



Magnetic Materials

Elixir Magnetic Materials 50 (2012) 10609-10612

Elixir
ISSN: 2229-712X

Structural and magnetic properties of LiFePO_4 cathode material prepared by polyol technique

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ARTICLE INFO

Article history:

Received: 1 August 2012;

Received in revised form:

31 August 2012;

Accepted: 20 September 2012;

Keywords

Cathode material,
Polyol technique,
Magnetic properties.

ABSTRACT

Nano-crystallite LiFePO_4 cathode material has been prepared by polyol technique. The crystalline structure, functional group vibration analyses of the prepared cathode material were characterized by X-ray diffraction (XRD), Fourier transfer infrared spectroscopy (FT-IR) and Raman Studies. The surface morphology of synthesized material has been studied by scanning electron microscopy (SEM) and the compositional analysis has also been carried out through EDX analysis. It is inferred from XRD result that LiFePO_4 powder have an orthorhombic structure with a space group of Pmna. The magnetic properties of the fine particles of LiFePO_4 were examined by vibrating sample magnetometer (VSM) at room temperature, which showed that the prepared sample exhibited a tiny hysteresis loop with the coercivity of 401.81 G.

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Introduction

Since Goodenough et al. [1] first reported lithium iron phosphate (LiFePO_4) with olivine structure as a new cathode material for rechargeable lithium-ion batteries, LiFePO_4 has become one of the most promising cathode materials for application in electric vehicles (EV) and hybrid electric vehicles (HEVs) because of its high theoretical capacity (170 mAhg^{-1}), safety, environmental benignity and low raw materials cost, which can be fully implemented in practice. It consists of polyoxybionic frame work where LiO_6 , FeO_6 octahedra and PO_4 tetrahedra are present, and Li, Fe and P atoms occupy octahedral 4a, octahedral 4c, and tetrahedral 4c sites, respectively. The strong P–O covalence, stabilizes the anti-bonding $\text{Fe}^{3+}/\text{Fe}^{2+}$ state through the Fe–O–P inductive effect to generate high operating potential (3.4–3.5Vvs.Li/Li⁺). However, one of the main problems of Olivine LiFePO_4 materials lies in its poor rate capability, which is attributed to its low electronic conductivity and slow kinetics of lithium ion diffusion through the LiFePO_4 – FePO_4 interfaces [2]. One of the approach is to improve the intrinsic electronic conductivity by cation doping [3]. The other one is to synthesize LiFePO_4 with small particle size [4, 5] and/or add conductive additives such as carbon [6, 7] and metal powders [8]. The reason is that a small particle size of LiFePO_4 could shorten the diffusion length of lithium ion while the electronic conductive phase coating would increase the surface electronic conductivity.

Based on this concept, currently many of the synthetic routes are both time and energy consuming also need for an inert or reductive atmosphere to enhance crystallinity and avoid the oxidation of Fe^{2+} state. Driven by the energy crisis, researchers presently focused on low-temperature synthesis methods, such as hydrothermal process [9], ionothermal synthesis [10], solvothermal technique [11] and polyol process [12] are low temperature effective method to prepare materials with well-defined morphology, scarcely used in the synthesis of LiFePO_4 particles. Among these, polyol process is a versatile chemical approach, which refers to the use of polyol (for example

ethylene glycol, diethylene glycol and TTEG) to reduce metal salts to metal particles, that has been successfully used to prepare a great variety of inorganic compounds. The polyol medium itself not only acts as a reducing agent and dissolving medium but also as a stabilizer and controls the particles growth [13]. Especially, the polyol process provides a reducing environment, which is extremely advantageous for synthesizing LiFePO_4 , because, it is very difficult to obtain divalent iron containing LiFePO_4 . In this work, the LiFePO_4 powder was prepared by polyol process without post heat treatment. The structure and magnetic properties of the synthesized LiFePO_4 were also investigated in detail in the view point of its crystal structure, functional group vibration, surface morphology, magnetic properties, etc.

Experimental

Synthesis of LiFePO_4

LiFePO_4 material was synthesized via polyol process. Iron (II) sulphate (99.9% of Alfa-Acer) ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), Lithium hydroxide ($\text{LiOH} \cdot 2\text{H}_2\text{O}$) (99.9% of SRL, India) and Ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) (98.9% of Alfa-Acer) were taken in stoichiometric amount, which were dissolved in tetra ethylene glycol (TTEG) and heated in a reflex condenser near to the boiling point of the polyol solvent (320°C) for 12 h. In order to remove the TTEG and partial organic compounds, the resulting solution was washed several times with acetone and ethanol. The resulting particles were separated and dried in a vacuum oven at 150°C for 24 h and finally the LiFePO_4 fine particles were obtained [12].

Characterization of LiFePO_4

The Powder X-ray diffraction (PXRD) patterns of LiFePO_4 samples were obtained using a PANalytical X-pert diffractometer (Netherlands) with a Cu K_α radiation operated at 40 kV and 30 mA. And the radiation of $\lambda = 1.54060 \text{ \AA}$ in the range of 15 – 60° was used to determine the crystal structure of the prepared material. The functional group vibration was analyzed using thermo Nicolet 380 FT-IR spectrophotometer by preparing KBr pellets technique. The surface morphology of the

samples was observed on a scanning electron microscope (SEM) coupled with Energy dispersive X-ray spectra (EDX). Room temperature magnetic measurement was carried out by vibrating sample magnetometer (VSM).

Results and discussion

XRD

Figure.1 shows the XRD pattern of LiFePO_4 sample prepared by polyol process. All the peaks are indexed as an orthorhombic olivine-type structure with a space group of Pmna . All diffraction peaks are strong and narrow, which indicates the high crystallinity of the LiFePO_4 and the lattice parameter is $a=6.021 \text{ \AA}$, $b=10.379 \text{ \AA}$, $c=4.686 \text{ \AA}$ and $V=292.867 \text{ \AA}^3$. From the XRD pattern it is observed that high intensity diffraction peak at the angle of $2\theta=29.6^\circ$ corresponding to the (121)/ (200) crystal plane of the olivine LiFePO_4 cathode material. This implies a preferentially oriented growth of LiFePO_4 cathode material. The average crystallite size of the LiFePO_4 calculated from the Scherrer equation is 40 nm. This is in good agreement with the literature values JCPDS 81-1173 [14].

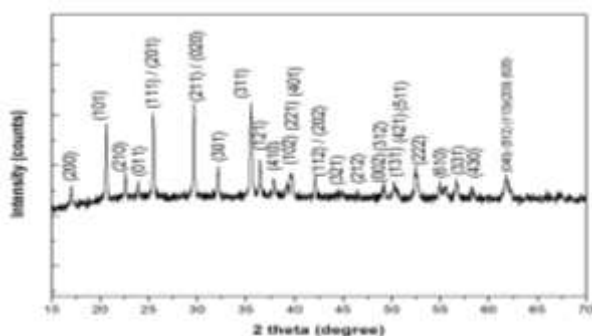


Fig. 1 XRD pattern of LiFePO_4 cathode material prepared by polyol process

FT-IR

The local structure of LiFePO_4 material was studied by FT-IR in the spectral range of $400\text{--}4000 \text{ cm}^{-1}$. Figure 2 (a), shows the FT-IR spectra of the LiFePO_4 sample prepared by polyol process. There are broad bands at $940\text{--}1120$ and $540\text{--}650 \text{ cm}^{-1}$ range, which can be attributed to P-O vibrations of the $(\text{PO}_4)^{3-}$ polyanion respectively. The bending OPO vibrations appear in the region of $450\text{--}600 \text{ cm}^{-1}$. From Fig.2 (a), the band at 1141 cm^{-1} originates from the symmetric and antisymmetric stretching vibrations of O-P-O. The frequency at 579 , 550 , and 467 cm^{-1} originate from antisymmetric and symmetric bending vibrations of O-P-O [15]. A weak IR band at 423 cm^{-1} is attributed to a small amount of Li_3PO_4 [16]. In these observation denoted that more sensitive than PXRD was unable to detect these impurities in the prepared sample. The bands observed at 497 cm^{-1} and 634 cm^{-1} corresponds to intra-molecular antisymmetric and symmetric stretching vibrations of the Fe-O band in FeO_6 unit. The band centered at 1451 cm^{-1} might be identified as the vibration of the P-O-Fe [17]. The bands at $3500\text{--}3200$, $3000\text{--}2800 \text{ cm}^{-1}$ represented the O-H, CH stretching vibration of prepared material and O-H bending vibration observed at 1617 cm^{-1} . The small band observed at 2347 cm^{-1} denoted that the stretching vibration of CO_2 [18]. The FT-IR spectra showed that there is a negligible amount of organic residue and water present in the prepared sample, because of the low temperature (320°C) synthesis. This concludes that the sample has been fired at above 400°C will result the elimination of all organic residue.

Raman Study

Fig. 2 (b) shows the Raman spectra of the LiFePO_4 sample prepared by polyol process without post heat treatment and two

peaks were observed at 1591 and 1365 cm^{-1} . The sharp Raman band at 1591 cm^{-1} is one of the E_{2g} modes (or mode G), which has been assigned to the vibrational mode corresponding to the movement in opposite directions of two neighbouring carbon atoms in a graphene sheet. The 1365 cm^{-1} band is assigned to the D mode which originally is not a Raman-active mode of the graphene sheet. This mode is generally associated with the defects in the curved graphene sheet and staging disorder. The presences of carbon enhance the electronic conductivity of LiFePO_4 [19].

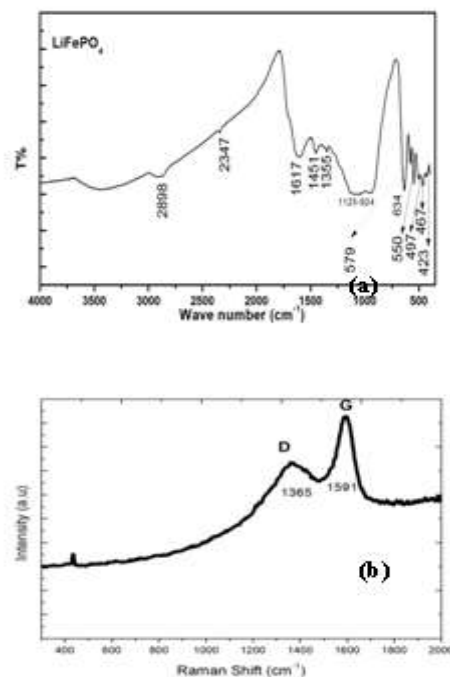


Fig. 2 (a) FT-IR Spectra (b) Raman Spectra of LiFePO_4 cathode material prepared by polyol process

SEM

SEM was used to analyze the particle morphology and size of LiFePO_4 powders, which are shown in Fig.3. From SEM image, two types of particles were observed, some plates and spherical shape. In this reason may be compare with similarly previous reported data like that N. Lyczko et. al [20] observed the SEM image of the lithium precursor alone showed rounded particles; while observation of the iron precursor revealed flat particles. These observations are consistent with the type of particle present in the final product. It is smaller size particles with aggregation were produced at the low temperature method and without annealing process. The SEM observation indicates that the average particle size of the sample prepared by polyol process is about less than 100 nm . From the SEM images it is observed that the agglomeration of particles when refluxing temperature is low. The presence of carbon content is probably ascribed to the glycol solvent acts as a carbon source and adsorption of CO_2 on the sample [21]. The primary particle size is very important vital role of electrochemical performance as well as the electrode process. However, the material with larger primary particles has a relatively lower special capacity because of two reasons. First, larger primary particles perhaps lead to an increase on the diffusive path of Li^+ and electrons. Secondly, it is difficult for the material with larger primary particles to adequately absorb electrolytes. While this reason, the aim of preparing the nano crystalline sized LiFePO_4 material with low temperature is fulfilled.

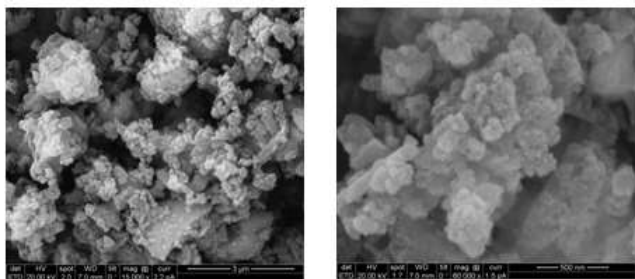


Fig. 3 SEM image of LiFePO_4 cathode material prepared by polyol process

EDX

An Energy dispersive X-ray (EDX) analysis was carried out to identify the elemental atoms presents. The result of obtained sample is presented in Figure 4. The EDX analysis of LiFePO_4 showed the atomic percentage of C, O, P and Fe range is 67.10, 23.01, 4.83 and 5.06% respectively. From this analysis, calculated the ratio of the elemental atoms and found Fe/P is equal to 1 and O/Fe or O/P equal to 4. This is confirmed the LiFePO_4 formation. This results good agree with reported data [20]. From the EDX analysis Li element can't be found in the spectrum because it is a light element.

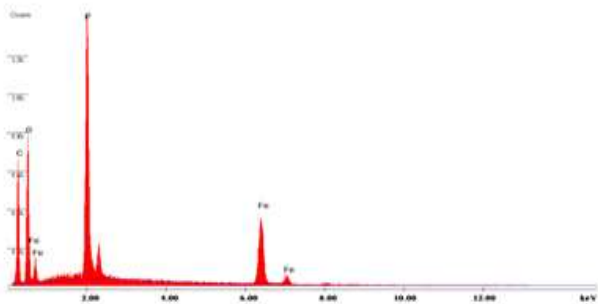


Fig. 4 EDX Spectra of LiFePO_4 cathode material prepared by polyol process

Magnetic properties

The specific magnetization curves of LiFePO_4 cathode powder obtained from room-temperature magnetic measurement using VSM is shown in Fig.5. From the Figure is designate that ferromagnetic material characteristics involved that the prepared LiFePO_4 using three sources of raw materials. From M-H curve of LiFePO_4 was refluxed at 320°C without annealing process. From the observed data the prepared material with a significant remanence, indicating a characteristic of antiferromagnetic behaviour and the observed values of the coercivity force and retentivity are 401.81 G and $30.366 \times 10^{-3} \text{ emu/g}$ respectively. The magnetization M –H of the prepared sample is linear in the magnetic field up to H 20 kOe at room temperature, so that the material is free from the $\gamma\text{-Fe}_2\text{O}_3$ and Fe_2P impurity phases [22, 23].

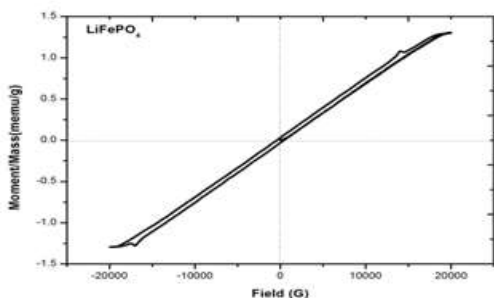


Fig. 5 Magnetic study of LiFePO_4 cathode material prepared by polyol process using VSM

Conclusions

Nano-crystallite LiFePO_4 particles were prepared by polyol technique without any post heat treatment steps under air atmospheres. The XRD pattern was indexed on orthorhombic olivine structure type with space group of Pmna. From the FT-IR spectra has been analysed small amount of Li_3PO_4 impurity and also identified the Lithium iron orthophosphate $(\text{PO}_4)^{3-}$ group. The prepared particles were observed of various shapes like plate and spherical with an average size of 100 nm. Raman spectra and EDX spectra has been demonstrated the carbon content. The magnetic measurements shows that the evidence of ferromagnetic behaviour without magnetic impurities of LiFePO_4 at room temperature. Furthermore, the polyol technique is less energy, low cost precursor, significantly less expensive and easier to carry out.

Acknowledgements

The authors M.Sivakumar and R.Muruganantham gratefully acknowledge for the financial support for this work by Department of Science and Technology (DST), New Delhi, Govt. of India under DST-SERC major research project (SR/S2/CMP-0049/2008).

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