IOP Conf. Series: Materials Science and Engineering **735** (2020) 012037 doi:10.1088/1757-899X/735/1/012037

Research on Preparation of Nano-porous Lithium Iron Phosphate for Lithium-ion Battery Electrode Materials

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Abstract. Citric acid, nitric acid, ferrous phosphate and lithium carbonate as raw materials, the precursor $Fe_3(PO_4)_2$ were synthesized by precipitation method, and nano-porous lithium iron phosphate ($LiFePO_4$) was prepared by modified sol-gel method. The influence of pH to purity and yield of precursor $Fe_3(PO_4)_2$ and sintering temperature to purity of $LiFePO_4$ were studied. X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and transmission electron microscopy techniques (TEM) were used to character the phase and morphology of nano-porous lithium iron phosphate ($LiFePO_4$).

1. Introduction

$LiFePO_4$ has been largely used as electrode materials for lithium-ion batteries due to its environmentally friendly, low cost, high safety, excellent charge and discharge, reversible performance [1–3]. However, $LiFePO_4$ has considerable low lithium-ion diffusion coefficient (10^{-14} $cm^2\ s^{-1}$) [4], which make batteries have longer charging time and smaller specific capacity and batter energy density. These short comes limit its practical applications in high energy density batteries using in electric vehicles (EVs) and other high power equipment [5].

Much work has been done to improve lithium-ion diffusion coefficient or 'effective Li^+ density' in $LiFePO_4$ electrode materials lithium-ion batteries to improve the specific capacity and batter energy density [6-10]. Among them, 'decreasing the $LiFePO_4$ particles size to improve effective Li^+ density' is one of theoretical ideal method [8–10]. Because Li^+ can only passed through a few nanometres thickness of the $FePO_4$/$LiFePO_4$ electrode material interface at the charging and discharging process of the batteries, the 'effective Li^+ concentration' of the large crystal grain (such as particle size >1μm) $LiFePO_4$ electrode material is not high. On the contrary, Nano-size $LiFePO_4$ can provide more 'effective Li^+' due to the larger surface portion volume fraction. The large specific surface and porous structure improve the diffusion of Li^+ extraction and embedding during charging and discharging of the battery, thereby increasing the capacity of the battery. Zhang [11] synthesized $LiFePO_4$ quantum dots, the first discharge capacity at 0.1C rate to 197 $mAhg^{-1}$, which is much higher capacity than that of $LiFePO_4$ materials synthesized by traditional methods.

In this paper, we synthesized ferrous phosphate precursor material by precipitation method. Then used low costs, green and low temperature Modified Sol-Gel method synthesize Nano-porous $LiFePO_4$.

2. Experimental

2.1. Materials

All chemicals and materials used in this research were analytical-grade reagents (A.R.) and purchased from Sinopharm Chemical Reagent Co., Ltd. They were Ammonium Dihydrogen Phosphate ($NH_4H_2PO_4$), Potassium Dihydrogen Phosphate (KH_2PO_4), Citric Acid ($C_6H_8O_7$), Lithium Carbonate ($LiCO_3$), Ferrous Sulfate ($FeSO_4$), Urea (CH_4N_2O), Nitric acid (HNO_3) and Sodium Hydroxide (NaOH). $NH_4H_2PO_4$, KH_2PO_4, $LiCO_3$ and $FeSO_4$ were the source materials for supplying P, Li and Fe, respectively.

2.2. Synthesis

The preparation process has precursor $Fe_3(PO_4)_2$ synthesized by precipitation method and nano-porous lithium iron phosphate ($LiFePO_4$) prepared by modified sol-gel method. KH_2PO_4 is dissolved in deionization water, and then the solution pH is adjusted by NaOH. $FeSO_4$ is dissolved in deionization water. And then fully mix the solutions till the precipitate is repeatedly. Then wash the precipitate with deionization water. Finally, pure $Fe_3(PO4)_2$ is got after the mixture is dried at 80℃ in a vacuum.

Figure 1 shows the Nano-porous $LiFePO_4$ synthese process. $C_6H_8O_7$, $NH_4H_2PO_4$ and $LiCO_3$ are mixed and dissolved in deionization water. Then mixes the solution with $Fe_3(PO_4)_2$ solution. Add dilute HNO_3 into the solution till $Fe_3(PO_4)_2$ is completely dissolved. Adjust the pH by Urea. Dry the solution at 80℃ till it become colloid. Finally the colloid is sintered in nitrogen gas.

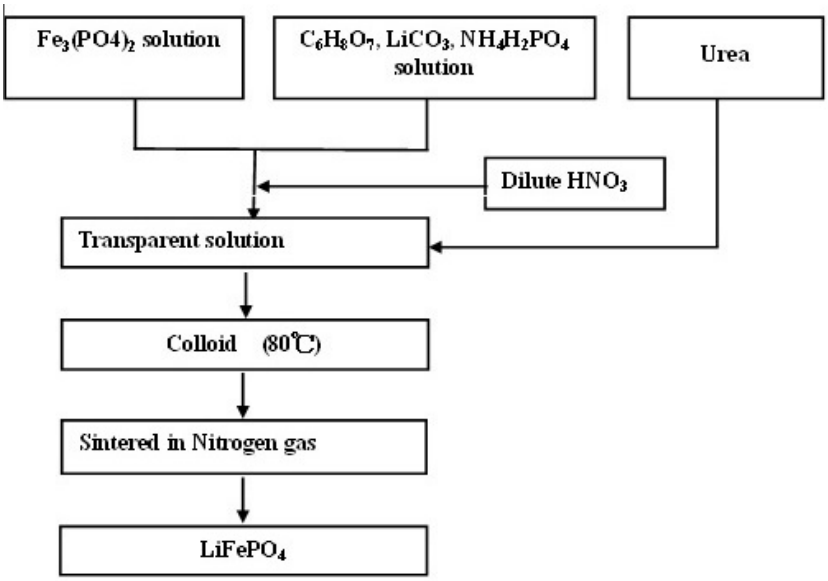

Figure 1. Schematic Diagram of Preparation Process of Nano-porous $LiFePO_4$

2.3. Characterization

The phases were characterized by X-ray diffraction (XRD) Rigaku D/max-rB (Rigaku Co., Japan, Cu-Kα1). The powders size, morphology and structure were characterized by field emission scanning electron microscopy (FESEM, S-3000H, Hitachi Co., Japan) and transmission electron microscopy (TEM, H-7000, Hitachi Co., Japan).

3. Results and discussion

3.1. Influence of pH to Purity and Yield of $Fe_3(PO_4)_2$

Figure 2 shows XRD patterns of $Fe_3(PO_4)_2 \cdot 8H_2O$ prepared in different pH (from 4.0 to 6.0). It indicates that the $Fe_3(PO_4)_2 \cdot 8H_2O$ phase is very pure by precipitation method in different pH. But our research results indicate that the pH value effects the precursor $Fe_3(PO_4)_2 \cdot 8H_2O$ yield when the molar ratio of KH_2PO_4 to $FeSO_4 \cdot 7H_2O$ is 1:1. The $Fe_3(PO_4)_2 \cdot 8H_2O$ yield is 70.0% (wt.) when the solution pH keeps at around 4.0. The $Fe_3(PO_4)_2 \cdot 8H_2O$ yield is 94.0% (wt.) when the solution pH keeps at around 5.0. The $Fe_3(PO_4)_2 \cdot 8H_2O$ yield is 98.0% (wt.) when the solution pH keeps at around 6.0. However, there will be yellow-white precipitate (Fe^{2+} are oxidized to Fe^{3+}) when the pH above 6.0.

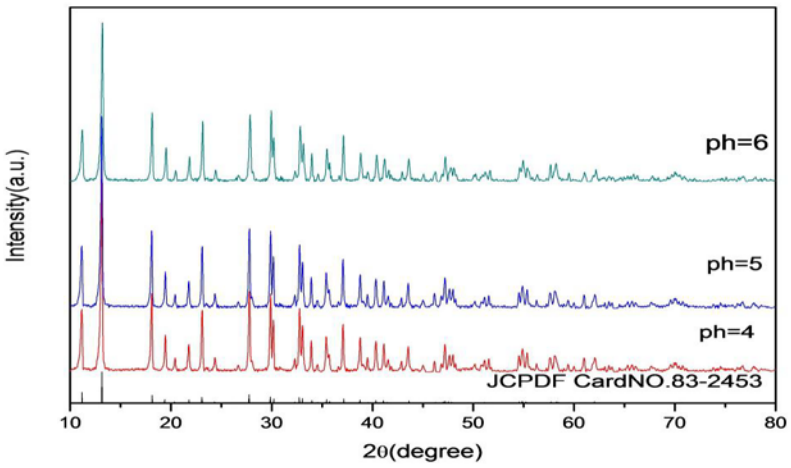

Figure 2. XRD Patterns of $Fe_3(PO4)_2 \cdot 8H_2O$ Precipitate at Different pH

3.2. Influence of Sintering Temperature to Purity of $LiFePO_4$

Figure 3 shows the XRD pattern of $LiFePO_4$ prepared at different sintering temperatures. The diffraction peaks of $LiFePO_4$ by sol-gel method match well with the standard card (40-1499). But the heights of corresponding peaks rise with the sintering temperature arise from 500℃ to 600℃. However, the corresponding peaks strength at 450℃ are stronger than those of at 500℃, mainly because the amount of $C_6H_8O_7 \cdot H_2O$ added at 450℃ is more than those of at 500℃, which resulting in higher temperature caused by intense instantaneous combustion of citric acid nitrate. (However, if the amount of $C_6H_8O_7 \cdot H_2O$ added at 450℃ was same as 500℃, the red Fe^{3+} compound would appear.)

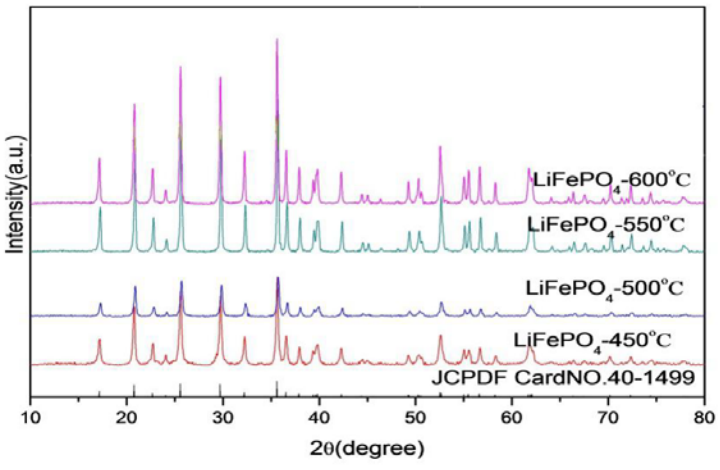

Figure 3. XRD Patterns of $LiFePO_4$ Sintering at Different Temperature

3.3. Morphology Characterization of $LiFePO_4$

Figure 4 shows the FESEM image of $LiFePO_4$ sintered at 500℃ for 30minutes. The $LiFePO_4$ particles are homogeneously distributed spherical-like. The $LiFePO_4$ powders loosely agglomerate together forming porous constructions.

Figure 5 shows the TEM image of $LiFePO_4$ sintered at 500℃ for 30minutes. The $LiFePO_4$ particles have the sizes of about 100 nm and shape of sphere or ellipsoid.

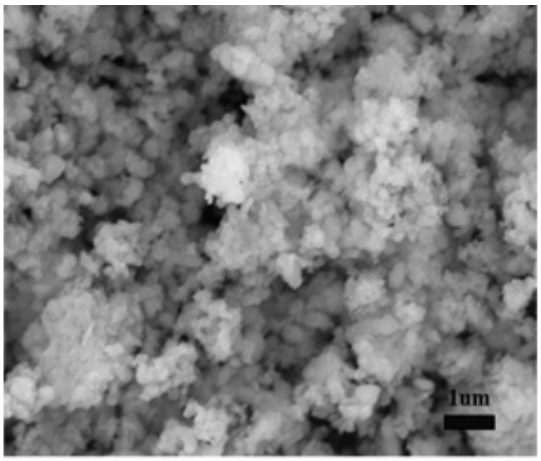

Figure 4. FESEM Image of Nanoporous $LiFePO_4$

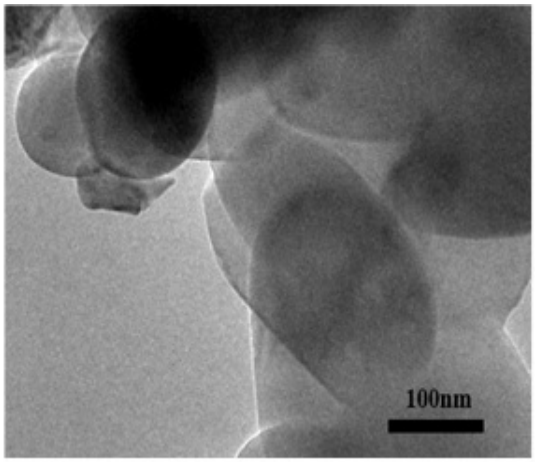

Figure 5. The TEM Image of $LiFePO_4$ Powers

4. Conclusion

Nano-porous $LiFePO_4$ with particle size about 100 nm for Lithium-ion Battery Electrode Materials was synthesized by Citric-Urea-Nitrate Combustion aid modified Sol-Gel method. The pure precursor $Fe_3(PO_4)_2 \cdot 8H_2O$ synthesized by precipitation method had the yield of 98.0% (wt.) when the precipitation solution pH was 6.0 with molar ratio of KH_2PO_4 to $FeSO_4 \cdot 7H_2O$ is 1:1. The Nano-porous pure $LiFePO_4$ with the particle size of about 100 nm is prepared sintering 30 minutes at 500℃ in nitrogen gas.

5. Acknowledgements

This work was supported by the Key Science Project of Jiangxi Provincial Department of Education (No. GJJ180246).

6. Reference

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