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Preparation and structural analysis of catalysts by XAFS for rechargeable PEM fuel cells using cyclohexane and 2-propanol as organic hydrogen reservoirs generating electric power with no CO_2 emissions.

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Introduction.

Recently, the utilization of the “organic hydrogen reservoirs (OHR)” such as cyclohexane and decalin, [1] which release and absorb hydrogen reversibly by dehydrogenation and hydrogenation reactions have been proposed for application to infrastructures of hydrogen energy systems. Unlike steam reforming and water-gas shift reactions of methanol and hydrocarbons, reaction of OHR emits no CO_2 in producing hydrogen, and the dehydrogenated reservoirs can be hydrogenated at high efficiency for recycle use and saving surplus hydrogen. Since electrochemical dehydrogenation and hydrogenation of the OHR is reversible[2], the “rechargeable” fuel cell is available by combination with electrolysis of H_2O and electrochemical hydrogenation of OHR. To our knowledge, there has been no report on the “rechargeable” fuel cells using organic fuels. In this paper, we report the details of the electro-oxidation of typical OHR and structural analyses of the catalysts by XAFS.

Experimental.

Catalyst preparation.

The 20 wt.% Pt/C and 30 wt.% Pt-M/C (M= Rh, Zn) catalysts were prepared by an alcohol reduction method. $H_2PtCl_6 \cdot 6H_2O$, $RhCl_3 \cdot 3H_2O$ (for only Pt-Rh/C case), support Ketjen black EC were mixed in a ethylene glycol-water (volumetric ratio 1:3) solvent mixture to form a suspension. The resulting suspension was stirred and refluxed in air and then filtered and washed. Pt-Zn/C catalyst was prepared by successive impregnation method using Pt/C prepared by above-mentioned method. and $Zn(NO_3)_2 \cdot 6H_2O$, followed by hydrogen reduction at 300 °C under 20 % H_2 /N_2 gas stream.

I-V curve measurement.

The fuels were vaporized and fed with N_2 carrier gas into anode, where the N_2 gas was saturated with vapor. Potentials were scanned by a galvanostat for the polarization measurement in the range of 0 - 1000 mV.

XAFS data collection and analyses.

XAFS data were acquired at BL-10B of KEK-PF at room temperature. The data were analyzed using the program of REX2000.

Result and discussion.

For discharging process, cell voltages are compared for several anode catalysts, Pt, PtRu, PtPd, and PtRh, in the electro-oxidation of cyclohexane at 100 °C. PtRh anode showed the best performance (16 mW cm^{-2}), while PtRu and PtPd gave lower activity toward cyclohexane than Pt (12 mW cm^{-2}).

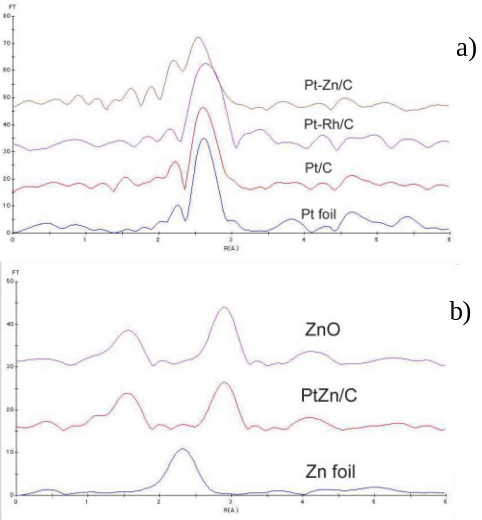

Figure 1. Fourier-transformed EXAFS spectra at (a) Pt L_{III} edge of Pt/C, PtRh/C, and PtZn/C, (b) Zn K edge of PtZn/C

On the other hand, PtZn catalyst showed better conversion (4.2 % @ 2000 mV) than Pt catalysts (3.6 % @ 2000 mV) in the electro-reduction (charging process) of acetone at 70 °C.

Fourier-transformed EXAFS spectra were shown in Figure 1. Pt/C and Pt-Rh/C catalysts showed similar spectra with the Pt L_{III} edge absorption of Pt foil, suggesting the both Pt catalysts have similar electronic state with metallic Pt in spite of the difference of the discharging cell performance. Contribution of ZnO was observed for Pt-Zn/C, thus indicating that ZnO species promote the electroreduction of acetone.

References

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