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Roles of Iron in Metal-Phthalocyanine Based Carbon Alloy Catalysts for Polymer Electrolyte Fuel Cells Investigated by X-Ray Absorption Spectroscopy

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Introduction

Carbon alloy catalysts (CACs) are promising cathode catalysts for polymer electrolyte fuel cells (PEFC) due to low cost and potential of good durability. To prepare active CACs, elucidation of the Oxygen Reduction Reaction (ORR) active sites is essential. Heat-treated metal-macrocycles in the temperature range of ~600 °C have been reported to show good ORR activity [1]. The structure of ORR active sites are metal sites in iron-phthalocyanine (FePc) or metal-N_4 moieties [1]. If CACs are heat-treated in ~1000 °C, shell like carbon structure develops and the metal-N_4 moieties decompose almost completely, but CACs still show good ORR activity [1]. Our recent experiments have shown that iron-phthalocyanine (FePc) based CACs show much higher ORR activity than H_2-phthalocyanine (Pc) based CACs [2], and first principles calculation has suggested that zigzag edge of graphene shows ORR activity [3]. In iron containing carbon-based materials, iron in the precursors seems to be responsible for the formation of ORR active carbon structures [2]. In this experiment, we obtained C 1*s* XAS of Pc and FePc based CACs to clarify the roles of iron in the formation of active carbon structures.

Experimental

Samples were prepared by pyrolyzing the mixture of Pc and phenolic resin (PhRs) denoted as Pc/PhRs, and the mixture of FePc and PhRs, FePc/PhRs. The amount of iron in FePc/PhRs was adjusted to be 3 wt% [2]. Nitrogen concentration of Pc/PhRs is adjusted to that of FePc/PhRs. The temperature range for the pyrolysis was from 700 °C and 800 °C. Here, Pc700 and Fe700 denote the Pc/PhRs and FePc/PhRs pyrolyzed at 700 °C, respectively.

C 1*s* 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 1*s* XAS spectra of the Pc/PhRs and FePc/PhRs based CACs. Fe800 and Fe700 show clear peaks at 291.1 eV, which is due to exiton in graphite [3]. Peak height at 288.0 eV, which is characteristic for amorphous components (*sp*^{3} carbon) [3], decreases from Fe700 to Fe800. FePc/PhRs based CACs have smaller shoulder components at ~284 eV, which is assigned as edge states of graphene [4]. These results suggest that Pc/PhRs based CACs are composed of more amorphous carbon atoms than FePc/PhRs CACs, and iron in FePc/PhRs based CACs promotes development of larger graphitic structures.

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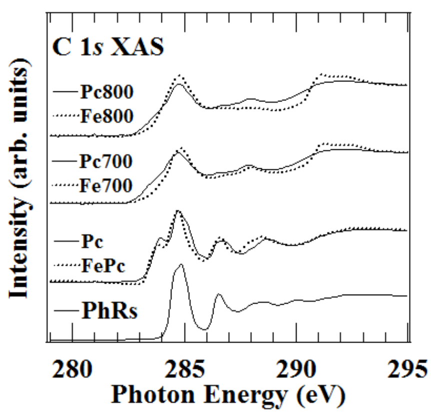

Fig. 1 C 1*s* XAS of CACs.