

XAFS characterization of Pt-Gd alloy nanoparticles on hollow mesoporous sphere carbon support for efficient electrochemical oxygen reduction reaction

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1 Introduction

We prepared Pt₂Gd alloy nanoparticles with narrow size distribution by using Pt and Gd organometallic complexes as precursors and a hollow mesoporous carbon sphere (HMCS) as a support (denoted as Pt₂Gd/HMCS). The structure of Pt₂Gd alloy nanoparticles in Pt₂Gd/HMCS was characterized by XRD, TEM/HAADF-STEM-EDS, XAFS, and XPS, and electrochemical oxygen reduction reaction (ORR) performances of Pt₂Gd/HMCS was investigated.^[1]

2 Experiment

Pt *L*_{III}-edge and Gd *L*_{III}-edge XAFS of the as-prepared samples were measured in a transmission mode at the BL-9C and BL-12C stations. Ionization chambers filled with pure N₂/Ar (8.5/1.5 v/v) and pure Ar were used to monitor incident and transmitted X-rays for Pt *L*_{III}-edge, respectively. Ionization chambers filled with pure N₂ and pure N₂/Ar (7.5/2.5 v/v) were used to monitor incident and transmitted X-rays for Gd *L*_{III}-edge, respectively.

Pt *L*_{III}-edge XAFS of the sample after acceleration degradation test (ADT) was measured in fluorescence mode at the BL-9C station. Ionization chambers filled with pure N₂/Ar (8.5/1.5 v/v) and a 7-channel Ge solid-state detector were used to monitor the incident and fluorescent X-rays, respectively. Inelastically scattered X-rays were cut off using a Zn filter ($\mu t = 3$), the characteristic X-rays from the Zn filter were cut off using a solar slit, and the fluorescent X-rays from Pt (*L* _{α} line) were selected. The rotating disk electrode with sample after ADT was directly measured.

3 Results and Discussion

Figure 1(a) shows the Pt *L*_{III}-edge XANES spectrum of Pt₂Gd/HMCS and control samples. The white line intensity of the Pt *L*_{III}-edge XANES spectrum of Pt₂Gd/HMCS (Figure 1(a)) was similar to those of metallic Pt species in Pt/HMCS (prepared in a similar manner to Pt₂Gd/HMCS but without Pt precursor) and Pt foil, suggesting that Pt in Pt₂Gd/HMCS was metallic. The slight positive shift of the XANES spectrum of Pt₂Gd/HMCS supported the alloying of Pt with Gd.^[1]

Figure 1(b) shows the Pt *L*_{III}-edge EXAFS oscillation of Pt₂Gd/HMCS and control samples. The oscillation of Pt₂Gd/HMCS had a different period and smaller amplitude than that of Pt/HMCS and Pt foil. Figure 1(c) shows the Pt *L*_{III}-edge EXAFS Fourier transform of

Pt₂Gd/HMCS and control samples. The peak attributed to the Pt-Pt bond (0.265 ± 0.001 nm, coordination number (CN): 4.2 ± 0.2) was much smaller than the peak attributed to the Pt-Pt bond in Pt foil (0.277 ± 0.001 nm, CN: 12). Together with the structural analyses of XRD, TEM/HAADF-STEM-EDS, and XPS, the formation of Pt₂Gd alloy nanoparticles with narrow size distribution were clarified.^[1]

Pt₂Gd/HMCS showed higher ORR activity and durability (from ADT) than Pt/HMCS and commercially available Pt/C catalyst.^[1] One of the reasons for high ORR performance was suggested to be the formation of Pt₂Gd core - Pt shell type nanoparticles as active species, as suggested from HAADF-STEM/EDS analyses of Pt₂Gd/HMCS after ADT. The Pt *L*_{III}-edge EXAFS oscillation of Pt₂Gd/HMCS after ADT became closer to that of Pt species as shown in Figure 1(d), supporting this observation.^[1]

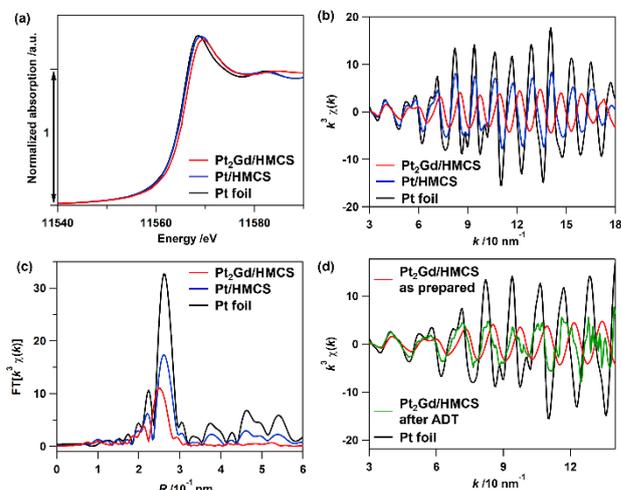


Figure 1 (reproduced from Ref. [1]): (a) Pt *L*_{III}-edge XANES spectra, (b) Pt *L*_{III}-edge EXAFS oscillations, and (c) Pt *L*_{III}-edge EXAFS Fourier transforms of as-prepared Pt₂Gd/HMCS and control samples. (d) Pt *L*_{III}-edge EXAFS oscillations of Pt₂Gd/HMCS (as prepared and after ADT) and control samples.

References

[1] T. Moriyama *et al.* *J. Am. Chem. Soc.* **147**, 1262-1270 (2025).

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