

Exploitation of Novel Spectroscopic Methods for Material and Surface Science

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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 x-ray absorption fine structure (XAFS) spectroscopy. XAFS is a quite powerful technique for investigating quantitative local structures of very low concentrated non-crystalline element by using the energy-resolved x-ray fluorescence detection technique. We have investigated local geometric and electronic structures of the photoexcited states of photocatalysts as WO_3 and BiVO_4 which are known to be active for visible light. In WO_3 , the photoexcited state around W is ascribed to the electron polaron like state since W is reduced from hexavalent to pentavalent and the local geometric structure around W is significantly distorted.

Within this one year, two assistant professors Drs. Takagi and Uemura moved out and a new assistant professor Dr. Koitaya has just joined our group and one position is now open. 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. Local Thermal Expansions and Lattice Strains in Elinvar Alloy¹⁾

It is well known that local structures in mixed crystals are often different from lattice structures that are expected crystallographically. Even when the crystal shows clear x-ray diffraction patterns, there should exist strains in the crystal that cannot be solved by the x-ray diffraction analysis. In this work, we have investigated local thermal expansions and lattice strains in the Elinvar alloy $\text{Fe}_{49.66}\text{Ni}_{42.38}\text{Cr}_{5.49}\text{Ti}_{2.47}$ (Ni Span C) and the stainless steel SUS304 $\text{Fe}_{71.98}\text{Ni}_{9.07}\text{Cr}_{18.09}\text{Mn}_{0.86}$ (AISI304) were investigated by the temperature-dependent Cr, Fe, and Ni *K*-edge EXAFS measurements, combined with the path-integral effective classical potential Monte Carlo (PIECP MC) theoretical simulations. From the EXAFS analysis of the Elinvar alloy, the local thermal expansion around Fe is found to be considerably smaller than the ones around Ni and Cr (see Figure 1). This observation can be understood simply because Fe in the Elinvar alloy exhibit an incomplete Invar-like effect. Moreover, in both the Elinvar and SUS304 alloys, the local thermal expansions and the lattice strains around Cr are found to be larger than those around Fe and Ni. From the PIECP MC simulations of both the alloys, the first-nearest neighbor Cr-Fe pair shows extraordinarily large thermal expansion, while the Cr-Cr pair exhibits quite small or even negative thermal expansion. These findings consequently indicate that the lattice strains in both the Elinvar and SUS304 alloys are concentrated predominantly on the Cr atoms. Although the role of Cr in stainless steel has been known to inhibit corrosion by the formation of surface chromium oxide, the present investigation may interestingly suggest that the Cr atoms in the bulk play a hidden new role of absorbing inevitable lattice strains in the alloys.

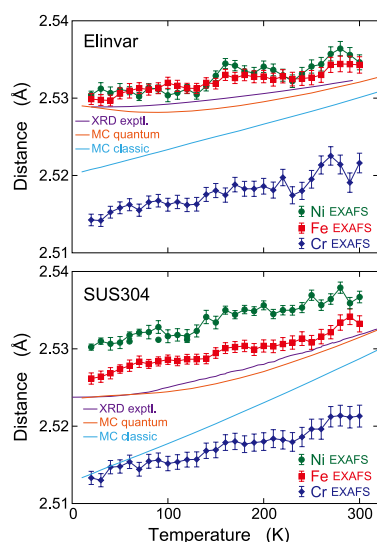


Figure 1. Temperature dependence of the interatomic distances in the Elinvar and SUS304 alloys. The Fe, Ni, and Cr *K*-edge EXAFS analysis are given, together with the results from the powder x-ray diffraction and the calculated results obtained by the present PIECP and the classical MC simulations.

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2. Direct Electric Potential Measurements of Electrode Components in an Operating Fuel Cell by Ambient Pressure XPS²⁾

X-ray Photoelectron spectroscopy is usually utilized to investigate chemical states of the elements of interest in various materials. This technique also has the advantage of providing electric potentials of each component in functional materials without using probe electrodes. We performed operando hard X-ray photoelectron spectroscopy (HAXPES) measurements with an 8 keV excitation source to measure the shift in electron kinetic energies as a function of the voltages of all the components at the anode and cathode electrodes of a polymer electrolyte fuel cell (PEFC). At the cathode electrode, when we increase the voltage between the cathode and anode from 0.2 to 1.2 V, the O 1s and F 1s peaks shift to a lower binding energy and the magnitude of the energy shift is equal to the voltage. The Pt 3d and C 1s peaks do not shift with the voltage since platinum nanoparticles and carbon supports at the cathode electrode have ground contact. In contrast to the cathode electrode, the peak shifts of all the components at the anode electrode show the same amount of shift as the voltages. The results are summarized in Figure 2. It is clear that the change in the potential difference occurs only in an electrical double layer at the interface between the cathode electrode (Pt/C) and the electrolyte (Nafion and water), and that the anode electrode is in equilibrium as a pseudo-hydrogen electrode. It should be noted that the electric potential variation of the cathode electrode in a PEFC under a power generation condition was also directly detected by operando HAXPES, although the electric double layer is a well-established concept but is not easy to observe directly.

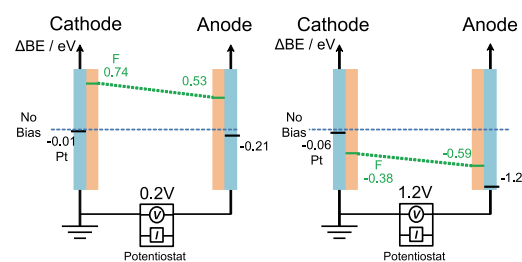


Figure 2. Electric potential diagram of each component in PEFC, where light blue bars correspond to cathode and anode electrodes of Pt (C shows the same potential) and orange to electrolyte Nafion (F and O). At the voltage of 1.2 V between the cathode and anode, a well-known two-step electric double layer is clearly observed (right panel). On the other hand, at 0.2 V, the electrolyte interestingly shows more positive potentials at both the cathode and anode electrodes (left panel).

References

- 1) T. Yokoyama, A. Koide and Y. Uemura, *Phys. Rev. Mater.* **2**, 023601 (2018).
- 2) L. Yu, Y. Takagi, T. Nakamura, O. Sekizawa, T. Sakata, T. Uruga, M. Tada, Y. Iwasawa, G. Samjeské and T. Yokoyama, *Phys. Chem. Chem. Phys.* **19**, 30798 (2017).