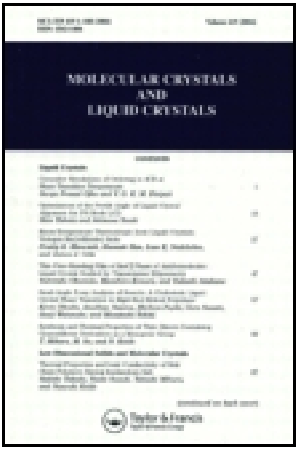

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Anodic Performance of Polyparaphenylene (PPP)-Based Carbons Heat-Treated at Various Temperatures

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Anodic Performance of Polyparaphenylene (PPP)-Based Carbons Heat-Treated at Various Temperatures

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The microstructure and electrochemical properties of polyparaphenylene (PPP)-based carbons prepared by the Kovacic and the Yamamoto methods have been comparatively studied after heat-treatment up to 3000°C. The results obtained by X-ray diffraction can clarify the specific electrochemical properties of PPP-based carbons and graphites.

Keywords: polyparaphenylene-based carbon; X-ray diffraction; Li ion battery

INTRODUCTION

Recent developments of Li ion secondary batteries have been achieved by the use of well-designed carbonaceous materials as an anode. Typically two types of carbon materials, highly-ordered graphite heat-treated at temperatures as high as 3000°C and non-graphitizable carbon heat treated at temperatures as low as 1100°C, have been used in anodes for commercial batteries. Actually, non-graphitizable carbon has attracted attention as an anode material because of its low cost and higher capacity compared with graphite anodes. On the other hand, for non-graphitizable carbons with high capacity, elucidation of the lithium insertion mechanism and improvement of the irreversible capacity are important issues. In particular, polyparaphenylene (PPP)-based carbons show different Li insertion capacities for different preparation methods, such as the Kovacic and the Yamamoto methods. Several authors reported the structural characterization and the electrochemical properties of polyparaphenylene-based non-graphitizable carbons heat-treated at different temperatures[1]. However, electrochemical properties of PPP-based carbons heat-treated at different temperatures have not been reported systemically. In the present paper, we discuss the correlation between the microstructural parameters and the electrochemical properties of the PPP-based carbons prepared by the Kovacic and the Yamamoto methods.

EXPERIMENTAL

The starting polyparaphenylene (PPP) material was obtained by the Kovacic[2] and the Yamamoto methods[3]. The former was obtained by a polymerization of benzene or of a benzene-derived reagent by using an $AlCl_3$-$CuCl_2$ catalyst. The polymerization occurs through the loss of one π electron and the formation of a benzene radical carbon that propels the polymerization process. This procedure leads to the formation of long polymer chains that exhibits some structural defects, such as branching in ortho- or meta- positions and the presence of radical carbons. The Kovacic-based PPP is a granular form with a dark brown color. The latter was prepared from 1,4-dibromobenzene by using a Grignard reagent and a transition metal catalyst and the resultant polymer (PPP) has a shorter chain and yellow color. The samples of these materials were subsequently heat-treated at various temperatures up to 3000°C in high purity argon gas (99.999%). Thermogravimetric analysis (TGA) and X-ray diffraction of the samples have been carried out. Electrochemical measurements were performed by using three-electrode test cells made of pyrex glass. The working electrodes were prepared by mixing the PPP-based carbons at 90 weight percent (wt.%) with poly (tetrafluoroethylene) (PTFE) of 10wt. % as a binder. The paste-like mixture of ca. 1mg was spread thinly onto a nickel mesh (5mm × 5mm) and pressed at a pressure of 200kgf/cm^2. The electrolyte used was *1M* solution of $LiClO_4$ in propylene carbonate (PC). Li metal was used as counter and reference electrodes. The specific capacity of the PPP-based electrode was measured by a potentiostat/galvanostat (Hokuto Denko Co., Ltd., HA-151) during the charge and discharge cycles in the ranges 0 to 2.8V, with a current density of 30mA/g-carbon.

RESULTS AND DISCUSSION

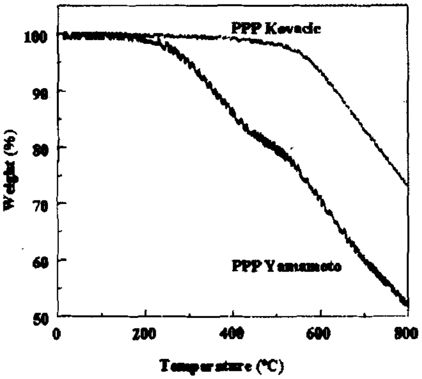

Figure 1. Thermogravimetric analysis (TGA) of PPP under flowing of N_2

Fig. 1 shows the result of thermogravimetric analysis for the PPP Kovacic method and the Yamamoto method under flow of N_2 gas. The weight decrease of the PPP Yamamoto, as shown in this figure, started at a temperature of 200°C, and the carbon yield obtained at 800 °C was about 50%. On the other hand, the weight loss of PPP Kovacic starts at 500°C, and the carbon yield obtained at 800°C is about 70%. These results may be related to the fact that the PPP Kovacic method is branched and have more cross-linked polymer structure and a longer phenylene chain length than that of the PPP Yamamoto method. From the view point of cost and carbon yield, the PPP Kovacic method is a more effective process than the PPP Yamamoto method. Fig. 2 shows the XRD patterns of PPP Kovacic-(a) and PPP Yamamoto-based carbons (b) as a function of heat treatment temperature (HTT). The XRD curve of pristine Yamamoto-based PPP shows strong and sharp peaks, indicating that the polymer has high crystallinity and regularly repeated units related to the polymer chain. However, the PPP prepared by the Kovacic method shows only broad signals that might be due to the irregularities caused by the presence of both cis-trans, trans-trans, and polynuclear configuration components[1]. The Kovacic- and Yamamoto-based PPP shows polymeric peaks, which are broad and then disappear with increasing heat treatment temperatures up to 600°C and 500°C, respectively. These temperatures region may be related to the departure of hydrogen atoms and the breaking of the phenylene-chain. These results are very consistent with the TGA curves.

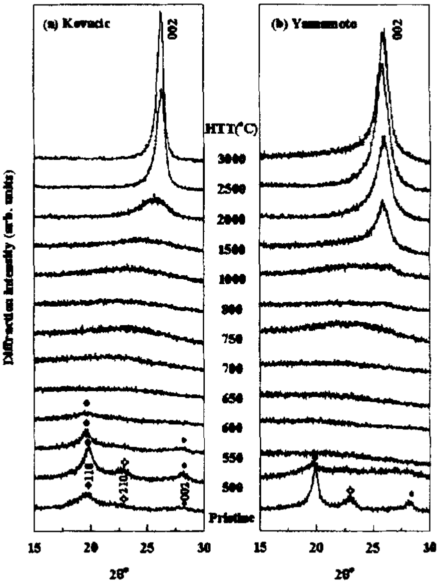

Figure 2. XRD patterns of (a) PPP Kovacic- and (b) PPP Yamamoto-based carbon as a function of HTT.

In Figs. 3 and 4, the voltage changes for PPP Kovacic- and PPP Yamamoto-based carbons are shown, respectively as a function of HTT from 700 to 3000°C during the galvanostatic discharge and charge examination. In particular, PPP Kovacic-based carbons HTT with below 2000°C show larger lithium insertion capacity than that of PPP Yamamoto-based carbons. On the other hand, for HTT above 2000°C, Yamamoto-based carbon shows a larger battery capacity than that of PPP Kovacic-based carbons. These results may be related that the PPP Kovacic-based carbons HTT below 2000°C have a more porous structure than the PPP Yamamoto-based carbons determined by SEM observations[1]. Namely, the porous texture of PPP Kovacic-based carbon could be useful as an anode in Li ion batteries for penetration of the electrolyte and Li ion. Especially, PPP Kovacic-based carbon heat-treated at 700°C shows the largest lithium insertion capacity. This might be related the quinoid type of plate-like graphene structure[4] and the homogeneously developed disordered carbon structure. The PC (propylene carbonate) was not a good electrolyte for samples HTT above 2000°C for both the Kovacic and Yamamoto samples, though that is one of the most popular electrolyte solvents. During the first discharging of both samples heat-treated at 3000°C, irreversible capacity and long plateaus are observed at about 0.8V, which is caused by electrolyte (PC) decomposition on the new surface of the carbon materials.

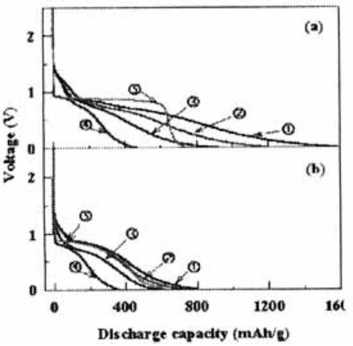

Figure 3. Discharging curves of PPP Kovacic- (a) and PPP Yamamoto-based carbons (b) as a function of HTT. ① 700°C, ② 800°C, ③ 1000°C, ④2000°C, and ⑤3000°C.

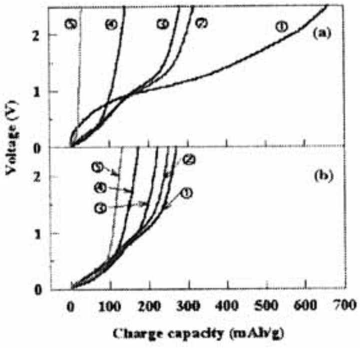

Figure 4. Charging curves of PPP Kovacic- (a) and PPP Yamamoto-based carbons (b) as a function of HTT. ①700°C, ② 800°C, ③ 1000°C, ④ 2000°C, and ⑤3000°C.

CONCLUSIONS

We have examined the correlation between microstructural and electrochemical properties of the PPP Kovacic- and the PPP Yamamoto-based carbons prepared at different heat-treatment temperatures. The electrochemical properties of PPP-based carbons characteristically depend on the starting materials and their microstructures.

References

[1] M. Endo, C. Kim, T. Hiraoka, T. Karaki, K. Nishimura. M. J. Matthews, S. D. M. Brown, and M. S. Dresselhaus, *J. Mater. Res.*, **13,** 2023 (1998).

[2] P. Kovacic and A. Kyriakis, *J. Am. Chem. Soc.*, **85,** 454 (1963).

[3] T. Yamamoto, Y. Hayashi, and A. Yamamoto, *Bull. Chem. Soc.*, Jpn. **51,** 2091 (1978).

[4] M. Endo, C. Kim, T. Karaki. T. Fujino. M. J. Matthews, S. D. M. Brown, and M. S. Dresselhaus, *Synthetic Metals*, **98,** 17 (1998).