

XAFS study on PtRu/C catalyst synthesized by electron-beam irradiation

Hiroaki NITANI¹, Ryo HORIOKA¹, Kosuke OHARA¹, Takuya KAWAGUCHI¹, Satoru KAGEYAMA¹, Kazuhiro MATSUDA¹, Takashi NAKAGAWA², Takao A. YAMAMOTO¹
¹Graduate School of Engineering, Osaka Univ., 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan
²Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan

Introduction

PtRu nanoparticle catalysts have been attracting much attention as an anode catalyst of direct methanol fuel cell, because of its high CO tolerance. However, effective cell voltage is much lower than its thermodynamic one due to high overpotential at anode PtRu catalyst. Therefore, it is important to improve catalytic activity of the PtRu catalyst. In our previous work, we showed the correlation between the catalytic activity and the surface structure of PtRu nanoparticles by using a “pairing factor” and concluded that a random alloy structured surface led to high catalytic activity for PtRu nanoparticle [1]. In this work, we tried to synthesize random alloy structured PtRu nanoparticles with electron-beam irradiation method. XAFS spectra of synthesized samples were measured, and we checked whether the “pairing factor” would be valid for these samples.

Experimental

PtRu alloy nanoparticles loaded on a carbon support (PtRu/C) were synthesized as follows. Aqueous solution containing H_2PtCl_6 , $RuCl_3$, carbon nanoparticles and 2-propanol were prepared. Then the solution was irradiated by 4.8 MeV of electron-beam for a few seconds in order to reduce metallic ions. The irradiated dose was about 10 kGy. After washing with water and ethanol and drying, PtRu/C catalyst was obtained. For XAFS measurements, PtRu/C samples were mixed with boron nitride and shaped into 7-mm diameter pellets.

Pt- L_{III} (11549 eV) and Ru- K (22120 eV) edges XAFS spectrum of PtRu/C were obtained at the BL-12C beam line of KEK-PF and at the BL-14B2 beam line of the SPring-8, respectively. Monochromator was Si(111) double crystals. Unwanted higher harmonic waves were eliminated by detuning (KEK-PF) and a Rh mirror (SPring-8). Measurements were performed in air at room temperature with the transmission mode. The intensities of incident and transmitted X-rays were obtained with ion chambers.

Results and Discussions

The theoretical EXAFS analyses were performed by “IFEFFIT” and “FEFF7” software with assuming of

single scattering paths of Pt-Pt, Pt-Ru, Ru-Pt and Ru-Ru bonds. In least square fitting, the structural parameters; R , N , σ^2 , and ΔE_0 were optimized for each paths. The pairing factors were calculated as $P_{Pt} = N_{Pt-Ru} / (N_{Pt-Pt} + N_{Pt-Ru})$, and $P_{Ru} = N_{Ru-Pt} / (N_{Ru-Pt} + N_{Ru-Ru})$. The relationships between these “pairing factor” and catalytic activity were evaluated. The results showed that there was a clear correlation between P_{Ru} and catalytic activity. Furthermore we also found relationships between Debye-Waller factor of Ru and catalysis as depicted in Figure. These results indicated that synthesized PtRu/C catalysts consisted of Pt-rich core and Ru-rich shell region and that the catalytic activity of PtRu/C catalysts were enhanced by Ru-Pt pairs according to the “bi-functional mechanism” [2]. Thus we concluded that the “pairing factor” was good indicator to evaluate the catalysis of PtRu nanoparticles even if they were synthesized various methods.

References

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*Now at National Institute of Advanced Industrial Science and Technology (AIST).
 E-mail: nitani.hiroaki@aist.go.jp

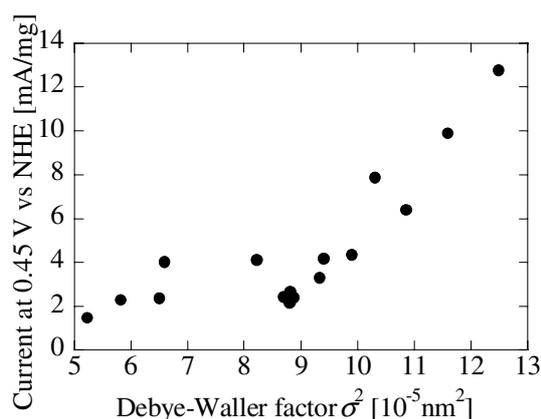


Fig. Relationship between Debye-Waller factor and catalytic activity.