

Characteristics of carbon-coated graphite prepared from mixture of graphite and polyvinylchloride as anode materials for lithium ion batteries

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Abstract

A carbon-coated graphite is investigated as the negative electrode for Li-ion batteries. The carbon-coated graphite particles are prepared by simple heat-treatment of mixtures of graphite and poly(vinyl chloride), PVC, at 800–1000°C in an argon flow. The carbon coating reduces significantly the initial irreversible capacity of the graphite in a propylene carbonate-based electrolyte, by suppressing the solvated lithium ion intercalation, and also improves the initial charge–discharge coulombic efficiency. By carbon coating, the specific surface area of graphite particles is greatly increased. These findings can be explained by assuming that a turbostratic structure of PVC-carbon resists irreversible side-reactions which are controlled predominantly by active, edge surface sites. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Many types of carbons have been widely studied as the negative electrode for lithium-ion batteries [1–5]. Graphite is still one of the most promising materials because it exhibits a high specific capacity, charge–discharge reversibility, and a desirable charge potential profile. Graphite suffers, however, from a large irreversible capacity loss during the first charge–discharge cycle due to electrolyte decomposition followed by the formation of a solid electrolyte interface (SEI) film [6–8] and solvated lithium intercalation between the graphene layers [6,8,9].

The irreversible capacity loss associated with the use of graphite is considerably dependent on the electrolyte used. Among the solvents that cause exfoliation of graphene layers, propylene carbonate (PC) is the worst. For example, the irreversible reactions are more severe in PC-based electrolyte than in ethylene carbonate (EC)-based

electrolyte [10,11]. Nevertheless, the use of PC as a solvent is desirable for low-temperature performance of batteries because of its low melting point (–55°C).

Recently, some attempts to suppress the solvent co-intercalation and reduction of PC-based solvents and reduce the first irreversible capacity have been made through a surface modification procedure which is based on coating the graphite with carbon [12–14]. It has been found that carbon coating of the fine particles of some ceramics is successfully accomplished by a simple mechanical mixing of ceramic particles with poly(vinyl chloride) (PVC) powders and heating to a temperature of around 1000°C in an inert atmosphere to carbonize the PVC [15]. The PVC is known to be carbonized through a liquid phase with very low viscosity, which would allow a coating with uniform carbonaceous layers. This method is expected to be a powerful process for carbon-coating because of its simplicity.

In the present study, carbon-coated graphite has been prepared by utilizing pyrolysis of PVC, as described above, and the effect of carbon coating on the electrochemical performance in both EC-based and PC-based electrolytes has been investigated.

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2. Experimental

The graphite used in this experiment was MCMB6-28 (Osaka Gas Co.). Carbon-coated graphite was prepared by mechanically mixing graphite particles in a mortar with 70 wt.% PVC and heating the mixture in an alumina boat to a temperature between 800 and 1000°C for 1 h under an argon flow. The heating rate was 5°C per min. To increase the extent of the coating on the graphite, “double coating” was carried out by a second application of the same procedure.

The charge (de-intercalation of lithium ions from a graphite anode) and discharge (intercalation of lithium ions) characteristics of the graphite electrode were examined in a coin cell (2016 type). The cell comprised a lithium metal electrode and a carbon electrode that were separated by a separator. The carbon electrode consisted of 90 wt.% carbon powder and 10 wt.% poly(vinylidene fluoride) (PVDF) as a binder. The *n*-methyl pyrrolidinone (NMP) was added to the mixture and the resulting slurry was spread on to a copper grid. The electrodes were dried for 12 h at 120°C in a vacuum oven and pressed at about 0.4 t cm⁻². The electrolyte solution was 1 M LiPF₆ in PC/EC/DEC (diethyl carbonate) (3:2:5 by volume) or EC/DEC mixed solvents. Cells were cycled in the range 0.0–2.0 V. The typical charge/discharge current density was 0.3 mA cm⁻² except where specified otherwise.

3. Results and discussion

Carbonization of PVC is known to occur above 500°C [16]. When the heating temperature is increased to 1000°C, the crystallite size (L_a) increases slightly and the H/C atomic ratio decreases monotonically, although the width and position of the broad X-ray diffraction peak do not change greatly. This suggests that the carbon has an amorphous structure.

In electrochemical testing of cells using carbon made from PVC and with an electrolyte of PC/EC/DEC, both the capacity and irreversible capacity during the first cycle decrease as the heating temperature is increased. The characteristics of carbon prepared from pyrolysis of PVC are summarized in Table 1.

Typical discharge–charge curves of the original graphite (MCMB6-28) and PVC carbon pyrolyzed at 1000°C, in 1 M

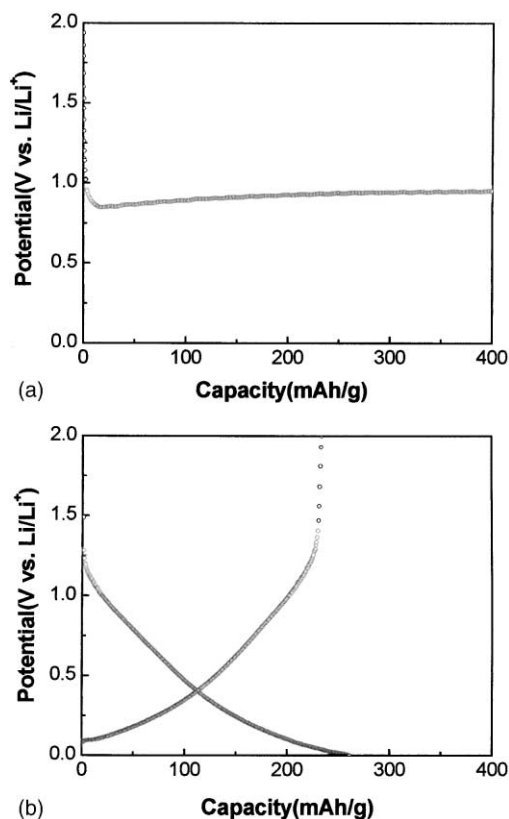


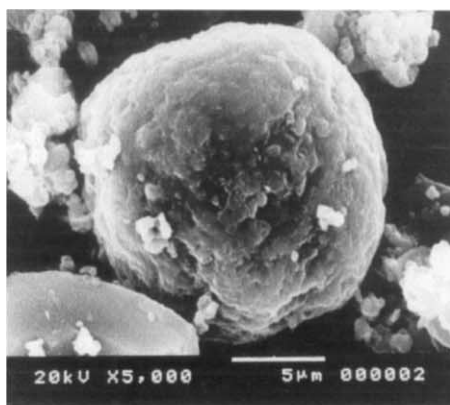
Fig. 1. Charge–discharge curves of graphite electrodes in 1 M LiPF₆/PC electrolyte for first cycle: (a) original untreated graphite; (b) PVC carbon pyrolyzed at 1000°C.

LiPF₆, PC electrolyte are shown in Fig. 1. In the first discharge curve of the original graphite (Fig. 1a), a very long plateau is observed near 0.9 V. This plateau is due to PC decomposition and exfoliation of the graphite electrode [8]. It has been suggested [10,11,14] that this decomposition occurs continuously without forming a stable passive SEI layer on the edge surface of the graphite particles. On the other hand, in the first charge–discharge curve of the PVC carbon in the same electrolyte (Fig. 1b), the plateau due to PC decomposition is not observed. This indicates that PVC carbons with turbostratic structure show good compatibility with PC-based electrolytes. Therefore, if the original graphite is coated with PVC carbon particles, the disordered carbon on the surface will protect the graphite from the electrolyte decomposition and exfoliation problems encountered in a PC-based electrolyte.

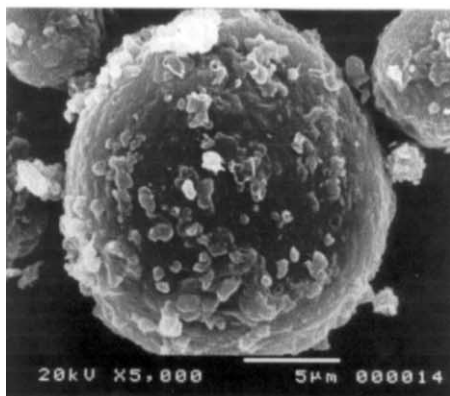
Table 1
Electrochemical properties of PVC

Pyrolysis temperature (°C)	H/C (atomic ratio)	$d_{0\ 0\ 2}$ (Å)	$L_{a\ 1\ 0\ 0}$ (Å)	Half-width _{0 0 2} (2θ)	First discharge (mAh/g)	First charge (mAh/g)	Q_{irr}^a (mAh/g)
800	0.1339	3.546	32.8	5.274	380	306	74
900	0.0762	3.564	38.0	5.021	298	258	40
1000	0.0452	3.571	43.4	4.870	261	233	28

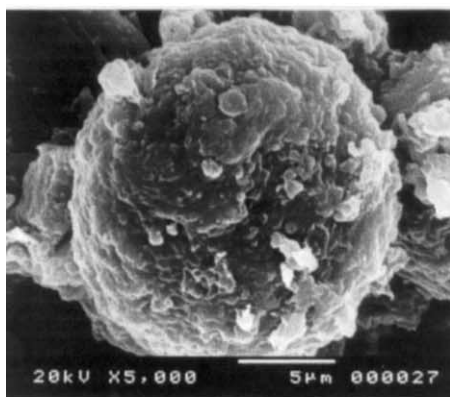
^a Q_{irr} : irreversible capacity on first cycle.



(a)



(b)



(c)

Fig. 2. Scanning electron micrographs of graphite samples: (a) original untreated graphite; (b) graphite after single coating; (c) graphite after double coating.

Scanning electron microscope (SEM) images of the untreated graphite and carbon-coated graphite are presented in Fig. 2. There are no differences in the shape between the particles before and after heating with PVC powders and all the particles are separated even after carbon coating, i.e. no coagulation of particles by residual carbon is observed. Raman spectra and the R -value of the original graphite and graphite double-coated with PVC carbon at 800, 900 and 1000°C are given in Fig. 3. The R -value is defined as the intensity ratio of the peak height at 1360 and 1580/cm, which

is known to be an indicator of crystallinity in near surface regions [17,18].

The carbon coating at each temperature induces broadening of the peak at about 1580/cm and increase of the peak height at 1360/cm. This results in a corresponding increase of the R -value. This indicates that the surface of the particle becomes more disordered, i.e. the graphite particles are covered with disordered PVC-carbon.

To identify the contribution of the PC solvent to the initial irreversible capacity, Q_{irr} , galvanostatic first discharge–charge cycles for the original bare graphite and the graphite double-coated with PVC carbon at 1000°C were carried out in 1 M LiPF₆ in PC/EC/DEC and 1 M LiPF₆ in EC/DEC electrolytes separately. The first cycle discharge–charge curves are given in Fig. 4. For PC/EC/DEC electrolyte, the first-cycle discharge curve of the original graphite has two shoulder-like plateaus at about 0.7 and 0.5 V as shown in Fig. 4a. The capacities arising from those plateaux are irreversible and cannot be recovered during subsequent cycles. For the carbon-coated graphite, the two plateaux are reduced significantly in the first-cycle discharge curves. In the case of EC/DEC electrolyte (Fig. 4b), the first discharge curves of both samples decline monotonously, although the PVC-carbon coated sample shows a higher initial discharging potential as expected from the electrode reaction of disordered PVC-carbon.

In order to reveal more clearly the features of irreversible reactions, differential capacity curves (dq/dv versus potential) for each cell are plotted in Fig. 5 for the first and second discharges of the original graphite and carbon-coated graphite electrodes in PC/EC/DEC electrolyte. Two peaks, which are located near 0.7 and 0.5 V, respectively, are observed in the first discharge curve. Each peak corresponds to a plateau in the voltage profile of Fig. 4. The peaks are absent in the second discharge curve. These features indicate clearly that the peaks in the first discharge derivative curves, or the corresponding first discharge plateaux in the voltage profile, are due to irreversible reactions. A previous study [8] has ascribed the irreversible peak near 0.7 V to electrolyte decomposition and the formation of the SEI layer, both of which take place simultaneously at the surfaces of the carbon particles. The irreversible peak near 0.5 V is caused by side reactions, which take place at the edges of the graphite, i.e. a process called “exfoliation”. The carbon-coated sample, especially the double-coated one (Fig. 5c) shows a considerably smaller peak near 0.5 V than does the original graphite sample (Fig. 5a). This suggests that the concentration of active edge sites at the surfaces of the graphite sample is reduced significantly by coating the graphite with PVC-carbon. Note that the single-coated graphite has a much larger peak at 0.5 V and a larger irreversible capacity than the double-coated one.

The differential capacity curves for each electrode in EC/DEC electrolyte are shown in Fig. 6 for comparison. In contrast to the case of PC/EC/DEC electrolyte, only the peak near 0.5 V is observed, (there is no peak at 0.7 V). This

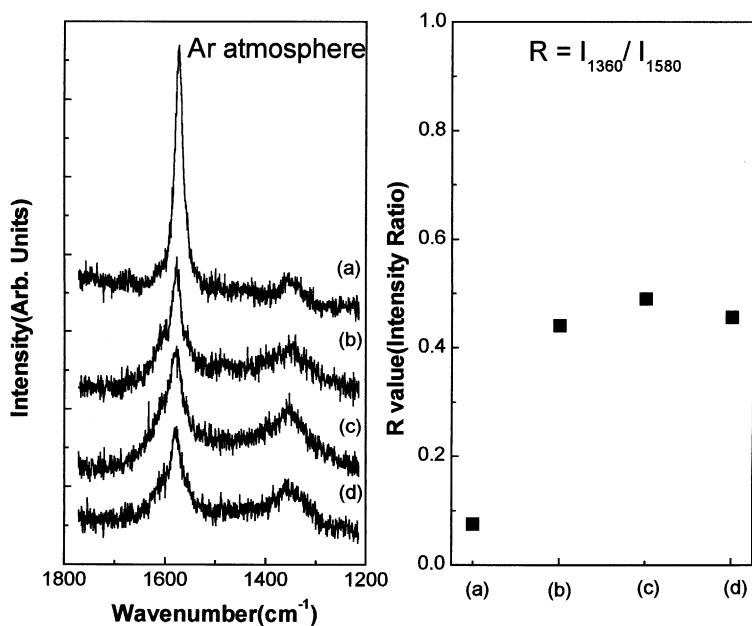


Fig. 3. Raman spectra and *R*-value of: (a) original graphite and carbon-coated graphites prepared by heating mixture of graphite and PVC at (b) 800°C, (c) 90°C, (d) 1000°C.

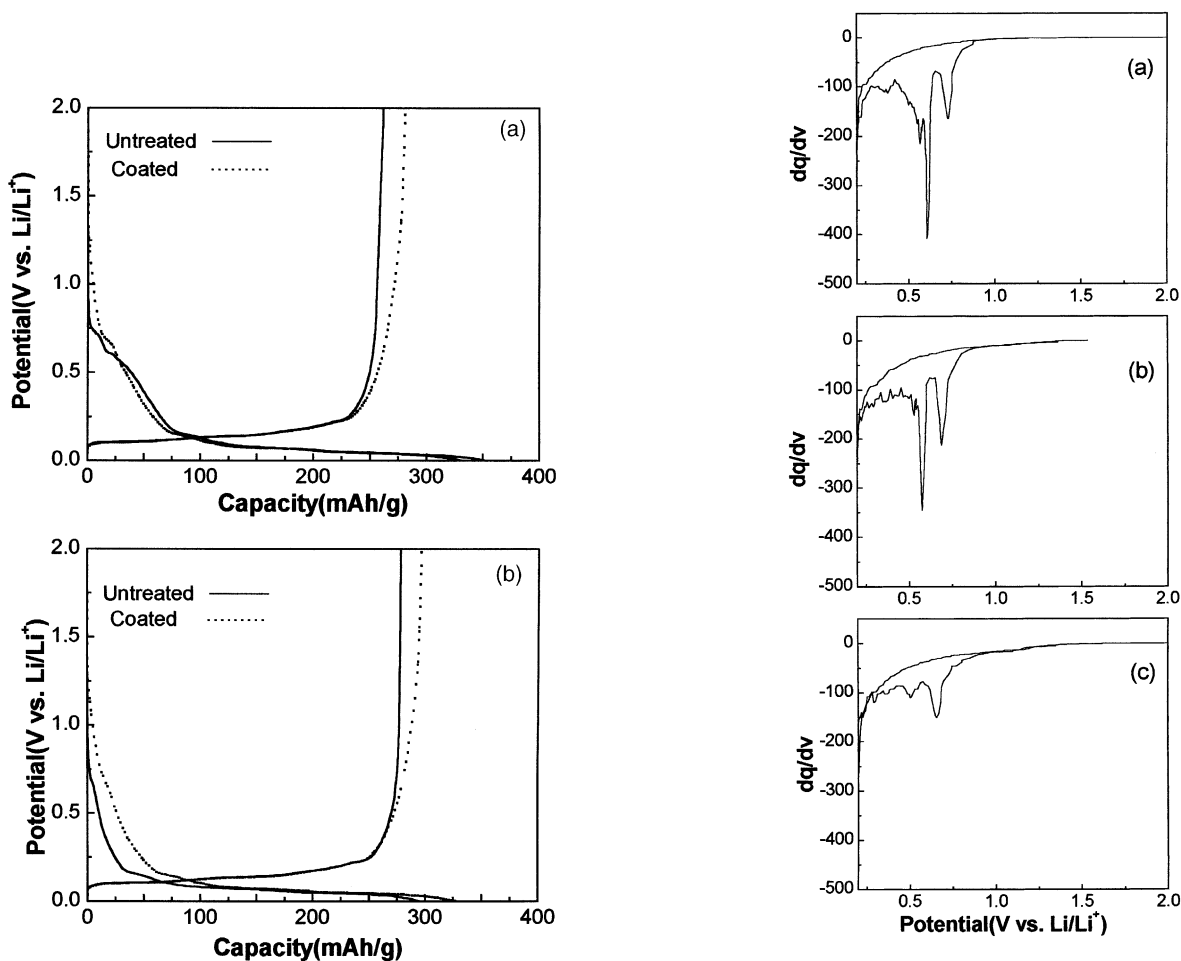


Fig. 4. Initial charge–discharge curves for original untreated graphite and carbon-coated graphite in: (a) 1 M LiPF₆/PC/EC/DEC (3:2:5 by volume); (b) 1 M LiPF₆/EC/DEC (1:1 by volume).

Fig. 5. Differential capacity vs. voltage for first and second lithium intercalation in 1 M LiPF₆/PC/EC/DEC electrolyte for: (a) untreated graphite; (b) single carbon-coated graphite; (c) double carbon-coated graphite.

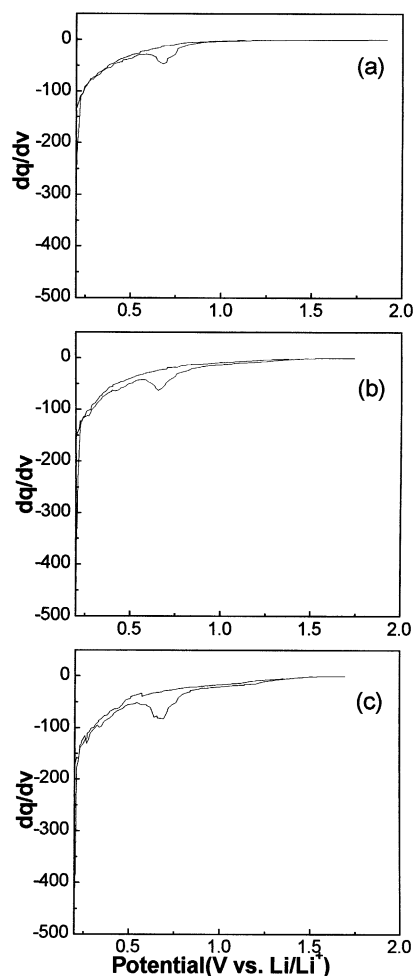


Fig. 6. Differential capacity vs. voltage for first and second lithium intercalation in 1 M LiPF₆/EC/DEC electrolyte for: (a) untreated graphite; (b) single carbon-coated graphite; (c) double carbon-coated graphite.

distinction supports the conclusion that the peak near 0.7 V in the discharge derivative curve is due to exfoliation of the graphite in PC-based electrolyte, which is the main irreversible reaction in the original graphite electrode.

The coulombic efficiency (Fig. 7a) and the irreversible capacity (Fig. 7b) as a function of both the heating temperature for PVC pyrolysis and the coating times of graphite electrodes are shown in Fig. 7 for the first cycle in PC/EC/DEC electrolyte. As the coating times increases, the coulombic efficiency increases and the irreversible capacity becomes smaller. This trend is confirmed by the data given in Fig. 5 which show that double coating provides much better performance in inhibiting the solvated lithium intercalation than does single coating.

As the heating temperature for PVC pyrolysis increases, the irreversible capacity decreases. This seems to be related to the fact that the irreversible capacity of PVC-carbon itself decreases with increasing pyrolysis temperature, as demonstrated in Table 1.

The variation in irreversible capacity per surface area with specific surface area is shown in Fig. 8 for before and after

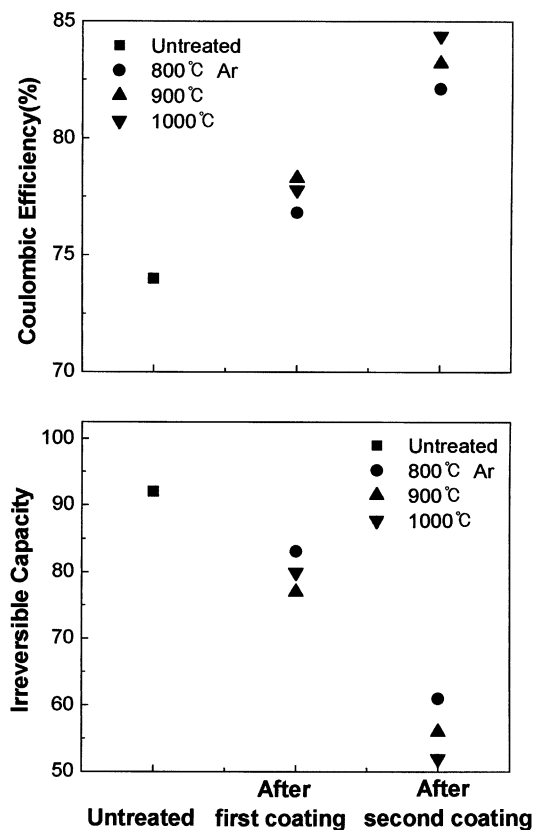


Fig. 7. Coulombic efficiency and irreversible capacity for first cycle of graphite electrodes as function of heating temperature for carbon-coating and coating times (the electrolyte: 1 M LiPF₆, PC/EC/DEC).

PVC-carbon coating of the original graphite. The irreversible capacity per surface area decreases significantly when the specific surface area increases. The capacity data of carbon samples tested in PC/EC/DEC electrolyte are summarized in Table 2. The irreversible reactions, which occur during the first cycle, can be divided into two broad potential

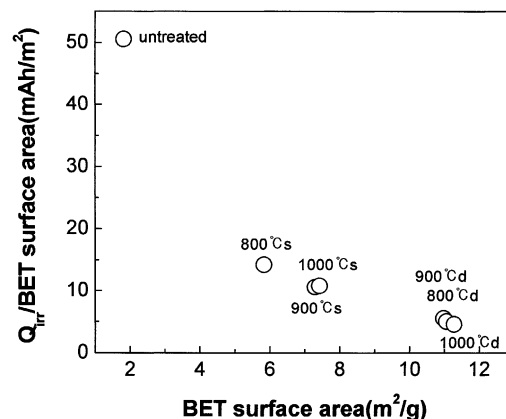


Fig. 8. Variation in initial irreversible capacity per surface area with specific surface area for untreated graphite and carbon-coated graphites obtained from graphite-PVC mixture at various temperatures (s: single coating, d: double coating).

Table 2
Charge–discharge characteristics of the original untreated graphite and carbon-coated graphites

Sample ^a	Surface area (m ² /g ⁻¹)	First discharge capacity (mAh/g ⁻¹)	First charge capacity (mAh/g ⁻¹)	(2.0–0.6 V) $Q_{\text{irr A}}$ (mAh/g)	(0.6–0.1 V) $Q_{\text{irr B}}$ (mAh/g)	Total ($Q_{\text{irr A}} + Q_{\text{irr B}}$) (mAh/g)
Untreated	1.92	354	262	20	72	92
800°C, s	5.83	358	275	24	59	83
800°C, d	10.97	341	280	28	33	61
900°C, s	7.29	356	279	20	57	77
900°C, d	11.05	333	277	27	29	56
1000°C, s	7.47	361	281	23	57	80
1000°C, d	11.27	333	281	25	27	52

^a s: single coating; d: double coating.

regions based on the differential capacity curve shown in Fig. 5. The irreversible capacities in the potential ranges 2.0–0.6 and 0.6–0.1 V are termed to $Q_{\text{irr A}}$ and $Q_{\text{irr B}}$, respectively. The irreversible loss due to exfoliation of graphite $Q_{\text{irr B}}$, is significantly suppressed after PVC-carbon coating, especially after double coating. Note that $Q_{\text{irr A}}$ (which arises from SEI layer formation) increases slightly after double coating despite the large increase in specific surface area. These results, along with the findings shown in Fig. 8, suggest that the irreversible capacity is not directly proportional to the BET surface area of the graphite samples, but is controlled predominantly by the surface structure. Previous studies on the electrochemical reactivity of graphitic carbon have revealed that the irreversible capacity of the edge surface is substantially larger than that of the basal surface, due to solvent co-intercalation in the layer spacing. This is particularly true for PC-based electrolytes [19]. Moreover, it should be noted that the SEI layer is formed at the edge sites on graphite and that these sites are the dominant active sites for electrolyte decomposition [10]. Therefore, it is believed that low-temperature carbons with disordered structure can effectively resist exfoliation and electrolyte decomposition. From the results of this study, it is inferred that PVC-carbon coated on the surface of the graphite, by virtue of having a turbostratic structure, suppresses effectively electrolyte decomposition and graphite exfoliation by covering the active edge sites. This feature leads to reduction of the initial irreversible capacity.

The cycle characteristics of PVC-carbon coated and untreated graphites in terms of charge capacity are presented in Fig. 9. The PVC-carbon coated sample displays better cycleability than the untreated counterpart. Again, this improved cycling ability seems to be due to PVC-carbon suppressing PC solvent intercalation into, and subsequent solvent reduction within, the graphite, since if such reaction is not properly inhibited, exfoliation would take place continuously.

It is found that surface modification of graphite by PVC-carbon is effective in preparing an anode material for lithium-ion batteries. Clearly, the carbon-coating conditions, e.g. the coating amount, coating times and heating temperature, need to be optimized to improve further the electrochemical performance.

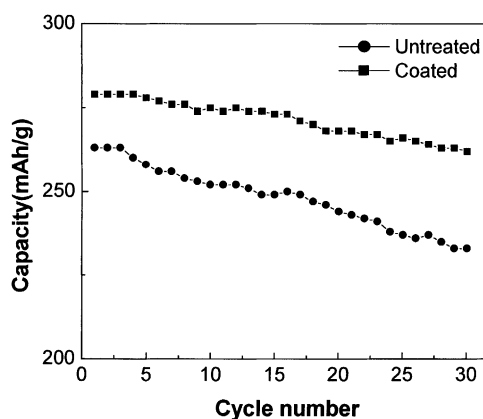


Fig. 9. Cycling behavior of untreated graphite and carbon-coated graphite.

4. Conclusions

Carbon-coated graphite particles have been prepared by simple mechanical mixing and heating of graphite particles with PVC powders. Graphite coated with PVC-carbon exhibits much better electrochemical performance as an anode material for lithium-ion batteries in PC-based electrolyte than original untreated graphite. The PVC-carbon coating significantly reduces the irreversible capacity due to SEI film formation and exfoliation of graphite during the first cycle, despite the fact that the BET specific surface area greatly increased after the carbon-coating. The initial irreversible capacity is therefore not determined by surface area. It is concluded that the irreversible side reactions are depressed by the disordered nature of the turbostratic structure of PVC-carbon.

Acknowledgements

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