

Hydrothermal Process Synthesizing of LiFePO₄ with High-rate Capability and High Tap Density

Xiaoming Lou, Bonian Hu, Jiali Huang, Tanping Li

Department of Chemistry and Chemical Engineering, Hunan Institute of Technology, Hunan, 421002, China

Abstract—LiFePO₄/C microspheres were synthesized by a rheological phase method using nanoplates assembled quasi-microspheres of FePO₄·2H₂O as raw materials, and the FePO₄·2H₂O precursors were synthesized via a hydrothermal process. The FePO₄·2H₂O precursors were characterized by XRD and SEM, and the LiFePO₄/C were characterized by XRD, SEM, TEM, and charge-discharge test. The LiFePO₄/C, with ~2 nm thick amorphous carbon layer coating at the surface, showed excellent high-rate performance; the discharge capacities reaching 116, 96 and 75 mAh g⁻¹ at 10 C, 20 C and 30 C current rates, respectively. Moreover, the LiFePO₄/C had a high tap density (1.4 g cm⁻³). Therefore, this material can be the cathode material for large-scale applications.

Keywords—LiFePO₄/C; FePO₄·2H₂O; High-rate performance; High tap density; Lithium ion batteries.

I. INTRODUCTION

Energy production and storage have key issues concerning our welfare in daily life. Compared with other battery systems, Li-ion batteries (LIBs) show the advantages of high energy density, long cycle and shelf life, and no memory effect [1]. However, for use as power supplies for EVs and HEVs, it is still a challenge to achieve the same high power densities using LIBs as are currently achieved with supercapacitors. For high power densities, the electrode materials must possess rapid ionic and electronic diffusion, and high tap density.

Lithium iron phosphate (LiFePO₄), with its olivine structure, was first studied by J.B. Goodenough and co-workers in 1997[2], has attracted extensive interest as a cathode material for LIBs because of its particular advantages with regard to low cost, nontoxicity, environmental friendliness, and high safety. Although LiFePO₄ possesses so many advantages, the inherent very poor electronic conductivity (~10⁻⁹ S cm⁻¹) and Li-ion diffusion coefficient (~1.8×10⁻¹⁴ cm² s⁻¹) at room temperature[3] brings difficulties for high-rate batteries applications.

These problems may be surmounted through two ways. One is coating the LiFePO₄ particles with an electron-conducting layer or doping with supervalent ions [4-5]. Another way is to shorten Li⁺ diffusion distance by minimizing the particle size [6-7] or making it porous [4] through controlling the synthesis conditions.

Herein, based on the preceding outstanding work, by using inexpensive and stable Fe³⁺ as iron source, we developed a method to synthesize LiFePO₄ microspheres which were composed of many densely compact nanoplates with ~2 nm thick amorphous carbon layer evenly coated at

the surface. This LiFePO₄/C composite not only showed excellent high-rate performance, but also had a high tap density.

II. EXPERIMENTAL

To synthesizing nano-sized FePO₄ • 2H₂O, sodium dodecylsulfate, H₃PO₄ were dissolved in deionized water. Then Fe(NO₃)₃ • 9H₂O was added into the solution. The mixture was sealed in a teflonlined stainless steel autoclave, and heated at 170°C for 4h. After cooled to room temperature, the products were separated by centrifugation and washed with ethanol and water several times. After heated the product at 100°C for 4 h in air, nano-sized FePO₄ • 2H₂O, were obtained.

LiFePO₄/C composite was synthesized by a rheological phase method. First, stoichiometric amount nano-sized FePO₄ • 2H₂O, polyethylene glycol (PEG-10000) and LiOH were mixed in a mortar to get a homogeneous mixture. Finally, the slurry-like mixture was calcined at 650°C for 10h in Ar flow. After cooling to room temperature, the LiFePO₄/C composite was obtained.

X-Ray Diffraction (XRD) was performed on a Bruker D8 Advance X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The powders were observed using a JSM-5610LV scanning electron microscope (SEM, JEOL Ltd. Japan) and JEM 2010-FEF transmission electron microscopy (HRTEM, JEOL Ltd. Japan). The cells were galvanostatically charged and discharged on a battery cycler (Neware TC481 China).

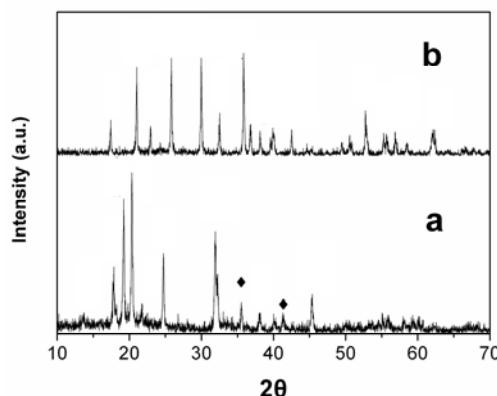


Figure 1. XRD patterns of FePO₄ • 2H₂O (a) and LiFePO₄/C (b).

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of $\text{FePO}_4 \bullet 2\text{H}_2\text{O}$ precursor (a) and the LiFePO_4/C (b). As shown in fig.1a, the XRD results matches with standard data JCPDS card No.33-666 ($\text{FePO}_4 \bullet 2\text{H}_2\text{O}$, phosphosiderite, monoclinic, space group: P21/n, $a = 0.53290$ nm, $b = 0.9798$ nm, $c = 0.8710$ nm). There were two peaks ($2\theta = 35.44, 41.30$) can be found corresponding to the another phase of $\text{FePO}_4 \bullet 2\text{H}_2\text{O}$ (strengite, No. 33-667, orthorhombic, space group: Pcab, $a = 1.0122$ nm, $b = 0.9886$ nm, $c = 0.8723$ nm). The diffraction peaks of the LiFePO_4 in fig. 1b can be well indexed to pure LiFePO_4 with JCPDS card No. 83-2092.

Figure 2a presented an SEM image of the FePO_4 particles, which showed the nanoplates assembled quasi-spheres had a uniform size distribution about 1 μm . Figure 2b and Figure 2c clearly displayed the $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ microsphere was composed of densely aggregated nanoplates which about 100 nm length and 30 nm thick. Figure 2d gave the SEM image of LiFePO_4/C . The picture clearly showed the carbon layer was orbicular covered on the LiFePO_4 surface. The carbon connected network also could be seen from Figure 2e. inset. Moreover, HRTEM image (Figure 2f) displayed clear crystal lattices with d-space 0.3497 nm which consistent with the theoretical value (0.34870 nm) of (111) planes in orthorhombic phase LiFePO_4 . In addition, it could also be clearly seen from the HRTEM image that an amorphous carbon layer with a thickness of 2-3 nm even covered the surface of LiFePO_4 . Figure 2f inset showed the selected area electron diffraction (SAED) that presented the single LiFePO_4/C particle was very well crystallized with pure olivine phase.

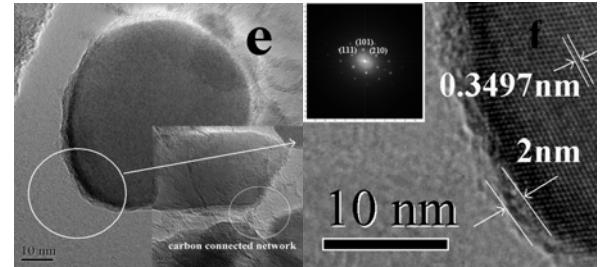
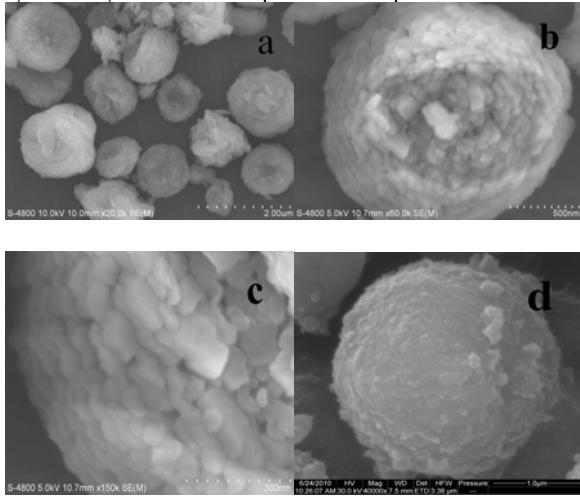


Figure 2. SEM images of a (a) panorama, (b) individual, (c) partial of FePO_4 , (d) LiFePO_4/C , HRTEM (high resolution transmission electron microscopy) pattern of (e) LiFePO_4/C (inset is the carbon network), (f) enlarge picture of circle part in Figure 2e (inset is the SAED (select area electron diffraction) image).

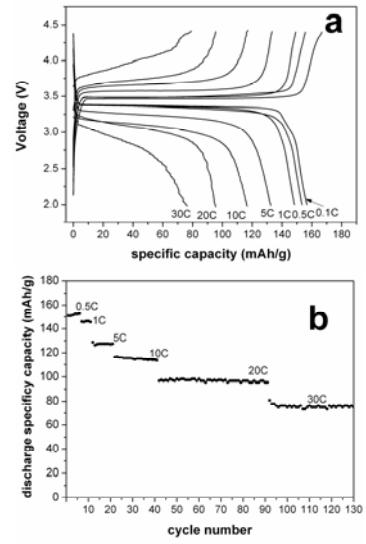


Figure 3. (a) Typical charge/discharge curves at various charge/discharge rates in the potential window 2.0-4.4V (vs. Li^+/Li); (b) The rate and cycling performances.

Figure 3a and b exhibited the typical charge/discharge curves of the LiFePO_4/C composite at various rates from 0.1C to 30C. At a low rate of 0.1C, the material got a discharge capacity of 158 mAh/g, about 93% of the theoretical capacity of LiFePO_4 . The more remarkable advantage of this material was the high-rate capability. The discharge capacity of the LiFePO_4/C was 116 mAh/g and 96 mAh/g at a high rate of 10C and 20C. Even the current was increased to 30C the discharge capacity could also reach 75 mAh/g. Furthermore, these microspheres could be densely packed and had a high tap density 1.4 g/cm³. So, this synthesis strategy could give an excellent electrochemical performance without sacrificing the volume energy density.

IV. CONCLUSION

LiFePO_4/C composite was synthesized with the carbon coating process via a rheological phase method by using the nanoplates self-assembled quasi-microspheres FePO_4 which was made by using inexpensive Fe^{3+} as iron source via a hydrothermal reaction. Thanks to the small and thin amorphous carbon completely coating on the thin primary

plates, this material had excellent electronic conductivity and good cycling performance. Moreover, this material had a high tap density, which was very important for enhancing the volumetric energy density. So, this synthesis strategy may be a good supplement to high-rate lithium ion batteries. And we would explore synthesize the special LiFePO₄ by water-bath method to simplify the steps, cut the cost and Promote industrialization.

V.ACKNOWLEDGEMENTS

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