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

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 apparatus is extensively open for public usage. Recently, assistant professor Kohei Yamamoto is developing the soft x-ray resonant magnetic reflectivity (SXRMR) system for the clarification of depth resolved magnetism of magnetic thin films with the atomic layer resolution scale, and is conducting coherent diffraction imaging (CDI) experiments for the observation of magnetic domain structures of magnetic thin films, using highly coherent SR x-rays from SPring-8 hard x-ray undulators and x-ray free electron laser SACLA. By combining the SXRMR and CDI experiments, the magnetic structures along both the vertical and lateral directions can be revealed with atomic to nm spatial resolution.

The second subject is the exploitation of ambient pressure hard x-ray photoelectron spectroscopy (AP-HAXPES) for polymer electrolyte fuel cells (PEFC) under working conditions. Although photoelectron spectroscopic measurement is usually 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. Moreover, we designed and constructed the subsecond time resolved AP-HAXPES measurement system, and successfully investigated electrochemical reaction dynamics for the cathode Pt oxidation/reduction and the S^2- adsorption/desorption processes upon an abrupt step of the cathode-anode bias voltages. These works were supported by the NEDO Fuel Cell project. More recently, assistant professor, Takanori Koitaya, has been investigating various kinds of surface chemical reactions such as methane activation and CO\textsubscript{2} hydrogenation using the AP-HAXPES system combined with the near ambient pressure soft x-ray photoelectron spectroscopy system installed at Beamline 07LSU of SPring-8.

Selected Publications

1. Sulfur Poisoning Pt and PtCo Anode and Cathode Catalysts in PEFC Studied by operando AP-HAXPES \(^1\)

In practical performance of polymer electrolyte fuel cells (PEFC), the PtCo alloy electrode is known to be superior to the pure Pt electrode because of a longer life time and a less amount of noble Pt metal. In this work, in order to evaluate the tolerance of S poisoning between Pt\(_2\)Co and Pt electrodes comparatively, we have investigated the S adsorption behaviours on Pt (average particle size ~2.6 nm) and Pt\(_2\)Co (~3.0 nm) anode and cathode electrode catalysts in PEFC under working conditions for the fresh state just after the aging process and also the degraded state after accelerated degradation tests (ADT), by recording near ambient pressure HAXPES.

The S 1s HAXPES of both the anode and cathode electrodes show not only the principal S species from the sulfonic acid group (-SO\(_3\)H) in the Nafion electrolyte (~2478 eV in the left panel of Figure 1) but also other characteristic S species such as zero-valent S (S\(^0\)) adsorbed on the carbon support (~2471 eV) and anionic S (S\(^2-\)) adsorbed on the Pt electrode (~2470 eV). The S\(^2-\) species on Pt should be ascribed to S contamination poisoning the Pt catalyst electrode. The S\(^2-\) species on the cathode can be oxidatively removed by applying a high cathode–anode bias voltage (≥ 0.8 V) to form SO\(_4^{2-}\), while at the anode the S\(^2-\) species cannot be eliminated because of reductive environment in hydrogen gases. The important finding is the different S adsorption behaviour between the Pt/C and Pt\(_2\)Co/C electrodes after ADT. After ADT, the Pt/C anode electrode exhibits much larger S\(^2-\) adsorption than the Pt\(_2\)Co/C anode electrode. This indicates that the Pt\(_2\)Co/C anode is more desirable than the Pt/C one from the view point of S poisoning.

The reason for more tolerance of the Pt\(_2\)Co/C anode catalyst against S poisoning after ADT can be ascribed to more negative charge of the surface Pt atoms in the Pt\(_2\)Co/C catalyst than the Pt/C one, this yielding weaker interaction between the surface Pt and the anionic S species as S\(^2-\), SO\(_3^{2-}\), and SO\(_4^{2-}\).

A similar behaviour was observed also in the cathode catalyst. The present findings will nevertheless provide important information to design novel Pt-based PEFC electrodes with higher performance and longer durability.

2. Negative Thermal Expansion of Zinc-Blende CdTe from the View Point of Local Structure

Since the discovery of anomalously large negative thermal expansion (NTE) in ZrW\(_2\)O\(_8\) over an extremely wide temperature range in 1996, NTE has revived as a hot topic in structural solid-state chemistry and physics. The origin of zero thermal expansion and/or NTE is known to be categorized into two mechanisms. The first one is a so-called Invar effect as observed in the Fe\(_{64}\)Ni\(_{36}\) Invar alloy, in which the electronic structure of some atoms in the system is temperature dependent. The second one is derived from vibrational anomaly. The materials with zinc blende or diamond structure mostly show NTE at low temperature due to the presence of vibrational anomaly. In this work, thermal expansion of zinc-blende CdTe was investigated from the view point of local structure using the extended x-ray absorption fine structure (EXAFS) spectroscopic data and the path-integral effective classical potential (PIECP) Monte Carlo computational simulations. Figure 2 shows the experimental (EXAFS as orange open circles and XRD as light-blue filled circles) and theoretical (PIECP as solid lines and classical MC as dashed lines). Although the origin of NTE is known as a result of classical vibrational anomaly within the Newton dynamics theory, the quantum statistical simulation is found to be essential to reproduce the negative thermal expansion of CdTe. It is emphasized that the vibrational quantum effect and classical anharmonicity are of great importance for the understanding of low-temperature thermal expansion as well as the elastic constants.

![Figure 1](image1.png)

**Figure 1.** (left) Typical S 1s HAXPES from the anode Pt/C and Pt\(_2\)Co/C electrodes at the cathode-anode voltage \(V_{CA} = 0.6\) V for the aged (before ADT and degraded (after ADT) PEFC. The S\(^2-\) peak intensity (~2470 eV) is found to increase significantly in Pt/C, while it is not so much in Pt\(_2\)Co/C. (right) The relative amount of S\(^2-\) with respect to S\(^0\) originating from Nafion -SO\(_3\)H, for the aged and degraded anode Pt/C and Pt\(_2\)Co/C electrodes, as a function of \(V_{CA}\). It is clearly exemplified that the Pt\(_2\)Co/C anode electrode is more tolerant against S poisoning than the Pt/C.

![Figure 2](image2.png)

**Figure 2.** Experimental and theoretical thermal expansion of CdTe. Experimental XRD result for the lattice constant (light-blue closed circles) gives small NTE at <100 K, while experimental EXAFS result for the 1st nearest neighbor shell (orange open circles with error bars) provides quite normal thermal expansion even at low temperature. Computational PIECP results (solid lines) agree qualitatively well with both the experimental EXAFS and XRD data, while the classical MC results failed in the reproduction of the NTE (see black dashed lines).

Reference

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 Imχ^{(2)} SFG spectra (χ^{(2)}: The second-order nonlinear susceptibility) obtained by the heterodyne 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 Imχ^{(2)} SFG has a great advantage to 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.

**Keywords**  
Surface & Interface Science, Nonlinear Optical Spectroscopy, Water Molecules

**Selected Publications**


**Figure 1.** Infrared-visible sum-frequency-generation (SFG) spectroscopy of water molecules on solid surface.
1. Interface Engineering of the Thermodynamic Properties of Strongly Correlated Many-Body Protons in Crystalline Ice

The static and dynamic behavior of strongly correlated protons play crucial roles in rendering exotic properties and enabling a wide range of applications of nanoscale hydrogen-bonded (HB) materials in physics, chemistry and biology. However, because of the difficulty in probing and manipulating the proton configuration in nanomaterials, controlling the cooperative behavior of many-body protons has not been realized.

In this study, we demonstrate the possibility of designing and controlling the physical properties of strongly correlated many-body protons through systematic sum-frequency generation (SFG) spectroscopy of crystalline-ice nanofilms. Since the second-order nonlinear susceptibility tensor \( \chi^{(2)} \) is nonzero for non-centrosymmetric systems, the homodyne-detected SFG intensity \( |\chi^{(2)}|^2 \) increases with increasing the number of water molecules with net orientational preference, and thus can be used as the signature of the emergence of ferroelectric proton ordering. Because of the strong correlation of many-body protons imposed by the ice rules,\(^2\,^3\) protons in the hydrogen-bond (HB) network of crystalline ice provide an interesting platform for studying fundamental emergent properties of strongly correlated proton systems. Here, we employ SFG spectroscopy of heteroepitaxial crystalline-ice nanofilms grown on Pt(111) surface precovered by a well-defined single layer of either carbon monoxide (CO) molecules or oxygen (O) atoms to study the effects of interface termination on mesoscopic characteristics of many-body protons.

The intensities of the \( |\chi^{(2)}|^2 \)-SFG spectra were shown as a function of ice thickness for these substrates (Figure 1). We found that the SFG signal derived from ice film on CO precovered Pt(111) continues to increase as that on bare Pt(111).\(^2,^3\) In contrast, negligibly small \( |\chi^{(2)}|^2 \)-SFG intensity (Figure 1) suggests that ice film on oxygen precovered Pt substrate is paraelectric. Our observations on the two different types of intercalated layer directly demonstrate that the thermodynamic properties of emergent ferroelectric proton ordering are extensively tuned by the interface engineering at the angstrom scale.

2. Operando FT-IR Spectroscopy of Steam-Methane-Reforming Photocatalyst under Irradiation of Intensity Modulated UV Light

Photocatalytic steam-methane reforming is an attractive chemical technology for hydrogen production from abundant resources of methane and water. In the case of photocatalytic reaction, photo-generated electron plays key roles in hydrogen production. However, the dynamics of photogenerated electrons under reaction condition have been unclear. To uncover the behavior of reactive photo-excited electrons, we conducted operando FT-IR spectroscopy of metal loaded Ga\(_2\)O\(_3\) photocatalysts under irradiation of intensity modulated UV light. We succeeded in observing a correlation between the reaction activity and a broad mid-infrared absorption band derived from the photo-generated electrons shallowly trapped at the photocatalyst surfaces.

3. Critical Role of Interfacial Water Molecules on the Photocatalytic Methane Activation

Recent expectations for effective use of natural gas have led to an interest in chemical technology for methane activation. Photocatalytic approach has a potential to convert methane at ambient conditions. However, the microscopic understanding on photocatalytic reaction mechanism, especially robust C–H bond activation mechanism, remains an open question. Here, combining in-situ MS-IR spectroscopy and systematic reaction measurements under various partial pressures of methane and water, we demonstrate that photoactivated interfacial water molecules facilitate the first C–H dissociation and shift the rate-determining step. Our reaction observation on typical three photocatalysts (Ga\(_2\)O\(_3\), NaTaO\(_3\), TiO\(_2\)) clarified the existence of critical partial pressure of methane at approximately 0.5 atm, around which the reaction rates markedly increased with methane partial pressure. Operando IR measurements showed that H atom extraction from methane by photo-activated water was accelerated at the same critical partial pressure of methane, suggesting that the first C–H activation and adsorption of methane was directly assisted by interfacial water.

References
Organic Solar Cells

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Education
1984 B.E. Osaka University
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Professional Employment
1984 Technical Associate, Institute for Molecular Science
1988 Research Associate, Osaka University
1997 Associate Professor, Osaka University
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Awards
2021 Outstanding Achievement Award, Molecular Electronics & Bioelectronics Division, Japan Society of Applied Physics
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

Keywords
Organic Semiconductors, ppm-Doping, Lateral Junction

Organic solar cells have been intensively studied due to many advantages like flexible, printable, light, low-cost, fashionable, etc. Last year, we proposed a novel concept of the structure of organic solar cell, namely, a lateral multilayered junction (Figure 1). An essential point is that the photo-generated holes and electrons are laterally transported and extracted to the respective electrodes. We also investigated the reduction of open-circuit voltage ($V_{oc}$) loss due to non-radiative recombination in organic solar cells by using high-mobility organic semiconductors. We observed the $V_{oc}$ reaching to thermodynamic (Shockley-Queisser) limit (Figure 2, double red dot). On the other hand, we have been focused on the research on the ppm-level doping effects in organic semiconductor films and organic single crystals for organic solar cells. 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$^{-1}$, 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. Lateral multilayered junction.

Figure 2. $V_{oc}$ vs. Charge Transfer (CT) state energy of donor/acceptor type organic solar cells. By using high carrier mobility organic semiconductors, $V_{oc}$ reaching SQ-limit was observed (double red dot).

Selected Publications

1. Efficient Solid-State Photon Up-conversion Enabled by Spin Inversion at Organic Semiconductor Interface

Energy of photons, i.e., the wavelength of light, can be upgraded through interactions with materials—a process called photon upconversion (UC). Although UC in organic solids is important for various applications, such as in photovoltaics and bioimaging, conventional UC systems, based on intersystem crossing (ISC), suffer from low efficiency.

In this study, we report a novel UC mechanism at hetero-junctions of organic semiconductors in bilayer structures. The UC occurs through spin inversion during the charge separation and recombination at the interface (Figure 3(a)). This spin inversion can efficiently convert the incident photons to triplets without relying on the ISC, whose rate is typically accelerated by the heavy-atom effect. As a result, a solid-state UC system is achieved with an external efficiency of two orders of magnitude higher than those of the conventional systems. Using this result, efficient UC, from near-infrared to visible light, can be realized on flexible organic thin films under a weak light-emitting diode-induced excitation, observable by naked eyes (Figure 3(b)).


Recently, we reported a lateral alternating multilayered junction using a high mobility organic semiconductor. In this study, we fabricated lateral junction cells having lateral distance \(L\) reaching cm order (Figure 4(a)). A donor [C8-BTBT (hole mobility: 43 cm\(^2\)V\(^{-1}\)s\(^{-1}\)]-acceptor [PTCDI-C8 (electron mobility: 1.7 cm\(^2\)V\(^{-1}\)s\(^{-1}\)] combination was used. Buffer layers of BCP and MoO\(_3\) were used for the selective carrier collection of electrons and holes, respectively. Surprisingly, even lateral cells with \(L = 1.8\) cm (Figure 4(b)) showed clear photovoltaic behavior (Figure 4(c), red curve). Figure 4(d) shows the \(L\) dependence of observed \(J_{sc}\) (red curve) and calculated \(J_{sc}\) (blue curve) obtained from diffusion lengths of electrons (4.7 mm) and holes (5.5 mm), which are dominated by traps. These diffusion lengths were obtained by the experiments using the moving photomask covering the irradiated surface from respective electrodes. Thus, considerable decrease in photocurrent is attributed to the trap-assisted recombination indicated by the blue curve. A further difference between the observed and calculated curves is due to bimolecular recombination and its effect is small. Thus, we concluded that trap-assisted recombination can be the main reason for photocurrent loss of the long lateral cells. Hence, identifying and removing the defects acting as traps can be done to improve cell performance.

References

Awards
HIRAMOTO, Masahiro; Outstanding Achievement Award, Molecular Electronics and Bioelectronics Division, Japan Society of Applied Physics (2021).
IZAWA, Seiichiro; The Young Scientist Award, Molecular Electronics and Bio Electronics Division in the Japan Society of Applied Physics (2021).
IZAWA, Seiichiro; Konica Minolta Imaging Science Encouragement Award (2021).
IZAWA, Seiichiro; The Outstanding Presentation Award of the 31\(^{st}\) Japan OLED Forum (2021).
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 characterizations 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

1. Structural Characterization of Amyloid-β Protein Oligomer Promoted on Model Neuronal Cell Membranes Using State NMR

Amyloid β (Aβ) 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 Aβ 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 considered to be 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 Aβ (1-40) induced on DMPC bilayers based on solid-state NMR. We have been collaborated with Prof. Kato group in IMS for those Aβ studies.

In the current study, Aβ (1-40) oligomer induced on model neuronal cell membranes consisting of GM1 and DMPC have been attempted to characterize using solid-state NMR. Based on information of intra- and intermolecular distances and torsion angles of back born obtained from solid-state NMR analyses, precise molecular structure of Aβ oligomer was determined from restrained molecular dynamics simulations in collaboration with Prof. Okumura group in IMS. The determined Aβ structure conforms disordered N-terminus followed by center and C-terminus β-sheets. Aβ takes intermolecular configuration of antiparallel β-sheet among adjacent molecules, in which different from Aβ fibrils prepared in solution and also Aβ oligomer induced on DMPC bilayers. Those suggest specific roles of GM1 for the formation of Aβ oligomers. We expect the significant contribution of our determined Aβ oligomer structure to reveal the molecular mechanism of Aβ fibrils on neuronal cell membranes, and thus understanding of Alzheimer’s disease. The manuscript of this study is under preparation.

2. Characterizations of Lipid Binding of Prion Fragment Based on Solid-State NMR

“Prion” protein is amyloid protein responsible for class of neurodegenerative diseases such as Bovine spongiform encephalopathy, (BSE), Creutzfeldt-Jakob disease (CJD) of human, scrapie of sheep. Those are collectively known as transmissible spongiform encephalopathies (TSEs). The onset of TSEs has been considered to be arisen by conformational conversion of the native monomeric cellular prion protein (PrPc) into misfolded β-sheet rich form (PrPs), resulting in their insoluble aggregations. Recent studies suggest that those processes are facilitated through interactions with biomembranes, in particular, through binding with ganglioside GM1 in lipid raft. Despite of many studies of prion, molecular mechanism of structural conversion of prion protein and the cytotoxicity have not been clarified yet.

Ultimate goal of this project is provision of molecular basis of prion disease through the characterizations of molecular structure of prion and their interactions with specific lipids based on solid-state NMR analyses. As the first stage, we start study of PrP(106-126) fragment which has been considered as minimum prion fragment to understand their fibrillation mechanism, because of conservations of important properties of formation of amyloid fibrils, membrane binding ability and cytotoxicity. We explore to clarify PrP(106-126) specific binding site in GM1 has been explored through the analyses of chemical shift perturbations of 13C signals from GM1 in POPC/GM1 vesicles from the comparisons of 13C-solid-state NMR spectra in the presence and absence of PrP(106-126). None of 13C signals from POPC exhibited peak shift, but several signals in GM1 exhibited peak shifts due to PrP(106-126) bindings, suggesting specific interactions of PrP(106-126) with GM1 in GM1/POPC lipid bilayers. Further detail is under investigation.

3. Characterization of Protein Using Solid-State NMR

The secretary abundant heat soluble protein (SAHS) from water bear which has ability of torpor under dry-condition, and recovery from torpor by water supply. The biological functions of SAHS at dry-state has not been identified yet, but SAHS has been considered to play key roles during torpor. This is collaboration project with Prof. Kato group in IMS. SAHS consisting of more than 200 amino acid residues and its dry-state is expected to be inhomogeneous. Therefore, in order to investigate structural homogeneity and obtain local conformational information, 2D 13C- homonuclear correlation solid-state NMR measurements were carried out for the dry-state SAHS protein which only isoleucine residues are specifically 13C and 15N isotope labeled. The 6 sets of signals were observed and assigned successfully.

4. Development of Solid-State NMR Probe

We have built a variety of solid-state NMR probes such as static and MAS 1H-X double resonance probes for 400 MHz NMR, and a variable temperature 1H-X double resonance MAS probe for 920 MHz ultra-high field NMR at past. During the past few years, we have been working on building an original solid-state NMR probe which is fully compatible with commercial instruments currently used. Those developed probes were built with originally designed parts except for spinning and spinning rate detection modules which were purchased from NMR company. To replace remained commercial modules, we attempted to design original spinning module. At first stage, two different types of original spinning modules were designed for 4.0 mm sample tube. Those exhibited moderate performances but slightly lower performance respect to commercial module. Based on various tests, we identified the key parts to govern the performance of the spinning. The improved version of spinning module is under developments.

Reference
Hydrogen has a charge flexibility and can take various charge states such as proton (H⁺), atomic hydrogen (H₀), and hydride (H⁻) depending on the different bonding states in materials. Due to this feature, whereas hydrogen diffusing in metals behaves a state close to H₀, H⁺ becomes the charge carrier in many types of chemical compounds, including polymer, solid acid, MOF, and ceramics. In the former case, hydrogen absorbing alloys and hydrogen embrittlement of metals have been studied, and in the latter case, materials research for fuel cell applications has been actively carried out over the past few decades. In contrast, H⁻ is a relatively rare state that can only be taken when hydrogen is coordinated to metals with low electronegativity such as alkali metals and was not well recognized as a charge carrier. Therefore, even though H⁻ has attractive features such as suitability for fast ionic conduction in terms of size, valence, and polarization and strong reduction properties (Eº(H⁻/H₂) = −2.35 V vs. SHE), its electrochemical applications have not been considered. Against this background, we developed a series of H⁻ conductive oxyhydrides, La₂₋ₓSrₓHₓO₃₋₀.₃, in 2016 and found its function as an H⁻ solid electrolyte for the first time. Based on the results, our group is challenging the progress of materials science on H⁻ conductors and the development of novel electrochemical devices utilizing H⁻ conduction phenomena.

Selected Publications
1. Study on H⁻ Conductive Oxyhydrides¹⁻³

In 2016, we synthesized a series of K₂NiF₄-type oxyhydrides, La₂₋ₓSrₓCr₂₋ₓLiH₁₋ₓO₃₋ₓ (LSLHO), which are equipped with anion sublattices that exhibit flexibility in the storage of H⁻, O²⁻, and vacancies (Figure 2 upper) and demonstrated pure H⁻ conduction properties in the oxyhydrides.¹ The Li-based oxyhydrides acted as solid electrolytes and the all-solid-state Ti/LSLHO/TiH₂ cell showed a redox reaction based on hydrogen storage/desorption on the electrodes, which is a first battery reaction using H⁻ conduction phenomena.  

More recently, we synthesized novel H⁻ conductive oxyhydrides, Ba₂MHo₃ (M = Sc, Y)²,³ 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 Ba₂MHo₃ 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). The cation size at the octahedral center influences the anion arrangement within the rock-salt layer, and in the Y-oxyhydride, the complete ordering of H/O in the mixed conducting oxyhydrides was tuned by anion sublattices that exhibit flexibility in the storage of H⁻, O²⁻, and vacancies (Figure 2 upper) and demonstrated pure H⁻ conduction properties in the oxyhydrides.¹ The Li-based oxyhydrides acted as solid electrolytes and the all-solid-state Ti/LSLHO/TiH₂ cell showed a redox reaction based on hydrogen storage/desorption on the electrodes, which is a first battery reaction using H⁻ conduction phenomena.  

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For Li-based oxyhydrides (LSLHO) with the K₂NiF₄-type structure, we have successfully established the solid-state reaction method under ambient-pressure.⁴,⁵ Electroductive force measurements using hydrogen concentration cells became possible by preparing the LSLHO sintered pellets with sufficient size.

We have also succeeded in direct synthesis of barium titanium oxyhydride BaTiO₃₋ₓHₓ by mechanochemical reaction, allowing gram-scale and speedy preparation of the functional material. Its unique reaction condition without external heating might be suitable for materials exploration of oxyhydrides. We also confirmed that the prepared polycrystalline BaTiO₃₋ₓHₓ worked as a hydrogen-permeable electrode. This result suggests that H⁻/e⁻ mixed conducting oxyhydrides are promising for electrode use in electrochemical chemical/energy conversion devices (Figure 3).⁶

Figure 3. BaTiO₃₋ₓHₓ synthesized by a mechanochemical method and its performance as hydrogen permeable electrodes.

References
4) A. Watanabe, G. Kobayashi* et al., Electrochemistry 85, 88–92 (2017).

2. Materials Processing of Oxyhydrides for Electrochemical Applications⁴⁻⁶

Synthesizing oxyhydrides usually requires unique methods such as solid-state reactions at high-pressure and topochemical reactions using CaH₂ reductant. Since the former method is a sealed reaction system, loss of light elements, such as hydrogen, can be prevented, making it a suitable synthesis method for composition control and, ultimately, exploration for new materials. On the other hand, the latter is an O²⁻/H⁻ exchange reaction using oxides as precursors and is useful for preparing metastable phases that the conventional sintering process cannot obtain. However, the low synthesis volume in the high-pressure method and less reproducibility of composition due to complicated multi-step processes such as washing in CaH₂ reduction have prevented expanding the study on oxyhydrides to applicable research for electrochemical devices. To resolve the above problems, we have been trying to establish a suitable synthesis method for oxyhydrides.

For Li-based oxyhydrides (LSLHO) with the K₂NiF₄-type structure, we have successfully established the solid-state reaction method under ambient-pressure.⁴,⁵ Electroductive force measurements using hydrogen concentration cells became possible by preparing the LSLHO sintered pellets with sufficient size.

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References
4) A. Watanabe, G. Kobayashi* et al., Electrochemistry 85, 88–92 (2017).

* carrying out graduate research on Cooperative Education Program of IMS with High Energy Accelerator Research Organization
At the interface between solid and liquid, energy conversion reactions in the physical, chemical, and biological process proceed. The details of such a energy conversion process is yet to be clarified completely. Scanning probe microscopy (SPM) is a powerful method to clarify such mechanisms because it can explore structural, mechanical, electric and electronic properties in atomic (or molecular) scales. As shown in an atomic resolved SPM image of CaCO$_3$(104) surface in 5 mM NaCl aqueous solution (Figure 1), atomic scale properties are investigated by SPM.

Figure 1. An atomically resolved friction image of CaCO$_3$(104) surface in 5 mM NaCl aqueous solution. image size: 5 nm × 5 nm.

Rechargeable battery plays an important role in the development of new systems of energy storage and transfer. Currently, lithium-ion batteries have been widely used for energy systems. Recent demands for rechargeable batteries require more developments in the capacity, cyclic performance and lifetime. For these developments, the clarification of the reaction mechanism at the interface between electrode and electrolyte during the charge and discharge reactions is crucial.

During the charge and discharge reactions of rechargeable battery, solvent, carrier ions, additive and solute produce specific states at the interface between electrode and electrolyte. The interface states are believed to change the physical properties depending on the potential and strongly correlate the battery performances. However, detecting the interface states is challenging. By setting up SPM system which can operate in electrochemical conditions, we detected and investigated physical properties of interface states. Figure 2 shows force curves obtained at the interface between organic electrolyte for lithium-ion battery and gold electrode. The force curve was changed by the sample potential between +1.0 (blue) and −1.0 V (red) (vs Pt). The changes of the force curves were caused by the interface states, exhibiting the evidence of the formation of the thick interface states by electrolyte at −1.0 V. By the analysis of the force curves, the mechanical properties of the interface states were also clarified. The analysis of the electrode/electrolyte interface will be applied to innovative battery systems that can overcome current battery performances.

Figure 2. A schematic model of electrode/electrolyte interface in a rechargeable battery and force curves obtained by electrochemical SPM systems at the interface between organic electrolyte for lithium-ion battery and gold electrode with changing the sample potential. The blue and red curve were obtained at +1.0 and −1.0 V (vs. Pt), respectively. The force curves were measured during the approaching the tip to the interface. The distance was determined from the point detecting 0.4 nN.

References
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 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. During this one year, we have focused on theoretical description of the chirality-induced phonon in non-centrosymmetric crystals.

Visiting Associate Professor

FURUKAWA, Ko *(from Niigata University)*

Advanced ESR Study of Molecule-Based 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 advanced electron spin resonance (ESR) spectroscopy such as high-field/high-frequency ESR, time-resolved ESR, pulsed-ESR and so on. Recently, our themes are following three (I) spin dynamics study of molecule-based materials with the complex function combined to photoconductivity and photo-induced magnetic properties, (II) operand ESR study of the novel oxygen reduction reaction (ORR) catalyst for fuel cell, and (III) the soil environments were investigated by using ESR spectroscopy for the vegetable food such as the rice and tea leaves.

Visiting Associate Professor

OSHIMA, Yugo *(from RIKEN)*

Development of ESR Probe for Molecular Field-Effect Transistor (FET) Devices

Recently, a novel type of ferromagnet (Et-4BrT)[Ni(dmit):] has been developed by Kusamoto Group and Yamamoto Group in IMS (dmit is 1,3-dithiol-2-thiole-4,5-dithiolate and Et-4BrT is ethyl-4-bromotheiazolium). We have found that this ferromagnet is the first realization of the Nagaoka-Penn ferromagnetism, where the ferromagnetism is achieved by the light hole-doping of the insulating Ni(dmit): layer owing to the internal dipole moment of the monovalent cation Et-4BrT (*Sci. Rep.* **11**, 1332 (2021)). Our latest interest is whether the ferromagnetism of this material can be controlled by electrical doping or not. In collaboration with Yamamoto Group, we have newly developed an ESR sample holder for field-effect transistors (FETs), so that we can control precisely the electrical doping of (Et-4BrT)[Ni(dmit):] by means of FET structure. We will investigate the magnetic properties of (Et-4BrT)[Ni(dmit):] by carrier doping from ESR spectroscopy.