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A monodispersed nano-hexahedral $LiFePO_4$ with improved power capability by carbon-coatings

Jing Li, Qunting Qu, Longfei Zhang, Li Zhang *, Honghe Zheng *

School of Energy & School of Physical Science and Technology, Soochow University, Suzhou, Jiangsu 215006, PR China

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ABSTRACT

A monodispersed nano-sized hexahedral $LiFePO_4$ of regular angularity was prepared through hydrothermal process. Different carbon precursors were employed to create carbon-coating layers onto the nanoparticles to improve the electrochemical performances of the material. Structure and morphology of the $LiFePO_4$ material without and with carbon-coating layer were studied using a combination of X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and Raman spectroscopy. It confirms that carbon-coating plays an important role inhibiting the agglomeration of the nanoparticles. A uniform carbon-coating layer of higher graphitization degree was developed on the $LiFePO_4$ particles with sucrose precursor. The electrode exhibits discharge capacities of 148.3 mA h g^{-1}, 138.7 mA h g^{-1}, 117.8 mA h g^{-1} at 0.1 C, 1 C and 10 C, respectively. Very close Li ion diffusion coefficient of around 8×10^{-14} cm^2 s^{-1} for all the $LiFePO_4$/C composites with different carbon sources implies that the improved power capability is mainly attributed to the small particle size and low contact resistance between the $LiFePO_4$ nanoparticles.

1. Introduction

Lithium-ion batteries (LIBs) are very promising for powering electric vehicles (EVs) and plug-in hybrid electric vehicles (PHEVs). In the recent years, numerous approaches have been developed for key materials and high performance battery systems. Among the main components of lithium-ion batteries, cathode material plays a significant role in limiting the cell capacity, reversibility and cost. Compared with the typical lithium insertion oxides including $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC), $LiNi_{0.08}Co_{0.15}Al_{0.05}O_2$ (NCA), $LiMn_2O_4$, and conventional $LiCoO_2$, olivine-structured $LiFePO_4$ (LFP) cathode has the advantages of high specific capacity (170 mA h g^{-1}), good safety attribute, attractive cost competitiveness, and low toxicity [1–3]. In recent years, it has been extensively investigated as one of the most promising cathode candidates for EVs and PHEVs [4,5]. However, low electronic conductivity (10^{-9}–10^{-10} S cm^{-1}) and poor ionic conductivity (1.8×10^{-14} cm^2 s^{-1}) in the LFP phase have posed a bottleneck for its large commercial applications [6,7], especially for large-scale PHEV and EV applications [8].

Reducing particle size [9,10], conducting surface coating [11,12], doping the host framework with supervalent cations [13,14], and controlling morphology [15,16] are the most common strategies to mitigate these limitations. Among all these approaches, reducing primary particle size not only shortens the diffusion length of Li ion during electrochemical process, but also increase ionic diffusion constant to a certain extent as Li diffusion within nano-sized particle is faster than that in the bulk phase [17]. Surface coating with electronically conductive layers [18,19] is extraordinary effective to increase the electronic conductivity of this material. Many different coating materials including Cu, Ag, carbon, and conducting polymers have been attempted in the previous studies [11,20,21]. Among them, carbon coating is particularly attractive due to its high conductivity, electrochemical stability, low cost, and simplicity of implement [22–24]. This approach contributes to a great improvement of reversible capacity and the kinetics for Li insertion and extraction. Although carbon coating of LFP has been widely studied and successfully commercialized, there are still a lot of fundamentals and technical issues, which require thorough investigations. According to Dominko et al. [19], the lowest amount of carbon in LFP/C composite was 3.2 wt.% and the optimal carbon coating thickness was about 1–2 nm. However, Sun et al. [22] believe that too much carbon in the LFP-based cathode will inevitably decrease the energy density and even hinder the migration at the particle surface. Therefore, in-depth understanding the role of carbon coating layer is of great significance for designing quality LFP electrode to meet the aggressive EV and PHEV requirements [25–27].

Hydrothermal is a very promising synthetic approach for nano-sized LFP production. This method shows great potential for LFP nanoparticles are formed at very low temperature at around

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* Corresponding authors. Tel.: +86 512 69153523.
E-mail addresses: zhangli81@suda.edu.cn (L. Zhang), hhzheng@suda.edu.cn (H. Zheng).

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200 °C. Most importantly, the particle size and morphology can be tailored by the solution concentration, pH value, temperature and surfactant. In this study, a monodispersed nano-hexahedral LFP of *ca.* 200 nm wide and 100 nm thick was prepared with hydrothermal method under an optimized condition.

Although the impacts of carbon coating onto LFP material have been widely investigated, most of the studies were performed with polydispersed and irregular particles made from solid-phase, co-precipitation, and sol–gel processes. Impact of carbon coating on a mono-dispersed hexahedral LFP with clear sides and edges has never been reported. Herein, a nano-sized long hexahedral LFP material is coated with different carbon sources and heated at various sintering temperatures for different heat-treatment time. Key parameters involved in the coating progress were investigated. The role of the carbon coating layer on the materials' structure and morphology, electrochemical performance, and Li diffusion property of the special LFP particles is discussed.

2. Experimental

The LFP was synthesized through an optimized hydrothermal method. The starting materials of $FeSO_4·7H_2O$ (AR grade), H_3PO_4 (85 wt.%) and $LiOH·H_2O$ (AR grade) were used as received. First of all, 0.25 mol $LiOH·H_2O$ and 0.083 mol H_3PO_4 were dissolved into 150 mL de-ionized water under magnetic stirring. Then, 0.83 mol/L $FeSO_4$ aqueous solution was slowly added to the $LiOH/H_3PO_4$ solution. The molar ratio of Li:Fe:P was kept at 3:1:1. After stirring for 30 min under the protection of Ar-gas, the resulting mixture was transferred into a 500-mL-capacity Teflon-lined stainless steel autoclave. The sealed autoclave was then placed into a 200 °C oven for 10 h. Subsequently, the autoclave was cooled down to room temperature and a gray white precipitate (LFP powder) was filtered with de-ionized water and ethanol for several times. Finally, the obtained powder was dried at 120 °C in vacuum for 2 h.

Fabrication of the LFP/C composites was performed as follows: the obtained LFP powder was added into a certain amount of sucrose solution, glucose solution and ascorbic acid (VC) solution, respectively. The mass ratio between LFP and carbon contained in the precursor was kept at 95:5. The mixtures were heated while vigorous stirring till the water was completely evaporated. The LFP powder without and with carbohydrate coatings was heated at 450–850 °C for 1–10 h under Ar/H_2 (95:5 by volume ratio) atmosphere. The percentage (wt.%) of carbon in the final product was estimated using a high-precision thermogravimetric analysis system (TG/DTA 7300, SII Nano Technology Inc., Shanghai) in a dry flowing air environment. A weight ratio of *ca.* 2.5 wt.% for the carbon coatings was obtained for all the three carbon-coated samples. The different samples are referred to as bare LFP (heat-treated LFP sample without carbon precursor), LFP-Glucose (glucose as the carbon source), LFP-Sucrose (sucrose as the carbon source), and LFP-VC (VC as the carbon source), respectively.

Structural analyses of the samples were characterized by X-ray diffraction (XRD, PANalytical X'Pert PRO, Ni-filtered Cu Kα radiation, Netherlands). Raman spectroscopy measurements (LabRam HR800, Jobin Yvon, France) were carried out using the excitation line of 514 nm from an Ar-ion laser with 10 s exposure time, 70 mW power, 200 μm pinhole, 100 μm slit and 600 grating. Morphological observation was carried out with scanning electron microscopy (SEM) using a Hitachi S-4700 operated at 15 kV accelerating voltage. Transmission electron microscopy (TEM) images were captured on the JEM-2100 instrument microscopy at an acceleration voltage of 200 kV.

LFP cathode electrode was prepared by casting slurries onto the aluminum foil with doctor blade method. The slurries consisting of 84% active material, 8% polyvinylidene difluoride (PVDF) and 8% conductive carbon were prepared by mixing in 1-methyl-2-pyrrolidone (NMP) solvent. All the laminates were controlled to have an active material loading of *ca.* 5 mg cm^{-2}. The electrodes were dried at 60 °C for 5 h in air in order to completely remove NMP solvent and followed by drying at 120 °C for 16 h under vacuum.

Electrochemical properties of the cathodes were measured using two-electrode coin cells (type CR2032). Assembly of the coin cells was carried out under an argon atmosphere in a glove box. Li foil was used as the counter electrode and 1 M $LiPF_6$ ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by weight ratio) as the electrolyte. A polypropylene film (Celgard 2400) was used as the separator. Galvanostatic charge–discharge performance of the LFP/C cathode was tested on a Maccor Battery Test Cycler at 30 °C in the voltage range of 2.5–4.2 V. Electrochemical impedance spectroscopy (EIS) was measured by applying an alternating voltage of 10 mV over the frequency ranging from 10^{-2} to 10^5 Hz. All impedance measurements were carried out at 40% DOD (depth of discharge) after rate tests. Prior to AC impedance measurements, the cell was rested for at least 3 h to attain the condition of sufficiently low residual current.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the as prepared LFP, bare LFP and LFP/C composites obtained by using different carbon sources. All the patterns show well-crystallized diffraction peaks indexed to orthorhombic olivine $LiFePO_4$ (JCPDS No. 83-2092). No noticeable diffraction peaks associated with impurities (Fe_2O_3, Li_3PO_4, Fe_2P), which was usually reported in the literature [28,29], is perceived in this study, reflecting high purity of the LFP sample obtained in this study. In addition, the peak intensity of the LFP is obviously stronger than other three LFP/C composites because the signal can be decreased by the carbon coating layer. Meanwhile, typical diffraction peak associated with carbonaceous material is not detected. This is due to the predominantly amorphous nature of the carbon layer obtained through pyrolysis of the selected carbon precursors [22,30]. Lattice parameters for the as prepared LFP, bare LFP and the LFP/C composites with different carbon sources were listed in the Table 1. The calculated crystal lattice parameters, a varies from 10.2419 to 10.2828 Å, b varies from 5.9861 to 5.9942 Å and c varies from 4.6535 to 4.6857 Å, which are well indexed with the orthorhombic lattice parameters, a = 10.32 Å, b = 6.01 Å and c = 4.69 Å. No considerable difference exists between the lattice parameter of all the LFP samples, indicating the crystallinity of the LFP material is not much affected by carbon-coating during the calcinations. The values obtained are well comparable with reported data [31,32]. By comparison, no considerable difference exists between the lattice parameter of the LFP samples, indicating the crystallinity of the LFP material is not much affected by the carbon-coating during the calcinations.

Fig. 2 displays the SEM images of the as-prepared LFP from hydrothermal process, bare LFP, LFP-Glucose, LFP-Sucrose, and LFP-VC samples, respectively. Clearly, the as-prepared LFP (see Fig. 2a and b) was monodispersed nanoparticles of regular long hexahedron. The length of the particle is around 500–800 nm, the width about 200–300 nm and the thickness about 80–100 nm. The angularity is seen very clear and sharp at each side of the particle. It is generally accepted that 200–400 nm is the optimal particle size for LFP material of high electrochemical performance [33]. In this aspect, our hydrothermal sample is very ideal in terms of physical dimensions. As is shown in Fig. 2c, the heat-treated LFP without the protection of organic compound layer shows serious agglomeration and the diameter of the particle is increased to *ca.* 1 μm scale. The original shape of long hexahedron completely disappeared. By comparison, the LFP covered with carbon layer (Fig. 2d–f) well maintained their original morphology

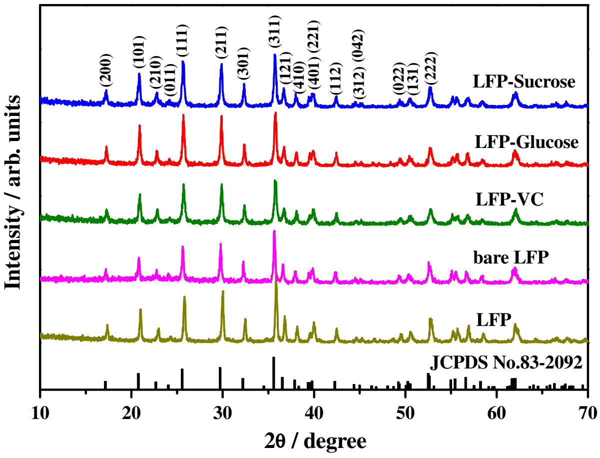

Fig. 1. X-ray diffraction patterns of the as prepared LFP, bare LFP and LFP/C composite prepared with different carbon sources.