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A core–shell $LiFePO_4$/C nanocomposite prepared via a sol–gel method assisted by citric acid

Gang Xie, Hua-Jun Zhu, Xiao-Min Liu *, Hui Yang *

College of Materials Science and Engineering, Nanjing University of Technology, 5 Xinmofan Road, Nanjing, Jiangsu 210009, PR China

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A B S T R A C T

Nanosized $LiFePO_4$ particles, each covered with a complete but thin carbon shell, are synthesized via a sol–gel process using citric acid (CA) as both chelating agent and organic carbon source in this study. Several precursors are prepared with various mole ratio of CA to total metal ions (n_{CA}/n_m) first. Then the prepared precursors are investigated by thermogravimetry and derivate thermal analysis. The $LiFePO_4$/C samples obtained via calcining the precursors at different temperatures are characterized by X-ray diffraction, field emission scanning electron microscope, transmission electron microscope and galvanostatic charge/discharge test. The systematic study shows that the $LiFePO_4$/C nanocomposite, calcined from the precursor with a composition of n_{CA}/n_m equal to 1:3 at 650 °C, delivers discharge capacities of 166 and 153 mA h g^{-1} at 0.1 and 1C, respectively, and exhibits almost no capacity fade up to 50 cycles.

1. Introduction

Over the past two decades, Lithium ion batteries have become the technology of choice for powering portable electronic devices which revolutionizes our everyday life. They are currently primed to make a great impact on a wide range of green applications, including hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs), and stationary energy storage for solar and wind electricity generation as well as smart grids. Accordingly, these new applications demand that lithium-ion batteries offer high energy/power density, high safety and long cycle life. In all the cathode materials for next generation of Li-ion battery, olivine structure $LiFePO_4$ first reported by Goodenough et al. [1]. in 1997, has been considered as the most promising candidate due to its low toxicity, low cost, high safety and long cyclability compared to Co-based materials. However, the main weakness of bulk $LiFePO_4$, intrinsically sluggish mass and charge transport [2–6] as demonstrated by recent work on single crystals of $LiFePO_4$ [7,8], might necessitate being overcome in order to achieve a high power performance required in transportation and energy storage fields [9]. Various strategies, generally focusing on improving the electrical conductivity of bulk and/or surface of the material, and reducing the Li^+ diffusion distance, have been adopted. Among them, utilizing tailored nanosize particles and in situ carbon coating, have brought the most success in preparing high power $LiFePO_4$ powders by many studies [10–15]. Nanosized particles can provide a high surface area and short the diffusion paths for ionic transport and electron tunneling. A complete but thin coating with a conductive phase can ensure that (1) the $LiFePO_4$ particles get electrons from all directions; (2) Lithium ions can penetrate through the coat without appreciable polarization. From above we conclude that in order to realize the practical application of inherently low-cost and non-polluting $LiFePO_4$ successfully, a low-cost and clean manufacturing process, which can control the morphology, particle size, cation order, and other important parameters, as well as a thin but complete in situ carbon coating during synthesis, is critical.

Tremendous efforts have been made in recent years to develop various synthesis routes to prepare nano-sized $LiFePO_4$ with excellent electrochemical performance. Compared to the most common and traditional ceramic power techniques, sol–gel method is preferred in preparing nano-particles since it can form homogeneous precursors mixed at a molecular level, thus enabling the nanoscale control of the structure, ensuring potentially high purity and lowering processing temperatures [16]. In addition to that, a carbon layer could be in situ generated from decomposing the organic solvents [17–19] and/or carbon-based compounds during calcining process. A uniform carbon layer may facilitate the nano-particle formation since it can act as a diffusion barrier by blocking particle contact to hinder the grain growth [20,21]. In this work, the $LiFePO_4$/C nano-composites with carbon shell structure are synthesized by a sol–gel process using citric acid (CA) as both chelating agent and organic carbon source. CA possesses lone pair electrons in carboxyl which could combine with the unoccupied orbital of metal ions to form stable complexes. The thickness of the pyrolytic carbon layer in situ formed on the $LiFePO_4$ particle surface during CA decomposition is optimized by adjusting the mole ratio of CA to

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* Corresponding authors. Tel./fax: +86 25 83587762 (X.-M. Liu), tel./fax: +86 25 83587275 (H. Yang).

E-mail addresses: liuxm@njut.edu.cn (X.-M. Liu), yanghui@njut.edu.cn (H. Yang).

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total metal ions (n_{CA}/n_m). Although a complete carbon layer on the surface of $LiFePO_4$ facilitates the electron transfer between the weak-conductive particles and current collector to improve the particle conductivities, excess carbon content may suppress the Li^+ diffusion across the carbon layer due to the lower electrolyte penetration, which lowers the reversible capacity [22]. Therefore, in order to achieving the high electrochemical performance of the resulting $LiFePO_4/C$, it is important to optimize the content of residual carbon. The calcining temperature is also optimized in this paper since it affects the particle size, carbon residue, crystallinity, and even the electrochemical performance of the resulting $LiFePO_4$ [23]. The results show that the $LiFePO_4/C$ nanocomposite, calcined from the precursor with a composition of n_{CA}/n_m equal to 1:3 at 650 °C, delivers discharge capacities of 166 and 153 mA h g^{-1} at 0.1 and 1C, respectively, and exhibits almost no capacity fade up to 50 cycles.

2. Experimental

2.1. Synthesis of $LiFePO_4/C$ composites

The $LiFePO_4/C$ composites were prepared by a sol–gel method using lithium acetate dihydrate ($CH_3COOLi{\cdot}2H_2O$, AR), ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$, AR), phosphoric acid (H_3PO_4, AR) as precursors. The starting materials were dissolved in ethanol with the stoichiometric amounts. The resulting solution was then mixed well with an aqueous solution of citric acid (AR) and stirred for 48 h at room temperature to form a sticky gel. The amount of citric acid was adjusted according to the molar ratio of citric acid to total metal ions (n_{CA}/n_m = 1:4, 1:3, and 1:2 were employed in this study). The gel precursors, dried in an oven, were preheated at 350 °C for 5 h and then calcinated at 600 °C, 650 °C, 700 °C, 750 °C under a redox flow gas (93 vol% Ar and 7 vol% H_2), respectively, for another 10 h to obtain the $LiFePO_4/C$ powders.

2.2. Characterization of $LiFePO_4/C$

The thermal behavior of the dried gel precursors was analyzed using the gravimetric apparatus (Pyris Diamond, PerkinElmer Thermal Analysis) under nitrogen flow from ambient temperature to 800 °C at a scan rate of 10 °C min^{-1}. The structure of the synthesized materials was identified by X-ray diffraction analysis (XRD, Model X'TRAX) using nickel filtered Cu Kα radiation (λ = 0.15406 nm) over the 2θ range from 10° to 80°. The particle morphology of the powders was observed using a JSM-6700F field emission scanning electron microscope (FESEM) and a Joel JEM-1010 transmission electron microscope (TEM).

2.3. Electrochemical characterization

The obtained $LiFePO_4/C$ was mixed with carbon black and polyvinylidene fluoride (PVDF) (weight ratio is 80:10:10) in N-methylpyrrolidinon (NMP) to form a slurry. The viscous slurry was cast on an aluminum foil and dried at 120 °C under vacuum for 12 h. The dried foil was then punched to a disk with the diameter of 13 mm. Electrochemical properties of the cathode material were tested by fabricating 2032 coin-type cells using lithium foil as negative electrode. The electrolyte employed was 1 M $LiPF_6$ in ethylene carbonate and diethyl carbonate (volume ratio is 1:1). The galvanostatic charge/discharge were tested at room temperature in the voltage range of 2.5–4.2 V vs. Li^+/Li at various current rates.

3. Results and discussion

Coating the $LiFePO_4$ particle surface with a thin layer of carbon is very effective to improve its electronic conductivity [24]. In this study, citric acid is involved in the sol–gel process as both chelating agent and carbon source. In order to clarify the effect of the molar ratio of citric acid to total metal ions (n_{CA}/n_m) on the properties of the final product, three precursors with different n_{CA}/n_m values (1:4, 1:3 and 1:2), are prepared and marked as p1, p2 and p3, respectively. For clarify, the $LiFePO_4$ calcined at *y* °C from p*x* is marked as LFP-*x*–*y* in the following text.

Thermogravimetry (TG) and derivate thermal analysis (DTA) profiles of the sample p2 obtained under an Argon atmosphere, at a heating rate of 10 °C min^{-1}, is presented in Fig. 1. The TG curve shows that the mass loss of this sample has two clear stages. The first stage is the quick mass loss of 17 wt% (i.e., 83 wt% of its original mass in the temperature range from 50 °C to 120 °C). In addition, the DTA curve shows that the first stage is an endothermic reaction with peak centered at 60 °C. The mass loss in this stage corresponds to the volatilization of the absorbed water in the precursor. Further mass loss of 39 wt% (i.e., 83–44 wt%) is observed in the second stage between 120 °C and 350 °C with another endothermic peak detected at 220 °C in the DTA curve. This stage can be attributed to the removal of crystal water and decomposition of organic. There is no obvious mass loss observed when scan temperature exceeds 350 °C, but one exothermic effect occurs at 600 °C in the DTA curve which is attributed to the formation of $LiFePO_4$. Therefore, in order to obtain a single-phase olivine-type $LiFePO_4$, the precursors are preheated at 350 °C for 5 h, followed by calcining at a higher temperature (from 600 °C to 750 °C) for 10 h.

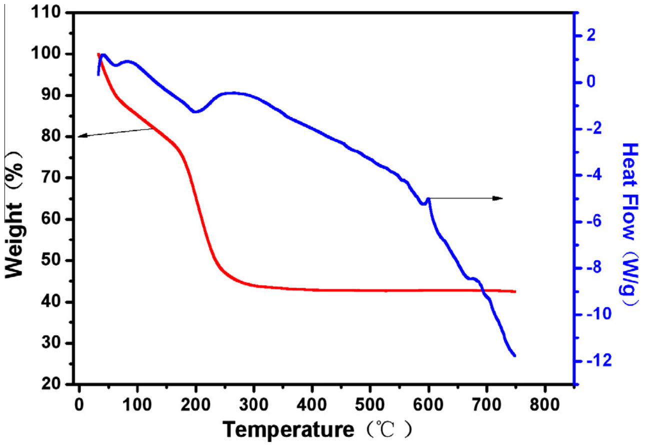

Fig. 1. TG–DSC curves for the sample p2 from room temperature to 800 °C with a heating rate of 10 °C min^{-1} in an argon atmosphere.

The X-ray diffraction patterns of several calcined samples are presented in Fig. 2. As shown in Fig. 2, all three samples present olivine structure (Pnma space, JCPDS NO. 40-1499) without any detectable impurity phase. In addition, with increasing the amount of the citric acid in the precursors, more carbon is in situ produced during calcining process which effectively inhibits the size growth of the $LiFePO_4$ crystalline grain [23]. As a result, the diffraction peak intensities decrease with the increase of citric acid in the XRD patterns.

As shown in the field emission scanning electron microscopy (FESEM) images of the obtained $LiFePO_4/C$ composites (Fig. 3), all

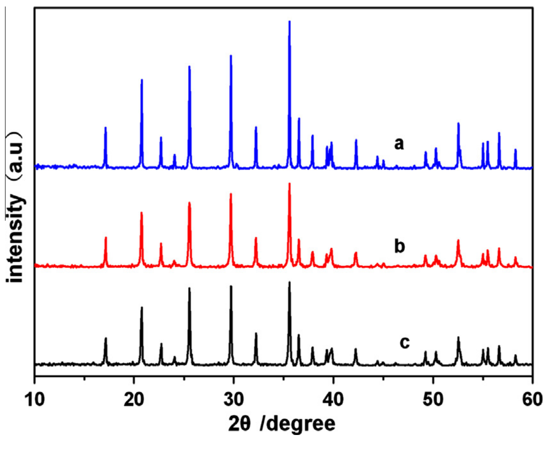

Fig. 2. XRD images of the LFP-1-650 (a), LFP-2-650 (b) and LFP-3-650 (c).