ISBN: 978-1-948012-12-6

New Materials and Intelligent Manufacturing (NMIM)

Contents List available at VOLKSON PRESS
DOI : <http://doi.org/10.26480/icnmim.01.2018.21.23>
Journal Homepage: <https://topicsonchemeng.org.my/>

HYDROTHERMAL SYNTHESIS OF LITHIUM IRON PHOSPHATE CATHODES AND ITS ELECTROCHEMICAL PERFORMANCE

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ARTICLE DETAILS

Article History:

Received 26 June 2018

Accepted 2 July 2018

Available online 1 August 2018

ABSTRACT

LiFePO₄ powders were prepared via hydrothermal synthesis. The effects of synthesis conditions on structure and electrochemical behavior of LiFePO₄ were studied. The samples were characterized by X-ray Diffraction, Scanning Electron Microscope (SEM) and charge-discharge test. The study showed that LiFePO₄ had an ordered layered structure and good electrochemical properties. The results showed that the performance of the powder was affected by the stoichiometric of the reactants and the synthesis parameters.

KEYWORDS

Hydrothermal synthesis, Lithium ion battery, Cathode material, Olivine LiFePO₄

1. INTRODUCTION

Transition metal oxides, such as LiCoO₂, LiNiO₂ and spinel LiMn₂O₄ have been studied as cathode materials in lithium batteries. These materials have shown good cyclability and high capacity at high potential (around 4V versus Li/Li⁺). Spinel compounds, such as LiMn₂O₄, are promising candidates because of low toxicity and cost compared to LiCoO₂ and LiNiO₂, but they still have problems with Mn dissolution and they are low energy density. Recently, the phosphate LiFePO₄ has been studied as the cathode-active material in Li batteries, because of it is expected low-cost, low toxicity and high theoretical specific capacity of 170 mAh/g [1-4].

LiFePO₄ is one of the olivine formula MNXO₄, where M and N are cations with different sizes. Its structure is composed of PO₄ tetrahedra and FeO₆ octahedra. Each FeO₆ octahedron shares edge with one tetrahedron along c-axis and two corners in the ab-plane. This compound is environmentally benign and cheap, making it ideal for battery applications. A group researchers reported that 0.8 mol of lithium can be reversibly extracted at 0.05 mA/cm² [5]. The polyanion group stabilizes the structure and lowers the Fermi level of this redox couple through the Fe-O-X inductive effect, thus providing a higher voltage. Its discharge voltage is 3.5V, almost 0.7V higher than Li₃Fe₂(PO₄)₃. Since its formula has 1 mol of lithium, it should be charged first, and its theoretical capacity is 170 mAh/g. During the recharge, its volume shrinks only about 6.8%, comparable to that of LiTiS₂, thus minimizing mechanical decrepitation and the resulting loss of electrical contact during cycling.

In all of these studies, LiFePO₄ was synthesized by a solid-state reaction using electric furnaces, which require a lengthy firing at 300~800°C [6,7]. Besides, the solid-state reaction needs N₂ or Ar, which increase the cost of reaction. Comparatively the hydrothermal synthesis cost less, so it is worth to be investigated. In this paper, we exploited the advantages of hydrothermal synthesis, quick easy synthesis at low energy cost and readily scalable. We report the rapid formation of LiFePO₄, where no impurities were observed, making it an excellent alternative to high-temperature synthesis. This method involves reaction at low temperature (100~20°C) for a short period (3h to 10h), which is very good for commercialization of these compounds.

2. EXPERIMENT

2.1 Synthesis procedure

LiFePO₄ was prepared by direct hydrothermal synthesis of FeSO₄, H₃PO₄ and LiOH in the stoichiometric ratio 1.0:1.0:3.0. FeSO₄ and H₃PO₄ solution were mixed first to avoid Fe(OH)₂, because it is easily oxidized to Fe(III), then LiOH solution was added to the mixture with stirring for 1 min. pH was 7.56 and the solution was quickly transferred to reactor for up to 5h at 120°C. After the sample was cooled, the pH was 6.91. The light green precipitate was filtered and air-dried at 40°C for 2h. For several similar syntheses, pH was slightly different, and it had no effect on the final product. Several attempts had been tried with Fe(II) salt and Li₃PO₄, all of them had some impurities. When FeCl₂ and (NH₄)₂Fe(SO₄)₂ were used instead of FeSO₄, the same compound was synthesized reddish impurities will be produced, especially when the iron salt is not new, but they can be easily separated from LiFePO₄ in a centrifuge.

2.2 Structural and morphological characterization

Phase characterization was done by powder X-ray diffraction technique on a Philips 1830 X-ray diffractometer using Ni filtered Cu Kα radiation (λ = 1.5406 Å) in the 2θ range of 10~100° at scan rate of 0.1°/s. Surface morphology of the particles was examined through SEM images obtained from Jeol S-3000 H Scanning Electron microscope and the charge-discharge studies were carried out using BTS-5V/3mA charge-discharge cycle life tester.

3. RESULTS AND DISCUSSION

3.1 SEM analysis of LiFePO₄ by different synthesis routes

The synthesis routes of LiFePO₄ can be classified into two kinds according as the reaction medium, they are solid-state reaction and hydrothermal synthesis. The solid-state reaction needs a higher temperature and requires inert gases. Moreover, the diameter of the powder is much larger. In order to diminish the granularity of the productions, and decrease the impurities at the same time, the research always used liquid method to synthesize the powder, such as sol-gel method and hydrothermal

synthesis. We used both solid-state reaction and hydrothermal synthesis to compose LiFePO_4 . The SEM images of LiFePO_4 by these two methods are as Figure 1.

Figure 1: The SEM of LiFePO_4 synthesized by different synthesis routes (a) hydrothermal (b) solid state reaction

The particle size of the LiFePO_4 which was synthesized by hydrothermal route is homogeneous and small, the average particle size is about $3\mu\text{m}$, and this is smaller than the $20\mu\text{m}$ average size of LiFePO_4 produced by solid-state reaction.

3.2 Electrochemical performance of LiFePO_4 with different Li:Fe

The reactant proportion usually decides the product's final stoichiometric, chooses the suitable Li:Fe may suppress the mixed production, and obtains pure olivine LiFePO_4 . The experiment synthesizes LiFePO_4 under the different Li:Fe reactant proportion. Figure 2. are the discharge curves and cycling performance of the product obtained under different reactant proportion at 0.1C discharge rate. when the Li:Fe ratio is 1.5:1, the discharge capacity is 44.26mAh/g^{-1} , the platform is not obvious, this is due to the impurity FePO_4 , its existence causes the product capacity greatly to reduce. Along with the Li content increase, the platform elevates and changes slow. When the Li:Fe is 3:1, the discharge capacity is 77.23mAh/g^{-1} . Although this four kinds of products have good cycling performance, but when Li content is lower, the first ten discharge capacities will rise.

Figure 2: The 10th discharge curve (a) and cycling performance (b) for LiFePO_4 with different Li:Fe

3.3 Electrochemical performance of LiFePO_4 by different synthesis parameters

When the pH value is a constant ($\text{pH}=8\pm0.05$), the reaction temperature has the certain influence to the electrochemistry performance of the LiFePO_4 . The experiment carries in the different reaction temperature (110°C , 120°C , 130°C). The discharging curve and cycling performance are shown in the Figure 3.

Figure3: The 10th discharge curve (a) and cycling performance (b) for LiFePO_4 with different reactive temperature

The result of Figure 3. indicates that products obtained under 120°C and 130°C have similar discharging curves, but the discharge capacity and the platform of products obtained under 110°C are lower. Under three kinds of reaction temperatures the first ten discharge capacities all have the certain enhancement.

The reaction time also has a tremendous influence on the structure and electrochemistry performance of the powder. The reaction time is 5h, 6h, 10h, 24h, and the discharging curve and cycling performance of the powders obtained under different reaction time are shown in Figure 4. Along with reaction time lengthen, the voltage platform elevates, the discharge capacity increase. All of these show that the inside impedance has reduced, and the crystal lattice distortion are less. Along with the cycle time increase, the discharge capacity slightly rises.

Figure4: The 10th discharge curve (a) and cycling performance (b) for LiFePO_4 with different reactive time

The choice of drying time influences the crystal process, as well as the electrochemistry performance. The experiment operates under the same drying temperature; the products obtained by different dry time are analyzed as Figure 5.

Figure 5: The 10th discharge curve (a) and cycling performance (b) for LiFePO_4 with different evaporation hours

We may see from the Figure 5, when the drying time surpasses 6h, the discharging curves nearly superpose. The 10th discharge capacity is all about 91mAh/g^{-1} . Through the contrast of the discharging curves and cycling performance of products which obtained by different drying time, may discover the product which has a longer drying time has a good charge-discharge performance. As the drying time prolong, the discharge capacity of the battery has risen, as well as the discharge platform. After the drying time surpasses 6h, the tendency is not obvious.

4. CONCLUSIONS

Studied the synthesis condition of LiFePO_4 , the optimized conditions are as follow: the reactant mole ratio is $\text{FeSO}_4:\text{H}_3\text{PO}_4:\text{LiOH} = 1:1:3$; the reaction temperature is 120°C , the reaction time is 10h, in inert gas dry 6h.

ACKNOWLEDGMENTS

This project was supported by the Science and Technology Research Project in Jilin Institute of Chemical Technology under Contract No.2018073.

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