Study on C_xN and C_xS with disordered carbon structure as the anode materials for secondary lithium batteries

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Abstract

C_xN ($x = 12.5$ and 7.3) and C_xS ($x = 31.8$ and 28.0) with disordered carbon structure was synthesized by chemical vapor deposition (CVD) from pyridine and thiophene, respectively, at 800 °C in the absence or presence of chlorine. Lithium was reversibly inserted into these materials. In addition, C_xN and C_xS had larger capacities than pyrolytic carbon synthesized by CVD from benzene at 800 °C. The capacities of C_xN and C_xS increased with increase in nitrogen or sulfur content. In particular, $C_{7.3}N$ had a first cycle discharge capacity of 507 mAh/g in the potential range of 0–3 V versus Li/Li^+, which exceeds the theoretical capacity of graphite (372 mAh/g). $C_{28.0}S$ had a large first cycle discharge capacity of 551 mAh/g. The average interlayer spacing of $C_{7.3}N$ increased during charging and decreased during discharging like that of pyrolytic carbon. On the other hand, the average interlayer spacing of $C_{28.0}S$ hardly changed during charging and discharging. © 1997 Published by Elsevier Science S.A.

Keywords: Lithium batteries; Anode material; Disordered carbon structure. Carbon

1. Introduction

Lithium-ion secondary batteries with carbon as the anode material have been developed. In order to increase the energy density, it is necessary to find carbon materials which have larger reversible capacities. Some researchers already reported carbon materials heat-treated below 1000 °C whose capacity exceeded the theoretical discharge capacity of graphite (372 mAh/g) [1–6]. On the other hand, new anode materials such as B_xC [7,8]. C_xN [9,10] and BC_xN [11,12] with disordered carbon structure have been studied by different research groups. In this study, we synthesized C_xN. rich in nitrogen. and C_xS. The electrochemical behavior and the structural change of these materials during charging/discharging were investigated by constant current measurements and X-ray diffraction (XRD). respectively.

2. Experimental

C_xN ($x = 7.3$ and 12.5) with disordered carbon structure was synthesized by chemical vapor deposition (CVD) proposed by Kouverakis et al. [13] from pyridine or pyridine with chlorine at 800 °C. C_xS ($x = 28.0$ and 31.9) was synthesized, by CVD. from thiophene or thiophene with chlorine at 800 °C. Pyrolytic carbon was also synthesized, by CVD, from benzene at 800 °C for comparsion. The flow rates of pyridine, thiophene and chlorine are shown in Table 1. The compositions and structures were investigated by chemical analysis and XRD, respectively. XRD measurements were performed using a RIGAKU X-ray diffractometer with Cu $K\alpha$ radiation.

The working electrodes were prepared as follows. The carbon powder with a particle size of less than 45 μm was mixed with 10 wt.% polyvinylidene fluoride (PVDF) binder dissolved in N,N-dimethylformamide solution. The mixture was coated on copper foil and dried at 110 °C. It was cut into 1.2 cm × 1.2 cm and pressed by a roll press machine.

Electrochemical measurements were performed at 20 °C using coin-type cells. The electrolyte was 1 M solution of $LiPF_6$ in a 50:50 vol.% mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). Lithium metal was used as a counter electrode. The cells were assembled in an air-filled dry box. Constant-current charge (lithium insertion)/discharge (lithium extraction) measurements were carried out between 0 and 3.0 V (versus Li/Li^+) at a constant-current density of 0.28 mA/cm².

The average interlayer spacing was calculated from the position of the Bragg peak at around 25° using the Bragg

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Table 1
Results of elemental analysis and compositional formula of materials synthesized by CVD from benzene, pyridine or thiophene and pyridine or thiophene with chlorine at 800 °C

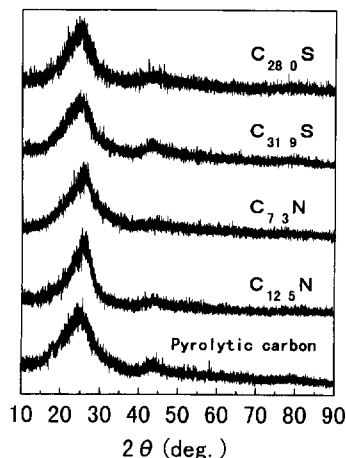| Sample	C (wt %)	N (wt.%)	S (wt %)	H (wt.%)	Cl	Formula
Benzene (0.033 M/h)	97.7			0 81		
Pyridine (0.033 M/h)	89.7	8.40		0 40		$C_{12.5}N$
Pyridine (0.033 M/h) + chlorine (0.144 M/h)	81.2	13 0		0.14	2.82	$C_{7.30}N$
Thiophene (0.033 M/h)	86.0		7 2	0.20		$C_{31.9}S$
Thiophene (0.033 M/h) + chlorine (0 120 M/h)	84.0		8.0	0.10	0.50	$C_{28.0}S$

Fig. 1. XRD patterns of C_xN ($x = 12.5$ and 7.3), C_xS ($x = 31.9$ and 28.0) and pyrolytic carbon powders
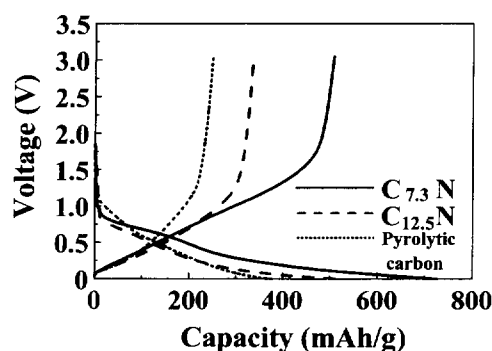

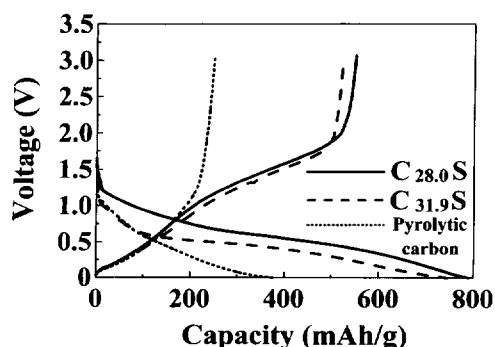Fig. 2 Charge and discharge curves of C_xN ($x = 12.5$ and 7.3) and pyrolytic carbon electrodes

Fig 3 Charge and discharge curves for C_xS ($x = 31.9$ and 28.0) and pyrolytic carbon electrodes.

equation. All ex situ XRD samples were prepared in an air-filled dry box as follows. The cell was disassembled after charging or discharging. The electrode sample was washed with diethylene carbonate and dried under vacuum. The electrode sample was mounted on a glass holder and sealed with a thin aluminium foil to avoid the reaction with water.

3. Results and discussion

The results of elemental analysis and compositional formula of the materials synthesized by various conditions are shown in Table 1. The nitrogen content and sulfur content increased and the hydrogen content decreased in the presence of chlorine. The values of C:N (carbon:nitrogen atomic ratio) in the materials synthesized from pyridine or pyridine with chlorine were 12.5 and 7.3, respectively. The values of C:S (carbon:sulfur atomic ratio) in the materials synthesized from thiophene or thiophene with chlorine were 31.9 and 28.0, respectively. These results indicate that chlorine works to promote the elimination of hydrogen as HCl and prevents the elimination of nitrogen in pyridine or sulfur in thiophene heat-treated at 800 °C.

Fig. 1 shows the XRD patterns of C_xN, C_xS and pyrolytic carbon. In all materials, broad d_{002} peaks were observed at around 25°. These data indicate that C_xN and C_xS have an amorphous structure like disordered carbons.

Figs. 2 and 3 show the charge/discharge curves of C_xN, C_xS and pyrolytic carbon. Table 2 shows also first cycle charge, discharge and irreversible capacities of C_xN, C_xS and pyrolytic carbon. C_xN and C_xS had larger charge and dis-

Table 2
Charge, discharge and irreversible capacities of C_xN ($x = 7.3$ and 12.5), C_xS ($x = 31 9$ and 28.0) and pyrolytic carbon electrodes in EC/DEC containing 1 M $LiPF_6$

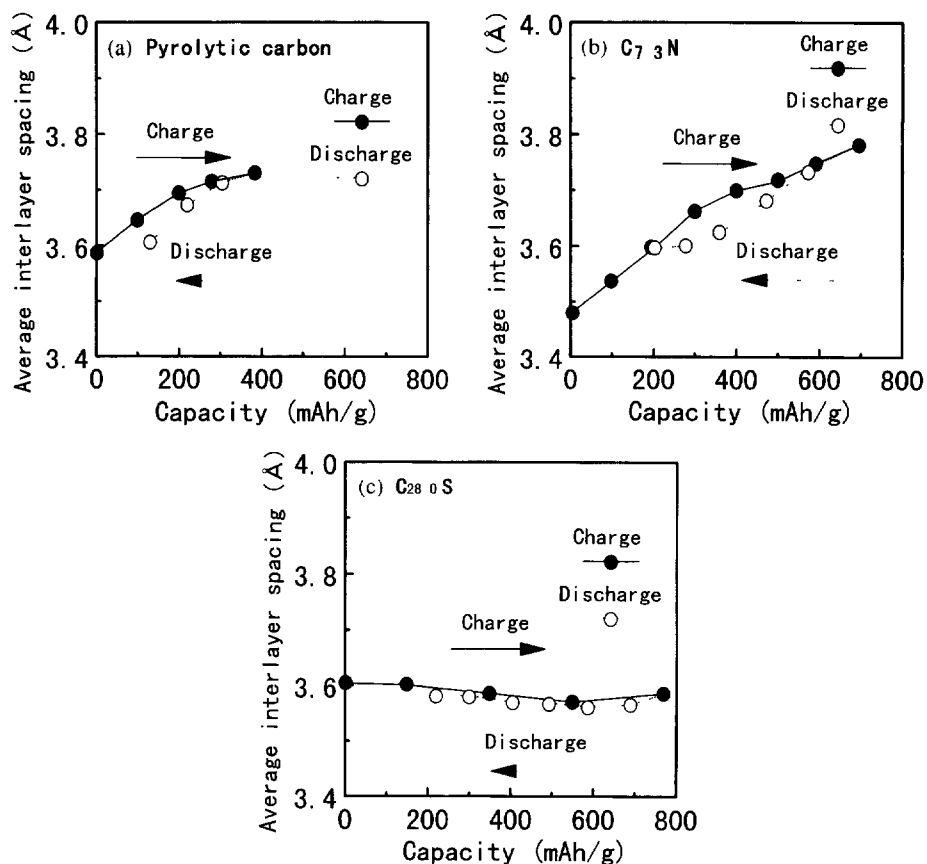| Formula	First charge capacity (mAh/g)	First discharge capacity (mAh/g)	Irreversible capacity (mAh/g)
Pyrolytic carbon	376	249	127
$C_{12.5}N$	516	335	181
$C_{7.30}N$	725	507	218
$C_{31.9}S$	746	523	223
$C_{28.0}S$	791	551	240

Fig. 4 Change of average interlayer spacing of (a) pyrolytic carbon, (b) $C_{7.3}N$, and (c) $C_{28.0}S$ at various charge/discharge states.

charge capacities than pyrolytic carbon. The capacities of C_xN and C_xS increased with increase in nitrogen or sulfur content. In particular, $C_{7.3}N$ had a first discharge capacity of 507 mAh/g, which exceeds the theoretical capacity of graphite (372 mAh/g). C_xN retained 70–76% of initial discharge capacities after the third cycle. $C_{28.0}S$ had a first discharge capacity of 551 mAh/g. C_xS retained 68–85% after third cycle. On the other hand, the irreversible capacities of C_xN and C_xS increased with increase in nitrogen or sulfur content. It has been already reported by Dahn et al. that less nitrogen-containing C_xN (nitrogen content 2.41–5.65 wt.%) synthesized from pyridine by CVD at 850–1050 °C have discharge capacities of about 300 mAh/g and that their irreversible capacities increase with an increase in nitrogen content [9]. Our results were consistent with these results. Furthermore, we found that C_xN richer in nitrogen had an even larger capacity.

It has been already reported by Yata et al. [5] that the capacity of PAS increases with increase in the value of H:C (hydrogen:carbon atomic ratio) in PAS [5]. On the other hand, the hydrogen content in C_xN or C_xS synthesized in this study was less than that in PAS. From these results, we consider that the content of nitrogen in C_xN or sulfur in C_xS has the dominant influence on capacities.

Fig. 4 shows the changes of the average interlayer spacing of $C_{7.3}N$, $C_{28.0}S$ and pyrolytic carbon at various charge/discharge states. In all materials, the staged structures found in

the case of lithium-intercalated graphite were not observed. The average interlayer spacing of $C_{7.3}N$ increased during charging and decreased during discharging like that of pyrolytic carbon. However, it did not completely return to the initial position after full discharging. This result indicates that lithium inserted in C_xN interacts strongly with the disordered carbon sheets and that it is mainly located between the disordered carbon sheets. This result also suggests that some of lithium inserted in C_xN remains between them after full discharging. On the other hand, the average interlayer spacing of $C_{28.0}S$ hardly changed during charging and discharging. From this result, we assume that lithium inserted in C_xS is located not only between the disordered carbon sheets, but also in the cavities or at the edge of them [14–16]. However, the measurements with detailed evidence for this assumption have not yet completed.

It is necessary to investigate in detail the reaction mechanism of C_xN and C_xS during charging/discharging.

4. Conclusions

Major findings in this study are:

1. The charge and discharge capacities of C_xN and C_xS increased with increase in nitrogen or sulfur content.
2. $C_{7.3}N$ and $C_{28.0}S$ had large first cycle discharge capacities of 507 and 551 mAh/g, respectively, in the potential

range of 0–3 V versus Li/Li$^+$, which exceed the theoretical capacity of graphite (372 mAh/g).

3. Lithium inserted in C_xN is mainly located between disordered carbon sheets.

4. C_xN rich in nitrogen and C_xS are interesting anode materials for high energy density secondary lithium batteries.

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