

USE OF CARBON FROM NANOCOMPOSITES FOR THE STORAGE OF ENERGY

*L. Duclaux, R. Benoit, T. Gibinski, F. Béguin and *E. Frackowiak*

CRMD, CNRS-Université, 1B rue de la Férollerie, 45071 Orléans Cedex 2, France

**ICTE, Poznan University of Technology, ul. Piotrowo 3, 60-965 Poznan, Poland*

Introduction

It has been shown that chars formed by the pyrolysis of pyrene in the pores of pillared clay minerals offer a large reversible storage capacity of lithium [1]. This was attributed to lithium insertion in the micropores which are liberated after dissolution of the inorganic part of the nanocomposite. Recently, we demonstrated that carbons produced in nanocomposites free of pillars had comparable performance [2]. We suspected a redox reaction between the clay layers and interlamellar carbon to explain the properties observed. Additionally, a rectangular shape of the voltammetry curves suggested that the carbon produced by this process could be better utilized in electrodes of supercapacitor.

Experimental

The substrate for the synthesis of the nanocomposites was lithium taeniolite (TNL), $\text{Li}(\text{Mg}_2\text{Li})\text{Si}_4\text{O}_{10}\text{F}_4 \cdot n\text{H}_2\text{O}$ ($M=410.8 \text{ g}\cdot\text{mol}^{-1}$ in the dehydrated form, cationic exchange capacity : CEC = 262 meq/g). An aqueous suspension of taeniolite was allowed to react with Safranin (SF) or Indoine Blue (IB) excess (1.5 equivalent amount of CEC), under continuous stirring, in order to form Taeniolite/Safranin (TNL/SF) and Taeniolite/Indoine Blue (TNL/IB) complexes.

After elimination of the filtrate, the complexes were washed several times, freeze dried and pyrolysed in a nitrogen flow for 1 hour at various temperatures ranging from 700°C to 1150°C, giving taeniolite/carbon lamellar nanocomposites. The silicate matrix was dissolved in hydrofluoric acid (73%) at room temperature and the insoluble fluorides were eliminated by hydrochloric acid (37%) treatment at 70°C. The mass of carbon extracted (\cong 30-40% of the total mass of the composite) is compatible with the theoretical value expected from CEC of taeniolite. For a comparison, pure SF and IB precursors were pyrolysed in the same conditions.

The surface composition of the chars and the type of heteroatom-carbon bonding were studied by XPS (VG ESCALAB MKII spectrometer). Nitrogen adsorption was realized on carbons using Micromeritics ASAP 2010. Prior to experiment, the samples were outgassed (10^{-6} mbar) at 350°C for 12 hours.

Carbon electrodes were pressed from a mixture of carbon as active material (80%), acetylene black (10%) and

polyvinylidene fluoride (Kynar flex, Atochem, 10%). Electrochemical insertion of lithium was investigated in Li/C cells using 1M LiPF_6 dissolved in a 1/1 mixture of ethylene carbonate (EC)/diethyl carbonate (DEC) as electrolyte. The cells were cycled between 3V and - 0.005 V vs Li/Li^+ at a constant current of 10 mA/g using a Mac Pile multichannel generator (Biologic). Capacitors were built with two carbon electrodes and the electrolyte was either 1M LiPF_6 in EC/DEC or 6M KOH in water. 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 formed from nanocomposites were found to be mesoporous, with quite important specific surface area, ranging from 150 to 300 m^2/g , depending on the preparation conditions. They also contain an extremely high amount of oxygen, from 11 to 18% by weight, that could be due to oxidation of the inserted carbon by the silicate matrix during the pyrolysis.

XPS analyses confirmed the presence of oxygen and nitrogen, which amount slightly decreases with heat-treatment temperature. From the fitting of C1s, O1s and N1s peaks, C-N (3-4%), C=N- (1-3%), C-O-C (2-3%), C=O (3-5%), RCOO- (2%) surface groups were identified in the chars from nanocomposites. The C-O-C ether bridges could not be detected in the chars obtained from pure IB, and only C-O groups were identified in this case, that shows that the pyrolysis in the constrained space of a nanocomposite can create specific functionality.

The carbon from nanocomposites pointed out a high reversible storage capacity of lithium (Table 1) and an important polarization between charge and discharge potentials (Figure 1) [2]. On the other hand, the chars coming from the direct pyrolysis of the pure precursor presented a small surface area and more moderated irreversible and reversible capacities.

The main difference between the two kinds of materials is an additional contribution for the carbon from TNL/IB and TNL/SF in the range 1.5 V - 3 V vs Li/Li^+ , with almost linear variation of voltage versus capacity typical of a faradaic effect (Figure 1).

The O/C and N/C atomic ratios considerably decreased after a reduction treatment of the chars under hydrogen/nitrogen flow at 1000°C, and the storage capacity

Table 1. Reversible capacities of lithium insertion received from the first galvanostatic charge, in mAh/g

Precursor of char, T°C	Capacity (1.5 -3 V)	Capacity (0 -1.5V)	Total capacity
IB, 1000°C	20	358	378
TNL/IB, 700°C	383	442	825
TNL/IB, 1000°C	186	379	565
TNL/IB, 1000°C, reduced by H ₂	108	372	480

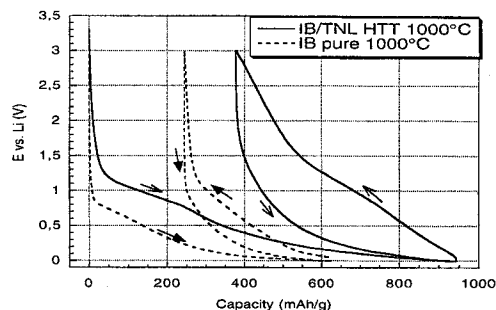


Figure 1. Charge/discharge of Li/C cells containing carbon obtained by the pyrolysis of IB or TNL/IB at 1000°C. Current load of 10 mA/g.

between 1.5 V and 3 V vs Li/Li⁺ was noticeably reduced, but still remained important (Table 1). That means that the pseudofaradaic character of the chars from nanocomposites is due to the combined presence of surface groups and mesopores. Finally, if one considers the three chars prepared from TNL at 1000°C (Table 1), there are only little differences in the value of reversible capacity for the range 0 V - 1.5 V vs Li/Li⁺. Therefore, it can be concluded that the improvement of capacity using the constrained medium of a nanocomposite is only due to oxidation of carbon during the pyrolysis, creating mesopores and surface groups. A capacitive effect was clearly demonstrated between 1.5 V and 3 V vs Li/Li⁺ from cyclic voltammetry experiments giving flat curves with a constant value of current.

The real values of capacitance were deduced from cyclic voltammetry investigations on capacitor cells built from two carbon electrodes (Table 2). The response for each capacitor cell has been found to be dependent on scan rate. The voltammograms are close to the ideal rectangular shape at low scan rate (<10 mV/s) for cells built in KOH electrolyte but not in LiPF₆ one.

Theoretically the double layer capacitance should be proportional to the value of the specific surface area. Carbons from TNL/SF heat treated at 700°C or 850°C are mesoporous due to their oxidation by the adjacent layers of taeniolite in this range of temperature. Since their specific surface area is almost identical, they give comparable values of capacitance. Above 850°C, the effect of lattice constraints is so important on the interlayer carbon that the

basic structural units tend to be almost parallel to the silicate layers [3]. As a result, the carbon extracted from TNL/SF heat-treated at 1150°C presents a lamellar microtexture and its capacitance is very low (Table 2, Figure 2).

Surface groups can give an additional pseudocapacitance contribution which improves the total capacitance. Since their amount decreases with HTT, this can be another explanation for the decrease of capacitance with temperature.

The values for capacitance are more important in KOH than in LiPF₆ due to the different physicochemical properties of electrolyte (dielectric constant ϵ , resistivity ρ , wettability, dimensions of the ions which form the electrical double layer). The distribution of porosity for the investigated carbons centered on small mesopores with a diameter of less than 5 nm plays an important adsorption and transporting role for the ions.

Table 2. Specific capacitance (F/g) of the carbon electrodes deduced from cyclic voltammetry on capacitor cells. Chars obtained from TNL/SF at various HTT. Electrolyte: 6M KOH or 1M LiPF₆ in EC/DEC.

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

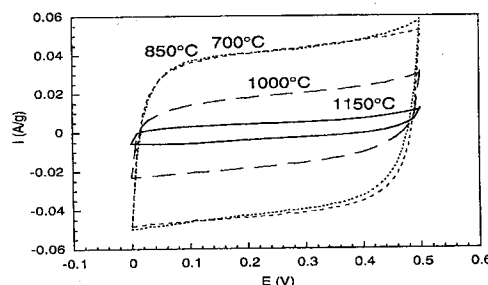


Figure 2. Voltammograms obtained from SF/TNL chars as a function of HTT. Electrolyte: 6M KOH.

Conclusion

Mesoporous chars of well developed surface functionality were produced by pyrolysis of organic precursors in the constrained medium of a layered silicate. This method enables to prepare electrode materials for double layer supercapacitors.

References

- [1] Sandi G, Winans RE, Carrado KA. *J. Electrochem. Soc.* 1996; 143: 95-98.
- [2] Duclaux L, Frackowiak E, Béguin F. *J. Power Sources* 1999, in press.
- [3] Béguin F, Rouzaud JN, Ben Maimoun I, Seron A. *J. Phys. Chem. Solids* 1996; 57: 1019-1029.