

New solid-state synthesis routine and mechanism for LiFePO_4 using LiF as lithium precursor

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Abstract

Li_2CO_3 and $\text{LiOH} \cdot \text{H}_2\text{O}$ are widely used as Li-precursors to prepare LiFePO_4 in solid-phase reactions. However, impurities are often found in the final product unless the sintering temperature is increased to 800°C . Here, we report that lithium fluoride (LiF) can also be used as Li-precursor for solid-phase synthesis of LiFePO_4 and very pure olivine phase was obtained even with sintering at a relatively low temperature (600°C). Consequently, the product has smaller particle size (about 500 nm), which is beneficial for Li-extraction/insertion in view of kinetics. As for cathode material for Li-ion batteries, LiFePO_4 obtained from LiF shows high Li-storage capacity of 151 mAh g^{-1} at small current density of 10 mA g^{-1} (1/15 C) and maintains capacity of 54.8 mAh g^{-1} at 1500 mA g^{-1} (10 C). The solid-state reaction mechanisms using LiF and Li_2CO_3 precursors are compared based on XRD and TG–DSC.

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1. Introduction

In recent years, the demand for developing new cathode materials for high-performance lithium ion batteries has increased continuously. LiFePO_4 is one of the most promising materials due to its moderate Li-storage capacity and excellent safety. However, its insulating nature leads to poor kinetic performance. It becomes a barrier for practical applications in high-power batteries. Therefore, much effort has been made to improve the performance of this material [1–11] since the first report from Goodenough et al. in 1997 [12,13]. In view of transport properties of ions and electrons and reversible Li-storage, LiFePO_4 possessing small particle size and pure phase simultaneously is the favorite.

Synthesis of LiFePO_4 is mainly performed via solid-state reaction using Li_2CO_3 or $\text{LiOH} \cdot \text{H}_2\text{O}$ as Li-precursor [1,5,6,10–13]. However, we have noticed that Li_3PO_4 is

often detected in the final products unless the sintering temperature was increased to 800°C . High-reaction temperature always leads to large particle size. The presence of impurities or large particle size is not good for achieving satisfactory electrochemical performances. Therefore, new synthesis routine should be developed.

Compared with Li_2CO_3 , $\text{LiOH} \cdot \text{H}_2\text{O}$, and other Li salts, LiF is generally regarded as a stable compound and rarely used for preparing lithium-containing electrode materials. Here, we report that LiF precursor as single lithium source is suitable for preparing LiFePO_4 . The reaction temperature to obtain pure phase LiFePO_4 can be decreased to 600°C . Consequently, the obtained material shows superior electrochemical performance.

2. Experimental

LiFePO_4 was prepared by a two-step solid-state synthesis. Stoichiometric amounts of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$

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(Aldrich, 99%), $\text{NH}_4\text{H}_2\text{PO}_4$ (Beijing Chemicals, 99.5%), and LiF (Beijing Chemicals, 98.5%) were mixed and ground in an agate mortar for 30 min. Then, the powder was calcinated in a tube furnace with flowing Ar-H_2 (92:8 v/v) at 400 °C for 8 h. After it cooling down to room temperature, the sample was reground and maintained at 400, 500, 600, 700 or 800 °C for 24 h under the same atmosphere. Another sample was sintered at 300 °C for 8 h. After grinding, it was maintained at 300 °C for 24 h.

For comparison, samples using Li_2CO_3 , $\text{LiOH}\cdot\text{H}_2\text{O}$ or Li_3PO_4 as Li-precursor were also prepared. For these other raw materials, the preparing process was the same as that for samples obtained from LiF. Samples were prepared from 400 to 800 °C.

In addition, a mixture of $\text{FeC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ (1:1 in mole) was also sintered under the same condition at 400 and 500 °C, named Inter400 and Inter500, respectively.

A LiFePO_4 electrode is composed of LiFePO_4 , carbon black, and polyvinylidene fluoride (PVDF) at a weight ratio of 75:15:10. Lithium foil was used as the counter electrode, 1 mol L^{-1} LiPF_6 dissolved in ethylene carbonate/dimethyl carbonate (1:1 v/v) as electrolyte, and Celgard[®] 2340 as the separator. Test cells were assembled in a M-Braun glove box filled with pure argon. The cells were cycled between 2.0 and 4.5 V vs. Li/Li^+ at the current density of 10 mA g^{-1} on Land automatic battery tester (Wuhan, China) at room temperature.

Thermal analysis was performed by a thermo-gravimetric differential scanning calorimetry (TG–DSC) apparatus STA-449C (Netzsch, Germany). Heating rate is $10\text{ }^\circ\text{C min}^{-1}$ in argon atmosphere. The X-ray diffraction (XRD) with $\text{CuK}\alpha$ radiation (D/MAX-RC) was used to characterize the structure of the materials. The surface morphology of the powder was observed on Philips XL30S-F1G field emission scanning electron microscope (FMSEM). The fluorine in the sample was detected with SA720 ion selective electrode (ISE).

3. Results and discussion

3.1. Solid-reaction mechanism of LiF as Li-precursor

Fig. 1 shows the XRD patterns of LiFePO_4 synthesized at different temperatures. At 300 °C as shown in Fig. 1a, LiFePO_4 phase is not observed and LiF is the only crystalline substance. At 400 °C, LiFePO_4 phase appears (Fig. 1b). As the sintering temperature is further increased to 500 °C, LiFePO_4 becomes the dominant phase, but LiF and two unidentified peaks still exist (Fig. 1c). When the mixture is sintered at 600–800 °C, single-phase LiFePO_4 are obtained with well-defined olivine structure (orthorhombic $Pnma$) as shown in

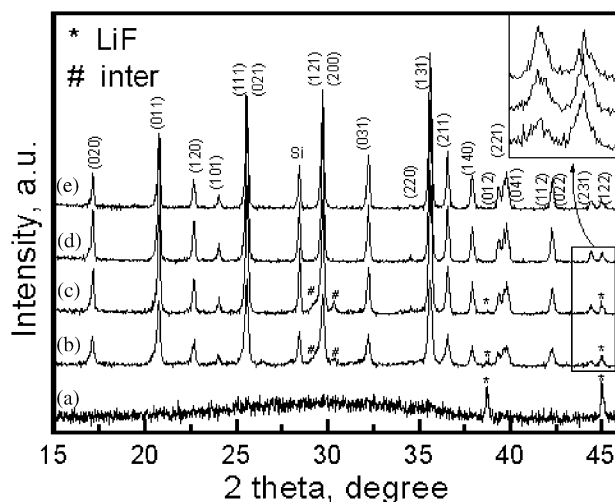


Fig. 1. The XRD patterns of the samples obtained from LiF (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C, and (e) obtained at 800 °C. * marked in figure belongs to LiF: (111) at 38.70° and (200) peak at 45.00°, partially overlapped with the (122) peak of LiFePO_4 (determined from relative intensities of (122) and (231) peak²²).

Figs. 1d and e. These results indicate that LiF does not react with other precursors below 300 °C and the formation of LiFePO_4 starts around 400 °C.

Chemical composition of the final compound prepared at 600 °C was $\text{Li:Fe:P} = 0.99:1.00:1.00$ determined by inductive coupled plasma (ICP) analysis. No fluorine was detected in the same material by ISE method (resolution $> 10^{-9}$ g fluorine in a liter solution). On the other hand, fluorine was found in the distilled water that was used to absorb the tail gas from the tube furnace. In addition, crystalline NH_4F was detected from the species on the inner wall of the low-temperature end of the furnace. These facts indicate that LiF is decomposed and fluorine is released in the form of HF during the sintering process as discussed later.

The TG/DSC measurement of the starting materials for LiFePO_4 with LiF as Li-precursor is presented in Fig. 2. Two endothermic peaks at 183 and 221 °C in the DSC curve are observed, corresponding to the decomposition of $\text{NH}_4\text{H}_2\text{PO}_4$ and losing lattice water of $\text{FeC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$, respectively [14]. No other peaks are found in DSC curves under 390 °C, but continual weight loss is observed in TG curve. The weight loss under 390 °C is 40%. It indicates that FeC_2O_4 should be decomposed and reacted with the decomposed product of $\text{NH}_4\text{H}_2\text{PO}_4$.

From 390 to 460 °C, an endothermic peak and an exothermic peak appear at 417 and 448 °C in DSC curve, respectively, implying the formation of LiFePO_4 as confirmed by XRD data. There is slight change from 460 to 750 °C in the DSC curve. This may reveal the further nuclearization and grain growth of LiFePO_4 . The weight of raw materials does not decrease over

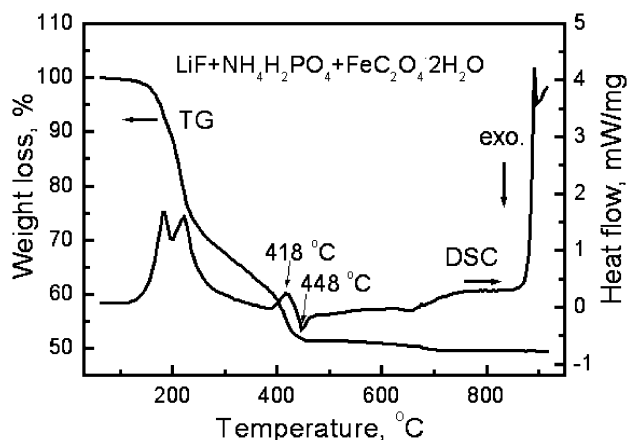


Fig. 2. TG and DSC curves of the precursors composed of LiF, $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (1:1:1 in mole). The measurement was done over the temperature range from ambient to 900°C at a heating rate of $10^\circ\text{C min}^{-1}$ in argon.

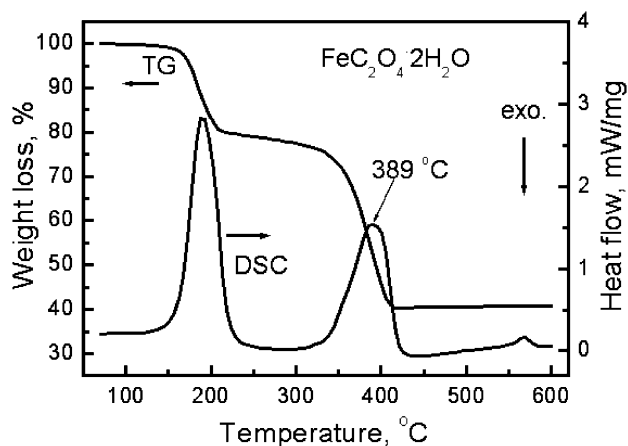


Fig. 3. TG–DSC curves of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ between ambient and 600°C in argon.

730°C . The total weight loss from 390 to 730°C is 10.5% .

In order to understand the mechanism of this solid-state reaction clearly, thermal analysis of precursors is done. Fig. 3 is the TG/DSC curves of pure $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. The appearance of two peaks in the DSC curve indicates that $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ loses lattice water first and then decomposes. In the TG curve, raw materials lose 20.0% of total weight under 220°C , the same as predicted weight loss of losing lattice water. From 220 to 300°C , the weight decreases slightly (2.7%), and weight loss is 37.2% when the temperature increases to 420°C . The total weight loss from 220 to 420°C is consistent with the weight loss of FeC_2O_4 decomposition, but main weight loss occurs above 300°C . When the sintering temperature is over 420°C , the weight does not decrease any more.

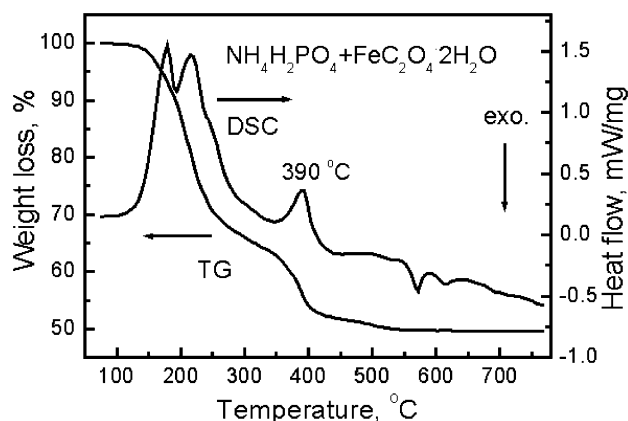


Fig. 4. TG–DSC curves of mixture including $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (1:1 in mole) between ambient and 600°C in argon.

Fig. 4 is the TG/DSC curves of the mixture of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ (1:1 in mole). Except for $\text{NH}_4\text{H}_2\text{PO}_4$ decomposition and $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ losing lattice water, an endothermic peak at 390°C is found. It corresponds to the decomposition of FeC_2O_4 confirmed by the thermal analysis of pure $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Fig. 3). However, the weight loss from 300 to 420°C is 13.1% , much less than the theoretical value (24.4%). Considering the results of Fig. 3, it means that more FeC_2O_4 decomposes under 300°C due to the existence of $\text{NH}_4\text{H}_2\text{PO}_4$. Similarly, the disappearance of the decomposing peak of FeC_2O_4 in Fig. 1 is caused by the addition of LiF and $\text{NH}_4\text{H}_2\text{PO}_4$. According to the above results, the peaks at 417 and 448°C in Fig. 1 should be related to further reaction of an intermediate with LiF.

The mixture of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ (1:1 in mole) was sintered alone under the same condition at 400°C and 500°C , respectively, named Inter400 and Inter500. Fig. 5 is their XRD patterns. The strongest peaks of two samples are located at 29.38° and 30.26° , and at 29.34° and 30.28° , respectively. They are at the same positions with the peaks of the two unidentified peaks in the final compound prepared at 400 and 500°C as shown in Figs. 1b and c. It indicates clearly that the unidentified compound should be an intermediate resulted from the solid-state reaction between $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$. Unfortunately, the phase cannot be identified based on current knowledge.

Based on the above result and analysis, we suppose that the whole solid-state reaction process can be divided into two main steps when LiF is used as Li-precursor.

Firstly, $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ decompose and form an intermediate, as shown in Eq. (1). In this step, the weight loss should be 44.7% , higher than weight loss under 390°C in experiments (40.0%). The second step is the reaction between the intermediate and

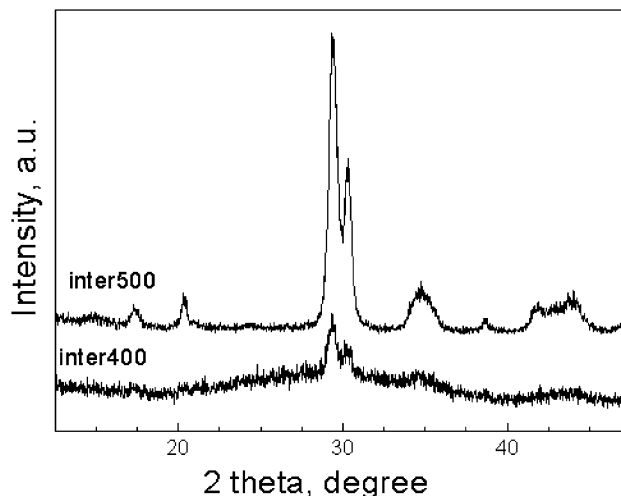
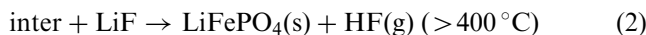
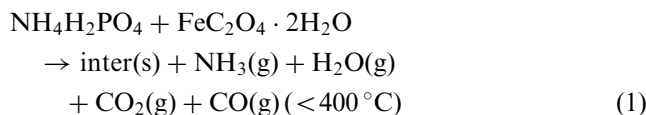


Fig. 5. The XRD patterns of the Inter400 and Inter 500.

LiF to produce LiFePO_4 and give off HF gas (in Eq. (2)). This step starts around 400°C . The weight loss above 390°C is 10.5%, which includes the decomposition of LiF (6.2%, the calculated value) and the uncompleted reaction in the first step.

HF produced in Eq. (2) is taken away by flowing gas (Ar/H_2) and reacts partly with ammonia to form NH_4F (Eq. (3)). This is the reason why white powder was stuck on the inner wall in the low temperature end of the tube furnace. The rest of HF gas is flown into the distilled water, so fluorine was detected in the distilled water that absorbed the protected air.



Based on the above discussion, we believe that the Inter400 (or Inter500) should include Fe, H, and P in a mole ratio of 1:1:1. Actually, the mole ratio of Fe and P are equally determined by ICP. In addition, the Inter400 contains 0.58 wt% hydrogen detected by Vario EL, roughly equal to the theoretical amount of 0.66 wt%. Therefore, it is plausible that the intermediate compound (Inter400 or Inter500) is FeHPO_4 . However, structural information of FeHPO_4 is not available, and a clear identification of the intermediate needs further study.

3.2. Li_2CO_3 as Li-source for comparison

For comparison, the TG–DSC curves using Li_2CO_3 as the Li-precursor to prepare LiFePO_4 is shown in Fig. 6.

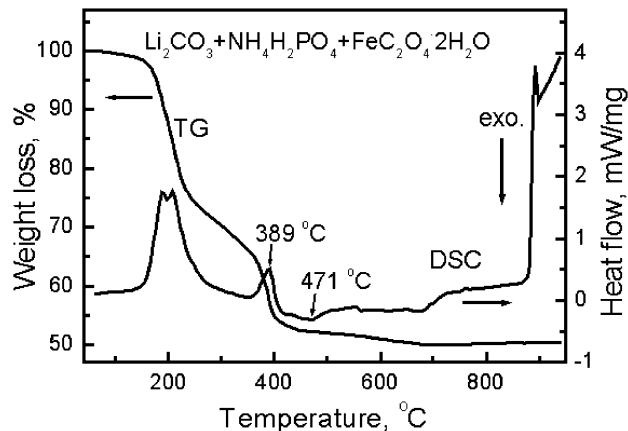


Fig. 6. TG and DSC curves for the precursors composed of Li_2CO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (0.5:1:1 in mole). The measurement was done over the temperature range from ambient to 900°C at a heating rate of $10^\circ\text{C min}^{-1}$ in argon.

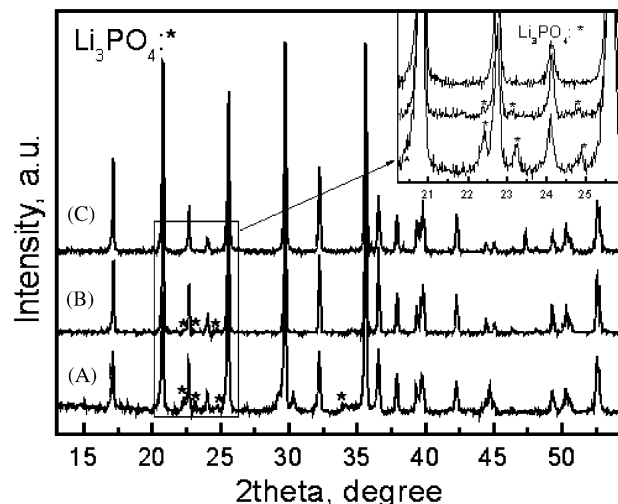


Fig. 7. The XRD patterns of the samples from Li_2CO_3 . (A) 600°C , (B) 700°C , and (C) 800°C .

The DSC curve under 420°C is similar to that of Fig. 4. The weight loss under 420°C is 49.3% higher than the total weight loss of $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (43.1%), indicating that Li_2CO_3 starts to decompose at a lower temperature. From 420 to 770°C , a hump exothermic peak appears at 471°C , which should correspond to the formation of LiFePO_4 .

The XRD patterns of LiFePO_4 synthesized from Li_2CO_3 at 600 – 800°C are shown in Fig. 7. Although LiFePO_4 is the dominant phase sintered at 600°C , Li_3PO_4 and another intermediate (perhaps $\text{Fe}_3(\text{PO}_4)_2$) obviously exist (Fig. 7A). When the sintered temperature is increased to 700°C , the peaks of Li_3PO_4 are still apparent (Fig. 7B). Only the sample prepared at 800°C shows a pure olivine structure without any impurity.

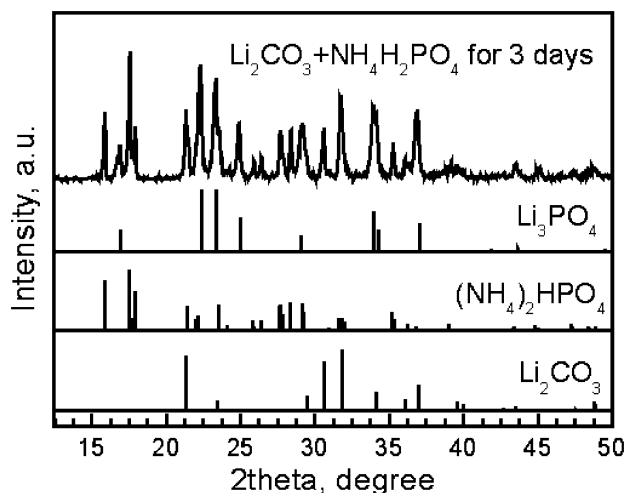


Fig. 8. The XRD patterns of a mixture of Li_2CO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$ (1.5:1 in mole) kept for 3 days after grinding by hand.

It is noticed that Li_2CO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$ can react at room temperature to form Li_3PO_4 (1.5:1 in mole, XRD confirmed, Fig. 8) and $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ cannot react. So it is believed that certain amount of Li_3PO_4 should be formed firstly during grinding in practical production.

According to the above results, the formation of Li_3PO_4 is unavoidable when Li_2CO_3 is used as Li-precursor. So we also used Li_3PO_4 as Li-precursor to prepare LiFePO_4 . It is only at 800°C that impurities are not detected in the sample prepared. Intense grinding may decrease the final temperature to obtain pure LiFePO_4 when Li_2CO_3 or Li_3PO_4 is used as lithium source.

3.3. SEM and electrochemical performance

Fig. 9 shows the SEM images of LiFePO_4 from Li_2CO_3 and LiF . The particles of samples prepared at 600°C (Figs. 9a and b) are homogeneous with the particle size of about 500 nm . When the sample from Li_2CO_3 is sintered at 800°C , the particle size is over $5\text{ }\mu\text{m}$ (Fig. 9c), much larger than that of samples prepared at 600°C .

Fig. 10 presents the charge–discharge curves of LiFePO_4 prepared from LiF and Li_2CO_3 . The cell voltage profile of the samples shows a flat plateau around 3.4 V . The sample from LiF shows a capacity of 151 mAh g^{-1} , and a capacity of only 97 or 45 mAh g^{-1} for the samples from Li_2CO_3 . Samples from Li_2CO_3 exhibit poor capacity due to the existence of impurities (sintered at 600°C) or the large particle size of LiFePO_4 (sintered at 800°C).

As-mentioned above, one of the serious drawbacks of olivine LiFePO_4 is poor rate capability. However, the best sample in our experiments exhibits relatively good

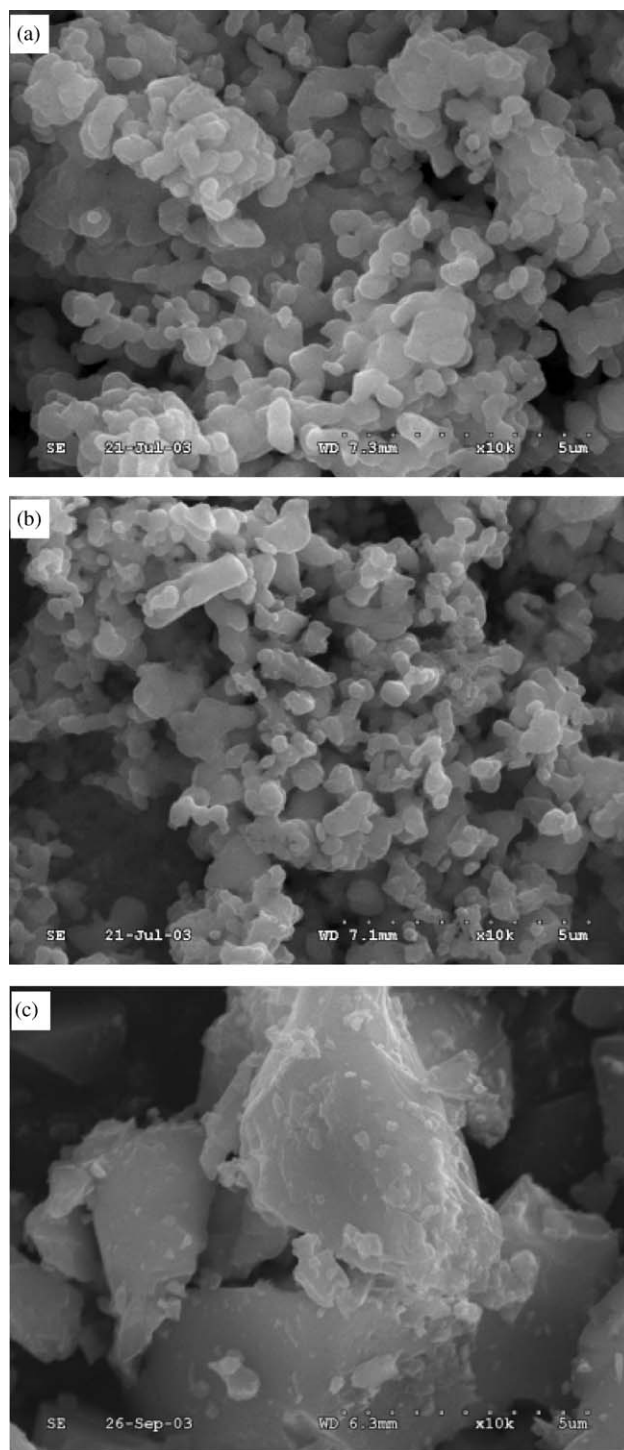


Fig. 9. SEM images of samples investigated in this study: (a) sample prepared from LiF at 600°C , (b) the sample obtained from Li_2CO_3 at 600°C , and (c) the sample sintered from Li_2CO_3 at 800°C .

rate performance, as shown in Fig. 11. All cells were charged under the current density of 10 mA g^{-1} to 4.5 V and discharged under specific current density to 2.0 V . When the applied current density is 1000 mA g^{-1} (7 C), the delivered capacity is 72.5 mAh g^{-1} . The LiFePO_4 cell

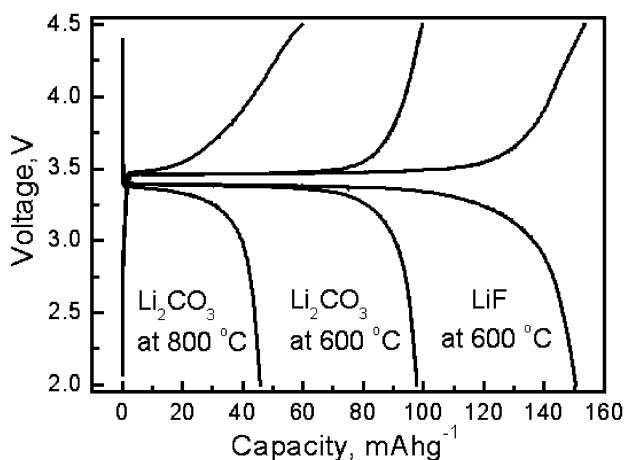


Fig. 10. The second charge–discharge curve of prepared samples.

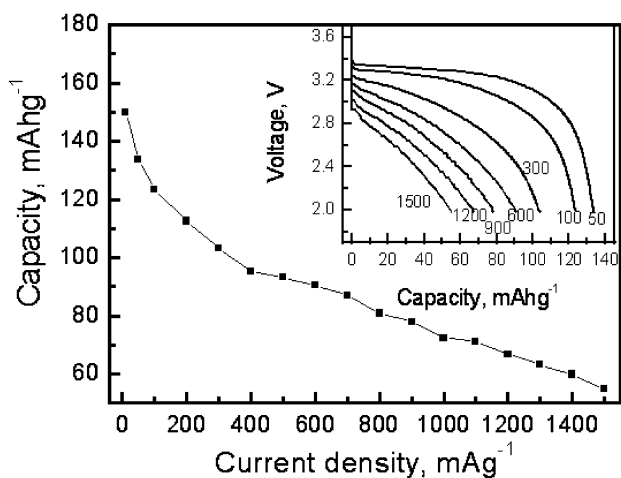


Fig. 11. The rate performance of LiFePO₄ from LiF prepared at 600 °C. Inset means the discharge curves of the same material at the various current densities.

still exhibits 54.8 mAhg⁻¹ when the current density is increased to 10 C. The insets of Fig. 11 are the profiles of discharge curves of LiFePO₄ with the various current densities from 50 to 1500 mA g⁻¹. The rate performance of LiFePO₄ is better than expected.

In brief, LiFePO₄ prepared from LiF shows good electrochemical performance. Our studies show that LiF is a better Li-precursor for scale-production in all aspects except producing HF gas during preparation.

Fortunately, HF is not very difficult to deal with in industry.

4. Conclusion

We demonstrated that pure phase LiFePO₄ can be prepared using LiF as the single lithium source in a solid-state reaction at 600 °C. This reaction could be divided into two main steps. Firstly, FeC₂O₄·2H₂O and NH₄H₂PO₄ are decomposed and reacted to produce an intermediate. Then LiFePO₄ is obtained through the reaction of LiF and the intermediate. Our experiments show that LiF is more suitable than Li₂CO₃ and Li₃PO₄ for the preparation of LiFePO₄. Consequently, the sample prepared from LiF shows good electrochemical performance.

Acknowledgment

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