

## Operando observation of sulfur species that poison polymer electrolyte fuel cell studied by near ambient pressure hard X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a powerful tool for investigating surface physical and chemical properties of functional materials and systems. Although conventional photoelectron spectroscopy can only be operated under high vacuum, we recently succeeded in ambient pressure ( $10^5$  Pa) XPS measurements [1] using brilliant microfocused hard X-rays from SPRING-8 BL36XU undulator beamline. The beamline and XPS apparatus are dedicated to investigating degradation and poisoning mechanisms in polymer electrolyte fuel cells (PEFCs) and are maintained by University of Electro-Communications and supported by New Energy and Industrial Technology Development Organization (NEDO). In this work, we performed *operando* S 1s hard X-ray photoelectron spectroscopic (HAXPES) measurements to observe various sulfur species that poison PEFCs under working conditions.

One important methodological achievement in this work is that one can directly measure the electric potential of the electrolyte constituting the membrane-electrode assembly (MEA) as the power generation part in PEFCs. Although it is easy to measure the electrode voltage using a tester probe, the electrolyte voltage is difficult to obtain because the insertion of the tester probe induces the appearance of an electric double layer (EDL) at the electrolyte-probe interface, resulting in an electric potential difference at the interface. On the other hand, the technique of electric potential measurements using XPS is already well known and voltage distributions such as those of transistors have been reported. Owing to the exploitation of the (near) ambient pressure XPS technique, the electrolyte voltage in wet electrochemical cells is expected to be measurable, providing essential information for understanding electrochemical reactions at the interface between the working electrode and the electrolyte. Figure 1 shows the electric potentials of a Pt cathode and anode and a Nafion electrolyte determined, respectively, by Pt 3d<sub>5/2</sub> and F 1s XPS, in which cathode-anode voltages of 0.2 and 1.2 V were applied with the cathode grounded [2]. Variation of the EDL is clearly observed; even the polarity of the EDL at the cathode changes by 1.12 V between 0.2 and 1.2 V. It is here noted that the anode-electrolyte voltage does not differ between 0.2 and 1.2 V because the anode works well as a pseudo-standard hydrogen electrode, while the cathode-electrolyte voltage drastically changes, allowing

essentially different electrochemical reactions.

We have applied this novel method of electric potential measurement in electrochemical cells to sulfur species that poison PEFCs [3]. Figure 2 shows the S 1s XPS spectra around the cathode and anode under working conditions. Without artificial introduction of S-containing species to the MEA, we observed several kinds of S species depending on the applied cathode-anode voltage  $V_{CA}$ . Peak S1 can immediately be assigned to the sulfonic acid group ( $-\text{SO}_3\text{H}$ , +6 valent) of Nafion, while other peaks, S2 (+4 valent), S3 (zero valent), and S4 (−2 valent) ascribed on the basis of their binding energies (BE) to  $\text{SO}_3^{2-}$  in the electrolyte, thioether or embedded S in the C support, and anionic atomic S species adsorbed on the Pt nanoparticles, respectively. With increasing  $V_{CA}$ , the number of anionic S species adsorbed on the Pt nanoparticles at the cathode electrode gradually decreased and they completely disappear at  $V_{CA} \geq 0.8$  V owing to oxidation reactions from adsorbed S to  $\text{SO}_3^{2-}$  and possibly  $\text{SO}_4^{2-}$ , but S4 reappeared again with decreasing  $V_{CA}$ . With the introduction of oxygen to the cathode electrode, no sulfur species other than the sulfonic acid group of Nafion was detected even at the lowest voltage (not shown in Fig. 2).

Figures 3(a)-3(c) respectively give the S 1s BE of S1, S2, and S4 as a function of  $V_{CA}$ . Note that the cathode is always grounded. The BE of S4 species in Fig. 3(c) are found to be constant at the cathode and decreasing with a slope of  $-1$  eV/V at the anode, implying that the S4 species is S adsorbed on the Pt electrode. The S1 species (sulfonic acid group in Nafion electrolyte) exhibits similar  $V_{CA}$  dependence on the anode as in Fig. 2. The most interesting finding in Fig. 3 is that the S2 species (see Fig. 3(b)) ascribed to

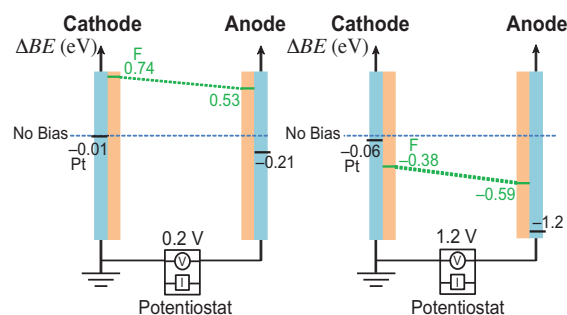


Fig. 1. Electric potential diagrams of the PEFC at the cathode-anode voltages of 0.2 V (left) and 1.2 V (right).

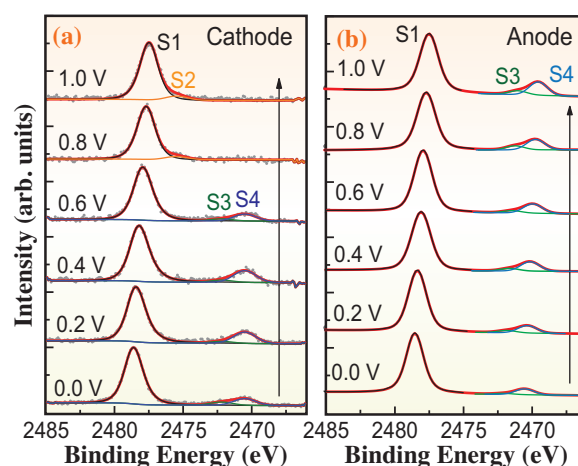


Fig. 2. S 1s HAXPES of (a) the cathode and (b) the anode in the PEFC with a cathode-anode voltage  $V_{CA}$  of 0.0–1.0 V. The cathode was always grounded.

tetravalent  $\text{SO}_3^{2-}$  also shows similar  $V_{CA}$  dependence to S1 in Fig. 3(a), clearly indicating that  $\text{SO}_3^{2-}$  is not adsorbed on the Pt or C electrode but is dissolved in the electrolyte. Consequent redox reactions concerning sulfur species are depicted in Fig. 3(d).

The present work has successfully demonstrated that the measurements of electric potentials of

chemical species in electrochemical cells, such as PEFCs, using ambient pressure HAXPES allow us to identify the locations of the phase (cathode, anode, or electrolyte) of the chemical species of interest, thus paving the way to new useful methodologies that can be applied to electrochemical cells such as fuel cells and batteries.

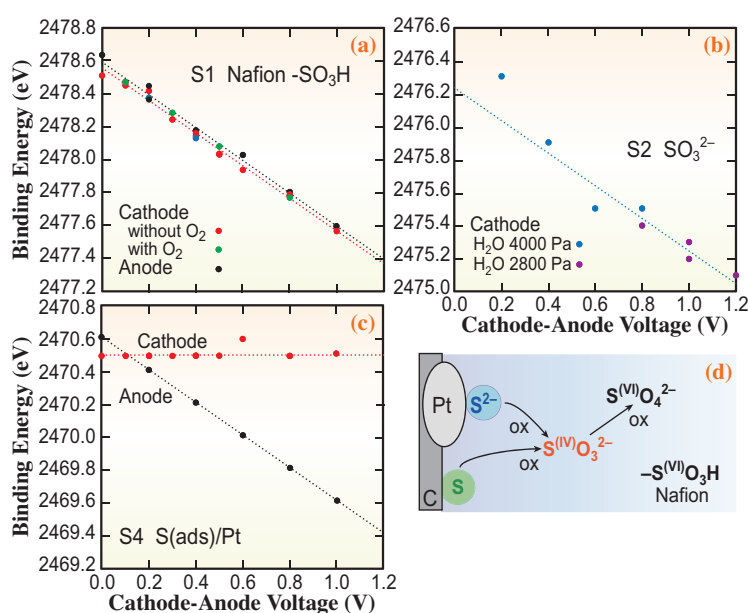


Fig. 3. S 1s binding energies of (a) S1, (b) S2, and (c) S4 species near the cathode or anode. The cathode was always grounded. (d) Schematic redox reactions of S species around the electrode. The  $\text{SO}_4^{2-}$  species was not detected in this work because of overlap of its peak with the Nafion sulfonic acid peak S1.

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## References

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