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Surface Modification of Natural Graphite by Phenolic Resin Carbon Coating for Improvement of Cyclic Performances in Lithium Ion Batteries

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Natural graphite was coated with different concentrations of phenolic resin and methane solution. To obtain modified graphite, the coated natural graphite was further carbonized at a temperature of 1000°C for 1 h under a N_2 stream after removing the solvent of methane. The surface morphology and microstructure of modified graphite were investigated with scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. The computer-controlled constant-current cycler investigated charge and discharge performances. Results showed that the phenolic resin carbon with disordered structure formed on the surface of graphite could protect the graphite from exfoliation and improve its cyclic performances successfully. The reversible capacity and coulombic efficiencies of modified graphite were higher than that of natural graphite during charge and discharge cycling tests at a rate of 50 mA $\cdot g^{-1}$. It is confirmed that modified graphite has an advantage for an application of high power density lithium ion battery.

Keywords natural graphite, lithium ion battery, carbon anode, phenolic resin

It is recognized that lithium secondary batteries using lithium metal exhibit problems, which make it difficult for their wide usage in the consumer market. The problem is the unsafe characteristics, such as combustion and explosion due to dendrites formed at the surface of lithium metal during charge-discharge cycles. Therefore much effort in the last decade has been focused on searching for suitable materials to act as an alternative anode for lithium secondary batteries (Mochida et al., 1998; Zaghib et al., 1997). At

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present, graphite has been found to be the most desirable candidate among many types of materials reported (Novak et al., 2001; Zane et al., 2001). Moreover, most commercial cells manufactured today use graphitic carbons (Sato et al., 2001; Broussely et al., 1997; Rifat and Hikmet, 2001).

Graphite has a nearly perfect lamellar structure where lithium intercalated and deintercalated during charge and discharge. It can be explained that the following are 2 advantages of anode material. One is a high storage capacity, as the faradaic capacity of the graphite compound fully intercalated by lithium (LiC_6) is 372 mAh $\cdot$ g^{-1} carbon. The other is a relatively flat potential profile near the redox potential of the Li/Li^+ couple during charge and discharge processes. However, cointercalation resulting from solvent-based electrolytes between the layers of graphite electrode during charge and discharge cycling would lead to a huge expansion and total disintegration of some layers of exfoliation (Funabiki et al., 1999). Consequently, the cyclic performances are very poor. In order to solve these problems, carbon-coated graphite has drawn much attention recently (Wang and Yoshio, 2001; Kuribayashi et al., 1995). However, whether the surface of graphite is completely covered by carbon coating is a difficult problem. The attempt made in this study is to overcome the above question and further improve the cyclic performances of graphite by phenolic resin carbon coating.

Experimental

Preparation of Carbons

Natural graphite (NG) power with an average particle diameter of 13 μm was used in this study. Prior to the experiment, phenolic resin (PR) was mixed with hexamethylenetetramine (HEX) (PR: HEX = 87:13, wt) and then dissolved in methanol to get phenolic resin solution. Natural graphite dipped in different concentrations of phenolic resin solution in an airtight flask at 78°C for 1 h. The mixture solution was filtrated at 78°C, and the residues were dried under a vacuum at 80°C for 24 h. After solidifying at 150°C for 5 h, the residues were heated up to 1,000°C for 1 h in a nitrogen atmosphere. The products obtained were milled to 3–35 μm in a carnelian mortar. For the purpose of comparison, we physically prepared a mixture composed of PR carbon and natural graphite (PR: NG = 30:100, wt) and PR carbon, which had been heated at a temperature of 1000°C for 1 h under a N_2 stream.

Analysis of SEM

The surface morphology of the samples by heat treatment at 1000°C were observed with a scanning electron microscope (SEM; Hitach H-600).

XRD

X-ray power diffraction (XRD) measurements were made using a D/max-rA diffractometer equipped with a copper target tube and a diffracted beam monochromator.

Electrochemical Measurements

Working electrodes were fabricated by mixing carbon powder with 10 wt% of PTFE (poly-tetrafluroethylene) binder in a carnelian mortar. The gumlike mixture was spread

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to form a film on copper foil substrates, then pressed at a pressure of 300 kg/cm^2, and dried for 12 h at 120°C under a vacuum. Typical electrodes were 10 mg · cm^{-2}. Electrochemical measurements were performed with 3-electrode cells. A carbon electrode was used as the work electrode. Lithium metal was used as a counter electrode and a reference electrode. The electrolyte was 1 M $LiPF_6$ (Merck) dissolved in a mixture of 50 wt% ethylene carbonate (EC, Merck) and 50 wt% diethyl carbonate (DEC, Merck). The cell assembly was carried out in the glove box filled with high pure argon gas. The cells were tested with a computer-controlled constant current cycler at a constant temperature of 25°C. The cut-off voltage was 0.001 V in charge and 2.0 V in discharge Galvanostatic cycle was respectively carried out at a constant current density of 15 mA · g^{-1} carbon and 50 mA · g^{-1} carbon.

Results and Discussion

Morphology Analysis

Figures 1a–1d present the SEM images of the NG and modified graphites (MPGs) coated by a phenolic resin solution concentration from 5 wt% to 40 wt% before being carbonized at 1000°C. From Figure 1a, the surface shape of NG is smooth, and its grains are identified clearly. For MPG-05 shown in Figure 1b, the surface shape is similar to that of NG. The others are rough. Due to a relatively lower concentration of phenolic resin in methanol (5 wt%) for MPG-05, the formed carbon layer on the surface of NG is very thin. So this only influences the shape of graphite slightly. With the increasing of phenolic resin concentration, the formed carbon layers on the surface of graphite become thicker, which result in some difference between the surface shapes of MPGs and pure NG.

Power XRD Analysis

The XRD patterns are shown in Figure 2. The results obtained are for NG and MPGs by phenolic resin carbon coating. Peaks (002 and 004) at 26.5° and 54.7° are observed for them corresponding to typical graphite structures. The intensity of the peak (004) becomes weaker with decreasing graphite content from NG to MPG-40. This is consistent with the result that the stronger intensity of peaks in XRD corresponds to the higher content of graphite for a carbon-graphite composite (Li et al., 1999).

Electrochemical Studies on NG and MPGs

Charge-Discharge Characteristics of NG and MPGs at a Rate of 15 mA · g^{-1}. The charge capacity, the discharge capacity (Crev), and the irreversible capacity (Cirr) are defined as the lithium ion intercalation capacity, the lithium ion deintercalation capacity, and the difference between the charge capacity and the discharge capacity, respectively. The first charge and discharge curves of NG, phenolic resin carbon, and MPGs are presented in Figure 3. In addition, the results are summarized in Table 1. As shown in Figure 3 and Table 1, both graphite and modified graphites deliver a higher charge capacity than the theoretical faradaic capacity of the graphite (372 mAh · g^{-1}) in the first cycle, but the charge capacity is not fully discharged, which gave rise to an irreversible capacity (Cirr) of 120–190 mAh · g^{-1}. But Cirr of modified graphites was higher than that of graphite. The Cirr is recognized to relate to the following 3 factors. The first is electrolyte decomposition on nominally clean carbon surface. The second is the reactions

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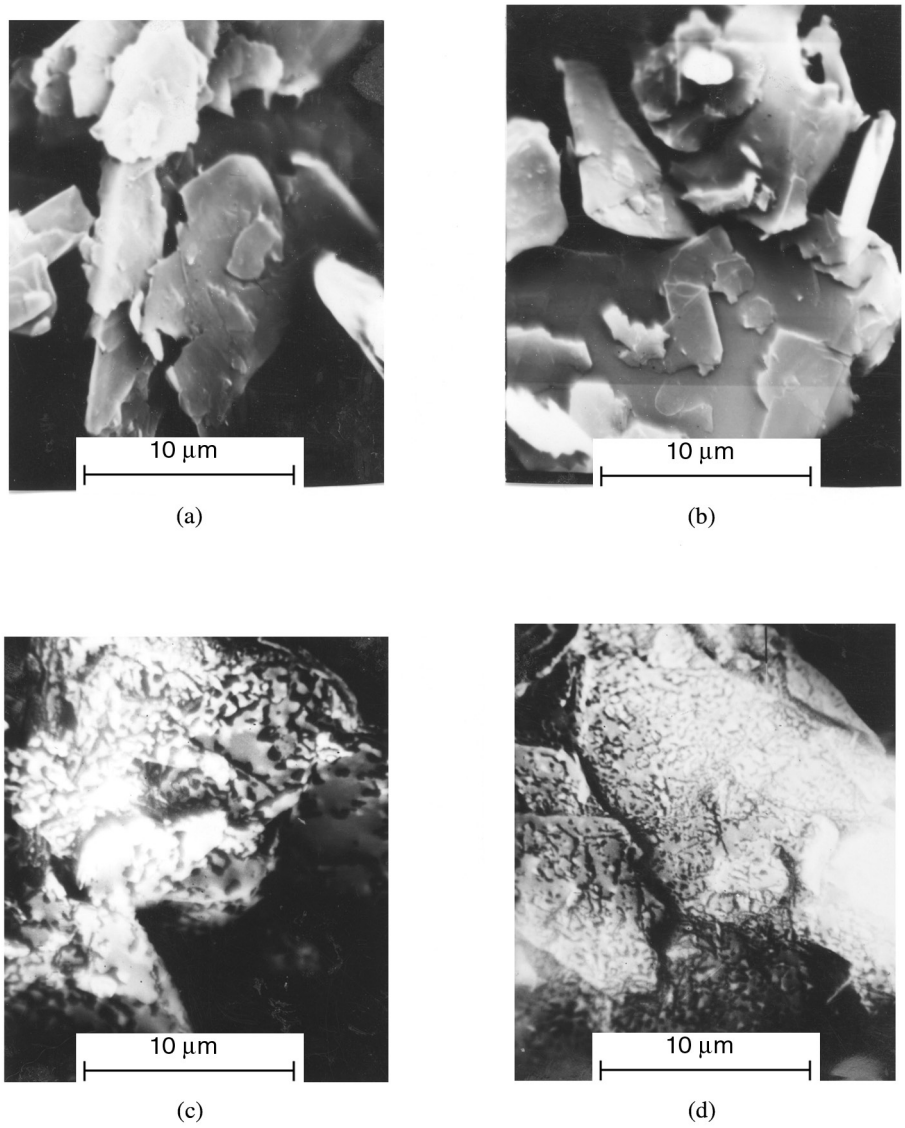

Figure 1. SEM micrograph of natural graphite, phenolic resin carbon, and modified graphites by phenolic resin carbon coating: times 4,800, (*a*) graphite, (*b*) MPG-05, (*c*) MPG-20, and (*d*) MPG-40.

between solid electrolyte and surface functional groups formed on carbons exposed to reactive gases. The third is that the interface (SEI) formation on the carbon surface occurred normally at 0.5–1.0 V (versus Li/Li^+) (Jiang et al., 1995), which is evidenced in this study by the voltage plateau appearing at nearly 0.7 V in the first charging. For graphite, the Cirr mainly resulted from the third factor. However, the reactions between solid electrolyte and surface functional groups are also a significant reason for Cirr of phenolic resin carbon. In fact, modified graphites coated by phenolic resin carbon may have many active sites in which surface oxides may be formed due to their many defect

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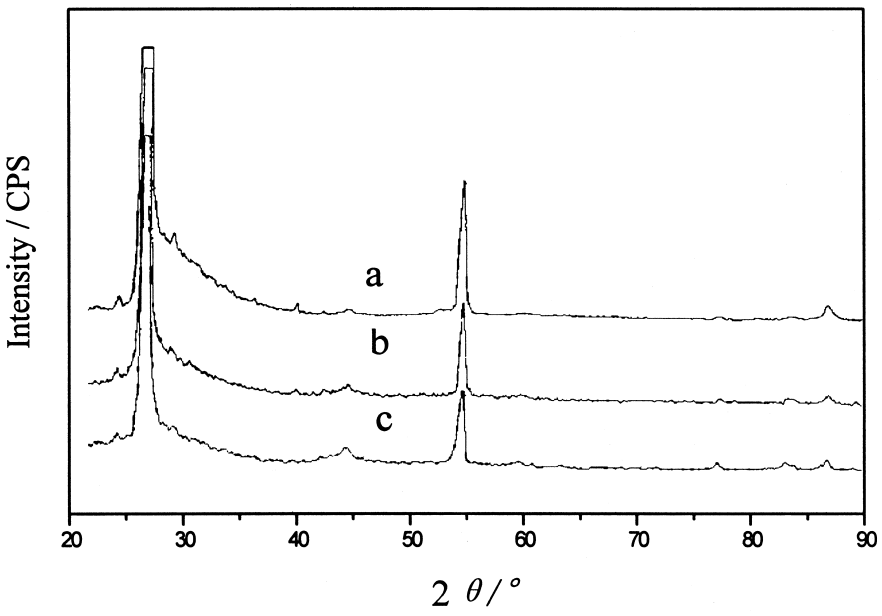

Figure 2. XRD patterns of graphite and modified graphite coating with phenolic resin carbon: (*a*) graphite, (*b*) MPG-30, and (*c*) MPG-40.

sites. Some additional Cirr of modified graphites may be caused by the irreversible reaction of lithium with surface functional groups such as −COOH and −OH. From Figure 3, the first discharge capacity of modified graphites is less than that of natural graphite in the first cycle. Pled (Pled et al., 1996) discovered that graphite had some micropores to store lithium ions. However, some micropores of natural graphite were filled due to natural graphite dipping in phenolic resin and methanol solution. Next, the discharge capacity (202 mAh · g^{-1}) of PR carbon is far less than that of graphite. Consequently, both reasons lead to a decrease in the storage of lithium ions during charge and discharge. On the other hand, the first discharge capacity of modified graphite showed only a slight change when phenolic resin carbon content exceeded 30 wt%. This may suggest that MPG-30 and MPG-40 had been completely coated by phenolic resin carbon.

Stability in the Capacity of the Carbon Materials During Charge-Discharge Cycling at a Rate of 15 mA · g^{-1}. In order to further examine the charge and discharge cycling performances of carbon materials, Crev of carbon materials were recorded for up to 10 cycles during the cycling tests at a rate of 15 mA · g^{-1}. The results are presented in Figure 4, both natural graphite and MPG-05 showed high beginning Crev. However, with the increasing cycles, the Crev of them decreased to lower than other modified graphites after the fifth cycle. This makes them unsuitable for consumer-market applications. Modified graphites (not including MPG-05) show more stable Crev in the total cycles. For unmodified graphite, cointercalation of solvent-based electrolytes between the graphemes of graphite electrodes during the charge and discharge cycle would lead to a huge expansion and total disintegration of the LiC_6 exfoliation (Funabiki et al., 1999; Besenhard et al., 1995). Therefore the cycle performance of graphite was very poor. On the contrary, phenolic resin carbon with the microstructure of low crystallite, disorder, and microlayer

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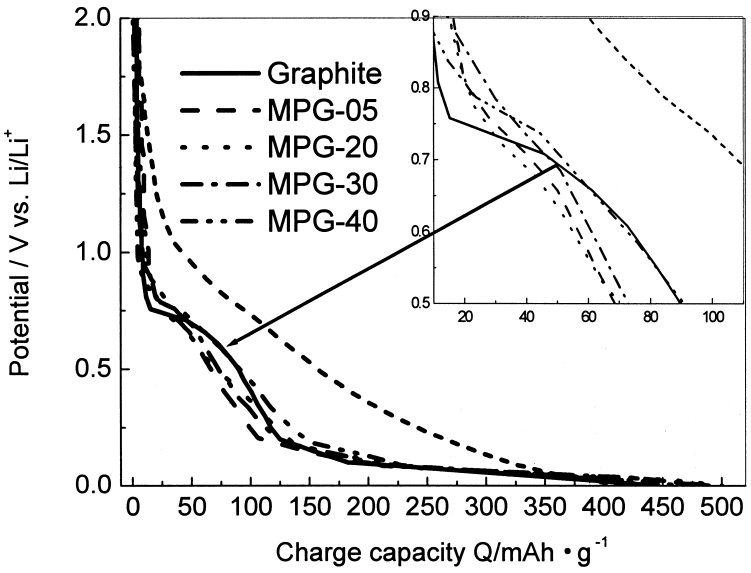
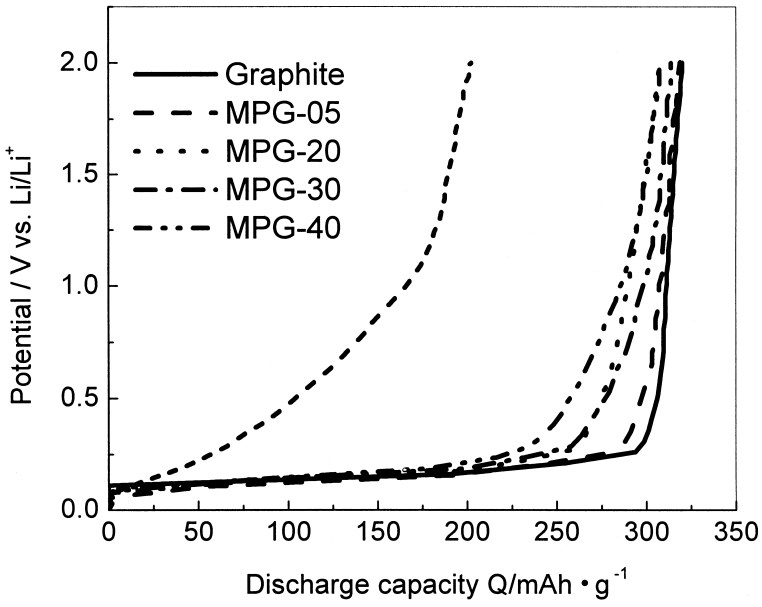


(a)



(b)

Figure 3. Charge and discharge curves of graphite and modified graphite coating with phenolic resin carbon in the first cycle at a rate of 15 mA · g^{-1}: (*a*) charge, and (*b*) discharge.

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Table 1
Electrochemical properties of graphite, phenol resin carbon, and modified graphite coating with phenol resin carbon

Sample No.	Concentration of phenolic resin solution (%)	Current density ($mA \cdot g^{-1}$)	First reversible capacity ($Q/mAh \cdot g^{-1}$)	First irreversible capacity ($Q/mAh \cdot g^{-1}$)
Graphite	0	15	320	127
		50	232	153
MPG-05	5	15	318	194
		50	309	117
MPG-20	20	15	308	192
		50	302	125
MPG-30	30	15	314	175
		50	305	123
MPG-40	40	15	308	156
		50	288	130
PR	100	15	202	217

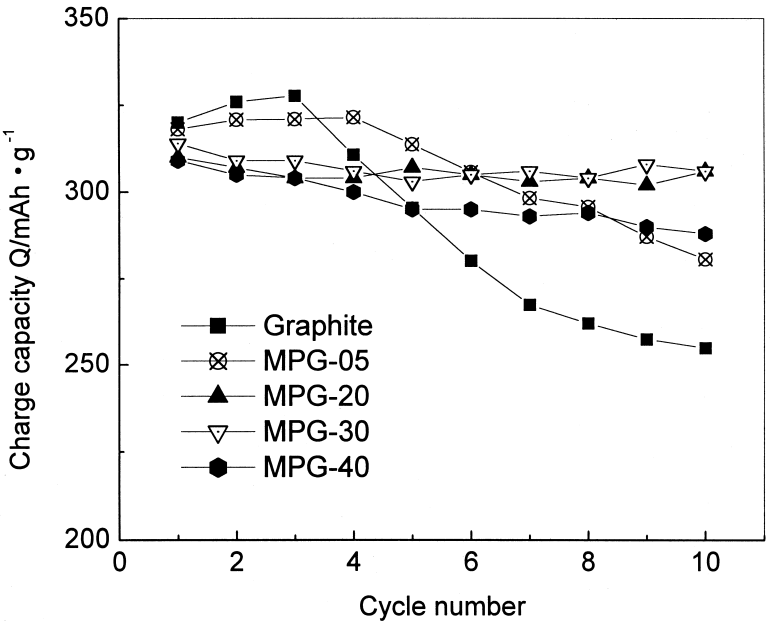

Figure 4. The discharge capacity of modified graphite coating with phenolic resin carbon during charge and discharge cyclic tests at a rate 15 $mA \cdot g^{-1}$.

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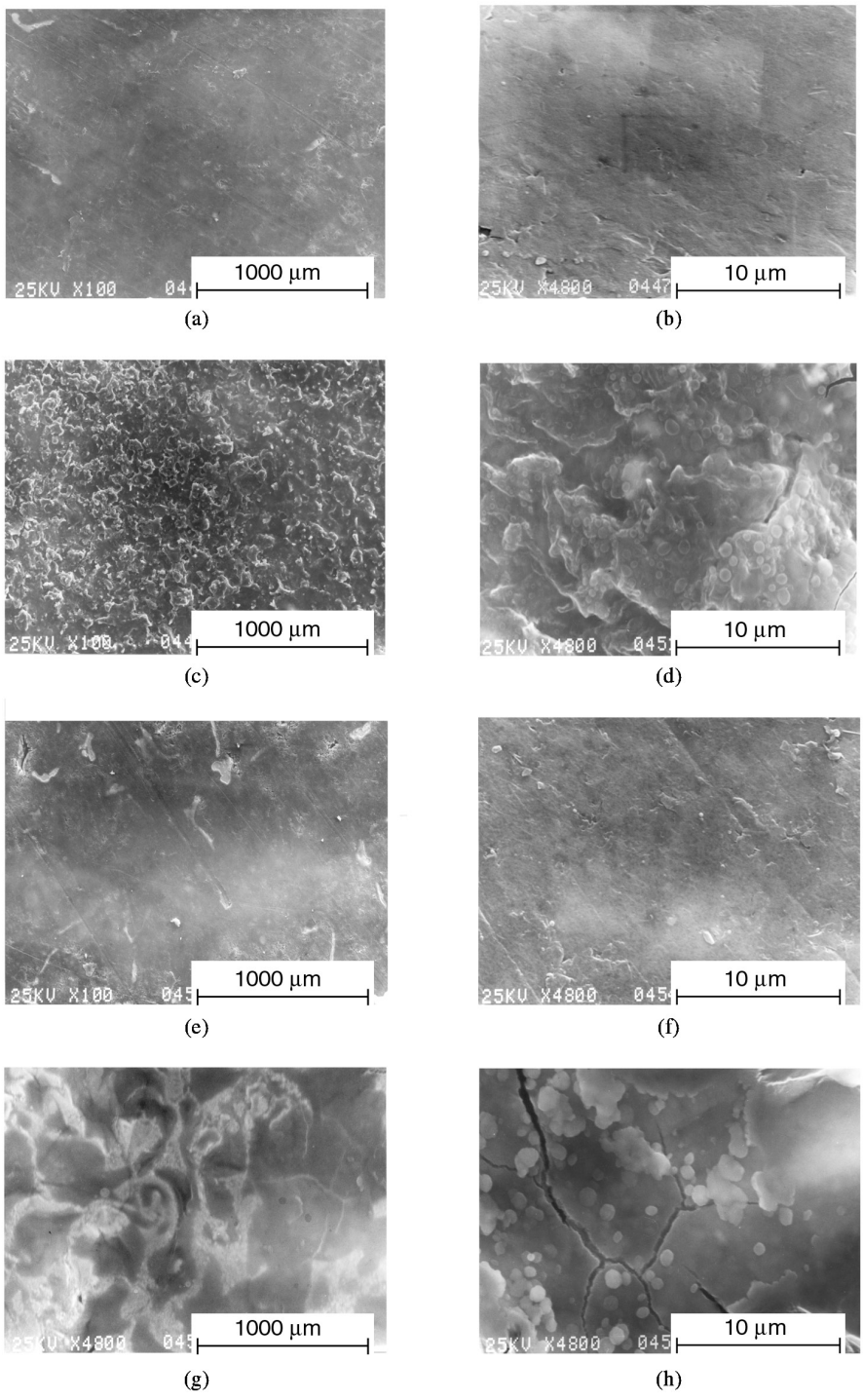

Figure 5. SEM micrograph of surface on a graphite electrode and a modified graphite (MPG-30) electrode before and after charge-discharge cycling: a, c, e, g, ×1,000; b, d, f, h, ×4,800; (*a*, *b*) graphite electrode, before first charge; (*c*, *d*) graphite electrode after tenth charge-discharge cycling; (*e*, *f*) modified graphite (MPG-30) electrode, before first charge; (*g*, *h*) modified graphite (MPG-30) electrode after tenth charge-discharge cycling.

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twist each other restrain exfoliation during charge-discharge cycling. Furthermore, for modified graphites the phenolic resin carbon completely coated graphite and tacked in its inner. So modified graphites may be recognized as the structure composed of core (natural graphite) and shell (phenolic resin carbon). The shell can protect the core from exfoliation, which resulted in perfect cycle performance for MPG-20, MPG-30, and MPG-40 during charge-discharge cycling. However, this is not for MPG-05, mainly originating from the fact that the formed shell layer is too thin to completely restrain the core from exfoliation.

Further work has been done to validate the exfoliation of natural graphite during charge and discharge cycling. As shown in Figure 5, the results are obtained for a SEM micrograph of the surface on a natural graphite electrode (a, b, c, d) and a modified graphite (MPG-30) electrode (e, f, g, h) before and after charge and discharge cycling. Compared to their change of SEM micrograph before and after charge and discharge cycling, formation of solid electrolyte interface (SEI) film and exfoliation can clearly be seen for the surface on a natural graphite electrode but exfoliation not for modified graphite.

Charge-Discharge Characteristics of Modified Graphite with Different Current Density. Taking into account the practicality of modified graphite, we study their charge-discharge characteristics with different charge-discharge current density. The data are shown in Table 1. The Crev of graphite (232 mAh $\cdot$ g^{-1}) in the first cycle at the rate of 50 mA $\cdot$ g^{-1} was far less than that at the rate of 15 mA $\cdot$ g^{-1} and that of modified graphite, which showed a constant value with the increasing of current density. It may have resulted from enhanced kinetics of modified graphites. This suggests that modified graphite has an advantage for high energy density batteries.

Stability in Capacity of the Carbon Materials During Charge-Discharge Cycling at a Rate of 50 mA $\cdot$ g^{-1}. Figure 6 shows the Crev of carbon materials during the cycling tests at a rate of 50 mA $\cdot$ g^{-1}. The Crev of natural graphite are $<$ 250 mAh $\cdot$ g^{-1} and cycle performance was not stable. However, the Crev of modified graphite are more than 250 mAh $\cdot$ g^{-1} and cycle performances were very stable.

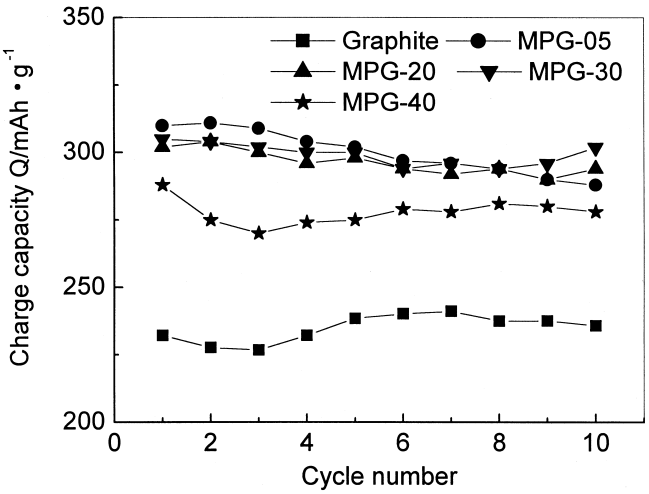

Figure 6. The discharge capacity of modified graphite coating with phenolic resin carbon during charge and discharge cyclic tests at a rate of 50 mA $\cdot$ g^{-1}.

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Conclusions

Modified NGs were prepared by depositing phenolic resin on the graphite surface. Modified graphite electrodes showed good charge and discharge cyclic stability, higher reversible capacity, and smaller irreversible capacity than natural graphite's during the cycling tests at a rate of 50 mA $\cdot$ g^{-1}. These results showed that the phenolic resin carbon with disordered structure on the surface of graphite could successfully protect the graphite from exfoliation and improve its cyclic performances. This also further confirmed that modified graphite has an advantage for an application of high power density lithium ion batteries.

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