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Morphology controllable synthesis and electrochemical performance of LiCoO₂ for lithium-ion batteries



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ABSTRACT

In this work, morphology-controlled lithium cobalt oxides (LCO) were obtained by a simple two-step method that involves a Co_3O_4 synthetic process, in which cubic and spherical Co_3O_4 were prepared by a hydrothermal method and a subsequent lithiation process with Li_2CO_3 . The structures and morphologies of two materials were investigated by XRD, SEM and TEM. In contrast with the LCO prepared by using commercial Co_3O_4 precursor, the cubic and spherical LCO materials have an excellent performance in cyclic stability and rate capacity which is attributed to the better fluidity and less agglomeration with specific morphology of LCO materials.

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1. Introduction

LiCoO₂ has been widely applied as one of the most attractive cathode materials in the field of lithium-ion batteries due to its unique advantages including superior cyclic stability, excellent cycle life, high open circuit voltage and easy preparation [1]. By now, LiCoO₂ has been researched for tens of years and largely used in the field of commercial applications. Although it has a few disadvantages, such as high price and toxicity, LiCoO₂ still has an important role in the market of cathode materials. People's attentions to LiCoO₂ have not been cooled down, and lots of studies about LiCoO₂ have been reported in recent years [2–9].

Morphology control of particles for cathode materials plays an important role in material packing density. Powder materials with irregular morphologies are prone to be agglomerated and "bridge formation", which results in a number of vacancies among particles and reduces the fluidity of the particles [10]. In contrast, materials with specific morphology particles have the advantage of high packing density and specific volumetric capacities. When the particles have an ideal size distribution, the smaller particles could fill up the gaps among large particles and the stacking density increases, which is helpful for achieving high energy density in lithium ion batteries. According to Ying's study [11], the tapdensity of powder $LiCoO_2$ are usually $2.2-2.4 \,\mathrm{g\,cm^{-3}}$, which limits the energy density of $LiCoO_2$ materials. Furthermore, the materials have better dispersity and fluidity, which are beneficial to be the electrode materials. The materials with regular morphologies are easier for further modification by uniform and stable coated layer. Many materials with regular particles [12–15] exhibited better electrochemical performance than the materials with irregular particles. Therefore, morphology controllable particles are the tendency in the development of industrial production for lithiumion batteries.

In recent years, persons pay more attentions to morphology control for cathode materials. Various electrode materials, such as nanoparticles, nanowires, nanotubes, hollow cubes and hollow spheres, have been reported [16–20]. For example, Xiao et al. [17] synthesized uniform LiCoO_2 nanoplates with a capacity of 113 mAh g⁻¹ at a rate of 1000 mA g⁻¹ after 100 cycles. Hao et al. [21] prepared single-crystalline LiMn_2O_4 hollow nanocones via a template-engaged reaction, which maintained a capacity of 100 mAh g⁻¹ even at a high rate of 50 C and retained 94.8% after over 1000 cycles at 5C. Xiao et al. [18] prepared LiCoO_2 nanowires composed of nanoparticles, which showed excellent rate capability, and its capacity retention was higher than 80% after 100 cycles

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at a high rate of 1000 mAg^{-1} . Our group [16] has also made an attempt on the synthesis of porous sphere $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ via an impregnation method and the material showed much better electrochemical properties than that synthesized by commercial source and conventional approaches. All these have demonstrated that materials with specific morphologies are beneficial to the electrochemical performance of cathode materials in Li-ion batteries.

Considering above-mentioned reasons, the cubic and spherical $LiCoO_2$ were synthesized by a solid phase method using morphology controllable Co_3O_4 obtained by a simple hydrothermal method as engaged template in this work. The cubic and spherical $LiCoO_2$ is in a size range of $10 \sim 15 \,\mu$ m. Such big particles can reduce the contact area and weaken the side reactions on interfaces between electrolyte and electrode. Resultantly, both cubic and spherical $LiCoO_2$ showed excellent performance in cyclic stability and rate capability.

2. Experimental

2.1. Material preparation

Cubic Co_3O_4 synthesis (a modified hydrothermal method [22]): 1.70 g cobalt acetate, 2.10 g urea and 1.40 g triethanolamine were dissolved in 70.0 ml deionized water. After stirring for 1 h, the mixed solution was transferred to a 100 ml teflon-lined stainless steel autoclave. The autoclave was kept at 160 °C for 12 h, and then cooled naturally to the room temperature. The prepared pink powders were first filtered and washed for more than three times by deionized water and ethanol, then dried in the electric oven at 110 °C for 3 h, and finally calcined in muffle furnace at 600 °C for 10 h with a heating rate of 10 °C min⁻¹.

Spherical Co₃O₄ synthesis (a modified hydrothermal method [23]): 1.00 g cobalt chloride hexahydrate and 2.00 g urea were dissolved in a mixture solution of 20.0 ml deionized water and 60.0 ml glycerol, after stirred to transparent, the mixed solution was transferred to a 100 ml teflon-lined stainless steel autoclave. The autoclave was kept at 120 °C for 12 h, and then cooled naturally to the room temperature. The prepared pink powders were firstly filtered and washed for more than three times by deionized water and ethanol, then dried in the electric oven at 110 °C for 3 h, and finally calcined in muffle furnace at 600 °C for 10 h with a heating rate of 10 °C min⁻¹.

The Co₃O₄ prepared above was mixed with appropriate Li₂CO₃ by a grinding process and calcined in air at 850 °C for 12 h with a heating rate of 2 °C min⁻¹, then cooled down to room temperature slowly. The obtained LCO maintained the morphology of Co₃O₄. The LCO sample using cubic Co₃O₄ as cobalt source was denoted as cubic-LCO, while that using spherical Co₃O₄ was marked as spherical-LCO.

In order to make a contrast with this two regular shaped LCO, the LCO using commercial Co_3O_4 materials (99.99% aladdin) as cobalt source were synthesized in the same condition, which is labelled as powder-LCO.

2.2. Material characterization

The XRD patterns were collected on a Rigaku miniflex 600 instrument equipping with Cu K α radiation operated at 40 kV and 15 mA from 10° to 90° at 2° min⁻¹ with a recording interval of 0.02°. Field emission scanning electron microscopy (SEM, HITACHI S-4800) was used to characterize the morphologies of samples. Transmission electron microscopy (TEM, JEOL-2100) was used to confirm the morphologies and identify the structures of the asprepared samples. The particle sizes were analyzed by Malvern laser particle size analyzer (Mastersizer2000).

2.3. Electrochemical measurements

The electrochemical properties were evaluated in CR2016-type coin-cell configuration The active materials were mixed with acetylene black and polyvinylidene difluoride (PVDF) (weight rate 80: 10: 10) in N-methyl pyrrolidone. The slurry was spreading onto an aluminum foil and dried in a vacuum oven at 80 °C overnight. The electrodes were punched out and roll-pressed. The coin cells were assembled in an argon-filled glove box (MBraun, Germany). The lithium metal foil was as the counter electrode and the polypropylene membrane (Celgard 2400) was as the seperator. The electrolyte used was 1 mol L⁻¹ LiPF₆ salt dissolved in a mixed solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of 1: 1.

The charge-discharge tests were performed on LAND battery test system (CT-2100A, Wuhan, China) in the voltage window $3.0 \sim 4.3$ V at room temperature. The charge process was involving constant current charge and constant voltage charge [24]: the constant current charge step to the desired voltage and the constant voltage charge was executed till the current decreased to one tenth of the constant current value. The electrochemical impedence spectra (EIS) were performed on Solartron (SI 1287) electrochemical workstation with a frequency range from 100 kHz to 0.01 Hz.

3. Results and discussion

The morphologies and structures of LiCoO₂ and Co₃O₄ were characterized by SEM, XRD and TEM. The SEM images of cubic and spherical Co_3O_4 precursors are shown in Fig. 1. The cubic samples possess regular and uniform mesoporous structure with diameters of about $10 \sim 15 \,\mu m$ (Fig. 1a and b). The micron-size particles are stacked by nano-sheet layers and each layer is consisted of irregular nanoparticles with diameters of about $50 \sim 200 \text{ nm}$ assembling together. The spherical samples (Fig. 1c and d) show uniform spherical structure with diameters of about $10 \sim 15 \,\mu m$ which are accumulated by small cubic particles that are further composed of nanoparticles with diameters of about $50 \sim 100$ nm. After blending and calcining with lithium carbonate, the LCO were obtained. Fig. 1e and f show that the obtained cubic LCO particles with diameters of $10 \sim 15 \,\mu m$ are consisted of dense particles with diameters of about $0.5 \sim 1 \,\mu$ m. Fig. 1g and h indicate that the spherical LCO samples with diameters of $10 \sim 15 \,\mu m$ are also composed of dense particles with diameters of about $1 \sim 2 \,\mu$ m. The SEM images indicate that the LCO inherit the Co₃O₄ morphology successfully with uniform distribution in size and the less pores can be seen on the surfaces. The sizes of particles were also analyzed by Malvern laser particle size analyzer (Fig. 2), and the results are consistent with the SEM results. In comparison, commercial Co₃O₄ are consisted of uniform and irregular particles (Fig. 1i) and the obtained powder-LCO (Fig. 1j) using commercial Co₃O₄ as cobalt source are composed of pulverous particles (about $0.5 \sim 1 \,\mu m$) without specific morphology. Moreover, some agglomeration phenomena of particles exist in the powder-LCO material. The particle size of the powder-LCO was analyzed as shown in Fig. S1. It can be seen that the particle size of powder-LCO is around 100 nm and $3 \sim 5 \,\mu$ m. The nanoparticles may be the broken ones. Also a few particles are in size of about $20 \sim 30 \,\mu\text{m}$, it could be attributed to the agglomeration of particles. It is tested that the tap-density values of cubic and spherical LCO are 2.63 and $2.72\,g\,cm^{-3}$, which are higher than that of powder LCO (2.23g cm^{-3}).

X-ray diffraction (XRD) analysis was conducted to confirm the structures of materials. As shown in Fig. 3, three Co_3O_4 samples match well with the standard pattern of Co_3O_4 (JCPDS Card No: 43-1003), and there are no other impurity peaks in the patterns. All-



Fig. 1. SEM images of samples: (a, b) cubic-Co₃O₄, (c, d) cubic-LCO, (e, f) spherical-Co₃O₄, (g, h) spherical-LCO, (i) commercial-Co₃O₄, (j) powder-LCO.

prepared LCO samples can be assigned to LiCoO₂ (JCPDS Card No: 50-0653). The obvious diffractive peak splitting at I(006)/I(102) and I(108)/I(110) (about 39° and 66°) indicates superior hexagonal

layer structure. The lattice parameters are obtained by the PDXL2 software (Rigaku, Japan), and the results are shown in Table 1. The ratio of I(003)/I(104) values of cubic-LCO, spherical-LCO and



Fig. 2. Particle size analysis of cubic-LCO and spherical-LCO.

powder-LCO are 1.67, 1.57 and 1.73, respectively, and the c/a values are all about 4.99, indicating low extent of cation disorder, which is beneficial for electrochemical performance [25]. The lattice parameters of cubic-LCO and spherical-LCO are close to that of powder-LCO. All LCO samples show no impurities.

TEM was employed to further characterize the structure of cubic-LCO and spherical-LCO samples as shown in Fig. 4. It can be seen the cubic-LCO and spherical-LCO particles are all dark in the images, which means a solid construction with no hollow areas inside. These results are according with the results of SEM images. After fully grinding, the submicron-sized particles as shown in Fig. 4c and g are obtained from the micron-sized cubic-LCO and spherical-LCO, respectively. The patterns of selected-area electron diffraction (SAED) in Fig. 4d and h with the electron beam in the [12–1] direction corresponding to Fig. 4c and g present well-organized array of diffraction spots that index typical layered lattice structure. This means the cubic-LCO and spherical-LCO micron-sized particles are composed of mono-crystalline nano-sized polyhedrons, which is favorable to Li-ion transport [16].

The electrochemical performances of cubic-LCO, spherical-LCO and powder-LCO are shown in Fig. 5. The discharge capacity at a current density of 100 mAg^{-1} and the corresponding coulomb efficiencies for the three LiCoO₂ electrode materials are given in Fig. 5a. The first discharging capacities of cubic-LCO and spherical-LCO are 157.3 and 154.1 mAh g⁻¹, and after 100 cycles their capacities are 145.0 and 139.7 mAh g⁻¹, with a capacity retention of 92.1% and 90.6%, respectively. The electrochemical performance of cubic-LCO is slightly superior to that of spherical-LCO, which may be attributed to some rolling out of spherical-LCO caused by the unstable structures of spherical Co₃O₄ during sintered process as shown in Fig. 1g. In contrast, the first discharging capacity of the

Table 1

The lattice parameters and integrated intensity ratios for all LCO samples.

	a(Å)	b(Å)	c(Å)	c/a	I(003)/I(104)
Cubic-LiCoO ₂	2.8130	2.8130	14.039	4.990	1.67
Spherical-LiCoO ₂	2.8110	2.8110	14.010	4.984	1.57
Powder-LiCoO ₂	2.8149	2.8149	14.046	4.989	1.73

powder-LCO is also up to 153.2 mAh g^{-1} , however, it remains 112.0 mAh g^{-1} with only 73.1% retention after 100 cycles. In addition, the first coulomb efficiencies of cubic-LCO, spherical-LCO and powder-LCO are 96.5%, 95.5% and 95.2%, respectively, and after several cycles the coulomb efficiencies of two regular morphology samples are all above 99%, while the powder-LCO sample has a little low efficiencies value ($98\% \sim 99\%$). This may be attributed to the solid structure of spherical-LCO and cubic-LCO, which lowers the interaction between electrolyte and LCO and decreases the side reactions at interfaces. Fig. 5b shows the differences of electrochemical performance of these LCO at successive-changed charge/ discharge rates of 50, 100, 200, 500 and 1000 mA g^{-1} (0.35 C, 0.7 C, 1.4C, 3.5C and 7C), respectively. The discharging capacities of cubic-LCO sample at 50, 100, 200, 500 and 1000 mAg^{-1} rates are 153.5, 151.3, 146.7, 132.5 and 112. mAh g⁻¹, while that of spherical-LCO are 149.3, 147.1, 144.0, 136.1 and 124.2 mAh g⁻¹, respectively. The powder-LCO shows decreased performance at all rates, the capacities are only 141.5, 130.6, 123.0, 111.0 and 81.0 mAh g⁻¹ . at above same rates, respectively. It is attributed to the ohmic polarization and electrochemical polarization caused by the poor electronic conductivity and Li-ion transfer rate [26]. The rate capabilities of cubic-LCO and spherical-LCO have apparent differences. The cubic-LCO exhibits slightly higher discharge capacity than spherical-LCO at low rate of $50\,{\sim}\,200\,mA\,g^{-1}$ (0.35 C ${\sim}\,1.4\,C).$ However, at high rates of $500 \sim 1000 \text{ mAg}^{-1}$ (3.5 C \sim 7C), the specific capacity of spherical-LCO becomes larger than that of cubic-LCO. This may be attributed to that, at high rate, Li-ion transport holds dominant position and the broken particles existing in spherical-LCO are favorable for Li-ion transport to some extent. While for powder-LCO, the particles are too small to maintain stable structure at interface, which also intensify the interaction between electrolyte and LCO. This is why the discharging capacities of powder-LCO are lower than other two samples at all rates. After 30 cycles at successive-changed charge/ discharge rate, all the samples can recover to the discharge capacities in the first 6 cycles at 50 mAg^{-1} .

Furthermore, for the discharge curves (Fig. 5c, d and e) at different rates, it can be observed that discharge platforms of spherical sample drop slowly, and that of cubic-LCO follow tightly, while the discharge platforms of powder-LCO drop sharply. This could be ascribed to the increased ohmic polarization and cell



Fig. 3. XRD patterns of samples: (a) Co₃O₄, (b) LCO.



Fig. 4. TEM images of samples: (a, b) cubic-LCO, (e, f) spherical-LCO, (c) submicron-sized particles of cubic-LCO, (g) submicron-sized particles of spherical-LCO. SAED patterns: (d) cubic-LCO, (h) spherical-LCO.



Fig. 5. Electrochemical properties of as-prepared samples at 25 °C: (a) cycle performance at a current density of 100 mA g⁻¹, (b) rate cycling performance, (c) discharge curves of cubic-LCO at different rates, (d) discharge curves of spherical-LCO at different rates, (e) discharge curves of powder-LCO at different rates.

polarization accompanying by the increasing of discharge current density. The special structure with less contact area between the LCO and electrolyte relieves the polarization and slows down the generation of solid surface film [10,27,28]. Two types of LiCoO₂ materials with specific morphology show excellent performance in cyclic stability and rate capability, and the spherical-LCO presents a little better performance than the cubic-LCO.

To illustrate the difference in capacity fading among these three materials, electrochemical impedance spectroscopic (EIS) analysis was carried out as shown in Fig. 6. After 6 and 60 full cycles, the cells were charged to 4.3 V, then EIS was measured in the range from 100 kHz to 0.01 Hz. The Nyquist plots display the same profile, two semicircles in the high-frequency region and low-frequency region, respectively. The plots can be fitted with same equivalent



Fig. 6. EIS spectra of the samples in the frequency range between 0.01 Hz and 100 kHz at 25 °C.

circuits as insets shown in Fig. 6. In the equivalent circuit, the R_s is assigned to the electrolyte resistance, the first high-frequency semicircle corresponds to the solid surface film resistance (R_f), and the second low-frequency semicircle is attributed to the charge transfer resistances (R_{ct}) at the interface of electrolyte and electrodes [24]. CPE represents the double layer capacitance and passivation film capacitance. After 6 cycles (Fig. 6a), the plots of three samples are similar, the Rf and Rct values of them are almost the same. While after 60 cycles (Fig. 6b), the R_{ct} values of cubic, spherical and powder LCO are 50.8, 68.7 and 444 Ω , respectively. The R_{ct} value of powder-LCO is much bigger than that of other specific morphology materials, which could be attributed to the agglomerations and polarization of small particles. The spherical and cubic samples have better fluidity and less side-reactions at interfaces, which is beneficial to electron and charge transfer in Liion batteries. While for powder-LCO, active interfacial reaction accompanying with electrochemical polarization and ohmic polarization is disadvantageous for electron and ion transferring.

Furthermore, the corresponding dQ/dV curves for charge/ discharge profiles of three samples at 1st, 5th, 10th and 50th cycles at 100 mAg^{-1} are given in Fig. 7. Three main oxidation/reduction peaks (A/A', B/B', C/C') for each curve could be observed, indicating the existence of four different phases [29–31]. The peaks at 3.95, 4.08 and 4.19V are corresponding to the consecutive phase transitions. Two different hexagonal phases are coexisting around peaks A/A' and the phase transition is related to the electronic effect of $Co^{3+} \rightarrow Co^{4+}$. Peaks of B/B' and C/C' are related to the transition of order/disorder structure accompanying with the phase transition between hexagonal and monoclinic phases [29,32]. As shown in Fig. 7, potential differences between the first cycle and the following cycles in oxidation/reduction peaks are large, which means large polarization between oxidative and reductive peaks, resulting by the formation of solid surface film at first cycle [27,28,33]. The polarization is alleviated in the following cycles. However, the intensity of peaks is gradually decreased and the polarization is increased upon the 50th cycle, which is an indicative of the degradation of LiCoO₂ crystal structure, resulting from the repetition of crystallographic change during Li-ion extraction and insertion processes [29,34–36]. Among three samples. B/B' and C/C' peaks of the cubic-LCO and spherical-LCO are almost invisible after 50 cycles in Fig. 7c, while that of powder-LCO are almost disappeared. It is demonstrated that the cell polarization is serious in the powder-LCO electrode materials, which may be an explanation for the sharply decreased capacity of powder-LCO after 50 cycles. The cubic-LCO and spherical-LCO samples have a better inhibition of the polarization in comparison with the powder-LCO.

In order to further estimate the morphologies of samples after long cycle, the coin cells were disassembled in the glove box after 300 cycles at 100 mA g^{-1} . The positive electrode laminate was

immersed in the dimethyl carbonate (DMC) for several minutes to move away the residual electrolyte, and then the electrode materials were scraped and dispersed in N-2-methyl pyrrolidone (NMP) to remove the binder in electrode. The corresponding



Fig. 7. dQ/dV curves of charge/discharge profiles: (a) cubic-LCO, (b) spherical-LCO, (c) powder-LCO.



Fig. 8. (a) Electrochemical performance of samples, (b) SEM images of powder-LCO sample after 300 cycles at 100 mA g^{-1} (c) SEM images of cubic-LCO sample after 300 cycles at 100 mA g^{-1} , (d) SEM images of spherical-LCO sample after 300 cycles at 100 mA g^{-1} .

discharge cycle and SEM images after 300 cycles of samples are shown in Fig. 8. The discharge capacities of the cubic-LCO and spherical-LCO are 131 and 128 mAh g⁻¹ with a retention of 82% and 83% after 300 cycles, respectively, while the capacity of powder-LCO is only 71.6 mAh g⁻¹ with a retention of 46.5%. There are obvious pulverized and agglomerated phenomena for powder-LCO after 300 cycles. However, the particle structures of cubic-LCO (Fig. 8c) and spherical-LCO (Fig. 8d) remained unchanged after 300 cycles, which demonstrates a stable structure of cubic-LCO and spherical-LCO and it is favorable to cyclic performance.

As Table S1 shown, the $LiCoO_2$ in our work exhibited better cyclic stability and rate capacity performance comparing with those previous literatures. Among them, some $LiCoO_2$ materials are micron-sized with irregular morphology, and others possess specific morphology but most of their electrochemical performances are not so excellent. The $LiCoO_2$ materials with higher capacity are always charged to higher voltage, so the capacity retention is poor.

For example, the Ref. [S3] reported flake-like $LiCoO_2$ (about 10 µm) synthesized by a sacrificial template method, this $LiCoO_2$ delivered a discharge capacity of 179 mAh g⁻¹ at 0.1 C, but only 116 mAh g⁻¹ at 5 C even with a high cutoff voltage up to 4.5 V. The reported flake-like $LiCoO_2(2-4 \mu m)$ in Ref. [S7] exhibited a discharge capacity of 163 mAh g⁻¹ at 0.1 C rate in a voltage window of 2.5–4.4 V, but the discharge capacity is less than 60 mAh g⁻¹, when the rate is up to 5 C. In our work, the discharge capacities of cubic and spherical $LiCoO_2$ are 112 and 124 mAh g⁻¹ at 1000 mA g⁻¹(7 C), and the cutoff voltage is only 4.3 V.

In the Ref. [S8], $20 \,\mu$ m spherical LiCoO₂ was synthesized. The initial discharge capacity is $148 \,\text{mAh g}^{-1}$ at 0.2 C rate with a capacity retention of 97.6% after 40 cycles. Although the sample showed excellent cyclic stability, however the initial capacity at 0.2 C is lower than that of our samples at the rate of 0.7 C and the data after 40 cycles was not given.

As for the reports about nano-sized $LiCoO_2$ in Ref. [S4] and Ref. [S6], the discharge capacities of samples are lower than that of ours

at low rate. The Ref. [S9] delivered an initial discharge capacity of 166 mAh g⁻¹ at a rate of 0.1 C, but the capacity retention is only 81% after 50 cycles. In conclusion, we can believe the $LiCoO_2$ in our work exhibited excellent electrochemical performance.

4. Conclusion

In summary, the cubic and spherical lithium cobalt oxides were successfully synthesized by a simple two-step method including regular Co₃O₄ preparation and subsequent lithiation process. Asprepared cubic-LCO and spherical-LCO are in a range sizes of $10 \sim 15 \,\mu$ m. The LCO particles composed of small primary particles with a size of about 1 µm inherit the morphologies of Co₃O₄ precursor materials perfectly. The above two LCO materials show much better performance than the LCO material prepared by commercial Co₃O₄ as cobalt source. The cubic-LCO and spherical-LCO deliver a same capacity of above 150 mAh g^{-1} , with capacity retention of 92.1% and 90.6% after 100 cycles, respectively. In contrast, the powder-LCO also delivers a capacity of 153.2 mAh g^{-1} at the first cycle, but only 112.0 mAh g^{-1} remains with a retention of 73.1% after 100 cycles. The cubic-LCO and spherical-LCO also exhibit excellent rate capability at large current densities, attributing to the better fluidity and less side-reactions at interfaces between electrolyte and LCO, which alleviates the polarization in comparison with powder-LCO. After 300 cycles, the morphologies of cubic-LCO and spherical-LCO are still maintained, which is also responsible for good electrochemical property. Therefore, we can believe the morphology-controllable LCO will have a promising prospect as the cathode materials for lithium-ion batteries.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. electacta.2016.05.085.

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