

Short communication

Effects of preparation methods of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode materials on their morphology and electrochemical performance

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Received 5 April 2004; accepted 3 May 2004

Available online 19 July 2004

Abstract

$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ as the cathode material for a lithium ion battery was prepared by two different methods, sol–gel method and the solid-state reaction process. The samples were characterized and tested by means of XRD, SEM, particle size analysis, BET, and electrochemical methods. The results of XRD show that both the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ samples prepared by two different methods are isostructural with $\alpha\text{-NaFeO}_2$ with a space group $R\bar{3}m$. The results of electrochemical studies show that the sample prepared by the solid-state reaction process is superior to that by the sol–gel method in electrochemical performance.

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Keywords: Li-ion battery; Sol–gel; Solid-state reaction process; $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$

1. Introduction

Lithium nickel cobalt oxide has been widely studied as the alternative cathode material to LiCoO_2 for lithium-ion batteries because it has the advantage of a large capacity and an inexpensive material cost [1–4]. Extensive studies have been devoted to the preparation by sol–gel methods [5–7] and solid-state processes [8–12]. Generally there has been a strong correlation between the preparation method and the electrochemical performance of these oxide materials. Thus, it is important to compare the electrochemical performance of the materials prepared by different methods.

In this study, the effects of two different preparation methods (sol–gel method and solid state reaction process) of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ on their structure, morphology and electrochemical performance were investigated. It is believed that it will be beneficial to develop an improved, simple and high efficiency synthetic method for $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode material.

2. Experimental

2.1. Preparation of cathode materials

$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders were prepared by two different preparation methods in this work. For method A

[7], the sample was prepared by the sol–gel method using citric acid as a chelating agent. Lithium hydroxide, cobalt hydroxide (CP) and nickel hydroxide (CP) were used as starting materials. Hydroxides of Ni and Co in stoichiometric amounts were dissolved in distilled water, and mixed well with citric acid (the acid-to-metal ions ratio was 1:1), which was also dissolved in distilled water. The mixture was stirred at 353 K for 3 h to form a transparent dark-green solution. Then, the solution of lithium hydroxide were added to the above mixture, and stirred at 353 K for 6 h to form a sol, and then to a gel under constant heating and stirring to evaporate water for about 12 h. The gel was heated at 393 K for 12 h to form a dry-gel, which was put into a Mullf oven for pre-calcination at 773 K for 6 h. Lastly, the dark-brownish decomposed powder was heated in a horizontal quartz tube oven and calcinated at 948 K for 24 h with a fixed oxygen flux (500 sccm/min). For method B, the sample was prepared by the solid-state method, which used lithium hydroxide, cobalt hydroxide (CP) and nickel hydroxide spheres (industrial grade, Changsha Research Institute of Mining and Metallurgy, China) as starting materials. The powders of starting materials in stoichiometric amounts were mixed well by ball milling at 500 rpm for 6 h to form a powder mixture. Then, the powder mixture was heated in a horizontal quartz tube oven and calcinated at 973 K for 24 h with a fixed oxygen flux (500 sccm/min). All of the chemicals were AR grade unless mentioned otherwise.

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2.2. Characterization

The XRD patterns of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ samples were obtained using a Rigaku Rotaflex D/max-C X-ray diffractometer with a graphite monochromator and $\text{Cu K}\alpha$ radiation operated at 40 kV and 30 mA.

The morphology of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particles were observed with a scanning electron microscopy (SEM) (LEO 1530 Field Emission Scanning Electron Microscope, Oxford Instrument) operated at 15 kV.

The particle size and particle size distributions were obtained using a laser granulometer (CILAS-1604L) which is based on a laser wavelength of 830 nm, power of 3 mW, and a multielement 42-channel detector.

The specific area of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ samples were deduced from nitrogen adsorption experiments (BET method) at boiling temperature (77 K).

2.3. Electrochemical measurements

The capacity and cyclability of the prepared materials were assessed using CR2025 coin cells. The cathode was prepared by mixing 85% of the active material with 10% carbon black and 5% poly(vinylidene fluoride) (PVDF). The mixture was made into a slurry by ball milling using *N*-methyl-2-pyrrolidone (NMP) (water content was below 0.01 wt.%) as the solvent. The electrodes were formed by coating the slurry onto Al foils and pressing at 16 MPa after drying overnight at 393 K in a vacuum. The cells were assembled with the cathode as prepared, with lithium metal as the anode, and with Celgard 2400 film as a separator. The electrolytes were 1 M LiPF_6 dissolved in EC + DMC (1:1 volume ratio). Cell assembly was carried out in an argon-filled glove box (Master 100 Lab, Braun, Germany), where water and oxygen concentrations were kept less than 3 ppm. Charge–discharge testing was performed galvanostatically at various charge and discharge rates (0.2C and 1C rate) between 3.0 V and 4.3 V by an Arbin BT-2043 battery test system.

3. Results and discussion

3.1. XRD characterization

XRD patterns of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ compounds prepared by methods A and B are shown in Fig. 1. All of the patterns can be indexed to a single phase of the $\alpha\text{-NaFeO}_2$ type with space group $R\bar{3}m$. As reported in the literature [13,14], the ordering of the structure is indicated from the XRD spectra with the intensity ratios of $I_{(003)}/I_{(104)}$, the ratios of lattice parameters of c/a and the degree of either (108)/(110) or (006)/(102) peak splitting. The intensity ratios of $I_{(003)}/I_{(104)}$ and the ratios of lattice parameters of c/a of the materials prepared by two different preparation methods are listed in Table 1. For the compounds pre-

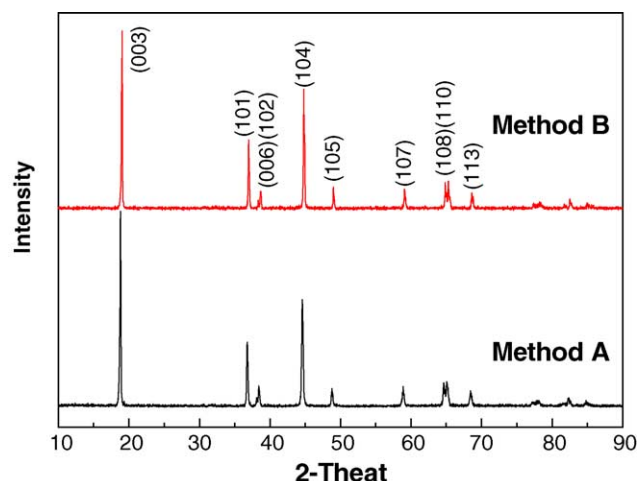


Fig. 1. X-ray diffraction patterns of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ materials prepared by methods A and B.

pared by methods A and B, there is no distinct difference in the ratio of $I_{(003)}/I_{(104)}$, the ratios of lattice parameters of c/a and the degree of either (108)/(110) or (006)/(102) peak splitting. This indicates that both $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ compounds prepared by methods A and B formed a pure phase with good crystallinity.

3.2. Electrochemical studies

The electrochemical properties of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ compounds prepared by methods A and B were tested galvanostatically at various charge and discharge rates (0.2C and 1C rate) between 3.0 V and 4.2 V. The corresponding charge–discharge curves of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ compounds prepared by methods A and B are shown in Figs. 2 and 3, respectively. The effects of the preparation methods on the cycle life of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ at various charge and discharge rates (0.2C and 1C rate) are shown in Figs. 4 and 5.

When cycled at the 0.2C rate, the materials prepared by methods A and B all have a high first discharge capacity. The first discharge capacity is 187 and 185 mAh/g, respectively. But the capacity retention of the material prepared by method B is superior to that of method A. After 100 cycles, the discharge capacity of the material prepared by method B is 158 mAh/g and the capacity retention is 85.4%, however, the material prepared by method A is only 143 mAh/g and the capacity retention is 77.3%. When cycled at the 1C rate, the material prepared by method B has a higher first discharge capacity than that of method A. The first discharge

Table 1

Intensity ratios of (003) to (004) ($I_{(003)}/I_{(104)}$), lattice parameter a , c and c/a ratios of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ materials prepared by methods A and B

Preparation method	$I_{(003)}/I_{(104)}$	a	c	c/a
A	1.45	2.876	14.180	4.93
B	1.45	2.879	14.194	4.93

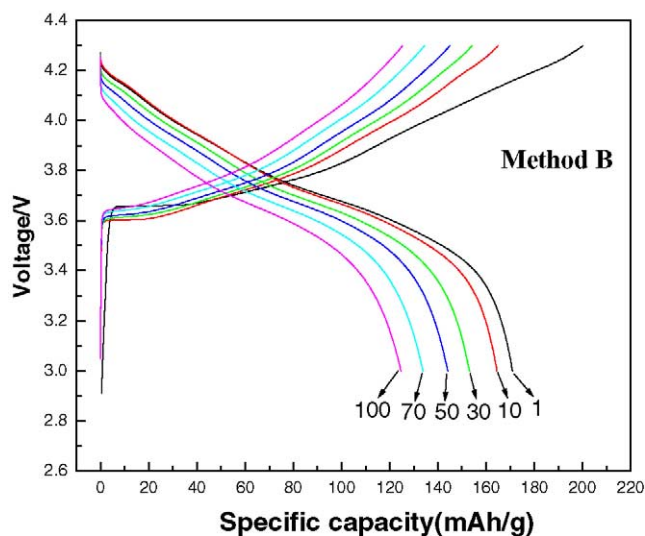
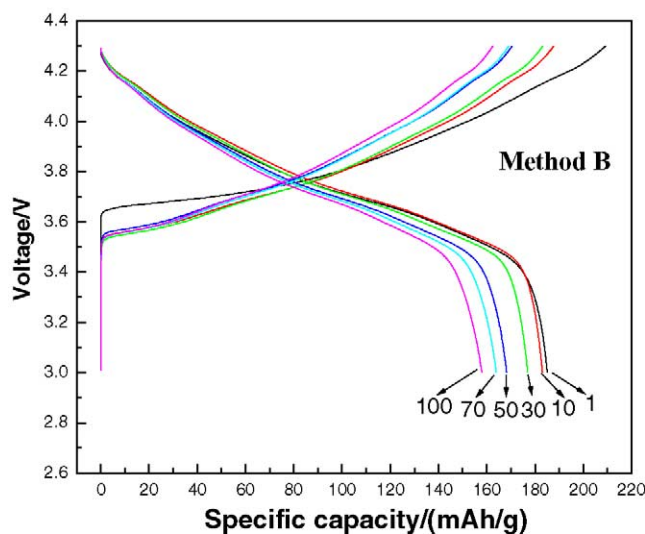
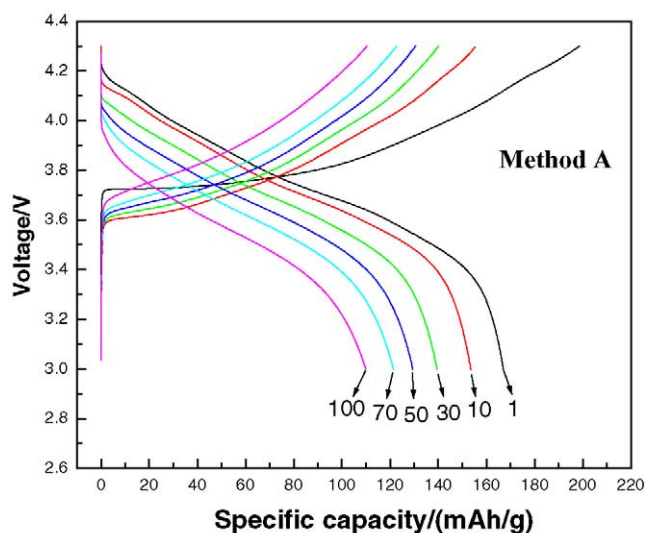
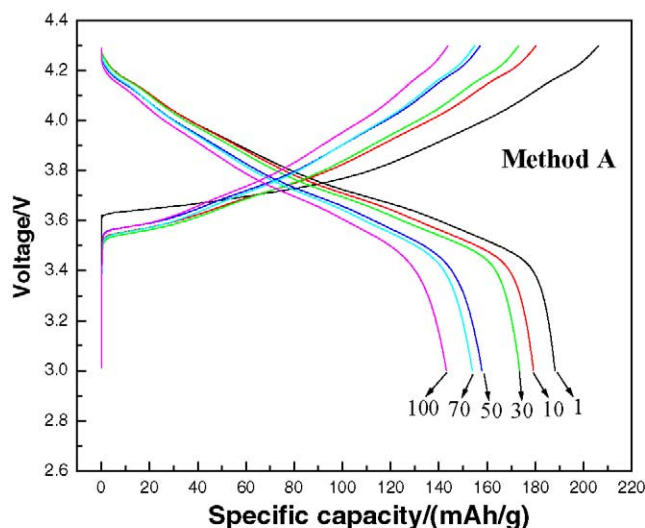


Fig. 2. Charge–discharge curves of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ materials prepared by methods A and B with a $0.2C$ ($\sim 36\text{mA/g}$) current at the range of 3.0V – 4.3V .

Fig. 3. Charge–discharge curves of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ materials prepared by methods A and B with a $1C$ ($\sim 180\text{mA/g}$) current at the range of 3.0V – 4.3V .

capacity of the material prepared by methods A and B is 167 and 171 mAh/g, respectively. At the same time, the capacity retention of the material prepared by method B is apparently superior to that by method A. After 100 cycles, the discharge capacity of the material prepared by method B is 124 mAh/g and the capacity retention is 72.7%, however, the material prepared by method A is only 110 mAh/g and the capacity retention is 65.9%. This shows that the electrochemical performance of the materials prepared by method B is superior to that of method A whether with low or high charge–discharge rate (i.e. $0.2C$ and $1C$).

Normally, the crystal structure and morphology are two main factors which affect the electrochemical performance of the materials. As the results of XRD show that there is no distinctive difference in the crystal structure of the materials prepared by methods A and B, we think that the difference in the morphology may be the main factor which

results in the difference in the electrochemical performance of the materials prepared by methods A and B. In order to study the effects of preparation method of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode materials on their morphology, the morphology of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powder materials prepared by methods A and B were studied by means of SEM, particle size analysis and BET methods.

3.3. SEM examination

Scanning electron microscopy pictures of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powder materials prepared by methods A and B are shown in Fig. 6. Typical SEM micrographs showed that all the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ compounds prepared by methods A and B comprise secondary particles that are composed of faceted primary particles. But there is an obvious difference in particle morphology, particle size and particle size distribution

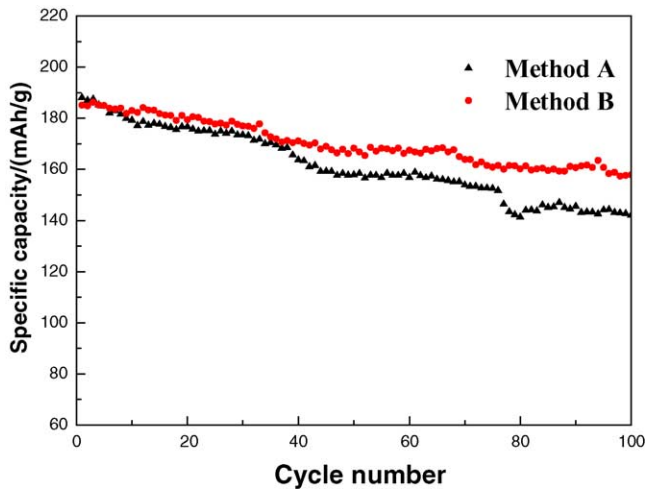


Fig. 4. Specific discharge capacity as a function of cycle number for $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ materials prepared by methods A and B with a 0.2C ($\sim 36 \text{ mA/g}$) current at the range of 3.0 V–4.3 V.

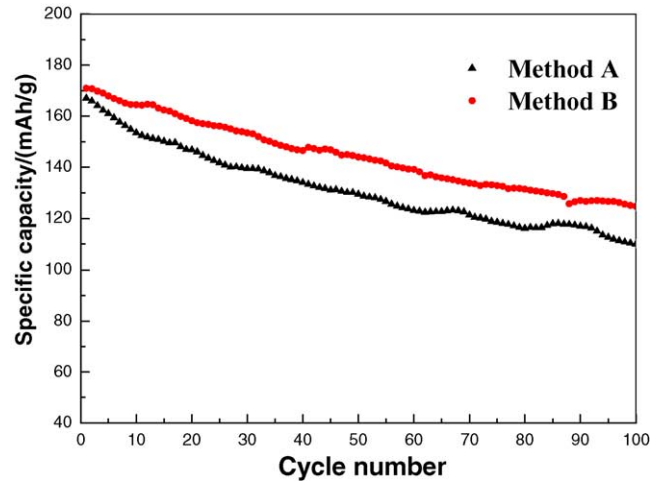


Fig. 5. Specific discharge capacity as a function of cycle number for $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ materials prepared by methods A and B with a 1C ($\sim 180 \text{ mA/g}$) current at the range of 3.0 V–4.3 V.

among the materials prepared by methods A and B. The secondary particles prepared by method A are irregularly faceted pebbles (Fig. 6a), whereas by method B are irregularly spherical (Fig. 6c). The particle size of the materials

prepared by method B is more uniform than that by method A. Compared with method A, the structure of the material prepared by method B is looser (Fig. 6b and d). It may facilitate electrolyte soaking into particles and the insertion

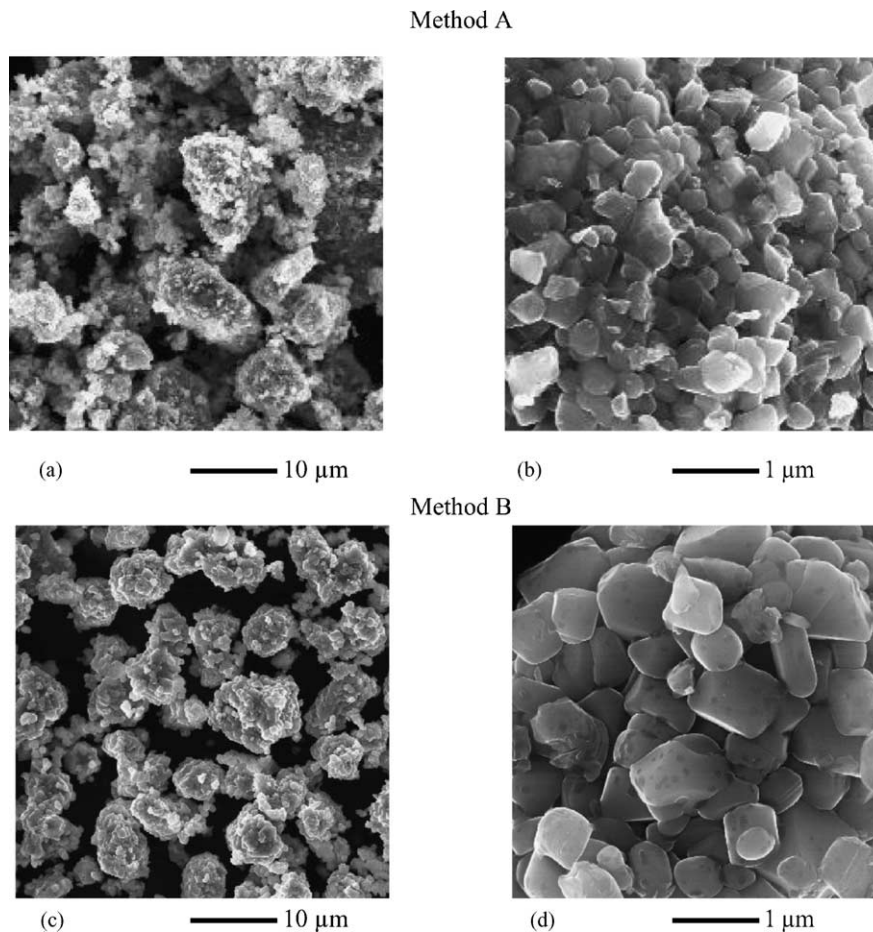


Fig. 6. SEM images of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ which were prepared by method A: (a) 500 \times , (b) 5000 \times , and by method B: (c) 500 \times , (d) 5000 \times .

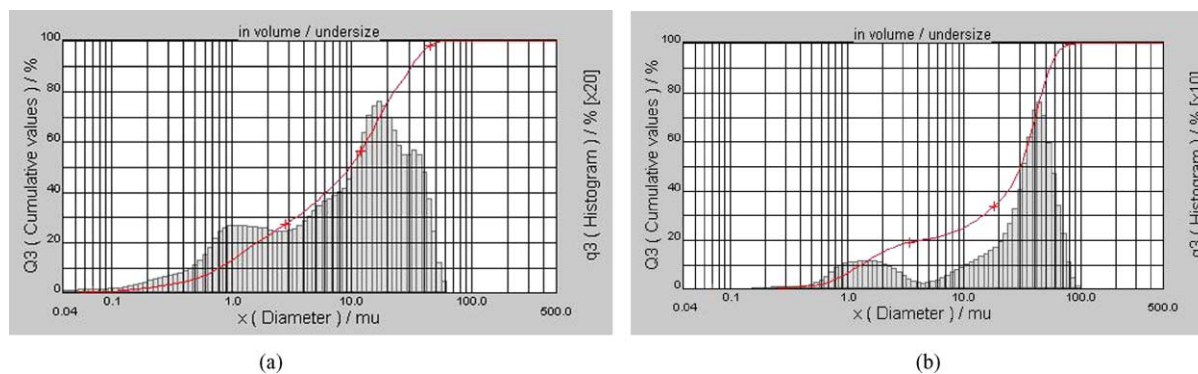


Fig. 7. Particle size distribution of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ synthesized by methods A (a) and B (b).

and de-insertion of lithium ions during the charge–discharge process and hence may improve the electrochemical performance of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ material.

3.4. Particles size studies

The particle size and particle size distributions of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ compounds prepared by methods A and B are shown in Table 2 and Fig. 7. The average particle size of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ compounds prepared by methods A and B are 9.65 and 30.36 μm based on the experimental analysis, respectively.

3.5. BET examination

The specific area of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ compounds prepared by methods A and B are 1.4765 and 1.0708 m^2/g , respectively. It has been known that the electrolytes decompose on the surface of the cathode and form surface layers during the charge–discharge cycles, which was the main cause of capacity fade [15,16]. The capacity fading also occurs by active material dissolution and phase changes of the materials. The specific area of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ compounds prepared by method B is less than the specific area of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ compounds prepared by method A. Less specific area can reduce the interface of the cathode materials with the electrolytes, and reduce the decomposition of electrolytes and the dissolution of active material. This decreases the capacity fade and improves the cycle performance of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode material.

Table 2
Particle size of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ materials prepared by methods A and B

Preparation method	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)
A	0.79	9.65	31.46
B	1.31	30.36	54.18

4. Conclusions

$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ as the cathode material for lithium ion battery was prepared by the sol–gel method (method A) and the solid-state reaction process (method B). The results of XRD showed that both $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ compounds prepared by methods A and B all formed a single phase with good crystallinity. The effects of preparation methods on their morphology and electrochemical performance were investigated. The results showed that the morphology (such as particle shape, particle size, particle size distribution and specific area) of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ compounds prepared by method B was superior to that by method A, which resulted in the electrochemical performance of the materials prepared by method B being superior to that of method A. At the same time, the process of method B is simpler than method A. Method B has been shown here to be a promising technique for preparation of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode materials with enhanced electrochemical performance.

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