

ELECTRICAL PROPERTIES OF FILM AND LITHIUM ION BATTERY COMPOSED OF NATURAL GRAPHITE PARTICLES GROUND UNDER VARIOUS ATMOSPHERES

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Introduction

Highly crystalline natural graphite has a high electrical conductivity and an excellent lubricant properties [1]. Since the shape of natural graphite particles present aspects similar to flakes due to their lamellar crystal structure, they are used as raw materials to produce electrically conductive films and pastes such as the CRT mask in television sets. Recently, attempts have been made to use them in negative electrode materials for lithium ion batteries for mobile computers, mobile telephones and the likes.

Very recently, we ground natural graphite particles in a ball-mill under a well-controlled dry atmosphere such as N₂, H₂, O₂ or vacuum to investigate the relationship between the electrical conductivity, the size, and the shape of the ground particles [2]. Hayashi et al. reported that the shape of graphite particles ground in the presence of added liquid alcohol as a grinding aid became flaky [3].

The aim of the present study is to investigate the effects of grinding atmosphere such as alcoholic vapors on the electrical conductivity of films, as well as the electrochemical performance of lithium ion batteries, whose negative electrode is made from ground natural graphite particles. The investigation included grinding highly crystalline natural graphite particles in various kinds of alcoholic vapor under well-controlled atmosphere, and evaluating the size and the shape of the ground products as well as the specific resistance of films composed of the graphite particles, and testing the

electrochemical performance of home-made lithium ion batteries.

Experimental

Grinding of natural graphite particles in alcoholic vapors

First, five grams of highly crystalline natural graphite particles that were sieved to yield a range of particle size under 63 μm were placed with 4-mm stainless steel balls (33% apparent packing fraction) in a stainless steel ball mill pot (480 cm³), having a valve attached for the evacuation of gases. After the mill pot containing feed graphite particles was vacuum-dried at 80 °C for one night, various alcohols in the form of iso-C₃H₈OH, C₂H₅OH, or CH₃OH vapors were fed into the mill pot. The amount of alcohol was 1.6 x 10⁻⁴ mol per gram of graphite. Then, the graphite was ground for the time listed in **Table 1**, at a rotation speed of 120 rpm of the mill pot (method I). When alcoholic vapors disappeared due to the grinding, we increased the fraction of alcohol to five times of the 1.6 x 10⁻⁴ mol/g of graphite. Natural graphite particles were also ground in dry air at 800 Torr, in a mixture of 1 % O₂ and 99 % N₂, and in a low pressure corresponding to a vacuum atmosphere of 10⁻³ Torr (0.1 Pa).

Next, to investigate the characteristics of the graphite particles used as constituents of the negative electrode of a lithium ion battery, 20 grams of natural graphite particles were ground in a similar way to that described above (method II).

Table.1 Grinding conditions

grinding atmosphere	grinding time [h]
O ₂ 1%, N ₂ 99%	2, 4, 8, 24, 48
O ₂ 21%, N ₂ 79% (dry air)	2, 4, 8, 24
Vacuum 10 ⁻³ Torr	2, 4, 8, 24
CH ₃ OH (1.6 x 10 ⁻⁴ mol/g of graphite)*	2, 4, 8, 24, 48*
C ₂ H ₅ OH (1.6 x 10 ⁻⁴ mol/g of graphite)*	2, 4, 8, 24, 48*
n-C ₃ H ₇ OH (1.6 x 10 ⁻⁴ mol/g of graphite)	2, 4, 8, 24, 48
iso-CH ₃ H ₇ OH (1.6 x 10 ⁻⁴ mol/g of graphite)	2, 4, 8, 24, 48

In the cases of CH₃OH and C₂H₅OH, grinding for 48 h with a fraction of alcoholic vapor of 8.0 x 10⁻⁴ mol/g of graphite was also performed.

Evaluation of the size and the shape of ground particles

The particles ground as described above were carefully collected from the mill pot and dispersed in water containing ammonium acrylate as a dispersion agent using a supersonic oscillator. Then, the sizes of the particles were measured by two different methods as follows. The diameter for the Stokes region, called the Stokes diameter X_{st} , determined by gravitational sedimentation, is defined by

$$X_{st} = \sqrt{\frac{18\eta u_{st}}{\Delta\rho g}}, \quad (1)$$

where η is the viscosity of water, u_{st} is the terminal velocity of the particle, $\Delta\rho$ is the difference of density between the particles and water, and g is the gravitational acceleration [4,5]. By definition, the Stokes diameter of a particle is equivalent to the diameter of a sphere which has the same sedimentation velocity as the particle. The Stokes diameters of the particles were measured with the SACP-3 (Shimadzu Co.). Another particle diameter, called the laser diffraction diameter, X_{dif} , was calculated from the diffraction pattern based on the Fraunhofer theory using an inversion technique [6,7]. The laser diffraction diameter was measured with the SALD-1100 (Shimadzu Co.). Since the laser diffraction diameter mainly depends on the cross-section of the particle in the laser beam [8], it tends to be overestimated for flaky particles [8,9].

The theory and discussion were detailed elsewhere [8,9]. We used the ratio between the 50 wt% Stokes diameter and the 50 wt% laser diffraction diameter, X_{dif50} / X_{st50} , as an index for the flakiness of the particles. It was theoretically and experimentally established that the particle size ratio X_{dif50} / X_{st50} , is greater than unity when the flakiness of the

particle increased, and that it asymptotically approaches unity when the particle shape comes blocky [8,9]. The apparent bulk density of 20 grams of graphite particle samples was measured with a 100 milliliter measuring cylinder, after tapping 40 and 80 times in a similar way to JIS standard K5101.

The specific surface area of particles was measured with the ASAP 2010 microscope analyzer (Micromeritics Inc.) by the Burnauer-Emmett-Teller (BET) method.

Measurements of specific electrical resistance

One gram of graphite particles was dispersed in 5 ml of water containing 0.1g ammonium acrylate as a dispersion agent. Then, five glass slides were coated with the graphite particles suspended as described above, and dried at 50 °C to form graphite films. The electrical resistance of these films was measured with a mercury electrode. The measurement was repeated 10 times for each of the five films. The specific electrical resistance was then determined from the measured electrical resistance and the thickness of the film which was calculated from the weight of the film and the size of the glass slides. The average electrical resistance determined in this way was used as an index of the electrical conductivity.

Measurements of the performance of home-made lithium coin type cells

The detailed measurement procedures were described elsewhere [10]. Briefly, the electrodes were prepared by coating slurries of graphite powder (90wt %) and polyvinylidene fluoride (10wt %) dissolved in 1-methyl-2-methyl pyrrolidinone over a copper foil current collector. After coating, the electrodes were dried at 120 °C

for 10 min in air, then pressed by a roll press machine. Typically, the electrode density was 1.4 g/cm^3 , and the thickness was $60 \text{ }\mu\text{m}$. These electrodes were further vacuum-dried for 3h at $120 \text{ }^\circ\text{C}$.

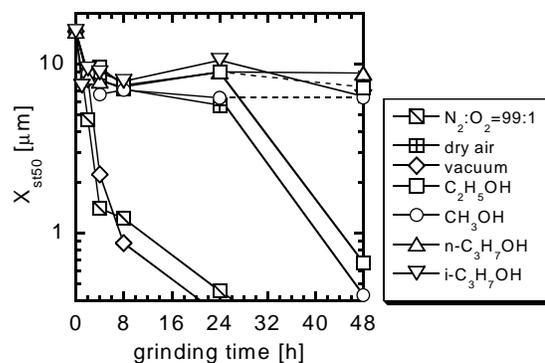
All the electrochemical measurements were carried out using 2016 coin type cells at $25 \text{ }^\circ\text{C}$. Lithium metal was used as the counter electrode, and a porous film of polypropylene was used as separator. The electrolyte was a solution of 1 M LiPF_6 in a 50:50 (volume) solvent mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). All the cells were assembled in a glove box filled with dry argon.

The cells were charged, i.e., lithium was intercalated within the graphite electrode, from the open-circuit voltage to 0.01 V (vs. Li/Li^+) at a constant current density of 0.5 mA/cm^2 . Then, the cells were discharged i.e., lithium was de-intercalated of from the graphite electrode, to 1.1V (vs. Li/Li^+) at constant current density of 0.5 mA/cm^2 .

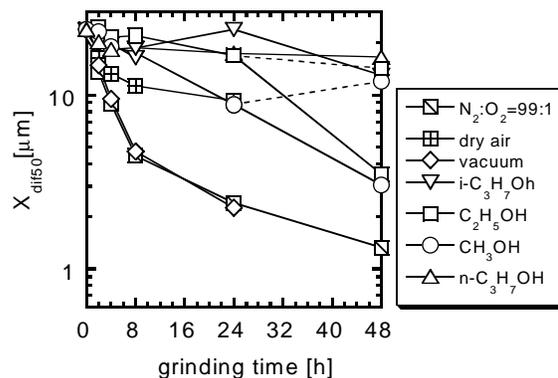
Results and discussion

Size and shape of ground particles

Figure 1 (a) and (b) show the values of the 50 wt% Stokes diameter, X_{st50} , and the 50 wt% laser diffraction diameter X_{dif50} , of the graphite particles in various alcoholic vapors (method I) as a function of grinding time, respectively. For the data associated with solid line, the fraction of alcoholic vapor was $1.6 \times 10^{-4} \text{ mol/g}$ of graphite. The X_{st50} of particles ground in alcoholic vapors, except those ground for 48 h in CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ vapors, are relatively close to those ground in dry air. The data associated with the broken line corresponds to the grinding with an alcoholic vapor of $8.0 \times 10^{-4} \text{ mol/g}$ of graphite. In this case, the progression of the grinding in CH_3OH vapor and $\text{C}_2\text{H}_5\text{OH}$ vapor were similar to the grinding in the other alcoholic vapors. It was considered that the drastic decrease in X_{st50} of the products ground for 48 h in CH_3OH vapor and $\text{C}_2\text{H}_5\text{OH}$ vapor, for which **Figure 1** 50 wt% diameter of ground particles as a function of grinding time.



(a) 50 wt% Stokes diameter, X_{st50}



(b) 50 wt% diffraction diameter, X_{dif50}

the fraction was $1.6 \times 10^{-4} \text{ mol/g}$ of graphite, was caused by the lack of alcoholic vapor during progression of the grinding. Although the detailed effects on the grinding process due to the use of different alcoholic vapor cannot be discussed here, the differences in molecular size and electrical polarity of alcohols used in this study probably caused a difference in the grinding process as shown in Fig. 1, and the electrical properties of ground products described later such as in Fig. 2.

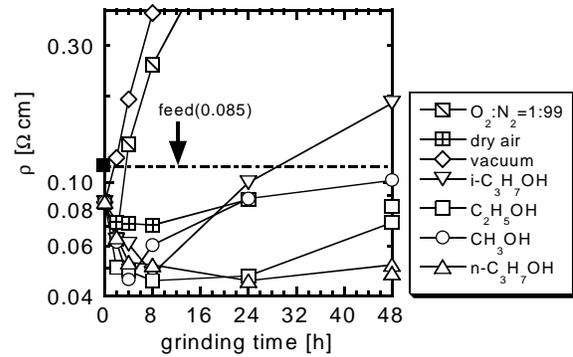
The decrease in the X_{dif50} of ground products in alcoholic vapor was rather smaller than those in dry air grinding (see Fig. 1 (b)). Therefore, the particle size ratio X_{dif50}/X_{st50} of the products ground in alcoholic vapor was greater than the products ground in dry air. Since the flakiness of the particles increases with the increase in their particle size ratio X_{dif50}/X_{st50} [8,9], the grinding in alcoholic vapor could produce flaky particles.

Electrical conductivity of films made from the ground graphite particles

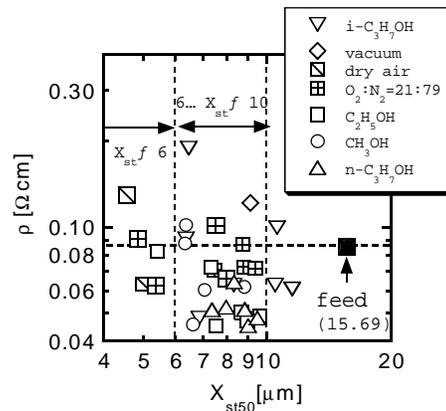
Figure 2 shows the changes of specific resistance of the film ρ , as a function of grinding. In the figure, the specific resistance of the feed particles is also shown as a reference. The specific resistance of products ground in vacuum increased monotonously with the grinding time. The other products had a minimum value for the specific resistance, although the grinding time which gave the minimum value, depended on the grinding atmosphere. As previously reported by the author's group [2], the ground products tend to have high specific resistance. Therefore, the results are un expected in that the product ground in alcoholic vapors present approximately half the specific resistance of the feed particles.

Figure 3 (a) shows the relationship between the specific electrical resistance ρ , of the film and the 50 wt% Stokes diameter X_{st50} of the ground particles. In the figure, the specific resistance of the feed particles is also shown as a reference. Although the values of specific resistance of the films were rather scattered, the figure shows that the specific resistances of products ground in alcoholic vapor, of which the sizes ranged from 6 to 10 μm , are lower than the products ground in dry atmospheres such as dry air, the gas mixture of 1 % O_2 and 99 % N_2 , and vacuum. Higher specific resistance was obtained for products ground for 24 h or longer. This was probably caused by the long time grinding which destroyed the crystalline nature of the particles [11,12].

Figure 3 (b) shows the relationship between the specific electrical resistance ρ , of the film and the 50 wt% laser diffraction diameter X_{dif50} of the ground particles. In the figure, the specific resistance of the feed particles is also shown as a reference. The figure shows that the specific resistance increases with the decreasing laser diffraction



diameter of the ground particles. This result is probably due to the reduction in the size of the a multiplication of the number of the contact points between the particles in

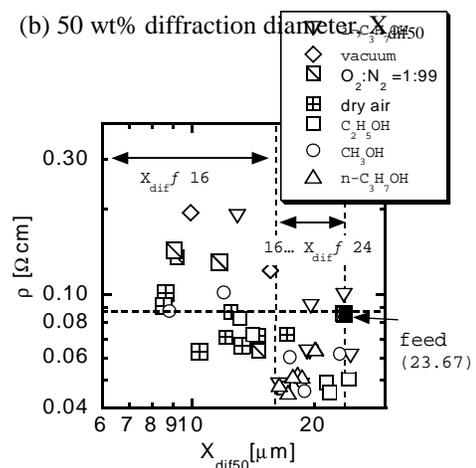


(a) 50 wt% Stokes diameter, X_{st50}

the films, increasing the resistance at the boundary of particles' contact. Furthermore, as mentioned in the discussion in Fig. 3(a), the crystalline nature of the

Figure 2 Changes in the specific resistance ρ , of films made of ground particles as a function of grinding time.

Figure 3 Relationship between the specific electrical resistance ρ , of the films and the 50 wt% diameter of the ground particles.



particles ground for a long time in order to obtain a smaller size was substantially destroyed as the grinding time increased.

The specific resistances of the products ground in alcoholic vapors, which ranged from 16 to 25 μm in size, are clearly lower than those of feed particles and products ground in dry atmospheres.

Figure 4 shows the relationship between the specific resistance of the film ρ , and the particle size ratio $X_{\text{dif}50}/X_{\text{st}50}$. The values of ρ decrease with an increase in the particle size ratio $X_{\text{dif}50}/X_{\text{st}50}$, although the correlation was not strong. This result shows that the graphite film composed of particles with greater flakiness has a higher electrical conductivity, and is similar to the results obtained for dry atmosphere grinding previously reported [2].

Figure 5 (a) shows typical microscopic images of products ground for 8 h in $n\text{-C}_3\text{H}_7\text{OH}$, as an example of particles with a lower specific resistance than the feed particles. **Figure 5 (b)** shows typical microscopic images of products ground for 2 h in vacuum, as an example of particles with a higher specific resistance than the feed particles. The particle sizes are similar to products ground for 8 h in $n\text{-C}_3\text{H}_7\text{OH}$. Figs 5 (a) and (b) show that the photo images of products ground in $n\text{-C}_3\text{H}_7\text{OH}$ are larger than the products ground in vacuum, although these particles have approximately the same Stokes diameter, i.e., the same sedimentation velocity. Especially, in the case of products ground for 8 h in $n\text{-C}_3\text{H}_7\text{OH}$, the particle size in the figure is apparently much larger than the 50 wt% Stokes diameter $X_{\text{st}50}$ ($7.35 \mu\text{m}$) and 50 wt% laser diffraction diameter $X_{\text{dif}50}$, ($18.6 \mu\text{m}$) measured. This observation can be qualitatively explained as follows: First, the products ground in alcoholic vapor agglomerate easily. Second, taking into account that the products ground in alcoholic vapors have a greater particle size ratio $X_{\text{dif}50}/X_{\text{st}50}$, than the products ground in vacuum, the former has a greater flakiness than the latter. Therefore, their flat surfaces tend to orient stably in a horizontal direction on the sampling plate for microscopic observation, even when we attempted to disperse them randomly over the plate.

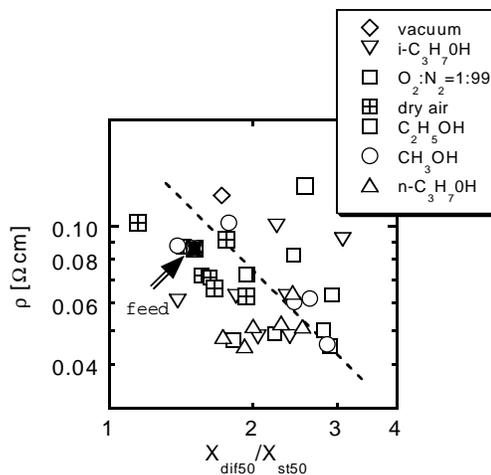
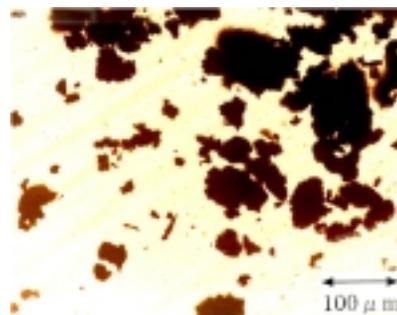
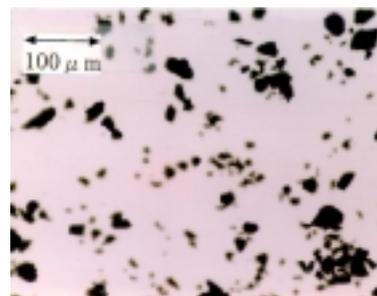


Figure 4 Relationship between the specific resistance ρ , of the film made of ground particles and the ratio between the 50 wt% diffraction diameter and the 50 wt% Stokes diameter, $X_{\text{dif}50}/X_{\text{st}50}$.



(a) ground for 8 h in $n\text{-C}_3\text{H}_7\text{OH}$
 $(X_{\text{st}50}=18.6 \mu\text{m}, X_{\text{dif}50}=7.35 \mu\text{m},$
 $X_{\text{dif}50}/X_{\text{st}50}=2.54, \rho=0.0515 \Omega\text{cm})$



(b) ground for 2 h in vacuum
 $(X_{\text{st}50}=14.6 \mu\text{m}, X_{\text{dif}50}=9.11 \mu\text{m},$
 $X_{\text{dif}50}/X_{\text{st}50}=1.72, \rho=0.122 \Omega\text{cm})$

Figure 5 Typical micrograph images.

Charge-discharge performance of negative electrode for lithium ion battery

Since 20 grams of graphite particles are required to investigate charge and discharge performance of negative electrode for home-made lithium ion coin-type cells, we subsequently ground 20 grams of natural graphite particles (method II). Nevertheless five grams of natural graphite particles were ground in all the cases described in Figs. 1-4.

Figure 6 (a) and (b) show the relationship between the discharge capacity of lithium ion coin cell made from the ground graphite particles and their laser diffraction diameter X_{dif50} , and their BET specific surface area, respectively. In both figures, data are shown for feeds, products ground in vacuum for 8 h, products ground in dry air for 8 h and 24 h, and products ground in $n\text{-C}_3\text{H}_7\text{OH}$ for 8 h and 24 h. For the case of the products ground for 24 h in vacuum, the coin-type cells could not be assembled due to a lack of adhesion of the electrode film to a copper foil. Since we performed the grinding in different atmosphere, the size, the particle shape, the surface condition, and the distortion of crystal structure of the ground products also changed upon grinding in different atmosphere, which did not allow us to estimate separately the effects of the size or the specific surface area on the discharge capacity. Both figures show, however, that the discharge capacity has a maximum value at a given X_{dif50} or a BET surface area. Therefore, it is considered that a suitable size or a suitable specific surface area exist for use as raw materials for negative electrode of the lithium ion batteries.

Figure 7 shows the relationship between the specific resistance of films composed of the ground graphite particles, and the discharge capacity. The figure shows that the discharge capacity also has a maximum value at a given specific resistance. However, as mentioned before, not only the specific resistance, but also the other characteristics of ground particles varied simultaneously by grinding in different atmosphere. Therefore, we should carefully investigate the relationship between the discharge capacity and the specific resistance.

(a)

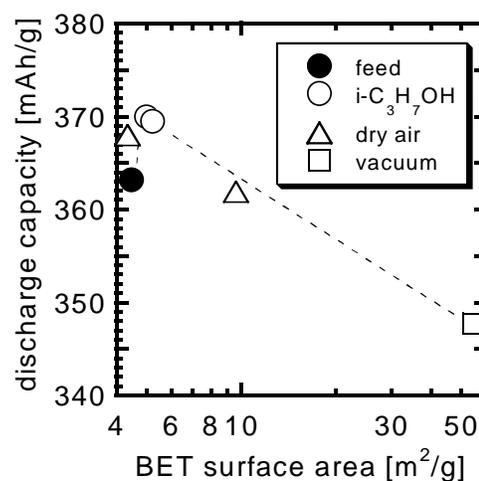
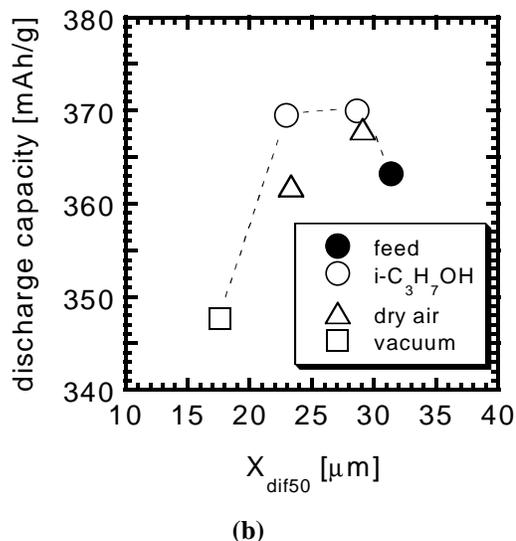


Figure 6 Relationship between the discharge capacity of the negative electrode for lithium ion coin-type cells made from the ground graphite particles and (a) the laser diffraction diameter X_{dif50} , and (b) the BET specific surface area.

Conclusions

Highly crystalline natural graphite particles were systematically ground with a ball mill under various well-controlled alcoholic vapors. Then, the size, the flakiness, the electrical conductivity of films made of the ground products, and the discharge capacity of negative electrode for lithium ion coin-type cells were experimentally evaluated, and the following results were obtained.

- (1) The products ground in alcoholic vapors have approximately half the specific resistance of the feed particles.
- (2) The graphite films composed of particles with a greater flakiness, and ground in alcoholic vapor display a higher electrical conductivity.
- (3) Since the discharge capacity has a maximum value at a given X_{dif50} or a BET surface area, a suitable size or a suitable specific surface area of the particles exist for use as raw materials for the negative electrode of lithium ion batteries.

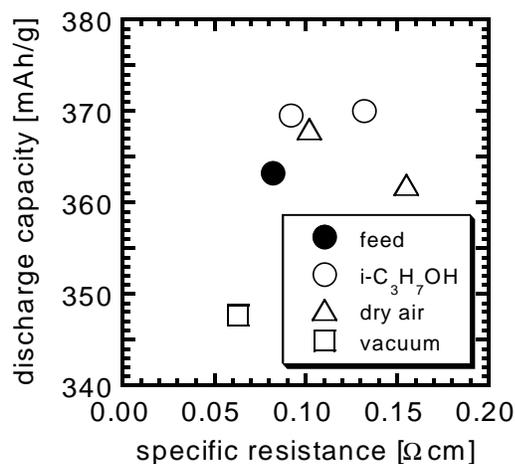


Figure 7 Relationship between the specific resistance of films composed of the ground graphite particles and the discharge capacity.

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