Sulfur poisoning of Pt and PtCo anode catalysts in polymer electrolyte fuel cells studied by *operando* near ambient pressure hard X-ray photoelectron spectroscopy

Ambient pressure X-ray photoelectron spectroscopy has become a powerful tool for the investigation of surface chemical reactions of functional catalytic systems. The SPring-8 **BL36XU** beamline was dedicated to the investigation of the degradation and poisoning mechanisms in polymer electrolyte fuel cells (PEFCs), and was maintained by University of Electro-Communications and financially supported by New Energy and Industrial Technology Development Organization (NEDO). We installed an ambient pressure hard X-ray photoelectron spectroscopy (AP-HAXPES) apparatus at BL36XU. In the present work, we investigated the sulfur poisoning phenomenon in Pt and PtCo anodes of polymer electrolyte fuel cells (PEFCs) before and after acceleration degradation tests (ADTs) and found significant dissimilarities in the sulfur poisoning feature between the Pt and PtCo electrodes. The PtCo anodes catalyst is revealed to be much more tolerant to S poisoning even after ADTs [1].

We investigated the S adsorption behaviors on Pt (average particle diameter of ~2.6 nm) and Pt_3Co (~3.0 nm) anode and cathode catalysts in PEFCs under working conditions for fresh specimens immediately after aging as well as degraded specimens after ADTs by recording the HAXPES data. Figure 1 shows the results of S 1*s* HAXPES at the anodes. The principal peaks appearing at ~2478 eV are ascribed to the S species from the sulfonic acid group (–SO_3H) in the Nafion electrolyte. Peaks of other characteristic S species such as anionic S (S^{2-}) and zero-valent S (S^0), which are regarded as poisonous S species, are also found in Fig. 1. By plotting the electric potentials evaluated from the binding energies (see Figs. 2(b) and 2(d) below), both the S^{2-} and S^0 species are found to have the same potential as the Pt and C electrodes. This implies that S^{2-} is the S species absorbed on the Pt electrode, while S^0 is the species adsorbed on the C support. In all the samples shown in Fig. 1, the amount of S^{2-} increases significantly with an increase in cathode-anode bias voltage, indicating that reductive conditions at the anode induce poisonous S^{2-} adsorption. This observation can be understood easily because S^{2-} adsorption occurs through the reductive reaction between the Pt electrode and the SO_3^{2-} or SO_4^{2-} species dissolved in the electrolyte.

The most striking result found in Fig. 1 is an appreciable difference in the amount of S^{2-} between the Pt and Pt_3Co anodes after ADTs. The amount of S^{2-} are depicted in Figs. 2(a) and 2(b). Although the aged (fresh) Pt and Pt_3Co electrodes give similar amounts of S^{2-}, the degraded Pt anode after ADTs

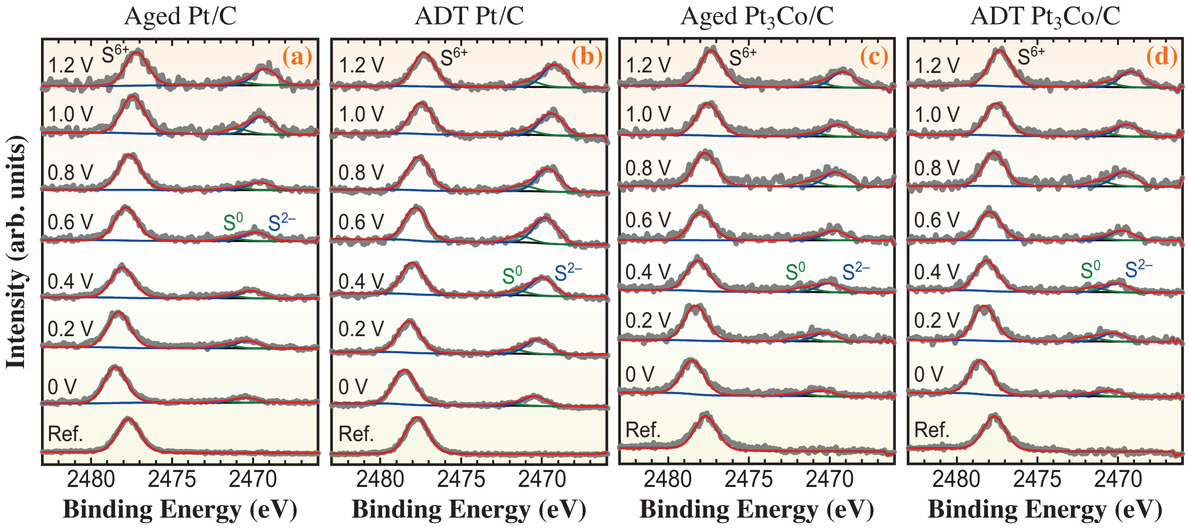

Fig. 1. S 1*s* HAXPES of **(a)** the fresh Pt/C anode immediately after the aging treatment before ADTs, **(b)** the degraded Pt/C anode after ADTs, **(c)** the fresh Pt_3Co/C anode (aged), and **(d)** the degraded Pt_3Co/C anode after ADTs. The main peaks at ~2778 eV are the S^{6+} species originating from the sulphonic acid group in the Nafion electrolyte, and other species (S^0 and S^{2-}) are the poisonous S impurities. The amount of S^{2-} is found to be much more significant at the Pt/C anode than at the Pt_3Co/C anode.

exhibits much more S^{2-} adsorption than the Pt_3Co anode. This finding implies that the Pt_3Co anode is more tolerant to the adsorption of poisonous S^{2-} than the Pt anode.

It is well known that the Pt_3Co cathode exhibits a higher activity in the oxygen reduction reaction (ORR). The reason for this higher ORR activity could be applied to gain an understanding of the present finding. It is reported that the surface Pt atoms are significantly negatively charged in the Pt(skin)/Pt_3Co(111) system compared with the pure Pt case [2] because of the difference in electronegativity between Pt and Co. It is believed that, as a result, the negatively charged surface Pt destabilizes O^{2-} adsorption on the Pt cathode, leading to a higher ORR activity. In the present electrode, a similar structure of the Pt skin and Pt_3Co core is elucidated by scanning transmission electron microscopy (STEM) energy dispersive X-ray spectroscopy (EDS) measurement [3]. The surface Pt atoms are thus negatively charged in the Pt_3Co electrode, which exhibits a weaker (repulsive) interaction with anionic sulfur species such as SO_3^{2-}, SO_4^{2-}, or S^{2-}. The adsorption of poisonous S^{2-} may eventually be suppressed.

S^{2-} adsorption is much more serious in the anode because, at the cathode, adsorbed S^{2-} on the Pt catalyst is desorbed at a high bias voltage owing to the oxidative environment, while the anode is in a more reductive environment at a higher bias voltage. The adsorbed S^{2-} cannot be removed easily. The Pt_3Co electrode has a higher tolerance to poisonous S^{2-} adsorption at the anode and a higher ORR activity at the cathode. The Pt_3Co electrode is found to be suitable not only at the cathode but also at the anode.

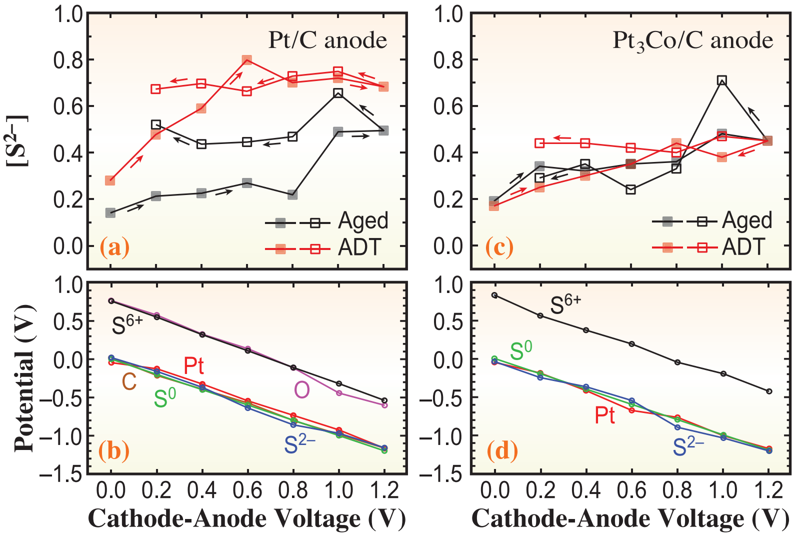

Fig. 2. **(a, c)** Amounts of S^{2-} species on the fresh (black) and degraded (red) Pt/C (a) and Pt_3Co/C (c) anode, and **(b, d)** electric potentials of S^{6+} (electrolyte), S^{2-}, S^0, O (liquid H_2O), C, and Pt (electrode). Because of the potential difference between the electrode and the electrolyte, the S^{2-} and S^0 species are found to adsorb on the electrode.

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References

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