

X-Ray Absorption Spectroscopy Study on Fe Phthalocyanine-Based Carbon Alloy Catalysts for Polymer Electrolyte Fuel Cells

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Introduction

As cathode catalysts for polymer electrolyte fuel cell (PEFC), carbon alloy catalysts (CACs), which are composed of C with a little amount of B, N, O, transition-metal etc., without precious metal like Pt have potential to be alternative to Pt catalysts. It has been reported that CACs which are synthesized from metal complexes through heat treatment have high oxygen reduction reaction (ORR) activity [1-2]. To clarify the origin of the high catalytic activity for ORR, it is important to investigate the chemical states of these catalysts. It has been revealed that CACs containing more nitrogen at certain positions have higher ORR activity [3, 4], while nitrogen-coordinated metals can be ORR active sites [2, 5]. However, further studies are needed to correlate the catalytic activity to the chemical states. In this study, in order to clarify the chemical states of carbon, we have investigated the electronic structures of carbon in CACs which were synthesized from Fe-phthalocyanine (FePc) by x-ray absorption spectroscopy (XAS).

Experimental

FePc and a polymer were mixed in acetone, and the mixture was heat-treated at 800 or 1000 °C. The residuals were pounded to prepare Fe800 and Fe1000. The numbers in sample names represent the treatment temperatures. A part of each was washed with hydrochloric acid to remove iron. These acid-washed samples were named as Fe800aw and Fe1000aw, respectively.

The XAS experiments were conducted at PF BL-7A. The C 1s spectra of the samples were measured at room temperature in the total electron yield mode by collecting the photocurrent. As reference, highly oriented pyrolytic graphite (HOPG) and a carbon black (Vulcan XC-72) were also measured.

Results and discussion

The XAS spectra are shown in Fig. 1. These spectra were normalized to height of the peak at 285.0 eV, which is characteristic to HOPG composed of sp^2 hybridized carbon atoms. The result that all the samples have a peak at 285.0 eV shows that all measured CACs contain sp^2 hybridized carbon. The spectra shows that the peak intensities at 288.1 eV, which is characteristic for amorphous carbon (carbon black), decreases with

increasing the heat treatment temperature, indicating that the heat treatment temperatures largely influence the chemical states of carbon. The difference of spectra between the samples also reflects the interaction between carbon and oxygen, like oxygen adsorption on carbon or the chemical bond between carbon and oxygen [6]. The peak intensities at 288.1 eV decrease after the acid washing and the decreases of the intensity change with the treatment temperatures. These results show that the treatment temperature is an important factor to determine the chemical states of carbon or interaction between oxygen and carbon. For detailed analysis, discrimination of the contribution from amorphous carbon and interaction between oxygen and carbon to the peak intensity at 288.1 eV should be made.

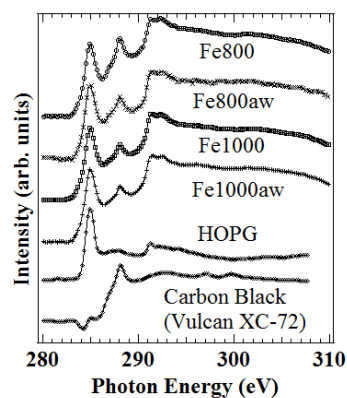


Fig. 1: The C 1s XAS spectra of Fe phthalocyanine-based CACs, HOPG and a carbon black.

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