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STRUCTURAL AND ELECTRONIC PROPERTIES OF PLATINUM NANOPARTICLE SURFACE IN AN AQUEOUS SYSTEM PROBED BY *IN SITU* X-RAY ABSORPTION SPECTROSCOPY

There is a strong demand for new mobile batteries for powering mobile electronics, such as laptop computers, mobile phones, and personal digital assistants (PDAs), in the upcoming ubiquitous networking society, because the energy capacity of the currently widely used Li-ion batteries is insufficient to power the state-of-the-art electronics for long period of use. The micro-direct methanol fuel cells (DMFCs), that generate electricity by an electrochemical reaction between methanol and oxygen, are considered to be a potential successor to Li-ion batteries as its energy capacity is potentially more than ten times larger than that of Li-ion batteries. One of the main technological issues in developing DMFCs is the improvement of the efficiency of cathode catalysts. Currently, platinum nanoparticles are the best cathode catalysts for use in DMFCs. Their performance, however, is unsatisfactory for real wide spread commercial use.

The detailed mechanism of the cathode reaction in DMFCs, i.e., the oxygen reduction reaction (ORR) on platinum, at the atomic or molecular scale, has been a long-period problem in electrochemistry and is still controversial. Since this is directly related to the catalytic activity of platinum in the ORR, the elucidation of the ORR mechanism is important for developing new catalysts. As the first step toward a full understanding of the ORR mechanism, we investigated the structural and electronic properties of platinum nanoparticles in an aqueous system by X-ray absorption spectroscopy. [1]

In situ XAFS measurements were performed in an anodic oxidation process in an aqueous system in a wide potential range. Carbon supported platinum nanoparticles (ca. 3 nm, 50 wt%-Pt loading) were spread onto a carbon electrode. This electrode was placed in an originally designed electrochemical cell with $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ electrolytes, and the potential of the electrode was controlled by an electrochemical analyzer. XAFS measurements were made in the transmission mode at beamlines **BL16B2** and **BL19B2**.

The results of *in situ* XAFS studies clearly showed the surface reconstruction and the formation of surface oxygen species in the ORR region (from 0.8 V to 1.2 V vs. reversible hydrogen electrode, RHE). As shown in Fig. 1, above 0.8 V vs. RHE, the amplitude

of Fourier transforms that occur due to the interaction with the nearest neighbor Pt atoms significantly decreases, indicating that the surface is roughened by oxidation in this potential range. Simultaneously, the peak associated with Pt-O bonds appears and the amplitude increases upon increasing the potential.

Figure 2 shows the potential dependence of the interatomic distance and the coordination number

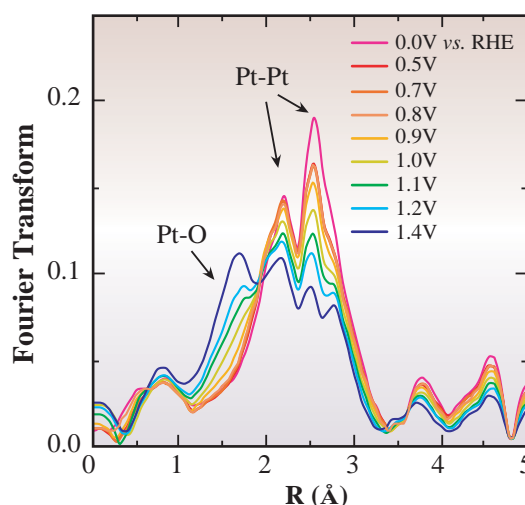


Fig. 1. Potential dependence of k^1 -weighted Fourier transforms of Pt L_3 EXAFS.

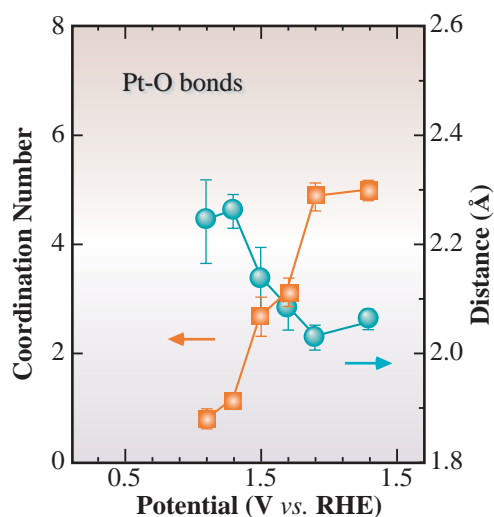


Fig. 2. Potential dependence of interatomic distance and coordination number.

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(CN) for the surface Pt-O bonds. At 0.8 V, the Pt-O bond length is almost 2.3 Å and it gradually decreases and becomes 2.0 Å at 1.0 V. These oxygen-containing species can be assigned as waterlike Pt-OHH species and Pt-OH species at on-top sites, on the basis of comparison with theoretical studies [2-4]. Above 1.0 V, since the CN approaches three, which corresponds to the fully occupied hollow-site Pt-O bonds, the OH species gradually change to atomic oxygen at hollow sites and release protons. Above 1.2 V, the CN exceeds three. This indicates that some oxygen atoms go inside the surface and form amorphous oxides.

Considering the results described above, the surface structure of platinum in an aqueous system near the ORR potential regions are summarized and shown in Fig. 3. First, at 0.8 V, waterlike species begin to adsorb weakly on the surface. Then they change into Pt-OH species at on-top sites. Near 1.1 V, the OH species move to the hollow sites, and

change to atomic oxygen. Finally, above 1.2 V, the amorphous oxides are formed on the surface.

Regarding the electronic properties of platinum nanoparticles, we can estimate the number of vacancies in the platinum 5d orbitals from the results of the analysis of the XANES spectra at L_3 and L_2 absorption edges. As shown in Fig. 4, the number of the vacancies is clearly correlated with the electrochemical reaction on the platinum surface. In the potential range from 0.8 V to 1.2 V, the number of vacancies slightly increases, indicating that charge transfer from platinum occurs to surface oxygen-containing species, and these adsorbates strongly adsorb on the platinum surface.

Since these surface OH species or atomic oxygen species block the adsorption of oxygen molecules, they may reduce the catalytic activity of platinum for ORR. The removal of such surface OH species would play a crucial role in improving the performance of catalysts.

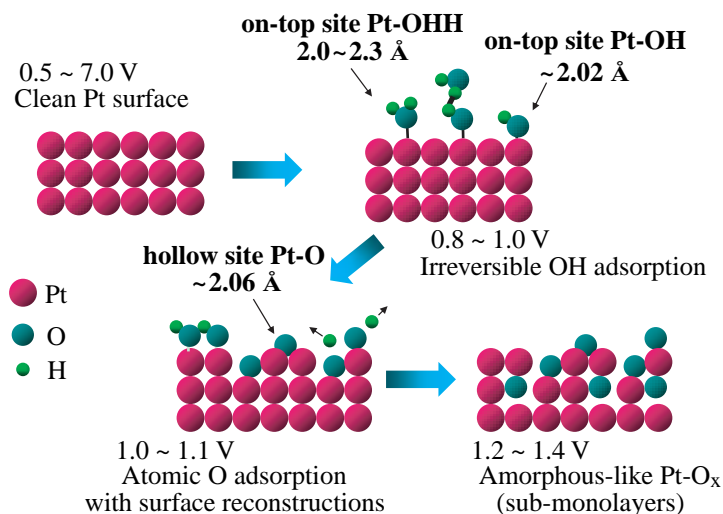


Fig. 3. The structural models for platinum surface near the ORR region.

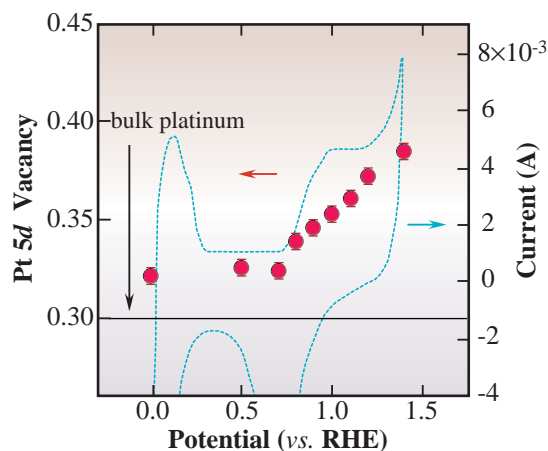


Fig. 4. Potential dependence of the number of vacancies in Pt 5d orbital. The dashed line shows the cyclic voltammetry for platinum nanoparticles supported on carbon in the same electrolyte.

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References

- [1] H. Imai, K. Izumi and Y. Kubo - in preparation.
- [2] T. Jacob and W. A. Goddard: J. Am. Chem. Soc. **136** (2004) 9360.
- [3] M. T. Koper *et. al.*: J. Phys. Chem. B **106** (2002) 686.
- [4] T. Li and P. B. Balbuena: J. Phys. Chem. B **105** (2001) 9943.