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Electronic states of the carbon support in Pt-Co cathode catalysts for PEFC

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Introduction

The Polymer Electrolyte Fuel Cell (PEFC) system has been developed as an environmentally friendly power source for stationary, transportation and portable applications. The electrochemical surface area (ECA) loss of Pt nano-particle catalyst is one of the major causes to reduce the PEFC performance. For Pt cathode catalyst, the carbon corrosion, that is carbon oxidization, induces the Pt detachment from the carbon support and decreases the ECA [1]. Chizawa *et al.* [2,3] have detected the carbon dioxide from Pt cathode catalyst during the acceleration cycle testing, which suggests the carbon support corrosion. In this study, the electronic states of C have been investigated to determine the corrosion of the carbon support in Pt-Co catalyst.

Experiment

Pt-Co nano-particles were loaded on the carbon support, which is carbon black. The Pt-Co catalyst was mixed with Nafion® dispersion as an ionomer in the catalyst layer to make a cathode catalyst layer in a membrane electrode assembly (MEA). Five MEAs were stacked for this testing. The open circuit voltage holding and the constant current operation followed by the nitrogen purge consist the acceleration cycle [2]. After each step of 2,000 cycles up to 10,000 cycles, continuous current operation was conducted for 250 hours to induce the flooding in the cathode catalyst layer.

The electronic states of C in the cathode catalyst layer of MEAs were measured using the soft X-ray absorption spectroscopy (XAS) in BL-7A of the Photon Factory. The measurements were conducted for the initial and cycle-tested MEAs.

Results and discussion

The electrochemical surface area of the cathode catalyst after 10,000 cycles decreased to 32% from the initial state. It means that the cathode catalyst has been deteriorated severely. The C 1*s* XAS spectra of the initial and the 10,000 cycle-tested MEAs normalized by the maximum peak height are shown in Fig. 1. Carbons not only in the carbon support but also in the ionomer in the catalyst layer contribute to the spectra. Although the line shapes of the spectra are quite similar, a difference between the initial MEA and 10,000 cycle-tested MEAs shows little increase at 288 eV. This peak is reported to belong to the C-C bond [4]. The observations suggest that no evidence of the production of any additional functional group by carbon corrosion can be seen in XAS spectra of the Pt-Co cathode catalysts.

As the Pt nano-particles induce the carbon corrosion [5], the carbon corrosion might occur in localized area around the catalyst particle. A SEM observation of the MEAs suggests that the cathode catalyst layer thickness didn't change after 10,000 cycles. It is possible that carbon corrosion occurs locally and might not be reflected on the XAS spectra.

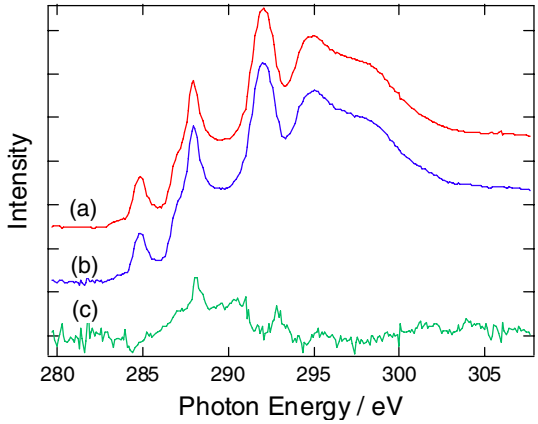

Fig. 1 C 1*s* XAS spectra of (a) initial MEA, (b) 10,000 cycle-tested MEA and (c) difference between (a) and (b), whose magnitude is enhanced 5 times.

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