

Preparation of LiFePO₄ for lithium ion battery using Fe₂P₂O₇ as precursor

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Abstract: In order to obtain a new precursor for LiFePO₄, Fe₂P₂O₇ with high purity was prepared through solid phase reaction at 650 °C using starting materials of FeC₂O₄ and NH₄H₂PO₄ in an argon atmosphere. Using the as-prepared Fe₂P₂O₇, Li₂CO₃ and glucose as raw materials, pure LiFePO₄ and LiFePO₄/C composite materials were respectively synthesized by solid state reaction at 700 °C in an argon atmosphere. X-ray diffractometry and scanning electron microscopy(SEM) were employed to characterize the as-prepared Fe₂P₂O₇, LiFePO₄ and LiFePO₄/C. The as-prepared Fe₂P₂O₇ crystallizes in the C₁ space group and belongs to β-Fe₂P₂O₇ for crystal phase. The particle size distribution of Fe₂P₂O₇ observed by SEM is 0.4–3.0 μm. During the Li⁺ ion chemical intercalation, radical P₂O₇⁴⁻ is disrupted into two PO₄³⁻ ions in the presence of O²⁻, thus providing a feasible technique to dispose this poor dissolvable pyrophosphate. LiFePO₄/C composite exhibits initial charge and discharge capacities of 154 and 132 mA·h/g, respectively.

Key words: lithium ion battery; cathode material; preparation; precursor; LiFePO₄; Fe₂P₂O₇

1 Introduction

The original work of PADHI et al^[1] for LiFePO₄ has aroused researchers' interest in this new cathode material for lithium ion batteries. With the advantages of cheap raw materials, environmental friendliness, high safety, good cycle stability and appreciable specific capacity of 170 mA·h/g, LiFePO₄ has established itself as a potent competitor in cathode material field and challenged the widely used LiCoO₂ and other cathode material candidates such as LiMn₂O₄, LiMnO₂ and LiNiO₂^[2–4]. In particular based on the listed characteristics, LiFePO₄ has highly potential application in hybrid electric vehicles(HEVs)^[5].

Presently, the work of the preparation of LiFePO₄ has centered on different synthetic methods: solid state reactions at high temperature^[6], hydrothermal synthesis^[7] and sol-gel methods^[8] etc. In most cases, lithium salts or lithium hydroxide, ferrous or ferric compounds and phosphates are used as raw materials to obtain LiFePO₄ either in solid or liquid state^[9–11]. Here, enlightened by the concept of precursor Ni_{1/3}Co_{1/3}Mn_{1/3}CO₃ with molar ratio $n(\text{Ni}):n(\text{Mn}):n(\text{Co})=1:1:1$ for LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂, a new precursor Fe₂P₂O₇ for LiFePO₄ was presented. The compound has the following characteristics.

1) Besides O²⁻, the component includes only Fe and P with molar ratio of 1:1.

2) The valences of elements Fe and P in Fe₂P₂O₇ are

the same as those in LiFePO₄, namely +2 and +5 respectively, and during the synthesis of LiFePO₄ they stay unchanged.

In this work, the precursor Fe₂P₂O₇ with high purity was prepared and then chemically intercalated with Li⁺ ion to successfully synthesize LiFePO₄ through solid state reaction.

2 Experimental

Fe₂P₂O₇ was prepared by a solid state reaction using FeC₂O₄ and NH₄H₂PO₄ as raw materials. The detailed procedure was as follows: the stoichiometric amount of raw materials FeC₂O₄ and NH₄H₂PO₄ were mixed and milled in a planetary mill at a speed of 300 r/min for 4 h in acetone to get them thoroughly mixed. The slurry was then dried at 80 °C to remove acetone. The dried mixture was heated to 650 °C in an argon atmosphere to start the reaction of FeC₂O₄ and NH₄H₂PO₄, and finally Fe₂P₂O₇ was prepared.

Fe₂P₂O₇, stoichiometric Li₂CO₃ and some glucose were ball-milled at a speed of 300 r/min for 4 h in acetone to ensure a homogenous mixing. After being dried at 80 °C overnight, the mixture was ground and then sintered at 700 °C under a flowing argon gas. Composite cathode material LiFePO₄/C (simply denoted as LiFePO₄/C) was synthesized in the sintering procedure. Carbon content of LiFePO₄/C was determined as follows: dissolve LiFePO₄/C in hydrochloric acid, filtrate the solution, wash the indissoluble carbon

thoroughly, finally calculate mass fraction of the dried carbon.

X-ray powder diffraction of $\text{Fe}_2\text{P}_2\text{O}_7$ and LiFePO_4 was performed on Philips X'pert powder diffractometer with Cu K_α radiation. The morphology of $\text{Fe}_2\text{P}_2\text{O}_7$ was characterized using scanning electron microscope (SEM) (JSM-5600LV, JEOL).

The electrochemical performance test of LiFePO_4/C was carried out with coin cell 2025 which was assembled in an argon atmosphere glove-box. The electrolyte was 1 mol/L LiPF_6 in a 1:1 (volume ratio) mixture of ethylene carbonate (EC) and dimethyl carbonate (DEC). Membrane used is Celgard2300 and the metal lithium was used as the anode electrode. N-methyl pyrrolidinone was used as organic solvent, and the cathode electrode was made, which consisted of 80% LiFePO_4 , 10% PVDF (polyvinylidene fluoride) binder and 10% carbon black (in mass fraction) coated onto an aluminum foil current collector. The cathode was dried under vacuum at 120 °C for 24 h before cell assembly procedure. The coin cells were galvanostatically charged and discharged at 0.1C rate and cut-off of 2.5–4.1 V.

3 Results and discussion

3.1 Preparation and characterization of $\text{Fe}_2\text{P}_2\text{O}_7$

The preparation of $\text{Fe}_2\text{P}_2\text{O}_7$ using FeC_2O_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ as raw materials in an argon atmosphere can be described as follows:



Actually, the divalent metal pyrophosphates $\text{M}_2\text{P}_2\text{O}_7$ ($\text{M}=\text{Fe}, \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$) are polymorphic, including α , β and γ phases. Radical $\text{P}_2\text{O}_7^{4-}$ is the common ion in pyrophosphates, among which the $\text{P}-\text{O}-\text{P}$ bond angles are different from each other in the range of 120°–180°, and the bond length of $\text{P}-\text{O}$ in $\text{P}-\text{O}-\text{P}$ is longer than that in tip $\text{P}-\text{O}$ (Fig.1). HOGGINS^[12] reported that $\text{P}-\text{O}-\text{P}$ bond angle of $\text{Fe}_2\text{P}_2\text{O}_7$ is linear as a result of extensive π bonding with the p orbital on the bridge oxygen atom.

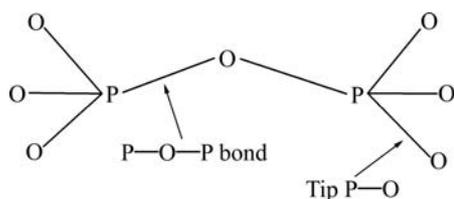


Fig.1 Plane configuration of structure of radical $\text{P}_2\text{O}_7^{4-}$

The X-ray diffraction pattern of $\text{Fe}_2\text{P}_2\text{O}_7$ prepared is shown in Fig.2. According to Ref.[13], the as-prepared $\text{Fe}_2\text{P}_2\text{O}_7$ crystallizes in the $\bar{C}1$ space group and belongs

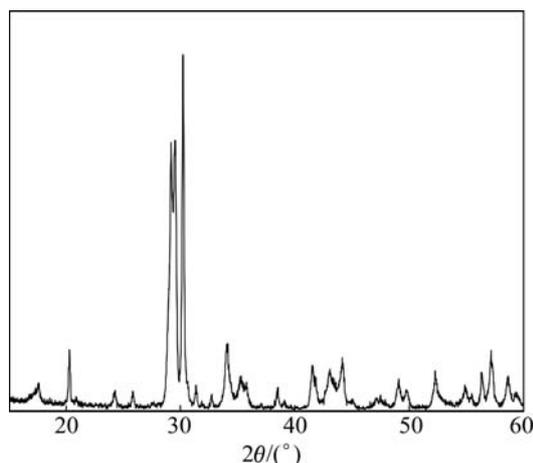


Fig.2 X-ray diffraction pattern of $\text{Fe}_2\text{P}_2\text{O}_7$ prepared at 650 °C

to $\beta\text{-Fe}_2\text{P}_2\text{O}_7$ for crystal phase, which is isostructural with high temperature form of $\beta\text{-Mg}_2\text{P}_2\text{O}_7$.

In this experiment, fully crystallized $\text{Fe}_2\text{P}_2\text{O}_7$ was made at 700–900 °C using FeC_2O_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ as raw materials in an argon atmosphere. Here, it must be mentioned that according to the experiment results, there is, to a certain extent, no difference in electrochemical performance between LiFePO_4/C samples with same carbon content using either $\text{Fe}_2\text{P}_2\text{O}_7$ prepared at 650 °C as precursor or fully crystallized ones obtained at higher temperature.

The SEM image of the as-prepared $\text{Fe}_2\text{P}_2\text{O}_7$ is shown in Fig.3. The powders have a narrow particle size distribution ranging from 0.4 to 3.0 μm . An average primary crystal size can be roughly estimated using Schererr equation^[14]:

$$d = \frac{0.89\lambda}{B \cos \theta} \quad (2)$$

where d is the average crystal size, 0.89 is Schererr constant, $\lambda=0.154$ nm is the wavelength of X-ray, B is the

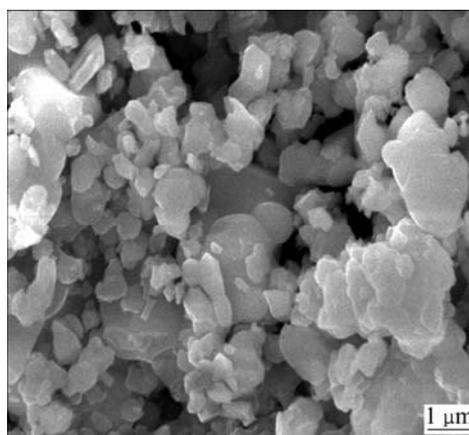


Fig.3 SEM image of $\text{Fe}_2\text{P}_2\text{O}_7$ powder prepared at 650 °C using FeC_2O_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ as raw materials

width (in radian) of the X-ray diffraction peak at half maximum intensity and θ is Bragg diffraction angle. With the reference of the X-ray diffraction data, the calculated crystal size is 91 nm. The small primary crystallinity and fine particles of the as-prepared $\text{Fe}_2\text{P}_2\text{O}_7$ allow its easily homogenous mixing and reaction with Li_2CO_3 , ensuring a thorough Li^+ chemical intercalation in the synthesis procedure of LiFePO_4 .

3.2 Synthesis of LiFePO_4 and mutual transformation between PO_4^{3-} and $\text{P}_2\text{O}_7^{4-}$

The synthesis of LiFePO_4 using $\text{Fe}_2\text{P}_2\text{O}_7$ and Li_2CO_3 as raw materials in an inert atmosphere can be expressed by the following reaction:



It should be noticed that in the procedure of synthesis of $\text{Fe}_2\text{P}_2\text{O}_7$ and thereafter LiFePO_4 an exciting mutual conversion between PO_4^{3-} and $\text{P}_2\text{O}_7^{4-}$ is realized: $\text{PO}_4^{3-} \rightarrow \text{P}_2\text{O}_7^{4-} \rightarrow \text{PO}_4^{3-}$. In this work, PO_4^{3-} is converted into $\text{P}_2\text{O}_7^{4-}$ in the reaction of $\text{NH}_4\text{H}_2\text{PO}_4$ and FeC_2O_4 . There are some other cases for this conversion. Generally, $\text{Fe}_2\text{P}_2\text{O}_7$ is prepared by the reduction of FePO_4 in a reductive atmosphere containing H_2 via a long and strict process^[15]. Some divalent metal pyrophosphates can be obtained by heating their corresponding ammoniated or acidic phosphates. For example:



In aqueous solution, dilute phosphoric acid H_3PO_4 becomes viscid when heated to 422 K and then dehydrates into $\text{H}_4\text{P}_2\text{O}_7$ when heated to 485–486 K, and finally pure $\text{H}_4\text{P}_2\text{O}_7$ is obtained at 528–533 K.

For the transformation from $\text{P}_2\text{O}_7^{4-}$ to PO_4^{3-} , however, there are few cases reported ever. In this work, pure LiFePO_4 was prepared by disrupting the $\text{P}_2\text{O}_7^{4-}$ radical into two PO_4^{3-} ions in the presence of O^{2-} at elevated temperature in an inert atmosphere. Though $\text{Fe}_2\text{P}_2\text{O}_7$ can be dissolved in acidic solution, it is sluggish in kinetics. Due to the high dissolubility of LiFePO_4 in acidic solution, the structural conversion from $\text{P}_2\text{O}_7^{4-}$ to PO_4^{3-} provides a feasible technique to dispose those pyrophosphates of low dissolubility.

3.3 XRD characterization of pure LiFePO_4 and LiFePO_4/C

The X-ray powder diffraction patterns of pure LiFePO_4 prepared using the as-prepared $\text{Fe}_2\text{P}_2\text{O}_7$ and Li_2CO_3 and LiFePO_4/C obtained using $\text{Fe}_2\text{P}_2\text{O}_7$, Li_2CO_3 and glucose are shown in Fig.4. The two diffraction lines are indexed to an orthorhombic crystal structure (space group $Pnma$). The peaks in both curves are very sharp

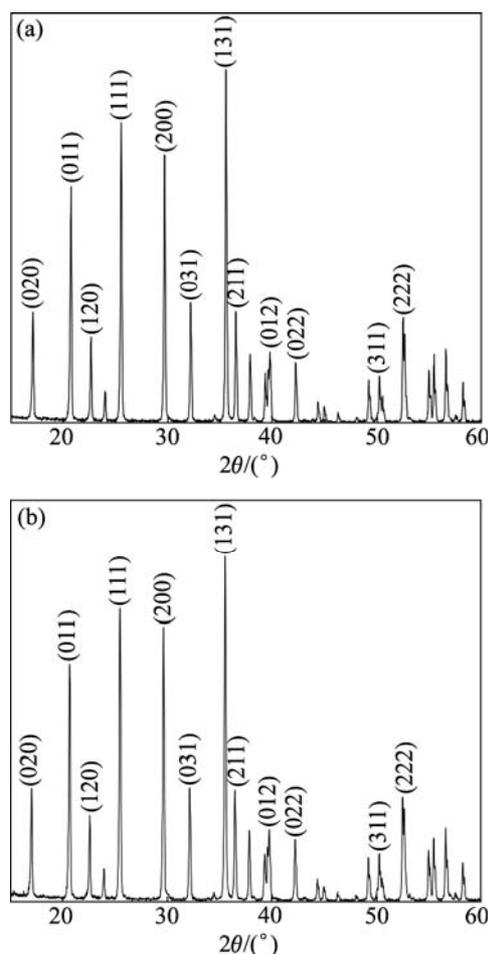


Fig.4 X-ray diffraction patterns of pure LiFePO_4 (a) and LiFePO_4/C (b)

and perfect, suggesting a high degree of crystallinity. The patterns agree well with that of phospho-olivine LiFePO_4 , and no impurity phase is detected. For the diffraction of LiFePO_4/C , no peaks of carbon are revealed, indicating the amorphous property of the electron conductor.

3.4 Electrochemical test of LiFePO_4/C

The charge/discharge curves of LiFePO_4/C (Fig.5) reveal a flat potential plateau of 3.45 V (vs Li^+/Li). At this voltage, the lithium extraction/insertion proceeds at the room-temperature in a two-phase reaction between LiFePO_4 and FePO_4 that belongs to the same space group. A 0.08 V voltage difference between charge and discharge plateaus is shown in Fig.5, which represents very small polarization in electrodes and electrolyte of coin cell during charge and discharge process.

The first charge and discharge capacities of LiFePO_4/C are 154 and 132 mA·h/g, accounting for 90.6% and 77.6% of the theoretical value (170 mA·h/g), respectively. Here, it can be concluded the ecumenic electrochemical performance and low efficiency of the initial cycle (85.7%) of the LiFePO_4/C are ascribed to the

non-optimal coating of carbon and calcining temperature and time. Furthermore, the appearance of LiFePO_4/C is a medium to dark grey, and according to Ref.[16], the conductivity of the as-prepared LiFePO_4/C in this color is not high enough to ensure an appreciable electrochemical performance. More evidence about the poor conductivity of LiFePO_4/C is the low efficiency of the initial charge/discharge. Further work will be carried out to study charge/discharge capacity and improve initial charge/discharge efficiency of LiFePO_4/C .

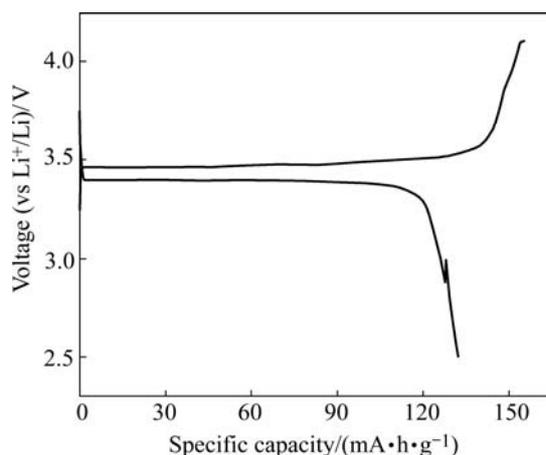


Fig.5 Initial charge/discharge curves of LiFePO_4/C (mass fraction of carbon is 9%)

4 Conclusions

1) $\beta\text{-Fe}_2\text{P}_2\text{O}_7$ with high purity is prepared through solid phase reaction at $650\text{ }^\circ\text{C}$ using starting materials of FeC_2O_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ in an argon atmosphere. Pure LiFePO_4 and LiFePO_4/C can be synthesized by solid state reaction at $700\text{ }^\circ\text{C}$ in an argon atmosphere using the as-prepared $\text{Fe}_2\text{P}_2\text{O}_7$ and Li_2CO_3 .

2) Radical $\text{P}_2\text{O}_7^{4-}$ is disrupted into two PO_4^{3-} ions in the presence of O^{2-} during the synthesis procedure of LiFePO_4 , thus an important mutual transformation is realized: $\text{PO}_4^{3-} \rightarrow \text{P}_2\text{O}_7^{4-} \rightarrow \text{PO}_4^{3-}$, which offers a feasible technique to deal with this hardly dissolvable pyrophosphate.

3) Composite material LiFePO_4/C shows appreciable initial charge and discharge capacities of 154 and 132 $\text{mA}\cdot\text{h}/\text{g}$, respectively.

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