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Charge/discharge characteristics of the coal-tar pitch carbon as negative electrode in Li-ion batteries

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Abstract

The charge/discharge characteristics were studied for the coal-tar pitch-based carbon (CTPC), which was pyrolyzed under the condition to form anisotropic mesophase pitch and then heat treated at temperatures ranging from 500 to 1300°C in N_2 atmosphere. As the heat treatment temperature increased, the reversible capacity for the CTPC increased progressively up to 1000°C, while the irreversible capacity decreased continuously. Carbons synthesized through the extraction of anisotropic mesophases showed higher reversible and lower irreversible capacities than the directly pyrolyzed ones.

Keywords: Lithium-ion battery; Coal-tar pitch carbon; Electrochemical properties; Carbon electrode

1. Introduction

As most carbons, including graphite, can insert lithium reversibly with high capacity, have good electronic conductivity and low electrochemical potential with respect to lithium metal, they are attractive candidates as anode materials for rechargeable lithium batteries. The types of carbonaceous materials studied for the lithium battery range from completely layered graphites to non-graphitizable hard carbons. Structural variations of carbonaceous materials play an important role in the electrochemical performance of the lithium-intercalated carbon, such as capacity reversibility, cycleablility, and stability. Recent works [1–5] showed that carbons obtained by pyrolyzing organic precursors such as phenolic and epoxy resins at low temperature can reversibly intercalate Li atoms with capacity greater than that of graphite (≅372 mAh/g). Most of these carbons were found to be disordered and to contain a large fraction of single graphene layers that have large amount of nanoporosity. In the present study, carbon was synthesized by pyrolyzing the organic precursor of coal-tar pitch under the condition forming preferentially anisotropic mesophases which was then extracted, and its electrochemical performance as an anode for the Li-ion cell was investigated.

2. Experimental

In pyrolyzing process, the coal-tar pitch was held in a quartz tube furnace under flowing N_2 gas at 300°C for 3 h at the first stage to remove the low molecular weight compounds, then heated at 400°C for 3 h to enhance the formation of anisotropic mesophase at the second stage prior to being cooled down to room temperature. In order to extract anisotropic mesophases, the pitch was dissolved in tetrahydrofuran (THF) solution for a day and washed by ethanol. The solidified pitch was then heat treated at various temperatures ranging from 700 to 1300°C for 1 h in N_2 atmosphere. Carbon electrodes were prepared by coating slurries of carbon powders and polyvinylidene fluoride (PVDF) dissolved in *N*-methyl pyrrolidinone (NMP) on a copper foil.

Electrochemical experiments were carried out in a 10 ml, three-electrode cylindrical glass-cell in which the electrodes and the separators (Celgard 2400) were placed vertically. Li foils were used as the counter electrode and the reference electrodes. The electrolyte was prepared by dissolving 1 M $LiPF_6$ in a mixture of 50% ethylene and 50% diethyl carbonate by volume. Half-cells were fabricated in a dry argon-atmosphere glove box. The electrochemical tests were performed using a potentiostat/galvanostat (EG&G Inst. 263A). The cells were discharged at a constant current of $C/10$ rate to a cutoff voltage of 10 mV versus Li/Li^+. Charging was performed at the same rate up to 1.5 V versus Li/Li^+.

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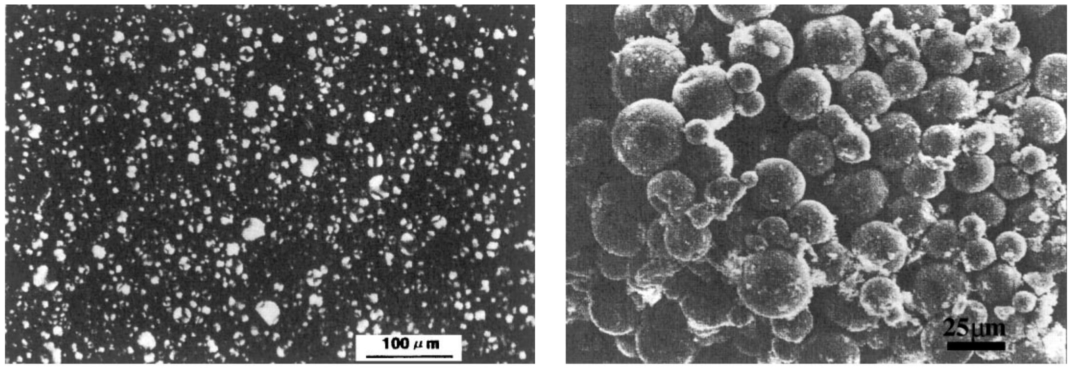

(a) (b)

Fig. 1. (a) Polarization micrograph of the directly pyrolyzed CTPC and (b) SEM micrograph of the extracted anisotropic mesophase pitches.

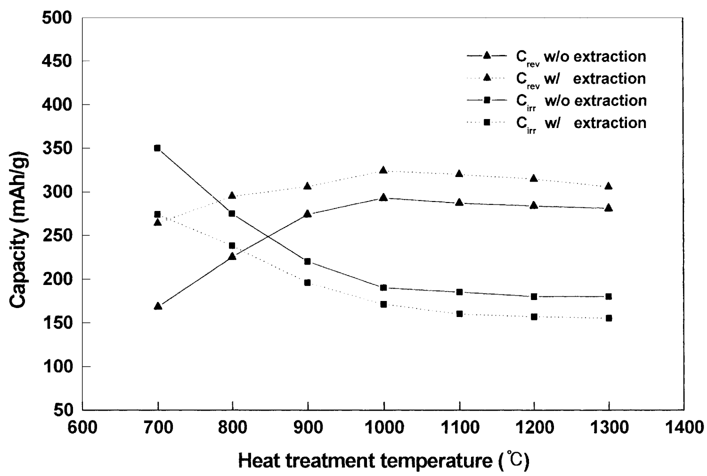

Fig. 2. Reversible capacity and irreversible capacity vs. heat treatment temperature for carbons pyrolyzed from the coal-tar pitch without extraction (solid line), and with extraction of mesophase (dotted line).

3. Results and discussion

Fig. 1(a) shows a polarization micrograph of CTPC directly pyrolyzed at 400°C for 3 h, in which the bright spherical particles are anisotropic mesophases. Fig. 1(b) is the SEM micrograph for the anisotropic mesophase pitches extracted by THF solution, showing the homogeneous distribution of spherical particles with around 20 μm diameter. Fig. 2 shows the reversible capacity and irreversible capacity as a function of heat treatment temperature for the pyrolyzed carbons without extraction (solid lines) and with extraction of anisotropic mesophases from the coal-tar pitch (dotted lines), respectively. As a heat treatment temperature increased, the reversible capacity for the coal-tar pitch carbon increased progressively up to 1000°C, while the irreversible capacity decreased continuously. Also, a carbon of anisotropic mesophase by the THF extraction shows higher reversible capacity (C_{rev}) and lower irreversible capacity (C_{irr}) than carbons without extraction. Fig. 3 shows the charge/discharge capacities with cyclic number for the CTPC which was pyrolyzed, extracted and heat-treated at 900°C. Discharge capacity decreased significantly at the first cycle, and then did gradually down to 220 mAh/g after the second cycle. Also, the difference in capacity between discharge and charge occurred with large amount of about 300 mAh/g at the first cycle and a little amount of less than

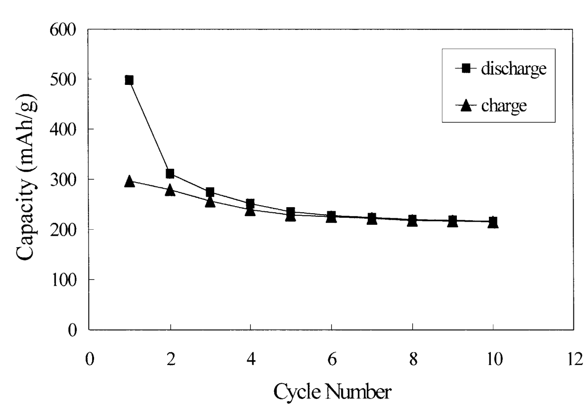

Fig. 3. Capacity as a function of cycle number for carbons extracted and heat treated at 900°C.

30 mAh/g after second cycle number. The work in progress is devoted to the crystallographic analysis and Li intercalation/deintercalation process for the anisotropic mesophase based carbon in order to understand its enhanced cell performance, in detail.

4. Conclusions

The electrochemical performance of Li-ion batteries based on the coal-tar pitch carbons was carried out under two different synthesizing conditions, i.e. direct pyrolyzation and pyrolyzation with extraction of anisotropic mesophases. Coal-tar pitch carbons synthesized by extracting anisotropic mesophases showed a higher reversible capacity and lower irreversibility, compared with the directly pyrolyzed carbons.

Acknowledgements

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