In situ hard X-ray photoelectron study of O$_2$ and H$_2$O adsorption on Pt nanoparticles

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In order to clarify the effect of water adsorption on fuel cell cathode catalysis surface, we have investigated electronic structure of Pt and Pt-Co nano-particles with O$_2$ adsorption and O$_2$/H$_2$O co-adsorption by in situ hard X-ray photoelectron spectroscopy (HAXPES) together with in situ high resolution fluorescence detected X-ray absorption (HERFD-XAS). The valence band (mainly Pt 5d) and Pt 4f spectra were successfully obtained under up to 1 mbar with an ambient cell for the first time by in situ HAXPES. Both valence band and Pt 4f spectra show that O$_2$/H$_2$O co-adsorption hindered oxygen adsorption. Based on our first principles calculation of valence band density-of-states (DOS) we have found that H$_2$O molecules may occupy the oxygen adsorption sites on Pt surface more easily than oxygen, resulting in hindering the successive oxygen adsorption. However, under the more realistic condition at atmospheric pressure the formation of higher oxidation states of Pt in Pt L$_3$-edge absorption spectra was enhanced by water adsorption, which was obtained by high resolution (Pt M$_5$, FWHM about 2.5 eV) in situ HERFD-XAS. These changes in white line cannot be observed by conventional XAFS spectra due to large life-time broadening of Pt L$_3$ (FWHM about 5.2 eV). At 1 bar more frequent attack by oxygen molecules onto water-adsorbed Pt surface may occur, resulting in the formation of hydrated hydroxyl intermediates and higher oxidation states. This enhanced oxygen adsorption is more clearly observed for Pt than Pt-Co nano-particles, probably because Pt nano-particles with stronger Pt-O bonding than Pt-Co nano-particles may further stabilize Pt-O bonding by additionally adsorbed water leading to less water effect on oxygen adsorption on Pt-Co. These results would be helpful to understand the reason why Pt-Co nano particles show higher ORR activity than Pt nano particles.

Figure 1: (a) Valence band spectra under in situ/ex situ reductions, (b) Calculated projected Pt d-pDOSs of bare Pt(111) surface with various adsorbates, (c) experimental difference spectra of ex situ reduced, H$_2$O, and O$_2$ adsorbed condition (solid lines) obtained by subtracting the in situ reduced spectrum, together with calculated difference spectra of H$_2$O and O$_2$ adsorption (dashed lines).

Biography

Masaharu Oshima is a Project Researcher of Institute for Solid State Physics (ISSP), University of Tokyo. He completed his Bachelor degree in Dpt. of Industrial Chemistry, University of Tokyo in 1972, and Doctor of Engineering degree at University of Tokyo in 1984. After he started his experience at Stanford University in 1981-82, he is continuing synchrotron radiation science for semiconductors, magnetic materials and catalysts for more than 35 years. He became a Professor in Dpt. of Applied Chemistry, University of Tokyo in 1995. He was the President of the Japanese Society for Synchrotron Radiation Research (JSSRR) in 2009-2011, and the President of the Surface Science Society of Japan (SSSJ) in 2013-2015. He had received many research awards including ECS Best Paper Award in 2010 and Ministry of Education, Science and Technology (MEXT) Award in 2014.

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