

Preparation and characterization of LiFePO_4 from $\text{NH}_4\text{FePO}_4 \cdot \text{H}_2\text{O}$ under different microwave heating conditions

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Abstract Olivine-type LiFePO_4 is a very promising polyanion-type cathode material for lithium-ion batteries. In this work, LiFePO_4 with high specificity capacity is obtained from a novel precursor $\text{NH}_4\text{FePO}_4 \cdot \text{H}_2\text{O}$ via microwave processing. The grains grow up in the duration of sintering until they reach the decomposition temperature. The apparent conductivity of the samples rises rapidly with the irradiation time and influences the electrochemical performance of the material greatly at high current density. As a result, the LiFePO_4 cathode material obtained with a sintering time of 15 min has good electrochemical performance. Between 2.5 and 4.2 V versus Li, a reversible capacity is as high as 156 mAh g^{-1} at 0.05 C.

Keywords Lithium-ion batteries · Cathode material · LiFePO_4 · $\text{NH}_4\text{FePO}_4 \cdot \text{H}_2\text{O}$

Introduction

Olivine-type LiFePO_4 is a potential candidate for the cathode material of the lithium-ion secondary batteries. It becomes attractive recently for its high capacity and good stability and for its being inexpensive and environmentally benign [1–7].

Microwave processing is thought as the most promising method to synthesize olivine-type LiFePO_4 . Because the microwave energy is directly absorbed by the sample, uniform and rapid heating can be achieved within a short

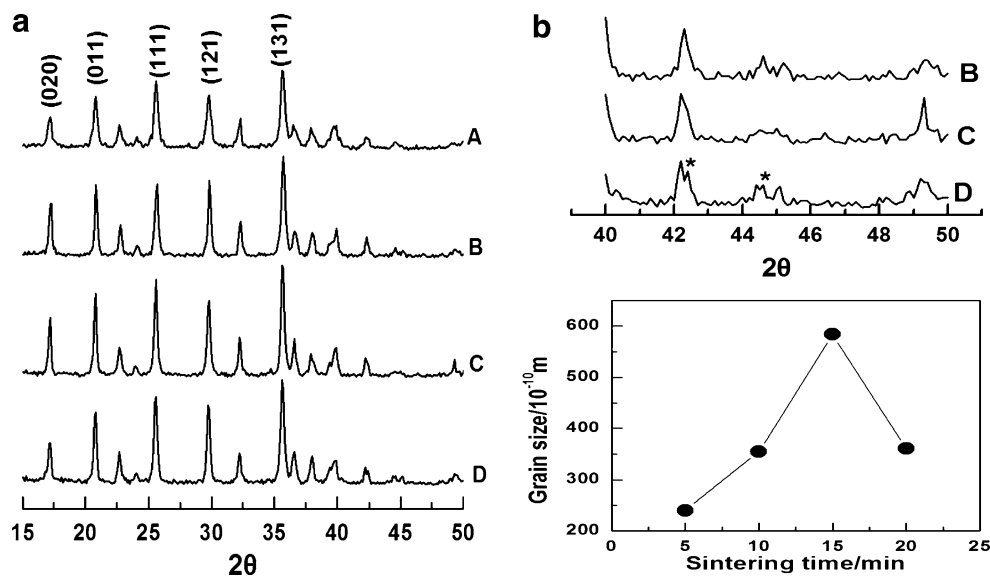
period of time and at temperatures lower than that required for furnace heating. This process has been applied in the preparation of many ceramics as a novel sintering method, such as PTZ, an oxide superconductor, and other ceramics [8, 9]. Park et al. [10] and Higuchi et al. [11] synthesized olivine LiFePO_4 cathode materials by microwave process. In Higuchi et al.'s case, iron precursors act as microwave absorbers and the initial discharge capacity of the product is just 125 mAh g^{-1} at 60°C . Park et al. reform the method by using activated carbon as the heat source. This improvement receives soul-stirring result. The initial discharge capacity of LiFePO_4 is up to 151 mAh g^{-1} at 0.1 C.

Synthesizing LiFePO_4 from ferrous ions precursor is easier than from trivalence iron ions precursor, as the electrovalence of iron in LiFePO_4 is also 2, and ferrous ions do not need to be deoxidized. But, the precursors that are mainly used are FeC_2O_4 and $\text{Fe}(\text{OOCCH}_3)_2$. They are expensive, and these multistage preparative strategies are not considered commercially favorable. Furthermore, a part of Fe(II) in FeC_2O_4 tends to be oxidized to Fe(III).

In our study, a novel precursor, $\text{NH}_4\text{FePO}_4 \cdot \text{H}_2\text{O}$, is presented in the synthesis of LiFePO_4 . This precursor is cheap and easy to prepare. It is stable at room temperature and can be stored for a long time. The ratio of Fe to PO_4 in this ferrous phosphate precursor is 1:1, so the carbothermal reduction is not necessary. Based on this precursor, LiFePO_4 with good electrochemical properties is obtained with a power of 320 W, which is much lower than the results from the former research. We also use sucrose as co-heat source, which can provide pyrolytic carbon at high temperature. In addition, the pyrolytic carbon can absorb microwave and gives heat among the particles. The carbon generated from the sucrose coats on the surface of LiFePO_4 , which improves the electronic conductivity and reduces the particle size.

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Fig. 1 XRD pattern and the grain size in the direction of [020] of LiFePO_4 . **a** XRD patterns of the LiFePO_4 . **b** The existence of Fe_7C_3 in sample D (top) and grain size of the samples in the direction of [020] (bottom). Asterisks= Fe_7C_3

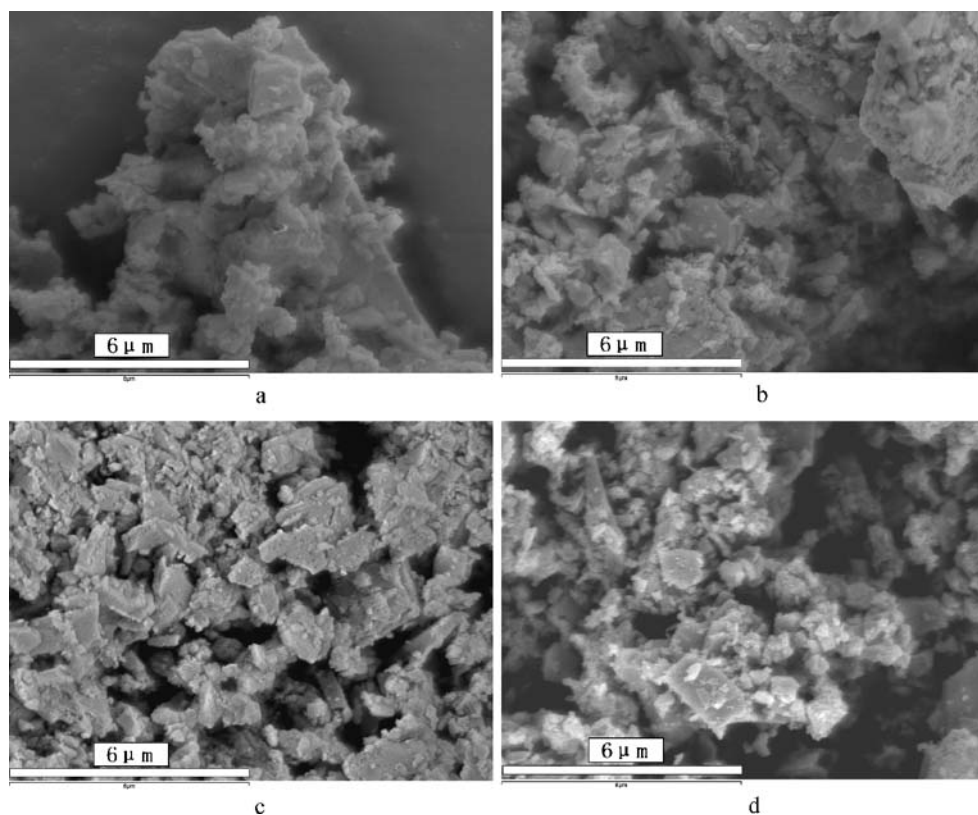


Experimental

The mixed solution of FeSO_4 , H_3PO_4 and a reducing and chelating agent was pumped continuously into a special reactor. At the same time, the solution of $\text{NH}_3\cdot\text{H}_2\text{O}$ was also pumped into the reactor. The precipitate was filtered, washed and dried in an oven at $80\text{ }^\circ\text{C}$ for 4 h. $\text{NH}_4\text{FePO}_4\cdot\text{H}_2\text{O}$ and Li_2CO_3 and sugar were mixed by ball milling (with a rotation speed of 250 rpm, agate balls) for 24 h and

then pressed into pellets. The pellet was put inside the alumina crucible filled with activated carbon, and the alumina crucible was placed inside the microwave oven. The microwave irradiation to the crucible was conducted with the use of a domestic microwave oven (Galanz, China) that operated at 2.45 GHz with a maximum power level of 800 W. A power of 320 W was added. The irradiation times were 5, 10, 15 and 20 min, and the samples obtained from each sintering time were labeled as A, B, C and D,

Fig. 2 SEM images of LiFePO_4



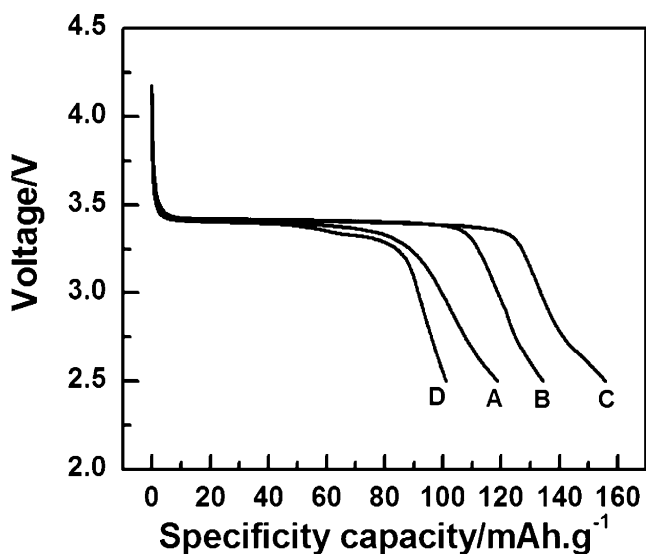


Fig. 3 Discharge curves of the initial cycle of LiFePO_4 at current density of 0.05 C

correspondingly. The atmosphere was air, and no additional inert or reductive gas was given. When the alumina crucible with the pellet and activated carbon was naturally cooled down to room temperature, the pellet was taken out and pulverized into powders.

During microwave irradiation, the activated carbon could absorb microwave intensively, resulting to a very high rate of temperature rising. The activated carbon surrounding the pellet acted as the strong heat sources, which could heat the pellet to a high temperature in a short time. In addition, the activated carbon could partly be oxidized to CO (reducing agent), acting as the reductive atmosphere. During microwave irradiation, the sucrose in pellet would pyrolyse at high temperature. Pyrolytic carbon, which could also absorb microwave, was generated. This heat source helped to heat the precursors among the particles. In addition, the pyrolytic carbon coated on the surface of the particles keeps the ferrous ions from oxidation at high temperature effectively.

Powder X-ray diffraction (XRD, D/max-rB) using $\text{Cu K}\alpha$ radiation was used to identify the crystalline phase and crystal lattice parameters of the $\text{NH}_4\text{FePO}_4\cdot\text{H}_2\text{O}$ and LiFePO_4 . The particle morphology of the powders was observed using a scanning electron microscopy (SEM, JSM6301F). The grain size was calculated by using the software JADE 5.0 (Materials Data) and Scherrer formula. The margin of error is below 5%.

The apparent conductivity is measured as follows. First, the material is pressed at 30 MPa and formed into a pellet. Then, the resistance, diameter and thickness of the pellet are measured. The apparent conductance of the samples can be calculated by these figures.

Experimental test cells for measurements used the cathode with the composition of 80 wt% LiFePO_4 , 10 wt%

carbon black and 10 wt% polytetrafluoroethylene. The separator used was a Celguard 2400 microporous polypropylene membrane. The electrolyte was 1 M LiPF_6 ethylene carbonate+diethyl carbonate (1:1, v/v). A lithium metal anode was used in this study. The cells were assembled in a glove box filled with argon gas. The charge–discharge cycling was galvanostatically performed at a current of 0.05 and 0.5 C with cut-off voltages of 2.5–4.2 V (versus Li/Li^+) at room temperature.

Results and discussion

The XRD patterns of the LiFePO_4 synthesized by the microwave sintering method are shown in Fig. 1a. The products are all identified as crystal-type LiFePO_4 according to the comparison with PDF. It is surprising that even the sample that was heated 5 min with a power of 320 W was identified as well-crystallized LiFePO_4 . In our opinion, the reasons may be as follows. $\text{NH}_4\text{FePO}_4\cdot\text{H}_2\text{O}$ is a kind of ferrous phosphate and the Fe/PO_4 ratio in the precursor is 1:1, so that the Fe^{2+} and PO_4^{3-} ions do not need to diffuse in the solid. Moreover, $\text{NH}_4\text{FePO}_4\cdot\text{H}_2\text{O}$ is a kind of poor thermal stable compound and is easy to react with other compounds at high temperature. There is no evidence of diffraction peaks for carbon, indicating that the residual pyrolytic carbon in product is amorphous. The temperature rises rapidly during the irradiation, which makes it possible for synthesizing LiFePO_4 in a very short period of time. But if the sintering time is not well controlled, the temperature will rise as high as a terrible reductive reaction may occur. In this experiment, as shown in Fig. 1b, sample D contains an amount of iron carbide, mainly Fe_7C_3 , which is caused by overheating. This kind of reductive reactions damages the crystal structure of the LiFePO_4 and does harm to the electrochemical performance of the material.

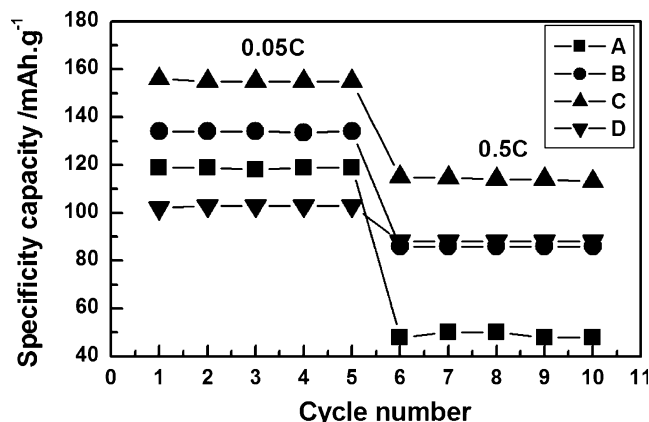


Fig. 4 Discharge capacity with increasing cycles for LiFePO_4 at different current density

Figure 1b shows the grain size of the samples in the direction of [020]. The grain sizes of samples A to D are 240, 355, 584 and 361 Å, respectively. It is obvious that the grains grow up in the duration of sintering. The grain size of LiFePO₄ is 240 Å after 5 min sintering, whereas it grows to 355 Å after 10 min and 584 Å after 15 min. The grain size enlarged more than two times in 10 min. The phenomenon is explained by the deductions that the LiFePO₄ obtained in short sintering time has isotropic and strain-free crystallites and has the smaller grains than that obtained in long sintering time. If the sintering time lasts more than 15 min, the grain size will tend to decrease rapidly. The grain size of sample D is only 361 Å. As discussed above, the terrible reductive reactions caused by overheating damage the crystal structure of LiFePO₄ and of course reduce the grain size.

Figure 2 shows the morphology of the LiFePO₄ powders. There is little difference among the samples in particle morphology for the short sintering time, and the low power did not destroy the structure and the morphology of NH₄FePO₄·H₂O. The particles still maintain the flake-like crystal structure of the precursor. The particle size is around 2 μm, and carbon can be seen on the surface of the crystal. The powders conglomerated during sintering because the carbon generated from sucrose agglutinated the particles of LiFePO₄ together.

The samples obtained by microwave process have high specific capacity and good cycling stability. The samples with different sintering time and grain size have different electrochemical performance. Figure 3 shows the initial discharge curves of the LiFePO₄ obtained by microwave process at different conditions. As Fig. 3 illustrates, voltage plateaus of the samples are observed at around 3.4 V in all the curves. It indicates that the charge and discharge reactions are two-phase reactions. Sample A has the initial discharge capacity of 119 mAh g⁻¹. Sample B, which was heated for 10 min, has the initial discharge capacity of 134 mAh g⁻¹. Sample C, which was heated for 15 min, has the initial discharge capacity of 156 mAh g⁻¹. Obviously, with the increase of sintering time, the initial discharge capacity of the product increases. This might be explained by a solid-state reaction and decomposition rate. The solid-state reaction between Li₂CO₃ and NH₄FePO₄·H₂O needs enough time to complete and form perfect crystal of LiFePO₄, which is believed to have good reversible capacity. The decomposition of sucrose also needs a certain period of time and proper high temperature. The apparent conductivity of the samples rises with the irradiation time. Sample A exhibits a conductivity of 1.57×10⁻⁵ S·cm⁻¹, whereas sample C exhibits 5.66×10⁻² S·cm⁻¹ and sample D exhibits 8.09×10⁻² S·cm⁻¹. The conductivity rises more than a thousand times from sintering 5 to 15 min. Proper long sintering time allows the solid reaction to complete

thoroughly, and the grains grow up at the same time. But if the sintering time lasts more than 15 min, the initial discharge capacity will fade fast. Sample D has the initial discharge capacity of only 102 mAh g⁻¹, which is much less than that of sample C. It is proved that overheating does great harm to the performance.

Figure 4 shows the cycle performance of the discussed four LiFePO₄ samples. All the products showed excellent cycling stability. The cycle capacity of sample C is more than 155 mAh g⁻¹ at 0.05 C and remains 115 mAh g⁻¹ at 0.5 C. The cycle capacity of sample A is around 119 mAh g⁻¹ at 0.05 C and fades to 48 mAh g⁻¹ at 0.5 C. The rate performance of samples A and B (86 mAh g⁻¹) are even worse than sample D, which has a capacity of 88 mAh g⁻¹. The electronic conduction is more important to the performance of the material at high current density than at low current density. The apparent conductivity of sample D is the highest among the four samples, and it shows the least capacity lose from 0.05 to 0.5 C. Sample C shows excellent reversible capacity even at high current density. As a result, the electrochemical performance of the product is very sensitive to the sintering time, and the best sintering time is about 15 min.

Conclusion

LiFePO₄ powders with high specific capacity have been synthesized from a novel precursor and via a low-power microwave process. The sample prepared with a sintering time of 15 min results in the attainment of higher discharge capacity (156 mAh g⁻¹ at 0.05 C). The grains grow up in the duration of sintering until they reach the decomposition temperature. The excellent electrochemical performance and the low synthesizing power of the LiFePO₄ cathode material are partly attributed to the good reaction character of the precursor. This method should be a promising way to synthesize LiFePO₄ cathode material and is significant to be further studied.

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