

EXAFS study on PtRu nanoparticle catalyst for DMFC

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Introduction

Direct methanol fuel cell (DMFC) is expected candidate for the next generation's mobile power source. PtRu has been studying as an anode catalyst of DMFC, because it shows excellent CO tolerance during oxidation reaction of methanol. However, effective cell voltage is much lower compared with thermodynamic one due to very high overpotential at anode. Therefore, it is important to improve catalytic activity of PtRu anode catalyst for realization of DMFC. In this work, we synthesized PtRu nanoparticle catalyst and investigated a relationship between catalytic activity and atomic structure of it.

Experimental

PtRu nanoparticles supported on carbon particle catalysts were synthesized by polyol reduction method in which ethylene glycol was used as solvent and reducer [1]. Appropriate amount of Vulcan XC72R carbon support, Pt(acac)₂ and Ru(acac)₃ were added into ethylene glycol so as to keep an atomic ratio of Pt and Ru ions 1:1. In addition, pH of synthetic solution was adjusted to 3.0 and 5.5 by adding sulfuric acid. Then the solution was refluxed at 473 K for 4 hours with mechanical stirring under nitrogen atmosphere. Catalytic activity for methanol oxidation of synthesized PtRu nanoparticles were estimated by linear sweep voltammetry (LSV). XAFS spectrum of PtRu nanoparticles were obtained at Pt-L_{III} edge. All the measurements were performed at the BL-7C beam line of KEK-PF in air at room temperature in the transmission mode. Synchrotron radiation was monochromated by using a Si(111) crystal. Unwanted high harmonics were eliminated with detuning. Incident and transmitted intensities of X-rays were measured with ionization chambers filled with N₂(85 %)+Ar(15 %) mixed gas and Ar(100 %) gas, respectively. The energy of X-ray was calibrated by setting the first inflection point on the L_{III} edge jumps of Au foil to 11913 eV.

Results and Discussions

The result of LSV measurements is shown in Fig. 1. It indicated that the PtRu nanoparticle synthesized at pH 3.0 has higher catalytic activity for methanol oxidation compared with one synthesized at pH 5.5. However, XRD and TEM analyses did not find out a significant difference between these two samples.

EXAFS oscillation of PtRu nanoparticle synthesized at pH 3.0 and theoretically calculated fitting curve are depicted in Fig. 2. The theoretical fit was performed with

the "Artemis" and "FEFF7" code assuming the single scattering path of Pt-Pt and Pt-Ru bonds. Optimized values of structural parameters are shown in Table I. Coordination numbers of Pt-Ru bonding in PtRu nanoparticle synthesized at pH 3.0 and at pH 5.5 are 1.4 and 0.6, respectively. This result indicates that Pt and Ru atoms of PtRu nanoparticle synthesized at pH 3 exist more randomly compared with PtRu catalyst synthesized at pH 5.5. Based on bifunctional mechanism theory, when Pt and Ru atoms exist contiguously each other, Ru becomes an associate catalyst for oxidation of CO which chemisorbs on active site of Pt [2]. LSV measurement and EXAFS analysis revealed that PtRu nanoparticle in which Pt and Ru atoms stand close shows higher catalytic activity for methanol oxidation, which strongly supports bifunctional mechanism theory.

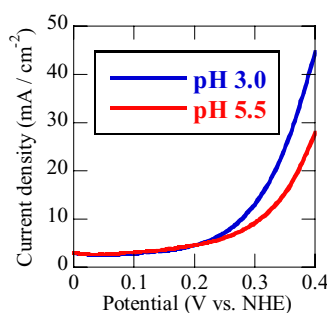


Fig. 1. Catalytic activity for methanol oxidation reaction of synthesized PtRu.

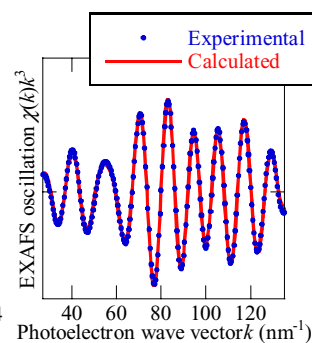


Fig. 2. Experimentally and theoretically obtained EXAFS oscillation of PtRu synthesized at pH 3.0.

Table 1: Optimized structural parameters evaluated from Pt-L_{III} edge EXAFS analysis

Sample	Bond	<i>N</i>	<i>R</i> [nm]	σ^2 [nm ²]	ΔE [eV]
pH 3.0	Pt-Pt	5.9	0.272	7.1×10^{-5}	5.1
	Pt-Ru	1.4	0.270	5.0×10^{-5}	3.4
pH 5.5	Pt-Pt	6.2	0.273	6.5×10^{-5}	5.1
	Pt-Ru	0.6	0.271	3.3×10^{-5}	3.4

References

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[2] M. Watanabe et al., J. electroanal. chem. interfacial electrochem. 60, 267 (1975).

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