

Platinum L₃-edge X-ray absorption spectra directly see and evaluate the triple phase boundary of replica Pt–C catalysts in fuel cells

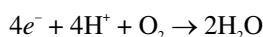
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Introduction

New preparation method of platinum–carbon composite was recently developed for polymer electrolyte fuel cells (PEFCs) [1]. 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 fluoric acid (HF) washing. This preparation route was named as replica method.

On the cathode of PEFCs, reaction proceeds over Pt sites at triple phase boundary (carbon, electrolyte, and air).



Our replica Pt–C has an advantage of greater contact of C with embedded Pt particles. However, suitable coverage of polymer electrolyte over the Pt surface is not known. Pt surface needs to be covered with PE for the proton transport and at the same time to be reserved for the active sites for O₂ reduction. Thus, the change of Pt electronic states in contact with PE was investigated for our replica Pt–C composite and commercial Pt/C catalysts by means of Pt L₃-edge XAFS.

Experimental section

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; 1.3 wt% Pt). The sample was at 973 K in 20 mL/min of acetylene (10%) flow diluted in N₂ to give Pt–C–Al–MCM-41. Al–MCM-41 was removed from the Pt–C–Al–MCM-41 with 15 % HF washing. Obtained replica Pt–C composite was suspended in Nafion solution and dried. The Nafion concentration was 2.5 % (Nafion-2.5) or 1.25 % (Nafion-1.25). Commercial Pt/Ketjen black EC300J (IFPC40-II; Ishifuku metal ind.) was used as reference. Pt L₃-edge XAFS spectra were measured at beamline 9C and 12C in transmission mode at 290 K.

Results & discussion

Pt L₃-edge XANES spectra for replica Pt–C composite, Pt/Ketjen black EC300J both in ambient air, and PtO₂ (Figure 1c,f,b) were similar to one another except for gradual intensity decrease of peak at ≈11566 eV from spectrum b to spectrum f then to spectrum c. This indicates that a part of the surface Pt sites was oxidized if they are not in contact with support carbon.

The spectra for the mixture of Pt–C catalyst and Nafion (Figure 1d,e,g,h) corresponded to transition states starting from PtO₂ to metallic Pt. The reduction of Pt

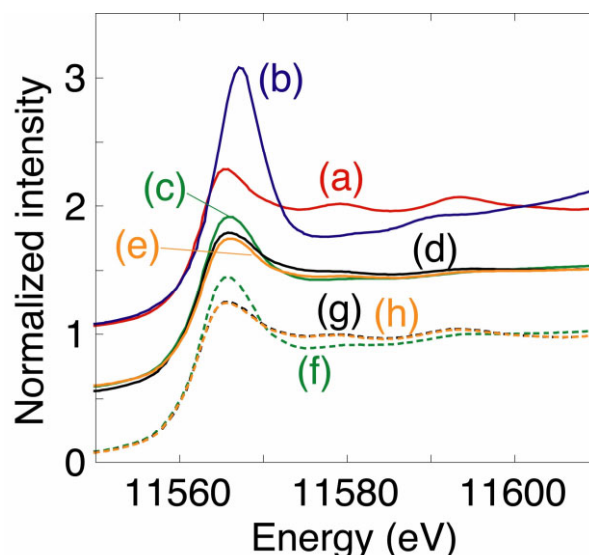


Figure 1. Pt L₃-edge XANES spectra for 5 microns of Pt foil (a), PtO₂ (b), replica Pt–C (c), replica Pt–C with Nafion-2.5 (d), replica Pt–C with Nafion-1.25 (e), Pt/Ketjen black (f), Pt/Ketjen black with Nafion-2.5 (g), and Pt/Ketjen black with Nafion-1.25 (h).

surface sites was spectroscopically demonstrated by the protons derived from Nafion. Among cathode catalysts in ambient air and (partially) in contact with Nafion, energy positions of edge peaks negligibly shifted but the peak intensity varied as much as 1.24 – 2.07 (Table 1). Thus, the edge peak intensity of Pt L₃-edge XANES spectra can be utilized as a key index to optimize PE coverage over Pt sites.

Reference

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

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Table 1. Energy positions (eV) and normalized intensity of Pt L₃ white-line peak for Pt–C composites and references

Sample	Energy (eV)	Normalized Intensity
Pt metal foil	11565.5	1.28
PtO ₂	11567.3	2.07
Replica Pt–C	11566.2	1.41
Replica Pt–C & Nafion-2.5	11566.1	1.28
Replica Pt–C & Nafion-1.25	11565.1	1.24
Pt/Ketjen black	11565.9	1.44
Pt/Ketjen black & Nafion-2.5	11565.7	1.24
Pt/Ketjen black & Nafion-1.25	11565.7	1.24