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Short communication

Hydrothermal synthesis of monodispersed $LiFePO_4$ cathode materials in alcohol–water mixed solutions

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Abstract

Monodispersed $LiFePO_4$ powders were prepared by thermal decomposition of Fe(II)–citric acid complex precursor and application of isopropanol as a dielectric constant tuner. The powders morphology was greatly influenced by the volume ratio of isopropanol to water (RH ratio). Monodispersed short rod-like $LiFePO_4$ crystals were obtained when RH ratio was 1.0, while column-like $LiFePO_4$ particles composed of much smaller crystals were produced when isopropanol was absent.

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Keywords: Hydrothermal synthesis; Dielectric tuner; Monodispersed particles; Cathode materials

1. Introduction

Owing to its high capacity, stability, low toxicity and low raw materials cost, $LiFePO_4$ (triphylite) has become one of the most promising cathode materials for next generation rechargeable lithium ion batteries [1,2]. Since Goodenough group's discovery, great efforts have been made to improve the performances of this material till now [3–6]. One of the main problems for commercialization is its very low electronic conductivity. The synthesis of $LiFePO_4$ cathode materials with a small particle size and narrow size distribution was believed to be an effective way to enhance electronic conductivity [7].

Almost all of the intensively studied cathode materials, such as $LiFePO_4$, $LiNiVO_4$ and $LiMnO_2$ were synthesized successfully by the hydrothermal process [8–11]. Starting materials were suspensions of solid ferrous salts and lithium salt solutions, so the hydrothermal reaction system was inhomogeneous. As a result, particle nucleation and growth processes were uncontrollable, and the microstructures of products were largely unpredictable and undesignable.

Typical methods for the synthesis of inorganic monodispersed particles and fibers included: (1) homogeneous precipitation through the dissociation or decomposition of metal ion chelated complex precursors [12] and (2) thermal hydrolysis of alkoxide compounds or inorganic salt in alcohol–water mixed solutions [12–14]. In cases, both the particle nucleation and growth processes were controlled elaborately.

A new synthesis method for $LiFePO_4$ cathode materials by using Fe(II) chelated complex precursor and isopropanol as Fe(II) source and a dielectric constant tuner is presented.

2. Experimental

2.1. Preparation of the starting solution

The starting materials were analytical reagents: $LiOH\cdot H_2O$ ($\geq$98.0%), $FeSO_4\cdot 7H_2O$ ($\geq$99.0%), H_3PO_4 (85 wt.% solution) and citric acid (CA) ($\geq$99.8%) and isopropanol (99.7 wt.% solution). The hydrothermal synthesis process was carried out as follows. First, a desired amount of H_3PO_4 was added to distilled water. Fe(II)–CA solution was prepared by dissolving $FeSO_4\cdot 7H_2O$ and citric acid in the phosphoric acid solution in the molar ratio of Fe(II)/citric acid = 1.0:1.0. Then an appropriate amount of isopropanol was added, and the $LiOH\cdot H_2O$ solution was poured into it. The molar ratio of Li:Fe:P was 3.0:1.0:1.0. All the reagents were added under vigorous stirring. The concentration of Fe(II) in the mixed solution was 0.05 M. The experiment conditions and partial results are shown in Table 1.

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Table 1
Hydrothermal experiment conditions and partial results in the present work.

	Group 1	Group 2
Starting Li:Fe:P	3.0:1.0:1.0	3.0:1.0:1.0
Starting RH ratio	0	1.0
Starting [Fe^{2+}] (mol L^{-1})	0.05	0.05
Treatment time (h)	3	3
Starting pH	7.80	7.80
Product microstructure	Particles composing of subunits	Monodispersed single crystals
Product phase	Lithium iron(II) phosphate	Lithium iron(II) phosphate

2.2. *Preparation of samples*

The as-prepared starting solution was rapidly poured into a stainless autoclave and sealed, hydrothermally treated at 180 °C under 1.5 MPa for 3 h. After the sample was cooled, the solution was removed by centrifugation. The product was washed with distilled water and absolute ethyl alcohol, then dried at 40 °C in air overnight.

2.3. *Characterization*

The crystalline phases, chemical composition and morphology were characterized by X-ray powder diffraction (XRD; Model D/max, Rigaku Co., Japan) with Cu Kα radiation (40 kV, 150 mA), energy dispersive X-ray spectroscopy (Oxford Instruments' INCA EDS system), and scanning electron microscopy (SEM; Model JSM-840, JEOL Co, Japan), respectively. Particle size and distribution of the powders were measured by a particle size analyzer (ZETASI ZER 300, Malvern).

3. Results and discussions

Fig. 1 shows the XRD patterns of the as-prepared products. After 3 h hydrothermal treatment, the final products were all orthorhombic $LiFePO_4$ (triphylite) with almost identical XRD patterns. No other impurity phases were found. There was a good agreement with the reported results so far [7]. Diffraction peaks were narrow and sharp, index of well-crystallized powders. The intensity of corresponding diffraction peaks was higher at RH ratio of 1.0. So it was concluded that the presence of isopropanol enhanced the crystallinity of the final products.

The EDS spectra of the synthesized powders of Fig. 2 show presence in the final products of Fe, P, and O (Li could not be detected by EDS detector), and there were no other impurity peaks in the spectra except carbon, which derived by the absorption of absolute ethyl alcohol used as a cleaning agent. The EDS results corresponded to the XRD results, further demonstrating that the final product was $LiFePO_4$.

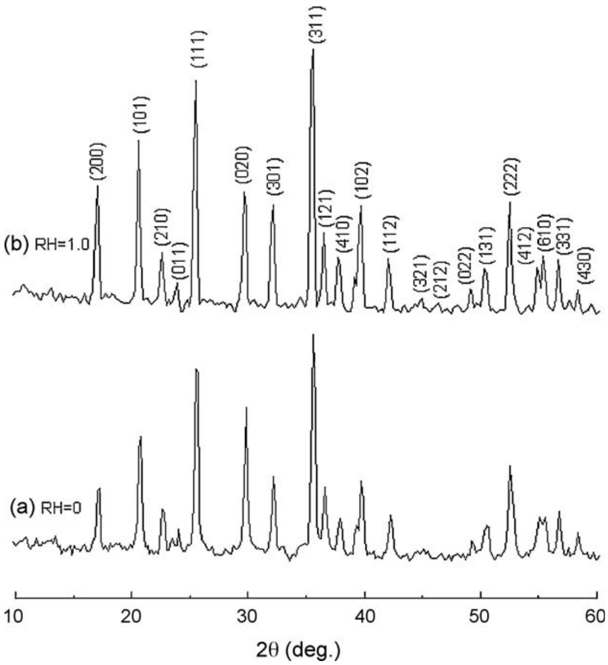

Fig. 1. XRD patterns of $LiFePO_4$ powders prepared from different starting RH ratios.

Fig. 3 shows the SEM images of the as-prepared powders. When isopropanol was not applied (i.e., the RH ratio was 0), the obtained $LiFePO_4$ powders were short column-like particles

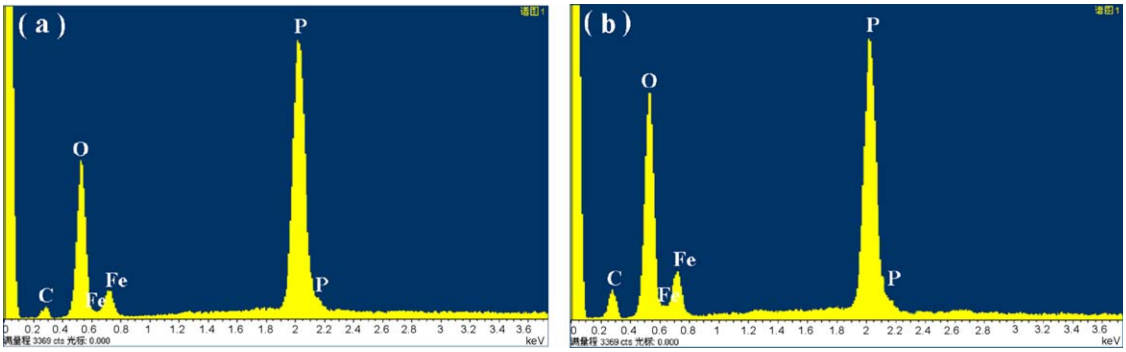

Fig. 2. EDS spectra of the products prepared from different starting RH ratios: (a) RH = 0 and (b) RH = 1.0.

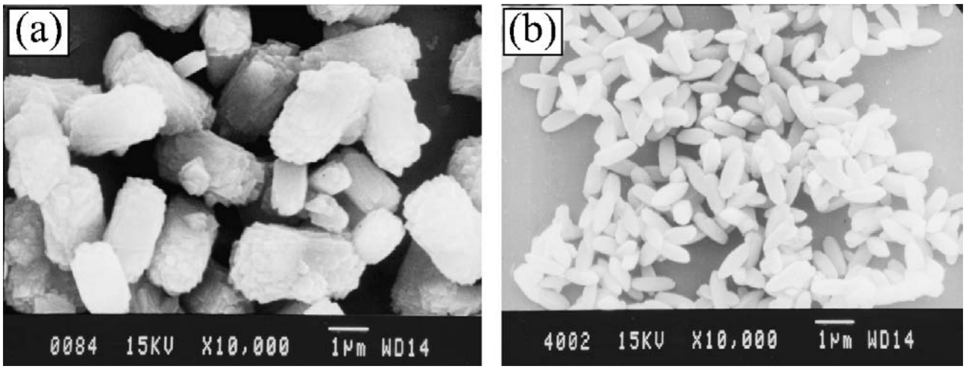

Fig. 3. SEM images of $LiFePO_4$ powders prepared from different starting RH ratios: (a) RH = 0 and (b) RH = 1.0.

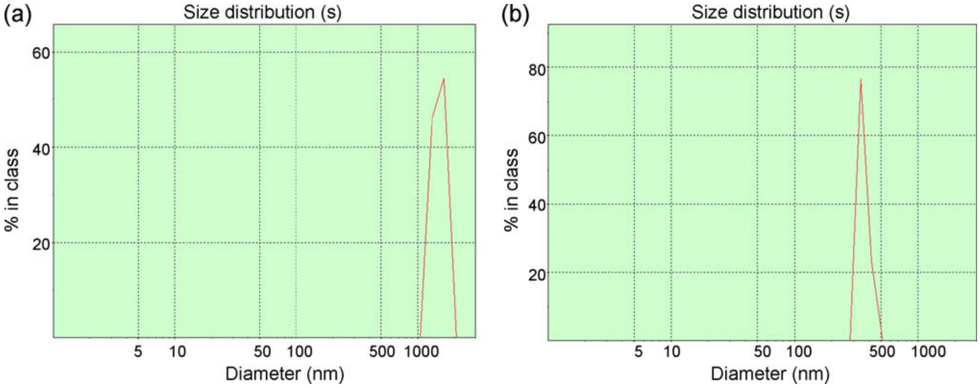

Fig. 4. Particle size distribution of the products obtained from different starting RH ratios: (a) RH = 0 and (b) RH = 1.0.

composed of much smaller crystals. The particles had length, diameter and aspect ratio in the range of 1–4 μm, 1–2 μm and 2–3 μm, respectively (Fig. 3(a)). When the RH ratio was 1.0, the obtained $LiFePO_4$ powders changed dramatically in morphology. All of the individual crystals took the shape of discrete short rods with a uniform size about 1 μm in length and 0.4 μm in diameter (Fig. 3(b)).

Fig. 4 shows the particle size and distribution of the products. The powders sizes were in the range of 800–1100 nm (Fig. 4(a)) and 200–500 nm (Fig. 4(b)), respectively. By comparison, the particle size distribution in Fig. 4(b) was narrower than in Fig. 4(a) which demonstrated that isopropanol played an important role in to obtain monodisperse powders.

Since metal salts applied here were almost insoluble in isopropanol, the homogeneous mixing of the isopropanol and the aqueous solution promoted the supersaturation of the metal salts in the mixed solvent. The supersaturation of solute led to the nucleation and the growth of solid hydrous metal oxide (i.e., $LiFePO_4$) crystals. Furthermore, when isopropanol was added into the aqueous solution, the dielectric coefficient of solvent and zeta potential of the crystals decreased, which results in the chemical adsorption of isopropanol molecules on the crystal surfaces [13]. So, isopropanol acted as a dielectric constant tuner as well as a steric hindrance agent, restraining the aggregation of the crystals as previously experienced as the formation of monodispersed titania and zirconia, respectively [13,14].

Simultaneously, the Fe(II)–CA complex began to decompose when the solution reached to 180 °C, the chelated Fe(II) ions released into the solution at a rate determined by the rate of the decomposition of the Fe(II) citric acid precursor. This approach allowed a comparatively slow rate of nucleation and growth of the particles in a clear solution, obtaining a narrow size distribution of the $LiFePO_4$ particles.

4. Conclusions

Monodispersed $LiFePO_4$ powders were successfully synthesized by homogeneous hydrothermal precipitation at 180 °C through the decomposition of Fe(II)–CA complex precursor and application of isopropanol as the dielectric constant tuner. The product was characterized by XRD, EDS, and SEM tests, and the particle size and distribution of powders were measured, which indicated that the obtained product was pure and well crystallized $LiFePO_4$. It was shown the volume ratio of isopropanol to water (RH ratio) had a great influence on the morphology of the obtained particles. Monodispersed short rod-like $LiFePO_4$ crystals were synthesized when the RH ratio was 1.0, while column-like $LiFePO_4$ particles composed of much smaller crystals were produced when isopropanol was absent.

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