MECHANISM OF LITHIUM INSERTION IN MESOCARBON MICROBEADS USED AS ANODES

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Introduction

Carbons are good candidates as anode materials for rechargeable lithium-ion batteries, allowing the lack of dendrites, low self-heating, safety and harmlessness for environment [1]. Poorly organized carbons have the best performances in terms of capacity, but the reasons are not well understood. Among disorded carbons, mesocarbon microbeads (MCMB) heat-treated at 700-1000°C appear to be very efficient anode materials [2]. We have examined the correlation between the charge-discharge characteristics and the multiscale organization (structure and microtexture) of MCMB. ^{7}Li-NMR investigation has been performed at different steps of the charge-discharge process for getting better information on lithium state in these materials.

Experimental

Coal tar pitch was heat-treated for 1h at 450°C and MCMB were extracted with coal tar derived wash oil. After washing with toluene, they were heat-treated at 900°C under argon for 15 minutes. A carbon pellet was formed by pressing a mixture of MCMB (85%) with acetylene black (5%) and polytetrafluoroethylene binder (10%). Cycling was performed in a two electrodes cell with 1M $LiPF_6$/EC+DEC electrolyte using a Mac-Pile controller working at 0.5mA. From galvanostatic experiments, we calculated discharge capacity for lithium insertion into carbon and charge capacity for deinsertion of lithium. Multiscale organization of MCMB was analyzed by high resolution TEM (Philips CM 20) especially using the 002 lattice fringes mode. The lithiated and delithiated MCMBs were examined by solid state ^{7}Li-NMR on a Bruker DSX 360 spectrometer using $LiNO_3$ solution as external standard.

Results and discussion

Charge and discharge curves of the MCMBs during the first cycle are shown in figure 1. The plateau observed at *ca.* 0.8V *vs* Li^+/Li during discharge is attributed to the decomposition of electrolyte which results in the formation of a passivating film at the surface of carbon. The reversible capacity, of the order of 340mAh/g , is comparable to that of graphite, in good agreement with the data already published by Mabuchi et al. [2]. Lamellar and mesoporous microtextures were brought out by TEM on the MCMB (figures 2 and 3). It is proposed that the mesoporous phase could be due to spheres stabilization during extraction process. The interesting electrochemical performances of MCMB are attributed to a mesoporous component which allows easy diffusion of lithium towards the lamellar phase. In order to obtain more information about lithium insertion into MCMB, ^{7}Li-NMR spectra were recorded ex situ at the end of discharge, i.e. -0.020V, and after the end of charge, i.e. +3.0V. The fully lithiated MCMB (figure 4) presented two lines of Knight shift at 1.8ppm (40%) and at 0ppm (60%). It is remarkable that these two lines do not correspond to the positions which could be expected either for metallic lithium (262ppm) or for a saturated first stage like graphite intercalation compound LiC_6 (45ppm) [3]. Even if reversibly stored in rather large amount, lithium inserted in MCMB appears to have no metallic character. This implies that no extended layer of lithium is present contrarily to the one existing in LiC_6. Limited clusters or Li-C bonds are more likely responsible for the shift observed. The line of the delithiated sample, formed after the first charge (figure 5), had to be decomposed into two contributions: at 1.25 ppm (47%) and at 0.7 ppm (53%). These two peaks show that the passivating layer contains only pure ionic lithium. Previous observations by X ray diffraction already identified Li_2CO_3 coming from the decomposition of the electrolyte [4].

Conclusion

MCMB show a specific multiscale organization including lamellar and mesoporous textures. This particular arrangement of the basic structural units (BSU) could be responsible for the electrochemical performances observed. ^{7}Li-NMR spectra of fully lithiated MCMBs indicated only ionic character for lithium species. We can assume that in the low temperature (700-900°C) carbons, insertion is probably not between the extended layers of BSU but rather in the intercrystallite spaces. However, further study is needed to better analyze the kind of interaction existing between lithium and low temperature carbons with various organization.

Acknowledgments

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References

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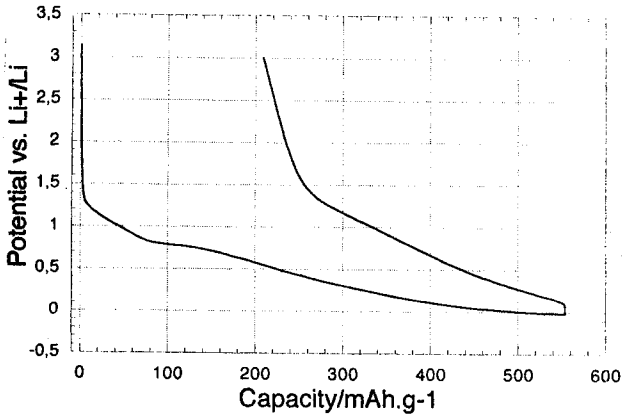

Figure 1 : discharge and charge profiles of MCMB in 1M $LiPF_6$/EC+DEC

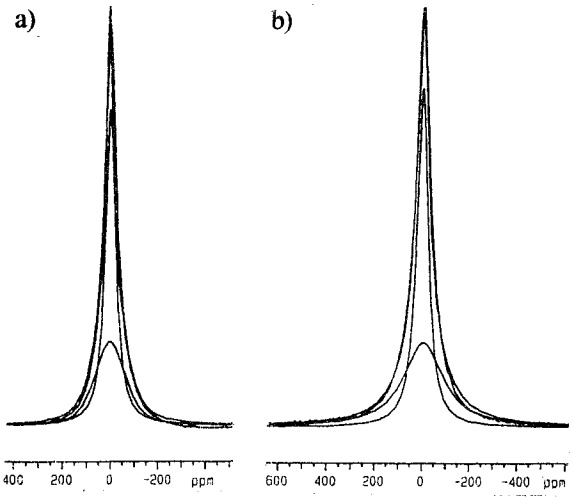

Figure 2 : ^{7}Li NMR spectra of a) fully lithiated MCMB, b) MCMB after the first charge at +3.0V

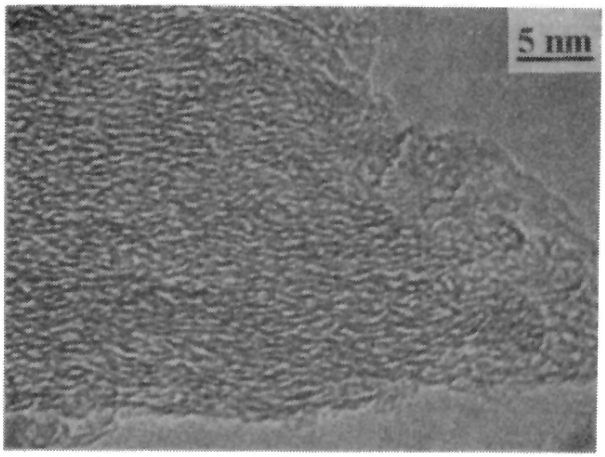

Figure 3 : TEM image of lamellar texture of MCMB.

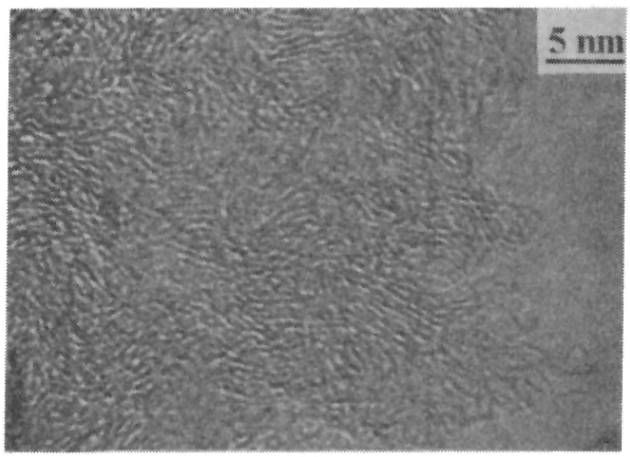

Figure 4 : TEM image of mesoporous texture of MCMB.