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Pt L_{III}-Edge EXAFS Studies on Pt-Cu-Fe Alloy Electrocatalysts Supported on Carbon

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Abstract. Carbon supported Pt-Cu-Fe alloys with compositions of Pt:Cu:Fe=6:1:1 and 2:1:1 have been prepared. Both catalysts exhibit higher specific activities for oxygen reduction than Pt alone. In order to reveal the local structure around Pt, we have performed X-ray absorption experiment at the Pt L_{III}-edge. The local structure around Pt has been analyzed by fitting the first shell including the Pt-Pt, Pt-Cu, and Pt-Fe contributions to EXAFS spectra. The fitted C.N. for both alloys are similar to that for bulk Pt, indicating that the particle size is not small. The Pt-Pt distances for both alloys are found to be slightly shorter than that of bulk Pt, and the Pt-Cu and Pt-Fe distances decrease as the amounts of Cu and Fe increase. It is therefore concluded that the catalytic activity is strongly influenced by the bonding character.

1. INTRODUCTION

Highly dispersed platinum on carbon supports is well-known electrocatalyst for oxygen cathode in low temperature fuel cells such as phosphoric acid or polymer electrolyte fuel cells. Alloying supported platinum with one or several transition metals has improved the electrochemical activity for oxygen reduction reaction. Several investigators [1] have studied the alloying effect, but there still remains debate on the reason of enhanced activity. In this study, we prepared carbon supported Pt-Cu-Fe ternary alloy electrocatalysts with two compositions of Pt:Cu:Fe = 6:1:1 and 2:1:1 that are useful for oxygen cathode in low temperature fuel cells. We have investigated the local structure of those supported metal clusters by means of the extended X-ray absorption fine structure (EXAFS) spectroscopy. The application of EXAFS to such a highly dispersed material can give us information on the local structure, which otherwise can be hardly obtained.

2. EXPERIMENTAL

Alloy catalysts were prepared from commercially available Pt catalyst supported on Vulcan XC-72R (Johnson Matthey, 10 wt% Pt, about 120 m²/Pt g). Pt/C (1 g) were dispersed in 25 ml of deionized water and ultrasonically blended for 10 minutes. Appropriate amount of 0.1 M solution of transition metal salts (FeCl₂, CuCl₂) was added to this suspension. Pt:Cu:Fe atomic ratio was adjusted to 6:1:1 (Pt₆CuFe/C) and 2:1:1 (Pt₂CuFe/C) in resulting catalysts. Then the pH of the solution was adjusted to 8. After stirring, the suspension was filtered and dried at 100 °C for 2 hours. The quantitative analysis of the loaded metal amount was achieved with an ICP-AES. The dried catalysts were heated at 900 °C (Pt₆CuFe/C) or 1100 °C (Pt₂CuFe/C) for 2.5 hours in reducing atmosphere and cooled to RT under flowing inert gas. The Pt L_{III}-edge EXAFS spectra were measured at the BL 10B of the Photon Factory (Tsukuba). In order to determine the structural parameters, a curve fitting was performed for the first shell in the Fourier transform (FT). The electrochemical performance of the oxygen reduction was measured in a half cell apparatus. The reference electrode was a dynamic hydrogen electrode (DHE, 50 mV lower than NHE) and the counter electrode was a large area platinum gauze. Polarization curve of oxygen reduction was obtained by potentiostatic method.

3. RESULTS AND DISCUSSION

Figure 1 shows the k³-weighted Pt L_{III} - edge EXAFS spectra of the Pt₆CuFe and Pt₂CuFe, in which the k range between ~2.5 Å⁻¹ and ~15.5 Å⁻¹ was Fourier transformed as shown in Figure 2. It is clearly seen that FT of Pt₆CuFe is very similar to that of bulk platinum metal, whereas FT of Pt₂CuFe shows a larger shoulder peak at the lower distance compared to Pt₆CuFe, indicating significant contributions of Cu and Fe as expected. But the consideration of only Pt-Pt bonding pair in the curve-fitting for Pt₆CuFe could not give a reasonable result. Therefore, the three shell curve-fitting with the Pt-Pt, Pt-Cu, and Pt-Fe contributions has been carried out for both compounds. Because the contributions of Fe and Cu to EXAFS oscillation cannot be distinguishable, we put the constraint that Pt-Cu distance is shorter than Pt-Fe one from the consideration of ionic radii. The best-fitted spectra for both compounds are shown in Figure 2, and the resulting structural parameters are given in Tables 2. The fitted Pt-Pt distances for both compounds are similar to each other, and slightly shortened compared to that (2.772 Å) of the bulk Pt metal. These reduced Pt-Pt bond distances well reflect the reduced unit cell parameters estimated by XRD. In addition, the Pt-Cu and Pt-Fe distances decrease as the relative amounts of Cu and Fe increase. The observed total coordination numbers (C.N.) of Pt-(Pt/Cu/Fe) pair for both compounds are also similar to the coordination of twelve for Pt metal. It has been well

Figure 1: The k^3 -weighted EXAFS spectra at the Pt L_{III} -edge for Pt_2CuFe/C (a) and Pt_6CuFe/C (b).

Figure 2: The experimental (o) and best-fitted (—) FTs for Pt_2CuFe/C (a) and Pt_6CuFe/C (b). The contributions of Pt-Pt (---), Pt-Fe (---), and Pt-Cu (—) pairs to the best-fitted FT are shown.

accepted that EXAFS analysis for material of small particle size might induce the smaller C.N. due to the enhanced surface areas than those expected for bulk material.[2] In this regard, the resulting C.N. suggests that particle sizes for both catalysts are not so small, even though considering that experimental errors for C.N. is generally $\pm 20\%$. It is of great interest the ratio of C.N. is Pt:Cu:Fe = 73:13:14 for Pt_6CuFe/C and Pt:Cu:Fe = 55:21:24 for Pt_2CuFe/C , which are consistent with the compositional ratio. Such a fact suggests that Cu or Fe is well penetrated into the interior of the Pt lattice giving rise to the formation of homogeneous and long range ordered alloys, irrespective of the compositional ratio. Both compounds do not display the peak at low distance due to Pt-C distances, indicating that these materials are resistant to carbon deposition and oxidation.

The electrocatalytic activities for oxygen reduction (Table 2) are measured to see the alloying effect under operating conditions of phosphoric acid fuel cell. The alloy catalysts show enhanced mass activity, which means a higher current density normalized to the weight of Pt in the tested electrode. To see the net enhancement exhibited by alloy catalysts, it is reasonable to compare specific activity or real activity per unit surface area because metal surface area may be changed upon heating. As shown in Table 2, the alloy catalysts exhibit higher specific activities than the Pt alone catalyst by about 50 %. We suppose that the enhanced catalytic activity obtained in this study is not solely due to the roughness effect [1], as the kinetics of oxygen reduction is also influenced by the bond strength or coverage of oxygen molecules on the surface of the electrocatalyst [3]. Since the absorption properties of Pt should be changed by forming alloy with Cu and Fe, the enhanced activity of the alloy catalysts seems to be related to this changed property in addition to the roughness effect.

Table 1: Structural parameters obtained by curve-fittings of Pt L_{III} -edge EXAFS spectra for Pt_2CuFe/C and Pt_6CuFe/C .

compounds	scatterer	C.N. ^a	R (Å) ^a	σ^2 (Å ²) ^a	ΔE_0 (eV) ^a
Pt_6CuFe	Pt	8.0	2.71 ₄	0.0055	5.9
	Cu	1.4	2.69 ₉	0.0073	
	Fe	1.5	2.70 ₅	0.0078	
Pt_2CuFe	Pt	6.7	2.71 ₉	0.0054	4.9
	Cu	2.5	2.62 ₅	0.0065	
	Fe	2.9	2.63 ₂	0.0077	

^a C.N. is the number of scatterers. R is the metal-scatterer distance. σ^2 is a mean square deviation in R. ΔE_0 is the shift in E_0 for the theoretical scattering function.

Table 2: Electrochemical activity for oxygen reduction reaction.

compounds	mass activity ^a (A g ⁻¹)	ECMSA ^b (m ² g ⁻¹)	specific activity ^c (μA cm ⁻²)
Pt_6CuFe	86.1	52.9	163
Pt_2CuFe	69.1	38.5	179
Pt/C ^d	58.6	53.2	110

^a Measured at 0.9 V (vs. DHE) in 100 % H_3PO_4 at 200 °C.

^b Electrochemical metal surface area measured by cyclic voltammetry at the scan rate of 10 mV s⁻¹ in 1 M H_2SO_4 at 20 °C.

^c The specific activity is obtained by dividing the mass activity with specific metal surface area measured electrochemically.

^d Pt alone catalyst heat-treated at 900 °C for 2.5 hr.

4. Conclusion

The structures of Pt-Cu-Fe ternary alloy electrocatalysts elucidated by the Pt L_{III} -edge EXAFS analyses suggest that both catalysts are homogeneous and consist of relatively large particles. The reduced Pt-Pt distance upon the formation of alloy indicates that alloying effect gives an influence on the local structures, consequently resulting in variation of the electronic structures of constituent metal atoms. According to the electrochemical test, these alloy exhibit enhanced catalytic activity towards oxygen reduction reaction.

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