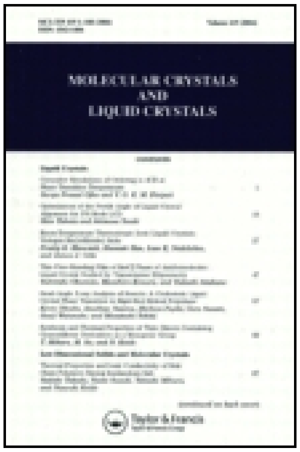

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Mechanism of Lithium Insertion in Different Kinds of Carbons

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Mechanism of lithium insertion in different kinds of carbons

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Effects of microtexture were analyzed using mesocarbon microbeads (MCMB) and two reference cokes heat-treated at 1000°C, a mesoporous saccharose coke and a lamellar anthracene coke. The electrochemical performance of MCMB heat-treated at 900°C (340mAh/g for the reversible capacity) are attributed to the specific microtexture of the beads, which are both lamellar (inner part) and mesoporous (outer part). The disorganised phase present at the surface of MCMB favors lithium sorption and further intercalation in the bulk. The electrochemical characteristics of saccharose coke were drastically changed by a mild oxidation at 450°C. The presence of oxygen at the surface plays an important role by enhancing lithium adsorption on surface sites prior to diffusion into the grains.

Keywords: carbonaceous materials; lithium intercalation; mesocarbon microbeads; lithium batteries

INTRODUCTION

Carbons are good candidates as anode materials for rechargeable lithium-ion batteries, allowing the lack of dendrites, low self-heating, safety and harmlessness for environment [1]. Poorly organized carbons have the best performance in terms of capacity, but the reasons are not well understood. It is assumed that microtexture and chemical composition are mainly responsible for lithium insertion [1]. Among disordered carbons, mesocarbon microbeads (MCMB) heat-treated between 700 and 1000°C appear as efficient anode materials [2] . We used them to analyze the effect of microtexture by comparison to two reference cokes obtained after heat-treatment at 1000°C: a saccharose coke (mesoporous) and an anthracene coke (almost pure lamellar carbon).

Influence of oxygen was analyzed through mild oxidation of saccharose coke and anthracene coke trying to keep microtexture unchanged.

EXPERIMENTAL

Mesocarbon microbeads were produced at a laboratory scale using a conventional extraction method. Coal tar pitch was carbonized in argon under atmospheric pressure for one hour at 450°C. The resultant mesophase pitch contained about 53% vol. of mesophase, predominantly in the form of spherical units. The spherules (MCMB) were separated from pitch matrix by extraction with coal-tar derived wash oil, followed by filtration and rinsing with toluene to remove the residual oil. The produced MCMB, of average diameter of 18µm, were thermally stabilized for two hours at 500°C and then heat-treated at 900°C for 15 min. Both treatments were carried out with the heating rate of 5°C/min.

The saccharose coke and the anthracene coke were prepared by Le Groupe Français d'Etude des Carbones (GFEC). Saccharose semi-coke was obtained at 400°C, then pyrolysed at 1000°C under argon. Anthracene semi-coke was obtained at 450°C under a pressure of 2 MPa and pyrolysed under argon at 1000°C. For a part of the experiments, saccharose coke and anthracene coke heat-treated at 1000°C were oxidized at 450°C for two hours under air atmosphere.

Carbon pellets were formed by pressing a mixture of carbon (85%) with acetylene black (5%) and polytetrafluoroethylene binder (10%). They were heated at about 140°C for 12h under vacuum before cell assembling. Cycling was performed in a two electrodes cell with 1M $LiPF_6$/EC+DEC electrolyte using a Mac-Pile controller (Biologic) working at 0.5mA. From galvanostatic experiments, we calculated discharge capacity for lithium insertion into carbon and charge capacity for lithium deinsertion.

Multiscale organization of the samples was analyzed by high-resolution Transmission Electron Microscopy (Philips CM 20) especially by using the 002 lattice fringes mode. The XPS measurements were carried out with a VG ESCALAB MKII multidetection spectrometer using $Mg(K_{\alpha1,2})$ radiation with a pressure of about 10^{-7} Pa.

RESULTS AND DISCUSSION

First cycle charge and discharge curves of MCMB heat-treated at 900°C are shown in Fig. 1. The plateau observed at *ca.* 0.8V *vs* Li^+/Li during discharge is attributed to the decomposition of electrolyte which results in the formation of a passivating film at the surface of carbon. The reversible capacity, of the order of 340mAh/g, is comparable to that of graphite, in good agreement with data already published [2].

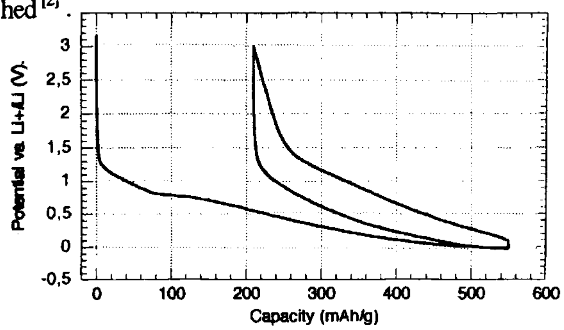

FIGURE 1 Discharge-charge profiles of MCMB heat-treated at 900°C.

According to Mabuchi, the charge capacity decreases with increasing heat-treatment temperature, for example MCMB heat-treated at 1600°C give a reversible capacity of 190mAh/g[2]. For a comparison, the reversible capacity of anthracene coke heat-treated at 1000°C is about 200mAh/g whereas saccharose coke treated at the same temperature has a reversible capacity of 250mAh/g (Figs. 2).

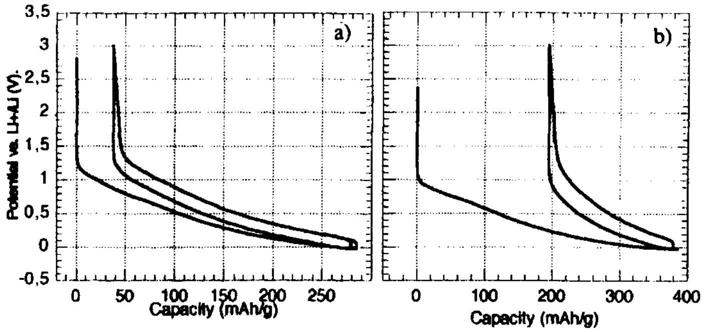

FIGURE 2 Discharge-charge profiles of a) anthracene coke heat-treated at 1000°C, b) saccharose coke heat-treated at 1000°C.

The multiscale organization of the carbonaceous materials is the result of the arrangement in space of nanometric polyaromatic Basic Structural Units (BSU). The BSU are oriented approximately in parallel within domains. Semi-cokes obtained at about 500°C from oxygen free precursors as anthracene show large domains (more than 10μm) and have a lamellar microtexture (soft carbons). By contrast, semi-cokes from oxygen rich precursors, such as saccharose, are mesoporous, each domain forming a pore wall (less than 10 nm in diameter). Residual hydrogen and oxygen atoms are assumed to be grafted on the BSU edges and especially the domains boundaries. Submitted to a further heat-treatment, heteroatoms are released (Table 1) allowing a progressive increase of the BSU parallelism within the domains. Above 1500°C, the neigbouring BSU coalesce to form continuous distorded aromatic layers [3].

TABLE 1 Elemental composition of saccharose coke and anthracene coke

		400°C	1000°C	1500°C
Saccharose coke	H/C	0.53	0.15	0.01
	O/C	0.123	0.041	0.003
		450°C	900°C	
Anthracene coke	H/C	0.41	<0.03	

In the case of MCMB, the decrease of capacity with increasing heat-treatment temperature was interpreted by a depression of the total amount of micropores. On our side, we rather assume that changes in microtexture are more responsible for lithium insertion in MCMB. In order to check it, multiscale organization of MCMB was analyzed by high resolution TEM at two heat treatment temperatures, 900°C and 1500°C (Figs. 3 and 4), for which the electrochemical performances are rather very different.

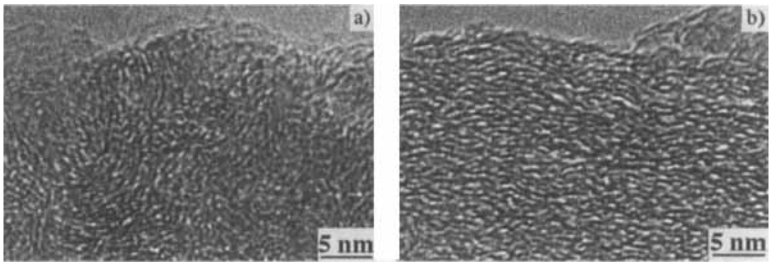

FIGURE 3 TEM images of MCMB heat-treated at 900°C, a) mesoporous texture, b) lamellar texture.

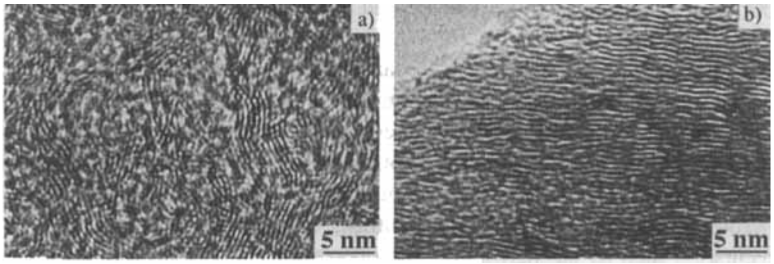

FIGURE 4 TEM images of MCMB heat-treated at 1500°C, a) mesoporous texture, b) lamellar texture.

MCMB prepared at 900°C consist of a lamellar phase, comparable to anthracene coke, and a mesoporous phase, comparable to saccharose coke. This last phase has probably its origin in the composition of the original pitch used for preparing MCMB. Its presence is attributed to the fraction which is insoluble in quinoleine (about 6% for the sample studied here). This is well demonstrated also by SEM images which show a rough surface in this case, whereas for pitches with low quinoleine insoluble fraction the surface appears almost regular. After heat treatment at 1500°C, the basic structural units (BSU) tend to coalesce to form disordered continuous layers. The mesoporous phase, with closed pores, forms a kind of shell and prevents easy access of lithium to the edge planes of the lamellar phase . Therefore in this case, the reversible capacity is very low [2] .

As compared to anthracene coke which has almost the same elemental composition as MCMB, the interesting electrochemical performances of MCMB heat-treated at 900°C could be attributed to the mesoporous component which allows lithium sorption prior to diffusion in the lamellar phase.

In some cokes, it can also be expected that heteratoms are responsible for at least a part of lithium insertion. Therefore, the two reference cokes were submitted to mild oxidation in order to demonstrate any effect of oxygen. In the case of anthracene coke, the electrochemical behavior remained unchanged after oxidation.

Non-oxidized saccharose coke gave, in the first discharge, a capacity of 400mAh/g whereas it was only 200mAh/g for the second discharge. The capacity of the first discharge for the oxidized saccharose coke was 1200mAh/g and the reversible capacity was of the order of 400mAh/g (Fig. 5).

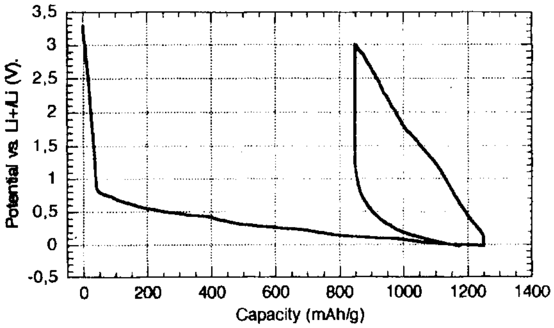

FIGURE 5 Discharge-charge profiles of oxidized saccharose coke

This experiment shows that oxidation could have a strong influence on the passivating layer formation and also on lithium insertion. Since TEM image of the oxidized sample did not show any striking modification as compared to non-oxidized saccharose coke, a textural effect cannot be considered as responsible of these important differences. Consequently, the oxygen present at the surface is rather considered at the origin of these differences, as demonstrated by XPS investigations. The atomic percentage of carbon involved in C-O bonds slightly increased from 10% in as-received saccharose coke to 14% in the oxidized saccharose coke.

CONCLUSION

MCMB show a specific multiscale organization including lamellar and mesoporous microtextures. This particular arrangement of BSU could be responsible of the electrochemical performance observed in MCMB heat-treated at 900°C for which mesopores appear to be still open. The disorganized phase present at the surface of MCMB heat-treated at 900°C favors the extended lithium sorption and further insertion in the bulk. At 1500°C, BSU tend to coalesce to form continuous layers and the mesoporous phase forms a shell surrounding the lamellar phase, preventing any easy access of lithium to the edge planes. For anthracene coke heat-treated at 1000°C, we can assume that the BSU, oriented in parallel, give only few lithium sorption sites. For the saccharose coke heat-treated at 1000°C, the aromatic layers are disordered such as the mesoporous phase of MCMB heat-treated at 900°C. Its lower performance as compared to MCMB are attibuted to differences in the chemical composition of these two materials; The influence of surface oxygen was shown with oxidized saccharose coke. It appeared that the presence of oxygen at the surface plays an important role by enhancing lithium adsorption on surface sites [4] prior to diffusion into the grains.

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