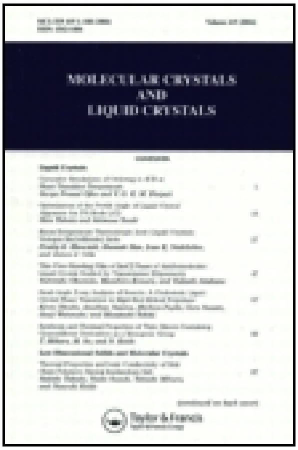

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Electrochemical Insertion of Lithium into Carbonaceous Materials Derived from Pyrolyzed Polyparaphehylene : Effects of the Pyrolysis Time

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Electrochemical Insertion of Lithium into Carbonaceous Materials Derived from Pyrolyzed Polyparaphenylene : Effects of the Pyrolysis Time

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In order to optimise the thermal treatment of PPP at 700°C, we report on the electrochemical studies using solid polymer electrolytes composed of polyethylene oxide (PEO) and $LiClO_4$ of the insertion of lithium ions into PPP pyrolyzed at 700°C in argon atmosphere during increasing pyrolysis times (0.5 ; 1, 2 and 6 hours).

The electrochemical measurements reveal that two parameters are necessary to improve the affinity of these materials for lithium : i) the density of crosslinking (or the lateral extension of the graphene sheets for the longest pyrolysis times) must be large. ii) a high molar ratio H/C.

Keywords: polyparaphenylene; pyrolysis; lithium; electrochemical insertion

INTRODUCTION

During these last years, several studies[1-5] have shown that carbon obtained by pyrolysis of polyparaphenylene (PPP) at 700°C could insert lithium ions with capacities higher, ie 500 to 900 mAh/g, than those reported with graphite (372 mAh/g). Electrochemical performances of these carbons depend strongly on the nature of the organic precursor and of the treatment conditions (temperature and pyrolysis atmosphere, morphology of the precursor, ...). Although many mechanisms have been proposed to explain the exceptional affinity for lithium[1-5], none of them is indisputable. This work is a contribution to the understanding of the mechanisms of accommodation of lithium in this kind of materials. We have studied the insertion of lithium ions into the materials derived from the pyrolysis of PPP at 700°C in argon gas during increasing pyrolysis times (PPP*). The structural and spectroscopic (Raman and infrared) characterisations of these materials[6] reveal that, at the beginning of the PPP decomposition, disordered carbons exhibiting a high cross-linking density were formed. Then, when the samples were pyrolyzed during 4 and 6 hours, the derived materials were totally disorganised and can be described as disordered carbons containing small graphene precursors. The atomic H/C ratio decreased continuously from 0.59 to 0.24 respectively for PPP and samples treated for 6 hours[6].

EXPERIMENTAL

Polyparaphenylene, synthesized according to the method of KOVACIC[7], was treated at 700°C in argon atmosphere during increasing times (0.5; 1; 2; 4 and 6 hours). The electrochemical system $Li/P(EO)_8LiClO_4/PPP^*$-PEO (60/40 by weight w/w) was mounted in a button type cell using a PEO-$LiClO_4$ film obtained by classical procedures[8]. Insertion and deinsertion were investigated using a computer-controlled potentiostat-galvanostat Mac Pile (Biologic).

RESULTS AND DISCUSSION

The galvanostatic curves for the different samples (fig. 1) are similar with : i) an important irreversible capacity in the first cycle (tab. 1 and fig. 1a). This one is related to the side reactions of the electrolyte, such as the decomposition of the electrolyte at the carbon/electrolyte interface and the reduction of the binder PEO. The irreversible capacity decreases drastically during the second cycle then after this one, the electrochemical cells exhibit a good reversibility. ii) a large hysteresis between the charge and the discharge curves; the insertion processes take place at low potentials (near zero volt) and the deinsertion ones occurred in the range 0.6-1.0 Volts.

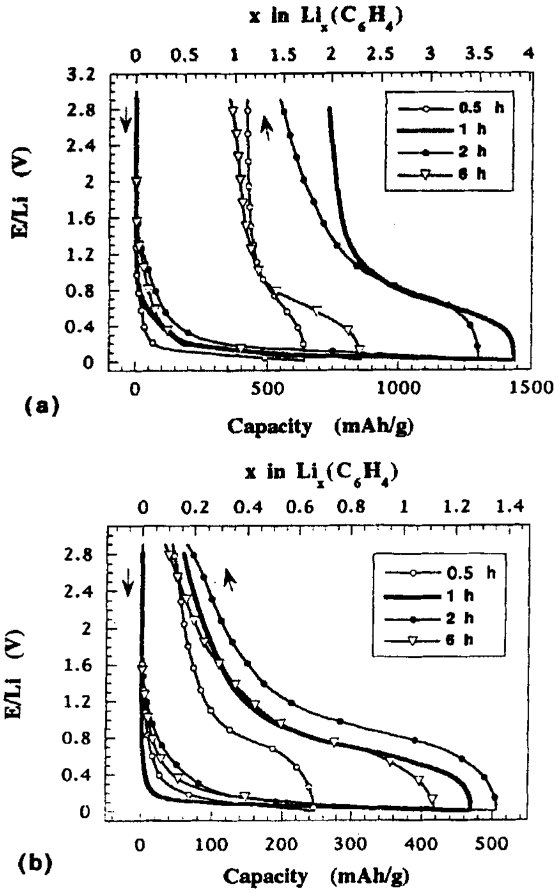

FIGURE 1 Galvanostatic curves of the first (a) and tenth cycles (b) of the electrodes processed during increasing pyrolysis times
(7.1 $\mu A.mg^{-1}$ <specific current <$9.1 \mu A.mg^{-1}$; T=80°C)

The reversible capacity depends on the pyrolysis times. Except for the sample pyrolyzed during 0.5 hour, which exhibits a value close to x=0.5 (x refers to $Li_x(C_6H_4)$) whatever the number of cycle, high reversible capacities were obtained. The best performances during the first cycles were obtained with PPP pyrolyzed for 2 hours. However, even if the reversible capacity during the first cycle was as high as x=2.1, it decreases with cycling.

TABLE 1 Evolution of the electrochemical capacities with cycling

Pyrolysis time (h)	Molar ratio H/C	Cycle	$x_{reduction}$	$x_{reversible}$	Δx
0.5	0.52	1	1.72	0.61	1.11
		2	0.76	0.57	0.19
		10	0.66	0.53	0.13
1	0.45	1	3.85	1.90	1.95
		2	2.80	1.85	0.95
		10	1.30	1.15	0.15
2	0.37	1	3.55	2.10	1.45
		2	2.50	2.05	0.45
		10	1.35	1.17	0.18
6	0.24	1	2.31	1.47	0.84
		2	1.80	1.40	0.40
		10	1.13	1.03	0.10

The profiles of potentials seem to be equivalent for all the samples, but an analysis by electrochemical potential spectroscopy (ECPS) indicates that the position and the width of the peak, which appears at high potentials in the oxidation process, depend on the hydrogen content of the samples : when the pyrolysis times is higher than 0.5 hour, this peak broadens when H/C increases. Moreover, its position is slightly shifted towards the highest potentials (the maximum of this peak is shifted to 0.65 V for the PPP*(6h) and to 0.8 V for the PPP*(2h)) in relation with the hydrogen content which is higher in PPP*(2h) than in PPP*(6h) and PPP*(0.5h). This parameter could modify the profile of the potentials[5]. The ECPS data curve of the fifth cycle for PPP*(1h) (not shown here) is similar to that of PPP*(2h).

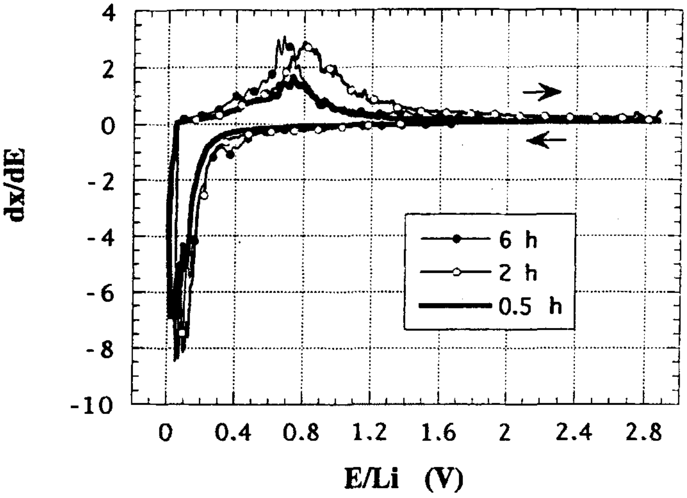

FIGURE 2 ECPS data curves of the fifth cycle

CONCLUSION

The excess of lithium, as compared to the composition LiC_6, could be accommodated by the fixation of lithium with the hydrogenated carbon atoms, which are present at the edge of the aromatic plans[5]. These mechanisms are compatible with the profiles of the galvanostatic curves and of their ECPS curves, which show two peaks in the oxidation process at about 0.5 and 0.8 V. The first one could be attributed to the deinsertion of the lithium ions adsorbed on the small graphene plans formed during the thermal treatment and the second peak at higher potentials, could be related to the fixation of lithium near the hydrogenated carbons at the edge of the aromatic plans. If this last mechanism is not totally reversible (a part of these connections are not broken), the quantity of available hydrogen for the fixation of Li^+ decreases, that would explain the loss of the reversible capacity with cycling. During the reduction process, the two mechanisms (intercalation and fixation of lithium with C - H) would occur simultaneously at low potentials. A high H/C ratio and a large density of cross-linking (or a large lateral extension of the graphene sheets for the longest pyrolysis times[6]) are necessary to obtained high electrochemical capacities. As a matter of fact, when the pyrolysis time increases, H/C decreases continuously since the density of the aromatic plans increases[6]. The best electrochemical performances have been obtained with PPP^*_{Ar}(2h).

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