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Effect of Carbon Coating on Electrochemical Performance of Treated Natural Graphite as Lithium-Ion Battery Anode Material

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Carbon-coated natural graphite has been prepared by thermal vapor decomposition treatment of natural graphite at 1000°C. Natural graphite coated with carbon showed much better electrochemical performance as an anode material in both propylene carbonate-based and ethylene carbonate-based electrolytes than "bare" natural graphite. The effect of carbon coating on the electrochemical performance was investigated by solid-state ⁷Li-NMR in conjunction with standard electrochemical techniques. © 2000 The Electrochemical Society. S0013-4651(99)08-083-0. All rights reserved.

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Accompanying the development of lithium-ion batteries, worldwide efforts have been devoted to the application of carbonaceous materials as anodes (negative electrodes) in these batteries. Among the wide spectrum of carbonaceous materials, natural graphite appears to be the most suitable candidate because of its many advantages, such as its high capacity of 372 mAh/g (with a stoichiometry of LiC₆), low and flat potential profile, and reasonable cost. As far as we are aware, graphite and graphitized carbon have been used in many lithium-ion battery commercial products on the market to date. However, graphite has an important disadvantage which may limit its further utilization as the anode material in lithium-ion batteries: its sensitivity to certain electrolytes. Ethylene carbonate (EC) and propylene carbonate (PC) are the most commonly used high permittivity solvents for lithium-ion batteries. It is well known that ECbased electrolytes are always used with graphite anodes in lithiumion batteries, whereas PC-based electrolytes are not compatible with graphite anodes because PC decomposes on graphite's surface accompanied by graphite exfoliation.¹⁻⁵ Nevertheless, EC-based electrolytes exhibit inferior low temperature performance compared to PC-based electrolytes, mainly due to their different melting points $(mp_{EC} 39^{\circ}C, mp_{PC} - 49^{\circ}C)$. Therefore, one problem to be solved is: How can we apply graphite anodes in PC-based electrolytes?

In our opinion, a one-word answer to this question is "modification." It is the modification of graphite or PC-based electrolytes, or both, that may lead to acceptable stability.

Several papers have been published on modifying PC-based electrolytes using additives such as catechol carbonate, crown ether, ethylene sulfite, and sulfur dioxide.⁶⁻⁹ However, from the viewpoint of graphite modification, one approach is to coat carbon onto the graphite surface to protect it from PC. In fact, the prototype of this concept, the core-shell-structured carbon composite was first applied as an anode material in lithium-ion batteries by Kuribayashi et al.¹⁰ More recently, other groups have also reported the electrochemical performance of core-shell-structured carbon composites.11,12 Reported processes of preparing composite carbons include common procedures such as mixing the carbon precursors with graphite or graphitized carbon and heating the slurry mixtures at temperatures of about 1000°C or above. In contrast, we have prepared carboncoated natural graphite by thermal vapor decomposition (TVD). In this paper, we discuss the excellent electrochemical performance of TVD-treated natural graphite in both EC-based and PC-based electrolytes. The effect of carbon coating has also been studied.

Experimental

Carbon-coated natural graphite (Mitsui Mining Co., Ltd., Japan) was prepared by the TVD technique. Toluene vapor and nitrogen carrier gas were fed into a reaction tube at flow rates of 2 mL/min

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and 1 L/min, respectively. Natural graphite was stirred in the reaction tube to make a fluid-bed layer and to expose the surfaces of the graphite particles to the vapor. The temperature of the reaction tube was maintained at 1000°C. At such a high temperature, the toluene vapor flowed into the reaction tube, decomposed, and deposited on the graphite surface as a carbon coating. The carbon coating thickness was controlled by the feed time of the toluene vapor. In the studies, three carbon-coated natural graphite samples with 17.6, 13.4, and 8.6 wt % of carbon coatings, respectively, were tested as well as the original natural graphite. Selected physical properties for all of these samples are listed in Table I.

Graphite electrodes were prepared by spreading the graphite powder slurry (90 wt %) and poly(vinylidene fluoride) (10 wt %) dissolved in 1-methyl-2-pyrrolidinone onto a copper foil substrate. The electrodes were then dried overnight at 105° C under vacuum and pressed between two flat steel plates at about 0.2 ton/cm².

Both EC-based and PC-based electrolytes were used in our studies. The electrolyte EC:dimethyl carbonate (DMC) (1:2 by volume)/ 1 M LiPF₆ (Ube) was chosen as representative for EC-based electrolytes. The PC-based electrolytes were 1 M LiPF₆ (Tomiyama, battery grade) in PC/DMC (Wako, high purity) mixed solvents. The water content in all these electrolytes was < 20 ppm.

The electrochemical measurements included galvanopotentiostatic charge-discharge tests and cyclic voltammetric experiments on the graphite electrodes. In the galvanopotentiostatic charge-discharge tests, two-electrode cells were used. The two-electrode cells included a lithium metal electrode and a graphite electrode, held apart by a separator (Celgard 2400) and glass fiber.

The test procedures were as follows. (*i*) The cells were discharged (intercalation of lithium into the graphite electrode) from the open-circuit voltage (OCV) to 0 V at a constant current density of 0.4 mA/cm², (*ii*) the cell voltages were held at 0 V until the current density decreased to < 0.08 mA/cm², (*iii*) the cells were rested for 10 min, (*iv*) the cells were charged (deintercalation of lithium from the graphite electrodes) at a constant current density of 0.4 mA/cm² to 1.5 V, and (*v*) the cells were rested for 10 min; then the cycles were repeated.

In the cyclic voltammetric experiments, three-electrode cells were used. In these cells, lithium metal electrodes were used as both the counter and reference electrodes, and graphite electrodes were used as the working electrodes. The cells were cycled between the OCV (*ca.* 3 V *vs.* Li⁺/Li) and 0 V *vs.* Li⁺/Li at a scan rate of 0.1 mV/s.

All cells were fabricated in a glove box filled with a dry argon atmosphere.

To gain more insight into our studies on carbon-coated natural graphite, all graphite samples, together with carbon sample MCMB 6-10 (Mesocarbon Microbeads, Osaka Gas, nominal diam 6 μ m, heat-treated at 1000°C) as a reference, were fully lithiated electrochemically in the electrolyte of EC:DMC (1:2 by volume)/1 M

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Figure 1. SEM images of graphite samples: (a) original natural graphite; (b) natural graphite coated with 17.6 wt % carbon.

LiPF₆ (Ube) and examined by ⁷Li-NMR spectroscopy. Carbon lithiation was performed by discharging the two-electrode cells at a constant current density of 0.4 mA/cm² to 5 mV and holding the cells at this potential for *ca*. 5 h. Then these cells were disassembled inside the glove box and the graphite electrodes were washed with dried DMC solvent. After evaporation of the DMC solvent from these electrodes under vacuum at room temperatures for *ca*. 3 h (in the side box of the glove box), the graphite was scraped off the copper foil substrates and sealed in NMR sample tubes inside the glove box. The sample tubes were set into a ⁷Li-NMR spectrometer (external magnetic field **B**₀ = 7.05 T, resonance frequency for ⁷Li 116.7 MHz; DSX-300, Bruker). Line shifts were measured with LiCl aqueous solution as the external standard at room temperature; magic angle spinning spectroscopy was not used.

Results and Discussion

Scanning electron microscopy (SEM) images of the original natural graphite and graphite coated with 17.6 wt % carbon are shown in Fig. 1a and b, respectively. These two images show that the outer surface morphology of graphite particles is retained even after carbon coating. Therefore, we conclude that TVD is a very effective technique for uniformly depositing carbon coating on the surfaces of graphite particles. However, graphite particle size appears to increase after carbon coating, which also can be seen from Table I.

A transmission electron microscopy (TEM) image of the carbon coating on the graphite surface is presented in Fig. 2. The highly ordered structure with well-defined layer planes is clearly evident. It is believed that the lattice image of the layers is observed along the [110] direction of the coated carbon with TEM. In other words, the coated carbon covers the original graphite particles with highly oriented (110) planes toward their surface. This kind of treatment of natural graphite, by covering the active surface, is thought to be an alternative way to suppress PC decomposition and exfoliation of the graphite.

Because the principal goal of coating carbon on the natural graphite surface is to prevent PC decomposition and graphite exfoliation, all carbon-coated natural graphite samples, along with the original bare natural graphite, were first tested in the PC-based electrolytes to study the effect of carbon coating on the suppression of PC decomposition. Figure 3 shows typical first-cycle cyclic voltam-

 Table I. Some physical properties of the original and carboncoated graphite samples.

Amount of Carbon coating on graphite (wt %)	Brunauer, Emmett, and Teller method surface area (m ² /g)	Average particle size (µm)	<i>d</i> ₀₀₂ (nm)	<i>Lc</i> ₍₀₀₂₎ (nm)	
0	5.6	12.6	0.33544	102.4	
8.6	4.5	18.5	0.33555	83.8	
13.4	3.1	20.4	0.33553	135.2	
17.6	2.5	22.3	0.33553	93.3	

mograms (CVs) of carbon-coated and original natural graphite electrodes in PC-based electrolytes. The effects of carbon coating can be clearly observed. In the cyclic voltammogram of original bare natural graphite, which is drawn as a thin solid curve, there is a large irreversible peak near 0.5 V *vs.* Li⁺/Li which can be definitely ascribed to PC decomposition and graphite exfoliation. In addition, there are three small peaks at potentials lower than 0.2 V *vs.* Li⁺/Li during the cathodic sweep. These small peaks are due to the intercalation of lithium ions into the graphite electrode and the transformations between different stages of the intercalation compounds (from dilute stage 1 to stage 4 (LiC₃₆), from liquid-like stage 2 (LiC₁₈) to stage 2 (LiC₁₂), and from stage 2 (LiC₁₂) to stage 1 (LiC₆), respective-



Figure 2. TEM image of the carbon coating on the surface of natural graphite.



Figure 3. CVs of the graphite electrodes in PC-based electrolyte PC:DMC (1:1.86 by volume)/1 M LiPF₆ for the first cycle: (a) natural graphite coated with 17.6 wt % carbon; (b) original natural graphite. Scan rate: 0.1 mV/s.

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ly).¹³⁻¹⁶ During the anodic sweep, there are also three small peaks which can be attributed to the deintercalation of lithium ions from the graphite electrode. These peaks appear symmetrical to the three small peaks in the cathodic sweep. However, the reversible capacity, which is mainly composed of the integrated area under the three peaks is rather small. We observed that a large part of the graphite was stripped from the copper foil substrate and fell to the bottom of the three-electrode cell after the first-cycle sweep. Thus, it is expected that the small reversible capacity of natural graphite in the PCbased electrolyte, e.g., PC:DMC (1:1.86 by volume)/1M LiPF₆, originates from the residual graphite bound to the copper foil substrate. This agrees with the conclusion of Aurbach et al. that besides the exfoliation of graphite, fractures leading to electronic disconnection of graphite particles from the bulk contribute to electrode degradation.¹⁷ In contrast to the cyclic voltammogram of the original natural graphite in PC-based electrolyte, that of carbon-coated natural graphite demonstrates different performance in PC-based electrolyte. In the CV of natural graphite coated with 17.6 wt % carbon, as drawn in the thick solid curve, the irreversible peak near 0.5 V vs. Li⁺/Li is barely visible, whereas the reversible peaks due to stage transformations of lithium-graphite intercalation compounds are prominent and clear. The disappearance of the irreversible peak results from the effective suppression of PC decomposition and graphite exfoliation by carbon coating. However, other than this phenomenon, the CV shows no signs of lithium insertion into or deinsertion from the carbon-coating phase. By comparing the CVs of the carbon-coated and original natural graphite electrodes in the PCbased electrolyte, the superiority of carbon-coated natural graphite to the original bare natural graphite becomes clear.

Corresponding to the CVs, the effect of carbon coating can also be observed in the charge-discharge tests. As shown in Fig. 4a, in the first-cycle discharge curve of the original natural graphite in PCbased electrolyte, a very long plateau can be observed near 0.7 V. This long plateau is due to PC decomposition and exfoliation of the graphite electrode. This plateau is so long that it exceeded the testing time scale in our experiment, and no charge capacity could be obtained. In contrast, in the first-cycle charge-discharge curve of natural graphite coated with 17.6 wt % of carbon in the same PC-based electrolyte (Fig. 4b), considerable charge capacity could be obtained. Moreover, the plateaus due to lithium intercalation-deintercalation can be clearly observed below 0.2 V.

For comparison with the charge-discharge characteristics of the graphite electrodes in the PC-based electrolytes as discussed above, the charge-discharge tests were also carried out for graphite electrodes in the EC-based electrolyte. Figure 5 shows typical first-cycle charge-discharge curves of the carbon-coated and original natural graphite electrodes in EC:DMC (1:2 by volume)/1 M LiPF₆. In the first-cycle discharge curve of the original natural graphite electrode, two shoulder-like plateaus at about 1.4 and 0.6 V can be seen. These plateaus can be attributed to the decomposition of the electrolyte to build up a solid electrolyte interphase (SEI) on the graphite surface. For the carbon-coated natural graphite electrodes, these types of plateaus are difficult to detect in the first-cycle discharge curves. Instead, the discharge curves drop down smoothly from the OCV to about 0.2 V. For all the graphite electrodes, coated with carbon or not, in the potential range from 0.2 to 0 V the charge-discharge curves demonstrate plateaus relating to lithium intercalation-deintercalation. Moreover, for natural graphite coated with 17.6 wt % carbon, the irreversible capacity is remarkably decreased compared to that of the original natural graphite.

To gain more insight into the electrochemical performance of carbon-coated natural graphite, we tested the charge-discharge characteristics of graphite electrodes in electrolytes with different components. Table II lists some of these results. The blanks in this table indicate cases for which the plateaus at ca. 0.7 V due to PC decomposition and exfoliation of graphite electrodes are very long, as



Figure 4. Charge-discharge curves of graphite electrodes in PC-based electrolyte PC:DMC (1:1.86 by volume)/1 M LiPF_6 for the first cycle: (a) original natural graphite; (b) natural graphite coated with 17.6 wt % carbon.



Capacity (mAh/g)

Figure 5. Charge-discharge curves of graphite electrodes in EC-based electrolyte EC:DMC (1:2 by volume)/1 M LiPF₆ for the first cycle.

a

Amount of carbon coating (wt %)	EC:DMC (1:2) 1 M LiPF ₆	PC:DMC (1:4) 1 M LiPF ₆	PC:DM (1:3) 1 M LiPF ₆	PC:DMC (1:2.33) 1 M LiPF ₆	PC:DMC (1:2.08) 1 M LiPF ₆	PC:DMC (1:2) 1 M LiPF ₆	PC:DMC (1:1.86) 1 M LiPF ₆
0	392.0^{a} 341.7^{b} 50.3^{c} $87.2\%^{d}$	408.6 313.1 95.5 76.6%	450.9 314.7 136.2 69.8%	582.9 307.9 275.0 52.8%	_		—
8.6	411.6 347.5 64.1 84.4%	436.0 330.4 105.6 75.8%	467.1 328.0 139.1 70.2%	434.5 318.5 116.0 73.3%	_	_	_
13.4	381.2 335.1 46.1 87.9%	337.0 295.1 42.5 87.4%	383.4 291.8 91.6 76.1%	403.5 308.7 94.8 76.5%	677.8 270.7 407.1 39.9%		
17.6	357.4 337.8 19.6 94.5%	360.7 333.4 27.3 92.4%	377.1 332.0 45.1 88.0%	397.3 316.8 80.5 79.7%	427.4 311.8 115.6 73.0%	430.3 305.4 124.9 71.0%	422.5 303.3 119.2 71.8%

Table II. Charge-discharge characteristics of graphite electrodes in different electrolytes.

^a The discharge capacity at the first cycle (mAh/g).

^b The charge capacity at the first cycle (mAh/g).

^c The irreversible capacity at the first cycle (mAh/g).

^d Coulombic efficiency at the first cycle.

shown in Fig. 4a. From Table II, some general understanding can be acquired; the more PC content in the electrolyte, the more dramatically PC decomposes and the more easily graphite electrodes exfoliate. In addition, the more carbon that is coated on the graphite's surface, the more compatible are the graphite electrodes toward PCbased electrolytes.

From the data listed in Table II, we provide two figures (Fig. 6 and 7) to show the relationships between the amount of carbon coating and the irreversible capacity and coulombic efficiency, respectively. From Fig. 6, it can be seen that for each kind of electrolyte, as the coating amount increases, the irreversible capacity becomes smaller. Some previous studies have indicated that the irreversible capacity of carbonaceous anode materials is closely related to their specific surface areas.^{2,18} In this study, the trend appears to be similar because as the carbon coating amount on the surface of natural graphite particles increases, the specific surface area of carbon-coated graphite decreases as illustrated in Table I, and then the irreversible capacity decreases accordingly. However, it is assumed that the remarkable decrease of irreversible capacity with the increase of carbon coating amount cannot be simply explained by the fact that the specific surface area of graphite decreases with increasing carbon coating amount. Rather, it is believed that the carbon coating provides a buffer phase between the graphite and the electrolyte. The decomposition of the electrolytes on this phase to build up the SEI film passivating the electrodes is much milder than for pure graphite. As the carbon coating thickness increases, the coverage of this phase over the graphite particles becomes denser and thus protects the graphite from electrolyte attack more effectively. From Fig. 7, it can be observed that as the carbon coating amount increases, the coulombic efficiency increases.

As illustrated above, the electrochemical performance of carboncoated natural graphite is quite different from that of the original natural graphite, so it can be expected that for a single particle of carbon-coated natural graphite, the electrochemical performance of the shell part must differ from that of the core part. That is, the carbon coating may store some lithium in a distinct way compared with that of natural graphite in the core. However, in our previous attempts using techniques such as *in situ* X-ray diffraction, cycle voltammetry, and charge-discharge tests, it was difficult to differentiate the role each part plays in determining the overall electrochemical performance (especially in the case of EC-based electrolytes). Here, we applied a more powerful technique, ⁷Li-NMR, to clarify the storage sites for lithium in carbon-coated natural graphite. In the ⁷Li-NMR



Figure 6. Relationship between carbon coating amount and irreversible capacity of graphite electrodes for the first cycle in different electrolytes.



Figure 7. Relationship between carbon coating amount and coulombic efficiency of graphite electrodes for the first cycle in different electrolytes.

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Figure 8. ⁷Li-NMR spectra of fully lithiated carbons: (a) original natural graphite; (b) natural graphite coated with 17.6 wt % carbon; (c) MCMB 6-10.

spectra of fully lithiated carbon-coated natural graphite, as shown in Fig. 8b, there are two peaks at 43.74 and 15.83 ppm, respectively. Compared with the 7 Li-NMR spectra of fully lithiated natural

graphite (Fig. 8a), the peak at 43.74 ppm in ⁷Li-NMR spectra of fully lithiated carbon-coated natural graphite can be ascribed to lithium intercalated into graphite (LiC_6).^{19,20} For the peak at 15.83 ppm,





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Figure 10. Relationship between the ratio of the peaks' (ca. 15 and 44 ppm) intensities in ⁷Li-NMR spectra and the coating amount of carbon on the graphite surface.

we take the ⁷Li-NMR spectra of fully lithiated MCMB 6-10 (Fig. 8c) as a reference; *i.e.*, there is one peak at *ca*. 11.43 ppm. Because these peaks' chemical shifts are near each other and MCMB 6-10 is a kind of soft carbon, we can attribute the peak at 15.83 ppm to the presence of lithium in the crystallized soft-carbon-type shell part.²⁰⁻²⁵

Moreover, from the ⁷Li-NMR spectra of fully lithiated natural graphite coated with different amounts of carbon, as shown in Fig. 9, we find that the ratios of these two peaks' intensities change with the amount of carbon coating. Figure 10 shows the relationship between the ratio of the peaks' intensities (the intensity of the peak at *ca*. 15 ppm to that of the peak at *ca*. 44 ppm) and the amount of carbon coating. A linear relationship can be clearly observed. In turn, from the ratio of these two peaks' intensities in the ⁷Li-NMR spectra of the fully lithiated carbon-coated natural graphite, the coating amount can be calculated from the straight line in Fig. 10.

Conclusions

Carbon-coated natural graphite was prepared by a TVD technique. This material shows superior electrochemical performance as an anode for lithium-ion batteries in both EC- and PC-based electrolytes compared to original natural graphite. The amount of carbon coating on the natural graphite can affect the electrochemical performance significantly; as the coating amount increases, the irreversible capacity decreases while the coulombic efficiency increases. ⁷Li-NMR spectra of the fully lithiated carbon-coated natural graphite show that there are two types of storage sites for lithium insertion in this kind of carbon material: the graphite core part for lithium intercalation and the soft-carbon-type shell part for lithium storage. Moreover, the ratio of the peaks' intensities (the intensity of the peak at *ca*. 15 ppm to that of the peak at *ca*. 44 ppm) in the ⁷Li-NMR spectra of fully lithiated carbon-coated natural graphite bears a linear relationship to the amount of carbon coating.

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