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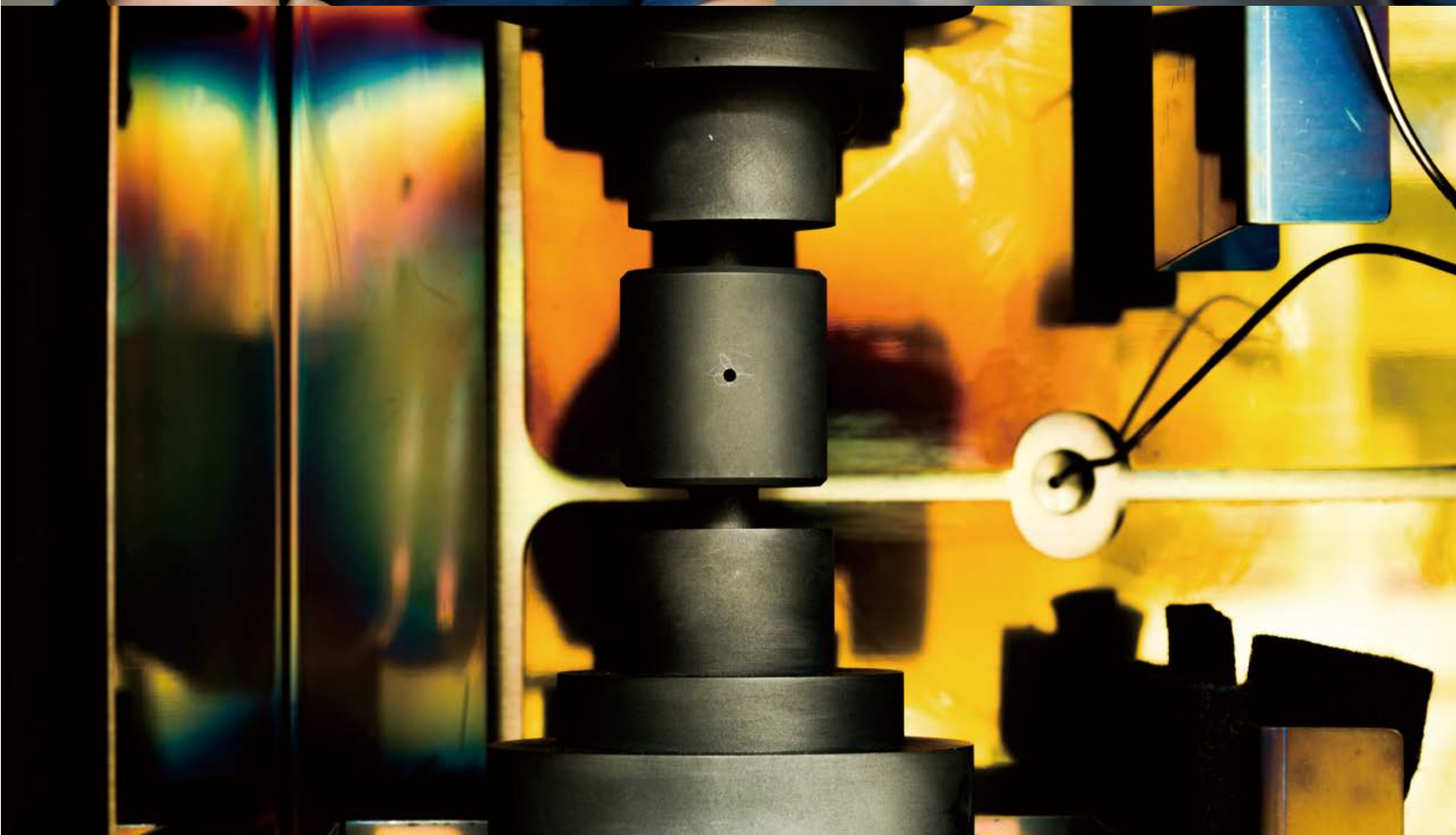
Strategic integration of innovative materials

Effective combination of next-generation materials vital to the development of a sustainable society



Center for Green Research on Energy and Environmental Materials

Strategic integration of innovative materials

Effective combination of next-generation materials vital to the development of a sustainable society

The energy market is expected to experience radical change in the immediate future. The growing global economy has dramatically increased demand for electricity, while the fossil fuels used for power generation are nearly depleted and CO_2 emissions remain a cause of serious environmental problems.

What is required to ensure the stable energy supply vital to making society more sustainable? Two particularly urgent measures are increasing the diversity of available energy sources to ensure a continuous electricity supply and boosting the use of environmentally friendly renewable energy to make it a major power source.

In addition, a new community-wide energy management plan has been proposed. It advocates utilizing emerging IoT (internet of things) technologies—which connect all types of devices via the internet—for more effective energy management. The plan recommends the development of energy management systems that would monitor and control overall energy production, distribution and consumption by gathering relevant data through the internet. Such systems may, for example, be capable of dramatically increasing a community's energy efficiency by instantaneously analyzing sensor-collected data on the amount of electricity being generated, automatically assigning power sources with excess electricity reserves and properly distributing electricity across a city or between buildings in relation to power demand.

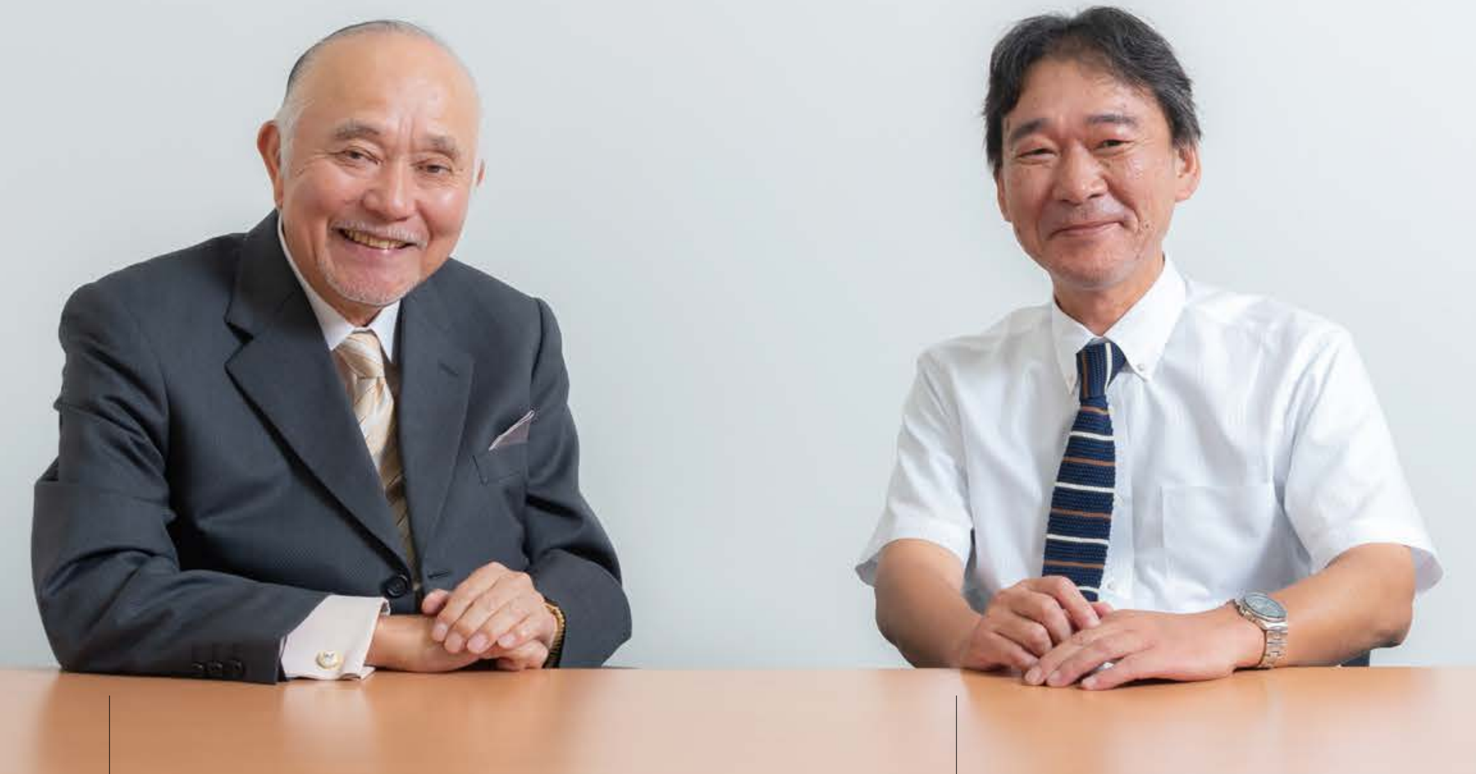
The Center for Green Research on Energy and Environmental Materials at NIMS has been engaged in research activities with the goal of satisfying future societal needs. Its researchers are striving to significantly increase the capabilities of different types of energy generation, develop large-capacity rechargeable batteries and create highly efficient energy transport infrastructure. The strategic application of diverse and effective materials will be crucial in meeting these R&D goals. Through these activities, NIMS has been making key contributions to the development of a next-generation, IoT-based energy network.

Special Talk

Fifth Strategic Energy Plan launched

Future energy policy and the materials it needs

In July 2018, the Cabinet of Japan approved energy policy guidelines for the country under the title of the Fifth Strategic Energy Plan. What are the main points of this Plan, which focuses on energy-related options in 2030 and in the more distant future of 2050? Takao Kashiwagi, a Distinguished Professor at the Tokyo Institute of Technology, has been involved in the formulation of Japan's energy policy for many years. He discussed the Plan's key points and the development of materials vital to its successful implementation with Kazunori Takada, Director of the Center for Green Research on Energy and Environmental Materials at NIMS.



Takao Kashiwagi
Distinguished Professor and Professor Emeritus, Tokyo Institute of Technology, Chairman of the Advanced Cogeneration and Energy Utilization Center JAPAN (ACEJ)

Kazunori Takada
Director, Center for Green Research on Energy and Environmental Materials
National Institute for Materials Science (NIMS)

Boosting renewable energy use to make it a major power source

Takada: At the NIMS Center for Green Research on Energy and Environmental Materials, we are developing energy and environment-related materials that will contribute to the construction of energy network systems enabling the utilization of various types of energy. The Fifth Strategic Energy Plan, which was approved by the Cabinet in July, will provide us with new direction in the development of materials. Could you give us an overview of Japan's energy policy, including the newly implemented energy plan?

Kashiwagi: The most significant event that took place during the four-year implementation of the Fourth Strategic Energy Plan was the entry into force of the Paris Agreement in November 2016, which requires all parties to put forward measures to slow global warming starting in 2020. As you know, energy and the environment are linked. The agreement had a great impact because many countries around the world joined it with the common goal of reducing their carbon emissions. The agreement drove these countries to make major revisions to their policies on energy systems.

In Japan, retail sales of electricity and gas were fully deregulated in 2016 and 2017, respectively. I expect various forms of energy supply and demand to be deregulated in the future.

In the light of this movement, the Fifth Strategic Energy Plan aims to greatly increase renewable energy use to make it a major power source. Some newspapers extensively covered this subject. However, I do not presume that any companies will launch business models that rely on renewable energy as a major power source because securing a stable power supply using this type of energy is difficult.

Because current technology does not allow large amounts of electricity to be stored, electricity consumers have to rely on the present power supply system, in which proper amounts of electricity need to be generated constantly for immediate use. To stably integrate power sources susceptible to weather conditions, such as solar cells, into the electricity supply and demand system, effective rechargeable battery materials need to be developed at first.

Takada: Rechargeable battery material research at NIMS has focused on the development of all-solid-state batteries, due to their high reliability, and lithium air batteries, due to their high energy densities. To expedite lithium air battery R&D, NIMS and SoftBank Corp. jointly established the SoftBank-NIMS Advanced Technologies Development Center in April 2018. Our goal is to achieve practical use of lithium air batteries with advantageous characteristics, such as light weight, compactness and low cost (see p. 12).

Energy production must be economically feasible

Kashiwagi: The Strategic Energy Plan contains language to the effect that the generation of electricity using renewable energy must be economically feasible in order for it to serve as a major power source. At present, electricity generated using renewable energy is expensive and thus less competitive in electricity markets than that generated through other means. The feed-in tariff (FIT) system has therefore been implemented to mandate that power companies buy renewable energy-derived electricity, thereby promoting the utilization of renewable energy. However, the economic viability of renewable energy power generation is a critical issue.

For solar cell power generation to become economically sustainable, its efficiency must be doubled and its cost must be halved. Thus, energy policy cannot be updated unless innovative materials, including much more efficient electronic devices, are developed to resolve these issues.

Takada: Most solar cells in current use are silicon wafer-based. It would be difficult to dramatically increase their power generation efficiencies because of the physical limitations of silicon. To address this issue, we are currently developing solar cells comprising group III and IV nitrides or quantum dots whose theoretical power generation efficiencies are higher than that of silicon. We are also conducting research on perovskite solar cells with many advantageous characteristics, such as flexibility and lower production cost. We have succeeded in increasing the stability and durability of these cells (see p. 13).

Putting these batteries under develop-

Balanced utilization of diverse energy sources will be indispensable to maintaining and strengthening the prosperity of Japan.

Takao
KASHIWAGI

ment into practical use would be very challenging. However, we must expedite this effort in order to meet the goals set in Japan's energy plans.

Preserving all available energy options

Kashiwagi: The Fifth Strategic Energy Plan contains language to the effect that Japan will consider and take full advantage of all available power source options. As an island nation, Japan does not have the ability to share energy with neighboring countries that EU nations possess. It is therefore crucial for Japan to secure diverse power sources, including the use of renewable energy mentioned earlier and nuclear power generation, which is proven to be economically sustainable and to emit no carbon.

Next-generation energy must be safer, more economical and more manageable. From this viewpoint, I expect that the current nuclear reactors in Japan will be replaced with smaller ones, in line with the reactor miniaturization trend in the United States. Because small nuclear reactors do not require water cooling, they can be constructed in more disaster-resistant areas away from coastlines. In addition, the operation of a varying number of small reactors will allow more precise adjustment of power output in response to varying demand.

The optimum energy mix will change naturally as renewable energy-derived electricity becomes a major power source. Balanced utilization of various energy sources is indispensable to maintaining and strengthening the prosperity of Japan.

Takada: I presume that an "optimum energy mix" means optimization of the power source composition through the combined use of diverse energy sources. Our mission as material developers is to provide as many material options as possible that contribute to enhancing energy systems so that energy policy makers can consider a wide range of options without making compromises.

Materials for smart communities

Kashiwagi: Optimization of the power source composition through combined use of diverse energy sources requires complex and advanced energy management within an energy-sharing community. This can be accomplished by using the internet of things (IoT) and artificial intelligence (AI).

By analyzing the lifestyles of residents using energy-related data collected from IoT devices, new businesses—such as monitoring services to ensure the safety of elderly people—may be created. The launch of these completely new "value chain" businesses may stimulate economic growth. This so-called "smart community" represents the model future society—known as Society 5.0—advocated by the Cabinet Office of Japan. The Society 5.0 concept supports the vision that a human community is capable of both achieving economic growth and solving social issues through sophisticated integration of the "cyber layer," consisting of IoT and AI, and the "physical layer," representing the real world. The establishment of a smart community requires placement of many sensors to collect real world data.

Takada: Sensors are indeed the key technology. NIMS recently founded the Center for Functional Sensors & Actuators this year and its members have since been fully engaged in sensor R&D.

A rapid increase in the number of sensors to be installed will in turn increase the demand for power sources to operate the sensors. This energy issue can be addressed by incorporating independent power sources—capable of converting very low level energy sources, such as light, vibration and heat, into electricity—into sensors. Thermoelectric devices capable of converting human body heat into electricity would be ideal for this purpose. Devices under development capable of operating at low temperatures are designed to efficiently utilize heat generated by the physical activities of humans (see p. 8).

Fuel cells can potentially serve as a power source option for smart communities. Research is underway to develop systems capable of efficiently producing, storing or processing hydrogen, which is used by fuel cells to generate electricity. There is great potential for material studies to make breakthroughs in this endeavor. For example, development of the following materials is in progress: materials capable of converting renewable energy-derived surplus electricity into hydrogen and storing it, materials capable of extracting hydrogen from compounds in naturally occurring gases and separation membranes capable of further purifying extracted hydrogen (see p. 10).

As the name of our research center implies, our mission is to research and develop energy and environment-related materials by quantifying energy use flow across a smart community and identifying the most effective materials for specific purposes.

Kashiwagi: I have great expectations for NIMS. The true value of the innovative materials that comprise a system is often appreciated only after the system is proven to be effective. We are attempting to optimize the combination of various energy sources with the goal of making Japan more prosperous. This comprehensive approach may be applicable to the development of materials: rather than taking the approach of choosing the superior of two options, it is more desirable to find the optimum combinations within a wider range of options.

(by Akiko Ikeda, Sci-Tech Communications)

Kazunori
TAKADA

Our mission as material developers is to provide as many energy policy options as possible.

ENERGY Materials of NIMS

Thermoelectric generators

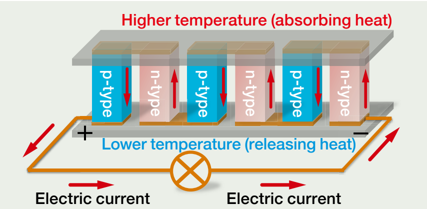
(From left to right) Iron, silicon and aluminum. These abundant elements are the primary resources exploited by the research group led by Shinohara and Takagiwa to develop thermoelectric materials.

Converting exhaust heat into electricity using ubiquitous chemical elements

Thermoelectric materials are capable of converting heat directly into electricity. Elements made of thermoelectric materials are called thermoelectric power generators (hereinafter referred to simply as "thermoelectric generators"). The research group led by Yoshikazu Shinohara and Yoshiki Takagiwa has been developing thermoelectric generators using readily accessible chemical elements. These thermoelectric generators are intended for use as autonomous power sources to be installed in various sensors—technology vital to putting the "super smart society" concept into practice.

The National Aeronautics and Space Administration (NASA) of the United States launched the Voyager 2 space probe in 1977. The probe completed long-term space missions far from the light of the sun to seek clues to unravel some of the mysteries of outer space and to explore a world previously unknown to humankind. These space missions were indeed made possible by thermoelectric generators.

Thermoelectric materials are capable of converting heat flows across internal temperature gradients into electricity. A thermoelectric generator contains alternately installed p-type and n-type semiconductors. This arrangement causes temperature differences between the two opposite ends of these semiconductors. This temperature difference is then used to generate a large electromotive force (figure).



The magnitude of electromotive force is determined by the type of thermoelectric material and the temperature difference between the opposite ends of the thermoelectric materials. The thermoelectric generator contains alternately installed p-type and n-type semiconductors. This arrangement causes temperature differences between the two ends of the semiconductors, and this temperature difference is then used to produce a large electromotive force, leading to power generation. P-type semiconductors carry positive charges while n-type semiconductors carry negative charges. The alternating arrangement of these two types of semiconductors allows electric current to flow in specific directions indicated by the red arrows in the diagram.

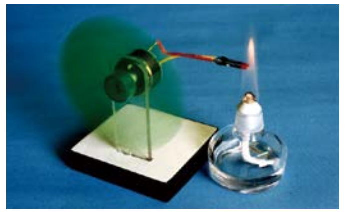
Only a few thermoelectric generators intended for use by the general public have been developed. This is partly because thermoelectric material R&D had not been focused on designing materials that function optimally at various operational temperatures. In addition, common thermoelectric materials developed for use at specific temperatures, such as bismuth-tellurium-based and lead-tellurium-based materials, are expensive and environmentally harmful.

Shinohara has been engaged in thermoelectric generator R&D for more than 20 years. He said, "About two-thirds of all energy produced by humans today is lost as exhaust heat and 90% of such exhaust heat occurs at temperatures below 200°C. I believe that development of thermoelectric generators capable of producing high power using small temperature differences between room temperature and 200°C would contribute to slowing global warming."

Such thermoelectric generators are expected to serve as ideal power sources for various sensors. "Compact and lightweight thermoelectric generators that require no maintenance can be used as very effective power sources for sensors," Shinohara said. "Our goal is to develop thermoelectric generators using abundantly available chemical elements."

Development of environmentally friendly manufacturing process

"Candle radios" are a rare example of thermoelectric generators developed for use by the general public. The iron silicide ($FeSi_2$)-based thermoelectric generator, which was integrated into the candle radio as an independent power source, was invented about 30 years ago by the National Research Institute for Metals (NRIM), a predecessor of NIMS (the upper right photo). Inspired by the predecessor's invention, Shinohara has been researching and developing iron-silicon-based thermoelectric generators.



U-shaped, $FeSi_2$-based thermoelectric generator developed in 1990 by the National Research Institute for Metals, a predecessor of NIMS. It can produce up to 35 milliwatts of power. The p-type and n-type semiconductors in the generator are doped with manganese and cobalt, respectively. This rare-metal-free thermoelectric generator capable of producing large amounts of electricity received global attention.

"The power density of the U-shaped thermoelectric generator invented by NRIM is not sufficient as an independent power source for a single sensor," Shinohara said. "To address this issue, I have been collaborating with companies to develop higher-power thermoelectric generators."

Increasing power density requires techniques to install thermoelectric generators in a particular arrangement. In addition, low-cost, environmentally friendly manufacturing techniques need to be developed.

"Manufacturing processes must be energy-efficient in addition to being capable of producing high-quality thermoelectric generators," Shinohara said. "To achieve this, we are developing a MIM (metal injection mold) manufacturing process in which a mixture of $FeSi_2$ powder and a binder (or a binding agent) kneaded together is injected into a mold to form a desired shape and then sintered. Injection molding has several major advantages: it allows continuous, speedy mass production, is environmentally friendly, and allows materials to be shaped into various forms with precise dimensions."

Discovery of a new material using computational and data science

While Shinohara is developing thermoelectric generators and manufacturing processes, Takagiwa is researching new thermoelectric materials and has made significant discoveries.

Takagiwa said, "I discovered a semiconducting material composed of aluminum (Al), iron (Fe) and silicon (Si). Because numerous studies had been focusing on Fe-Si-based materials, my research initially focused on Fe-Al-based materials. However, these materials did not serve as semiconductors. I subsequently decided to develop Al-Fe-Si-based materials based on the idea that adding Si to a Fe-Al-based material might strengthen its semiconducting properties."

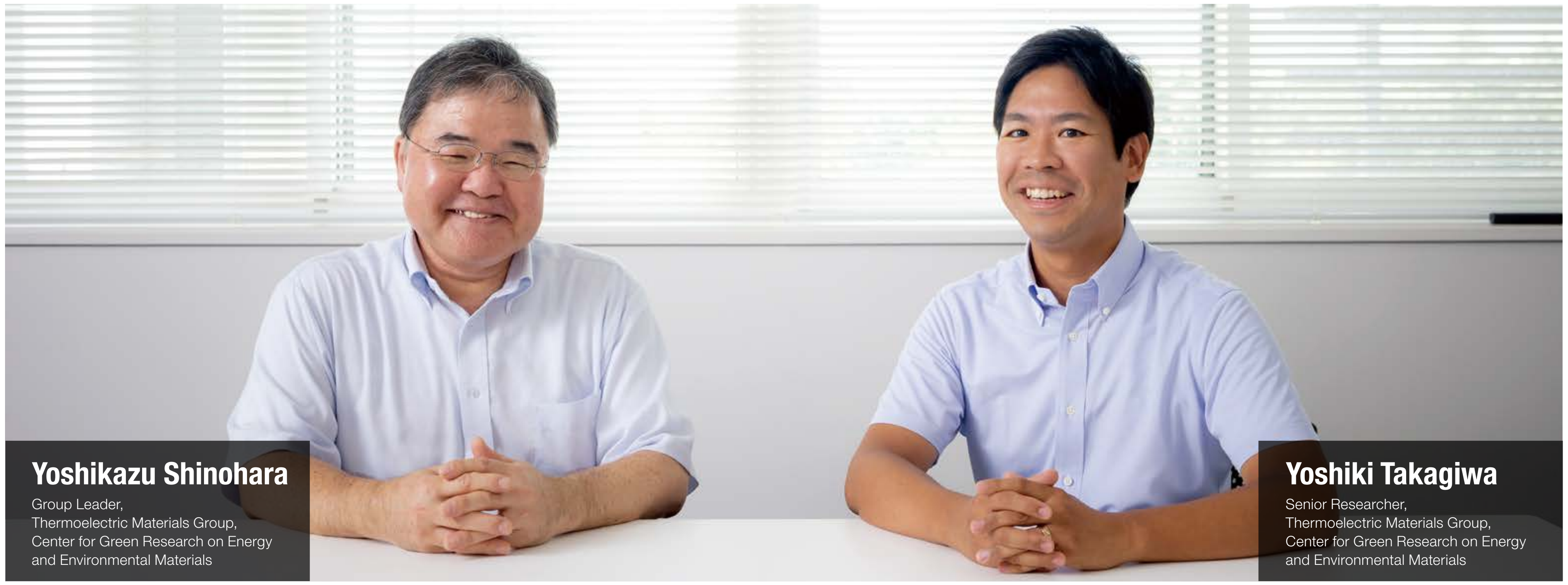
In his initial study, Takagiwa preformed first-principles calculations on the properties of Al-Fe-Si-based materials and discovered $Al_2Fe_3Si_3$ with semiconducting properties. Takagiwa then closely examined the phase diagram of $Al_2Fe_3Si_3$. A phase diagram is a "map of a material," so to speak, illustrating the relationships between the ratio of chemical elements to be mixed, processing temperatures and the properties of resulting compounds.

Takagiwa said, "The phase diagram of $Al_2Fe_3Si_3$ indicated that successive and extensive changes in the Al/Si ratio would not cause deterioration of the stability of the compound. Then a flash of inspiration came to me. I thought that simple adjustment of the Al/Si ratio within an allowable range might enable me to create both p-type and n-type semiconductors. This idea excited me because creating the two types of semiconductors without doping the compound with other chemical elements is truly innovative."

Takagiwa later succeeded in determining precise Al/Si ratios to create p-type and n-type semiconductors by means of materials informatics (MI) which takes both data science and experimental approaches. He found that $Al_2Fe_3Si_3$ is capable of generating sufficient power to operate a sensor using temperature differences between 5°C and room temperature. He also found that this effective temperature range can be expanded to approximately 200°C, an intermediate temperature. Takagiwa made these significant discoveries after two years of R&D effort using a variety of techniques. He is currently conducting joint research with an industrial company to process $Al_2Fe_3Si_3$ into thermoelectric generators.

Both Shinohara and Takagiwa are truly enjoying studying thermoelectric materials. They expect that thermoelectric materials will play a key role in putting the "super smart society" concept into practice. Their goal is to achieve practical application of the thermoelectric materials invented by NIMS.

(by Kumi Yamada)



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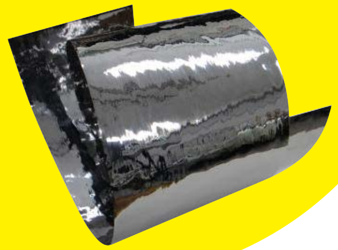
Y. Shinohara, O. Umezawa, Thermoelectric Power Generation from Waste Heat, Handbook of Ecomaterials, Springer (in printing)
Y. Takagiwa et al., J. Phys. Chem. Solid 118, 95-98 (2018). DOI: 10.1016/j.jpcs.2018.03.003

ENERGY Materials of NIMS

Hydrogen production and utilization

Materials enabling production of hydrogen, a promising major energy source for the future society



Vanadium (V) alloy foil enabling separation and purification of hydrogen developed by Nishimura. The rate of hydrogen passing through the foil can be increased by reducing the thickness of the foil.

Combustion of hydrogen does not produce any polluting byproducts but rather only clean water. Due to this property, the importance of hydrogen as a green energy source is expected to grow. However, because almost all hydrogen on the earth exists in compound forms, hydrogen molecules must be extracted from these compounds. If this hydrogen production process requires spending large amounts of energy, large-scale hydrogen utilization will be difficult to achieve. We asked Chikashi Nishimura and Hideki Abe about materials critical to achieve this.

Extracting hydrogen from natural gas using catalysts with "anchoring roots"

Future energy sources are required to meet the need for zero-emission of environmentally harmful gases such as carbon dioxide. In addition, diversification of these energy sources is important to ensure stable energy supply. Because combustion of hydrogen does not generate any polluting byproducts but rather only clean water, it is a viable energy source option. Hydrogen stations to fuel hydrogen vehicles, which are analogous to gas stations to fuel gasoline vehicles, have already been installed in some areas. The "hydrogen society" plan promotes public use of hydrogen-powered fuel cell vehicles. Expectations for putting this plan into practice are growing. Development of a hydrogen society, however, necessitates a chain of infrastructure capable of producing, purifying and transporting hydrogen.

Abe said, "Most hydrogen production methods today use natural gas as a hydrogen source. However, these methods have not yet become economically viable as they require large amounts of energy input. I have been developing catalysts that will allow more energy-efficient and low-cost hydrogen production." A catalyst is a substance capable of increasing the rate of specific chemical reactions while itself remains unchanged. Catalysts are commonly used in the chemical industry. They are used in hydrogen production to facilitate high-temperature chemical reactions leading to the conversion of methane and water vapor, the main natural gas components, into hydrogen and carbon monoxide.

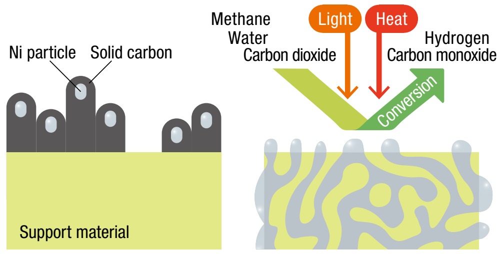


Figure 1. Conventional (left) and rooted (right) catalysts

A conventional catalyst is composed of a support material (yttrium oxide, Y_2O_3) and catalytic nickel (Ni) particles scattered over the Y_2O_3 surface. Hydrogen producing reactions yield solid carbon byproducts which deposit on the Y_2O_3 surface, weakening catalytic functions of conventional Ni particles. On the other hand, when the rooted catalyst is used, catalytic Ni particles remain attached to the support material in the presence of solid carbon by means of extensive root-like structures which penetrate into the support material.

The currently used catalysts are composed of a base material (support material) and nickel (Ni) particles scattered over the support material surface. Byproducts of the hydrogen production reactions include solid carbon which grows on the support material surface like frost columns, pushing Ni particles away from the support material and weakening catalytic function. To prevent this problem, these reactions have been subjected to high temperatures of approximately 1,000°C to burn out solid carbon using methane. This heat treatment has required large amounts of methane: more than 10% of annual methane production, significantly increasing the energy cost of hydrogen production.

In the hope of reducing the excessive methane use, Abe has developed a so-called "rooted catalyst" capable of properly functioning at lower temperatures. Because individual Ni particles in this catalyst have elongated plant root-like structures which penetrate into the support material, they are able to remain attached to the material surface even when solid carbon is produced (Figure 1). The use of rooted catalysts has enabled hydrogen production below 500°C.

How was Abe able to come up with such catalyst structure? "During earlier research on catalysts used to treat automobile exhaust gases, I once exposed alloy-based automobile catalysts to high temperatures in a gas mixture which simulated an exhaust gas. Then, to my surprise, the alloy transformed into a peculiar nanostructure composed of very fine fibrous metals and oxides entangled together like plant roots." Later, a flash of inspiration came to Abe. He thought that the rooted catalyst might be used to solve the problem associated with solid carbon deposition. "The results were fantastic," Abe said. "I am now more confident that this catalyst may be used practically because it has demonstrated the ability to perform effectively without deterioration after 1,000 hours of continuous hydrogen production."

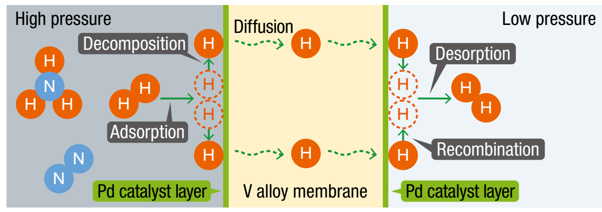
Vanadium alloy membrane capable of quickly and completely separating large amounts of hydrogen

Extraction of hydrogen from natural gas does not represent the whole process. Natural gas contains impurities and hydrogen producing reactions generate unwanted byproducts. These impurities and byproducts must be removed during the hydrogen separation and purification process before hydrogen becomes acceptable in quality as an appropriate energy source. To achieve this, Nishimura has been devoted to the development of membranes penetrable only by hydrogen for 30 years.

A hydrogen atom is the smallest chemical element. It is capable of traveling though metallic lattices at an astonishing speed—10 billion times faster than carbon and nitrogen. Global research efforts have been made to extract pure hydrogen from natural gas by allowing the gas to pass through a metallic membrane penetrable only by hydrogen. As a result, practical use of palladium (Pd) alloy membranes for this purpose has been achieved. However, Pd is a scarce and expensive metal and it takes a long time for Pd membranes to separate hydrogen. To address these issues, Nishimura designed a new membrane composed of a vanadium (V) alloy membrane and Pd surface layers.

Like Pd alloy membranes, V alloy membranes also allow hydrogen atoms to pass through them. However, hydrogen can travel faster through a V alloy membrane than through a Pd alloy membrane due to different crystalline structures. While Pd has a very dense atomic structure, V has slightly larger space in its atomic structure, allowing hydrogen atoms to more easily pass through it. Thus, a V alloy membrane was expected to be able to separate hydrogen more quickly. With this theoretical basis, Nishimura began developing V-containing membrane materials.

Figure 2. Mechanism of hydrogen separation by the vanadium (V) alloy membrane. Both sides of the V alloy membrane are coated with a palladium (Pd) catalyst layer. The Pd layer on the high pressure side causes hydrogen molecules to decompose into individual atoms. Hydrogen atoms then pass though the Pd layer, diffuse though the V alloy membrane, surface on the low pressure side of the membrane and bond together to form hydrogen molecules. Because only hydrogen atoms and no other atoms can pass thorough the membrane, this process enables production of highly pure hydrogen.



Although V membrane could separate hydrogen more quickly, this property was also problematic: as the entry of too many hydrogen atoms into the membrane causes it to expand and rupture. To prevent this, Nishimura added Ni to V to create an alloy membrane. He then processed the membrane into a foil of several tens of micrometers in thickness and coated both sides of the foil with a very thin Pd layer. This combination was effective because Pd atoms, and not V atoms, are capable of catalyzing decomposition of hydrogen molecules into individual atoms. Thus, Nishimura successfully developed an innovative alloy membrane capable of speedily separating and purifying hydrogen (Figure 2).

Nishimura said, "The performance of the V alloy membrane has been increasingly recognized in Japan and overseas in recent years. I am currently working with several domestic organizations to optimize alloy design for practical application and develop devices." The device in which the V alloy membranes are incorporated has already been confirmed to be capable of separating and purifying approximately 9 L of hydrogen per minute. This device with proven processing capacity has potential to be used practically in hydrogen refueling stations.

"Technologies for hydrogen production and purification must be enhanced to establish hydrogen as a major energy source. I would like to contribute to the implementation of the "hydrogen society" initiative using the materials I have developed," Nishimura said energetically.

(by Akiko Ikeda, Sci-Tech Communications)

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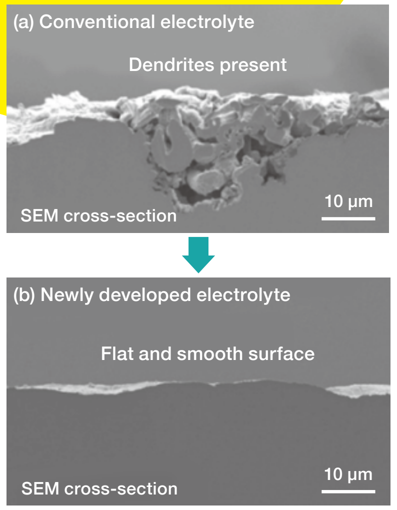
C. Nishimura et al., J. Alloys. Compd 330-332, 902-906 (2002). DOI: 10.1016/S0925-8388(01)01648-6

ENERGY Materials of NIMS

Next-generation rechargeable batteries

Development of ultralight, large-capacity lithium air battery in partnership with SoftBank

Lithium (Li) ion batteries are currently the most commonly used rechargeable batteries. However, the effort to further increase their capacity is approaching the limit. On the other hand, lightweight, large-capacity Li air batteries (hereinafter referred to simply as "air batteries") are considered by many as the ultimate rechargeable batteries. The SoftBank-NIMS Advanced Technologies Development Center was established in April 2018 to expedite air battery R&D. We asked Kimihiko Ito, who is conducting joint research with SoftBank Corp., about challenges in air battery research and the future prospects.



Detailed observation of anode cross-section using an electron microscope. Ito found that the formation of lithium oxide (Li_2O) film over the metal lithium surface prevents dendrites from occurring. "This effect presumably resulted from the synergy of LiBr and $LiNO_3$ comprising the electrolyte." (Ito)

The currently prevalent Li ion battery is composed of a transition metal oxide cathode, a carbon-based anode and an electrolytic solution. Charging and discharging of the battery are driven by the back and forth movement of Li ions between the cathode and anode. In air batteries, the cathode is composed of oxygen reactive compounds and the anode is composed of lightweight metal Li. Air batteries are the lightest rechargeable batteries and can be produced at low cost, owing to their ability to use the surrounding air as an oxygen source, rather than storing oxygen internally. The theoretical energy density by weight of air batteries is more than five times higher than that of Li ion batteries.

Due to these great advantages of air batteries, SoftBank began joint research with NIMS at the SoftBank-NIMS Advanced Technologies Development Center. SoftBank hopes to integrate lightweight air batteries into sensors of IoT devices and wearable devices.

Modification of electrolytes led to increased power generation efficiency and charge cycles

Putting air batteries into practical use requires overcoming many challenges, such as increasing their power generation efficiencies, charge cycles and charge capacities. Ito has been working to improve battery materials for many years. He reported one of his accomplishments in 2017.

"The voltage of air batteries was known to hike sharply during charging, which leads to decreased energy efficiency of the batteries," Ito said. "The voltage hike results from chemical reactions occurring during the charging phase. When the air battery is discharged, lithium peroxide (Li_2O_2) is deposited on the cathode and when it is charged, Li_2O_2 is decomposed, releasing Li ions, which move to the anode side. Because Li_2O_2 is difficult to break down, its decomposition requires a high voltage. I decided to modify the electrolyte to facilitate Li_2O_2 decomposition reactions."

Voltage hike had been thought to be diminishable by adding redox reaction promoting substances to electrolytes. Ito's group therefore added iodine (I), a candidate for bringing such an effect, to electrolytes without achieving significant improvement. The group then added bromine (Br), which belongs to the same group in the periodic table as I, to develop an electrolyte containing a mixture of lithium bromide (LiBr) and lithium nitrate ($LiNO_3$).

"As a result, we succeeded in lowering charge voltages from 4.5 V to 3.5 V, which led to increasing energy efficiency from approximately 60% to approximately 77%," Ito said. "The improved energy efficiency may reflect more effective decomposition of Li_2O_2 on the cathode driven by changed valence of Br ions in the electrolyte at about 3.5 V during charging."

The new electrolyte also alleviated another problem: when air batteries containing a conventional electrolyte were being charged, metal Li dendrites (branching, tree-like structures) had been formed on the anode, shortening its life and acting as a cause of short-circuiting. However, dendrites did not develop when the new electrolyte was used (photo).

"The modification of electrolytes resulted in increased charge cycles from 20 to more than 50. Although the battery in its current form is still far from practical use, we will continue to enhance battery materials, including electrolytes. The joint research with SoftBank is a great opportunity for us," Ito said with excitement.

(by Kumi Yamada)

Kimihiko Ito

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X. Xin et al., ACS Appl. Mater. Interfaces 9, 25976-25984 (2017). DOI: 10.1021/acsami.7b05692
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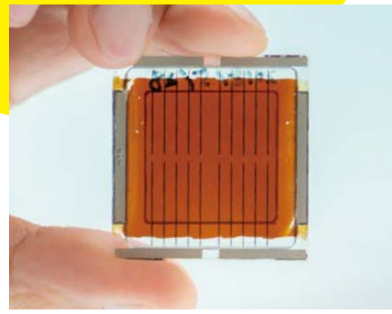
ENERGY Materials of NIMS

Solar cells

Perovskite solar cells with improved power generation efficiency and durability



Translucent perovskite solar cell developed by Shirai's research team

The perovskite solar cell is drawing a great deal of attention for its potential to serve as a next-generation solar cell that is lightweight, is bendable and can be produced at low cost. Its energy conversion efficiency is rapidly catching up with that of silicon solar cells. Practical use of perovskite solar cells in the near future is eagerly awaited. However, such achievement requires overcoming a major challenge: they need to be more durable. Yasuhiro Shirai has been addressing this challenge from two different angles—developing materials and developing fabrication processes.

A perovskite solar cell has a five-layered structure. A perovskite layer—capable of generating electrons and holes when exposed to sunlight—lies between an electron transport layer and a hole transport layer. Then, these three layers lie between two electrode layers. The perovskite, electron transport and hole transport layers are fabricated by dissolving materials for respective layers in solutions and layering them on top of a film substrate one by one in the proper order.

Because the perovskite solar cell was derived from "dye sensitized solar cell" research, its structure and the materials used to create it tend to be similar to those used for dye sensitized solar cells. On the other hand, Shirai, whose research focus had been organic photovoltaics (OPV), incorporated his expertise on OPV into the development of perovskite solar cells. As a result, in 2016 he succeeded in fabricating a perovskite layer free of porous titanium oxides.

Shirai said, "I developed a new fabrication method by integrating a step to add a chlorine-containing material into the conventional interdiffusion method. The resulting layer had even thickness and a flat and smooth surface. I was also able to meet the goal of making the layer more stable and durable. Furthermore, I was able to achieve sufficiently lower processing temperatures to the level which the film substrate could withstand."

Translucent perovskite solar cell with dramatically increased durability

In addition to the research activities mentioned above, Shirai has been studying the tandem solar cell in which a perovskite solar cell is placed on top of a silicon solar cell.

In the case of crystalline silicon solar cells, for example, their energy conversion efficiency peaks when they are exposed to wavelengths in the near-infrared region. On the other hand, perovskite solar cells most efficiently absorb visible light wavelengths in the vicinity of 500 nanometers. Thus, a tandem structure in which a perovskite solar cell is placed over a crystalline silicon solar cell can absorb a greater range of wavelengths and therefore produce greater amounts of electricity than when either of these solar cells is used alone.

"Principal Researcher Masatoshi Yanagida, a member of my research team, worked to increase the transparency of the perovskite solar cell in order to allow more light to penetrate into the underlying silicon solar cell. Yanagida used a so-called sputtering method to form a hole transport layer made of nickel oxide and the back contact electrode layer made of indium tin oxide (ITO)."

Yanagida's work produced unexpected results: the durability of the fabricated translucent perovskite solar cell was significantly extended. Shirai said, "We continuously monitored the power generation efficiency of the solar cell over a period of time. The power generation efficiency of our earlier perovskite solar cell declined by approximately 20% after 1,000 hours of continuous operation. In comparison, the efficiency of the modified perovskite solar cell was nearly unaffected by more than 4,000 hours of continuous operation. I consider the extended durability to be an added advantage of Yanagida's method of fabricating high-quality interface layers. However, the expected durability of solar cells is generally accepted to be more than 20 to 30 years. We therefore aim to develop devices that will meet this expectation." In the future study, Shirai plans to identify mechanisms of perovskite solar cell deterioration by conducting experiments under more severe conditions such as at high temperatures.

"The energy conversion efficiency of the current translucent perovskite solar cell is approximately 12%," Shirai said. "We hope to develop more efficient perovskite solar cells. Our ultimate goal is to develop tandem solar cells with conversion efficiency higher than 30%."

Shirai's team is making steady progress in solar cell R&D to achieve practical use.

(by Kumi Yamada)

Yasuhiro Shirai

Principal Researcher,
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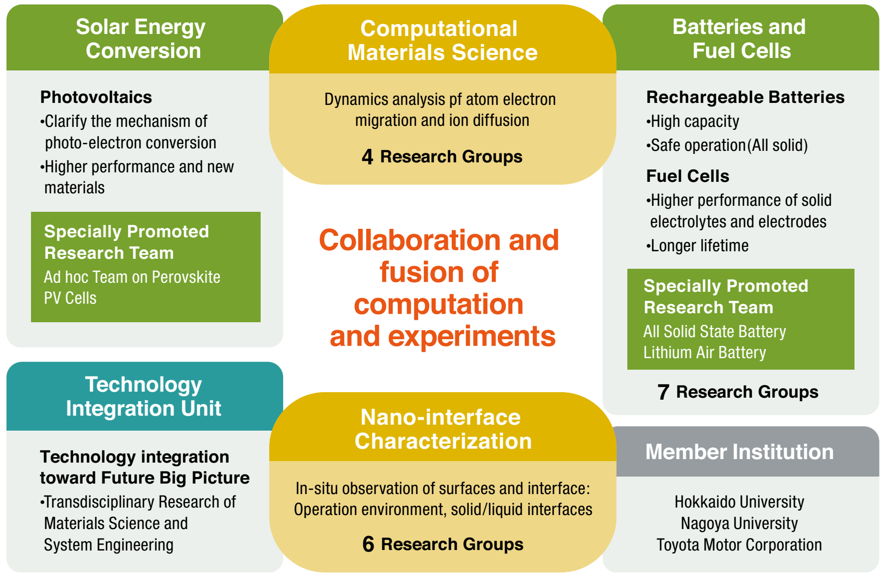
D. B. Khadka et al., ACS Appl. Mater. Interfaces 10 (26), 22074(2018). DOI: 10.1021/acsami.8b04439
M. B. Islam et al., ACS Omega 2 (5), 2291(2017). DOI: 10.1021/acsomega.7b00538

What is GREEN ?

GREEN (Global Research Center for Environment and Energy based onNano-materials Science) was established in October 2009 as a collaborative research center to contribute to solving global environmental issues under the auspices of the MEXT program for the Development of Environmental Technology Using Nanotechnology. Many experts in various fields from NIMS, universities and private companies participate in GREEN to help establish solar-based energy conversion/storage/transport systems through understanding and control of the interfacial processes of energy conversion devices (e.g., fuel cells, rechargeable batteries and solar cells) based on a fusion of experimental materials development, advanced characterization and theoretical/computational approaches. In addition, GREEN serves as an "open laboratory" by making its state-of-the-art equipment and facilities available for use by external researchers and providing them with know-how.

Since 2016, GREEN is under the "Integrated Materials Development Project" and its stress now is to develop materials, devices and systems, which are directly related to future societal needs, including sustainable energy systems, by combining traditional materials research with systems engineering and information science. GREEN will hold a symposium in January 2019 to summarize its activities over the past 10 years (see below).

Organization of GREEN



What is the NIMS Battery Research Platform?

The NIMS Battery Research Platform was established by the support of the supplementary budget in FY2012 as a leading-edge facility equipped with virtually all resources necessary to accelerate R&D of next-generation rechargeable batteries, from fabrication of small/medium-sized batteries to analysis and evaluation of battery materials. It became fully operational in 2014.

It is located in the NanoGreen Building at the Namiki Site and the most notable feature of the Platform is the 80-m2 super-dry room capable of providing the extremely dry environment (dew point of supply air: -90 °C), which is essential for next-generation battery R&D. Another important feature is the availability of a variety of world-class analytical equipment (SEM, TEM and XPS, etc.), enabling researchers to efficiently carry out a series of R&D steps, including assembly/disassembly, analysis and evaluation of batteries, under one roof without exposure to ambient air.

Although the main objective of the Platform is to support the ALCA-SPRING project (MEXT program for next-generation battery R&D), it is also available to researchers from universities, research institutes and private companies working in next generation battery R&D. Please visit the Platform' s website for details at **http://www.nims.go.jp/brp/nims**.


Super-dry room

19th
GREEN Symposium
GREEN 2009 ～ 2018

Solving common issues related to solar-based energy flow systems
—Understanding and controlling interfacial phenomena in device development—

Time and date:
Wednesday, January 23, 2019
10:30-17:15
Venue:
Hitotsubashi Hall
(National Center of Sciences, 2F)

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Science is even more amazing than you think maybe...

Microplastics

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

The use of plastic straws is expected to be banned in the United States in the near future due to their potential environmental impact. Abandoned plastics break down into small pieces. Organisms that ingest these pieces and accumulate them in their bodies may suffer from abnormalities.

Vast amounts of single-use plastics are used in our society. Lightweight, easy to process and cheap, these plastics are continuously manufactured, used and disposed.

Due to their stable molecular structures, plastics are strong and versatile materials. However, stable plastics are resistant to complete decomposition. Deteriorated plastics accumulate unnoticed as microscopic pieces (i.e., microplastics) in natural environments, which has been a growing problem in recent years.

Marine pollution represents a major environmental issue associated with microplastics. Many of the once beautiful beaches around the world are now filled with washed up trash. While drifting in the sea, plastics are exposed to waves, winds and ultraviolet rays, causing them to break down into microplastics. Planktons ingest microplastics, and these planktons are in turn eaten by fish and clams. Humans consuming these affected fish and clams then accumulate microplastics in their bodies.

According to the recent surveys conducted in Tokyo Bay, microplastics were found in 80% of the Japanese anchovies and 100% of the blue mussels. Some of these marine animals reportedly exhibit signs of growth failure or reproductive abnormalities.

Other recent research and surveys discovered that not only seawater but also bottled drinking water may contain large amounts of microplastics.

A research team at the State University of New York at Fredonia sampled and analyzed 259 plastic bottles of drinking water produced in the US, Brazil, China, Indonesia, India, Kenia, Lebanon, Mexico and Thailand. The team found that 93% of the samples were contaminated with some types of plastics, such as polypropylene, nylon and polyethylene terephthalate (PET).

Ninety five percent of plastic contaminants were minute particles between 6.5 and 100 micrometers in size (1 micrometer = 0.001 millimeter). Averaging across all samples, one liter of water contained 325 pieces of contaminants.

Even the most uninterested scientists would react to these shocking findings. Research efforts have been expedited to develop environmentally and eco-friendly plastic products.

Plant-based plastics are a type of such plastics. Most plastic products used today are petroleum based. Unlike petroleum-based products, biodegradable plastics—synthesized using corn or sugar cane—are ultimately decomposable to water and carbon dioxide by soil-dwelling microorganisms. In addition, resource depletion is of less concern for the production of biodegradable plastics than of petroleum-based plastics. If future research finds ways to make these plastics more durable and mass producible, they might become common everyday items.

Many inventions throughout human history have made our life more convenient. However, overly excessive amounts of convenient items may impact our environment. I believe that we have a responsibility to protect the global environment by dealing with various environmental issues, including those related to global warming, endocrine disruptors and CFCs.

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.

NIMS NEWS

1 Principal Researcher Kazunori Sugiyasu wins Friedrich Wilhelm Bessel Research Award

Kazunori Sugiyasu (Principal Researcher, Research Center for Functional Materials) won the Friedrich Wilhelm Bessel Research Award presented by the Alexander von Humboldt Foundation.

The award ceremony is set to be held in Bamberg, Germany in March 2019.

The foundation—named after Prussian naturalist Alexander von Humboldt—is an independent, non-profit German organization established in 1953. Friedrich Wilhelm Bessel Research Awards are bestowed upon accomplished overseas scientists who have earned their doctorates within the past 18 years and who are expected to continue producing cutting-edge achievements. Award winners receive 45,000 Euros and are invited to join a long-term research project in Germany.

The foundation recognized Sugiyasu for his development of a technique enabling precision synthesis of supramolecular polymers. Sugiyasu said, "I am very delighted that my research at NIMS has been so well recognized. I would like to create innovative materials using the synthesis technique we developed."

2 NIMS and University of Waterloo sign International Cooperative Graduate Program agreement

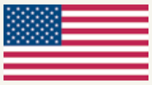
On October 12, 2018, an International Cooperative Graduate Program (ICGP) agreement was concluded between NIMS and University of Waterloo (UW) in Canada, which conducts quantum computer and nanotechnology research. This agreement stipulates that NIMS will accept doctoral students from UW for 6 to 12 months of research training. Qualified students will have opportunities to use NIMS' state-of-the-art facilities and receive advice from leading researchers while conducting their dissertation research projects. NIMS is also expected to benefit from the opportunities the ICGP affords to strengthen research collaboration, train student researchers, discover talented researchers and enhance partnership with overseas organizations.

Signing ceremony at the Embassy of Canada to Japan. Professor Sushanta Mitra (Executive Director of the Waterloo Institute for Nanotechnology, UW; right) and NIMS President Kazuhito Hashimoto.

Hello From NIMS

Hey there! My name is Ken Pradel, and I am a JSPS fellow from the United States. My mother is of Japanese descent, so growing up I was constantly exposed to Japanese culture in the form of food, movies, and a bit of the language, so the transition to working and living in Japan was not a difficult one. To this day, I have a deep love for Japanese pop culture, and I frequently make my way into Tokyo on the weekends for concerts, voice actor meet and greets, and comic conventions. The fan culture here is completely different from the United States, and I love being able to experience it first-hand. My research focuses on p-type doping of zinc oxide and its optoelectronic applications. The work can be frustrating at times, but I hope that one day it will find practical application.

Me with the Unicorn Gundam in Odaiba.



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