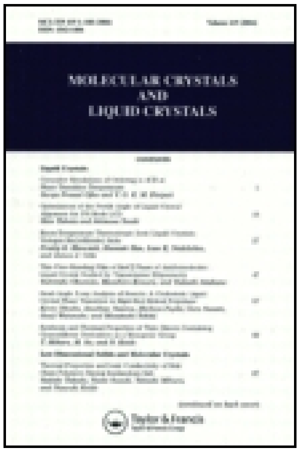

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Synthesis and Electrochemical Behavior of Carbon Alloy C_xN

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Synthesis and electrochemical behavior of carbon alloy C_xN

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Abstract- C_xN compounds were coated on two kind of graphites, natural graphite treated with 94%HNO_3 solution and the natural graphite without treatment, by chemical vapor deposition. XPS and Raman spectroscopy revealed that these materials were not mixtures of C_xN and graphites, but C_xN coated-graphites. As anodes of secondary lithium battery, the C_xN-coated graphites demonstrated the higher capacity than that of natural graphite, good cycleability, and gradual increase in the potential at the last stage of lithium deintercalation reaction.

Keywords: C_xN-coated graphite; secondary lithium battery

INTRODUCTION

Carbon materials such as natural graphite, synthetic graphite, non-graphitizable carbon and so on are currently employed as anodes of rechargeable lithium ion batteries. Many kinds of carbon materials with different morphologies and crystallinity were examined as negative electrodes. Recently nitrogen- and boron-substituted carbons were synthesized and their electrochemical behaviors were also investigated [1-8]. The electrode potentials of these materials gradually increase along with lithium deintercalation process, while the potential of graphite sharply increases at the last stage of discharge. To modify the sharp increase in the potential of graphite anode at the end of lithium ion deintercalation process, we have attempted the coating of natural graphite powder with C_xN by chemical vapor deposition (CVD) using acetonitrile. In this paper, we report the synthesis and electrochemical behavior of C_xN-coated graphite.

EXPERIMENTAL

C_xN-coated carbons were prepared by CVD. Graphites used as starting materials were 94%HNO_3-treated natural graphite (average diameter:ca.7 μm, abbreviated to HNO_3-TNG), and the natural graphite without treatment, (abbreviated to NG). Acetonitrile vapor was introduced into an alumina reactor with nitrogen gas after the temperature of the reactor reached the deposition temperature, 950℃. The flow rate of nitrogen gas mixture was 50mlmin^{-1}. Partial pressure of acetonitrile and total pressure of the gases were 0.9×10^4Pa and 1.0×10^5Pa, respectively. Deposition reactions were performed for 0.5, 1.5 and 3hrs. The following carbon materials were also prepared for comparison:heat-treated HNO_3-TNG, carbon-coated (duration:1.5hr, feed:benzene) HNO_3-TNG and a mixture of heat-treated HNO_3-TNG with 15wt% C_xN. These samples were analysed by X-ray diffractometry, Raman spectroscopy and XPS. Electrode was prepared by mixing 8wt% PVDF with a carbon material as reported in a previous paper [3]. Electrochemical mesurement was conducted by using a three electrodes beaker type cell with 1M $LiClO_4$-EC/DEC(1:1) solution. Charge-discharge cycling was made at a current density of 60mAg^{-1} at 25℃ between 0 and 3.0V vs. Li/Li^+.

RESULTS AND DISCUSSION

Table I shows the surface compositions of the samples examined in the present study. The surface compositions were calculated from the peak areas of XPS spectra taken with different incident angles. The amounts of C_xN deposited on HNO_3-TNG or NG were ca.10wt%, 15wt% and 35wt% for 0.5, 1.5 and 3hrs reactions, respectively. Detection depth increases with increasing incident angle. With decreasing detection depth, the larger amounts of nitrogens were detected in the C_xN-coated samples. With increase in the duration of deposition, the amount of nitrogen detected also increased. The nitrogen concentration thus increases from the inside to the surface of the sample. These results suggest that HNO_3-TNG and NG are coated by C_xN layers. All the samples contained also small amounts of oxygen species, the amount of which was higher around the surface than in the inside of the sample. Oxygen contents in C_xN-coated graphites were comparable to those of NG and carbon-coated HNO_3-TNG.

TABLE I Compositions of natural graphite, surface-treated graphite and C_xN- or carbon-coated graphites, calculated from peak areas of XPS spectra taken with different angles of Mg Kα line.

Sample	Duration of deposition (hour)	Incident angle (°)		
		15°	45°	75°
NG	0	$C_{36.7}O$	$C_{61.5}O$	$C_{78.4}O$
HT-94NG[a]	0	$C_{41.9}O$	$C_{84.5}O$	$C_{104}O$
CN-NG1[b]	1.5	$C_{24.9}NO_{0.6}$	$C_{39.5}NO_{0.5}$	$C_{41.2}NO_{0.5}$
CN-94NG1[c]	0.5	$C_{34.4}NO_{1.2}$	$C_{68.6}NO_{1.1}$	$C_{70.1}NO_{0.9}$
CN-94NG2[c]	1.5	$C_{24.3}NO_{1.3}$	$C_{38.8}NO_{0.5}$	$C_{40.7}NO_{0.4}$
CN-94NG3[c]	3.0	$C_{25.6}NO_{1.3}$	$C_{30.2}NO_{0.6}$	$C_{34.3}NO_{0.6}$
C-94NG[d]	1.5	$C_{40.7}O$	$C_{57.8}O$	$C_{63.5}O$

NG:Natural graphite (average diameter:ca.7μm). a:Heat-treated natural graphite after oxidized with 94%HNO_3. b:C_xN-coated natural graphite. c:C_xN-coated natural graphite after oxidized with 94%HNO_3. d:Carbon-coated natural graphite after oxidized with 94%HNO_3.

Fig 1. shows Raman spectra of heat-treated HNO_3-TNG, the same one mixed with 15wt% C_xN, and C_xN- and carbon-coated HNO_3-TNGs.

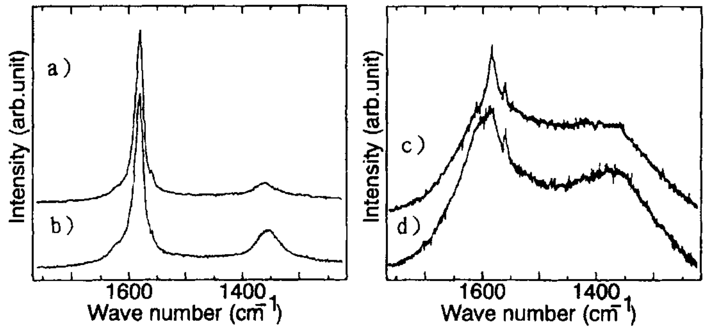

FIGURE 1 Raman spectra of surface-treated graphite, surface-treated graphite mixed with 15wt% C_xN and C_xN- or carbon-coated graphites. a) Heat-treated natural graphite after oxidized with 94%HNO_3. b) Heat-treated natural graphite after oxidized with 94%HNO_3, mixed with 15wt% C_xN. c) C_xN-coated natural graphite after oxidized with 94%HNO_3 (C_xN deposition:1.5hr). d) Carbon-coated natural graphite after oxidized with 94%HNO_3 (carbon deposition:1.5hr).

There is a large difference between the spectrum of the heat-treated HNO_3-TNG mixed with 15wt% C_xN and the spectra of C_xN- and carbon-coated HNO_3-TNGs, while the X-ray diffraction profiles of the C_xN- and carbon-coated samples were almost the same as those of NG and the C_xN-mixed sample. Since detection depth by Raman spectroscopy is much shallower than that by X-ray diffractometry, the result coincides with that C_xN and carbon are coated on HNO_3-TNGs. Coated C_xN or carbon gave two broad peaks at ca.1580cm^{-1} and 1360cm^{-1} or ca.1600cm^{-1} and 1360cm^{-1}, respectively, the profiles of which are similar to those reported in a previous paper [2]. This suggests that the coated C_xN and carbon have the similar crystallinity to that of C_xN and carbon prepared with nickel catalyst.

Fig 2. shows the charge curves at 10th cycle for NG and C_xN-coated HNO_3-TNG samples prepared by 0.5, 1.5 and 3hrs reactions.

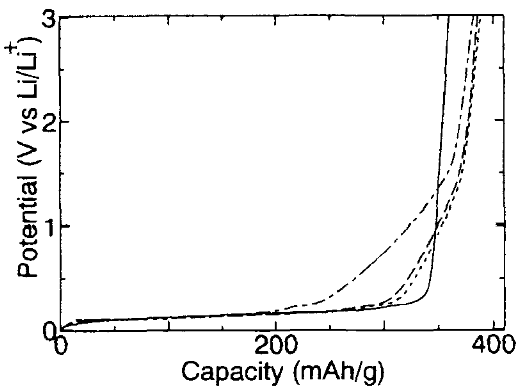

FIGURE 2 Charge curves at 10th cycle of natural graphite and CxN-coated natural graphites.

———— : Natural graphite.
- - - - - - - : CxN-coated natural graphite after oxidized with 94%HNO_3 (C_xN deposition:0.5hr).
— — — — : CxN-coated natural graphite after oxidized with 94%HNO_3 (C_xN deposition:1.5hr).
— - — - - : CxN-coated natural graphite after oxidized with 94%HNO_3 (C_xN deposition:3hr).

Table II shows the charge-discharge capacities and coulombic efficiencies at 1st and 10th cycles of the samples examined in the present study.

TABLE II Charge and discharge capacities between 0 and 1V vs. Li/Li and coulombic efficiencies of natural graphite, surface-treated natural graphite and C_xN- or carbon-coated graphites.

	1st cycle			10th cycle		
Sample name	Discharge $(mAhg^{-1})$	Charge $(mAhg^{-1})$	Q (%)	Discharge $(mAhg^{-1})$	Charge $(mAhg^{-1})$	Q (%)
NG	444	348	78.4	364	354	97.3
HT-94NG[a]	451	320	71.0	350	332	94.9
CN-NG[b]	497	349	70.2	354	328	92.7
CN-94NG1[c]	542	351	64.8	384	355	92.6
CN-94NG2[c]	529	353	66.7	380	351	92.4
CN-94NG3[c]	588	354	60.3	362	323	89.3
C-94NG[d]	452	314	69.5	334	308	92.3

NG:Natural graphite (average diameter:ca.7μm). a:Heat-treated natural graphite after oxidized with 94%HNO_3. b:C_xN-coated natural graphite. c:C_xN-coated natural graphite after oxidized with 94%HNO_3. d:Carbon-coated natural graphite after oxidized with 94%HNO_3.
Current : 60mAg^{-1}.

NG shows a sharp increase in the potential at the last stage of lithium ion deintercalation with the first charge capacity of 348mAhg^{-1} at 60mAg^{-1}. The profile of the charge curve of heat-treated HNO_3-TNG was almost the same as that of NG, showing low and constant potential at early stage and sharply increasing at last stage, whereas the first charge capacity was 320mAhg^{-1} lower than that for NG. The cycleability of heat-treated HNO_3-TNG was comparable to that of NG. On the other hand, C_xN-coated HNO_3-TNG samples prepared by 0.5 and 1.5hrs reactions demonstrated gradual increase in the potential at the last stage of charging with the first charge capacities of 351mAhg^{-1} and 353mAhg^{-1}, respectivery, which were slightly higher than that of NG. No decrease in the charge capacity was observed for these two C_xN-coated HNO_3-TNG samples. The potential of C_xN-coated HNO_3-TNG prepared by 3hrs deposition started to increase at the earlier stage than those for other two C_xN-coated HNO_3-TNG samples. It is due to the larger amount of C_xN deposited by longer duration of the reaction. A slight decrease in the charge capacity was found at 10th cycle, though it is smaller than that observed of C_xN-coated NG without surface oxidation. Carbon-coated HNO_3-TNG also showed gradual increase in the potential at the last stage of the reaction. However, the first charge capacity was 314mAhg^{-1} lower than that of NG.

The present study has revealed that C_xN coating to graphite induces the gradual increase in the potential at the last stage of lithium ion deintercalation process, keeping the comparable capacity to that for NG between 0 and 1V. Thus the thin C_xN coating to HNO_3-TNG would have several advantages without decrease in the cycleability. The deposition of C_xN to NG and to HNO_3-TNG for 3hrs, however, did not give sufficient results. Because the C_xN deposition to the HNO_3-TNG proceeds in a reductive atmosphere, it may be possible that carbon-carbon bond formation occurs in part between HNO_3-TNG and deposited C_xN by eliminating the oxygen atoms as carbon oxide gases. If carbon-carbon bonds are formed to some extent, one can expect the growth of crystallized C_xN layers on HNO_3-TNG, which is consistent with the result indicated by the Raman spectra. There is a distinct difference in the cycleability between the samples prepared by C_xN coating to NG and HNO_3-TNG. The C_xN coating to NG may have less possibility for carbon-carbon bond formation. Even if the C_xN coating is made to HNO_3-TNG, the longer duration of the coating (3hrs) would cause the growth of less crystallized C_xN layers as the thickness of the coated C_xN layers increases.

A problem on C_xN-coated HNO_3-TNG is the slightly low coulombic efficiencies at first cycle. The coulombic efficiencies at first cycle were about 8~10% lower than that of NG. Oxygen and nitrogen in the samples may be responsible for the low coulombic efficiencies. Coulombic efficiencies of heat-treated HNO_3-TNG and carbon-coated HNO_3-TNG are close to those of C_xN-coated HNO_3-TNG samples, because the oxygen contents in these samples were comparable to those of C_xN-coated graphites.

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