Chemistry

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Monitoring of triple phase boundary of polymer electrolyte fuel cells by Platinum L_3-edge X-ray absorption spectra

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Introduction

New preparation method of platinum-carbon composite was developed for polymer electrolyte fuel cells (PEFCs). First, Pt complex was supported in ordered mesopores of silica. Next, acetylene was decomposed catalytically on the Pt metal surface. Then, Pt–C composite was obtained after the removal of silica by hydrofluoric acid (HF) washing. This reprica preparation and the characterization were already reported [1]. The preparation of membrane-electrolyte assembly (MEA) was also monitored by using Pt L_3-edge XANES. Especially, MEA preparation and the chemicals used were studied in this report.

Methods

$Pt(NH_3)_4(OH)_2$ was ion-exchanged with Al–MCM-41 at 353 K for 48 h. Obtained white powder was heated at 573 K in H_2. The sample was at 973 K in 20 mL/min of acetylene (10%) flow diluted in N_2. Then, Al–MCM-41 was removed with 15 % HF washing. 50 mg of obtained replica Pt–C composite (6.1 wt% Pt) was suspended in 0.2 mL Nafion solution and dried. The Nafion concentration was 2.5% (Nafion-2.5) or 1.25% (Nafion-1.25) prepared from DE521, Dupont. Also, replica Pt–C composite was immersed in ethanol. Commercial Pt/Ketjen black EC300J (IFPC40-II; Ishifuku metal ind.) was used as reference. Pt L_3-edge XAFS spectra were measured at beamline 9C and 12C in transmission mode at 290 K.

Results and discussion

Samples in air exhibited higher whiteline peak intensities (1.44–1.59) for replica Pt–C (Table 1a) and Pt/Ketjen black (e) than 1.28 for Pt metal foil (h). In Table 1, the whiteline peak intensities for replica Pt–C with Nafion (b, c) were 1.28–1.27, lower than 1.44 for replica Pt–C in air. Moreover, these whiteline peak intensities were dependent on Nafion concentration used for MEA preparation. The whiteline peak intensity for replica Pt–C in ethanol was 1.26, that was the lowest intensity among replica Pt–C samples. In the case of Pt/Ketjen black catalyst, whiteline peak intensities followed same trend as for replica Pt–C samples.

These results were explained by redox of surface Pt sites (Figure 1). In air, the valence of surface Pt sites was δ+ – 4+ (Figure 1A). Next, the oxidic surface Pt sites were reduced to Pt^0 when the Pt–C catalyst was immersed in Nafion solution (Figure 1B). 1-propanol and ethanol contained (75–89 vol%) in Nafion solution was found to reduce the surface Pt sites. A part of the reduced Pt^0 sites was reserved covered with the Nafion film, but other part of Pt^0 sites exposed to air, not covered with Nafion re-oxidized (Figure 1C). The active Pt sites in cathode catalyst of PEFCs are at triple phase boundary, with proton conductor (Nafion), carbon (electron conductor), and air. Thus, whiteline peak intensity for Pt–C catalyst with Nafion is a nice indicator of the Nafion coverage over the Pt surface and can predict the activity of the cathode catalysts.

Table 1. Energy positions (eV) and normalized intensity of whiteline peak at Pt L_3

Sample name	Energy (eV)	Normalized Intensity
(a) Replica Pt–C in air	11566.7	1.59
(b) Replica Pt–C with Nafion-1.25	11566.8	1.28
(c) Replica Pt–C with Nafion-2.5	11566.8	1.27
(d) Replica Pt–C in ethanol	11566.7	1.26
(e) Pt/Ketjen black in air	11566.5	1.44
(f) Pt/Ketjen black with Nafion-1.25	11566.5	1.24
(g) Pt/Ketjen black with Nafion-2.5	11566.4	1.23
(h) 5 microns of Pt metal foil	11565.6	1.28
(i) PtO_2	11567.3	2.07

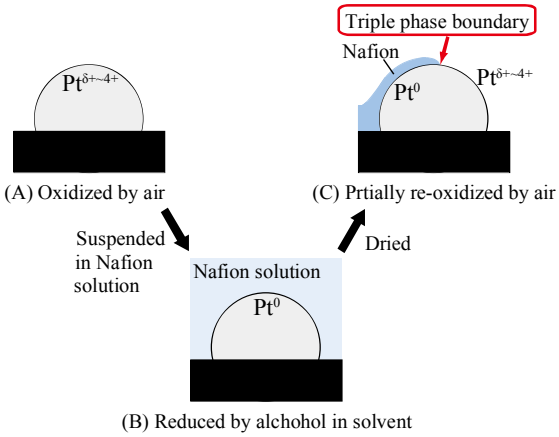

Figure 1. Redox of surface Pt particles in Pt–C catalyst with Nafion.

Reference

[1] Oka et al., *J. Phys. Chem. C* **114**(2), 1260–7 (2010).
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