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Electrochemical performance of modified synthetic graphite for lithium ion batteries

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The carbon-coated composite has been manufactured and investigated as the negative electrode for Li-ion batteries. The carbon-coated composite powders are prepared by a simple mixing of two types of synthetic graphite particles (SFG6 and SFG44) with polyvinylchloride powders and heating to a temperature between 800 and 1100°C under an argon gas flow.

As a result of the carbon-coating treatment, the flake particles of the original graphites changed into a bulky shape of carbon-coated composite with a largely increased particle size due to aggregation through the treatment. It is shown that carbon-coated composite electrodes for the two types of graphite have much lower irreversible loss than the original graphites and coulombic efficiency of ~91% in the first cycle in a PC-based electrolyte. The carbon coating treatment improves the cycling performance. Despite their coarse morphology due to aggregation, carbon-coated composite electrodes show the enhanced high rate capabilities. *© 2005 Springer Science + Business Media, Inc.*

1. Introduction

Carbon materials are available in a wide range of crystal structures and morphologies for the negative electrode of lithium ion batteries. It has been found that the host structure has large effects on the electrochemical properties of carbonaceous anodes [1, 2].

Of crystalline carbon powders currently used in Li-ion batteries, artificial or natural graphite typically shows a plate-like shape with the shorter dimension along the crystallographic *C*-axis. This gives rise to an undesirable orientation in rolled or pressed graphite anode films with the *C*-axis of graphite particles perpendicular to the electrode film surface. Since the lithium intercalation into graphite carbon layer takes place at the edges of graphite plates, the plate-like shape of graphite powder and undesirable orientation of graphite particles used in anodes for Li-ion batteries would deteriorate the performance of the battery by limiting the lithium intercalation rate [3].

A major problem in using graphite is a large irreversible capacity loss between the first discharge and charge cycle due to the formation of a solid electrolyte interface (SEI) film on the graphite and other side reactions such as decomposition of electrolyte, exfoliation of the graphite (especially in PC-based electrolyte) and reduction of the functional groups on the graphite surface [4, 5].

These irreversible reactions, in practical Li-ion cells, lead to a decrease in the specific energy density, and moreover may result in safety problems [6]. Therefore, the amount of irreversible capacity must be minimized.

The irreversible capacity has been controlled by coating the graphite particle surface with metal [7] and carbon [8, 9], and modifying the electrolyte [10, 11]. In our previous study [12], it has been shown that carbon coating of the carbon particles with spherical morphology is successfully accomplished by a simple mechanical mixing of graphite particles with poly(vinyl chloride) (PVC) powders and heating to a temperature of around 1000°C in an inert atmosphere to carbonize the PVC. It is expected that we can modify the shape and surface of the flake-like graphite particles, by producing the composite particles, and then alter the corresponding electrochemical performance. Of the flaky synthetic graphites, SFG6 and SFG44 are known to have different particle size and surface structure [13], which influences on the electrochemical performance such as the irreversible capacity and high rate capability.

Based on the knowledge gained from our previous study, in the present study, we made an attempt to modify the surface and shape of flaky synthetic graphites (Timrex SFG44 and SFG6) by heat treating the mixture of PVC powders and graphite particles in inert atmosphere, and to study its influence on the physical and electrochemical properties.

2. Experimental

We have used two types of Timrex synthetic graphites, SFG44 and SFG6. These materials have a flaky

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morphology but different surface area, particle size distribution and crystal structure (or rhombohedral phase content).

To obtain carbon-coated composite graphites, a mixture of graphite particles and PVC powders was pressed into a pellet, then heated to a temperature between 800 and 1100°C with heating rate of 5°C/min, and soaked at the temperature for 1 h under an argon flow. The different amounts of PVC powders (70, 100, 130 and 170 wt%) were used, in which the weight of residue carbon from PVC is about 10% of PVC mixed. The product was ground into powder to be used as the active material in the negative electrodes of Li-ion batteries. The ball milling for grinding was performed on a Fritsch planetary mill set.

Electrochemical cell testing was performed galvanostatically in a coin cell (2016 type). The cell comprised a lithium metal electrode and a carbon electrode that were separated by a separator. All cells were fabricated in an argon filled glove box in which the moisture level was less than 2 ppm. The carbon electrode of 90 wt% carbon powder and 10 wt% poly(vinylidene fluoride)(PVDF) as a binder. The *n*-methylpyrolidinone (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 tcm^{-2}. The electrolyte solution was 1M $LiPF_6$ of propylene carbonate (PC)/ ethylene carbonate (EC)/ diethyl carbonate (DEC) (3:2:5 by volume) or EC/DEC (1:1 by volume) mixed solvents, provided by Cheil industries Inc., Korea. The charge-discharge behavior of the Cell was investigated using a Toyo system(Toscat 3000) at a current density of 0.3 mAcm^{-2} with cut-off potentials of 0.01 and 2 V vs. Li/Li^+.

3. Result and discussion

Fig. 1 shows the typical first-cycle charge (delithiation)-discharge (lithiation) curves of the original graphites in the electrolytes of 1 M $LiPF_6$ dissolved in the mixed solvents of EC/DEC and EC/PC/DEC. The type of graphite has a more dramatic effect on the reaction behavior of the electrolyte containing PC. As illustrated in Fig. 1a and b, in the first discharge curve obtained with the PC-based electrolyte, SFG44 shows a long plateau-like profile between 0.5 and 0.8 V due to electrolyte decomposition/SEI film formation [4, 13] with a 56% loss of capacity but in SFG6 sample, the plateau is significantly reduced. This observation is attributed to the difference in the degree of structural imperfections [13]. SFG6 contains large amounts of rhombohedral phase and its surface is rich in the basal planes relative to that of SFG44. It is also known that graphite containing more rhombohedral phase tends to resist exfoliation in PC-based electrolytes [1] and the edge sites are more reactive than the basal planes [14, 15].

On the contrary, when 1 M $LiPF_6$ EC/DEC electrolyte is used, an irreversible plateau in SFG44 considerably was reduced as shown in Fig. 1c but the lithium intercalation behavior of SFG6 seemed to be independent of the electrolyte used. In the PC/EC/DEC electrolyte, the two types of graphite show rather different behaviors of lithium intercalation. It is known that PC has a strong effect on the irreversible capacity with the surface structure of graphite. In order to evaluate the effectiveness of the surface modification of graphite on the electrochemical performance, it would be desirable to use the PC-based electrolyte. Therefore, the following experiments to investigate the effect of carbon-coating treatment on the initial irreversible capacity were carried out in 1 M $LiPF_6$ PC/EC/DEC

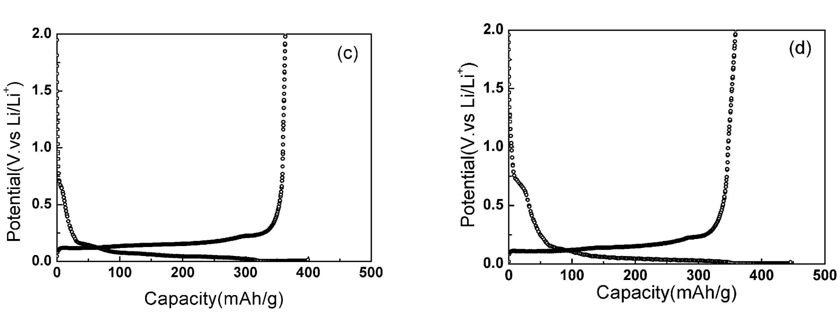


Figure 1 Initial charge-discharge curves for original graphites in different electrolytes: (a) SFG44 in 1 M $LiPF_6$/PC/EC/DEC, (b) SFG6 in 1 M $LiPF_6$ / PC/EC/DEC, (c) SFG44 in 1 M $LiPF_6$/EC/DEC, and (d) SFG6 in 1 M $LiPF_6$ /EC/DEC.

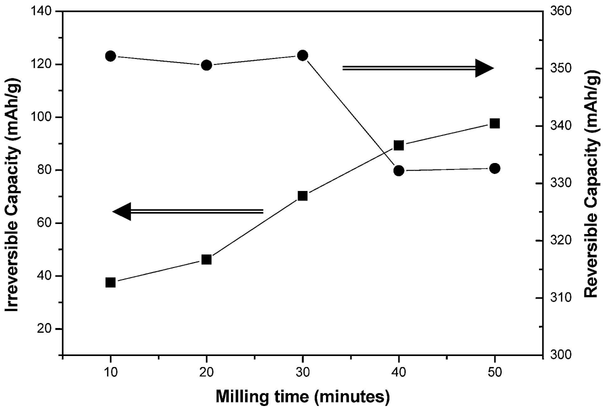


Figure 2 Irreversible and reversible capacity of the milled carbon-coated graphite (SFG6) powders as a function of milling time (The electrolyte: 1 M $LiPF_6$ PC/EC/DEC).

electrolyte. Moreover, this study would be practically meaningful because PC-based electrolytes exhibit superior low temperature performance compared to EC-based electrolytes, mainly due to their different melting points.

To prepare the carbon-coated composite graphite powders, a mixture of graphite and PVC powders were heat treated for the carbonization of PVC and the resultant product was ball-milled for different durations. Fig. 2 presents the typical irreversible and reversible capacity of the milled carbon-coated composite powders as a function of milling time. When the milling duration is extended beyond 20 min, the irreversible capacity increases significantly. The carbon-coated composite graphite electrodes, therefore, were prepared by 10 min milling.

Fig. 3 shows the scanning electron microscopy (SEM) micrographs of the graphite samples (SFG44 and SFG6) before and after carbon-coating treatment with 170 wt% PVC at 1000°C. The original graphite particles have a flaky shape but the carbon-coated composite graphite shows a bulky nugget-type shape. This is due to aggregation of the flaky particles with PVC carbon. It should be noted that carbon-coated particles obtained by heating the mixture of graphite particles and PVC powders without pressing into a pellet retain their original morphology, as shown in previous study [12].

Powder X-ray diffraction (XRD) profile (not shown here) of carbon-coated composite sample shows a shoulder at around $2\theta = 25^{\circ}$C, which is a characteristic

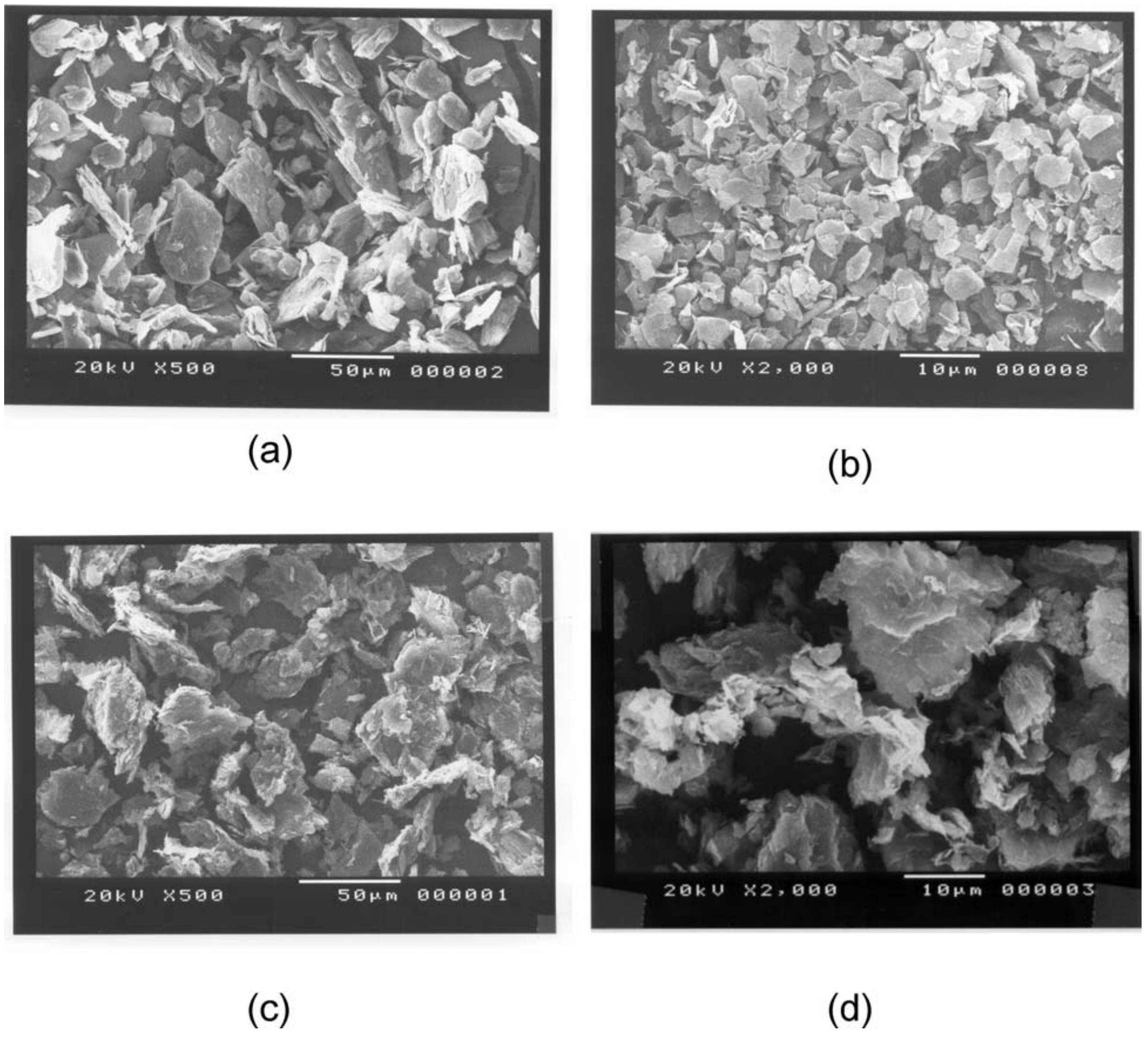


Figure 3 Scanning electron micrographs of graphite samples: (a) original untreated SFG44, (b) original untreated SFG6, (c) carbon-coated SFG44, and (d) carbon-coated SFG6.

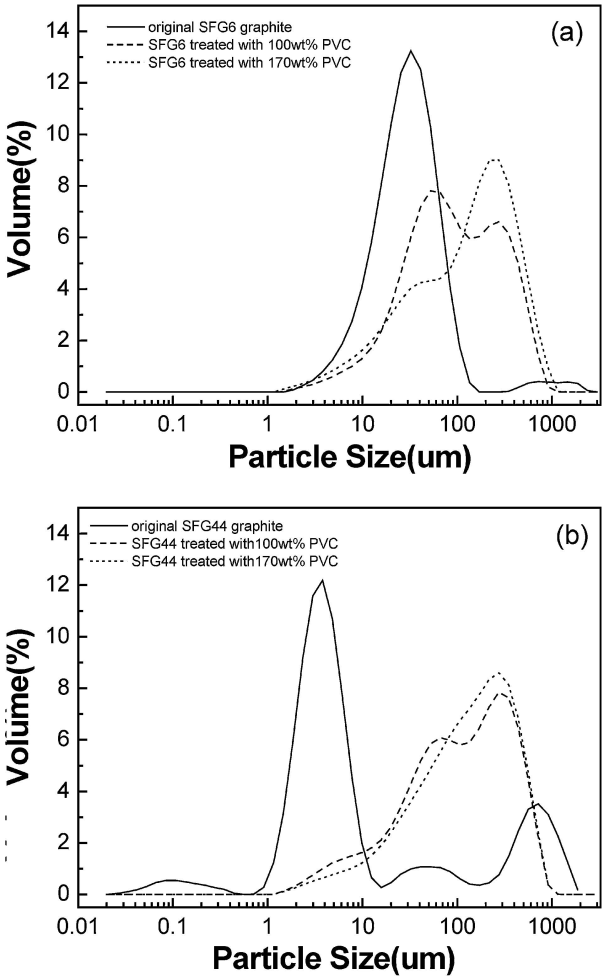


Figure 4 Particle size distribution of the original and carbon-coated composite graphite powders: (a) SFG44 samples and (b) SFG6 samples.

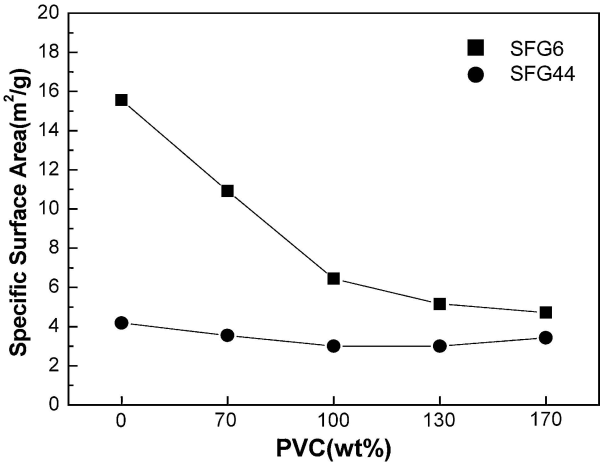


Figure 5 Specific surface areas for carbon-coated composite graphites as a function of PVC Content in the starting mixture.

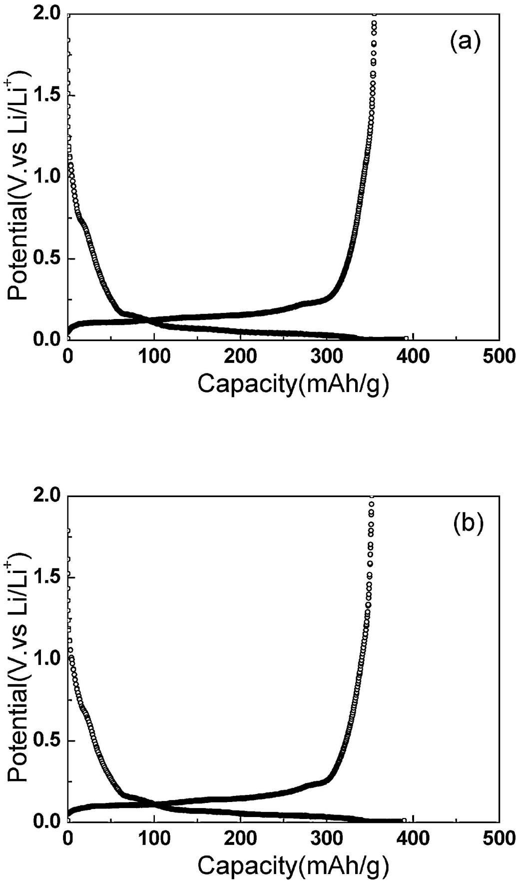


Figure 6 Initial charge-discharge curves for: (a) SFG44 and (b) SFG6 treated at 1000°C with 170 wt% PVC.

of the amorphous PVC carbon. However, the interlayer (d_{002}) distance does not change. This suggests that the carbon-coating treatment has not brought about any crystallographic changes to the graphite structure.

Fig. 4 shows the particle size distribution of the original and carbon-coated composite powders. As the results of aggregation of particles through carbon-coating process as shown in Fig. 3, the particle size distribution is shifted towards the larger size. Two types of graphite treated with 170 wt% PVC appear to have similar mean particle size of about 120 μm.

Fig. 5 shows the surface area of SFG44 and SFG6 graphites before and after carbon-coating treatment as a function of PVC content in the starting mixture. The surface area of SFG6 samples decreased, from 15.5 to 4.7 m^2/g, with an increase in PVC content, while the surface area of SFG44 samples slightly decreased. Considering that the mean particle size greatly increased by carbon-coating treatment, as shown in Fig. 4, the latter case is interesting.

Fig. 6a and b show the first charge-discharge profile for SFG44 and SFG6 treated at 1000°C with 170 wt% PVC in the starting mixture, respectively. The plateau of the first discharge curve is decreased substantially by carbon-coating treatment as compared with that given in Fig. 1a and b. Our previous study [12] confirms that the pyrolyzed PVC carbon shows good compatibility with PC-based electrolytes.

To better understand the difference in the initial intercalation behavior of original and carbon-coating treated samples, the first and second discharge capacities were differentiated with respect to the potential; the resulting differential capacity curves (dq/dv versus potential) for original and carbon-coating treated SFG44 and SFG6 are plotted in Figs 7 and 8, respectively.

A voltage plateau in the cycling would transform into a peak in the differential capacity plot. In the original

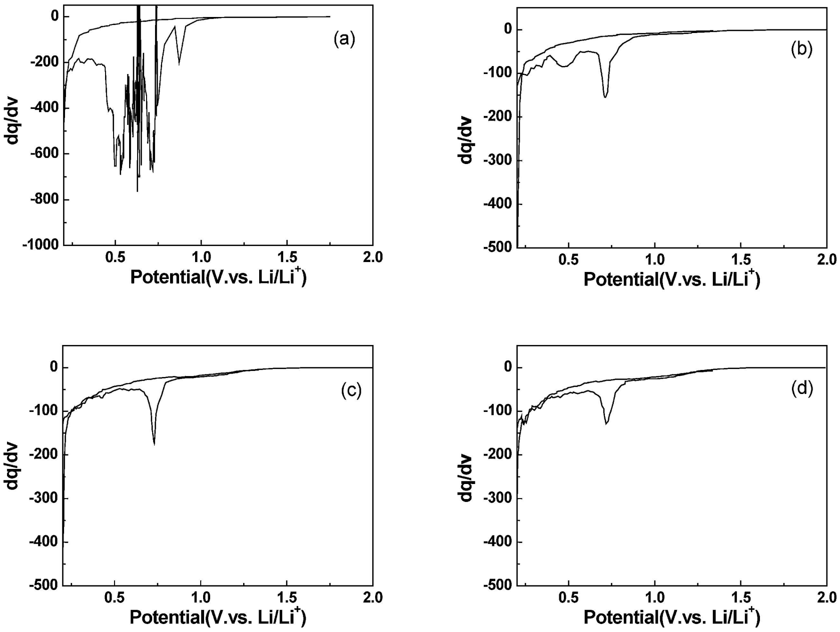


Figure 7 Differential capacity vs. voltage for first and second lithium intercalation in 1 M $\mathrm{LiPF_6}$ /PC/EC/DEC electrolyte for: (a) original SFG44 graphite and carbon-coated composite graphite prepared with, (b) 70 wt% PVC, (c) 130 wt% PVC and (d) 170 wt% PVC.

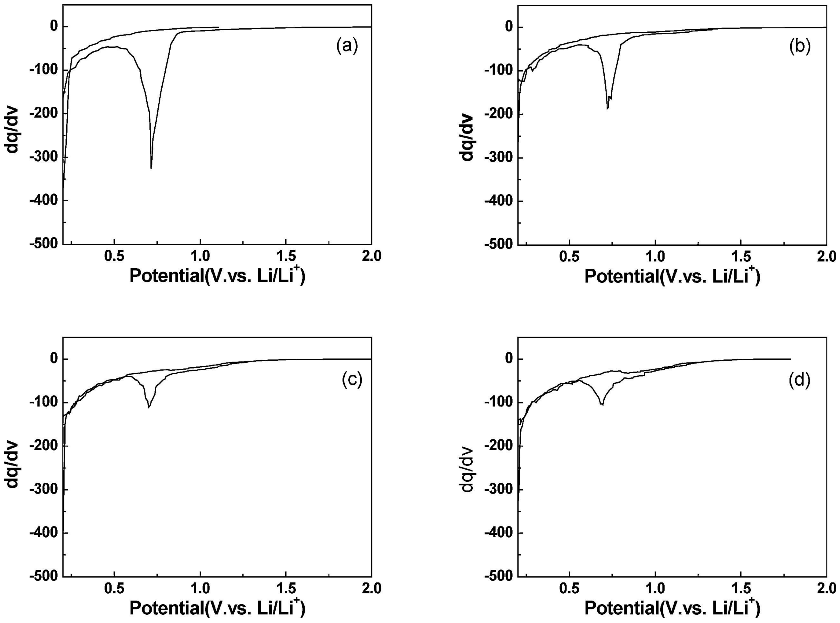


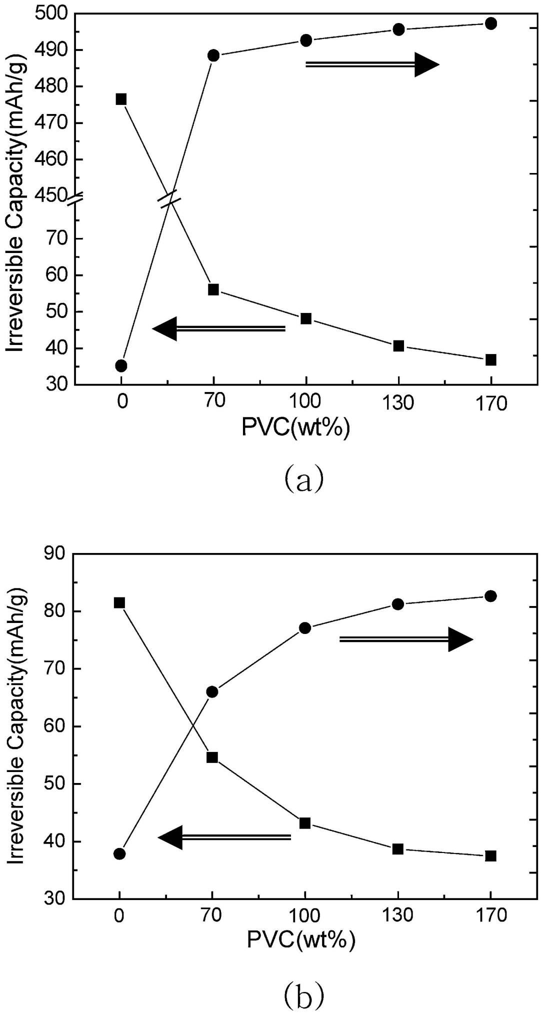
Figure 8 Differential capacity vs. voltage for first and second lithium intercalation in 1M $\mathrm{LiPF_6}$/PC/EC/DEC electrolyte for: (a) original SFG6 graphite and carbon-coated composite graphite prepared with, (b) 70 wt% PVC, (c) 130 wt% PVC and (d) 170 wt% PVC.

SFG44, three peaks were observed in the differential capacity plot for the first discharge process, as shown in Fig. 7a. According to previous reports [4, 13], the irreversible peaks located between 0.7 and 0.9 V and near 0.5 V are due to the electrolyte decomposition and formation of the SEI layer, and exfoliation, respectively.

However, with the increase of carbon-coating amount, by increasing the PVC content in the starting mixture, the peak near 0.5 V mostly disappears and the height of the peak near 0.7 V is significantly reduced as illustrated in Fig. 7b–d. It is apparent that irreversible losses caused by voltage plateau related reactions were effectively suppressed after carbon-coating treatment.

On the other hand, Fig. 8a shows that the irreversible capacity in the original SFG6 is dominantly related to electrolyte decomposition/SEI formation as the differential capacity plot exhibits a major peak near 0.7 V. This observation, as compared with Fig. 7a, indicates that SFG6 has better mechanical integrity against exfoliation in PC-based electrolytes than SFG44, and also supports the previous explanations for Fig. 1a and b.

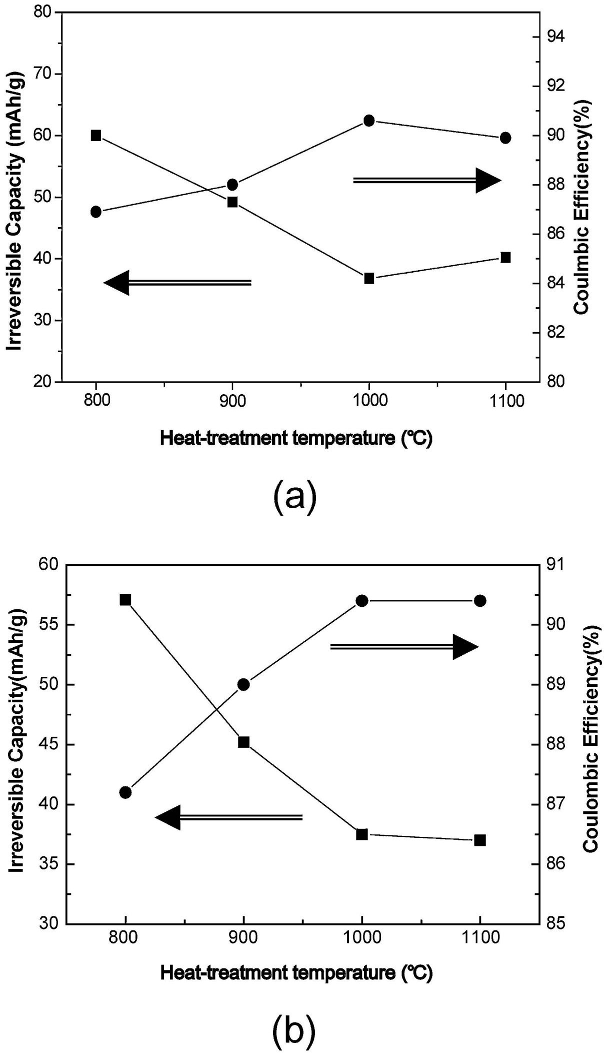
When the carbon-coating treatment was carried out at 1000°C, the irreversible capacity and coulombic efficiency are presented as a function of the PVC wt% in the starting mixture (Fig. 9). As the PVC content in the starting mixture (i.e., the coating amount) increases, the irreversible capacity for both types of graphite became smaller, and the coulombic efficiency increased to ~90.6 and ~90.4% for SFG44 and SFG6, respectively. These trends are consistent with the results given in Figs 7 and 8.



(a)

(b)

Figure 9 Irreversible capacity and Coulombic efficiency for first cycle of: (a) SFG44 samples and (b) SFG6 samples as a function of PVC content in the starting mixture.



(a)

(b)

Figure 10 Irreversible capacity and Coulombic efficiency for first cycle of: (a) SFG44 samples and (b) SFG6 samples prepared at different temperatures with 170 wt% PVC.

The irreversible capacity of the original SFG44 is considerably larger than that of the original SFG6, although the former has a smaller specific surface area than the latter. The remarkable decrease of irreversible capacity after carbon-coating treatments for SFG44 samples, although the change in specific area is slight, cannot be simply explained by a surface area reduction. From the fact that the graphite exfoliation and electrolyte decomposition reaction occur preferentially at edge sites of the graphite surface [14, 15], it is supposed that the original graphite particles are uniformly covered by a disordered PVC carbon through the carbon-coating process. The disordered PVC carbon is resistant against exfoliation and the electrolyte decomposition on its surface to form the SEI film is mild even in the pure PC electrolyte [12].

Therefore, if the graphite particles are covered by the PVC carbon more completely and densely, the coverage would protect the graphite from electrolyte attack and thus reduce the irreversible capacity more effectively, as inferred from the data of Fig. 9.

Fig. 10a and b show the irreversible capacity and coulombic efficiency for SFG44 and SFG6 samples prepared at different temperatures with 170 wt% PVC in the starting mixture, respectively. With increasing the temperature the irreversible capacity decreases and the coulombic efficiency increases to the values for the sample treated at 1000°C for each case. The samples treated at 1000°C also show a maximum reversible capacity. These results indicate that 1000°C is the optimum temperature to produce high-efficiency carbon-coated composite powder.

The charge-discharge capacities versus cycle number for original SFG6 and coating-treated SFG6 (heat treated at 1000°C) are given in Fig. 11. The coating-treated graphite shows superior cyclability to original one. The rate of capacity loss of the coated graphite is significantly lower than that of original graphite as the cycle number increases. The columbic efficiencies as a function of cycle number are presented in Fig. 12. The carbon-coating treatment on SFG6 increases not only the first coulombic efficiency, but also improves subsequent charge-discharge cycle efficiencies.

Fig. 13 presents the reversible capacity of the original and carbon-coating treated SFG6 samples as a function of the current density, in which the result for original graphite cycled in EC/DEC electrolyte is also compared. In the EC/PC/DEC electrolyte, the capacity of the original graphite decreases rapidly with increasing the current density while the carbon-coated composite

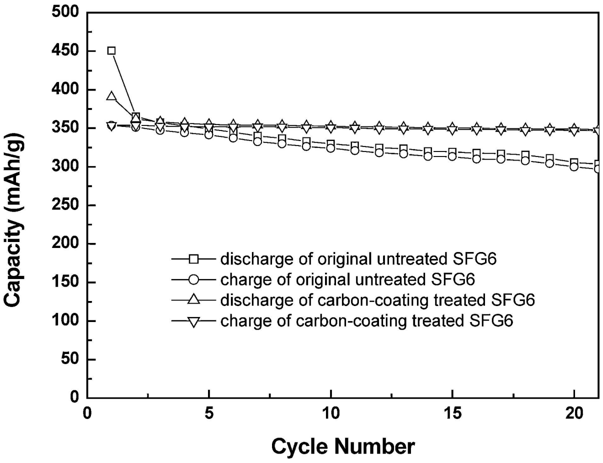


Figure 11 Charge-discharge capacities as a function of the cycle number for untreated and carbon-coating treated SFG6. The carbon-coating treatment was performed at 1000°C with 170 wt% PVC.

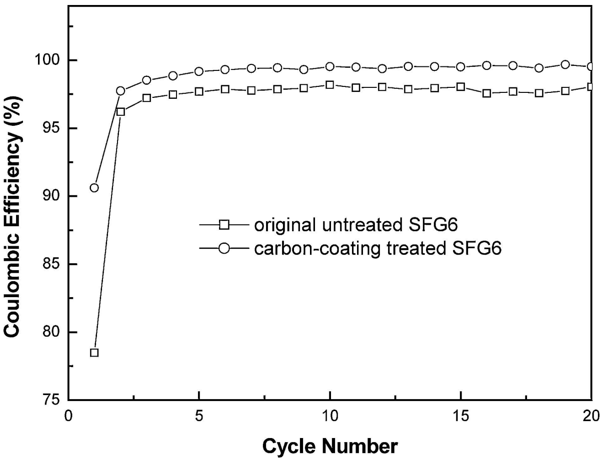


Figure 12 Charge-discharge efficiencies as a function of the cycle number.

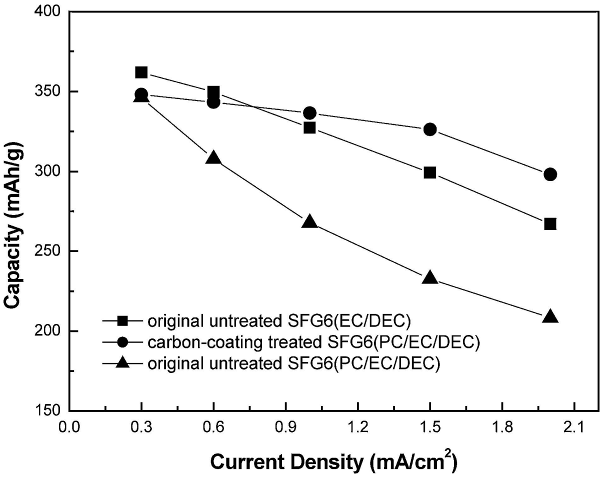


Figure 13 Rate capabilities of original and carbon-coating treated SFG6 graphite electrodes.

sample shows a gradual decrease. The rate capability of the carbon-coated composite appears to be better than that of the original graphite in EC/DEC. Considering that the composite powders have a larger particle size than the original graphite, as shown in Figs 3 and 4, its prominent high rate capability seems to be remarkable.

4. Conclusions

Carbon-coated composites were prepared by a simple mixing of two types of synthetic graphite (SFG6 and SFG44) and PVC powders, pressing into a pellet, then heating to a temperature between 800 and 1100°C. After the carbon-coating treatment, the particles showed an aggregated bulky shape with a largely increased particle size. These materials show superior electrochemical performance as an anode for lithium ion batteries in PC-based electrolyte compared to original graphites.

The irreversible capacity was significantly reduced and the first cycle coulombic efficiency reached to $\sim$91%.

Those electrochemical properties were affected by the amount of carbon coating on the original graphite and heat-treatment temperature. The treatment at 1000°C with 170 wt% PVC in the starting mixture appeared to be optimum to produce high-efficiency composite powder. The improved electrochemical performance are attributed to that a disordered PVC carbon layer coated on the original graphite protects the graphite particles from electrolyte attack and has the enhanced resistance against exfoliation/ electrolyte decomposition in PC-based electrolyte.

Acknowledgements

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