Journal of Power Sources 288 (2015) 337–344

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Surfactants assisted synthesis and electrochemical properties of nano-$LiFePO_4$/C cathode materials for low temperature applications

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HIGHLIGHTS

- Nano-$LiFePO_4$/C have been prepared by a facile solid–state reaction method.
- The nano-$LiFePO_4$/C yields a specific capacity of 130 mAh g^{-1} under 0.1 C at −20 °C.
- The nano-$LiFePO_4$/C shows an excellent rate capability and cycle performance.

ARTICLE INFO

Article history:
Received 17 March 2015
Received in revised form
17 April 2015
Accepted 20 April 2015
Available online

Keywords:
Lithium ion battery
Lithium iron phosphate
Cathode material
Nanoparticles
Electrochemical performance

ABSTRACT

Nano-$LiFePO_4$/C cathode materials have been synthesized by a solid–state reaction method using Tween60-Span60 composite as surfactant and carbon source. The Tween60-Span60 composite surfactants together lead a strong space steric effect, which ensures a high surface energy and reaction kinetic of the precursors. Consequently, it contributes to the formation of uniformly distributed $LiFePO_4$ particles coated with a thin layer of carbon. The unique structured $LiFePO_4$/C cathode materials can deliver high electrochemical capacities of 166, 150.5 and 130.1 mAh g^{-1} under 0.1 C at 25, 0 and −20 °C, respectively. Moreover, the $LiFePO_4$/C cathode materials demonstrate an excellent rate capability and cycle performance, no discernible specific discharge capacity fading has been observed after over 400 cycles under the rate of 0.1–5 C at 25 °C, or after over 100 cycles under the rate of 0.1–0.5 C at −20 °C.

1. Introduction

Recently, lithium ion battery (LIB) has attracted significant interests for its applications in energy storage and electric or hybrid electric vehicles [1–3]. Among the state-of-art cathode materials, lithium iron phosphate ($LiFePO_4$) has been considered as one of the promising cathode materials, due to its advantages including large theoretical capacity, high operating voltage and long cycle life, low toxic, environmental compatibility and high safety [4–6]. However, $LiFePO_4$ generally suffers from poor rate performance as a result of its lower mass- and charge-transport kinetics, caused by its low electronic conductivity and Li-ion diffusivity at room temperature, and which become even worse at low temperatures [7,8]. Many strategies have been proposed to overcome the limitations inherent to $LiFePO_4$ to improve its rate capability, such as carbon or conductive materials coating [9–12], metal ions doping [13,14] and nanofabrication [15,16]. Experiments demonstrate that good control over physical and chemical properties of $LiFePO_4$ particles, e.g. shape, size, and thickness of the carbon coating layer, etc., is critical to achieve an optimal electrochemical performance [5,17–19]. Especially, fabrication of nano-sized $LiFePO_4$ has been considered as an effective way to improve its electrochemical performance, since reduction the grain size of cathode materials can greatly facilitate the lithium ions diffusion [5,8].

In the past decades, various methods have been developed to

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http://dx.doi.org/10.1016/j.jpowsour.2015.04.126

fabricate nano $LiFePO_4$ cathode materials, for example, sol–gel [20–22], hydrothermal [23,24], solvothermal method [25], co-precipitation [26] and spray pyrolysis [27] et al. Although these approaches are promising, they might be time consuming and costly, the electrochemical performances of fabricated $LiFePO_4$ are much lower than that of the $LiFePO_4$ fabricated by solid–state reaction method. Thus, solid–state reaction method has been widely recognized for large-scale $LiFePO_4$ cathode materials fabrication [28]. However, the synthesized particles are often randomly orientated and the minimum dimension of $LiFePO_4$ particles along the Lithium ion diffusion direction cannot be assured, since the solid particles react through surface diffusion at high temperature during the formation process. The addition of surfactants has been reported to be an effective approach to block reactants diffusion and hinder the growth of $LiFePO_4$ particles in the solid state reaction process, and prepare nano-sized $LiFePO_4$/C cathode materials. For example, polyvinylpyrrolidone (PVP) [29], ethylene oxide (PEO) and propylene oxide (PPO) [30], $C_{12-15}H_{24-31}(OC_2H_4)_nSO_3Na$ [31], and cetyltrimethylammonium bromide (CTAB) [32] et al. have been used as the surfactants to synthesize nano-sized $LiFePO_4$/C by the solid state reaction methods, and the obtained nano-$LiFePO_4$/C composites possess advanced electrochemical properties. As it is reported, surfactants assisted synthesis of $LiFePO_4$ nanoparticles is cost effective and easy to scale up approach. Considering the limiting factors that can affect $LiFePO_4$ particle growth and morphology, $LiFePO_4$ nanoparicles can be rational designed and prepared by adding appropriate surfactants, which can bond to and form a tight adsorption layer on the surface of the precursor in the solid state reaction process [33,34]. Moreover, the carbon sources could be directly induced and homogenously coated on the $LiFePO_4$ nanoparticles by using proper surfactants and fabrication processes.

Herein, we report a facile method to fabricate nano-$LiFePO_4$/C cathode materials by employing Tween60, Span60, and Tween60 and Span60 composite as surfactant and carbon source. The effects of surfactants on the morphology and electrochemical properties of $LiFePO_4$ will be discussed in detail. The formation mechanisms of $LiFePO_4$ with various morphologies will be analyzed and interpreted.

2. Experimental

$LiFePO_4$/C powders were synthesized by solid–state reaction method using LiH_2PO_4, FeC_2O_4, and Tween60, Span60, or Tween60 and Span60 composite surfactants as raw materials. Stoichiometric amount of the reactants were mixed by ball milling for 3 h and using deionized water as the liquid medium. The obtained mixture was dried at 80 °C for 12 h and disintegrated through crusher to get the fine precursor powders. The $LiFePO_4$/C products were obtained by calcining the as-prepared precursors in high purity N_2 atmosphere at 600, 700 and 800 °C for 10 h, respectively. Tween60-Span60 represents raw materials were firstly mixed with Tween60, and then the mixture was mixed with Span60, while Span60-Tween60 represents raw materials were mixed with the surfactants in the reverse order. The $LiFePO_4$/C fabricated by using Tween60, Span60 and Tween60-Span60 (the weight ratio of Tween60 to Span60 equals to 3) surfactants will be shorted as $LiFePO_4$/C-T and $LiFePO_4$/C-S, $LiFePO_4$/C-TS for convenience, respectively.

The powders X-ray diffraction (XRD) patterns were recorded on Rigaku D/Max 2100 Powder X-ray Diffractometerwith a Cu-K$_{\alpha}$radiation ($\lambda = 1.5418$ Å), employing a scan rate of 5°/min in the 2θ range from 10 to 80°. The microstructure of the $LiFePO_4$/C powders was characterized with scanning electron microscopy (SEM, Philips, FEI Quanta 200 FEG) and transmission electron microscopy (TEM, JEM-2010, JEOL). Fourier transform infrared spectroscopies (FTIR) were carried out on the samples employing an AVATAR370 spectrometer.

The electrochemical performances of the $LiFePO_4$/C-T, $LiFePO_4$/C-S and $LiFePO_4$/C-TS cathode fabricated at 700 °C were evaluated using CR2025 coin cells with lithium metal as the reference electrode, and a Celgard 2500 separator. The cathodes were made by dispersing the $LiFePO_4$/C, acetylene black, and polyvinylidene fluoride (PVDF) binder evenly in a weight ratio of 90:5:5 in NMP solvent, casting the viscous slurry uniformly on the aluminum foil and drying at 90 °C under vacuum for 12 h. A 1:1 volumetric ratio mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) containing 1 M $LiPF_6$ was utilized as the electrolyte. Galvanostatic charge–discharge curves were recorded between 2.5 and 4.2 V at the temperature of 25, 0 and −20 °C. Electrochemical impedance spectroscopy (EIS) of the coin cells was carried out using IM6 (Zahner) electrochemical station by applying with an AC signal amplitude of 5 mV in the frequency range of 0.01 Hz–1 MHz.

3. Result and discussion

The XRD patterns of $LiFePO_4$/C synthesized with Tween60, Span60, and Tween60-Span60 composite surfactants (the weight ratio of Tween60 to Span60 equals to 3) are shown in Fig. 1. The prepared materials are single phase of orthorhombic olivine-type structure $LiFePO_4$, no impurity phase was observed. As indicated in the Figure, the intensities of diffraction peaks increase with increasing sintering temperature from 600 to 800 °C, due to the improvement of crystallinity. The crystallite sizes of the synthesized $LiFePO_4$/C composites have been calculated by Debye—-Scherrer equation, and the results are listed in Table 1. The average crystal size of fabricated $LiFePO_4$/C-TS powders is much smaller than that of the $LiFePO_4$/C-T and $LiFePO_4$/C-S powders.

Fig. 2 shows the SEM micrographs of $LiFePO_4$/C-T, $LiFePO_4$/C-S and $LiFePO_4$/C-TS composites prepared by solid state reaction

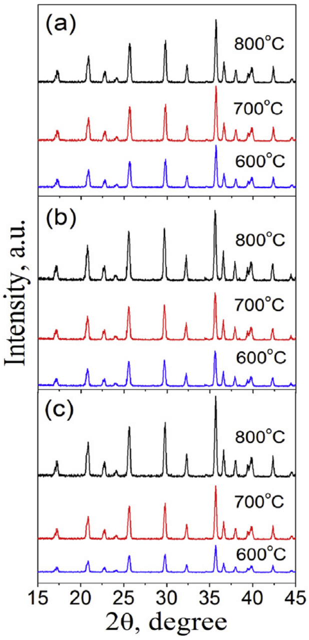

Fig. 1. X-ray diffraction (XRD) patterns of $LiFePO_4$/C composites prepared by using Tween60-Span60 composite (a), Tween60 (b), or Span60 (c) as surfactants at 600, 700 and 800 °C, respectively. Tween60-Span60 represents the raw materials were firstly mixed with Tween60, and then the mixture was mixed with Span60. The weight ratios of Tween60 to Span60 was set to 3.