



RESEARCH ACTIVITIES

Materials Molecular Science

Extensive developments of new functional molecules and their assemblies are being conducted in three Divisions of Electronic Structures, Electronic Properties, and Molecular Functions, and one division for visiting professors and associate professors, in an attempt to discover new phenomena and useful functions. The physical (electric, optical, thermal and magnetic) properties on new functional materials, the chemical properties like enzymes, catalysis and photochemistry, the exploitation of new spectroscopic methods for materials molecular science, and technological applications like batteries, photocatalysts, fuel cells, solar cells and field effect transistors are investigated in this department.

Exploitation of Novel Spectroscopic Methods for Material and Surface Science

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1994 Lecturer, The University of Tokyo
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Keywords

X-Ray Absorption Spectroscopy, Surface & Thin Film Magnetism, Ambient Pressure Hard X-Ray Photoelectron Spectroscopy

For the developments of novel functional materials, it is quite important to exploit simultaneously new analytical methods based on advanced technology. Novel materials and devices often require spatial and/or time resolved analysis to optimize their qualities. In our group, we have been exploiting spectroscopic methods for material and surface science using mainly synchrotron radiation (SR) and partly lasers.

The first subject in our group is the spectroscopic analysis systems of magnetic thin films. In 2006, we successfully invented a novel magnetic nanoscope using ultraviolet magnetic circular dichroism (UV MCD) photoelectron emission microscopy (PEEM), which allows us to perform real-time and ultrafast magnetic imaging to investigate magnetic dynamics. We have also constructed *in situ* x-ray magnetic circular dichroism (XMCD) system using an ultrahigh vacuum superconducting magnet and a liq. He cryostat, which is installed at Beamline 4B of the IMS SR facility UVSOR-III. The XMCD measurement system contains ultrahigh vacuum sample preparations chamber, with which one can clean substrates (substrate single crystals *etc.*), deposit materials (metallic and molecular magnets *etc.*) and characterize the samples using low energy electron diffraction, reflection high energy electron diffraction and Auger electron spectroscopy. The apparatus is extensively open for public usage and many domestic and foreign researchers visit us every year.

The second subject is the exploitation of ambient pressure hard x-ray photoelectron spectroscopy (HAXPES) for polymer

electrolyte fuel cells (PEFC) under working conditions. Although usually photoelectron spectroscopic measurement is done under ultrahigh vacuum, recent material science requires ambient pressure measurements under working conditions. In 2017, we succeeded in real ambient pressure (10^5 Pa) HAXPES measurements for the first time using Beamline 36XU of SPring-8. This work is supported by the NEDO Fuel Cell project.

The third subject is the pico- and femtosecond pump-and-probe time resolved measurements using x-ray. Time-resolved x-ray absorption fine structure spectroscopy of photocatalysts WO_3 and BiVO_4 was performed and we have investigated those local geometric and electronic structures. Time-resolved measurement can be also applied to investigate the dynamics of magnetic materials with XMCD and other magneto-optical effects. We captured XMCD spectra of the photoinduced transient state. The real space image of magnetic domains can be retrieved from the diffraction patterns. We succeeded in capturing diffraction from magnetic domains and now considering the possibility of its application for time- and space-resolved imaging.

Within two years, two assistant professors Drs. Takagi and Uemura moved out and new assistant professors Drs. Koitaya and Yamamoto have joined our group. We will further perform surface physics and chemistry researches for materials science including methodological exploitation using synchrotron radiation and lasers.

Selected Publications

- T. Nakagawa *et al.*, *Phys. Rev. Lett.* **96**, 237402 (2006).
- T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **107**, 065901 (2011).
- M. Dabrowski *et al.*, *Phys. Rev. Lett.* **113**, 067203 (2014).
- Y. Uemura *et al.*, *Angew. Chem., Int. Ed.* **55**, 1364 (2015).
- Y. Takagi *et al.*, *Appl. Phys. Express* **10**, 076603 (2017).
- Y. Uemura *et al.*, *Chem. Commun.* **53**, 7314 (2017).

1. Operando Observation of Sulfur Species Poisoning PEFC Studied by Near Ambient Pressure HAXPES¹⁾

PEFC is currently one of the most promising electrochemical energy conversion and storage technology. To achieve more highly efficient PEFC with longer life time, a continuous supply of more powerful materials and a further detailed understanding of the electrochemical properties of PEFC are essentially important. We have been investigating the degradation and poisoning mechanisms of PEFC using near ambient pressure *operando* HAXPES of PEFC under working conditions. We will here emphasize that the electric potentials of all chemical species in PEFC can be determined by HAXPES measurements and allow us to distinguish the location of the specimen; whether the S-containing species in PEFC is adsorbed on the electrode or solved in the electrolyte *etc.* In this work, we performed S 1s HAXPES measurements to observe sulfur species poisoning the PEFC cathode and anode electrodes, C-supported Pt nanoparticles in PEFC. Without artificial introduction of S-containing species, we observed several S species other than sulfonic acid group of Nafion: Anionic atomic S species adsorbed on the Pt nanoparticles, SO_3^{2-} in the electrolyte, and S in the C support. As a voltage applied between the cathode and anode increases, the adsorbed S species on the Pt nanoparticles at the cathode electrode are gradually diminished and completely disappear at ≥ 0.8 V due to oxidation reactions from adsorbed S to SO_3^{2-} and possibly SO_4^{2-} , but is reproduced with a decrease in the voltage. With oxygen introduction to the cathode electrode, no sulfur species except sulfonic acid group of Nafion were detected even at the lowest voltage. Schematic electric potential diagrams of the cathode, electrolyte and anode are depicted. Upon the voltage change, the electric double layer varies on the cathode, while it is kept constant (~ 1.0 V) on the anode. It is emphasized that the electric potentials of the chemical species observed by HAXPES can distinguish the location of the specimen; the SO_3^{2-} species is found not to be adsorbed on the electrode but to be solved in the electrolyte.

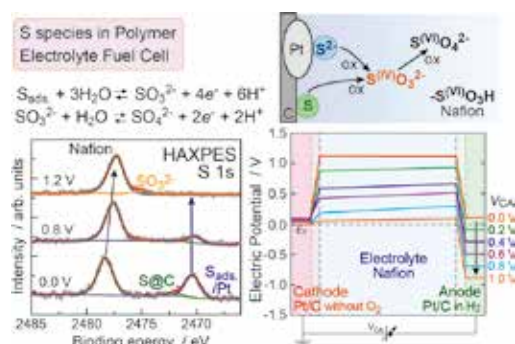


Figure 1. Various sulfur species observed in working PEFC that poison the electrode Pt nanoparticles. It is most important to note that HAXPES can determine the electric potentials of the electrolyte as well as the electrodes that are impossible fundamentally by any conventional electric method as probe contact *etc.*

2. Operando Observation of Methane Oxidative Coupling on Pd(110) by Soft X-Ray Ambient Pressure XPS

Chemical transformation of methane to valuable chemicals is an attracting but challenging research topic. Activation of inert methane molecules on metal or metal-oxide surfaces is an important process for catalytic conversion. In order to reveal reaction mechanisms of weakly adsorbed methane, spectroscopic measurements under ambient pressure condition are indispensable because of a small reactive sticking probability of methane. In this study, the oxidative coupling of methane to ethane on Pd(110) was investigated by ambient pressure soft x-ray photoelectron spectroscopy (XPS) and quadrupole mass spectroscopy (QMS). Figure 2(a) shows the QMS signal of produced ethane and the sample temperature as a function of elapsed time. The sample was exposed to 2.0 mbar O_2 and 5.7 mbar CH_4 throughout the entire experiment. The sample was first heated to 615 K (I). At this point, the reactivity of the sample was low, and the amount of produced ethane is negligible. The reactivity was significantly enhanced by temporary heating to 780 K. The produced ethane was clearly detected by QMS after cooling to 615 K (II). Figure 2(b) shows Pd 3d AP-XPS spectra at 615 K measured before and after heating the sample to 780 K. Observed three peaks were attributed to Pd oxide (PdO), oxygen-adsorbed Pd ($\text{O}_{\text{ad}}\text{-Pd}$), and metallic Pd (Pd). The relative intensity of the $\text{O}_{\text{ad}}\text{-Pd}$ and Pd peaks was increased after heating to 780 K, indicating partial reduction of the PdO thin film formed on Pd(110). These results show that the reactivity of Pd(110) significantly depends on the oxidation state of the surface; partially reduced PdO–Pd(110) is active for the methane oxidative coupling reaction.

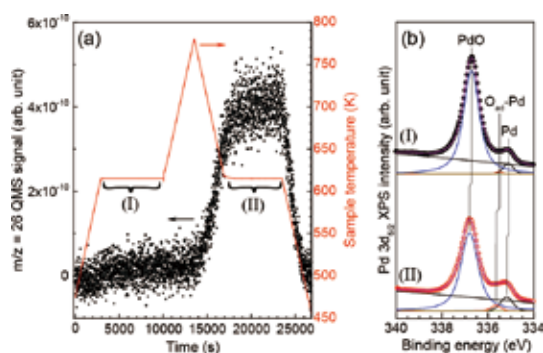


Figure 2. (a) The QMS signal of produced ethane ($m/z = 26$) and the sample temperature as a function of elapsed time. The Pd(110) sample was heated and cooled in the presence of 2.0 mbar O_2 and 5.7 mbar CH_4 gas mixture. AP-XPS measurements were performed at 615 K (I) and (II). (b) Pd $3d_{5/2}$ AP-XPS spectra ($h\nu = 1100$ eV) measured (I) before and (II) after heating the sample to 780 K. The sample temperature was kept at 615 K during the AP-XPS measurements.

Reference

- 1) L. Yu *et al.*, *J. Phys. Chem. C* **123**, 603–611 (2019).

* IMS International Internship Program

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Unique Structures, Physicochemical Properties and Quantum Dynamics of Interfacial Water

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Awards

2014 Young Scientist Award, 33rd Annual Meeting of the SSSJ
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2018 CSJ Presentation Award 2018
2018 Encouragement Award, The Spectroscopic Society of Japan
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Keywords Water Molecule, Molecular Spectroscopy, Surface Science

Interfacial water is ubiquitous in nature and plays crucial roles in a variety of disciplines, including physics, chemistry and biology. In such a symmetry-breaking system, not only adsorption geometry but also anisotropic molecular orientation (H-up/H-down configuration) is a key structural parameter that determines unique physicochemical properties of interfacial water systems. Nevertheless, orientation of water molecules, *i.e.* configuration of hydrogens, in the interfacial hydrogen-bond network is extremely hard to investigate with traditional experimental techniques such as electron diffraction, grazing X-ray scattering and even scanning probe microscopy, because hydrogen has only a single electron and responds extremely weakly to the probes of these techniques. Therefore, the determination of molecular orientation of interfacial water has been an experimental challenge.

We have used recently developed heterodyne-detected sum-frequency generation spectroscopy for unveiling molecular orientation of interfacial water system. The remarkable feature of this technique is that $\text{Im}\chi^{(2)}$ SFG spectra ($\chi^{(2)}$: The second-order nonlinear susceptibility) obtained by the hetero-

dyne detection exhibit positive or negative sign for net orientation of OH with hydrogen pointing away (H-up) or toward substrate (H-down), respectively. Thus, the heterodyne-detected $\text{Im}\chi^{(2)}$ SFG has a great advantage for direct observation of water orientation that cannot be investigated through other traditional experimental methods. With this sophisticated molecular spectroscopy technique, we have conducted a series of pioneering research on unique structures and physicochemical properties of hydrogen bonds of interfacial water molecules.

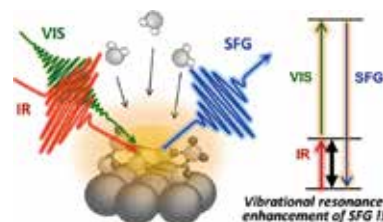


Figure 1. Infrared-visible sum-frequency-generation (SFG) spectroscopy of water molecules on solid surface.

Selected Publications

- T. Sugimoto *et al.*, “Emergent High- T_c Ferroelectric Ordering of Strongly Correlated and Frustrated Protons in Heteroepitaxial Ice Film,” *Nat. Phys.* **12**, 1063–1068 (2016).
- O. Yuji *et al.*, “Unveiling Subsurface Hydrogen-Bond Structure of Hexagonal Water Ice,” *Phys. Rev. B* **96**, 115405 (14 pages) (2017).
- K. Shirai *et al.*, “Water-Assisted Hole Trapping at Highly Curved Surface of Nano-TiO₂ Photocatalyst,” *J. Am. Chem. Soc.* **140**, 1415–1422 (2018).
- N. Aiga *et al.*, “Origins of Emergent High- T_c Ferroelectric Ordering in Heteroepitaxial Ice Film: Sum-Frequency Generation Spectroscopy of H₂O and D₂O Ice Films on Pt(111),” *Phys. Rev. B* **97**, 075410 (21 pages) (2018).
- T. Sugimoto *et al.*, “Topologically Disordered Mesophase at Topmost Surface of Crystalline Ice Between 120 and 200 K,” *Phys. Rev. B* **99**, 121402(R) (2019).

1. Isotope Effects on Emergent High- T_c Ferroelectric Ordering of Strongly Correlated and Frustrated Proton in Ice¹⁾

In the hydrogen-bond network of crystalline water ice, orientation of water molecules, *i.e.* configuration of protons, is strongly correlated and highly frustrated under the Pauling's ice rules. Materials with these constraints have a potential to exhibit dramatic and unusual responses to external stimuli. In fact, we have recently demonstrated that inversion-symmetry breaking at a heterointerface in isotope diluted HDO crystalline-ice film grown on Pt(111) induces high- T_c ferroelectric proton ordering.²⁾ However, the molecular-level origin of the emergent high- T_c ferroelectric ordering has been unclear.

We have tackled this problem to elucidate fundamental physics behind the heterointerface-induced ferroelectric proton ordering in the crystalline-ice film. Because an isotope shift in the critical temperature of ferro-to-paraelectric transition gives essential information about the mechanism of emergent ferroelectric ordering, we have conducted temperature programmed sum-frequency generation (SFG) spectroscopy of H₂O and D₂O ice films on Pt(111). Then, we found that the ferroelectric proton orderings in these films are extremely thermally robust: $T_c = 164$ K (H₂O) and 168 K (D₂O); these are more than twice as large as that of ferroelectric bulk ice XI ($T_c \sim 72$ K for H₂O, $T_c \sim 76$ K for D₂O). The observed small isotope shift in T_c of the ferroelectric ice films is beyond the conventional belief: High- T_c hydrogen-bonded ferroelectrics typically have large isotope shifts in T_c . This result indicates that not only nuclear quantum effects in the hydrogen-bond network of ice film but also the inter-adsorbate and adsorbate-substrate interactions at the ice/Pt interface are responsible for the thermal stability of ferroelectric ordering and its small isotope effect.

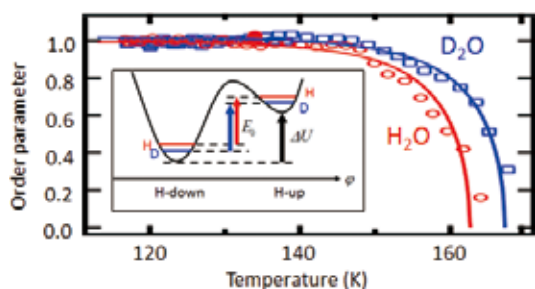


Figure 2. Temperature dependence of the ferroelectric order parameter of crystalline H₂O (red) and D₂O (blue) grown on Pt(111).

2. Unveiling Topologically Disordered Hydrogen-Bond Network at Surface Layer of Hexagonal Crystalline Ice^{3,4)}

The surface of crystalline water ice (hexagonal ice Ih) ubiquitous in nature plays a crucial role in a variety of phenomena in physics, chemistry, biology, geology, atmospheric and astronomical sciences. In 1859, Faraday first proposed that a layer of liquid water (quasi liquid) is present on the surface of crystalline ice below the bulk freezing temperature

of 273 K. Ever since, the nature of ice surface and the onset temperature of surface premelting have been intensely explored. Nowadays it is generally believed that the onset temperature of surface disordering of ice Ih is 200 K and the surface structure of ice Ih is perfectly ordered below this temperature. However, we have demonstrated for the first time that surface disordering of ice emerges at 120 K that is much lower than the traditionally believed premelting temperature of 200 K.

By combining surface-specific SFG spectroscopy and the state-of-the-art molecular dynamics simulations, we found that the topmost surface layer of ice Ih(0001) undergoes a cascade of structural transitions from solid to quasi-liquid phase via a liquid-crystal-like mesophase with a topologically disordered hydrogen-bond network between 120 and 200 K; this is in stark contrast to the traditional concept of premelting of ice surface as well as bulk melting of ice where a single first-order phase transition takes place from solid to liquid state at the melting temperature. Our result sheds new light on the effects of undercoordinated water molecules at the surface on melting behavior of ice and thus advances physics of two-dimensional surface phase transition of molecular crystal.

In addition, our finding casts profound impacts on many disciplines. Since the lower limit of temperature of the earth's atmosphere is ~ 120 K, the surface of crystalline ice Ih on earth is unlikely to be the perfectly ordered solid. The existence of glassy mesophase in the temperature range 120–200 K makes the structural and electronic features of ice surface in nature more inhomogeneous than they have ever been expected. The molecular-level structure and dynamics of ice surface clarified in the present study provide a new basis for elucidating the key properties of ice surface that are of great interest in a variety of heterogeneous processes in nature such as cloud seeding and electrification in atmosphere, catalytic destruction of Earth's ozone layer, and even molecular evolution in interstellar space.

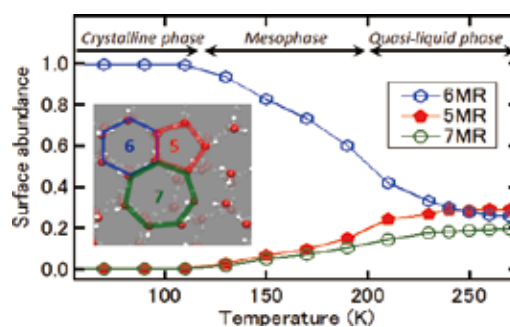


Figure 3. Temperature dependence of relative abundance of 5-, 6- and 7-membered rings at the topmost surface layer of hexagonal crystalline ice-Ih(0001).

References

- 1) N. Aiga, T. Sugimoto, Y. Otsuki, K. Watanabe and Y. Matsumoto, *Phys. Rev. B* **97**, 075410 (21 pages) (2018).
- 2) T. Sugimoto *et al.*, *Nat. Phys.* **12**, 1063–1068 (2016).
- 3) T. Sugimoto, Y. Otsuki, T. Ishiyama, A. Morita, K. Watanabe and Y. Matsumoto, *Phys. Rev. B* **99**, 121402(R) (2019).
- 4) Y. Otsuki, K. Watanabe, T. Sugimoto and Y. Matsumoto, in press.

Magnetic Resonance Studies for Functional Molecular-Based Solids

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Keywords Organic Conductor, Electron Spin Resonance (ESR), Nuclear Magnetic Resonance (NMR)

Magnetic resonance measurements are advantageous for studying fundamental electronic properties and for understanding the detailed electronic structures of molecular based compounds. Developing an understanding of the electronic phases and functionality of these materials enables us to perform systematic investigations of low-dimensional, highly-correlated electron systems and functional materials. Competition between the electronic phases in molecular-based conductors has attracted much attention. The investigations of such electronic phases by magnetic resonance measurements are important to understanding unsolved fundamental problems in the field of solid state physics, and to explore novel functionalities in the field of material science.

In this study, we performed broad-line NMR and ESR measurements on molecular-based conductors to understand electron spin dynamics and functionality in low-temperature electronic phases.

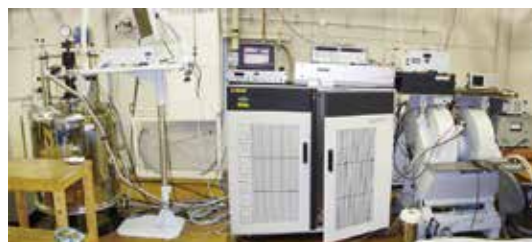
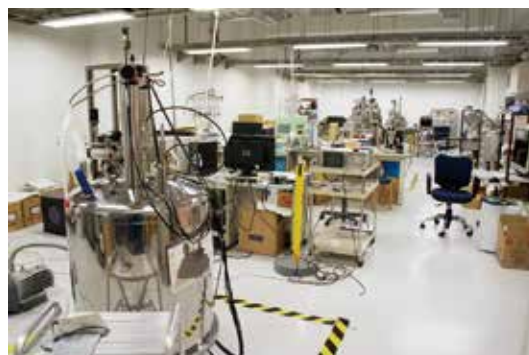


Figure 1. Solid-state broad-line NMR system (above). Multi-frequency pulsed ESR system (below).

Selected Publications

- S. Kitou, T. Fujii, T. Kawamoto, N. Katayama, S. Maki, E. Nishibori, K. Sugimoto, M. Takata, T. Nakamura and H. Sawa, *Phys. Rev. Lett.* **119**, 065701 (2017).
- T. E. Jin, M. Asada, Q. Xu, S. Dalapati, M. A. Addicoat, M. A. Brady, H. Xu, T. Nakamura, T. Heine, Q. Chen and D. Jiang, *Science* **357**, 673–676 (2017).

1. Possibility of Dielectric Material: Magnetic Resonance Study of Oxo-Bridged Dinuclear Ruthenium Mixed-Valence Complex

Solid-state broad line $^1\text{H-NMR}$ (nuclear magnetic resonance) and ESR (electron spin resonance) were performed for an oxo-bridged dinuclear ruthenium $[\text{RuORu}]^{5+}$ ($\text{Ru}^{3.5+}\text{ORu}^{3.5+}$) mixed-valence complex. The $^1\text{H-NMR}$ spin-lattice relaxation rate T_1^{-1} was significantly enhanced, to below 100 K with a peak at approximately 33 K. The T_1^{-1} peak temperature was frequency-independent, indicating that this anomaly is a possible phase transition. Below approximately 40 K, an abrupt decrease of $^1\text{H-NMR}$ spin-spin relaxation time T_2 provides evidence of the appearance of inequivalent ^1H -sites (sudden decrease in symmetry). ESR spectra suddenly disappeared above 35 K. The electronic properties and possible charge ordering ($\text{Ru}^{3+}\text{ORu}^{4+}$) states in this mixed-valence compound are discussed from a microscopic point of view.

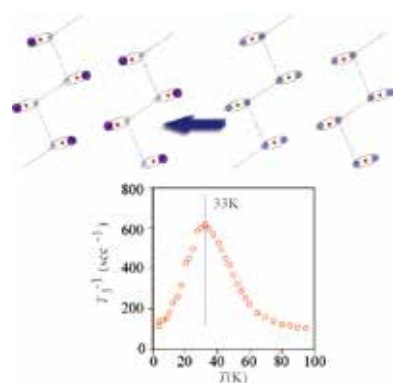


Figure 2. Temperature dependence of the $^1\text{H-NMR}$ spin-lattice relaxation rate T_1^{-1} of the $[\text{RuORu}]^{5+}$ complex. A schematic diagram of the ac -plane: The inter-molecular Ru–Ru interactions between each dinucleus are described here. Possible schematic charge configuration within the ac -plane below 33 K. Color code: Ru^{3+} , dark blue; Ru^{4+} , gray; $\text{Ru}^{3.5+}$, blue; O, red.

2. Effect of Cu Intercalation and Pressure on Excitonic Interaction in 1T-TiSe_2

1T-TiSe_2 has a semimetallic band structure at room temperature and undergoes phase transition to a triple- q charge density wave (CDW) state with a commensurate superlattice structure ($2a \times 2a \times 2c$) below $T_c \approx 200$ K at ambient pressure. This phase transition is caused by cooperative phenomena involving electron–phonon and electron–hole (excitonic) interactions, and cannot be described by a standard CDW framework. By Cu intercalation or the application of pressure, this phase transition temperature is suppressed and superconductivity (SC) appears. However, it is not clear what kinds of order parameters are affected by these two procedures. We investigated the crystal structure of Cu_xTiSe_2 and pressurized 1T-TiSe_2 around the SC state by synchrotron x-ray diffraction on single crystals. In the high-temperature phase, the variation of structural parameters for the Cu intercalation and application of pressure are considerably different. The relationship between the critical points of the CDW phase transition and

the SC dome are also different. The excitonic interaction appears to play an important role in the P – T phase diagram of 1T-TiSe_2 , but not in the x – T phase diagram.

3. Honeycomb Lattice Type CDW Formed by Cooperative Interaction in Cu Intercalated 1T-TiSe_2

1T-TiSe_2 has attracted attention as an excitonic insulator. However, since the phase transition accompanying superlattice peaks has the q -vector connecting the Fermi surfaces of the three-dimensional shape of hole- and electron-pockets, it also suggests the CDW state due to the electron–phonon interaction. In order to understand the electronic state at the low-temperature, the control of chemical potential was attempted by electronic doping by Cu^+ intercalation. It has been found that phase transition occurs as a cooperative phenomenon between the honeycomb lattice type CDW corresponding to the nesting vector and the ordered state of the Cu^+ ions between TiSe_2 layers at a specific doping amount. The behavior of Cu^+ ions in highly doped regions suggests the two-dimensional liquid–solid state transition from the temperature dependence of the x-ray diffuse scattering.

4. Synthesis of a Protected Ribonucleoside Phosphoramidite-Linked Spin Label via an Alkynyl Chain at the 5' Position of Uridin

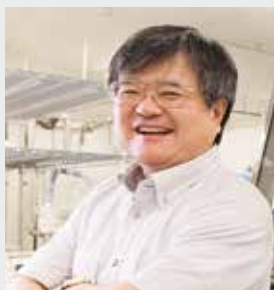
New spin-labeled nucleosides and an efficient synthetic route for the modified uridine amidite were developed. The spin-labeled part was the 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) group, and TEMPO was linked via an alkynyl chain at the 5' position of uridine. Three typical protecting groups, such as the *t*-butyldimethylsilyl (TBDMS) group at 2', the dimethoxytrityl (DMTr) group at 5', and the phosphoramidite group at 3', were introduced to induce an automated nucleic acid synthesizer. The TEMPO group at the 5' position in the uridine structure affected the introduction of the bulky protecting groups, such as the DMTr group at the 5' position and the TBDMS group at the 2' position. The EPR data revealed the presence of a nitroxyl radical in the structure of synthetic nucleoside compounds; however, RNA synthesized by an automated synthesis using TEMPO linked uridine phosphoramidite building block which was protected by TBDMS at 3' and DMTr at 5' was EPR silent.

References

- 1) T. Nakamura, M. Asada, M. Yoshida, M. Kondo and S. Masaoka, *ChemistrySelect* **3**, 10526–10531 (2018).
- 2) S. Kitou, A. Nakano, S. Kobayashi, K. Sugawara, N. Katayama, N. Maejima, A. Machida, T. Watanuki, K. Ichimura, S. Tanda, T. Nakamura and H. Sawa, *Phys. Rev. B* **99**, 104109 (2019).
- 3) S. Kitou, S. Kobayashi, T. Kaneko, N. Katayama, S. Yunoki, T. Nakamura and H. Sawa, *Phys. Rev. B* **99**, 081111(R) (2019).
- 4) A. Hatano, N. Terado, Y. Kanno, T. Nakamura and G. Kawai, *Synth. Commun.* **49**, 136–145 (2019).

Organic Solar Cells

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Education

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Professional Employment

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1988 Research Associate, Osaka University
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Awards

2017 Fellow Award of Japan Society of Applied Physics
2006 Paper award, Molecular Electronics & Bioelectronics division, Japan Society of Applied Physics
2006 Research and Education Award, Osaka University
2004 Editor Award, Japanese Journal of Applied Physics

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Keywords Organic Semiconductors, Organic Solar Cells, ppm-Doping

Organic solar cells have been intensively studied due to many advantages like flexible, printable, light, low-cost, fashionable, etc. We have been focused on the research on the ppm-Level doping effects in organic semiconductor (OSC) films and organic single crystals for organic solar cells. We believe that the following features are indispensable. (i) A ppm-doping strategy should be performed on sub-ppm purified OSCs together with the total removal of oxygen from the air, which acts as an external dopant. (ii) Perfect *pn*-control, namely, any single or blended OSCs should exhibit either *n* or *p*-type behavior only by impurity doping. (iii) To precisely clarify the nature of the doping effects, ppm doping in the bulk of OSC single crystals with few grain boundaries should be performed.

So far, we have reported complete *pn*-control, doping sensitization, ppm-level doping effects using an extremely low-speed deposition technique reaching 10^{-9} nm s⁻¹ (Figure 1), in organic single crystals measured by the Hall effect, which shows a doping efficiency of 24%, and enhancement of

open-circuit voltage of organic solar cells by doping. These results can be regarded as a foundation for the construction of high efficient organic solar cells.

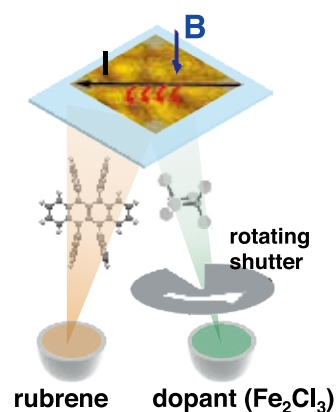


Figure 1. Ultra-slow co-deposition technique to produce the doped rubrene single crystal for Hall effect measurements.

Selected Publications

- M. Hiramoto, M. Kikuchi and S. Izawa, "Parts-per-Million-Level Doping Effects in Organic Semiconductor Films and Organic Single Crystals," *Adv. Mater.* **30**, 1801236 (15 pages) (2018). [Invited Progress Report]
- S. Izawa, N. Shintaku and M. Hiramoto, "Effect of Band Bending and Energy Level Alignment at the Donor/Acceptor Interface on Open-Circuit Voltage in Organic Solar Cells," *J. Phys. Chem. Lett.* **9**, 2914–2918 (2018).
- M. Kikuchi, M. Hirota, T. Kunawong, Y. Shinmura, M. Abe, Y. Sadamitsu, A. M. Moh, S. Izawa, M. Izaki, H. Naito and M. Hiramoto, "Lateral Alternating Donor/Acceptor Multilayered Junction for Organic Solar Cells," *ACS Appl. Energy Mater.* **2**, 2087–2093 (2019).

1. Lateral Multilayered Junction for Organic Solar Cells¹⁾

Bulkheterojunctions (blended junctions) are indispensable for organic solar cells. However, the fabrication of electron and hole transport routes in blended junction remains quite challenging. We proposed a novel concept of the structure of organic solar cell, namely, a lateral alternating multilayered junction (Figure 2). An essential point is that the photo-generated holes and electrons are laterally transported and extracted to the respective electrodes.

Minimum units of proposed junction are hole highway and electron highway. At first, we demonstrated that lateral extraction of photogenerated holes and electrons of the order of 1 mm in the hole and electron highways using ultra-high mobility organic films. Observed macroscopic value of milli-meter order is surprising long compared to the conventional value below 1 μm . Next, we demonstrated the successful operation of organic solar cell having a lateral alternating multilayered junction by combining the hole highway and electron highway. A total of 93% of the photogenerated electrons and holes are laterally collected over a surprising long distance (0.14 mm). The exciton-collection efficiency reaches 75% in a lateral alternating multilayered junction with a layer thickness of 10 nm. Therefore, the lateral junction is proved to have an ability to collect both excitons and carriers almost completely.

A lateral alternating multilayered junction can be regarded to be an alternative blended junction for organic solar cells. Advantage of a lateral cell is its unlimited thickness in the vertical direction. Therefore, tandem solar cells that can utilize the full solar spectrum can be freely designed. The present new concept paves the way to exceed the conversion efficiency of organic solar cells above 20%.

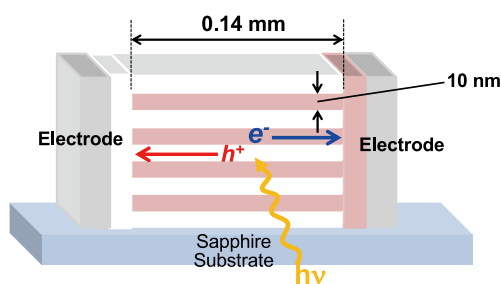


Figure 2. Lateral alternating multilayered junction. Present junction has layer thickness of 10 nm and lateral distance of 0.14 mm, *i.e.*, aspect ratio reaches 1.4×10^4 .

2. Organic *pn*-Homojunction Solar Cell²⁾

Formation of *pn*-homojunction in a single semiconductor material through doping is key for photocurrent generation in inorganic solar cells. In contrast, a donor/acceptor heterojunction is generally utilized in organic solar cells to split coulombically bound exciton forming in organic semiconductors. We reported an organic *pn*-homojunction solar cell showing high internal quantum efficiency of about 30%. *pn*-homojunction was created by co-deposition of *p* or *n* type dopants and an organic semiconductor. An increase of the photocurrent density by more than 8 times, from the undoped device to *pn*-homojunction device with 5% doping, was observed. The increase of photocurrent due to charge separation assisted by the built-in potential near the *pn*-homojunction interface that was controlled by doping concentration (Figure 3). The result demonstrated that the *pn*-homojunction interface in a single organic semiconductor layer formed by doping can achieve efficient charge separation and provide a suitable alternative to the donor/acceptor interface that has been considered necessary for photoconversion in organic solar cells.

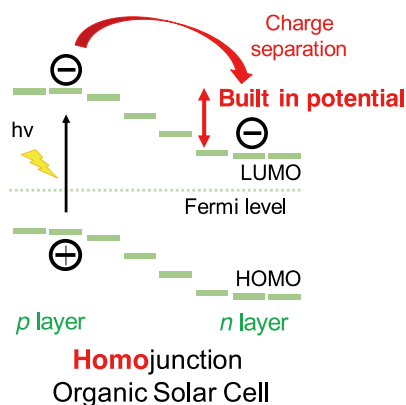


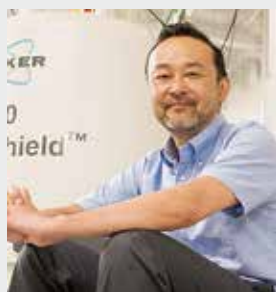
Figure 3. Schematic diagram of the working mechanism of organic *pn*-homojunction solar cells.

References

- 1) M. Kikuchi, M. Hirota, T. Kunawong, Y. Shinmura, M. Abe, Y. Sadamitsu, A. M. Moh, S. Izawa, M. Izaki, H. Naito and M. Hiramoto, *ACS Appl. Energy Mater.* **2**, 2087–2093 (2019).
- 2) S. Izawa, A. Perrot, J. Lee and M. Hiramoto, *Org. Electron.* **71**, 45–49 (2019).

Solid-State NMR for Molecular Science

Department of Materials Molecular Science Division of Molecular Functions



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Education

1994 B.S. Himeji Institute of Technology (University of Hyogo)
1999 Ph.D. Himeji Institute of Technology (University of Hyogo)

Professional Employment

1999 Postdoctoral Fellow, National High Magnetic Field Laboratory, Florida State University
2001 Assistant Professor, Yokohama National University
2006 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies

Award

2002 The Young Scientist Poster Award, The Nuclear Magnetic Resonance Society of Japan

Member
Secretary
YOKOTA, Mitsuyo

Keywords Solid State NMR, Biomolecules, Developments

In order to elucidate functions of molecules, characterization of the molecule is the first step. There is a variety of important molecules, which are insoluble in any solvents and functional at amorphous state. Solid-state NMR enables us to obtain a variety of information at atomic resolution without damage to molecules and significant restrictions. Thus, solid-state NMR is one of the essential tools for the characterization of those molecules.

We have been working on methodology and hardware developments of solid-state NMR and their application to structural biology and materials science. We study characterization of membrane proteins and peptides, organic materials, natural products and synthetic polymers. Characterization of those molecules based on solid-state NMR is underway through collaborations with several research groups.

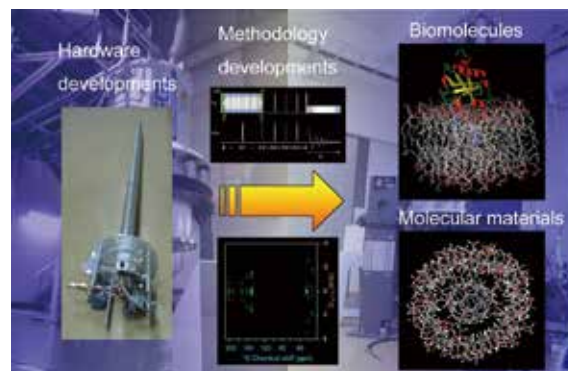


Figure 1. Outline of our studies.

Selected Publications

- N. Uekama, T. Aoki, T. Maruoka, S. Kurisu, A. Hatakeyama, S. Yamaguchi, M. Okada, H. Yagisawa, K. Nishimura and S. Tuzi, "Influence of Membrane Curvature on the Structure of the Membrane-Associated Pleckstrin Homology Domain of Phospholipase C- δ 1," *Biochim. Biophys. Acta, Biomembr.* **1788**, 2575–2583 (2009).
- T. Iijima and K. Nishimura, " ^2H Quadrupolar Carr-Purcell-Meiboom-Gill NMR for Paramagnetic Solids," *Chem. Phys. Lett.* **514**, 181–186 (2011).
- K. Yazawa, F. Suzuki, Y. Nishiyama, T. Ohata, A. Aoki, K. Nishimura, H. Kaji and T. Asakura, "Determination of Accurate ^1H Positions of Alanine Tripeptide with Anti-Parallel and Parallel β -Sheet Structures by High Resolution ^1H Solid State NMR and GIPAW Chemical Shift Calculation," *Chem. Commun.* **48**, 11199–11201 (2012).
- M. Tanio and K. Nishimura, "Intramolecular Allosteric Interaction in the Phospholipase C- δ 1 Pleckstrin Homology Domain," *Biochim. Biophys. Acta, Proteins Proteomics* **1834**, 1034–1043 (2013).
- M. Yagi-Utsumi, K. Kato and K. Nishimura, "Membrane-Induced Dichotomous Conformation of Amyloid β with the Disordered N-Terminal Segment Followed by the Stable C-Terminal β Structure," *PLoS One* **11**, 0146405 (10 pages) (2016).
- N. Ousaka, F. Mamiya, Y. Iwata, K. Nishimura and E. Yashima, "'Helix-in-Helix' Superstructure Formation through Encapsulation of Fullerene-Bound Helical Peptides within a Helical Poly(methyl methacrylate) Cavity," *Angew. Chem., Int. Ed.* **56**, 791–795 (2017).

1. Characterization of Fluorinated Synthetic Polymer Based on Solid-State NMR¹⁾

We have collaborated with a research group of Prof. Hiroki Fukumoto in Ibaraki university for the characterizations of fluorinated polymers newly designed in his group. Molecular design of polyaromatic hydrocarbons with fluorine unit is one of the central themes in investigation of functionalized organic materials such as *n*-type organic semiconductors and polymers for electronic devices. They have successfully developed new schemes of synthesis and copolymerization of fluorinated phenanthrene derivatives with hydroxyl groups based on the Mallory reaction using commercially available octafluorocyclopentene (OFCP). Since final polymers are insoluble in any organic solvents, we have utilized solid state NMR to characterize a polymerization state of this compound.

¹⁹F possesses as large a gyromagnetic ratio as ¹H. Therefore, ¹⁹F-X hetero-, and ¹⁹F homonuclear dipolar couplings are as large as those for ¹H. In order to observe ¹³C spectra in the presence of ¹⁹F, it is essential to decouple ¹⁹F during ¹³C detection, which requires a ¹H-¹⁹F-¹³C triple resonance probe. Since a ¹⁹F resonance frequency is very close to that for ¹H, it is usually difficult to isolate ¹H and ¹⁹F channels well. Therefore, although a ¹H-¹⁹F-X triple resonance probe is commercially available, it is commonly significantly expensive and their performances are limited. In addition, we do not possess such a probe. In order to overcome those problems, we have used high-speed magic angle spinning (MAS) techniques to attenuate ¹⁹F homonuclear- and ¹⁹F-¹³C heteronuclear dipolar couplings as much as possible.

¹³C observed solid-state NMR measurements for all the raw materials and polymers were carried out at spinning speed of 20 kHz using a ¹H-¹³C-¹⁵N triple resonance probe with an outer diameter of 2.5 mm at the ¹H-¹³C double resonance mode. ¹³C solid-state NMR spectra for the raw materials exhibited quite sharp signals, suggesting homogeneous local structures. In contrast, those for polymers showed broad signals, suggesting inhomogeneous local structures. Unfortunately, 2D correlation experiments were unable to be performed due to low sensitivity to the polymers. Only ¹³C signals for the carbons directly attached to fluorine disappeared due to the strong ¹³C-¹⁹F heteronuclear dipolar couplings. However, most of the observed ¹³C signals were successfully assigned based on a variety of 1D NMR spectra in combination of spectral editing techniques. Based on those analyses, the polymerization state of fluorinated phenanthrene derivatives was successfully characterized.

In addition, we have been working on collaboration work with two other research groups for the characterization of newly designed materials based on solid-state NMR.

2. Development of Solid-State NMR Probe

We have built a variety of solid-state NMR probes such as static and MAS probes for 400 MHz NMR, and a variable temperature MAS probe for 920 MHz ultra-high field NMR so far. Most of these probe buildings were achieved through major modifications of commercial probes. Since last year, we have been working on building an original solid-state NMR

probe which is fully compatible with commercial instruments currently used. Probe developments enable us to reduce costs for acquiring probes and open up possibilities to design new experiments which are tightly related to specifically designed hardware. Currently, we are building a solid-state ¹H-X double resonance MAS probe. It will be extended to triple resonance probes for ¹H-¹³C-¹⁵N. In the near future, we would like to incorporate special functions into our original probes.

3. Structural Characterization of Amyloid β Protein Oligomer Promoted on Lipid Bilayers Using Solid-State NMR

Amyloid β (A β) protein is disordered in solutions under diluted conditions, however it conforms insoluble amyloid fibrils, which are found in senile plaque as a hallmark of Alzheimer's disease. Although molecular structures of amyloid fibrils have been determined, its molecular process for fibrillation in vivo has not been clarified yet. However, accumulated evidences suggest that the fibrillation process may be promoted on neuronal cell membrane. Especially, it has been reported that A β specifically interacts with ganglioside GM1 which is one of the key lipids in lipid raft. Therefore, GM1 embedded into lipid bilayers composed of neutral lipid DMPC may be regarded as the most simplified model neuronal cell membrane. In order to clarify the role of GM1 in the fibrillation process, first, we have successfully determined the oligomeric structure of A β (1-40) induced on DMPC bilayers based on solid-state NMR.²⁾

In the current study, to clarify the contribution of GM1 in the fibrillation process, we have attempted to characterize the oligomeric structure of A β (1-40) bound to lipid bilayers consisting of GM1 and DMPC. In order to achieve reliable signal assignments, we have re-examined ¹³C-¹⁵N heteronuclear solid-state NMR correlation experiments because of low sensitivities for previously obtained spectra. Then the signal assignments have been completed together with 2D ¹³C homonuclear correlation data. Analysis of the secondary structure of A β based on the chemical shifts of assigned signals revealed that a disordered N-terminus was followed by two β -sheet structures from the middle region to the C-terminus. Comparison of secondary structures of A β in the absence and presence of GM1 in lipid bilayers suggests that the β -sheet structure in the middle region may be promoted through the interaction with GM1. In order to clarify intermolecular packing, ¹³C space through homonuclear correlation experiments were carried out at various mixing times for the sample with spin labeled A β at the C-terminus. The correlation spectra for spin labeled sample, Ser²⁶ signal clearly disappeared, suggesting the close location of Ser²⁶ residue and C-terminal spin center. Based on the obtained data, a molecular packing model is currently under construction.

References

- 1) S. Kataoka, H. Fukumoto, T. Kawasaki-Takasuka, T. Yamazaki, K. Nishimura, T. Agou and T. Kubota, *J. Fluorine Chem.* **218**, 84–89 (2019).
- 2) M. Yagi-Utsumi, K. Kato and K. Nishimura, *PLoS One* **11**, 0146405 (10 pages) (2016).

Study on Ion Conductive Materials for Novel Energy Storage/Conversion Devices

Department of Materials Molecular Science Division of Molecular Functions



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Education

2006 B.E. Kanazawa University
2008 M.E. Tokyo Institute of Technology
2010 D.S. Tokyo Institute of Technology

Professional Employment

2010 Postdoctoral Fellow, Tokyo Institute of Technology
2011 Assistant Professor, Kanagawa University
2012 JST-PRESTO Researcher (Additional post)
2013 Research Associate Professor, Institute for Molecular Science
2018 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies

Awards

2010 ACerS Spriggs Phase Equilibria Award, American Ceramics Society
2011 Tejima Doctoral Dissertation Award, Tokyo Institute of Technology
2018 The 39th Honda Memorial Young Researcher Award, The Honda Memorial Foundation
2018 The 7th Ishida Award, Nagoya University
2019 Tagawa Solid State Chemistry Awards, Division of Solid State Chemistry, The Electrochemical Society of Japan

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IMAI, Yumiko
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NISHIKAWA, Masako
Secretary
SUZUKI, Ai

Keywords Solid State Ionics, H⁻ Conductor, Battery

Chemical energy conversion/storage using electrochemical devices such as fuel cells and batteries will become increasingly important for future sustainable societies. As ion transport in solids is key for determining the performance of these devices, an improved understanding of the characteristics of existing electrode and electrolyte materials is required. For example, crystal structure, thermal stability, and reaction mechanisms are important to enhancing battery performance. Furthermore, the development of novel ion conduction phenomena through the synthesis of a new class of substances will be expected to lead to the creation of novel battery systems. In this context, I have concentrated my research efforts into two main areas: (i) Studies into the reaction mechanisms of cathodic materials for lithium secondary batteries; and (ii) The synthesis of new materials exhibiting hydride ion (H⁻) conductivity and the development of a novel battery system utilizing both the H⁻ conduction phenomenon and the H⁻/H₂ redox reaction.

Selected Publications

- G. Kobayashi, Y. Hinuma, S. Matsuoka, A. Watanabe, M. Iqbal, M. Hirayama, M. Yonemura, T. Kamiyama, I. Tanaka and R. Kanno, *Science* **351**, 1314–1317 (2016).
- G. Kobayashi, Y. Irii, F. Matsumoto, A. Ito, Y. Ohsawa, S. Yamamoto, Y. Chui, J.-Y. Son and Y. Sato, *J. Power Sources* **303**, 250–256 (2016).
- A. Watanabe, G. Kobayashi, N. Matsui, M. Yonemura, A. Kubota, K. Suzuki, M. Hirayama and R. Kanno, *Electrochemistry* **85**(2), 88–92 (2017).
- Y. Iwasaki, N. Matsui, K. Suzuki, Y. Hinuma, M. Yonemura, G. Kobayashi, M. Hirayama, I. Tanaka and R. Kanno, *J. Mater. Chem. A* **6**, 23457–23463 (2018).
- F. Takeiri, A. Watanabe, A. Kuwabara, H. Nawaz, N. Ayu, M. Yonemura, R. Kanno and G. Kobayashi, *Inorg. Chem.* **58**, 4431–4436 (2019).
- N. Matsui, G. Kobayashi, K. Suzuki, A. Watanabe, A. Kubota, Y. Iwasaki, M. Yonemura, M. Hirayama and R. Kanno, *J. Am. Ceram. Soc.* **102**, 3228–3235 (2019).

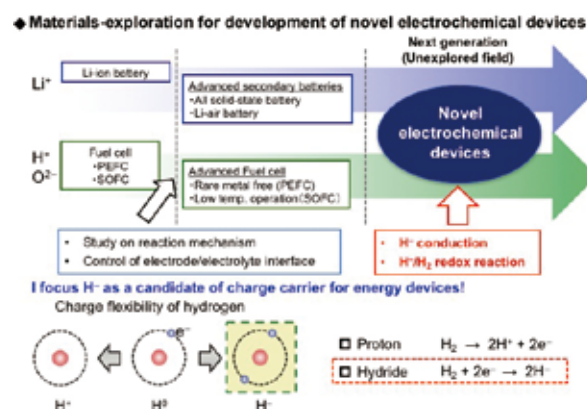


Figure 1. The concept of our research toward the realization of new energy storage/conversion devices.

1. Study on H⁻ Conductive Oxyhydrides¹⁻⁴⁾

Ionic charge carriers include a variety of species, such as Li⁺, H⁺, Ag⁺, Cu⁺, F⁻, and O²⁻, and their conductors have found applications in energy devices such as fuel cells and batteries. The conduction of hydride ions, H⁻, is also attractive. These are similar in size to oxide and fluoride ions and show strong reducing properties with a standard redox potential of H⁻/H₂ (-2.3 V) which is close to that of Mg/Mg²⁺ (-2.4 V). Hydride ion conductors may therefore be applied in energy storage/conversion devices with high energy densities. Here, we prepared a series of K₂NiF₄-type oxyhydrides, La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}, which are equipped with anion sublattices that exhibit flexibility in the storage of H⁻, O²⁻, and vacancies (Figure 2). An all-solid-state Ti/La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}/TiH₂ cell showed a redox reaction with hydrogen storage/desorption on the electrodes. The present success in the construction of an all-solid-state electrochemical cell exhibiting H⁻ diffusion confirms not only the capability of the oxyhydride to act as an H⁻ solid electrolyte but also the possibility of developing electrochemical solid devices based on H⁻ conduction.

More recently, we synthesized Ba₂SchO₃, a novel H⁻ conductive Sc-oxyhydride with the K₂NiF₄-type structure and confirmed its unique site selectivity for H⁻. In accordance with the electrostatic valence rule, it was found that the hydride ions in Ba₂SchO₃ selectively occupied the rock salt layer, in contrast to those of the observed isostructural Li-based oxyhydrides that preferentially occupy the perovskite layer (Figure 2). This result indicated that anion arrangements in oxyhydrides could be tuned by appropriate element substitutions, which is a new insight for designing H⁻ conducting materials.

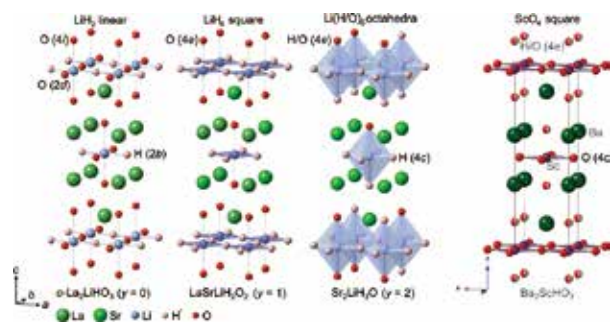


Figure 2. Crystal structures of H⁻ conductive oxyhydrides La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y} ($x = 0, y = 0, 1, 2$) and Ba₂SchO₃.

2. High-Performance of Li-Rich Layered Cathode Materials through Al₂O₃-Surface Modification⁵⁾

Awards

KOBAYASHI, Genki; Tagawa Solid State Chemistry Awards (2019).

KOBAYASHI, Genki; 7th Ishida Award (2018).

Controlling the cathode/electrolyte interface by modifying the surface of the cathode material with metal oxides or phosphate is being explored as a possible strategy for improving the electrochemical performance of such materials. In this study, we synthesized Al₂O₃-coated Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O₂ and investigated the crystal structure, the chemical bonding state from bulk to surface, and the influence of the surface modification on the electrochemical performance by X-ray diffraction, hard X-ray photoelectron spectroscopy (HAXPES), and galvanostatic charge/discharge reaction. It revealed that the surface-modification layer was composed of Li-Al oxides and Al oxides and that a LiM_{1-x}Al_xO₂ ($M =$ transition metals) interlayer was formed between the modification layer and the Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O₂ particles (Figure 3). The cycling performance of the Li-rich layered oxide was enhanced by the surface modification with Al₂O₃. A discharge capacity of more than 310 mA h⁻¹ and excellent cycling stability at 50 °C were achieved by the combination of the gradual Li-insetion/de-insertion process (stepwise precycling treatment) and the surface-modification.

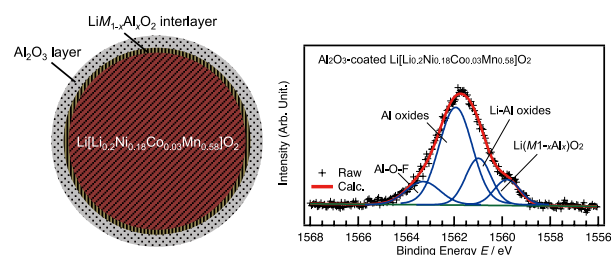


Figure 3. Schematic illustration and Al 1s HAXPES spectra of the 2 wt% Al₂O₃-coated Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O₂ particle.

References

- 1) F. Takeiri, A. Watanabe, A. Kuwabara, H. Nawaz, N. Ayu, M. Yonemura, R. Kanno and G. Kobayashi*, *Inorg. Chem.* **58**, 4431–4436 (2019).
- 2) N. Matsui, G. Kobayashi*, K. Suzuki, A. Watanabe, A. Kubota, Y. Iwasaki, M. Yonemura, M. Hirayama and R. Kanno*, *J. Am. Ceram. Soc.* **102**, 3228–3235 (2019).
- 3) A. Watanabe, G. Kobayashi*, N. Matsui, M. Yonemura, A. Kubota, K. Suzuki, M. Hirayama and R. Kanno, *Electrochemistry* **85**, 88–92 (2017).
- 4) G. Kobayashi*, Y. Hinuma, S. Matsuoka, A. Watanabe, M. Iqbal, M. Hirayama, M. Yonemura, T. Kamiyama, I. Tanaka and R. Kanno*, *Science* **351**, 1314–1317 (2016).
- 5) G. Kobayashi*, Y. Irii, F. Matsumoto, A. Ito, Y. Ohsawa, S. Yamamoto, Y. Chui, J.-Y. Son and Y. Sato, *J. Power Sources* **303**, 250–256 (2016).

* carrying out graduate research on Cooperative Education Program of IMS with High Energy Accelerator Research Organization

Visiting Professors



Visiting Professor

KISHINE, Jun-ichiro (*from The Open University of Japan*)

Theoretical Studies on Chiral Material Science

The concept of chirality is ubiquitous in natural sciences. However, until only recently, research fields on chirality had been fragmented into separated branches of physics, chemistry and biology. Even inside physics, a term “chiral” has been used in different meanings in condensed matter and high-energy physics. One of the most important mission of our project, on which the present workshop is based, is to integrate the scattered concepts of chirality and make a roadmap toward an attempt at synthesis of chiral material sciences. Let us remind the Laurence Barron’s definition of the true chirality, *i.e.*, true chirality is shown by systems existing in two distinct enantiomeric states that are interconverted by space inversion, but not by time reversal combined with any proper spatial rotation. The space inversion is a matter of geometrical symmetry, while time reversal is a matter of dynamical motion. This unambiguous definition clearly indicates that the concept of chirality ties geometry and dynamics. Conversion of geometry into dynamics naturally leads to material functionalities. The main purpose of this research project is to integrate these concepts in a unified manner.



Visiting Associate Professor

FURUKAWA, Ko (*from Niigata University*)

Electron Spin Dynamics of the Functional Materials

To develop the high-efficiency molecule-based device, it’s vital to clarify the mechanism of the functional molecules/materials. We investigate the mechanism of the solid-state functional materials in terms of the advanced electron spin resonance (ESR) spectroscopy such as high-field/high-frequency ESR, pulsed-ESR, time-resolved ESR, and so on. In recently, my main targets are the photo-induced conductivity/magnetic materials composed of a donor–acceptor (D–A) dyad. The charge-separated (CS) state induced by the electron transfer from the donor to the acceptor after the photolysis plays an important role of the functional efficiency of the photo-induced conductivity/magnetic properties. We investigated the CS state in the D–A dyad in terms of the spin dynamics by using the time-resolved ESR spectroscopy.



Visiting Associate Professor

OSHIMA, Yugo (*from RIKEN*)

Electron Spin Resonance Studies of a Bilayer-Type Molecular Ferromagnet (Et-4BrT)[Ni(dmit)₂]₂

Recently, several novel bilayer-type molecular magnets X[Ni(dmit)₂]₂, where dmit is 1,3-dithiol-2-thiole-4,5-dithiolate and X is a monovalent cation, have been developed by Kusamoto Group and Yamamoto Group in IMS. By taking the advantages of molecular design and the degree of freedom of the molecular arrangements, these novel molecular magnets take a bilayer structure, and the intralayer exchange interactions can be controlled by just substituting the asymmetric cation X. (Et-4BrT)[Ni(dmit)₂]₂ is one of these novel bilayer molecular magnets, which becomes a ferromagnet below 1 K. However, the magnetic moment only shows the half of the full saturation, and the mechanism of the ferromagnetism in this system is still under debate. In collaboration with Kusamoto Group and Yamamoto Group, we have studied the microscopic magnetic properties of (Et-4BrT)[Ni(dmit)₂]₂ by means of ESR spectroscopy. We have found that the ESR origin is only from one of the two layers and the other layer remains non-magnetic up to 24 T.