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DESIGNING NANOSTRUCTURED CARBONS FOR THE NEGATIVE ELECTRODE OF LITHIUM BATTERIES

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Various parameters such as mesopore volume, microtexture, surface area, dangling bonds which can affect the value of irreversible capacity C_{irr} of a carbon anode have been considered. A new hypothesis is suggested and confirmed that active surface sites are at the origin of C_{irr} but not the specific surface area of carbon. An ideal proportional dependence has been found between C_{irr} and mesopore volume in the case of nanotubular materials. Surface modification of carbon fibres by a pyrolytic carbon coating has been successfully realized with an improvement of lithium insertion characteristics.

Keywords: lithium batteries; anode; nanostructured carbons; nanotubes; irreversible capacity

INTRODUCTION

During the last five years, important effort has been devoted to improving the performance of secondary lithium batteries. The main drawback of graphite which is currently used for the negative electrode is a possible exfoliation during cycling and a rather moderate value of reversible capacity (C_{rev}). Among the few materials that are considered for being substituted to graphite, the so-called ≪hard carbons≫ which in general demonstrate a high reversible capacity seem to be promising [1]. However,

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an important irreversible capacity (C_{irr}) and a marked polarization (hysteresis) between the reduction and the oxidation processes preclude an immediate application [2] unless they will be partly cured of these disadvantages. The objective of this paper is to consider some structural parameters of carbon which affect mainly the irreversible lithium electrochemical insertion and to propose some strategy for the manufacture of composite materials with improved performance.

EXPERIMENTAL

Catalytic MWNTs have been synthesized by decomposition of acetylene using cobalt supported on silica at 700°C and 900°C (A/CoSi700, A/CoSi900) or on zeolite at 600°C (A/CoNaY600). Chemical vapour deposition of propylene at 800°C within an alumina membrane supplied bamboo-like nanotubes (P/A1800). In all cases, after the preparation of the nanotubes, the catalyst support or the alumina template were dissolved with 72% hydrofluoric acid, that allowed also to eliminate an important part of cobalt. The samples A/CoSi700 and A/CoSi900 were additionally treated in dilute nitric acid for a further elimination of the free Co particles. After these treatments, the samples were filtered, washed several times with distilled water and dried at 150°C under vacuum.

Pristine graphite (UF2 from Kropfmühl $<5\,\mu m$) was ball-milled for 72 h in argon atmosphere using a vibration type crushing mill (Retch MM 2000). For a comparison, graphite was also milled 72 h in air.

Self-standing disks of carbon tissue have been prepared by carbonisation of a cellulose precursor under neutral atmosphere at 1000°C. For some experiments, the chemical vapor deposition technique was used for coating the fibres by a pyrolytic carbon film; the feedstock was propylene diluted in nitrogen as a carrier gas and the temperature was selected at 900°C.

Surface area and micro/mesopore volume were obtained from nitrogen adsorption/desorption isotherms at 77 K (Micromeritics ASAP 2010). Prior to the adsorption experiments, the samples were outgassed (10^{-6} mbar) at 350°C during 12 hours. Profile of the aromatic carbon layers has been imaged by high resolution mode (HRTEM, Philips CM 20); a home made image analysis procedure allowed an access to structural and microtextural characteristics of these disordered carbons.

Electrochemical lithium insertion into the nanostructured carbon hosts has been performed in a two electrode Swagelok® cell where a lithium disk was the counter as well as the reference electrode. The carbon electrodes were either disks of tissue or in the form of pellets with 85 wt.% of carbon material, 5 wt.% of acetylene black and 10 wt.% of binding substance (Polyvinylidene fluoride, PVDF-Kynar flex 2801, Atochem, France). The

electrolytic solution was 1M $LiPF^6$ dissolved in a mixture (1:1) of ethylene carbonate (EC) and diethylcarbonate (DEC) (Merck). Galvanostatic charge/discharge cycling with a current load of 20 mA/g of carbon has been performed in order to estimate the degree of lithium insertion and extraction, using a multichannel potentiostatgalvanostat MacPile II (Biologic, France).

RESULTS AND DISCUSSION

Among the literature reports, there is quite a general agreement for considering that irreversible capacity is more or less directly related to the specific surface area of carbon [3]. Actually, this seems to be the case for microporous carbons, however with mesoporous carbons, such as nanotubes [4] or lamellar carbons prepared from nanocomposites [5], the value of irreversible capacity is always very high and practically not dependent on the specific surface area.

Therefore, we have plotted C_{irr} measured after the first discharge/charge cycle versus the mesopore volume for the different types of multiwalled carbon nanotubes (Fig. 1). The almost perfect proportionality $C_{irr} = f(V_{meso})$ indicates that the central canal and/or mesopores formed by nanotubes entanglement allow an easy access of the voluminous solvated lithium ions to the active surface where they can be transformed into decomposition products giving rise to the solid electrolyte interphase (SEI). On the other hand there is a complete lack of proportionality between C_{irr} and the specific surface area (Fig. 1 inset). Moreover, during subsequent cycling of electrodes from nanotubes, an additional passivation layer is formed, as it is well demonstrated by the continuous increase of C_{irr}

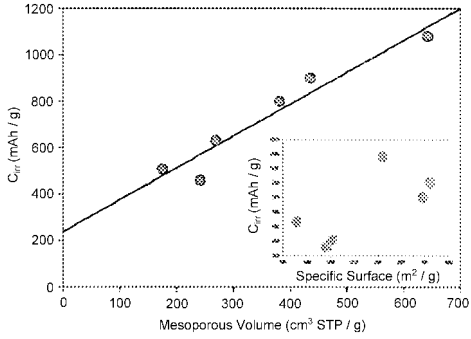

FIGURE 1 C_{irr} of various nanotubes *vs* mesopore volume and *vs* specific surface area (inset).

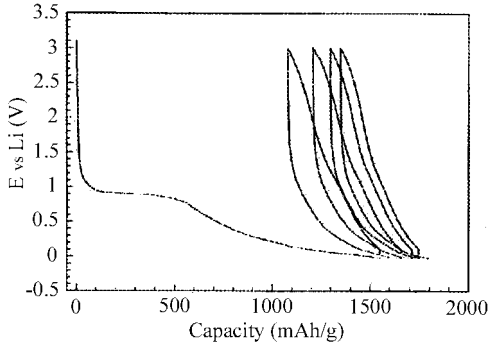

FIGURE 2 Few subsequent cycles of Li insertion into nanotubes (P/A1800). Current load of 20 mA/g.

in Figure 2. It means that, in the case of carbons with open mesopores, solvated ions can still penetrate to the interior of the electrode where they can be further decomposed. Hence, an optimal carbon for getting the highest proportion of reversible lithium insertion must be constituted only of small micropores.

The BET model assumes a flat surface, and the specific surface area is expressed by multiplying the number of molecules adsorbed in the pores by their area. This is essentially a geometric factor based on the physisorption of nitrogen on the carbon surface, whereas the SEI formation involves higher energies and is rather related to the active surface area, i.e. the presence of free radical, so-called dangling bonds. In order to sustain this proposition, reactive milling of graphite has been performed in different conditions. Changing the atmosphere from argon (Fig. 3) to air (Fig. 4) leads to a considerable decrease of C_{irr}, proving that in the later case the

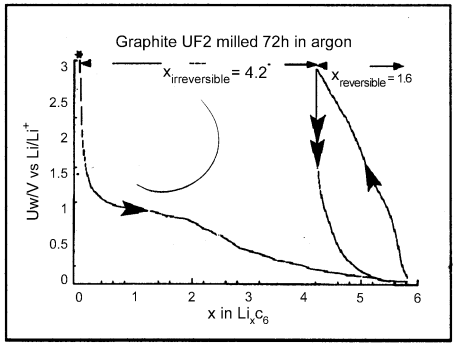

FIGURE 3 Lithium insertion into graphite milled 72 h in argon.

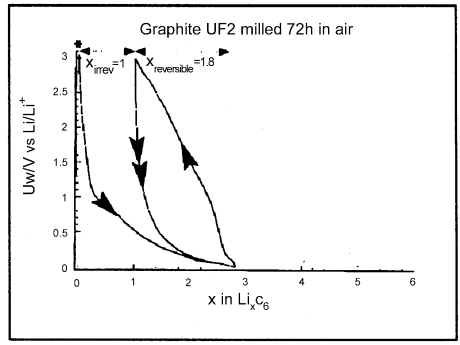

FIGURE 4 Lithium insertion into graphite milled 72 h in air.

free radicals formed by breaking the graphite sheets are saturated by oxygen, giving rise to a less active surface due to its passivation by a rich oxygenated functionality. A more marked decrease of C_{irr} was noticed when a mixture of graphite and lithium powders was milled under argon. With an atomic ratio Li /C = 1/6, all lithium is characterized by a unique ^{7}Li NMR line at 0 ppm, which is attributed to the formation of Li-C bonds as free radicals appear during the milling process. The lithium proportion in the mixture had to be increased up to Li /C = 1/2 for observing the appearance of the X ray diffraction lines corresponding to LiC_6. The presence of two lines at 40 ppm and 0 ppm in the ^{7}Li NMR spectrum was attributed to LiC_6 and Li-C, respectively. Despite a marked surface area provoked by milling, C_{irr} becomes quasi negligible due to the blockage of the active surface. Hence, the extent of SEI formation is directly related to the concentration of surface free radicals accessible to solvated lithium.

Taking into account all these observations, our strategy was to design carbon materials with essentially blocked dangling bonds and with smaller voids in order to hinder the penetration of solvated lithium in the bulk. Figure 5 shows the galvanostatic lithium insertion/deinsertion in a microporous viscose carbon tissue degassed at 150°C under primary vacuum in order to remove adsorbed water. Reversible capacity is quite high and hysteresis is rather moderate for a hard carbon. However, despite a small specific surface area (ca. 20 m^2/g), the irreversible capacity is very high. This value keeps at a comparable value even after degassing the carbon substrate at 900°C under secondary vacuum prior to its use in a lithium cell. One must rule out the proposition that surface functional groups could be responsible for a large C_{irr} and rather consider that this is again due to dangling bonds which favour an important SEI formation. Therefore the viscose carbon fabric has been coated by CVD pyrolytic carbon using a

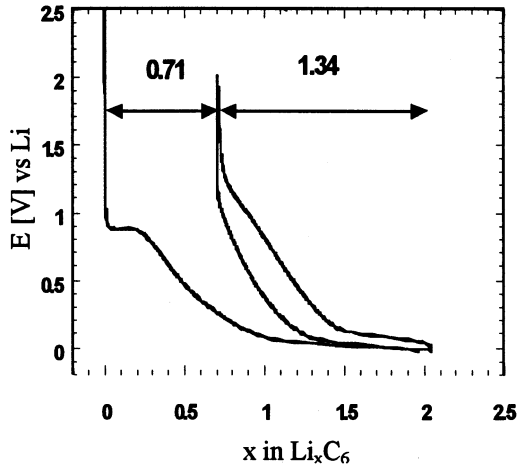

FIGURE 5 Li insertion into carbon fibers after outgassing of 150°C.

hydrocarbon feed-gas at 800–900°C. The galvanostatic charge/discharge on the resulting composite is shown in Figure 6.

While the reversible capacity is about 1.5 higher than in graphite, with a small value of hysteresis, the irreversible capacity is now very small, with $C_{irr}/C_{rev} < 0.1$ which is considered as the acceptable limit for a material of lithium battery anode.

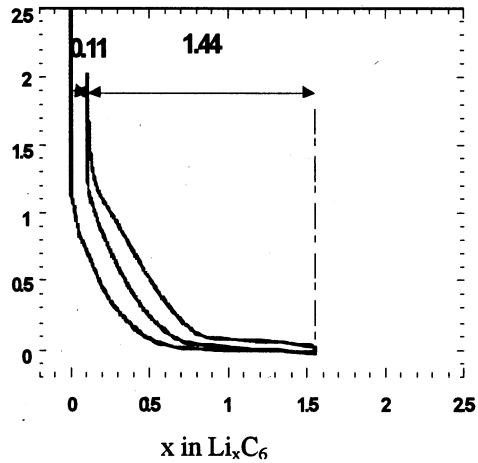

FIGURE 6 Li insertion into carbon fibres after CVD coating at 800°C.

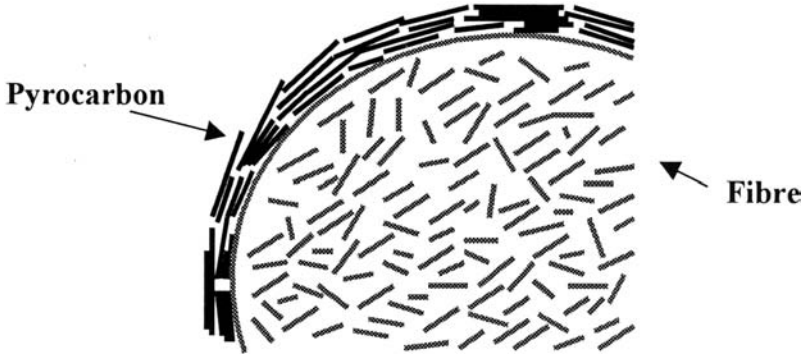

FIGURE 7 Model of pyrolytic carbon coating of a fibre by a CVD method.

During pyrolytic decomposition of propylene, the first step is the reaction of the surface dangling bonds with the free radicals formed in the gas phase. Continuing the CVD process, that gives a shell of soft carbon at the surface of the fibres which plays the role of a protecting layer preventing the diffusion of the solvated lithium ions to the core, while lithium can still reversibly penetrate. Hence, the use of these hard carbon based composites seems realistic for the negative electrode of lithium-ion batteries.

REFERENCES

[1] Wakihara, M. & Yamamoto, O. (1998). *Lithium ion batteries*, Wiley-VCH: Tokyo.
[2] Gautier, S., Frackowiak, E., Machnikowski, J., Rouzaud, J. N., & Béguin, F. (1998). *Mol. Cryst. Liq. Cryst.*, *310*, 359.
[3] Winter, M., Novak, P., & Monnier, A. (1998). *J. Electrochem. Soc.*, *145*, 428.
[4] Frackowiak, E., Gautier, S., Gaucher, H., Bonnamy, S., & Béguin, F. (1999). *Carbon*, *37*, 61.
[5] Duclaux, L., Frackowiak, E., & Béguin, F. (1999). *J. Power Sources*, *81–82*, 323.