

# Characteristics of coke carbon modified with mesophase-pitch as a negative electrode for lithium ion batteries

Yuichi Sato <sup>a</sup>, Yasuo Kikuchi <sup>a</sup>, Takeshi Nakano <sup>a</sup>, Gaku Okuno <sup>a</sup>, Koichi Kobayakawa <sup>a</sup>,  
Takanobu Kawai <sup>b,\*</sup>, Akira Yokoyama <sup>b</sup>

<sup>a</sup> Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, 3-27-1 Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan

<sup>b</sup> Nippon Carbon, 1-1 Shin-Urashimacho, Kanagawa-ku, Yokohama 221-0042, Japan

## Abstract

To increase the charge–discharge capacity of carbon electrodes for lithium ion secondary batteries, coke carbon, a relatively cheap material, was modified with mesophase-pitch carbon by a heat treatment. While coke carbon powder, mesophase-pitch, and a mixture thereof (4:1 by weight) supplied between 0 and 1.5 V vs. Li/Li<sup>+</sup> an initial discharge capacity of about 295 mAh/g, 310 mAh/g, and 310 mAh/g, respectively, the modified coke deintercalated 400 mA h/g of lithium with a high degree of reversibility. The difference in capacity between the modified carbon and mixture are discussed based on the shape of their current–potential curves and their galvanostatic charge–discharge curves. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Lithium secondary battery; Anode material; Coke carbon; Mesophase-pitch carbon; Surface modification

## 1. Introduction

Much effort has gone into the search for high-capacity carbons for use in lithium-ion secondary batteries. These carbons are disordered and have capacities exceeding the 372 mAh/g for graphite. Disordered carbons are categorized into (1) materials heat-treated from 550 to 1000°C and (2) hard carbons heated at about 1000°C. The carbons heat-treated from 550 to 1000°C are prepared from meso-carbon microbeads (MCMB) [1,2], phenolic resin [3], poly-paraphenylene [4,5], mesophase-pitch based carbon fiber (MCF) [6] and perylene-based disordered carbon fiber (PBDCF) [7] and have a specific capacity of 500 to 700 mA h/g with large potential hysteresis. Hard carbons prepared from pyrolyzed polyfurfuryl alcohol [8] and an isotropic carbon [9] have capacities near 600 mAh/g with little potential hysteresis. Some researchers have tried to increase the charge–discharge capacity by surface modifications such as coverage with metals [10], milling graphite, coke, or carbon fibers [11], mild air oxidation [12], heating natural graphite to 3000°C in an inert atmosphere, followed by fluorination or ozonization [13] and chemical oxidation [14].

MCMB and MCF have a lamella or radial texture and charge–discharge characteristics, related to layer spacing, show large capacities as cited above. We attempted to improve the capacity of coke, which is relatively cheap, but has a capacity of only 170–250 mAh/g, by covering coke carbon with mesophase-pitch carbon and we evaluated this material as an anode material for lithium secondary batteries.

## 2. Experimental

Mesophase-pitch carbon powder was prepared by heating  $\beta$ -resin at 400°C in a nitrogen atmosphere, where  $\beta$ -resin was extracted from coal-originated pitch and then ground. Graphitized coke carbon powder, which was obtained by heating cokes at 3000°C in a reductive atmosphere, and mesophase-pitch carbon powder were mixed at 4:1 by weight and mechanochemically heat-treated at 2.0 kg/cm<sup>2</sup> in air, i.e., when the mixture was ground using a grinding machine at the above pressure, the higher-softening-point powder (coke) was covered with lower-softening-point mesophase-pitch powder. This mixture was then heated at 1000°C in nitrogen to obtain coke carbon modified with mesophase-pitch carbon, which is named treated carbon or modified carbon hereafter.

\* Corresponding author

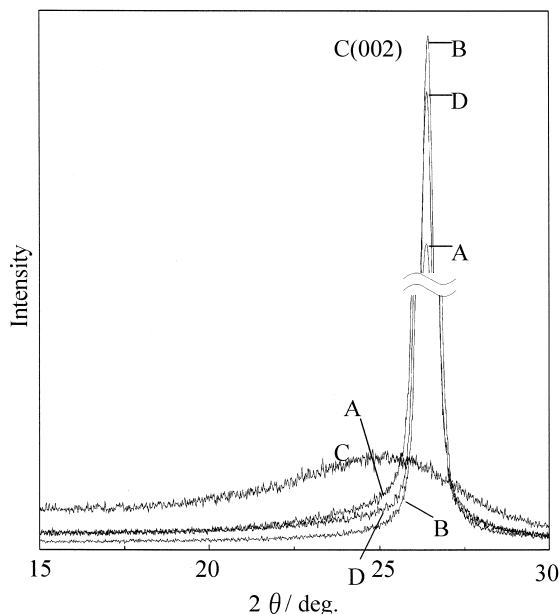


Fig. 1. X-ray diffraction patterns of various carbons. (A) Modified coke, (B) coke, (C) mesophase-pitch carbon, (D) mixed carbon of coke and mesophase-pitch carbon by 4:1 in weight ratio.

X-ray diffraction (XRD) patterns were recorded with a Rigaku diffractometer (Rad- $\gamma$ A) using monochromatic Cu K $\alpha$ . Raman spectra were measured using a Ramanscope (Renishaw). BET surface areas of carbon powders were analyzed by nitrogen adsorption measurement. Average particle sizes of carbon powders were measured using a laser diffraction particle size distribution analyzer (Seishin Enterprise)

To confirm the effect of modification by mesophase-pitch on coke carbon, cyclic voltammograms and charge–discharge cycling tests were conducted for (A) modified carbon, (B) coke carbon, (C) mesophase-pitch carbon, and (D) a mixture of coke and mesophase-pitch carbon (4:1 by weight).

The composite anode for cyclic voltammogram measurements and charge–discharge cycling tests was fabricated by mixing 95 wt.% carbon with 5 wt.% conductive binder (66% acetylene black, 33% PTFE, and 1% surface active agent). The mixture was pressed onto a nickel mesh collector at 3.76 t/cm<sup>2</sup> to form a tablet of 13 mm in diameter. Carbon electrodes were dried in vacuum at 150°C for 5 h before use. The reference and counter electrodes were lithium foils. A glass filter, which served as the separator, and the reference electrode were sandwiched between the carbon and counter electrodes. The electrolyte was a solution of 1 M LiClO<sub>4</sub> in a 50 vol.% ethylene carbonate (EC) and 50 vol.% diethylcarbonate (DEC) solvent (Mitsubishi Chemical). Test cells were assembled in a glove box filled with argon. Cyclic voltammograms were measured at a scan speed of 50  $\mu$ V/s. Charge–discharge cycling tests were conducted at a constant current of 0.1 mA/cm<sup>2</sup> between 0 and 1.5 V at 30  $\pm$  1°C using a PC-controlled battery tester (Toyo System, TYS-30TUOO).

### 3. Results and discussion

#### 3.1. Properties of the modified carbon

Powder XRD profiles of carbon samples were obtained to confirm that mesophase-pitch was modified by coke carbon. Fig. 1 shows XRD peaks for the (002) plane for different carbons. The treated carbon (A), untreated carbon (coke) (B) and mixed carbon (D), which was a mixture of coke and mesophase-pitch carbon of 4:1 by weight showed a sharp diffraction peak at  $2\theta = 26.5^\circ$ , suggesting that each carbon had a high crystallinity and a graphite structure. Mesophase-pitch carbon showed a broad peak at around  $2\theta = 25^\circ$ . The peak intensity order—peak A < peak D < peak B—proved to be reasonable, because the amount of coke in carbon D was 80% of that of carbon B making peak D smaller than peak B. At  $25^\circ \leq 2\theta \leq 26^\circ$ , however, the intensity order reversed  $I_B < I_D < I_A$  suggesting that the treated carbon (A) consisted of coke carbon covered by mesophase-pitch carbon which contributed to the diffracted intensity in this Bragg-angle range.

The Raman spectra of the four carbons are shown in Fig. 2, where the  $R$  value is the intensity ratio of the peak height at 1360/cm and 1580/cm, i.e.,  $R = I_{1360}/I_{1580}$  and is known as an indicator of crystallinity [15,16]. Unmodified carbon (B, coke) has a small value of  $R$  (0.2) indicating a graphitic structure. Mesophase-pitch carbon has the largest value,  $R = 0.85$ , which suggests that the structure is turbostratic. Since carbon D contains 80% graphitized coke and 20% mesophase-pitch carbon, it shows a larger value ( $R = 0.30$ ) compared to coke ( $R = 0.20$ ). Carbon A

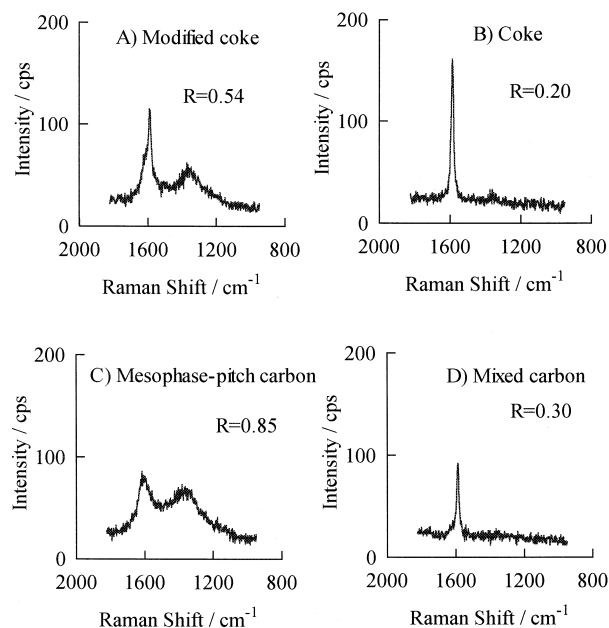


Fig. 2. Raman spectra of various carbons. Mixed carbon = coke and mesophase-pitch carbon (weight ratio 4:1).

Table 1  
Carbon characteristics

Sample	Description	$d(002)$ (Å)	$L_c(002)$ (Å)	BET surface area (m <sup>2</sup> /g)	Average particle diameter (μm)
A	After modifying coke B with mesophase-pitch carbon, heated at 1000°C.	3.363	853	2.74	8.9
B	Coke powder treated at 3000°C.	3.365	> 1000	1.13	9.3
C	Mesophase-pitch treated at 1000°C.	3.520	28	0.61	13.4
D	Mixed carbon of B and C (4:1 by weight)				

has a relatively high value of  $R$  (0.54), which suggests that coke is covered with mesophase-pitch carbon. The treated carbon (A) will be called modified carbon hereafter.

Table 1 shows the characteristics of the four carbons. Even though the lattice spacing  $d(002)$  for modified carbon (A) and unmodified carbon (coke, B) is almost the same,  $L_c(002)$  of the modified carbon, the size of the crystallite domains for  $c$ -axis direction [17,18], is slightly lower than that of unmodified carbon. The fact that the mesophase-pitch has a higher value ( $d(002) = 3.520$  Å) than that of the other carbons and a smaller  $L_c(002)$  suggests that the mesophase-pitch is a carbon with low crystallinity. The BET surface area of the modified carbon is larger than that of the unmodified carbon, which was caused by a smaller average particle diameter of the modified carbon compared to the unmodified carbon.

### 3.2. Cyclic voltammograms

To clarify the effect of modifying coke carbon, cyclic voltammograms were measured (Fig. 3). Modified carbon

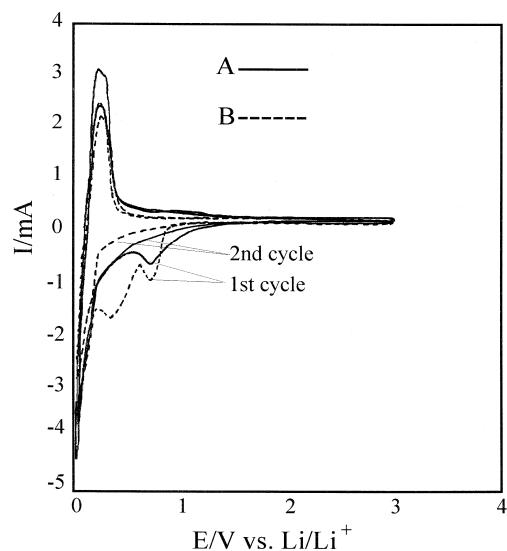


Fig. 3. Cyclic voltammograms of carbons in 1 M LiClO<sub>4</sub>/EC+DEC at 0–3 V. Sweep rate: 50 μV/s. (A) Modified coke, (B) coke.

(A) had a cathodic peak at about 0.8 V, and unmodified coke (B) had two peaks at about 0.8 and 0.4 V. The cathodic current of unmodified coke is larger than that of modified, suggesting greater Li<sup>+</sup> ion doping and larger capacity, but these cathodic peaks disappeared in the second cycle. These cathodic currents were due to an irreversible reaction and did not contribute to the reversible capacity. They appear to be caused by the formation of a solid-electrolyte interface (SEI) due to the decomposition of the solvent or the reaction of functional groups present on the carbon surface [19,20] rather than Li<sup>+</sup> intercalation. Although both carbons gave an anodic peak at about 0.25 V, the higher anodic peak of the modified carbon and its higher anodic current at about 1.0 V suggests that the capacity of the modified carbon may be greater than that of the unmodified carbon. Reducing the potential range from 0–3.0 V to 0.25–3.0 V (Fig. 4) revealed that the unmodified carbon showed a large cathodic current, but no anodic peak which makes the unmodified coke electrochemically useless in this voltage range. The modified carbon, however, still showed an anodic peak even at a

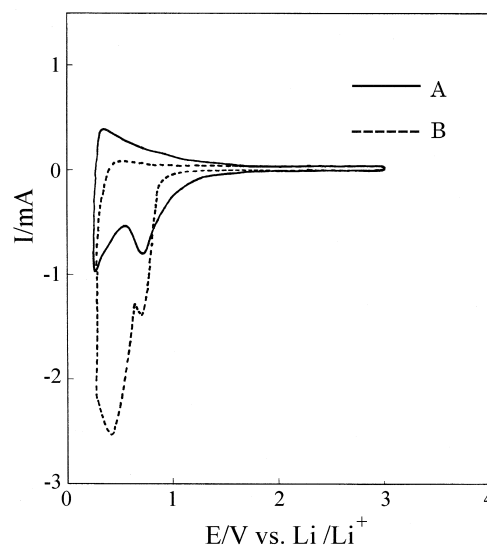


Fig. 4. Cyclic voltammograms of carbons in 1 M LiClO<sub>4</sub>/EC+DEC at 0.25–3 V. Sweep rate: 50 μV/s. (A) Modified coke, (B) coke.

switching potential of 0.25 V, indicating that this material may be usable as an electrode above 0.25 V vs. Li/Li<sup>+</sup>, thus avoiding plating of lithium. Cyclic voltammograms of modified carbon (A), mesophase-pitch carbon (C), and mixed carbon (D) showed cathodic peaks at about 0.8 V and one peak at 0.4 V (carbon D only) and an anodic peak at about 0.25 V (Fig. 5). The electrode reaction of the mixed carbon differed from that of the modified carbon although the ratio of coke and mesophase-pitch carbon was the same. The cathodic peak at about 0.4 V for the mixed carbon (D), which may have been due to coke carbon as expected from the cyclic voltammogram B in Fig. 4, disappeared for the modified carbon (A). Due to the modification, the electrode reaction at about 0.4 V was suppressed and the anodic peak observed at 0.25 V became larger than that of the mixed carbon (D), i.e., the modification treatment could improve the capacity of the simple powder mixture D. In contrast, mesophase-pitch carbon (C) alone showed lithium deintercalation at a wider potential range than the other carbons. Coating carbon B with a small amount of carbon C reduced the irreversible capacity (Figs. 3–5). This could be used to reduce the irreversible capacity of carbon materials that are otherwise very attractive.

### 3.3. Charge–discharge curves and cycleability

Fig. 6 shows the first charge–discharge curves for the investigated carbons. Mesophase-pitch carbon (C) showed a higher initial charging potential (lithium intercalation), which was monotonously sloping, in contrast to that of the other carbons. This is expected from the cyclic voltammogram (C) in Fig. 5 and suggests that the electrode reaction differs from the other carbons. The modified carbon (A)

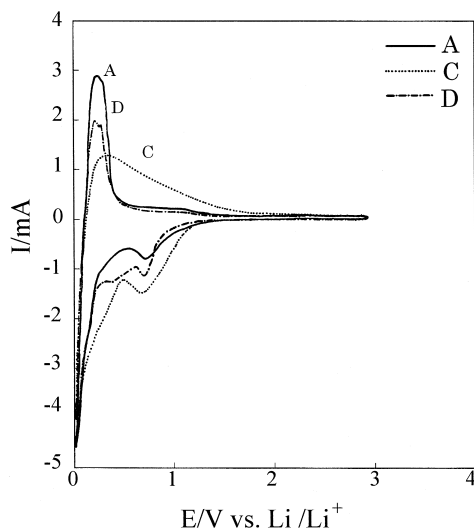


Fig. 5. Cyclic voltammograms of carbons in 1 M LiClO<sub>4</sub>/EC+DEC at 0–3 V. Sweep rate: 50 μV/s. (A) Modified coke, (B) coke, (C) mesophase-pitch coke, (D) mixed carbon.

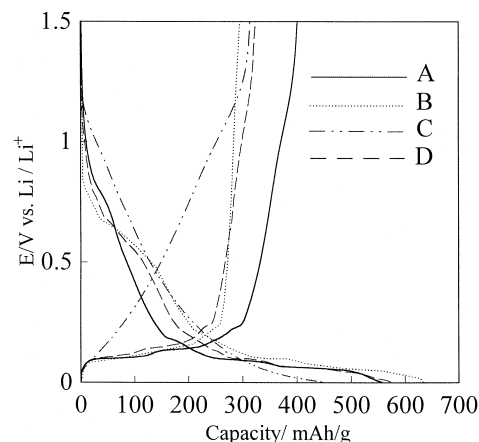


Fig. 6. Charge and discharge curves of carbons A, B, C, and D in 1 M LiClO<sub>4</sub>/EC+DEC at 0.1 mA/cm<sup>2</sup> between 0 and 1.5 V. The capacity is based on the mass of the respective electrode material excluding the conductive binder. (A) Modified coke, (B) coke, (C) mesophase-pitch coke, (D) mixed carbon.

showed an onset of a plateau at about 0.8 V and a long plateau at around 0.12 V. Compared to the modified carbon (A), the unmodified carbon (B) exhibited a higher charge capacity. As discussed above for the cyclic voltammogram of B in Fig. 3, the electrode reaction of unmodified carbon (B) between 0.8 and 0.2 V involved the irreversible formation of the SEI layer, which was partially suppressed by the modification (curve A, Fig. 6). The discharge capacity of the modified carbon (A) was not only greater than that of the simple mixture (D), but also exceeded the discharge capacity of B and C. The discharge curves of the carbons A, B, and D show a similar behavior up to about 0.25 V, above which all of these discharge curves rose steeply and where about 90 mA h/g of lithium could be deintercalated from the modified carbon A above this voltage. We explain the discharge behavior of the modified carbon (curve A, Fig. 6) according to Tatsumi et al. [21]. They stated that the discharge capacity in the potential range 0–0.25 V is due to the deintercalation of Li<sup>+</sup> from the graphitic structure, while the discharge capacity above 0.25 V is attributed to the turbostratic structure where stacking structure orientation is random. Considering that the modified carbon consists of two phases, i.e., where graphitic coke carbon powder is covered with nongraphitized mesophase-pitch carbon, the capacity in the potential range from 0 to 0.25 V seems mainly due to Li<sup>+</sup> deintercalation from the inner coke part and the capacity above 0.25 V mainly due to that from the outer mesophase-pitch carbon where many crystal defects, which offer additional sites for lithium storage, are present [2]. The separation of these two voltage ranges also indicates that the surface layer does not significantly interfere in the Li<sup>+</sup> ion deintercalation from the inner coke part. Although some scientists may argue that the capacity above 0.25 V, especially that above 1.0 V, is not useful from a practical point of view, we believe, however, this is not true in the

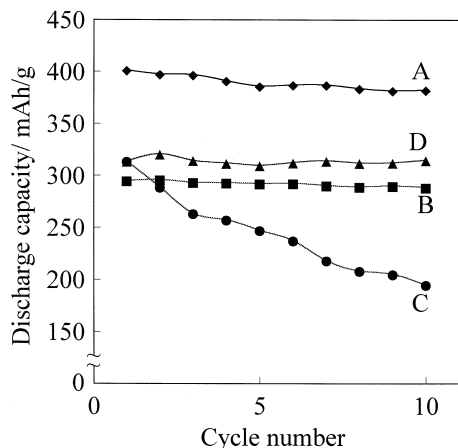


Fig. 7. Cycleability of the carbons A, B, C, and D in 1 M LiClO<sub>4</sub>/EC + DEC at 0.1 mA/cm<sup>2</sup> between 0 and 1.5 V. The capacity is based on the mass of the respective electrode material excluding the conductive binder. (A) Modified coke, (B) coke, (C) mesophase-pitch coke, (D) mixed carbon.

light of an advancing electronic technology using lower operating voltage.

Fig. 7 shows the discharge cycle characteristics of the four carbons. The capacity of mesophase-pitch carbon (C) decreased with cycling, whereas the other three types of carbon show good cycleability. Modified carbon (A) shows the largest capacity and a relatively good cycleability. Thus, surface modification of coke by mesophase-pitch carbon is found to be effective in preparing a negative electrode material for lithium secondary batteries.

#### 4. Conclusion

Coke carbon modified with mesophase-pitch carbon on the surface was studied as a negative electrode material for lithium secondary batteries by cyclic voltammetry and constant current charge–discharge cycling. Modified carbon had a cathodic peak at about 0.8 V, and unmodified coke two peaks at about 0.8 and 0.4 V. The cathodic current of unmodified coke is larger than that of modified, but these cathodic peaks disappeared in the second cycle. They appear to be caused by the formation of SEI. Although both carbons gave an anodic peak at about 0.25 V, the higher anodic peak of the modified carbon suggests that the capacity of the modified carbon was greater than that of the unmodified carbon. Modified coke carbon

shows about 400 mA h/g with a high degree of reversibility. About 90 mA h/g of increasing capacity compared to that of unmodified carbon, mesophase-pitch and mixture of thereof could be deintercalated of lithium from the outer mesophase-pitch carbon layer of modified carbon.

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