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Journal of Power Sources 93 (2001) 123–129

JOURNAL OF
POWER
SOURCES

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Carbon-coated natural graphite prepared by thermal vapor decomposition process, a candidate anode material for lithium-ion battery

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Received 6 April 2000; accepted 2 August 2000

Abstract

The electrochemical performance of thermal-vapor-decomposition carbon-coated natural graphite was studied in both propylene carbonate (PC)-based electrolytes and ethylene carbonate (EC)-based electrolytes. In the cyclic voltammograms of carbon-coated natural graphite, the hump in the range of 1.3–0.7 V versus Li^+/Li can be observed when the potential was swept at higher scan rates. This hump was investigated with reference of carbon black. The effect of electrode-fabrication pressure on the electrochemical performance of carbon-coated in the PC-based electrolyte has also been studied. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbon-coated; Graphite; Lithium-ion battery

1. Introduction

Recently, carbon-coated graphite has drawn much attention as the substitute for graphite used as the anode material in lithium-ion battery [1–3]. The main advantage of the composite material over the constitutional materials lies in the “hybrid” characteristics, which can overcome most of the drawbacks whereas keep the benefits of both of the “parents” (graphite and carbon) materials. However, whether the surface of graphite is completely covered by carbon coating is an open question before standard methods were developed to evaluate it. In our previous study of carbon-coated natural graphite prepared by thermal vapor decomposition technique [4], the durability towards propylene carbonate (PC)-based electrolytes was correlated with the coating amount of carbon. Moreover, the storage mechanisms of lithium in both the “core” and the “shell” parts were investigated by solid state ^7Li NMR.

With the progress of the study, some new phenomena have been discovered [5]. In this paper, we would like to demonstrate these new insights as a complimentary work in detail.

2. Experimental

Most experimental details, including carbon-coated natural graphite samples, electrode preparations, electrolytes,

glove box operation, instrumentation, cells, etc. have been previously described [4]. Carbon-coated natural graphite samples from Mitsui Mining Co. Ltd., with carbon-coating amount of 17.6, 13.4, 8.6 wt.%, respectively, were used as well as the original natural graphite. In some cases for comparison, carbon black (Katayama Chemical) was selected to resemble some aspects of the electrochemical performance of carbon coating. Carbon black as received had been heated in nitrogen flow at 1000°C for over 6 h before use.

3. Results and discussion

It is well known that PC will decompose drastically on the surface of graphite and exfoliate graphite [6]. This fact makes it difficult to charge–discharge graphite electrodes reversibly in direct contact with the PC-based electrolytes. The carbon-shell–graphite-core concept as illustrated in Fig. 1 is aimed at solving this problem since carbon coating with turbostratic-structured can suppress the intercalation of lithium ions solvated by single PC molecules. In turn, PC-based electrolytes can become the probe into the coverage degree of carbon coating on the surface of graphite. However, the selection of PC-based electrolyte as the standard of the above test must be careful.

It is generally taken for granted that electrolytes containing PC equal to PC-based electrolytes. This conception is too vague. If ethylene carbonate (EC), which always stands for the counterpart of PC as high-permittivity solvents

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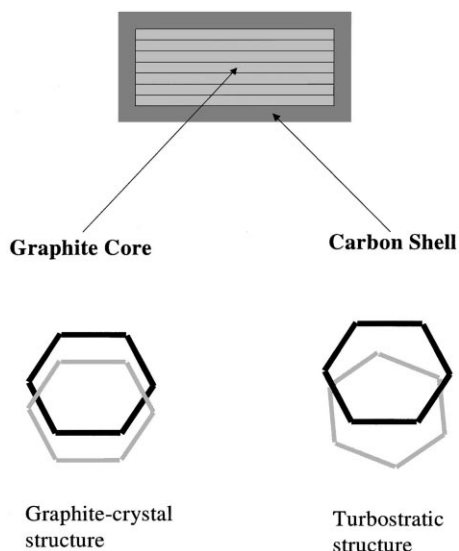


Fig. 1. Schematic of the core-shell structured carbon.

commonly used in lithium-ion battery, was mixed with PC with comparable amount in the electrolyte, how can we ascribe it to the categories of either PC, or EC-based electrolyte. In fact, graphite can be fairly cycled in the electrolyte of EC-PC-DMC (dimethyl carbonate) (1:1:1 by volume). Fig. 2 shows the typical cyclic voltammogram of the original natural graphite in the electrolyte of 1 M LiPF₆ dissolved in mixed solvents of EC-PC-DMC (1:1:1 by volume). At the first cycle, there are two small irreversible peaks at 0.7 and 1.2 V versus Li⁺/Li, respectively, which can be attributed to the decomposition of the electrolyte to build up the SEI film. These irreversible peaks disappear from the second cycle. At potential lower than 0.4 V versus Li⁺/Li, there are roughly three couples of reversible redox peaks. Actually, four cathodic peaks and

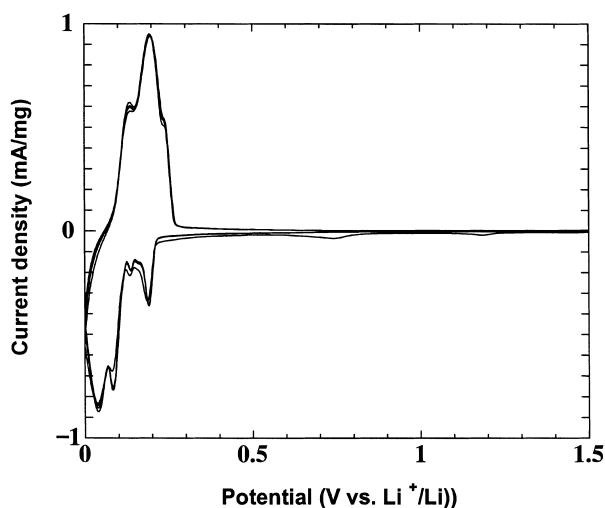


Fig. 2. Cyclic voltammogram of the original natural graphite in the electrolyte of 1 M LiPF₆ dissolved in PC-EC-DMC (1:1:1 by volume) in the first five cycles; scan rate: 0.1 mV/s.

three anodic peaks can be observed. The reversible peaks are due to the reversible stage transformations between Li-graphite intercalation compounds [7–10]. The current densities of these reversible peaks barely decrease with cycles, which implies the good cycleability of the graphite electrode in the electrolyte. As described above, it seems that the EC-PC-based electrolyte is not suitable for the test of coverage degree of carbon coating on the surface of graphite.

In a more strict sense, the electrolytes with binary solvents of PC and low viscosity solvents such as DMC, diethyl carbonate (DEC), methyl ethyl carbonate (MEC) are proper for the test of the coverage degree of carbon coating. The prerequisite for the choice of the “probe” electrolyte is the big decomposition of PC accompanied by graphite exfoliation when the “bare” graphite is used in the electrolyte. Fig. 3 shows the cyclic voltammograms of the original natural graphite in the electrolytes of 1 M LiPF₆ dissolved in the binary mixed solvents of PC and DMC with different volume ratios. For the electrolytes containing PC volume fraction exceeding 30 vol.%, there is one big irreversible peak at ca. 0.5 V versus Li⁺/Li at the first cycle, which is due to the decomposition of PC and graphite exfoliation. Besides, the reversible peaks lower than 0.3 V versus Li⁺/Li are very small. This means that small amount of lithium can be reversibly intercalated and de-intercalated into and from the original natural graphite electrode in these electrolytes. With the decrease of PC fraction in the electrolytes, the irreversible peak will become smaller whereas the reversible peaks become bigger. In the case of 20 vol.% PC, good electrochemical performance can be got. This phenomenon was first discovered by Nakamura et al. [11]. As described above, to demonstrate the difference between the electrochemical performances of carbon-coated natural graphite and the original natural graphite remarkably, PC content in the PC-DMC mixed solvents should be over 30 vol.%.

Fig. 4 shows the typical first-cycle charge-discharge curves of carbon-coated and the original natural graphite samples in the electrolyte of 1 M LiPF₆ dissolved in the mixed solvents of PC-DMC (35:65 by volume). As illustrated in Fig. 4a, in the first-cycle discharge curve of the original natural graphite, a very long plateau can be observed near 0.7 V, which is due to the decomposition of PC on the graphite electrode. This plateau is so long that it exceeds the testing time scale in our experiment, no charge capacity can be obtained. In contrast, in the first-cycle charge-discharge curve of natural graphite coated with 17.6 wt.% carbon, the long plateau at 0.7 V can hardly be seen whereas considerable charge capacity can be got. Besides, the discharge curve extends down smoothly to the low voltage of 0 V and the plateaus due to lithium intercalation can be clearly observed below 0.2 V. In the cases of natural graphite coated with 13.4 and 8.6 wt.% carbon, the long plateau due to decomposition of PC also appears. However, these discharge curves demonstrate a little different trend with that of the original natural graphite.

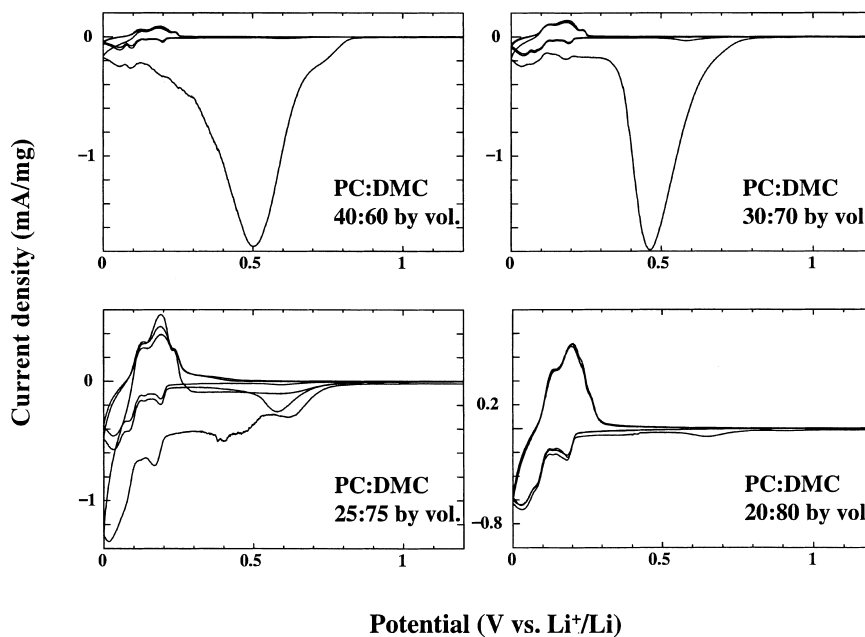


Fig. 3. Cyclic voltammogram of the original natural graphite in PC-based electrolytes of 1 M LiPF₆-PC-DMC; scan rate: 0.1 mV/s.

The discharge curve of the original natural graphite drops down slopingly and makes a sharp turn at ca. 0.7 V, leveling off at this voltage. In contrast, for natural graphite coated with both 13.4 and 8.6 wt.% carbon, the discharge curves go

down to voltages lower than the plateau, turn around in the arc shape, and then level off at the plateau voltage. Moreover, the lowest voltage in the discharge curve of natural graphite coated with 13.4 wt.% carbon is lower than that of natural graphite coated with 8.6 wt.% carbon. Comparing discharge curves of graphite samples, we can estimate that carbon coating covers almost the whole surface of natural graphite for natural graphite coated with 17.6 wt.% carbon, whereas the coverage of carbon coating is not adequate for natural graphite coated with 13.4 and 8.6 wt.% carbon. Moreover, the coverage is more complete for carbon coating amount of 13.4 wt.% than that for 8.4 wt.% carbon coating.

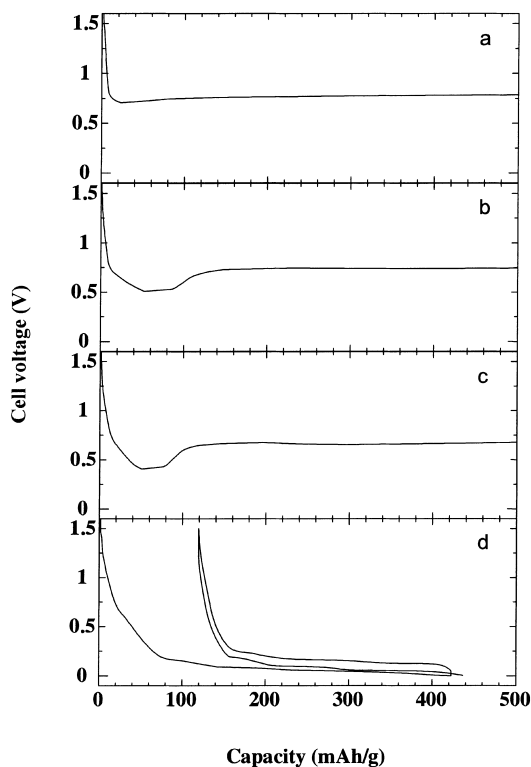


Fig. 4. Charge–discharge curves of graphite electrodes in the PC-based electrolyte of PC–DMC (35:65 by volume)/1 M LiPF₆ at the first cycle; (a) the original natural graphite; (b) natural graphite coated with 8.6 wt.% carbon; (c) natural graphite coated with 13.4 wt.% carbon; (d) natural graphite coated with 17.6 wt.% carbon.

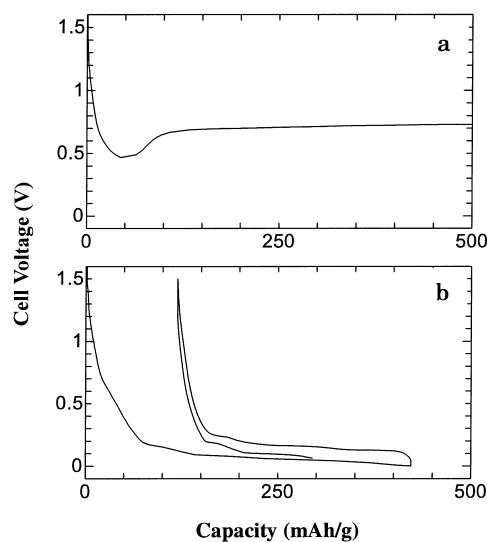


Fig. 5. Charge–discharge curves of natural graphite coated with 17.6 wt.% carbon in the electrolyte of PC–DMC (35:65 by volume)/1 M LiPF₆; (a) graphite electrode fabricated at the pressure of 1 tonne/cm²; (b) graphite electrode fabricated at the pressure of 0.2 tonne/cm².

Although carbon coating on the surface of natural graphite for coating amount of 17.6 wt.% is dense enough to protect the “core” graphite from PC attack, the big decomposition of PC accompanied by exfoliation can happen if the graphite electrode was fabricated in a wrong way. During the course of fabrication of graphite electrode, any procedures capable of destroying the carbon coating must be prohibited. For instance, rolling or pressing process is always applied to graphite electrodes. If the pressure upon the electrode is too high, carbon coating on the outer surface of natural graphite could be broken up. Thus, the PC-based electrolyte will penetrate through the cracks of carbon coating and touch the “core” graphite. In such a case, the big decomposition of PC and the graphite exfoliation will occur. Fig. 5 shows the first-cycle discharge curve of natural graphite coated with 17.6 wt.% carbon in the electrolyte of 1 M LiPF₆ dissolved in PC–DMC (35:65 by volume). The pressures applied to the

graphite electrode were 1 and 0.2 tonne/cm², respectively. As shown in Fig. 5a, the long plateau of PC decomposition and graphite exfoliation can be observed at ca. 0.7 V if the pressure was 1 tonne/cm². On the contrary, as illustrated in Fig. 5b, the long plateau at 0.7 V can't be seen if the pressure is as low as 0.2 tonne/cm². For the same carbon-coated natural graphite, in the same electrolyte, the electrochemical performance is quite different after fabrication of graphite electrode at different pressures.

The differences between the electrochemical performances of carbon-coated and the original natural graphite are not only responses to the big decomposition of PC, but also the storage mechanisms of lithium. In the differential capacity curves of carbon-coated natural graphite, dedicated features indicative of the presence of carbon phase can be observed [5]. The “fingerprint” feature is the hump in the potential range from 0.7 to 1.3 V versus Li⁺/Li. In principle,

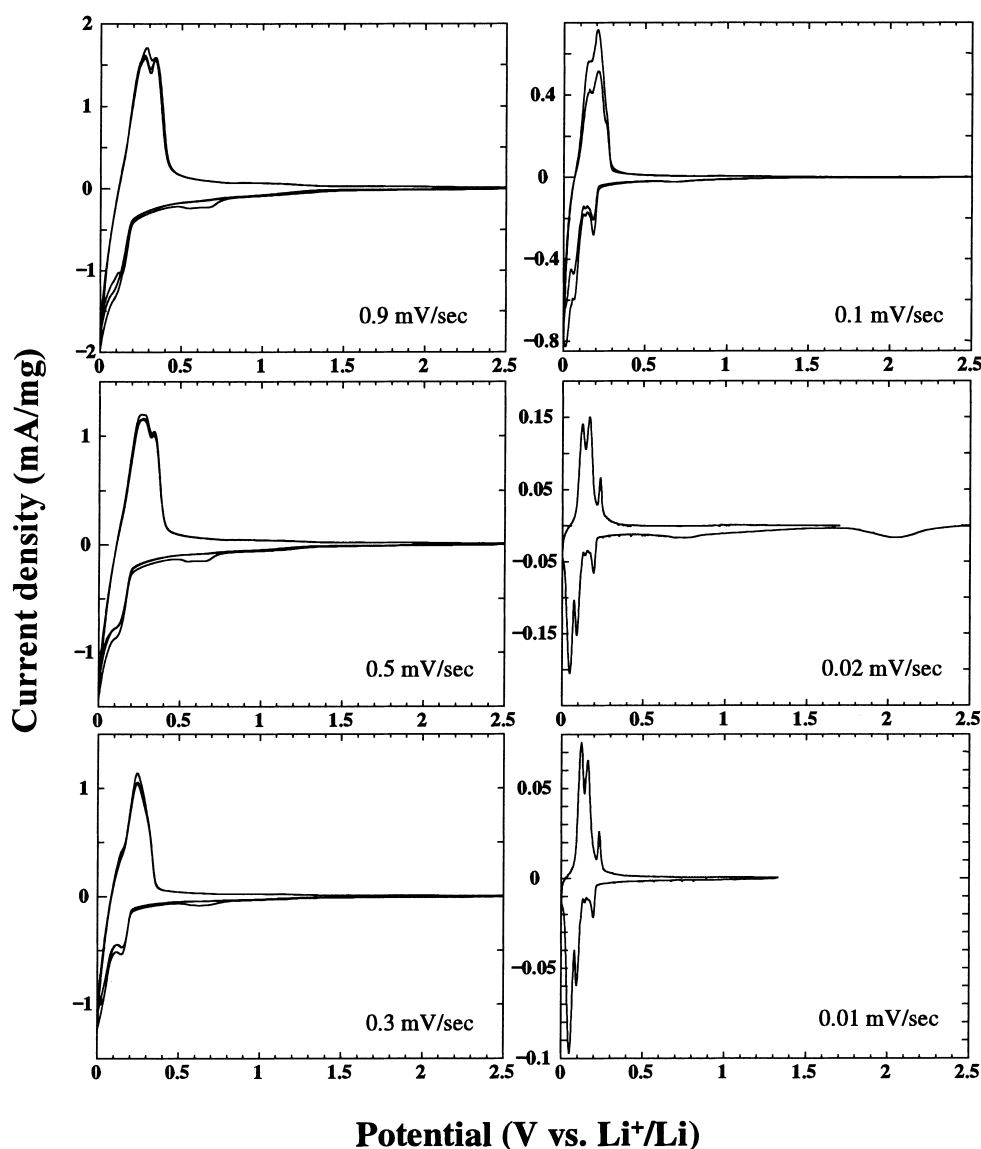


Fig. 6. Cyclic voltammograms of natural graphite coated with 17.6 wt.% carbon in the electrolyte of 1 M LiPF₆ dissolved in EC–DMC (1:2 by volume).

cyclic voltammetric results are very similar to differential capacity curves [12]. However, in our previous study, such kind of hump couldn't be detected in the cyclic voltammogram of carbon-coated natural graphite when the scan rate was 0.1 mV/s [4].

Fig. 6 shows the cyclic voltammograms of natural graphite coated with 17.6 wt.% carbon in the electrolyte of 1 M LiPF₆ dissolved in EC–DMC (1:2 by volume) at different scan rates. It can be observed that with the decrease of the scan rate, the reversible redox peaks lower than 0.4 V versus Li⁺/Li due to lithium intercalation and de-intercalation become well-separated and the cathodic peaks shift towards the negative potential which means that the redox processes become more reversible. Moreover, as the scan rate increases, the hump range from ca. 1.3 to 0.7 V versus Li⁺/Li appears. This hump can be seen in both the cathodic and the anodic scans, with almost the same size, which indicates it is also a reversible electrochemical process. This feature can be enlarged only at higher scan rates, say 0.9 mV/s. At lower scan rates, for example, 0.1 and 0.02 mV/s, this feature diminishes. It is believed that the hump originates from the carbon coating. The electro-

chemical process of this hump, as was already suggested, corresponds to the storage of lithium into cavities of carbon [13,14]. On the other hand, this process was also ascribed to lithium residence in the non-orientated phase of carbon [15]. In the previous cyclic voltammetric study on carbon black heated at temperatures from 1200 to 1600°C, two electrochemical processes were observed at ca. 0.2 and 0.9 V, respectively [16]. It was found that the current of the peak at 0.2 V bear a linear relationship with the square root of scan rate, whereas the current of the peak at 0.9 V is proportional to the scan rate. This means that the change rate for the current of the peak at 0.9 V is much higher than that of the peak at 0.2 V when the scan rate in cyclic voltammetric tests is altered. We believe that carbon black is very similar to carbon coating on the surface of natural graphite since both of these carbon materials need the decomposition of organic gas at temperatures around 1000°C. So it can be estimated that carbon coating can also have two electrochemical processes. One is at lower potential of ca. 0.2 V due to lithium intercalation and de-intercalation. The other is at higher potential range from 1.3 to 0.7 V versus Li⁺/Li. The peak corresponding to the electro-

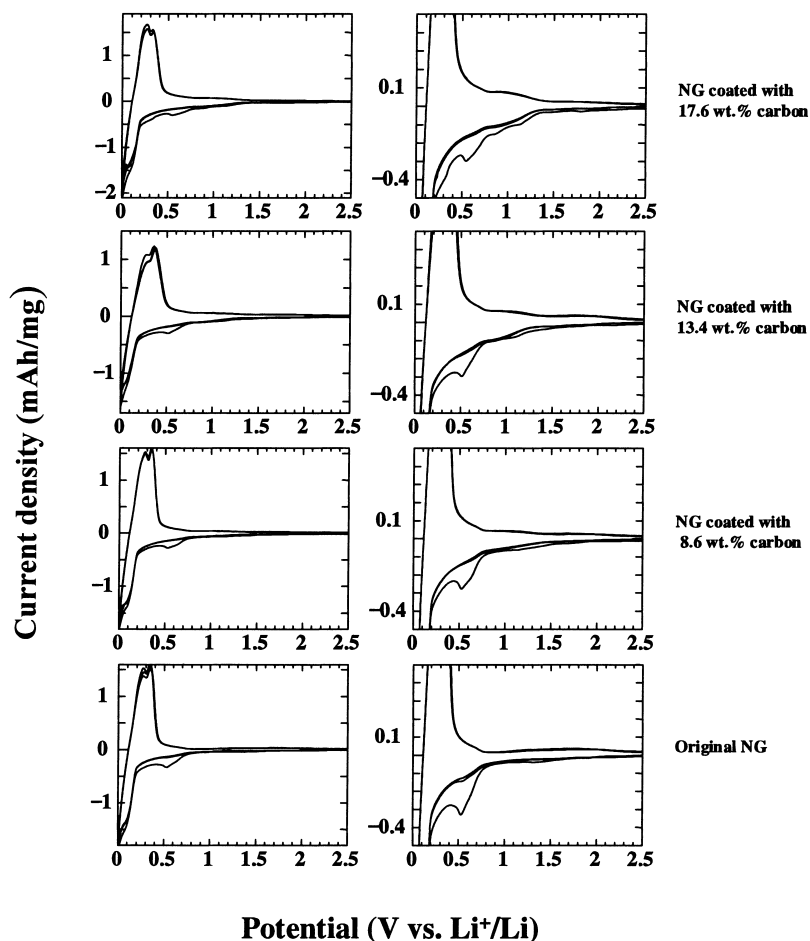


Fig. 7. Cyclic voltammograms of graphite samples in the electrolyte of 1 M LiPF₆ dissolved in EC–DMC (1:2 by volume); scan rate: 1 mV/s.

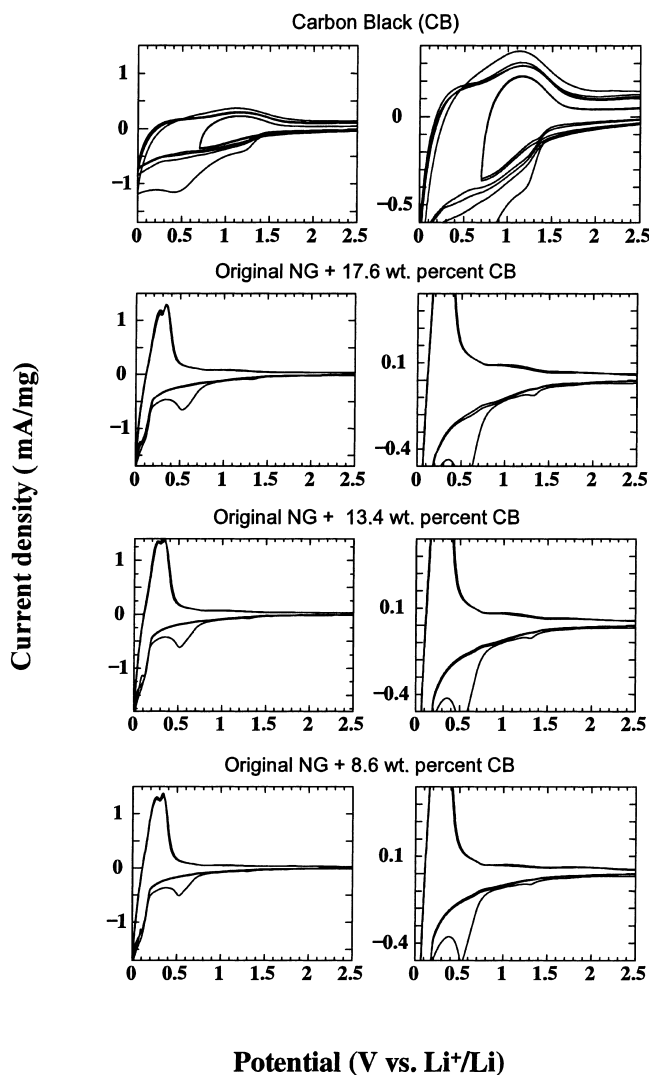


Fig. 8. Cyclic voltammograms of carbon black and the mixtures of the original natural graphite (NG) and carbon black (CB) in the electrolyte of 1 M LiPF₆ dissolved in EC–DMC (1:2 by volume); scan rate: 1 mV/s.

chemical process at lower potential in cyclic voltammogram will be overlapped by the peaks corresponding to lithium intercalation and de-intercalation into and from the “core” graphite phase. At common scan rates, say 0.9 mV/s, the magnitude of the hump range from 1.3 to 0.7 V versus Li⁺/Li is comparable with that of the peaks due to lithium intercalation and de-intercalation in the cyclic voltammogram of carbon-coated natural graphite. With the decrease of scan rate, the magnitude of the hump will decrease more quickly than that of the peaks at ca. 0.2 V. Thus, this hump almost disappears at low scan rates as compared with the peaks at ca. 0.2 V.

Fig. 7 shows the cyclic voltammograms of carbon-coated natural graphite samples, together with the original natural graphite sample in the electrolyte of 1 M LiPF₆ dissolved in EC–DMC (1:2 by volume) at the scan rate of 1 mV/s. Left side demonstrates the cyclic voltammograms in whole scale.

Right side demonstrates the cyclic voltammogram in a smaller scale to observe the hump more clearly. It can be seen that, with the increase of coating amount, the height of the hump increases. For the original natural graphite, no hump can be observed in the range from 1.3 to 0.7 V versus Li⁺/Li.

Fig. 8 shows the cyclic voltammograms of carbon black and the mixtures of the original natural graphite (NG) and carbon black (CB) in the electrolyte of 1 M LiPF₆ dissolved in EC–DMC (1:2 by volume) at the scan rate of 1 mV/s. The hump can also be observed in all these cyclic voltammograms. With the increase of carbon black content in the mixture, the height of the hump increases. Comparing Figs. 7 and 8, we can conclude that carbon coating on the surface of natural graphite resembles carbon black in the electrochemical responses of cyclic voltammetry.

4. Conclusion

So far, we have shown the electrochemical performance of carbon-coated natural graphite in both PC and EC-based electrolytes. It can be concluded as follows:

1. The electrolytes of the binary mixed solvents of PC and DMC (PC content more than 30 vol.%) can be chosen as the standards to test whether the surface of natural graphite is completely coated with carbon.
2. Carbon coating on the surface of natural graphite can be destroyed in the process of rolling and pressing if the pressure is too high, and thus can't protect natural graphite from PC attack.
3. Cyclic voltammetry is a powerful technique to investigate the electrochemical performance of carbon-coated natural graphite. By altering the scan rate, two electrochemical performance indicative of both the “core” graphite and the “shell” carbon phases, respectively, can be clarified.

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