Industrial Application — Hard X-ray Photoelectron Spectroscopy (HAXPES)

Mechanism of Adhesion between High-Performance Fluororesin Coating and Metal Substrate Clarified at Atomic Level

Fluororesin has excellent heat resistance and chemical resistance. Cooking utensils such as metal frying pans and the inner pots of rice cookers are often coated with fluororesin. On the other hand, the adhesion between fluororesin and metals has not been sufficient for fluororesin coatings to be used in medical equipment and automobiles, where high reliability is required, which has been an obstacle to the widespread adoption of fluororesin in those areas. To commercialize fluororesin in areas where high reliability is required, it is necessary to clarify the adhesion mechanism and demonstrate the reliability of products.

Chemical state analysis by X-ray photoelectron spectroscopy (XPS) is effective for revealing the chemical state of the interface between the resin and a metal, the key factor for understanding the adhesion mechanism. However, only depths of up to a few nanometers from the surface can be analyzed by conventional equipment in a laboratory. Although depths of up to ~20 nm can be analyzed by hard X-ray photoelectron spectroscopy (HAXPES*) at SPring-8, the analysis of the interface between the resin and a metal in actual products has been impossible because the interface is located at a depth of 10 µm or more from the surface.

In this study, an original sample fabrication technique was developed to reduce the thickness of a metal layer to 20 nm or less. With this technique, we fully demonstrated the ability of HAXPES to accurately analyze the chemical state of the interface between a resin and a metal (Fig. 1). In addition to performing HAXPES using BL16XU and BL46XU, we used multiple analytical techniques, including transmission electron microscopy, to perform a comprehensive analysis. As a result, it was revealed for the first time that high adhesion is due to the formation of new carbon–oxygen–metal bonds between fluororesin and the metal produced by electron beam irradiation (Fig. 2). As a result of this breakthrough, we gained credibility with our customers by disclosing the mechanism of adhesion as well as the characteristic values for high adhesion, contributing to the increased use of fluororesin coatings (product name: cross-linked fluororesin FEX®). *HAXPES: hard X-ray photoelectron spectroscopy

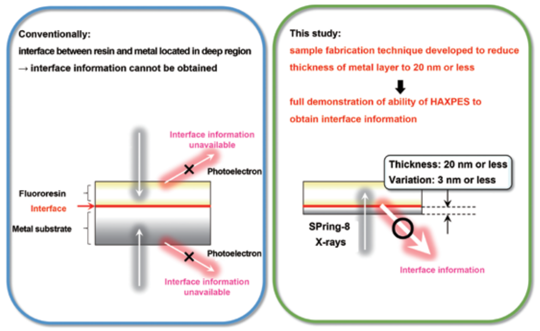
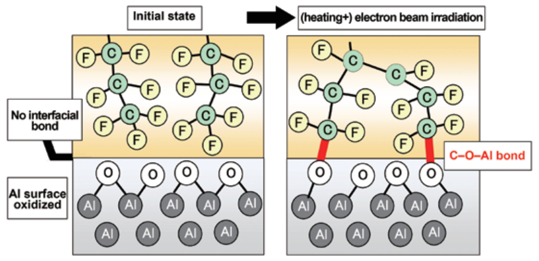


Fig. 1 Chemical state analysis of interface between resin and metal by HAXPES.



*Metal = Al in this figure

Fig. 2 Mechanism of high adhesion between fluororesin and metal (C: carbon; O: oxygen; F: fluorine; Al: aluminum).

BL16XU, BL46XU Yugo Kubo (Sumitomo Electric Industries, Ltd.)

Article: Yugo Kubo *et al., ACS Applied Materials & Interfaces* **10**, 44589 (2018)
Yugo Kubo *et al., ACS Applied Nano Materials* **5**, 6757 (2022)

Industrial Application — Hard XPS under Atmospheric Pressure

World's First Photoelectron Spectroscopy under Atmospheric Pressure and Tracking of Sulfur Poisoning Process of Fuel Cells

Fuel cells are a promising next-generation energy source and are expected to be widely used in automobiles. However, the performance and durability of the electrode catalyst made of the precious metal platinum must be improved to accelerate the implementation of fuel cells. We therefore investigated and clarified the mechanism of the sulfur poisoning process of polymer electrolyte fuel cells, which reduces their lifetime, using photoelectron spectroscopy under atmospheric pressure. Although photoelectron spectroscopy is generally performed under vacuum conditions, we developed a method of photoelectron spectroscopy that can be performed under atmospheric pressure.

X-ray photoelectron spectroscopy (XPS) is an analytical technique used to reveal the chemical state of target elements. The kinetic energy of photoelectrons emitted when a sample is irradiated with X-rays is accurately measured using the apparatus shown in Fig. 1(a). The chemical state is determined on the basis of the electron binding energy obtained by this method. Soft X-rays are usually used as the light source for XPS in a laboratory. However, the use of hard X-rays allows us to observe more deeply inside a substance or to investigate the chemical state of a sample in a gaseous atmosphere. Figure 1(b) shows the photoelectron spectra observed under atmospheric pressure (10^5 Pa) for the first time in the world, which was realized using the high-luminosity hard X-ray microbeam from the undulator insertion light source at SPring-8.

Figure 2(a) shows the photoelectron spectra of sulfur near the cathode of a polymer electrolyte fuel cell during operation. Not only the identification of existing chemical species but also the determination of the electrical potential of each chemical species is possible by the analysis of fuel cells by photoelectron spectroscopy. It is therefore easy to determine in which of the three phases, i.e., cathode, anode, and electrolyte phases, each chemical species is present. In our experiment, S^{2-} is sulfur that is adsorbed on the platinum electrode and poisons the electrode. The S^{2-} on the cathode oxidized to SO_3^{2-} and dissolves in the electrolyte as the voltage increases, whereas the S^{2-} on the anode remains as S^{2-} on the electrode. In addition, poisoning by S^{2-} is drastically reduced by the use of a platinum–cobalt electrode, demonstrating the effectiveness of such an electrode.

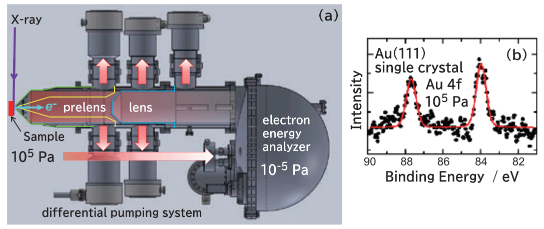


Fig. 1 (a) Schematic diagram of apparatus for hard XPS under atmospheric pressure. (b) Au4f photoelectron spectra of Au(111) single crystal observed under atmospheric pressure for the first time in the world.

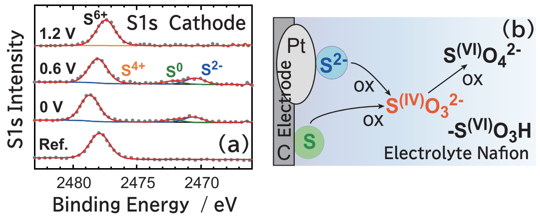


Fig. 2 (a) S1s photoelectron spectra of sulfur from cathode of polymer electrolyte fuel cell during operation. The chemical species of sulfur present depends on the voltage between the cathode and anode. (b) Schematics of chemical species of sulfur adsorbed on and desorbed from the electrode.

BL36XU Toshihiko Yokoyama (Institute for Molecular Science)

Article: Y. Takagi *et al.: Appl. Phys. Express* **10**, 076603 (2017).

Industrial Application — X-ray Radiography

Visualization of Micro-Water Generated in Polymer Electrolyte Fuel Cell Supporting Development of New-Generation Toyota Mirai Hydrogen-Powered Car

Hydrogen is a promising energy source for realizing a sustainable society. The spread of fuel cell electric vehicles as "ultimate eco-cars" is expected because they use hydrogen as fuel and emit only water. The performance of polymer electrolyte fuel cells (PEFCs) is affected not only by the properties of materials such as catalysts and electrolytes but also by the drainage efficiency of water produced by power generation. It is thus necessary to understand the behavior of water inside PEFCs.

The information needed for the design of PEFCs includes the micro-level distribution of water inside the PEFCs and its second-order changes. We developed a small evaluation bench for simulating the operation of a fuel cell electric vehicle, a special power-generating tool that transmits X-rays, and a high-speed and high-sensitivity X-ray camera system at the Toyota beamline (BL33XU). Using these devices, we developed an X-ray radiography technique that can "visualize" the water inside PEFCs (Fig. 1).

These measurement techniques are used for the design of channels and materials of PEFCs. A partially narrowed flow channel newly developed by Toyota Motor Corporation supplies air from the channel to the gas diffusion layer, which reduces the oxygen transport resistance and improves the performance. However, the effects of supplied air on water drainage are not yet fully understood. The water distribution in a conventional channel (Fig. 2, left) and that in the partially narrowed flow channel (Fig. 2, right) were compared at SPring-8. In the partially narrowed flow channel, the air supplied to the gas diffusion layer pushed the accumulated water forward and accelerated water drainage, resulting in improved power generation performance even in the presence of water. These technologies developed at SPring-8 were used in the design of the channel separator and gas diffusion layer of the PEFC in the new-generation Mirai hydrogen-powered car launched by Toyota Motor Corporation in December 2020, contributing to its improved performance and reduced cost.

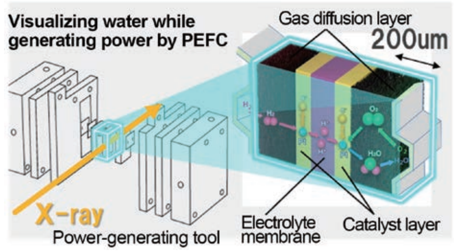


Fig. 1 Schematics of visualization of micro-level water behavior in PEFC by synchrotron radiation X-ray radiography.

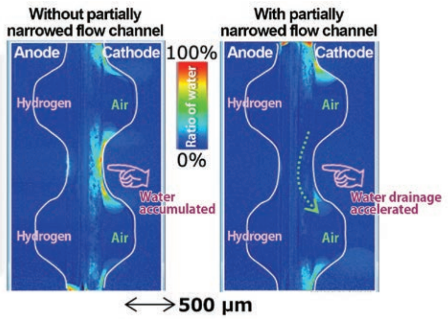


Fig. 2 Observed water distribution. "Without partially narrowed flow channel" and "with partially narrowed flow channel" denote the conventional channel and the newly developed channel adopted in the new-generation Mirai car, respectively.

BL33XU Toyota Central R&D Labs., Inc., SOKEN, Inc., and Toyota Motor Corporation

Industrial Application — Infrared Microspectroscopy Imaging

Success in visualization of localizations of proteins and lipids in hair

Around the age of 35 years, people's hair concerns shift from hair damage to hair aging. Curliness, waviness, and dryness are included in the top common hair problems and cause people to feel a change in their hair quality. A well-known change in hair caused by aging is the increase in the number of curly hairs. The localization of proteins in such curly hair has been studied by various methods. However, the localization of lipids in the hair has remained unclear. In this study, the localizations of proteins and lipids were visualized using an infrared (IR) microspectroscopy system at SPring-8. This system combines a microscope and an IR spectrophotometer and can be used to determine the localization of components in a specific region. Information on fine regions has been difficult to obtain with general IR measurement systems. Detailed data on the cross-sectional localization of components in hair have not been available.

Cross-sectional imaging revealed that proteins (amide bonds) and lipids (CH bonds) were uniformly localized in hair with a nearly round cross section and that the inside of the hair had a uniform composition localization (Fig. 1). For curly hair, however, lipids were sparsely localized (the number of CH bonds was small) at sites where proteins were densely localized (the number of amide bonds was large). In contrast, the lipids were densely localized at sites where proteins were sparsely localized (Fig. 2). That is, the localizations of proteins and lipids were in an inverse relationship.

In this study, an uneven localization of hair components, such as proteins and lipids, in curly hair was confirmed at the microlevel by visualizing a more detailed localization of hair components than before. It was found that the localization of proteins is different from that of lipids in curly hair; this is the so-called state of "hair distortion". Therefore, the curliness of hair can be improved by correcting the uneven localizations of proteins and lipids throughout the curly hair.

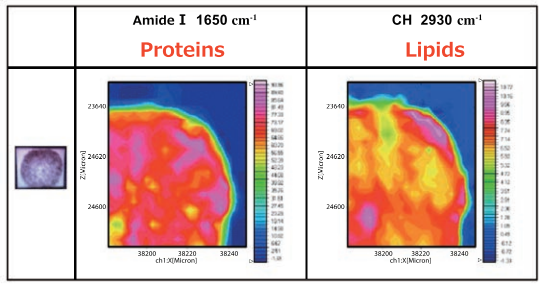


Fig. 1 Mapping of components in hair with a nearly round cross section Red region has a dense localization of components

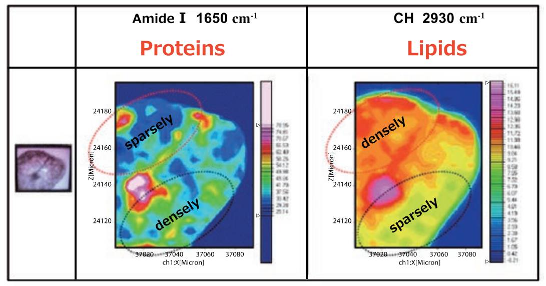


Fig. 2 Mapping of components in curly hair

BL43IR Satoshi Inamasu (Kracie Home Products, Ltd.,)