

Electronic Structure of Carbon Alloy Cathode Catalysts for Polymer Electrolyte Fuel Cells

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Introduction

Drastic cost down of Polymer Electrolyte Fuel Cells (PEFC) is strongly required. Conventionally, Pt, which is a precious metal, has been used as cathode catalyst for slow oxygen reduction reaction (ORR). So far, almost no cathode catalysts whose performances are comparable to Pt catalysts have been reported yet. Quite recently it was reported that some carbon alloys doped with nitrogen or/and boron showed high oxygen reduction activities [1]. However, the mechanism for these activities of nitrogen-doped carbon alloys has not been elucidated yet. In this study, we have investigated the electronic structures by soft X-ray absorption spectroscopy (XAS) of these carbon alloys in order to clarify the origin of cathode catalyst activity of the N-doped carbon alloys.

Experimental

Experiments were carried out at the BL-2C of the Photon Factory. For XAS measurements, samples were synthesized in air and transferred to an ultrahigh vacuum chamber at room temperature. XAS spectra were recorded in a total electron yield (TEY) mode.

We have measured five samples; Nano-shell carbon derived from pyrolyzed cobalt phthalocyanine and polymers (CoPc-ph-900), N-doped carbon alloys prepared by the anmo-oxidation method (AO50, AO90), and N-doped carbon materials prepared by kneading method (N1, N2)[1]. Although AO50 and AO90 have different nitrogen contents, they show similar ORR activities. On the other hand, N2 containing more nitrogen shows higher ORR activities than N1. Among all samples, CoPc-ph-900 shows the highest ORR activity.

Results and Discussion

X-ray absorption is resonantly enhanced when N 1s core electrons are excited to π^* or σ^* states. In the σ^* region, there are little differences except σ^* edge peak position. The value Δ_σ which is an energy difference between the σ^* peak energy and the ionization potential energy is reportedly well correlated with the C-N bond length (R) by the equation: $R=0.148\text{nm}-(0.00243\text{nm/eV})\Delta_\sigma$ [2]. Rough estimation of C-N bond length suggests the existence of the sp^2 hybridized nitrogen, not

the sp^3 hybridized C-N bonds. In contrast, in the π^* region, two prominent peaks A1, A3 and a small peak A2 are clearly observed. The widely accepted peak interpretation is that the peak A1 at $\sim 399\text{eV}$ is due to sp^2 hybridized pyridine-like nitrogen which has two carbon neighbors with a double bond C=N, and peak A3 at $\sim 401.4\text{eV}$ is due to sp^2 hybridized graphite-like nitrogen which has three carbon neighbors [3]. Here, peak A2 at $\sim 400\text{eV}$ is assigned as cyanide-like nitrogen which has a triple bond.

To correlate the chemical states of nitrogen with the ORR activity, all XAS spectra were compared. First, the fact that AO50 and AO90 spectra consisting of the main peak A1 (pyridine-like) and the small peak A3 (graphite-like) are very similar is consistent with that there is not much difference in ORR activities. Second, N2 containing more nitrogen than N1 shows enhanced intensity of peak A3. Finally, CoPc-ph-900 showing the highest ORR activity also shows quite high intensity of the graphite-like nitrogen (peak A3). Thus, higher ORR activity catalysts contain larger amount of graphite-like nitrogen than the others. According to molecular dynamics simulation, it is revealed that carbon atoms bonded to graphite-like nitrogen exhibit higher ORR activity than those bonded to pyridine-like nitrogen.

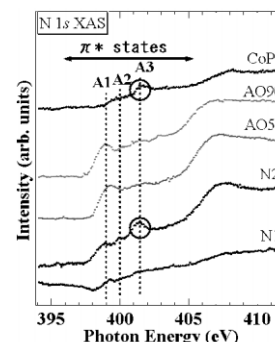


fig 1: N 1s XAS spectra

Conclusion

We have measured XAS of carbon alloy cathode catalysts with various ORR activities for PEFC, and correlated nitrogen geometry well with ORR activities.

References

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