

Novel carbons from nanocomposites for high lithium storage

L. Duclaux ^{a,*}, E. Frackowiak ^b, F. Béguin ^a

^a CRMD, CNRS-Université, 1B Rue de la Férellerie, 45071 Orléans Cedex 2, France

^b Poznan University of Technology, ul. Piotrowo 3, 60-965 Poznań, Poland

Abstract

Carbons obtained by the pyrolysis of Taeniolite/Indoine blue and Taeniolite/Safranine nanocomposites were investigated for the lithium storage in Li/carbon cells. A high reversible capacity (900 mA h/g) was found, especially for carbons prepared at 700°C. The mesoporous character due to the oxidation of the interlayer carbon by the neighbour SiO₄ tetrahedra during the pyrolysis is responsible for the important insertion of lithium and for the capacitive properties (90 F/g). The high polarisation between insertion and extraction of lithium is strictly connected with these properties. For comparison, carbons reduced with hydrogen and obtained from the pure precursor (Indoine blue) were investigated to elucidate the role of heteroatoms. Voltammetry experiments proved that insertion of lithium is kinetically limited. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The research of anodic materials which could be substituted to graphite in lithium-ion batteries leads to a considerable effort for creating novel carbons [1]. Recently, it has been shown that, despite a large hysteresis, chars formed by the pyrolysis of pyrene in the pores of pillared montmorillonite have a large reversible storage capacity (800 mA h/g) [2]. It was proposed that an important amount of lithium is inserted in the micropores which are liberated when the pillars are eliminated by demineralisation. In order to elucidate if this interpretation is reasonable, we have synthesised cokes from lamellar nanocomposites free of pillars, and their electrochemical properties have been determined in carbon/lithium cells.

Pillar-free silicate/carbon nanocomposites can be formed through the exchange of the interlayer cation of a clay mineral by an aromatic ammonium cation, and subsequent pyrolysis at ca. 700°C to 1000°C [3]. The carbon which is extracted by demineralisation of the inorganic part of the nanocomposite is easily transformed into graphite through a thermal treatment at 2800°C, whereas carbonisation of the precursor outside of the constrained space of the clay mineral gives a hard carbon which is not graphitizable. This difference is due to the lattice constraints which impose a preferential orientation of the

carbonaceous basic structural units in the interlamellar space of the clay structure [3].

In this work, chars have been prepared either from the direct pyrolysis of a free carbon precursor or from the precursor heat treated in the interlayer space of taeniolite [4]. Their performance for the electrochemical storage of lithium were determined and compared to those of the carbons extracted from pillared clays [2].

2. Experimental

Taeniolite/Safranine (SF/TNL) and Taeniolite/Indoine Blue (IB/TNL) complexes were obtained by adding an excess of Safranine (SF) or Indoine blue (IB) (1.5 equivalent amount of the cationic exchange capacity—CEC = 262 meq/g) to an aqueous suspension of taeniolite, followed by stirring at 80°C during 24 h. By atomic absorption spectroscopy (Perkin Elmer, 3300) on the filtrate after reaction, it was estimated that almost 90% of the lithium cations were exchanged by the aromatic ammonium cations of SF or IB. X-ray diffraction (SIEMENS D500, $\lambda = 1.5405 \text{ \AA}$) on the nanocomposites confirmed the swelling of the layers due to the intercalation of the ammonium aromatic cation of Indoine blue and Safranine.

Comparing the dimensions of these cations to the basal distances d_{001} , indicates that the molecules lay almost vertically between the layers [3].

* Corresponding author

Table 1

Elemental composition of the chars (O% was obtained by difference), reversible and irreversible capacities obtained after the first charge

Samples of chars (precursor, HTT)	%C	%H	%N	%Si	%O	Reversible capacity	Irreversible capacity
Pure IB, 700°C	76.6	1.6	9.1	–	12.7	469	338
Pure IB, 1000°C	85.2	1.2	4.5	–	9.2	378	244
IB/TNL, 700°C	74.4	1.7	8	0.04	15.6	825	473
IB/TNL, 1000°C	78.2	1	6	0.2	14.6	565	377
IB/TNL, 1000°C, after reduction	88	1.1	3.8	0.2	6.9	480	415
SF/TNL, 700°C	70.5	2	9.8	0.05	17.9	900	599
SF/TNL, 1000°C	80.7	1	7	0.2	11.1	550	598

After careful elimination of excess water by freeze drying, the SF/TNL and IB/TNL nanocomposites were pyrolysed at 700°C, 850°C, 1000°C and 1150°C, respectively, during 1 h (heating rate 200°C/h) in a nitrogen flow, giving lamellar taeniolite/carbon nanocomposites. The silicate matrix was dissolved in hydrofluoric acid (73%) at room temperature and the insoluble fluorides formed were eliminated in hydrochloric acid (37%) at 70°C. From the mass of carbon extracted, we found that IB/TNL and SF/TNL contained 47% and 36% of C, respectively. The chars were characterized by X-ray diffraction measuring the position and the width of the 002 line. For a comparison, indoine blue was carbonised in N₂ atmosphere in the same conditions at 700°C and 1000°C. Carbons obtained at 700°C and 1000°C from IB/TNL were reduced at 700°C and 1000°C, respectively, in a mixture of H₂ and N₂ (25 vol.% H₂). Elemental analyses on the chars were performed in Centre d'Analyses du CNRS, Vernaison, France. Nitrogen adsorption measurements were performed at 77 K on some carbons using Micromeritics ASAP 2010.

Pellets (10 mm diameter) were pressed from a mixture of carbon (80%), Kynar flex 2801 (Atochem) PVDF (10%) and acetylene black (10%). NH₄HCO₃ additive, through its decomposition at 150°C under vacuum, enabled to

obtain an additional porosity which facilitates the ionic diffusion. The pellets were investigated in Li/C cells with Merck 1M LiPF₆ electrolytes either in a mixture of ethylene carbonate/diethyl carbonate (1/1 vol.) for the galvanostatic experiments or in a mixture of ethylene carbonate/dimethyl carbonate (1/1) for the cyclic voltammetry.

The cells were cycled between 3 V and –0.005 V at a constant current of 10 mA/g using a Mac Pile multichannel potentiostat/galvanostat (Biologic). Cyclic voltammetry was also performed on carbon pellets from IB/TNL pyrolysed at 700°C and 1000°C, respectively, at scan rates of 0.23 mV/s, 1 mV/s and 2.3 mV/s between 3V and –0.005 V.

3. Results and discussion

The chars obtained from pure Indoine blue are mainly composed of C together with H, N, and O heteroatoms, whereas those formed in the constrained space of taeniolite contain also Si (Table 1) and traces of F and Mg. In all cases, the proportion of carbon is increasing with the pyrolysis temperature and the content of N, H, and O is decreasing. Silicon could not be totally eliminated from the chars formed in the nanocomposites, though a few HF

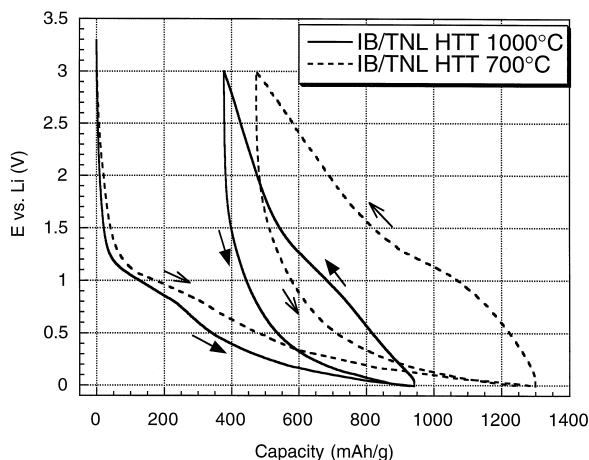


Fig. 1. Charge–discharge of a Li/C cell. Carbon from IB/TNL 1000°C and 700°C. Current load 10 mA/g.

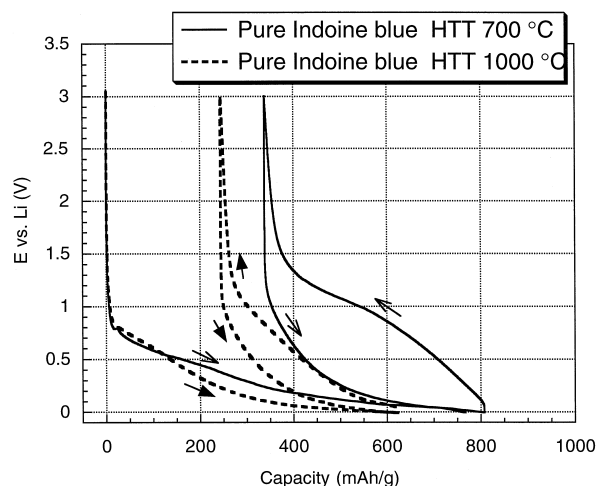


Fig. 2. Charge–discharge of a Li/C cell. Carbon from pure IB prepared at 700°C and 1000°C. Current load 10 mA/g.

treatments were applied in order to dissolve silicates. Moreover, the oxygen content of these chars is a little more high than for those obtained from the thermal decomposition of pure IB. These two facts suggest that the interlayer carbon is oxidised during the pyrolysis by the neighbour (SiO_4) tetrahedra belonging to the silicate matrix, and that a small amount of silicon is incorporated to the framework. Hydrogen reduction at 1000°C of the char obtained from IB/TNL at 1000°C successfully depressed the contents of N and O, suggesting that a part of these elements is probably involved in easily accessible surface groups (Table 1).

Large BET specific surface area were found, respectively $196\text{ m}^2/\text{g}$ for the char from IB/TNL at 700°C , and $139\text{ m}^2/\text{g}$ and $144\text{ m}^2/\text{g}$ for the chars from SF/TNL at 700°C and 1000°C . Taking into account our previous remark about Si and O content, one can suspect that these important values of BET surface area could be partly due to an additional porosity created when the interlayer carbon is oxidised. The essentially mesoporous character of these samples, with an average pore size distribution of 50 \AA could be also the consequence of this redox reaction during the pyrolysis.

All the chars are characterized by asymmetric hk. bands (10 and 11) typical of a turbostratic stacking of the aromatic layers. The most important contribution in the diffractograms is the 002 line, which parameters give indications on the structural evolution with temperature. For the chars from nanocomposites, as heat treatment temperature increases, the coherence length along the c axis, L_c , increases and the d_{002} interlayer distance is progressively decreasing, showing an improvement of the structural organisation. Further heat treatment at 2700°C during 1 h under argon atmosphere gives graphite ($d_{002} = 3.36\text{ \AA}$).

This property proves that, despite a high proportion of heteroatoms, carbons formed in the interlamellar space of a

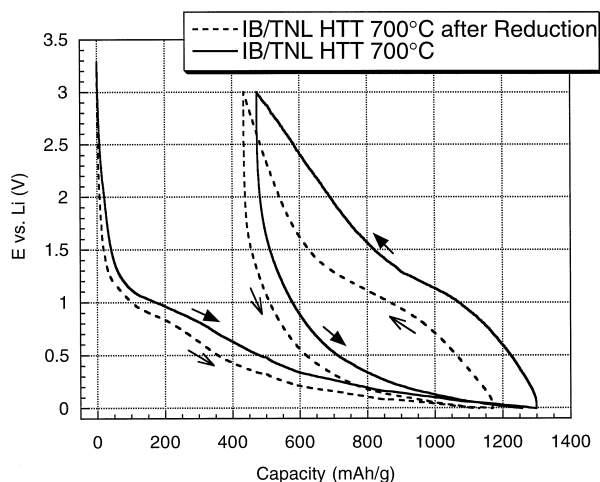


Fig. 3. Charge–discharge of a Li/C cell. Carbon from IB/TNL 700°C before and after reduction by hydrogen. Current load 10 mA/g .

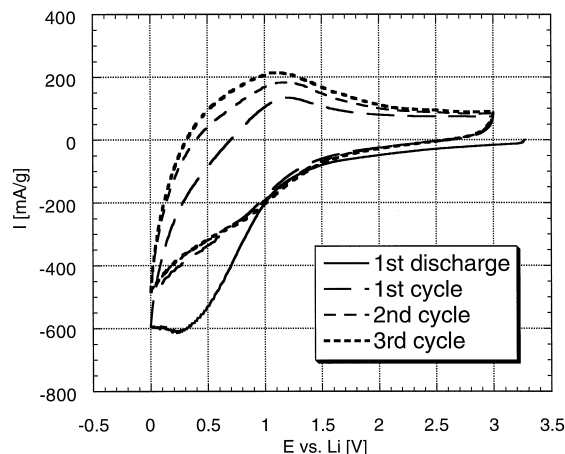


Fig. 4. Voltammetry of a Li/C cell (IB/TNL 1000°C). Scan rate of potential 1 mV/s .

nanocomposite are lamellar, and therefore graphitisable. It confirms the important role of the constraints imposed by the silicate matrix during the pyrolysis leading to the orientation of the basal units in parallel with the host layers [3].

On the other hand, chars produced by the direct pyrolysis of the precursor are poorly crystallised whatever the temperature of their formation. Carbon remains turbostratic and non-graphitizable even after heat treating up to 2700°C .

Whatever the temperature of formation, the general trends of the charge–discharge characteristics are comparable for all the carbons produced from nanocomposites. An example is given in Fig. 1 for IB/TNL carbons. The curves recorded for the chars prepared from the pure precursor are shown in Fig. 2 for a comparison. The most striking fact is that the shape of the galvanostatic curves (Fig. 1) and the values of capacity are comparable to those of chars coming from pillared clays [2]. However, in our case, the large capacity cannot be attributed to micropores liberated by the elimination of pillars. Comparing Figs. 1 and 2, we notice a big difference in the charge profile. The curve of positive polarisation (charge) can be divided in two parts separated by a break in the slope at about 1.5 V . The first domain in the range $[0\text{ V}–1.5\text{ V}]$ corresponds to lithium deinsertion. The second one in the range $[1.5\text{ V}–3\text{ V}]$, very remarkable on Fig. 1, presents a linear dependence of potential with capacity where lithium is extracted with high overvoltage, due to the overlapping of Faradaic and non-Faradaic processes. This additional capacitive effect caused by the presence of oxygen, as compared to the pure precursor (Fig. 2) and more marked for low HTT, contributes to the high storage capacity of these chars derived from nanocomposites. We assume that lithium is trapped in the mesopores and partly attracted through electrostatic forces. The high polarisation remarked during deinsertion is assigned to the strong electrostatic attraction of lithium due to a pseudocapacitive character of these carbons. Lithium interacts with different oxygenated, e.g.,

–C–O–H or –COOH groups created on the edge planes through the oxidation of carbon by the silicate host during pyrolysis: one can suspect –C–O⁽⁻⁾ Li⁽⁺⁾ ionic interactions [5].

A proof of this proposition is given by the comparison with the voltage profile after reduction (Fig. 3). Reduction mainly affects the domain [1.5 V–3 V] for which hysteresis is slightly depressed. It indicates that the reversible process related to this domain of potential is probably an interaction of Li with the carbon surface, and that the part of active surface groups are eliminated by hydrogen treatment.

Polarisation in the range [0 V–1.5 V] is always very high whatever the kind of char. It means that intercalated lithium is strongly trapped in the network due to the high content of heteroatoms. This is supported by the fact that the hysteresis decreases with the increase of heat treatment temperature, i.e., with a partial elimination of O, H, and N heteroatoms. For a given temperature, there is not a significant difference of capacity in the domain (0 V–1.5 V], whatever the kind of char, coming from the pure precursor or from the nanocomposite. It means that, for these kinds or carbons, there is not an influence of the change of microtexture, from misoriented to lamellar, imposed by the constraints in the host taeniolite.

The high irreversible capacity for the chars from nanocomposites is related with their quite important specific surface area, due to the reaction of interlamellar carbon with silicate layers during the preparation.

The lithium/carbon cells have been also investigated by cyclic voltammetry at different scan rates in the range of potential from 3.0 V to –0.005 V. Fig. 4 represents the electrochemical behaviour at a scan rate of 1 mV/s for carbon from IB/TNL nanocomposite obtained at 1000°C. During the first discharge, apart from lithium insertion, an irreversible reduction process is remarkable which is connected with the formation of the passive layer. Upon scan reversal, the current takes on the anodic values and the

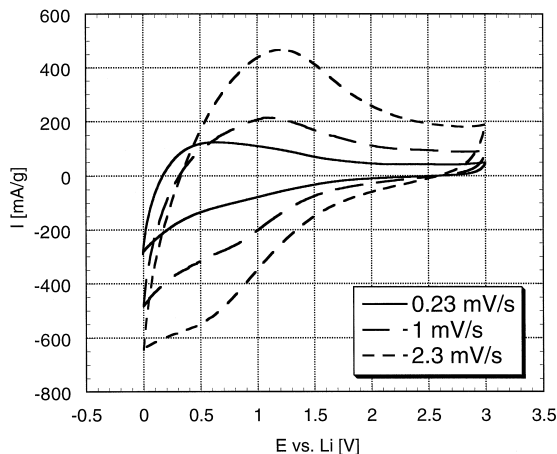


Fig. 5. Voltammetry of a Li/C cell (IB/TNL 1000°C) with different potential scan rates.

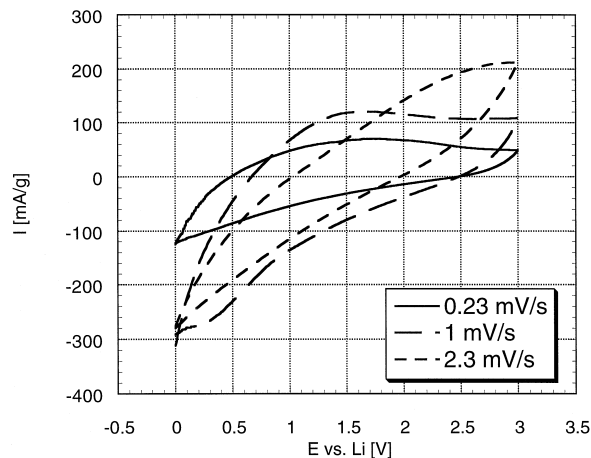


Fig. 6. Voltammetry of a Li/C cell (IB/TNL 700°C) with different potential scan rates.

lithium is deintercalated from carbon. The decrease of anodic current when the potential approaches 1 V is due to the depletion of the lithium reactant. Lower values for reduction and oxidation processes were observed in the early cycles, that is attributed to a relatively fast sweep rate compared to the kinetics of lithium insertion/extraction. The enhancement of the anodic current during repeated cycles can be explained by the increase of the internal pathways for Li diffusion due to the progressive structural expansion. More lithium is inserted into the deep inner parts of carbon particles by solid–state diffusion but also by the transformation of SEI during the cycles for better insertion/removal. The dependence of lithium insertion into carbon from IB/TNL 1000°C for different scan rates of potential, i.e., 0.23; 1.0; 2.3 mV/s is shown in Fig. 5. The higher the sweep rates the higher the values of currents and of the maximum of anodic currents which are shifted to more positive potentials. The position of this maximum depends on the diffusion resistance as the lithium diffusion in solid is hindered. It is well proved in Fig. 6 where the voltammetry investigation was performed on the carbon from IB/TNL prepared at 700°C. The kinetics of lithium insertion and removal is definitively lower for this carbon than for the same carbon treated at 1000°C. The maximum anodic current is only 120 mA/g whereas it reaches the value of 200 mA/g in Fig. 4 for carbon from IB/TNL 1000°C. Undoubtedly the carbon prepared at a higher temperature possesses a higher conductivity that facilitates the redox processes. For all the voltammetry characteristics over 1.5 V, the region connected with charging an electrical double layer is well defined. Values of the order of 80 to 100 F/g for the specific capacitance were found but only for carbons from nanocomposites. The relatively high surface area of these carbons, their microtexture of mesoporous character, their electronic properties due to the heteroatoms (mainly oxygen) and the presence of surface functional groups are responsible for the capacitive properties.

Finally, the chars prepared by cationic exchange in taeniolite appear to be comparable to those formed in pillared clays. In the two cases it may be suspected that mesopores created during pyrolysis by a redox reaction between carbon and the host are responsible for the high storage of lithium and the capacitive properties of carbons.

Acknowledgements

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