

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

Satoshi MURATSUGU*¹, Kentaro ICHIHASHI¹, Mizuki TADA^{1,2}

¹ Department of Chemistry, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya, 464-8602, Japan.

² Research Center for Materials Science (RCMS) & Integrated Research Consortium on Chemical Science (IRCCS), Nagoya University, Furo-cho, Chikusa, Aichi 464-8602, Japan.

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 L_{III}-edge and Gd L_{III}-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 L_{III}-edge and Gd L_{III}-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 L_{III}-edge), and pure N₂ and N₂/Ar (75:25) gas (for Gd L_{III}-edge) were used to monitor incident and transmitted X-rays, respectively. EXAFS spectra were analysed using ATHENA and ARTEMIS programs. *k*³-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 (σ^2), and correction-of-edge energy (ΔE_0). 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 L_{III}-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 L_{III}-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 oxidation state of Gd species for **A-PtGd** was analyzed by Gd L_{III}-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 of **A-PtGd** was analyzed by Gd L_{III}-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 co-existence of Gd species suppressed Pt oxidation and accelerated Pt oxide reduction.^[1]

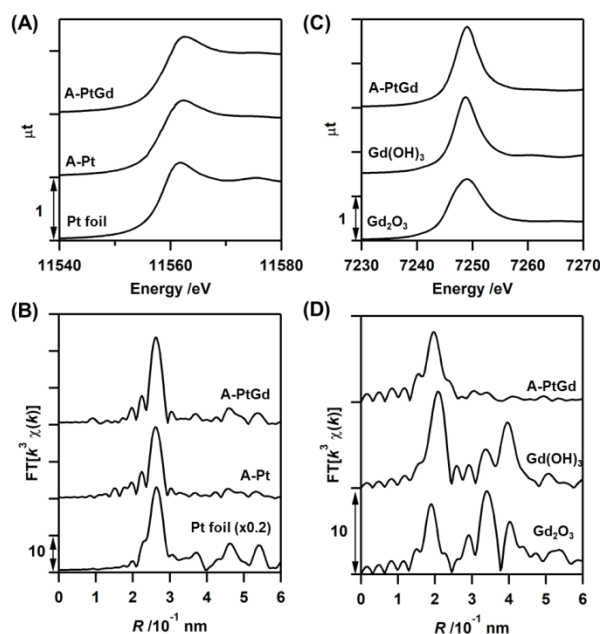


Figure 1. (A) Pt L_{III}-edge XANES and (B) *k*³-weighted Pt L_{III}-edge EXAFS FT (*k* = 30–180 nm⁻¹) of **A-PtGd**, **A-Pt**, and Pt foil. (C) Gd L_{III}-edge XANES and (D) *k*³-weighted Gd L_{III}-edge EXAFS FT (*k* = 30–120 nm⁻¹) of **A-PtGd**, Gd(OH)₃, and Gd₂O₃.

References

[1] K. Ichihashi *et al.*, *J. Phys. Chem. C* **124**, 26925-26936 (2020).

* smuratsugu@chem.nagoya-u.ac.jp