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Preparation and characterization of high-density spherical $LiCoO_2$ cathode material for lithium ion batteries

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Abstract

The high-density spherical $LiCoO_2$ is expected as an important direction for $LiCoO_2$ cathode material. Spherical $Co(OH)_2$ powders were prepared via a "controlled crystallization" method using $Co(NO_3)_2$, NaOH and NH_3. To mix $Co(OH)_2$ and lithium sources in a molar ratio of Li:Co = 1.05:1.00, the Li_2CO_3 was uniformly coated on the surface of the spherical $Co(OH)_2$ precursor using $LiOH\cdot H_2O$ and NH_4HCO_3. The mixed powders were sintered at 700–800 °C for 12–16 h to obtain spherical $LiCoO_2$ powders. The structures of $Co(OH)_2$, Li_2CO_3 coated $Co(OH)_2$ and $LiCoO_2$ were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Electrochemical test of charge–discharge proved the spherical $LiCoO_2$ cathode material had excellent electrochemical performance. At the current of 0.2 and 1.0 C, the cathode material showed initial discharge capacity of 148.4 and 141.7 mAh g^{-1}, and retention of 97.6 and 91.7% after 40 cycles, respectively. The lax pile-density and tap-density of the powders are as high as 1.9 and 2.8 g cm^{-3}, respectively, which are remarkably higher than the non-spherical $LiCoO_2$ powders available as commercial cathode materials. The high-density spherical $LiCoO_2$ cathode material can be used in the lithium ion batteries to greatly increase the batteries' energy density.

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1. Introduction

Though $LiCoO_2$ cathode material has been widely used in lithium ion batteries, there are still a lot of publications [1–14] reporting new methods to further improve the material's performance. The surface modification [6–9], metal ion substitution [10–14] have draw a lot of attention. The high specific capacity, long cycling life, high charge–discharge rate and safety are expected by the researchers. However, little attention has been fixed on particle morphology in relation to high density.

The high energy density lithium ion batteries need $LiCoO_2$ cathode materials with both high specific capacity and high density. The commercialized $LiCoO_2$ powders are usually prepared via conventional solid state reaction of mechanically mixed lithium compounds and cobalt compounds. The obtained $LiCoO_2$ powders always show irregular particle morphology with broad particle size distribution. According to our test, the lax pile-density and tap-density of the powders are usually 1.0 and 2.2–2.4 g cm^{-3}, respectively. The low density of $LiCoO_2$ cathode materials limits the energy density of lithium ion batteries.

As has been reported in our previous publication [15], the particle morphology is a very important factor on the density of the $LiNi_{0.8}Co_{0.2}O_2$ powders. The powders composed of spherical particles have higher density than the powders composed of irregular particles. The reasons may be as follows. In general, there are serious agglomeration and "bridge formation" of particles within the powders composed of irregular particles. The phenomena result in a lot of vacancies among the particles and the bad fluidity of the powders. In contrast, there are much less agglomeration and "bridge formation" of particles within the powders composed of spherical particles because the spherical particles have less contacting interface among each other. The phenomena result in less vacancy among the particles and the excellent fluidity of the powders. The spherical powders have higher density because there is smaller quantity of space within the powders. Thus, to obtain high-density $LiCoO_2$ cathode material, preparing spherical powders is expected as an effective way. In addition, it's easier to coat spherical particles than irregular particles. The coated layer on the surface of spherical particles is well distributed, stable, intact and firm [16]. Thus, surface modification will become a more

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promising way to further improve the spherical $LiCoO_2$ cathode materials' performance. Furthermore, the spherical powders have excellent fluidity and dispersivity, which may be beneficial to manufacture high quality electrode pellets. As a whole, we conclude the spherical $LiCoO_2$ is an important direction for $LiCoO_2$ cathode materials.

In our laboratory, the high-density spherical $LiNi_{0.8}Co_{0.2}O_2$ cathode material has been prepared via a "controlled crystallization"—solid state reaction method [15]. Recently, we synthesized high-density spherical $LiCoO_2$ cathode material via the similar method. In this paper, the preparation, structure and electrochemical performance of the spherical $LiCoO_2$ powders have been discussed in detail.

2. Experimental

To synthesize spherical $LiCoO_2$ powders, we need spherical $Co(OH)_2$ powders as the precursors. Referring to the "controlled crystallization" methods of preparing spherical $Ni(OH)_2$ described in references [17–20], the spherical $Co(OH)_2$ was synthesized as the follows. The solution of $Co(NO_3)_2$ was pumped continuously into a special reactor. At the same time, the solution of NaOH and NH_3 (as the chelating agent) was also pumped into the reactor. $Co(OH)_2$ was obtained according to the reaction:

$$Co(NO_3)_2 + 2NaOH = Co(OH)_2 \downarrow + 2NaNO_3$$

The concentration of the two solutions, average rest time (or the feed-in velocity), agitating intensity, temperature, and pH of the mixture being agitating vigorously in the reactor should be controlled carefully. Thus, the crystallization and growth of $Co(OH)_2$ particles in the reactor could be controlled effectively. The irregular particles changed gradually into spherical particles after enough time of reaction and agitation. The mixture in the reactor was filtered, washed and dried. Thus, the spherical $Co(OH)_2$ powders were obtained. In this work, the "controlled crystallization" parameters were as follows. The concentration of the $Co(NO_3)_2$ solution was 2.0–3.0 $mol\,l^{-1}$. The concentration of the NaOH solution was 4.0–6.0 $mol\,l^{-1}$. The concentration of the NH_3 solution was 0.8–1.2 $mol\,l^{-1}$. The agitating intensity was 50–60 $W\,l^{-1}$. The average rest time was 8–12 h. The temperature was 40–60 °C. The pH was 10.5–11.5.

To synthesize spherical $LiCoO_2$ powders, we will mix spherical $Co(OH)_2$ precursors and lithium compounds (for example Li_2CO_3) uniformly. However, if we use the traditional mechanically mixing methods, such as ball milling, the uniform spherical $Co(OH)_2$ particles will be broken to pieces. Thus, to keep $Co(OH)_2$ precursor and $LiCoO_2$ product particles as ideal spheres, we have to use special mixing methods. In this work, we used a kind of similar "controlled crystallization" method to uniformly coat Li_2CO_3 on the surface of $Co(OH)_2$ precursor. The process was as the follows. The spherical $Co(OH)_2$ powders and distilled water were put into a special reactor and agitated vigorously. The solution of $LiOH{\cdot}H_2O$ was pumped continuously into the reactor. At the same time, the solution of NH_4HCO_3 was also pumped into the reactor. Li_2CO_3 was obtained according to the reaction:

$$2LiOH \cdot H_2O + NH_4HCO_3 = Li_2CO_3 \downarrow + NH_4OH + 3H_2O$$

The obtained Li_2CO_3 was uniformly coated on the surface of spherical $Co(OH)_2$ particles. The mixture in the reactor was filtered and dried. Thus, the Li_2CO_3 coated spherical $Co(OH)_2$ powders were obtained. We can control the quantity of $LiOH{\cdot}H_2O$ and NH_4HCO_3 pumped into the reactor to ensure the Li_2CO_3 and $Co(OH)_2$ being mixed in a molar ratio of Li:Co = 1.05:1.00.

The Li_2CO_3 coated spherical $Co(OH)_2$ powders were sintered at 700–800 °C for 12–16 h to obtain spherical $LiCoO_2$ powders.

Powder X-ray diffraction (XRD, D/max-rB) using Cu Kα radiation was used to identify the crystalline phase and crystal lattice parameters of the $Co(OH)_2$, Li_2CO_3 coated $Co(OH)_2$ and $LiCoO_2$ powders. The particle morphology of the powders was observed using a scanning electron microscopy (SEM, JSM6301F). The lax pile-density and tap-density of the powders were tested using the method described in reference [20].

Experimental test cells for measurements used the cathode with the composition of 80 wt.% $LiCoO_2$, 10 wt.% carbon black, and 10 wt.% PTFE. The separator was a Celguard 2400 microporous polypropylene membrane. The electrolyte was 1 M $LiPF_6$ EC + DEC (1:1, v/v). A lithium metal anode was used in this study. The cells were assembled in a glove box filled with argon gas. The charge–discharge cycling was galvanostatically performed at a current of 0.2 and 1.0 C with cut-off voltages of 3.0–4.3 V (versus Li/Li^+) at 20 °C.

3. Results and discussion

The underside of Fig. 1 shows the XRD spectra of the obtained $Co(OH)_2$ powders. It can be observed that the spectra is almost the same as the spectra of pure β-$Co(OH)_2$. The absence of any other signals indicates there are no else phases in the product. The crystal lattice parameters of the layered β-$Co(OH)_2$ are $a = 3.1867$ Å and $c = 4.6628$ Å.

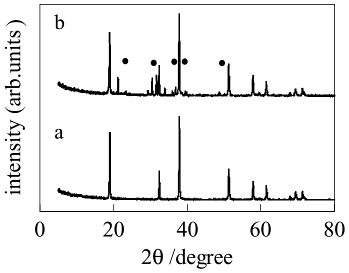

Fig. 1. X-ray diffraction patterns of the $Co(OH)_2$ powders (a) and Li_2CO_3 coated $Co(OH)_2$ powders (b); (●) Li_2CO_3.

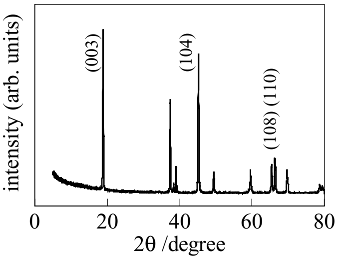

Fig. 2. X-ray diffraction pattern of the $LiCoO_2$ powders.

The upside of Fig. 1 shows the XRD spectra of the Li_2CO_3 coated $Co(OH)_2$ powders. Obviously, this is the composite spectra of the individual spectra of Li_2CO_3 and β-$Co(OH)_2$. The result proves the powders are only the mixtures of Li_2CO_3 and β-$Co(OH)_2$.

The X-ray diffraction pattern of $LiCoO_2$ powders is shown in Fig. 2. The spectra shows the Li_2CO_3 coated $Co(OH)_2$ powders calcined at 750 °C for 16 h were well crystallized into phase-pure $LiCoO_2$ powders without any development of minor phases. The spectra also shows a large integrated intensity ratio $I(0\,0\,3)/I(1\,0\,4) = 1.45$ and a clear split of the (1 0 8) and (1 1 0) peaks which are indicative of order layered structure. The crystal lattice parameters of the layered $LiCoO_2$ are $a = 3.1867$ Å and $c = 14.0643$ Å.

According to X-ray diffraction analysis, $Co(OH)_2$ and $LiCoO_2$ are both hexagonal system. They have very similar order layered structure. During the heat treatment of Li_2CO_3 coated $Co(OH)_2$ powders, the CoO_2 layer framework of $Co(OH)_2$ holds the line, while the H^+ is substituted by Li^+ and the Co^{2+} becomes Co^{3+}. The similar layered structure of precursors and products is the reason of easier synthesizing process of $LiCoO_2$ from $Co(OH)_2$. The order layered structure of $Co(OH)_2$ precursor ensures the order layered structure of $LiCoO_2$, as has been indicated by the X-ray diffraction patterns.

Fig. 3 shows the morphology of the $Co(OH)_2$ powders. The powders are composed of well-dispersed spherical particles. It is tested the particle size distribution is $D_{10} = 9.3\,\mu m$, $D_{25} = 11.8\,\mu m$, $D_{50} = 14.6\,\mu m$, $D_{75} = 17.4\,\mu m$ and $D_{90} = 19.8\,\mu m$. Each of the spherical particles is made up of a large number of sheet crystalline grains, as shown in Fig. 3(b). The $Co(OH)_2$ powders are amaranthine, with excellent fluidity and dispersivity. It is tested that the lax pile-density and tap-density of the powders are as high as 1.8 and 2.3 g cm^{-3}, respectively. The high-density precursor is the precondition of high-density product.

Fig. 4 shows the morphology of the Li_2CO_3 coated $Co(OH)_2$ powders. Almost all the spherical particles are uniformly coated by Li_2CO_3 and become larger and rough, as shown in Fig. 4(a). Fig. 4(b) and (c) show the surface coated Li_2CO_3 have nubby crystalline grains. Within the mechanically mixed Li_2CO_3 and $Co(OH)_2$ powders, Li_2CO_3 particles and $Co(OH)_2$ particles are contacting more loose. During the heat treatment, Li^+ ions have to firstly diffuse from Li_2CO_3 particles' surface to $Co(OH)_2$ particles' surface by a long distance, then diffuse from $Co(OH)_2$ surface into the inside. In comparison, within the Li_2CO_3 coated $Co(OH)_2$ powders, Li_2CO_3 and $Co(OH)_2$ are contacting at the "zero" distance. During the heat treatment, Li^+ ion can easily diffuse from the spherical $Co(OH)_2$ surface into the inside. As a result, lower temperature, shorter sintering time and simpler process are used to produce spherical $LiCoO_2$ cathode materials in this work.

Fig. 5 shows the morphology of the $LiCoO_2$ powders. Fig. 5(a) is very similar with Fig. 3(a), showing the particle morphology, particle size, and particle size distribution of $LiCoO_2$ products are almost the same as the $Co(OH)_2$ precursors. The $LiCoO_2$ powders are also composed of well-dispersed spherical particles. As shown in Fig. 5(b) and (c), each of the spherical particles is made up of a large number of granular crystalline grains which are different

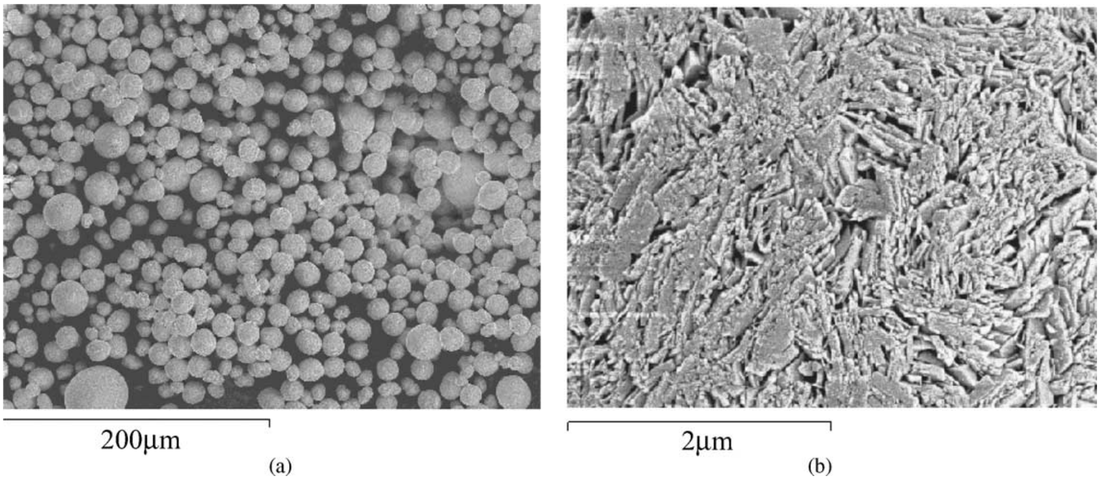

Fig. 3. SEM images of the $Co(OH)_2$ powders.

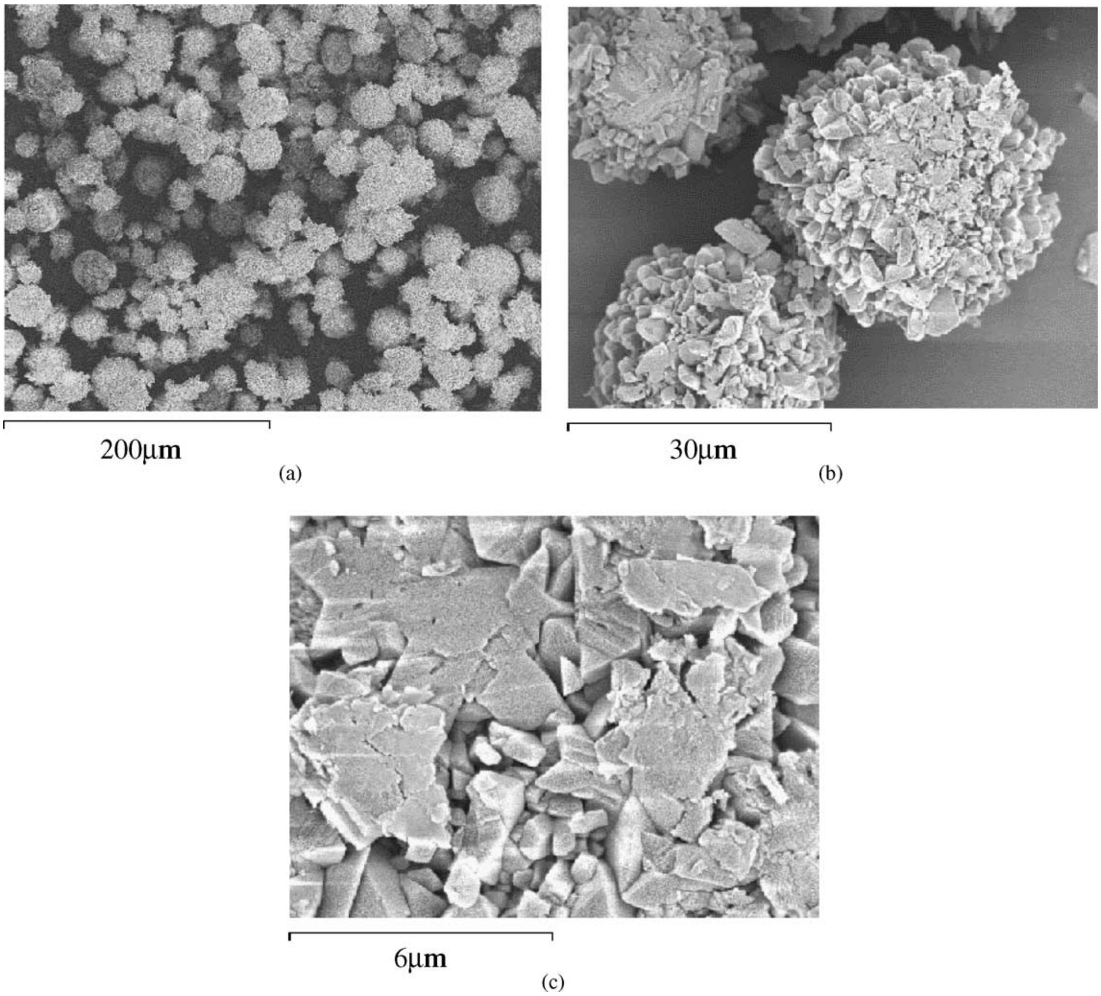

Fig. 4. SEM images of the Li_2CO_3 coated $Co(OH)_2$ powders.

from the sheet crystalline grains of the $Co(OH)_2$ particles. The surface of the spherical particles is very clean, indicating the surface coating Li_2CO_3 has completely decomposed and Li^+ has completely diffused into the inside during sintering. The solid state reaction of Li_2CO_3 and $Co(OH)_2$ is almost 100%, and no remnants phases exist within the $LiCoO_2$ products, which accord with the X-ray diffraction analyzing result of $LiCoO_2$ powders. Fig. 5(c) shows there are some interspaces among the granular crystalline grains. When the $LiCoO_2$ cathode material is used in lithium ion batteries, $LiCoO_2$ contacts with liquid electrolyte. The liquid electrolyte can soak into the interspaces and directly contacts with the crystalline grains. Thus, the Li^+ in the liquid electrolyte can easily diffuse throughout the $LiCoO_2$ particle, which is beneficial to good electrochemical performance of the material at high current density. The spherical $LiCoO_2$ powders are black, with excellent fluidity and dispersivity. It is tested that the lax pile-density and tap-density of the powders are as high as 1.9 and 2.8 g cm^{-3}, respectively, which are remarkably higher than the non-spherical $LiCoO_2$ powders available as commercial cathode materials.

The spherical $LiCoO_2$ cathode materials not only have high density, but also have high specific capacity and good cycling stability. We tested the Li/1.0 M $LiPF_6$ EC/DEC/$LiCoO_2$ cells using spherical $LiCoO_2$ powders prepared in this work. Cycling was carried out galvanostatically at constant charge–discharge current of 0.2 and 1.0 C between 3.0 and 4.3 V at 20 °C. As Figs. 6 and 7 illustrate, at current of 0.2 C, the cathode material has a first cycle charge capacity of 166.3 mAh g^{-1} followed by a discharge capacity of 148.4 mAh g^{-1}. After 40 cycles, the reversible discharge capacity is 144.8 mAh g^{-1}, showing the retention of 97.6%. However, at current of 1.0 C, the cathode material shows initial discharge capacity of 141.7 mAh g^{-1}, and retention of 91.7% after 40 cycles. The result indicates the high-density spherical $LiCoO_2$ cathode material has good electrochemical performance at high charge–discharge current.

The capacity density (mAh cm^{-3}) of the cathode material equals the product of the specific capacity (mAh g^{-1}) and density (g cm^{-3}) of the powders. Since the spherical $LiCoO_2$ cathode material prepared in this work has higher

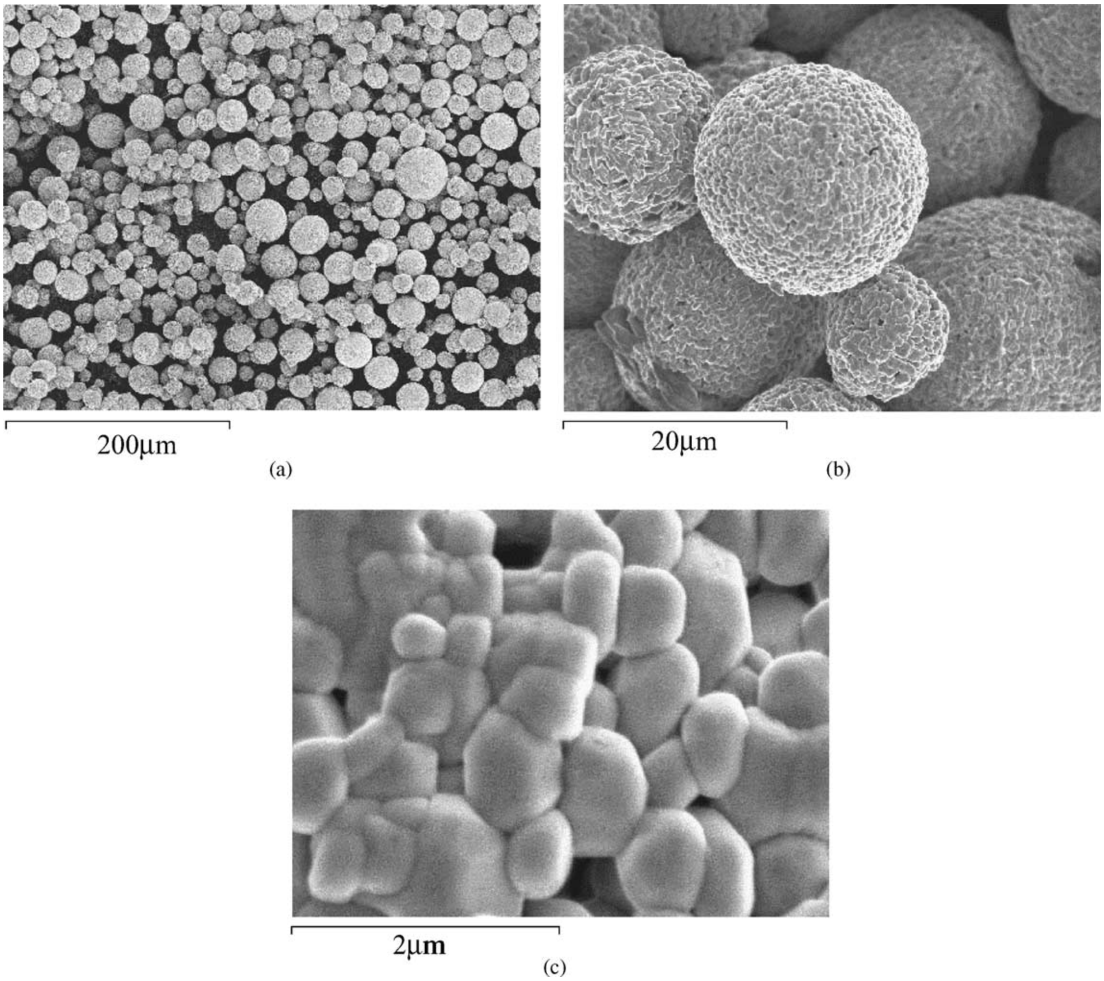

Fig. 5. SEM images of the $LiCoO_2$ powders.

specific capacity and much higher density than commercialized $LiCoO_2$ powders, it has much higher capacity density. The higher the capacity density, the more the energy can be stored in the same volume of the lithium ion batteries. The high-density spherical $LiCoO_2$ cathode material is then a very promising candidate to be used in the lithium ion batteries to greatly increase the batteries' energy density.

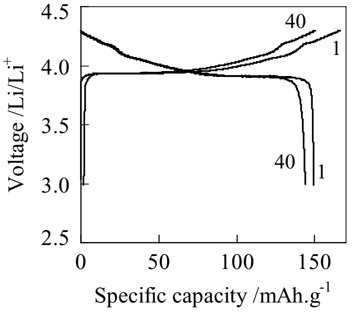

Fig. 6. Charge–discharge curves of the first cycle and 40th cycle at current of 0.2 C.

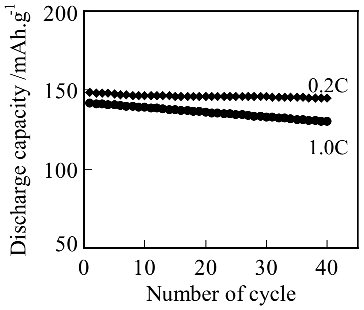

Fig. 7. Variation of specific discharge capacity with number of cycles at current of 0.2 and 1.0 C.

4. Conclusions

The spherical $LiCoO_2$ cathode material has been synthesized via a "controlled crystallization"—surface coating—solid state reaction method. The material has excellent electrochemical performance, including high specific capacity, good cycling stability, and high charge–discharge rate. The most promising virtues of this material are the extraordinary high density and capacity density. The high-density spherical $LiCoO_2$ cathode material provides significant incentive for battery manufacturers to consider it as a very promising candidate to be used in the lithium ion batteries with high power density.

The "controlled crystallization"—surface coating—solid state reaction process proposed in this work has a lot of advantages. By this new process, lower temperature, shorter sintering time and simpler process are used to synthesize high-density spherical $LiCoO_2$ cathode materials with excellent physical and electrochemical performance. We expect the new process can also be used to synthesize high-grade spherical cathode materials, such as $LiNiO_2$, $LiMn_2O_4$, LiV_3O_8, $LiFePO_4$ and the derivatives. Further studies in this field are very promising and significative.

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