

Preparation and Properties of LiFePO_4 /C Cathode Material by the Sol-gel Method

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Abstract: The nanosized cathode material LiFePO_4/C composites were prepared through the sol-gel method using $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ as the carbon source. Meanwhile, the effect of sintering temperature on the structure and property of LiFePO_4/C was investigated. It was found that the LiFePO_4/C sample had only LiFePO_4 phase when the sintering temperature ranging from 600 to 750 °C. When the sintering temperature was 700 °C, the corresponding electrode exhibited the best electrochemical performance. The initial discharge capacity of LiFePO_4/C reached $153.1 \text{ mAh} \cdot \text{g}^{-1}$ at 0.1 C, and retained $114.2 \text{ mAh} \cdot \text{g}^{-1}$ at 5 C between 2.5 and 4.2 V, and this capacity almost preserved after 20 cycles.

1. Introduction

Lithium ion secondary battery which has high working voltage, long cycle life and friendly with environment features become the research hot spot. The positive electrode material is an important component of lithium battery, which is one of the key factors affecting the battery performance. And olivine type lithium iron phosphate (LiFePO_4) has high specific capacity (theoretical specific capacity is $170 \text{ mAh} \cdot \text{g}^{-1}$), good reversible cycle performance, high safety, as well as the low price advantage. It is one of the most promising lithium ion battery cathode material. But it is difficult to synthesize and the electron conductivity and lithium ion migration rate are low, which seriously hinders its practical application process. At present researchers mainly used in a variety of synthetic methods, by controlling the particle size, surface coating (such as carbon coated) and ion doping methods to improve the electric conductivity and high rate charge and discharge performance of LiFePO_4 [1]. There are many methods to prepare LiFePO_4 , including solid phase method, hydrothermal method, sol-gel method, microwave synthesis method and so on. The sol-gel method is widely used for its advantages such as low consumption, uniform mixing, high purity crystallinity, small particle size and easy operation. However, in improving the life of LiFePO_4 conductivity, the addition of carbon materials is a simple and efficient method. Join carbon ways mainly has two kinds: one is the reaction of LiFePO_4 powder evenly mixed with carbon derived from organic matter, and under the condition of high temperature heat treatment for carbon decomposition of organic matter and conductive carbon; Another is the addition of carbon to organic compounds in the process of preparing LiFePO_4 to produce the carbon coated LiFePO_4 materials under heat treatment. In this paper, using the sol-gel method in situ synthesized conductive carbon film coated LiFePO_4 nanomaterials, the properties are studied under different sintering temperature.

2. Experimental part

2.1 Material synthesis

Figure 1 is the synthesis process of sol-gel for LiFePO_4/C material. $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$ as source of lithium, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as source of iron, with $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ as chelating agent, reducing agent

and carbon source, will first 10% $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ (the relative quality of LiFePO_4) dissolved in a certain amount of deionized water, form a homogeneous solution under the action of a magnetic stirring; The molar ratios of $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ were added to the solution, and the mixture was mixed for 2 h in the mixer. The solution is then heated to 80°C to slowly vaporize the excess water until the dried gel is formed. Dry the dry gelatin in a vacuum drying oven for 24 h under 100°C ; Finally transfer the precursor to filled with argon hydrogen (H_2) 5% of the mixer tube furnace, heat treatment, respectively, in 600°C and 650°C and 700°C and 650°C sintering temperature insulation 12h, at last LiFePO_4/C material natural cooled to room temperature.

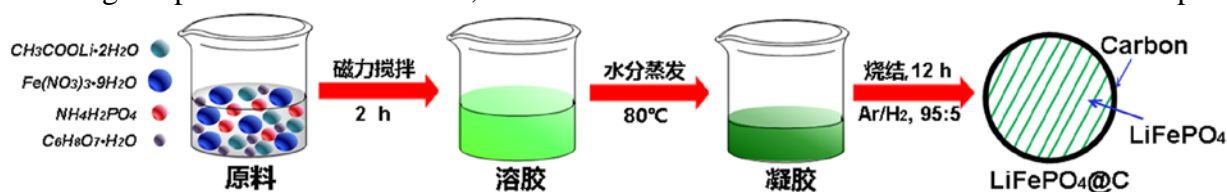


Figure 1 Schematic illustration of the synthesis of LiFePO_4/C by using the sol-gel method

2.2 Material characterization

The thermogravimetric analysis (TGA) was carried out with the Model Q50 thermal analyzer of American TA company in the nitrogen atmosphere condition. the X-ray diffraction (XRD) analysis was performed on the rigaku-d/max-2550pc X-ray powder diffractometer; X-ray photoelectron spectroscopy (XPS) analysis of ESCALAB250 MgK α radiation of symerfjet technology co.LTD. The scanning electron microscope (SEM) analysis and energy conversion dispersion (EDS) analysis were performed on the XL30ESEM-TMP type scanning electron microscope in Philips, Netherlands.

2.3 Battery assembly and testing

The quality of LiFePO_4 , acetylene black and polyvinylidene fluoride at 85:10:5 is weighed, and it is mixed in the mortar of agate mortar, and the amount of n-methylpyrrolidone solvent is added in the grinding process. Mix and apply on aluminum foil, drying 12 h in vacuum drying oven of 120°C . In the end, the plate is pressed into thin slices with a roller press, and a round positive plate with a diameter of 14 mm is made. In the glove box full of argon, in preparation of electrodes for the anode, metal lithium as negative, with polypropylene microporous membrane Celgard - 2400 for the diaphragm, with 1 mol/L LiPF_6 ethylene carbonate + diethyl carbonate (1:1, volume) solution as the electrolyte, assemble CR2032 battery buckle type experiment. The Land battery test system manufactured by wuhan jinnuo electronics co, LTD was tested for charging and discharging.

3. Results and discussion

3.1 TGA and XRD analysis

FIG. 2(a) is the thermal failure analysis diagram (TGA) of the precursor of sol-gel. It can be seen from the TGA curve that with the increase of sintering temperature, the phenomenon of material weightlessness occurred in LiFePO_4/C precursor, which indicates that the precursors began to undergo chemical reaction under the influence of temperature. When the temperature is higher than 450°C , the weight loss rate of raw materials starts to slow down, indicating that the by-products of CO_2 , NH_3 , NO_2 and H_2O are evaporating. When the temperature is higher than 550°C , the TGA curve gradually enters the constant weight region. It can be inferred that the precursors begin to crystallize at the time of 550°C , forming the product of LiFePO_4/C . According to the analysis results of TGA, it is appropriate to select $600 \sim 750^\circ\text{C}$ as the sintering temperature of LiFePO_4/C material.

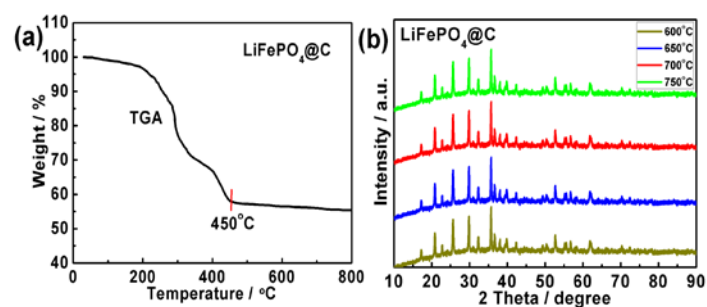


Figure 2 The TGA curve (a) and XRD profiles (b) of the LiFePO_4/C products prepared at different temperature

Figure 2(b) shows the XRD diagram of the synthetic LiFePO_4/C material at different sintering temperatures. According to the standard atlas of LiFePO_4 , the samples of LiFePO_4/C prepared are all crystalline and complete LiFePO_4 phases, which show that at four temperatures, the crystallinity of LiFePO_4/C material can be synthesized. The corresponding materials of different temperatures are single olivine type LiFePO_4 phase, and the peak is sharp, and there is no Li_3PO_4 , FeP or Fe_2P hybrid. This result is consistent with relevant literature reports [2-5].

3.2 XPS analysis

Figure 3. XPS of LiFePO_4/C material prepared at 700°C temperatures. By figure 3 (a), XPS curves clearly contain $\text{Li}1s$, $\text{Fe}2p$, $\text{P}2p$, $\text{C}1s$ and $\text{O}1s$ corresponding to the peak, the peak position respectively at 55.6 eV (FIG. 3 (b)), 724.6 eV (FIG. 3 (c)) (FIG. 3 (d)), 133.8 eV and 531.5 eV (FIG. 3 (e)), and 284.8 eV (FIG. 3 (f)), in addition to this, no other impurity elements in XPS curves of characteristic peak. It shows that there are C elements in LiFePO_4/C material.

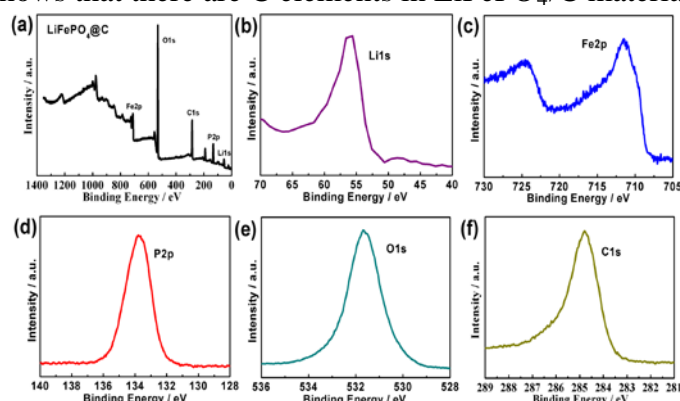


Figure 3 XPS curves of LiFePO_4/C prepared at 700 oC

3.3 SEM, EDS

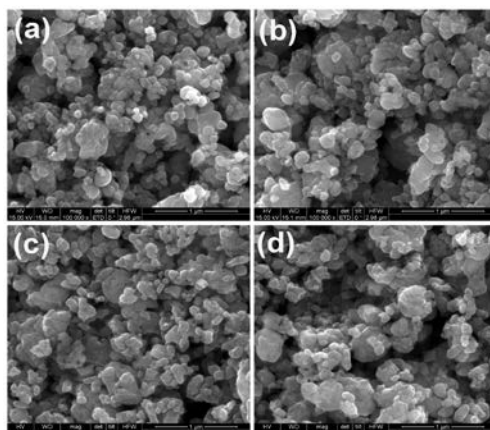


Figure 4 SEM images of LiFePO_4/C composite prepared at different temperature

Fig.4 (a) and (b) are the sintered products under 600°C and 650°C. The particle size of the two materials is not uniform and the morphology of the particles is significantly different. Figure 4 (c) is 700°C temperature preparation of SEM figure of LiFePO₄/C material, its grain size is even, average particle size is 100 nm, and the grain size is in the shape of a ball which greatly increased the specific surface area of the interface, can promote the interface of the electrode reaction rate [6, 7]. FIG. 4(d) is a sintered product of 750°C. It can be seen that as the temperature rises, the particle has a tendency to grow, which will lead to the degradation of the electrochemical properties of the material. Figure 5 is the EDS spectra of LiFePO₄/C material synthesized at 700 °C temperatures. As shown in figure 5 (b-d), Fe, P, and O elements are uniformly dispersed in composite materials. In addition, the C element (FIG.5(e)) is also distributed evenly in the LiFePO₄/C granules to further prove the existence of carbon materials.

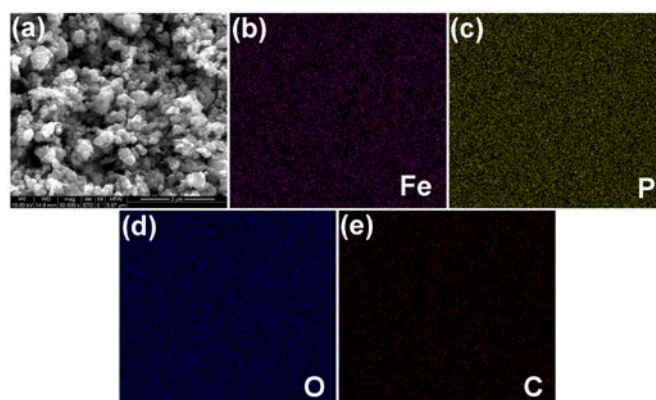


Figure 5 EDS mapping images of LiFePO₄/C prepared at 700 oC

3.4 Electrochemical performance test analysis

Fig. 6 shows the first charge and discharge curve and cyclic stability of LiFePO₄/C materials synthesized at different temperatures. The figure 6 (a) shows that when the sintering temperature is 700°C, the first discharge specific capacity of the sample is the largest, 153.1 mAh•g⁻¹ close to the 90% of the theoretical capacity (170 mAh•g⁻¹). The capacity value is higher than the literature reported by solid instead of synthesis method of the capacity of the sample [8-11]. In the case of four materials, their charge-discharge curve has a flat voltage platform near 3.5v, which is caused by Li⁺ in the LiFePO₄ structure and embedded in the two opposite causes [12-13]. The figure 6 (b) shows that 700°C corresponding sample has the best cycle stability, after 30 cycles, its capacity to keep at a rate of 98.2%.

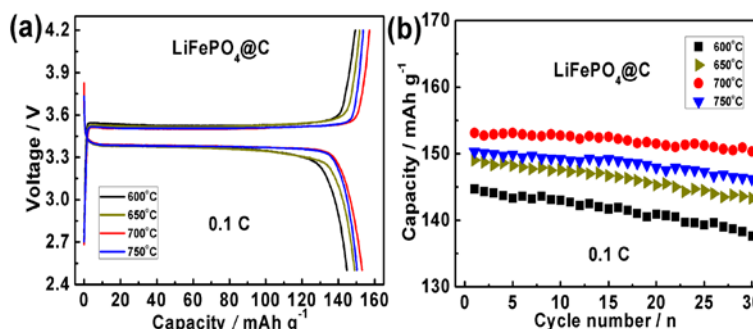


Figure 6 Initial charge-discharge curves and cycling stability of the obtained LiFePO₄/C materials at a rate of 0.1 C

Fig. 7 is the relationship between discharge ratio and current density of LiFePO₄/C material synthesized at different sintering temperatures. As can be seen from the figure, the discharge ratio of all LiFePO₄/C materials gradually decreases with the increase of charging current density. In particular, samples prepared under the conditions of 600°C, the volume attenuated rapidly and the discharge ratio of 0.2c was 141.2 mAh•g⁻¹ When the multiplier was increased to 5 C, its capacity

decreased rapidly to $81.6 \text{ mAh}\cdot\text{g}^{-1}$. On the contrary, the samples corresponding to 700°C have a good multiplier performance, and even in the case of high magnification and discharge of the 5C, its capacity remains at $114.2 \text{ mAh}\cdot\text{g}^{-1}$. Figure 8 is the cyclic performance of LiFePO_4/C material synthesized at different temperatures. It can be seen from the figure that the discharge ratio of four samples at the same ratio is maintained in a certain numerical range, with no significant attenuation. 700°C temperature synthesis of electrode samples under different ratio of cycle performance are better than the other three samples, under 2 C and 5 C high-magnification cycle after 20 times, its specific capacity remains at 128.2 and $108.7 \text{ mAh}\cdot\text{g}^{-1}$, capacity rate were 96.7% and 95.2% respectively.

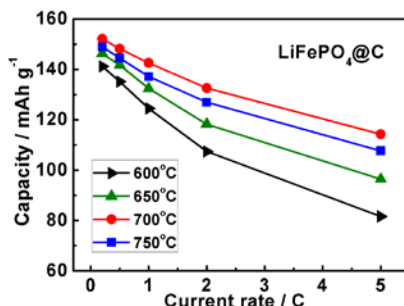


Figure 7 The rate capability of LiFePO_4/C electrode materials prepared at different temperature

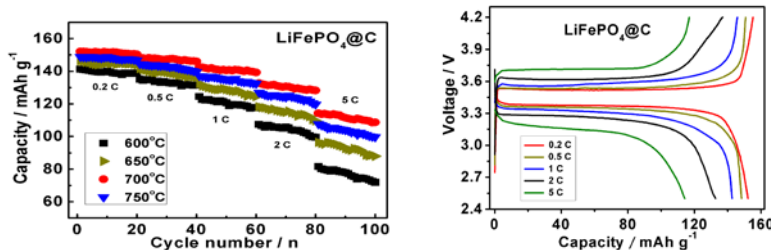


Figure 8 The cycling performances of the as-fabricated LiFePO_4/C at various temperature

Figure 9 the charge-discharge curve of LiFePO_4/C synthesized at different times of the 700°C

FIG. 9 is the charge-discharge curve of LiFePO_4/C synthesized at different times of the 700°C temperature. As can be seen from the figure, the discharge ratio of 0.2c is $152.1 \text{ mAh}\cdot\text{g}^{-1}$, and the voltage of the charging and discharging platform is relatively stable. As the multiplying ratio increases, especially at the 5 C high ratio, the voltage of the charging and discharging platform changes, which indicates that the electrode material is polarized during charging and discharging. Andersson etc[14] believed that the main step affecting the charging and discharging process was the diffusion of Li^+ in the $\text{LiFePO}_4/\text{FePO}_4$ phase interface when reembedding the FePO_4 structure. As of lithium, FePO_4 interface is falling, when the interface through the unit area of the lithium ions at constant rate, will reach a critical interface area, and through the interface of the total transfer rate of lithium ion is not enough to maintain the current, the size of this leads to large reversible capacity attenuation when current density and the polarization phenomenon. The above analysis shows that the carbon coating of the conductive agent only increases the surface conductivity of LiFePO_4 , and the conductivity of the material is not effective.

4. Conclusion

(1) Using citric acid as a chelating agent and carbon source, precursor is synthesized by sol-gel method. The in-situ decomposition of citric acid at high temperature makes the surface of LiFePO_4 particles coated with a conductive carbon film, which greatly improves the surface conductivity of LiFePO_4 .

(2) Without any impurity phase, the LiFePO_4/C composites prepared by sol gel method are all

LiFePO₄ phase of olivine type structure within 600~750 °C range. It indicates that sol-gel method is a simple and effective way to synthesize LiFePO₄.

(3) Sintering temperature plays a significant role in controlling the morphology and particle sizes of LiFePO₄/C, which will affect the lithium storage performance of the electrode material. The results show that the particles synthesized at 700°C temperature are uniformly fine and basically spherical, which will shorten the diffusion path of Li⁺ and improve the electrochemical performance of the material.

(4) Under the optimized condition (700°C), the LiFePO₄/C electrode materials have good lithium storage properties. In the voltage range of 2.5-4.2 V, the initial discharge specific capacity of the material at 0.1 C low rate reaches 153.1 mAh g⁻¹. In the condition of 5 C capacity is still as high as 114.2 mAh g⁻¹, and the electrode in different magnification has good cycle stability.

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