

Preparation of LiFePO_4 powders by co-precipitation

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Abstract

Pure olivine LiFePO_4 can be successfully prepared with co-precipitation from aqueous solution containing trivalent iron ion. The introduction of hydrolyzed sugar before heating give the best result, because the poor conductivity of the powders can be improved by synthesizing small and homogeneous powders with coatings of electronically conductive materials. The resultant LiFePO_4/C composite with carbon scaffold and LiFePO_4 embedded can achieve high specific capacity (143 mAh g^{-1}) after the 100th cycle with 1 C charge/discharge rate at 50°C . The excellent cycle life and stability as well as cheap precursor solution make the process feasible commercially. Moreover, since the only auxiliary product of thermal treatment in this process is water vapor, the process is more environmental friendly than other synthesized methods. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

In the several materials under development for use as cathodes in lithium-ion batteries, orthophosphates LiMPO_4 ($M = \text{Mn, Fe, Co, Ni}$) structure to olivine are intensively studied as lithium insertion compounds [1–3]. Among the LiMPO_4 , lithium iron phosphate, LiFePO_4 , has been recognized as a promising candidate for Li batteries cathode due to the low cost, environmental benignity, cycling stability and high theoretical capacity of 170 mAh g^{-1} [4–7].

However, the poor conductivity, resulting from the low lithium-ion diffusion rate and low electronic conductivity in the LiFePO_4 phase, shows that approximately 0.6 lithium atoms per formula unit can be extracted at a closed-circuit voltage of 3.5 V Li/Li^+ [1]. The schemes to solve this major problem are to prepare a small and homogeneous particle size distribution [8–11] and to provide a novel coating technology to obtain an electronic conductive particle coating or LiFePO_4 /electronic conductor composite compound [12–14].

The co-precipitation method, a commercially feasible process, can prepare a fine, chemically uniform and more

homogeneous powder size distribution of LiFePO_4 . Up to date, the bivalent iron precursors, which are usually expensive, are used as the precursors for co-precipitation. Barker et al. have successfully synthesized LiFePO_4 from trivalent iron ion (Fe_2O_3) by carbothermal reduction method [20]. However, the reducing atmosphere produced at high temperature ($>650^\circ\text{C}$) is required for iron reduction. The high temperature ($>600^\circ\text{C}$) will lead to the undesired particle grow [3].

In this study, we synthesize the fine precursor particle of LiFePO_4 by co-precipitation with aqueous precursor solution containing trivalent iron ion that has never been reported literature.

2. Experimental

2.1. Synthesize precursor

The aqueous precursor mixture of $\text{Fe}(\text{NO}_3)_3$, LiNO_3 , $(\text{NH}_4)_2\text{HPO}_4$, ascorbic acid and appropriate amount of ammonia was used. The purpose of ascorbic acid had reduced Fe^{3+} to Fe^{2+} in the aqueous precursor [15]. The amount of sugar added into the precursor solution is 20 wt% of LiFePO_4 to be formed. That co-precipitated powder can be easily separated in a centrifuge and then the co-precipitated powder

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was dispersed in the hydrolyzed sugar solution, followed by drying and heating. The sugar-coated powder was calcined at 350 °C for 10 h and subsequently sintered at 600 °C for 16 h in nitrogen atmosphere. The sugar will be converted to carbon and distributed evenly on the LiFePO₄ powders.

2.2. Structural and morphological characterization

X-ray diffraction (XRD) profiles of the sample were measured with a Shimadzu XRD-6000 diffractometer (Cu K α radiation). Structural parameters were determined by GSAS analysis of diffraction profiles. A simultaneous thermogravimetric–differential thermal analysis (TG–DTA) apparatus SDT 2960 (TA instrument) was used for the thermal characterization. The particle size distribution was determined by the optical particle size analyzer (Mastersizer X). The morphology and particle size distribution can be observed by SEM (Hitachi S-800). The BET specific surface area of LiFePO₄/C compound powder measurement was performed by N₂ adsorption–desorption method (Micromeritics Gemini 2375). Elemental composition of the compound powder (Li, Fe) was determined by ICP-AES (Perkin-Elmer Optima 2000), and amount of C, N and H was determined by element analyzer (Heraeus VarioEL-III for CNH).

2.3. Electrochemical characterization

Electrochemical properties of the lithium iron phosphate powders were studied by assembling 2032 coin cells with lithium metal as an anode and 1 M LiPF₆ in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume) as an electrolyte. All the manipulations were made in an argon-filled glove box with oxygen and moisture control less than 2 ppm. The cathode for the cells was prepared by mixed 75 wt% active materials with 20 wt% of carbon additive

(including conducting carbon black and carbon converted from sugar) and 5 wt% polyvinylidene fluoride (PVDF) binder in *N*-methyl-2-pyrrolidone (NMP). The intensively mixed slurry was blade-coated onto aluminum foil and dried overnight at 120 °C in an oven. The circular electrodes were punched after roller-pressing the dried foil. The cells were cycled between 2.5 and 4.3 V in a multi-channel battery tester.

3. Results and discussion

3.1. Thermal analysis

Fe³⁺ in aqueous precursor solution can be reduced to Fe²⁺ by the addition of ascorbic acid. It can be verified from the fact that the color of the aqueous solution can change from brown to greenish color after the addition of ascorbic acid. According to reaction formula (1), the products of the co-precipitated powder could be the Fe₃(PO₄)₂·*n*H₂O and Li₃PO₄. These mixed powders were subsequently calcined at 350 °C for 10 h and then sintered at 600 °C for 16 h in nitrogen atmosphere can obtain LiFePO₄ powder. The formula (2) could be the formation reaction of LiFePO₄ from these as-calcined powders. Fig. 1 shows the TG/DTA curves of the powders co-precipitated from aqueous precursor with hydrolysis-sugar coating. The weight losses at temperatures between 60 and 170 °C can be associated with desorption of the water and carbonization of hydrolysis-sugar, respectively. The steep weight loss at temperatures between 180 and 250 °C can be ascribed to the decomposition of nitrate. The organic materials that residual ammonia and hydrolysis-sugar were decomposed and carbonized before 350 °C. The DTA curve shows two exothermic peaks at 436 and 490 °C. One peak around 436 °C can be associated with the oxidation of carbon, which produce carbon monoxide or carbon dioxide

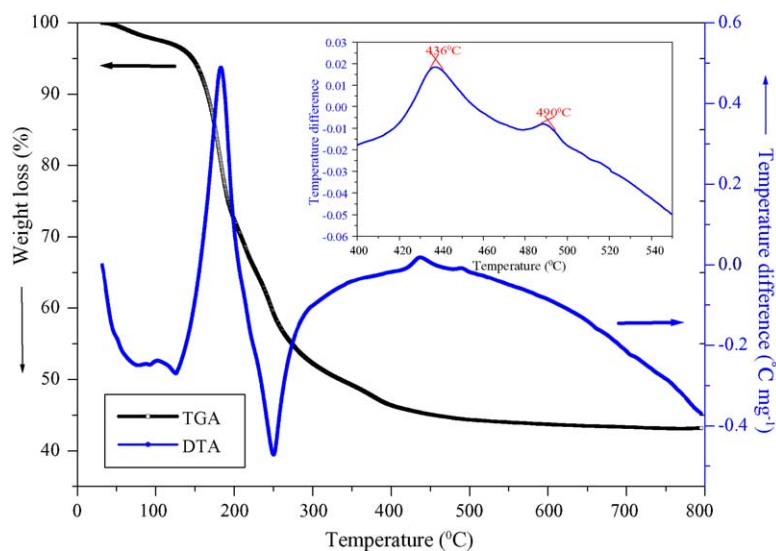


Fig. 1. The DTA/TGA curves for the precursor recorded over the temperature range from ambient to 800 °C at a heating rate of 5 °C min⁻¹ in N₂ atmosphere at 100 mL min⁻¹ flow rate.

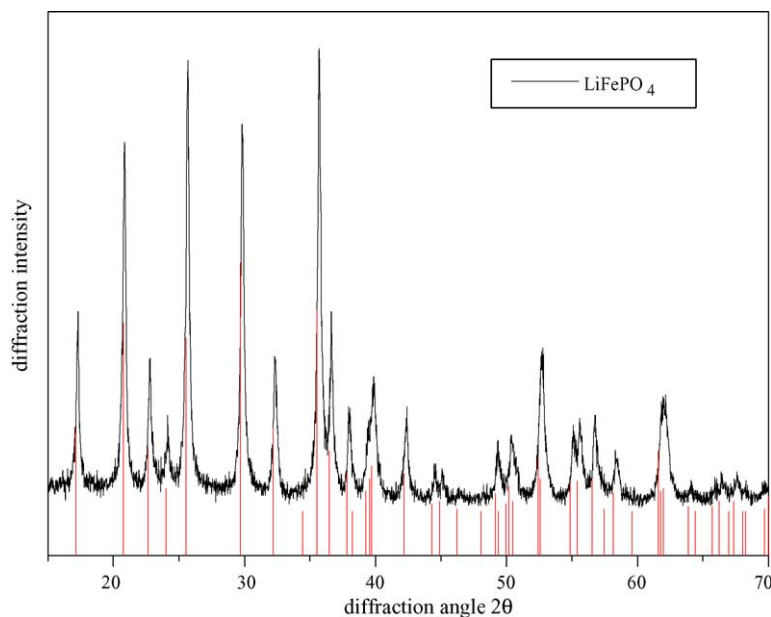
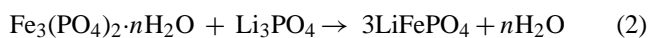
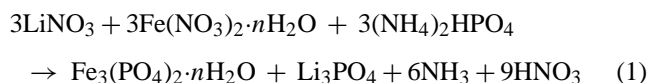


Fig. 2. The X-ray diffraction profiles of as-prepared LiFePO₄ power (Cu Kα radiations, potential 15 kV, current 40 mA, scan rate 0.02° s⁻¹).

[17]. From X-ray diffraction results, the peaks at 490 °C can be ascribed to crystallization of the amorphous LiFePO₄ [10]. The amount of carbon in LiFePO₄/C was of about 15.76 wt% determined with element analyzer.



3.2. Crystalline structure analysis

As shown in the XRD patterns of Fig. 2, the precursor with hydrolysis-sugar additive could be synthesized to the pure LiFePO₄ phase even with the presence of substantial amount of carbon in the powders. Through the GSAS software calculation, the lattice constants are $a = 10.328 \text{ \AA}$, $b = 6.006 \text{ \AA}$ and $c = 4.708 \text{ \AA}$, which are very similar to the reports [18]. Since the a - c planes containing the Li atoms are bridged by PO₄ tetrahedral [19], Li ions could diffusion along c -axis which has lowest diffusion energy barriers. Since the larger inter-plane spacing between a - c planes (i.e. c -axis) will facilitate the passage for Li ion movement, the powders with larger lattice constant c will give better electrochemical property even for higher charge/discharge rate at ambient temperature.

3.3. Microstructure of the powders

Chen and Dahn reported that the carbon was distributed on the surface of the as-sintered powder through the introduction of solid sugar into the as-calcined powders [13]. In this study, the carbon distribution, as shown in Fig. 3, is entirely different from the literatural reports. According to the reports

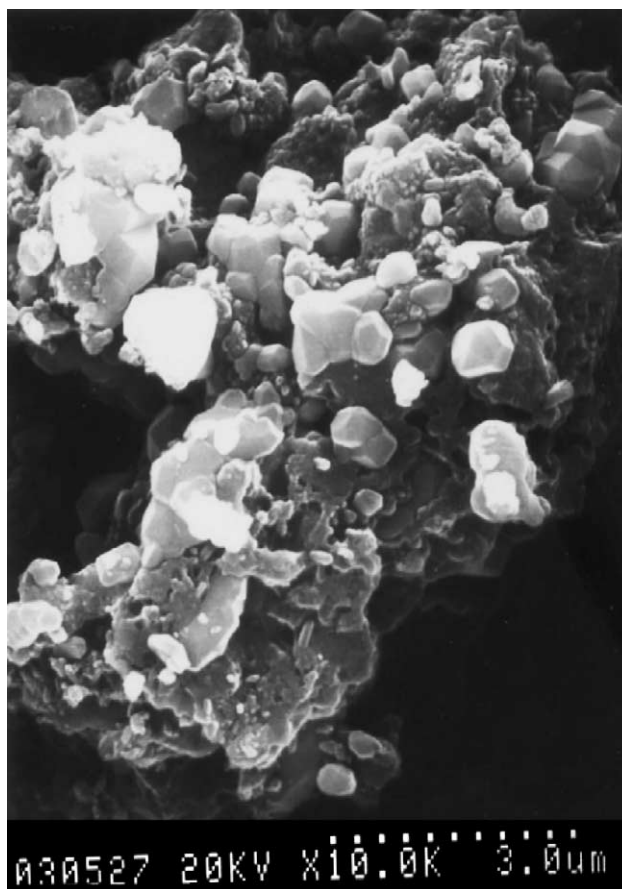


Fig. 3. SEM morphology of the LiFePO₄/C compound (calcined at 350 °C for 10 h and then heated at 600 °C for 16 h).

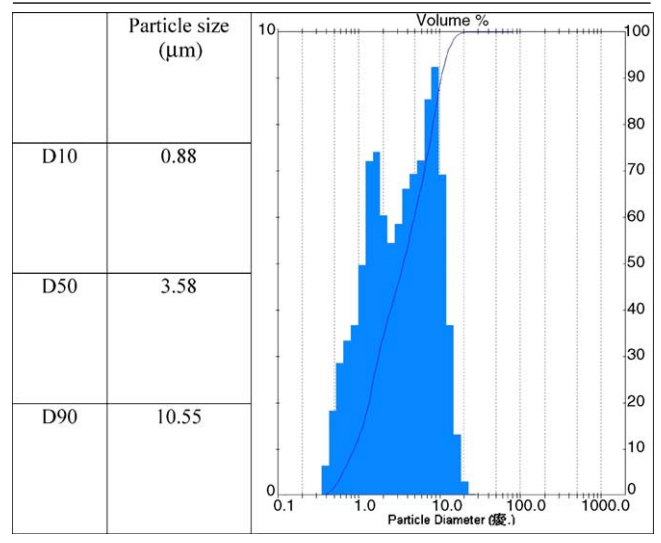
regarding to the preparation of zirconium oxide and alumina, the carbon reduced from the decomposition of hydrolyzed sugar will develop a porous structure [16,17]. The sugar ($C_{12}H_{22}O_{11}$) gets hydrolyzed to glucose ($C_6H_{12}O_6$) and fructose ($C_6H_{12}O_6$), which ultimately oxidizes to gluconic acid or a polyhydroxyl acid. The polyhydroxyl similar to polymer has cross-link property. The cross-link like precursor was calcined at 350°C for 10 h, the cross-link part would be decomposed to porous structure of carbon and metal ions were well distributed into porous structure. After heat treatment at 600°C for 16 h, the LiFePO_4 was embedded in the porous structure of carbon. The novel structure of carbon scaffold with LiFePO_4 embedded has the following advantages:

- (i) The LiFePO_4 powder was well distributed and avoided agglomerations.
- (ii) The porous structure of carbon would limit/prohibit the particle size to grow during heating.
- (iii) The conductivity of LiFePO_4/C composite would be enhanced due to the embedding of the LiFePO_4 powder in the carbon scaffold.
- (iv) The carbothermal reaction would readily induce the reaction of Fe^{3+} to Fe^{2+} by only burning out the oxide ($\text{C} \rightarrow \text{CO}$) [20].

3.4. Powder characterization

Since the porous structure of carbon, the surface area, determined by the BET method, is as high as $97.19\text{ m}^2\text{ g}^{-1}$. Ray and co-workers reported that the porosity structure of carbon would effectively control the particle size about $1\ \mu\text{m}$ [16,17]. For LiFePO_4 , similar result can be seen, as shown in Fig. 3.

Table 1

The particle size distribution of the LiFePO_4/C compound

The particle size distribution of LiFePO_4 , as listed in Table 1, was measured by the optical particle size analyzer (Mastersizer X). The particle distribution is bimodal. The population peak around smaller particle size is LiFePO_4 powder (about $1.51\ \mu\text{m}$) and another population peaks at larger particle size (about $8.04\ \mu\text{m}$) can be attributed to the LiFePO_4/C particles composed porous carbon structure with LiFePO_4 embedded. The results correspond well with SEM observation. The molar ratio of Li:Fe of lithium iron phosphate powder, determined with ICP analysis, is 1:1.001, which is very close to stoichiometry.

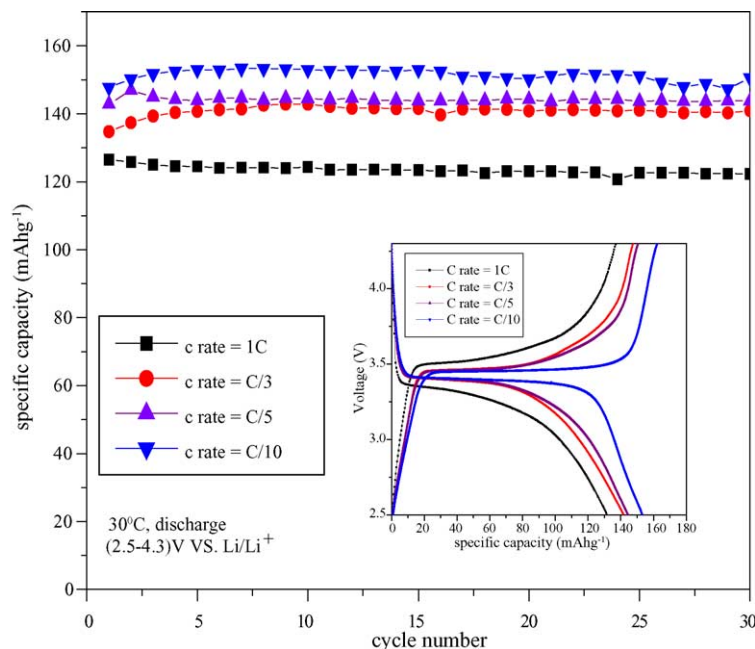


Fig. 4. The cyclability of LiFePO_4/C composite electrode at 30°C . Inset means the charge–discharge curves of LiFePO_4/C at 10th cycle at 30°C .

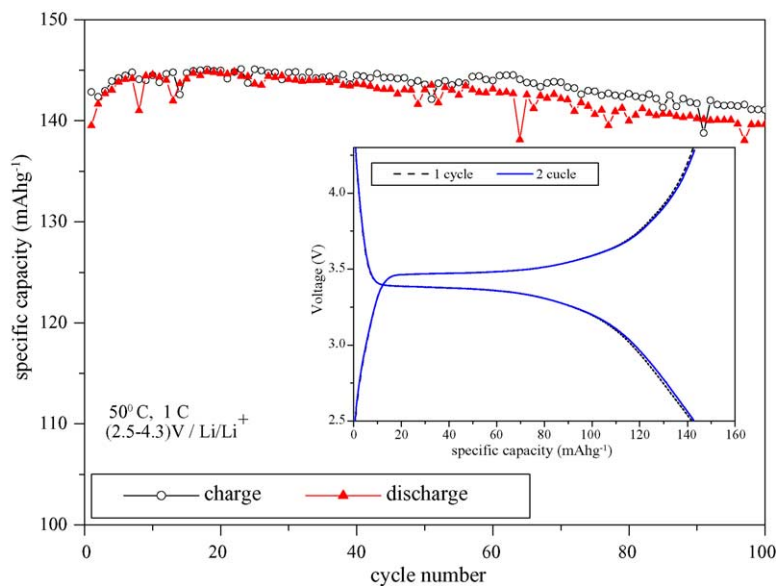


Fig. 5. The cyclability of LiFePO₄/C composite electrode at 50 °C. Inset means the 1 C charge–discharge curves of LiFePO₄/C at 100th cycle at 50 °C.

3.5. Electrochemical performance

Fig. 4 shows that specific capacity of the LiFePO₄/C powder in function of the cycle number with various charge/discharge rates at ambient temperature. With slow charge–discharge rate (C/10–C/3), the powder exhibits good capacity retention, 85% of theory capacity 169 mAh g⁻¹. The inset in Fig. 4 shows that a voltage plateau can be observed even after 10th cycle. At 50 °C, the capacity is more than 140 mAh g⁻¹. It is still remained good stability and reversibility (3.4 V plateau can be seen) even after 100 cycles, as shown in Fig. 5.

4. Conclusions

Pure olivine LiFePO₄ can be successfully prepared with co-precipitation from aqueous solution containing trivalent iron ion. The resultant LiFePO₄/C composite achieves high specific capacity (143 mAh g⁻¹) after the 100th cycle with 1 C charge/discharge rate at 50 °C due to homogenous distribution of carbon and small pure olivine LiFePO₄ embedded. The excellent cycle life and stability as well as cheap precursor solution make the process feasible commercially. Moreover, since the only auxiliary product of thermal treatment in this process is water vapor, the process is more environmental friendly than other synthesized methods.

Acknowledgement

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