XAFS Characterization of Pt Nanoparticle Catalysts on MWCNT Functionalized by Gd Species for Oxygen Reduction Reaction

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1 Introduction
We prepared fine Pt nanoparticle catalysts functionalized with Gd hydroxide/oxide species on multi-wall carbon nanotubes (MWCNTs) (denoted as A-PtGd), and the prepared catalysts exhibited superior oxygen reduction reaction (ORR) performance compared with the similarly prepared Pt nanoparticles without Gd species (denoted as A-Pt).[1] The oxidation states and the local coordination structures of the prepared Pt nanoparticles with/without Gd species (A-PtGd and A-Pt) were investigated by Pt LIII-edge and Gd LII-edge XAFS.[1]

2 Experimental
Pt nanoparticles with/without Gd species (A-PtGd and A-Pt) were prepared according to the literature.[1] The loading of Gd species in A-PtGd was estimated to be 1/5 of the loading of Pt species in a molar ratio.
Pt LIII-edge and Gd LII-edge XAFS were measured in a transmission mode at 20 K at the BL-12C station with a Si(111) double-crystal monochromator. Ionization chambers filled with pure N2 and N2/Ar (85:15) gas (for Pt LIII-edge), and pure N2 and N2/Ar (75:25) gas (for Gd LII-edge) were used to monitor incident and transmitted X-rays, respectively. EXAFS spectra were analysed using ATHENA and ARTEMIS programs. k²-Weighted EXAFS oscillations were Fourier transformed into R-space, and curve-fitting analysis was performed in R-space with coordination number (CN), interatomic distance (R), Debye-Waller factor (σ²), and correction-of-edge energy (ΔE0). Phase shifts and backscattering amplitudes were calculated by the FEFF8 code.

3 Results and Discussion
The oxidation state of the Pt nanoparticles for A-PtGd was analyzed by Pt LIII-edge XANES (Figure 1(A)), and the spectrum was compared with that of A-Pt. The white line heights of A-PtGd and A-Pt were similar to that of Pt foil, indicating that the Pt nanoparticles of A-PtGd and A-Pt were both basically metallic. The local coordination structure of A-PtGd was analyzed by Pt LIII-edge EXAFS (Figure 1(B)), and it was also compared with that of A-Pt. The CN and bond distances of the Pt-Pt coordination for A-PtGd were fitted as 6.2 ± 0.6 and 0.275 ± 0.002 nm, respectively, and these values were similar to that of A-Pt (6.1 ± 1.8 and 0.275 ± 0.002 nm), indicating that the size of Pt nanoparticles was similar in both catalysts.[1]

The loading of Gd species for A-PtGd was analyzed by Gd LIII-edge XANES (Figure 1(C)), and it was estimated to be 3+. The XANES spectrum showed similar features to that of Gd(OH)3 rather than Gd2O3, suggesting that the major Gd species would be Gd³⁺ hydroxides. The local coordination structure of Gd species for A-PtGd was analyzed by Gd LIII-edge EXAFS (Figure 1(D)), and the bond distance of the Gd-O coordination was fitted as 0.239 ± 0.009 nm (CN = 7.6 ± 1.6). The fitted Gd-O distance was in between of Gd2O3 (0.230 nm) and Gd(OH)3 (0.246 nm), suggesting that the Gd species in A-PtGd would be mainly Gd(OH)3 with a small amount of Gd2O3.[1]

A-PtGd showed higher activity for ORR than A-Pt, and one of the reasons was clarified that the coexistence of Gd species suppressed Pt oxidation and accelerated Pt oxide reduction.[1]

Figure 1. (A) Pt LIII-edge XANES and (B) k²-weighted Pt LIII-edge EXAFS FT (k = 30–180 nm⁻¹) of A-PtGd, A-Pt, and Pt foil. (C) Gd LIII-edge XANES and (D) k²-weighted Gd LII-edge EXAFS FT (k = 30–120 nm⁻¹) of A-PtGd, Gd(OH)3, and Gd2O3.

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References

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