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Clay/Carbon Nanocomposites as Precursors of Electrode Materials for Lithium-Ion Batteries and Supercapacitors

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Chars prepared by pyrolysis of organic precursors (Indoine Blue, Safranine, Pyrene) in the interlayer space of taeniolite were used as electrode materials in lithium/carbon cells. Due to oxidation of interlayer carbon by the silicate host, they contain a high amount of surface groups, and their essentially mesoporous character is attributed to the space liberated by the elimination of the clay template. A large reversible capacity for lithium insertion, up to 900 mAh/g, was detected for these materials. The chars presented a high capacitance which could reach 85 F/g in KOH electrolyte if they were formed below 850°C. Such a high value relatively to the low BET surface area of the chars is strictly related to the important mesopore volume and to the rich surface functionality.

Keywords: intercalation; nanocomposites; lithium batteries; energy storage; capacitance

INTRODUCTION

Intensive research is focused on the synthesis of new carbon materials that could be substituted to graphite in lithium-ion batteries. For example chars prepared by the pyrolysis of organic precursors intercalated either in pure clay or in pillared clay derivatives possess a very high reversible capacity for lithium storage (800-900 mAh/g) [1-2], but with an important polarization between lithium insertion/de-insertion processes. A capacitance effect makes them promising materials for an use as supercapacitor electrodes [1].

Chars with various structure, microtexture and chemical composition can be obtained in the constrained medium of clay/carbon nanocomposites by varying the nature of the precursor and pyrolysis temperature. For this work, taeniolite (TNL) was selected as a host and the organic precursors were Safranine (SF), Indoine Blue (IB), or Pyrene (PY). The properties of the chars were tested in lithium/carbon and capacitor cells and they were compared to those prepared by pyrolysis of the pure organic molecules.

EXPERIMENTAL

Clay/carbon lamellar nanocomposites were formed by exchanging lithium cations of Li-taeniolite with aromatic cations (Safranine, Indoine blue or Pyrene) and subsequent pyrolysis in nitrogen atmosphere at temperatures ranging from 700°C to 1150°C [3].

Taeniolite/Safranine (TNL/SF) and Taeniolite/Indoine Blue (TNL/IB) 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/100 g) to an aqueous suspension of taeniolite, followed by stirring at 80°C during 24 hours.

For the preparation of Taeniolite/Pyrene (TNL/PY) complex, taeniolite was first out-gassed (10^{-4} mbar) at 300°C during one day. Pyrene (4 g) was dissolved in toluene (125 cm^3) and added to a solution of bromine (1.2 cm^3) in acetonitrile (500 cm^3). After 5 days of reaction of dried TNL with the pyrene solution, the suspension was filtered, and the solid washed with toluene in order to remove the excess of pyrene.

After a careful elimination of excess water by freeze drying, the TNL/SF and TNL/IB nanocomposites were pyrolyzed for 1 h at 700°C, 850°C, 1000°C and 1150°C in a nitrogen flow, giving lamellar TNL/carbon nanocomposites. For a comparison, indoine blue was carbonized in N_2 atmosphere in the same conditions at 700°C and 1000°C. The TNL/PY nanocomposites were pyrolyzed in a sealed stainless steel reactor filled with argon during 1 h at 400°C and at 700 °C or 850°C for 1 h.

The taeniolite matrix was dissolved in hydrofluoric acid (73%) at room temperature, and the insoluble fluorides formed were eliminated by hydrochloric acid (37%) at 70°C. From the mass of carbon extracted, we found that TNL/IB, TNL/SF and TNL/PY pyrolyzed nanocomposites contained 50%, 30% and 30% of C, respectively, against theoretical values of 49.8%, 37.8% and 33.9%, if lithium would be completely exchanged and in the hypothesis that pure carbon is formed.

Elemental analyses on the chars were performed in Centre d'Analyses du CNRS, Vernaison, France. The surface composition of the chars from TNL/SF and TNL/IB and the type of carbon-heteroatom bonds were estimated from the C1s, O1s, N1s core level peaks detected by XPS on a VG ESCALAB MKII multidetector spectrometer. Nitrogen adsorption measurements were performed at 77 K on the chars using Micromeritics ASAP 2010. Prior to nitrogen adsorption, carbon samples were out-gassed at 350°C until the pressure was 10^{-4} mbar (≈ 12 hours). Micropore and mesopore volumes were estimated from t-plot and BJH treatments of the data, respectively.

Composite electrodes were pressed from a mixture of carbon as active material (80%), polyvinylidene fluoride binder (Kynar flex 2801, Atochem, 10%) and acetylene black (10%). NH_4HCO_3 additive, through its decomposition at 150°C under vacuum, enabled to obtain an additional porosity which facilitates electrolyte diffusion. Electrochemical insertion of lithium was

investigated in Li/C cells using 1M $LiPF_6$ electrolyte dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1/1vol.). The cells were cycled between 3 V and - 0.005 V *vs* Li/Li^+ at a constant current of 10 mA/g using a Mac Pile multichannel potentiostat/galvanostat (Biologic). For cyclic voltammetry, the scan rates were 0.23 mV/s, 1 mV/s and 2.3 mV/s. Capacitors were built with two carbon electrodes and the electrolyte was either 1M $LiPF_6$ in EC/DEC or 6M aqueous KOH. They were investigated by cyclic voltammetry at scan rates from 0.5 mV/s to 10 mV/s, and the potential range was 0-2.5 V and 0-0.5 V for aprotic and protic medium, respectively.

RESULTS AND DISCUSSION

The chars extracted from thermally treated nanocomposites contain a high proportion of heteroatoms (O, N, H) which decreases upon increasing heat treatment temperature (HTT) of the composite. For carbons formed in TNL at 700°C the elemental mass content was: oxygen (18% or 16%), nitrogen (10% or 8 %), hydrogen (2%), respectively for SF or IB precursors; traces of silicon and chlorine were also found. The presence of the extremely high amount of oxygen suggests an oxidation reaction of interlayer carbon by the silicate host during the pyrolysis.

From the fitting of C1s, O1s and N1s core level XPS spectra, C=O (3-5%), RCOO- (1.5-2%), C-N< (4%), aromatic C=N- (1-3%) and C-O-C (2-2.5 %) surface groups were detected in the chars from nanocomposites. C-O- groups were identified in the chars obtained from pure IB, instead of C-O-C, that shows that the pyrolysis in the constrained space of a nanocomposite can create a specific functionality.

Nitrogen adsorption data show that the chars prepared from nanocomposites are essentially mesoporous. Another characteristic feature common to all the samples is the infinite adsorbed quantity of nitrogen close to the bulk gas/liquid transition ($P/P_0 = 1$). Taking into account that flaky morphology was confirmed by Transmission Electron Microscopy [3], the absence of saturation plateau can be interpreted by the swelling of a flake-like carbon. It is clear that the peculiar mesoporous character of carbon is created by the elimination of the clay template. Hence, the mesopore volume appears to be little sensitive to HTT, while BET surface area and micropore volume decrease with increasing HTT (Table I). On the other hand, we already showed

TABLE I BET surface area (m^2/g), micropore and mesopore volumes (cm^3/g) of the chars

Origin of char	TNL/IB 700°C	TNL/IB 850°C	TNL/IB 1000°C	TNL/SF 700°C	TNL/SF 850°C	TNL/SF 1000°C
BET	265	166	114	76	33	40
Micropore	0.093	0.060	0.034	0.019	0.003	0.006
Mesopore	0.139	0.083	0.140	0.067	0.100	0.099

that the orientation in parallel of the carbon Basic Structural Units (BSU) is more marked with increasing of HTT [3], therefore micropore volume decreases.

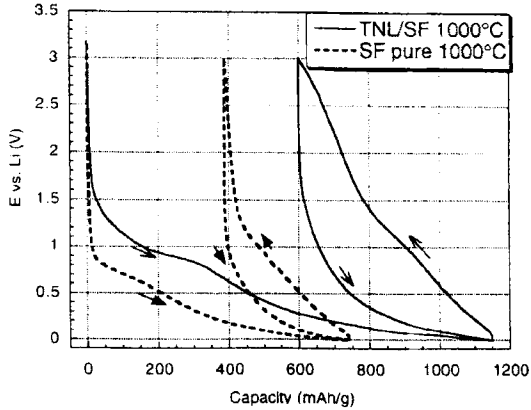

Figure 1. Charge/discharge of Li/C cells in which carbon was obtained by pyrolysis of SF and TNL/SF at 1000°C. Current load 10 mA/g.

An example of galvanostatic charge-discharge curve is given in Figure 1 for the char from TNL/SF. Even if the reversible capacity is higher than for graphite (372 mAh/g), there is a high irreversible capacity and a large hysteresis which makes such a carbon non-appropriate to be used as negative electrode for Li-ion batteries. The high value of irreversible capacity (600 mAh/g), with a surface area of carbon from TNL/SF 1000°C which does not exceed 40 m^2/g, can be explained by a significant penetration of solvated Li^+ in the mesopores and subsequent decomposition. The linear variation of potential with capacity in the range 1.5 - 3 V *vs* Li is typical of a capacitive character related to the presence of mesopores. The char prepared from pure safranine presents a very limited hysteresis between 1.5 and 3 V, and its irreversible capacity is lower than for the one from the nanocomposite.

Table II compares the values of reversible capacity for the chars from nanocomposites and for those prepared from the pure precursors in the two

TABLE II Reversible capacities (mAh/g) for lithium insertion received from the first galvanostatic charge: in the ranges 0 V - 1.5 V, 1.5 V - 3 V *vs* Li and total reversible capacity

Origin of char	Pure IB 700°C	Pure IB 1000°C	TNL/IB 700°C	TNL/IB 1000°C	TNL/SF 700°C	TNL/PY 700°C
0 V-1.5 V	419	358	442	379	516	557
1.5 V-3 V	50	20	383	186	384	218
Total	469	378	825	565	900	775

potential ranges below and above 1.5 V *vs* Li. Taking the particular case of IB precursor, the reversible capacity measured below 1.5 V is comparable for the chars from pure IB or from TNL/IB. For all the chars from nanocomposites there is an additional contribution to the total capacity in the range of potential 1.5 - 3 V, which is due to a pseudocapacitance character related with the presence of mesopores and rich functionality.

Cyclic voltammetry on carbon from TNL/SF pyrolyzed at 1000°C is shown in Figure 2. Increasing the scan rate, the anodic response is shifted to higher potential, that is characteristic of kinetically controlled de-insertion of lithium. A capacitive effect was clearly demonstrated by almost constant value of current on the voltamogramms between 1.5V and 3V *vs* Li (Figure 2 inset). Even if this carbon has limited surface area (≈ 40 m^2/g), it may be concluded that the mesopores are at least partly responsible for this capacitance, favoring ions diffusion to the active surface.

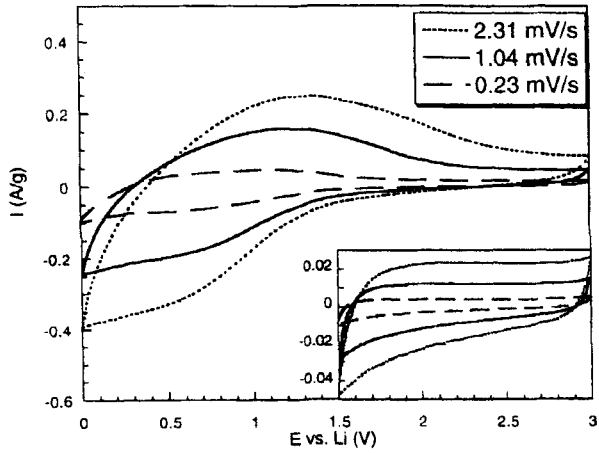

Figure 2: Voltammetry on a Li/C cell (TNL/SF 1000°C) at various potential scan rates. The inset corresponds to cycling between 1.5 and 3 V.

The real values of specific capacitance of the chars were measured by cyclic voltammetry on capacitor cells with two carbon electrodes using either 1M $LiPF_6$ in EC/DEC or 6M KOH electrolyte (Table III). The voltammograms were close to the ideal rectangular shape at low scan rate (<10 mV/s) for cells built in KOH but not in $LiPF_6$ electrolyte.

The values of capacitance are more important in KOH than in $LiPF_6$ medium due to the different physicochemical properties of the two electrolytes(dielectric constant ε, resistivity ρ, wettability, dimensions of the ions which form the electrical double layer). Relatively to their moderate specific surface area, the chars extracted from TNL/SF have a very high capacitance. However, comparing the values given in Tables I and III, there is

TABLE III Specific capacitance (F/g) of chars obtained from TNL/SF at various HTT. Electrolyte: 6M KOH or 1M $LiPF_6$ in EC/DEC.

HTT	700°C	850°C	1000°C	1150°C
6M KOH	85	83	36	8
1M $LiPF_6$	25	25	20	-

not a proportional dependence between capacitance and the value of the specific surface area. Due to the fact that specific capacitance decreases with the amount of heteroatoms, it confirms that surface are involved in a pseudocapacitance contribution. Since the chars are essentially mesoporous, it may also be expected that the samples formed at 1000°C differ by the distribution of small mesopores of less than 5 nm which play an important adsorption and transporting role for the ions.

CONCLUSION

Pyrolysis of organic cations in the constrained space of taeniolite and elimination of the clay template produces chars with swelling mesopores.

The amount of lithium reversibly inserted in these chars is very high. Mesopores and surface groups are responsible for an important overvoltage between insertion and de-insertion, and they induce a capacitive effect which contributes to the value of the reversible capacity. Solvated lithium ions are easily trapped in the mesopores, therefore, despite a low specific surface area, the irreversible capacity is very high. For this reason these chars are not applicable in lithium-ion cells.

On the other hand, the chars from nanocomposites obtained at low temperature (700-850°C) are very promising electrode materials for supercapacitors. Swelling mesopores play an important role for the accumulation of charges. Specific capacitance of 85 F/g was obtained on capacitor cells in aqueous electrolyte.

Acknowledgments

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