

ANODE PERFORMANCE OF PPP-BASED CARBONS

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Introduction

Recent development of the lithium ion secondary batteries has been achieved by the use of well-designed carbon and graphite materials as an anode. By the contribution of the carbon materials used in anode, in last five years the capacity of the typical Li ion battery have been improved by 1.7 times. However, the Li insertion mechanisms, especially into disordered carbon system, are not yet fully understood to explain to electrochemical insertion process.

In the present work, in order to explain the electrochemical Li insertion and extraction phenomena in PPP-700 (polyparaphenylene, HTT=700°C, in Ar) *in-situ* Raman scattering experiments have been carried out, using an experimental Li cell with propylene carbonate (PC) as an electrolyte.

Experimental

The starting PPP material was obtained by the Kovacic method, as described elsewhere. The electrode assembly was a two-electrode experimental cell for *in-situ* Raman experiments using 1 M LiClO₄ in a propylene carbonate electrolyte. The PVDF binder has been examined to show no Raman peaks in the region where Raman lines appear for PPP and graphite. Raman ($\lambda=632.8\text{nm}$ HeNe laser, optical power 25mW) spectra were measured at various cell voltages during charging and discharging of the experimental cell.

Results and discussion

Fig. 1 shows the charging and discharging second cycle of the ppp-700. PPP-700 shows a very high reproducible charge capacity of about 1100mAh/g, which is almost near to the capacity of LiC₂.

The extremely enhanced charge capacity in PPP-700 can be explained as follows, based on *in-situ* Raman spectroscopy (Fig. 2).

The results of lineshape analysis for the high frequency mode near 1600cm⁻¹ are expressed in Fig. 3, which provides interesting information about the Raman frequency shift in the Li/PC/PPP-700 battery system during discharging and charging. The high frequency peak position as a function of electrode voltage, in the range between about 2.8V and 0.0V for both of the discharging and charging processes, is reflecting the Li⁺ uptake and

release in PPP-700. It is worthwhile to note that the curves have thresholds at about 1.0V, and are divided into two zones by the threshold voltages. That is to say, in Zone I (2.8V~1.0V) the Raman peak wave number shows no change with decreasing voltage up to 1.0V, and the other Zone II (1.0V~0.3V) corresponds to the downshift of the wave number with decreasing the voltage for discharging. On the other hand, for charging, the change in peak position takes place almost reversibly with some histerises effect indicating some amount of residual Li. Present result suggests that in Zones I and II the Li⁺ ions have different insertion behaviors. The change in Zone II could be due to a charge transfer effect like in GIC occurring in the PPP-700 electrode, which would modify the localized electron density and electrical conductivity which is reflected to the final diminishing of the peaks. It is noteworthy also that even in the present very disordered structure of PPP-700, same behavior as charge transfer in GIC can take place to store Li⁺ ions between the defective or primitive carbon layers, and this result is phenomenologically consistent with the Li storage model proposed before [1]. On the other hand, Li storage in Zone I might be different from that occurred in Zone II. Though, it is still difficult to clarify the Li storage mechanism, it could be suggested that Li in Zone I may be firstly stored at preferable sites, and charge localization affecting the peak wave number does not occur. Inaba et al. reported the *in-situ* Raman study on MCMB heat-treated at around 1000°C, and showed no change in 1580cm⁻¹ Raman peak. These different results indicate that charge and discharge mechanism taking place especially in such a low temperature carbon with super high Li storage capacity should be different in each cases depending upon the each delicate structure of carbons, and it is difficult to explain systematically by the common scheme by proposed models [1,4,5].

Conclusions

In-situ Raman spectroscopy is used to investigate the electrochemical Li insertion into disordered PPP-700, obtained by the Kovacic method after heat-treatment at 700°C. The Raman spectrum provides insight into the mechanism of lithium insertion into the PPP-700 electrode.

References

1. Sato K, Noguchi M, Demachi A, Oki N and Endo M., Science 1994;264:556.

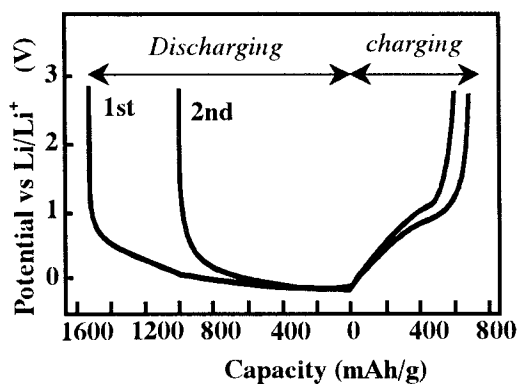


Figure 1. Change in potential during the first and second charging and discharging cycle of the PPP-700.

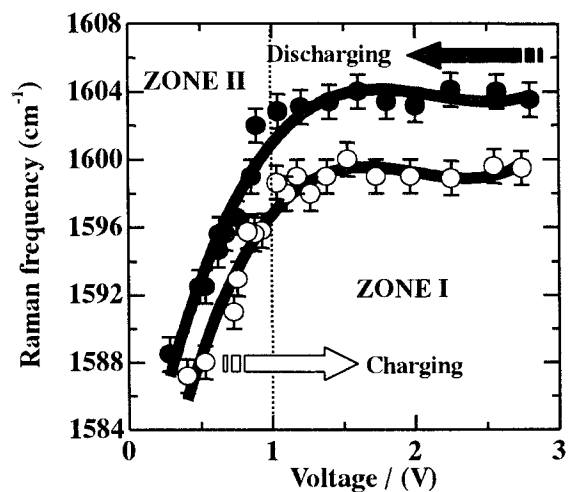


Figure 3. The voltage dependence for the high frequency Raman modes of the PPP-700 electrode obtained by fits to a Lorentzian line shape.

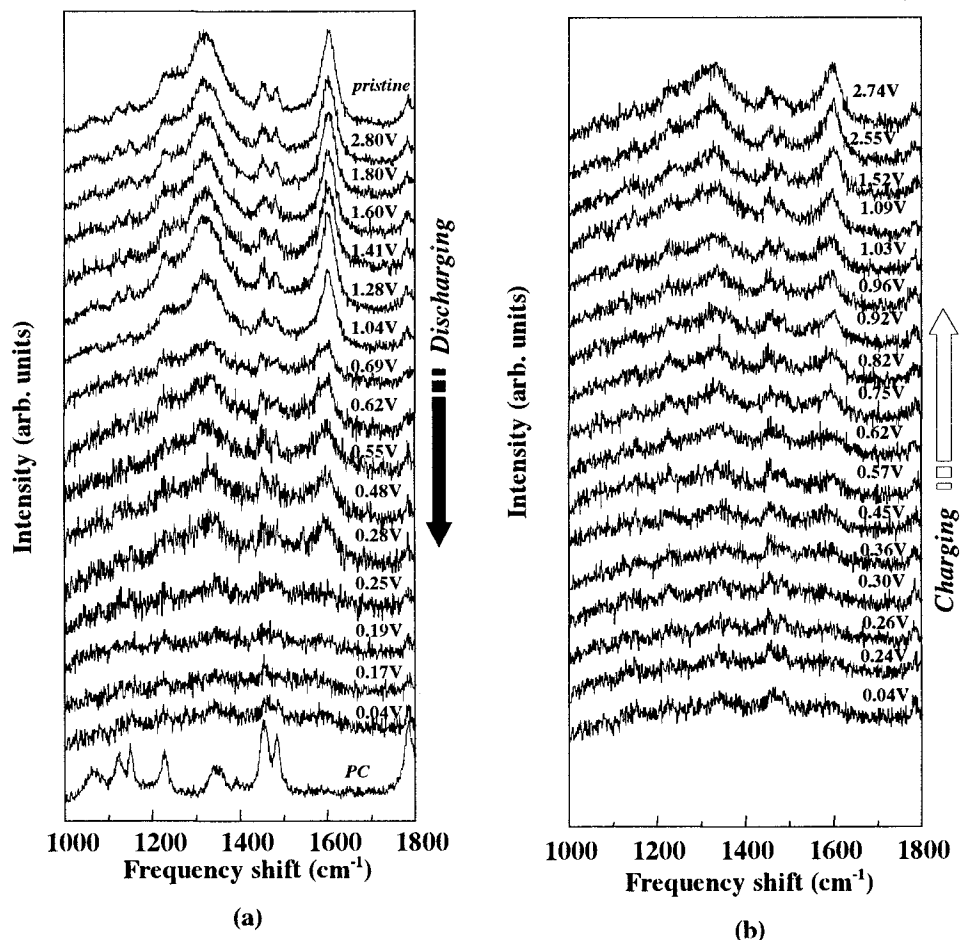


Figure 2. In-situ Raman spectra of PPP-700 at various cell voltages for discharging from 2.8V to 0.04V (a) and for charging from 0.04V to 2.7V (b).