniques and increasing the temporal resolution. I would also like to achieve in-situ observation of the formation of a space charge layer, a key event which needs to be understood to enhance the performance of all-solid-state batteries. It would be very exciting to determine the cause of space charge layer formation, a source of increased ionic resistivity."

Investigating the working principle of perovskite solar cells

Another focus of Ishida's research has been operando measurement of perovskite solar cells—a subject of intensive next-generation solar cell R&D—using a KPFM.

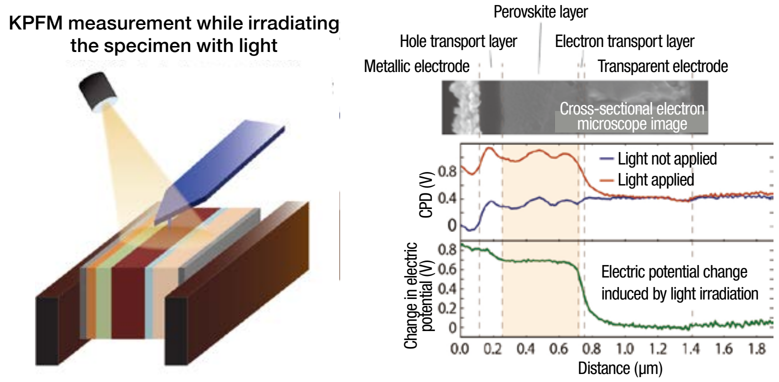


Figure 2. Ishida measured electric potential distribution across the p-i-n junction of a perovskite solar cell using a KPFM while the cell was maintained in an operational state by irradiating it with light. This enabled him to find a drastic change in electric potential at the interface between the perovskite and charge transport layers when light was applied to the cell. These results indicate that this solar cell may operate as a p-n junction device rather than a p-i-n device.

Perovskite solar cells can be produced at lower manufacturing cost than conventional inorganic solar cells and may be used to fabricate lightweight, flexible devices. However, the working principle of perovskite solar cells is not fully understood. A deeper understanding of them is critical to increasing their power generation efficiency.

A perovskite solar cell is composed of a perovskite layer—which generates holes and electrons by absorbing light—and hole and electron transport layers, which together facilitate the migration of holes to the cathode and electrons to the anode.

The hole/electron transport layers function as p-type and n-type semiconductors, respectively. The perovskite layer (the intrinsic [i-type] semiconductor) is sandwiched between these layers, forming a p-i-n junction structure.

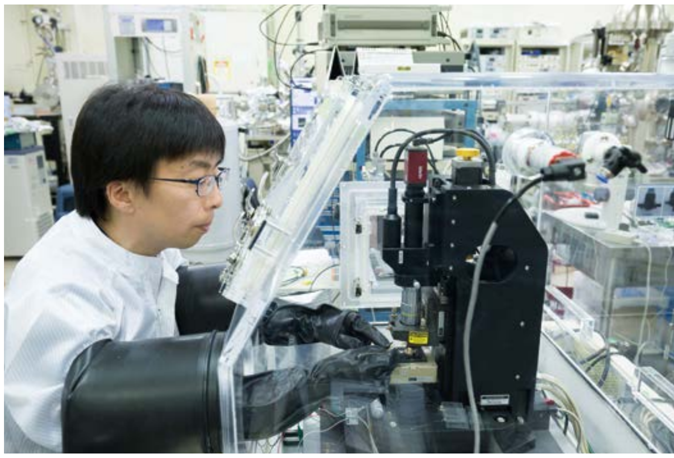
"Some of the important working principles of perovskite solar cell devices were not well understood," Ishida said. "For example, we did not know the exact location within the p-i-n junction at which the separation of holes and electrons (charge separation) occurs. I decided to perform operando measurements using a KPFM. I first cut out small sections of a perovskite solar cell and measured changes in electric potential distribution within them while irradiating them with light."

In June 2017, Ishida discovered that the location of the charge separation site varies greatly depending on the structure and material composition of a perovskite solar cell. Ishida's results also suggested that cells in perovskite solar cell devices may operate as p-n junction solar cells—in which strong charge separation occurs at the interface between the perovskite and charge transport layers—rather than p-i-n junction solar cells, in which charge separation occurs in the perovskite layer.

These findings are expected to be useful in the continued optimization of perovskite solar cells and in increasing their power generation efficiency.

"KPFM is a young technology," Ishida said. "Research and development of it began only in the 1990s. We are still uncertain of its maximum potential in terms of spatial resolution, electric potential resolution and many other functions. I am currently evaluating the performance of the KPFM and working to enhance its capabilities while using it to conduct R&D. I will continue to pursue progress in materials R&D by leveraging and enhancing KPFM techniques."

(by Kumi Yamada)



Ishida created this KPFM measurement system, which enabled him to connect the battery specimen to an electrode and irradiate the specimen with light in the presence of nitrogen gas (see p. 2 for an image of the actual KPFM measurements being made in a glovebox).

H. Masuda, N. Ishida et al., Nanoscale 9, 893-898 (2017). DOI:10.1039/c6nr07971g
M. Cai, N. Ishida et al., Joule. 2, 296-306 (2018). DOI:10.1016/j.joule.2017.11.015

Determining electron spin arrangements Innovative idea that enabled neutron transmission measurements

Various novel functions of materials and devices had been developed by leveraging the charge properties of electrons. More recently, a number of publications have reported the use of novel properties of electron spins and their arrangements to develop such functions. Chief Researcher Hiroaki Mamiya succeeded for the first time in the world in analyzing electron spin arrangements in materials using a neutron transmission technique. Because the technique is applicable in extreme environments and when various devices are in actual operation, it may facilitate the discovery of new functions and the development of new materials that take advantage of electron spin.

Hiroaki Mamiya
Chief Researcher
Neutron Scattering Group
Research Center for Advanced Measurement and Characterization

Technique that break the mold in magnetic materials research

"Interest has been increasing recently in research on and development of materials and devices with novel functions by leveraging novel properties of electron spins and their arrangements," Mamiya said.

What is spin? "Simply put, the spins of electrons produce magnetic fields around these particles like small magnets," Mamiya explained. The north magnetic pole of individual electron spins in a material may point upward or downward. When all electron spins in a material are oriented either upward or downward, the material as a whole exhibits magnetic behavior. The use of such simple magnets has a long history, however, recent studies have revealed that unique spin arrangements, such as alternating upward and downward spin orientations, can generate novel functions. High-density, high-speed magnetic storage devices and magnetic refrigeration, which can reduce energy use and requires no refrigerant, are an example of a technology that takes advantage of unique spin arrangements.

"It had been unnecessary until recently to determine spin orientations and arrangements in magnets because we knew that all spins in a magnet were oriented in the same direction," Mamiya said. "However, materials and devices with novel functions derived from novel spin arrangements are now drawing greater attention. This has inspired us to investigate spin arrangements. Conventional methods of determining spin arrangements have some issues. We therefore decided to take a completely different approach to this challenge."

Visualizing spin arrangements without using scattered neutrons

Neutrons can be effectively used to determine electron spin arrangements. Neutrons and protons together constitute an atomic nucleus which electrons orbit. Electrons and protons are negatively and positively charged, respectively. Unlike these particles, neutrons are electrically neutral. On the other hand, neutrons are similar to these particles in having a spin and therefore magnetic properties. Because of these characteristics, neutrons are capable of effectively passing through various materials. In addition, the wave properties of neutrons can be exploited to determine spin arrangements in materials.

When a material sample is irradiated with a neutron beam, neutrons scatter in various directions in relation to spin arrangements in the sample. In conventional diffractometry, the intensities of diffracted neutrons are measured using large arrays of detectors. This information is then used to determine the sample's spin arrangement. "Many detectors need to be positioned around a sample to record all of the neutrons scattered from the sample at various angles in relation to spin arrangements," Mamiya said. "Spin arrangements that produce novel functions are often discovered by subjecting samples to extreme conditions, such as high pressure, high and low temperatures and strong magnetic fields. For this reason, it is desirable to perform neutron mea-

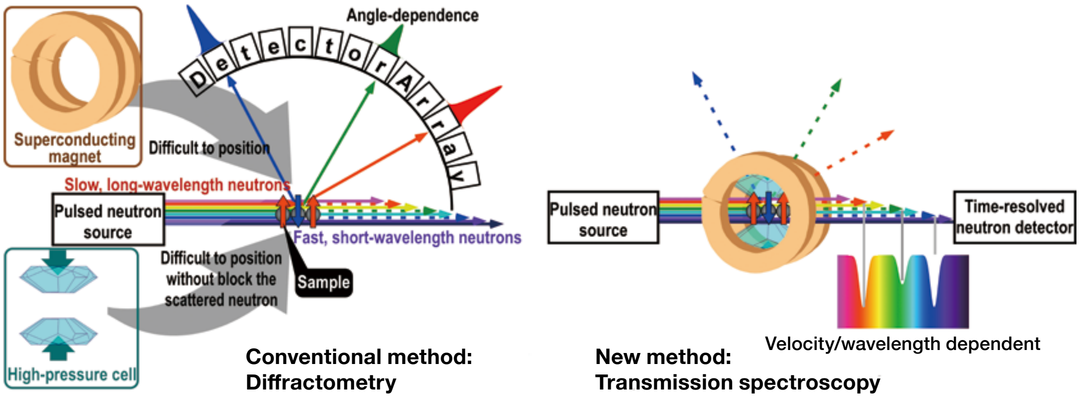


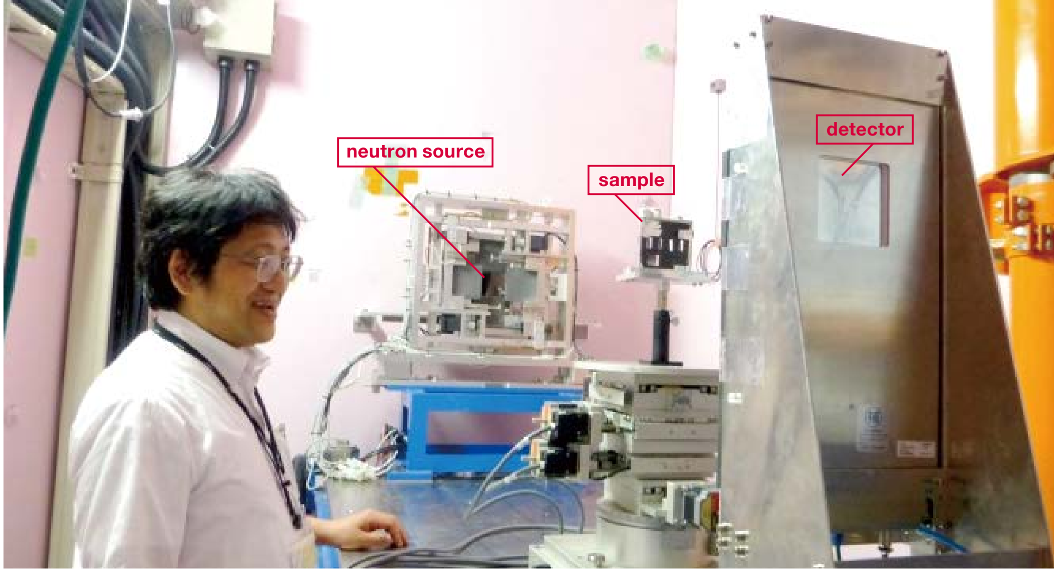
Figure 1. (Left) Conventional diffractometry in which neutrons which interact with electron spin arrangements in a material sample and scatter are measured using an array of many detectors. It is difficult to position the various devices properly to avoid obstructing the trajectories of the diffracted neutrons. (Right) Novel transmission spectroscopy in which neutrons transmitted though the sample are measured by a single detector. This method offers greater flexibility in the positioning of equipment.

surements in extreme environments. However, such experiments, require the proper positioning of various equipment, such as high-pressure cells, superconducting magnets, high-temperature furnaces and refrigerators to avoid obstructing the trajectories of the diffracted neutrons. This is very difficult to achieve. We eventually decided to take a different approach. We aligned a neutron beam source, a sample and a single detector in a straight line to measure only those neutrons that pass straight through the sample." This arrangement only required Mamiya to secure a neutron trajectory the size of the eye of a sewing needle and afforded him great flexibility in the positioning of equipment necessary to create extreme environments.

New spin arrangement measurement method

Mamiya carried out experiments at the Japan Proton Accelerator Research Complex (J-PARC). Specifically, he irradiated a nickel oxide sample with a pulsed neutron beam, measured the intensities and wavelengths of neutrons that passed through the sample and analyzed the relationship between the two measurements. As a result, he found that the intensity of transmitted neutrons of specific wavelengths was very low. Because the spin arrangement of the nickel oxide sample was known in advance, he incorporated this information into the interpretation of the experimental results. Consequently, he found that his method allows adequate estimation of spin arrangement within a sample by measuring transmitted neutrons, in line with the rationale that increased scattering of incident neutrons of certain wavelengths caused by the spin arrangement of the sample decreases the intensity of transmitted neutrons of these wavelengths. This groundbreaking study demonstrated that spin arrangements within materials can be determined effectively by measuring neutrons transmitted through a sample.

"When a neutron beam is applied to a specimen, the number of transmitted neutrons decreases with an increase in the number of diffracted neutrons. As such, measurement of the transmitted neutrons enables determination of spin arrangements in a material. This is a simple principle and the concept itself is not particularly new. In fact, the spectra of transmitted waves have been analyzed as commonly as that of diffracted, scattered or reflected waves. Nevertheless, as far as I know, we are the first to report the measurement of spin arrangements using transmitted neutrons. I believe that this method may drive rapid popularization of neutron utilization in research."



Measurement of transmitted neutrons in progress at J-PARC. The material sample is irradiated with a neutron beam emitted from the neutron source on the far side of the photo. Neutrons transmitted though the sample are measured by the detector on the near side.

Enabling observations in actual operational conditions

Neutrons can also be used for non-destructive inspection of the internal states of metals and concrete. They are highly sensitivity to light elements, such as hydrogen and lithium. Because of these characteristics, interest in using neutrons is growing in materials science, life science and industrial research. However, current opportunities to use neutrons in scientific experiments are significantly restricted by the need to use a massive particle accelerator. Integration of a compact neutron source into the method of measuring transmitted neutrons using only a single detector which Mamiya's group developed will enable the construction of a transmission spectroscopy system small enough to fit in common laboratories. This more accessible technology is expected to dramatically increase experimental opportunities and may expedite research efforts related to producing novel functions derived from electron spin.

"The measurement of transmitted neutrons has another major advantage," Mamiya said. For example, where magnetic materials are integrated into devices under development, it may be desirable to take "X-ray photographs" of spin arrangements within the magnetic materials while devices are in operation (i.e., operando measurements). The use of conventional neutron diffractometry is inadequate for this purpose because it is difficult to take an image of spin arrangement by measuring neutrons that scatter in various directions from the target magnetic material present within a device. By contrast, the new transmission spectroscopy technique may even enable a computed tomography scan of the magnetic material in an operating device because equipment can be positioned beyond the trajectory of the transmitted neutrons.

In future studies, Mamiya plans to explore other potential applications of this method by directing neutron beams at different types of materials and magnetic devices and measuring the transmitted neutrons under different conditions in various environments.

(by Shino Suzuki, PhotonCreate)

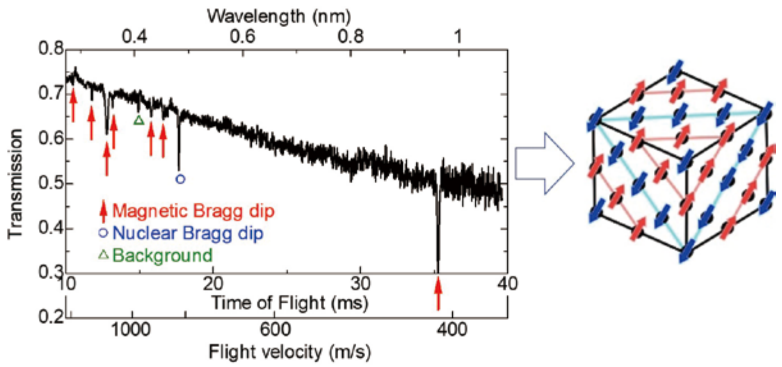


Figure 2. Spectrum of neutrons transmitted through a single-crystal nickel oxide sample. Transmission of neutrons are measured as a function of time of flight. Decreased transmission (intensity) of neutrons of various wavelengths are represented by dips in the graph (indicated by arrows). Analysis of magnetic Bragg dips enables estimation of electron spin arrangement in the sample (right).

Hiroaki Mamiya et al,. Scientifi c Reports. 7 (2017) DOI:10.1038/s41598-017-15850-3

Research Highlight 4

Identifying hydrogen pathways using a microscope capable of measuring diffused hydrogen

Hydrogen embrittlement is thought to be one of the major causes of metal material breakage. No effective means of preventing hydrogen embrittlement has been developed because its mechanisms remain unknown. A research group led by Akiko Itakura has developed a microscope capable of measuring diffused hydrogen in metal materials. This microscope has been attracting a great deal of attention as a promising tool for elucidating hydrogen embrittlement mechanisms.

Akiko N. Itakura
Leader of the Surface Physics and Characterization Group
Research Center for Advanced Measurement and Characterization

Hydrogen makes materials brittle

One of Itakura's research interests has been to visualize the distribution of hydrogen in materials. Corrosion and hydrogen embrittlement are thought to be two major causes of metal material breakage. Because corrosion in materials—as rust and oxidation—is observable, substantial advancements have been made in the understanding of corrosion mechanisms and the development of anticorrosion treatments. By contrast, hydrogen embrittlement of materials is not visible and research on this subject has therefore progressed slowly. Japan is planning to create a "hydrogen fuel economy," in which hydrogen will serve as a major energy source, in the near future. The development of this hydrogen society will require the construction of hydrogen storage tanks and piping systems. From this perspective, understanding hydrogen embrittlement mechanisms and developing materials resistant to it are urgent issues. An understanding of hydrogen distributions within materials, including hydrogen entrances and pathways, is required to resolve these issues.

Several methods of observing hydrogen distributions have been developed. In the silver (Ag) decoration technique, a material sample is immersed in an aqueous solution containing potassium silver cyanide, allowing hydrogen atoms on its surface to react with silver ions to form silver atoms, making hydrogen distribution on the surface of the sample observable. The etching technique—another method of observing hydrogen distributions—enables electron microscope observation of hydrogen within a sample by etching the surface of the sample and revealing its internal structure.

Itakura noted the limitations of these conventional techniques. "They are only capable of determining the hydrogen distribution at a certain point in time. The fact that no hydrogen is detected in a sample examined using one of these techniques does not establish that hydrogen is always absent from the sample; the technique may simply have been applied immediately after the hydrogen moved away from the area examined. In addition, these techniques can be applied to a sample only once because they either deposit silver particles on the sample or etching it." Itakura continued, "I wanted to measure hydrogen distributions repeatedly and non-destructively in order to map all of the hydrogen pathways. None of the available equipment allowed us to do that, so we ended up building our own machine."

Continuous supplementation of hydrogen enables its observation

In 2016, Itakura's group succeeded in developing a scanning electron microscope (SEM) component enabling the measurement of diffused hydrogen. When the surface of a sample placed in this SEM is irradiated with an electron beam, secondary electrons are released from the surface. The SEM then scans the surface, detects secondary electrons emitted in response to incident electron beams and produces a SEM image of the surface of the sample. Irradiation of the surface with an electron beam also causes hydrogen present on the surface to ionize and be released. This phenomenon—detachment of atoms and molecules from the surface of a material in response to irradiation by electrons or photons—is called

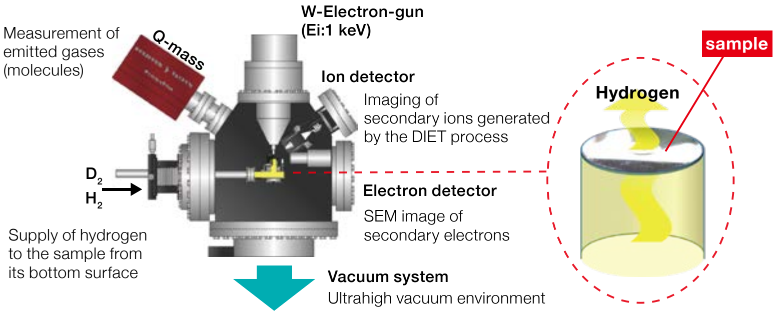


Figure 1. Schematic diagram of the scanning electron microscope (SEM) component enabling measurement of diffused hydrogen within a material sample. Imaging of hydrogen ion distribution within a sample while hydrogen is supplied to it from the bottom surface. This imaging is achieved by utilizing a SEM image and taking advantage of the DIET process in Ultra-high vacuum chamber (UHV).

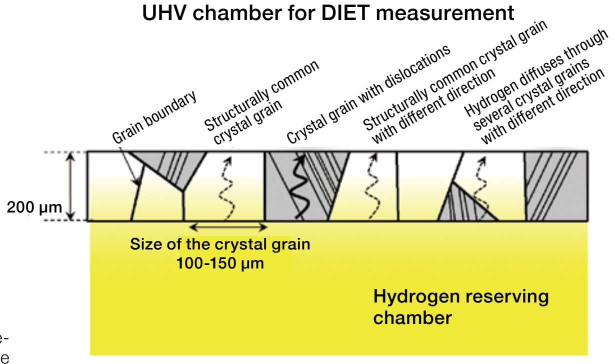


Figure 2. Schematic diagram of the structure of a thin plate sample and diffusion of hydrogen through the sample.

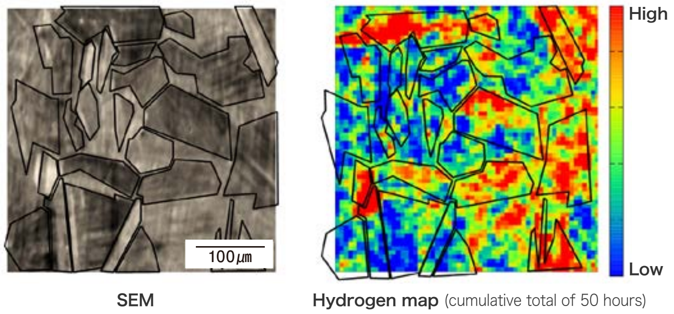


Figure 3. Measurement of diffused hydrogen within a thin stainless steel plate. (Left) SEM image. (Right) hydrogen map. Many hydrogen ions are released from martensitic (body-centered cubic) grains with dislocations (shown as darker shades in the SEM image).

the DIET (desorption induced by electronic transitions) process. Itakura wanted to construct a "hydrogen map"—an image of the hydrogen distribution on the surface of a sample—by adding an ion detector to the SEM capable of observing released hydrogen ions. In addition, Itakura thought it would be feasible to analyze the relationship between crystal grains and their boundaries in samples by combining the hydrogen map with the SEM image.

In the conventional technique which has been used to observe hydrogen released from material samples for about 20 years, a sample is first exposed to high temperature and injected with hydrogen under high pressure. Hydrogen released from the surface of the sample due to the DIET process is then observed. The technique has a major limitation, however: hydrogen atoms are extremely light and small, and as a result, hydrogen injected under high pressure quickly leaves the sample. It is impossible to measure hydrogen in materials into which it is difficult to inject hydrogen and materials from which hydrogen leaves easily.

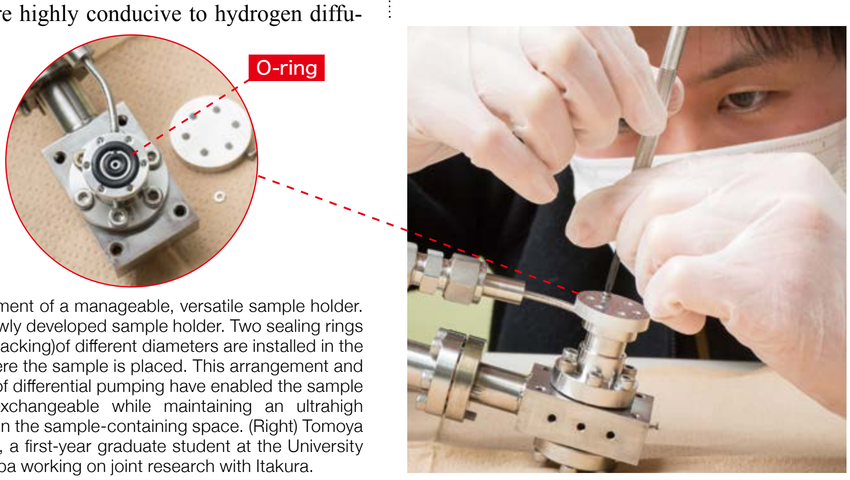
To solve this issue, Itakura came up with one idea. "The problem of hydrogen quickly leaving a material sample can be resolved by supplying hydrogen to the sample from its bottom surface continuously," she said. To implement her concept, she added an ion detector to the SEM and attached a hydrogen supply tube to the sample stage. She then worked with Naoya Miyauchi (then a Researcher at Toho University) to make a major change to the measurement program. These modifications led to the completion of a SEM component that enabled the measurement of diffused hydrogen (Figure 1).

Uncovering hydrogen pathways

"The types of crystal grains and the types of boundaries between them that make up a metal material through which hydrogen can diffuse easily can be identified using the SEM component we developed," Itakura said. Metal materials are composed of crystal grains. Crystal orientations and the presence/absence of dislocations—a type of crystal defect—differ among individual crystal grains. In addition, the properties of a boundary between two adjoining crystal grains vary depending on the grain combinations. The ease with which hydrogen diffuses through a material is influenced by these factors (Figure 2). However, these differences are too subtle for the conventional technique to be effective.

"The SEM component we developed continuously supplies hydrogen to the sample from its bottom surface, allowing operando measurement of diffused hydrogen and calculation of the cumulative amount of diffused hydrogen over time," Itakura said. "The hydrogen diffusion rate can also be accurately estimated. This information can be used to clearly differentiate between crystal grains and boundaries through which hydrogen can pass easily from those through which it cannot."

Itakura also measured diffused hydrogen within a thin stainless steel plate (main structure is austenite (face-centered cubic [FCC])) composed of martensitic (body-centered cubic [BCC]) grains with dislocations and found that BCC grains with dislocations can be identified in SEM images as darker shades. The hydrogen ion distribution shown in Figure 3 demonstrates that many hydrogen ions are released from BCC grains with dislocations. These results indicated that BCC grains with dislocations are highly conducive to hydrogen diffusion. It was also found that diffused hydrogen slowly reaches the surface via grain boundaries and that the amount of hydrogen that diffuses though crystal grains increases with time. This operando technique in which hydrogen is continuously supplied to the sample enabled these discoveries.



Development of a manageable, versatile sample holder. (Top) Newly developed sample holder. Two sealing rings (O-ring packing)of different diameters are installed in the area where the sample is placed. This arrangement and the use of differential pumping have enabled the sample to be exchangeable while maintaining an ultrahigh vacuum in the sample-containing space. (Right) Tomoya Iwasawa, a first-year graduate student at the University of Tsukuba working on joint research with Itakura.

Contributing to create hydrogen society

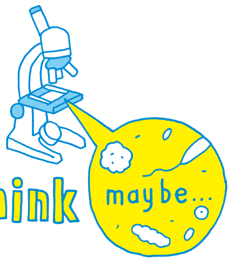
After her lecture on this result at a scientific conference and on other occasions, attendees have asked Itakura questions and expressed great interest. The majority have been researchers from various types of companies. "I was surprised to learn that so many industries are faced with the hydrogen embrittlement issue," Itakura said. Expectations are high that the newly developed SEM component can achieve a breakthrough, clarifying hydrogen embrittlement mechanisms, a crucial challenge in the creation of a hydrogen society.

Another major advantage of the SEM technique is that it allows hydrogen measurements at a wide range of temperatures and pressures. Itakura had a particularly strong desire to acquire this capability when developing the SEM component. "My area of expertise is physics," Itakura said. "It is important for physicists to carry out experiments under systematically selected conditions and discover new laws that explain the results in relation to different experimental conditions. I really wanted to develop a device that would allow me to take a physicist's approach to my research."

Itakura continued enthusiastically. "I would like to add a device capable of measuring the orientations of multiple crystals simultaneously to the current system so that we can use it to understand the phenomena leading to hydrogen embrittlement in greater detail."
(by Shino Suzuki, PhotonCreate)

N. Miyauchi et al,. Scripta Materialia 144 (2018) 69–73. DOI:10.1016/j.scriptamat.2017.09.026

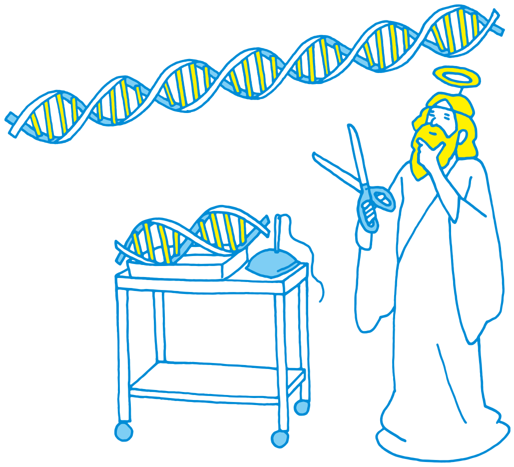
Science is even more amazing than you think



CRISPR genome editing technique:

a revolutionary invention attracting global attention

Text by Akio Etori
Illustration by Joe Okada (vision track)



Nobel Prize winner Susumu Tonegawa once asked me, "What do you think is the greatest biological achievement ever?" I replied instantly: "Isn't it a discovery of DNA?" Professor Tonegawa surprised me by saying no. "I think that Darwin's theory of evolution represents the greatest biological achievement, because the concept that humans evolved from primitive animals was completely mind-blowing for people everywhere."

It is true that the theory of evolution presented a novel idea about living organisms that now serves as a fundamental biological concept. However, I still insist that the discovery of DNA also represents one of humanity's greatest biological achievements by facilitating our understanding of fundamental genetic mechanisms and processes. All living organisms have DNA (genes) in their cells. DNA is transcribed to RNA, which is then translated into proteins. The establishment of this "central dogma of molecular biology" has led to a series of revolutionary biological achievements, including genetic engineering and the cloning of animals.

The CRISPR-Cas9 gene editing technique which is attracting global attention is a recent biological discovery with a similar impact. The use of this technique allows the genome, or "blueprint," for any organism—including humans—to be freely rewritten.

CRISPR is an abbreviation for "clustered regularly interspaced short palindromic repeats." Genes are composed of double-stranded DNA (deoxyribonucleic acid) molecules to which a sequence of four nitrogenous bases—A, G, C and T—is attached. In 1986, a research team led by Yoshizumi Ishino and Atsuo Nakata—who were both then at the Research Institute for Microbial Diseases, Osaka University—discovered short palindromic sequences of nitrogenous bases on DNA. A Dutch research team later named these unique base sequences "CRISPR" in 2002.

Professor Emmanuelle Charpentier and Professor Jennifer Doudna worked on CRISPR research in an attempt to apply it to the development of an easy-to-use genome editing tool.

In 2012, these researchers demonstrated a technique capable of freely cutting and editing genes using CRISPR and an associated gene (the Cas9 gene). CRISPR is composed of alternating short palindromic repeats and "spacers"—base sequences that differ from those of the repeats. The Cas9 protein can be guided to cut out a targeted CRISPR region of a DNA molecule.

Although other genome editing techniques, such as ZFN and TALEN, have already been developed, the CRISPR-Cas9 technique is considerably more precise, more versatile and easier to implement.

The use of the CRISPR-Cas9 technique has led to the production of hornless dairy cattle, chickens that give birth to only female chicks, tomato plants capable of bearing fruit without pollination and red seabream with larger amounts of muscle.

In the future, the CRISPR-Cas9 technique may be applied to humans to make us taller, enhance our appearance, increase our intelligence or improve our athletic talents. In other words, this technique may allow humans to freely reconstruct any plants and animals, including themselves. As with nuclear energy technology, the technique may be used for either good or evil.

What if humans acquire the capability to freely design the appearance and competence of their potential children? What if certain researchers and countries attempt to create extremely unnatural organisms for their own benefit? We are facing a grave moral issue: What are the acceptable applications of a genome editing technique which enables the manipulation of the physical and mental traits of humans?

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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