

Effect of milling on the electrochemical performance of natural graphite as an anode material for lithium-ion battery

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Abstract

The electrochemical performance of natural graphite as the anode material for lithium-ion batteries can be improved by both jet milling and turbo milling. The effect of milling on electrochemical performance of natural graphite was discussed in terms of morphological change in graphite. The correlations between some aspects of morphology and electrochemical performance of natural graphite were studied. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

During the past years there have been a lot of research work carried out on different kinds of carbonaceous materials used as anode in lithium-ion batteries. More recently, considerable effort has been focused on heat-treated soft and hard carbons with specific capacities higher than that of lithium intercalated graphite (LiC_6 , 372 (mA h)/g). Although the theoretical limit of the specific capacity of 372 (mA h)/g is the major disadvantage of graphitic carbons, they are commonly found in most commercial products on the market today due to their advantages such as flat and low working voltage with respect to lithium metal, high coulombic efficiency, etc.

In the family of graphitic carbons, natural graphite seems to be the most promising candidate for anode in lithium-ion battery in terms of economy. Sanyo has already succeeded in applying natural graphite as the anode in the product [1]. However, from the previous works [2,3], we found that the rather “raw” natural graphite flakes as

received directly from the mines cannot deliver reversible specific capacity as high as the theoretical limit of lithium intercalated graphite. There are many aspects of morphology that can affect the electrochemical performance of natural graphite anode in lithium-ion cell, for example, lattice parameter, crystallite size, particle size, surface area, ash content, porosity, etc. We believe it is the compromise of the aspects altogether that determines the electrochemical behavior of natural graphite at last. An attractive way of getting some insight into the correlation between the electrochemical performance and morphology of natural graphite is to find an effective treatment method which can significantly change some aspects of natural graphite's morphology and then alter the corresponding electrochemical performance. Powdering has been adopted by some research groups as a powerful treatment method to change the morphology of carbons [3–5]. For example: Fukuda et al. [3] have obtained foliated natural graphite with specific capacity near 372 (mA h)/g mainly by chemical flaking of natural graphite along cleavage planes.

By contrast, Disma et al. [4] applied two kinds of mechanical grinding techniques (impact/shock mode and shear mode of ball milling) to the treatment of graphite and soft carbons. They found that the morphology of the milled graphitic powders depend strongly upon the kind of mills used.

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There are many mechanical grinding techniques other than ball milling. So we can expect there should be much more possibilities in finding different types of morphologies of carbons than those already present in the literature. Herein we report the study of the application of two kinds of milling (jet milling and turbo milling) effective for industrial use for the treatment of natural graphite.

2. Experimental

Two kinds of Brazilian natural graphite were used as the starting materials. These two kinds of graphite were ground in jet mill and turbo mill, respectively, and classified. The samples' name details are listed in Table 1. In the jet mill (Fig. 1), namely, Fluidized Bed Jet Mill CGS (Netzsch-Condux Maschinenbau, Germany), Brazilian natural graphite designated as B-1 was fed into the milling area in a "bed" form which was fluidized by the air stream from the Laval jets. Then particles of natural graphite from the fluidized bed were accelerated to a high velocity about 500 m/s by the air stream in contact. In the center of the bed the accelerated particles collide with each other and thus reduce their sizes. In contrast to the jet milling, in the turbo mill (Fig. 2), namely, Turbo-Mill T-400-4J (Turbo Kogyo, Japan), Brazilian natural graphite designated as B-2 was pulverized by the high-frequency-vibrating air vortexes which were generated by high speed rotation of the wings.

The charge and discharge characteristics of graphite samples were tested in two-electrode cells. The cell comprised a graphite electrode and a lithium metal with a separator between them. The graphite (10 mg) was mixed with 10 wt.% PVDF as a binder dissolved in *N*-methyl-2-pyrrolidone. The paste mixture was spread thinly on a stainless-steel mesh and pressed at 1 ton/cm². The graphite electrodes were dried under vacuum at 200°C for 2 h. The electrolyte used in the cells was 1 M LiPF₆-ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:2 in volume).

Table 1
Details of Brazilian natural graphite samples' names

Sample's name	Type of mill used	Classification
B-1	None	No classification
B-1-JM-N	Jet mill	No classification
B-1-JM-2M	Jet mill	Middle particle size
B-1-JM-2F	Jet mill	Fine particle size
B-1-JM-M	Jet mill	Middle particle size
B-1-JM-F	Jet mill	Fine particle size
B-2	None	No classification
B-2-TM-N	Turbo mill	No classification
B-2-TM-2M	Turbo mill	Middle particle size
B-2-TM-2M-F	Turbo mill	Middle/fine particle size
B-2-TM-M	Turbo mill	Middle particle size
B-2-TM-F	Turbo mill	Fine particle size

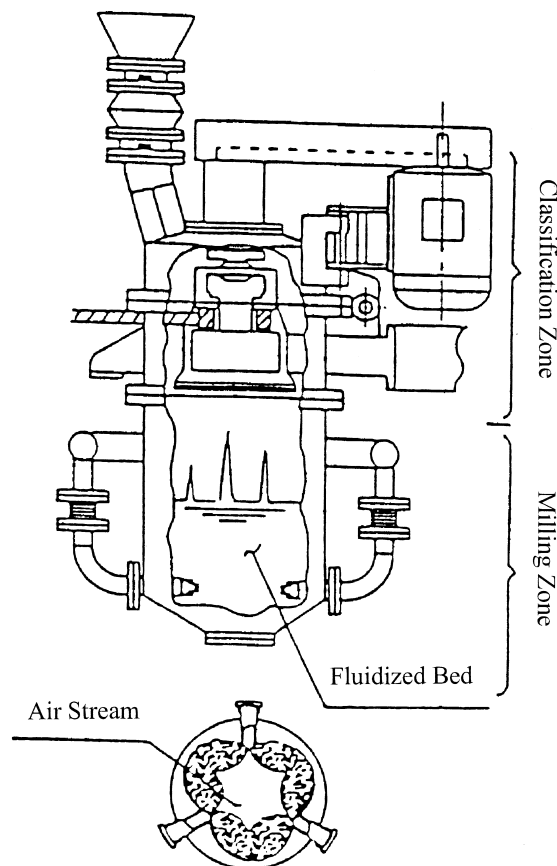


Fig. 1. Schematic diagram of fluidized bed jet mill CGS construction.

The cells were discharged at a constant current density of 0.4 mA/cm² (100 mA/g) to a cutoff voltage of 1 mV and held at this potential for 1 h. After resting the cells for 10 min, the cells were charged at the same current density to 1.5 V.

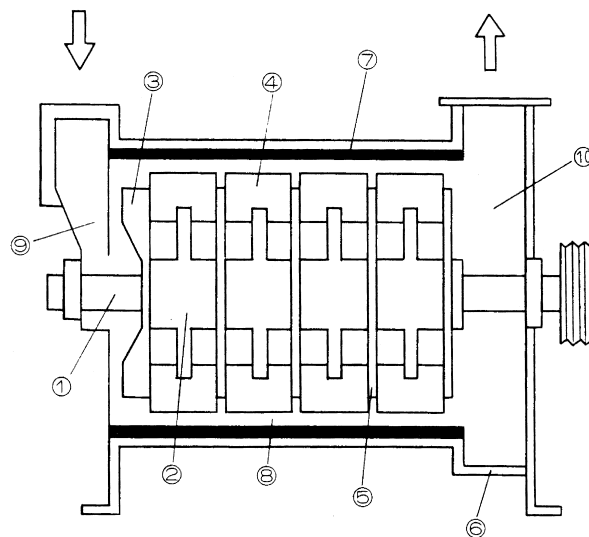


Fig. 2. Schematic diagram of turbo mill construction: (1) shaft; (2) rotor; (3) distributor; (4) wings; (5) partition discs; (6) casing; (7) liner; (8) chamber; (9) inlet spiral chamber; (10) outlet spiral chamber.

3. Results and discussion

Fig. 3 presents SEM micrographs of the graphite samples before and after milling-treatment. From this figure it can be seen that:

1. All the graphite particles are thin plate-like flakes. Their thickness is much smaller than their average particle size which relates to their wide dimensions parallel to the cleavage planes of the particles.
2. Both jet milling and turbo milling can cut graphite particles into smaller ones in the directions of both perpendicular and parallel to the basal planes.

Table 2 presents some physical properties and the corresponding electrochemical performance of the graphite samples. From Table 2, it can be seen clearly that both of these two kinds of milling make the particle size of graphite, the thickness of graphite flakes, and crystallite size decrease while cause the B.E.T. specific surface area increase remarkably. On the other hand, for both jet milling and turbo milling, the changes in d_{002} ((002) plane spacing) of graphite samples after milling are very small. This is the main point which may differentiate both jet milling and turbo milling from other milling techniques which may inevitably introduce considerable defects into graphene

layers and then increase the value of d_{002} more markedly. In other words, both jet and turbo millings can provide much softer and milder destructive effect on graphite particles than those of other milling techniques. In Disma et al.'s work [4], it is demonstrated that the value of d_{002} can be changed markedly besides the changes of particle size and crystallite size after the treatment of ball milling. In the case of impact/shock type of ball milling, the interactions vertical to the graphite cleavage planes are so strong that graphite particles are torn to pieces of disordered carbons with both a very high reversible specific capacity and a high irreversible capacity in a sloping voltage range. While as for both jet milling and turbo milling, the graphitic layered structure still persists in the graphite samples after the treatments in spite of the cutting effects vertical to the cleavage planes.

As mentioned above, both jet milling and turbo milling can change the morphology of graphite via the decreases of particle size, the thickness of flakes and crystallite size as well as the increase of B.E.T. specific surface area. So it can be expected there may be some relationships among these four aspects of morphology and electrochemical performance of graphite. In order to clarify the roles the aspects play in the influences on electrochemical perfor-

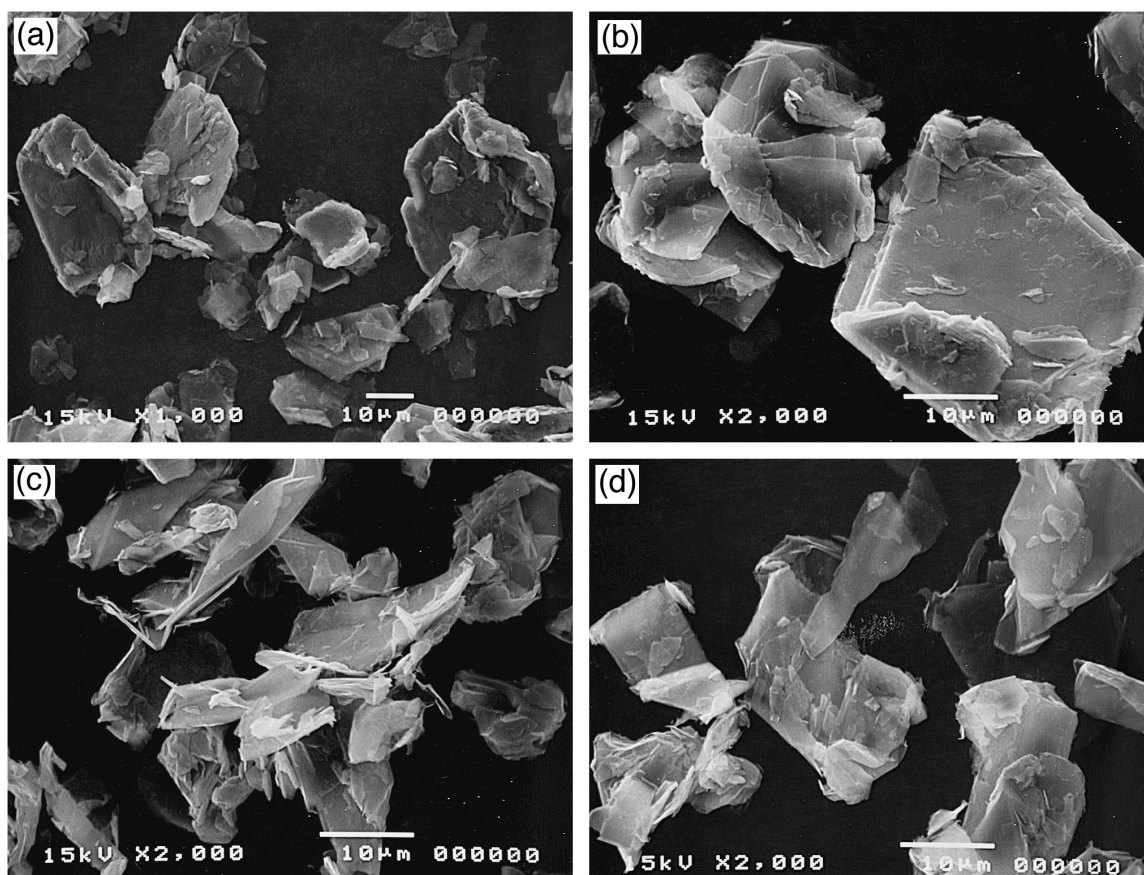


Fig. 3. SEM graphs of Brazilian natural graphite samples: (a) Brazilian natural graphite as received, B-1; (b) Brazilian natural graphite as received, B-2; (c) Brazilian natural graphite treated by jet milling, B-1-JM-2M; (d) Brazilian natural graphite treated by turbo milling, B-2-TM-2M.

Table 2
Some physical properties and electrochemical performance of natural graphite samples

Sample's name	Ash content (wt.%)	Mean particle size (μm)	Thickness (nm)	n	B.E.T. specific surface area (m^2/g)	d_{002} (nm)	Lc(002) (nm)	Initial discharge capacity ((mA h)/g)	Initial charge capacity ((mA h)/g)	Coulombic efficiency (%)
B-1	0.18	20.75	2000	6.2	4.24	0.33549	322	395	349	88.4
B-1-JM-N	0.18	9.56	300	1.7	6.88	0.33565	177	417	363	87.1
B-1-JM-2M	0.18	12.54	400	1.6	5.61	0.33563	255	415	366	88.2
B-1-JM-2F	0.18	6.26	200	1.1	9.06	0.33578	178	431	359	83.3
B-1-JM-M	0.18	14.12	400	2.2	5.32	0.33582	178	404	361	89.4
B-1-JM-F	0.18	7.69	200	1.1	6.69	0.33577	176	422	358	84.8
B-2	0.19	33.09	3000	9.2	3.16	0.33543	326	361	323	89.5
B-2-TM-N	0.19	9.35	350	2.5	8.03	0.33569	138	424	362	85.4
B-2-TM-2M	0.19	11.36	400	2.8	6.98	0.33584	145	422	362	85.8
B-2-TM-2M-F	0.19	6.52	300	2.4	8.13	0.33612	124	437	361	82.6
B-2-TM-M	0.19	14.45	400	2.7	8.84	0.33572	148	419	363	86.6
B-2-TM-F	0.19	7.8	300	1.6	9.86	0.33573	187	426	361	84.7

mance of graphite, we correlated these aspects with electrochemical performance separately although this kind of investigation may be too simplified to see the coordination of all these aspects.

Fig. 4 shows the relationship between particle size and the electrochemical performance of graphite. Fig. 4(A) shows the relationship between particle size and the discharge capacity. For each set of the graphite samples, it can be seen that the discharge capacity increases with the

decrease of particle size. Fig. 4(B) shows the relationship between the charge capacity and particle size. The charge capacity, in contrast with the discharge capacity, does not show very direct correlation with the particle size. The unmilled graphite samples with large particle size have as low charge capacity as 323 mA h or 349 (mA h)/g, respectively. After being milled, the mean particle size of graphite decreases to less than $15 \mu\text{m}$, and then the values of charge capacity keep around 360 (mA h)/g independent

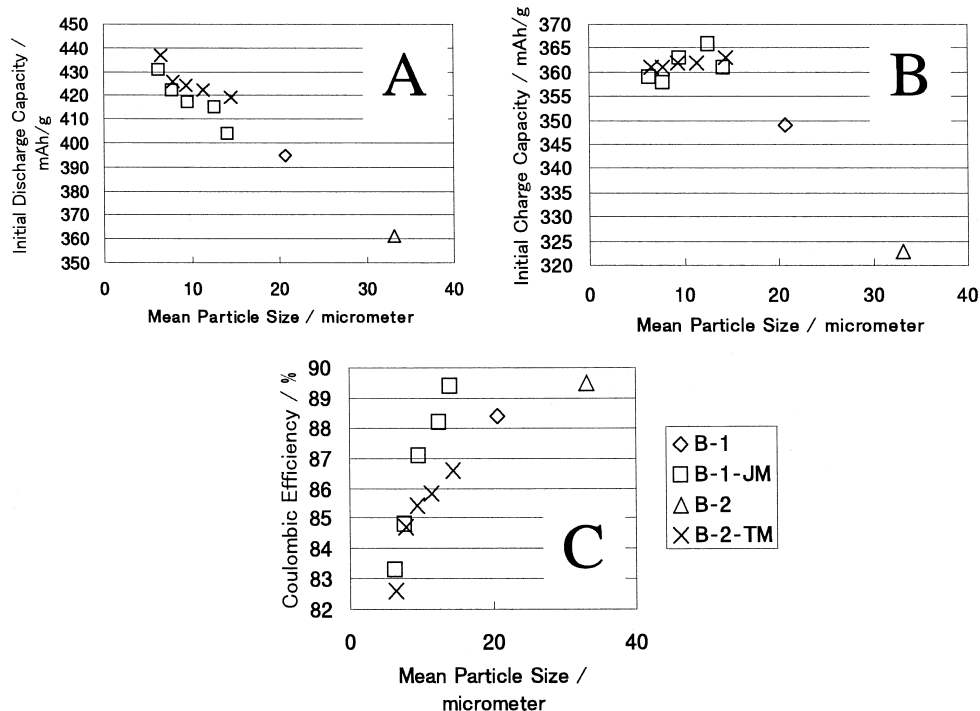


Fig. 4. Relationship between the particle size and the electrochemical performance ([A] the initial discharge capacity; [B] the initial charge capacity; [C] the coulombic efficiency).

of the variation of particle size. Fig. 4(C) shows the relationship between coulombic efficiency and particle size. For milled graphite samples, it can be seen clearly that as the particle size increases, the coulombic efficiency increases. On the other hand, turbo milling shows a negative effect on the coulombic efficiency of natural graphite anodes. The graphite samples turbo-milled have lower coulombic efficiencies than the original natural graphite. For jet milling, the coulombic efficiency of natural graphite anode generally decrease after being jet-milled. However, with a little increase in particle size of jet-milled natural graphite samples by classification, it is found that the jet-milled natural graphite anode can have a higher coulombic efficiency than the original natural graphite. It can be conceived that too big particle-sized natural graphite cannot deliver high reversible capacity because of the lack of exposure of the edge planes towards the electrolyte. So the reversible capacity of natural graphite can be increased with the decrease of particle size of natural graphite. However, too fine-particle natural graphite will inevitably incur very big irreversible capacity due to the big surface area and then decrease the coulombic efficiency. Thus it can be concluded that in order to obtain natural graphite suitable for lithium-ion batteries, the particle size of graphite must be controlled strictly.

With the decrease of particle size, the B.E.T. specific surface area of graphite will increase after milling-treat-

ment. Fig. 5 shows the relationship between the B.E.T. specific surface area and the electrochemical performance of graphite samples. From Fig. 5(A) it can be observed that in the range from about 3 to 7 m^2/g for the B.E.T. specific surface area, the initial discharge capacity of graphite increases with the increase of B.E.T. specific surface area while keeps the values around 430 (mA h)/g when the B.E.T. specific surface area is about over 8 m^2/g . Fig. 5(B) shows the relationship between the B.E.T. specific surface area and the initial charge capacity for graphite samples. Fig. 5(B) demonstrates similar trend as that in Fig. 5(A). However, the range for the monotonic increase of initial charge capacity with the change of the B.E.T. specific surface area becomes narrower (from about 3 to 6 m^2/g). Moreover, the values of the initial charge capacity fluctuate around 360 (mA h)/g when the B.E.T. specific surface area is more than 6 m^2/g . Fig. 5(C) shows the relationship between the B.E.T. specific surface area and coulombic efficiency. It can be seen that the rough trend is: the smaller the B.E.T. specific surface area is, the larger the coulombic efficiency is. As mentioned above, natural graphite with too small B.E.T. surface area is not preferable for the anode material in lithium-ion batteries because it cannot provide enough surface (especially edge plane) for lithium intercalation. On the other hand, too big B.E.T. specific surface area is also not advisable for graphite because of the big amount of decomposition of

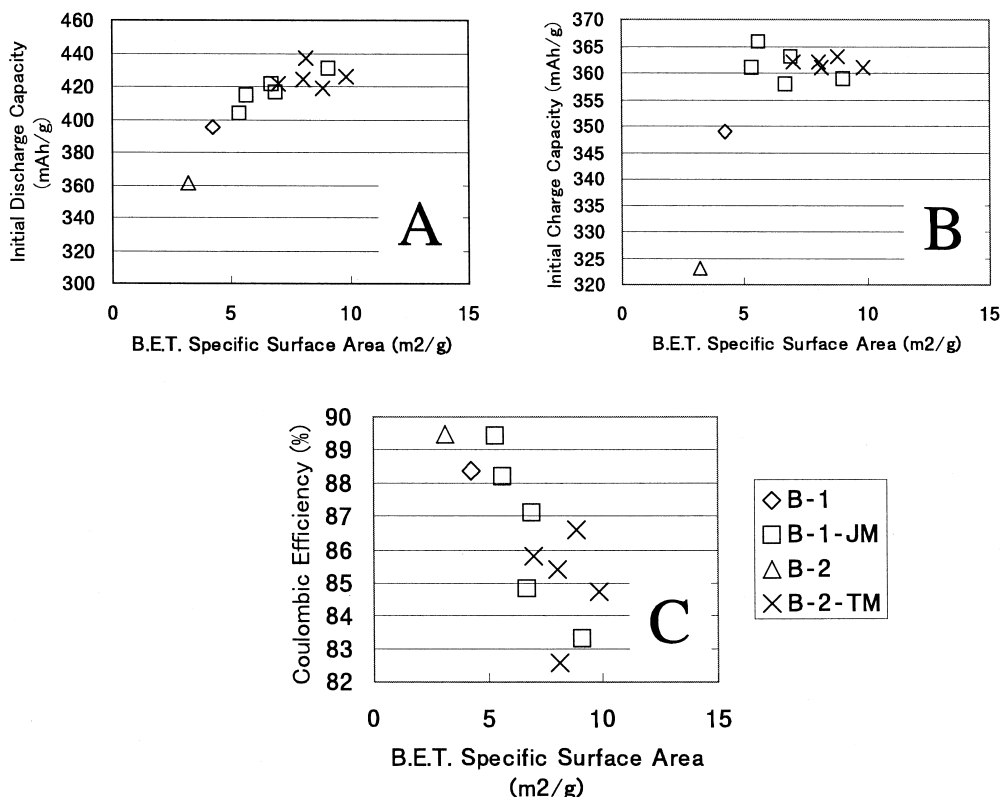


Fig. 5. Relationship between the B.E.T. specific surface area of natural graphite and the electrochemical performance ([A] the initial discharge capacity; [B] the initial charge capacity; [C] the coulombic efficiency).

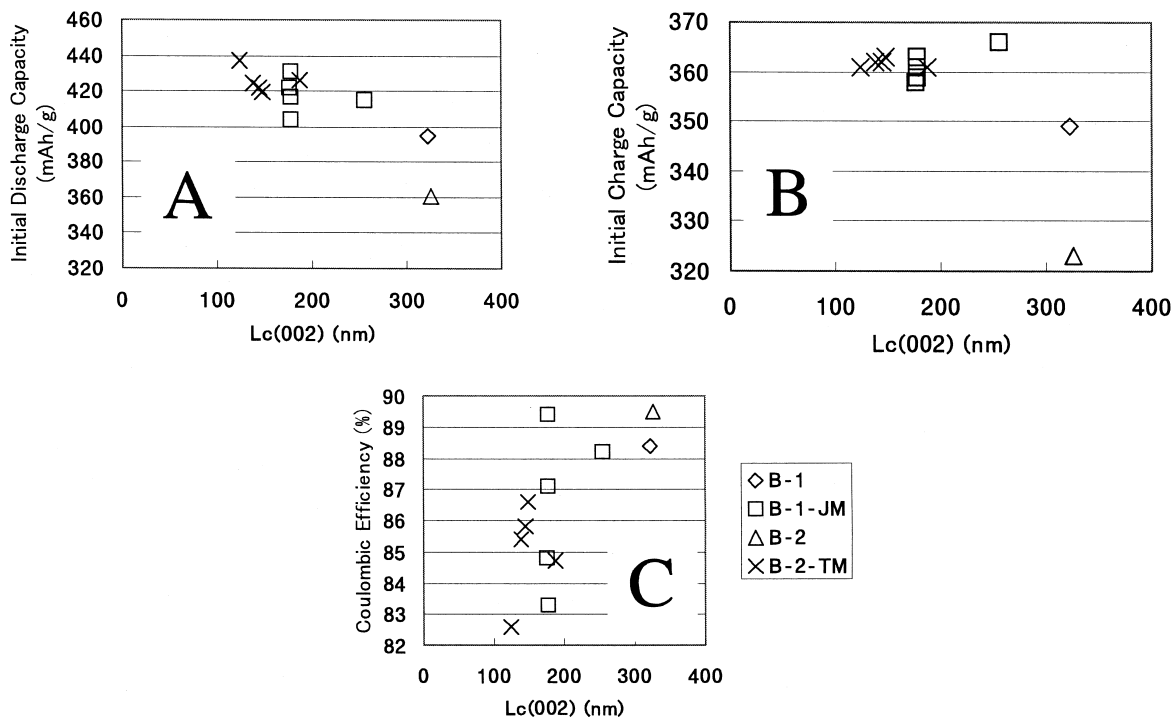


Fig. 6. Relationship between Lc(002) and the electrochemical performance ([A] the initial discharge capacity; [B] the initial charge capacity; [C] the coulombic efficiency).

electrolyte to build up the SEI (Solid Electrolyte Interface) film covering all the surfaces of graphite particles. In this study we found that by classification after jet milling the

graphite sample with B.E.T. specific surface area near 6 m²/g shows satisfactory electrochemical performance in terms of reversible capacity and coulombic efficiency.

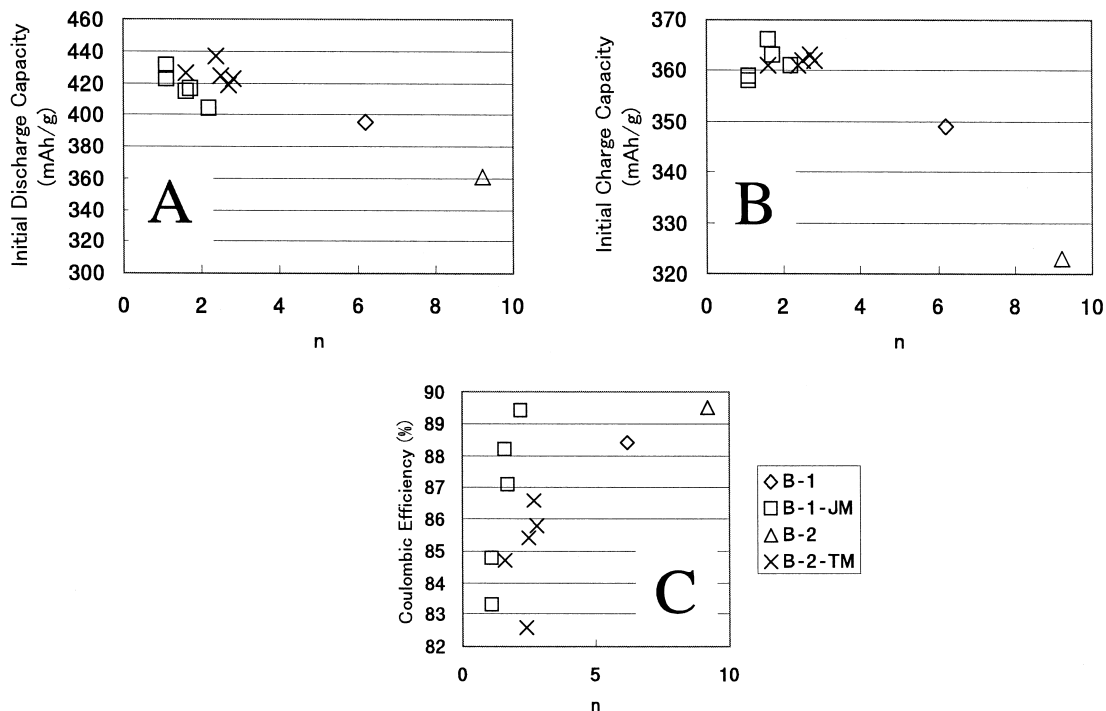


Fig. 7. Relationship between n and the electrochemical performance ([A] the initial discharge capacity; [B] the initial charge capacity; [C] the coulombic efficiency).

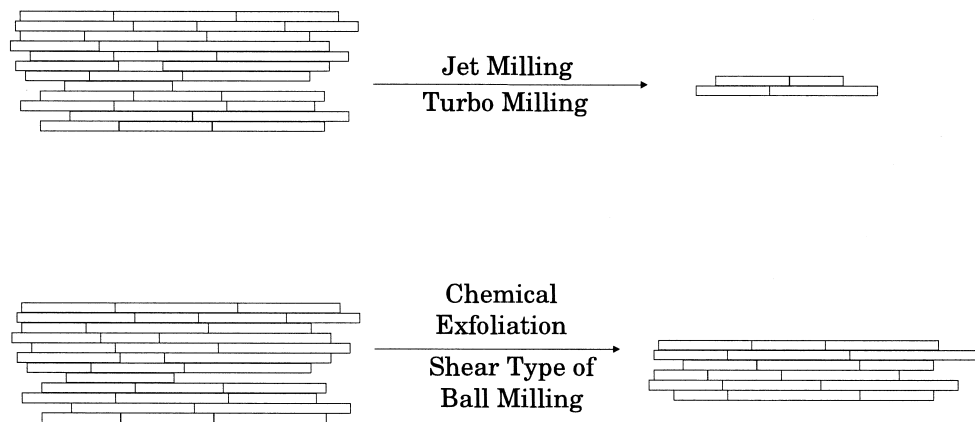


Fig. 8. Schematic of the morphological changes of different kinds of powdering methods for natural graphite.

For both jet milling and turbo milling, not only does the particle size of graphite but also crystallite size decreases. So the correlation between crystallite size and electrochemical performance should also be investigated. Fig. 6(A)–(C) show the relationships between $L_c(002)$ and the initial discharge capacity, initial charge capacity, and coulombic efficiency, respectively. From Fig. 6 it is difficult to find some strong function relationships between $L_c(002)$ and the electrochemical performance. Fujimoto et al. [6] have proposed relationship between the reversible specific capacity and the crystallite parameters of graphite. However, their equation is not applicable to this study since particle size shows much more pronounced effect on graphite's electrochemical performance than that of crystallite size as illustrated above.

Together with the decrease of particle size, the thickness of graphite flakes decreases after milling-treatment. In Fukuda et al.'s work, [3] an empirical parameter, “ n ”, was introduced to quantify the degree of graphite foliation in the thickness direction, and defined as the mean stacking number of crystallites along the thickness direction in every graphite particle. Here we adopt this parameter to evaluate the milling effect on graphite flake thickness. Fig. 7(A)–(C) show the relationships between n and the initial discharge capacity, initial charge capacity and coulombic efficiency, respectively. Fig. 7(A) and (B) demonstrate almost the same trend. That is: the lower the n value is, the higher both initial discharge capacity and initial charge capacity are. More interestingly, the “ n ” values of milled graphite samples seem to be around 1 and 2. Compared with the “ n ” values of foliated natural graphite samples in Fukuda et al.'s work [3] which also shows that graphite flakes with the “ n ” value of about 1 and 2 have good electrochemical performance, it can be concluded that natural graphite with low “ n ” value as 1 to 2 can be

intercalated by lithium adequately. For comparison of different powdering techniques, a schematic of the morphological changes in natural graphite from the viewpoint of “ n ” value is shown in Fig. 8. From this figure it can be seen all these powdering techniques can cut graphite flakes along the cleavage planes. However, jet milling and turbo milling seem more effective than chemical exfoliation and shear type of ball milling.

4. Conclusion

By applying jet milling or turbo milling to the treatment of natural graphite, suitable anode materials for lithium battery can be obtained. The effect of both kinds of milling on the electrochemical performance of graphite is mainly due to the decrease of the particle size and thickness of graphite flake which cause the change of morphology for graphite. These two kinds of milling can make natural graphite a promisingly economical source for anode material in rechargeable lithium-ion battery.

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