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Short communication

Hydrothermal synthesis of Ni-doped carom-like $LiFe_{0.95}Ni_{0.05}PO_4$ powders

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Abstract

Ni-doped $LiFe_{1-x}Ni_xPO_4$ ($x = 0.00, 0.03, 0.05, 0.07$) powders were synthesized via the hydrothermal method. The samples were characterized by XRD, SEM and EDS tests, indicating that the obtained products were pure and well crystallized. All the doped samples took the shape of spheres and had much smaller size. Monodispersed spindle-like $LiFePO_4$ powders were obtained without Ni doping ($x = 0.00$); while carom-like spherical $LiFe_{0.95}Ni_{0.05}PO_4$ powders were produced when the doping concentration was 5 wt% ($x = 0.05$).

Keywords: Hydrothermal synthesis; Carom-like; $LiFe_{0.95}Ni_{0.05}PO_4$

1. Introduction

The olivine $LiFePO_4$ is an attractive electrode material for its remarkable advantages, such as low toxicity, low cost, long cycle life and high safety [1]. In addition, $LiFePO_4$ has a theoretical specific capacity of about 170 mAh g^{-1}, good cycle stability and a technically attractive flat voltage versus current profile of 3.45 V versus Li^+/Li, due to the two-phase extraction/insertion mechanism. However, one of the main problems of $LiFePO_4$ lies in its poor conductivity, which is resulting from its low electronic conductivity and slow kinetics of lithium ion diffusion in the $LiFePO_4$ phase [2,3]. Many approaches have been developed to overcome this problem recently. One of the approaches took advantage of the conductive coating such as carbon on $LiFePO_4$ to increase the electronic conductivity [4,5]. Another approach was reducing particle size to nanometer scale, which can shorten the lithium-ion transport distances and enhance ionic diffusion rate [6,7]. In addition, doping with alien ion is a critical way to improve overall electrochemical properties to some extent [8–14], which attracted many researchers since Chiang et al. [15] firstly reported an increase by 8 orders of magnitude in the electronic conductivity of the cation doped olivine-type materials $LiFePO_4$. Simultaneously, doping with alien ion can make $LiFePO_4$ form specific morphology so as to affect its electrochemical performance. According to Zhao's result [16], the spherical structure will supply a big specific surface area for the subsequent reactions, which can improve the electrochemical performance of $LiFePO_4$ [17]. Lots of effort has been devoted to the realization of spherical $LiFePO_4$ products.

More recently, hydrothermal synthesis has been preferentially chosen to prepare $LiFePO_4$ for its advantages of mild synthesis conditions, high degree of crystallinity, high purity and narrow particle size distribution of product. In this study, hydrothermal method was adopted to synthesize pure $LiFePO_4$ and that doped with Ni in different doping concentrations. Monodispersed spindle-like $LiFePO_4$ powders were obtained without Ni doping; while carom-like spherical $LiFe_{0.95}Ni_{0.05}PO_4$ powders with much smaller particles were produced when the doping concentration was 5 wt% ($x = 0.05$) and hydrothermally treated at 180 °C for 6 h.

2. Experiments and characterizations

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)

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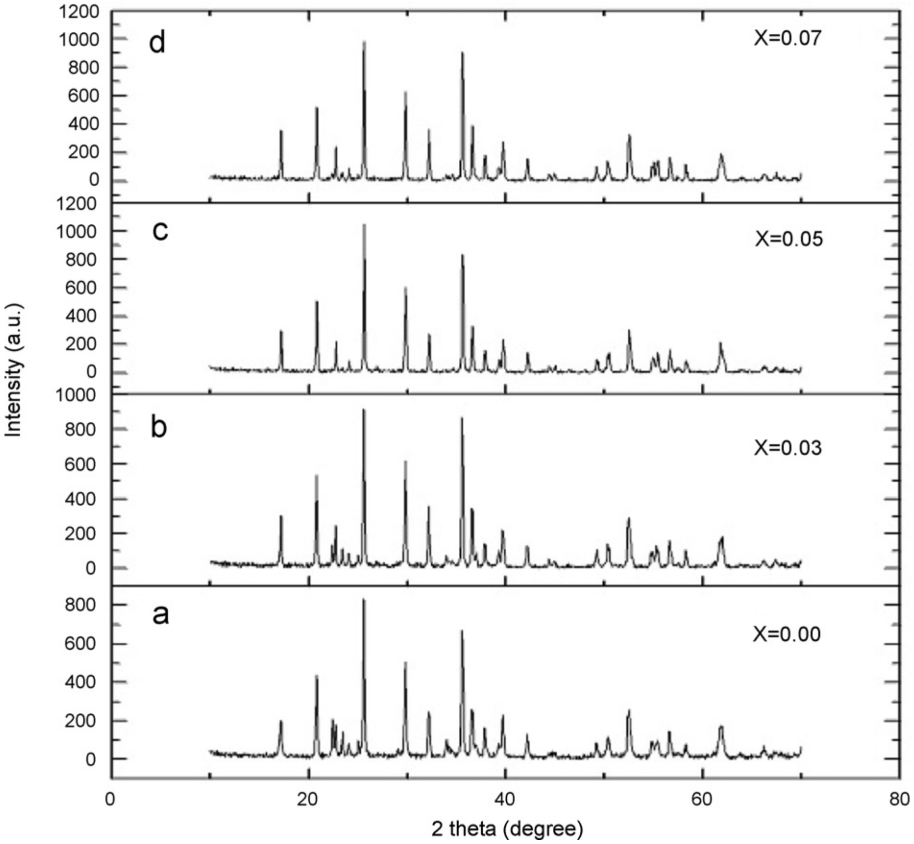

Fig. 1. XRD patterns of $LiFe_{1-x}Ni_xPO_4$ powders from different doping concentrations: (a) $x = 0.00$; (b) $x = 0.03$; (c) $x = 0.05$; and (d) $x = 0.07$.

and $NiSO_4 \cdot 6H_2O$ (≥98.0%). The molar ratio of Li:Fe:P:Ni was 3:1 − x:1:x ($x = 0.00$, 0.03, 0.05, 0.07). The hydrothermal synthesis process was carried out as follows. First, a desired amount of H_3PO_4 was added to distilled water. Then the appropriate amount of $FeSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 6H_2O$ were added, and the $LiOH \cdot H_2O$ solution was poured into the mixed solution above-mentioned. All the reagents were added under vigorous stirring.

2.2. Preparation of samples

The as-prepared starting suspension was rapidly poured into a stainless autoclave and sealed, hydrothermally treated at 180 °C for 6 h. After being cooled to room temperature, the obtained precipitate was washed several times with deionized water and absolute ethylalcohol. Later, the products were dried at 110 °C for 2.0 h in a vacuum oven.

2.3. Characterizations

The crystalline phases, chemical composition and morphology were characterized by X-ray powder diffraction (XRD; Model D/max, Rigaku Co., Japan) with Cu K_α radiation (40 kV, 150 mA), energy dispersive X-ray spectroscopy (Oxford Instruments' INCA EDS system), and scanning electron microscopy (SEM; Model JSM-6700F, JEOL Co, Japan), respectively.

3. Results and discussions

Fig. 1 shows the X-ray diffraction (XRD) profiles of the $LiFe_{1-x}Ni_xPO_4$ ($x = 0$, 0.03, 0.05, 0.07) samples. The dominant diffraction peaks can be indexed as the orthorhombic $LiFePO_4$ (triphylite) phase with space group Pnmb (62), according to the standard pattern of JCPDF 40-1499. And there are no obvious impurity phases detected. Diffraction peaks are narrow and sharp, index of well-crystallized powders. Table 1 lists the rietveid refined lattice parameters of $LiFe_{1-x}Ni_xPO_4$ powders from different doping concentrations. It shows that the values of a and b decrease while c without obvious change with the Ni doping and. The smaller radius of Ni^{2+} ion (0.780 Å) than that of Fe^{2+} ion (0.830 Å) leads to the shrinkage of lattice parameters [18]. The results indicate that Ni^{2+} has been successfully doped into the sites of Fe^{2+} without affecting the lattice structure of $LiFePO_4$.

Table 1
Lattice parameters of $LiFe_{1-x}Ni_xPO_4$ powders from different doping concentrations: (a) $x = 0.00$; (b) $x = 0.03$; (c) $x = 0.05$; (d) $x = 0.07$.

Samples	a (Å)	b (Å)	c (Å)
$LiFePO_4$	10.3379	5.9937	4.6966
$LiFe_{0.97}Ni_{0.03}PO_4$	10.3261	5.9886	4.6966
$LiFe_{0.95}Ni_{0.05}PO_4$	10.3246	5.9873	4.6967
$LiFe_{0.93}Ni_{0.07}PO_4$	10.3233	5.9870	4.6965

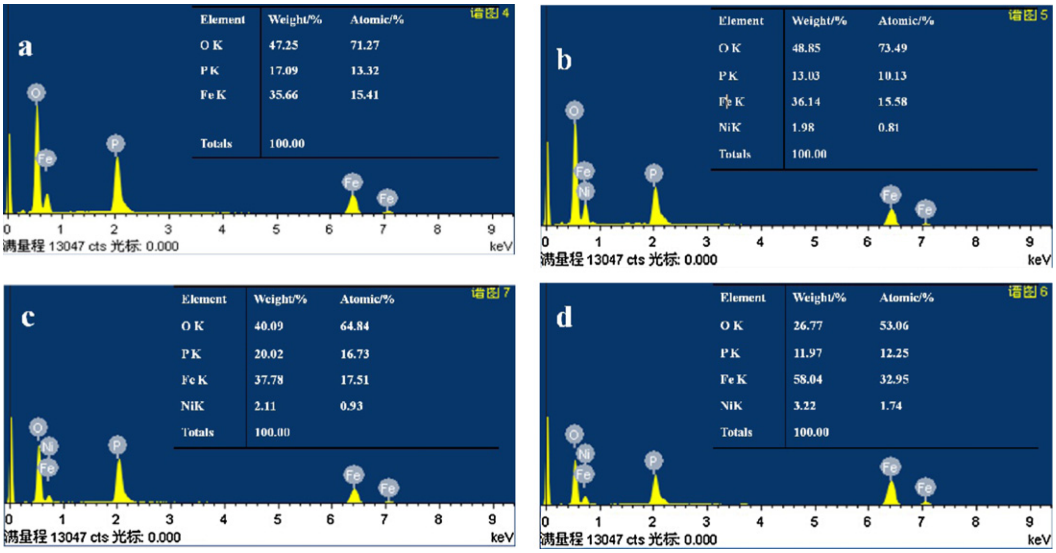

Fig. 2. EDS spectra of $LiFe_{1-x}Ni_xPO_4$ powders from different doping concentrations: (a) $x = 0.00$; (b) $x = 0.03$; (c) $x = 0.05$; and (d) $x = 0.07$.

The EDS results of Fig. 2 unambiguously confirm that the particles in the Ni-doped $LiFe_{1-x}Ni_xPO_4$ ($x = 0.00$, 0.03, 0.05, 0.07) included Fe, P, and O components with a trace of Ni (Li could not be detected by EDS detector), while the weight of Ni gradually increases with the rise of doping concentrations.

Fig. 3 shows SEM images of the synthesized $LiFe_{1-x}Ni_xPO_4$ powders from different doping concentrations by hydrothermal method. The undoped sample is mainly composed of discrete spindle-like particles with 10–15 μm in length and 3–5 μm in width (Fig. 3a). An interesting morphological change can be observed when Ni is doped into $LiFePO_4$. All of the doped samples take the shape of spheres with much smaller size. The size of the obtained particles is unevenly distributed in the range of 3–10 μm in diameter as shown in Fig. 2b ($x = 0.03$). When the doping concentration is 5 wt%, the sample is composed of homogeneous carom-like spheres with particles of 1–2 μm in diameter (Fig. 3c). The carom-like spheres disappear as the doping concentration rise to 7 wt% almost without any particle size modification (Fig. 3d). According to Fig. 4, the surface of the spindle-like $LiFePO_4$ displays lamellar architectures apparently (Fig. 4a), while the surface of the carom-like spherical $LiFe_{0.95}Ni_{0.05}PO_4$ particles shows hierarchical architectures apparently (Fig. 4b).

It is shown that the particle size of Ni-doped $LiFePO_4$ is much smaller than the undoped sample and decreasing as the rising of doping concentrations. Meanwhile, the formation of the carom-like spherical $LiFe_{0.95}Ni_{0.05}PO_4$ grains results from the Ni doping, too. Ni^{2+} can occupy the site of Fe^{2+} via doping, which induces the lattice distortion of $LiFePO_4$ crystal. This lattice distortion could reduce the surface energy

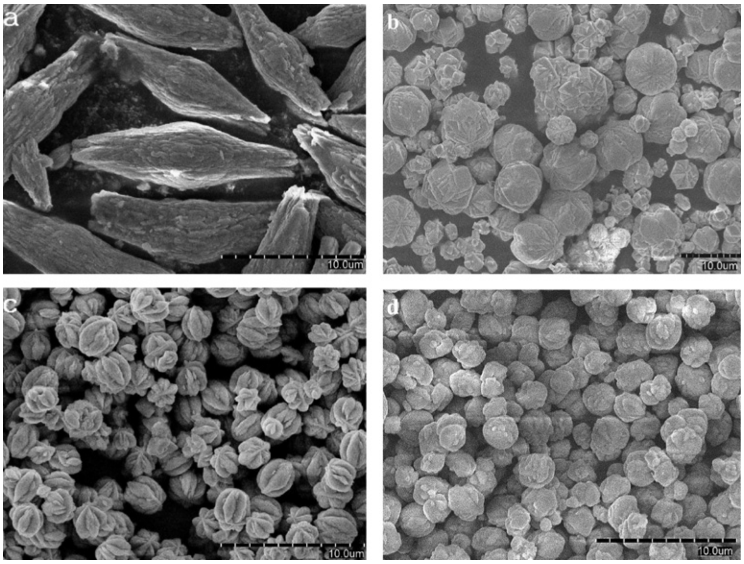

Fig. 3. SEM images of $LiFe_{1-x}Ni_xPO_4$ powders from different doping concentrations: (a) $x = 0.00$; (b) $x = 0.03$; (c) $x = 0.05$; and (d) $x = 0.07$.

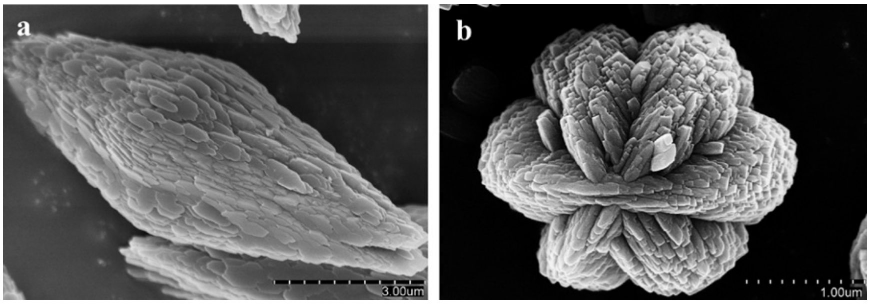

Fig. 4. SEM images of as-prepared powders: (a) the feature of a spindle-like $LiFePO_4$ particle, and (b) the feature of a carom-like $LiFe_{0.95}Ni_{0.05}PO_4$ particle.

of $LiFePO_4$ crystal and then impede the growth of $LiFePO_4$ crystal [18]. So $LiFePO_4$ crystal can be controlled in a small size and specific shape.

4. Conclusions

Well-crystalline and pure phase lithium iron phosphate and its doped derivatives have been successfully synthesized through hydrothermal route. The products were characterized by XRD, EDS, and SEM tests, which indicated that the obtained products were pure and well crystallized. The Ni doping did not destruct the lattice structure of $LiFePO_4$, while the weight of Ni in the products gradually increased with the rise of initial doping concentrations. All the doped samples took the shape of spheres and had much smaller size. Particularly, carom-like spherical $LiFe_{0.95}Ni_{0.05}PO_4$ powders with much smaller particles of 1–2 μm in diameter were produced when the doping concentration was 5 wt% ($x = 0.05$).

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