



Synthesis of LiFePO_4/C cathode material from ferric oxide and organic lithium salts

Zhongqi Shi^{a,b}, Ming Huang^{a,b}, Yongjian Huai^{a,b,c}, Ziji Lin^{a,b}, Kerun Yang^{a,b}, Xuebu Hu^{d,e}, Zhenghua Deng^{a,b,e,*}

^a Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, Sichuan 610041, PR China

^b Graduate School of Chinese Academy of Sciences, Beijing, 100039, PR China

^c China Aviation Lithium Battery Co., Ltd, Luoyang, Henan 471003, PR China

^d Department of Chemistry and Materials, Sichuan Normal University, Chengdu, Sichuan 610068, PR China

^e Zhongke Laifang Power Science & Technology Co., Ltd., Chengdu, Sichuan 610041, PR China

ARTICLE INFO

Article history:

Received 30 October 2010

Received in revised form 17 January 2011

Accepted 22 January 2011

Available online 28 January 2011

Keywords:

Lithium iron phosphate

Organic lithium salt

Ferric oxide

Lithium-iron batteries

ABSTRACT

LiFePO_4/C cathode material has been simply synthesized via a modified in situ solid-state reaction route using the raw materials of Fe_2O_3 , $\text{NH}_4\text{H}_2\text{PO}_4$, $\text{Li}_2\text{C}_2\text{O}_4$ and lithium polyacrylate (PAALi). The sintering temperature of LiFePO_4/C precursor is studied by thermo-gravimetric (TG)/differential thermal analysis (DTA). The physical properties of LiFePO_4/C are then investigated through analysis using by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscope (TEM) and the electrochemical properties are investigated by electrochemical impedance spectra (EIS), cyclic voltammogram (CV) and constant current charge/discharge test. The LiFePO_4/C composite with the particle size of ~ 200 nm shows better discharge capacity (156.4 mAh g^{-1}) than bare LiFePO_4 (52.3 mAh g^{-1}) at 0.2 C due to the improved electronic conductivity which is demonstrated by EIS. The as-prepared LiFePO_4/C through this method also shows excellent high-rate characteristic and cycle performance. The initial discharge capacity of the sample is 120.5 mAh g^{-1} and the capacity retention rate is 100.6% after 50 cycles at 5 C rate. The results prove that the using of organic lithium salts can obtain a high performance LiFePO_4/C composite.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

With a high voltage and energy density, lithium-ion batteries have become a new generation of green rechargeable batteries and have an increasingly diverse range of applications, from portable electronic devices to electric vehicle (EV) and hybrid electric vehicle (HEV). Widespread attentions have been paid upon the development of cathode material. Compared with LiNiO_2 , LiCoO_2 and LiMn_2O_4 , the most promising cathode material, olivine-type LiFePO_4 [1] presents several advantages, such as low material cost, no toxicity, high theoretical capacity (170 mAh g^{-1}), thermal stability at rather high temperature, safety and so on. However, LiFePO_4 suffers from two drawbacks of poor ionic conductivity and poor electronic conductivity, which are the major limitations of its large-scale application such as in electric vehicle. To overcome the problems, several methods have been developed, such as coating

electronically conductive additives (carbon or metal) [2–5], doping with supervalent cation [6,7] and minimizing the particle size [8–10].

Currently, solid-state reaction [1,4,11] is considered as the appropriate method for commercial production of LiFePO_4 . Meanwhile, Li_2CO_3 [1,5,12–14], $\text{LiOH} \cdot \text{H}_2\text{O}$ [15–18] or CH_3COOLi [3,19,20] have been used frequently as the lithium source to synthesize LiFePO_4 . It is well known that the divalent iron is stable in the acidic systems, but is inclined to be oxidized in the alkaline environment. The using of these lithium compounds in aqueous system will lead the precursor slurry to display alkalinity, which may impact the stability of the divalent iron. Moreover, the precursor may suffer from composition segregation which is caused by the fusion of these lithium compounds, because the fusion temperature of them is lower than the decomposition temperature. The segregation will gravely damage the homogeneity of the precursor, and then affect the performance of LiFePO_4 .

From the above reviews, we use two organic lithium salts of $\text{Li}_2\text{C}_2\text{O}_4$ and lithium polyacrylate (PAALi) as the lithium source, Fe_2O_3 as the iron source and $\text{NH}_4\text{H}_2\text{PO}_4$ as the phosphorus source to synthesize carbon coated LiFePO_4 via solid-state reaction. Contrasted with the method by using divalent iron compounds, only

* Corresponding author at: Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, Sichuan 610041, PR China. Tel.: +86 2885229252; fax: +86 2885233426.

E-mail address: zh Deng@cioc.ac.cn (Z. Deng).

after reducing ferric iron to divalent iron can we obtain the LiFePO_4 when we use ferric oxide as iron source. As is well known, carboxylic acid free-radicals obtained from the pyrolysis of $\text{Li}_2\text{C}_2\text{O}_4$ have strong reducibilities, which can reduce ferric iron to divalent iron by a sequence of free-radical reactions [21–23]. PAALi can also generate carboxylic acid free radicals and is an effective dispersant in the mixture of starting materials. $\text{Li}_2\text{C}_2\text{O}_4$ and PAALi, which are different from inorganic lithium salts, can avoid the composition segregation and ensure the homogeneity of the precursor because the decompositions of the two organic lithium salts precede the fusions.

Meanwhile the aqueous PAALi is also used as carbon source. So we can use environmentally friendly and low cost distilled water as the dispersion medium, to replace the organic solvents, such as acetone and ethanol. Moreover, the using of ferric oxide can further reduce the production cost of LiFePO_4 .

2. Experimental

Fe_2O_3 , $\text{NH}_4\text{H}_2\text{PO}_4$, $\text{Li}_2\text{C}_2\text{O}_4$, and PAALi were used as starting materials to synthesize LiFePO_4/C . PAALi was obtained via dissolving a stoichiometric amount of $\text{LiOH} \cdot \text{H}_2\text{O}$ into an aqueous solution of polyacrylic acid (PAA). $\text{Li}_2\text{C}_2\text{O}_4$ and PAALi with an appropriate mixture mole ratio of 1.17:1, were used as lithium sources. Starting materials were placed in a stainless steel cylindrical container with zirconia ball and grounded in a planetary ball-miller for 8 h in water at a rotation speed of 400 rpm. The above mixture was dried in an oven at 100°C for 10 h to get precursor and then preheated at 450°C for 2 h and held at 700°C for 10 h in an N_2 atmosphere. Bare LiFePO_4 was prepared without using PAALi.

TG–DTA measurements have been performed (NETZSCH STA 409 PC/PG) from 20 to 800°C at a heating rate of $10^\circ\text{C min}^{-1}$ under argon atmosphere. The crystalline phase of the sample was identified by XRD analysis using $\text{Cu K}\alpha$ radiation (X'Pert Pro MPD, PHILIP). The morphology of powder was observed by scanning electronic microscope (SEM, INSPECT F, FEI) and transmission electron microscope (TEM, JEM-100C, JEOL). The carbon content of samples was determined by an elemental analyzer (CARLO ERBA 1106, CARLO ERBA).

The cathodes were prepared via mixing 90 wt.% LiFePO_4/C composite, 5 wt.% conductive carbon black (Super P, TIMCAL) and 5 wt.% an aqueous binder LA132 (from Indigo, China) in distilled water. The resultant slurry was then coated onto an aluminum foil. The coated aluminum foil was dried for 10 h in a vacuum oven at 100°C and then punched into circular discs with active material loading of about $4\text{--}5 \text{ mg cm}^{-2}$.

The lithium foil was used as the counter electrode and 1 M LiPF_6 in EC:DEC:EMC = 1:1:1 was used as the electrolyte. The 2032 type coin cells were assembled in an argon-filled glove box. The charged/discharged test was performed at various C rates in the voltage range of 2.5–4.3 V (versus Li/Li^+) at ambient temperature. Electrochemical impedance spectra (EIS) were investigated by a Solartron SI 1260/1287 (UK) impedance analyzer in the frequency range of 10^{-1} – 10^6 Hz. Cyclic voltammetry (CV) tests were carried out in the voltage range of 2.5–4.3 V at a scan rate of 0.1 mV s^{-1} (Arbin-001 MITS Pro 3.0-BT2000, Arbin). All the tests were carried out at room temperature.

3. Results and discussion

Fig. 1 shows the TG/DTA curves for the precursor of LiFePO_4/C from 20 to 800°C with a heating rate of $10^\circ\text{C min}^{-1}$ in an argon flow rate of 30 mL min^{-1} . The mass-loss process in the TG curve is related to exothermic and endothermic peaks in the DTA curve. An initial mass loss of 2.84% before 160°C and an endothermic peak

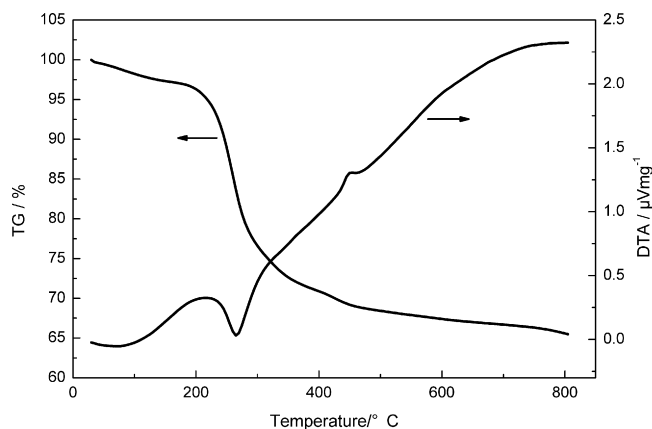


Fig. 1. TG–DTA curves of the LiFePO_4/C precursor recorded from 20 to 800°C with a heating rate of $10^\circ\text{C min}^{-1}$ under an argon flow of 30 mL min^{-1} .

was observed. This is attributed to the volatilization of moisture of the precursor. A continuous mass loss between 200 and 450°C can be related to the thermal decomposition of the partial reactants. There is a solely petite exothermic peak at 452.2°C in the DTA curve, but no appreciable mass loss is observed in TG curve, this is suggesting that the crystallization of LiFePO_4 takes place in this temperature [24–26]. The mass of the precursor is almost unchanged after 600°C , which may indicate that the reaction was complete. In this study, the precursor was preheated at 450°C and finally held at 700°C to get the well-crystallized LiFePO_4 .

Fig. 2 shows the X-ray diffraction patterns for the bare LiFePO_4 and the LiFePO_4/C composite. All the two patterns can demonstrate a well-ordered olivine LiFePO_4 , indexing to be an orthorhombic *Pmnb*, in good agreement with the JCPDS No. 83-2092. It indicates that LiFePO_4 can also be obtained from Fe_2O_3 by the reducibility of carboxylic acid free radicals, without adding carbon source PAALi. However, a petite Fe_2O_3 peak was detected in the bare LiFePO_4 , whereas no impurities were observed in the LiFePO_4/C composite. The result means that reduction of Fe_2O_3 is not thorough only using $\text{Li}_2\text{C}_2\text{O}_4$ as reducing agent, but the problem is dissolved by the cooperation of $\text{Li}_2\text{C}_2\text{O}_4$ and PAALi. Meanwhile, no characteristic diffraction peaks of crystallized carbon was detected in the XRD pattern for LiFePO_4/C composite, it suggests that the presence of carbon delivered from PAALi does not influence the structure of LiFePO_4 .

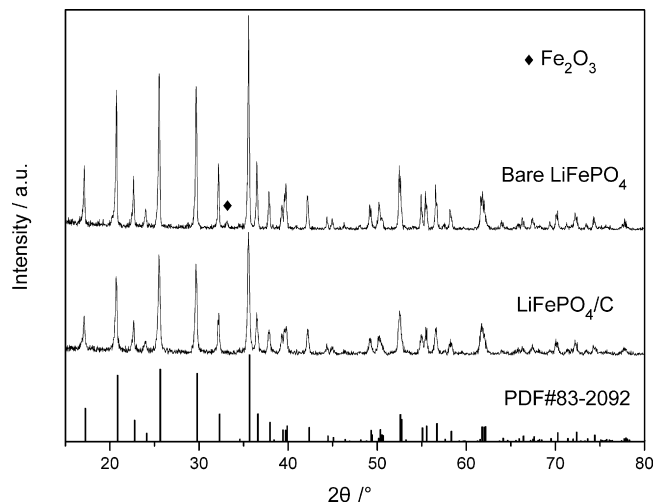


Fig. 2. XRD pattern of the LiFePO_4/C composite.

Download English Version:

<https://daneshyari.com/en/article/190294>

Download Persian Version:

<https://daneshyari.com/article/190294>

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