

Structural Analysis of Low Crystalline Carbons by High Energy X-Ray

*Kyoichi Oshida, Tatsuo Nakazawa, Kozo Osawa, Katsuyuki Fujiwara, Nagano National College of Technology,
716 Tokuma, Nagano, Japan, 381-8550
Morinobu End, Shinshu University, 4-17-1 Wakasato, Nagano, Japan, 380-8553*

Abstract

The structure of polyparaphenylene (PPP)-based carbon was analyzed by using high energy X-ray diffraction at Spring-8. The PPP-based carbon contains the small turbostratic particles with graphite like stacking. This suggests the existence of basic structural unit (BSU) in the highly disordered carbon like PPP-based carbon. The structure was verified by transmission electron microscopy and image analysis.

Introduction

Energy density of Lithium (Li) ion secondary batteries is larger than that of other secondary batteries. The mobile systems can be more compact in size and weight by using high performance Li ion secondary battery as an energy storage module [Endo, M. 2000]. In this study we used polyparaphenylene (PPP)-based carbon heat-treated at 720°C as the sample for the analysis. PPP consists of very small molecules which are made of about 10 benzene rings connecting like straight chain. Consequentially, PPP-based carbon is a kind of low crystallized material which contains many very small pores. PPP-based carbon has a very large charge and discharge capacity, which is much larger than the theoretical maximum capacity of graphite-Li intercalation compound of LiC_6 (372mAh/g). PPP-based carbon as the anode of Li ion batteries, however, has some problems such as high resistivity, large irreversible capacity, and poor cycle characteristic in practical applications. The mechanisms of charge-discharge of Li in the low crystalline carbons are not well understood. The first step to improve the high capacity Li ion batteries is to know the structure of the low crystalline carbons. The structure of PPP-based carbon was analyzed by using high energy X-ray diffraction at Spring-8.

Methods

The high energy X-ray we used is monochromatic X-ray of synchrotron radiation (SR). The SR is an electro-magnetic wave emitted from an electron traveling at almost the speed of light, toward its running-direction when its path is bent by a magnetic field. The beam line used for the experiment is BL04B2 at Spring-8. The monochromator is Si220 (61.7keV, $\lambda=0.020\text{nm}$). The brightness of radiation is about hundred thousand times higher than that of normal rotating anode type X ray tube at laboratories.

The samples are PPP-based carbon heat-treated at 720°C and the Li charged PPP-based carbon with binder and organic solvent (propylene carbonate and lithium perchlorate 1mol liquid solution) at 1st cycle. They were encapsulated in borosilicate capillary tubes with an inside diameter of 3 mm. Each samples were irradiated the X-ray for 8 hours.

The PPP-based carbon is observed by transmission electron microscopy (JEOL, acceleration voltage of 200kV, defocus value (Δf) = -60 nm).

Results and discussion

The X-ray diffraction pattern (XRD) of PPP-based carbon heat-treated at 720°C is shown in Figure 1 (a). The X-ray diffraction data was standardized to total structure factor, $S(Q)$ (see Figure 1 (b)). The pair distribution function (PDF) was obtained by Fourier transformation of $S(Q)$. The total correlation functions $T(r)$ calculated from PDF is shown in Figure 2. For comparison $S(Q)$ and $T(r)$ of graphite are plotted in Figure 1 (b) and Figure 2, respectively.

The XRD pattern of PPP-based carbon heat-treated at 720°C in Figure 1 is broad; however, it shows clear pattern up to highly angle. The PPP-based carbon has graphite order because there are peaks of $S(Q)$ of PPP-based carbon at the same places in Figure 1 (b).

The peaks of dotted curve labeled from A1 to A8 shown in Figure 2 correspond to interatomic distances in the same hexagonal layer of graphite. The labels of B1 to B3 indicate the peaks corresponding to interatomic distances of atoms of the adjacent hexagonal layers of ABAB stacking of graphite. The peak labeled C1 shows interatomic distance between the atoms of every other hexagonal layers of ABAB stacking. The solid line in Figure 2 shows $S(Q)$ of PPP-based carbon. The peaks of PPP-based carbon corresponding to the peaks of graphite of A4 and A5 are weak in intensity in comparison to that of graphite; however, there is correlation of graphite structure up to peak of A8 in the same hexagonal layer. This shows the existence of the hexagonal layers of PPP-based carbon which size is up to about 0.8nm. On the other hand, the atoms shift from atom positions of graphite between the different hexagonal layers because the spectral intensity of peaks of B1, B2, B3

and C1 is very weak. The small number of the minute layers are stacked at random one another. The experimental results show the existence of basic structural units (BSU) [Oberlin, A. 1984] in the highly disordered carbon like PPP-based carbon. The pores of the carbon are seemed to be formed between the small structures of the BSU.

TEM image of PPP-based carbon is shown in Figure 4. There are many small stacks of hexagonal layers of short length in the TEM image. The stacking number is two of three. The TEM image is in good agreement with the results of X-ray diffraction.

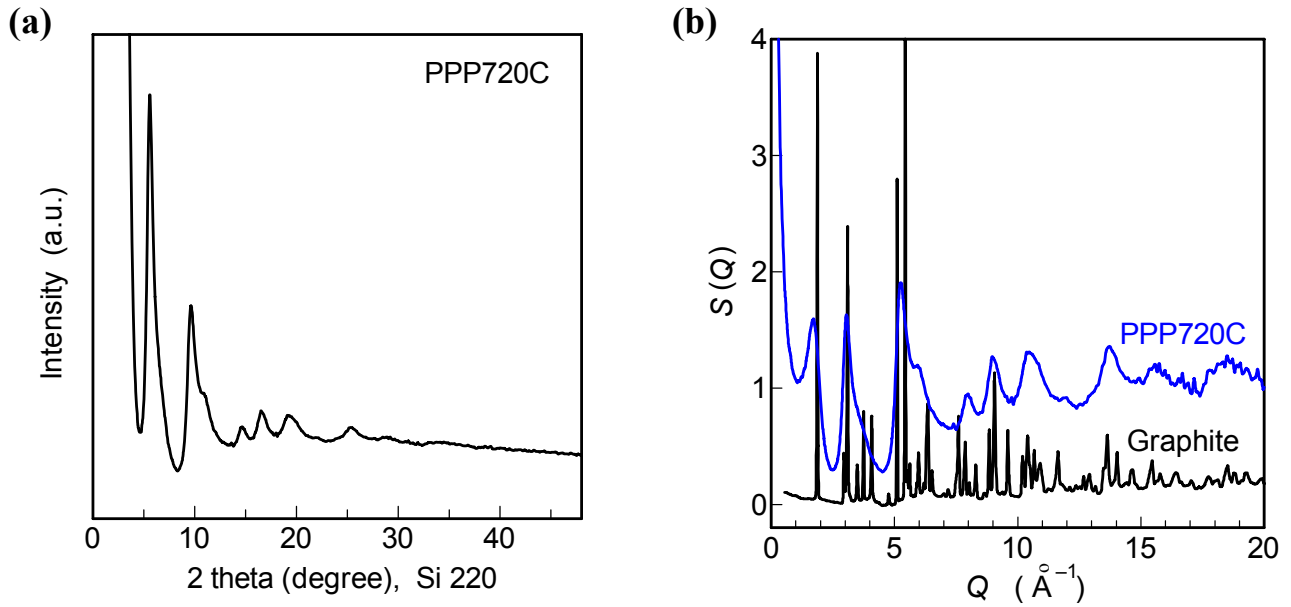


Figure 1. (a) High energy X-ray diffraction pattern of PPP based carbon heat treated at 720°C. (b) $S(Q)$ obtained from high energy X-ray diffraction pattern of (a).

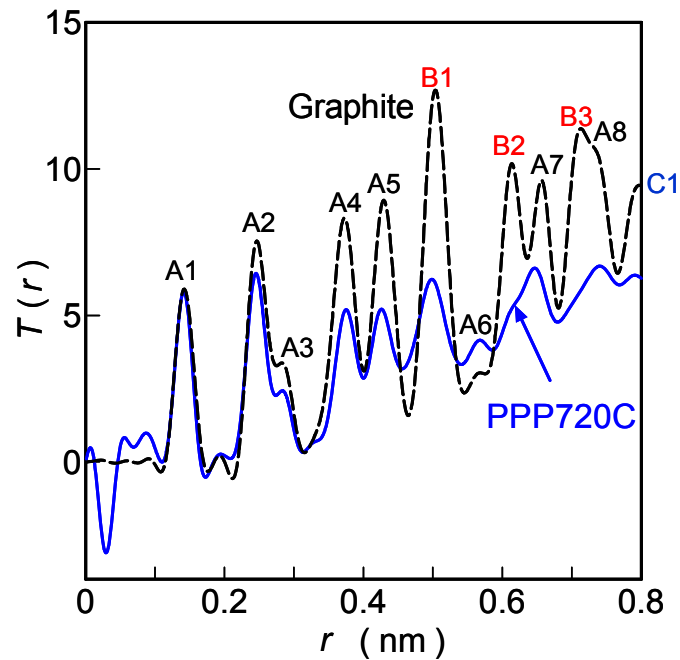


Figure 2. The total correlation functions $T(r)$ of PPP based carbon heat treated at 720°C and graphite.

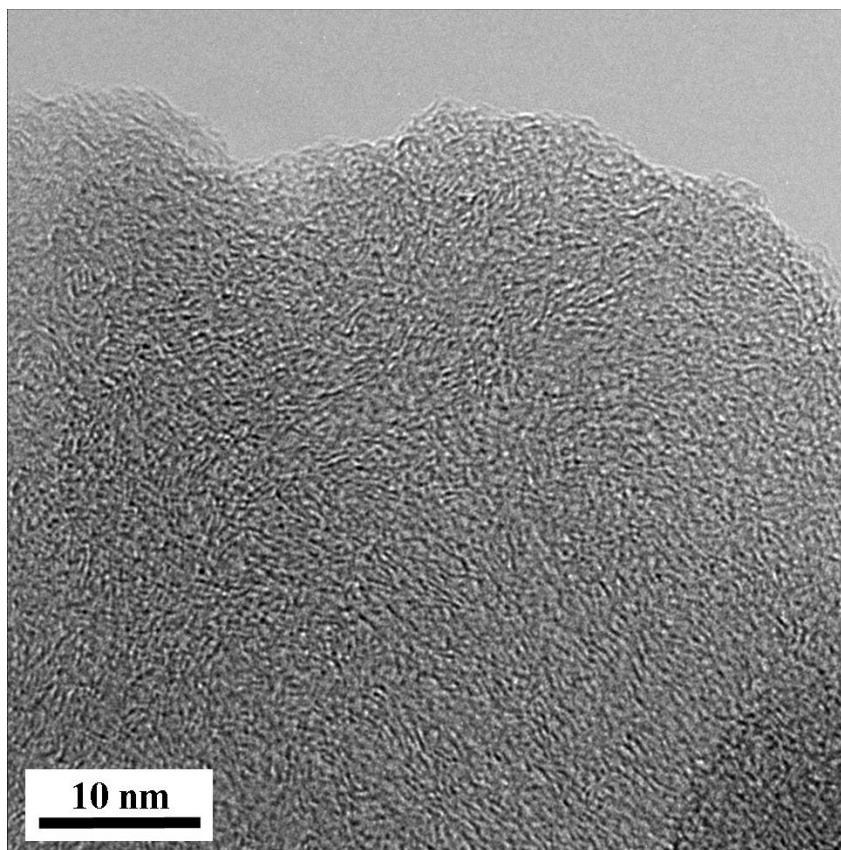


Figure 3. Transmission electron microscopy (TEM) image of PPP based carbon heat treated at 720°C.

Conclusions

The structure of PPP-based carbon was analyzed on atomic size by high energy X-ray at Spring-8. The PPP-based carbon of which structure seemed to be amorphous was estimated to have graphite like particles up to 0.8 nm in size. Existence of basic structural unit (BSU) is clarified in the highly disordered carbon like PPP-based carbon. The TEM observation has supported the experimental results.

Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research (No.17560296) of the Ministry of Education, Sports, Culture, Science and Technology of Japan. The synchrotron radiation experiments were performed at the BL04B2 in the Spring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal N0.2007A1178).

References

- Endo, M. 2000. Recent development of carbon materials for Li ion batteries. *Carbon* 38(2):183-197.
Oberlin, A. 1984. Carbonization and graphitization, *Carbon* 22(6):521-541.