



Hierarchical structured $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ spheres synthesized by template-engaged reaction as cathodes for high power Li-ion batteries



Wei Xiang^a, En-Hui Wang^a, Ming-Zhe Chen^a, Hui-Hui Shen^a, Shu-Lei Chou^c,
Hong Chen^b, Xiao-Dong Guo^{a,c}, Ben-He Zhong^a, Xinlong Wang^{a,*}

^a College of Chemical Engineering, Sichuan University, Chengdu 610065, PR China

^b Zigong Innovation Center of Zhejiang University, Zigong 643000, PR China

^c Institute for Superconducting and Electronic Materials, University of Wollongong, Wollongong, NSW 2522, Australia

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ABSTRACT

Porous hierarchical $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ spheres were synthesized via a novel template-engaged method using pre-synthesized hollow spherical Li_3PO_4 as template and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}/\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ as $\text{Fe}^{2+}/\text{Mn}^{2+}$ source. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) show that the porous hierarchical spheres exhibit hollow structure and have a size distribution of 0.4–1 μm consisting of aggregated ~ 50 nm nanoparticles. A mechanism of the reaction from Li_3PO_4 to $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ was proposed on the basis of the phase and morphology transformation of the intermediates. With the short Li^+ diffusion path and porous structure, the carbon coated $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ spheres show high specific capacity and superior rate capability with the discharge capacities of $159.3 \text{ mA h g}^{-1}$ at 0.1C and 80.6 mA h g^{-1} at 20C. The porous hierarchical spheres also exhibit an excellent cycling stability with about 90.7% of the initial value at 1C after 100 cycles.

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1. Introduction

Since the first introduction by Goodenough et al. in 1997, olivine-type LiMPO_4 (M = Mn, Fe, Co and Ni) compounds with high thermal stability, cycling stability and superior safety properties have been extensively investigated as promising alternative cathode materials for the conventional layered lithium transition metal oxide LiMO_2 [1]. Among them, the LiFePO_4 (LFP) cathode has been successfully developed and commercialized for application in electric vehicles (EV) or in grid scale energy storage. To further increase the energy density, the isomorph LiMnPO_4 (LMP) is a more exciting cathode material than LFP as a result of its higher operation voltage of 4.1 V vs. Li/Li^+ (3.4 V for LFP) [2]. Nevertheless, LMP suffers from poor electrochemical performance due to its inherently low electronic and ionic conductivities, Jahn-teller distortion caused by unstable Mn(III) [$d^4:t_{2g}^3e_g^1$] of MnPO_4 and interfacial strain between the lithiated and delithiated phase [3]. In response, efforts have been focused on overcoming the kinetic limitations of the LMP material through particle-size reduction coordinated with external conductive layer coating and internal cationic substitution, especially Fe substitution at Mn site. $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$ solid solution systems which

combine the advantages of relative high electrical conductivity of LFP and relative high voltage of LMP have been widely studied. Nano-sized $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4/\text{C}$ solid solution systems have shown improved lithium diffusion and charge transfer, as well as attractive electrochemical performances. However, monodispersed nano-sized materials usually have very large surface area and inferior packing of particles, leading to the low volumetric energy density and difficulties in electrode fabrication. Therefore, advances in preparation strategy and geometrical structure design are required to improve the electrochemical performance of olivine based phosphate cathodes [4].

Materials with micro-nano hierarchical structures have attracted great interest, because the unique geometrical structures are beneficial to the fast and efficient transport of mass and charge [4]. Among many different types of hierarchical microstructure, porous hierarchical spheres assembled by interconnected primary nanoparticles are most suitable for electrode materials to achieve both high power density and high energy density [5,6]. The highly porous LFP microspheres composed of nanoscale carbon-coated primary particles have exhibited much improved rate capability, considerable reversible capacity and excellent cyclic stability in comparison with the samples without hierarchical nanostructures [4,7–13]. Until now, a variety of strategies have been adopted for the synthesis of porous hierarchical olivine-type phosphate spheres. As the most common method used for the synthesis of

* Corresponding author.

E-mail address: wangxl@scu.edu.cn (X. Wang).

hierarchical spheres, template process is a versatile approach to control the morphology of products [14]. Lim et al. prepared hierarchical LFP micro hollow spheres by using KIT-6 silica as the hard templates [15]. Huang et al. synthesized tri-layer composite microspheres consisting of a carbon shell, a porous LFP layer and a carbon core with a hierarchical conductive structure by using carbon spheres as hard templates [10]. Kim et al. reported $\text{LiMn}_{0.75}\text{Fe}_{0.25}\text{PO}_4/\text{C}$ microspheres prepared by a microwave-assisted process with the assistance of a complexing agent [12].

However, fabrication route based on hard templates (colloid polystyrene beads, silica particles, or carbon spheres) or soft templates (vesicles, emulsions, or micelles) is somewhat a complex process [16]. The recent upsurge in the reports of template-engaged reaction routes for the preparation of hollow spheres presents a special view to the fabrication of hierarchical spheres. As the templates are engaged in chemical reactions and could be completely converted into target products, the method underscores its facile operation in fabrication [17–19]. Recently, Lee et al. synthesized hierarchical LFP hollow microspheres by hydrothermal reaction using hollow spherical Li_3PO_4 as precursor and CTAB as a surfactant [20]. The inheritance of morphology and dimensions from hollow spherical Li_3PO_4 precursor provide a new strategy to prepare hierarchical structured olivine-type phosphate spheres.

Herein, we report on the synthesis of porous hierarchical $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ spheres via a template-engaged routes by reacting pre-synthesized hollow spherical Li_3PO_4 with $\text{Fe}^{2+}/\text{Mn}^{2+}$ under solvothermal condition. By virtue of the direct ion exchange reaction between Li_3PO_4 nanoparticles and Mn^{2+} (Fe^{2+}) ions in ethylene glycol (EG) medium, the morphology and size of $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ successfully inherited the characteristic of Li_3PO_4 precursor. After carbon coating, the porous hierarchical $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ spheres showed high specific capacity and superior rate capability for the $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$ type of cathode materials.

2. Experimental

2.1. Sample preparation

The hierarchical structured $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ spheres (denoted as LMFP) were synthesized using a two-step solution-based method. In the first step, hollow spherical Li_3PO_4 templates, the precursor for the synthesis of LMFP, were synthesized by a precipitation method. In specific, 0.01 mol of H_3PO_4 (85 wt% solution) was quickly poured into 12 ml of aqueous solution containing 0.03 mol of LiOH with vigorous magnetic stirring. After being stirred at 30°C for 3 h, the product was filtrated and dried at 60°C for 24 h. In the second step, 0.005 mol of $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ and 0.005 mol $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ were dissolved into 25 ml of ethylene glycol solvent, and then 0.01 mol of the as-synthesized Li_3PO_4 from the first step was dispersed into the solvent by stirring for 30 min. Subsequently, the mixture was sealed in a Teflon lined stainless steel autoclave filled with N_2 , and heated up to 180°C for 6 h. After ambient cooling to room temperature, the products was filtrated, washed several times with water and ethanol, and dried at 80°C for 3 h. To achieve the carbon-coated $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ spheres (denoted as LMFP/C), the solvothermal products were mixed with 20 wt.% of glucose solution. After magnetically stirring and drying at room temperature naturally, the mixture was sintered at 650°C for 6 h under argon atmosphere with a heating rate of 5°C min^{-1} .

2.2. Materials characterization

The crystalline phase of the as-prepared materials was identified by X-ray diffraction (XRD, D/max-rB, Rigaku, Japan) measurements using $\text{Cu-K}\alpha$ radiation in the 2θ range of $10\text{--}70^\circ$.

Particle morphologies were observed by scanning electron microscopy (SEM, SPA400 Seiko Instruments) and field-emission transmission electron microscopy (TEM, JEOL 2100F). The carbon content in composites was measured by a carbon-sulfur analyzer (CS-902, Wanlianda Xinke, Beijing, China).

2.3. Electrochemical measurements

The electrochemical performances of the as-prepared composite were evaluated using CR2032 coin-type cells. To prepare the working electrodes, the active materials, acetylene black, and poly(vinylidene fluoride) were mixed at a weight ratio of 80:13:7 in *N*-methyl pyrrolidone. The mixed viscous slurry was uniformly spread on an Al foil current collector with loading mass of active materials fixed about 5 mg cm^{-2} . The electrodes dried under vacuum at 120°C for 12 h were subsequently assembled into cells in glove box filled with argon using Li metal foil as anode and a polypropylene micro-porous film as separator. Then, 1 mol L^{-1} LiPF_6 dissolved in a mixture of ethylene carbonate and dimethyl carbonate (1:1 by volume) was used as the electrolyte. The cells were tested in a voltage range of 2.5 V–4.5 V (vs. Li/Li^+) using a constant-current protocol at various rates ($1\text{C} = 170\text{ mA h g}^{-1}$) on a battery testing system (Neware BTS-610).

3. Results and Discussion

Fig. 1a shows the XRD pattern of the Li_3PO_4 precursor. The XRD pattern of the as prepared Li_3PO_4 can be well indexed to orthorhombic Li_3PO_4 (JCPDS No. 25-1030). The average sizes of the Li_3PO_4 crystallites were calculated as $\sim 20\text{ nm}$ by Scherer equation. XRD patterns of the products after solvothermal treatment and carbon coating are presented in Fig. 1b and Fig. 1c, respectively. All diffraction peaks for both samples can be indexed as a single phase with an ordered olivine structure indexed to the orthorhombic $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ *Pmnb* (62) space group (PDF#42-0585). No obvious carbon is observed in the LMFP/C sample, which is attributed to the low content or amorphous structure of the carbon layer. The carbon content measured by elemental analysis is 3.2 wt% in LMFP/C. Moreover, the increased intensity of diffraction peaks of LMFP/C suggests the crystallinity is enhanced after calcination. Chemical analysis of the as-synthesized LMFP/C using inductively coupled plasma optical emission spectrometry (ICP-OES) revealed a olivine phase $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ with Li: Mn: Fe: P = 0.93: 0.52: 0.55: 1.

The morphology and structure of the as-prepared Li_3PO_4 were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fig. 2a displays that most of the Li_3PO_4 sample consists of monodispersed spherical

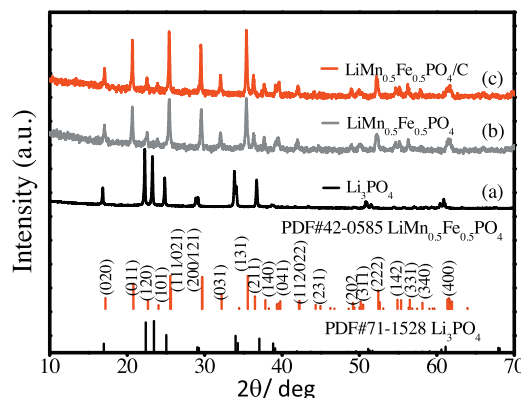


Fig. 1. XRD patterns of Li_3PO_4 (a), LMFP (b) and LMFP/C (c).

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