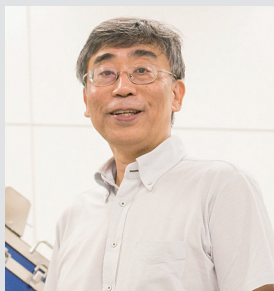


Exploitation of Novel Spectroscopic Methods for Material and Surface Science

Department of Materials Molecular Science
Division of Electronic Structure



YOKOYAMA, Toshihiko
Professor
[yokoyama@ims.ac.jp]

Education

1983 B.S. The University of Tokyo
1985 M.S. The University of Tokyo
1990 Ph.D. The University of Tokyo

Professional Employment

1987 Research Associate, Hiroshima University
1993 Research Associate, The University of Tokyo
1994 Lecturer, The University of Tokyo
1996 Associate Professor, The University of Tokyo
2002 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies

Member

Assistant Professor
KOITAYA, Takanori
YAMAMOTO, Kohei
Secretary
ISHIKAWA, Azusa

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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_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

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- Y. Takagi *et al.*, *Acc. Chem. Res.* **51**, 719 (2018).
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- T. Nakamura *et al.*, *J. Phys. Chem. C* **124**, 17520 (2020).
- S. Chaveanghong *et al.*, *Phys. Chem. Chem. Phys.* **23**, 3866 (2021).

1. Sulfur Poisoning Pt and PtCo Anode and Cathode Catalysts in PEFC Studied by *operando* AP-HAXPES¹⁾

In practical performance of polymer electrolyte fuel cells (PEFC), the Pt₃Co 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 Pt₃Co and Pt electrodes comparatively, we have investigated the S adsorption behaviours on Pt (average particle size ~2.6 nm) and Pt₃Co (~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 (-SO₃H) in the Nafion electrolyte (~2478 eV in the left panel of Figure 1) but also other characteristic S species such as zero-valent S (S⁰) adsorbed on the carbon support (~2471 eV) and anionic S (S²⁻) adsorbed on the Pt electrode (~2470 eV). The S²⁻ species on Pt should be ascribed to S contamination poisoning the Pt catalyst electrode. The S²⁻ species on the cathode can be oxidatively removed by applying a high cathode–anode bias voltage (≥ 0.8 V) to form SO₃²⁻, while at the anode the S²⁻ 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 Pt₃Co/C electrodes after ADT. After ADT, the Pt/C anode electrode exhibits much larger S²⁻ adsorption than the Pt₃Co/C anode electrode. This indicates that the Pt₃Co/C anode is more desirable than the Pt/C one from the view point of S poisoning.

The reason for more tolerance of the Pt₃Co/C anode catalyst against S poisoning after ADT can be ascribed to more negative charge of the surface Pt atoms in the Pt₃Co/C catalyst than the Pt/C one, this yielding weaker interaction between the surface Pt and the anionic S species as S²⁻, SO₃²⁻, and SO₄²⁻.

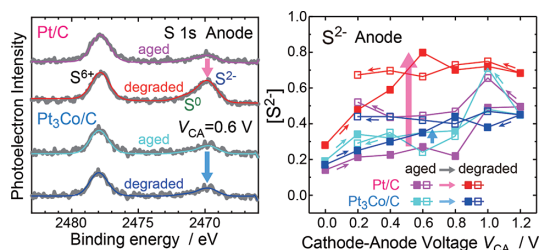


Figure 1. (left) Typical S 1s HAXPES from the anode Pt/C and Pt₃Co/C electrodes at the cathode–anode voltage $V_{CA} = 0.6$ V for the aged (before ADT) and degraded (after ADT) PEFC. The S²⁻ peak intensity (~2470 eV) is found to increase significantly in Pt/C, while it is not so much in Pt₃Co/C. (right) The relative amount of S²⁻ with respect to S⁶⁺ originating from Nafion -SO₃H, for the aged and degraded anode Pt/C and Pt₃Co/C electrodes, as a function of V_{CA} . It is clearly exemplified that the Pt₃Co/C anode electrode is more tolerant against S poisoning than the Pt/C.

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 ZrW₂O₈ 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 Fe₆₄Ni₃₆ 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.

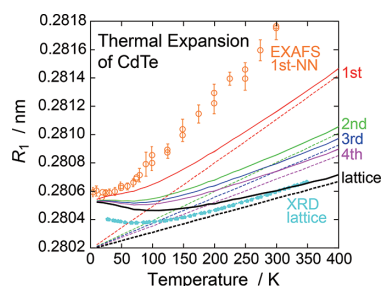


Figure 2. Experimental and theoretical thermal expansion of CdTe. Experimental XRD result for the lattice constant (light-blue closed circles) gives small NTE at <100 K, while experimental EXAFS result for the 1st nearest neighbor shell (orange open circles with error bars) provides quite normal thermal 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

- 1) S. Chaveanghong *et al.*, *Phys. Chem. Chem. Phys.* **23**, 3866–3873 (2021).

Award

KOITAYA, Takanori; 2021 Vacuum and Surface Science Journal Award of the Japan Society of Vacuum and Surface Science (2021).