



Short communication

## Effect of cathode active materials produced by a wet-type jet mill on lithium cell performance

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## ABSTRACT

We prepared slurries by dispersing  $\text{LiMn}_2\text{O}_4$  and  $\text{LiCoO}_2$  into toluene or  $\text{NaPO}_3$  aqueous solution. The slurries were then milled with a high-pressure wet-type jet mill to form fine particles. In estimating the performance of Li cells containing the materials, we found that the cell capacity improved with a decrease in the materials' particle size. Maximum cell capacity was obtained using materials produced by milling  $\text{NaPO}_3$  slurry to reduce the particle diameter to 2–3  $\mu\text{m}$ . Such the maximum value was disappeared by treating the materials with toluene. The treatment, however, did not provide remarkable increase in the cell capacity. We found that the cell cycle life tended to increase with a decrease in the mean diameter of the material particles.

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### 1. Introduction

Lithium-ion batteries have long been considered one of the most promising candidates for next-generation automotive and industrial batteries. Accordingly, intensive efforts have been made to increase or improve such factors as their capacity, rate capability, lifetime, and safety. Towards this end,  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  has been studied as a cathode active material due to its high capacity and low cost [1]. Recently, olivine-type lithium iron phosphate has also come to be considered a promising material because of its advantage of low cost, thermal stability and excellent cycleability [2–5]. The use of cathode active material/carbon composite systems has also been studied as a means of prolonging cell cycle life [6,7].

One effective way to increase cell capacity and improve rate capability is to increase the cathode reaction area by finely milling the cathode active materials. Fine particles, however, diminish the pore sizes of cathode sheets and inhibit the supply of electrolyte into the pores.

The authors have used a high-pressure wet-type jet mill to fabricate fine powder with optimum distribution as a means of improving cell capacity and rate capability. This paper describes the effect of the powder treatment on cell performance.

### 2. Experimental

#### 2.1. Cathode active material preparation

Three types of slurries were prepared by dispersing  $\text{LiCoO}_2$  (Nippon Chemical Industrial Co., Mean diameter: 10  $\mu\text{m}$ ) or  $\text{LiMn}_2\text{O}_4$  (Yunan Yuxi Heolo Technology Co., Mean diameter: 10  $\mu\text{m}$ ) into toluene or 2 wt%  $\text{NaPO}_3$  aqueous and rotating the mixture overnight.

*Slurry A:* 100 g of  $\text{LiCoO}_2$  in 500 ml of toluene.

*Slurry B:* 100 g of  $\text{LiCoO}_2$  in 400 ml of 2 wt%  $\text{NaPO}_3$  aqueous solution.

*Slurry C:* 100 g of  $\text{LiMn}_2\text{O}_4$  in 400 ml of 2 wt%  $\text{NaPO}_3$  aqueous solution.

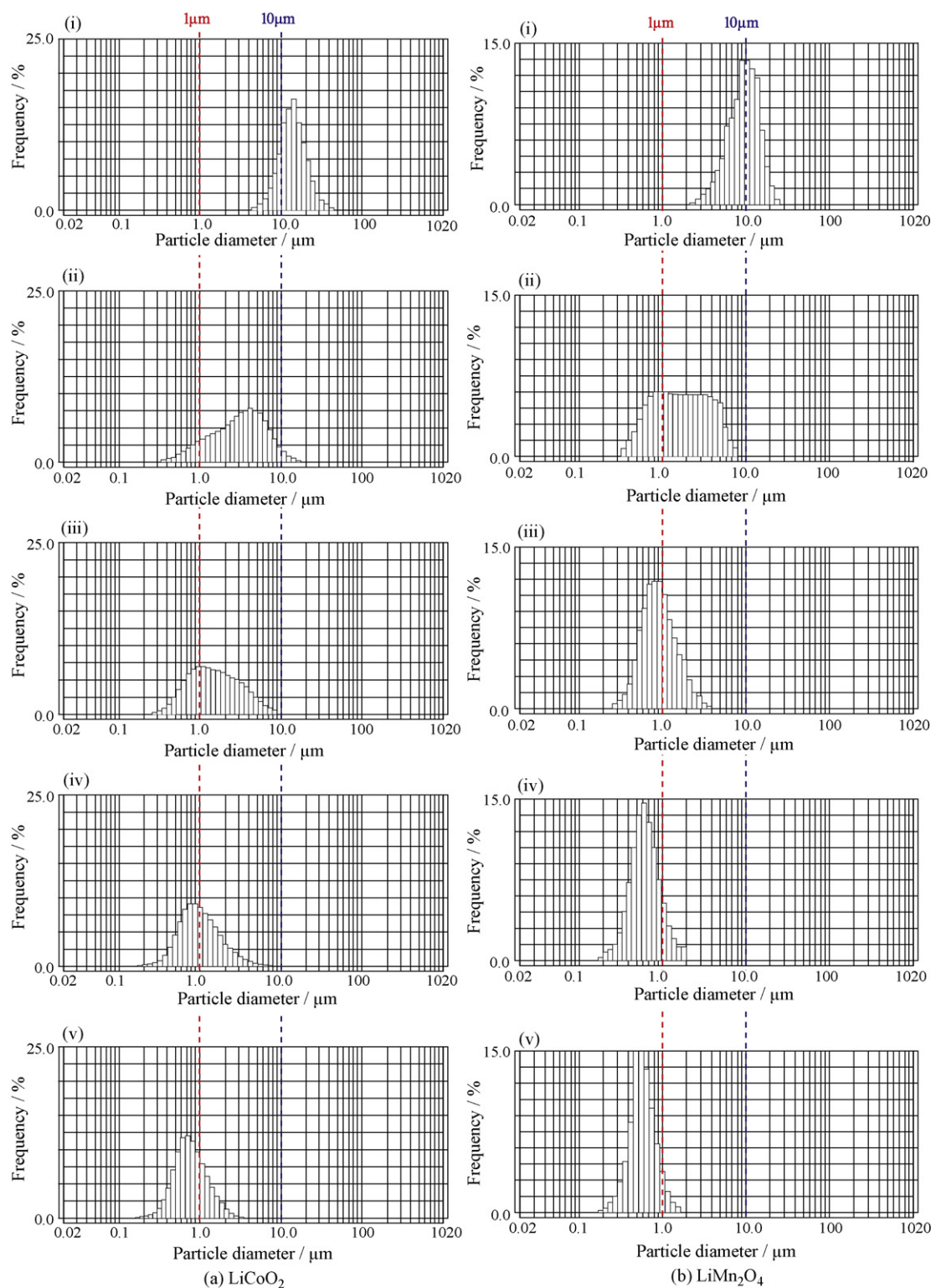
The slurries were subjected to ultrasonic vibration for three minutes before milling. In the milling process, opposing slurry jets were made to collide by spurting them from two opposite nozzles 5, 10, 15, or 20 times under pressure of 100, 200, or 245 MPa with a high-pressure wet-type jet mill (Sugino Machine Ltd.). Milled powder was then obtained by filtering the resultant slurries and drying them overnight under vacuum at 80 °C.

#### 2.2. Toluene treatment

We dispersed 7 g of  $\text{LiCoO}_2$  obtained from Slurry B into 35 ml of toluene. The mixture was stirred for 10 min and then subjected to

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**Fig. 1.** Particle distribution of the materials produced with the wet-type jet mill. (i) As received, (ii) 5 collisions, (iii) 10 collisions, (iv) 15 collisions, and (v) 20 collisions. (a)  $\text{LiCoO}_2$  and (b)  $\text{LiMn}_2\text{O}_4$ .

ultrasonic vibration for 3 min. The powder was obtained by filtering the mixture and drying it overnight under vacuum at  $80^\circ\text{C}$ .

### 2.3. Electrochemical measurements

For each of the resultant powder, we fabricated a  $1.33\text{ cm}^2$  cathode disk by using an automatic agate motor to produce a mixing

comprising the powder (70 wt%), acetylene black (25 wt%), and PTFE powder (5 wt%), followed by rolling the mixture. We then fabricated a coin-type cell with the cathode, Li anode (Honjo Metal Co., Disk area:  $1.13\text{ cm}^2$ ) and 1 M  $\text{LiPF}_6$ -ethylene carbonate/dimethyl carbonate (1/1 of volume ratio) (Tomiyama Pure Chemical Industrial Ltd.). We estimate the initial cell characteristics by charging at  $0.75\text{ mA cm}^{-2}$  to 4.3 V and discharging at  $0.75\text{ mA cm}^{-2}$  to 3.0 V

twice, with 10-min breaks, at 21 °C. When we estimate the rate capability, we measured the capacities by discharging the cells at 12.0 mA cm<sup>-2</sup> first and then by discharging at current density steadily decreased, with 10-min breaks in-between, after the third charging at 0.75 mA cm<sup>-2</sup>. For estimating the cycling performance, the cells were cycled at the charge and discharge current density of 0.75 mA cm<sup>-2</sup>.

### 3. Results and discussion

#### 3.1. Milled powder

The particle size of the milled LiCoO<sub>2</sub> and LiMn<sub>2</sub>O<sub>4</sub> powder decreased with the number of collisions. The mean diameter became less than 1 μm after 20 millings, as shown in Fig. 1. The LiMn<sub>2</sub>O<sub>4</sub> particles were milled smaller than those of LiCoO<sub>2</sub>; the mean diameter for the former being 0.60 μm and that for the latter being 0.91 μm after 20 millings at 245 MPa.

#### 3.2. Discharge efficiency

Fig. 2 shows dependence of the ratio of the second discharge capacity (Cd) to the second charge capacity (Cc) on particle size of LiCoO<sub>2</sub> and LiMn<sub>2</sub>O<sub>4</sub>. The ratio decreases with decrease in the particle size of LiCoO<sub>2</sub> and LiMn<sub>2</sub>O<sub>4</sub> although the change for LiMn<sub>2</sub>O<sub>4</sub> is smaller than that for LiCoO<sub>2</sub>. This suggests that an increase in specific surface area affects discharge efficiency. Further investigation will be needed to clarify this.

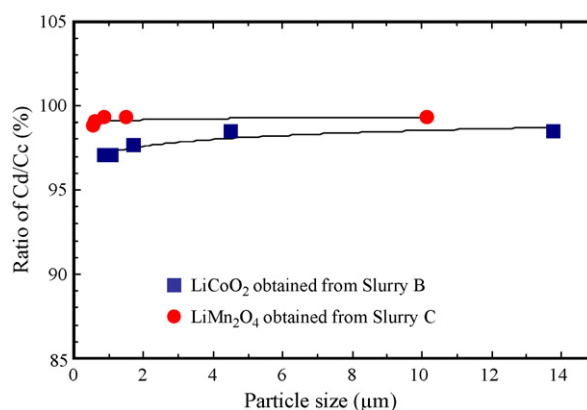


Fig. 2. Dependence of the ratio of Cd/Cc on the particle size of LiCoO<sub>2</sub> and LiMn<sub>2</sub>O<sub>4</sub> obtained from Slurries B and C.

#### 3.3. Rate capability

Relationships between the specific capacity and particle size of the cathode active materials are shown in Fig. 2(a) and (b) for LiCoO<sub>2</sub> and LiMn<sub>2</sub>O<sub>4</sub> obtained from Slurries B and C, and shown in Fig. 2(c) for LiCoO<sub>2</sub> obtained from Slurry A. Fig. 2(a) and (b) show that, at discharge current density of larger than 5 mA cm<sup>-2</sup>, the specific capacity for LiCoO<sub>2</sub> and LiMn<sub>2</sub>O<sub>4</sub> obtained from Slurries B and C increased as the particle size was reduced until it reached a maximum at mean particle diameter of around 2–3 μm and then decreased thereafter. On the other hand, Fig. 2(c) shows that, at discharge current density of 12 mA cm<sup>-2</sup>, the specific capacity

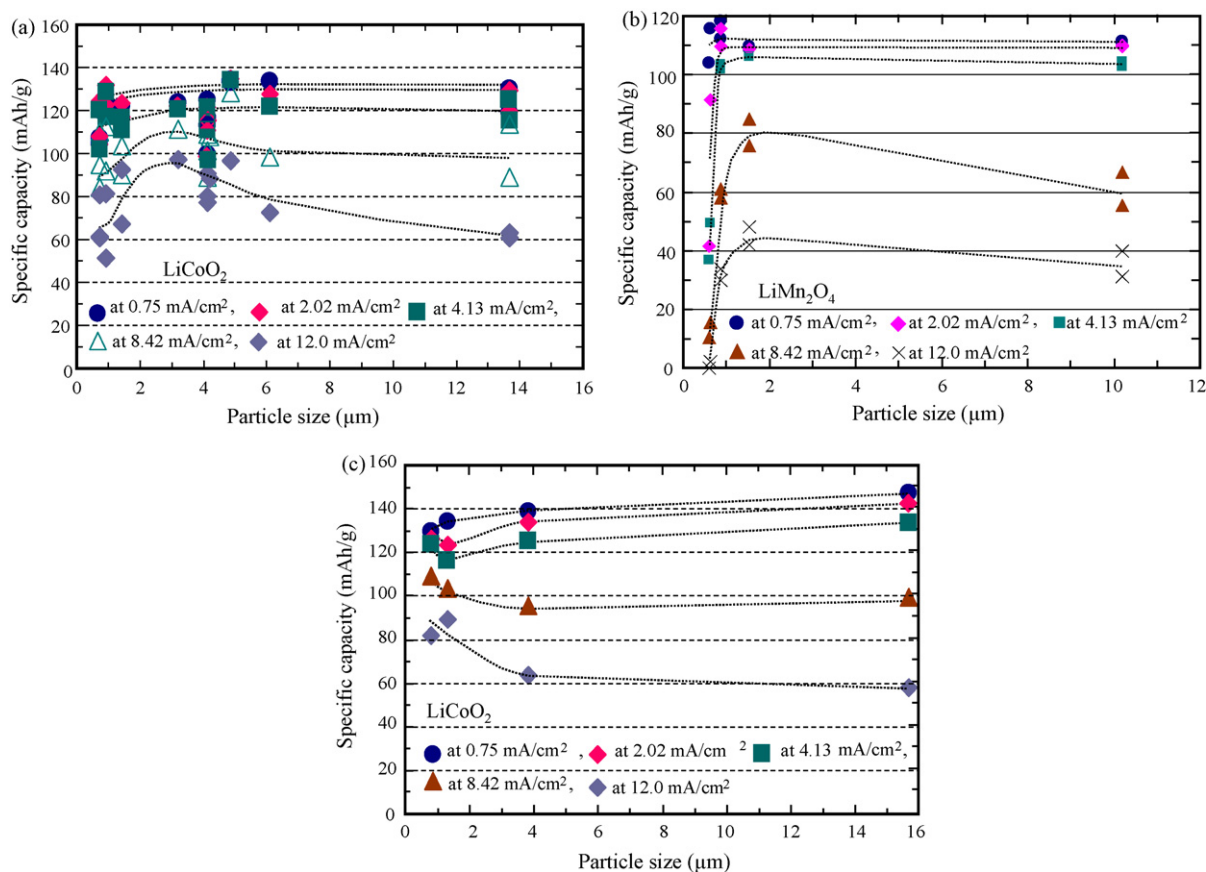


Fig. 3. Dependence of specific capacity on particle size of cathode active materials produced with a wet-type jet mill. (a) LiCoO<sub>2</sub> in 2 wt% NaPO<sub>3</sub>/H<sub>2</sub>O at 245 MPa. (b) LiMn<sub>2</sub>O<sub>4</sub> in 2 wt% NaPO<sub>3</sub>/H<sub>2</sub>O at 245 MPa. (c) LiCoO<sub>2</sub> in toluene at 200 MPa.



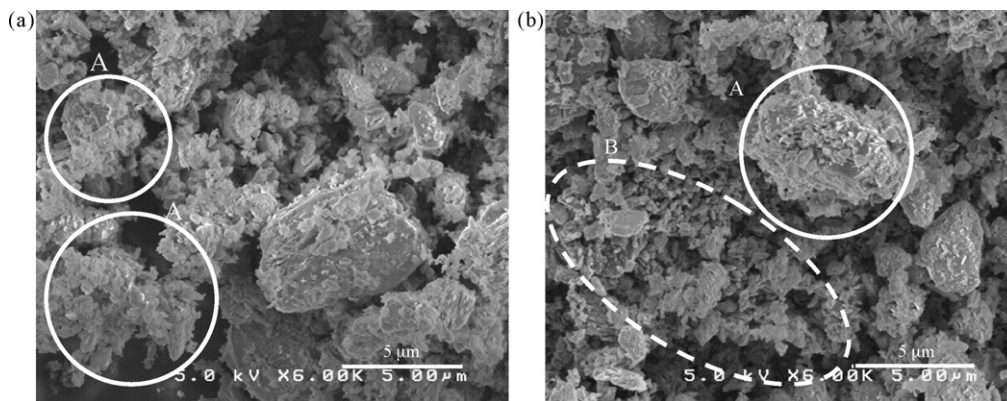


Fig. 4. SEM photos of LiCoO<sub>2</sub> milled with 15 slurry jet collisions. (a) From Slurry A at 200 MPa. (b) From Slurry B at 245 MPa.

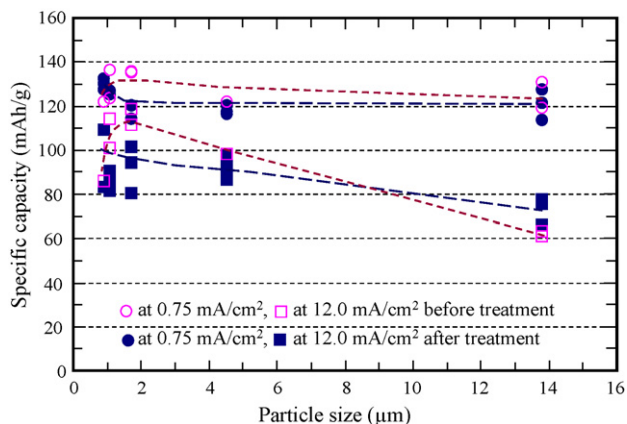


Fig. 5. Dependence of specific capacity on particle size of LiCoO<sub>2</sub> treated with toluene. Open symbols indicate pre-treatment LiCoO<sub>2</sub> capacities, and closed symbols indicate post-treatment capacities.

for LiCoO<sub>2</sub> obtained from Slurry A increased as the particle size decreased throughout the particle size range used in this study.

#### 3.4. Particle distribution

Fig. 3 shows SEM photos of LiCoO<sub>2</sub> particles obtained from Slurries A and B through use of the wet-type jet mill. They suggest that the powder distribution conditions affected the rate capability of

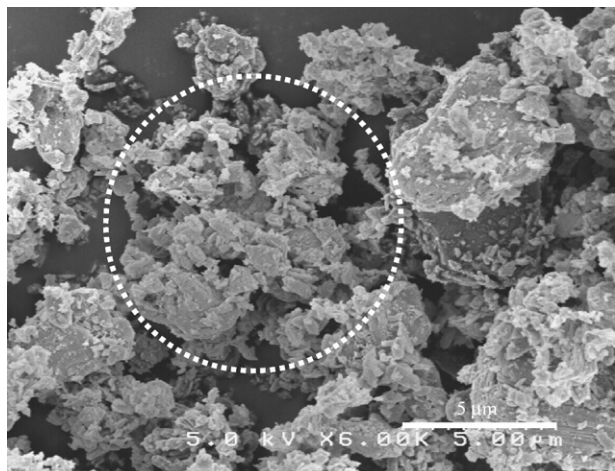


Fig. 6. SEM photos of LiCoO<sub>2</sub> obtained from Slurry B and after treatment with toluene.

the cells. Both photos indicate that smaller particles were dispersed on the surface of larger particles for the materials obtained from all the slurries (Circle A in the figures); the distribution can produce an electrode with a large reaction area and pore diameter large enough to enable electrolyte to be supplied to the pores. In Fig. 3(b), it can also be seen that smaller particles agglomerate in the powder obtained from Slurry B (Circle B). This agglomeration may produce an electrode with smaller pores that inhibit the electrolyte supply if the electrode is fabricated from a powder with particle diameter of less than 2 μm.

#### 3.5. Effect of treatment with poor dispersant on cell capacity

Our belief is that the smaller particles were well dispersed in the NaPO<sub>3</sub> solution, which is a good dispersant, and they agglom-

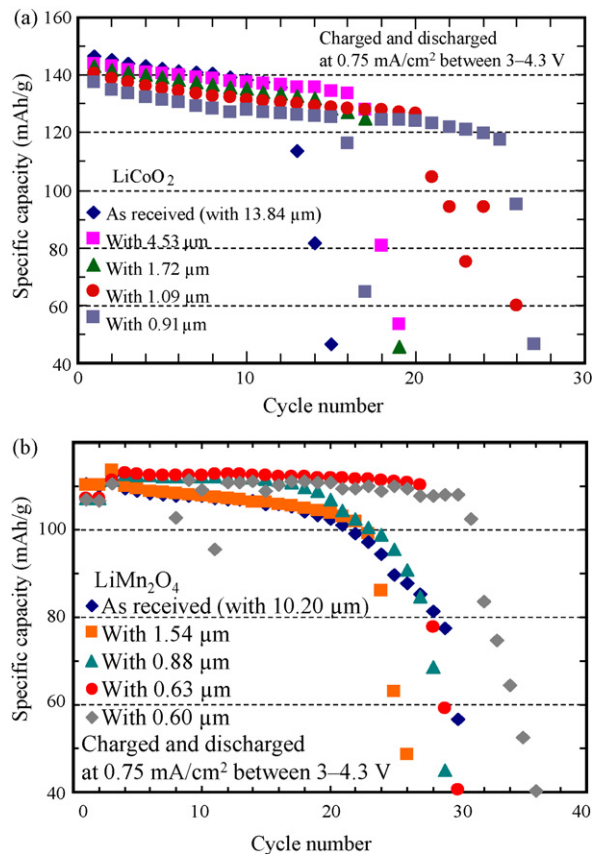


Fig. 7. Change in capacity with cycle number. (a) Cells with LiCoO<sub>2</sub> obtained from Slurry B. (b) Cells with LiMn<sub>2</sub>O<sub>4</sub> obtained from Slurry C.

erated when the mixture was filtered. To solve the problem of the smaller particle agglomeration, we tried to treat the  $\text{LiCoO}_2$  powder obtained from Slurry B by dispersing into toluene, a poor dispersant, and then collecting the powder by filtering and drying the mixture.

Fig. 4 shows relationship between the specific capacity and particle size of  $\text{LiCoO}_2$  after treatment with toluene. The specific capacity increased as the  $\text{LiCoO}_2$  particle size decreased throughout the particle size range used. The treatment, however, did not provide any notable increase in current cell capacity levels. Fig. 5 shows SEM photo of  $\text{LiCoO}_2$  particles after treatment. The circle in the figure shows the agglomeration of the larger particles on the surface of which smaller ones were distributed, which suggests a reason as to why the expected increase in cell capacity was inhibited.

### 3.6. Cycling properties

Fig. 6(a) and (b) shows changes in specific capacity with cycle number for the cells containing  $\text{LiCoO}_2$  and  $\text{LiMn}_2\text{O}_4$  obtained from Slurries B and C after charging at  $0.75 \text{ mA cm}^{-2}$  to 4.3 V and discharging at  $0.75 \text{ mA cm}^{-2}$  to 3.0 V with 10-min intervals. For both of these cathode active materials, the cells having smaller particle sizes tended to have longer cycle lives.

## 4. Conclusion

We fabricated fine particles of  $\text{LiCoO}_2$  and  $\text{LiMn}_2\text{O}_4$  powder by using a high-pressure wet-type jet mill to mill slurries obtained by dispersing these materials into toluene and  $\text{NaPO}_3$  aqueous solution (Fig. 7). We then estimated the performance of the cells fabricated using these particles. The results we obtained are summarized as follows:

- (1) The wet-type jet mill produced submicron powder of  $\text{LiCoO}_2$  and  $\text{LiMn}_2\text{O}_4$  with mean diameter less than  $1 \mu\text{m}$ .
- (2) At discharge current larger than  $5 \text{ mA cm}^{-2}$ , the specific capacity of the cells fabricated using the powder as cathode active material as the mean particle diameter was decreased until

it dropped to  $3 \mu\text{m}$ . The specific capacity, however, decreased when the mean diameter was decreased to less than  $2 \mu\text{m}$ .

- (3) SEM measurements showed that smaller particles were dispersed on the surface of larger particles; which can produce a cathode having a large reaction area and pores large enough to receive supplied electrolyte. It also showed that smaller particles agglomerated, which resulted in a specific capacity that reached a maximum at a mean diameter of  $2\text{--}3 \mu\text{m}$ .
- (4) To solve smaller particle agglomeration, the  $\text{LiCoO}_2$  powder was dispersed into toluene and collected by filtering the mixture. The maximum in the capacities depending on the particle size was disappeared by treating the materials with toluene. The treatment, however, did not provide remarkable increase in the cell capacity.
- (5) The cycle life of the cells tended to increase with a decrease in the mean diameter of the cathode active materials.

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