

Short communication

Sub-micron LiCoO_2 manufactured in a single synthetic step using eutectic self-mixing method

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Abstract

Sub-micron LiCoO_2 as a cathode material for lithium rechargeable battery with high rates is easily and economically prepared using eutectic self-mixing method without any artificial mixing procedures of reactants and ultra-miniaturization of products. While the micro-sized LiCoO_2 exhibits the discharge capacities of 134.8 mAh g^{-1} at 0.1C and 118.6 mAh g^{-1} at 5.0C, those of the sub-micron LiCoO_2 are 137.2 mAh g^{-1} at 0.1C and 131.7 mAh g^{-1} at 5.0C.

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1. Introduction

From the dawning of Li ion batteries, LiCoO_2 is ceaselessly used as the cathode material for almost all commercialized lithium rechargeable batteries due to its suitable performances such as high energy density, ease of manufacture, etc. In the past two decades, a wealth of research on LiCoO_2 has achieved advances in technology in terms of synthetic techniques, electrochemical properties, effect of doping and/or coating, thermal stability, etc. [1–6]. Nonetheless, to accommodate the increasing user's demands especially in the fields of multi-functioned mobile electronics and high power applications such as electric vehicle, intensive efforts seem to be concentrated to good battery performance at high rates. The diffusion of lithium ion in the cathode material, as a function of concentration gradient, must be fast enough to grant a good rate capacity. Thus, to obtain lithium rechargeable batteries with high rates, cathode material needs to be encouraged by ultra-miniaturization in a nano-size. Nano-sized cathode materials can be obtained by controlling of crystal nucleation and crystal growth.

The preparation of LiCoO_2 using eutectic self-mixing method and the good battery performances of the prepared

LiCoO_2 are described in our previous report [7]. Using this method, the manufacturing procedure is easily made up just thermal reaction at high temperature in air without any pulverization, grinding, particle morphology controlling, and particle size controlling of reactants as well as products. When lithium and cobalt acetates are exposed to the temperature of 80°C , they can be fluidized substances by themselves without any solvents and then spontaneously and homogeneously mixed together [7]. In addition, it is found that the heat treatments of lithium and cobalt acetates at 350°C are required to obtain the steady phase transition and the enhanced battery performances [7,8].

Here, we present the results of the simple but successful preparation of sub-micron LiCoO_2 in a single synthetic step using advanced eutectic self-mixing method, as well as a good example of how to accomplish material preparation and simultaneous ultra-miniaturization in a nano-size by design of the experimental conditions based on the elucidation of the reaction mechanism study.

2. Experimental

2.1. Materials

To prepare LiCoO_2 smaller, both 0.105 mol of $\text{LiCH}_3\text{CO}_2 \cdot 2\text{H}_2\text{O}$ and 0.1 mol of $\text{Co}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ were heated

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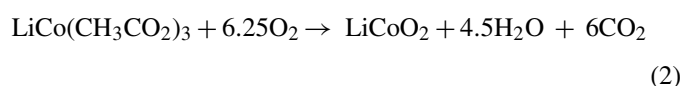
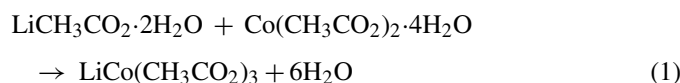
consecutively at 80 °C for 40 min in air, 270 °C for 8 h in a fixed CO₂ pressure between 0.001 and 1.0 kgf cm⁻², and 900 °C for 20 h in air without any artificial mixing procedures and intermittent cooling. Separately, micro-sized LiCoO₂ was also prepared as follows: 0.105 mol of LiCH₃CO₂·2H₂O and 0.1 mol of Co(CH₃CO₂)₂·4H₂O were heated consecutively at 80 °C for 40 min, 350 °C for 8 h, and 900 °C for 20 h in air without an external CO₂ stream. Excess LiCH₃CO₂·2H₂O was used to compensate for the loss of Li during the heating.

2.2. Characterization

X-ray diffraction (XRD) pattern analyses were achieved by using a Mac Science M03XHF²² diffractometer and Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$) operated with 30 mA and 40 kV. The diffractograms were recorded in the 2θ range of 5–90° with 0.02° intervals at a scanning rate of 2° min⁻¹. The scanning electron microscope (SEM) images of the LiCoO₂ phases prepared without external CO₂ stream and with external CO₂ stream were obtained using an Hitachi SEM S-4500. Electrochemical tests were carried out at room temperature using coin cells. The prepared cathode materials were mixed with 7 wt.% super-P carbon black and 8 wt.% poly-vinylidene fluoride (PVDF) binder dissolved in *N*-methyl-2-pyrrolidone (NMP) until a slurry was obtained. The slurry was laminated on an Al foil using a hot-roller press. The electrolyte was a 1.0 M solution of LiPF₆ in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with 1:2 volume ratio. Lithium foil was used as anode; cell assembly was performed in an Ar-filled glove box; and cells were charged and discharged at 0.1, 0.5, 1.0, 2.0, and 5.0C.

3. Results and discussion

In our previous report [8], the TG-DTA data during the preparation of LiCoO₂ without external CO₂ stream ascertain that the first weight loss (experimental value of 30.8%) between room temperature and 80 °C together with small endothermic DTA peaks up to 80 °C correspond to the removal of hydrated 6H₂O (theoretical value of 30.8%). It is also reported, beyond 80 °C up to 350 °C, decomposition of lithium acetate and cobalt acetate results in the second weight loss of 41.3% and a large exothermic DTA peak at 260 °C [8]. This result is exactly in accordance with the theoretical value, 41.3% for the release of 4.5H₂O and 6CO₂, as well as the gain of 6.25O₂. Therefore, the reaction pathway can thus be given as follows:



While the temperature of 350 °C is the end-point for all of thermal weight loss, endothermic and exothermic, the practical temperature of the second weight loss and the huge exothermic heat is 260 °C. During the heating around 260 °C, the decomposition

of both acetates occurs, and 6 mol of CO₂ gas are simultaneously emitted. The crystallization process actually occurs in two stages, crystal nucleation and crystal growth. While the driving force for crystal growth is exclusively attached to just reaction temperature, the rate of crystal nucleation is the result of two competing factors; contributions of thermal motion and phase instability. Here, providing externally CO₂ gas during the self-emission of CO₂ gas promotes crystal nucleation and dispersion of crystal nuclei, but, at the same time, inhibits crystal growth.

The XRD patterns of LiCoO₂ prepared without external CO₂ stream and LiCoO₂ prepared with external CO₂ stream are shown in Fig. 1. All XRD peaks of the prepared phases are characteristic for the space group *R*-3*m* as layered LiCoO₂ phase [9]. Both of the prepared LiCoO₂ phases crystallize in the hexagonal system (LiCoO₂ prepared without CO₂ stream: $a = 2.855 \text{ \AA}$, $c = 13.98 \text{ \AA}$, LiCoO₂ prepared with external CO₂ stream: $a = 2.870 \text{ \AA}$, $c = 14.06 \text{ \AA}$).

Fig. 2 shows the SEM images of the morphologies in LiCoO₂ prepared without external CO₂ stream, LiCoO₂ prepared in the external CO₂ pressure of 0.01 kgf cm⁻², and LiCoO₂ prepared in the external CO₂ pressure of 0.03 kgf cm⁻². These images directly demonstrate the effect of the injection of external CO₂ gas on the particle size of LiCoO₂. It is easily found that those particle sizes are significantly different. While the LiCoO₂ prepared without external CO₂ stream consists of micro-sized particles, the LiCoO₂ prepared with external CO₂ stream consist

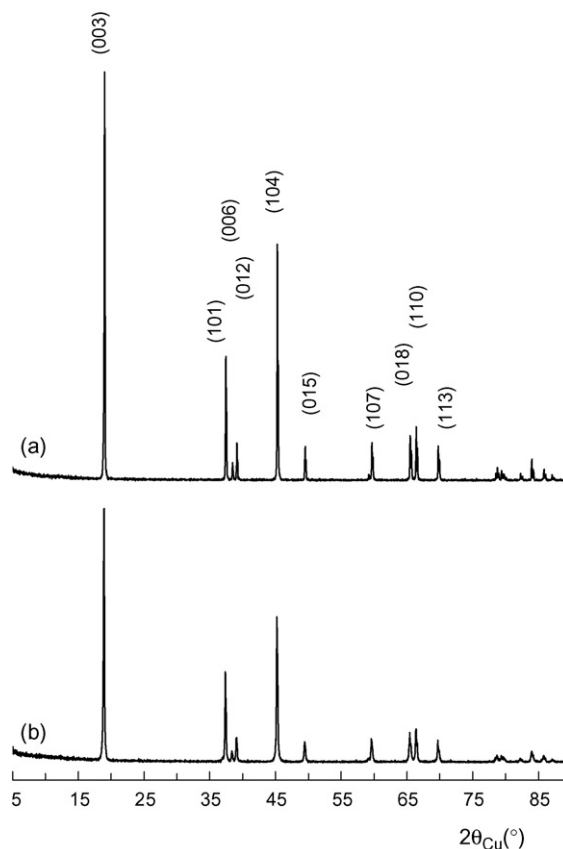


Fig. 1. X-ray diffraction patterns for: (a) LiCoO₂ prepared without CO₂ stream, and (b) LiCoO₂ prepared with CO₂ stream.

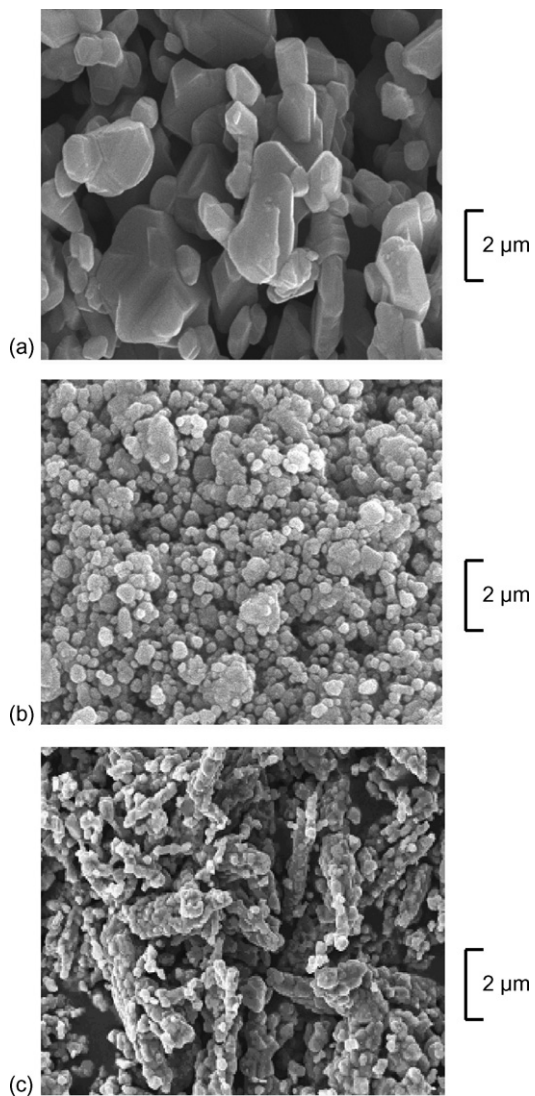


Fig. 2. SEM images of: (a) LiCoO_2 prepared without CO_2 stream, (b) LiCoO_2 prepared in CO_2 pressure of 0.01 kgf cm^{-2} , and (c) LiCoO_2 prepared in CO_2 pressure of 0.03 kgf cm^{-2} .

of sub-micron and aggregated grains. In fact, the aggregation of the sub-micron LiCoO_2 is not in itself, but ascribed to a gold-coating on the sub-micron LiCoO_2 before the SEM observation to prevent a flying of sub-micron LiCoO_2 .

As shown in Fig. 3, the LiCoO_2 prepared in CO_2 pressure of 0.03 kgf cm^{-2} exhibits the discharge capacities of 137.2 mAh g^{-1} at 0.1C and 131.7 mAh g^{-1} at 5.0C . However, the LiCoO_2 prepared without external CO_2 stream exhibits the discharge capacities of 134.8 mAh g^{-1} at 0.1C and 118.6 mAh g^{-1} at 5.0C (Fig. 4). Needless to say, the difference in the discharge capacity retentions of the two LiCoO_2 at 5.0C versus 0.1C ; 95.9 and 87.9%, results from the effect of concentration polarization with those different particle sizes. Although sub-micron LiCoO_2 is economically and easily prepared by just direct thermal reaction without any artificial mixing procedures of reactants and ultra-miniaturization of products, its battery performances are on the whole excellent.

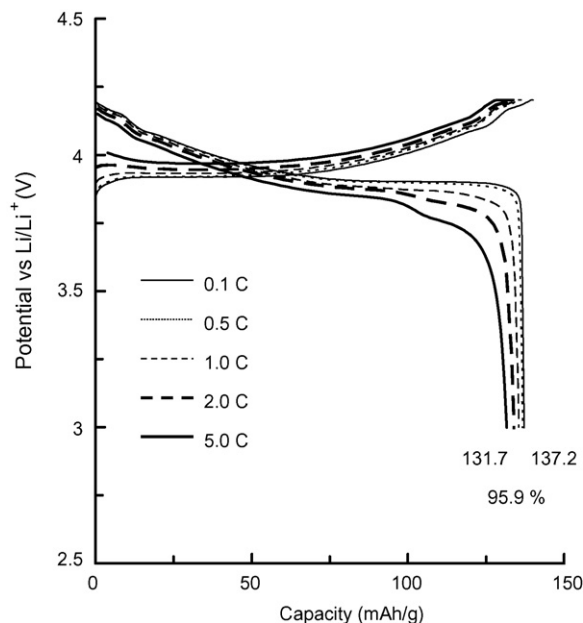


Fig. 3. Voltage vs. capacity profiles of sub-micron LiCoO_2 at the 0.1, 0.5, 1.0, 2.0, and 5.0C .

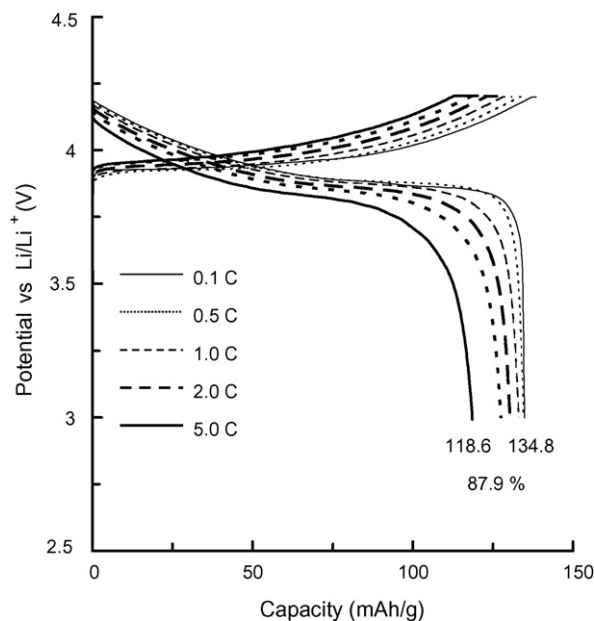


Fig. 4. Voltage vs. capacity profiles of micro-sized LiCoO_2 at the 0.1, 0.5, 1.0, 2.0, and 5.0C .

4. Conclusion

Sub-micron LiCoO_2 as a cathode material for lithium rechargeable batteries is prepared using eutectic self-mixing method without any artificial mixing procedures of reactants and ultra-miniaturization of products. During the thermal reaction, just providing externally CO_2 gas promotes crystal nucleation and dispersion of crystal nuclei, but, at the same time, inhibits crystal growth, which results in material preparation and simultaneous ultra-miniaturization in a sub-micron size. The

prepared sub-micron LiCoO_2 exhibits the discharge capacities of 137.2 mAh g^{-1} at $0.1C$ and 131.7 mAh g^{-1} at $5.0C$.

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