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Soft X-ray Absorption Spectroscopy of Carbon Alloy Catalysts for Oxygen Reduction Reaction

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Introduction

The carbon based materials such as carbon alloy catalysts (CACs) show high oxygen reduction reaction (ORR) activities[1,2] and are expected to be cathode catalyst alternative to Pt for Polymer Electrolyte Fuel Cells (PEFC). The origin of their ORR activities should be elucidated to further enhance the activities. So far, we have studied the cobalt phthalocyanine-based CACs and have reported the importance of graphite-like nitrogen and the neighboring carbon at the zigzag edge of graphite.[3,4] In this study, the electronic structure of residual cobalt in the CACs is investigated by synchrotron radiation analyses to clarify the role of cobalt for ORR activity.

Experimental

The CACs were derived from pyrolyzed cobalt phthalocyanine (CoPc) and phenol resin followed by ball milling. The amount of cobalt in the precursor was adjusted to be 3 wt.% in the mixture of cobalt phthalocyanine and phenol resin. The temperature of the pyrolysis was 1000 °C. After ball milling, some samples were washed with hydrochloric acid to remove cobalt (acid washing). Prepared samples are Co1000 (the CAC before acid washing) and Co1000aw (the CAC after acid washing).

In order to investigate the electronic structure of the CACs, X-ray absorption spectroscopy was performed at BL-7A of the Photon Factory. The XAS spectra were recorded in a total electron yield (TEY) mode under an ultrahigh vacuum of 2×10^{-9} Torr at room temperature.

Results and Discussion

The electrochemical activities for ORR measured by the rotating disk electrode voltammetry showed that Co1000 and Co1000aw had similar values of oxygen reduction potential (E_{O2}), indicating that the acid washing does not change E_{O2} for the CAC.

As shown in Fig. 1, the Co 2*p* XAS spectra have revealed that there are certain amounts of residual cobalt in the CACs after pyrolysis and the residual cobalt in the CACs is different from the precursor (CoPc: planer cobalt 2+). The spectra of the CACs are much closer to that of Co metal but have broader peaks, indicating the presence of other oxidized states. The Co $2p_{3/2}$ peak width at half-height of Co1000 is 2.0 eV and that of Co1000aw is 1.8eV. These results suggest that the acid washing process reduces the oxidized cobalt species in the CACs. Since the ORR activity does not change by the acid washing which reduces the oxidized cobalt species, there is no correlation between the oxidized cobalt and the ORR activity. Furthermore, considering that metallic cobalt is not active for ORR[5], the residual cobalt should not be the active site.

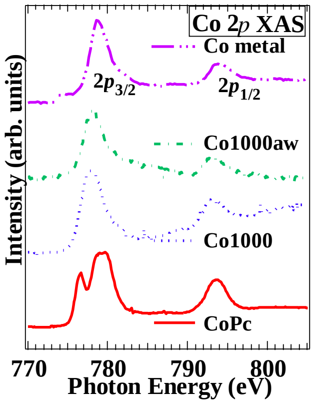

Fig. 1. Co 2*p* XAS

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