Effect of iodine treatment on the electrochemical performance of natural graphite as an anode material for lithium-ion batteries

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Abstract

After being heated with iodine at certain temperatures in nitrogen, natural graphite shows superior electrochemical performance compared to the original one as the anode material in lithium-ion batteries. The electrochemical behavior of iodine-treated natural graphite was studied and the improvement for the electrochemical performance of natural graphite after iodine treatment was mainly ascribed to the chemically bonded iodine on the surface of natural graphite. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the past decade, many kinds of carbon materials have been investigated as the anode materials for lithium-ion batteries. Among them, natural graphite seems a very promising candidate due to its many advantages such as its high capacity at low and flat potential, its low price. However, from previous work, we have found that the rather raw natural graphite received directly from mines cannot deliver satisfactory electrochemical performance [1]. There are many factors which may contribute to its poor electrochemical performance. One of the factors, namely, the exposure degree of edge planes to the non-aqueous electrolytes plays a very important role in the capacity for lithium intercalation [2]. This factor will become much more pronounced in the case of flake-shaped, especially big particle-sized natural graphite. One way to solve this problem is by cutting the graphite flakes into smaller ones in order to expose more edge planes to the electrolytes [3].

On the other hand, there are many kinds of functional groups on the edge planes which can influence the effectiveness of edge planes' exposure to the electrolytes and thus affect the electrochemical performance of carbon. So far, more and more work has been carried out on modifying the functional groups to make full use of the exposed edge planes for smooth lithium intercalation, and consequently more and more insights have been gained on the effect of functional groups on the electrochemical performance of carbon anodes. For example, it was found that hydroxyl groups on the surface of carbon retard the entrance of lithium ions into carbon, whereas carboxylic acid groups on the surface help in building up solid electrolyte interface (SEI) films and provide extra lithium accommodation sites other than graphite layers for lithium intercalation, etc. [4,5].

In this paper, we will show that introducing iodine onto the surface of natural graphite can improve the electrochemical performance of graphite anode remarkably.

2. Experimental

2.1. Iodine treatment of natural graphite

Madagascar natural as-received graphite (with ash content of ca. 9 wt.%) was mixed with iodine in the weight ratio of 4:1 at room temperature. Then, in a tube furnace flushed with nitrogen flow, the mixture was heated from room temperature to desired treating temperature in about 1 h and heated at the final temperature for 3 h. The furnace was then turned off and cooled to near room temperature in a few hours.

2.2. Cell assembly and electrochemical measurements

Graphite electrodes were fabricated by spreading slurry, which consists of 20 mg graphite, 1 mg ethylene/propylene/ diene polymer (EPDM) as a binder dissolved in cyclohexane,

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evenly onto the surface of a stainless steel mesh substrate. After cyclohexane was evaporated, the electrodes were pressed at the pressure of about 2.8 t/cm^2 and then heated in vacuum at 200°C for over 6 h.

The charge (de-intercalation of lithium ions from graphite electrodes) and discharge (intercalation of lithium ions) characteristics of graphite electrodes were examined in two-electrode cells. The cell comprised a lithium metal electrode and a graphite electrode that were separated by a polypropylene separator and glass fiber. The electrolyte solution was 1 M LiPF$_6$-ethylenecarbonate (EC)/dimethyl-carbonate (DMC) (1:2 by volume).

All the operation for the cell assembly was carried out in a glove box filled with argon gas where both the moisture and oxygen concentrations were very low.

Galvano-potentiostatic charge and discharge were applied on the testing cells, i.e. at first, discharged the cells from open circuit voltage (OCV) to 0 V at the constant current density of 0.4 mA/cm^2; second, kept the potential of the cells at 0 V until the current density dropped down from 0.4 to 0.08 mA/cm^2; third, rested the cells for 10 min; fourth, charged the cells at the constant current density of 0.4 mA/cm^2 to 1.5 V; at last, rested the cells for 10 min and repeated the cycling as above.

Cyclic voltammetry (CV) of graphite samples were measured in three-electrode cells. In these cells, lithium metal chips were used as both the counter and reference electrodes while graphite electrodes were applied as the working electrodes. The electrolyte solution was 1 M LiPF$_6$-EC:DMC (1:2 by volume). In the cyclic voltammetric tests, the potential was scanned from OCV (ca. 3 V versus Li$^+$/Li) to 1.2 V at a higher scan rate of 0.5 mV/s at first, then cycled between 1.2 and 0 V versus Li$^+$/Li at a slower scan rate of 0.05 mV/s.

3. Results and discussion

Table 1 lists some physical characteristics of both the original and the iodine-treated natural graphite samples. From this table, it is difficult to find some marked physical
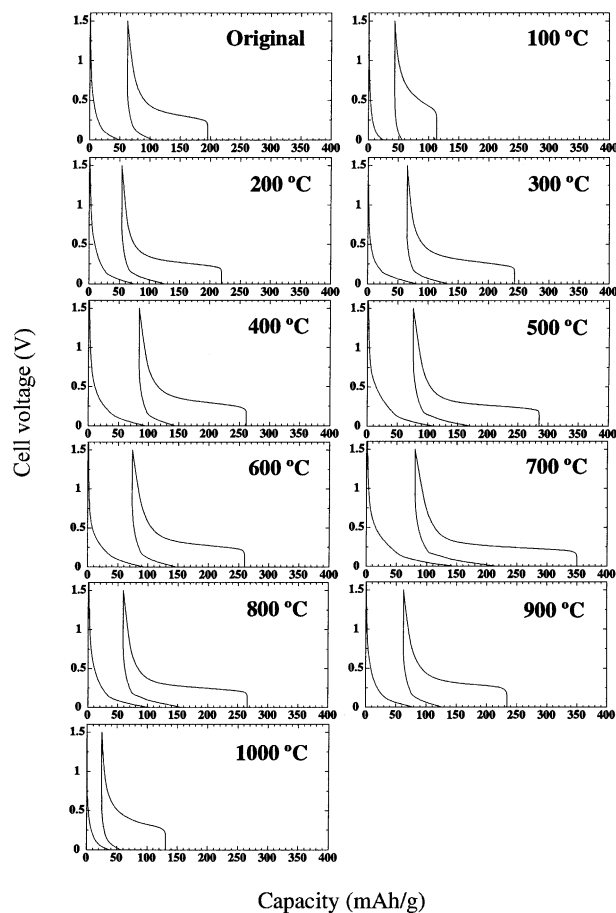

Fig. 1. Typical charge–discharge curves at the first-cycle for the original and iodine-treated natural graphite samples heated at various temperatures.

changes caused by the iodine treatment. But the iodine treatment does alter the electrochemical performance of natural graphite greatly as follows.

Fig. 1 shows the typical charge and discharge curves at the first-cycle of the graphite samples before and after the iodine treatments at different temperatures. It can be observed that for all the graphite samples, the majority of the capacity exhibits large hysteresis and lithium is mainly inserted near

Table 1
Some physical properties of graphite samples

Natural graphite type	Ash content (wt.%)	Specific surface area (m^2/g)	d_{002} (nm)	Lc (0 0 2) (nm)
Original	9.2	2.2	0.335	>100
Iodine-treated at 100°C	9.3	1.8	0.335	>100
Iodine-treated at 200°C	9.4	2.3	0.335	>100
Iodine-treated at 300°C	9.0	2.3	0.335	>100
Iodine-treated at 400°C	9.5	2.0	0.335	>100
Iodine-treated at 500°C	9.1	1.9	0.335	>100
Iodine-treated at 600°C	9.4	2.1	0.335	>100
Iodine-treated at 700°C	9.3	1.9	0.335	>100
Iodine-treated at 800°C	9.7	2.0	0.335	>100
Iodine-treated at 900°C	9.2	2.2	0.335	>100
Iodine-treated at 1000°C	9.3	2.3	0.335	>100

0 V. This phenomenon can be attributed to the big particle size and high anisotropy characteristic of these graphite samples (iodine-treated or not). As shown in Fig. 2, all the graphite particles are in the shape of flakes with much wider dimensions parallel and much thinner dimensions perpendicular to the basal planes. As for such kind of graphite, it can be conceived that the surface area of edge plane amounts to only a small part of the whole surface area of the graphite particles and thus the entrance of lithium through edge planes into the bulk of graphite particles becomes very difficult. So the initial insertion of lithium into graphite proceeds at a very low potential (<0.2 V) and the majority of the first-cycle discharge capacity is at ca. 0 V. Moreover, since the lithium transportation along the galleries between graphite layers is a long journey due to the big dimensions parallel, the intercalation and the de-intercala-

tion of lithium will show big hysteresis in the charge–discharge curves.

Comparing the first-cycle charge–discharge curves of natural graphite before iodine treatment or after being heated with iodine at different temperatures, it can be seen that the iodine treatment can change the electrochemical performance of natural graphite greatly. To show the change of natural graphites electrochemical performance more clearly, we plotted the graphs of the first-cycle discharge capacity, charge capacity, irreversible capacity and Coulombic efficiency against treating temperature, respectively, in Fig. 3. From Fig. 3(a), it can be observed that both the first-cycle charge capacity and discharge capacity of natural graphite increase with the iodine treatment except for treating temperatures at 100 and 1000°C. In the case of treating temperature at 700°C, both the discharge capacity and the
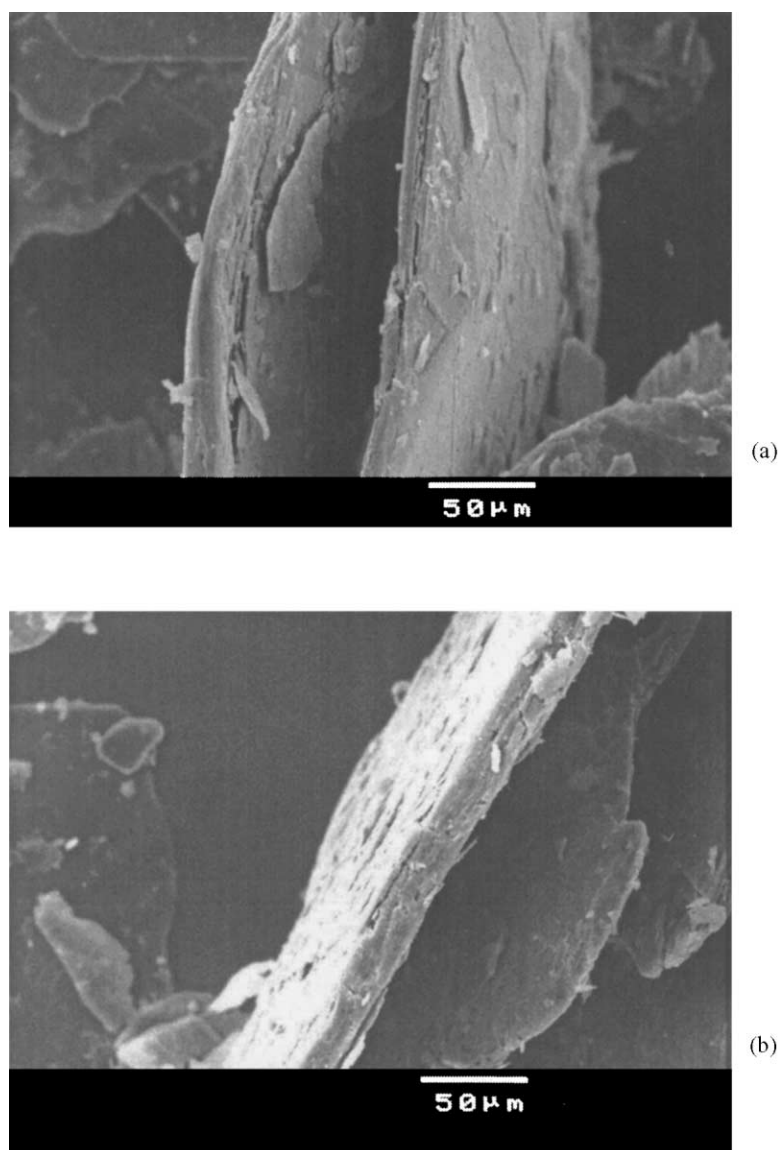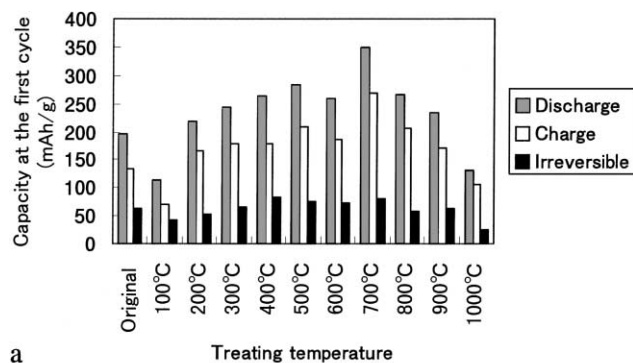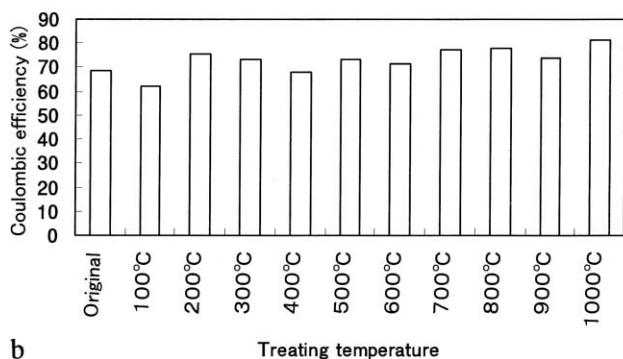

(a)

(b)

Fig. 2. SEM graphs of natural graphite samples: (a) the original Madagascar natural graphite; (b) natural graphite iodine-treated at 700°C.

a   Treating temperature

b   Treating temperature

Fig. 3. Histograms of the charge–discharge characteristics for iodine-treated natural graphite samples: (a) capacity at the first-cycle vs. treating temperature; (b) Coulombic efficiency at the first-cycle vs. treating temperature.

charge capacity at the first-cycle show the maximums in all the natural graphite samples. It is notable that the charge capacity of natural graphite iodine-treated at 700°C is as high as twice the value of that for original natural graphite. Although, this value (269.3 mAh/g) is smaller than the theoretical value of fully lithiated graphite (LiC$_6$, 372 mAh/g), it shows that iodine treatment is an effective method of enlarging charge capacity of natural graphite. On the other hand, from Fig. 3(b), it can be seen that the Coulombic efficiency of iodine-treated natural graphite seems to fluctuate around the value of that for the original natural graphite.

Before correlating the relationship between the so-called "iodine-treatment" and the improvement of natural graphite's electrochemical performance, it should be noted that only heating in some inert atmosphere like nitrogen also alters the surface states of natural graphite and thus changes its electrochemical performance. For comparison with the iodine treatment, we performed a complementary experiment as the "blank test", i.e. heating the natural graphite in nitrogen flow without the addition of iodine at different temperatures. Since, the iodine treatment seems effective at temperatures higher than 300°C as shown in Fig. 3, the treating temperatures in the "blank test" started from 400°C. Fig. 4 shows the relationship among the first-cycle discharge capacity, charge capacity, irreversible capacity and heating
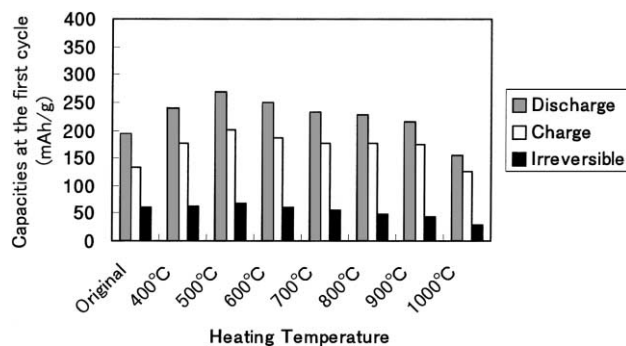

Fig. 4. Histogram of capacities at the first-cycle for natural graphite heated in nitrogen.

temperature. By a careful comparison of Figs. 3 and 4, it is interesting to note that the first-cycle charge capacities of natural graphite heated at 400, 500, 600, and 900°C in nitrogen almost equal to those of natural graphite treated with iodine at the same temperatures, respectively. In contrast, the natural graphite heated in nitrogen at 700 and 800°C show much lower first-cycle charge capacity than those of natural graphite treated with iodine at the same temperatures, respectively. Moreover, the first-cycle discharge capacities of natural graphite heated in nitrogen at the temperatures from 400 to 900°C are lower than those of the natural graphite iodine-treated at the same temperatures, respectively. Consequently, the irreversible capacity at the first-cycle shows the same trend for both series of graphite samples. From the comparison of the results as shown in Figs. 3 and 4, the improvement of natural graphite's electrochemical performance after iodine treatment at temperatures of 400, 500, 600 and 900°C can be mainly attributed to the heat treatment in nitrogen atmosphere, especially for the charge capacity at the first-cycle. In the case of natural graphite treated with iodine at 700 and 800°C, the effect of iodine addition becomes more pronounced for the increase of the charge capacity at the first-cycle.

In the previous work carried out by Takamura's and coworkers [4], it was proposed that heating carbon in vacuum removes some kinds of functional groups which can retard lithium intercalation into carbon and make the entrance of lithium into carbon become more smooth. We believe that this mechanism also holds for the case of heat treatment in the nitrogen atmosphere. As for iodine treatment, especially at the temperatures of 700 and 800°C, other factors should be taken into account in addition to the mechanism mentioned above. These factors must bear some relationships with the addition of iodine. Actually, almost all the iodine mixed with natural graphite will sublime and be blown out with nitrogen flow during the course of heating at temperatures above 200°C as shown in Fig. 5. However, for most of the iodine-treated natural graphite samples, iodine element did be detected in the tail gas by iodo-starch reaction, when we flushed the graphite sample with air at about 900°C in a clean tube furnace although we have not
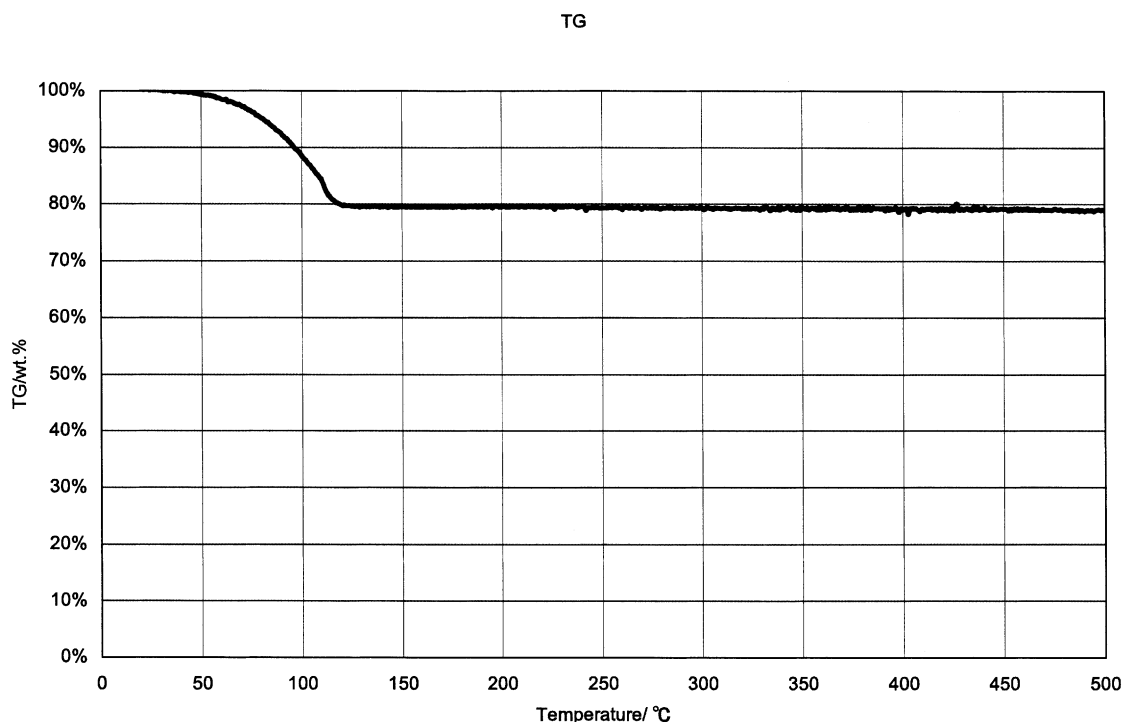
TG

Fig. 5. Thermogravimetry (TG) for the mixture of Madagascar natural graphite and iodine (in the weight ratio of 4:1) in nitrogen flow.

measured the exact amount of iodine. As shown in Fig. 6, if the tail gas was passed through the aqueous solution of starch, the colorless solution became light purple in the cases of natural graphite iodine-treated at temperatures from 100 to 800°C. On the contrary, for natural graphite iodine-treated at 900 and 1000°C, the color of the aqueous solution did not change. If there is some residual iodine left with natural graphite after iodine treatment, its amount must be very small (except for natural graphite iodine-treated at 100°C). It is the trace amount of iodine that plays some role on the electrochemical performance of natural graphite. From Table 1, we do not expect that iodine can intercalate into graphite since the value of d_{002} does not change after iodine treatment. Instead, iodine seems to reside on the surface of

natural graphite, especially on the edge plane. Iodine on the surface of natural graphite may be classified into two types: physically adsorbed and chemically bonded. On the surface of natural graphite iodine-treated at 100°C, all the iodine can be ascribed to the physically adsorbed type (I_2) since the temperature is too low to proceed some chemical reactions adequately between iodine and the functional groups on the surface of natural graphite. To test this assumption, we carried out a kind of "washing" experiment to get rid of physically adsorbed I_2 on the surface of graphite and flushed the resultant graphite samples with air. The washing experiment included the following steps: (1) dispersed the iodine-treated natural graphite sample (about 0.5 g) into the aqueous solution of $Na_2S_2O_3$ (0.1 M, 50 ml) and added in a little
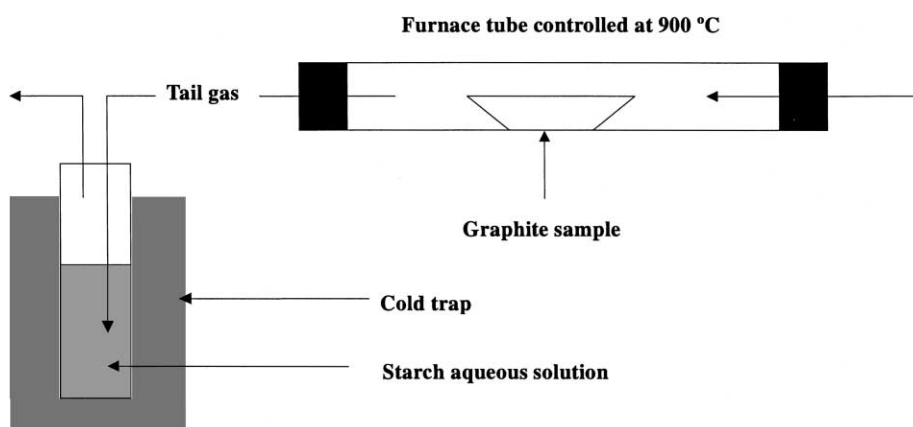

Fig. 6. Schematic of the detection of iodine in graphite samples.

of surface-active agent to make the surface of graphite be wetted by the solution very well; (2) put the resultant suspension solution into ultrasonic bath for 0.5 h; (3) filtered off the solution and rinsed the graphite particles with distilled water for many times; (4) dried the washed graphite in electric oven at 120°C. In this way, the physically adsorbed iodine can be removed from the surface of graphite and thus be separated from chemically bonded iodine species. For the washed 100°C iodine-treated natural graphite, iodine cannot be detected in the tail gas when being burned with air. From the poor charge–discharge characteristics of natural graphite iodine-treated at 100°C, it seems that the physically adsorbed iodine will decrease the charge capacity. We believe that the physically adsorbed iodine will react with lithium to form LiI on the surface of natural graphite when the natural graphite electrode is discharged in the electrolyte. The resultant LiI from the physically adsorbed iodine will block the entrance of lithium into graphite. For the natural graphite, iodine-treated at 100°C, considerable amount of iodine will be adsorbed on the surface of natural graphite since the treating temperature is too low to sublime and take away most of the iodine within the starting mixture subject to treatment. So the amount of LiI is big on the surface of natural graphite and thus cause the coverage layer on the edge plane to become too thick to intercalate–deintercalate lithium easily. As a result, the charge capacity is as low as 70.2 mAh/g and the hysteresis is very large as shown in Fig. 1. This expectation is schematically shown in Fig. 7. As for natural graphite iodine-treated at temperatures from 200 to 800°C, both the physically adsorbed and the chemically bonded iodine may be present on the surface but the amount of iodine will be very small. Comparing the charge–discha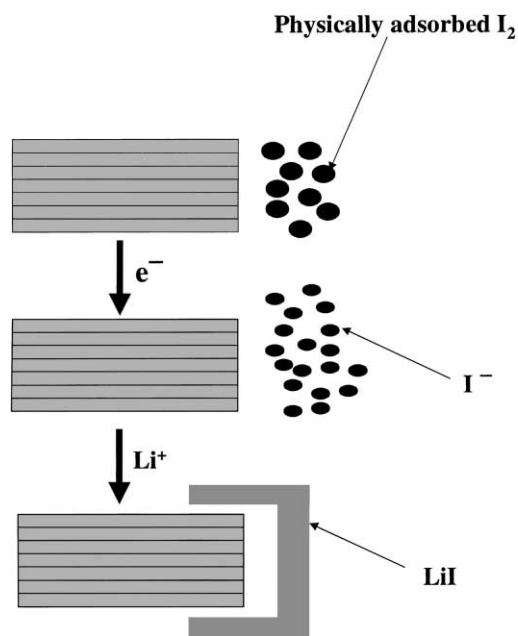rge characteristics of iodine-treated natural graphite with those of heat-treated ones in nitrogen atmosphere at the same temperatures, we can distinguish to what degree iodine affect the overall electrochemical performance of natural graphite. In the range of treating temperatures from 200 to 600°C, iodine has little effect on charge capacity of natural graphite, whereas seems to enlarge the irreversible capacity and decrease Coulombic efficiency. In contrast, for natural graphite iodine-treated at 700 and 800°C, iodine demonstrates its important role in increasing the charge capacity of natural graphite. Since the physically adsorbed iodine does not contribute to the increase of charge capacity as shown in the case of natural graphite iodine-treated at 100°C, it is expected that the improvement of electrochemical performance is mainly due to the presence of the chemically bonded iodine on the surfaces of natural graphite treated at 700 and 800°C. For natural graphite iodine-treated at lower temperatures, the chemically bonded iodine maybe only amounts to a very small portion of all the iodine on the surface. With the rise of treating temperature, the physically adsorbed iodine can chemically react with some functional groups on the surface of natural graphite more adequately. This expectation can be verified by the detection of iodine in the tail gas by iodo-starch reaction when "washed" iodine-treated graphite samples were burned with air. For the natural graphite iodine-treated at temperatures from 100 to 400°C, the change of color can hardly be observed in the starch solution. On the contrary, for natural graphite iodine-treated at temperatures from 500 to 800°C, iodine in the tail gas could change the color of starch solution into light purple. The iodine left with the "washed" iodine-treated natural graphite can be ascribed to the chemically bonded species. As the treating temperature rise to over 800°C, it seems that iodine on the surface of natural graphite is depleted since we did not discover the presence of iodine element (either physically adsorbed or chemically bonded) in the tail gas when flushing the natural graphite iodine-treated at 900 and 1000°C (non-washed) with air at the high temperature. Accordingly, the charge capacity of iodine-treated natural graphite decreases with the rise of temperature in the range from 800 to 1000°C. The surface states of iodine-treated natural graphite at different treating temperatures is schematically shown in Fig. 8.

In order to get more insight into the effect of the chemically bonded iodine on the electrochemical performance of natural graphite, cyclic voltammetric experiments were performed for the original natural graphite and natural graphite iodine-treated at 100, 700 and 1000°C, respectively. Fig. 9 shows the cyclic voltammograms of these natural graphite samples in the first five cycles. The cyclic voltammograms of the original natural graphite, the natural graphite iodine-treated at 100 and 1000°C are very similar, whereas the cyclic voltammogram of 700°C iodine-treated natural graphite is quite different from others. The distinctive features which the cyclic voltammogram of the natural graphite iodine-treated at 700°C shows may be noticed in two aspects.
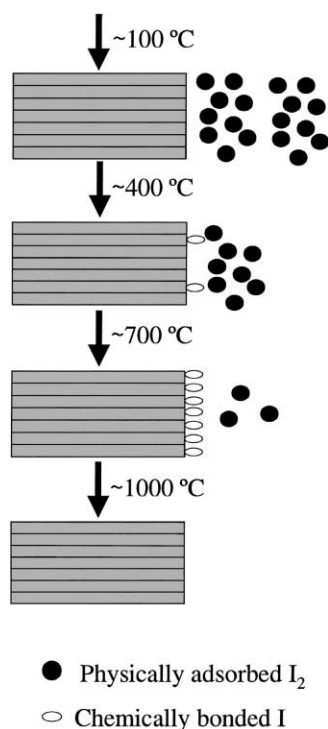

Fig. 7. Schematic of the reaction of physically adsorbed iodine on natural graphite surface with Li$^+$ during the first-cycle discharge.

Fig. 8. Schematic of the surface states of natural graphite at different treating temperatures.

Firstly, the peak near 0.6 V versus Li$^+$/Li during the cathodic scan is very small. This peak becomes weaker as the cycles proceed and almost disappears after the second cycle. On the contrary, in other samples' cyclic voltammograms, the corresponding peaks are bigger and still appear until the fifth cycle.

Secondly, both the cathodic peak at the potential below 0.2 V versus Li$^+$/Li and the anodic peaks are larger than the corresponding peaks in the cyclic voltammograms of other samples.
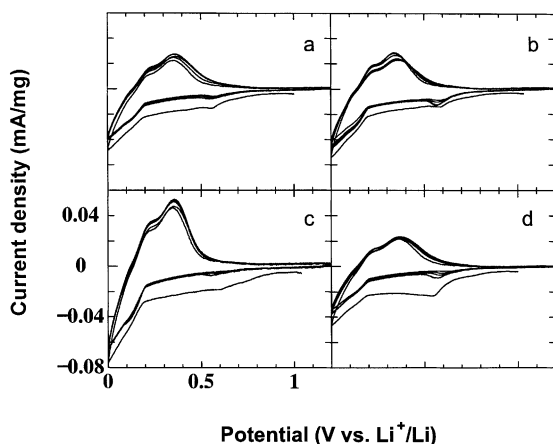

Fig. 9. Cyclic voltammograms of natural graphite samples (scan rate: 0.05 mV/s) in the electrolyte of 1 M LiPF$_6$-EC:DMC(1:2 by volume): (a) the original natural graphite; (b) iodine-treated at 100°C; (c) iodine-treated at 700°C; (d) iodine-treated at 1000°C.

Considering the first aspect, it is generally believed the peak near 0.6 V versus Li$^+$/Li is concerned with the solid electrolyte interface (SEI) formation through decomposition of the electrolyte. By comparing these cyclic voltammograms, it seems that the natural graphite iodine-treated at 700°C only needs milder decomposition of the electrolyte to build up the SEI on its surface and the SEI formed is more stable toward charge–discharge cycles than those in other cases.

As for the second aspect, it shows that more lithium is intercalated into and de-intercalated from the natural graphite iodine-treated at 700°C during charge–discharge cycles than in other cases.

The main difference between the natural graphite iodine-treated at 700°C with others lies in the presence of the chemically bonded iodine on its surface. If taking all these as mentioned above together into consideration, we may contribute the effect of the chemically bonded iodine to the improvement of building up SEI on the surface of natural graphite. Actually, SEI is a key factor which can affect the electrochemical performance of graphite [6]. In the work of Peled and coworkers [5], it was assumed that chemically bonded SEI on the surface of graphite improves the electrochemical performance markedly. We believe the chemically bonded iodine in our experiments is the same case with theirs.

4. Conclusion

Based on the observations above, it can be summarized that the chemically bonded iodine on the surface of natural graphite can help improve the electrochemical performance remarkably. Nevertheless, in the present work, the amount of chemically bonded iodine on the surface is too small to investigate its effect on the electrochemical performance of natural graphite quantitatively. Moreover, the iodine treatment seems not to be an effective and economic way to introduce chemically bonded iodine onto the surface of natural graphite. Further work relates to how to exactly analyze chemically bonded iodine on the surface of natural graphite and how to graft iodine chemically onto the surface of natural graphite more effectively is under way.

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