

Effect of nano-size LiCoO_2 cathode powders on Li-ion cells

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Abstract

Lithium ion batteries are widely used in many portable devices; however, their power density is not sufficient for use in electric vehicles. One of the most effective methods to improve the power density is the use of very fine cathode particles. We investigated a new excess lithium method of preparing nano-sized LiCoO_2 powders. To begin with, lithium acetate and cobalt acetate are mixed by the molar ratio 9, 13 or 21 to 1, uniformly. The mixture is then calcined at 600°C for 6 h. Finally, obtained powders are washed with a large amount of water to remove impurity and then dried. Using this method, we obtained nano-sized spherical LiCoO_2 particles with a diameter of about 25 nm or needlelike LiCoO_2 particles with a diameter of about 5 nm and a length of about 60 nm. The discharge capacity of a $\text{Li}/5\ \mu\text{m}$ LiCoO_2 cell is $51\ \text{mAh g}^{-1}$, but when the nano-sized LiCoO_2 was used, the capacity increased to about $100\ \text{mAh g}^{-1}$ at the same cycling condition.

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1. Introduction

The technology for making materials into nano-sized particles has been studied energetically in recent years. Nano-technology has been used to improve remarkably the performance of nano-sized materials or allowed new characteristics of the materials to be discovered. Nano-technology can be applied to lithium ion batteries, too. Li et al. [1] reported that nanostructured Sn-based electrodes showed improved rate capabilities relative to thin-film control electrodes prepared from the same material. On the other hand, Larcher et al. [2] produced nano-sized $\alpha\text{-Fe}_2\text{O}_3$ and reported that the discharge potential of the nanostructured $\alpha\text{-Fe}_2\text{O}_3$ became higher than that of microstructured $\alpha\text{-Fe}_2\text{O}_3$.

The reason for making cathode materials of lithium ion batteries from fine particles is to achieve high-powered output. Lithium ion batteries are used as a power source for portable electric devices all over the world for their high

power density and high discharge voltage, but they are seldom used as a power source for large electric equipment, for instance, hybrid electric vehicles (HEVs) or electric vehicles (EVs) because of safety problems and power output limitations. The power output of lithium batteries is smaller than those of lead-acid batteries and nickel–hydrogen batteries, which are used as the power source in EVs or the power source in HEVs. Finer particles of cathode materials are desirable for high power output by lithium batteries, because of the larger surface area of the cathode.

Researchers have investigated some of the techniques used to make LiCoO_2 that are generally used for cathode material of lithium ion batteries for making nano-sized particles. Kumta et al. [3] mixed equimolar amounts of $\text{LiCH}_3\text{COO}\cdot 2\text{H}_2\text{O}$ and $\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ in water, and after heat treatment at 400°C they obtained fine LiCoO_2 particles in the range of about 70 nm. However, this LiCoO_2 was the low-temperature polymorph of LiCoO_2 that is known to exhibit poor electrochemical behavior [4]. Sol–gel methods have also been tried. Peng et al. [5] mixed LiCH_3COO and $\text{Co}(\text{CH}_3\text{COO})_2$ (Co/Li = 1:1 atom ratio) with citric acid in

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ethylene glycol solution and heated the mixture at 140 °C to form a gel. They obtained about 30 nm of LiCoO₂ particles by calcining the gel at 750 °C. Yoon et al. [6] dissolved a stoichiometric amount of Li and Co acetate salts in distilled water and mixed them with an aqueous solution of acrylic acid, and they obtained a clear viscous gel by heating the mixture at 70–80 °C for several hours. The precursor was calcined at 600–700 °C. Finally, they obtained about 300 nm of LiCoO₂ particles. There are other techniques, for example, a spray drying method [7], a coprecipitation method [8] and a hydrothermal method [9], resulting in LiCoO₂ particles of 200–700 nm, 20–100 nm and 70–200 nm, respectively.

We focused on the report of Arai et al. [10], who used the excess lithium method to synthesize LiNiO₂. However, their purpose was to obtain pure LiNiO₂, and they did not pay any attention to the rate capability of the fine LiNiO₂. In this paper, we report a new method of synthesizing nano-sized LiCoO₂ particles using a method similar to that of Arai et al. We also investigated the electrochemical properties of these nano-sized LiCoO₂ powders were investigated.

2. Experimental

LiCH₃COO·2H₂O (Wako Pure Chemical Industries Ltd.) and Co(CH₃COO)₂·4H₂O (Wako Pure Chemical Industries Ltd.), with molar ratios of 5:1, 9:1, 13:1 and 21:1, were dis-

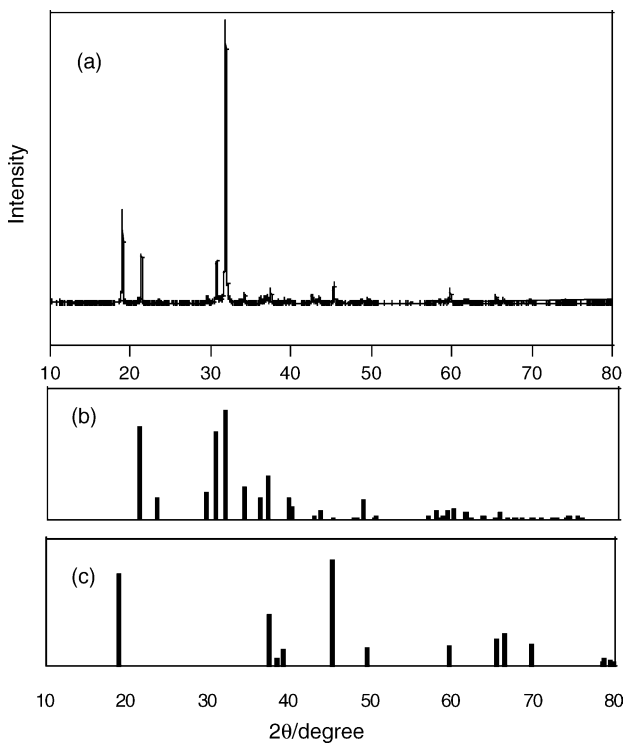


Fig. 1. XRD pattern of powders obtained by calcining, at 800 °C for 6 h, the mixture of a large amount of LiCH₃COO·2H₂O and a small quantity of Co(CH₃COO)₂·4H₂O at molar ratios of 5:1 (a) and XRD patterns of LiCoO₂, (b) Li₂CO₃ and (c) as references.

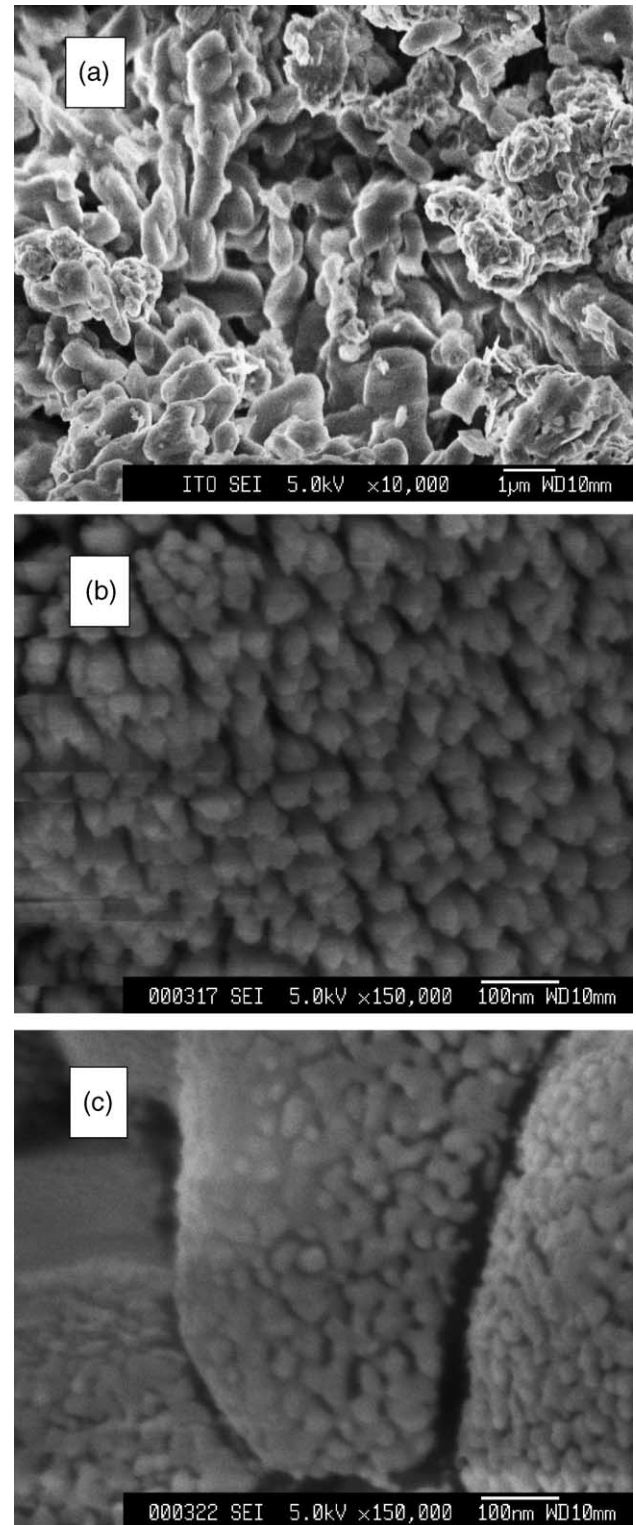


Fig. 2. SEM images of products obtained by calcining, at 600 °C for 6 h, the mixture of a large amount of LiCH₃COO·2H₂O and a small quantity of Co(CH₃COO)₂·4H₂O at molar ratios of 5:1 (a), 9:1 (b) and 13:1 (c) (products before washing with water).

solved in deionized water, and the solution was heated at 230 °C under stirring and then dried to form a mixed precursor in atmosphere. The dried product obtained was then heat treated in a furnace using an alumina crucible at 600 °C for 6 h. After heat treatment, a gray lump with a sponge-like structure was obtained. This product was washed with a large amount of water by using a centrifugal separator (5200, KUBOTA) to separate Li_2CO_3 and LiCoO_2 after grinding the gray product in an agate mortar. After washing, the black powder obtained was dried in an incubator at 80 °C for 12 h in atmosphere. After that, the product was ground again, and fine powders were obtained. The gray products and the black powders were analyzed for their structure using X-ray diffraction (RINT2100HLR/PC, Rigaku). The morphology and microstructure of the powders were examined using a scanning electron microscope (JSM-6340F, JEOL).

The electrochemical properties of LiCoO_2 powders were investigated using a $\text{Li}/1\text{M LiPF}_6 \text{ EC}$ (ethylene carbonate) + DMC (dimethyl carbonate) (1:1 in vol.)/ LiCoO_2 cell. The composite cathode was prepared by mixing the LiCoO_2

powder, acetylene black and polyvinylidene fluoride (PVDF) at a weight ratio of 90:5:5 in *n*-methylpyrrolidinone (NMP) and then coating the resultant paste on an Al foil. The coated cathode sheet was dried, pressed and cut into samples 15 mm in diameter. Celgard® 3501 (Celanese Co.) was used as a separator. The cell elements were fabricated into coin-type cells (20 mm in diameter, 3.2 mm thick) in a dry box filled with Ar gas. The cells were cycled using a cell cycler (HJSM6, HOKUTO DENKO Co.) at a constant current density of 12 or 24 mA cm^{-2} between 4.2 and 2.6 V at 25 °C.

3. Results and discussion

3.1. Morphology of the particles

At first, we mixed $\text{LiCH}_3\text{COO}\cdot 2\text{H}_2\text{O}$ and $\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ at a molar ratio of 5:1 and calcined the mixture at 800 °C for 6 h. Fig. 1 shows the XRD pattern of the resulting substance, and the pattern indicates the formation of LiCoO_2

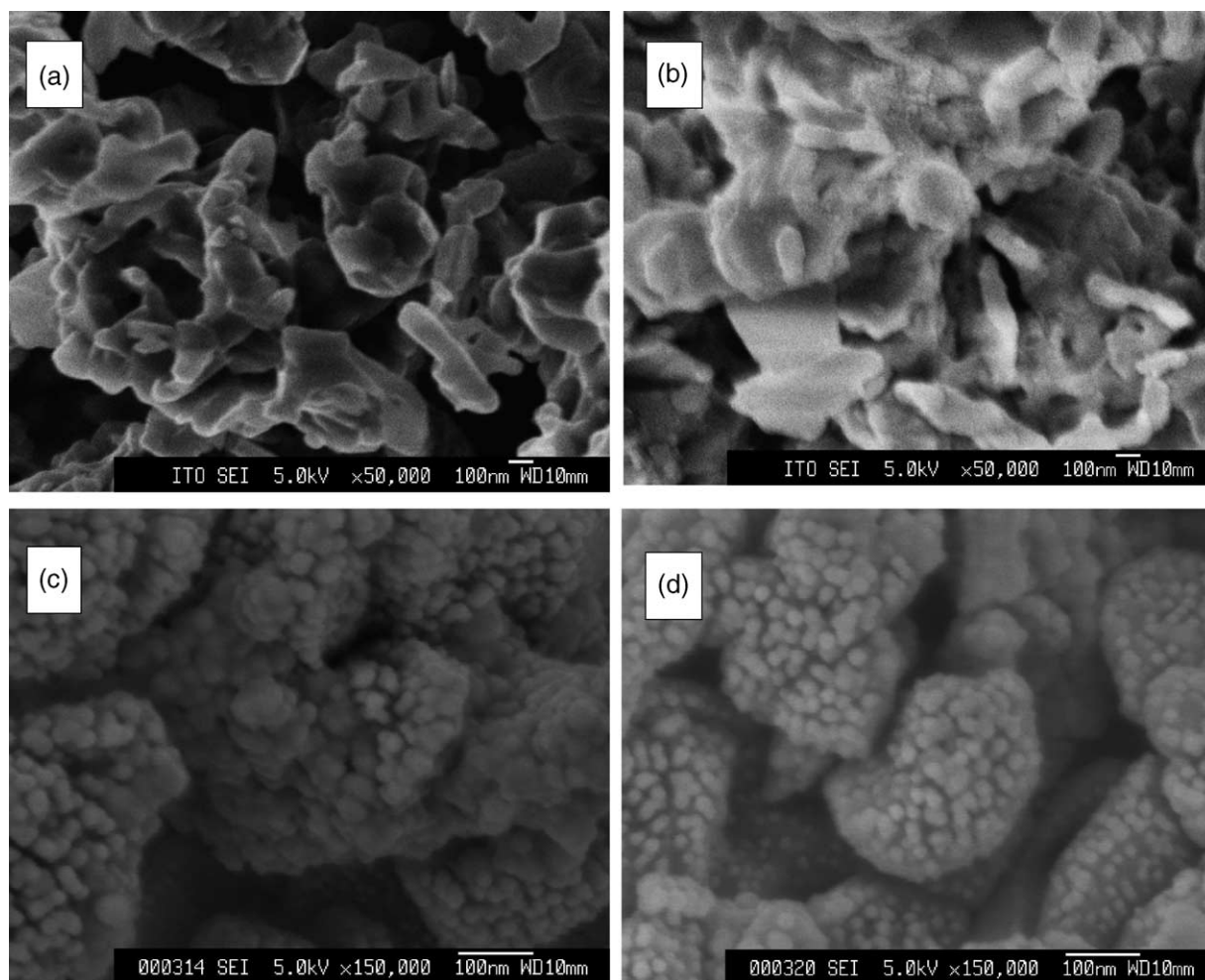


Fig. 3. SEM images of LiCoO_2 powders obtained by calcining, at 600 °C for 6 h, the mixture of $\text{LiCH}_3\text{COO}\cdot 2\text{H}_2\text{O}$ and $\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ at a molar ratio of 1:1 (a), and of LiCoO_2 obtained by washing the products obtained by calcining, at 600 °C for 6 h, the mixture of a large amount of $\text{LiCH}_3\text{COO}\cdot 2\text{H}_2\text{O}$ and a small quantity of $\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ at molar ratios of 5:1 (b), 9:1 (c) and 13:1 (d) (products after washing with water).

belonging to the space group $R\bar{3}m$ and Li_2CO_3 . Calcining above the melting point of lithium carbonate (618°C), lithium carbonate melted and LiCoO_2 sedimented under a white crystal of lithium carbonate. Therefore, the mixture was not mixed uniformly at 800°C . After this experiment, in subsequent experiments, we decided to calcine at 600°C , which was below the melting point of lithium carbonate, to prevent separation of the LiCoO_2 phase and Li_2CO_3 phase.

Fig. 2a–c are SEM images of powders made by heat treatment of mixtures of lithium acetate hydrate and cobalt acetate hydrate whose molar ratios are 5:1, 9:1 and 13:1 respectively. Those samples were heat treated but not washed with water; therefore, those products included an impurity of Li_2CO_3 . XRD patterns of all three samples indicated the formation of LiCoO_2 and Li_2CO_3 , as shown in Fig. 1.

Next, the three samples were washed with a large amount of water and dried well. In XRD patterns of all products after washing, only LiCoO_2 could be seen and no other impurity could be observed. In order to compare LiCoO_2 powders made by using the excess lithium method with LiCoO_2 powders synthesized by using the normal method, we took SEM micrographs of LiCoO_2 obtained by calcinations, at 600°C for 6 h, of a mixture of equimolar amounts of corresponding acetate salts, lithium acetate and cobalt acetate as shown in Fig. 3a. The particle form was not uniform, and particles were about 500 nm or larger. Fig. 3b is a SEM image of the LiCoO_2 powders obtained from the sample (Li:Co = 5:1 atom ratio) shown in Fig. 2a by washing with a large amount of water. The micrograph is very similar to Fig. 3a, with particles of 500 nm or more and not uniform. From this result, we concluded that the excess lithium method was ineffective when $\text{LiCH}_3\text{COO}\cdot 2\text{H}_2\text{O}$ and $\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ were mixed at a molar ratio of 5 to 1.

Fig. 3c and d are SEM images of LiCoO_2 powders obtained by washing the powders, which were made by calcining mixtures of lithium acetate and cobalt acetate with molar ratios of 9:1 and 13:1, respectively, with a large amount of water. Samples of Fig. 3c and d were obtained by removing lithium carbonate from samples of Fig. 2b and c, respectively. LiCoO_2 powders made from a mixture of Li compound and Co compound at a molar ratio of 9 to 1 consisted of uniform and very fine particles whose size was about 25 nm (Fig. 3c). LiCoO_2 particles obtained by mixing lithium acetate and cobalt acetate at a molar ratio of 13 to 1 are very small, about 23 nm, and uniform. The primary particles formed a larger secondary particle, whose size was about 500 nm. From these results, we concluded that nano-sized LiCoO_2 powders can be obtained when $\text{LiCH}_3\text{COO}\cdot 2\text{H}_2\text{O}$ is added nine or more times to $\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ in molar ratio.

The mechanism for obtaining nano-sized LiCoO_2 particles by using the excess lithium method is very simple. First, a large amount of $\text{LiCH}_3\text{COO}\cdot 2\text{H}_2\text{O}$ and a small quantity of $\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ are mixed uniformly with water. Next, the dried mixture is calcined. By calcining, LiCoO_2 is synthesized and any excessive lithium acetate becomes lithium carbonate simultaneously. At that time, excessive lithium car-

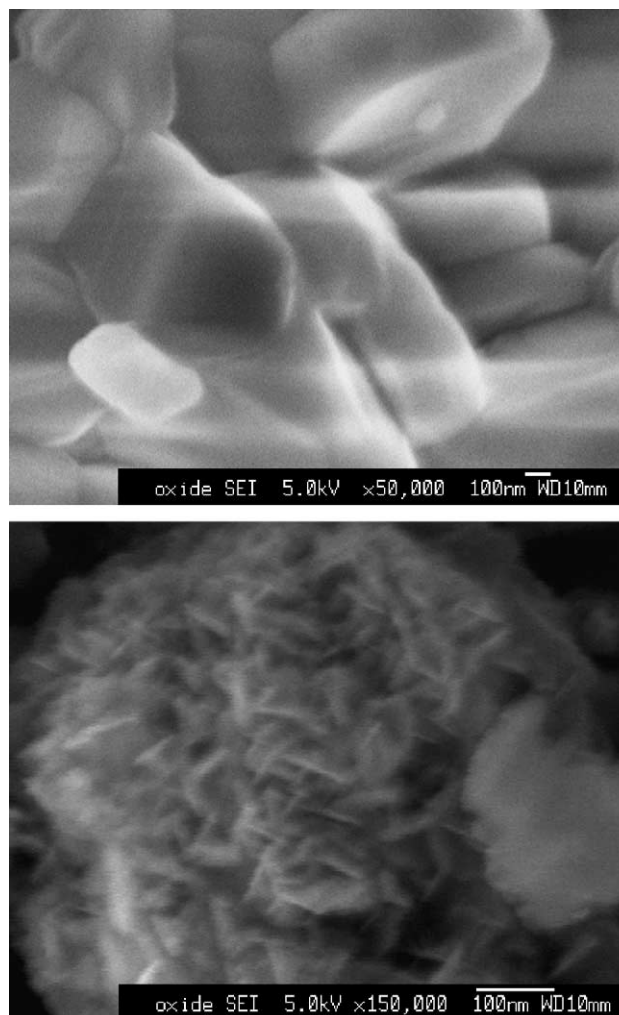


Fig. 4. SEM image of products obtained by calcining, at 600°C for 6 h, the mixture of a large amount of $\text{LiCH}_3\text{COO}\cdot 2\text{H}_2\text{O}$ and a small quantity of $\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ at a molar ratio of 21:1, before washing with water (a) and the SEM image of LiCoO_2 obtained by washing the products (b).

bonate covers LiCoO_2 particles, and it suppresses the growth of LiCoO_2 particles. After the lithium carbonate is removed, very fine LiCoO_2 powders are obtained. It is important to mix the lithium acetate and cobalt acetate uniformly and to calcine the mixture below the temperature of the melting point of lithium carbonate.

Next, we mixed lithium acetate and cobalt acetate at a molar ratio of 21 to 1 and calcined the mixture at 600°C for 6 h. We confirmed that this sample consisted of LiCoO_2 and Li_2CO_3 by XRD measurement. Fig. 4a shows a SEM image of this heat-treated sample. The particles are about one micrometer and are very large in comparison with samples made prior to the treatment. We next washed the mixture of LiCoO_2 and Li_2CO_3 with a large amount of water and subjected it to a centrifugal separator. Finally, very fine LiCoO_2 powders were obtained. Fig. 4b shows a SEM image of the powders. Unlike the LiCoO_2 particles obtained by mixing Li compound and Co compound at a molar ratio of 9 to 1 or 13

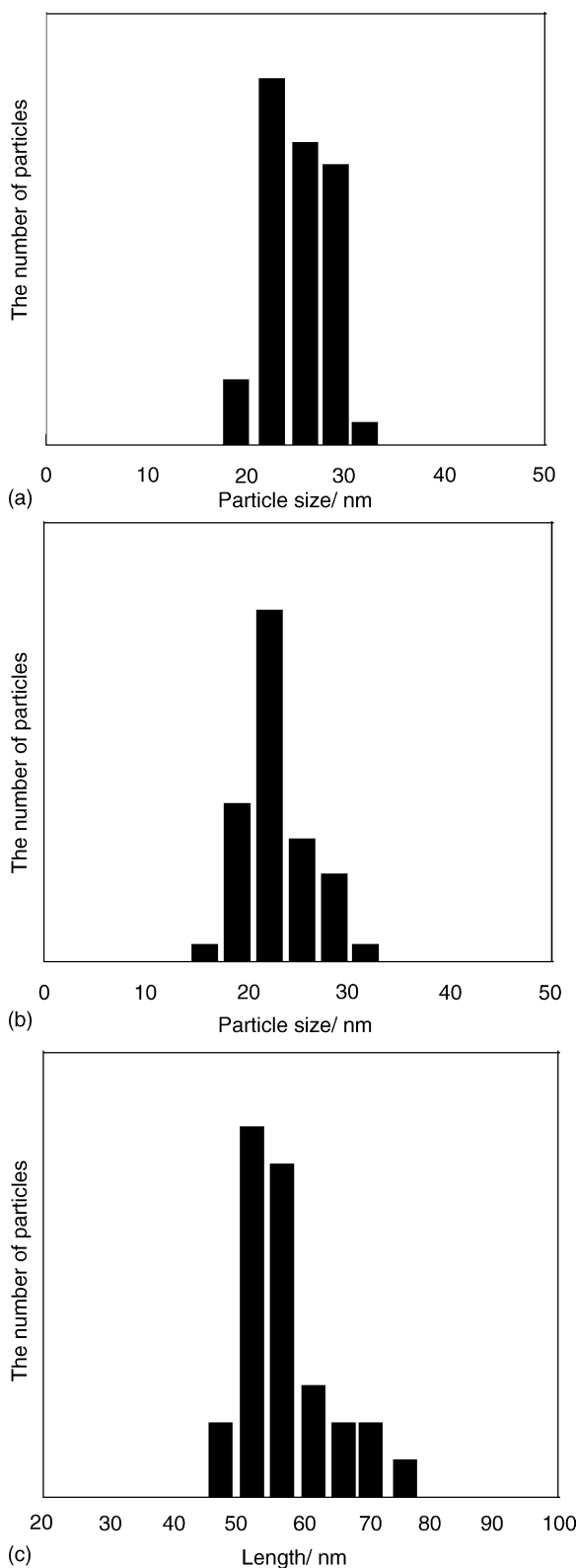


Fig. 5. LiCoO_2 particles synthesized by using the excess lithium method, with size distribution measured from SEM images, from samples of $\text{LiCH}_3\text{COO}\cdot 2\text{H}_2\text{O}$ and $\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ at molar ratios of 9:1 (a), 13:1 (b) and 21:1 (c).

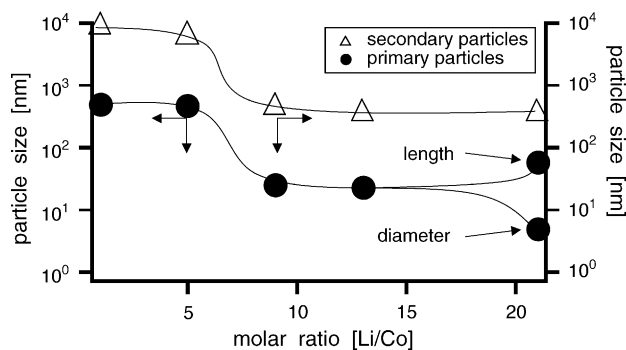


Fig. 6. Relationship between primary and secondary particle size and Li/Co molar ratio when the excess lithium method was used to synthesize LiCoO_2 at 600 °C for 6 h.

to 1, needlelike particles about 5 nm in diameter and 60 nm long appeared in the micrograph. Needlelike LiCoO_2 particles have more surface area than do spherical particles, so the former are more suitable for a cathode material of lithium batteries for a HEV and an EV than are the latter. We do not yet know why the particles became needlelike. It is likely that a lot of lithium carbonate affected the grain growth of nano-sized LiCoO_2 .

Particle size distribution measured from SEM images is shown in Fig. 5. Fig. 6 is a summary of the relationships between primary and secondary particle size and Li/Co molar ratio.

3.2. Electrochemical properties

The discharge characteristics of the LiCoO_2 samples obtained by using the excess lithium method are shown in

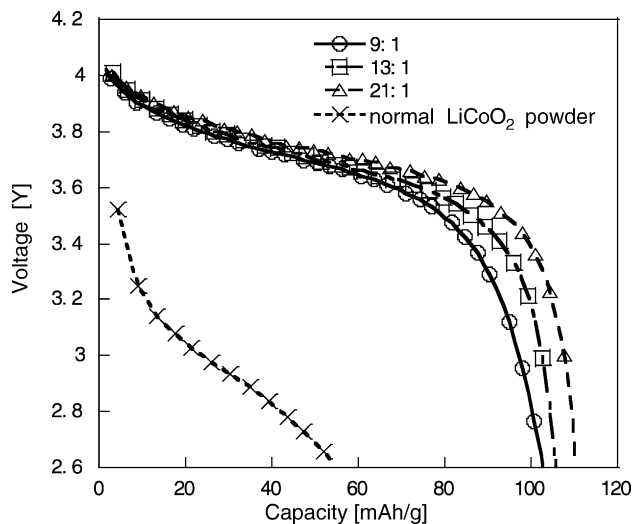


Fig. 7. Discharge curves of Li/1M LiPF_6 EC + DMC (1:1 in vol.)/ LiCoO_2 cells, with LiCoO_2 obtained by washing powders made by calcining mixtures of lithium acetate hydrate and cobalt acetate hydrate at molar ratios of 9:1 (open circle), 13:1 (square) and 21:1 (triangle), respectively, and obtained by the normal solid phase method using Li_2CO_3 and Co_3O_4 (cross) at constant current density 12 mA cm^{-2} .

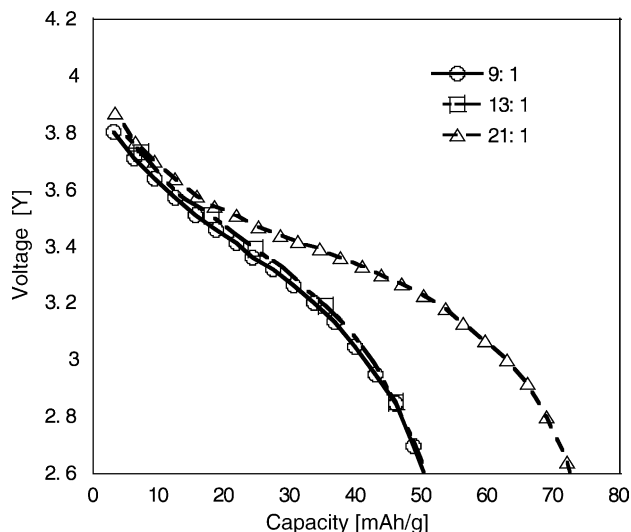


Fig. 8. Discharge curves of Li/1M LiPF₆ EC+DMC (1:1 in vol.)/LiCoO₂ cells, with LiCoO₂ obtained by washing powders, those were made by calcining mixtures of lithium acetate hydrate and cobalt acetate hydrate at molar ratios of 9:1 (open circle), 13:1 (square) and 21:1 (triangle), respectively, at constant current density 24 mA cm⁻².

Figs. 7 and 8. The open circle, square and triangle represent nano-sized LiCoO₂ powders obtained by our study, and the cross represents LiCoO₂ powder obtained by the normal solid phase method using Li₂CO₃ and Co₃O₄, with a particles size of about 5 μm, as shown in Figs. 7 and 8. The cathode electrode densities of cells including LiCoO₂ particles obtained by mixing lithium acetate and cobalt acetate at a molar ratio of 9, 13 and 21 to 1 are 1.60, 1.47 and 1.52 g cm⁻³, respectively. The cathode density of a cell including LiCoO₂ particles obtained by the usual solid phase method is 1.41 g cm⁻³. The cathode thickness of all cells is about 80 μm.

Fig. 7 shows discharge curves of four samples at a constant current density of 12 mA cm⁻² between 4.2 and 2.6 V. The rate capability of Li cells was very much improved by using cathodes made of nano-sized LiCoO₂, compared with that made of the usual 5 μm LiCoO₂. Fig. 8 shows discharge curves of the same samples at a constant current density of 24 mA cm⁻² without the sample of micro-order LiCoO₂ because the cell capacity using micro-order LiCoO₂ was under

10 mAh g⁻¹ at this current density. The discharge capacity of the sample of 21:1 is over 70 mAh g⁻¹. This capacity is very large in comparison with the capacity of samples of 9:1 and 13:1 molar ratios. It seems that these differences were caused by the difference of surface area of each size of LiCoO₂ granule.

4. Conclusion

We investigated a new method, the excess lithium method, of preparing nano-sized LiCoO₂ powders. In this method, lithium acetate hydrate and cobalt acetate hydrate are mixed at molar ratios of 9, 13 and 21 to 1, uniformly, and the mixture is calcined at 600 °C for 6 h. Finally, obtained powders are washed with a large amount of water to remove impurity and then dried. Using this method, we obtained nano-sized spherical LiCoO₂ particles with a diameter of about 25 and 23 nm at Li/Co at molar ratios of 9/1 and 13/1, respectively. Needlelike LiCoO₂ particles with a diameter of about 5 nm and a length of about 60 nm appeared at Li/Co = 21/1. The rate capability of Li cells was very much improved by using cathodes made of nano-sized LiCoO₂, compared with that of cathodes made with the usual 5 μm LiCoO₂.

References

- [1] N. Li, C.R. Martin, B. Scrosati, J. Power Sources 97–98 (2001) 240.
- [2] D. Larcher, C. Masquelier, D. Bonnin, Y. Chabre, V. Masson, J.B. Leriche, J.M. Tarascon, J. Electrochem. Soc. 150 (1) (2003) 133.
- [3] P.N. Kumta, D. Gallet, A. Waghay, G.E. Blomgren, M.P. Setter, J. Power Sources 72 (1998) 91.
- [4] E. Rossen, J.N. Reimers, J.R. Dahn, Solid State Ionics 62 (1993) 53.
- [5] Z.S. Peng, C.R. Wan, C.Y. Jiang, J. Power Sources 72 (1998) 215.
- [6] W.S. Yoon, K.B. Kim, J. Power Sources 81–82 (1999) 517.
- [7] Y. Li, C. Wan, Y. Wu, C. Jiang, Y. Zhu, J. Power Sources 85 (2000) 294.
- [8] H. Chen, X. Qiu, W. Zhu, P. Hagemuller, Electrochem. Commun. 4 (2002) 488.
- [9] A. Burukhin, O. Brylev, P. Hany, B.R. Churagulov, Solid State Ionics 151 (2002) 259.
- [10] H. Arai, S. Okada, H. Ohtsuka, M. Ichimura, J. Yamaki, Solid State Ionics 80 (1995) 261.