Colloids and Surfaces A: Physicochem. Eng. Aspects 495 (2016) 54–61

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Electrospun polycrystalline $Li_xFe_{0.2}Mn_{0.8}PO_4$/carbon composite fibers for lithium-ion battery

Fangfang Leng[a,b], Xu Yan[a,c], Laiying Jing[a,b], Ruirui Liu[a,b], Yun-Ze Long[a,c,*], Hongliang Li[a,b,*], X.S. Zhao[a,b], Peizhi Guo[a,b,*]

[a] *State Key Laboratory Breeding Base of New Fiber Materials and Modern Textile, Collaborative Innovation Center for Marine Biomass Fibers, Materials and Textiles of Shandong Province, Qingdao University, Qingdao 266071 PR China*

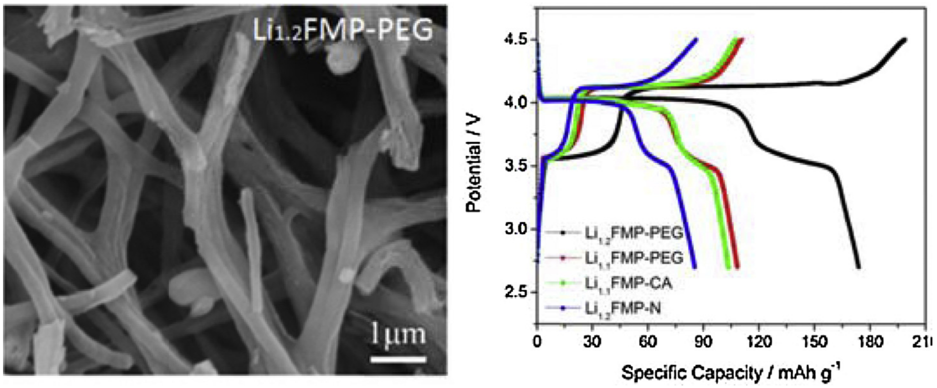
[b] *Institute of Energy and Environmental Materials, School of Materials Science and Engineering, Qingdao University, Qingdao 266071 PR China*

[c] *College of Physics, Qingdao University, Qingdao 266071, PR China*

HIGHLIGHTS

- $Li_xFe_{0.2}Mn_{0.8}PO_4$/C composite fibers were synthesized based on the electrospinning method.
- The content of lithium of $Li_xFe_{0.2}Mn_{0.8}PO_4$/C fibers has a strong effect on their electrochemical properties.
- The molecular structure of carbon sources plays an important role in determining the electrochemical properties of composite fibers.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 October 2015
Received in revised form 15 January 2016
Accepted 29 January 2016
Available online 1 February 2016

Keywords:
$Li_xFe_{0.2}Mn_{0.8}PO_4$/C composite fibers
Lithium-ion battery
Electrospinning method
Electrochemical performance

ABSTRACT

$Li_xFe_{0.2}Mn_{0.8}PO_4$/C (Li_xFMP/C, $x = 1.2$, 1.1, 1.05) composite fibers were successfully prepared by stabilization and calcination of the electrospun fibers from the precursor solution. The structural and morphological characterizations revealed that the $Li_xFe_{0.2}Mn_{0.8}PO_4$ with high purity was evenly coated with an amorphous carbon layer. Experimental data testified the well-crystalline structure of composite fibers based on the results of the X-ray diffraction (XRD) and selected area electron diffractions (SAED). The galvanostatic charge–discharge measurements indicated that $Li_{1.2}Fe_{0.2}Mn_{0.8}PO_4$ displayed the highest capacity of 174 mA h g^{-1} at 0.05 C and the best cycling stability. The charge-transfer impedance of $Li_xFe_{0.2}Mn_{0.8}PO_4$/C was decreased negatively with the content of lithium. It was found that the molecular structure of carbon sources and calcination procedure played key factor in determining the electrochemical properties of the composite fibers. These results suggested that electrospinning should be a promising method for fabricating crystalline LFMP/C composite fibers as electrode materials for lithium-ion battery.

---

* Corresponding authors at: State Key Laboratory Breeding Base of New Fiber Materials and Modern Textile, Collaborative Innovation Center for Marine Biomass Fibers, Materials and Textiles of Shandong Province, Qingdao University, Qingdao 266071, PR China. Fax: +86 532 859 55529.

E-mail addresses: yunze.long@163.com (Y.-Z. Long), lhl@qdu.edu.cn (H. Li), guopz77@yahoo.com, pzguo@qdu.edu.cn (P. Guo).

http://dx.doi.org/10.1016/j.colsurfa.2016.01.054

1. Introduction

Tremendous efforts have recently been dedicated to improve the performance of Li-ion batteries for large-scale usages, such as cell phones, plug-in hybrid vehicles and energy storage systems [1–8]. Since the pioneering studies of Padhi et al. [9], olivine structured $LiMPO_4$ (M = Mn, Fe, Co, Ni) cathode materials have attracted great interest for the advantages including low cost, environmental friendliness and excellent structural stability due to the strong P—O bonds [10–13]. Among these materials, $LiFePO_4$ is considered as the most promising one (now considered to have great prospect in large scale application) due to the low toxicity and most importantly high safety [1,14,15]. However, an inherent low electronic and ionic conductivity leads to a poor rate capability, which constrains its developments as a candidate for cathode materials [12]. Thanks to the increasing research of $LiFePO_4$, $LiMnPO_4$, which is an isomorph of $LiFePO_4$, is attracting an increasing attention [16–18]. It has advantages of the higher energy density and the higher operation potential of 4.1 V which is compatible with the present electrolytes compared with $LiFePO_4$ (3.4 V vs. Li/Li^+) [16,19,20]. However, the performance of $LiMnPO_4$ is not so satisfactory for the low electronic conductivity, low tap density and poor cycle life caused by Mn dissolution [9,21]. It was found that the $LiMn_yFe_{1-y}PO_4$ solid solution achieved better electrochemical performance than $LiMnPO_4$, because the coexistence of Mn and Fe could ameliorate the kinetics to speed up the charge–discharge process [19]. Besides, recent reports indicate that energy density of the solid–solution increases with the content of Mn in the composite [22–26].

Nanostructured olivine materials have been prepared and used as electrode materials for Li-ion batteries with high performances [20,27]. The structural features of such materials provided decreased length for lithium-ion diffusion, which would increase the rate capability of the active materials [27]. Nevertheless, the large surface area of nanomaterials results in a high solid–electrolyte interfacial (SEI) area, leading to capacity fade in the cycle life [28]. Carbon coating is a practicable strategy to remedy the defect of nanostructured electrode materials. Except for restraining the particle growth, the carbon layer can improve the electronic and ionic conductivity to enhance electrochemical performance. Moreover, the coating can prevent side reactions that produce undesired Fe^{3+} and Li_3PO_4 and deteriorate the properties of $LiMPO_4$. Citric acid was found to be a favorable agent to improve the electrochemical properties of active materials [29–31]. In this regard, preparing nano/submicrofibers is an effective method to combine the improvement of conductivity and the reduction of size. Moreover, nano/submicrofibers can provide better percolation property than particles [28,32].

Electrospinning is a simple, inexpensive, and effective technique to fabricate diverse fibers of various materials, such as composites, polymers and carbons. Besides, hollow or core/shell structured nano/submicrofibers can be obtained by electrospinning [29,33]. This technique has been the focus of attention of researchers due to the simplicity of preparing nanowires [34,35]. Recent reports indicated the great potential of nanowires with various morphologies in the lithium-ion batteries on account of better percolation properties compared with particles [36,37]. However, the electrochemical properties and morphology of those $LiFePO_4/C$ fibers are not satisfying and the long time of high-temperature calcination is not environmental friendly. Thus, it is necessary to fabricate LFMP/C fibers with excellent electrochemical performance.

In this study, $Li_xFe_{0.2}Mn_{0.8}PO_4$/carbon composite fibers for lithium-ion battery were prepared by electrospinning a viscous solution with Li, Fe, Mn, P sources, poly(4-vinyl) pyridine and the second carbon sources (citric acid or polyethylene glycol). The structure and morphology of the fibers were characterized by using X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Electrochemical measurements showed that $Li_{1.2}Fe_{0.2}Mn_{0.8}PO_4/C$ fibers prepared with polyethylene glycol precursor displayed the highest capacity of 174 mA h g^{-1} at 0.05 C and the best cycling property. The relationship between the structure, composition and properties of the composite fibers were discussed based on the experimental data.

2. Experiments

2.1. Materials

All chemical reagents, including $LiNO_3$, $Fe(NO_3)_3·9H_2O$, $Mn(NO_3)_2$ (aqueous solution, 49–51 wt.%), poly(4-vinyl) pyridine (PVP, M_w = 1,300,000), polyethylene glycol (PEG, M_w = 4,000), citric acid, $NH_4H_2PO_4$, ethanol, and nitric acid (65–68 wt.%) were analytical grade (Sinopharm Chemical Reagent Co., LTD.) and used without further purification. Polypropylene film (Celgard 2400) was purchased from Tianjin Jinniu Power Sources Material Co., LTD. Acetylene black was purchased from Strem Chemicals while polyvinylidiene fluoride and *N*-methylpyrrolidone from Aldrich.

2.2. Synthesis of $Li_xFe_{0.2}Mn_{0.8}PO_4$/carbon fibers

In a typical synthesis, $LiNO_3$, $Fe(NO_3)_3·9H_2O$, aqueous $Mn(NO_3)_2$ solution and $NH_4H_2PO_4$ were dissolved separately in a mixed solution composed of water, ethanol and nitric acid with a stoichiometric ratio of x:0.2:0.8:1 (x = 1.05, 1.1, 1.2). And then all the solutions were mixed under stirring, finally getting a transparent solution. An appropriate quantity of PEG was added into the solution. Then, a certain mass of PVP was added into the transparent solution above under stirring to obtain a homogeneous electrospinning solution which contains 8 wt.% PVP. The resultant precursor solution was placed in a 5 mL syringe with metal needle of 0.6 mm in internal diameter. A power supply (DW-P303-1ACFO) was used to provide a direct-current electric field of 25 kV between the needle and Al foil collector, and the distance between them was 20 cm. The ejection rate of the electrospinning solution from the syringe was 0.8 mL h^{-1}. The as-spun fibers were dried for 5 h in a vacuum at 100 °C and then were separated from the Al foil. First, the fibers were solidified at 280 °C for 4 h in air with an increment rate of 5 °C min^{-1}. Then, the fibers were calcined at 800 °C for 8 h under N_2 atmosphere at a ramp rate of 5 °C min^{-1} and the as-made $Li_xFe_{0.2}Mn_{0.8}PO_4$/carbon (LFMP/C) fibers were named as Li_xFMP-PEG. The fibers using citric acid as the second carbon source and fibers added no second carbon source, and undergone the same calcination procedure, were denoted as Li_xFMP-CA and Li_xFMP, respectively. The preparation procedure for Li_xFMP-PEG-2 was the same as that of Li_xFMP-PEG except the heating rate of 2 °C min^{-1}. For comparison purposes, the fibers without second carbon source were fabricated by calcining at 400 °C for 2 h and 280 °C for 4 h respectively, then 800 °C for 8 h with a heating rate of 5 °C min^{-1} in flowing N_2, which were respectively named as Li_xFMP-N and Li_xFMP-N-280.

2.3. Structure characterization

The XRD patterns of the samples were measured on Bruker D8 Advance X-ray diffractometer equipped with Cu Kα radiation (λ = 0.15418 nm) from 10 to 80° (2θ). The SEM images of the LFMP/C fibers were evaluated by using scanning electron microscope (JSM-6390LV) with an operating voltage of 20 kV. The microstructure of composite fibers was observed using transmission electron microscope (JEM-2000EX) operated at 160 kV.