

XAFS study on PtCo/C catalyst synthesized by electron-beam irradiation

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PtCo nanoparticles are one of the most promising materials as a cathode catalyst for polymer electrolyte membrane fuel cells (PEFCs) [1]. We challenged the synthesis of the carbon-supported PtCo bimetallic nanoparticle (PtCo/C) catalysts by an electron-beam irradiation reduction method (EBIRM) [2] because EBIRM is suitable for the mass-production of nanoparticle catalysts.

In order to investigate the relationships between the structure and catalytic activity, the structures of PtCo/C were characterized by TEM, ICP-AES, and the techniques of XRD and XANES, and the catalytic activity of PtCo/C was evaluated by LSV. In this report, only the results of XANES analysis are presented.

Experimental

Three kinds of PtCo/C samples were synthesized by an EBIRM under different Pt/Co millimolar ratios (i.e. Pt/Co = 0.50/0.00, 0.50/0.25, and 0.50/2.00). Aqueous 50-mL solutions that contained H₂PtCl₆, CoCl₂, carbon black powder (Vulcan XC-72R), 2-propanol, and NaOH were prepared in 100-mL glass vials. The glass vials that contained the precursor solution were then irradiated with a 4.8 MeV electron beam for several seconds at a commercial facility in order to reduce the metal ions. After irradiation was complete, the powder in each solution was separated from the supernatant by suction filtration and was dried at 70°C for one night. The obtained PtCo/C samples were denoted here as Pt_{0.50}Co_{0.00}/C, Pt_{0.50}Co_{0.25}/C, and Pt_{0.50}Co_{2.00}/C, respectively.

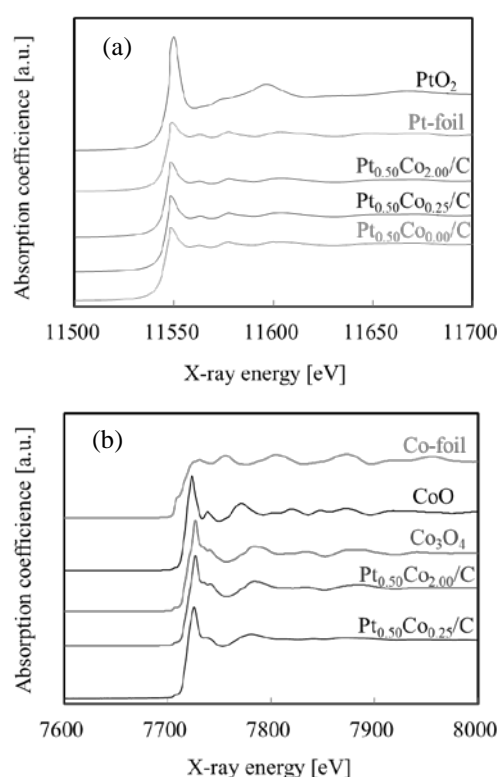
The XANES spectra around the Pt-L_{III} edge (11550 eV) and Co-K edge (7730 eV) were measured at the NW10A beam line of PF-AR. The X-ray beam was focused using a Si(311) crystal monochromator. The obtained PtCo/C samples were shaped into 7-mm-diameter pellets. The pellets were subsequently placed into the X-ray path. All XANES measurements were performed in air at room temperature in transmission mode. The Athena software (ver. 0.8.056) was utilized for the XANES analysis.

Results and Discussions

Figure 1 shows the normalized Pt-L_{III} edge and Co-K edge XANES spectra of the PtCo/C samples synthesized by an EBIRM under different Pt/Co millimolar ratios. Table 1 shows the Pt-foil/PtO₂ and Co-foil/CoO/Co₃O₄ ratios of the PtCo/C samples, as calculated from linear combination fitting using the XANES spectra of reference materials. The Pt-foil ratios of all the PtCo/C samples were approximately 90%, which means that most of Pt exist as a metal. In contrast, Co-foil ratios of Pt_{0.50}Co_{0.25}/C

and Pt_{0.50}Co_{2.00}/C were 0%, which indicates that Co exist as an oxide.

Although LSV results are not shown in this report, LSV results indicated the catalytic activity increases as the Co concentration increases, and the improvement of the catalytic activity was explained by the XANES results. Thus, XANES analysis was useful for characterization of catalytic nanomaterial.

Fig. 1: XANES spectra (a) Pt-L_{III} edge (b) Co-K edge.Table 1: Pt-foil/PtO₂ and Co-foil/CoO/Co₃O₄ ratios.

Sample ID	Pt-foil [%]	PtO ₂ [%]	Co-foil [%]	CoO [%]	Co ₃ O ₄ [%]
Pt _{0.50} Co _{0.00} /C	90	10	—	—	—
Pt _{0.50} Co _{0.25} /C	87	13	0	44	56
Pt _{0.50} Co _{2.00} /C	88	12	0	0	100

References

- [1] T. Toda et al., *J. Electrochem. Soc.* **146** (1999) 3750.
 [2] S. Seino et al., *J. Nanopart. Res.* **10** (2008) 1071.

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