

Preparation and electrochemical performance of $\text{LiFePO}_{4-x}\text{F}_x/\text{C}$ nanorods by room-temperature solid-state reaction and microwave heating

Yudai Huang · Dan Li · Dianzeng Jia ·
Zaiping Guo

Received: 22 December 2011 / Accepted: 4 June 2012 / Published online: 22 June 2012
© Springer Science+Business Media B.V. 2012

Abstract $\text{LiFePO}_{4-x}\text{F}_x/\text{C}$ nanorods were prepared by room-temperature solid-state reaction and microwave heating. The structure and morphology of the as-prepared materials were analyzed by X-ray diffraction and transmission electron microscopy. The results show that the $\text{LiFePO}_{4-x}\text{F}_x/\text{C}$ were well crystallized and consisted of nanoparticles with an average diameter of ten to several tens of nanometers, many round grains constituted solid rod-like structure. The length of the rods can be up to several hundreds of nanometers, and their diameters are around 100 nm. The results of electrochemical testing show that the initial discharge capacity of $\text{LiFePO}_{3.85}\text{F}_{0.15}/\text{C}$ is

124.7 mAh g^{-1} , with a negligible fading after 50 cycles at a constant current density of 1 C at room temperature. The capacity retention rate is 99.5 %, which is higher than that of LiFePO_4/C prepared by the same method. The doping of F helps improve electrical conductivity and Li^+ diffusion of LiFePO_4/C . This study may provide new insights and understanding on the effect of F-doping on the electrochemical performance of LiFePO_4/C .

Keywords Preparation · Microstructure · Electrochemical performance · $\text{LiFePO}_{4-x}\text{F}_x/\text{C}$ · Nanorods

Y. Huang · D. Li · D. Jia (✉)
Key Laboratory of Clean Energy Materials and
Technology of Ministry of Education, Xinjiang
University, Urumqi 830046, Xinjiang, People's Republic
of China
e-mail: jdz0991@gmail.com

Y. Huang · D. Li · D. Jia
Key Laboratory of Advanced Functional Materials of
Autonomous Region, Xinjiang University, Urumqi
830046, Xinjiang, People's Republic of China

Y. Huang · D. Li · D. Jia
Institute of Applied Chemistry, Xinjiang University,
Urumqi 830046, Xinjiang, People's Republic of China

Z. Guo
Institute for Superconducting and Electronic Materials,
University of Wollongong, Wollongong, NSW 2522,
Australia

Introduction

Since first proposed by Goodenough's group (Padhi et al. 1997), LiFePO_4 has been considered as a new and promising candidate for use as a cathode material because of its relatively large theoretical capacity (170 mAh g^{-1}), high safety, good cycling property, low cost, abundant raw materials, environmental benignity, and excellent thermal stability (Wang et al. 2008; Huang et al. 2011a). However, its power performance is greatly limited by slow diffusion of lithium ions across the two-phase boundary ($\text{LiFePO}_4/\text{FePO}_4$) and/or low electrical conductivity (Wang et al. 2008). For this reason, great endeavors have been

made into increase the conductivity of this cathode material and have suggested numerous solutions. Doping is considered to be an effective way to improve the lithium ions diffusion of LiFePO_4 . Several attempts have been made to synthesize improved lithium iron phosphate doped with supervalence cations. For example, $\text{Li}_{1-3x}\text{La}_x\text{FePO}_4$ composites (Li et al. 2010) were prepared and found that the conductivity was enhanced with increasing lanthanum doping content. Chung et al.'s (2002) controlled cation nonstoichiometry combined with solid-solution doping by metals supervalent to Li^+ increases the electronic conductivity of LiFePO_4 by a factor of $\sim 10^8$. It is reported that F is effective to improve cycling life for cathode materials. Liao et al. (2007) believed that a complete F-doping of LiFePO_4 may alleviate the iron dissolution, which enhances the cycling capability. However, up to now, the introduction of F-doping at oxygen sites in LiFePO_4 by room-temperature solid-state reaction and microwave heating is almost unheard of.

In recent years, nanomaterials have been used to as electrode materials in lithium ion batteries because of their diverse novel physicochemical and electrochemical properties. The use of nanostructures (i.e., nanoscale size or nanoporous structures) has been widely investigated to improve Li^+ transport in electrodes by shortening the Li^+ insertion/extraction pathway. Nanostructured materials have a high surface-to-volume ratio, which could facilitate charge transfer. In addition, the low diffusion/migration-length ratio of nanostructured materials exhibit high-power performance compared with conventional materials. In this article, $\text{LiFePO}_{4-x}\text{F}_x/\text{C}$ nanorods were prepared via room-temperature solid-state reaction and microwaving heating route. The structure, morphology, and electrochemical performance of the as-prepared materials were investigated.

Experimental

$\text{LiFePO}_{4-x}\text{F}_x/\text{C}$ ($x = 0, 0.05, 0.15, 0.25$) composites were prepared by room-temperature solid-state reaction and microwave heating technique. Stoichiometric $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, and $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ (worked as carbon source, molar ratio of citric acid to lithium acetate is 0.5:1) with/without LiF were mixed in an agate mortar and ground with a

pestle for 45 min. The start materials changed to a soft and pulpy mixture and then turned to solid powder. Later, the self-assembled carbon seal reactor (Huang et al. 2011a) with precursors inside, which could provide a reliable protective atmosphere, was put into a microwave oven (3.0 GHz, 800 W). Citric acid could absorb directly microwave energy, decompose to carbon, and thereby create a reductive atmosphere by carbon-thermal reaction. After 15 min of microwave irradiation, the samples were obtained, and the powders were further milled for testing.

An X-ray diffractometer (XRD, MXP18AHF, MAC, Japan) with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) was used for the identification of the crystalline phases of the particles. The morphologic characteristics of the products were investigated by transmission electron microscopy (TEM, H-600, Hitachi, Japan). The cells were assembled in an argon-filled glove box (Huang et al. 2011b). To prepare the working electrode, the cathode slurry for testing was prepared by thoroughly mixing 85 wt% $\text{LiFePO}_{4-x}\text{F}_x/\text{C}$ composites, 10 wt% acetylene black, and 5 wt% poly(vinylidene fluoride) in *N*-methylpyrrolidinone solvent. The obtained slurry was then spread onto aluminum foil substrates and dried in a vacuum oven at 120°C for 12 h. The cells consisted of the $\text{LiFePO}_{4-x}\text{F}_x/\text{C}$ composites as the positive electrode, a Li disk as the negative electrode, and an electrolyte composed of 1 M LiPF_6 in a 1:1 (volume ratio) mixture of ethylene carbonate and dimethyl carbonate. Celgard 2300 membrane was used as the separator. All the electrochemical tests were carried out at room temperature. Cyclic voltammetry (CV, CHI660B, Chenhua, China) experiments were conducted from 2.5 to 4.1 V at a scan rate of 0.1 mV s^{-1} . Charge/discharge tests were performed at a constant current density of 1 C within the potential range of 2.5–4.1 V.

Results and discussion

XRD patterns of $\text{LiFePO}_{4-x}\text{F}_x/\text{C}$ composites are shown in Fig. 1. All samples exhibit pure single phase of LiFePO_4 with an ordered olivine structure indexed with orthorhombic Pnmb space group (JCPDS card no. 40-1499) after microwave heating. As shown in Fig. 1, no impurity is detected, indicating that F-doping does not affect the lattice structure of LiFePO_4 because of the low doping content of F. In spite of

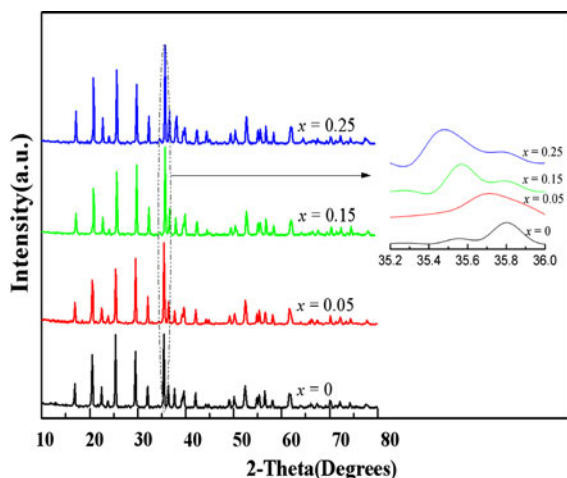


Fig. 1 XRD patterns of the as-synthesized $\text{LiFePO}_{4-x}\text{F}_x/\text{C}$ ($x = 0, 0.05, 0.15, 0.25$) samples

being subjected to a carbon-added treatment, no carbon peak is observed in each sample, which could be attributed to amorphous structure and low content of carbon in $\text{LiFePO}_{4-x}\text{F}_x/\text{C}$ composites. However, a close inspection of the XRD patterns reveals that the peaks shifted to smaller angles with increasing F-doping amount, which indicates an influence on the lattice after F-doping process. The peak position's variation of the (131) plane is magnified for clarity and shown in the right of Fig. 1.

The morphologies of different $\text{LiFePO}_{4-x}\text{F}_x/\text{C}$ composites are similar, and so the TEM images of $\text{LiFePO}_{3.95}\text{F}_{0.05}/\text{C}$ and $\text{LiFePO}_{3.85}\text{F}_{0.15}/\text{C}$ are given as examples in Fig. 2. It is clear that the as-prepared product consists of spherical-shaped nanoparticles. The average diameter of the particles changes from ten to several tens of nanometers. However, many round grains constitute solid rod-like structure. The length of the rods, as shown in Fig. 2, can be up to several hundreds of nanometers, and their diameters are ~ 100 nm. The formation of homogeneous nano-sized particles of $\text{LiFePO}_{4-x}\text{F}_x/\text{C}$ may be ascribed to the expansion of the added citric acid which reduces the surface tension of the precursors and prevent the particles from growing up in the heating process (Wang et al. 2007).

CVs of $\text{LiFePO}_{4-x}\text{F}_x/\text{C}$ samples between 2.5 and 4.1 V at a scanning rate of 0.1 mV s^{-1} for the first cycle are shown in Fig. 3. These samples have similar CV curves with a peak pair which consisting of an anodic and cathodic peak. The shape of CV profiles

become sharp with increasing F-doping content ($x = 0, 0.05, 0.15$). This can be ascribed to the enhanced electronic conductivity and decreased contact resistance because of the function of carbon network in the F-doping samples. However, it is obvious that the CV profiles of $\text{LiFePO}_{4-x}\text{F}_x/\text{C}$ ($x = 0.25$) have broadened peaks and lower peak height, which are due to immoderate higher content of F. It can be considered that the high F-doping content reduces the amount of Li^+ in the process of intercalation and deintercalation. The action of F-doping is further understood by comparing CV curves of virginal and other doped samples ($x = 0.05, 0.15$), which indicate that the latter have better electrochemical performance. For $\text{LiFePO}_{4-x}\text{F}_x/\text{C}$ ($x = 0.15$), the voltage separation is 0.143 V, which is smaller than that of LiFePO_4/C (0.252 V). Consequently, the narrower voltage separation and symmetric CV profiles indicate that $\text{LiFePO}_{3.85}\text{F}_{0.15}/\text{C}$ sample have a good reversibility of Li^+ extraction/insertion reaction by F-doping.

Figure 4 exhibits typical initial charge/discharge profiles of the as-synthesized $\text{LiFePO}_{4-x}\text{F}_x/\text{C}$ ($x = 0, 0.05, 0.15, 0.25$) in the potential range of 2.5–4.1 V (vs. Li/Li^+) at a current rate of 1 C. The flat charge/discharge profiles over a large compositional range imply that the two-phase redox reaction proceeds by a first-order transition between LiFePO_4 and FePO_4 (Padhi et al. 1997). The initial discharge capacities of LiFePO_4/C , $\text{LiFePO}_{3.95}\text{F}_{0.05}/\text{C}$, $\text{LiFePO}_{3.85}\text{F}_{0.15}/\text{C}$, and $\text{LiFePO}_{3.75}\text{F}_{0.25}/\text{C}$ are 113.8, 117.8, 124.7, and 114.8 mAh g^{-1} , respectively. $\text{LiFePO}_{3.85}\text{F}_{0.15}/\text{C}$ sample has the highest initial discharge capacity.

Figure 5 displays the discharge capacity versus cycle number curves of $\text{LiFePO}_{4-x}\text{F}_x/\text{C}$, with cycling between 2.5 and 4.1 V versus Li/Li^+ at a current density of 1 C at room temperature. The initial discharge capacity of LiFePO_4/C is 113.8 mAh g^{-1} , and a discharge capacity of 110.2 mAh g^{-1} is retained after 50 cycles, with its capacity retention rate being 96.8 %. However, the initial discharge capacity of $\text{LiFePO}_{3.95}\text{F}_{0.05}/\text{C}$ is 117.8 mAh g^{-1} , and its remaining discharge capacity is 115.5 mAh g^{-1} after 50 cycles, with its capacity retention rate being 98 %. Further, the initial discharge capacity of $\text{LiFePO}_{3.85}\text{F}_{0.15}/\text{C}$ is 124.7 mAh g^{-1} , and its remaining discharge capacity is 124.1 mAh g^{-1} after 50 cycles, representing a discharge capacity retention rate of 99.5 %. The initial discharge capacity of $\text{LiFePO}_{3.75}\text{F}_{0.25}/\text{C}$ is 114.8 mAh g^{-1} , and its remaining

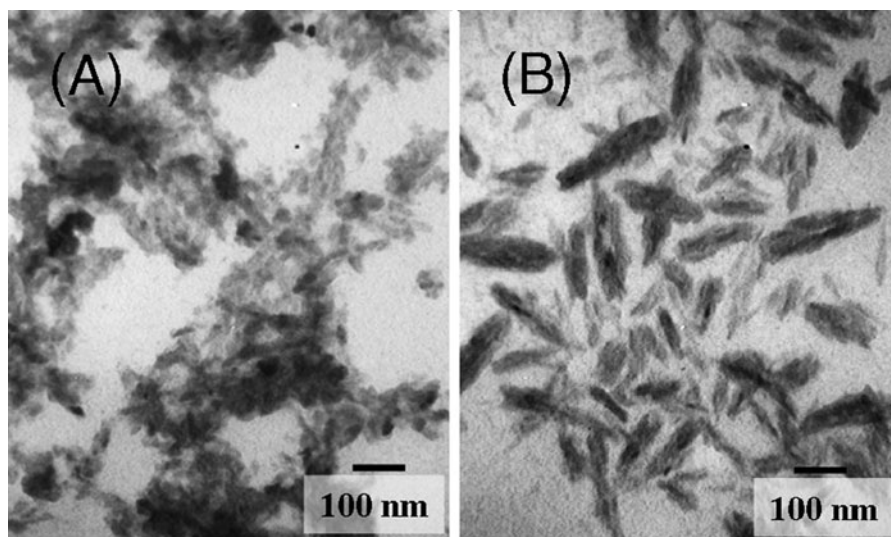


Fig. 2 TEM images of the as-synthesized $\text{LiFePO}_{4-x}\text{F}_x/\text{C}$: **a** $x = 0.05$, **b** $x = 0.15$

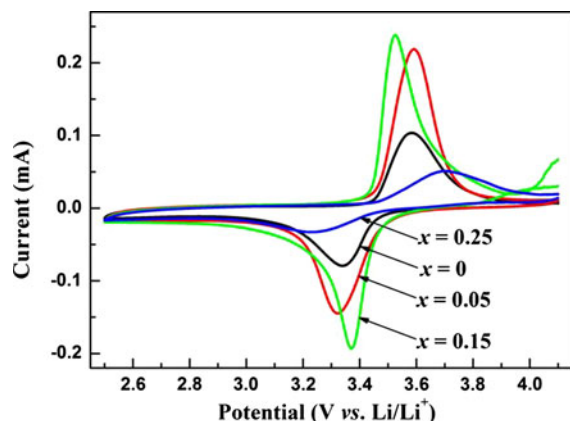


Fig. 3 CVs of the as-synthesized $\text{LiFePO}_{4-x}\text{F}_x/\text{C}$ ($x = 0, 0.05, 0.15, 0.25$) in the potential window of 2.5–4.1 V (vs. Li/Li^+)

discharge capacity is 113.6 mAh g^{-1} after 50 cycles, with its discharge capacity retention rate being 98.9 %. The initial discharge capacities and discharge capacity retention rates of $\text{LiFePO}_{3.75}\text{F}_{0.25}/\text{C}$ and LiFePO_4/C have no large difference, but the initial discharge capacities and discharge capacity retention rates of $\text{LiFePO}_{4-x}\text{F}_x/\text{C}$ ($x = 0.05, 0.15$) are higher than that of LiFePO_4/C . Pan and Wang (2011) reported that after F-doping in the LiFePO_4/C , the interatomic distances of Li–O increase by 1.09 %, 0.98 %, and 2.61 % for Li–O1, Li–O2, and Li–O3, respectively. This indicates that the extraction of Li from the lattice of LiFePO_4 could be facilitated via F-doping, because of the weakened interaction between Li and O. The F-doping improves

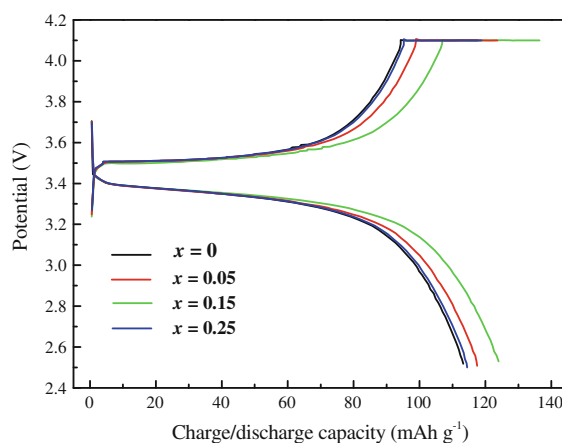


Fig. 4 The initial charge/discharge profiles of the as-synthesized $\text{LiFePO}_{4-x}\text{F}_x/\text{C}$ ($x = 0, 0.05, 0.15, 0.25$) in the potential range of 2.5–4.1 V (vs. Li/Li^+)

electrical conductivity and Li^+ diffusion of LiFePO_4/C , and therefore enhances electrochemical performance.

Conclusion

$\text{LiFePO}_{4-x}\text{F}_x/\text{C}$ nanorods were prepared by room-temperature solid-state reaction and microwave heating technique. The structure and morphology test results show that the $\text{LiFePO}_{4-x}\text{F}_x/\text{C}$ were well crystallized and consisted of nanoparticles with an average diameter of ten to several tens of nanometers,

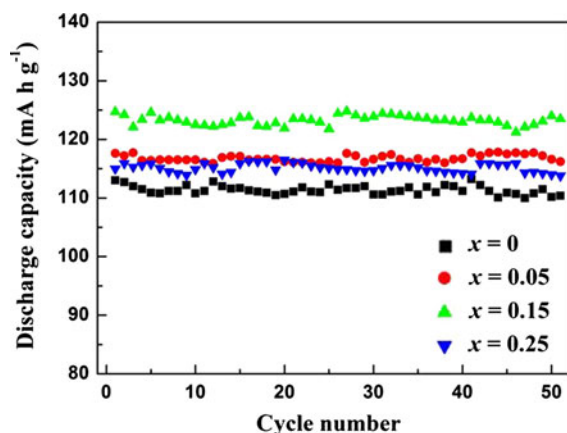


Fig. 5 Cycling performance of the as-synthesized $\text{LiFePO}_{4-x}\text{F}_x/\text{C}$ ($x = 0, 0.05, 0.15, 0.25$) samples

many spherical grains consisted of solid rod-like structure. The length of the rods can be up to several hundreds of nanometers, and their diameters are around 100 nm. The electrochemical performance results indicated that the initial discharge capacity of $\text{LiFePO}_{3.85}\text{F}_{0.15}/\text{C}$ was 124.7 mAh g^{-1} , and a discharge capacity of 124.1 mAh g^{-1} was retained after 50 cycles at a current density of 1 C at room temperature, with the discharge capacity retention rate being 99.5 %, which is higher than that of LiFePO_4/C prepared by the same method.

Acknowledgments This study was supported by the Nature Science Foundation of Xinjiang Province (nos. 200821121 and 2010211A09), the National Natural Science Foundation of China (nos. 21161021 and 21061013), the Science and Technology Foundation of Urumqi (no. y08231006), the Science and Technology Foundation of Xinjiang University

(no. BS100114), and the Program for Changjiang Scholars and Innovative Research Team in University of Ministry of Education of China (no. IRT1081).

References

- Chung S-Y, Bloking JT, Chiang Y-M (2002) Electronically conductive phospho-olivines as lithium storage electrodes. *Nat Mater* 1(2):123–128
- Huang Y, Li D, Jia D, Guo Z, Miao M, Cho WI (2011a) Preparation and characterization of Ag/C nanocables-modified nanosized C– LiFePO_4 . *J Nanopart Res* 13:4815–4820
- Huang Y, Jiang R, Jia D, Guo Z (2011b) Preparation, microstructure and electrochemical performance of nanoparticles $\text{LiMn}_2\text{O}_{3.9}\text{Br}_{0.1}$. *Mater Lett* 65:3486–3488
- Li D, Huang Y, Jia D, Guo Z, Bao S-J (2010) Synthesis and electrochemical properties of nanosized carbon-coated $\text{Li}_{1-3x}\text{La}_x\text{FePO}_4$ composites. *J Solid State Electrochem* 14:889–895
- Liao X-Z, He Y-S, Ma Z-F, Zhang X-M, Wang L (2007) Effects of fluorine-substitution on the electrochemical behavior of LiFePO_4/C cathode materials. *J Power Sources* 174: 720–725
- Padhi AK, Nanjundaswamy KS, Goodenough JB (1997) Phospho-olivines as positive-electrode materials for rechargeable lithium batteries. *J Electrochem Soc* 144(4):1188–1194
- Pan F, Wang W-l (2011) Synthesis and characterization of core-shell F-doped LiFePO_4/C composite for lithium-ion batteries. *J Solid State Electrochem*. doi:10.1007/s10008-011-1544-z
- Wang L, Huang Y, Jiang R, Jia D (2007) Preparation and characterization of nano-sized LiFePO_4 by low heating solid-state coordination method and microwave heating. *Electrochim Acta* 52(24):6778–6783
- Wang Y, Wang Y, Hosono E, Wang K, Zhou H (2008) The design of a LiFePO_4 /carbon nanocomposite with a core-shell structure and its synthesis by an in situ polymerization restriction method. *Angew Chem Int Ed* 47(39):7461–7465