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Synthesis of novel high-voltage cathode material $LiCoPO_4$ via rheological phase method

Long Tan[a], Zhimei Luo[a], Haowen Liu[a,*], Ying Yu[b]

[a] Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission & Ministry of Education, Hubei Province, South-Central University for Nationalities, Wuhan 430074, PR China
[b] Department of Physics, Center of Nano-Science and Technology, Central China Normal University, Wuhan 430079 PR China

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ABSTRACT

For the first time, rheological phase method, a simple and effective route, is applied to synthesize novel cathode material $LiCoPO_4$. X-ray diffraction spectrometer (XRD), X-ray photoelectron spectrometer (XPS), transmission electron microscope (TEM) and electrochemical impedance spectroscopy (EIS) are taken to investigate this material, respectively. XRD figure shows that the rheological sample is better crystallized than the solid-state one. XPS result of the rheological sample exhibits that the valence of Co is 2+. TEM images show that better dispersed particles with smaller size can be formed by rheological method comparing to the solid-state route. Charge–discharge test is carried out in the range of 3.0–5.0 V at 0.2 mA cm^{-2}. The initial discharge capacity for rheological phase and solid-state powder is 71.5 and 30.9 mAh g^{-1}, respectively. The better electrochemical property should be ascribed to the better crystallized rheological phase production with better dispersed and smaller particles, which can greatly facilitate the diffusion of Li^+.

1. Introduction

With the increasing demand for electric and hybrid electric vehicles to resolve energy and environmental problems, cathode material with high specific energy density, high power density, and excellent thermal stability is necessary for lithium-ion batteries (LIBs) [1]. Research of cathode materials, such as $LiCoO_2$, $LiMn_2O_4$, $Li_3V_2(PO_4)_3$, $LiFePO_4$, $LiCoPO_4$ and others lithium metal (metal = Ni, Co, Mn etc.) mixed oxide compounds, has been the hot spot, recently [1–9]. Among these materials, the $LiCoPO_4$ with an ordered olivine structure has the highest work voltage of 4.8 V [7], far above that of the other materials (3.4–4.1 V), which can increase the energy and power density of LIBs. Additionally, $LiCoPO_4$ with the framework based on poly-anion has more stably structure as the poly-anion phosphate is larger than O^{2-} ions comparing to the domain commercial cathode material $LiCoO_2$ [8]. Thus, $LiCoPO_4$ would be candidate for the new high-voltage cathode material with superior capacity [9].

Besides, the synthesis method also plays a significant role in the commercialization of this cathode material. Generally, the solid-state route is well known to be one of the simplest methods, which has been applied widely in synthesis of inorganic materials [10–13]. However, several disadvantages exist for this conventional method, such as heterogeneous composition and severe agglomerations between particles [9]. In this paper, we introduce another simple method, rheological phase method, to synthesize $LiCoPO_4$. This method has been widely applied in synthesizing other cathode materials, such as $Li_3V_2(PO_4)_3$ [14], $LiNi_{0.8}Co_{0.2}O_2$ [15,16], $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ [17,18]. Our group also has successfully synthesized $LiFePO_4$ using this simple route [19]. All these results reveal that excellent electrochemical properties could be obtained for the cathode materials synthesized by rheological phase method without the disadvantages of solid-state method [14–19]. To our knowledge, the investigation of synthesizing $LiCoPO_4$ by the rheological phase method has never been reported until now.

In this paper, we successfully synthesize the $LiCoPO_4$ via rheological phase method. Solid-state method is also used to synthesize $LiCoPO_4$ as a contrast to rheological phase reaction method. The influence of these two methods on the structure, morphology and electrochemical properties of $LiCoPO_4$ is investigated.

2. Experimental details

$LiCoPO_4$ was prepared using $Co(NO_3)_2{\cdot}6H_2O$, $NH_4H_2PO_4$ and $LiOH{\cdot}H_2O$ as the raw materials. Stoichiometric $Co(NO_3)_2{\cdot}6H_2O$ (4.365 g), $NH_4H_2PO_4$ (1.726 g), $LiOH{\cdot}H_2O$ (0.630 g) and 6.3 g of citric acid (Co:Li:citric acid = 1:1:2) were initially mixed roughly in an agate mortar. Then, about 2 ml distilled water were added to form rheological phase mixture which reacted in an oven at 150 °C for 6 h. The resulting precursors were calcined at 750 °C for 10 h.

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* Corresponding author. Tel.: +86 27 6784 2752; fax: +86 27 6784 2752.
E-mail address: liuhwchem@mail.scuec.edu.cn (H. Liu).

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$LiCoPO_4$ was also synthesized by a conventional solid-state method. The raw materials and proportion were the same as those of the above method. To obtain a pure olivine phase, the full mixed compounds was pre-calcined at 350 °C for 9 h [7], the compound was cooled down and ground again. Finally, the obtained precursor was calcined at 750 °C for 10 h.

All the reagents used in experiment were of analytical purity and were purchased from Shanghai Chemical Reagent Company and used without further purification. Powder X-ray diffraction (XRD) analysis using Cu Kα radiation was employed to identify the crystalline phase of the prepared powder with a Bruker D8-advance (German) at room temperature in the range of $10^\circ \leq 2\theta \leq 70^\circ$. The Rietveld analysis used the TOPS R refinement software. X-ray photoelectron spectrometry (XPS) of the reaction products was measured by an X-ray photoelectron spectrometer (Thermo VG Multi Lab 2000 America). Each spectrum was calibrated using the C 1s binding energy at 284.6 eV. The morphology was investigated with a transmission electron microscope (TEM, FEI, TECNAI G220 S-Twin, America). The simulate cells were assembled by using lithium foil as anode in an argon-filled glove box, the as prepared powders mixed with 12% acetylene black and 8% polytetrafluoroethylene (PTFE) as the cathode and 1 M $LiPF_6$ in a 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethylcarbonate (DMC) as the electrolyte, Celgard 2300 membrane as the cell separator. The electrochemical impedance spectroscopy (EIS) analysis was carried out by applying an ac voltage of 5 mV over the frequency range from 0.01 Hz to 100 kHz (BAS, EG and Ginstrument). The charge–discharge cycles were performed at 0.2 mA cm^{-2} in a potential range of 3.0 and 5.0 V using simulate cells. All the electrical measurements were carried out by a battery testing system (RFT-5 V/10 mA, corporation of LuHua electronic equipment, China) at room temperature.

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the XRD patterns of both productions. A single phase which can be indexed on the orthorhombic structure with the space group *Pmnb* is obtained by both routes [20]. It accords well with the theoretical pattern of $LiCoPO_4$ (PDF number: 32-0552). However, it can be obviously seen that the diffraction peaks of rheological powder are stronger and sharper than the solid-state sample which indicates that better crystallized structure was obtained for the rheological powder. It could be explained that the rheological phase process preparing the rheological phase precursor plays a vital role in the development of the better crystallized sample. In this process, the solid and liquid sections are in contact in molecule level, it is convenient for the heat exchange and should facilitate the diffusion of ions dissolved in solvent into the solid particles [17], and then, the crystal structure is improved. The refinement was performed by TOPS R software with a convincible Rwp value (1.721% for rheological phase production and 1.839% for solid-state production), and the lattice parameters of rheological phase production and the solid-state production are $a = 5.9086$ Å, $b = 10.178$, $c = 4.7068$ Å and $a = 5.9036$ Å, $b = 10.188$ Å and $c = 4.7012$ Å, respectively.

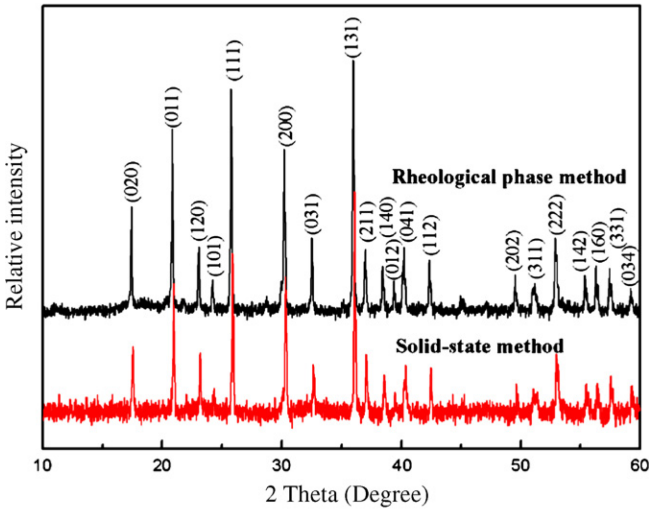

Fig. 1. XRD patterns of $LiCoPO_4$ synthesized by solid-state and rheological method.

3.2. TEM analysis

The morphology of the obtained powder are investigated by the TEM images and displayed in Fig. 2. It can be clearly seen that the rheological production has the well dispersed submicron particles with irregular shape. The average size for this production is about 0.5 μm. For the solid-state production, particles with irregular shape are severe agglomerate. It is difficult to evaluate the particle size. The size of rheological production is smaller than the sample (1–6 μm) obtained by using hydrothermal method [9]. It is obvious that the smaller and better dispersed particles of rheological production should be attributed to the effect of citric acid as a dispersant in the calcination step.

3.3. XPS analysis

Additionally, XPS is used to testify the compositions and valence of elements in $LiCoPO_4$ obtained by rheological phase method. As seen in the Fig. 3, the Co2p (Fig. 3b) binding energy for the sample is 783.2 eV. It is in agreement with the Co^{2+} in $CoF_2{\cdot}4H_2O$, which indicates that the Co in product is 2+. The P2p (Fig. 3c) binding energy is located at 135.4 eV, which explains that the oxide valences for P element are 5+. As for O 1s (Fig. 3d), a sharp peak is detected at 533.0 eV. It suggests that the valence of O element in $LiCoPO_4$

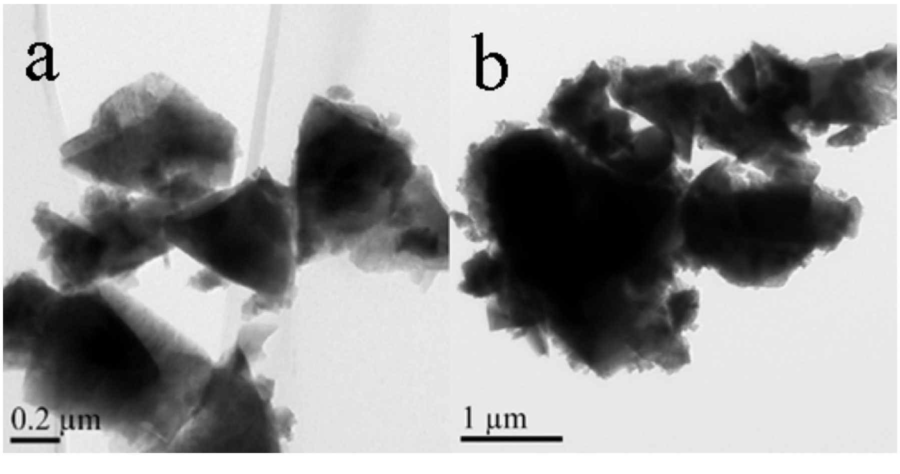

Fig. 2. TEM images of the sample synthesized by rheological (a) and solid-state method (b).

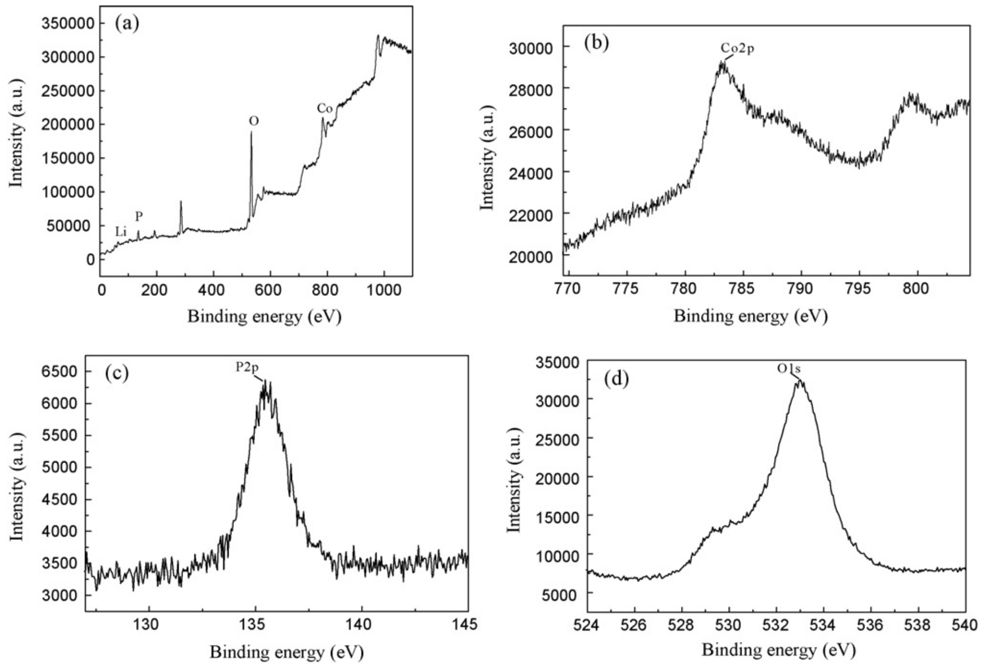

Fig. 3. (a) XPS survey spectrum and (b–d) high-resolution spectrum of Co, P, O of the $LiCoPO_4$ synthesized by rheological method.

is divalent. Combining with the XRD results mentioned above, the olivine $LiCoPO_4$ has been successfully synthesized.

3.4. *Electrochemical property of $LiCoPO_4$*

Initial charge–discharge curves of the $LiCoPO_4$ produced by both methods are displayed in Fig. 4. For the charge curve of rheological phase production, it consists of two plateaus indicating a two-step mechanism of lithium extraction [21,22], one is ~4.80 V and another is ~4.90 V. However, the two-step character is not observed in the discharge curve. Similar results were obtained by Bramnik et al. [21]. For the charge–discharge curve of solid-state production, a one-step mechanism of lithium insertion/extraction is observed. Both one-step and two-step mechanisms of lithium extraction have been observed in the literatures in lithium deficient olive and amorphous structure of the cathode material [21,22]. The initial discharge capacity is 71.5 mAh g^{-1} and 30.9 mAh g^{-1} for rheological phase and solid-state production, respectively. These results suggest that the rheological phase method can improve the electrochemical property of $LiCoPO_4$. The poor capacity (71.5 mAh g^{-1}) far below its theoretical value (167 mAh g^{-1}) should be attributed to low electronic conductivity and Li^+ diffusivity of $LiCoPO_4$ [1,23]. In our experiments, the capacity loss in the first cycle is noticeable, and the charge capacity is higher than the theoretical capacity of $LiCoPO_4$ for the both prepared materials. This behavior is due to the strong electrolyte decomposition [21,22,24,25], which leads to the irreversible charge/discharge process.

3.5. *EIS analysis of the pristine materials*

Resistances of the prepared samples, as a significant electrochemical property, are also studied by EIS and the results are displayed in Fig. 5. A semicircle is observed for both samples in

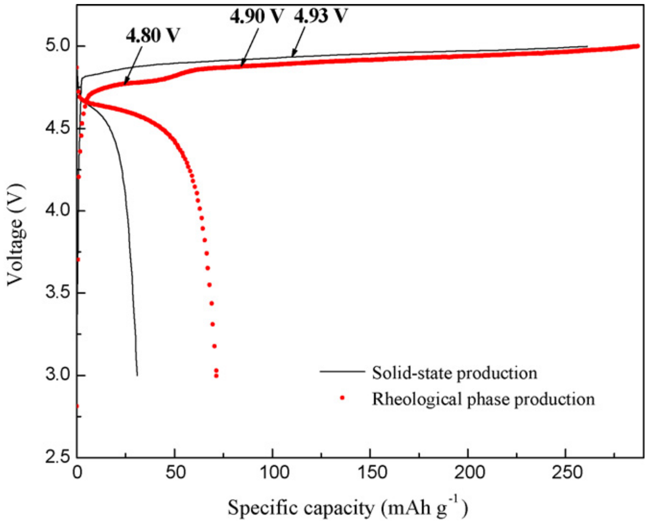

Fig. 4. The initial charge–discharge curves of $LiCoPO_4$ produced by rheological phase method and solid-state method.

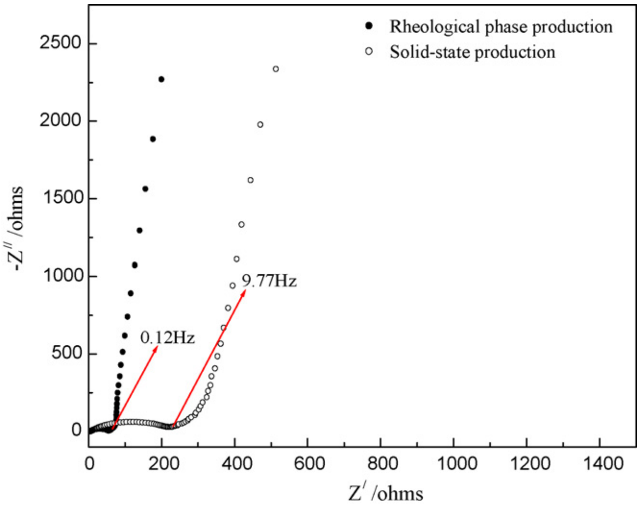

Fig. 5. EIS analysis of the $LiCoPO_4$ synthesized by rheological phase and solid-state method.

the high frequency domain, and its origin has been ascribed to the lithium-ion migration through the interface between the surface layer of the particles and the electrolyte, the inclined line in the low frequency region denotes the Warburg impedance, which is associated with lithium-ion diffusion in the $LiCoPO_4$ particles [26,27]. Obviously, the calculated surface layer resistance (∼80 Ω) for rheological production is much smaller than that of the solid-state one (∼220 Ω). It is obvious that the diffusion of Li^+ which determine the charge–discharge performance is greatly facilitated by rheological phase method. TEM results show that the particles of rheological production are smaller and better dispersed than the solid-state one. Thus, the rheological production and electrolyte are better contact with each other, shortening the Li^+ diffusion distance, which leads to its higher initial discharge capacity than that of the solid-state production.

4. Conclusions

Novel cathode material $LiCoPO_4$ has been synthesized by rheological phase and solid-state method. XRD results show that both of two samples have orthorhombic structure with the space group *Pmnb*, and the rheological production is better crystallized. Particles of rheological production with scale of 0.5 μm are smaller and better dispersed than the solid-state one. Galvanostatic test results show that the initial specific capacity of rheological phase and solid-state production is 71.5 mAh g^{-1} and 30.9 mAh g^{-1}, respectively. The surface layer resistance for the two productions is about 80 Ω and 220 Ω, respectively.

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