

Synthesis of LiCoPO_4 Powders as a High-Voltage Cathode Material via Solvothermal Method

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How to cite this paper: Ke, J.H., Han, Y. and Xie, K. (2017) Synthesis of LiCoPO_4 Powders as a High-Voltage Cathode Material via Solvothermal Method Synthesis of LiCoPO_4 Powders as a High-Voltage Cathode Material via Solvothermal Method. *Journal of Power and Energy Engineering*, 5, 21-27.

<https://doi.org/10.4236/jpee.2017.512004>

Received: November 1, 2017

Accepted: November 14, 2017

Published: November 21, 2017

Abstract

Lithium cobalt phosphate (LiCoPO_4 , LCP), having a high operating potential (4.8 V vs. Li/Li^+), a flat voltage profile and a good theoretical capacity (167 mAh/g), is considered a promising cathode material for improving the energy density of lithium-ion batteries (LIBs) [1] [2]. Here we report a category of method for synthesizing LCP, the solvothermal (ST) method with a binary solvent (deionized water: ethyl alcohol = 1:1), controlling the concentration of cobalt ion in 0.05 mol/L (ST-0.05) and 0.25mol/L (ST-0.25). The material phase was apparently identified via X-ray diffraction (XRD). Observed by scanning electron microscopy (SEM), the grain size of LCP powders synthesizing by solvothermal method with two kinds of the concentration of cobalt ion were $400 \times 400 \times 1000$ nm cuboids (ST-0.05) and $150 \times 150 \times 250$ nm hexagonal prisms containing nanoparticles (ST-0.25), respectively. Discharge capacities of LCP were 76.0 mAh/g (ST-0.05) and 94.5 mAh/g (ST-0.25), in the first cycle at 0.1 C, respectively.

Keywords

Lithium Cobalt Phosphate, Solvothermal Synthesis, High-Voltage Cathode, Lithium-Ion Batteries

1. Introduction

Since the cathode material of Lithium iron phosphate (LiFePO_4 , LFP) was first reported, lithium transition-metal phosphates [2], including the manganese (LMP), cobalt (LCP) or nickel (LNP) based phospho-olivines [3], have been receiving increasing attention as alternative cathode materials for lithium-ion batteries (LIBs) [4]. Compared to LFP (theoretical capacity: 167 mAh/g, gravimetric energy density: 580 Wh/kg) [5], the high-voltage cathode material LCP, which operates at 4.8 V [6] and shows a theoretical capacity of 166.56 mAh/g, provides

the high operating voltage to increase the gravimetric energy density to 800 Wh/kg, about 40% higher than LFP, so that might bring a significant improvement for LIBs [7].

Recently, there were many kinds of approach to synthesizing LCP powders, containing CAM sol-gel [8], hydrothermal method [9], solvothermal method [10] [11], polyol process [12], solid-phase method [13], microwave method [14] and so on. Among these, the mainstream method were hydrothermal method that synthetic crystals at relatively low reaction temperature and uniformity of product composition, phase and microstructure.

2. Experiment

LiOH·H₂O (≥95%, AR), CoSO₄·7H₂O (≥99.5%, AR) and H₃PO₄ (≥85 wt% in H₂O) were used in a Li: Co: P molar ratio of 3:1:1 and 2.5 g/L ascorbic acid (≥99.7%, AR) was added as a reducing agent, controlling the concentration of cobalt ion in 0.05 mol/L (ST-0.05) and 0.25mol/L (ST-0.25). The raw materials were dissolved in a binary solvents composed of deionized water and ethyl alcohol, controlling the initial PH value of solution was 8.5. The as-prepared suspension was poured into a stainless autoclave and sealed, hydrothermally treated at 220°C for 5 h. Testing the remaining solutions, the PH of the solvent environment after the reaction were 6.57 (ST-0.05) and 3.81 (ST-0.25). After natural cooling, the reaction products were washed several times with deionized water and ethanol to get rid of any remaining precursors or organic products. The recovered powders were heated to 700°C with a rate of 5°C/min and held at the temperature for 60 min under argon atmosphere.

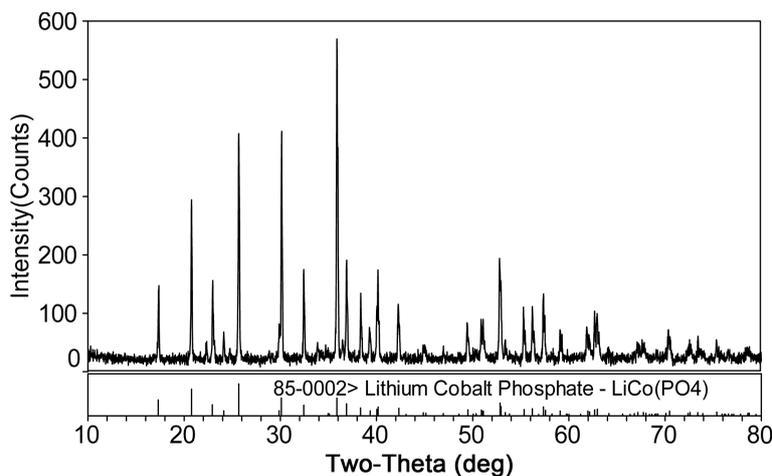
The LCP electrode was made by mixing 80 wt% of the as-prepared LCP powder, 10 wt% acetylene black (Timal) and 10 wt% polyvinylidene difluoride (PVdF, Arkema) in N-methyl-2-pyrrolidone (NMP), and then, was painted onto a thin Al foil and dried at 100°C for 12 h. The LCP composite electrode (15 mm in diameter) was set in a coin cell 2016 with a mixture of ethylene carbonate and ethyl methyl carbonate (volume ratio = 3:7) containing 1.2 mol·dm⁻³ LiPF₆ as an electrolyte, with lithium metal as a negative electrode and with polyethylene film as a separators (PE, Celgard 2400). Galvanostatic cycling was performed between 3.5 V and 5 V for 5 cycles at C/10 (C rates based on a theoretical capacity of 167 mAh/g). CV measurements were performed up to three cycles at a scanning rate of 0.05 mV/s for a voltage range of 3.0 V to 5.1 V.

X-ray diffraction (XRD) data were collected on a SIEMENS-500 diffractometer using Cu Kα1 radiation ($\lambda = 1.54 \text{ \AA}$), measured in a 2θ range of 10° - 80° (tube current: 200 mA; voltage: 40 kV; sweep rate: 7°/min). Scanning electron microscopy (SEM) image was performed on a HITACHI S-4800 Field Emission Scanning Electron Microscope.

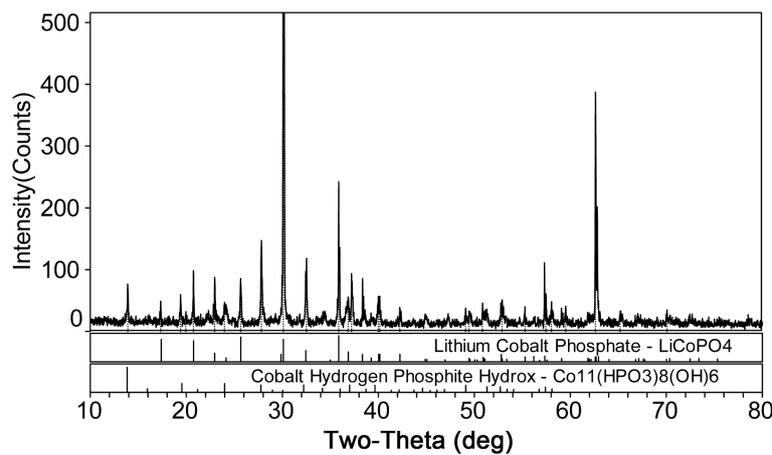
3. Results and Discussion

The X-ray diffraction (XRD) patterns of the as-prepared products were pre-

sented in **Figure 1 (a)** displayed that the XRD peaks correspond to the standard PDF (85-0002) of olivine structure with space group Pnma (62) which means LiCoPO_4 synthesized by solvothermal synthesis with the concentration of cobalt ion in 0.05 mol/L was successfully acquired without any undesirable impurities. **Figure 1(b)** shown that the powders synthesized by solvothermal synthesis with the concentration of cobalt ion in 0.25 mol/L were mainly LCP granule, containing some other unexpected impurities ($\text{Co}_{11}(\text{HPO}_3)_8(\text{OH})_6$). The concentration of raw materials in ST-0.25 was obvious higher than in ST-0.05. During the process of Solvothermal, the excessive concentration of phosphoric acid locally would give rise to the two steps dehydration decomposition under high reaction temperature and pressure conditions. The phosphoric acid dehydration decomposed to pyrophosphoric acid firstly, and then further decomposed to metaphosphoric acid. The process of dehydration decomposition as follows:



(a)



(b)

Figure 1. XRD patterns of LiCoPO_4 synthesized via (a) ST-0.05 and (b) ST-0.025.

Figure 2 displayed the scanning electron microscopy (SEM) of the as-prepared powders before heat treatment. The result verified that powders with an average size of $150 \times 150 \times 250$ nm for hexagonal prisms synthesizing by ST-0.25 were obviously smaller than with $400 \times 400 \times 1000$ nm cuboids synthesizing by ST-0.05. That was attributed to the higher concentration of cobalt ion, providing more necessarily nucleus for the nucleation and growth of the crystal granules. In addition, powders synthesizing by the both methods contained some other small granule, identified as the impurities and uncompleted crystallization granule. That would be solved effectively by the following heat treatment. The powders which formed by ST apparently had well dispersity, giving the credit to the binary solvent (deionized water: ethyl alcohol = 1:1) that homogeneous controlled the grain and morphology by selective adsorption mechanism. During the process of crystallization, the solvent molecules would be adsorbed on some specific surfaces of crystal granules selectively, limiting the growth of grain in some direction. Different solvents would express different results of selection.

Figure 3 revealed charge and discharge curves of LCP (ST). Discharge capacities of LCP were 76 mAh/g (ST-0.05) and 94.5 mAh/g (ST-0.25) in the first cycle at 0.1 C, respectively. The discharge voltage flat of LCP, acquiring from charge-discharge curves, were about 4.72 V (ST-0.05) and 4.67 V (ST-0.25), corresponding to lithium insertion into CoPO_4 to form a mixture of $\text{Li}_{0.67}\text{CoPO}_4$ and LiCoPO_4 phases that was exactly opposite during the process of charge.

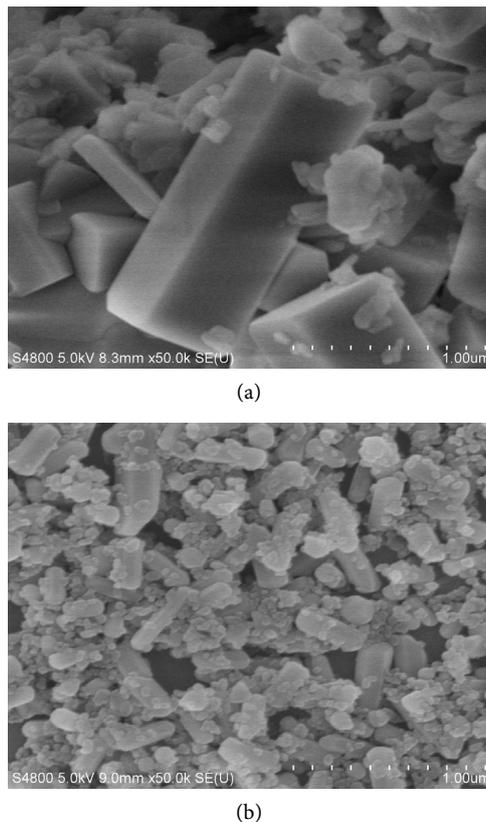


Figure 2. SEM image of LiCoPO_4 synthesized via (a) ST-0.05 and (b) ST-0.025.

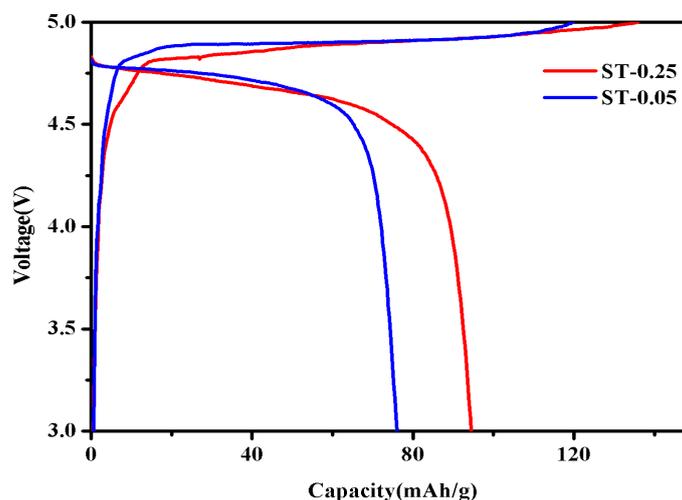


Figure 3. Voltage profiles measured at 0.1 C for the first cycle of the LCP synthesizing by ST-0.05 and ST-0.25.

4. Conclusion

In conclusion, the high-voltage cathode material LCP have been synthesized by a sample solvothermal synthesis method using a variety of 1:1 binary solvent blends of deionized water and ethyl alcohol with the different concentration of cobalt ion (0.05 mol/L, 0.25 mol/L). Compared to LCP powder synthesizing by ST-0.05, LCP powder synthesizing by ST-0.25 expressed smaller grain, higher discharge capacity and narrower diameter distribution, but easier to produce impurities of metaphosphate. The reason for the lower discharge capacity (94.5 mAh/g from ST-0.25) than the theoretical capacity (167 mAh/g) might be the heterogeneous component distribution and temperature, causing the heterogeneous nucleation and growth of LCP crystal particles, finally resulting in wide size distribution and uneven crystals morphology. Furthermore, the pH value of reaction solvent had the great impact on the crystallization, on account of the different case of ionization for phosphoric acid in different PH of solvent. Owing to these, we can improve the electrochemical performance of LCP in the following work by doping, changing a strring assisted modified hydrothermal instrument, adding some surfactants to control the morphology of LCP grain and coating carbon. Furthermore, changing a novel method to prepare LCP might bring a better result, such as the sol-gel-hydrothermal method that has the advantages of both sol-gel and hydrothermal synthesis [15], more specifically, the high degree of crystallinity, well-controlled morphology, high purity, and narrow particle size distribution [16] [17].

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