Greeting

Prof. Kazuhito Hashimoto
President, NIMS

It is my great pleasure to welcome you to the 20th GREEN International Symposium today.

Our theme for the symposium is environmental and energy issues, which are currently at the top of the international agenda. In Japan, the Council for Science, Technology and Innovation (CSTI) of the Cabinet Office, which I myself am a member of, has developed the National Energy and Environment Strategy for Technological Innovation towards 2050 two years ago.

The strategy selects promising target areas for technology innovation that require concentrated and reinforced research and development efforts, and organizes their impacts and challenges in development toward practical applications and widespread diffusion, thereby drawing up a scenario for deep cuts in greenhouse gas emissions by 2050 through energy saving, creation, and storage.

In the run-up to the formulation of this strategy, GREEN was established in 2009 as a research center within NIMS, as part of the MEXT Project for the Development of Environmental Technology Using Nanotechnology.

The past decade of GREEN represents a departure from the traditional materials development based on empirical rules, and has advanced the development of high-performance devices based on the understanding and control of interfacial phenomena through “coordination of theory and evidence,” with the aim of resolving shared challenges in the flow of energy that begins with sunlight.

By placing an initial priority on outputs such as fuel cells, secondary batteries, photovoltaics, and photocatalysts, and subsequently on lithium-air batteries, solid-state batteries, and perovskite solar cells since 2013, core research seeds have emerged and led to contributions in new national research projects and large-scale research collaborations with companies.

This fiscal year marks the tenth anniversary of GREEN and termination of its projects as government-commissioned projects as of March 2019.

In addition to the guest lectures by three leading scientists in solid-state batteries, perovskite solar cells, and lithium-air batteries, the symposium will consist of a number of oral and poster presentations that summarize the achievements of NIMS GREEN and participating institutions over the past decade.

Based on the achievements of the GREEN projects, we at NIMS hope to further contribute to resolving environmental and energy issues both in Japan and on a global scale, and we appreciate your continued support for our efforts. I sincerely hope that this symposium will build momentum for such efforts through active discussions among participants.

Greeting

Prof. Kohei Uosaki
Director-General of GREEN

Welcome to the 20th GREEN Symposium.

GREEN (Global Research Center for Environment and Energy based on Nanomaterials Science) was established in NIMS in October, 2009 supported by the Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT) as the core research center to carry out a MEXT project of the “Development of Environmental Technology using Nanotechnology” and has been engaged in fundamental research aiming at offering new scientific seeds to solve environmental and energy issues by taking mid- to long-term needs of industry and society into account.

The emphasis of GREEN was placed in understanding and control of interfacial processes of renewable/sustainable energy conversion systems such as fuel cell, secondary battery, and solar cell, by integrating the computational science and the advanced characterization/ measurement techniques. Three specially promoted research teams were established in 2013/2014 to speed up the researches of high social needs, namely “all solid state battery”, “Li-air battery”, and “perovskite solar cell”. They have achieved important results and are now recognized internationally. The former 2 teams play important roles in the MEXT/JST next generation battery project, ALCA-SPRING (https://www.jst.go.jp/alca/alca-spring/en/index.html), and a large-scale collaboration with an industrial partner on Li-air battery was started in April 2018. Perovskite solar cell team developed highly stable cells with world top class durability and is carrying out industrial collaboration.

Since April 2016, the target of the MEXT program was changed from “Development of Environmental Technology using Nanotechnology” to “Integrated Materials Development”, emphasizing the importance of the consideration of devices and systems where the materials to be used in the materials development. “Technology Integration Unit” was established in 0ctober 2016 and joint studies with existing groups and teams to achieve this goal have been carried out.

As GREEN completes its 10 year term at the end of March this year, this symposium was planned to sum up its activities. Achievements of GREEN are presented by oral and poster presentations by GREEN members. Internationally known experts in related fields are invited to give special lectures. Since GREEN’s another important mission is to provide scientists/engineers outside of NIMS with the most advanced equipment and knowledge and know-how of GREEN through open-laboratory system so that R&Ds of nanotechnology based energy and environmental materials in Japan are accelerated, the scientists who conducted open-laboratory research also present their results in the symposium. Researches on energy and environmental materials will be continued to be carried out in Center for Green Research on Energy and Environmental Materials Research (Greater GREEN) after GREEN ends its mission and introduction of all research groups of Greater GREEN are also presented as posters.

I hope this symposium will provide participants with ample opportunity to understand the GREEN’s 10 year activities and for future collaborations with NIMS scientists.

I would like to conclude my greeting by thanking all people who have participated GREEN activities.

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	Research Interest: SOFC, PEFC, Interface design in fuel cells

Design of functional interfaces in Intermediate Temperature Solid Oxide Fuel Cells (SOFCs) of NIMS

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Solid oxide fuel cells (SOFCs) are clean and efficient power source for generating electricity using variety of fuels. Especially, intermediate temperature SOFCs (IT-SOFCs) have attracted considerable attention as promising candidates to establish the GREEN innovation for our next generation. To achieve the radical innovation which is the gate way to GREEN innovation, the performance of SOFCs around 700ºC must be improved by the design of high quality active sites on the interface of the anode by multidisciplinary approach.

In the present work, we carefully observed subtle change of interfacial defect structure in IT-SOFC model material (i.e. doped CeO_2 system). For interpretation of microanalysis results, we performed the bulk and surface atomistic simulation using GULP code. Our combination work suggested the formation of the superstructure which consisted of C-type rare earth like structure in none equilibrium state during device fabrication.[1,2]

On the basis of our microanalysis results and bulk/ surface atomistic simulation data, we tried to design the high quality active sites on Ni with remained oxygen atoms in the anode layer. Then, we successfully created high quality active sites on three-phase boundaries in the anode of IT-SOFC.[3] In my talk, key concept (refer to Table 1) and data are shown in details.

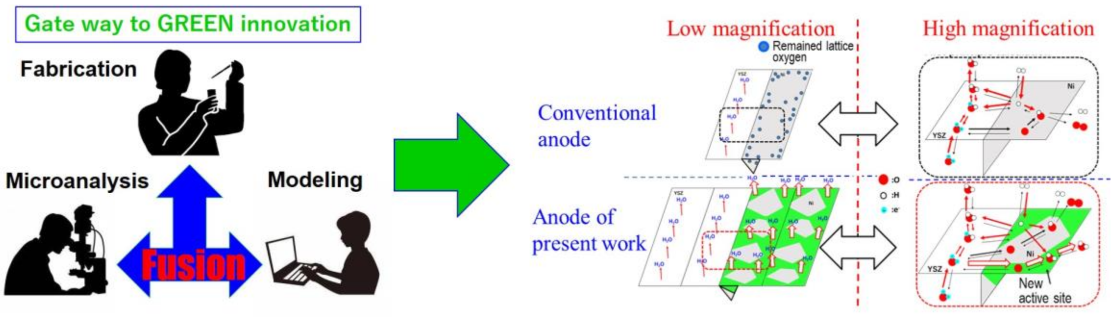

Table.1 Schematic diagram for introduction of research concept and target in the present work.

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Research Interest: electrochemistry, in situ, solid/liquid interfaces

in situ observation of intermediate species of oxygen reduction reaction and future perspective of interfacial analysis techniques

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Ultrathin metal films formed on foreign metal substrates often show very unique electrocatalytic activities for various multielectron transfer reactions. Underpotential deposition (UPD) is a powerful technique to form metal monolayers on a surface of single crystal electrodes with a well-defined atomic arrangement because metal atoms can be deposited on the metal substrate at potentials more positive than the reversible potential of the bulk deposition. For example, a Pd monolayer deposited on a Au(111) surface exhibit a catalytic activity for oxygen reduction reaction higher than bulk Au and Pd surfaces. Here, atomic arrangement and electronic structure of a Pd monolayer deposited on a Au(111) surface during the oxygen reduction reaction has been investigated by in situ surface x-ray scattering (SXS) and polarization-dependent total-reflection x-ray absorption fine structure (XAFS).

Specular rod profiles obtained by crystal truncation rod (CTR) measurements show that Pd atoms occupy the three-fold hollow sites with a coverage of approximately 1. According to the EXAFS oscillation at the Pd K-edge measured at s-polarization, distance of Pd-Pd bonds is estimated to be 2.88 Å which is longer than that of bulk Pd (2.76 Å) but in good agreement with that of bulk Au (2.88 Å). Thus, the pseudo-morphic deposition of the Pd monolayer on the Au(111) surface was confirmed by in situ structural analysis of SXS and XAFS.

Interestingly, not only Pd-Au bonds but also a small contribution of Pd-O bonds were observed in the EXAFS oscillation at the Pd K-edge measured at p-polarization, suggesting the adsorption of oxygenated species such as water, hydroxide groups, oxygen or intermediate species of oxygen reduction reaction. A peak corresponding to the super-structure of adsorbed oxygen was observed in the surface x-ray diffraction (SXRD) measurements. A similar peak was also observed at the Pt(111) surface during the oxygen reduction reaction and its intensity is indeed proportional to the cathodic current density for oxygen reduction reaction. Such substantial correlation between the current density and peak intensity suggest that the super-structure is an intermediate species of oxygen reduction reaction.

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Research Interest: electrochemistry, battery, fuel cell

Li Metal Anode for Next Generation Batteries

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Rechargeable batteries with high energy and power densities have been strongly required for electric vehicle and smart power grid applications. When using electric power generated in thermal power plant, LCA (Life Cycle Assessment of CO_2) of electric vehicles (EVs) is not so good. The electric vehicle with 80 kW h battery produces larger amount of CO_2 than that from vehicle with a thermal engine, because of CO_2 generation from battery production. Therefore, the CO_2 production from battery production should be reduced. By the way, another important point for rechargeable batteries is a cost of cell. The cost of battery is now very high. In fact, EVs is more expensive than standard vehicles. The cost of battery has to be reduced. Both CO_2 production and cost of rechargeable batteries partly depend on material cost, especially cathode and anode materials. When both cathode and anode materials have a larger capacity density (A h g^{-1}), practical cell cost can be reduced. The cost of battery is not per g, but is per A h g^{-1}. By using materials with larger capacity densities, the cost of cell can be reduced. The production of CO_2 is also reduced by using active materials with larger capacity density. This means that the energy density of cell is strongly related to both CO_2 production and cell cost. Therefore, the energy density of rechargeable batteries should be increased for future batteries. In the next generation batteries, high capacity density anode and cathode should be utilized to realize high energy density of cell. Li-sulfur, Li-air and Li-metal batteries contains higher capacity density cathode and anode. Especially, the anode in these batteries is Li metal. Li metal has 10 times larger capacity density than that of graphite. However, Li metal has some problems as anode material. The most serious problem is a formation of dendrite shape Li metal during charging process. The dendrite deposition of Li metal is strongly related to current distribution and surface film on Li metal. In order to realize uniform current distribution, the porous nature of cathode and separator should be precisely controlled by uniform porous structure. In addition, the surface film on Li metal anode have to be controlled to obtain more uniform nucleation and crystal growth of Li metal. In this study, three dimensionally ordered macroporous (3DOM) separator was employed to establish a highly uniform current distribution in the cell and a proper selection of electrolyte was conducted to improve stability and uniformity of the surface film on Li metal. Both effects provided an extremely stable discharge and charge performance. In fact, the symmetrical Li/3DOM separator/Li cell with ethylene carbonate based concentrated electrolyte exhibited reversible behavior more than 3000 cycles. This technology can be applied to next generation batteries. However, the proper electrolyte selection is a problem, because of cathode which requires a different kind of electrolyte in case.

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Strategies for Next Generation High Energy Batteries

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Many different approaches are pursued for next generation energy storage materials and technologies. Among the different materials, Li metal is a key electrode material for developing high energy batteries with a specific energy much higher than 300 Wh kg^{-1}. Despite of intensive efforts, significant challenges remain in direct utilization of Li metal anode in realistic high energy cells. This talk will summarize our current understanding of the scientific and technological challenges, discuss recent progress and propose potential directions based on a high-energy cell design, fabrication and testing. The fundamental relationship between the Li anode and other cell components, especially electrolytes, is explored at the cell level in order to inspire more new ideas to effectively address the grand challenges in high energy Li cells.

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High-throughput combinatorial screening of multi-component electrolyte additives to improve the performance of Li metal secondary batteries

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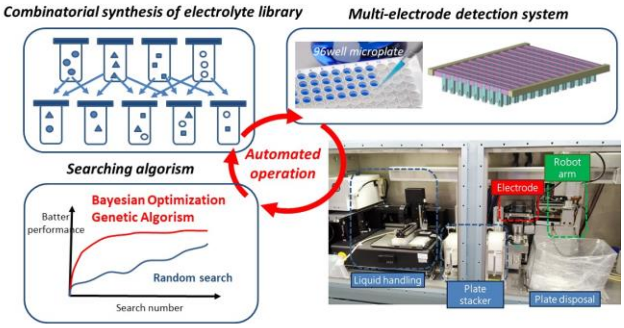
Data-driven material discovery has recently become popular in the field of next-generation secondary batteries [1,2]. However, it is important to obtain large, high quality data sets to apply data-driven methods such as evolutionary algorithms or Bayesian optimization. Combinatorial high-throughput techniques are an effective approach to obtaining large data sets together with reliable quality [3,4]. The application of such methods for searching electrolyte composition of lithium batteries is very much limited, due to difficulties in simultaneously performing automated sequential electrochemical operations based on robotics engineering together with big-data processing and highly sensitive analyses. Automated sequential electrochemical operation is essential so as to obtain data sets that are sufficiently large to allow the use of various data-driven methods.

In the present study, we developed a combinatorial high-throughput system with a screening rate of 400 samples/day, specialized for the evaluation of lithium battery components. Using this system, a specific combination of five chemical compounds was identified that improved the CE value during lithium deposition/stripping cycles. Analyses of the SEI film formed in this new electrolyte showed large amounts of lithium fluoride and lithium organic compounds that are known to enhance CE. Importantly, the CE was greatly decreased simply by the lack of one of the five additives, suggesting the cooperative effect of the five compounds. The results obtained in the present study confirm that the utilization of this HTB-system can accelerate the discovery of improved electrolyte compositions. While it is time-consuming or even unrealistic to find ideal combinations of multiple additives using a traditional bottom-up approach, the technique presented herein efficiently identifies complex electrolytes that can lead to superior lithium battery performance.



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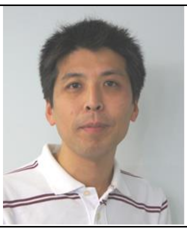

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Research Interest: photovoltaic devices

Recombination routes of the free carriers in Perovskite solar cells revealed by Impedance Spectroscopy

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Perovskite PV materials are unique polycrystalline semiconductors that can be deposited on surfaces using low-temperature solution-process to achieve high efficiencies with high open circuit voltage (Voc) over 1.2 V. We have developed Cl-mediated interdiffusion method and MACl annealing strategies to achieve high quality perovskite absorber layers, giving high efficiency and stability to the perovskite solar cells. The stable devices allowed us to study details of the working mechanism of devices under various bias voltage (V) and light power (P) conditions. From the impedance analysis in the (V, P) space, we suggest that the dynamics inside perovskite consist of two parts; the migration of mobile ions/vacancies and their capturing the free carriers at the boundary, and a classical diode involving the migration and recombination of free carriers. We show that the deep understanding of the lead halide perovskite and interface materials leads to the development of highly durable devices.

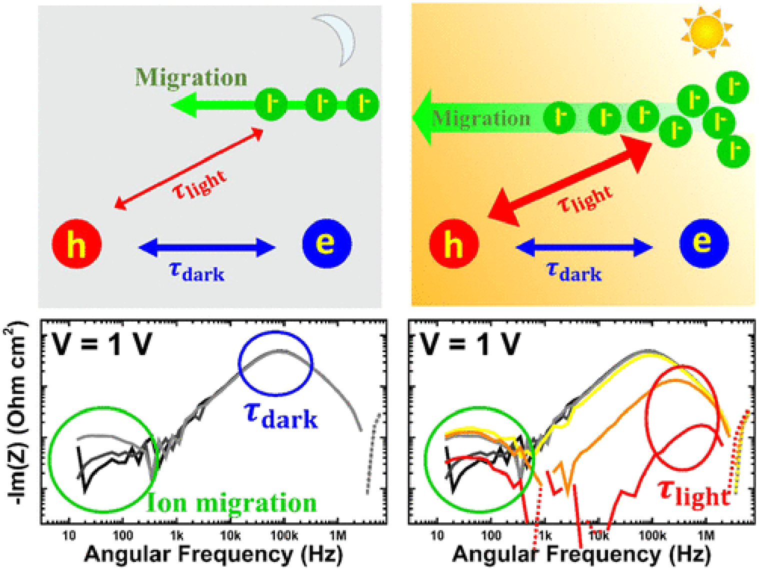

Figure 1. The voltage (V) and light-power (P) dependences of electrochemical impedance spectroscopy curves of perovskite solar cells.

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Research Interest: Perovskite solar cells, Dye sensitized solar cells

Co-additive engineering of perovskite layer for efficient and stable Sn perovskite solar cells

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Recently, Sn-based perovskite solar cells (PSCs) have attracted much attention as an alternative of toxic Pb-based PSCs. Though, the Sn-based perovskites show similar or even superior photovoltaic properties in compare with Pb-based perovskites, but the Sn-based PSCs show inferior device performance. This is because uncontrol crystallization rate of Sn-based perovskite films and facial tendency to Sn^{2+} oxidation. Diverse approaches have been proposed to enhance the performance of Sn-based PSCs by improving the film morphology or retarding Sn^{2+} oxidation [1]. We have demonstrated a co-additive engineering to simultaneously enhance the film morphology and retard Sn2+ oxidation by using hydrazinium chloride (N_2H_5Cl) as co-additive [2]. Recently, we have performed another co-additive engineering by using long carbon chain organic additive with bifunctional groups (i.e. 5-ammonium valeric acid iodide (5-AVAI)) to simultaneously improve the perovskite crystallinity and stability [3]. We observed that 5-AVAI affects the crystal growth of perovskites through its hydrogen bond with I^- of the SnI_6^{4-} octahedral and also form a protective layer on the surface of perovskite films. This made us able to enhance the PCE for Sn-based PSCs up to 7% in a 0.25 cm^2 aperture area. The 5-AVAI added PSCs showed high stability and maintained their initial PCE under 1 sun continuous illumination at maximum power point tracking for 100 h.

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Evolution of Efficient and Stable Perovskite Solar Cells

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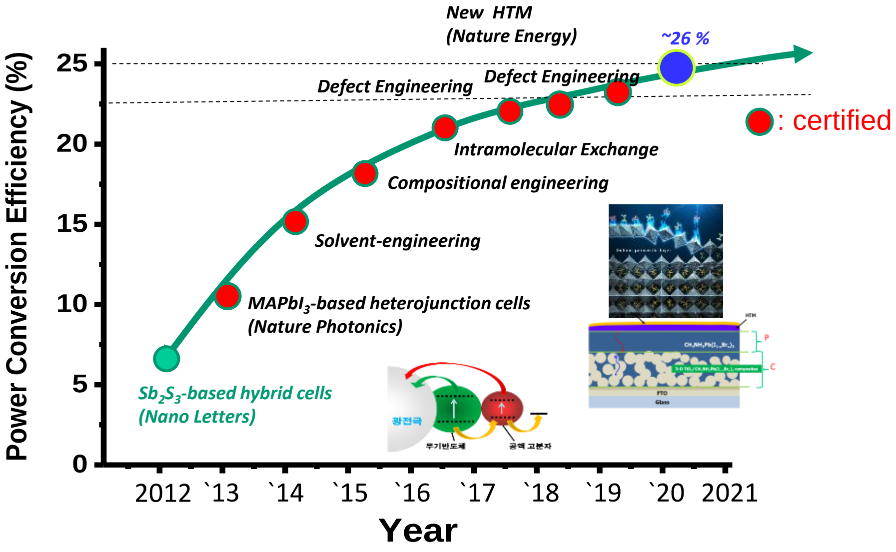
A long-standing dream in solar energy conversion is to fabricate solar cells of satisfying high-efficiency and long-term stability at low cost. In order to realize such a dream, we have long studied inorganic-organic hybrid solar cells that combine Sb_2S_3 as a light absorber and a polymeric hole conductor. After that, we have used inorganic-organic halide perovskite in place of Sb_2S_3, and as a high-efficiency perovskite solar cell, we have proposed a so-called bi-layer architecture consisting of nanostructured TiO_2 impregnated with perovskite and a thin perovskite layer on top. Since then, we have continuously improved efficiency through various fabrication processes including solvent engineering, compositional engineering and defect engineering etc. In addition, as far as the fabrication of perovskite solar cells by the solution process is concerned, it is necessary to consider not only the chemical factors of the precursor solution but also the physical properties of the coating solution such as viscosity, evaporation rate of solvents, the wettability and penetration onto substrates. This property requires an understanding of the precursor chemistry of the solution. In this presentation, I will introduce the evolution of perovskite solar cells based on our results.



Our progress in inorganic-organic hybrid solar cells

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Solid State electrolytes for Lithium Batteries, Materials, Synthesis and Applications

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All-solid-state lithium secondary batteries are considered to eliminate safety problems caused by flammable organic electrolyte in conventional commercial LIBs. The solid electrolyte membrane is essential to separate the lithium anode from redox mediators added aprotic Li-O_2 batteries, to suppress the internal “shuttle” phenomenon in Li-S batteries which decreases the active mass utilization and reduces the coulombic efficiency. In addition, the use of solid electrolyte also benefits the elimination of growth and penetration of lithium dendrite in the lithium batteries. New materials are being sought for next-generation batteries to provide higher energy density and lower cost factors comparing to conventional LIBs, such as solid lithium ion, Li-air and Li-S batteries. This review will focus on the materials design, fabrication and their use in the lithium metal-based batteries. A composite electrolyte based on the garnet structured oxide matrix and strategies to densify the ceramics are realized. Morphology, density and mechanical strength of the composite are all greatly enhanced compared to the pristine electrolyte. Furthermore, a novel two-step sintering strategy is applied to prepare Li-Garnet ceramics which involves one short-time high-temperature sintering process and one long-time low-temperature annealing process, effectively promote the densification and uniformity of the ceramics. Besides, LATP and Li_3N are also fabricated with modified routes. Li-S and lithium ion batteries consisting of Li metal anode and the above ceramic electrolytes exhibit good capacity, coulombic efficiency and improved cyclability, demonstrating positive effects of solid electrolytes in high energy density batteries.

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Research development of all solid-state batteries by using thin film technology

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Interface properties are essential in solid-state batteries. When battery materials are combined into a solid-sate battery, various kinds of interfaces are formed, and these play critical roles in determining the battery performance. Thin film synthesis of battery materials is an effective approach to investigating the interface properties, since it simplifies the interface geometry and provides important information about the interface.

Pulsed laser deposition (PLD) is used to form thin films of multication oxides since the deviation in composition between the solid target and the thin film is relatively small compared with other physical vapor deposition methods. However, even the PLD grown thin films often show somewhat different properties, usually degraded, from those of bulk single crystals by the inclusion of lattice defects in many cases caused by the composition deviating from stoichiometry. We use PLD to grow highly crystalline epitaxial thin films of a cathode material: $LiCoO_2$ [1-7].

Sputtering is widely used to form wide area thin films including battery materials with high deposition rate. We use sputtering to form amorphous thick films of an oxide solid electrolyte: Li_3PO_4. We use thermal evaporation to form metal Li film as an anode material.

I will talk about various properties of each film and show some battery performance of the samples consist of these films.

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Research Interest: Catalytic reaction, Excited-state dynamics

Theoretically inspired new catalyst: boron nitride with gold

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Recent advances in theoretical and computational chemistry have made it feasible to contribute to a design of new materials through a strong collaboration with experiment. In this talk, our recent research on theoretically inspired new catalyst, boron nitride with gold, is introduced. The main idea is that even catalytically inactive or completely inert materials can be functionalized at the nanoscale via the size, structure, morphology, and support effects. Oxygen reduction reaction (ORR) is a key process in fuel cells, and the most efficient catalysts for ORR are based on platinum. There are growing a lot of interests to develop non-platinum catalysts. As a totally new material, we focused on hexagonal boron nitride (h-BN), which is catalytically inert insulator with a wide band gap. Through theoretical consideration and computations, we examined the possibility to functionalize h-BN as an electrocatalyst for ORR, and discovered that the nitrogen doping or deposition of the BN nanosheets on some transition metals can make h-BN to be catalytically active [1]. Following theoretical suggestions, Uosaki group did the experiment, and succeeded in proving the ORR catalytic activities of h-BN on Au electrodes [2]. This is a valuable example of a success of theoretical suggestion and experimental proof in developing new materials. This success has inspired new experiments to increase the ORR activity by introducing gold nanoparticles on BN/Au, and to show the catalytic activity of h-BN/Au for hydrogen evolution reaction. Our finding has also stimulated the community in a research field of catalysis [3].

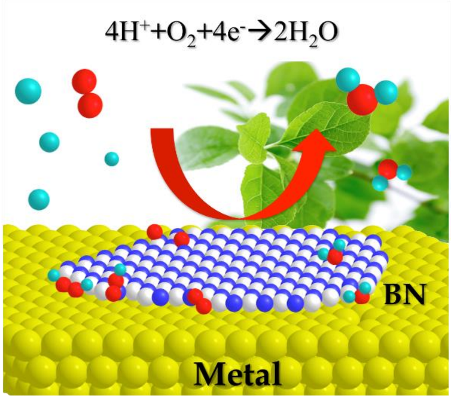

Figure 1. h-BN/Au works as catalyst for ORR.

Reference: [1] Lyalin, A.; Nakayama, A.; Uosaki, K.; Taketsugu, T. *Phys. Chem. Chem. Phys.* **2013**, *15*, 2809. [2] Uosaki, K.; Elumalai, G.; Noguchi, H.; Masuda, T.; Lyalin, A.; Nakayama, A.; Taketsugu, T. *J. Am. Chem. Soc.* **2014**, *136*, 6542. [3] Lyalin, A.; Gao, M.; Taketsugu, T. *Chem. Rec.* **2016**, *16*, 2324.

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Research Interest: Electrochemical Energy Conversion, Surface Physical Chemistry

GREEN 2009 - 2018: Towards Understanding and Control of Interfacial Processes, Common issues in Energy Flow from Solar Energy, Utilizing Computational Science and Advanced Measurements

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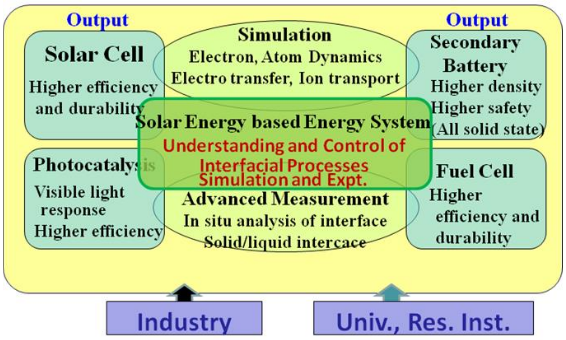
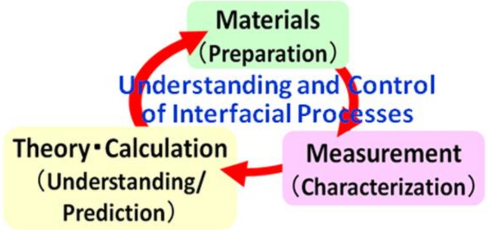
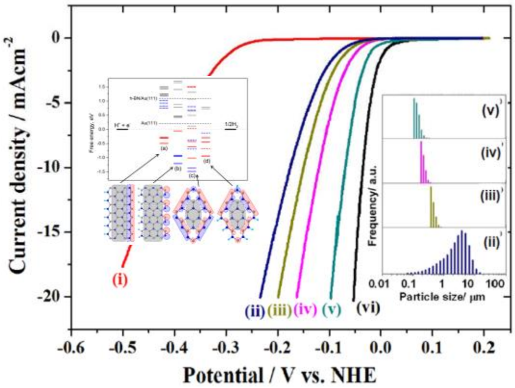
The GREEN’s target was set as understanding and control of interfacial processes, which are the common issues of solar energy based energy systems such as fuel cell, secondary battery, photocatalysis, and solar cell, and by integrating the computational science and advanced measurement techniques so that materials development can be carried out rationally and more effectively. Since most of the interfaces involved are of solid/liquid interfaces, techniques using electron cannot be used and various in situ methods are developed.[1] Several examples new developments will be presented.





Theoretical calculations are often used to understand and explain experimental results but are rather rare to predict results and propose new materials. We have predicted theoretically and proved experimentally that boron nitride, an insulator, nanosheets (BNNS) works as electrocatalyst for oxygen reduction reaction (ORR)[2-4] and hydrogen evolution reaction (HER).[5] This approach paved a new way to develop novel electrocatalysts.



LSVs at (i) bare Au, (ii-v) BNNS of various size shown in the inset/Au, and (vi) bare Pt in Ar sat 0.5 M H_2SO_4 solution.

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