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In situ XAFS studies on platinum-cobalt alloy nanoparticles

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The improvement of the efficiency of cathode catalysts is one of the main research interests in developing proton exchange membrane fuel cells (PEFCs). Currently, platinum nanoparticles are used as the best cathode catalysts in PEFCs, their performance is, however, not enough for the real wide use. Platinum based alloy catalysts, for examples, platinum alloys with *3d* transition metals, Cr, Mn, Fe, Co, and Ni, show better catalytic activity toward the cathode reaction (the oxygen reduction reaction, ORR) than that of the pure platinum catalyst. The electronic structure alternations as well as the surface structure modifications due to alloying are believed to the key factors in increasing the activity. The full understanding of the ORR on these alloy catalysts would give helpful information on the catalyst development. In order to clarify the relationships among the catalytic activity toward ORR, the electronic structure alternations, and surface structure modifications in these alloy catalysts, we have investigated structural and electronic properties of platinum alloy nanopercticles by using x-ray absorption spectroscopy under potential control.

Carbon supported platinum-cobalt alloy nanoparticles (ca. 3~6 nm, 50 wt% metal loading) were prepared by an oxide colloidal method. The nominal atomic ratios are Pt : Co = 3 : 1 and Pt : Co = 5 : 1. These catalysts were spread onto a carbon-paper electrode. This electrode was put in an electrochemical cell with 0.5 mol dm^{-3} H_2SO_4 electrolytes, and the potential of the electrode was controlled by an electrochemical analyzer. In situ XAFS measurements were made in the transmission mode on a beamline BL19B2 at SPring-8.

In situ XAFS studies clearly showed the electronic structures as well as surface structures are modified by both the cobalt concentration and the potential. As shown in Fig. 1, the slight differences in the white line intensity and also EXAFS oscillation were observed in platinum-cobalt alloys. This indicates the electronic and local structures around platinum were altered by alloying and it depends on the cobalt concentration. Figure 2 shows the potential dependence of XANES spectra for Pt_3Co nanoparticles. The white line intensity gradually increased as the potential increased due to the oxidation. This increase is, however, different from that for pure platinum. This difference may be important to understand the ORR. The detailed analyses are now in progress.

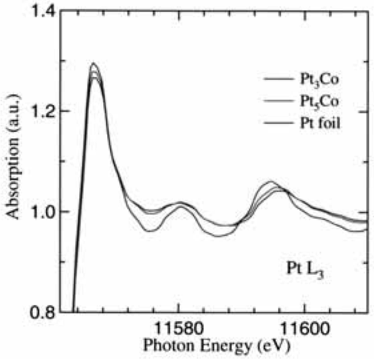

Fig. 1 The XAS spectra for two Pt-Co alloy nanoparticles taken at 0.5 V vs. RHE, after an electrochemical cleaning.

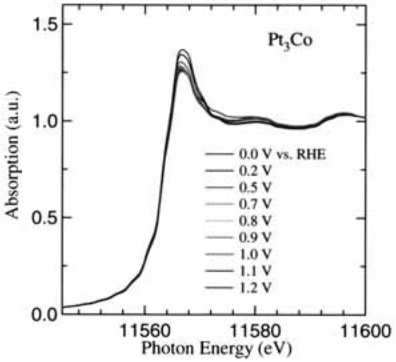

Fig. 2 The potential dependence of XANES spectra for Pt_3Co alloy nanoparticles.

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XAFS Speciation and Powder X-ray Diffraction of Pb in stabilized soil

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Soil contamination by heavy metals of natural origin exists in many sites in Japan partly because of the hydrothermal concentration of heavy metal–bearing minerals due to the volcanic activity. In addition, agricultural, industrial, and urban areas have been contaminated with various heavy metals via anthropogenic processes. "Stabilization" of contaminated soil is a technology that controls the elution of contaminants into aqueous phase by adding chemicals, minerals having adsorptive capacity etc.

Our company developed stabilization technology (Sealing Soil Method) in which only-natural minerals are used and the technology is low-cost and low-load to the environment. The minerals used are, allophanic clay, natural zeolites, baked dolomite, and iron hydroxide. Possible mechanism responsible for the stabilization of heavy metals are cation exchange by zeolite, and the formation of surface complexes by allophane and iron hydroxide as well as neo-formation of some silicate minerals incorporating heavy metals as impurity.

To obtain additional evidences to support the proposed mechanisms, we carried out XAFS and powder X-ray diffraction analyses on a Pb-contaminated soil with and without amendments for stabilization at BL19B2 in SPring-8. The amendments spiked with Pb were also analyzed as references.

The powder X-ray diffraction patterns for the Pb-containated soils that were stabilized and aged for 10, 30, and 60 days were almost identical to the original soil and no diffraction peaks indicative of newborn silicate minerals were detected. The XANES spectra of Pb in the contaminated soil and reference samples are shown in Fig. 1. The spectra from the original and stabilized soils were almost identical and they were very close to that from the allophanic soil spiked with Pb. On the other hand, the spectrum of the treatead soil was different only slightly from that of Pb-spiked smectite and significantly from those of Pb-spiked zeolite, dolomite, and iron hydroxide.

These observations suggest that the major chemical forms of Pb in the contaminated soil were surface complexes and the stabilization treatment enhanced their formation and increased their stability. These experimental results offered basic information that may be useful in improving the performance of the technology.

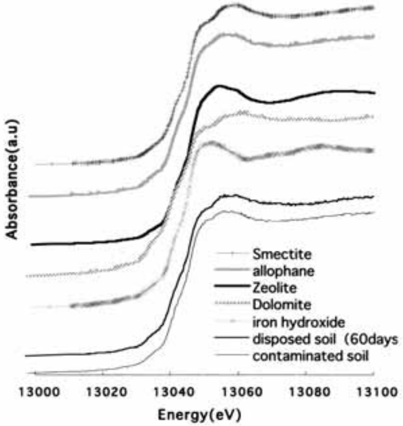

fig.1 Pb L-3 edge XANES spectra of the contaminated soil and reference samples