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S-K XANES Study on Adsorption of Nafion on Pt(111) and Glassy Carbon

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1 Introduction

Perfluorosulfonic acid polymer (Nafion) and Pt-particle catalysts supported by amorphous carbon (Pt/C) have been widely used for polymer electrolyte fuel cells (PEFCs). The Pt/C catalysts are surrounded by Nafion ionomer and the proton is transferred from the anode to the cathode catalysts via Nafion sulfonic group. However, the interaction between Nafion and the catalysts is still unclear although it should be one of key factors to the proton-transfer efficiency. In this work, adsorption of Nafion on a Pt(111) and a glassy carbon substrate has been studied by S K-edge XANES spectroscopy, particularly paying attention to the chemical state of Nafion sulfonic group and its electrochemical potential dependence.

2 Experiment

The S-K XAFS measurements of samples including sulphur standards in solution were performed at BL-11B using a He-path vessel with Si_3N_4 windows and a proportional counter. The substrate surfaces were cleaned by cyclic voltammetry (CV) with a Pd wire counter electrode and a Ag/AgCl reference electrode in a 2 M $HClO_4$ aqueous solution with Ar bubbling. Nafion was added into the solution with a concentration of 2 mM and after running several CV cycles the substrates were taken out from the solution under the potential kept at -0.2 and +0.6 V and subsequently rinsed with pure water.

3 Results and Discussion

The S K-edge XANES spectra of three sulphur standards in solution are shown in Fig. 1. The Nafion spectrum (black) exhibits a main peak at 2480.6 eV and a shoulder at 2483 eV, which are tentatively attributed to excitations to molecular orbitals with π^* and σ^* symmetries, respectively, with respect to the S=O bond of sulfonic group (-SO_3H). The CH_3SO_3H spectrum (blue) changes significantly in spite of replacement of only alkyl part. The S-K XANES spectrum varies depending on chemical environment of the sulphur atom. Fig. 2 shows S-K XANES spectra of the Pt(111) and the glassy carbon substrates after the Nafion adsorption treatment mentioned above. At -0.2 V, Nafion is adsorbed on the Pt(111) surface with the same chemical form as Nafion ionomer (see Fig. 1 top), which suggests that a major part of sulfonic groups are not directly interacting with the Pt(111) surface and Nafion is bound to the surface via van-der-Waals (vdW) interactions between the polymer chain and the Pt surface. This interaction seems to become weak at +0.6 V due to oxidation of the Pt(111) surface. The glassy carbon does not adsorb any Nafion irrespective of potential. These results suggest that Nafion is most strongly bound to metallic Pt surface via vdW interactions due to its hydrophobicity.

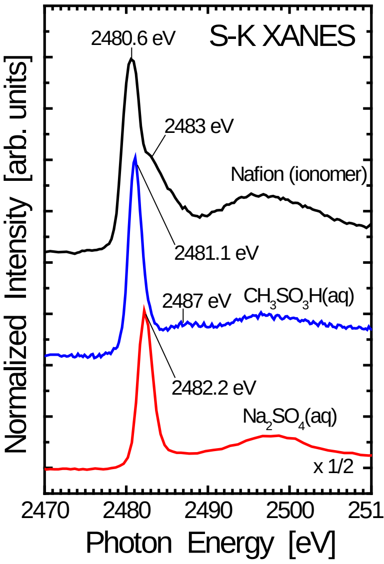

Fig. 1: S-K XANES spectra of three sulphur-containing molecules in solution. The solvent is a mixture of water and alcohol for Nafion and pure water for the others.

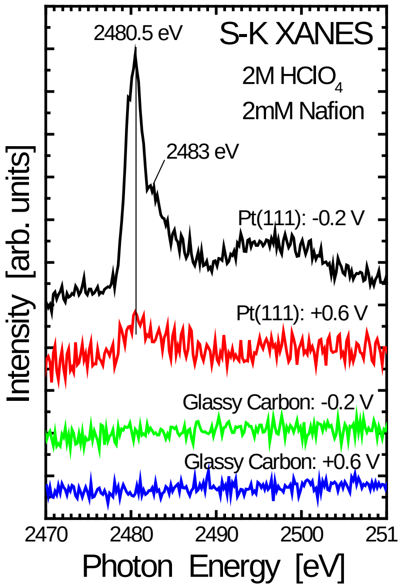

Fig. 2 : S-K XANES spectra taken for Pt(111) and glassy carbon substrates after taking out from 2 mM Nafion/2M $HClO_4$ aqueous solution at potentials of -0.2 and +0.6 V vs. Ag/AgCl and subsequent rinsing with pure water.

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