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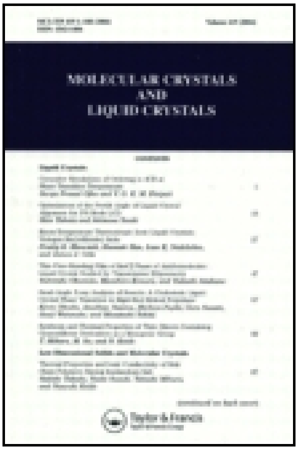

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Effect of Heteroatoms on Lithium Insertion into Carbons

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Electrochemical insertion of lithium into low temperature (below 1000°C) carbons such as cokes from various precursors and nanotubes has been correlated with their elemental composition, surface functionality and microtexture. The amount of heteroatoms (O, H, N) in the investigated carbons and especially the way of their bonding with the carbon matrix affects the reversible capacity of lithium storage which varies from 200 to 460 mAh/g. It has been found that heteroatoms, mainly oxygen, play more important role inbuilt in the carbon network as crosslinking element than present in the acidic surface functional groups. Essentially, the microtextural orientation of the pseudographitic layers and the kind of porosity at the nanometric scale determine the degree of reversible lithium insertion. The role of mesopores on irreversible capacity was also indicated.

Keywords: lithium insertion; heteroatoms; microtexture; surface functionality; hard carbon

INTRODUCTION

Much work has already been devoted for testing many carbons as possible anode materials in lithium-ion batteries. For perylene-based disordered cokes [1], nanotubes [2] and chars from nanocomposites [3-4], a high reversible specific capacity for lithium storage was found up to 900 mAh/g, however, simultaneously the deinsertion process was connected with a significant polarization. Apart from hysteresis, a high irreversible capacity during the first cycle and a subsequent loss of charge with cycling discriminate some materials from practical application even if the values of total capacity seem to be attractive. Hence, a full elucidation of the origin for divergence between lithium insertion and deinsertion, and seeking the optimal conditions for the preparation of cheap carbons is still very actual.

The objective of our study is to correlate the electrochemical storage of lithium in various carbons with their microtextural properties, the heteroatoms (O, H, N) content and the kind of their bonding with the network.

EXPERIMENTAL

The carbon samples investigated in this work were multi-walled nanotubes (MWNT) and cokes from lignite, anthracene, saccharose and polymeric precursor. The microtexture of the materials was characterized by nitrogen

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adsorption at 77K (Micromeritics, ASAP 2010) on samples carefully outgassed at 350°C under secondary vacuum. The proportion of heteroatoms was determined by elemental analysis. Back titration according to Boehm method allowed to estimate the nature and the amount of surface groups [5].

Specific capacity of lithium storage into the different types of carbons was evaluated from charge/discharge characteristics of lithium/carbon cells. Carbon pellets (ca. 10-20 mg) were prepared by pressing a mixture of carbon (85 wt%), acetylene black (10 wt%) and polyvinylidene fluoride binder – Kynar flex 2801, Atochem (5 wt%). After careful drying, they were mounted in two electrode cells under inert atmosphere in the glove box. A lithium disk played the role of counter as well as reference electrode. 1M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and diethylcarbonate (DEC) in 1:1 volume ratio (Merck) was the electrolytic solution. The electrochemical insertion of lithium was investigated between 3.0 V and –0.02 V *vs* Li using a multichannel potentiostat/galvanostat (Mac-Pile, Biologic). The current load in the galvanostatic mode was 20 mA/g, and the scan rate of potential for cyclic voltammetry ranged from 0.2 to 2 mV/s. For some samples, galvanostatic intermittent titration technique (GITT) was used where current pulses were followed by a relaxation period of 24 hours. Such a method allowed to perform insertion and removal of lithium close to equilibrium conditions and to distinguish the process controlled kinetically by diffusion of lithium ions from others, e.g. thermodynamics, ohmic polarization.

RESULTS AND DISCUSSION

The elemental composition of the carbons used for lithium storage is presented in Table I. The values for lignite cokes are ash-free due to demineralization prior to pyrolysis. The anthracene coke contained a negligible amount of oxygen. On the other hand, carbon nanotubes, lignite and saccharose cokes were rich in oxygen. It is remarkable that in the case of lignite cokes the amount of heteroatoms is only slightly affected by the thermal treatment.

TABLE I Elemental analyses (wt%) of the various carbon samples used for lithium insertion

Sample	C%	H%	N%	O%
Anthracene coke 1000°C	99.3	0.3	-	0.3
Saccharose coke 1000°C	85.8	1.3	-	9.8
Polymer coke 1000°C	93.5	0.6	-	1.4
MWNT 900°C	88.5	0.8	-	4.6
Lignite coke 700°C	89.8	2.3	0.8	7.1
Lignite coke 900°C	90.9	1.6	0.5	6.9
Lignite coke 1000°C	91.1	1.4	0.9	6.4

Taking into account the acid/base titrations of these cokes, it seems that the total number of acidic surface groups (over 2.5 meq/g) does not change significantly with temperature.

However, an increase of carboxylic groups from 0.8 to 1.8 meq/g for lignite cokes 700°C and 1000°C, respectively, indicates a mutual transformation between groups. It is also noteworthy that all the lignite cokes have a high amount of basic groups (over 1.5 meq/g) and in the case of the sample treated at 700°C (very remarkable hysteresis between lithium insertion and deinsertion), the amount of basic groups is extremely high (more than 2 meq/g). Nitrogen present in these cokes can partially contribute to the basic character together with oxygenated groups such as ether, pyrone and chromene.

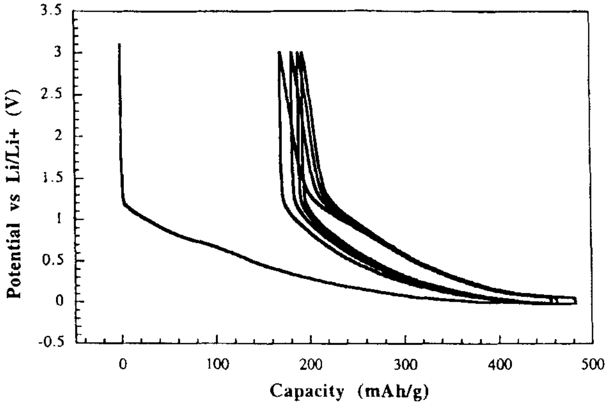

Figure 1. Galvanostatic charge/discharge characteristics for lithium insertion into lignite coke obtained at 1000°C. Current load 20 mAh/g.

As for many carbonaceous materials, it was proved that the irreversible specific capacity and hysteresis between lithium insertion and extraction for lignite cokes decrease with increasing heat-treatment temperature. Quite striking is the fact that even if lignite coke 1000°C has a rich surface functionality, the specific reversible capacity reaches 300 mAh/g without a harmful hysteresis (Figure 1). It looks that the total amount of hereoatoms does not play an important role but rather the way of their bonding with the carbon matrix. Cross-linking heteroatoms can strongly affect the microtexture of the material. Therefore, it is interesting to compare the nitrogen adsorption data of the carbons with the electrochemical characteristics for lithium insertion/deinsertion (Table II).

TABLE II Specific surface area (S_{BET}), irreversible capacity (C_{irr}) and reversible capacity (C_{rev}) for lithium storage of the various carbons

Sample	S_{BET} (m^2/g)	C_{irr} (mAh/g)	C_{rev} (mAh/g)
Anthracene coke 1000°C	0.5	60	280
Saccharose coke 1000°C	25	240	210
Polymer coke 1000°C	256	130	300
MWNT 900°C	396	860	460
Lignite coke 1000°C	173	170	300

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Except MWNT, all the other materials selected for this study presented a type I nitrogen adsorption isotherm, that is typical of a microporous character. Even if representative of two extreme categories of microtexture, oriented and highly misoriented, anthracene coke and saccharose coke gave comparable value of reversible capacity, with almost a lack of hysteresis. The main difference was in the value of irreversible capacity, due to the difference of specific surface area between the two cokes. These particular characteristics of saccharose coke, which contains a high amount of oxygen, can be explained by a closed porosity created for example by C-O-C bridges between polyaromatic units. This is supported by the fact that under mild oxidation, BET specific surface area of saccharose coke grew to 950 m^2/g. As a consequence, irreversible capacity reached 900 mAh/g and the hysteresis was very important.

Surprisingly, good characteristics for lithium insertion/deinsertion have been found, even if hard carbons had a quite developed specific surface area. For example, polymer hard coke and lignite coke obtained at 1000°C gave comparable specific reversible capacity, with almost lack of hysteresis and limited irreversible capacity. It appears that the value of irreversible capacity is strictly connected with the kind of porosity but not with the total BET surface area. The part of surface area originated from mesopores for polymer and lignite cokes 1000°C was 0.2 m^2/g and 6.7 m^2/g, respectively. Due to the relatively important basic character detected for lignite coke 1000°C, one may suppose that C-O-C ether bridges between polyaromatic units of this hard carbon could be responsible for the development of some mesopores.

This interpretation was confirmed from the experiments performed on carbon MWNT 900°C. They presented a type IV nitrogen adsorption isotherm characterizing a marked mesoporosity. On the other hand, the absence of a saturation plateau at $P/P_0 \approx 1$ is indicative of a network of mesopores which swells during adsorption of nitrogen [6]. MWNT 900°C provided an attractive value of reversible capacity, but irreversible capacity (Table II) and hysteresis were unfortunately very large. It is clear that the mesopores play an important role in the formation of the passivation layer during the first cycle of lithium insertion. Hence, the penetration of solvated Li ions with the following reductive decomposition of solvent takes place due to the great accessibility of the pores. The same characteristics, i.e. a great hysteresis and a large loss of lithium in the first cycle with simultaneously a high reversible capacity have been found also in the mesoporous carbon formed by template carbonisation in a lamellar nanocomposite [3]. It can be generalized that the mesoporous character of a carbon material is the cause for a hysteresis during lithium storage and precludes such materials from practical application as anode in lithium ion batteries.

The effect of different microtextures in the process of lithium insertion is well illustrated by the galvanostatic relaxation curves. In the case of microporous materials such as polymer hard coke or lignite coke 1000°C, the jumps of potential connected with returning of the electrode to the equilibrium state at $I = 0$ are very limited, of the order of 50 mV. For the electrode from MWNT (mesoporous), the oscillations are much more marked (Figure 2).

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Comparing MWNT 900°C and lignite coke 1000°C, the amount of heteroatoms does not differ significantly. Therefore, the great difference for the GITT characteristics is determined by the microtexture of the materials and especially the mesoporous character of MWNT. For explanation these important oscillations during lithium deinsertion the both polarization ohmic and diffusion should be considered (Figure 2).

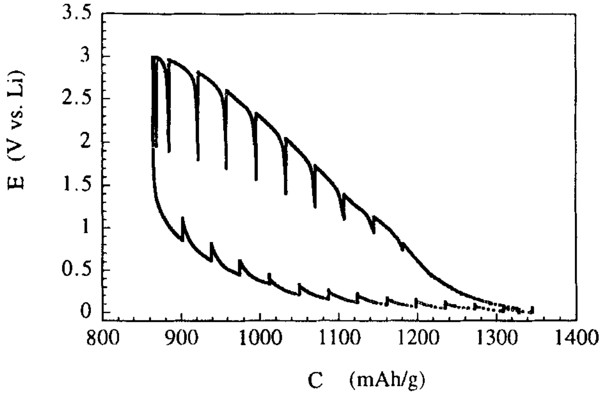

FIGURE 2 Relaxation galvanostatic charge/discharge characteristics (GITT) of carbon MWNT 900°C

Cyclic voltammetry was performed on lignite cokes formed at 700°C, 900°C and 1000°C at different scan rates of potential (from 0.2 to 2 mV/s). An example of experiment at 0.2 mV/s for lignite coke obtained at 900°C is presented in Figure 3. It looks that for such a low scan rate of potential the process of deinsertion is only slightly controlled by diffusion. The well developed anodic peak is remarked at 0.4 V vs Li what means that the lithium deinsertion involves only limited overvoltage.

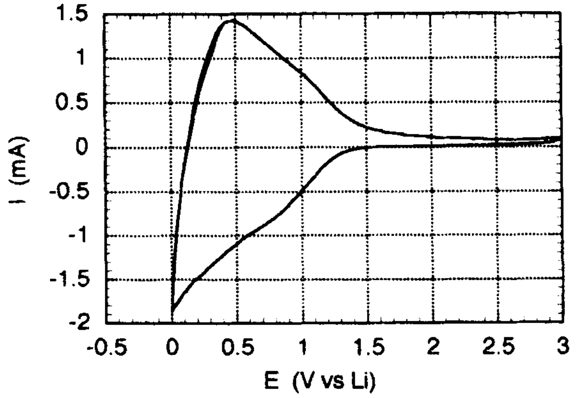

FIGURE 3 Voltammetry experiments at a scan rate of 0.2 mV/s on the lignite coke obtained at 900°C

CONCLUSION

Among the samples analyzed in this work, the great advantage of lignite precursor is the low cost of this natural coal and its high carbon content due to the condensed aromatic structure.

From the analysis of various carbons, only the microporous materials gave promising results. The amount of surface functional groups of acidic character below 2 meq/g does not seem to be harmful, however, a great amount of basic groups together with a mesoporous texture always gives a high divergence of potentials between insertion and extraction (hysteresis). Oxygen involved in crosslinking C-O-C ether bridges may be responsible for the development of mesopores in hard carbons. The mesoporous character of a carbon material facilitates the decomposition of electrolyte (great irreversible capacity, and in turn, ohmic polarization) and enables the charging of an electrical double layer.

Finally, it looks that the content of heteroatoms does not affect the charge/discharge characteristics but rather the microtexture and the kind of porosity play the most important role.

Acknowledgements

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References

[1] N. Takami, A. Satoh, T. Ohsaki and M. Kanda, *Electrochim. Acta* **42** (1997) 2537.
[2] E. Frackowiak, S. Gautier, H. Gaucher, S. Bonnamy and F. Béguin, *Carbon* **37** (1999) 61.
[3] L. Duclaux, E. Frackowiak and F. Béguin, *J. Power Sources* (1999) in press.
[4] G. Sandi, R. E. Winans and K. A. Carrado, *J. Electrochem. Soc.*, **L95** (1996) 143.
[5] H. P. Boehm, *Carbon* **32** (1994) 759.
[6] H. Gaucher, Y. Grillet, F. Béguin, S. Bonnamy and R.J.-M. Pellenq, in *Proceedings of the 6th International Conference of Fondamentals of Adsorption,* edited by F. Meunier (Elsevier, 1998) p. 243.

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