

XRD AND XAFS STUDIES OF CARBON SUPPORTED Pt-Ru ELECTROCATALYST IN A POLYMER-ELECTROLYTE-FUEL-CELL

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Structures of carbon supported Pt-Ru catalyst in a polymer-electrolyte-fuel-cell (PEFC) were analyzed by X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAFS). XRD analysis identified a face-centered-cubic (fcc) alloy structure for Pt-Ru. XAFS analysis revealed that Pt and Ru atoms were, however, not randomly distributed in the Pt-Ru fcc lattice. A Pt atom was more likely surrounded by Pt atoms, whereas a Ru atom was likely surrounded by Ru atoms.

1. Introduction

PEFC is a promising candidate for portable and mobile power sources. Ru atoms were added to Pt/C catalyst in PEFC to improve its CO tolerance, namely the electroactivity and the efficiency of PEFC [1, 2]. There have been few reports on the local structure of the Pt-Ru/C catalyst. In this study, we report the results on XRD identification of the crystal structure and on XAFS determination of local atom structures surrounding Pt and Ru atoms in PEFC.

2. Experimental

Two commercial samples, carbon supported Pt (40 wt%) and Pt (30 wt%)-Ru (15 wt%) catalysts were used in this study. XRD and XAFS measurements were performed using a conventional powder diffractometer (Cu-K α radiation) and a Rigaku laboratory XAFS measurement system, respectively. Pt L3-edge and Ru K-edge XAFS spectra were measured in the conventional transmission mode. Si(400) and Ge(840) single crystals were used to obtain a monochromatic incident beam from a Mo anode target. Intensities of the incident and the transmitted X-rays were measured using a gas-filled proportional counter and a scintillation counter, respectively. The Pt-Ru/C sample was diluted with BN and pressed to a tablet of 15-mm diameter prior to XAFS measurements.

3. Results and Discussion

3.1. XRD Analysis

XRD patterns of the Pt-Ru/C and Pt/C samples are plotted in Figure 1. For phase identification

purpose, the ICDD PDF standard diffraction pattern of Pt is also plotted at the bottom of Figure 1. Observed XRD peaks of both the Pt-Ru/C and Pt/C samples (marked by solid circles) match those of the ICDD standard pattern of Pt. This confirmed that both Pt-Ru/C and Pt/C formed a fcc structure.

The fcc XRD peaks from Pt-Ru/C appeared at higher 2θ angles than those from Pt/C. This indicates that the Pt-Ru alloy had a smaller fcc lattice than that of Pt/C.

3.2. XAFS Analysis

Pt L3-edge and Ru K-edge XAFS spectra were used for the study of the local atom structures surrounding Pt and Ru atoms.

Fourier transformations of the Pt L3-edge and the Ru K-edge EXAFS oscillation functions $k^3\chi(k)$ are shown in Figure 2. The peaks at 1.8-3.2 Å were due to the nearest neighbor

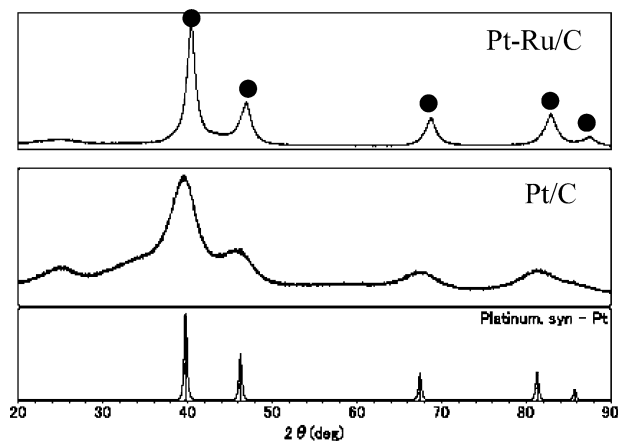


Fig. 1. XRD patterns of Pt-Ru/C and Pt/C.

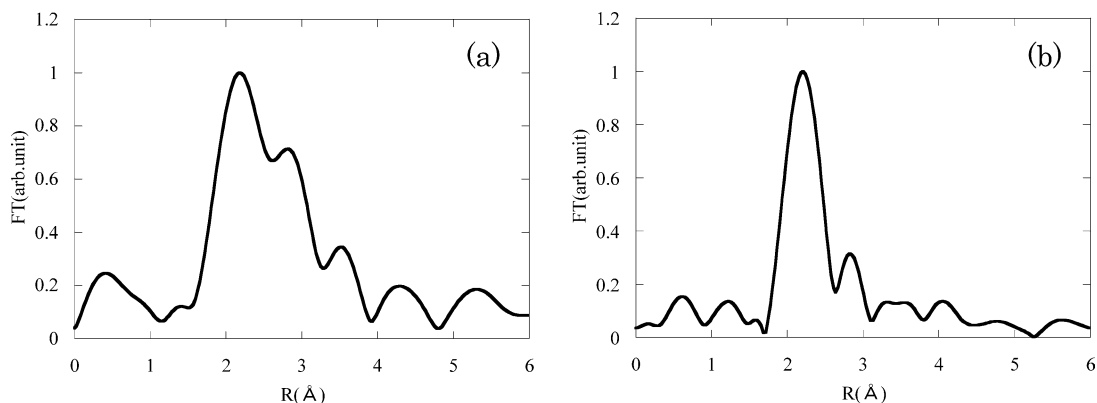


Fig. 2. Fourier transformation of Pt L3 (a) and Ru K-edge (b) EXAFS spectra for Pt-Ru/C.

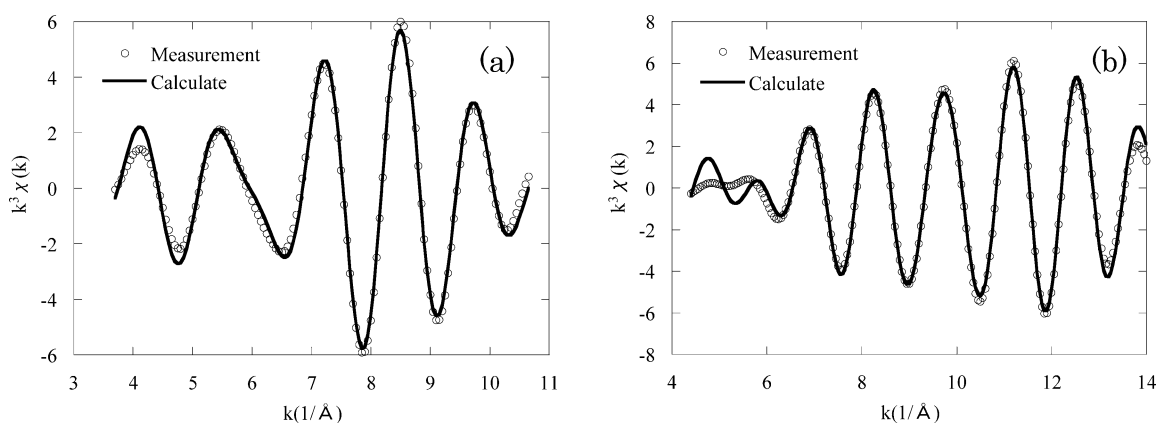


Fig. 3. Curve fitting results in the first peaks of Pt L3 (a) and Ru K-edge (b) for Pt-Ru/C.

Table 1. Atomic distances of Pt-Ru determined by XAFS analysis.

Pt L3-edge		Ru K-edge		Pt metal (FCC structure)
Shell	Atomic distance (Å)	Shell	Atomic distance (Å)	Atomic distance (Å)
Pt-Pt	2.71	Ru-Ru	2.66	2.77
Pt-Ru	2.68	Ru-Pt	2.69	

Pt-Pt, Pt-Ru and Ru-Ru, Ru-Pt shells for Pt L3-edge and Ru K-edge.

Curve fitting results in the k -space of the peaks at 1.8–3.2 Å of Pt L3-edge and Ru K-edge for Pt-Ru/C are shown in Figure 3 and Table 1. The backscattering amplitudes and the phase shifts for the Pt-Pt, Pt-Ru, Ru-Ru and Ru-Pt shells were obtained by FEFF calculation for fcc Pt-Ru [3]. Results show that the atomic distance of $R_{\text{Pt-Ru}}$ was practically equal to that of $R_{\text{Ru-Pt}}$. The difference between $R_{\text{Pt-Pt}}$ and $R_{\text{Ru-Ru}}$ was, however, significantly large. In addition, the atomic distances calculated from XAFS were shorter than that of metallic Pt, and these values were equal to those obtained by XRD. It is,

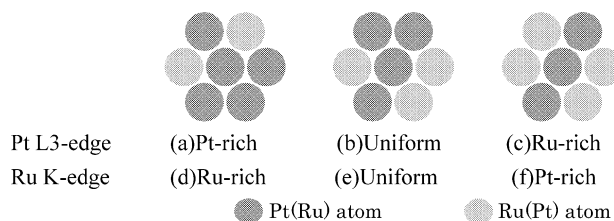


Fig. 4. Simulated models of Pt L3 (a)–(c) and Ru K-edge (d)–(f) for Pt-Ru/C.

therefore, suggested that the Pt and Ru atoms in Pt-Ru did not randomly distribute, although the average crystal structure of Pt-Ru was fcc. The local atom distributions surrounding Pt and Ru atoms were studied using simulated XAFS

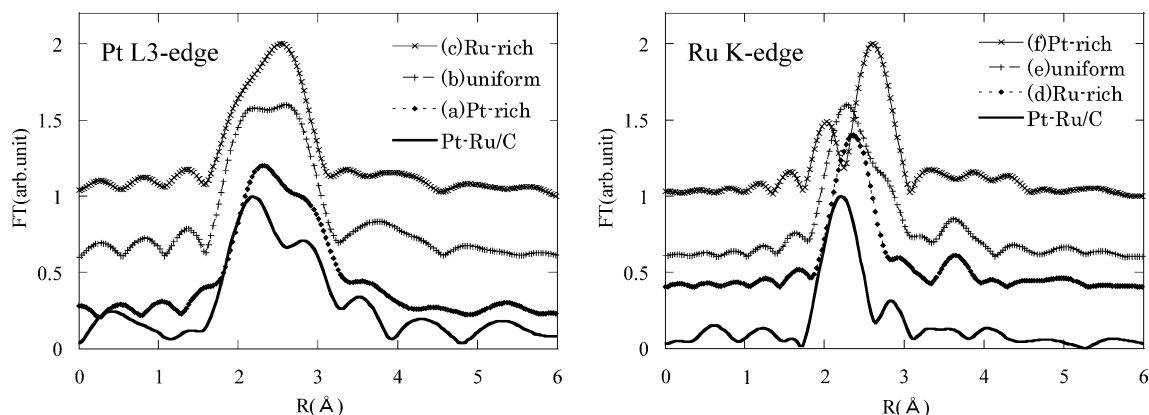


Fig. 5. Comparison the observed XAFS profiles and the simulated spectra.

spectra obtained by FEFF calculation.

3.3. XAFS Simulation

In XAFS simulation, it was assumed that the average crystal structure of Pt–Ru was fcc, and the atomic ratio of Pt and Ru was 1:1. Three models (namely, Pt-rich, uniform alloy, and Ru-rich) were used for the simulation of Pt L3-edge and Ru K-edge.

The experimental XAFS profiles were compared with the simulated spectra (Figure 5). It is found that the experimental Pt L3-edge profile matches that of the Pt-rich model, whereas Ru K-edge profile matches that of the Ru-rich model. This indicates that Pt and Ru atoms were not randomly distributed. And that Pt–Ru/C had two different local atom arrangements surrounding Pt and Ru, a Pt-rich and a Ru-rich regions, respectively.

4. Conclusions

The crystal structure and local atom arrangements surrounding Pt and Ru atoms were determined for carbon supported Pt–Ru catalyst using XRD and XAFS, respectively. XRD results identified Pt and Ru with a fcc alloy structure. XAFS analysis showed that experimental Pt L3 and Ru K-edge spectra matched those calculated from a Pt-rich and a Ru-rich models, respectively. This indicates that Pt and Ru atoms were not randomly distributed in the Pt–Ru fcc lattice. Pt atoms were more likely surrounded by Pt atoms, whereas Ru atoms likely surrounded by Ru atoms.

References

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