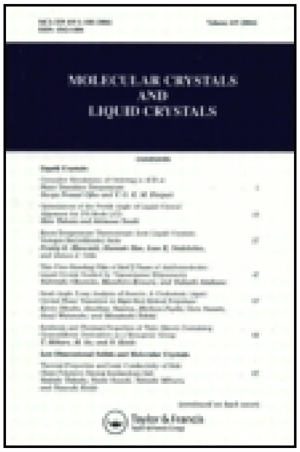

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Li Storage behavior in Polyparaphenylene(PPP)-based Disordered Carbon as a Negative Electrode for Li Ion Batteries

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Li Storage Behavior in Polyparaphenylene(PPP)-based Disordered Carbon as a Negative Electrode for Li Ion Batteries

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PPP-based carbons prepared by the Kovacic and the Yamamoto methods give rise to slightly different polymer structures. The low temperature forms of PPP-Kovacic-based carbon heat treated around 700℃ shows a Li storage capacity (1000mAh/g) which is 3 times larger than that of Yamamoto (280mAh/g) in the 2nd charging process. It is suggested that the texture as well as the microstructure of these carbons, as characterized by SEM, TEM, and Raman observations, affect the anode performance strongly.

Keywords: Li ion battery, Anode performance, Polyparaphenylene-based carbon

INTRODUCTION

The performance of Li ion batteries depends strongly on the crystallinity of the carbon used for the anode electrode. Generally, both disordered carbons and well-ordered graphites show higher charge and discharge capacity than that with intermediate crystallinity [1,2,3]. Especially PPP (poly p-phenylene)-based carbon, produced by the Kovacic method (denoted by PPP•Kovacic, with a dark brown color) exposed to heat treatment temperatures (HTT) as low as 700℃, has been shown to possess a superior Li storage capacity of 1000mAh/g or more[1,2]. This is about three times higher than that of the theoretical capacity of the 1st stage GIC (LiC_6). On the other hand, PPP-based carbon produced by another synthesis route, the Yamamoto method

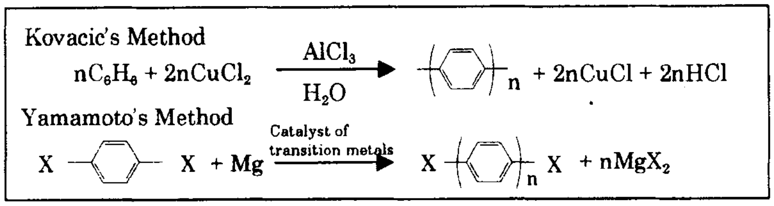

FIGURE 1 Chemical reaction for the formation of PPP.

(denoted by PPP•Yamamoto, with a yellow color) heat-treated at the same temperature as PPP•Kovacic, indicates very low charge and discharge capacity. In the present paper, the anode performance as well as the structure of PPP-based carbons obtained from the Kovacic and Yamamoto methods (see Fig. 1) are compared, and discussed with regard to their Li storage property from the view point that the structure of the resultant carbons is influenced by the starting polymer structure.

Experimental Results and Discussion

Fig.2 shows the charge-discharge characteristics of PPP-based carbons obtained by the Kovacic and Yamamoto methods, measured by using a cell of 1M $LiClO_4$ in propylene carbonate (PC)[1,2,3]. These PPP powders were heat-treated at 700℃ in an Ar atmosphere. PPP-based carbon from the Kovacic method shows a very high reproducible charge capacity of about 1000mAh/g (2nd and higher cycles), which is very close to the theoretical capacity of LiC_2. In contrast, PPP-based carbon from the Yamamoto method shows only a small reproducible charge capacity of about 280mAh/g (LiC_{10}, 2nd and higher cycles), which is as small as 1/3 of that from PPP•

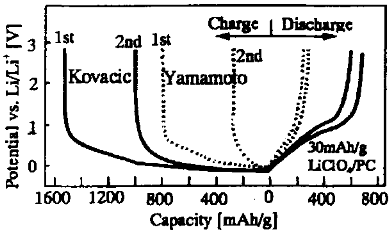

FIGURE 2 Charge and discharge properties (1st and 2nd cycle) of PPP-based carbons (HTT;700℃, in Ar) in a Li ion battery.

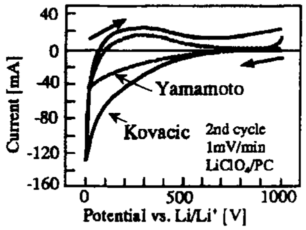

FIGURE 3 Voltammogram of PPP-based carbons (HTT;700℃, in Ar).

Kovacic.

Fig.3 shows the cyclic voltammogram (CV) of both samples. PPP • Yamamoto-based carbon shows no clear plateau at around 700mV as PPP• Kovacic-based carbon does. This potential corresponds to the plateau in the charge-discharge properties (see Fig.2) which can account for the higher charge-discharge capacity of Kovacic-based carbon relative to that of the Yamamoto-based carbon.

In order to discuss their microstructures, SEM and TEM images of PPP• Kovacic-based and PPP•Yamamoto-based carbons are shown comparatively in Figs.4 and 5. PPP•Kovacic-based carbon indicates a porous surface and granular texture, while PPP • Yamamoto-based carbon shows a smooth surface and a bulky structure by SEM observation. TEM images of both materials also demonstrate that PPP•Kovacic carbon shows a more porous non-graphitizing microstructure than PPP•Yamamoto-based carbon. It is suggested that the porous structure of PPP • Kovacic-based carbon is considered to be one of the factors responsible for the specific structure of the

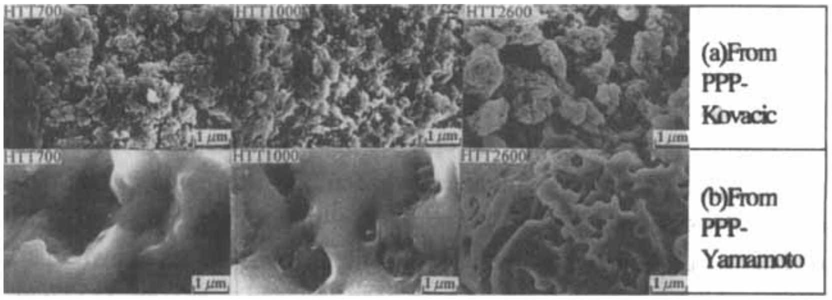

FIGURE 4 SEM images of PPP-based carbons.

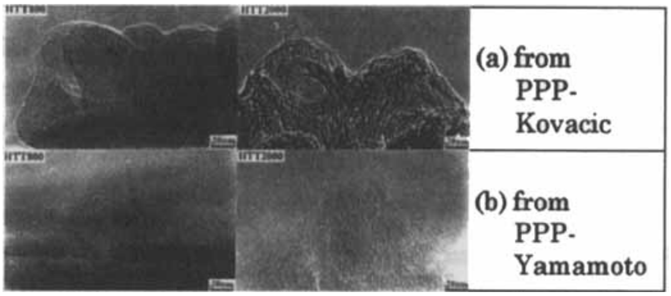

FIGURE 5 TEM images of PPP-based carbons.

low temperature form governing the high Li storage capacity.

Raman spectra of PPP•Kovacic-based carbon heat-treated at different temperatures has indicated that PPP•Kovacic carbon heat-treated around 700℃~750℃ exhibits a characteristic shoulder peak at about 1260cm^{-1}[4]. This is considered to be a partially carbonized structure formed by quenching the starting polymer through the low temperature carbonization. This special feature in PPP•Kovacic-based carbon could be an important characteristic that is responsible for the high Li storage capacity. PPP•Kovacic material includes some polymer components with a polynuclear structure, and PPP• Yamamoto contains only the pure para-phenylene component. This structural difference in the starting PPP could be responsible for the differences in the Raman spectra of the carbonized powder, as shown in Fig.6 for the low temperature forms. The characteristic shoulder observed in Kovacic-based carbons, heat treated at 700 and 750℃, are also found in the Yamamoto-based carbon treated at 675 and 700℃ with the HTT being 50℃ lower than in the Kovacic material. Fig.7 shows the Raman spectra for the Li doped samples, by charging up to 600mAh/g for Yamamoto-based carbon and 1000mAh/g for Kovacic-based carbon during the first charging cycle (each sample corresponding to a charging rate of about 70% against the maximum charge capacity in the 1st cycle as shown in Fig. 2). The Raman spectra were successfully taken by setting the charged flaky samples between two glass slides using the electrolyte for the experiments. Kovacic-based carbon shows clearly the disappearance of the shoulder while Yamamoto samples still retains the 1260cm^{-1} shoulder peak (see Fig. 7). It has been shown that Li GIC's exhibit two peaks[6] which have been assigned to interior- (1577cm^{-1})

and bounding-layer (1601cm^{-1}) phonon modes. It is reasonable that in the present samples the Raman spectra lack the peak corresponding to interior-layer mode because of the highly disordered structure. On the other hand, the slight shift of the 1600cm^{-1} peak after charging might be attributed to the random and homogeneous Li doping between the defective carbon layers. It could be suggested that the characteristic Raman shoulder at around 1260cm^{-1} plays an important role for Li storage in PPP carbons. Furthermore, the present doping mechanism is different from that in well-ordered graphite with stage fidelity upon intercalation, as discussed in detail elsewhere[2,3]. The structural differences existing in these carbons might give rise to the large differences in their anode performances. On the other hand, carbons from PPP (including a 10 % m-phenylene component), when heat-treated at 700℃, showed intermediate Li storage capacity between that of the Kovacic

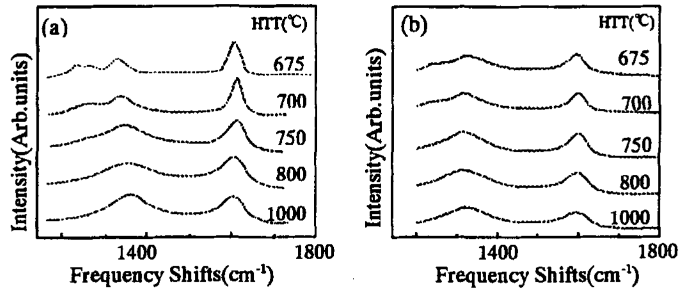

FIGURE 6 Raman spectra for PPP Kovacic(a) and Yamamoto(b) heat-treated between 700 and 1000℃ taken with 632.8nm light.

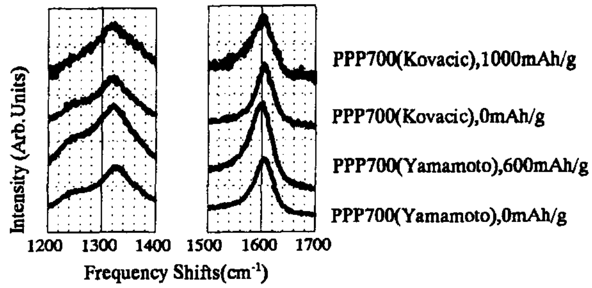

FIGURE 7 Raman spectra before and after Li doping for PPP Yamamoto- and Kovacic-based carbons heat-treated at 700℃, measured in propylene carbonate(PC) with 1M $LiClO_4$.

and Yamamoto samples. So, the slight differences in structure of the starting polymer, such as the inclusion of polynuclear components could influence the microstructure of the respective carbons, which is believed to be responsible for their different anode properties.

Conclusion

The different properties produced through carbonization, and Li storage characteristics in PPP-based carbons likely arise from the structural differences in the starting polymers. Because of the presence of the polynuclear component in PPP•Kovacic, the growth of carbon networks could be suitably controlled in diameter as well as in their parallel stacking[4,5], while PPP•Yamamoto forms a different structure of carbon networks because of the straight chains of polyphenylene. To improve the anode performance, such as capacity and efficiency of Li ion batteries, especially when based on disordered carbons, it is concluded that the precise control of the microstructure of the starting organic materials is very important. To gain further insight into the present work, a simulation of the Li storage behavior in the PPP-based disordered carbon will be carried out in future work.

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