

Electrochemical performance of Yb-doped LiFePO_4/C composites as cathode materials for lithium-ion batteries

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Abstract LiFePO_4/C and $\text{LiYb}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ composite cathode materials were synthesized by simple solution technique. The samples were characterized by X-ray diffraction, scanning electron microscope, and thermogravimetric–differential thermal analysis. Their electrochemical properties were investigated by cyclic voltammetry, four-point probe conductivity measurements, and galvanostatic charge and discharge tests. The carbon-coated and Yb^{3+} -doped LiFePO_4 sample exhibited an enhanced electronic conductivity of $1.9 \times 10^{-3} \text{ Scm}^{-1}$, and a specific discharge capacity of 146 mAhg^{-1} at 0.1 C. The results suggest that the improvement of the electrochemical performance can be attributed to the ytterbium doping, which facilitates the phase transformation between triphylite and heterosite during cycling, and the conductivity improvement by carbon coating.

Keywords Ytterbium · Cathode material · Lithium-ion batteries · LiFePO_4

Introduction

The mineral triphylite, having the formula of LiFePO_4 and showing an ordered olivine structure is believed to be one of the most promising replacements of the cathode materials currently being used, such as LiCoO_2 and LiMn_2O_4 [1]. Goodenough and co-workers first reported olivin-type LiFePO_4 cathode material in 1997 [2]. This material has the advantages of being nontoxic, inexpensive, and environmentally friendly [3–5]. Moreover, it has an interesting theoretical specific capacity of about 170 mAh g^{-1} , a good cycling stability, and a technically attractive flat voltage versus current profile of 3.45 V versus Li/Li, due to the two-

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phase extraction–insertion reaction. This reaction mechanism makes the theoretical capacity difficult to reach; the area of the interface between the LiFePO_4 – FePO_4 phases, where the insertion or deinsertion of Li ions takes place, is limited. Furthermore, the FePO_4 produced has a very low conductivity [6–8]. The low electronic conductivity and low lithium-ion diffusivity of LiFePO_4 restrict its commercial applications.

Various synthesis and processing approaches have been employed to overcome this problem. Initially, additives were introduced to synthesize LiFePO_4 /conductive material composites, such as dispersed carbon [9–14], metal powders [15, 16], and intrinsically conducting polymers [17]. However, the results have shown improvements on bulk conductivity without changes on any LiFePO_4 lattice parameters. Another method used was doping, where Li ions (on the M1 site) and/or Fe ions (on the M2 site) were substituted. It was reported that low-level doping of LiFePO_4 by a range of supervalent ions (e.g., Mg^{2+} , Al^{3+} , Ti^{4+} , Zr^{4+} , Nb^{5+}) increases the electronic conductivity to values greater than 10^{-2} Scm^{-1} at room temperature [18]. In addition, investigations of doping of other heteroatoms indicate that the electrochemical properties of LiFePO_4 could be improved by this modification [19–23].

Among these methods, expensive Fe^{2+} salts were often employed as the precursors, which increases the cost of the LiFePO_4 . For large-scale industrialization, inexpensive Fe^{3+} salts as raw materials and noncomplex craft should be proposed to prepare LiFePO_4 [24]. In this paper, we present a simple method for preparing LiFePO_4/C using cheap $\text{Fe}(\text{NO}_3)_3$ instead of Fe^{2+} salts as the iron source, and polyethylene glycol (PEG), a high temperature reducer and a carbon source. In this study, the synthesis and characterization of ytterbium-doped $\text{LiYb}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ cathode material and the improved electrochemical performances will be demonstrated.

Experimental

Virginal and 2 % doped $\text{LiYb}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ samples were prepared via a simple solution method using analytical grade reagents as starting materials. The stoichiometric amounts of $\text{Fe}(\text{NO}_3)_3 \times 9\text{H}_2\text{O}$ (Merck 98 %), $\text{NH}_4\text{H}_2\text{PO}_4$ (Merck 98 %) and LiNO_3 (Riedel-de Haen 95) were dissolved in distilled water. For the doped sample, the stoichiometric amounts of Yb_2O_3 solution in HNO_3 were added to the bare solution. This mixture was stirred slowly until a clear solution formed, followed by heating at 80 °C for 4 h with constant agitation to form a homogeneous suspension. Then, the gel was heated at 300 °C in air for 3 h to remove the water and for decomposition of nitrate in the absence of reductive atmosphere.

The precursor powder was ground and an adequate amount of polyethylene glycol (PEG; mean molecular weight 40,000) was added into the obtained powder as a reducing agent and carbon source. Finally, the resulting slurry was heated in a tube furnace at 700 °C for 10 h under argon gas flow. During the final heating of the PEG-contained precursor, Fe^{3+} was reduced to Fe^{2+} with the help of hydrogen and carbon as the reducing agent. These were generated from the decomposition of PEG, which produces a strong reductive atmosphere. As a result of this process, the LiFePO_4/C and $\text{LiYb}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ samples were synthesized.

The crystallographic structure of the samples was characterized by an X-ray diffractometer (Bruker). The diffraction data were collected for 2 s at each 0.02° step width over a 2θ range from 10 to 60° . The Diffrac Plus and Win-Metric programs were used to obtain information about the crystal structures and lattice parameters of the prepared samples.

Thermogravimetric (TG) analysis of the samples were studied on a Perkin-Elmer Diamond model thermal analysis apparatus with a heating rate of $10^\circ\text{C min}^{-1}$ from ambient to 800°C in an argon flow. The morphologies of the powders were observed using a scanning electron microscopy (LEO), operated at 20 kV . In order to measure the electronic conductivity, the powder was pressed into disc-shaped pellets at a pressure of 5 tons. Conductivity was measured by the four-point probe method, using an Iceblue Instrument (Kayseri, Turkey). The amount of carbon in the lithium iron phosphate was determined from the difference of weight loss t by heating at 700°C for 2 h in air [25].

The electrochemical studies were carried out in two-electrode Teflon cells. The cells were fabricated by using the LiFePO_4/C as a cathode and lithium foil as an anode. A glassfiber separator soaked in electrolyte separated the two electrodes. The electrolyte consisted of 1 M solution of LiClO_4 dissolved in a ethylene carbonate/diethyl carbonate (EC/DEC; 1:1 ratio by volume). For the preparation of the cathode composite, a slurry mixed with 80 wt% of cathode active material, 15 wt% of carbon additive (including carbon black and carbon converted from PEG) and 5 wt% of polyvinylidene fluoride binder in 1-methyl-2-pyrrolidinone (NMP) was pasted on the aluminium foil current collector with a diameter of 13 mm, followed by vacuum drying at 120°C overnight in a vacuum oven and uniaxial pressing between two flat plates at 2 tons for 5 min. The electrode loading was about 5–7 mg of the cathode active material. The test cell performance was measured on a computer-controlled multichannel charge/discharge apparatus (MLab100, Wenking). All cells were assembled in an argon-filled dry glove box and tested at room temperature. The cell was cycled galvanostatically between 2.1 and 4.3 V at different current density (0.1–2 C). Cyclic voltammetry measurements were performed using an MLab100 Instrument at a scan rate of 0.01 mVs^{-1} between 2.2 and 4.4 V.

Results and discussions

Figure 1 shows the XRD patterns of the LiFePO_4/C and $\text{LiYb}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ compounds. Both samples exhibited a single phase of LiFePO_4 with an ordered olivine structure indexed to the orthorhombic Pnma space group. The obtained lattice parameters agreed well with those reported in the literature (JCPDS card no. 81–1,173). The detailed cell parameters of LiFePO_4/C and $\text{LiYb}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ composites were calculated and are listed in Table 1. No impurity phase has been detected, which indicates that the 2 % doping could not destroy the lattice structure. Also, there is no obvious diffraction response of the carbon because of its low content or amorphous state. The results obtained from combustion analysis (700°C) showed that the amount of carbon in both LiFePO_4/C and $\text{LiYb}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ was

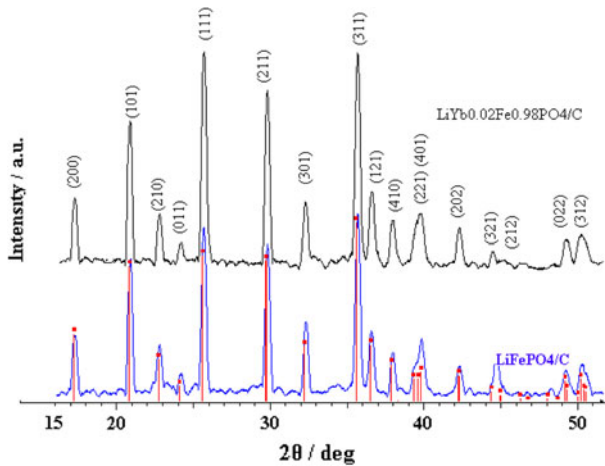


Fig. 1 XRD patterns of LiFePO_4/C and $\text{LiYb}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ samples

3 wt%. This residual carbon was uniformly dispersed in the compound, which improved the electroconductivity of the sample $2.7 \times 10^{-2} \text{ Scm}^{-1}$ presented in Table 1. According to the lattice parameters, the values of c are less affected than that of a and b . It has been reported that the lithium-ion intercalation–deintercalation proceeds through one-dimensional pathways along the c -axis [26].

The electrochemical performance of the electrode is greatly influenced by the particle size and the morphology of the particles [27]. The scanning electron microscopy (SEM) images of the LiFePO_4/C and $\text{LiYb}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ composites are shown in Fig. 2. It can be seen from Fig. 2 that the particle size of Yb-doped LiFePO_4/C was smaller than bare LiFePO_4/C . In general, the Yb-doped LiFePO_4 powder shown less agglomeration and the scatter was more uniform than the undoped one. It seems that the Yb ions in the solution prevent particles from conglomerating and form secondary particles during calcinations, which may be conducive to shorten the lithium diffusion distance.

The DTA/TG result of LiFePO_4/C is shown in Fig. 3. The weight loss at temperatures between 50 and 150 °C corresponding to the endothermic peak is due to water vaporization and carbonization of PEG, respectively. The weight loss in the next step at temperatures between 150 and 240 °C resulted from the decomposition of nitrates in the precursor. The residual organic materials of PEG were also decomposed and carbonized below 380 °C. A corresponding exothermic peak associated with the crystallization of LiFePO_4 was observed at around 460 °C. Therefore, the LiFePO_4 precursor was calcined above 500 °C to obtain the crystallized phase [28]. In order to

Table 1 Crystal parameters and electronic conductivity of prepared samples

Samples	$a(\text{Å})$	$b(\text{Å})$	$c(\text{Å})$	Volume (Å^3)	σ (S cm^{-1})
LiFePO_4/C	10.3166	5.5975	4.6914	290.27	1×10^{-4}
$\text{LiYb}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$	10.3236	6.0044	4.6920	290.98	2.7×10^{-2}

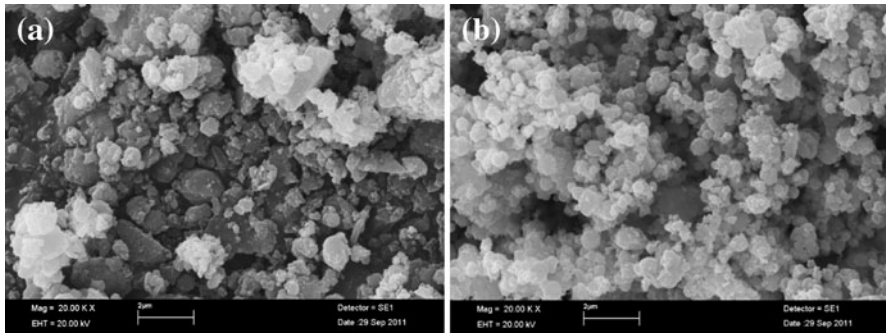


Fig. 2 Scanning electron micrographs of LiFePO_4/C (a) and $\text{LiYb}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ (b) samples

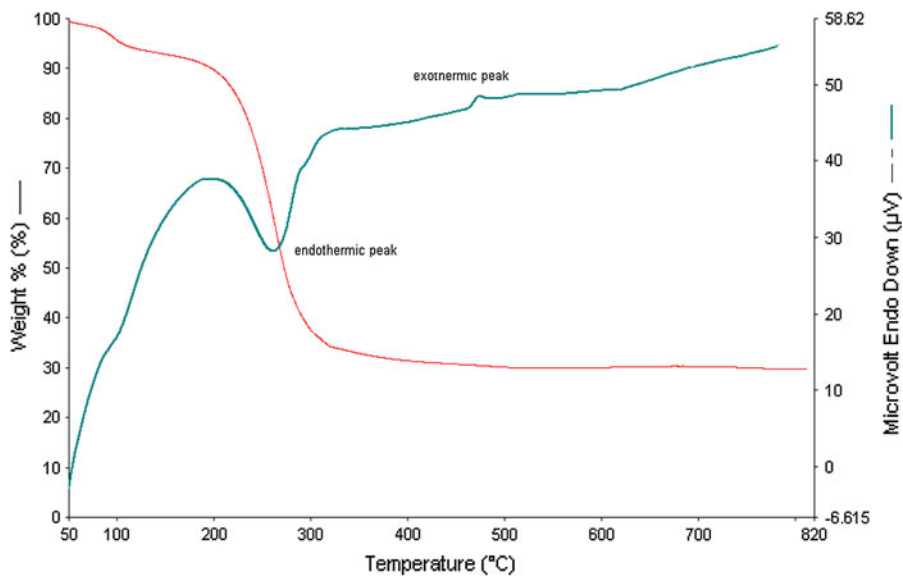


Fig. 3 The DTA/TGA curve for LiFePO_4/C over the temperature range from ambient to 800°C at a heating rate of $10^\circ\text{C min}^{-1}$ in argon atmosphere at 200 ml min^{-1} flow rate

gain a further insight into the effect of doping on the electrochemical performance of LiFePO_4/C , cyclic voltammetry was carried out. The CV curves of LiFePO_4/C and $\text{LiYb}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ samples were shown in Fig. 4. It can be seen from Fig. 4 that the two samples have similar redox peaks. The redox peaks of $\text{LiYb}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ and LiFePO_4/C were centered at 3.55/3.35 and 3.65/3.28 V, respectively. Apparently, the peak separation of $\text{LiYb}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ was narrower and the peak shape was sharper than that of LiFePO_4/C . These results may demonstrate that lithium insertion and extraction readily occurred in the $\text{LiYb}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ material [29].

The charge/discharge capacity of both LiFePO_4/C was tested at 0.1 C in the voltage range between 2.2 and 4.2 V. Figure 5 shows the charge/discharge curves with a flat voltage plateau at around 3.4 V. This demonstrates that the two-phase

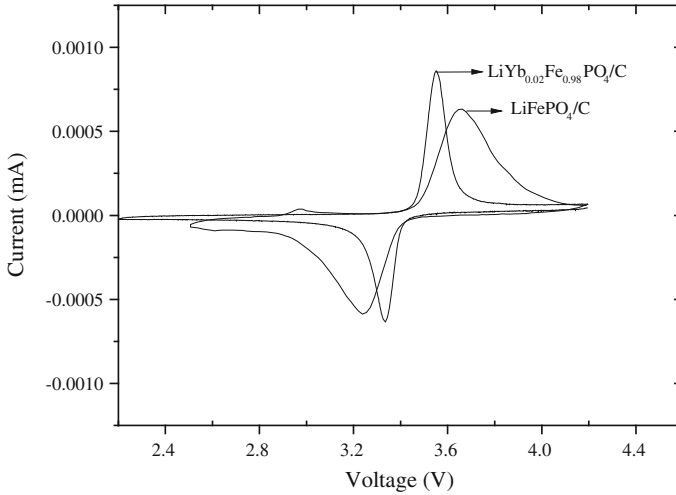


Fig. 4 The first cyclic voltammetry profiles of LiFePO_4/C and $\text{LiYb}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ samples

redox reaction occurs via a first-order transition between FePO_4 and LiFePO_4 [30]. A reversible capacity of about 146 mAh/g was obtained for the $\text{LiYb}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ carbon composite, which is higher than the capacity of undoped LiFePO_4/C . The capacity of undoped LiFePO_4/C , on the other hand, was observed as 136 mAh/g for the same condition. The higher discharge capacity for sample $\text{LiYb}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ was explained in terms of particle size, [31, 32] and the lowest electrochemical polarization of Yb-doped LiFePO_4/C which may suggest that the increased conductivity ($1.9 \times 10^{-2} \text{ Scm}^{-1}$) is induced by the doping and carbon coating [33].

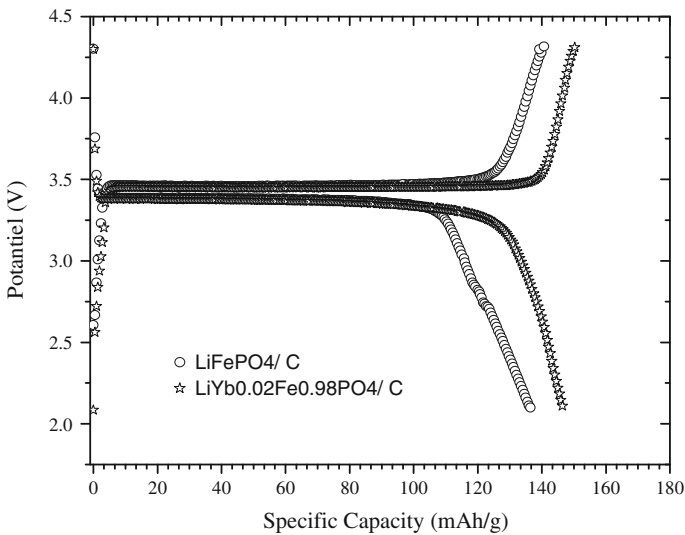


Fig. 5 Initial charge and discharge curves of LiFePO_4/C and $\text{LiYb}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ samples

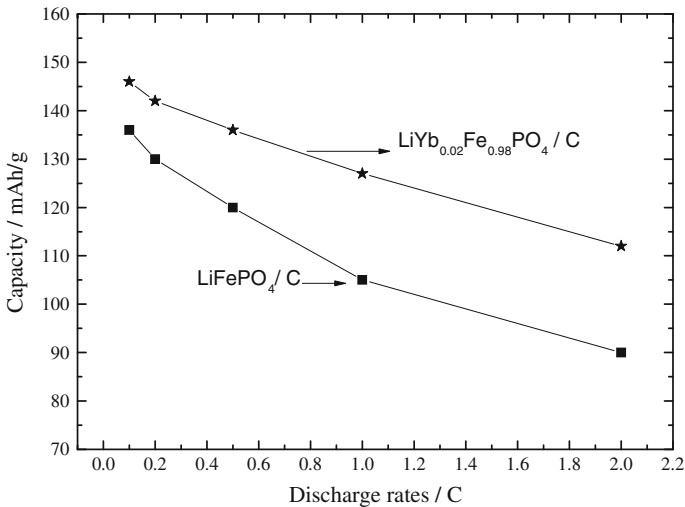


Fig. 6 Relationship between capacity and discharge rate of the LiFePO₄/C and LiYb_{0.02}Fe_{0.98}PO₄/C samples

Rate capabilities of both bare and Yb-doped LiFePO₄/C at different C rates were given in Fig. 6. The capacity of the Yb-doped LiFePO₄/C was larger than that of the bare LiFePO₄/C in all current densities. Also, the rate capability results were much better than those of the Yb-doped LiYb_{0.02}Fe_{0.98}PO₄/C. The capacity drop with an increase in the current density from 0.1 to 1 C was 14 % for the ytterbium doping and 24 % for the undoped LiFePO₄/C. Therefore, it seems that the ytterbium doping can be a powerful method to enhance the conductivity and preserve the capacity even at the high current densities.

Conclusion

Phase-pure, olivine LiFePO₄/C and ytterbium-doped LiYb_{0.02}Fe_{0.98}PO₄/C materials with carbon contents of 3 wt% have been synthesized by a simple and cheap solution method using PEG as the carbon source. The cell performance was improved and the initial capacity of LiYb_{0.02}Fe_{0.98}PO₄/C was 146 mAhg⁻¹ obtained at 0.1 C. As a result, ytterbium doping is very promising for the improvement of the electrochemical performance of LiFePO₄. Both discharge capacity and rate capability are well ameliorated.

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