

LITHIUM STORAGE IN HARD CARBONS PREPARED UNDER MECHANICAL STRAINS

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Introduction

Reversible lithium storage capacity of hard carbons ($Q_{rev.}$) has been often correlated to the final temperature of pyrolysis, the kind of precursor, the effect of milling or especially introduced oxygen, ... [1-3]. For the first time, we show in this paper that mechanical strains applied during two-step pyrolysis of an organic precursor can be profitable for improving $Q_{rev.}$

Experimental

Pyrolysis of polymeric films at 450°C for two weeks and at 1000°C for a short time gave sample 1. Sample 2 was the result of heat-treatment at 450°C for 7 minutes and at 1000°C for 7 minutes under mechanical strains.

Electrochemical investigations have been performed in a two-electrode cell, where carbon was the working electrode and a lithium disk was simultaneously the counter and the reference electrode. The electrolyte used was 1 M LiPF_6 in a 1:1 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC).

The galvanostatic investigations of the lithium/carbon cells were performed with a Mac Pile generator (Biologic, France) at 20 mA/g and in the potential range from 3 V to -0.020 mV vs Li/Li^+ , and for the potentiostatic experiments the voltage step was 10 mV/0.2h. The role of kinetics in the insertion/deinsertion process was estimated by the galvanostatic intermittent titration technique (GITT) with a charge of 0.05 Faraday per mole of 6C followed by 24 hours of relaxation.

The structure and the microtexture of the hard carbon films were characterized by high resolution transmission electron microscopy (TEM, Philips CM 20).

The carbon electrodes were examined at various steps of insertion/deinsertion by solid state ^7Li NMR (Bruker 360 spectrometer, frequency 139.9 MHz). The cell was relaxed one day after reaching the selected potential. Then, the electrode material was dried overnight in the glove box and sealed in a NMR probe for ex-situ experiments.

Results and Discussion

Even if the final temperature for the pyrolysis was the same for the two samples, we detected small differences in the oxygen composition (Table 1). The low oxygen

content of sample 1 is attributed to the long precarbonization treatment at 450°C.

Table 1. Elemental analyses (wt%) of the carbon samples

Sample	C%	H%	O%
1	93.5	0.6	1.4
2	93.2	0.6	3.8

Differences were detected in the TEM observations of the carbon films. The structure and the microtexture of sample 1 are typical of a hard carbon obtained at 1000°C. The basic structural units (BSU), made of stacks of 2-3 nanometric graphene layers, are strongly misoriented (Figure 1a). When mechanical strains are applied during the pyrolysis (sample 2), the size of graphene layers is more important and the BSU have a tendency to be oriented in parallel to a plane P (Figure 1b). However, in comparison with the microtexture of soft carbons, this preferential orientation is much less developed, as demonstrated by the non-graphitizability after heat treatment of sample 2 at 2800°C.

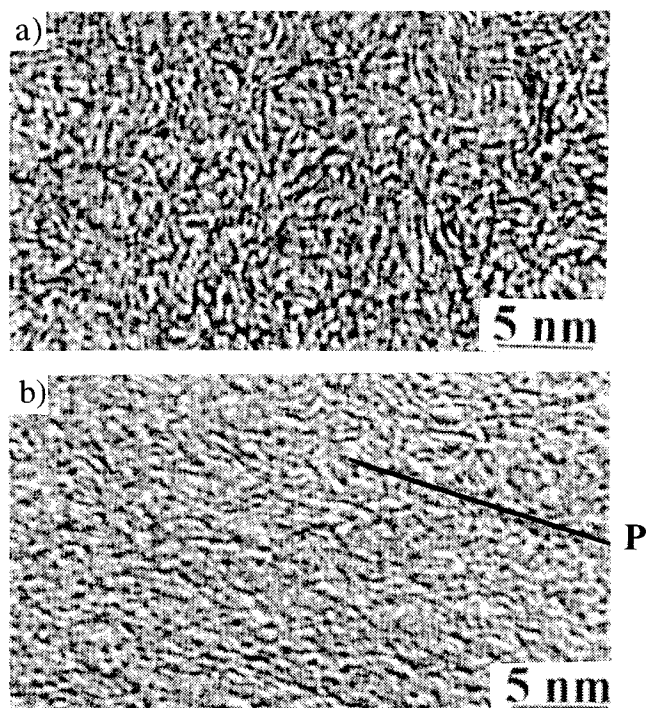


Figure 1. TEM images (002 lattice fringes) of: a) sample 1 (BSU at random); b) sample 2 obtained under strains (BSU preferentially oriented along P).

The galvanostatic profile of sample 2 is characterized by an extremely long plateau close to 0 V vs Li/Li⁺ (Figure 2). From the example of GITT experiment performed on sample 1 (Figure 3), it is clear that kinetic limitations play a negligible role for the small polarization between insertion and deinsertion of lithium. The reversible capacity for sample 2 reaches a high value of 450 mAh/g, which is definitively higher than in graphite (372 mAh/g for LiC₆). Well visible redox peaks close to 0 V vs Li/Li⁺ in the potentiostatic curves of sample 2 (Figure 2, inset) are connected to a part of lithium intercalated.

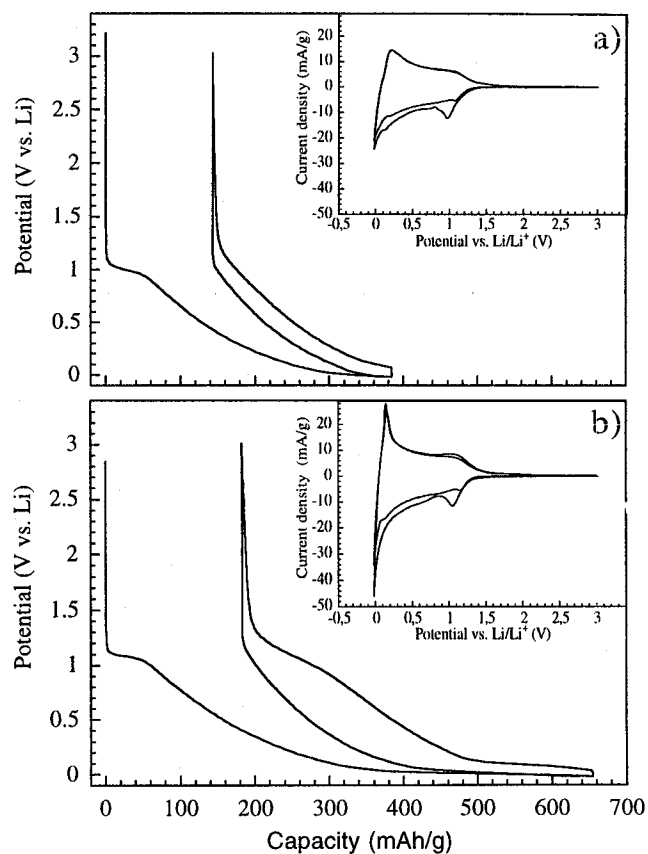


Figure 2. Li insertion/deinsertion at 20 mA/g: (a) sample 1; (b) sample 2. Insets: potentiostatic mode (10mV/0.2h).

⁷Li NMR spectra of sample 2 at different state of lithium insertion are shown in Figure 4. The shift of 60 ppm reached for the fully lithiated sample is greater than for LiC₆, confirming the existence of dense lithium islands.

In conclusion, a high oxygen content is related with a short precarbonization treatment. In this case, C-O-C ether bridges between BSU could favor the formation of slit-shape nanopores when mechanical strains are applied during carbonization. Such pores would be responsible for trapping lithium clusters. The more important polarization observed for sample 2 is also attributable to

the edge oxygenated groups which would interact with the inserted lithium ions.

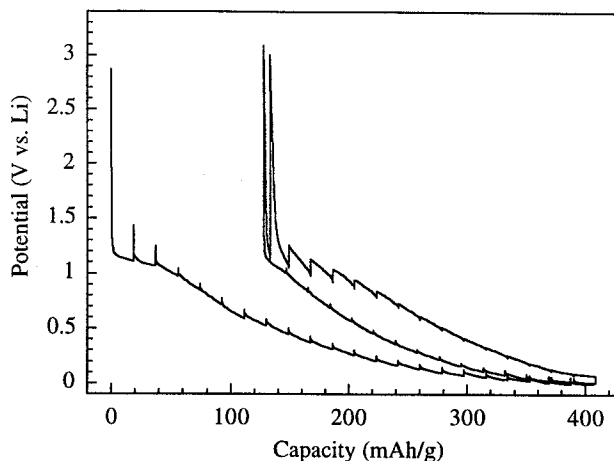


Figure 3. GITT experiments on sample 1

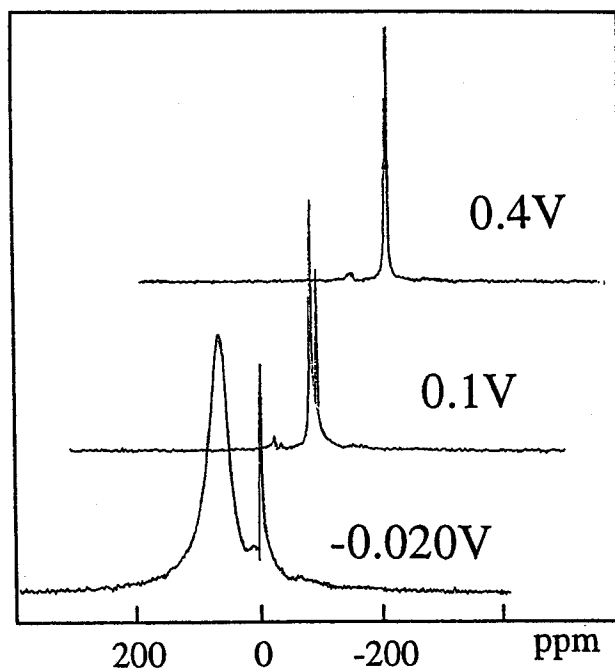


Figure 4. ⁷Li NMR on sample 2 at various steps of lithiation

References

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