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Boronated mesophase pitch coke for lithium insertion

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Abstract

Boronated carbons from mesophase pitch have been used as materials for lithium storage in Li/carbon cells. Doping by boron has been realized by co-pyrolysis of coal tar pitch with the pyridine–borane complex. Amount of boron in mesocarbon microbeads (MCMB) varied from 1.4 to 1.8 wt.% affecting the texture of carbon. Optical microscopy and X-ray diffractograms have shown tendency to more disordered structure for boron-doped carbon. The values of specific reversible capacity (x) varied from 0.7 to 1.1 depending significantly on the final temperature of pyrolysis (700–1150°C). The optimal charge/discharge performance was observed for boronated carbon heated at 1000°C.
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Keywords: Lithium insertion; Boronated carbon; Mesophase pitch; Coke; Mesocarbon microbeads

1. Introduction

The electrochemical insertion of lithium into non-boronated mesocarbon microbeads (MCMB) has been already studied [1]. The promising results encouraged us to the further modification of the mesophase carbon by boron as heteroatom.

Boron as a substitutional element in the carbon matrix facilitates graphitization, improves the oxidation resistance of carbon, the mechanical stability and the thermal conductivity [2,3].

Due to the fact that boronated carbon has an electronic deficiency, we can expect materials with better electron acceptor properties without any large distortion of structure.

Chemical and electrochemical intercalation of lithium into boronated carbons synthesized by chemical vapor deposition from acetylene and boron trichloride was investigated [4,5]. However, even if the amount of inserted lithium was enhanced, an aggravation of electrochemical characteristics was observed. Our target was to study the electrochemical properties of differently boronated mesophase pitch coke and boron-doped MCMB during the lithium insertion/deinsertion process and to analyze the effect of boron.

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2. Experimental

2.1. Preparation of carbons

The raw materials for the synthesis of boron-doped carbons were QI-free coal-tar pitch produced by bench scale distillation of centrifugated coke oven tar and pyridine–borane complex (Aldrich). The complex was introduced drop by drop to the molten pitch at 120°C with continuous stirring [3]. A total of 1 cm^3 (0.92 g) of the complex was added for each 6 g of the pitch that corresponds to the boron content in the mixture of 1.75 wt.% on pitch basis. The carbon materials prepared from the pitch/complex mixture were pitch semi-coke (PC) and MCMB. The semi-coke was produced by heat treatment until 520°C at 5°C min^{-1} with 2 h soak. To produce MCMB, the mixture was soaked for 9 h at 400°C with stirring and the mesophase formed was separated from the resultant mesophase pitch as insoluble in *N*-methylpyrrolidone (90°C, 0.5 h, pitch/NMP ratio 1:10). All treatments were performed in an inert atmosphere under atmospheric pressure. The MCMB yield was 35.3%. The final heat treatments of both semi-coke and MCMB were performed at 700, 850, 1000 and 1150°C at a heating rate of 5°C min^{-1} with 1 h soak.

The boron content in the carbons produced was calculated based on the yield of mineral residue remaining after heating in air for 12 h, assuming that all boron occurs as B_2O_3 and from inductively coupled plasma emission spectroscopy

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(ICP). ICP analysis was performed on JY 38s spectrometer using samples digested in nitric acid. Optical texture of semi-coke and mesophase pitch was evaluated using polarized light optical microscopy.

2.2. Electrochemical measurements

Boron-doped carbons (cokes and MCMB) treated in the wide range of HTT were used as materials for lithium insertion in aprotic medium: 1 M $LiPF_6$ in (EC:DEC) or (EC:DMC). Investigation of lithium insertion has been performed in carbon/lithium cells (two electrode swagelok construction) using a multichannel generator Mac Pile II (Biologic, France). Galvanostatic charge/discharge cycling with a current load of 20 mA/g has been performed in the range of potential from −0.02 to 3.0 V versus Li. For some experiments galvanostatic intermittent titration technique (GITT) was applied with a relaxation time of a few hours. Voltammetry technique at the scan rate of 0.2, 1 and 2 mV/s was also used to study the kinetics of lithium insertion.

3. Results and discussion

ICP analysis of mesophase pitch showed that about 70% of boron contained in the borane added to the pitch has been incorporated into carbonaceous material structure (Table 1). As could be expected based on high reactivity of borane, the mesophase is richer in boron than the isotropic pitch matrix. The determination of boron from ash content can lead to overestimated value due to inclusion of carbon material frequently associated with the boron oxide even if a long annealing in air is used.

Borane accelerates and modifies the transformation of pitch constituents into mesophase. In contrast to spherulitic mesophase of Brooks–Taylor morphology that is typically formed when QI-free coal tar pitch is carbonized, the irregular units of mesophase of size between 40 and 60 μm occur in mesophase pitch produced from pitch/borane mixture. Apparently, borane induced polymerization and cross-linking of pitch constituents result in small mesophase units which tend to form aggregates instead to coalesce. The semi-coke produced under conditions used in the study is characterized by heterogeneous texture with a considerable proportion of disordered material (fine-grained mosaics). The observation is consistent with a lower degree of structural ordering of boron-doped coke compared to the parent pitch coke as determined by X-ray study.

Table 1
Boron content in the carbonization products

Sample	Burning in air		ICP analysis
	Ash (%)	Boron (wt.%)	Boron (wt.%)
Semi-coke	7.17[a]	2.25	N.D.
Mesophase pitch	4.15	1.33	1.36
MCMB	5.85	1.84	1.48

[a] Residue contains inclusion of organic matter.

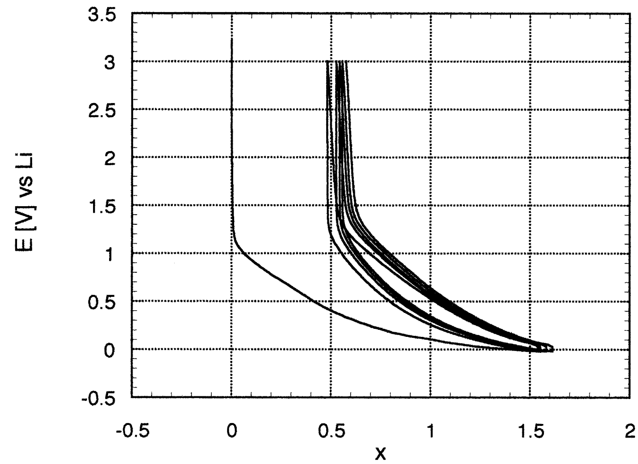

Fig. 1. Galvanostatic lithium insertion/extraction for boronated mesophase coke treated at 1000°C. Current load of 20 mA/g.

From the galvanostatic charge–discharge characteristics between 3 and −0.02 V versus Li at a current density of 20 mA/g, the reversible and irreversible capacity of lithium insertion was evaluated. A high value of 400 and 350 mAh/g was obtained for the boronated coke and MCMB, respectively, for both samples treated at 1000°C. An example of the galvanostatic characteristics for boronated coke (1000°C) are presented in Fig. 1. Very promising is the profile of curves and a lack of divergence between the lithium insertion and extraction for this boron-doped sample. However, in the case of cokes or MCMB treated at lower temperatures (700 and 850°C), even if the values of reversible capacity are higher ($x = 1.3$), the presence of hysteresis, more remarkable for carbon obtained at 700°C, discriminates this coke from practical application. Potentiodynamic investigations (0.2–2 mV/s) and GITT were used for detailed studies of all the kind of polarization during insertion and removal of lithium. Figs. 2 and 3 show voltammetry results at scan rates

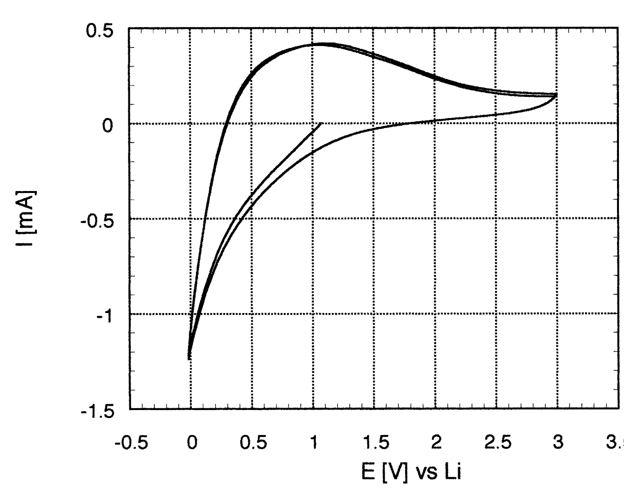

Fig. 2. Voltammetry experiments for boronated MCMB treated at 700°C. Scan rate of potential 0.2 mV/s.

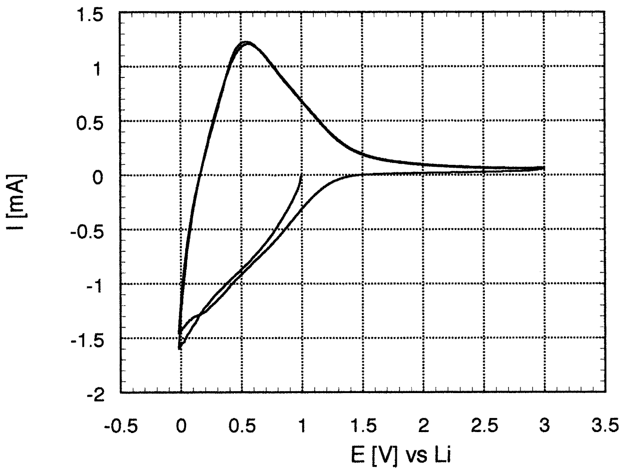

Fig. 3. Voltammetry experiments for boronated MCMB treated at 1000°C. Scan rate of potential 0.2 mV/s.

of 0.2 mV/s for boronated MCMB prepared at 700 and 1000°C, respectively. In the case of lower temperature MCMB, i.e. 700°C (Fig. 2), the wide region of potential is observed for lithium deinsertion that matches well with a hysteresis in galvanostatic experiments. The profile of characteristics shows that diffusion of lithium during deinsertion is limited (process proceeds above 1 V versus Li). Charging of electrical double layer is visible in very positive values of potential. Diffusion and ohmic polarizations were especially remarked during GITT experiments with relaxation intervals. Contrarily, for boronated MCMB treated at 1000°C (Fig. 3), the narrow region of potential with a maximum at 0.6 V versus Li, responsible for insertion and extraction of lithium, is observed. Even if the degree of lithium insertion does not increase rapidly after boronation of carbons, the electrochemical characteristics (for 1000 and 1150°C) are improved due to the lack of hysteresis. Finally, the effect of temperature dominates on the electrochemical characteristics.

Acknowledgements

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