

Electronic state analyses of platinum-carbon composite synthesized via replica method for polymer electrolyte fuel cells

Kazuki Oka, Yasuo Izumi*

Department of Chemistry, Graduate School of Science, Chiba University, Inage-ku, Chiba 263-8522

Introduction

We have developed new preparation method of platinum-carbon composite for fuel cells (FCs). First, platinum was supported in ordered mesoporous silica. Next, acetylene was decomposed catalytically on Pt metal surface. Then, Pt-C composite was obtained after the removal of silica by HF washing. This procedure was named as replica method.

In cathode of polymer electrolyte FCs (PEFCs), reaction is believed to proceed over Pt sites at triple phase boundary (C, electrolyte, fuel gas). Especially, Pt needs in contact with C in order to enable high conductivity. Thus, we examined Pt electronic states in contact with C or polymer electrolyte membrane of our replica Pt-C composite and of commercial Pt-C catalyst by means of Pt L₃-edge XAFS.

Experimental

Pt(NH₃)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 H₂ (Pt/Al-MCM-41, 1.4 wt% Pt). The sample was in 20 mL/min of acetylene (10%) diluted in N₂ at 973 K (Pt-C/Al-MCM-41). Al-MCM-41 was removed from Pt-C/Al-MCM-41 with 15 % HF washing. Obtained Pt-C composite was suspended in Nafion solution and dried at 290 K (Pt-C/Nafion). Commercial Pt/Vulcan XC-72/Nafion (1 mg-Pt/cm²) for FC was used as a reference. Pt L₃-edge XAFS spectra were measured at beamline 9C and 12C in transmission mode under ambient air.

Results & discussion

The peak positions of Pt L₃-edge XANES for Pt/Al-MCM-41 (Figure 1a) were similar to those for Pt metal (Figure 1e). The peak (absorption edge and post-edge peaks) intensity was weaker for Pt/Al-MCM-41 compared to data for Pt metal, indicating that the Pt particles in Pt/Al-MCM-41 were on nanometer scale.

The peak just above the absorption edge for Pt-C/Al-MCM-41 (Figure 1b) became weaker compared to data for Pt/Al-MCM-41 (Figure 1a, b). At present, we tentatively interpret this change due to negative charge transfer from C formed to Pt 5d band.

The spectral pattern of replica Pt-C composite (Figure 1c) was in transition from spectrum e for metallic Pt to spectrum f for PtO₂. The Pt-Pt coordination number *N* was evaluated to 6.1 at 0.265 nm for the replica Pt-C composite based on the EXAFS curve-fit analysis. Pt particle size was estimated to 1.0 nm based on the *N* value in consistent with size population given by TEM (0.69 – 1.8 nm). Thus, O₂ adsorption was suggested over

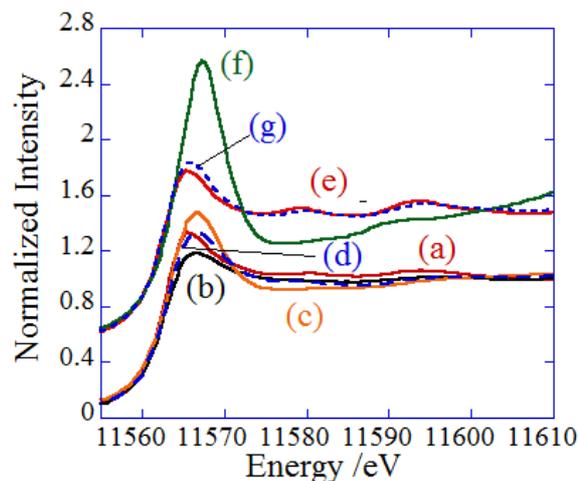


Figure 1. Pt L₃-edge XANES spectra for Pt/Al-MCM-41 (a), Pt-C/Al-MCM-41 (b), replica Pt-C (c), replica Pt-C/Nafion (d), 5 microns of Pt foil (e), PtO₂ (f), and Pt/Vulcan XC-72/Nafion (g).

Pt surface part not in contact with C derived from acetylene.

Finally, the spectrum for replica Pt-C/Nafion is depicted in Figure 1d. The peak just above the absorption edge was most similar to that for spectrum a (Pt/Al-MCM-41), but shifted by 1.0 eV toward higher energy. The post-edge pattern resembled most that of spectrum b (Pt-C/Al-MCM-41). Thus, the Pt particles were kept at metallic state in contact with Nafion and the negative charge transfer from C was not significant compared to the case of Pt-C/Al-MCM-41.

In comparison, XANES pattern of Pt/Vulcan XC-72/Nafion (Figure 1g) corresponded exactly to that for Pt metal foil. The Pt particles in Pt/Vulcan XC-72/Nafion were much greater than that in replica Pt-C composite and less effectively in contact with Nafion.

Table 1. Energy positions (eV) of Pt L₃ absorption edge and intense peak just above the edge

Sample	Absorption edge	Intense peak
Pt/Al-MCM-41	11562.5	11565.6
Pt-C/Al-MCM-41	11562.5	11566.6
replica Pt-C	11563.0	11566.8
replica Pt-C/Nafion	11562.5	11566.6
Pt metal foil	11562.0	11565.5
PtO ₂	11564.8	11567.3
Pt/Vulcan XC-72/Nafion	11562.4	11566.0

* yizumi@faculty.chiba-u.jp