

OUTERMOST SURFACE ANALYSIS OF DEFECTIVE ZIRCONIUM OXIDE FUEL CELL CATALYST USING RESONANT X-RAY PHOTOELECTRON SPECTROSCOPY (R-XPS)

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Polymer electrolyte fuel cells (PEFCs) have expected as one of the key energy devices in future sustainable society. PEFCs, however, have difficult issues such as insufficient oxygen reduction reaction (ORR) activity and expensive Pt consumption. To overcome such difficulties, various non-platinum ORR catalysts, such as, carbide, nitride, and oxide were examined as alternative of Pt [1]. Among them, Zr oxide-based catalysts attract much attention. Such transition-metal-oxide catalysts show the high ORR onset potentials, but ORR current is very low. Thus, identifying the ORR sites, and designing surface structure to have effective ORR sites, is main issues in developing oxide-base catalysts.

Previously, we reported that oxygen-vacancy sites could be ORR sites by surface-sensitive conversion-electron-yield x-ray absorption spectroscopy (CEY-XAS) [2]. However, we still lack detailed information on preferable electronic structure of oxide-base ORR catalyst. Since carbon is deposited at catalysts surface during partial oxidation preparation processes, conventional laboratory XPS does not provide effective information, especially at valence band (V.B.) region. Thus, we conducted highly brilliant soft X-ray synchrotron radiation (SR)-XPS measurements. First-principles calculation was adopted to interpret the partial density of state (PDOS) of V. B.

Zirconium chloride and phthalonitrile were put into aromatic solvents at ~473 K to synthesize oxy-zirconium phthalocyanine (ZrOPc). The obtained powders and multi-walled carbon nano-tube (MWCNT) powders were mixed in N-methylpyrrolidone (NMP) to prepare ZrOPc colloids-adsorbed MWCNTs. NMP was evaporated to prepare the MWCNT supported ZrOPc powders. The prepared precursors were heat-treated at 1173 K for several hours under an inert N₂ gas or 2% H₂ + 0.05 % O₂ /97.5% N₂ in a rotary quartz-tube furnace to generate ZrO_{2-x}/MWCNT. ZrO_{2-x} catalysts were ZrO₂-based compounds including a trace amount of C and N with deposited carbon and MWCNT.

Fig.1 shows TEM images of the ZrO_{2-x} catalysts. The grey tubules are MWCNT supports and the black spots are ZrO_{2-x} particles. The size of most ZrO_{2-x} particles was well-controlled in nanometer-scale from 5 to 10 nm. As shown in Fig. 1 (b), the oxide particles were covered with the deposited carbon derived from phthalocyanine. The thickness of the deposited carbon was ca. 1-2 nm. This deposited carbon covered with oxides prevented the oxide particle from growing.

The ORR activity was evaluated by cyclic voltammetry scans with a scan rate of 5 mV s⁻¹ in 0.1 mol dm⁻³ H₂SO₄ at 30°C. The ORR current, *i*_{ORR}, was based on the total mass of catalyst powders including the deposited carbon and MWCNT. Fig.2 shows the potential-current curves for the oxygen

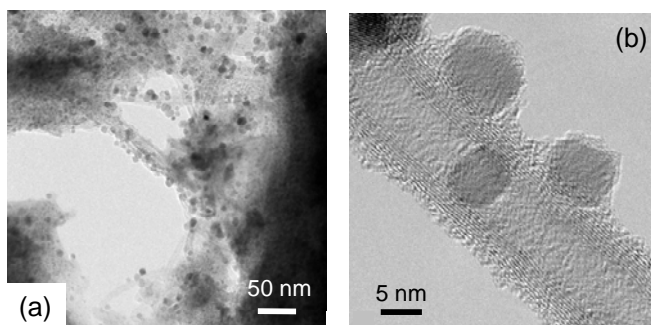


Fig.1 TEM images of ZrO_{2-x} catalysts.

reduction reaction of the ZrO_{2-x} catalysts with (a) high and (b) low activity. The ORR current of the ZrO_{2-x} with high activity started to flow about 0.95 V vs. RHE and reached about 0.4 A g^{-1} at 0.8 V. This current value was considerably high activity as a non-platinum.

The SR-XPS measurements were performed on BL-18A beam line at Photon Factory (PF) of High Energy Accelerator Research Organization (KEK). G3 (600 lines/mm, $R=4000 \text{ mm}$) and CLAM (VG) were used as diffraction grating and analyzer, respectively. ZrO_{2-x} catalysts with high and low ORR activity were measured with pass energy of 10 eV and excitation energy of 1 – 45 eV.

Fig.3 shows the constant initial state (CIS) curves of the ZrO_{2-x} with (a) high and (b) low ORR activity. The CIS curve plotted photoelectron intensity in each resonance energy. In Fig.3, CIS curves were displayed three-dimensionally by each binding energy. As shown in Fig.3 (a), the peaks appeared at resonance energy of ca. 36 eV. On the other hand, no peaks were observed at the same energy level on the ZrO_{2-x} with low ORR activity (Fig.3(b)). These peaks corresponded to the resonance from Zr 4p orbital to conduction band. Therefore, we successfully observed the electronic state due to the ZrO_{2-x} even if a part of surface was covered with carbon. In addition, the first-principles calculation suggested that the peaks occurred by the increase in the density of states at the bottom of the conduction band due to the formation of oxygen vacancies on the outmost surface.

Acknowledgement: A part of this work was performed under the “Non-precious metal oxide-based cathode for PEFC Project” supported by the New Energy and Industrial Technology Development Organization (NEDO).

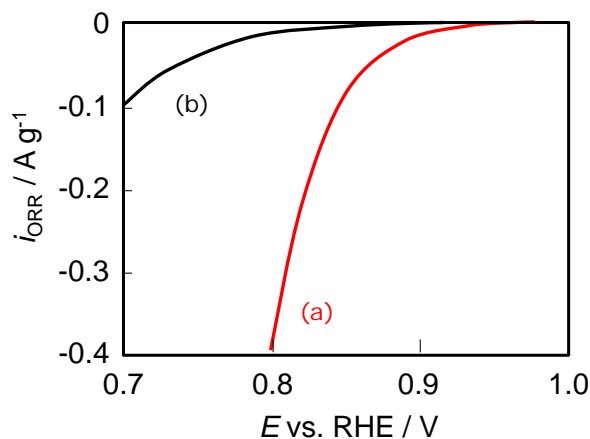


Fig.2 Potential-ORR current curves of ZrO_{2-x} with (a) high and (b) low activity.

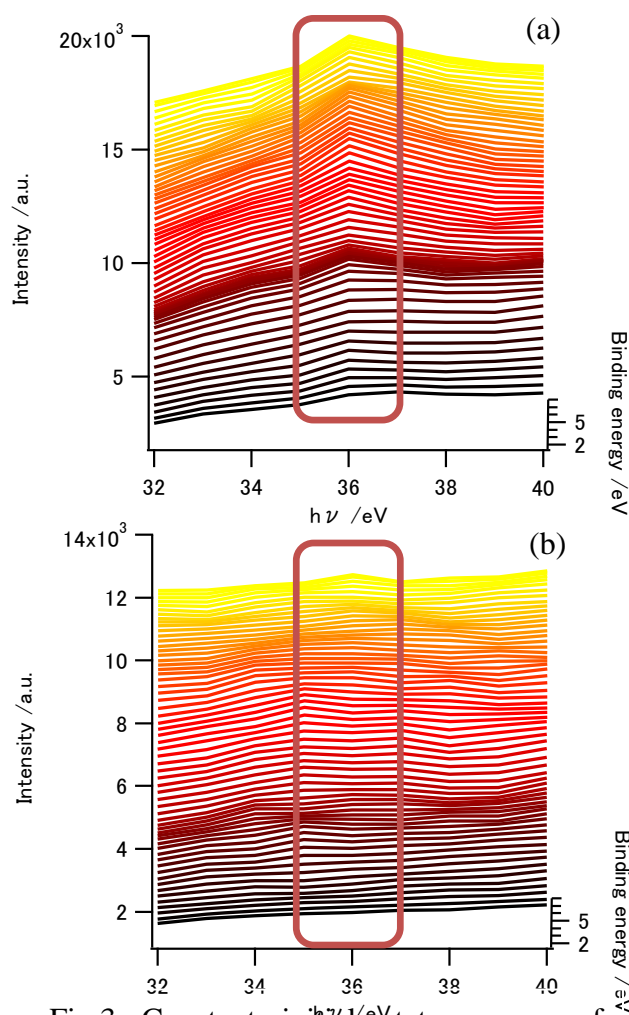


Fig.3 Constant initial state curves of ZrO_{2-x} with (a) high and (b) low activity.

REFERENCES

- [1] A. Ishihara, M. Tamura, Y. Ohgi, M. Matsumoto, K. Matsuzawa, S. Mitsushima, H. Imai, and K. Ota, *J. Phys. Chem. C*, 117, 18837 (2013).
- [2] H. Imai, M. Matsumoto, T. Miyazaki, S. Fujieda, A. Ishihara, M. Tamura, and K. Ota, *Appl. Phys. Lett.*, 96, 191905 (2010).