



Enhancement of electrochemical behavior of nanostructured LiFePO₄/Carbon cathode material with excess Li



K. Bazzi^a, M. Nazri^a, V.M. Naik^b, V.K. Garg^c, A.C. Oliveira^c, P.P. Vaishnava^d, G.A. Nazri^{a,*}, R. Naik^{a,**}

^a Department of Physics and Astronomy, Wayne State University, Detroit, MI 48201, USA

^b Department of Natural Sciences, University of Michigan-Dearborn, Dearborn, MI 48128, USA

^c Universidade de Brasilia, Instituto de Fisica, 70919-970 Brasilia, DF, Brazil

^d Department of Physics, Kettering University, Flint, MI 48504, USA

HIGHLIGHTS

- A new process is developed for preparation of conductive carbon coated LiFePO₄.
- Excess lithium significantly improved the electrochemical performance of LiFePO₄.
- Mössbauer spectroscopy identifies the presence of new impurity phases.
- LiFePO₄ with excess lithium made in presence of surfactant is a promising cathode.

ARTICLE INFO

Article history:

Received 24 June 2015

Received in revised form

30 October 2015

Accepted 22 November 2015

Available online 12 December 2015

Keywords:

Lithium battery

Lithium iron phosphate

Nanomaterial

ABSTRACT

We have synthesized carbon coated LiFePO₄ (C-LiFePO₄) and C-Li_{1.05}FePO₄ with 5 mol% excess Li via sol–gel method using oleic acid as a source of carbon for enhancing electronic conductivity and reducing the average particle size. Although the phase purity of the crystalline samples was confirmed by x-ray diffraction (XRD), the ⁵⁷Fe Mössbauer spectroscopy analyses show the presence of ferric impurity phases in both stoichiometric and non-stoichiometric C-LiFePO₄ samples. Transmission electron microscopy measurements show nanosized C-LiFePO₄ particles uniformly covered with carbon, with average particle size reduced from ~100 nm to ~50 nm when excess lithium is used. Electrochemical measurements indicate a lower charge transfer resistance and better electrochemical performance for C-Li_{1.05}FePO₄ compared to that of C-LiFePO₄. The aim of this work is to systematically analyze the nature of impurities formed during synthesis of LiFePO₄ cathode material, and their impact on electrochemical performance. The correlation between the morphology, charge transfer resistance, diffusion coefficient and electrochemical performance of C-LiFePO₄ and C-Li_{1.05}FePO₄ cathode materials are discussed.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The olivine structured LiFePO₄ has been established as an alternative cathode material to LiCoO₂ for lithium-ion battery technology due to its low cost, superior thermal stability, enhanced safety, and less potential for pollution. LiFePO₄ has a high theoretical capacity (170 mAh g⁻¹) with a flat voltage plateau (3.4 V vs. Li⁺/Li), indicating a two phase reaction [1–4]. However, LiFePO₄ has

poor electronic and ionic conductivities [5], which restrict its rate capability and electrochemical performance, particularly for high power applications. Several techniques have been used to increase the inherent electronic conductivity of LiFePO₄, such as, decreasing particle size [6–9], coating with electronic conducting agents [10–14], and doping with supervalent ions [15–17].

Recently, we studied the effects of carbon coating, particle size, and morphology, on the rate capability of C-LiFePO₄ synthesized with saturated and unsaturated fatty acid surfactants [18]. We have previously demonstrated that the particle size and the nature of the carbon coating depend on the type of surfactant used. For example, lauric acid, with a shorter carbon chain length (C₁₂H₂₄O₂), is able to effectively arrest particle growth and coat the LiFePO₄ particles

* Corresponding author.

** Corresponding author.

E-mail addresses: nazri@wayne.edu (G.A. Nazri), rnaik@wayne.edu (R. Naik).

uniformly with carbon. This leads to lower charge transfer resistance and enhanced electrochemical performance than that of LiFePO_4 prepared with myristic ($\text{C}_{14}\text{H}_{28}\text{O}_2$) and oleic ($\text{C}_{18}\text{H}_{34}\text{O}_2$) acids. Perhaps, a non-uniform coating and the presence of higher amount of ferric impurity phases account for the poor performance of C- LiFePO_4 cathode materials prepared with myristic and oleic acids. We found C- LiFePO_4 prepared with oleic acid had 17% amorphous ferric iron containing impurity phase that had negative effects on the overall performance of the cathode material. Although we synthesized all the C- LiFePO_4 samples with stoichiometric amounts of precursors, the lithium deficiency, due to heating at 600 °C in the protocol, may have resulted in a higher amount of ferric impurity phase. Our study, therefore, highlighted the importance of controlling the synthesis conditions and the choice of a suitable surfactant for carbon coating. Since the sample C- LiFePO_4 prepared [18] using oleic acid showed a larger amount of the impurity phase, perhaps due to loss of Li, we added extra 5 mol % Li with the expectation that the amount of Li lost due to heat treatment at 600 °C would be compensated for and may ultimately reduce the amount of ferric impurity. Our results show the extra 5 mol % Li not only reduced the amount of ferric impurity phase and the particle size, but also enhanced the electrochemical behavior of the cathode material.

Several studies [19–21] have reported on the impact of excess and deficient lithium in the C- Li_xFePO_4 ($x = 0.7$ to 1.1) system on electrochemical properties compared to those in a stoichiometric system ($x = 1.0$). Most of the studies have attributed the improvement to the reduced particle size in the samples with excess Li, and the lattice defects due to lithium deficiency. The effect of the amount and the nature of the impurity phases in the samples with excess and deficient lithium have not been investigated in detail. The purpose of our study is to investigate the effect of 5 mol% excess Li in C- LiFePO_4 on electrochemical performance, compared to that of C- LiFePO_4 without excess lithium. Here, we report on the preparation and characterization of C- $\text{Li}_{1+x}\text{FePO}_4$ ($x = 0, 0.05$) synthesized by sol gel method. Oleic acid was used as carbon source to enhance the electrical conductivity of the samples. The structural and physical properties of the composites were characterized by x-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). ^{57}Fe Mössbauer spectroscopy was used to identify and quantify the iron containing phases. The impact of excess lithium on electrochemical properties (charge transfer resistance, Li-ion diffusion coefficient, charge/discharge capacity, rate capability and cyclic stability) was determined.

2. Experimental details

2.1. Synthesis

C- LiFePO_4 and C- $\text{Li}_{1.05}\text{FePO}_4$ samples were prepared by sol–gel technique using $\text{CH}_3\text{CO}_2\text{Li} \cdot 2\text{H}_2\text{O}$ (Lithium acetate dihydrate, 99%, Alfa Aesar), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (ferrous chloride, Fisher Scientific), and P_2O_5 (phosphorous pentoxide, Fisher Scientific) as the initial precursors. Solutions of 1 M ferrous chloride and 1 M phosphorus pentoxide were made separately in dry ethanol (200 proof) and mixed together and stirred for three hours. After homogeneous mixing of ferrous chloride and phosphorous pentoxide solutions, in the case of C- LiFePO_4 , 1 M lithium acetate solution in dry ethanol was added to the previous solution under nitrogen environment to allow the sol formation. In the case of C- $\text{Li}_{1.05}\text{FePO}_4$, 1.05 M lithium acetate was added. After three hours of homogeneous mixing of lithium and iron solutions, 0.75 M of oleic acid as carbon source was added and kept for homogeneous mixing for the next three hours for sol formation. All the steps were performed under a nitrogen

atmosphere to prevent oxidation of the iron precursor. The final sol was dried at ~120 °C and annealed under reduced environment of H_2 (10%) and Ar (90%) at 600 °C for 5 h, to obtain a single phase material. This is a modification of synthesis process previously reported by us (18, 22). Carbon content of the samples was determined by CHN elemental analysis where the sample is combusted in a pure oxygen environment; the gases are carried through the system by helium, converted and measured as CO_2 , H_2O and N_2 . The product gases are separated under steady-state conditions and are detected by measuring thermal conductivity. The overall carbon content was found to be approximately 8% in both the samples.

2.2. Characterization

To determine the crystal structure of the materials, XRD patterns were obtained with a Rigaku Miniflex 600 powder diffractometer using Cu $K\alpha$ radiation. The morphologies of the samples were investigated using JSM-6510-LV-LGS SEM and JEOL 2010 TEM instruments.

^{57}Fe Mössbauer spectra were recorded in the transmission geometry using both sides of a (Wissel) transducer coupled to ^{57}Co in Rh matrix source of about 50 mCi and 256 channels of a multi-channel analyzer. The velocity calibration and the linearity verification were performed using a thin iron foil. For Mössbauer measurements, approximately 70 mg of the sample was uniformly dispersed in a Teflon circular cell of 1.7 cm diameter. The isomer shift values are reported with reference to α -Fe foil. The spectra were least square fitted with MossWin program.

The electrochemical properties were measured using a standard CR2032 coin cell geometry with lithium metal as an active anode. The fabrication details of the electrochemical cell are described in our previous report [22]. In brief, the active materials and Super P carbon, as a conducting material, were mixed in 80:20 ratio and ground for 20 min. The homogenous mixture was then put on an aluminum mesh and pressed between two steel cylinders. The aluminum mesh acts as a current collector and the advantage of its use are discussed in our previous study [18]. All cells were assembled in an argon filled glove box.

The cathode was charged and discharged against Li metal electrode that served as a counter electrode separated by Celgard 2400 polymeric separator soaked in a binary electrolyte consisting ethylene carbonate and dimethyl carbonate (50:50) containing 1 M LiPF_6 . Electrochemical impedance measurements were carried out using a Gamry electrochemical measurement system (EIS 300) in the frequency range of 0.1 Hz–100 kHz with AC amplitude of 10 mV. The room temperature cyclic voltammetry (CV) measurements were carried out using a Gamry electrochemical system (PHE 200) in the range of 2.6 V–4.2 V at 0.2, 0.5, 1, 2, and 5 mV s^{-1} scan rates. The galvanostatic charge and discharge measurements were performed at C/3, C/2, 2C and 5C rates in the voltage range of 2.2–4.2 V vs. Li^+/Li electrode.

3. Results and discussion

3.1. XRD measurements

Powder XRD patterns of crystalline C- LiFePO_4 and C- $\text{Li}_{1.05}\text{FePO}_4$ nanocomposites are shown in Fig. 1. For comparison, the bare LiFePO_4 was also prepared and its XRD is also included in Fig. 1. No evidence of crystalline impurities was detected in the three samples. This confirms formation of single phase olivine structure in LiFePO_4 , C- LiFePO_4 and C- $\text{Li}_{1.05}\text{FePO}_4$ composites. The addition of carbon, using oleic acid, has no negative influence on the crystal structure of LiFePO_4 . All the Bragg peaks can be indexed to a pure and well crystallized orthorhombic phase of tryphillite LiFePO_4 with

Download English Version:

<https://daneshyari.com/en/article/1292357>

Download Persian Version:

<https://daneshyari.com/article/1292357>

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