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The effect of ammonia concentration on the morphology and electrochemical properties of $LiFePO_4$ synthesized by ammonia assisted hydrothermal route

Hongbo Shu[a], Xianyou Wang[a,*], Qiang Wu[a], Li Liu[a], Qianqian Liang[a], Shunyi Yang[b], Bowei Ju[a], Xiukang Yang[a], Xiaoyan Zhang[a], Yingping Wang[a], Qiliang Wei[a], Benan Hu[a], Yuqing Liao[a], Huimin Jiang[a]

[a] *Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, School of Chemistry, Xiangtan University, Hunan, Xiangtan 411105, China*
[b] *BTR Battery Materials Co., Ltd, Guangdong, Shenzhen 518106, China*

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A B S T R A C T

The $LiFePO_4/C$ composites with different morphology are synthesized by an ammonia assisted hydrothermal method at various ammonia concentrations (from 0 to 1.6 mol L^{-1}) using inexpensive $Fe(NO_3)_3$ and LiOH as raw materials. The influences of the ammonia concentration on the structure, morphology and electrochemical properties of the $LiFePO_4/C$ composite are investigated by X-ray diffraction (XRD), scanning electron microscope (SEM), galvanostatic charge/discharge tests and electrochemical impedance spectroscopy (EIS). The results demonstrate that the ammonia concentrations markedly impact the morphology and electrochemical properties of the $LiFePO_4/C$. With the change of ammonia concentrations, the $LiFePO_4/C$ synthesized with 0.4 mol L^{-1} ammonia shows the smallest average particle size, the most uniform microsphere particle distribution and relatively high tap density (1.27 g cm^{-3}). In addition, the sample appears a high discharge capacity of 153.9 mAh g^{-1} at the first cycle as well as stable cycling performance (the capacity was not almost changed till 100 cycles) at a rate of 1*C* (170 mA g^{-1}). Moreover, it exhibits a good rate capability and still shows a high discharge capacity of over 125 mAh g^{-1} even at a rate of 5*C*.

1. Introduction

In the recent years, olivine-type $LiFePO_4$ has become one of the most promising cathode materials for lithium-ion batteries, owing to its nontoxicity, superior capacity retention, good thermal stability, remarkable tolerance to overcharge and discharge, excellent safety and potentially low cost. Usually, theoretical specific capacity of $LiFePO_4$ is 170 mAh g^{-1}, and the discharge/charge potential plateau is 3.45 V versus Li/Li^+ due to the Fe^{2+}/Fe^{3+} redox [1,2]. Unfortunately, the low intrinsic electronic conductivity (10^{-9} to 10^{-8} S cm^{-1}), ionic conductivity (10^{-11} to 10^{-9} S cm^{-1}) and ionic diffusivity (10^{-17} to 10^{-14} cm^2 s^{-1}) of $LiFePO_4$ have become a main obstacle for its applications [3–7].

In the past decade, tremendous efforts have been made to enhance the electronic conductivity, ionic conductivity and ionic diffusivity of $LiFePO_4$ [8–12]. One way is surface coating with a conductive layer (such as carbon, polymers, RuO_2, Ag and so on) around the $LiFePO_4$ particles to improve its surface electrochemical properties [9,13–20]. Especially, different carbon sources for carbon coating around $LiFePO_4$ particles have been extensively used for effectively enhancing the intrinsic electronic conductivity of $LiFePO_4$ [13,14,16]. As one of them, citric acid has been added as a chelating agent in quantities in the sol–gel method, thus resulting in carbon residues on the surface of $LiFePO_4$. Furthermore using citric acid as carbon source for good structure (low intensity ratio of D/G) $LiFePO_4$ can greatly improve its electrochemical performance [21]. Although the carbon residues are beneficial to the rate capability of $LiFePO_4$, addition of even relatively small amounts adversely affect its tap density and energy density [22]. Therefore, to avoid decreasing the volumetric energy density and maintain excellent electrochemical performance of $LiFePO_4$, the amount of the carbon residues should be kept or controlled at a reasonable level [22–24]. Another approach is to reduce particle size and obtain kinetically favorable morphology, which can shorten the diffusion distance for both Li^+ ions and electrons and thereby substantially improve the electrochemical performance [14,21,25–27]. To optimize the particle size and obtain kinetically favorable morphology of $LiFePO_4$, various synthetic techniques such as sol–gel, co-precipitation and hydrothermal processes have been utilized, and the positive results have been reported [11,28–31]. Among them, hydrothermal reaction arouses particular interest due to

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* Corresponding author. Tel.: +86 731 58292060; fax: +86 731 58292061.
E-mail address: wxianyou@yahoo.com (X. Wang).

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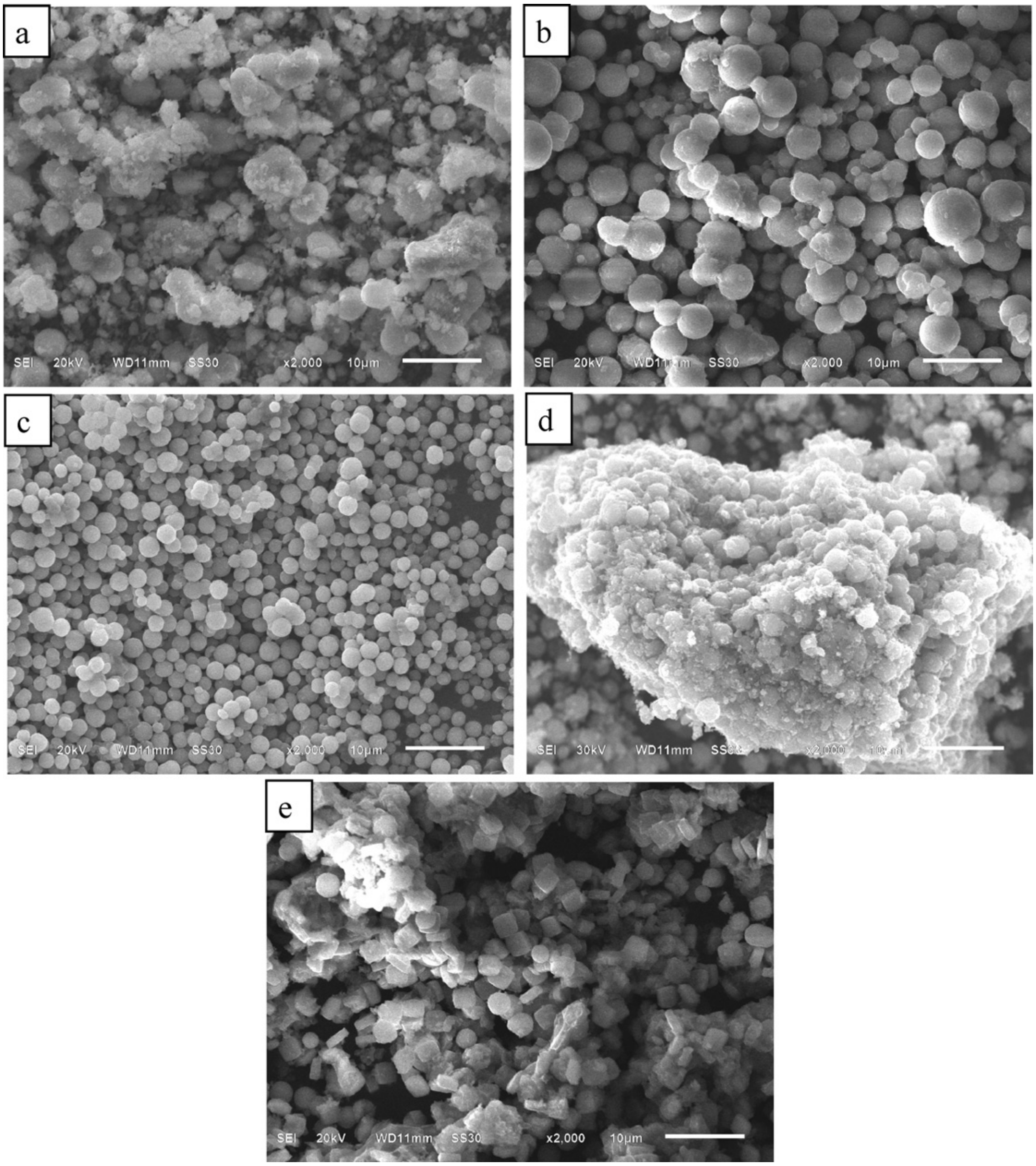

Fig. 1. SEM photographs of the precursors of $LiFePO_4/C$ synthesized with different ammonia concentrations of (a) 0 mol L^{-1}, (b) 0.2 mol L^{-1}, (c) 0.4 mol L^{-1}, (d) 0.6 mol L^{-1} and (e) 1.6 mol L^{-1}.

mild operating temperature, simple process and the potential for large-scale production. It is also considerably convenient to control the particle size and morphology of product by tuning experiment parameters such as solvent, temperature, pressure, concentration and additive. Although the low hydrothermal temperature facilitates experimental manipulation, it may result in a poor crystallinity of $LiFePO_4$ with olivine structure, and thus leading to a decreased electrochemical performance. Moreover, previous hydrothermal and other synthetic routes mostly used Fe^{2+} salt as a starting material [32], while Fe^{2+} salt is easily oxidized as compared with low-cost Fe^{3+} salt as a raw material.

Recently, we successfully prepared monodisperse $LiFePO_4/C$ microspheres synthesized by a ammonia assisted hydrothermal method with inexpensive $Fe(NO_3)_3$ and LiOH as raw materials [33]. It was found that the morphology and size of particle can be availably controlled due to the addition of ammonia. In this paper, the influence of the ammonia concentrations on the morphology and electrochemical properties of $LiFePO_4/C$ are studied in detail.

2. Experimental

The stoichiometric amounts of 0.028 mol of $LiOH{\cdot}H_2O$ (A.R.), $Fe(NO_3)_3{\cdot}9H_2O$ (A.R.), $NH_4H_2PO_4$ (A.R.), and citric acid (A.R.) (mole ratio is 1:1:1:1) were dissolved in 45 mL distilled water to form a transparent yellow–green solution. Then a certain amount of ammonia (NH_3) solution was added to the solution dropwise with continuous stirring. The molar ratios of ammonia and citric acid (CA) were 0:2, 1:2, 2:2, 3:2, and 8:2, and the corresponding ammonia concentrations were 0, 0.2, 0.4, 0.6 and 1.6 mol L^{-1}, respectively. Distilled water was added to above solution up to 70 mL. The solution mixture was stirred for 30 min with strong stirring before being transferred into a 100 mL Teflon-lined stainless steel autoclave. The autoclave was sealed, kept at 180 °C for 6 h in an electric oven, and