Pd-C-Fe Nanoparticles Investigated by X-ray Absorption Spectroscopy as Electrocatalysts for Oxygen Reduction

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Direct methanol fuel cells (DMFCs) have been regarded as potential next-generation power sources. Electrocatalysts have been extensively studied to promote catalytic activity. Platinum-based alloys have been demonstrated to be effective electrocatalysts in DMFCs. However, disadvantages such as low tolerance towardmethanol and the high cost of platinum restrict its application. Therefore, numerous nonplatinum catalysts, such as transition-metal oxides, transition-metal macrocycles, and palladiumbased catalysts, have been extensively investigated. Palladium is less expensive than platinum, but it performs less efficiently in oxygen reduction reactions (ORRs). Recent investigations have proven that an alloy of palladium with other transition metals can increase the catalytic activity toward ORRs. Shao et al. showed that electrocatalysts formed by alloying palladium and iron in a 3:1 molar ratio (Pd_3Fe/C) exhibit the greatest activity toward ORRs, with a half-wave potential that is -20 mV greater than that of Pt/C from ETEK. However, PdFe/C, which has been used as an electrocatalyst elsewhere, has a half-wave potential that is lower than that of Pt/C from ETEK. Most investigations on this subject take into account the change in catalytic activity that is associated with lattice distortion caused by the formation of the alloy. The change in interatomic distance is believed to influence the adsorption and transfer of oxygen-containing species in ORRs. Lattice distortion also influences the orbital overlap, altering the electronic properties on the active site of the electrocatalyst. Changing the electronic properties affects the surface reactivity, altering the performance of the electrocatalyst. Structure affects the intrinsic properties of an electrocatalyst. Therefore, structural analysis helps to elucidate the catalytic mechanism. Extended X-ray absorption fine structure (EXAFS) analysis is a powerful tool in obtaining structural information on noncrystalline and crystalline materials. A possible mechanism of formation of PdCFe/C electrocatalysts is proposed based on the structural parameter obtained from EXAFS.

Figure 1 presents the Pd K-edge XANES spectra of the PdCFe/C electrocatalysts. As shown in Fig. 1, all of the PdCFe/C samples yield almost the same near-edge absorption structures as palladium foil, indicating the metallic character of palladium in all of the samples. Because heat treatment was performed in an H_2 (5%)/N_2 atmosphere, palladium oxide species may be reduced to the metallic state during annealing.

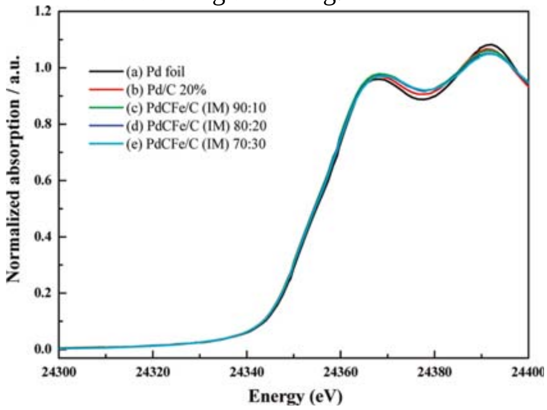

Fig. 1: Pd K-edgeXANES spectra of (a) palladiumfoil, (b) Pd/C 20%(500 ° C), (c) PdCFe/C (IM) 90:10, (d) PdCFe/C (IM) 80:20, and (e) PdCFe/C (IM) 70:30.

Figure 2 shows the Fourier transforms of Pd K-edge spectra of PdCFe/C electrocatalysts and palladium foil. The main peak centered at ca. 2.6 Å is corresponds to Pd-Pd and Pd-Fe coordination in the first coordination shell. The intensity of the main peak declines as the amount of added iron increases. Therefore, the drop in the height of the Fourier-transformed peak revealed destructive interference between Pd-Pd and Pd-Fe oscillations caused by the FePd alloy. Notably, the Pd-Pd bond distance did not vary with the PdFe content.

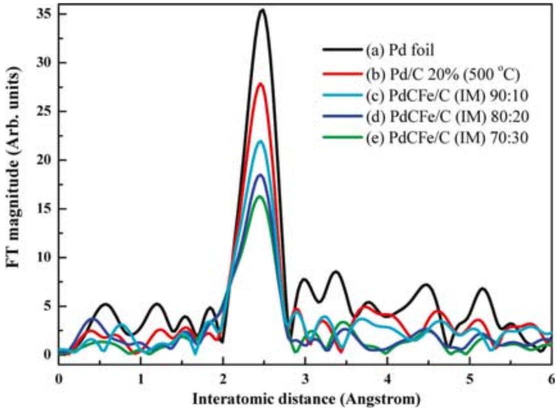

Fig. 2: Pd K-edge FT-EXAFS spectra of (a) palladium foil, (b) Pd/C20% (500 ° C), (c) PdCFe/C (IM) 90:10, (d) PdCFe/C (IM) 80:20, and (e) PdCFe/C (IM) 70:30.