9C, 12C, NW10A/2010G607

In situ XAFS analysis of electrochemical behavior of PtRu nanoparticle catalyst

Satoru KAGEYAMA[1*], Satoshi SEINO[1], Takashi NAKAGEWA[1], Takao A. YAMAMOTO[1],
Hiroaki Nitani[2]
[1]Osaka Univ., Yamadaoka 2-1, Suita, Osaka, 565-0871, Japan.
[2]KEK-PF, Tsukuba, Ibaraki 305-0801, Japan

Introduction

PtRu nanoparticles have been attracting much attention, because they are applicable to the anode catalysts for direct methanol fuel cell (DMFC) [1]. However, the degradation of catalysis during operating still remains as a critical issue for the commercialization of DMFCs. Therefore, the investigation of their electrochemical behavior in operating condition is required for a development of highly durable PtRu catalysts. We have performed in situ XAFS measurement of PtRu catalysts during operation with simulated electrochemical cell. The XANES spectra obtained implied that the preferential dissolution of Ru occurred at the surface.

Experimental

Source materials used were H2PtCl6 (99.9%, Wako), RuCl3 (n=2-3, 99.9%, Wako) as metal precursors, ultra pure water (18 MΩ•cm), carbon supports (Vulcan XC-72R, Cabot). All the chemicals were charged in a 100-ml glass vial. The vial was then irradiated with an electron beam at room temperature (20 kGy/sec for 10 second, at EBIS, Japan) [2]. In situ XAFS measurement was performed with simulated electrochemical cell. The fluorescence XANES spectra at the Pt-L_3 and Ru-K edges were measured with a multi-channel SSD at the beam line NW10A of PF-AR during CV cycling. A carbon paper with the catalysts powder was used as working electrode. The electrochemical behavior was examined by cyclic voltammetry, CV as giving potential loading cycles (0.6-1.1 V vs. NHE, 5 mV/sec, 50 cycles) in 1.5 M H_2SO_4 +methanol of 20 vol.%.

Results and Discussion

In table 1, the coordination numbers determined by EXAFS analysis of Ru-K edge are listed. The metallic bonds, $N_{\mathrm{Ru\text{-}Ru}}$ and $N_{\mathrm{Ru\text{-}Pt}}$ were confirmed. It should be noted that $N_{\mathrm{Ru\text{-}O}}$ is very large, as compared with other bonds. This result is consistent with the results on Pt core/PtRu shell structure [3].

Table 1 Coordination numbers determined by EXAFS analysis of Ru-K edge.

Coordination number	
$N_{\mathrm{Ru\text{-}Ru}}$	1.1±0.6
$N_{\mathrm{Ru\text{-}Pt}}$	2.5±1.1
$N_{\mathrm{Ru\text{-}O}}$	4.2±0.9
R-factor	0.002

Figure 2 shows the XANES spectra at the Pt-L_3 edge along with a spectrum of reference Pt metal: the spectra before CV and after 5, 10 and 50 CV cycles. The spectra of our sample have a metallic feature. No significant change of the states of Pt was observed. Figure 3 shows the XANES spectra at the Ru-K edge along with a spectrum of reference $RuCl_3$, Ru metal and RuO_2. The spectra of our as-made sample have a oxidized feature. In contrast to Pt-L_3, the spectra became steeper, and the peaks arose at lower energy with increasing of CV cycle number. It seems that this gradual change is not caused by the appearance of metallic feature, implying a change from Ru^{4+} to Ru^{3+} state by dissolution.

Our results imply that Ru located PtRu shell was dissolved preferentially by CV cycling.

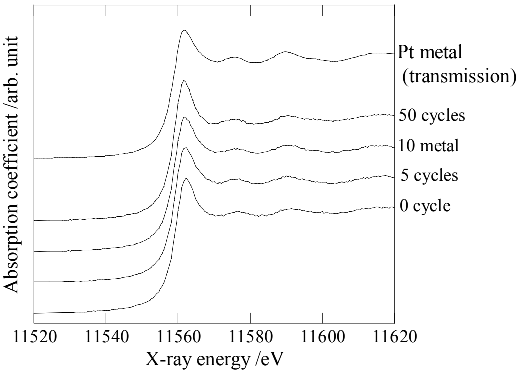

Fig.1 in situ XANES spectra at the Pt-L_3 edge.

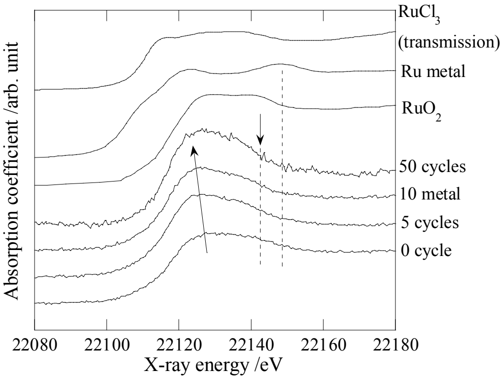

Fig.2 in situ XANES spectra at the Ru-K edge.

References

[1] H.S. Liu et al., J. Power Sources 155 95 (2006).
[2] S. Seino et al., J. Nanoparticle Res. 10 1071 (2008).
[3] H. Nitani et al., Appl. Catal. A: Gen. 326 194 (2007).

* s-kageyama@mit.eng.osaka-u.ac.jp