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 Fe3(PO4)2 were synthesized by precipitation method, and nano-porous lithium iron phosphate (LiFePO4) was prepared by modified sol-gel method. The influence of pH to purity and yield of precursor Fe3(PO4)2 and sintering temperature to purity of LiFePO4 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 (LiFePO4).

1. Introduction
LiFePO4 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, LiFePO4 has considerable low lithium-ion diffusion coefficient (10^{-14} \text{ cm}^2 \text{ 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 LiFePO4 electrode materials lithium-ion batteries to improve the specific capacity and batter energy density [6-10]. Among them, ‘decreasing the LiFePO4 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 FePO4/LiFePO4 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) LiFePO4 electrode material is not high. On the contrary, Nano-size LiFePO4 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 LiFePO4 quantum dots, the first discharge capacity at 0.1C rate to 197 mAhg^{-1}, which is much higher capacity than that of LiFePO4 materials synthesized by traditional methods.

In this paper, we synthesize ferrous phosphate precursor material by precipitation method. Then used low costs, green and low temperature Modified Sol-Gel method synthesize Nano-porous LiFePO4.
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 (NH₄H₂PO₄), Potassium Dihydrogen Phosphate (KH₂PO₄), Citric Acid (C₆H₈O₇), Lithium Carbonate (LiCO₃), Ferrous Sulfate (FeSO₄), Urea (CH₂N₂O), Nitric acid (HNO₃) and Sodium Hydroxide (NaOH). NH₄H₂PO₄, KH₂PO₄, LiCO₃ and FeSO₄ were the source materials for supplying P, Li and Fe, respectively.

2.2. Synthesis
The preparation process has precursor Fe₃(PO₄)₂ synthesized by precipitation method and nano-porous lithium iron phosphate (LiFePO₄) prepared by modified sol-gel method. KH₂PO₄ is dissolved in deionization water, and then the solution pH is adjusted by NaOH. FeSO₄ 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 Fe₃(PO₄)₂ is got after the mixture is dried at 80°C in a vacuum.

Figure 1 shows the Nano-porous LiFePO₄ synthesis process. C₆H₈O₇, NH₄H₂PO₄ and LiCO₃ are mixed and dissolved in deionization water. Then mixes the solution with Fe₃(PO₄)₂ solution. Add dilute HNO₃ into the solution till Fe₃(PO₄)₂ is completely dissolved. Adjust the pH by Urea. Dry the solution at 80°C till it become colloid. Finally the colloid is sintered in nitrogen gas.

2.3. Characterization
The phases were characterized by X-ray diffraction (XRD) Rigaku D/max-rB (Rigaku Co., Japan, Cu-Kα). 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 Fe₃(PO₄)₂

Figure 2 shows XRD patterns of Fe₃(PO₄)₂·8H₂O prepared in different pH (from 4.0 to 6.0). It indicates that the Fe₃(PO₄)₂·8H₂O phase is very pure by precipitation method in different pH. But our research results indicate that the pH value effects the precursor Fe₃(PO₄)₂·8H₂O yield when the molar ratio of KH₂PO₄ to FeSO₄·7H₂O is 1:1. The Fe₃(PO₄)₂·8H₂O yield is 70.0% (wt.) when the solution pH keeps at around 4.0. The Fe₃(PO₄)₂·8H₂O yield is 94.0% (wt.) when the solution pH keeps at around 5.0. The Fe₃(PO₄)₂·8H₂O yield is 98.0% (wt.) when the solution pH keeps at around 6.0. However, there will be yellow-white precipitate (Fe²⁺ are oxidized to Fe³⁺) when the pH above 6.0.

![Figure 2. XRD Patterns of Fe₃(PO₄)₂·8H₂O Precipitate at Different pH](image)

3.2. Influence of Sintering Temperature to Purity of LiFePO₄

Figure 3 shows the XRD pattern of LiFePO₄ prepared at different sintering temperatures. The diffraction peaks of LiFePO₄ 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 °C to 600 °C. However, the corresponding peaks strength at 450 °C are stronger than those of at 500 °C, mainly because the amount of C₆H₈O₇·H₂O added at 450 °C is more than those of at 500 °C, which resulting in higher temperature caused by intense instantaneous combustion of citric acid nitrate. (However, if the amount of C₆H₈O₇·H₂O added at 450 °C was same as 500 °C, the red Fe³⁺ compound would appear.)

![Figure 3. XRD Patterns of LiFePO₄ Sintering at Different Temperature](image)
3.3. Morphology Characterization of LiFePO₄

Figure 4 shows the FESEM image of LiFePO₄ sintered at 500°C for 30 minutes. The LiFePO₄ particles are homogeneously distributed spherical-like. The LiFePO₄ powders loosely agglomerate together forming porous constructions.

Figure 5 shows the TEM image of LiFePO₄ sintered at 500°C for 30 minutes. The LiFePO₄ particles have the sizes of about 100 nm and shape of sphere or ellipsoid.

4. Conclusion

Nano-porous LiFePO₄ 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 Fe₃(PO₄)₂·8H₂O synthesized by precipitation method had the yield of 98.0% (wt.) when the precipitation solution pH was 6.0 with molar ratio of KH₂PO₄ to FeSO₄·7H₂O is 1:1. The Nano-porous pure LiFePO₄ with the particle size of about 100 nm is prepared sintering 30 minutes at 500°C in nitrogen gas.

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6. Reference

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