

Short communication

LiFePO₄/carbon cathode materials prepared by ultrasonic spray pyrolysis

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Abstract

Small crystallites LiFePO₄ powder with conducting carbon coating can be synthesized by ultrasonic spray pyrolysis. Cheaper trivalent iron ion is used as the precursor. The pure olivine phase can be prepared with the duplex process of spray pyrolysis (synthesized at 450, 550 or 650 °C) and subsequent heat-treatment (at 650 °C for 4 h). The results indicate that the pyrolysis temperature of 450 °C is appropriate for best results. The carbon coating on the LiFePO₄ surface is critical to the electrochemical performance of LiFePO₄ cathode materials of the lithium secondary battery, since the carbon coating does not only increase the electronic conductivity via carbon on the surface of particles, but also enhance the ion mobility of lithium ion due to prohibiting the grain growth during post-heat-treatment. The carbon of 15 wt.% evenly distributed on the final LiFePO₄ powders can get the highest initial discharge capacity of 150 mA h g⁻¹ at C/10 and 50 °C.

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1. Introduction

Currently, LiFePO₄ is a promising candidate for use as a cathode material in lithium ion batteries, especially for low-cost, environmentally friendly, thermally stable and very good electrochemical performance. However, two major shortcomings of LiFePO₄, the poor electronic conductivity and lithium ion diffusion, pose a bottleneck for the commercial applications [1,2]. Some intimate carbon coatings can overcome those disadvantages, leading to the enhancement of capacity and rate capability [3–13]. The reductive carbon can avoid the formation of the Fe³⁺, and increase the electronic conductivity of these materials at the same time. Huang et al. [4] believe that both particle size minimization and intimate carbon contact are needed to optimize the rate capability of this material.

Ultrasonic spray pyrolysis (USP) is very suitable method for fabrication of high-density ceramic samples because the manufacturing process is one-step process and can prepare the well-crystallized and homogeneous small particles with the spherical shape, pure phase [14,15]. Although there is no report on the

USP to prepare LiFePO₄, USP seems to a feasible and deserved to investigate to prepare a homogeneous LiFePO₄/carbon powders.

2. Experimental

The precursor solution for atomization is an aqueous mixing solution of LiNO₃ (Wako), Fe(NO₃)₃·9H₂O (Wako, 99%), H₃PO₄ (Wako, 85%), and ascorbic acid (C₆H₈O₆, Wako, 99.5%) in the de-ionized water at the molar ratio 1:1:1 of Li:Fe:PO₄. The amount of white sugar added into the precursor solution is 60 wt.% of LiFePO₄ to be formed. The as-sprayed fine powders pyrolysis-synthesized at 450, 550, and 650 °C were heat-treated at 650 °C for 4 h in a tube furnace under a nitrogen atmosphere, and then furnace-cooled to room temperature.

The crystalline phase of the particles was investigated with X-ray diffraction (XRD, Shimadzu XRD-6000). Rietveld refinement was performed using the GASA (general structure analysis system) program to obtain the crystal structure parameters. The morphologies of the particles were observed with Scanning electron micrographs (SEM, Hitachi S-800), and high resolution transmission electron microscopy (HRTEM, JEOL JEM-2010). The carbon amount can be determined with a CHN analyzer (Heraeus Vario EL III) and thermogravimetric–differential thermal analysis (TG–DTA, SDT 2960).

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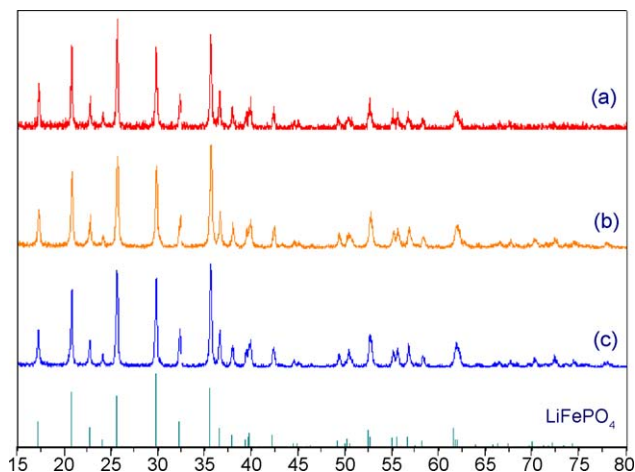


Fig. 1. XRD patterns for LiFePO₄/C composite prepared at various T_{sp} : (a) 450 °C, (b) 550 °C, (c) 650 °C and post-heat-treatment 650 °C, for 4 h under N₂ atmosphere.

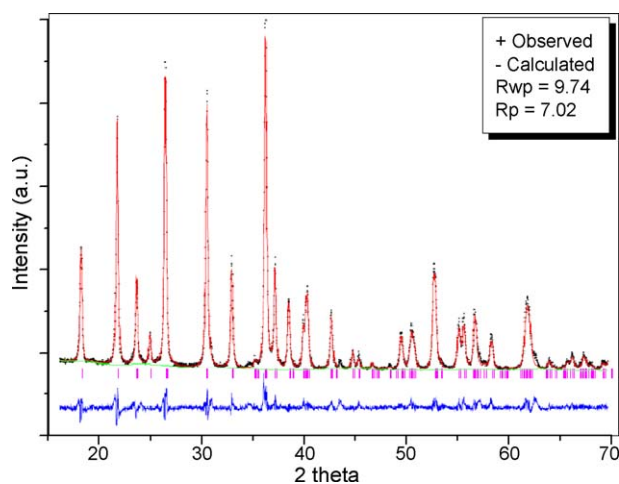


Fig. 2. Rietveld refinement of the XRD patterns of LiFePO₄/C composite prepared at $T_{sp} = 450$ °C, and post-heat-treatment 650 °C, for 4 h under N₂ atmosphere.

The electrochemical properties of the LiFePO₄/C powders were investigated in an electrochemical cell that comprised a cathode, and anode and an electrolyte of 1 M LiPF₆ in EC (ethylene carbonate)–DEC (diethyl carbonate) solution. The cathode

Table 1

Results of structural parameters obtained from Rietveld refinement of LiFePO₄/C composite prepared at $T_{sp} = 450$ °C, and post-heat-treatment 650 °C, for 4 h under N₂ atmosphere, in the orthorhombic *Pnma* space group, from XRD data

Atoms	Site	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy	U_{iso} (Å ²)
Li	4a	0	0	0	1	0.015 (5)
Fe	4c	0.2813 (0)	0.25	0.9737 (6)	1	0.014 (9)
P	4c	0.0954 (0)	0.25	0.4230 (2)	1	0.013 (1)
O(1)	4c	0.0902 (4)	0.25	0.7379 (6)	1	0.009 (6)
O(2)	4c	0.4555 (7)	0.25	0.2148 (6)	1	0.009 (1)
O(3)	8d	0.1638 (7)	0.0498 (6)	0.2832 (6)	1	0.009 (8)

Space group: *Pnma*, $R_p = 7.02\%$, $R_{wp} = 9.74\%$, $\chi^2 = 2.33$. Cell parameters: $a = 10.3205$ Å, $b = 6.0011$ Å, $c = 4.6899$ Å.

was prepared by mixing LiFePO₄/C-based powders with 8 wt.% carbon black and 7 wt.% polyvinylidene fluoride (PVDF) in *n*-methyl-2 pyrrolidone (NMP) solution. The charge and discharge characteristics of the cathode were evaluated at various current (C/10 and 1C rates) in the range of 2.5–4.3 V Li/Li⁺. All elec-

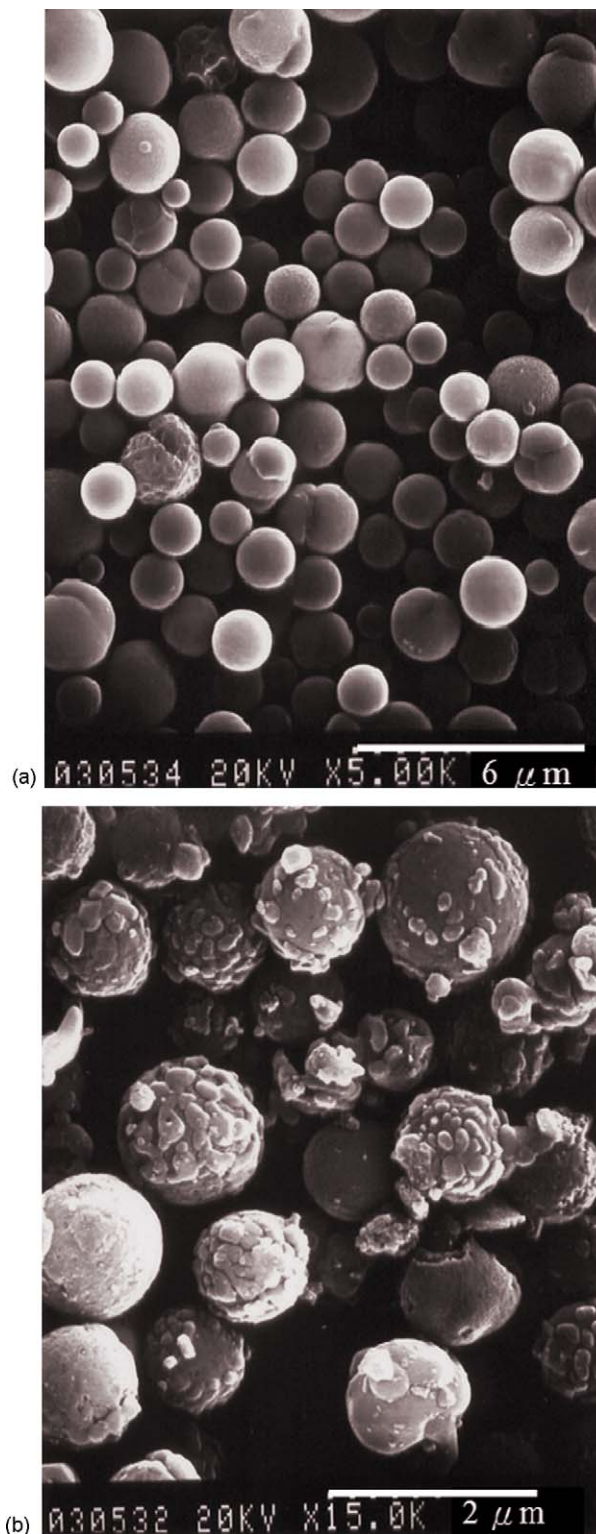


Fig. 3. SEM image of LiFePO₄/C composite prepared at T_{sp} : (a) 450 °C and (b) post-heat-treatment 650 °C, for 4 h under N₂ atmosphere.

trochemical experiments were conducted at room temperature in a glove box filled with high purity argon gas.

3. Results and discussion

The as-sprayed power is black, but the crystallinity of the as-spray power is not good (the intensity of diffraction peaks of olivine phase is low). The X-ray diffraction patterns of powder pyrolysis-synthesized at different temperatures (450, 550 and 650 °C) and post-heat-treated at 650 °C for 4 h are shown in Fig. 1. That indicates that on other diffractions peaks except olivine phase can be seen after heat-treatments. The amounts of carbon in the LiFePO₄/C composite pyrolysis-synthesized at 450, 550 and 650 °C and subsequent heat-treatment at 650 °C for 4 h are 15.33, 9.42, and 8.34 wt.%, respectively. It implied that

the residual carbon determined with CHN analyzer decreases with increasing pyrolysis-synthesized temperature. The TGA data agree with these results.

Fig. 2 and Table 1 show the Rietveld refinement results of the XRD pattern of the LiFePO₄/C composite sprayed at 450 °C and post-heat-treated at 650 °C for 4 h in the nitrogen atmosphere. All peaks are indexed according to an orthorhombic olivine structure without any secondary peaks in the entire patterns. A space group of *Pnma* was selected as the refinement model. The error between the observed and calculated patterns is acceptable ($R_{wp}=9.74$, $R_p=7.02$), the unit cell parameters for the orthorhombic cell were $a=10.3205$ Å, $b=6.0011$ Å, $c=4.6899$ Å and results data are shown in Table 1.

The particle morphologies of the LiFePO₄/C composites are non-agglomerated and exhibits extremely smooth surface

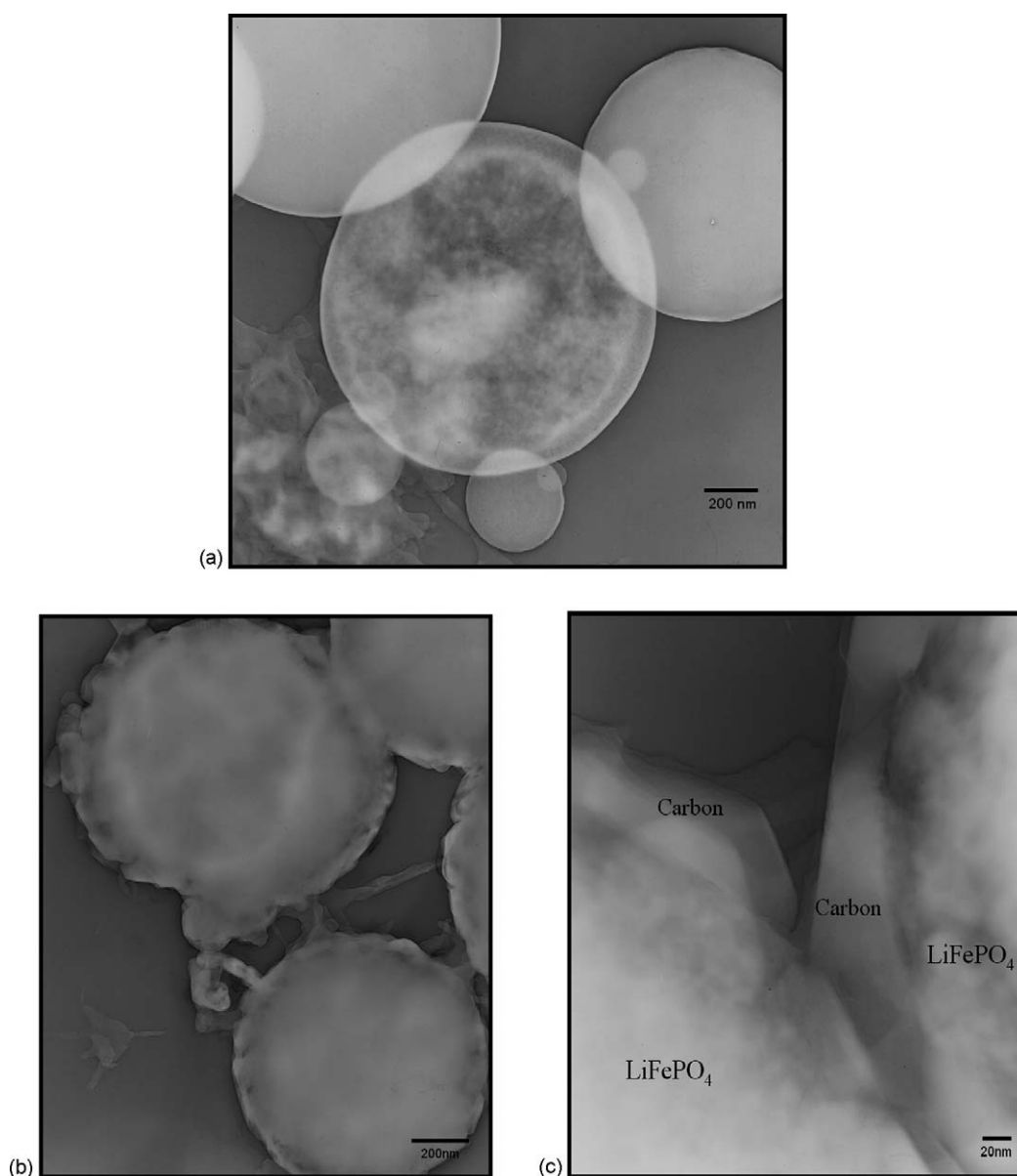


Fig. 4. HRTEM photography of LiFePO₄/C composite prepared at T_{sp} : (a) 450 °C, (b) post-heat-treatment 650 °C, for 4 h under N₂ atmosphere and (c) magnified image of (b).

appearance is shown in Fig. 3(a). The average particle size is around 1–2 μm . And the carbon is evenly distributed on the particles. From the HRTEM photography of Fig. 4(a), the outskirts of the particle is seemingly the carbon coating on the LiFePO_4/C composite compound and that carbon particles completely cover the surface of the LiFePO_4 particles. The evenly distributed carbon will enhance the electronic conductivity of the cathode materials and the presence of the carbon on the surface of particle is beneficial to the conductivity [11,12]. Moreover, carbon particles between LiFePO_4 particles can prevent particle coalescence. Even after the post-heat-treatment, particle size seemingly remains the same and the surface of the powder becomes rugged appearance, as shown in Figs. 3(b) and 4(b). The magnified image of Fig. 4(b), as shown in Fig. 4(c), reveals that the whole LiFePO_4 powder is covered with carbon. The small particle size of LiFePO_4 will also facilitate the lithium ion diffusion during intercalation/decalation processes, leading to the reduction of the cell resistance. The rugged appearance of the particles after post-heat-treatment may be attributed to the crystallization of LiFePO_4 and reduction of carbon content.

The charge and discharge curves shown in Fig. 5 were carried out between 2.5 and 4.3 V at a current density of C/10 rate. All samples have the plateau voltage of 3.4 V (versus Li/Li^+), indicative of a typical two-phase reaction between LiFePO_4 and FePO_4 [3]. The discharge capacity, however, increases with decreasing spray pyrolysis temperature and reaches to 124 mA h g^{-1} for powder spray-synthesized at 450°C . This value of discharge

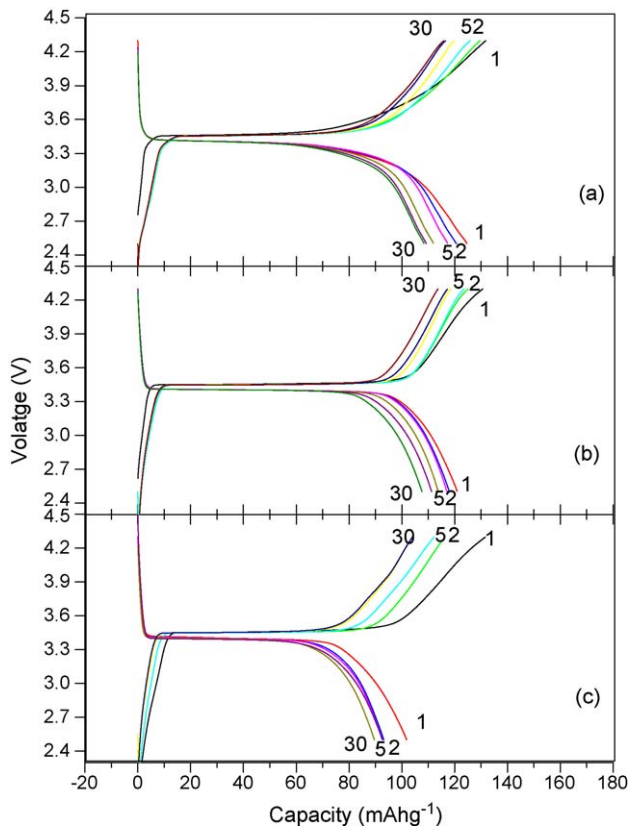


Fig. 5. Charge–discharge curves of LiFePO_4/C composite at C/10 rate prepared at various T_{sp} : (a) 450°C , (b) 550°C , (c) 650°C and heat-treatment 650°C , for 4 h under N_2 atmosphere.

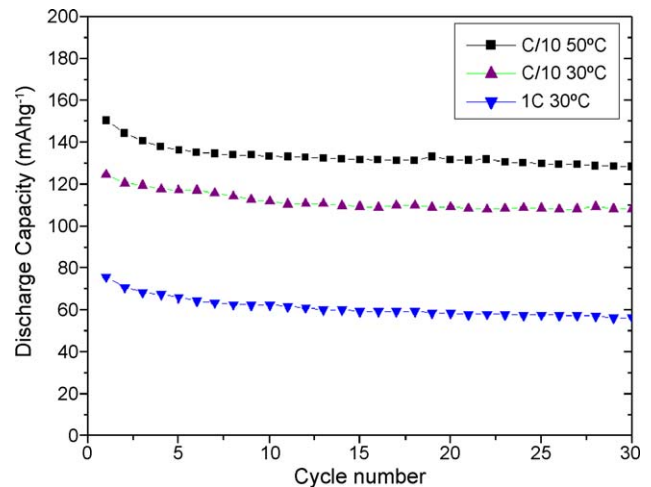


Fig. 6. Cycle-life of LiFePO_4/C composite prepared at $T_{\text{sp}} = 450^\circ\text{C}$ and heat-treatment 650°C for 4 h in N_2 atmosphere under the various rates and temperature.

capacity is similar to that reported by Konstantinov et al. [13], and they indicate that 15 wt.% carbon addition is the optimum level. With other reporters [3,11], the surface area and the carbon amount can influence the cell performance of LiFePO_4 as well. Thus, the largest discharge capacity for the $T_{\text{sp}} = 450^\circ\text{C}$ sample could have the highest electronic conductivity.

The charge–discharge test was carried out at 30 or 50°C under a charge/discharge rate of 1C or C/10 are shown in Fig. 6. The results indicated that the initial discharge capacity value of LiFePO_4 powder with 15 wt.% carbon addition at C/10 and 50°C can reach as high as 150 mA h g^{-1} . The specific discharge capacity after 30 cycles is about 128 mA h g^{-1} . The initial discharge capacity discharged with 1C rate at 30°C is reduced to only 75 mA h g^{-1} .

4. Conclusions

The homogeneous $\text{LiFePO}_4/\text{carbon}$ cathode materials have been successfully synthesized with ultrasonic spray pyrolysis from precursors contained cheaper trivalent iron ion. From the Rietveld refinement result, the USP can obtain a well-crystallized LiFePO_4 compound. The 15 wt.% carbon evenly distributed on the final LiFePO_4 powders cannot only prohibit the grain growth during post-heat-treatment, but also can enhance the conductivity of the LiFePO_4 cathode materials.

Acknowledgements

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