



Carbon-coated graphite for anode of lithium ion rechargeable batteries: Graphite substrates for carbon coating

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ABSTRACT

Anode performance in lithium ion rechargeable batteries (LIBs) was studied on four kinds of graphite powders, including synthetic graphite. Carbon-coated synthetic graphite gave a smaller irreversible capacity of about 20 mAh g⁻¹ and a better cyclic performance in an electrolyte solution of EC/DMC than natural graphite, though its discharge capacity of about 300 mAh g⁻¹ is a little smaller than natural graphite. Even in a PC-containing solution as EC/PC = 3/1, carbon-coated synthetic graphite had almost the same anode performance as in the solution without PC. Carbon coating of above 5 mass% on graphite particles was found to be effective to improve the anode performance at a low temperature of -5 °C, high retention in discharge capacity of about 90% being obtained. On both natural and synthetic graphite powders, carbon coating by the amount of 3–10 mass% at a temperature of 700–1000 °C was found to be optimum for the improvement of anode performance in LIBs, to have a lower irreversible capacity and higher retention in discharge capacity at -5 °C than without carbon coating.

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1. Introduction

Carbon coating of graphite was reported to improve the anode performance in lithium ion rechargeable batteries (LIBs) [1–15]. A simple coating process consisting of carbonization of mechanical mixture of graphite with carbon precursor in powder employed in most of works [8–15] seems to have a possibility to be applied to a large amount of production in industry. For the industrialization of this carbon coating process, however, many points have to be clarified, as pointed out in our previous paper [14]; the selection of substrate graphite and carbon precursor, mixing ratio of these two raw powders, heat treatment conditions, etc. In our previous work [14], poly(vinyl alcohol) (PVA) was shown to be one of applicable carbon precursors, although some papers used other precursors, poly(vinyl chloride) [8,9,12,13] and poly(urea) [11]. The amount of coated carbon of 4–13 mass% and heat treatment at 700–1000 °C on a natural graphite were shown to result in certain improvement in anode performance in LIBs [14].

However, the occurrence of natural graphite which can be used for the anode in LIBs is limited in the area in the world. On the other hand, synthetic graphite has been industrially produced mainly from petroleum coke in large amount as the electrodes for steel

refining and electrical discharge machining, and also as moderators and reflectors for atomic reactors, etc. [16]. Therefore, it is very important to explore the possibility to use these synthetic graphite powders as anode materials.

In the present work, three kinds of natural graphite and one kind of synthetic graphite were coated by carbon using PVA as carbon precursor. Anode performance of the resultant carbon-coated graphites in LIB was evaluated in different electrolytes with different charge/discharge rates. The possibility to use synthetic graphite as anode material was discussed by comparing with natural graphite. In addition, carbon coating was experimentally proved to improve the anode performance at a low temperature.

2. Experimental

2.1. Carbon coating

As the substrate graphite, three natural graphite and synthetic graphite were selected, as listed in Table 1. The substrate NG-1 was used in our previous paper [14,15] and SG was prepared from high-density isotropic graphite.

Average particle size of substrate graphite was selected to be around 20 μm. Three natural graphite have high crystallinity; relatively high immersion density, interlayer spacing d_{002} of 0.3354 nm, crystallite size along a -axis determined from 110 diffraction line $L_a(110)$ of more than 100 nm and R -value deter-

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Table 1
Graphite powders used as substrate.

	Sample code	Average particle size	D_{im} (g cm^{-3})	d_{002} (nm)	La(1 1 0) (nm)	R-Value
Natural graphite	NG-1	19	2.248	0.3354	>100	0.16
	NG-2	21	2.240	0.3354	>100	0.20
	NG-3	22	2.244	0.3354	>100	0.20
Synthetic graphite	SG	19	2.135	0.3368	89	0.36

mined by Raman spectroscopy of 0.16–0.20. However, synthetic graphite selected has a little poorer crystallinity than natural graphite; d_{002} is a little larger (0.3368 nm), La(1 1 0) is smaller (89 nm), and R-value is larger (0.36).

As the carbon precursor, PVA was selected, based on the result of our previous paper [14].

Carbonization of the powder mixtures of different graphite substrate with PVA in various mixing ratios P_{mixed} in a range from 10 to 100 g of PVA per 100 g of substrate graphite (i.e., 10–100 phg) was performed at a temperature of 700–1500 °C for 1 h in nitrogen flow. One batch of carbonization was about 100 g and a heating process with a step at 500 °C for 5 h before reaching a programmed temperature was employed.

2.2. Characterization

Morphology of the samples was observed in SEM with an acceleration voltage of 15 kV. The weight increase due to the carbonization of the mixture of the graphite substrate with PVA was determined as a measure of the amount of coated carbon C_{coated} . Density of the sample powder was determined by immersion of butanol (immersion density D_{im}).

Anode performance was measured on the sheet prepared from the mixture of carbon-coated graphite sample with poly(vinylidene fluoride) (PVdF) in 9:1 mass ratio using a n-methyl-2-pyrrolidone solution of 12 mass% PVdF. The solution dispersing sample powder was plated on a copper foil (18 μm thick), followed by drying at 65 °C for more than 1 h and then at 135 °C for 5 h under vacuum. The sample sheet thus prepared was rolled to make the density of

graphite sample in the film to be about 1.0 g cm^{-3} . On this sheet (40 mm \times 40 mm and 100–120 μm thick), the performance as the anode of LIB was determined at 25 °C by using three-electrode cell with counter and reference electrodes of lithium metal foils. The electrolyte used was 1 M LiClO_4 solution of a mixture of different solvents, ethylene carbonate (EC), dimethyl carbonate (DMC) and propylene carbonate (PC) in the different ratios in volume, i.e., EC/DMC = 1/1, EC/PC = 3/1 and EC/PC = 1/1. The battery was constructed in a glove box in argon atmosphere under a dew point below -65 °C. Charging was performed with a constant current density of about 1.6 mA cm^{-2} (condition of 0.5C) and discharging with either about 0.4, 1.6 or 9.4 mA cm^{-2} (0.1C, 0.5C or 3.0C, respectively) between 4 mV and 1.5 V. Anode performance was also checked by cycling about 10 times at room temperature on some of carbon-coated graphite samples.

In order to know the performance at low temperature, charge/discharge measurement was carried out at -5 °C on some of carbon-coated graphite samples. The retention rating in discharge capacity, C_{-5}/C_{25} , i.e., the ratio of discharge capacity at -5 °C, C_{-5} , to that at 25 °C, C_{25} , in percentage, was used to evaluate the low temperature performance.

3. Results and discussion

3.1. Carbon coated

In Fig. 1, SEM images of two samples prepared from NG-1 and SG at 900 °C by using P_{mixed} of 50 phg are shown in two different magnifications.

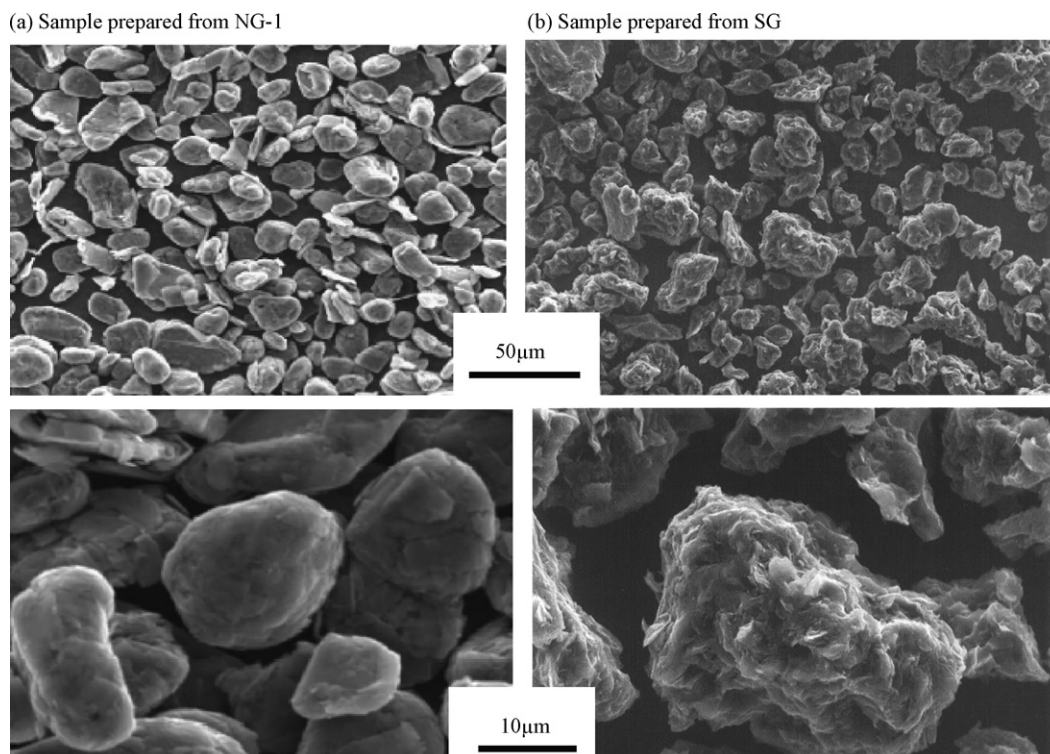


Fig. 1. SEM images of carbon-coated graphite particles. Sample prepared from NG-1 (a) and SG (b).

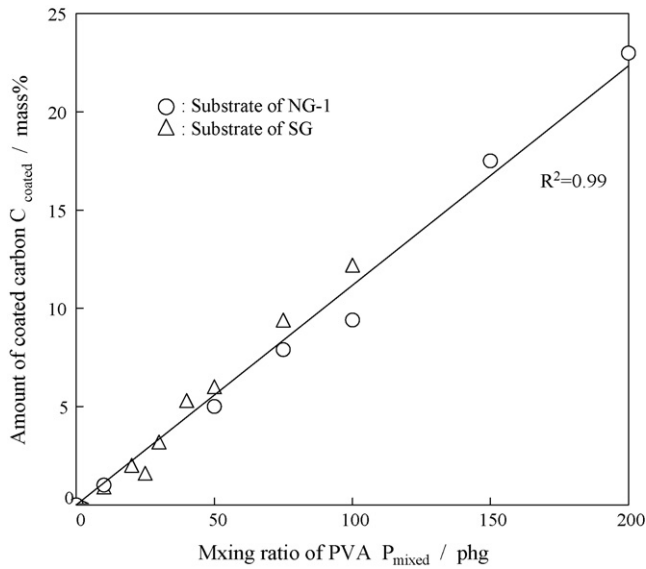


Fig. 2. Relation between mixing ratio of PVA P_{mixed} and amount of carbon C_{coated} coated at 900 °C on natural graphite NG-1 and synthetic graphite SG.

Morphology change in particles was not apparent on four graphite substrates before and after carbon coating, as shown in Fig. 1 and also reported in our previous paper [14]. After carbon coating, the samples prepared from natural graphite NG-1, NG-2 and NG-3 were easily crushed on the mesh of the sieve with an opening of the size of 63 μm . However, the samples prepared from SG agglomerated more markedly than those prepared from NGs and so crushing by gentle compression in a mortar was needed to pass through the sieve, particularly on the samples prepared with P_{mixed} of more than 75 phg.

In Fig. 2, amount of coated carbon C_{coated} was plotted against mixing ratio P_{mixed} for two substrates, NG-1 and SG.

The experimental points of C_{coated} obtained by using SG looks to locate slightly higher position than those obtained by using NG-1, but the difference is within the scattering range of the experimental points. Therefore, the relation between C_{coated} and P_{mixed} was approximated to be linear, common for different graphite substrates.

Immersion density D_{im} is plotted against C_{coated} on two carbon-coated graphite samples prepared from NG-1 and SG at 900 °C with different P_{mixed} in Fig. 3.

By carbon coating, D_{im} decreases with increasing C_{coated} on both substrates. Absolute values of D_{im} measured on the sample derived from NG-1 are always higher than those from SG, because the original NG-1 has higher density than the original SG. However, the decreasing curves for two samples are very similar with each other, in other words, a ratio in D_{im} between two samples is almost the same, irrespective to C_{coated} .

These experimental results suggest that the carbon formed on the particles of synthetic graphite SG cannot be differentiated from that on natural graphite NG-1, which has been demonstrated to have amorphous structure and low density in our previous paper [14].

3.2. Anode performance

3.2.1. Effect of carbon coating

In Fig. 4, discharge and irreversible capacities in 1 M LiClO_4 solution of EC/DMC = 1/1 with a rate of 0.5C/0.5C are plotted as a function of P_{mixed} on the samples prepared from four graphite substrates, though only the data obtained at P_{mixed} of 50 phg are shown on substrates NG-2 and NG-3.

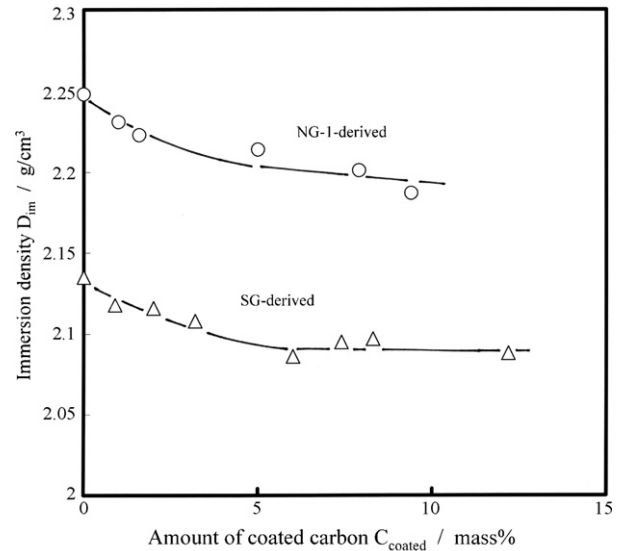


Fig. 3. Changes in immersion density D_{im} with amount of carbon C_{coated} coated on graphites NG-1 and SG at 900 °C.

The samples derived from natural graphite NG-1 show almost constant discharge capacity, about 360 mAh g^{-1} , in a P_{mixed} range from 0 (i.e., original) to 100 phg, but irreversible capacity increases a little for P_{mixed} of 10 phg and then becomes almost constant at a little smaller capacity (by about 30 mAh g^{-1}) for P_{mixed} of 20–100 phg. Natural graphite substrates NG-2 and NG-3 give almost the same discharge capacity but a little smaller irreversible capacity at P_{mixed} of 50 phg than NG-1. On the samples derived from synthetic graphite SG, both discharge and irreversible capacities decrease from the original by carbon coating. Discharge capacity becomes a constant at around 300 mAh g^{-1} by carbon coating with P_{mixed} above 20 phg. Irreversible capacity shows a plateau at about 20 mAh g^{-1} in a range of 10–40 phg and increases slightly above 50 phg. However, it has to be pointed out that irreversible capacity observed on SG becomes to a half of the original graphite by carbon coating.

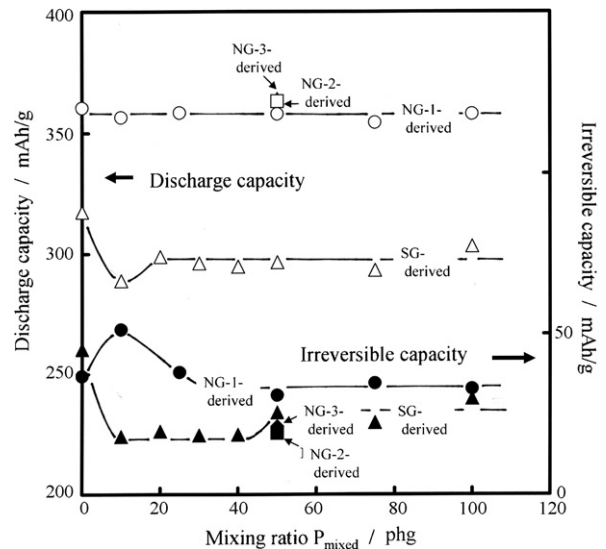


Fig. 4. Changes with mixing ratio of PVA P_{mixed} in discharge and irreversible capacities of two carbon-coated graphite derived from NG-1 and SG in 1 M LiClO_4 solution of EC/DMC = 1/1 with a rate of 0.5C/0.5C.

3.2.2. Effects of electrolyte solution and discharge rate

In Fig. 5a and b, discharge and irreversible capacities measured in an electrolyte solution of EC/DMC = 1/1 and EC/PC = 3/1, with the rate of 0.5C/0.5C are plotted against C_{coated} on two samples derived from NG-1 and SG. Fig. 5a is a re-plot of capacities in Fig. 4 as a function of C_{coated} , instead of P_{mixed} , in order to make a comparison with Fig. 5b easier.

Dependences of discharge and irreversible capacities on C_{coated} are similar in two solutions of EC/PC = 3/1 and EC/DMC = 1/1 on two samples (Fig. 5a and b). On the whole C_{coated} range examined, the samples derived from SG show smaller discharge capacity than those derived from NG-1 do, by about 50 mAh g^{-1} . Irreversible capacities on two samples are similar with each other, although those in EC/PC = 3/1 solution are slightly larger at C_{coated} above 8 mass% than that in EC/DMC = 1/1.

In EC/PC = 3/1 solution, the sample derived from SG shows very high irreversible capacity, more than 1000 mAh g^{-1} , at a low C_{coated} around 1 mass%. Similar but less pronounced anomaly in irreversible capacity at a low C_{coated} looks occurring on the sample derived from NG-1.

In Fig. 5c, discharge and irreversible capacities in EC/DMC = 1/1 solution with a rate of 0.5C/3.0C are shown as a function of C_{coated} on the sample derived from NG-1. This figure has to be compared with the data in Fig. 5a with 0.5C/0.5C rate on the same sample.

Discharge capacity shows only a small decrease by the increase in discharge rate, from about 360 mAh g^{-1} with a slow rate (0.5C) to about 350 mAh g^{-1} with a high discharge rate (3.0C), but irreversible capacity increases from 30 to 50 mAh g^{-1} .

In Table 2, capacities in different electrolyte solutions with different charge/discharge rates are listed for the original graphite NG-1 ($C_{\text{coated}} = 0.0$) and the carbon-coated graphite with C_{coated} of 5.0 and 17.5 mass%.

From Fig. 5 and Table 2, the carbon-coated graphite with C_{coated} of 5 mass% gives the same discharge capacity as the original graphite, but smaller irreversible capacity than the original under the different charge/discharge rates from 0.1C to 3.0C in the solution of EC/DMC = 1/1. In EC/PC = 3/1, a similar performance can be concluded. In the solution of EC/PC = 1/1 with larger amount of PC, however, extremely large irreversible capacity is observed on both the original and carbon-coated graphite with C_{coated} of 5 mass%. However, it is worth while to mention that carbon-coated graphite with C_{coated} of 17.5 mass%, which is obtained with P_{mixed} of 150 phg, gives relatively high anode performance even in the solution of EC/PC = 1/1, discharge capacity of about 360 mAh g^{-1} even though a large irreversible capacity for the first charge/discharge cycle (about 200 mAh g^{-1}).

3.2.3. Cyclic performance

Cyclic performance of LIB was preliminary studied by using the samples prepared from NG-1, NG-2 and SG with P_{mixed} of 50 phg (C_{coated} of about 5 mass%) in the electrolyte solution of EC/DMC = 1/1 with the rate of 0.5C/0.5C at room temperature. Discharge capacity and Coulombic efficiency are plotted against cycle number for three samples in Fig. 6.

Two samples derived from natural graphite show gradual decrease in discharge capacity with cycling, though the decreasing degree is very small, about 1% after 5th cycle. On the sample derived from SG, discharge capacity increases by about 15 mAh g^{-1} at 2nd cycle and then becomes constant at 300 mAh g^{-1} over 10 cycles. Coulombic efficiency increases from around 90% to 99% at 2nd cycle and saturated on three samples.

3.3. Low temperature performance of carbon-coated graphite

Anode performance of the samples derived from NG-1 was measured in the electrolyte solution of EC/DMC = 1/1 with the rate of

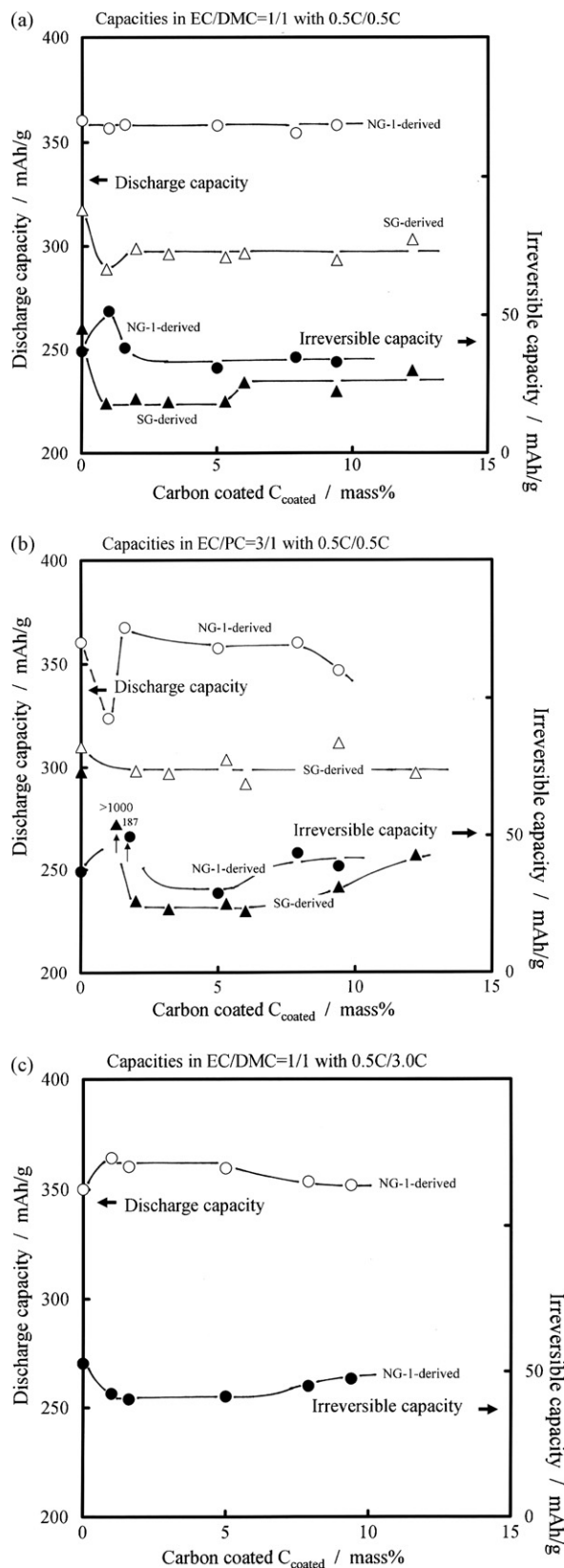


Fig. 5. Dependences of discharge capacity in different electrolyte solutions with different discharge rate on amount of coated carbon C_{coated} for two carbon-coated graphite derived from NG-1 and SG. Capacities in (a) EC/DMC=1/1 with 0.5C/0.5C, (b) EC/PC=3/1 with 0.5C/0.5C, and (c) EC/DMC=1/1 with 0.5C/3.0C.

Table 2
Capacities in different electrolyte solutions with different charge/discharge rates for the original and carbon-coated graphite NG-1.

	Electrolyte solution										
	EC/DMC = 1/1					EC/PC = 3/1		EC/PC = 1/1			
	0.1C/0.1C ^a		0.5C/0.5C ^a		0.5C/3.0C ^a	0.5C/0.5C ^a		0.5C/0.5C ^a			
Carbon coated, C _{coated} (mass%)	0.0	5.0	0.0	5.0	0.0	5.0	0.0	5.0	0.0	0.50	17.5
Charge capacity (mAh g ⁻¹)	406	394	397	389	403	401	435	386	1272	1718	560
Discharge capacity (mAh g ⁻¹)	394	366	360	358	350	360	354	357	358	332	361
Irreversible capacity (mAh g ⁻¹)	40	27	37	31	53	41	81	29	914	1386	199

^a Charge/discharge rate.

0.5C/0.5C at -5 °C and compared with that at 25 °C. The retention rating in discharge capacity, C₋₅/C₂₅, was calculated to be a measure of low temperature performance.

In Fig. 7a, discharge capacities measured at -5 and 25 °C and their ratio C₋₅/C₂₅ are plotted against C_{coated} for the carbon-coated graphite samples prepared at 900 °C with different P_{mixed}. Fig. 7b shows the changes in irreversible capacities at -5 and 25 °C with C_{coated}.

At -5 °C, the original graphite shows much smaller discharge capacity of about 250 mAh g⁻¹ and much higher irreversible capacity of about 150 mAh g⁻¹ than at 25 °C (about 360 and 35 mAh g⁻¹, respectively), and consequently a small C₋₅/C₂₅ of about 70%. These disadvantages of graphite anode at -5 °C are not improved by carbon coating of less than 5 mass%. Above 5 mass% C_{coated}, however, discharge capacity can keep at much higher value and irreversible capacity at much lower value than the original at -5 °C, about 310 mAh g⁻¹ and about 70 mAh g⁻¹, respectively. Therefore, the ratio C₋₅/C₂₅ keeps the value close to 90% with C_{coated} above 5 mass%, much higher than the original graphite (about 70% retention).

For the carbon-coated graphite samples prepared from NG-1 with P_{mixed} of 50 phg at different temperatures, discharge capacity becomes smaller at -5 °C than at 25 °C, as shown in Fig. 8. The dependence of discharge capacity at -5 °C on heat treatment temperature shows a maximum at around 800 °C, although the change in discharge capacity at 25 °C is comparatively small. As a consequence, the ratio C₋₅/C₂₅ shows a maximum of more than 90% at 900 °C. Above 1100 °C, discharge capacity at -5 °C decreases, although capacity at 25 °C does not change with heat treatment

temperature, and so retention rating C₋₅/C₂₅ approaches to that of the original graphite.

The present experimental results suggest that carbon coating is also effective to improve the performance at low temperature -5 °C. In order to get high C₋₅/C₂₅ ratio, i.e., high retention rating of about 90% in discharge capacity at -5 °C in comparison with that at 25 °C, the coating condition has to be controlled as follows; C_{coated} has to be more than 5 mass% and heat treatment temperature has to be 700–1000 °C.

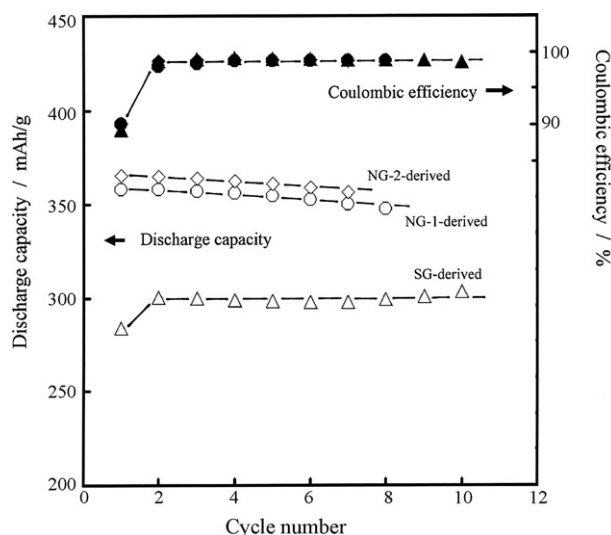


Fig. 6. Changes with charge/discharge cycle with a rate of 0.5C/0.5C of discharge capacity and coulombic efficiency for three carbon-coated graphite derived from NG-1, NG-2 and SG.

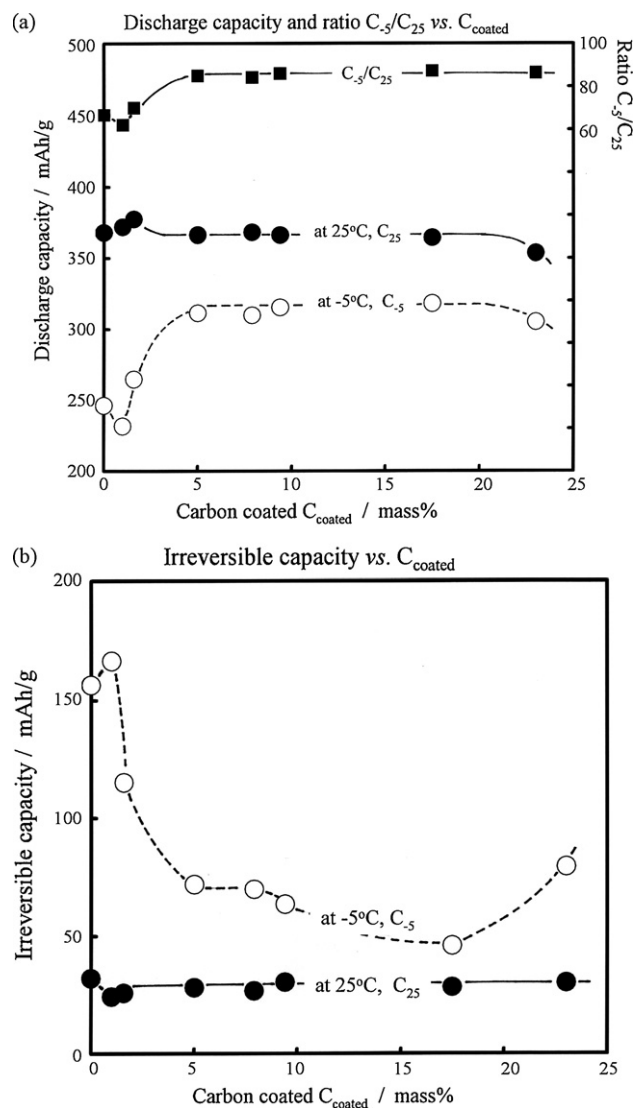


Fig. 7. Discharge and irreversible capacities at 25 and -5 °C with retention ratio C₋₅/C₂₅ as a function of amount of coated carbon C_{coated} on carbon-coated NG-1 at 900 °C. (a) Discharge capacity and ratio C₋₅/C₂₅ vs. C_{coated} and (b) irreversible capacity vs. C_{coated}.

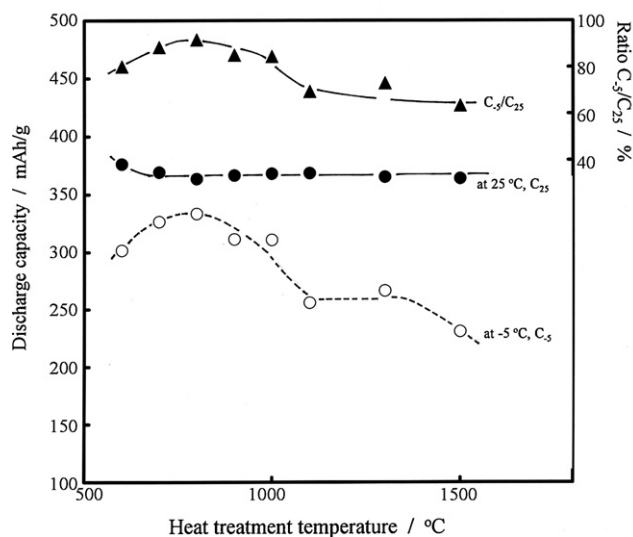


Fig. 8. Discharge capacities at 25 and -5°C with retention ratio C_{-5}/C_{25} as a function of heat treatment temperature of the mixtures of NG-1 with mixing ratio of PVA of 50 phg.

4. Conclusion

Synthetic graphite, a powdered high-density isotropic graphite, was shown to be used to anode material of LIBs as natural graphite did. By carbon coating, natural graphite gave discharge capacity of about 360 mAh g^{-1} and irreversible capacity of about 30 mAh g^{-1} . On the other hand, carbon-coated synthetic graphite gave smaller irreversible capacity of about 20 mAh g^{-1} and a good cyclic performance in an electrolyte solution of EC/DMC, though its discharge capacity was a little smaller than natural graphite. Even in a PC-containing solution as EC/PC = 3/1, carbon-coated synthetic

graphite had almost the same anode performance as in the solution without PC.

Carbon coating of graphite particles was found to be effective to improve the anode performance at low temperatures. By carbon coating above 5 mass%, high retention rating in discharge capacity, about 90%, was obtained at -5°C .

On both natural and synthetic graphite powders, carbon coating by the amount of 5–10 mass% at a temperature of $700\text{--}1000^{\circ}\text{C}$ were found to be optimum in order to improve anode performance in LIBs, to have a lower irreversible capacity and higher retention rating in discharge capacity at -5°C .

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