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Electrochemical behavior of carbon alloy $C_x N$ prepared by CVD using a nickel catalyst

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Abstract—Carbon–nitrogen layered compounds, $C_{14}N$ to $C_{62}N$ have been synthesized by thermal decomposition of acetonitrile at 800–1100°C in the presence of nickel catalyst. The C_xN samples prepared with nickel had higher crystallinity and less pyridine-type nitrogens existing at the edge of graphene layers than C_xN prepared in the absence of nickel. With an increase in the deposition temperature of C_xN , the cycleability for electrochemical intercalation–deintercalation of lithium ions was improved and the profile of the charge–discharge curve approached that of natural graphite powder due to an increase in the crystallinity and a decrease in the incorporated nitrogens. Surface oxidation of the C_xN by nitric acid solutions gave rise to an increase in the surface oxygens and a slight decrease in nitrogens without any change of crystallinity. The surface modification improved the cycleability for lithium ion intercalation–deintercalation reaction. © 1997 Elsevier Science Ltd. All rights reserved.

Key words: C_xN, CVD, lithium ion battery, surface modification.

INTRODUCTION

A graphite intercalation compound of lithium is employed as a negative electrode for the lithium ion secondary battery to avoid the dendrite formation at the negative electrode. Carbon material with various morphologies and crystallinity have been examined from the electrochemical and structural viewpoints [1,2]. It was discovered that highly crystallized graphites and low crystallinity carbons have high discharge capacities, whereas the capacities are less in carbons with intermediate crystallinity [1,2]. Recently boron- and/or nitrogen-substituted carbons BC_xN , BC_x and C_xN were synthesized by CVD and their electrochemical behavior as negative electrodes were investigated [3-10]. These compounds constitute a new class of candidates for negative electrodes with modified electronic structures, having different chemical interactions with lithium ions. On one hand, graphite with high crystallinity such as natural graphite shows flat and low

potentials in the lithium ion deintercalation process, however, the potential sharply increases at the end of the process. On the other hand, such carbon materials with lower crystallinity than natural graphite as petroleum coke or boron- or nitrogen-substituted carbon exhibit gradual increase in potential in lithium ion deintercalation process. It was reported that carbon-nitrogen compound C_xN was not suitable as a negative electrode because a significant amount of nitrogen existing at the edge of graphene layers was responsible for the irreversible capacity of $C_x N$, whereas the boron-carbon compound BC_x showed the high performance without such an irreversible capacity [6-8]. Substution of boron for carbon is more easily carried out than nitrogen substitution because of reduced structural strain in BC_x . This may be the main reason why nitrogen atoms are often replaced at the edge of graphene layers. It was also found that air oxidation of carbon materials at high temperatures effectively improved their electrochemical properties as negative electrodes in several cases [11-14]. Detailed studies were performed on the catalytic growth of

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Reaction temperature (°C)	Composition	Morphology	Diameter (µm)	<i>d</i> (002) (nm)	FWHM (°)	<i>L</i> _c (002) (nm)
1100	C ₆₂ N ^a	Particle	_	0.335	0.575	17
1050	$C_{33}N^a$	Particle	-	0.335	0.663	15
1000	$C_{20}N^a$	Particle	2-3	0.336	0.775	13
900	$C_{21}N^a$	Particle Fiber	2−3 ≈0.5	0.335	0.900	11
800	$C_{40}N^{a}$	Fiber	≈3, 0.3	0.337	1.250	8
1000	$\mathrm{C}_{14}\mathrm{NH}_{0.6}^\mathrm{b}$	_	_	0.340	2.850	3
900	C ^c	_	_	0.336	0.938	10

Compositions, morphologies and	XRD data of	$C_x N$ and carbor	samples
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^aPrepared from acetonitrile (partial pressure: 9.2×10^3 Pa) with Ni catalyst.

^bPrepared from acetonitrile (partial pressure: 9.2×10^3 Pa) without catalyst.

^cPrepared from benzene (partial pressure: 9.2×10^3 Pa) with Ni catalyst.

carbon filaments on iron–nickel alloy [15–18]. Growth of carbon filaments are influenced by the composition of iron–nickel alloy and additives. The C_xN filaments and particles with high crystallinity have been synthesized by thermal decomposition of acetonitrile or pyridine using nickel or cobalt catalyst at 800–1100°C [19]. The electrochemical behavior of C_xN samples thus prepared has been also reported in a short communication [20]. After that, we have obtained more better electrochemical data by using new C_xN electrodes instead of pellet electrodes. In this paper, we report the synthesis of a carbon–nitrogen compound C_xN with high crystallinity and the electrochemical behavior of various C_xN samples.

EXPERIMENTAL

Synthesis and surface oxidation of C_xN samples

The $C_x N$ samples were synthesized by thermal decomposition of acetonitrile (purity: 99%) at 800-1100°C. A mixture of acetonitrile and nitrogen gas (partial pressure of acetonitrile: 9.2×10^3 Pa) was allowed to flow over metallic nickel powder in an alumina boat, which was placed in an alumina reactor, with total flow rate 55 mL min⁻¹. The 400-500 mg of the $C_x N$ sample was obtained by a half day reaction. The C_xN samples were analyzed by elemental analysis, X-ray diffractometry, SEM, TEM and XPS. Binding energies for XPS peaks were determined relative to that of C1s electron of graphite, 284.3 eV without charging correction. The spectrometer used was Ulvac Phi Model 5500. The following carbon materials were used for comparison: natural graphite powder (average diameter: ca. 7 μ m), C_xN prepared at 1000°C in the absence of nickel, and carbon, prepared by pyrolysis of benzene at 900°C in the presence of nickel.

The surface oxidation of $C_x N$ samples was conducted in 3, 6 or 10 M (M: mol dm⁻³) HNO₃ solution under stirring for half a day and afterward

with ultrasonic agitation for 1 h. The oxidized samples were dried at 120°C under a vacuum for half a day prior to use.

Measurement of specific surface areas of $C_x N$ and carbon samples

Specific surface areas of as-prepared and surfaceoxidized $C_x N$ and carbon samples were measured by nitrogen gas adsorption (BET method) using Micromeritics ASAP 2000. Samples were pretreated at 120°C under 0.26 Pa for 3 h prior to nitrogen gas adsorption.

Electrochemical measurement

The working electrode was prepared as follows. $C_x N$ powder (ca. 30 mg) was dispersed into poly (vinylidene fluoride) (PVDF)-dissolved 1-methyl-2pyrrolidone (CH₃NC₄H₆O ca. 86 mg) so that the concentration of PVDF might be 8 wt% in CxN and PVDF mixture without solvent. The C_xN-suspended solution was then painted on a nickel grid, which was dried at 100°C for 2 h and further at 180°C overnight to remove the solvent. The amount of C_xN stuck on a nickel grid was calculated from the weight increase. The electrochemical measurement was conducted using a beaker-type three-electrodes cell with a cap in a dry box filled by argon. The electrolyte solution was 1 M LiClO₄-EC/DEC (1:1) supplied by Mitsubishi Chemical Corporation. The electrochemical behavior was evaluated by charge-discharge cycling at a current density of 30 mA g^{-1} at 25° C.

RESULTS AND DISCUSSION

Compositions, structure and crystallinity of asprepared and surface-modified $C_x N$ samples

Table 1 shows the typical examples of compositions, morphologies and X-ray diffraction data of C_xN samples prepared at 800–1100°C with nickel catalyst in comparison with those of C_xN prepared

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Table 1.

a)

b)



 $30 \,\mu$ m

Fig. 1. SEM images of $C_{20}N$ (a) and $C_{21}N$ (b) prepared with nickel catalyst at 1000°C and 900°C, respectively.

without the catalyst and carbon prepared from benzene with nickel. The catalytic effect of iron-nickel alloy on carbon filament growth was already investigated [15–18]. It was also found that metallic nickel or cobalt powder well catalyzes the growth of high crystalline C_xN filaments and particles [19]. It is known that iron is a good catalyst for the growth of well crystallized carbon fibers, however, the use of metallic iron powder was unsuccessful for the preparation of C_xN . Iron was deactivated during CVD probably due to the reaction with nitrogen [21].

 C_xN samples with compositions $C_{14}N$ to $C_{62}N$ were obtained in the temperature range 800-1000°C. No hydrogen was detected by elemental analysis for all the samples prepared using nickel catalyst, whereas less crystallized C14NH0.6 having hydrogen was obtained at 1000°C in the absence of the catalyst. The products prepared at 900°C and 1000°C had the highest nitrogen contents, as C14N to $C_{21}N$. Nitrogen concentrations were much less in the products deposited at the lower and higher temperatures, 800, 1050 and 1100°C (C₄₀N, C₃₃N and C₆₂N, respectively). Two different factors should be considered for the temperature dependency of nitrogen concentration. Nitrogen solubility in nickel is estimated to increase with increase in the temperature from the positive values of enthalpy and entropy changes for nitrogen dissolution in nickel [22], which would enhance the incorporation of nitrogen in $C_x N$. On the other hand, the temperature raise facilitates the crystallization of C_xN with reducing the structural strain induced by nitrogen incorporation in graphene layers. This effect would lead to the decrease in nitrogen content in $C_x N$.

The C_xN samples prepared were apparently black powder. However, SEM and TEM observations revealed that the products obtained at 800°C were fibrous C_xN with diameters of *ca*. 3 and 0.3 μ m, those at 900°C were mixtures of fibrous C_xN with diameters of *ca*. 0.5 μ m and fine C_xN particles with diameters of 2–3 μ m, and those at 1000°C were C_xN particles with diameters of 2–3 μ m. Typical SEM images of C_xN samples prepared at 900 and 1000°C are shown in Fig. 1.

It was also found by X-ray diffraction and elemental analysis that ca. 7 wt% nickel was mixed with $C_x N$. The $C_x N$ samples obtained using nickel catalyst exhibited the same (002), (004), (100), (101) and (110) diffraction lines as usual carbon materials, which indicates that $C_x N$ has the same layered sheet structure as carbon or graphite. In this paper, we use the same indexes for $C_x N$ samples as used for carbon materials. The d(002)values and half widths of (002) diffraction lines decreased from 0.337 to 0.335 nm and from 1.250 to 0.575°, respectively, with increasing thermal decomposition temperature of acetonitrile from 800 to 1100°C as given in Table 1. Both d(002) values and half widths were smaller than those for C14NH0.6 prepared without nickel, indicating that the $C_x N$ samples synthesized using nickel have much higher crystallinity than that prepared without nickel. Therefore, the crystallite sizes along the *c*-axis, that is $L_{c}(002)$ values calculated from the half widths of (002) diffraction lines were also much larger than that of C14NH0.6, increasing with an increase in temperature. On the other hand, the carbon prepared by pyrolysis of benzene at 900°C with nickel catalyst shows similar values in d(002), half width and crystallite size to those of C21N prepared at 900°C with nickel. The obtained results indicate that nickel effectively facilitates the growth and crystallization of C_xN filaments and particles as reported in the literatures [15–19].

The results of surface analysis by XPS are given in Figs 2 and 3 and Table 2. Figure 2 shows N_{1s} spectra for C_xN samples prepared at 1000°C with and without nickel catalyst. C_xN samples prepared at 900°C have the same profiles as those shown in Fig. 2. $C_{20}N$ prepared with nickel exhibits three peaks at 398.8, 400.9 and 402.3 eV, which are ascribed to pyridine-type nitrogen existing at the edge of graphene layer, quarternary nitrogen incorporated in graphene layer and pyridine-*N*-oxide,



at the edge of the graphene layer, respectively [23–26]. A small amount of oxygen detected may have been introduced into $C_x N$ by exposure to the air.



Fig. 2. N_{1s} XPS spectra of C_xN samples prepared at 1000°C. (a) $C_{20}N$ as-prepared with nickel, (b) $C_{20}N$ oxidized by 6 M HNO₃ solution and (c) $C_{14}NH_{0.6}$ as-prepared without nickel.

The peak at 400.9 eV indicating nitrogen atoms incorporated in the graphene layer has a higher intensity than other two peaks located at 398.8 and 402.3 eV, corresponding to nitrogen atoms existing at the edge of the graphene layer when C_xN is prepared using nickel catalyst [Fig. 2(a)], whereas C_xN prepared without nickel has a large amount of pyridine-type nitrogens [Fig. 2(c)]. The use of nickel catalyst is thus important not only because the crystallinity of C_xN is significantly improved as mentioned above, but also because the pyridinetype nitrogens existing at the edge of graphene layers are highly reduced. On the other hand, $C_{20}N$ oxidized by 6 M HNO₃ solution shows a new peak



Fig. 3. O_{1s} XPS spectra of C_xN samples prepared at 1000°C. (a) $C_{20}N$ as-prepared with nickel, (b) $C_{20}N$ oxidized by 6 M HNO₃ solution.

between those for quarternary and pyridine-Noxide. The spectrum was observed at slightly lower binding energy probably by the loss of charging due to the decrease of nitrogen in the sample. The new peak at 399.2 eV in Fig. 2(b) may be ascribed to amine (-NH₂), which may be formed along with a carboxyl group by carbon-nitrogen bond rupture of pyridine-N-oxide. In the Ols spectra shown in Fig. 3, two peaks indicating carbonyl and hyroxyl groups were observed at 531.0-531.2 and 532.4-532.8 eV, respectively, in both as-prepared and surface-modified samples with a small peak attributed to adsorbed water molecules at ca. 535 eV. Corresponding to Ols spectra, the shifted peaks were observed in Cls spectra at 285.6 and 287.9 eV, indicating carbonyl and hydroxyl groups, and carboxyl group, respectively. The contribution due to carbon-nitrogen bonds is included in the Cls peak located at 285.6 eV.

Table 2.

N/C and O/C ratios at the C_xN and carbon sample surfaces, obtained from peak areas of XPS spectra

	$C_{20}N^a$	3 M HNO ₃	6 M HNO ₃	10 M HNO ₃
N/C (×10 ²) O/C (×10 ²)	5.95 2.80	5.49 10.6	5.61 10.1	5.18 10.9
	$C_{21}N^b$	3 M HNO ₃	6 M HNO ₃	10 M HNO ₃
N/C (×10 ²) O/C (×10 ²)	6.49 2.60	4.52 10.1	3.70 11.9	5.32 11.0
	C ^c	_	6 M HNO ₃	_
O/C (×10 ²)	4.20	_	4.29	

^aPrepared from acetonitrile at 1000°C with Ni catalyst.

^bPrepared from acetonitrile at 900°C with Ni catalyst.

^cPrepared from benzene at 900°C with Ni catalyst.

Reaction		Specific surface areas			
temperature (°C)	Composition	As-prepared sample (m ² g ⁻¹)	Oxidized sample ^a (m ² g ⁻¹)		
1100	$C_{62}N^b$	1.55	-		
1000	$C_{20}N^b$	1.50	3.20		
900	$C_{21}N^b$	2.30	4.40		
800	$\mathrm{C}_{40}\mathrm{N}^\mathrm{b}$	10.5	-		
1000	$C_{14}NH_{0.6}^c$	16.0	_		
900	C^d	6.90	5.40		

Table 3.	
Specific surface areas of as-prepared and surface-oxidized C _v N and carbon samples	

^aOxidized by 6 M HNO₃ solution.

^bPrepared from acetonitrile (partial pressure: 9.2×10^3 Pa) with Ni catalyst.

^cPrepared from benzene (partial pressure: 9.2×10^3 Pa) without Ni catalyst.

^dPrepared from benzene (partial pressure: 9.2×10^3 Pa) with Ni catalyst.

Table 2 summarizes the surface concentrations of nitrogen and oxygen of as-prepared and surfacemodified samples and carbon derived from benzene. The amounts of nitrogens were somewhat decreased and at the same time those of oxygen were largely increased in both $C_{20}N$ and $C_{21}N$, whereas the amounts of oxygen in benzene-derived carbon were nearly the same before and after the oxidation. No



Fig. 4. Charge–discharge curves for $C_{21}N$ prepared from acetonitrile at 900°C with nickel catalyst. (a) As-prepared $C_{21}N$, (b) $C_{21}N$ oxidized by 6 M HNO₃ solution. lst, 5th and 10th cycles at 30 mAg⁻¹.

large dependency was found on the concentrations of nitric acid solutions used for the sample oxidation.

Table 3 shows the specific surface areas of asprepared and surface-oxidized CxN and carbon samples. The specific surface areas of C_xN samples prepared with nickel catalyst were significantly smaller than that of C14NH0.6 prepared without catalyst, having a trend to decrease with increasing deposition temperature. The carbon prepared at 900°C from benzene had a larger surface area than C₂₁N prepared at the same temperature. These trends well coincide with the difference in crystallinity of the $C_x N$ and carbon samples, shown by the X-ray diffraction data in Table 1, that is, the surface area is reduced with increasing crystallinity of the sample. The surface areas of $C_{20}N$ and $C_{21}N$ were enlarged approximately twice by the oxidation. The increased surface oxygens and areas given in Tables 2 and 3 suggest that C_xN samples were highly oxidized in addition to the formation of amine (-NH2) and carboxyl groups by carbonnitrogen bond rupture of pyridine-N-oxide. On the other hand, the specific surface area of benzenederived carbon slightly decreased by oxidation. In addition, the amount of surface oxygen was nearly constant before and after the oxidation as shown in Table 2. These results would imply that the disordered parts of benzene-derived carbon were lost as gaseous carbon oxides.

Charge-discharge behavior of C_xN samples

Figures 4, 5, 6 and 7 show typical charge–discharge curves for as-prepared and surface-modified $C_x N$ samples. For comparison, those of natural graphite powder and benzene-derived carbon are also shown in Figs 8 and 9. In the electrochemical cell used in this study, the electrodes of carbon materials are positive electrodes since the counter electrode is lithium metal, therefore, the deintercalation of lithium ions is a charge process. Flat potential curves and nearly constant charge capacities were observed for natural graphite electrode as seen in



Fig. 5. Charge–discharge curves for $C_{20}N$ prepared from acetonitrile at 1000°C with nickel catalyst. (a) As-prepared $C_{20}N$ and (b) $C_{20}N$ oxidized by 3 M HNO₃ solution. lst, 5th and 10th cycles at 30 mAg⁻¹.

Fig. 8. The charge capacities of natural graphite powder up to 3 V vs Li were as high as 360 mAh g^{-1} . The benzene-derived carbon, however, exhibited a gradual change in the potential with less charge capacity of 310 mAh g⁻¹ than natural graphite powder because of its lower crystallinity, as shown in Fig. 9. The cycleability of benzene-derived carbon was comparable to that of natural graphite powder, although the first coulombic efficiency was lower. The potentials of $C_x N$ electrodes gradually decreased and increased with lithium ion intercalation and deintercalation. Not only the variation of the potentials, but also the capacity and cycleability were dependent on the nitrogen content and crystallinity of C_xN samples. Nitrogen incorporation in carbon induced the large polarization for lithium ion deintercalation process and a small one for the intercalation process. The polarization observed suggests that the lithium ion interacts with a lone pair of the nitrogen atom in $C_x N$. Table 1 indicates that nitrogen content decreased and crystallinity increased with increase in the deposition temperature from 900 to 1100°C. According to this trend in the nitrogen content and crystallinity of $C_x N$, the profile of the charge-discharge curves of C_xN samples approached those of benzene-derived carbon and natural graphite powder as shown in Figs 6 and 7, while the capacity decreased with increasing



Fig. 6. Charge–discharge curves for $C_{33}N$ prepared from acetonitrile at 1050°C with nickel catalyst. lst, 5th and 10th cycles at 30 mAg⁻¹.

deposition temperature. The charge capacities somewhat decreased with increasing cycle number in both $C_{20}N$ and $C_{21}N$ as-prepared at 1000 and 900°C, respectively. The cycleability was, however, improved for $C_{33}N$ and $C_{62}N$ deposited at 1050 and 1100°C probably due to the increase in the crystallinity. Comparing the charge–discharge curves of $C_{20}N$ prepared at 1000°C with those of $C_{21}N$ prepared at 900°C, both charge and discharge capacities were larger in $C_{20}N$ than in $C_{21}N$. This may be because $C_{20}N$ has slightly higher crystallinity than $C_{21}N$ as given in Table 1.

Surface oxidation of C_xN samples by nitric acid solutions significantly improve the cycleability and changed the charge-discharge profiles as shown in Figs 4(b) and 5(b). The surface-modified $C_{21}N$ and $C_{20}N$ gave the similar charge-discharge curves to each other in spite of the different concentrations of nitric acid solutions employed for the oxidation. In Figs 4(b) and 5(b), the smaller polarization is observed for the first discharge curves and the larger one for the charge curves. The smaller polarization for the first discharge curves would be induced by the interaction of lithium ions with surface oxygen groups. In the charging process, the po-



Fig. 7. Charge–discharge curves for $C_{62}N$ prepared from acetonitrile at 1100°C with nickel catalyst. lst, 5th and 10th cycles at 30 mAg⁻¹.



Fig. 8. Charge–discharge curves for natural graphite (average diameter: 7 μ m). lst, 5th and 10th cycles at 30 mA g⁻¹.

tential varied almost linearly after *ca.* 170 mAh g⁻¹, which may be due to the interaction of lithium ions with amine (—NH₂) formed by nitric acid treatment. The charge and discharge capacities were slightly reduced at the 2nd cycle, but almost no change in the charge–discharge curves was observed after 2nd cycle in both $C_{21}N$ and $C_{20}N$. One reason for the improvement in cycleability may be the enlargement of surface areas by oxidation.

Surface oxidation using nitric acid solution did not improve the charge–discharge behavior of benzene-derived carbon. The charge–discharge curves of benzene-derived carbon in Fig. 9 are rather similar to those for $C_{21}N$ and $C_{20}N$ in the potential range between 0.0 and 1.0 V, whereas they were close to those for natural graphite in the range between 1.0 V and 3.0 V (Fig. 8). Considering that the crystallinity of benzene-derived carbon is similar to that of $C_{21}N$ prepared at 900°C, the main differences of $C_{21}N$ from benzene-derived carbon would be the nitrogen incorporation into carbon and higher surface oxygen concentration. These factors may give rise to an increase in the chemical interaction with lithium ions. The charge capacities of



Fig. 9. Charge–discharge curves for benzene-derived carbon prepared at 900°C and oxidised by 10 M HNO₃ solution. lst, 5th and 10th cycles at 30 mA g^{-1} .



Fig. 10. Change in the charge capacities of as-prepared and surface-modified $C_{20}Ns$, as-prepared $C_{14}NH_{0.6}$ and natural graphite as a function of cycle number. $\bigcirc C_{20}N$ as-prepared at 1000°C with nickel catalyst, $\spadesuit C_{20}N$ oxidized by 3 M HNO₃ solution, $\square C_{20}N$ oxidized by 6 M HNO₃ solution, $\blacksquare C_{14}NH_{0.6}$ as-prepared at 1000°C without nickel and \blacktriangle natural graphite (average diameter: 7 μ m). Current: 30 mA g⁻¹, potential: 0.0–3.0 V.

benzene-derived carbons are lower than that of natural graphite powder probably because of its lower crystallinity.

Figures 10 and 11 show the change in the charge capacities of $C_x N$ samples in comparison with other materials as a function of cycle number. As shown in Fig. 10, $C_{20}N$ prepared at 1000°C with nickel exhibited lower charge capacities than $C_{14}NH_{0.6}$



Fig. 11. Change in the charge capacities of as-prepared and surface-modified $C_{21}Ns$ and benzene-derived carbon as a function of cycle number. $\bigcirc C_{21}N$ as-prepared at 900°C with nickel catalyst, $\blacklozenge C_{21}N$ oxidized by 3 M HNO₃ solution, $\square C_{21}N$ oxidized by 6 M HNO₃ solution, $\blacksquare C_{21}N$ oxidized by 10 M HNO₃ solution and \blacktriangle carbon prepared from benzene at 900°C with nickel catalyst. Current: 30 mA g⁻¹, potential: 0.0–3.0 V.

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	1st cycle			10th cycle			
Composi- tion	Discharge (mAh g ⁻¹)	Charge (mAh g ⁻¹)	Q (%)	Discharge (mAh g ⁻¹)	Charge (mAh g ⁻¹)	Q (%)	
C ₆₂ N ^a	404	302	74.7	308	301	97.7	
C ₃₃ N ^a	487	332	68.2	325	320	98.5	
$C_{20}N^a$	567	408	72.0	387	391	98.4	
$C_{20}N^b$	657	414	63.0	420	411	97.8	
$C_{21}N^a$	560	390	69.6	367	362	98.6	
$C_{21}N^{c}$	697	424	60.8	418	408	97.6	
C ₁₄ NH ^d _{0.6}	677	430	63.5	393	382	97.2	
C ^e	435	306	70.3	312	306	98.1	

Charge and discharge capacities between 0 and 3 V vs Li/Li⁺ and coulombic efficiencies of C_xN and carbon samples

^aPrepared from acetonitrile (partial pressure: 9.2×10^3 Pa) with Ni catalyst.

^bOxidized by 3 M HNO₃ solution.

^cOxidized by 6 M HNO₃ solution.

^dPrepared from acetonitrile (partial pressure: 9.2×10^3 Pa) without Ni catalyst.

^ePrepared from benzene (partial pressure: 9.2×10^3 Pa) with Ni catalyst.

prepared without nickel at the same temperature. However, their capacities approached each other after the 7th cycle, showing the similar trend with cycle number. The surface oxidation of C₂₀N by 3 M and 6 M HNO3 solutions improved the cycling behavior. $C_{20}N$ as-prepared at $1000^\circ C$ with nickel exhibited higher charge capacities than C21N as prepared at 900°C probably because C₂₀N had slightly higher crystallinity than C21N. The oxidation of C₂₁N with 6 M and 10 M nitric acid solutions significantly improved cycling behavior as shown in Fig. 11. The charge capacity was increased and stabilized with increasing concentration of nitric acid. The optimum concentrations were 3 M and 6 M HNO₃ solutions for C₂₀N prepared at 1000°C and 6 M and 10 M HNO3 solutions for C21N pre-



Fig. 12. Coulombic efficiencies for carbon materials as a function of cycle number. $\blacklozenge C_{14}NH_{0.6}$ prepared at 1000°C without nickel, $\blacklozenge C_{20}N$ oxidized by 3 M HNO₃ solution, $\bigcirc C_{21}N$ oxidized by 6 M HNO₃ solution, \blacksquare natural graphite and \square benzene-derived carbon.

pared at 900°C. A possible explanation may be that the stronger oxidation is needed to enlarge the surface area of the fibrous component of $C_{21}N$ for easier lithium ion intercalation and deintercalation.

Figure 12 shows the coulombic efficiencies for $C_{14}NH_{0.6}$, $C_{20}N$, $C_{21}N$, natural graphite powder and benzene-derived carbon. The charge and discharge capacities and coulombic efficiencies at 1st and 10th cycles are summarized in Table 4. The coulombic efficiencies of $C_{14}NH_{0.6}$ were inferior to those of other samples. A problem in the electrochemical characteristics of C_xN samples as-prepared with nickel catalyst is that their coulombic efficiencies were 68–75% lower than that of natural graphite powder. Surface oxidation further reduced the first coulombic efficiencies by 9% in the case of $C_{20}N$ and $C_{21}N$ as given in Table 4. The decrease in the efficiencies may be due to an increase in the surface oxygen groups by oxidation.

Factors influencing the charge-discharge behavior

The charge-discharge behavior should be discussed in relation with several structural and compositional factors of carbon materials, which would be the crystallinity, surface area, chemical species interacting with lithium ions and so on. The influence of the crystallinity on the charge-discharge behavior was intensively investigated [1,2]. It is known that highly crystallized graphites and poorly crystalline carbons have high discharge capacities [1, 2]. In the present study, $C_x N$ samples with high crystallinity and less pyridine-type nitrogens were obtained by the use of nickel powder as a catalyst for the CVD reaction. With increasing deposition temperature, the crystallinity of $C_x N$ increases, while its nitrogen concentration and specific surface area decrease. The increase in crystallinity and decrease in nitrogen concentration improve the cycleability and induce the approach of the charge-

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Table 4.

discharge curve to that of natural graphite powder, while the capacity is somewhat reduced. It has been also shown that surface oxidation is a useful method to improve the cycleability of C_xN , however, the increased amount of oxygen reduces the first coulombic efficiency.

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