

# Synthetic optimization of spherical $\text{LiCoO}_2$ and precursor via uniform-phase precipitation

Ping He<sup>a</sup>, Haoran Wang<sup>b</sup>, Lu Qi<sup>a,\*</sup>, Tetsuya Osaka<sup>c</sup>

<sup>a</sup> Department of Applied Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China

<sup>b</sup> Beijing Green Power Technology Company Ltd., Beijing 100081, PR China

<sup>c</sup> Department of Applied Chemistry, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

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## Abstract

$\text{LiCoO}_2$  had been successfully prepared from spherical basic cobalt carbonate via a simple uniform-phase precipitation method at normal pressure, using cobalt sulfate and urea as the reactants. The preparation of spherical basic cobalt carbonate was significantly dependant on synthetic condition, such as the reactant concentration, reaction temperature and impeller speed, etc. The optimized condition resulted in spherical basic cobalt carbonate with uniform particle size distribution, as observed by scanning electron microscopy. Calcination of the uniform basic cobalt carbonate with lithium carbonate at high temperature led to a well-ordered layer-structured  $\text{LiCoO}_2$  without shape change, as confirmed by X-ray diffraction. Due to the homogeneity of the basic cobalt carbonate, the final product,  $\text{LiCoO}_2$ , was also significantly uniform, i.e., the average particle size was of about 10  $\mu\text{m}$  in diameter and the distribution was relatively narrow. As a result, the corresponding tap-density was also high approximately  $2.60 \text{ g cm}^{-3}$ , of which the value is higher than that of commercialized  $\text{LiCoO}_2$  of Hunan Ruixing, co. In the voltage range 2.8–4.2, 2.8–4.3, and 2.8–4.4 V, the discharge capacities of  $\text{LiCoO}_2$  electrode were 153, 159, and 168  $\text{mAh g}^{-1}$ , respectively, with better cyclability.

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**Keywords:** Cathode material; Spherical; High tap-density

## 1. Introduction

Although cathode material of Li-ion secondary battery— $\text{LiCoO}_2$  has been widely used, there are still some papers [1–3] reporting new methods to improve the performance of the material. Several researchers [4–6] explained synthesis of spherical powders could be an effective way to increase the tap-density and safety of the powder. Since cobalt oxide was the particular material for the synthesis of lithium cobalt oxide, what we need to study turned to gain the high purity and spherical precursor.

Since 1990, high density and spherical nickel hydroxide which was mainly used on nickel–hydrogen cell had been researched and more development was gained [7]. Just because the cobalt ion was easily oxidized, it is difficult to synthesize  $\text{Co(OH)}_2$  with good character by the same method as  $\text{Ni(OH)}_2$ .

It was demonstrated that homogeneous precipitation by urea offers the opportunity to produce discrete, uniform particles [8]. Furthermore, high purity can be obtained for the little metal ion existed in urea, which was an important factor for the cathode of lithium ion secondary cell. Now that the precipitation by urea offers an economically attractive and environmentally benign process as it is inexpensive and environmentally safe, it can be scaled-up for the preparation of precursor for lithium ion cell cathode material.

In this paper, particles were prepared via homogenous precipitation method using cobalt sulfate and urea as the reactants. The morphology of the as-synthesized cobalt carbonate and electrochemical characterization of  $\text{LiCoO}_2$  with as-prepared cobalt carbonate as one of the precursors are presented herein.

## 2. Experimental

Spherical basic cobalt carbonate was prepared as follows: an aqueous solution of  $\text{CoSO}_4$  with a concentration of  $0.2 \sim 1.0 \text{ mol dm}^{-3}$  was pumped into continuous stirred tank

\* Corresponding author. Tel.: +86 10 62753288; fax: +86 10 62755290.  
E-mail address: [qilu@pku.edu.cn](mailto:qilu@pku.edu.cn) (L. Qi).

Table 1  
Synthetic conditions of  $2\text{CoCO}_3 \cdot 3\text{Co}(\text{OH})_2$  powders

Sample	Cobalt concentration (mol dm <sup>-3</sup> )	Temperature (°C)	Impeller speed (rpm)	Tap-density (LiCoO <sub>2</sub> , g cm <sup>-3</sup> )
S1	0.2	80	500	2.44
S2	0.5	80	500	2.60
S3	1.0	80	500	2.11
S4	1.0	75	500	2.55
S5	1.0	85	500	1.77
S6	1.0	90	500	1.21
S7	1.0	80	400	1.44
S8	1.0	80	450	2.17
S9	1.0	80	550	2.28

reactor (CSTR, capacity 1 L). At the same time, urea solution of 4.0 mol dm<sup>-3</sup> was also fed into the reactor. All the reagents used in this study were of industrial grade and used without further purification. The concentration of the reactant, reaction temperature, and stirring speed of the mixture in the reactor were controlled with care. At the initial stage of the co-precipitation reaction, the irregular secondary particles from the agglomeration of the acicular primary structure were formed and the irregular particles changed gradually into spherical particles by vigorous stirring at 75–90 °C for 12 h. Then, the spherical  $2\text{CoCO}_3 \cdot 3\text{Co}(\text{OH})_2$  particles were filtered, washed, and dried at 110 °C. In synthesizing uniform spherical  $2\text{CoCO}_3 \cdot 3\text{Co}(\text{OH})_2$  particles, the concentration of the reactant, reaction temperature, and stirring speed during the precipitation reaction are the critical factors to the physicochemical properties of the powders. In this study, nine samples with different concentration of the reactant, reaction temperature, and stirring speed were prepared, as listed in Table 1.

The obtained spherical  $2\text{CoCO}_3 \cdot 3\text{Co}(\text{OH})_2$  dried at 110 °C to remove adsorbed water, then heated in an oven at 500 °C for its decomposing and  $\text{Li}_2\text{CO}_3$  was mixed thoroughly. The mixture was first heated at 700 °C for 12 h in air, and then it was calcined at 900 °C for another 12 h in air to obtain spherical  $\text{LiCoO}_2$  powders.

Powder X-ray diffraction (XRD) employing Cu K $\alpha$  radiation was used to identify the crystalline phase of the prepared powders by means of an X-ray diffractometer (MultFlex, Rigaku, Japan). The shape and size of the as-prepared samples were observed by scanning electronic microscope (SEM, JSM-5600LV, JEOL, Japan). The lithium and cobalt, etc. concentrations in the resulting materials were analyzed using an inductively coupled plasma spectrometer (ICP, Optima 4300DV, PE Ltd). Charge–discharge tests were performed with coin type cell (CR2032) applying a current density of 20 mA g<sup>-1</sup> at 25 °C. Composite positive electrodes were prepared by thoroughly mixing the active material (88%) with carbon black (3%), acetylene black (3%) and polyvinylidene fluoride (6%) in *N*-methylpyrrolidinone and extruding onto aluminium foils. Electrodes, with loading between 8 and 10 mg of active material cm<sup>-2</sup> were dried for 24 h at 120 °C in electric oven under vacuum. CR2032 simulated half cells were then assembled in a helium filled glove box (<1 ppm O<sub>2</sub>/H<sub>2</sub>O) using foils of Li metal as counter elec-

trodes and Celgard 3401 saturated with a 1 M  $\text{LiPF}_6$  (electrolyte) in ethylene carbonate/dimethylcarbonate/diethylene carbonate (1:1:1 in weight). Several simulated cells containing each sample were assembled and tested, to ensure reproducibility.

### 3. Results and discussion

#### 3.1. The effect of cobalt concentration

During the precipitation process, the crystal endured two steps: the formation of crystal nuclei and their growing up which includes the single crystal nuclei development and the agglomeration of some nuclei. The morphology of product depends on the interaction of the crystal nucleation speed and its growing speed [9]. Lower reactant concentration decreases the nucleation speed, which means that less nuclei are formed. Although the nuclei growth speed was lowered either, bigger crystal obtained by microcrystal agglomeration can be obtained for it is still higher than the nucleation speed, which is shown in Fig. 1(a). What most needed in the synthesis of cathode material is about 10  $\mu\text{m}$  in diameter considering of high discharge capacity and good circle life, which limited the use of bigger particle. Furthermore, lower reactant concentration need higher reaction volume and more energy, it has a disadvantage to scale up considering production cost.

With the increase of cobalt concentration, reaction time can be decreased correspondingly. But higher reactant concentration led to higher nucleation speed, which increased the ratio of nucleus collision and induced agglomeration of lots of nuclei, so the spherical extent was worsened and bigger sized particles are formed, which is shown in Fig. 1(c). And moreover, the fast growth speed resulted from the high reactant concentration lost the crystal lattice, and lowered particle density.

What we need is the particle less than 15  $\mu\text{m}$  in average diameter and high density [10]. Hence, suitable nucleus concentration need to be gained and grown in low speed. From the photographs of particles obtained at different concentrations, it is clear that the best reactant concentration is 0.5 M, which is shown in Fig. 1(b).

#### 3.2. The effect of reaction temperature

The effect of the reaction temperature to the crystallization was also manifested in changing the nucleation and growing rate [11]. The well-formed and high-density particles can be prepared with the decrease of temperature for the lower nucleus concentration and lower growing rate. When the reaction temperature is increased, higher nucleation rate led to high concentration of nucleus, which enhanced the ratio of nucleus collision and formed agglomerated particle, which is shown in Fig. 2(b) and (c). Moreover, high reaction temperature increased the growing speed of nucleus accordingly, and loose particle crystal lattice was obtained in that process.

Although good particle characteristics need low temperature, reaction time became too long and cobalt could not be precipitated entirely for urea would not be deposited ultimately when the temperature was less than 80 °C. Because there was little difference in particle morphology when the temperature was 75 °C

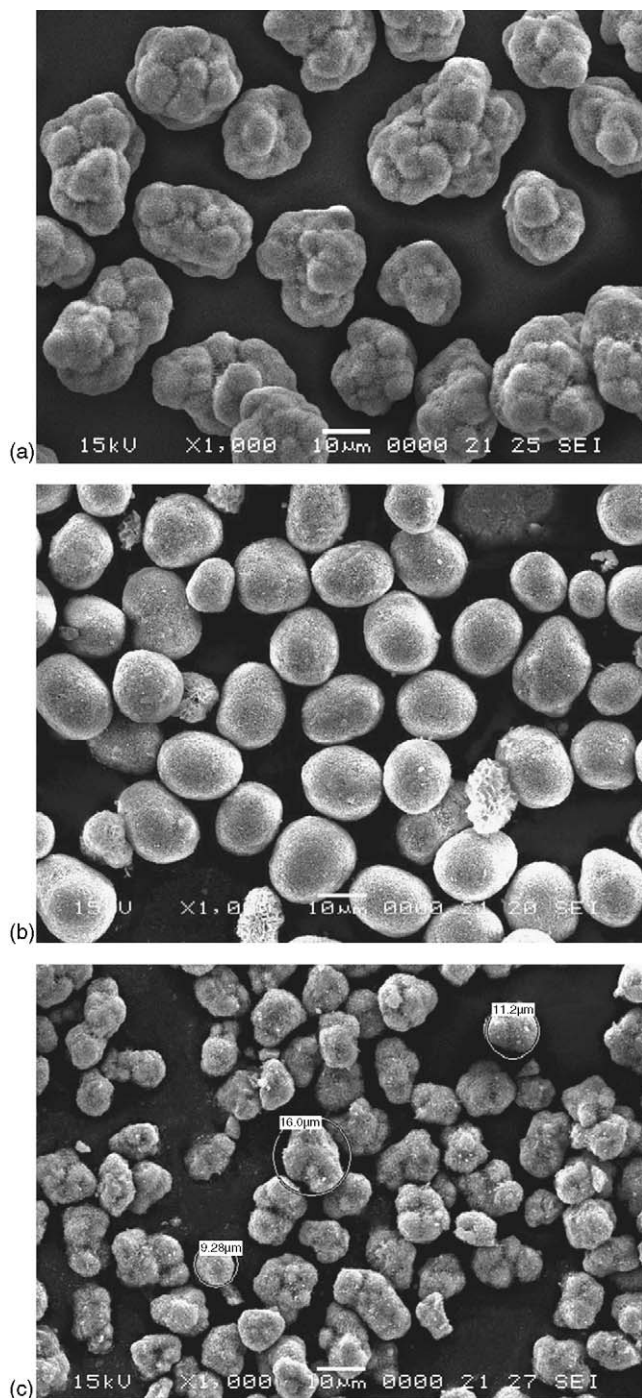


Fig. 1. SEM images of the basic cobalt carbonate at different cobalt concentrations (a) 0.2 M, S1; (b) 0.5 M, S2; (c) 1.0 M, S3.

as in Fig. 2(a), or 80 °C as in Fig. 1(b), the suitable reaction temperature can be chosen to be 80 °C.

### 3.3. The effect of impeller speed

Although high impeller speed leads to high agitation which improves the uniformity of reactant concentration in the bulk reactor, it also improves the collision rate of nucleus,

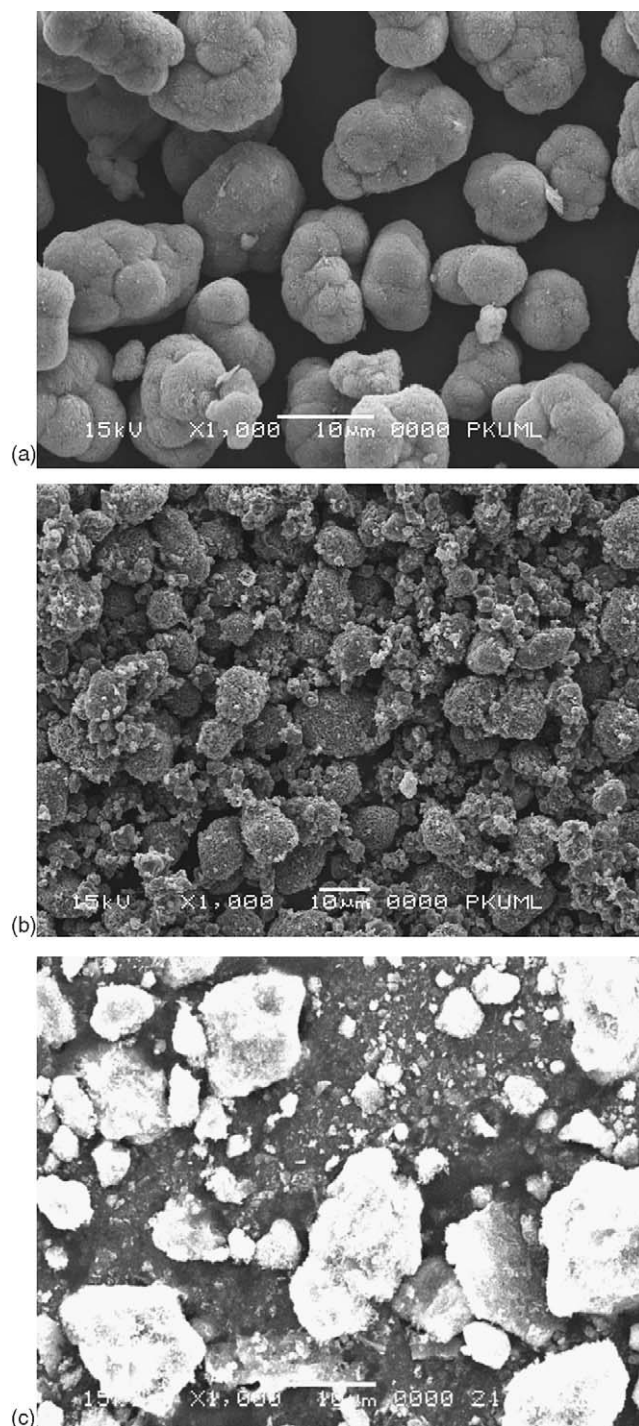


Fig. 2. SEM images of the basic cobalt carbonate at different reaction temperatures (a) 75 °C, S4; (b) 85 °C, S5; (c) 90 °C, S6.

and agglomerated particles will be obtained, as shown in Fig. 3(b).

With the decrease of impeller speed, the nucleation and growth rate of crystal recede both, with long reaction time being needed [12]. Furthermore, the weak agitation is brought on the high concentration grade of reactant, and wide particle distribution was obtained, which is shown in Fig. 3(a).

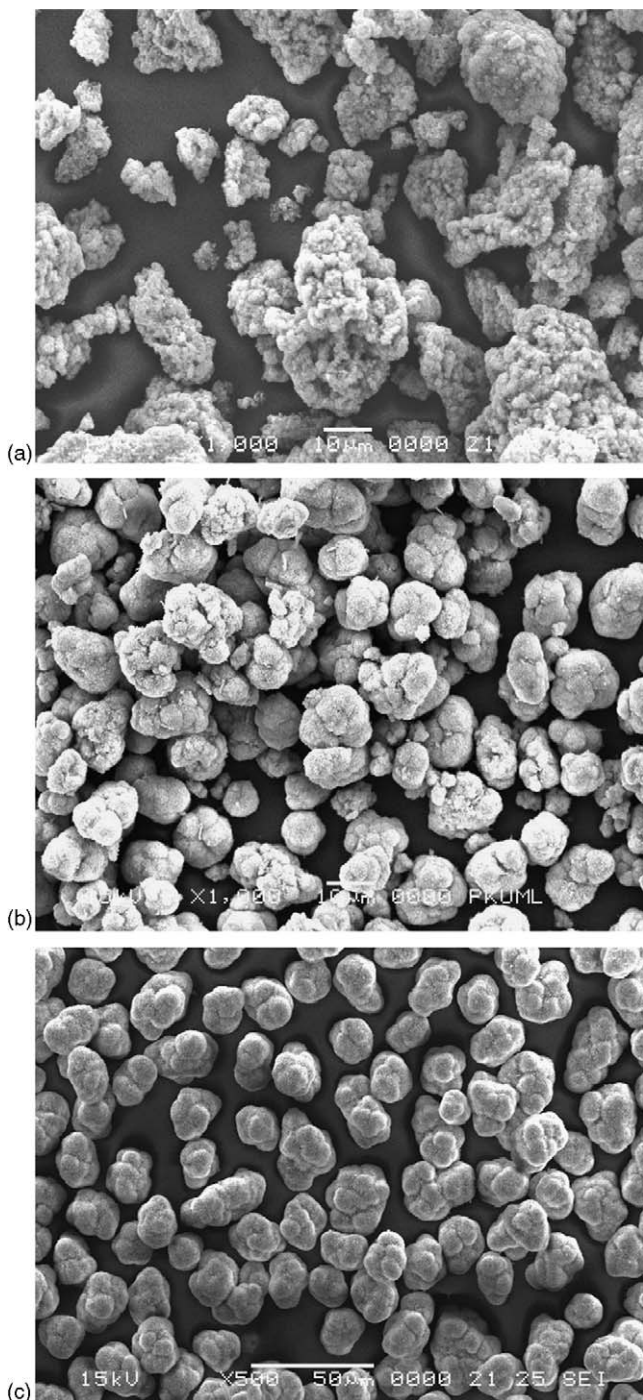


Fig. 3. SEM images of the basic cobalt carbonate at different impeller speeds (a) 400 rpm, S7; (b) 450 rpm, S8; (c) 550 rpm, S9.

Higher impeller speed enhanced the growth rate of crystal, and decreases the reaction time. During this experiment, the suitable impeller speed was 500 rpm.

#### 3.4. Preparation of $\text{LiCoO}_2$ by high temperature calcinations

Fig. 4 shows the SEM of the fired products using S2, which exhibited the highest tap-density, uniform particle size dis-

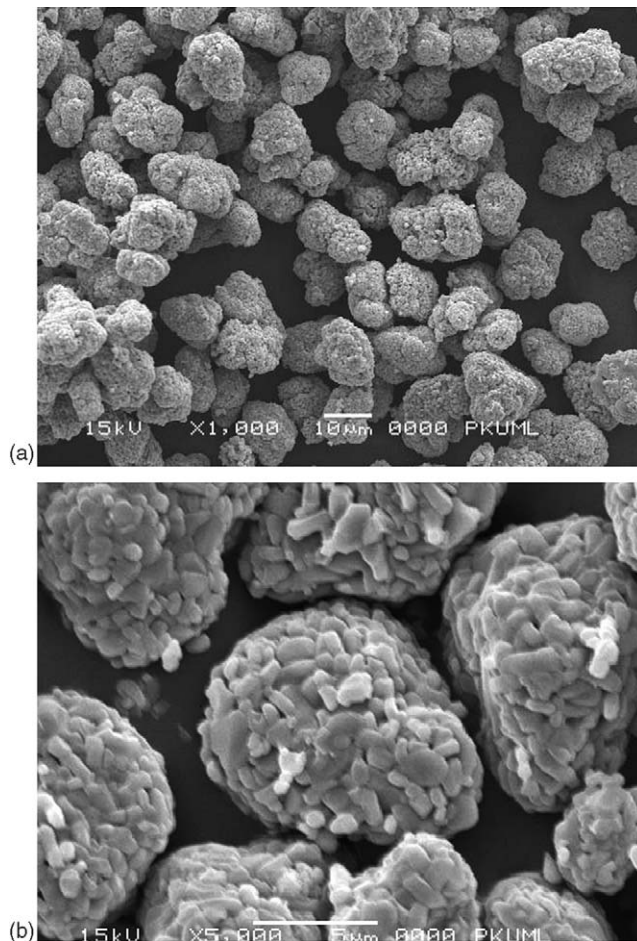


Fig. 4. SEM images of spherical  $\text{LiCoO}_2$  of (a) low and (b) high magnification calcined at 700 and 900 °C for 12 h in air.

tribution. The prepared basic cobalt carbonate was calcined with appropriate amount of  $\text{Li}_2\text{CO}_3$  at 700 and 900 °C for 12 h in air respectively. A little amount of excess lithium ( $\text{Li}/\text{Co} = 1.05\text{--}1.10$ ) was incorporated to compensate for the evaporation of lithium during high temperature calcinations, resulting in stoichiometric composition in the final products. All the synthesized powders showed a typical layered structure as shown in Fig. 5, and its composition was confirmed by ICP analysis which is presented in Table 2.

Table 2  
Element concentration of  $\text{LiCoO}_2$

	%
Li	6.83
Co	60.3
Fe	0.028
Ni	0.01
Na	0.0058
K	0.005
Mg	0.0054
Ca	0.013
$\text{SO}_4$	$\leq 0.01$

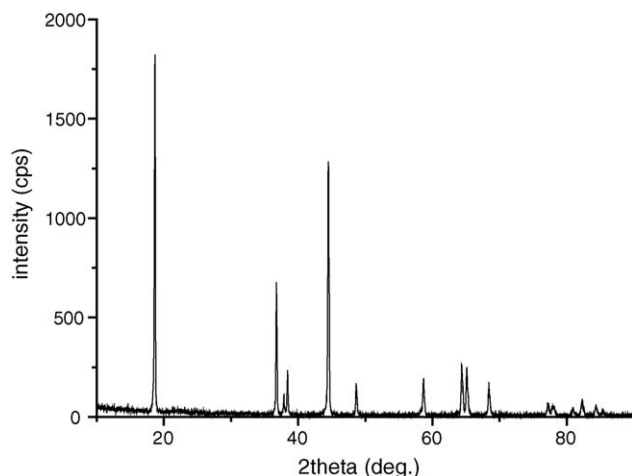


Fig. 5. Powder XRD pattern of spherical  $\text{LiCoO}_2$  calcined at 700 and 900 °C for 12 h in air.

Lithium insertion/extraction was monitored with an automatic cycling data recording system operating in galvanostatic mode, shown in Fig. 6. In order to observe cycling stability at higher voltage, the upper cut-off voltage was changed to 4.3 and 4.4 V. The discharge capacities increase gradually by raising the upper cut-off voltage limit. In the voltage range 2.8–4.2, 2.8–4.3, and 2.8–4.4 V, the capacities of  $\text{LiCoO}_2$  electrode are 153, 159, 168  $\text{mAh g}^{-1}$ , respectively, with good cyclability as can be seen in Fig. 6. In fact, it was reported that the occurrence of Co dissolution at higher voltage ( $>4.3$  V) is very detrimental effect on high voltage operation of  $\text{LiCoO}_2$ . The stable cyclability even at higher voltage limit in Fig. 6 also suggests that Co dissolution could be greatly suppressed in the spherical  $\text{LiCoO}_2$ , which need to be further considered in the future. From the SEM of spherical  $\text{LiCoO}_2$  (Fig. 4), we can learn that its shape did not appear as a single particle like what is in the market, the surface of the powder was an aggregate of many small particles. Each large particle was composed of these small particles about

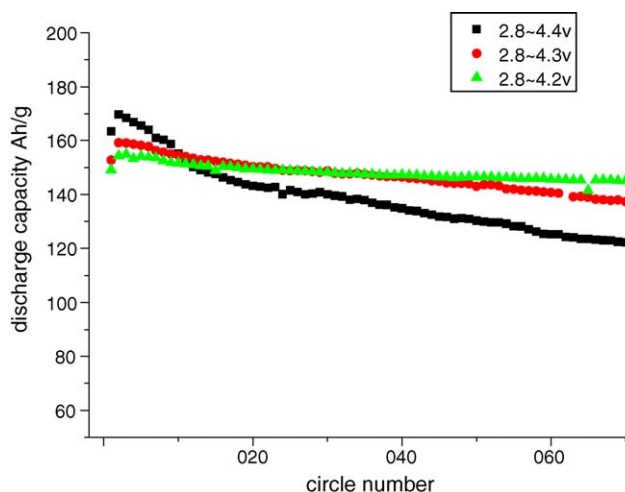


Fig. 6. Circle data of lithium ion cell with different cut-off voltages with current density of  $20 \text{ mA g}^{-1}$  at 25 °C.

$1 \mu\text{m}$ , which maybe the excuse for the good electronic property because of the easier insertion and dislocation of lithium. It is well known that the specific surface area is an important factor to stabilize the performance of lithium secondary batteries. When lithium and the pre-calcined precursors were calcined in the furnace, the small particles were agglomerated into large microsized particles by continuous calcination. Although there was a high possibility that a significantly increased surface area of  $\text{LiCoO}_2$  would result in the collapse of the structure due to an excess reaction between the very small particles and electrolyte, well optimized synthetic conditions using the uniform-phase precipitation process could maintain the most favorable powder properties of  $\text{LiCoO}_2$ , which existed in the form of agglomeration. Actually, even though the spherical crystal had 4–5 times smaller primary particle size, the surface area of it was nearly the same as that in the market. Therefore, we found that the average particle size and surface area of the resulting powder could be controlled during the synthesis and calcination processes.

For practical applications, tap-density of active material is also important to decide the capacity of battery. Because the inner space of battery is limited, if the tap-density is high, the higher volumetric capacity can be obtained, though the same gravimetric capacity remains. As a result, higher tap-density will lead to higher volumetric capacity in practical cells. Therefore, it is concluded that the preparation of homogeneous spherical precursor is a critical factor for the synthesis of high quality materials.

#### 4. Conclusion

In an attempt to synthesize spherical  $\text{LiCoO}_2$  powders, uniform-phase precipitation method has been employed. The precipitation and growth of primary basic cobalt carbonate particles could be controlled by regulation of reactant concentration, reaction temperature, and stirring speed during the precipitation. The optimized precipitation gave dense and uniform precipitates,  $2\text{CoCO}_3 \cdot 3\text{Co}(\text{OH})_2$ . After calcination of it with  $\text{Li}_2\text{CO}_3$  at high temperature, the final product became much denser, leading to the highest tap-density  $\text{LiCoO}_2$ , of which the density is close to  $2.60 \text{ g cm}^{-3}$ . In the voltage range 2.8–4.2, 2.8–4.3, and 2.8–4.4 V, the specific gravimetric discharge capacities of  $\text{LiCoO}_2$  electrode were 153, 159, 168  $\text{mAh g}^{-1}$ , respectively, with excellent cyclability by applying  $20 \text{ mA g}^{-1}$  of current density at 25 °C. This uniform-phase precipitation synthesis is an excellent powder preparation alternative method for high capacity positive electrode materials to be used in a Li-ion secondary battery.

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