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Investigation on the First-Cycle Charge Loss of Graphite Anodes by Coating of the Pyrolytic Carbon Using Tumbling CVD

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The first-cycle charge loss of graphite coated with pyrolytic carbon using a tumbling chemical vapor deposition (CVD) process has been studied for the active material of anodes in lithium-ion secondary batteries. Through the coating of pyrolytic carbons on the surface of graphite particles, carbon materials with a core (graphite)-shell (pyrolytic carbon) structure can be obtained. The irreversible capacity of these carbons at first charge/discharge cycle has been examined using a charge-discharge cycler. The coating of the pyrolytic carbon on the surface of graphite can effectively reduce the initial irreversible capacity, which leads to improvement of first cycle coulombic efficiency from 87.21 to 93.32%. The irreversible capacity formed above 0.8 V *vs.* Li/Li^+ at the first charging cycle is proportional to the surface area of the carbon, that is, the coating time of pyrolytic carbon. The plateau of the first-cycle charging curve disappears distinctly with the coating of pyrolytic carbon. The reduction of the initial irreversible capacity in graphite coated with pyrolytic carbon results from this disappearance of the plateau. This means that the coating layer of pyrolytic carbon is more compatible with the electrolyte than the surface of bare graphite. From electrochemical impedance spectroscopy spectra, the increase of contact resistance in bare graphite electrodes occurs at 0.8-0.2 V *vs.* Li/Li^+ in the first charging and the coating of pyrolytic carbon on the surface of graphite can suppress the increment of contact resistance.
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Graphite has been used widely for lithium (Li) ion secondary batteries because of its advantages of practical energy density, charge-discharge reversibility, and safety aspects.[1] Graphite consists of hexagonal arrays of carbon atoms arranged in benzene-type structures. The hexagonal arrays form ordered layer structures and the layer planes are separated by 3.354 Å. The surface of graphite particles consists of the basal planes and the prismatic (edge) planes of the hexagonal arrays. It has been recognized that the chemical reactivity of the prismatic plane was much higher than that of the basal plane.[2,3]

The irreversible capacity loss of graphite anodes in Li-ion secondary batteries originates from the decomposition of electrolyte to form both a solid electrolyte interface (SEI) layer and gaseous products on the electrode during the initial charge/discharge cycles. Winter *et al.*[4] reported that both the total surface area and the average ratio of the basal plane and edge thickness dimension influenced the irreversible capacity loss. Bar-Tow *et al.*[5] showed that the mechanism of electrolyte decomposition was different on the basal and prismatic planes in an electrolyte consisting of $LiAsF_6$ in ethylene carbonate (EC)—diethyl carbonate (DEC). The SEI layer formed on the prismatic planes is rich in inorganic compounds, whereas that formed on the basal planes is rich in organic compounds. Zaghib *et al.*[6] demonstrated that the distribution of basal and prismatic planes was associated with the extent of electrolyte decomposition and the prismatic planes (edge sites) were active sites for chemical/electrochemical reactions.

The factors responsible for the irreversible capacity loss are still a subject of intense research and debate. Both the catalytic properties and physical structure of graphite are believed to play important roles in the irreversible capacity loss. In an effort to investigate the irreversible capacity loss of graphite electrode for Li-ion secondary batteries, we made new-type carbon materials with a core (graphite)-shell (pyrolytic carbon) structure by a tumbling chemical vapor deposition (CVD) process.[7] In previous work, we reported that the coating of pyrolytic carbon could reduce significantly the irreversible capacity without the loss of reversible capacity. The coating of pyrolytic carbon is a useful process for modifying the surface structure of graphite particles. In the this study, we examine the cause of the first-cycle charge loss by investigating the electrochemical phenomena of graphite coated with pyrolytic carbon.

Experimental

Coating of pyrolytic carbons.—The new type of carbon materials with core (graphite)—shell (pyrolytic carbon) structure was obtained by the tumbling CVD process.[7] For improving the uniformity of the pyrolytic carbon shell, graphite particles tumbled in the rotating reactor tube during the pyrolytic carbon tumbling were deposited on the surface of graphite particles. The rotation speed of the reactor tube varied from 10 to 50 rpm. Four grooves parallel to the tube axis were placed on the inner wall of the tube to promote the tumbling action of the graphite particles. The coating of pyrolytic carbon on graphite was carried out by introducing a gas mixture of liquid propane gas (LPG) and argon under 1 atm pressure in the temperature range from 1000 to 1200°C. The coating time varied from 0.5 to 3 h. The concentration of LPG varied from 10 to 100%, and the total flow rate varied from 1 to 6 L/min. The specific surface area of each sample was determined with Brunauer-Emmett-Teller (BET) measurement with nitrogen gas. Prior to measurements, all samples were heated at 300°C for 10 h under vacuum to remove surface-adsorbed moisture and hydrocarbons.

Cell assembly and electrochemical measurement.—Carbon electrodes were prepared by coating slurries of the above new type carbon powder and polyvinylidene fluoride (PVDF) dissolved in *N*-methyl pyrrolidinone on copper foils. After coating, the electrodes were dried at 150°C for 3 h in vacuum (10^{-3} Torr) and then pressed at about 150 kg/cm^2. The diameter and thickness of the circular-shaped carbon electrodes were 16 mm and about 50 μm, respectively. Coin-type test cells were constructed from these electrodes. A microporous film (Celgard 2400) wetted with electrolyte [1 M LiPF6 dissolved in a 50/50 volume percent (vol%) mixture of EC DEC; Merck & Co., Inc.] was sandwiched between the carbonaceous cathode and Li metal foil anode. All cells were assembled in an argon-filled glove box. These cells were charged and discharged in the potential range of 0 to 2 V *vs.* Li/Li^+ using a galvanostatic cycler (Toscat-3100U; Toyo Corp.). The constant current density was 18.6 mA/g (0.05 C).

The irreversible capacity was defined as the difference between the charge and discharge capacity at the first cycle. For a detailed examination of the charge loss we subdivided the first charge curve

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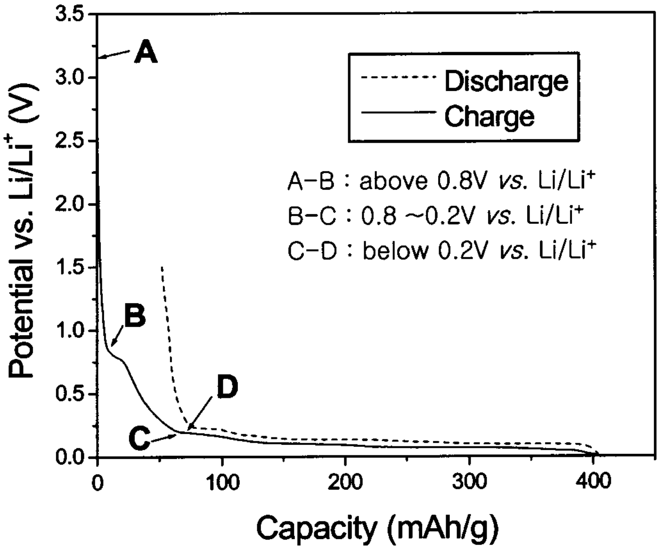

Figure 1. Typical charge-discharge profile of a graphite anode for the first cycle. The charge curve has been subdivided into three potential sectors; A-B, B-C, C-D.

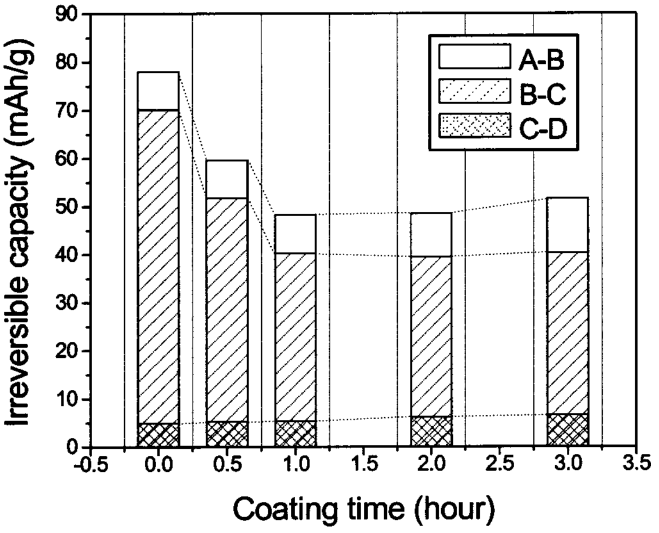

Figure 2. Irreversible capacity, C_{irr}, in A-B, B-C, C-D sectors of the graphite coated with pyrolytic carbons at various coating times.

in three sectors (A-B, B-C, and C-D) as shown in Fig. 1. $C_{irr,A\text{-}B}$ and $C_{irr,B\text{-}C}$ are the irreversible capacities in the sector A-B (above 0.8 V *vs.* Li/Li$^+$) and sector B-C (between 0.8 and 0.2 V *vs.* Li/Li$^+$), respectively. $C_{irr,C\text{-}D}$ means the irreversible capacity formed below the potential of 0.2 V *vs.* Li/Li$^+$. In order to estimate the internal resistance of the carbon electrodes at each potential, the impedance spectrum was investigated using electrochemical impedance spectroscopy (EIS). A Solatron 1255 frequency response analyzer was used in conjunction with the Solatron 1286 electrochemical interface. The electrochemical impedance measurement was carried out by applying an ac voltage of 5 mV over the frequency range from 1 mHz to 100 kHz for the carbon electrodes whose potentials were 0, 0.2, and 0.8 V *vs.* Li/Li$^+$ at the first charging.

Results and Discussion

New type of carbon materials with a core-shell structure were synthesized from the coating of pyrolytic carbon on the surface of graphite in the tumbling reactor tube. The electrochemical properties of these new carbons are characterized with charge-discharge cycling. Figure 2 shows the irreversible capacities obtained from the each sector A-B, B-C, and C-D in the first charge/discharge curve of the graphite coated with pyrolytic carbon at various coating times. As the coating time increases, the total irreversible capacity shows minimum behavior. The irreversible capacities of the sector A-B and C-D, $C_{irr,A\text{-}B}$ and $C_{irr,C\text{-}D}$ increase gradually with the coating time. However, the irreversible capacity of the sector B-C, $C_{irr,B\text{-}C}$ shows the saturation after drastic decrease as the coating time increases. The irreversible capacities of each sector are listed with the first cycle coulombic efficiencies and BET surface areas in Table I. The first cycle coulombic efficiency of the graphite coated with pyrolytic carbon for 1 h is 93.32% which is much higher than that of the bare graphite (87.21%). This result shows that the coating of pyrolytic carbon on the surface of graphite by tumbling CVD is very effective for improving the initial coulombic efficiency and especially decreasing the irreversible capacity which is formed in the potential range from 0.8 to 0.2 V *vs.* Li/Li$^+$ (in the sector B-C).

Figure 3a is the variation in the BET surface area of the graphite coated with pyrolytic carbon for various coating times. As the coating time increases, the BET surface area shows a trend of parabolic increase. The irreversible capacities of sector A-B are plotted in Fig. 3b as a function of coating time. They also show a parabolic increment, which is coincident with the increasing trend of the BET surface area. The irreversible capacity of graphite that is highly ordered carbon mainly results from the SEI layer formation on the surface. So the surface area and structure are very important factors for estimating the irreversible capacity of graphite. The irreversible capacity formed in above 0.8 *vs.* Li/Li$^+$ (in sector A-B) is results from a reaction of SEI layer formation that increases proportionally with the surface area of carbon material. The irreversible reactions in sector A-B are mainly associated with the surface area rather than the surface structure of graphite (highly ordered carbon) and pyrolytic carbon (disordered carbon). These reactions are side reactions from the reduction of solvent on the surface of carbon materials, that is, the formation of the SEI layer which consists of Li_2CO_3, CH_2OCO_2Li, Li_2O, *etc.*[8,9]

Figure 4 shows the variation of irreversible capacity in sector B-C for the coating time of pyrolytic carbon. The $C_{irr,B\text{-}C}$ decreases drastically up to 1 h and then saturates for the coating time. As the coating time increases, the surface of the graphite is covered gradually with pyrolytic carbon and the irreversible capacity which is formed in the potential range from 0.8 to 0.2 V *vs.* Li/Li$^+$ decreases. However, the coating effect on the $C_{irr,B\text{-}C}$ is reduced because the surface of graphite particles are fully covered with pyrolytic carbon after 1 h of coating time. The reduction of the total irreversible capacity in graphite anodes by the coating of pyrolytic carbon results mainly from that of the irreversible capacity which is formed in the potential range from 0.8 to 0.2 V *vs.* Li/Li$^+$.

The charge/discharge curves in Fig. 5a are the first cycle curves of half cells made with bare graphite and graphite coated with pyrolytic carbon. Figure 5b shows the magnified initial part of the first

Table I. First cycle coulombic efficiency, BET surface area, and irreversible capacity of the graphite coated with pyrolytic carbons.

Coating time		Uncoated (0 h)	Coated (0.5 h)	Coated (1 h)	Coated (2 h)	Coated (3 h)
1st cycle coulombic efficiency (%)		87.21	90.91	93.32	92.12	91.21
BET surface area (m^2/g)		14.9	15.2	15.7	18.3	22.8
Irreversible	Total	77.98	59.59	48.23	48.5	51.56
capacity	A-B	7.87	7.89	8.05	9.03	11.3
(mAh/g)	B-C	65.19	46.48	34.78	33.33	33.67
	C-D	4.92	5.22	5.4	6.14	6.59

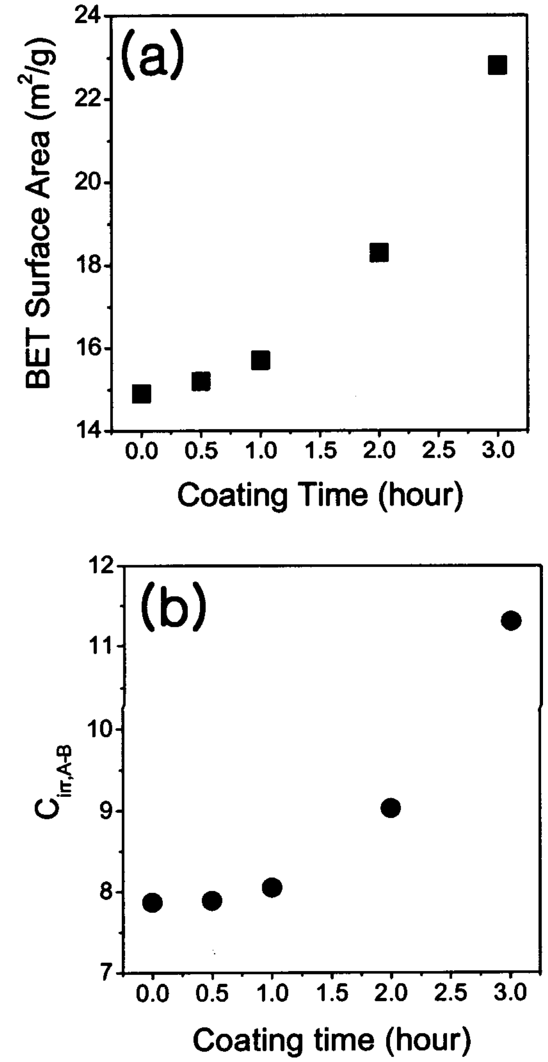

Figure 3. Variation of (a) the BET surface area and (b) the irreversible capacity in sector A-B of the graphite coated with pyrolytic carbons at various coating times.

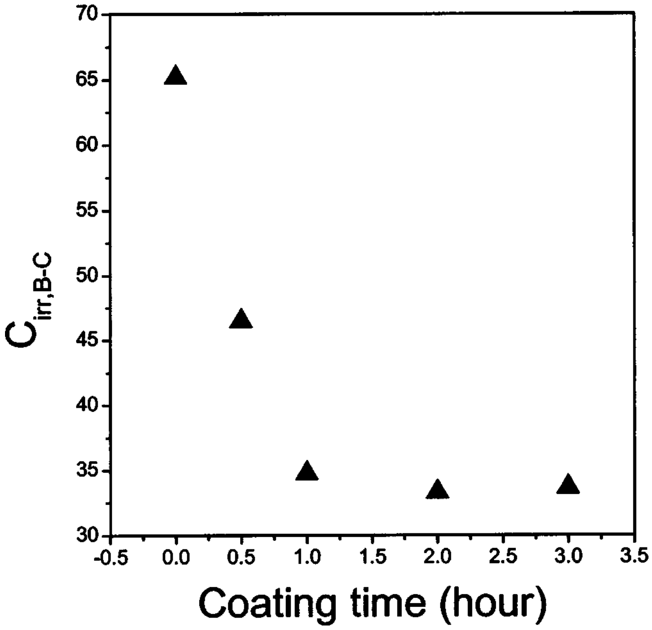

Figure 4. Variation of the irreversible capacity in sector B-C of the graphite coated with pyrolytic carbons at various coating times.

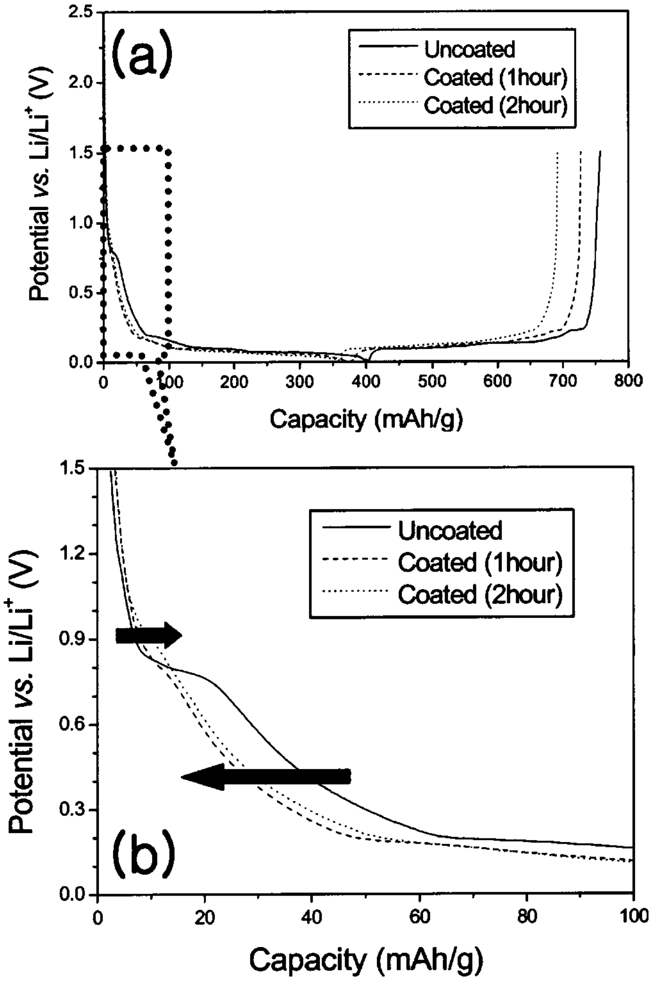

Figure 5. (a) First charge-discharge profiles and (b) magnified initial charging parts in the first charge curves of the bare graphite and coated graphite anodes.

cycle charge curves in Fig. 5a. As the coating time increases, the charge curves shift from left to right above 0.8 V *vs.* Li/Li$^+$ and from right to left below 0.8 V *vs.* Li/Li$^+$. In particular, the plateau around 0.8 V *vs.* Li/Li$^+$ that is observed in the charge curve of the bare graphite anode disappears by the coating of pyrolytic carbon. These phenomena are closely associated with the change of irreversible capacity loss. That is, the coating of pyrolytic carbon on the surface of graphite slightly increases the irreversible capacity formed above 0.8 V *vs.* Li/Li$^+$ but decreases drastically the irreversible capacity formed below 0.8 V *vs.* Li/Li$^+$.

Besenhard *et al.*[10] reported the plateau appeared about 0.8 V *vs.* Li/Li$^+$ in the first cycle charge curve of bare graphite anodes due to the co-intercalation of solvated ions with Li ions into graphene layers as shown in Fig. 6. These reactions between the electrolyte and the prismatic plane of graphite form SEI layers which consist of $Li_x(solv)_yC_6$ and cause large irreversible capacity loss. The carbon atoms in a graphene layer have strong covalent bonding. But the bonding between the graphene layers has a van der Waals force that is very weak. So when the basal plane of graphite contacts an electrolyte the co-intercalation of solvated ions does not occur, but it can occur when the prismatic plane of graphite contacts the electrolyte. On the other hand, the bonding force between graphene layers of pyrolytic carbon is much larger than that of graphite because the graphene layers of pyrolytic carbon are cross-linked to each other. That is, the pyrolytic carbon has a turbostratic structure.[11] Therefore, the co-intercalation of solvated ions cannot occur at the prismatic

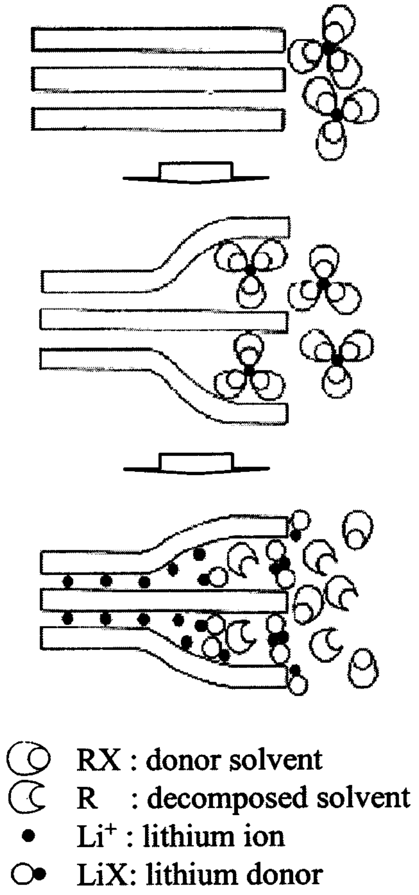

Figure 6. Model of co-intercalation of solvated ions between the graphene layers. (Adapted from Ref. 10.)

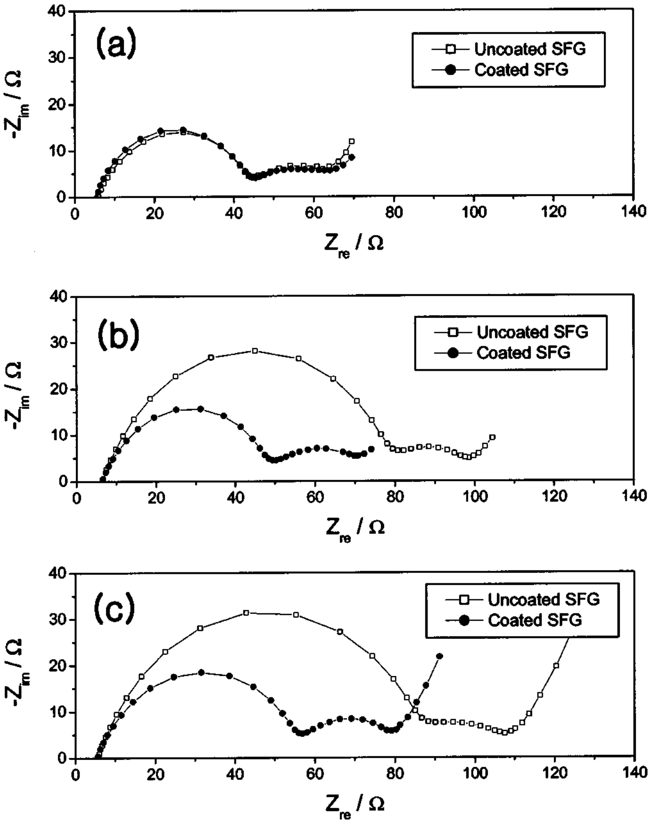

Figure 7. Nyquist plots of the bare graphite and coated graphite anodes at the potential of (a) 0.8, (b) 0.2, and (c) 0 V *vs.* Li/Li$^+$ in the first charging.

plane of pyrolytic carbon having a turbostratic structure. In this work, the decrease of irreversible capacity in graphite anodes by coating of pyrolytic carbon can be explained as follows. Covering prismatic planes of graphite with pyrolytic carbon having a turbostratic structure effectively inhibits the co-intercalation of solvated ions and it suppresses the formation of $Li_x(solv)_yC_6$ SEI layer which causes the irreversible capacity in the sector B-C.

In order to estimate the internal impedance of graphite electrodes, the Nyquist plots obtained from the results of EIS analysis are shown in Fig. 7. In the Nyquist plot, the first and second semicircles appear to be due to the contact resistance and charge-transfer resistance, respectively. The last linear part represents the Warburg impedance.[12] Figure 7a shows the Nyquist plots of bare graphite and coated graphite anodes at 0.8 V *vs.* Li/Li$^+$ of the first charge cycle (B point in Fig. 1). Figure 7b and c shows those at 0.2 V *vs.* Li/Li$^+$ (C point in Fig. 1) and at 0 V *vs.* Li/Li$^+$ (full charge state) of first charge cycle, respectively. The effects of coating do not appear when the charge proceeds until 0.8 V *vs.* Li/Li$^+$ as shown in Fig. 7a. However, the effects of coating appear apparent after charging in the B-C sector as shown in Fig. 7b. The contact resistance of the coated graphite electrode is much smaller than that of the bare graphite electrode. As mentioned above, this demonstrates that the SEI layer of $Li_x(solv)_yC_6$ does not form on the prismatic surface of graphite by coating of pyrolytic carbon. EIS spectra of fully charged electrodes in Fig. 7c do not differ greatly from those in Fig. 7b. This means that the coating effects on the electrochemical resistances of graphite electrode can be neglected in sector C-D.

Figure 8 is a plot for the variation of irreversible capacity in sector C-D. Sector C-D is the potential range below 0.2 V *vs.* Li/Li$^+$, in which lithium ions begin to intercalate between graphene layers of a graphite anode. Thus the irreversible capacity of this sector is mainly due to the loss of Li ions inserted within graphite. Internal defects (micropore, buckled layer, grain boundary, etc.) of carbon materials can play roles of irreversible sites for lithium ions. The irreversible capacity loss is proportional to the amount of lithium ions trapped in the internal defects. In general, disordered carbons (pyrolytic carbon) have many more internal defects than

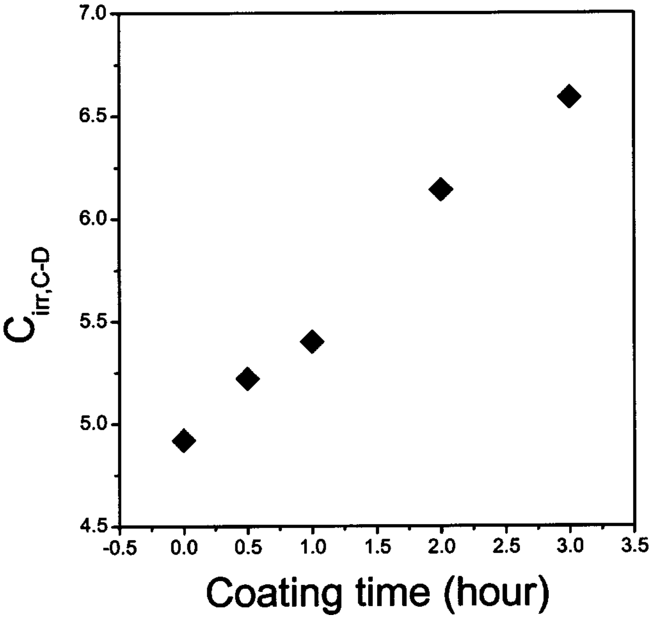

Figure 8. Variation of the irreversible capacity in sector C-D of the graphite coated with pyrolytic carbons at various coating times.

highly ordered carbons (graphite). From the viewpoint of the irreversible capacity loss owing to internal irreversible sites pyrolytic carbon can have more irreversible capacity than graphite. Therefore, as shown in Fig. 8, the linear increment of irreversible capacity in sector C-D with coating time is due to the linear increment in the amount of pyrolytic carbon covered on the surface of graphite, that causes the increase of internal irreversible sites.

Conclusions

We examined the irreversible capacity loss of graphite anodes for lithium ion secondary battery by coating with pyrolytic carbon on the surface of graphite particles. The irreversible capacity of graphite anodes was divided into three parts and we investigated the main irreversible reaction in each part. The irreversible capacity formed above 0.8 V *vs.* $\mathrm{Li/Li^+}$ was due to the electrochemical or chemical reduction between the electrolyte and graphite particles, which was proportion to the BET surface area of graphite particles. In the potential range of 0.2–0.8 V *vs.* $\mathrm{Li/Li^+}$, the main irreversible reaction was the co-intercalation of solvated ions with lithium ions into the graphene layer, which was closely related to the surface structure of graphite. This reaction can be suppressed effectively by a coating of pyrolytic carbon having a turbostratic structure on the surface of graphite particles. Below 0.2 V *vs.* $\mathrm{Li/Li^+}$, the irreversible capacity loss resulted from the trapping of lithium ions at internal irreversible sites of pyrolytic carbon, which were associated with the internal structure of carbon electrode materials.

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