Journal of Power Sources 248 (2014) 246–252

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Solvothermal synthesis of Fe-doping $LiMnPO_4$ nanomaterials for Li-ion batteries

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HIGHLIGHTS

- The Fe-doping $LiMnPO_4$ nanomaterials were synthesized by a solvothermal method.
- The particle morphology could be controlled simply by adjusting the pH values of precursor suspensions.
- The nanoplates along with [010] crystallographic axis with 20–30 nm could deliver the largest discharge capacity.
- Fe doping could significantly increase the initial reversible capacity.

ARTICLE INFO

Article history:
Received 6 July 2013
Received in revised form
9 September 2013
Accepted 11 September 2013
Available online 19 September 2013

Keywords:
Lithium ion batteries
Solvothermal
Cathode materials
Lithium manganese phosphate

ABSTRACT

The Fe-doping $LiMnPO_4$ ($LiMn_{1-x}Fe_xPO_4$, $x \leq 0.5$) nanomaterials are solvothermally synthesized in a mixed solvent of water and polyethylene glycol (PEG). The particle morphology can be controlled simply by adjusting the pH values of precursor suspensions. Electrochemical test shows that $LiMn_{0.9}Fe_{0.1}PO_4$ nanoplates with a thickness of 20–30 nm could deliver the largest discharge capacity, which is attributed to the fast Li^+ diffusion in the diffusion path of [010] crystallographic axis along the short radial direction of the nanoplates. It is demonstrated that Fe doping could significantly increase the initial reversible capacity, cycle performance and rate capability. The first discharge capacities of Fe-doped $LiMnPO_4$ are all above 150 mAh g^{-1} at the discharge rate of 0.05 C. Especially, $LiMn_{0.5}Fe_{0.5}PO_4$ delivers 100% capacity retention with the reversible capacity of 147 mAh g^{-1} at the discharge rate of 1 C, and losses only about 23.4% capacity with the discharge rate varying from 0.1 C to 5 C. The variation of energy density predicts that $LiMn_{0.5}Fe_{0.5}PO_4$ shows the potential application for high-power devices.

1. Introduction

Olive-type $LiMPO_4$ (M = Fe, Mn, Co, Ni etc.) have been extensively investigated as promising cathode materials since the pioneering work of Padhi et al. [1–3]. Among these phosphates, $LiFePO_4$ gets the most attention and has already been commercialized due to its excellent rate capability and preferable safety. However, low operating-potential (~3.5 V *vs.* Li^+/Li), meaning low energy density, limits its application in high-energy devices [4–6]. Recently, to develop the energy density of lithium ion batteries, many researchers have made great efforts to explore a more attractive member of this group. $LiMnPO_4$, which exhibits a higher energy density, is about 20% larger than that of $LiFePO_4$ due to its higher operating voltage (4.1 V *vs.* Li^+/Li). Moreover, compared to other high potential olivine-type cathode materials such as $LiNiPO_4$ (5.1 V *vs.* Li^+/Li) and $LiCoPO_4$ (4.9 V *vs.* Li^+/Li), the 4.1 V intercalation potential of $LiMnPO_4$ is compatible with conventional non-aqueous organic electrolytes of lithium ion batteries [7].

However, $LiMnPO_4$ suffers from poor electronic conductivity and low lithium diffusivity, even much worse than those of $LiFePO_4$, which lead to its low discharge capacity, high polarization and poor rate capability [8,9]. These have become the main obstacles for its practical application in lithium ion batteries. In order to improve the electrochemical performance of $LiMnPO_4$ cathode materials, many attempts have been reported [10–15]. The results confirmed that a great increase in the electrochemical performance when substituted some Mn^{2+} by Fe^{2+} to form the solid solution $LiMn_{1-x}Fe_xPO_4$, and it combines the good rate capability of $LiFePO_4$ and high potential of $LiMnPO_4$ [16–21]. Numerous synthetic methods to obtain $LiMn_{1-x}Fe_xPO_4$ with the improved electrochemical performance have been extensively investigated [22–30]. For example, Hong et al. reported $LiMn_{0.8}Fe_{0.2}PO_4$ prepared by a

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http://dx.doi.org/10.1016/j.jpowsour.2013.09.048

conventional solid-state method could deliver a specific capacity of 138 mAh g^{-1} at 0.1 C [26]. Chen et al. have synthesized $LiMn_{1-x}Fe_xPO_4/C$ on the basis of $FePO_4 \cdot 2H_2O$ nanocrystallites, and the samples with $x = 0.25$ have an improved discharge capacity of about 130 mAh g^{-1} at 0.05 C, which is mainly attributed to iron substitution, the appropriate Mn/Fe ratio, and the well-ordered crystal structure of raw materials [28]. Saravanan et al. have succeeded in synthesizing nanoplates of $LiMn_{1-x}Fe_xPO_4$ using a simple solvothermal method. Especially, $LiMn_{0.5}Fe_{0.5}PO_4/C$ composite materials exhibited a reversible capacity of 121 mAh g^{-1} at 0.1 C [27]. From above results, it is also confirmed that the electrochemical performance of $LiMn_{1-x}Fe_xPO_4$ cathode materials strongly depends on the synthetic method.

More recently, it is believed that particle morphology is also a key factor that affects the discharge capacity of olivine-type cathode materials [31–37]. Ceder et al. confirmed that lithium ions can move easily along the *b*-axis in the olivine structure due to the low activation barrier along this direction [38]. Recently, Kanamura et al. found the value of pH in the $LiFePO_4$ precursor was of importance to control the morphology, especially plate-like crystal growth [31]. In addition, Wang et al. also revealed that the sample with platelet morphology (only ~30 nm thick oriented in the *b* direction) presented a good rate capability [25]. It exhibited a specific capacity of 145 mAh g^{-1} at C/20, 141 mAh g^{-1} at C/10 and 113 mAh g^{-1} at 1 C. In our previous work, we have successfully synthesized $LiMnPO_4$ [36] and $LiFePO_4$ [37] cathode materials with certain morphology and nanoscaled particles using solvothermal method, and confirmed that $LiMnPO_4$ thin nanoplates display the largest specific capacity, compared with $LiMnPO_4$ thick nanoplates and nanorods [36]. Under the inspiration of these successes, we speculated that it would be possible to synthesize $LiMn_{1-x}Fe_xPO_4$ with the greatly enhanced electrochemical performance using solvothermal method.

Herein, we reported $LiMn_{1-x}Fe_xPO_4$ (with $x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$) nanoparticles synthesized through solvothermal method. The studies include two aspects. On one hand, efforts were tried to find out the optimal pH value of solvothermal reaction system. On the other hand, $LiMn_{1-x}Fe_xPO_4$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$) were synthesized under selected condition and their electrochemical performances were discussed in detail. To improve the conductivity, a small quantity of carbon was coated on materials, and the element analysis showed that carbon contents in the final cathode materials were *ca.* 2.7 wt. %.

2. Experimental

2.1. Sample synthesis

$LiMn_{1-x}Fe_xPO_4$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$) nanoparticles were prepared by solvothermal method, which have been reported for the synthesis of $LiMnPO_4$ and $LiFePO_4$ in our previous work [36,37]. First, polyethylene glycol 400 (PEG 400) was mixed with H_3PO_4 (1 mol L^{-1}), and then LiOH (1 mol L^{-1}) solution was dropwise added to the above mixture with vigorous stirring to regulate the pH value of the system. In this work, the pH value was set as 9, 11, 12.5, for purpose of controlling the morphology of products. After that, $MnSO_4$ (0.5 mol L^{-1}) and $FeSO_4$ (0.5 mol L^{-1}) solutions were slowly introduced into the system in sequence under stirring. The suspension obtained above was then taken in a Teflon lined stainless steel reaction vessel, which was subsequently autoclaved in an oven at 180 °C for 12 h after sealed tightly. After the vessel was allowed to cool down to ambient temperature, the claybank products obtained were collected and washed with ethanol and water each for several times, then dried under vacuum at 80 °C for 12 h. In the above processes, H_3PO_4, $MnSO_4$ and $FeSO_4$ were used in the molar ratio of $1{:}(1-x){:}x$. As LiOH was added to adjust the pH value of the system, the molar ratio of Li:(Mn + Fe) in the precursor was about 3:1.

Herein, carbon-coating was carried out via two steps: Firstly, $LiMn_{1-x}Fe_xPO_4$ and sucrose ($LiMn_{1-x}Fe_xPO_4$:sucrose = 9:1, weight ratio) were mixed using planetary ball milling containing appropriate ethanol at 350 rpm for 4 h with a weight ratio of sample: ball = 1:20; secondly, the mixture was annealed at 600 °C for 4 h in an Ar atmosphere. The carbon contents of all the final cathode materials were *ca.* 2.7 wt. % from the element analysis (CHNS/O Elemental Analyzer, PerkinElmer).

2.2. Structure and morphology characterizations

The as-prepared products were characterized by X-ray powder diffraction (XRD, D8 Advance diffractometer, Cu Kα radiation). Morphology was examined using field emission scanning electron microscopy (FESEM) (S-4800, Hitachi) and high-resolution transmission electron microscopy (HRTEM) (Tecnai F20, FEI).

2.3. Electrochemical measurements

Electrochemical properties of the $LiMn_{1-x}Fe_xPO_4$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$) electrodes were measured after assembling them into coin cells (type CR2032) in an argon-filled glove box using lithium metal as the anode and Celgard 2502 as the separator. The cathode was prepared by spreading a mixture of active material (80 wt. %), acetylene black (15 wt. %), and poly (vinylidene fluoride) binder (5 wt. %) dissolved in *N*-methyl pyrrolidone onto an aluminum foil current collector. The thickness of the electrode was about 20 μm and the loading density of active material on the electrode was about 2.5 mg cm^{-2}. The electrolyte (Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd., P. R. China), consists of a solution of 1 M $LiPF_6$ in a mixture of ethylene carbonate/dimethyl carbonate (3:7 vol. %). The coin-typed cells were tested in a voltage range of 2.0 V–4.5 V (*vs.* Li^+/Li) using a constant-current constant-voltage (CC–CV) protocol at various rates with potentiostatic steps at the cutoff potential on a battery tester (LAND-CT2001A, Jinnuo Wuhan Co., Ltd., P. R. China). Cyclic voltammetry (CV) measurements were carried out on an Autolab83710 at a scanning rate of 0.1 mV s^{-1} with the voltage ranging from 2.0 V to 4.6 V. All the tests were conducted at constant temperature (25 °C) and the forming current was 0.05 C.

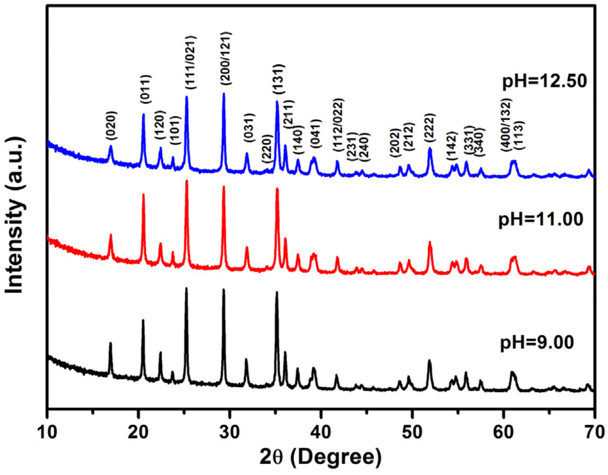

Fig. 1. XRD patterns of $LiMn_{0.9}Fe_{0.1}PO_4$ synthesized at different pH values.