

Oxygen-reduction reaction analysis of Zirconium-oxide catalysts by using EC-XPS

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Partially oxidized zirconium carbonitrides (Zr-CNOs) have been attracting a great deal of attention as a non-platinum-group oxygen reduction reaction (ORR) catalyst, which exhibits a high onset potential that is comparable to those of platinum-based catalysts. Since active sites and conduction mechanism is different from those of platinum-based catalysts, the ORR mechanism should also be different, although details of the reaction mechanism, remains unknown. Here, we report the results of electrochemical x-ray photoelectron spectroscopy (EC-XPS) measurements that provide new insights in to reaction mechanism of Zr-CNO catalysts.

Zirconium oxide-based catalysts (Zr-CNOs) were synthesized by oxidizing zirconium oxyphthalocyanine (Zr-OPc) at 1173 K under 2% H₂/N₂ containing 0.05% O₂ with gas flow rates of 50 mL min⁻¹ for 10 hours. The surface region of the obtained Zr-CNO catalyst consists of zirconium oxide (tetragonal ZrO₂) phase and partially graphitized carbon. The Zr-CNO catalysts electrodes for EC-XPS measurements were prepared by mounting Zr-CNO powders onto a glassy carbon disk electrode with Nafion. Zr-CNO catalysts electrodes were polarized at 0.6 V, 0.8 V, 1.0 V, and 1.2 V vs. RHE in an Ar or O₂ purged 0.1M HCl aqueous solution in the electrochemical chamber. The electrode was taken from the solution under polarizing at the potential, and it was transferred to the UHV analysis chamber quickly without exposure to the air. Then XPS measurements of the electrodes were performed.

Figure 1 shows the O1s spectra for adsorbed species on Zr-CNO catalysts polarized electrochemically in an Ar purged solution. The O1s spectra were decomposed by three singlets centered at 533.6 eV, 531.7 eV and 530.5 eV^{1,2} which were assigned to adsorbed H₂O (H₂O_{ad}) <533.6 eV>, adsorbed OH (OH_{ad}) <531.7 eV> and adsorbed O (O_{ad}) <530.5 eV>. The concentration ratio of H₂O_{ad}, OH_{ad} and O_{ad} was different depending on the polarization potentials (Fig.3 (a)). The ratio of OH_{ad} remains at same level up to 0.8V, then it increases up to 1.2V, while that of O_{ad} remains at same level up to 1.0V, then it increases up to 1.2V. This variation would correlate with the electrochemical oxidation behavior of the catalyst: OH_{ad} species is formed at 1.0V is formed by the electrochemical oxidation of H₂O adsorbed on the surface of Zr-CNO catalysts. (H₂O_{ad} → OH_{ad} + H⁺ + e⁻) Then O_{ad} species were also formed at 1.2V. (OH_{ad} → O_{ad} + H⁺ + e⁻) Zr 3d spectra for the electrochemically polarized Zr-CNO catalysts also changed in accordance with the polarization potentials (Fig.2). The Zr 3d spectra can be fitted with two doublets (peak 1 and peak 2 centered at 182.3 eV <4f7/2>, 181.3 eV<4f7/2>). Peak 1

can be assigned to ZrO₂² of the zirconium oxide phase. Peak 2 can be assigned to the zirconium oxides with lower valence number than ZrO₂. The ratio of peak 1 remains at same level up to 1.0V, then it increases at 1.2V (Fig.4). This behavior shows that the electrochemical oxidation of the surface (possibly catalytically active sites) occurs at the surface of zirconium oxide phases in the catalysts; The zirconium surface oxide with the same oxidation state as ZrO₂ forms at 1.2V due to the electrochemical oxidation of the zirconium surface oxide with lower valence number than ZrO₂ such as Zr-OH_{ad} → Zr-O_{ad} + H⁺ + e⁻.

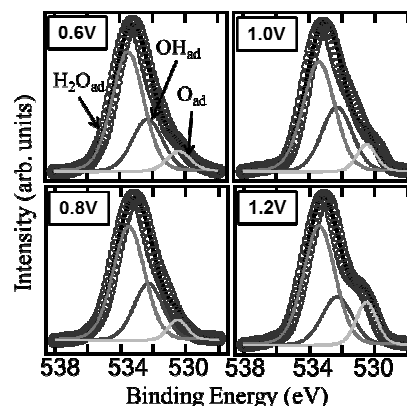


Fig.1 O 1s XPS spectra for adsorbed species on Zr-CNO catalysts polarized at 0.4V, 0.6V, 0.8V and 1.2V.

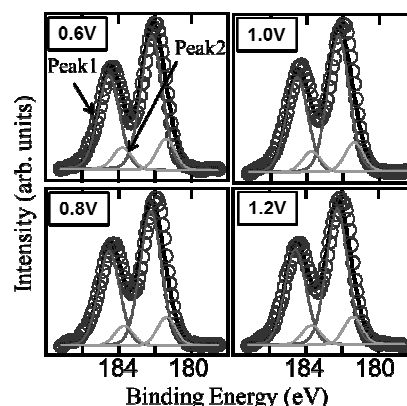


Fig.2 Zr 3d XPS spectra for adsorbed species on Zr-CNO catalysts polarized at 0.4V, 0.6V, 0.8V and 1.2V.

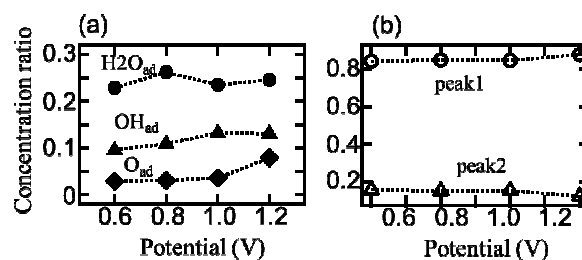


Fig.3 (a) O concentration ratio of H₂O_{ad}, OH_{ad} and O_{ad} and (b) Zr concentration ratio of peak1 and peak2 on the Zr-CNO electrode at 0.6V, 0.8V, 1.0V and 1.2V.

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