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) activities1, 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 Recently, it has been revealed that the catalysts synthesized from iron phthalocyanine/phenolic resin (FePc/PhRs) heat-treated at 600°C show the maximum ORR activity at certain temperature.5 In these iron containing carbon-based materials, iron in the precursors seem to be responsible for the formation of the ORR active carbon structure.5 In order to investigate the relationship between the carbon structure in FePc/PhRs catalysts and the heat treatment temperature, electronic states of carbon in the catalysts pyrolyzed at various temperatures have been analyzed by carbon 1s soft X-ray absorption spectroscopy (XAS).

Experimental

The samples were derived from pyrolyzed iron phthalocyanine and phenolic resin. The amount of iron in the precursor was adjusted to be 3 wt% in the mixture of iron phthalocyanine and phenolic resin. The temperature range for the pyrolysis was from 200°C to 800°C. Here, Fe200 denotes the FePc/PhRs sample pyrolyzed at 200°C.

C 1s XAS measurement was performed at BL-7A of the Photon Factory, KEK. The XAS spectra were recorded in a total electron yield mode under an ultrahigh vacuum of 2 x 10⁻8 Torr at room temperature.

Results and Discussion

Figure 1 shows C 1s XAS spectra of the FePc/PhRs catalysts. In each sample, π* resonance peak characteristic of a graphitic plane is observed around ~285 eV.6 A shoulder component around ~284 eV (E*) is observed in the highest ORR active catalysts such as Fe600. This may correspond to a unique electronic state called edge state, which is characteristic of the zigzag edge in graphite.6 This is well consistent with our previous study that graphite-like nitrogen and the neighboring carbon at the zigzag edge should be the ORR active site.3, 4

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References


Fig. 1. C 1s XAS spectra for various CACs. *shima@srg.t.u-tokyo.ac.jp