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journal homepage: www.jmst.orgSolvothermal-assisted morphology evolution of nanostructured LiMnPO₄ as high-performance lithium-ion batteries cathodeChongjia Zhu^a, Zhiqiu Wu^a, Jian Xie^{a,b,*}, Zhen Chen^c, Jian Tu^c, Gaoshao Cao^{b,**},
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ABSTRACT

As a potential substitute for LiFePO₄, LiMnPO₄ has attracted more and more attention due to its higher energy, showing potential application in electric vehicle (EV) or hybrid electric vehicle (HEV). In this work, solvothermal method was used to prepare nano-sized LiMnPO₄, where ethylene glycol was used as solvent, and lithium acetate (LiAc), phosphoric acid (H₃PO₄) and manganese chloride (MnCl₂) were used as precursors. The crystal structure and morphology of the obtained products were characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The electrochemical performance was evaluated by charge-discharge cycling, cyclic voltammetry and electrochemical impedance spectroscopy. The results show that the molar ratio of LiAc:H₃PO₄:MnCl₂ plays a critical role in directing the morphology of LiMnPO₄. Large plates transform into irregular nanoparticles when the molar ratio changes from 2:1:1 to 6:1:1. After carbon coating, the product prepared from the 6:1:1 precursor could deliver discharge capacities of 156.9, 122.8, and 89.7 mAh g⁻¹ at 0.05C, 1C and 10C, respectively. The capacity retention can be maintained at 85.1% after 200 cycles at 1C rate for this product.

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1. Introduction

The discovery of LiFePO₄ opened the research history of olivine-type cathode materials for lithium-ion batteries [1]. The successful commercialization of LiFePO₄ for electric vehicle (EV) or hybrid electric vehicle (HEV) is attributed to its low cost, environmental friendliness, good chemical/electrochemical stability, and high safety [2–5]. Besides, the olivine-type phosphate has a moderate theoretical capacity of 170 mAh g⁻¹. Compared with LiFePO₄, LiMnPO₄ is a more promising cathode with higher energy density due to its higher Mn²⁺/Mn³⁺ redox potential (4.1 V vs. Li/Li⁺) than that of LiFePO₄ (3.45 V) [6].

However, LiMnPO₄ shows much poorer electrochemical performance than LiFePO₄ although the two materials have a same crystal structure. There are some factors that limit the electrochemical activity of LiMnPO₄: low electronic conductivity (<10⁻¹² S cm⁻¹)

[7], low lithium-ion diffusion rate (<10⁻¹⁶–10⁻¹⁴ cm² s⁻¹), Jahn-Teller lattice distortion in Mn³⁺, the interface strain between the LiMnPO₄ and MnPO₄ phases, and metastability of the MnPO₄ phase [8]. Particle size or morphology control, surface modification [9] and supervalent ion doping [10] are three main strategies to overcome these limitations. Solvothermal route is widely used to prepare nanometer materials of olivine-type phosphates. For the solvothermal synthesis, the morphology and electrochemical performance of the LiMnPO₄ are determined by many factors such as precursor types [11], charging sequence [12], use of additives or surfactants [13–17], pH [18,19], and solvent types [20].

Previous work has shown that LiMnPO₄ with different orientations [21] or morphologies including spindles [22], dumbbells [23,24], balls [25,26], flowers [27–29], plates [30], and rods [31] has been prepared by adjusting the molar ratio and pH of the precursors. Generally, a nanostructure is necessary to obtain high performance of LiMnPO₄. However, the synthesis of nanostructured LiMnPO₄ with a facile route has been rarely reported to date. In this work, we proposed a facile method to decrease the particle size of LiMnPO₄ to nanoscale by simply adjusting the molar ratio of the precursors. In doing so, the electrochemical activity of LiMnPO₄

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was enhanced, leading to high capacity, excellent rate capability and long cycle life.

2. Experimental

The reagents include lithium acetate dehydrate (LiAc·2H₂O, Analytical reagent (AR) grade), phosphoric acid (H₃PO₄, 85 wt%), manganese chloridetetrahydrate (MnCl₂·4H₂O, AR grade), glucose (AR grade) and ethylene glycol (EG). LiMnPO₄ was synthesized by a facile one-step solvothermal route via the reaction $\text{H}_3\text{PO}_4 + 3\text{LiAc} + \text{MnCl}_2 \rightarrow \text{LiMnPO}_4 + 2\text{LiCl} + 3\text{HAc}$. First, 12 *x* mmol of LiAc·2H₂O (*x* = 2, 2.5, 3, 4, 5, 6) was dissolved in 30 mL of EG. Then, 820 μL (12 mmol) of H₃PO₄ was added dropwise to the above solution to form a suspension. After vigorous stirring for 10 min, a solution of 12 mmol MnCl₂·4H₂O in 30 mL EG was added dropwise into the above suspension. After stirring for another 10 min, the suspension was sealed in an 80 mL Teflon-lined stainless steel autoclave. The autoclave was then heated at 180 °C for 10 h in an electric oven followed by cooling to room temperature naturally. The as-obtained white precipitate was separated by centrifugation at a speed of 12000 rpm, washed with deionized (DI) water and ethanol for three times, and dried at 80 °C for 12 h in vacuum. The LiMnPO₄ samples synthesized with different *x* values are named LMP-*x*. To prepare carbon-coated LiMnPO₄ (LiMnPO₄/C), 1 g of LiMnPO₄ powder was mixed with 0.5 g of glucose in 3 mL of DI water. The mixture was ultrasonically dispersed for 1 h and the water was evaporated by heating at 80 °C in air. After being grounded in a mortar, the dried powder was heated to 600 °C at 5 °C min⁻¹ in a tube furnace and held for 4 h under Ar atmosphere. For simplicity, the names of the carbon-coated samples are same as the pristine ones.

The crystal structure and phase purity of the products were determined by X-ray diffraction (XRD) on a Rigaku D/Max 2550 pc powder diffractometer using CuK α radiation (wavelength = 0.1541 nm). The morphology of the samples was identified by scanning electron microscopy (SEM) on an S-4800 field emission scanning electron microscope (Hitachi, Japan). The microstructures were observed by transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and selected area electron diffraction (SAED) on an FEI Tecnai G² F20S-Twin high-resolution transmission electron microscope with an acceleration voltage of 200 kV. The amount of the coated carbon in LiMnPO₄/C was measured on a Flash EA 1112 tester.

The electrode slurry was fabricated by mixing 70 wt% LiMnPO₄/C active material, 20 wt% acetylene black and 10 wt% poly(vinylidene fluoride) binder in N-methylpyrrolidone with magnetic stirring. The slurry was uniformly coated onto polished aluminum foils, followed by drying in vacuum at 110 °C overnight to form working electrodes. The loading of the active material in electrode is about 2 mg cm⁻². The electrodes were pressed at 10 MPa before cell assembly. CR2025 coin-type cells were assembled in an argon-filled glove box using Celgard 2300 membrane as separators and lithium foils as counter electrodes. 1 mol L⁻¹ LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 in volume) was used as electrolyte. The cells were tested using a constant-current-constant-voltage (CC-CV) mode between 2.0–4.5 V (vs. Li/Li⁺) on a Neware BTS-5V–10 mA battery cycler (Shenzhen, China). The cells were charged at different current rates to 4.5 V, then held at 4.5 V until the current decreases to 0.01C (current rate 1C = 170 mA g⁻¹), and finally discharged to 2.0 V at the same current rate. The charge rate was the same as the discharge rate for all the tests. Cyclic voltammetry (CV) scanning was performed on a CHI660C electrochemistry work station in the voltage range of 3.0–4.8 V (vs. Li/Li⁺) at various scan rates. Electrochemical impedance spectroscopy (EIS) measurements were conducted by applying an alternative current voltage of 5 mV amplitude in

the frequency range from 10 mHz to 100 kHz on the electrochemistry work station. All of the electrochemical measurements were carried out at room temperature (25 °C).

3. Results and discussion

The crystal structure of olivine-type LiMnPO₄ perpendicular to the *b* axis and the lithium-ion diffusion pathway are shown in Fig. 1. The zigzag one-dimensional diffusion tunnels of Li ions along the *b* axis was verified by theoretical calculation [32] and experimental visualization [33]. The structure consists of a distorted hexagonal close-packed (hcp) oxygen framework. Li and Mn atoms are located in 1/2 of octahedral holes and P occupies 1/8 of the tetrahedral holes. This crystal structure results in rather low electronic conductivity and lithium-ion diffusion rate and thus poor electrochemical performance of LiMnPO₄.

Fig. 2 shows the XRD patterns of the as-synthesized LiMnPO₄ and LiMnPO₄/C. For all the LMP-*x* samples, the diffraction peaks can be indexed to an orthorhombic structure with a *Pnma* space group (JCPDS No. 74-0375). Although a minor Mn₇(PO₃OH)₄(PO₄)₂ phase is found in LMP-2 sample, it disappears after the carbon-coating step. It is expected that the carbon-coating process would enhance the crystallization of LiMnPO₄, besides the contribution to the electronic conductivity.

Fig. 3 shows the SEM images of LiMnPO₄ prepared with different molar ratios of the precursors. It is noted that the morphologies of the samples depend on the molar ratio of LiAc, H₃PO₄ and MnCl₂. The size of LiMnPO₄ particles tends to decrease with the increase in LiAc amount. LMP-2 sample consists of irregular plates with a length of around 500 nm and a thickness of 20 nm. For LMP-2.5, two shapes of plates and particles coexist, but the size of the plates is reduced to about 300 nm in length. For LMP-3, the size of the plates is further reduced to around 200 nm and more nanoparticles below 100 nm appear. All the plates transform to nanoparticles when the *x* value exceeds 4. At this *x* value, the size of the nanoparticles is below 100 nm as seen in Fig. 3(d)–(f). Further increasing the *x* value does not decrease the particle size of LiMnPO₄ obviously.

Fig. 4 shows the typical TEM image of LMP-5 after carbon coating. It can be seen that the particle size is smaller than 100 nm, agreeing with the SEM observation. It is noted that the size of some particles is as small as 20 nm, which is favorable for rapid lithium-ion transport. HRTEM image indicates that the LiMnPO₄ sample is well crystallized after the carbon-coating step. The lattice spacing of 0.4276 nm corresponds to (101) plane of LiMnPO₄. As shown in Fig. 4, a thin amorphous carbon layer of around 2 nm thickness can be observed on the surface of LiMnPO₄. The thin carbon layer is desirable for barrier-free lithium-ion diffusion. In addition, the carbon layer is uniform which is critical in increasing the electronic conductivity. The carbon contents of the above mentioned six samples are 9.0%, 12.2%, 11.0%, 10.1%, 10.9% and 10.8%, respectively.

The discharge profiles of the carbon-coated samples at different rates are shown in Fig. 5. For the rate capability tests, a CC-CV mode was applied at various current rates from 0.05C to 20C with 5 cycles at each current density. All the samples have a discharge plateau at around 4.1 V vs. Li/Li⁺. For LMP-2, its initial discharge capacity at 0.05C is only 39.3 mAh g⁻¹ indicating low electrochemical activity as seen in Fig. 5(a). Sample LMP-2.5 exhibits a much higher discharge capacity than LMP-2, but its capacity decreases rapidly to 34.9 mAh g⁻¹ at 20C, suggesting poor rate capability in Fig. 5(b). The rate capability of LMP-3 is slightly enhanced compared with LMP-2 and LMP-2.5 in Fig. 5(c). Clearly, the enhanced rate capability is closely related to the decrease in particle size since these samples have a similar carbon content. LMP-4 can deliver a discharge capacity of 156.8 mAh g⁻¹ at 0.05C, much higher than those of the above samples, indicating the considerably improved electrochem-

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