International Institute for Carbon-Neutral Energy Research

Grand Highway for a Carbon-Neutral Energy Society

I^{2}CNER's mission is to contribute to the advancement of low carbon emission and cost-effective energy systems, and improvement of energy efficiency. The array of technologies that I^{2}CNER's research aims to enable includes Solid Oxide Fuel Cells, polymer membrane based fuel cells biomimetic and other novel catalyst concepts, and production, storage, and utilization of hydrogen as a fuel. Our research also explores the underlying science of CO_2 capture and storage or the conversion of CO_2 to a useful product. Additionally, central to I^{2}CNER's mission is the establishment of an international academic environment that fosters innovation through collaboration and interdisciplinary research (fusion).

Research Center's Information (FY 2015)

Center Director: Petros Sofronis
Principal Investigators (PI): 26 (including 10 overseas researchers and 1 female researcher)
Other Researchers: 140 (including 70 overseas researchers and 17 female researchers)
Research Support Staff: 53
Administrative Division:
Administrative Director: Shunichi Masuda
Administrative Staff: 21 (percentage of bilingual staff: 81%)
Satellites and Cooperative Organizations:
University of Illinois at Urbana-Champaign, USA; and others
URL: http://i2cner.kyushu-u.ac.jp/en/

Major Research Achievements

1 Development of organic-inorganic perovskite solar cells with long lifetimes

The accumulation of lead originating from the breakdown of perovskite crystals upon reaction with water and oxygen was identified as a major mechanism leading to the degradation of organic-inorganic perovskite solar cells under operation. Device lifetime was extended by 17 times using a unique method to suppress this degradation mechanism.

2 Development of polymer-coated, highly durable carbon nanotube-based fuel cells

A new polymer electrolyte fuel cell cathode catalyst, in which the carbon nanotubes were doubly-coated with two different polymers, has been shown to be at least 100 times more durable than the conventional catalyst. In addition, this technology allows the smallest possible platinum particles to be used, leading to an overall reduction in the amount of platinum in the fuel cell.

3 Atomic level surface analysis with low energy ion scattering

The surface composition of perovskite, which had excellent oxygen molecule dissociation (catalytic activity), and is used as an air electrode, was analyzed at the atomic level using a new surface analysis method (the Low Energy Ion Scattering method). Degradation of cell performance was identified, and durability of the cell was improved.

4 Small Molecule Activation

An "Artificial molecular catalyst that can extract electrons from the hydrogen molecule (H_2) via a hydride ion (H^-)" was developed by mimicking a natural enzyme, hydrogenase. Furthermore, molecular fuel cells that make use of this molecular catalyst were successfully built.

5 Modeling of CO_2 behavior for safe and efficient CO_2 storage

A quantitative estimation of CO_2 saturation in rock was obtained using digital rock physics to investigate the behavior of CO_2 inside the rock, and conditions for effective CO_2 storage were clarified.

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Images shown in the background show blue emissions from a plasma plume during the pulsed laser deposition and observation of CO_2 behavior in natural rock.

Results of the research

The International Institute for Carbon-Neutral Energy Research (I^2CNER) of Kyushu University aims to promote advanced basic science research that will enable low carbon emission, highly efficient, and economically effective energy systems. As an Institute, we aspire to lead the way toward realizing an environment-conscious and sustainable society.

In an effort to create innovative solutions that will pave the way to the future, the Institute also addresses many major issues that currently hinder the realization of future clean energy societies.

1 Development of organic-inorganic perovskite solar cells with long lifetimes

Chihaya Adachi (PI)

Solar cells are currently garnering a lot of serious attention because they provide a promising solution to the growing concern over energy resources. A major advantage of solar cells is that no CO_2 is emitted through the power generation process, but this is offset to a certain extent by the substantial amount of power that is used and the amount of CO_2 that is emitted during the fabrication of the devices themselves.

In recent years, a class of solar cells called "perovskite solar cells" has drawn considerable attention because of their strong potential to achieve both a low carbon footprint and a high power conversion efficiency. Perovskite solar cells are composed of a mixture of organic and inorganic layers, and get their name from the crystalline perovskite layer that is used to absorb light.

The solar-to-electrical power conversion efficiency of perovskite solar cells is already greater than 20%, which is good enough for practical applications, but the devices degrade quickly under operation, which poses a major obstacle to commercialization. I^2CNER has set the goal of extending the lifetime–the time by which a device's efficiency decreases by a certain amount–while also increasing the conversion efficiency by clarifying and eventually elucidating the degradation mechanisms in perovskite solar cells.

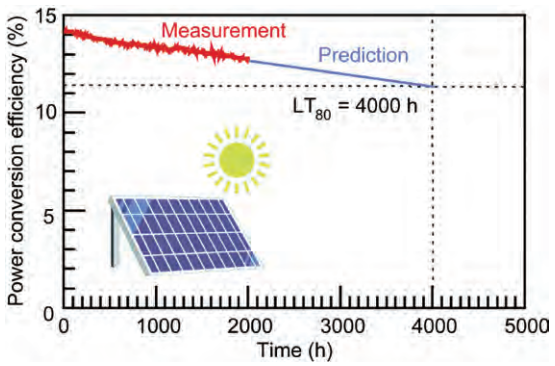

Fig. 1: Lifetime of a perovskite solar cell with benzoquinone added to the perovskite film

The dominant sources of degradation are thought to be water and oxygen from the atmosphere. To verify this, we produced prototype cells in a nitrogen environment free of water and oxygen, and compared them with those fabricated in an ambient atmosphere. The prototype cells were illuminated in the laboratory with simulated sunlight to measure the time until the conversion efficiency decreased to 80% of the initial, or a lifetime referred to as LT_{80}.

Whereas LT_{80} was at most 230 hours for the cells fabricated in an ambient atmosphere, LT_{80} increased to as long as 570 hours when the cells were made in a nitrogen environment. Thermally stimulated current measurements revealed that the cells produced in an ambient atmosphere had a large number of hole traps, i.e., positive charges that cannot move freely, and further analysis indicated that parts of the perovskite ($CH_3NH_3PbI_3$) had decomposed into CH_3NH_3I, PbI_2, and Pb. Thus, the efficiency degradation comes from the decomposition of perovskite in the presence of water and oxygen from the atmosphere, and hole traps formed by Pb produced after perovskite decomposition appear to play a particularly strong role in the reduction of efficiency.

Since we expect that the most likely source of Pb is the chemical reduction of Pb^{2+} created by the decomposition of perovskite, we developed a method to suppress this reduction by adding a small amount of an oxidizing agent called benzoquinone into the perovskite film. With the proper selection of benzoquinone concentration, the generation of hole-trapping Pb was controlled and the LT_{80} extrapolated from experimental measurements was extended to over 4,000 hours (Fig. 1).

These lifetimes are 17 times longer than those of conventional cells, and are the longest reported values to date. Furthermore, the addition of benzoquinone resulted in the formation of larger perovskite crystals, leading to an increase in conversion efficiency of about 30%. This research represents a major step toward the realization of perovskite solar cells with high conversion efficiency and long lifetimes for practical applications.

C. Qin et al: Adv. Mat., 28, 446, 2016

2 Development of polymer-coated highly durable carbon nanotube-based fuel cells

Naotoshi Nakashima (PI)

The fuel cells which have been used in "ENE FARM" (a home-use fuel cell cogeneration system) and fuel cell vehicles are an extremely clean electricity supply that generates electric power and water through the reaction between oxygen (i.e., air) and hydrogen with the help of catalysts. Polymer electrolyte fuel cells, in particular, in which a polymer membrane allows hydrogen ions to pass through and acts as the electrolyte membrane, are

considered to be the most promising fuel cells because of their small size, light weight, and high energy efficiency.

However, since platinum is used as the catalyst, driving up the overall device cost, the reduction of the amount of platinum used in the device and an increase in durability are important challenges.

In order to adsorb (or support) the nanometer-sized platinum particles on the catalyst, a conductive carbon material, carbon black, has been used. Carbon black poses a challenge, since it has a lot of chemically defective areas that cause functional degradation, although it supports platinum particles very well.

To resolve this dilemma, I²CNER's goal is to replace carbon black with carbon nanotubes (CNTs), which have almost no chemically defective sites. However, it is more difficult for CNTs to support platinum particles, and hence it is not simply a matter of switching from carbon black to CNTs.

Despite this difficulty, I²CNER has succeeded in supporting platinum particles by applying a thin polymer coating, polybenzimidazole (PBI), which has a strong affinity with the CNTs, to the surfaces of the CNTs. The schematic drawing of PBI-coating and platinum particle deposition on the CNTs is illustrated in the upper portion of Fig. 2. It can be said that PBI is playing the role of "double-sided tape" because it can be adsorbed strongly on the surfaces of the CNTs and at the same time, it can support platinum particles.

In Fig. 2, the durability of conventional fuel cells (shown by black dots), in which carbon black is used as the catalyst to support platinum particles, is compared with the durability of the fuel cells based on the PBI-coated CNTs (shown by red squares) to which platinum nanoparticles are deposited. The durability test based on the FCCJ protocol for the cells was carried out, in which high potential (1.5V) was applied in order to cause the carbon degradation/corrosion. In contrast to the distinctive degradation of the carbon black-based catalyst, the PBI-coated CNT-based catalyst shows almost no degradation and its durability is dramatically higher (Reference 1).

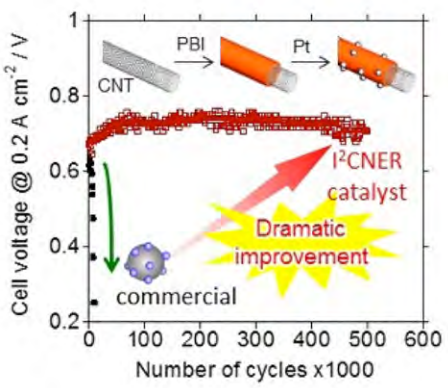

Fig. 2: Durability of fuel cells (cell voltage vs. durability cycling). Scheme of PBI coating is illustrated in the upper portion of the figure; black dots indicate durability of fuel cells with carbon black catalyst; and red squares indicate durability of fuel cells with PBI-coated CNT-based catalyst.

In addition to the above, the size of the platinum particles can be minimized with this new technology, leading to an overall reduction in the amount of platinum (Reference 2). This is, so to speak, a "trump card" for lowering the overall cost of the fuel cell.

These results indicate a strong possibility that this type of fuel cell (cells with the PBI-coated CNT-based catalyst) could be a promising next-generation fuel cell, and they have the potential to contribute to the wide-spread utilization of fuel cells in the near future.

M. R. Berber et al: Scientific Reports, 5, article number 16711, 2015

I. H. Hafez et al: Scientific Reports, 4, article number 6295, 2014

3 Atomic level surface analysis using the low energy ion scattering method

Tatsumi Ishihara (PI)

Solid Oxide Fuel Cells (SOFCs), in which the oxide ion conductor is a commonly used electrolyte that does not need to be humidified, is one type of fuel cell that is expected to be widely used in the future. Since SOFCs can operate at high temperatures, they do not require expensive precious metal electrodes, such as platinum, and achieve a high energy conversion efficiency. For these reasons, SOFCs are expected to have a wide array of practical applications.

In general, SOFCs use an oxide ion conductor as the electrolyte, with an oxide (i.e., perovskite) with high electrical conductivity acting as the air electrode (cathode) and a nickel-based metal acting as the fuel electrode (anode).

The lanthanum strontium cobalt ferrite (LSCF) perovskite used as the oxygen dissociation catalyst for air electrodes is susceptible to chemical reactions with substances from the air, such as sulphur, which causes the oxygen dissociation activity to degrade over time. This is one of the most difficult roadblocks in the development of SOFCs. In order to resolve this issue, I²CNER analyzed the aging (change with time) and spatial distribution of LSCF (perovskite-type oxide) composition in the vicinity of its surface using the latest analysis method (i.e., the low energy ion scattering, or LEIS method) and investigated the relationship between the composition of the outermost surface and the stability of the air electrode catalyst.

It was found that strontium, which was an additive to LSCF, tends to segregate on the surface as the temperature increases, and that strontium oxide was formed within a relatively short period (2 hours). The perovskite-type oxide is the chemical compound whose chemical formula is expressed as ABO_3 (where A and B are cations of different ionic sizes). In the case of LSCF,

the A ion is lanthanum and strontium ions, and the B ion is cobalt and ferrite ions, and it has been assumed that A, B, and O ions are uniformly distributed on the surface. However, this assumption was proven to be entirely incorrect through a detailed analysis of the catalytic LSCF surface. The composition of LSCF in the vicinity of the surface was investigated in detail using LEIS, and it was found that in the outermost layer (most surface one atomic layer of LSCF), the A ion is segregated and that the strontium ion in particular is occupied at the outermost surface layer (Fig. 3).

The above findings observed in this research clearly revealed that the degradation of catalytic activity at the air electrode caused by a reaction with a very small amount of impurities was closely related to the changes in surface composition. We have succeeded in finding an approach to improve the catalytic activity and durability of fuel cells by controlling the concentration of strontium that causes the activity to degrade. With this approach implemented, air electrode catalysts that can operate stably for long periods of time should be developed, which has the potential to lead to commercial viability for the SOFC.

J. Druce et al: Energy & Environmental Science, 7, 3593, 2014
A. Staykov et al: Chem. Mater., 27, 8273, 2015

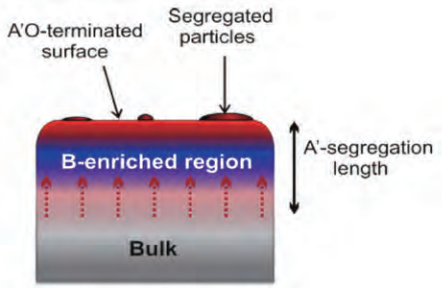

Fig. 3: Surface structure of perovskite oxides was clearly revealed by this research. A ions in the perovskite composition are concentrated in the uppermost surface and some of them have an island structure. Under the uppermost surface, there are regions that are abundant in B ions. Any one of these regions has a thickness of 3 to 5 atomic layers and, inside of (or under) these regions, the oxide is composed of ions (ABO_3).

4 Small Molecule Activation

Seiji Ogo (PI)

Small molecules such as H_2 (hydrogen molecules), O_2 (oxygen molecules), H_2O (water molecules), N_2 (nitrogen molecules), and CO_2 (carbon dioxide molecules) can be used effectively as energy sources when they are activated by oxidation and reduction. This process is called "Small Molecule Activation" and it is an area of research that has been gaining popularity rapidly in recent years. This report describes the results of I^{2}CNER research that is focused on the activation of hydrogen and oxygen molecules.

In nature, activation of the hydrogen molecule is achieved by a metalloenzyme, namely, hydrogenase. Hydrogenase plays a major role in many natural energy conversion systems. Under mild conditions, hydrogenase reversibly oxidizes the hydrogen with Fe and Ni, which is given by the following reaction equation: "$H_2 \rightleftarrows H^+ + H^- \rightleftarrows 2H^+ + 2e^-$". To date, no artificial catalyst has been developed that can catalyze this reaction. However, researchers at I^{2}CNER were the first in the world to succeed in developing "molecular catalyst extracting electrons (e^-) from the hydrogen molecule (H_2) via hydride ions (H^-)" by mimicking hydrogenase (Fig. 4 and Reference 1).

In addition, we are also the first in the world to have demonstrated that the oxygen molecule can be activated by making only minor changes to the molecular catalyst used to activate the hydrogen molecule, and that the peroxide species can be synthesized (Reference 2). In the peroxide species, the oxygen molecule is bound to an Fe center whose oxidation number is 4.

The key in designing the molecular catalyst is to configure the ligands surrounding the Fe center such that "they can withdraw the electron from the Fe center (Fig. 4)." Using this approach, the molecular catalyst can activate hydrogen molecules. We have also clarified that the molecular catalyst capable of activating oxygen molecules can be designed by "donating an electron to the Fe center."

By further deploying these approaches, we were successful in producing the first-in-the-world "molecular fuel cells" by making use of complexes (metal ions having molecules and ions bound) that activate hydrogen and oxygen molecules as the anode and cathode catalysts, respectively. This type of molecular catalyst can be manufactured less expensively than the platinum catalyst that is used as the electrode catalyst of fuel cells, with an added advantage being the ease with which the catalysts are designed. This type of catalyst has the potential to accelerate the development of precious-metal-free molecular fuel cells.

Ogo, S., et. al: Science 339, 682, 2013
Kishima, T., et. al: Angew. Chem. Int. Ed. 55, 724, 2016

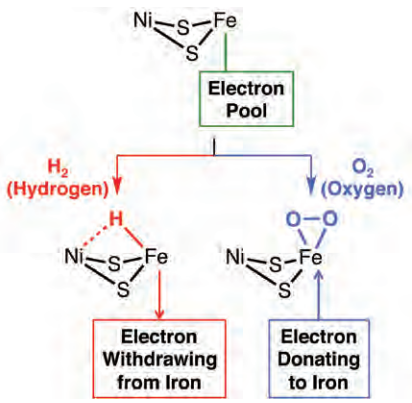

Fig. 4: Mechanism to control the activation of hydrogen (H_2) and oxygen (O_2). Fe: Ferrite, Ni: Nickel, S: Sulphur

5 Modeling of CO_2 behavior for safe and efficient CO_2 storage

Takeshi Tsuji (PI)

Carbon Capture and Storage (CCS) is a technology that can be used at a source which emits a large amount of CO_2, such as a coal-fired power station, to separate CO_2 and store it deep underground. The technology is well-known for its potential to reduce CO_2 emissions quickly in the near future. The storage of CO_2 does not require the construction of large, artificial underground spaces (e.g., tunnels). Instead, CO_2 is stored in the pore space of rocks (i.e., gaps in between the particles that make up rocks). Geologic strata in which a lot of pore spaces exist are called reservoirs. The porosity (i.e., a fraction of the pore volume over the total volume) of reservoirs is usually 20 to 30%. In ideal CO_2 reservoirs, CO_2 can be injected and stored using a small number of wells. However, around the Japanese Islands, the number of ideal reservoirs for CO_2 injection is limited, and thus, it is necessary to store CO_2 efficiently. As part of their efforts to develop ideal strategies for storing CO_2 underground, I²CNER researchers have developed a new approach making use of a novel approach called digital rock physics, which will allow them to consider specific factors, such as the geology of the Japanese islands or the limited number of reservoirs, when identifying potential CCS sites.

Using high-resolution CT equipment, we extracted the fine structure of pores in rocks at resolutions on the μm scale, which has allowed us to create a fine and precise digital (numerical) model of rocks. We have analyzed this model using the lattice Boltzmann fluid simulation method and precisely simulated and visualized CO_2 behavior as it runs through various networks of pores that exist inside rocks (Fig. 5).

Using the above-mentioned fluid simulation method, the behavior of CO_2 has been calculated under various reservoir conditions, and the amount of CO_2 (saturation) stored in the rock pores was investigated. It was found that saturation of CO_2 can be clearly estimated using two parameters: capillary number and viscosity ratio (i.e., ratio of CO_2 viscosity to water viscosity). The capillary number is a dimensionless parameter represented by surface tension and viscous forces. The capillary number and viscosity ratio are influenced by the conditions of reservoirs and the method used to inject CO_2 into the reservoir. Therefore, using the lattice Boltzmann method, it is possible to identify the conditions that allow for extremely efficient CO_2 storage. Furthermore, it could be possible to control CO_2 behavior in addition to the storage capacity. This technology is expected to contribute to the widespread use of CCS technology.

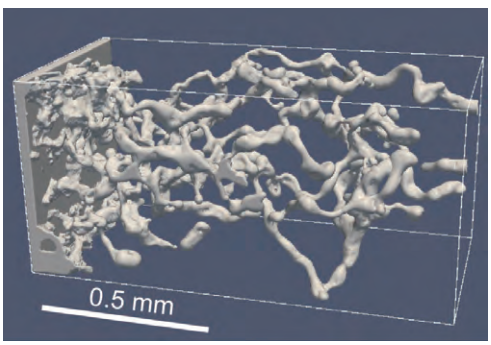

Fig. 5: CO_2 behavior running through rock pores. In this figure, only the injected CO_2 is color-coded in white, whereas formation water and rocks (solids) are shown as transparent. Conditions to effectively store CO_2 should be clarified by calculating CO_2 behavior under various conditions.

T. Tsuji et al: Advances in Water Resources, 95, 3-15, 2016
F. Jiang et al: Water Resources Research, 51, 1710, 2015

The unique influence of the only American WPI Director

When I²CNER was established in 2010, Professor Petros Sofronis (Ph.D.) of the University of Illinois became the first American to serve as the Director of a WPI Institute. Since the foundation of the Institute, we have held ourselves to the highest international operational standards, and our official language has been English.

In addition to creating a research environment that attracts some of the world's top researchers, we have adopted rigorous personnel performance evaluation systems based upon those used in the top US academic institutions. The Institute has also contributed to the cultivation of global human resources; implemented an efficient top-down decision-making system; sponsored international symposia which have attracted world-authorities in various fields; and cultivated some of the world's most cutting-edge fusion research efforts. All of these efforts by the Institute are expected to have widespread positive effects within Kyushu University, which will help increase KU's overall global recognition.

Thanks to the unceasing effort and dedication of Director Sofronis, I²CNER has created a unique network of research institutes and universities throughout the world. Most notable are the Institute's ongoing interactions with the United States Department of Energy (DOE) and the California Air Resources Board (CARB), among others.

As a world leading energy research institute, I²CNER aims to serve as a hub for accelerating the transition to a carbon-neutral energy society by promoting the circulation of ideas, information, and scientists in the area of energy research; expanding its basic science efforts; and proactively promoting the fusion of disciplines, including mathematics, sociology, and computational science, to create new research domains.

Shunichi Masuda (I²CNER)