Journal of Power Sources 245 (2014) 331–336

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

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

Short communication

The influence of temperature on a nutty-cake structural material: $LiMn_{1-x}Fe_xPO_4$ composite with $LiFePO_4$ core and carbon outer layer for lithium-ion battery

Zhen-Qing Huo, Yu-Ting Cui, Dan Wang, Yue Dong, Li Chen*

Department of Chemistry, Tianjin University, Tianjin 300072, People's Republic of China

HIGHLIGHTS

- A nutty-cake structural C–$LiMn_{1-x}Fe_xPO_4$–$LiFePO_4$ cathode material is synthesized.
- The calcination temperature has obvious influence on the crystal structure.
- Fe^{2+} diffused from the $LiFePO_4$ core to the outer $LiMnPO_4$ layer during calcination.

ARTICLE INFO

Article history:
Received 28 March 2013
Received in revised form
26 June 2013
Accepted 26 June 2013
Available online 4 July 2013

Keywords:
Cathode material
Ion diffusion
Nutty-cake structure
Lithium-ion batteries

ABSTRACT

The extremely low electronic conductivity, slow ion diffusion kinetics, and the Jahn–Teller effect of $LiMnPO_4$ limit its electrochemical performance. In this work, a nutty-cake structural C–$LiMn_{1-x}Fe_xPO_4$–$LiFePO_4$ cathode material is synthesized by hydrothermal method and further calcined at different temperatures. The influence of calcination temperature on the electrochemical behavior is investigated by X-ray diffractometer, scanning electron microscope, field-emission high-resolution transmission electron microscope, energy-dispersive X-ray spectroscopy, electrochemical impedance spectroscopy and charge–discharge tests. And the performance of C–$LiMn_{1-x}Fe_xPO_4$–$LiFePO_4$ materials has a relationship with its crystal structure. The well-crystallized Sample-600 calcined at 600 °C shows the smallest charge transfer resistance, the largest lithium ion diffusion coefficient (D_{Li}) and the best cycling stability. The discharge capacity of Sample-600 holds around 112 mAh g^{-1} after the 3rd cycle at 0.1 C rate. The performances improvement of C–$LiMn_{1-x}Fe_xPO_4$–$LiFePO_4$ material can be mainly attributed to the iron diffusion from the $LiFePO_4$ core to the outer $LiMnPO_4$ layer under appropriate calcination temperature.

1. Introduction

Olivine framed lithium metal phosphates [$LiMPO_4$ (M = Fe, Mn, Ni, and Co)] have recently attracted much attention as a potential cathode material for Li-ion battery due to their high safety, environment friendly nature, low cost, high thermal stability and high theoretical capacity (170 mAh g^{-1}) [1–5]. In the olivine family, $LiMnPO_4$ is another promising cathode material beside $LiFePO_4$, which can give a higher voltage of 4.2 V ($LiFePO_4$: 3.5 V) *vs.* Li/Li^+ and a higher theoretical energy density 684 Wh kg^{-1} ($LiFePO_4$: 578 Wh kg^{-1}) [1], but the electronic conductivity of $LiMnPO_4$ ($<10^{-10}$ S cm^{-1}) is much lower than that of $LiFePO_4$ (1.8×10^{-9} S cm^{-1}) [6,7]. The intrinsically low ionic and electronic conductivity of $LiMnPO_4$ has limited its practical application in high power batteries, and the Jahn–Teller distortion associated with Mn^{3+} also hinders the real application of $LiMnPO_4$. During cycling, the shrinkage of $LiMnPO_4$ is about 8.9%, but only 6.8% for $LiFePO_4$ [8].

The effective methods to improve the electrochemical performance of $LiMnPO_4$ include Mn-site doping [9–11], particle size minimization [12–14] and carbon coating [15,16]. Appropriate substitution iron for Mn is beneficial to produce small volume change of $LiMnPO_4$ during lithium extraction/insertion [8]. Further coating an electronically conducting phase is helpful to improve the poor electronic conductivity of $LiMnPO_4$. The $LiMnPO_4$ particles coating with $LiFePO_4$ and C has been reported by K. Zaghib et al. [17]. The carbon-coated $LiFePO_4$–$LiMnPO_4$ composite shows better electrochemical properties than the carbon-coated $LiMn_{2/3}Fe_{1/3}PO_4$ with the same composition. It is well known that the electronic conductivity and ionic conductivity of $LiMnPO_4$ is much lower than

* Corresponding author. Tel.: +86 22 27892379; fax: +86 22 27403475.
E-mail address: chenli_su@eyou.com (L. Chen).

0378-7753/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jpowsour.2013.06.148

that of $LiFePO_4$ [6,7]. The outward diffusion of Li^+ from the center of $LiMnPO_4$ particles should be more difficult, thus the electrochemical properties of internal $LiMnPO_4$ are severely hindered. At the same time, the dissolution of Fe^{2+} from $LiFePO_4$ is almost inevitable [18] which would lead to internal short circuit and low open circuit voltage of the battery. To solve those problems, a $Li(Mn,Fe)PO_4$ composite with $LiFePO_4$ core and a carbon outer layer is prepared to study its electrochemical properties in the present work.

2. Experimental details

2.1. Preparation of $LiFePO_4$

$LiFePO_4$ was synthesized by a hydrothermal route from starting materials $FeSO_4 \cdot 7H_2O$, H_3PO_4, and $LiOH \cdot H_2O$ in a molar ratio of 1:1:3. A 0.35 mol L^{-1} H_3PO_4 aqueous solution and a 0.35 mol L^{-1} $FeSO_4$ aqueous solution were mixed with vigorous agitation firstly, then a 1.05 mol L^{-1} LiOH solution was added drop-wise to the above solution. After stirring for 5 min under Ar atmosphere, the suspension was transferred into a hydrothermal autoclave reactor, heated at 220 °C for 7 h. After naturally cooling to room temperature, the $LiFePO_4$ powder was filtered, washed with water and ethanol for several times, and then dried at 80 °C in vacuum.

2.2. Coating with $LiMnPO_4$

Firstly, a 0.35 mol L^{-1} H_3PO_4 aqueous solution was mixed with a 0.35 mol L^{-1} $MnSO_4$ aqueous solution with vigorous agitation, then a 1.05 mol L^{-1} LiOH solution was added drop-wise into the above solution to obtain the precursor solution with a Li:Mn:P molar ratio of 3:1:1. Then $LiFePO_4$ prepared in step 2.1 and the precursor solution were mixed with a Mn:Fe molar ratio of 4:1 and added into a PTFE vessel again, and the subsequent process was the same as that described in step 2.1.

2.3. Carbon-coating

The composite obtained at the end of step 2.2 was mixed with a sucrose solution, and the weight ratio of composite/sucrose was 10:1. The mixture $LiMnPO_4$–$LiFePO_4$ was dried at 60 °C under vacuum firstly, then the mixture was heated at 300 °C for 1 h to carbonize the sucrose, and calcined at 550 °C, 600 °C and 650 °C for 3 h respectively under Ar gas flow to form C–$LiMn_{1-x}Fe_xPO_4$–$LiFePO_4$ composite named as Sample-550, Sample-600, Sample-650 respectively.

2.4. Apparatus

Thermo-gravimetric and differential scanning calorimetry (TG–DSC) analyses were used to understand the phase transformation of synthesized composite powder using a simultaneous thermal analyzer (STA 409 PC/PG, NETZSCH). The powder was heated from room temperature to 900 °C under N_2 atmosphere at a heating rate of 10 °C min^{-1}. X-ray diffraction analysis was carried out using a X-ray diffractometer (XRD, D/max 2500 V/PC, Rigaku, 40 KV, 150 mA) using Cu Kα radiation and a graphite monochromator. The samples were scanned over the 10–90° (2θ) range at a scan speed of 2°min^{-1} (step size 0.02°, step time 0.6 s). Morphology and external components of the samples were investigated using a scanning electron microscope (SEM, XL30, Philips) with an energy-dispersive X-ray spectroscopy (EDX). The interior structure of the samples was observed by a field-emission high-resolution transmission electron microscope (HRTEM, JEM-2100F, JEOL) with an energy-dispersive X-ray spectroscopy (EDX). Electrochemical impedance spectroscopy (EIS, Zennium, Zhaner Elektrik) was carried out in a frequency range from 0.1 Hz to 100 kHz with an AC signal of 5 mV.

The cathode was prepared by coating a viscous slurry with 80% C–$LiMn_{1-x}Fe_xPO_4$–$LiFePO_4$ composite, 10% conductive carbon black (Super P), and 10% polyvinylidene fluoride (PVDF) binder onto Al foils. The cathode was dried at 120 °C for 12 h to gain a coating layer with 150 μm. A mixture of ethylene carbonate (EC) and dimethyl carbonate (DEC) (volume ratio = 1:1) containing 1 M $LiPF_6$ was used as the electrolyte. All cells were assembled in an argon-filled glove box. The electrochemical properties of the cathodes were measured by a battery testing system (CT2001A, LAND) at a current density of 0.1 C rate (1 C = 170 mA g^{-1}) between 2.5 and 4.5 V *vs.* Li/Li^+ at room temperature.

3. Results and discussion

TG/DSC curves could help confirm the annealing program of precursor mixtures. Fig. 1 shows the TG/DSC curves of precursor mixtures. The TG curve exhibits a single weight loss stage about 5.58 wt. % between 180 °C and 300 °C, and there is no significant weight loss after 300 °C. The percent weight loss is mainly ascribed to the dehydration of sucrose [19,20], which is in accordance with the theoretical value (5.26 wt.%). However, a sharp endothermic DSC peak is observed at around 600 °C, which indicates that a solid solution $LiMn_{1-x}Fe_xPO_4$ *via* crystalline substitution is formed in this range. The supposition is proved further by the following detection technology.

Fig. 2(a) shows XRD pattern of $LiFePO_4$ synthesized in step 2.1. The diffraction peaks confirm the formation of the pure and well-crystallized $LiFePO_4$ with an orthorhombic olivine structure, and the pattern matches well with the standard $LiFePO_4$ (PDF#40-1499). Fig. 2(b) shows the XRD patterns and the inset shows the local enlarged XRD patterns between $2\theta = 50°$–$55°$. The JCPDS card data of $Li(Mn,Fe)PO_4$ (PDF#13-0336) and $LiMnPO_4$ (PDF#33-0804) are also shown in Fig. 2(b). All three samples are ordered olivine compounds with an orthorhombic structure (space group Pnma) and which is similar to that of $LiMnPO_4$, and $Li(Mn,Fe)PO_4$. Because the lattice parameters of $LiFePO_4$ and $LiMnPO_4$ are close, the XRD patterns show delicate difference only at high angle [17].

The inset shows the peaks shift slightly to higher angles with increasing calcination temperature. A small peak splitting is also observed around 52° only at 550 °C which disappears at temperatures higher than 600 °C. The crystal structure determined from XRD patterns by means of FOM value suggests that the samples at

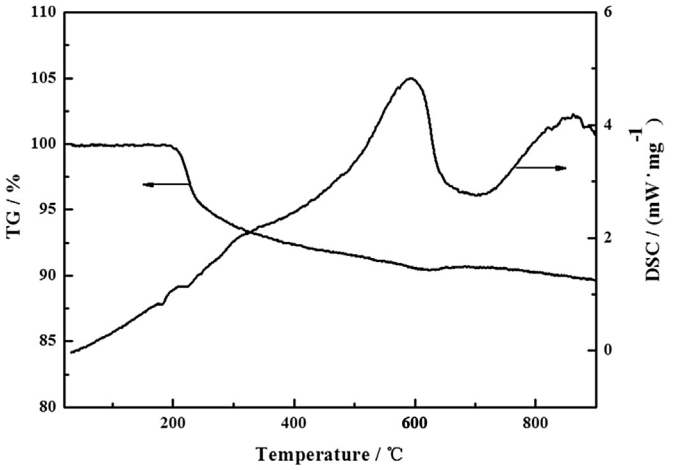

Fig. 1. TG/DSC curves of precursor mixtures.