

## Relationship between catalytic property and NEXAFS of P-doped graphite

Iwao SHIMOYAMA\*, Teruyuki HAKODA, Yuji BABA, Tetsuhiro SEKIGUCHI,  
Norie HIRAO, Kaveenga Rasika KOSWATTAGE  
Japan Atomic Energy Agency, Tokai-mura, Ibaraki 319-1195, Japan

### 1. Introduction

Recently, it has been reported B- and/or N-doped carbon electrodes and nanotubes have high catalytic property on oxygen reduction reaction [1,2]. Therefore, hetero-atom doping in  $\pi$ -conjugated carbon materials attracts much attention to design “carbon alloys” which are expected to have many functionalities. So far, study of carbon alloys with other dopants is behind those prepared with typical B and N dopants. Since P is one of the group V elements as well as N, we focused on P doping in graphite as a standard material of  $\pi$ -conjugated carbon, and investigated electronic structures at the dopant sites by NEXAFS in this work. Furthermore we studied catalytic property of P-doped graphite using electrochemical experiments, and found a relationship between catalytic property and NEXAFS.

### 2. Experimental

Experiments were performed at the BL27A.  $\text{PCl}_3$  was used for P doping. Fragment ions of  $\text{PCl}_3$  were formed by a cold cathode ion gun and irradiated on a highly oriented pyrolytic graphite (HOPG) with an acceleration energy of 3 keV. Three samples were compared. Sample A was prepared by ion doping at 700 °C with YAG laser heating. The fluences of the total fragment ions was  $3.5 \times 10^{16}$  ions/cm<sup>2</sup>. After doping, this sample was annealed at 800 °C. Samples B and C were prepared at room temperature with ion fluences of  $2.0 \times 10^{16}$  and  $2.6 \times 10^{15}$  ions/cm<sup>2</sup>, respectively, and then annealed at 800 °C. Contents of P were estimated by P2s/C1s photoelectron-peak intensity-ratios in XPS spectra measured with an MgK $\alpha$  source. Polarization dependence of NEXAFS was obtained by measuring total electron yield at various incidence angles  $\theta$  that is defined by the angle between the electric field vector of the linearly polarized X-ray and the surface normal of the HOPG. Electrochemical experiments were performed by rotatable disc electrode (RDE) system [3] in 0.5 M  $\text{H}_2\text{SO}_4$  solutions. P-doped HOPG samples were equipped on the RDE as the working electrode and cyclic voltammograms (CV) were measured in both  $\text{O}_2$  and  $\text{N}_2$  saturated solutions. The reference and counter electrodes were Ag/AgCl with a saturated KCl solution and a Pt wire, respectively. The RDE was operated at 1500 rpm.

### 3. Results and Discussion

Figure 1 shows P K-edge NEXAFS spectra of the P-doped HOPG measured at magic angle. Red, black, and blue curves show the results for samples A, B, and C,

respectively. Since the most intense peak around 2147 eV almost coincides with the  $\text{P1s} \rightarrow \sigma^*$  peak of  $\text{PCl}_3$  [4], it was difficult to distinguish carbon phosphide ( $\text{CP}_x$ ) compounds from phosphorous chloride without annealing. However, another peak appeared around 2144 eV for sample A, and samples B and C after the annealing. Since content of Cl drastically decreased by the heating procedures, this peak is attributed to some  $\text{CP}_x$  prepared by the ion doping.

Figure 2 shows polarization dependences of the P K-edge NEXAFS spectra. The top, middle, and bottom show results for samples A, B, and C, respectively. Solid, broken, and dotted curves correspond to the spectra measured at  $\theta = 20, 50$ , and  $90^\circ$ , respectively. Sample A showed clear graphite-like polarization dependence. This suggests that P atoms were incorporated in the *c*-plane of graphite and formed two-dimensional structure. Therefore, the peak at 2144.1 eV is assigned to  $\text{P1s} \rightarrow \pi^*$  out-of-plane transition of planar  $\text{CP}_x$  compounds. Since the peak around 2148 eV showed opposite polarization dependence, this peak can be assigned to  $\text{P1s} \rightarrow \sigma^*$  in-plane transition of same compounds.

Polarization dependences of samples B and C were smaller than that of sample A. We first supposed that the decrease of polarization dependence was caused by damage induced by ion beam irradiation. Polarization dependence can decrease when two-dimensional orientation of HOPG is disordered by ion beam irradiation. However, we noticed that the magnitude of polarization dependence was similar for samples B and C. Since the ion fluence of sample B was larger by almost

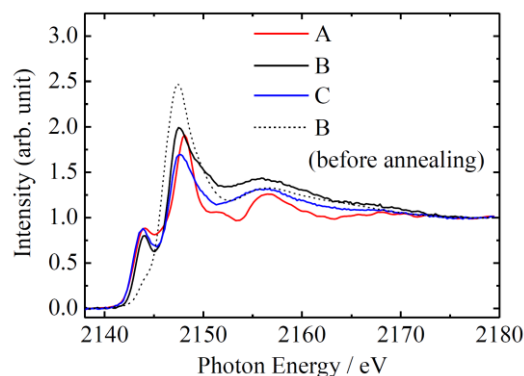


Figure 1. P K-edge NEXAFS spectra of P-doped HOPG. Red, black, and blue curves correspond to the results of samples A, B, and C, respectively. Dotted curve shows the result of sample B before annealing. (see text).

eight times than that of sample C, different magnitude of polarization dependences would be observed between these samples if degradation of polarization dependence was caused by damage effect. This implies that small polarization dependence was caused by the change of local configuration at P sites. We think distorted  $\pi$ -conjugated structures may be formed at P sites in samples B and C because some theoretical works indicated that substitution of P for C in  $\pi$ -conjugated carbon matrix can cause distortion of planar structure due to formation of "fullerene-like (FL) structure" [5,6].

Figure 3 shows reduction parts of CV for samples A, B, and C. Black and red curves correspond to the results obtained in  $N_2$  and  $O_2$  saturated solutions, respectively. P contents estimated from XPS spectra are also shown in the figure. Sample A shows almost identical CV for  $N_2$  and  $O_2$  saturated solutions. This means that the electrochemical reduction related to oxygen scarcely occurred on the surface of sample A. On the other hand, sample B and C showed different CV between  $N_2$  and  $O_2$  saturated solutions. For sample B, some electrochemical reduction related to oxygen was observed that around 0.1 V. This potential increased up to about 0.3 V (vs. Ag/AgCl) for sample C which showed the highest catalytic property among the samples. Since sample C had the smallest P content among them, we think amount of P was not the reason of the different catalytic properties. We consider that defects produced by ion

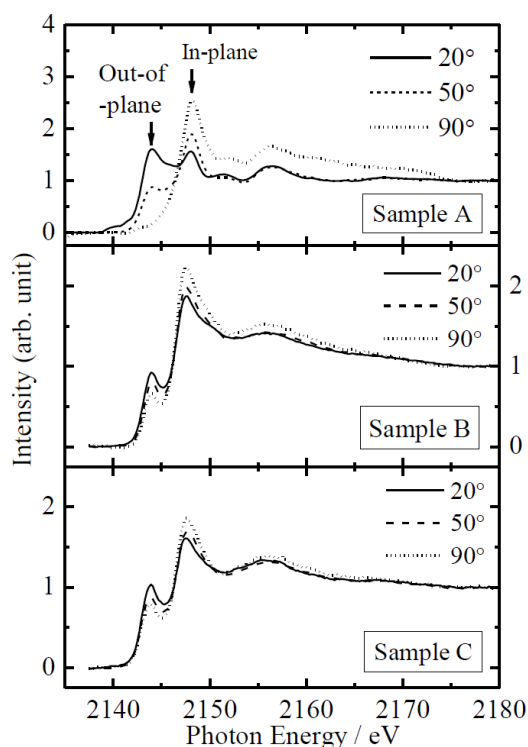


Figure 2. Polarization dependence of P K-edge NEXAFS spectra of samples A(top), B(middle), and C(bottom). Solid, broken, and dotted curves correspond to the spectra measured at  $\theta = 20, 50,$  and  $90^\circ$ , respectively.

beam were not the main cause of the catalytic property because the ion fluence of sample B was higher than that of sample C. Up to now, the reason why sample C had higher catalytic property than sample B is not clear. However, we noticed that both the samples B and C showed smaller polarization dependence of NEXAFS than sample A. This indicates that catalytic property was influenced by the local configuration at P sites, and distorted configuration can give better catalytic property to carbon alloys than planar configuration.

While the structure of the distorted configuration at P sites has not been clarified, our results indicate that P doping can also provide catalytic property for  $\pi$ -conjugated carbon materials. We also found that the catalytic property is related to the polarization dependence of NEXAFS. This suggests catalytic property can be designed by local configuration at dopant sites.

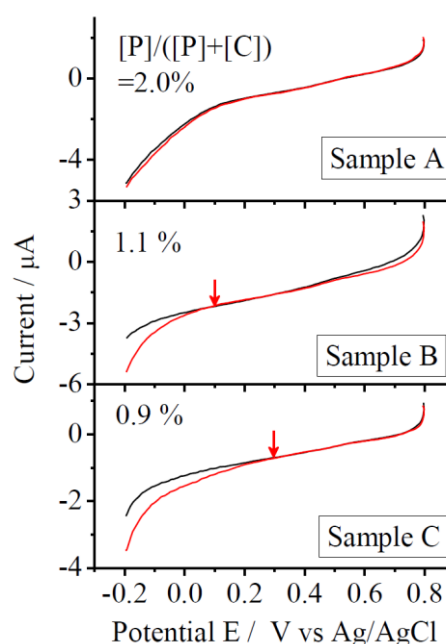


Figure 3. Cyclic voltammograms (CV) of P-doped HOPG in  $N_2$  (black) and  $O_2$  saturated  $H_2SO_4$  solutions. Top, middle, and bottom show results of sample A, B, and C, respectively. P contents were estimated from XPS measurements.

## References

- [1] J. Ozaki *et al.*, Carbon 45, 1847 (2007).
- [2] K. Gong *et al.*, Science 323, 760 (2009).
- [3] T. Hakoda *et al.*, Appl. Surf. Sci. 257, 1556 (2010).
- [4] Y. Baba *et al.*, Surf. Sci. 377-379, 699 (1997).
- [5] A. Furlan *et al.*, Thin Solid Films 515, 1028 (2006).
- [6] G. K. Georghiev *et al.*, Chem. Phys. Lett. 426, 374 (2006).

shimoyama.iwao@jaea.gp.jp