



Electrochemical performance comparison of LiFePO₄ supported by various carbon materials

Dan Zhao^a, Yun-long Feng^{a,*}, Yong-gang Wang^b, Yong-yao Xia^{b,**}

^a Zhejiang Key Laboratory for Reactive Chemistry on Solid Surfaces, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua, Zhejiang 321004, People's Republic of China

^b Department of Chemistry, Fudan University, Shanghai 200433, People's Republic of China

ARTICLE INFO

Article history:

Received 4 August 2012

Received in revised form

22 September 2012

Accepted 10 October 2012

Available online 1 November 2012

Keywords:

LiFePO₄

Acetylene black

Carbon nanotube

Graphene

Lithium-ion batteries

ABSTRACT

In the present work, various LiFePO₄/carbon composites were prepared through a facile solvothermal route followed by heat treatment. These as-prepared LiFePO₄/carbon composites, including LiFePO₄/acetylene black (95:5 wt.%), LiFePO₄/carbon nanotube (95:5 wt.%) and LiFePO₄/graphene (95:5 wt.%), were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Their electrochemical performances were also investigated and compared in detail. The achieved results indicate that both particle-size and electrochemical performance of LiFePO₄ much depend on the carbon supporter. When acetylene black and carbon nanotube were used as carbon supporter, the prepared LiFePO₄ particles were agglomerate together to form large-size second particles which cannot well connect with carbon supporter. In the LiFePO₄/graphene composite, ~50 nm LiFePO₄ particles uniformly loaded on the two-dimensional carbon supporter, and thus display much better rate ability. This result suggests that graphene should be a promising carbon supporter for LiFePO₄.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Since phospho-olivines (LiFePO₄) were first reported as cathode materials for lithium-ion batteries by Padhi et al. [1], a series of olivine-type lithium transition metal phosphates, LiMPO₄ (M = Fe, Mn, Co, Ni, and V), have been investigated intensively as attractive cathode materials for rechargeable lithium batteries [2–12]. In recent years, among all these materials, extensive attention has been focused on the LiFePO₄ which is considered to be the most promising candidate because of low cost, environmental compatibility, cycling stability and also this material has a relatively high theoretical specific capacity of 170 mAh g⁻¹ with a flat charge–discharge profile at intermediate voltage (3.45 V vs. Li⁺/Li) and reasonable cycle life [13–16].

Although it possesses so many advantages, LiFePO₄ as a cathode material still meets some problems on its way to the destination of a practical application. For example, there exists poor rate capability, and it is originated from the low electronic conductivity and the slow lithium-ion diffusion across the LiFePO₄/FePO₄ boundary at the room temperature [1]. In the first report about LiFePO₄, it could only have a reversible capacity of 110 mAh g⁻¹ at a potential of 3.5 V vs. Li/Li⁺ when cycled using a very low

current density at a constant test temperature of 30.0 °C [1]. The achieved capacity of 110 mAh g⁻¹ was much lower than the theoretical capacity of LiFePO₄ of 170 mAh g⁻¹. In 2001, Yamada et al. achieved 95% theoretical capacity of LiFePO₄ at room temperature by sintering it at 550 °C to make tailored particles [17]. According their report, decreasing the particle size is another effective way to overcome the diffusion limitation problems. Combining the both ideas of carbon coating and tailored particle-size, Huang et al. made LiFePO₄/C composites by mixing raw materials with a carbon gel before heating [18]. In this composite, LiFePO₄ has a particle size of 100–200 nm and there is about 15 wt.% carbon. This composite first demonstrated that LiFePO₄ could have excellent rate capability at room temperature. Even when cycled at a 5 C rate, it showed a capacity of about 120 mAh g⁻¹. During the following years, many efforts have been made to further improve the power performance of LiFePO₄ through low-temperature route to obtain tailored particles and carbon supporting to improve the conductivity of solid phase. Various kinds of carbon materials have been suggested as conductivity supporters (or additives) for LiFePO₄, such as carbon black [19–23], graphite [21–24], pyrolytic carbon [25–27], graphene [28–31], and carbon nanotube [32–36]. However, up to present, the comparative investigation about the effect of carbon supporters on the electrochemical performance is still rarely reported.

In the present work, acetylene black, carbon nanotube and graphene were employed as carbon supporter to prepare various LiFePO₄/carbon composites by a facile solvothermal route followed

* Corresponding author. Fax: +86 0579 82282269.

** Corresponding author. Tel.: +86 21 55664177; fax: +86 21 51630318.

E-mail addresses: sky37@zjnu.cn (Y.-l. Feng), yxia@fudan.edu.cn (Y.-y. Xia).

by heat treatment. The effect of these carbon supporters on the electrochemical performance of LiFePO_4 was investigated and compared in detail.

2. Experimental

2.1. Preparation of electrode materials

In the present work, we use graphene, carbon nanotube and acetylene black to synthesize three different LiFePO_4 /carbon composites. The LiFePO_4 /graphene sample was obtained as follows: some of graphene was added into the ethylene glycol (20 ml), and then $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (1.67 g) was added into the solution under stirring condition until it was completely dissolved. After that, H_3PO_4 (85%, 0.32 ml) was dropped to the solution gradually and stirred for 10 min. At the same time, $\text{LiOH} \cdot \text{H}_2\text{O}$ (0.68 g) was added into ethylene glycol (15 ml) to form a transparent solution. At last, the LiOH –ethylene glycol solution was slowly added into the FeSO_4 – H_3PO_4 –ethylene glycol solution with constantly stirring for some minutes. Then the mixture was sealed in a 50 ml teflon-lined stainless steel autoclave, and heated at 180°C for 10 h. After cooling to room temperature, the products were separated by centrifugation and washed with water and ethanol several times, and then dried at 60°C for 6 h. Then the mixture was calcinated at 200°C for 0.5 h, and then heated to 550°C in a tube furnace for 2.5 h under argon/ H_2 (95:5, v/v) flow. After cooling to room temperature, the LiFePO_4 /graphene composite was obtained. LiFePO_4 /carbon nanotube and LiFePO_4 /acetylene black were also prepared following the same procedure, and simply used carbon nanotube and acetylene black as conducting additives. All the reagents used in the experiment were analytical grade.

2.2. Characterization

The morphologies of LiFePO_4 /acetylene black, LiFePO_4 /carbon nanotube and LiFePO_4 /graphene powder were characterized using a scanning electron microscopy (SEM, Philips XL-60) and transmission electron microscopy (TEM, JEOL JEM2010). For structure and phase analysis, X-ray diffraction (XRD) was performed using a Bruker Advance D8 X-ray diffractometer with $\text{Cu K}\alpha$ radiation. Specific surface area of the samples was determined through nitrogen sorption isotherms at 77 K with a Quadrasorb SI Automated surface area and pore size analyzer. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas.

2.3. Electrochemical measurements

The LiFePO_4 electrodes supported different carbon sources were prepared according to the following steps. The mixture containing 75% LiFePO_4 /carbon composite and 15% carbon black, and 10% poly(vinylidene fluoride) (PVDF) was well mixed and then dispersed in N-methylpyrrolidone (NMP). The slurry was pressed on the current collector and tailored to a disk of $\Phi = 12$ mm. Finally, the electrode was dried at 80°C for 12 h to remove the solvent. The electrochemical tests were taken on a coin-type cell (CR-2016) assembled with positive electrode/a separator/and a negative electrode in an argon-filled glove box. The electrolyte was 1.0 M LiPF_6 in 1:2 volume ratio of ethylene carbonate (EC):dimethyl carbonate (DMC). The charge/discharge performance of the CR2016 coin cells was performed between 2.0 and 4.3 V at room temperature. Cyclic voltammetry (CV) was conducted by using Solartron Instrument Model 1278 at the scanning rates of 0.5, 1, 2 and 3 mV s^{-1} between 2.0 and 4.3 V. Solartron Instrument Model 1287 electrochemical interface and 1255B frequency response analyzer were employed for impedance measurements.

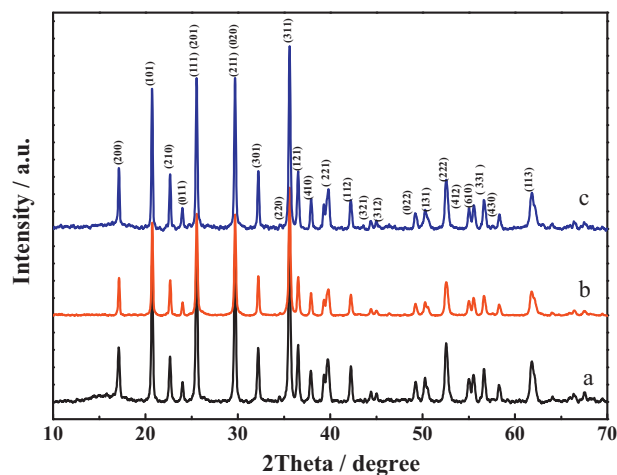


Fig. 1. XRD patterns of (a) LiFePO_4 /acetylene black, (b) LiFePO_4 /carbon nanotube, and (c) LiFePO_4 /graphene samples.

3. Results and discussion

Fig. 1 shows the XRD patterns of the LiFePO_4 supported different carbon sources. The XRD results note that the diffraction peaks of all the products are in full accord with the ordered LiFePO_4 olivine structure indexed by orthorhombic $Pmnb$ and no impurities such as Li_3PO_4 and others, which often appear in the LiFePO_4 product synthesized by traditional routes [37], are observed, which proved that introduction of acetylene black, carbon nanotube and graphene does not destroy the structure of LiFePO_4 . Furthermore, the half-peak widths of these XRD pattern for different LiFePO_4 /composites are almost same, indicating that they should have same primary crystalline size. According to the Scherrer equation, the grain sizes of these three samples are 42 nm (LiFePO_4 /graphene), 45 nm (LiFePO_4 /carbon nanotube) and 47 nm (LiFePO_4 /acetylene black), respectively. This result clearly indicates that these composites should have almost same primary crystalline size. However, it can be observed from SEM investigation that particle sizes of LiFePO_4 /acetylene black composite and LiFePO_4 /carbon nanotube composite are in the range from 300 to 500 nm (Fig. 2a and b), and obviously larger than that of LiFePO_4 /graphene (Fig. 2c). This is because that these primary crystals LiFePO_4 /acetylene black composite (or LiFePO_4 /carbon nanotube composite) agglomerate together to form larger size second particles. This point is confirmed by TEM investigation (Fig. 3). It can be detected from Fig. 3a or b that a lot of primary crystals of LiFePO_4 agglomerate together to form second particles in LiFePO_4 /acetylene black composite or LiFePO_4 /carbon nanotube composite. On the contrary, these primary crystals of LiFePO_4 are well dispersed on the graphene substrate (Fig. 3c). This clearly demonstrates that agglomeration of primary crystals of LiFePO_4 depends on the carbon supporter. In other words, the two-dimensional graphene facilitates the dispersion of primary crystals, compared with carbon nanotubes and acetylene black. The layered graphene is an ideal single-atom thick substrate for growth of LiFePO_4 nanoparticles to render them electrochemically active and electrically conductive to the outside current collectors. The BET surface areas of the prepared LiFePO_4 /carbon composite are given in Table 1.

Fig. 4 exhibits the charge and discharge profiles of the LiFePO_4 /acetylene black, LiFePO_4 /carbon nanotube and LiFePO_4 /graphene electrodes at 0.01 A g^{-1} for the first cycle and in the voltage range from 2 V to 4.3 V. All the electrodes show a reversible flat voltage plateau around 3.4 V during both charge and discharge, which corresponds to the redox couple of $\text{Fe}^{3+}/\text{Fe}^{2+}$.

Download English Version:

<https://daneshyari.com/en/article/187748>

Download Persian Version:

<https://daneshyari.com/article/187748>

[Daneshyari.com](https://daneshyari.com)