Morphology-controllable solvothermal synthesis of nanoscale LiFePO_4 in a binary solvent

WU Miao, WANG ZhaoHui, YUAN LiXia^{*}, ZHANG WuXing, HU XianLuo & HUANG YunHui

State Key Laboratory of Material Processing and Die and Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan 430000, China

Received October 25, 2011; accepted December 28, 2011; published online March 31, 2012

LiFePO_4 (LFP) nanobars, microplates and nanorods have been selectively synthesized via a solvothermal method in a water-ethylene glycol (EG) binary solvent with H_3PO_4 , $\text{LiOH}\cdot\text{H}_2\text{O}$, and $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ as starting materials. The morphology and size of the as-obtained LFP products can be deliberately controlled by varying the volume ratio of EG to water. The formation mechanism and electrochemical properties of different LFP morphologies have been investigated. With carbon coating, the Li-ion diffusion coefficients of LFP nanorods, nanobars and micro-plates are 2.58×10^{-9} , 2.91×10^{-10} , and 7.22×10^{-10} $\text{cm}^2 \text{s}^{-1}$, respectively. For the carbon-coated nanorods, excellent rate capability and cyclability were attained. At 5 C, the capacity was 141 mAh g^{-1} for the first cycle and maintained 120 mAh g^{-1} after 100 cycles; at 10 C, the capacity was still as high as 132 mAh g^{-1} .

lithium ion battery, lithium iron phosphate, solvothermal synthesis, morphology control, electrochemical performance

Citation: Wu M, Wang Z H, Yuan L X, et al. Morphology-controllable solvothermal synthesis of nanoscale LiFePO_4 in a binary solvent. *Chin Sci Bull*, 2012, 57: 4170–4175, doi: 10.1007/s11434-012-5019-0

Olivine lithium iron phosphate LiFePO_4 (LFP) is one of the most promising cathode materials for large-scale power systems because of its low cost, low environmental impact, high theoretical capacity (170 mAh g^{-1}), moderate voltage (3.4V vs. Li^+/Li), long cycle life, and safety. However, LFP suffers from poor ionic and electronic conductivity, which limits its application in high-rate lithium ion batteries [1].

Various synthetic and material modification approaches have been pursued to overcome the ionic and electronic-transport limitations of LFP. Among them, conductive agent coating [2–5] and supervalent cation doping [6–8] have been widely used for improving the electronic conductivity on the surface and in the bulk of LFP particles, respectively, though the doping effect is still a point of controversy [9,10]. Another common approach to improve the high-rate property of LFP is to use nano-sized particles, which can not only shorten the diffusion length for electrons and Li-ions but can also increase the effective reaction area [11–13].

Gibot et al. [14] claimed that downsizing the particles to less than 40 nm can drive the well-established two-phase insertion process into a single-phase process in LFP at room temperature. Jamnik et al. [15,16] reported that the nanosized electrode materials provide an interfacial Li-ion storage in addition to the classical Li insertion/deinsertion reaction, which can further improve the specific capacity of LFP. The smaller the particle size, the higher the surface electrochemical reactivity.

Alternatively, many attempts have been made to develop synthetic methods to prepare various LFP nanostructures with kinetically favorable morphologies [17]. While hydrothermal processes are efficient methods for preparing ultrafine LFP particles [18], selective morphological control in water or in the absence of surfactants is difficult. Solvothermal methods are alternative approach to prepare nanostructured materials using organic solvents [19–21], such as tetraethyleneglycol, benzyl alcohol and ethylene glycol. However, this method also has some disadvantages, such as, low precursor solubility, high cost, and high reac-

^{*}Corresponding author (email: yuanlixia@mail.hust.edu.cn)

tion temperature.

In this work, we report a facile solvothermal synthesis of LFP nanoparticles, nanorods, and microplates in a binary solvent containing water and ethylene glycol (EG) at a low reaction temperature. The size and morphology of LFP can be effectively controlled by simply varying the ratio of EG to water. Electrochemical measurements show that the carbon-coated LFP nanorods exhibit excellent rate capability and cyclability.

1 Materials and methods

1.1 Synthesis of materials

All chemicals used were purchased without further purification. H_3PO_4 (85 wt.% solution, AR), $\text{LiOH}\cdot\text{H}_2\text{O}$ (AR), $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ (AR), EG (AR), were from Sinopharm Chemical Reagent Co., Ltd.

Stoichiometric amounts of phosphoric acid (H_3PO_4 , 85 wt.%) and lithium hydrate ($\text{LiOH}\cdot\text{H}_2\text{O}$) were dispersed in an EG-water binary solvent under magnetic stirring to form a milky white suspension. Then, ferrous sulfate ($\text{FeSO}_4\cdot 7\text{H}_2\text{O}$) was added slowly while stirring, resulting in a green suspension. The molar ratio of $\text{Li}:\text{Fe}:\text{P}$ was 3:1:1, and the Li-ion concentration was 0.1 mol L^{-1} . The mixture was transferred into a 70 mL Teflon-lined stainless steel autoclave and maintained at 180°C for 9 h. After cooling to room temperature, the product was collected by centrifugation, washed several times with water and alcohol, and dried in air at 60°C for 12 h.

To obtain LFP samples with different morphologies, the volume ratio of EG to water was adjusted to 1:4, 2:3, and 3:2. The corresponding products were marked as L14, L23, and L32. Carbon coating was used to enhance the conductivities of the solvothermal samples. The as-synthesized LFP products were mixed with 12 wt.% of glucose, and annealed at 600°C for 5 h under a mixed 5% H_2/N_2 atmos-

phere. The carbon-coated LFP samples were referred to as L14/C, L23/C, and L32/C.

1.2 Characterization

The phase of the products was determined by X-ray powder diffraction (XRD, Panalytical X'pert PRO MRD, Holland) with a step of 0.017° in a 2θ range from 10° to 80° using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406\text{ nm}$, 40 kV, 40 mA). The morphology was observed with electron scanning electron microscopy (SEM, SIRION200).

1.3 Electrochemical measurements

Electrochemical performance was evaluated with CR2032 coin cells using Li foil as counter electrode. The working cathode was prepared by mixing the active material (LFP), acetylene black (AB) and polytetrafluoroethylene (PTFE) binder in N-methyl-2-pyrrolidone (NMP) solvent at a weight ratio of 8:1:1. The mixture was rolled into thin sheets, cut into circular electrodes and then dried at 80°C in vacuum for 24 h. Metallic lithium foil was used as the counter and reference electrodes. The electrolyte was 1 mol L^{-1} LiPF_6 dissolved in a mixed solution containing ethylene carbonate (EC) and dimethyl carbonate (DMC) with in a 1:1 volume. A microporous membrane (Celgard 2400) served as the separator. The cells were assembled in an argon-filled glove box. Electrochemical tests were performed with a battery tester (CT2001A LAND, China) by galvanostatic charge and discharge. Cyclic voltammetry (CV) was measured on a PARSTAT 2273 electrochemical workstation at the scan rate of $0.1\text{--}1\text{ mV s}^{-1}$.

2 Results and discussion

Figure 1 shows SEM images of the as-prepared LFP samples by the solvothermal process with different EG/water

Figure 1 SEM images of LFP particles prepared by solvothermal process with different volume ratio of EG to water. (a1) and (a2), L14 (EG:water = 1:4); (b1) and (b2), L23 (EG:water = 2:3); (c1) and (c2), L32 (EG:water = 3:2).

ratios. We can see that the morphology strongly depends on the EG/water ratio. When the ratio is low (EG : water = 1:4), the LFP sample (L14) consists of irregular bars with a wide size range of 100–500 nm and the particles agglomerate considerably (Figure 1(a1) and (a2)). When the ratio is changed to 2:3, plate-like LFP (L23) particles are obtained (Figure 1(b1) and (b2)); the particles show an elongated rhombic shape with lengths of 1–2 μm and thickness of 200–300 nm. When the ratio increases to 3:2, the resulting LFP (L32) sample shows uniform and well-crystallized rod-like shapes with lengths of 150–200 nm (Figure 1(c1) and (c2)). Clearly, the particle distribution and order are improved with increasing EG content. EG plays an important role in controlling the size and morphology of the products obtained during the solvothermal process. As a polar organic solvent with asymmetric $-\text{OH}$ groups, EG displays some unique physical and chemical effects for crystal growth of LFP [22–24]. (1) EG is a weak reducing agent that prevents the oxidation of Fe^{2+} to Fe^{3+} during the reaction process and helps ensure the purity of the products. (2) EG has a much higher viscosity than common solvents such as water and ethanol, which can slow down the ion diffusion rate and prevent large particle growth up. (3) EG molecules exist in long hydrogen-bonding chains, which may trap the cations in the reaction mixture and help LFP to nucleate and grow into particles with specific morphologies. (4) EG cannot only act as a solvent, but also as a soft template for crystal growth of LFP due to its special chelating ability. With the assistance of EG, the unequal growth rate in the two perpendicular directions for LFP crystals facilitates the formation of uniform LFP nanorods.

Figure 2 shows XRD patterns of the as-synthesized LFP samples. All of the diffraction peaks can be well indexed to the pure LFP phase with orthorhombic olivine structure (JCPDS No. 40-1499). No impurities are detected. Further information can be obtained by comparing the patterns for the LFP samples fabricated with different EG/water ratios.

Figure 2 XRD patterns for the LFP samples synthesized with different EG/water ratios: L14 (EG: water=1:4), L23 (EG: water = 2:3) and L32 (EG: water = 3:2).

It is found that the diffraction peak at $2\theta = 30^\circ$ corresponding to the (020) or (211) direction becomes stronger with increasing EG content, indicative of increasing regularity in the arrangement of the LFP crystals [24]. This can be attributed to differences in crystal growth orientation due to the directing ability of EG.

Figures 3 and 4 present the electrochemical performance of the LFP samples. Figure 3(a) compares the initial charge-discharge performance of the as-prepared nanobar (L14), microplate (L23), and nanorod (L32) LFP cathodes in the potential range from 2.0 to 4.2 V (vs. Li^+/Li) at a constant current of 34 mA g^{-1} (0.2 C). All the LFP electrodes demonstrate a single discharge plateau. The reversible capacities for LFP nanobars, microplates and nanorods are 96, 111 and 118 mAh g^{-1} , respectively. Obviously, the uniform and well-crystallized LFP nanorods which have the smallest particle size, show the best electrochemical properties. However, the low capacities indicate that the conductivities of the as-prepared samples are poor.

Carbon coating was used to enhance the electronic conductivity on the surface of LFP particles. Figure 3(b)–(d) shows the discharge performance of carbon-coated LFP nanobars (L14/C), microplates (L23/C), and nanorods (L32/C) at various current rates from 0.1 to 5 C. With carbon coating, the capacity is remarkably enhanced. As expected, C-coated LFP nanorods show the highest discharge capacity with 159 mAh g^{-1} at 0.1 C (17 mA g^{-1}), 153 mAh g^{-1} at 2 C (340 mA g^{-1}) and 141 mAh g^{-1} at 5 C (850 mA g^{-1}). The corresponding capacities are 152, 138 and 116 mAh g^{-1} for C-coated LFP microplates, and 114, 90 and 78 mAh g^{-1} for C-coated LFP nanobars.

Figure 4 displays the cycle stability of the LFP cathodes at various rates. Both the nano-rod LFP/C (L32/C) and microplate LFP/C (L23/C) show good cyclability at different current densities from 0.1 to 5 C. Notably, the nanorod LFP/C electrode shows high reversible capacity, especially at high rates. For example, it delivers a discharge capacity of 140 mAh g^{-1} for the first cycle at 5 C and 120 mAh g^{-1} after 100 cycles (Figure 4(c)). Even when the current density is increased to 1700 mA g^{-1} (10 C), the discharge capacity is still as high as 132 mAh g^{-1} (Figure 4(d)). On the contrary, the nanobar sample (L14/C) shows the poorest rate capability, which only delivers a discharge capacity of 80 mAh g^{-1} for the first cycle at 5 C and 60 mAh g^{-1} after 50 cycles.

The electrochemical behavior of the LFP/C cathodes is further characterized by cyclic voltammetry (CV). Figure 5 shows the CV curves of the C-coated LFP samples at scan rates from 0.1 to 1 mV s^{-1} (Figure 5(a)–(c)). In the CV curves, the oxidation and reduction peaks show good symmetry and the ratio of the anodic to the cathodic peak current is near unity ($I_{\text{pa}}/I_{\text{pc}} \approx 1$), demonstrating good reversibility of Li-ion insertion/extraction. From the figures, we also can see that the potential difference between the anodic

Figure 3 (Color online) Discharge curves of LFP at various current rates. (a) L14, L23, L32 at 0.2 C; (b) L14/C; (c) L23/C; (d) L32/C.

Figure 4 (Color online) Cycle performance at various rates for (a) L14/C, (b) L23/C, and (c) L32/C electrodes; (d) rate capability for L32/C.

and the cathodic peaks increases with scan rate. As shown in Figure 5(d), the peak current shows a good linear relationship with the square root of the scan rate, indicating that the Li-ion insertion/extraction in LFP is a diffusion-

controlled process [25]. Therefore, the Li-ion diffusion coefficient is the most important factor to influence the electrode kinetics [26]. In order to investigate the ability of Li-ions to diffuse in the LFP materials, we calculate the

Figure 5 CV curves at different scan rates for (a) L14/C, (b) L23/C and (c) L32/C; (d) linear relationship between peak current and square root of scan rate.

Li-ion diffusion coefficient, D_{Li^+} , based on the Randles Sevcik equation [27]:

$$I_p = 2.69 \times 10^5 A C^0 D^{1/2} n^{3/2} \nu^{1/2}, \quad (1)$$

where I_p (A) is the peak current in the CV curves, n is the number of electrons transferred in the oxidation/reduction reaction ($n=1$ for the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox pair), A (cm^2) is the surface area of the electrode, D ($\text{cm}^2 \text{s}^{-1}$) is the diffusion coefficient of Li-ions, C^0 (mol cm^{-3}) is the concentration of lithium ions in the electrode, and ν (V s^{-1}) is the potential scan rate. The calculated Li^+ diffusion coefficients are 2.91×10^{-10} , 7.22×10^{-10} , and $2.58 \times 10^{-9} \text{ cm}^2 \text{s}^{-1}$ for L14/C, L23/C, and L32/C, respectively. Obviously, the nanorod LFP/C exhibits the highest Li-ion diffusion coefficient and nanobar LFP/C the lowest, which agrees well with their electrochemical performance.

3 Conclusions

LiFePO_4 samples with nanobar, microplate, and nanorod morphologies have been selectively synthesized via a solvothermal route in a binary solvent by varying the volume ratio of water and ethylene glycol. EG plays a critical role in controlling the shape and size of the particles during the solvothermal process. Nanorods are the kinetically favored morphology due to the special LFP crystal orientation. With carbon coating, the nanorod LFP/C cathode delivers a dis-

charge capacity of 159 mAh g^{-1} at 0.1 C, 141 mAh g^{-1} at 5 C and 132 mAh g^{-1} at 10 C. Even after 100 cycles at a high rate of 5 C, the LFP/C cathode maintains a high capacity of 120 mAh g^{-1} , showing an excellent rate capability. Cyclic voltammetry measurement shows that nanorod LFP/C exhibits a much higher Li-ion diffusion coefficient than nanobar and microplate LFP/C samples, which is responsible for its excellent performance. The present work provides an efficient way to control morphology of the olivine cathode materials, and to improve the electrochemical performance.

This work was supported by the National Natural Science Foundation of China (50825203, 20803042 and 21175050), the National High Technology Research and Development Program of China (2009AA03Z225), and the Fundamental Research Funds for the Central Universities (HUST, 2010 QN048). The authors thank Analytical and Testing Center of Huazhong University of Science and Technology for SEM measurement.

- 1 Bewlay S L, Konstantinov K, Wang G X, et al. Conductivity improvements to spray-produced LiFePO_4 by addition of a carbon source. *Mater Lett*, 2004, 58: 1788–1791
- 2 Herle P S, Ellis B, Coombs N, et al. Nano-network electronic conduction in iron and nickel olivine phosphates. *Nat Mater*, 2004, 3: 147–152
- 3 Huang Y H, Park K S, Goodenough J B. Improving lithium batteries by tethering carbon-coated LiFePO_4 to polypyrrole. *J Electrochem Soc*, 2006, 153: A2282–A2286
- 4 Chen Z H, Dahn J R. Reducing carbon in LiFePO_4/C composite electrodes to maximize specific energy, volumetric energy, and tap

- density. *J Electrochem Soc*, 2002, 149: A1184–A1189
- 5 Xiong X Q, Jiang Y, Xia S A, et al. Synthesis and modification of well-ordered layered cathode oxide $\text{LiNi}_{2/3}\text{Mn}_{1/3}\text{O}_2$. *Chin Sci Bull*, 2010, 55: 3419–3423
 - 6 Wang Z H, Yuan L X, Wu M, et al. Effects of Na^+ and Cl^- co-doping on electrochemical performance in LiFePO_4/C . *Electrochim Acta*, 2011, 56: 8477–8483
 - 7 Chung S Y, Bloking J T, Chiang Y M. Electronically conductive phospho-olivines as lithium storage electrodes. *Nat Mater*, 2002, 1: 123–128
 - 8 Zeng L J, Gong Q, Liao X Z, et al. Enhanced low-temperature performance of slight Mn-substituted LiFePO_4/C cathode for lithium ion batteries. *Chin Sci Bull*, 2010, 56: 1262–1266
 - 9 Saiful I M, Driscoll D J, Fisher C A J, et al. Atomic-scale investigation of defects, dopants, and lithium transport in the LiFePO_4 olivine-type battery material. *Chem Mater*, 2005, 17: 5085–5092
 - 10 Meethong N, Kao Y H, Chiang Y M, et al. Aliovalent substitutions in olivine lithium iron phosphate and impact on structure and properties. *Adv Funct Mater*, 2009, 19: 1060–1070
 - 11 Saravanan K, Reddy M V, Balaya P, et al. Storage performance of LiFePO_4 nanoplates. *J Mater Chem*, 2009, 19: 605–610
 - 12 Dominko R, Bele M, Goupil J, et al. Wired porous cathode materials: A novel concept for synthesis of LiFePO_4 . *Chem Mater*, 2007, 19: 2960–2969
 - 13 Yamada A, Chung S C, Hinokuma K. Optimized LiFePO_4 for lithium battery cathodes. *J Electrochem Soc*, 2001, 144: A224–A229
 - 14 Gibot P, Casas-Cabanas M, Laffont L, et al. Room-temperature single-phase Li insertion/extraction in nanoscale Li_xFePO_4 . *Nat Mater*, 2008, 7: 741–747
 - 15 Jamnik J, Maier J. Nanocrystallinity effects in lithium battery materials—Aspects of nano-ionics. *Phys Chem Chem Phys*, 2003, 5: 5215–5220
 - 16 Balaya P, Bhattacharyya A J, Jamnik J, et al. Nano-ionics in the context of lithium batteries. *J Power Sources*, 2006, 159: 171–178
 - 17 Gong Z L, Yang Y. Recent advances in the research of polyanion-type cathode materials for Li-ion batteries. *Energy Environ Sci*, 2011, 4: 3223–3242
 - 18 Yang S F, Zavalij P Y, Whittingham M S. Hydrothermal synthesis of lithium iron phosphate cathodes. *Electrochem Commun*, 2001, 3: 505–508
 - 19 Muraliganth T, Murugan A V, Manthiram A. Nanoscale networking of LiFePO_4 nanorods synthesized by a microwave-solvothermal route with carbon nanotubes for lithium ion batteries. *J Mater Chem*, 2008, 18: 5661–5668
 - 20 Murugan A V, Muraliganth T, Manthiram A. Rapid microwave-solvothermal synthesis of phospho-olivine nanorods and their coating with a mixed conducting polymer for lithium ion batteries. *Electrochem Commun*, 2008, 10: 903–906
 - 21 Saravanan K, Reddy M V, Balaya P, et al. Storage performance of LiFePO_4 nanoplates. *J Mater Chem*, 2009, 19: 605–610
 - 22 Saravanan K, Balaya P, Reddy M V, et al. Morphology controlled synthesis of LiFePO_4/C nanoplates for Li-ion batteries. *Energy Environ Sci*, 2010, 3: 457–464
 - 23 Sun C W, Rajasekhara S, Goodenough J B, et al. Monodisperse porous LiFePO_4 microspheres for a high power Li-ion battery cathode. *J Am Chem Soc*, 2011, 133: 2132
 - 24 Nan C Y, Lu J, Chen C, et al. Solvothermal synthesis of lithium iron phosphate nanoplates. *J Mater Chem*, 2011, 21: 9994–9996
 - 25 Yu D Y W, Fietzek C, Weydanz W, et al. Study of LiFePO_4 by cyclic voltammetry. *J Electrochem Soc*, 2007, 154: A253–A257
 - 26 Li L X, Tang X C, Liu H T, et al. Morphological solution for enhancement of electrochemical kinetic performance of LiFePO_4 . *Electrochim Acta*, 2010, 56: 995–999
 - 27 Cho Y D, Fey G T K, Kao H M. The effect of carbon coating thickness on the capacity of LiFePO_4/C composite cathodes. *J Power Sources*, 2009, 189(Suppl): 256–262

Open Access This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and source are credited.