

# Exploitation of Novel Spectroscopic Methods for Material and Surface Science

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### Education

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### Professional Employment

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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  $\text{WO}_3$  and  $\text{BiVO}_4$  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.

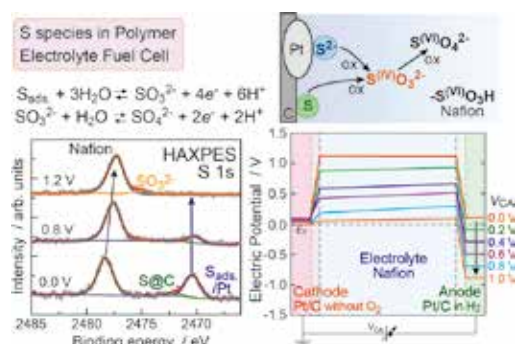
Within two years, two assistant professors Drs. Takagi and Uemura moved out and new assistant professors Drs. Koitaya and Yamamoto have joined our group. We will further perform surface physics and chemistry researches for materials science including methodological exploitation using synchrotron radiation 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 HAXPES<sup>1</sup>

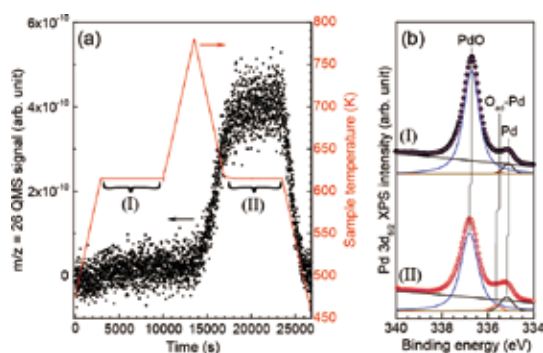
PEFC is currently one of the most promising electrochemical energy conversion and storage technology. To achieve more highly efficient PEFC with longer life time, a continuous supply of more powerful materials and a further detailed understanding of the electrochemical properties of PEFC are essentially 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,  $\text{SO}_3^{2-}$  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  $\geq 0.8$  V due to oxidation reactions from adsorbed S to  $\text{SO}_3^{2-}$  and possibly  $\text{SO}_4^{2-}$ , 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 ( $\sim 1.0$  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  $\text{SO}_3^{2-}$  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  $\text{O}_2$  and 5.7 mbar  $\text{CH}_4$  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  $\text{O}_2$  and 5.7 mbar  $\text{CH}_4$  gas mixture. AP-XPS measurements were performed at 615 K (I) and (II). (b) Pd 3d<sub>5/2</sub> 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).

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