

## Oxygen adsorption characteristics of nitrogen-doped graphite revealed by N 1s X-ray absorption spectroscopy

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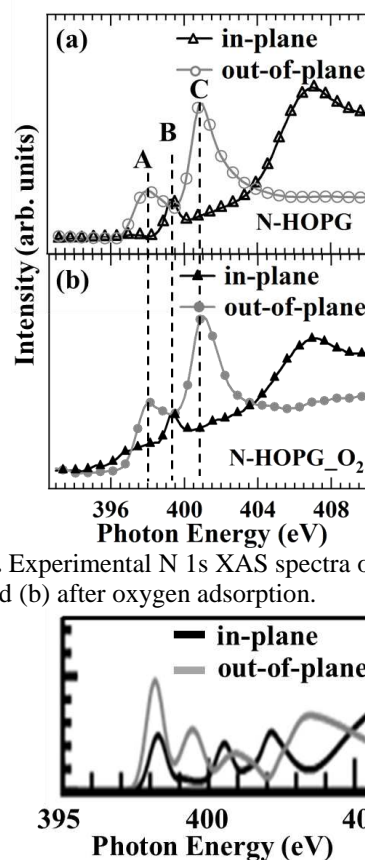
Recently carbon-based oxygen reduction catalysts have attracted much attention as cathode catalysts alternative to Pt for polymer electrolyte fuel cell [1-2]. These catalysts are modified by doping of light elements (such as nitrogen) and/or transition metals to accelerate oxygen reduction reaction (ORR). The role of the doped light elements and/or the transition metals on the ORR activity has been under debate [1-3]. In this study, we have investigated the role of nitrogen species on the first step of ORR, i.e. oxygen adsorption. We have synthesized a nitrogen doped graphite which models specific nitrogen species in carbon-based catalysts and observed changes in the electronic structure of nitrogen upon oxygen adsorption by X-ray absorption spectroscopy (XAS).

In order to synthesize the model catalyst, highly oriented pyrolytic graphite (HOPG, ZYA-grade, Panasonic Inc.) was first annealed at 1000 K for 30 minutes. Second, HOPG was irradiated by nitrogen ions using an ion gun (OMI-0730, Omegatron Inc.). Acceleration voltage and the amount of dosed nitrogen ions were 200 V and  $4 \times 10^{14}$  ions  $\text{cm}^{-2}$ , respectively. Finally, the nitrogen doped HOPG was annealed at 1000 K for 1 hour (N-HOPG). N 1s XAS of N-HOPG shows a graphite-like N rich surface with a small contribution of pyridinic N (Fig. 1(a)). Oxygen adsorption to N-HOPG was performed under 1 atm for 1 hour at R.T. (N-HOPG<sub>O<sub>2</sub></sub>). N 1s XAS measurements of N-HOPG before and after oxygen adsorption were performed at BL07LSU in SPring-8. X-ray incident angle to the sample surface was changed to 0°, 45° and 80° to extract information about in-plane and out-of-plane orbital in the unoccupied states. All experiments and the sample preparation were performed under  $2 \times 10^{-6}$  Pa.

Figure 1 shows in-plane and out-of-plane components in the  $\pi^*$  region (a) before and (b) after oxygen adsorption, extracted from the N 1s XAS spectra of N-HOPG for the three incident angles. The intensity of each spectrum was normalized by the intensity well above the absorption structures. Three sharp peaks in the  $\pi^*$  region are assigned to A: pyridinic N, B: cyano N and C: graphite-like N [3]. Upon oxygen adsorption following changes are observed in the XAS spectra; (1) appearance of pyridinic N  $\pi^*$  state in the in-plane component, (2) increase and decrease of graphite-like N and pyridinic N, respectively. The presence of the in-plane pyridinic N  $\pi^*$

component after oxygen adsorption indicates the appearance of pyridinic N where the C-N bond is tilted from the basal plane. The result (2) has also been observed in carbon-based catalysts synthesized from polyamide [4]. Since the graphite-like N has three C-N bonds while pyridinic-N has only two, the result suggests that C-N bond breaking of graphite-like N occurs and pyridinic N is produced after oxygen adsorption. After the bond breaking, the remaining C-N bond is tilted from the surface. Combined with a density functional theory (DFT) calculation, we found one of possible models that accounts for the C-N bond breaking and increase of pyridinic N  $\pi^*$  state in the in-plane component, i.e. nitrogen doped inverse-Stone-Wales (ISW) defect formed from a pair of joined pentagonal carbon rings placed between a pair of heptagonal rings. Figure 2 shows calculated N 1s XAS spectra of the ISW defect after oxygen adsorption, which well explains the appearance of pyridinic-N in the in-plane component at 398 eV.

In summary, we have performed polarization dependent XAS of nitrogen doped graphite before and after oxygen adsorption for three X-ray incident angles and extracted in-plane and out-of-plane components. Comparing the experimental results with the DFT calculation, we have taken a carbon close to the graphite-like N in ISW defects as a possible model for the oxygen adsorption site.



**Figure 1.** Experimental N 1s XAS spectra of N-HOPG (a) before and (b) after oxygen adsorption.

**Figure 2.** Calculated N 1s XAS spectra of the ISW defect after oxygen adsorption.

### References

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