



Doping supervalent rare earth ion in LiFePO_4/C through hydrothermal method

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ABSTRACT

Hydrothermal synthesized LiFePO_4/C and $\text{LiFe}_{0.95}\text{M}_{0.05}\text{PO}_4/\text{C}$ ($\text{M} = \text{Sm, Eu, Yb}$) are studied in this paper. The samples are characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive spectroscopy (EDS), thermogravimetric analysis and Brunauer–Emmett–Teller (BET). The electrochemical performance is evaluated via galvanostatic charge–discharge, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). The hydrothermal synthesized particles are nano scale level. The results show that the first discharge capacity of the as-prepared LiFePO_4/C and $\text{LiFe}_{0.95}\text{M}_{0.05}\text{PO}_4/\text{C}$ ($\text{M} = \text{Sm, Eu, Yb}$) is 109.4 mAh/g, 153.6 mAh/g, 144.0 mAh/g and 160.7 mAh/g at 0.2 C, respectively, and reduces to 65.1 mAh/g, 147.7 mAh/g, 141.3 mAh/g and 152.6 mAh/g after 20 cycles, respectively. The specific surface area of LiFePO_4/C and $\text{LiFe}_{0.95}\text{M}_{0.05}\text{PO}_4/\text{C}$ ($\text{M} = \text{Sm, Eu, Yb}$) is 18.3 m²/g, 25.2 m²/g, 21.5 m²/g and 25.4 m²/g, respectively. The exchange current density for $\text{LiFe}_{0.95}\text{M}_{0.05}\text{PO}_4/\text{C}$ ($\text{M} = \text{Sm, Eu, Yb}$) composite is 121 mA·g⁻¹, 89.8 mA·g⁻¹, 138.8 mA·g⁻¹, respectively, which is much larger than that for LiFePO_4/C , 12.5 mA·g⁻¹. The result of cyclic voltammetry indicates that the difference between anode peak potential and cathode peak potential reduces and the reversibility of electrochemical reaction is enhanced at doped electrode materials. The electrochemical performances are apparently improved due to doping supervalent rare earth ion in LiFePO_4/C .

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1. Introduction

Lithium battery plays a very important role in power system, especially in electric vehicle (EV) and hybrid electric vehicle (HEV) application [1,2]. The olivine structure LiFePO_4 is considered to be one of the most promising battery cathode materials [3,4]. It is expected that LiFePO_4 could replace the commercial LiCoO_2 as it has many advantages, such as low cost, low toxicity, high specific capacity and environmentally friendly [5,6]. Sylvain Franger investigated the influences of different synthesis routes on physico-chemical properties of LiFePO_4 [6]. Jaewon Lee synthesized LiFePO_4 micro and nanoparticles in supercritical water and found that temperature and pH of the solution affected the size and morphology of LiFePO_4 particles [7]. One of the most effective strategies to improve the electrochemical performance for Li-ion batteries is to control the dimensions in the nanometer scale of olivine-type LiFePO_4 [8].

Since the pioneering work of Padhi and co-workers in 1997 [9], many researchers have studied the synthesis methods of LiFePO_4 . The preparation method which controls the particle size and morphology of the cathode material is very critical to the material performances [10]. It is well known that solid-phase reaction is the traditional method for synthesizing LiFePO_4 while hydrothermal route is attracting more attention [10,11]. Hydrothermal synthesis as a soft chemical approach

expands short processing time and low energy, adopts simple instrument and makes the particle of target sample fine [3,9]. Jiajun Chen stated that the metal disorder increased at lower synthesis temperature, but decreased to nearly zero above 175 °C [10].

Though LiFePO_4 is famous for its safety, stable voltage platform, low toxicity and long cycle life, the intrinsic disadvantages of poor electronic conductivity and slow diffusion coefficient of lithium ion limit its application [12]. Carbon coating and doping some ion are primary approaches to solve the problems [13,14]. Especially, the addition of graphene to LiFePO_4 significantly improves the capacity and capacity retention of LiFePO_4 as a cathode material for Li-ion batteries [15]. The carbon coating can not only enhance its electronic conductivity, but meanwhile, the carbon can also protect Fe^{2+} from oxidizing to Fe^{3+} during the synthesis process. LiFePO_4/C composite has been a popular issue for many researchers [16].

Doping ion, especially doping supervalent ion, can improve the chemical activity obviously, and the effect of doping on electrochemical performances is very significant, and Sharma N has proved the existence state of doped ion within LiFePO_4 [17]. Jiezi Hu, Xian Zhao and Guo-rong synthesized $\text{Li}(\text{M, Fe})\text{PO}_4$ ($\text{M} = \text{La, Ce, Nd, Mn, Co, Ti}$) and $\text{Li}_{1-4x}\text{Ti}_x\text{FePO}_4/\text{C}$ through solid-phase reaction, respectively [12,18,19]. However, few people investigated the effect of doping rare earth element Sm, Eu, Yb via solid-phase reaction on the LiFePO_4 exception of

the papers published by our research group [20,21]. Recently Hüseyin Göktepe synthesized Yb-doped LiFePO_4/C composite by solution method, but the specific discharge capacity of 146 mAh/g at 0.1 C is too low [22]. In this paper, we have synthesized $\text{LiFe}_{0.95}\text{M}_{0.05}\text{PO}_4/\text{C}$ ($\text{M} = \text{Sm}, \text{Eu}, \text{Yb}$) by hydrothermal route, and their structure and electrochemical performance have been characterized in detail.

2. Experimental

$\text{LiFe}_{0.95}\text{M}_{0.05}\text{PO}_4/\text{C}$ ($\text{M} = \text{Sm}, \text{Eu}, \text{Yb}$) were synthesized from LiOH , H_3PO_4 , $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_2$, $\text{M}(\text{C}_2\text{H}_3\text{O}_2)_3$ ($\text{M} = \text{Sm}, \text{Eu}, \text{Yb}$) with the molar ratio of 3:1:0.95:0.05 through hydrothermal route at 190 °C for 6 h. In order to avoid Fe^{2+} oxidizing to Fe^{3+} , ascorbic acid was added into the reacting solution during the hydrothermal process. The resultant precipitate was washed with deionized water and filtered, and dried in the vacuum oven at 80 °C for 10 h. Then the hydrothermal product with the addition of 10 wt% glucose was calcined at 600 °C for 3 h under N_2 gas atmosphere. Finally, the LiFePO_4/C and $\text{LiFe}_{0.95}\text{M}_{0.05}\text{PO}_4/\text{C}$ ($\text{M} = \text{Sm}, \text{Eu}, \text{Yb}$) samples were synthesized.

The thermochemical behavior of sample was analyzed using Thermogravimetric apparatus (Pyris Diamond, PerkinElmer Thermal Analysis) under nitrogen gas flow. The sample was heated from ambient temperature to 800 °C at the rate of 10 °C min^{-1} . The crystallographic structure of the sample was characterized by powder X-ray diffractometer on a Rigaku D/max-2500/pc. The morphology of the sample was observed with a field-emission scanning electron microscope (FE-SEM) on S-4800 FE-SEM. The specific surface area of the sample was analyzed by Brunauer–Emmett–Teller (BET) (Micromeritics ASAP2010 specific surface area) instrument.

The charge–discharge tests of as-synthesized samples were carried on in a half cell in which lithium metal piece was used as the anode. The cathode was composed of 80 wt% active material, 15 wt% acetylene black and 5 wt% polyvinylidene fluoride (PVDF) binder in N-methylpyrrolidone (NMP) solvent to form a uniform slurry. The slurry was coated on Al foil and cut into square shape (8 × 8 mm). The mass of active material was about 1.5 mg/cm^2 . The foil dried in a vacuum oven at 120 °C for 12 h. The cell was assembled in the glove box filled up with argon gas of high purity. The electrolyte was 1 M $\text{LiPF}_6/\text{EC} + \text{DEC}$ (1:1, v/v). The cell was tested on the charge–discharge equipment over the voltage range 2.5–4.3 V at room temperature. Electrochemical impedance was tested on electrochemical workstation CHI660A. The sinusoidal excitation voltage applied to the cells was 0.5 mV and frequency range was between 0.01 Hz and 100 kHz. Cyclic Voltammetry (CV) was conducted by electrochemical workstation LK2005A at a scanning rate of 0.5 mVs^{-1} and the potential span from 2.3 V to 4.2 V.

3. Result and discussion

Fig. 1 shows the TG-DTA (Thermogravimetric Analysis and Differential Thermal Analysis) curves of $\text{LiFePO}_4/\text{glucose}$ before heat treatment. The weight loss under 100 °C corresponds to water absorbed in the sample. The weight loss during 100–250 °C results from the decomposition of the remaining organics, corresponding to the exothermic peaks at 154 and 214 °C. The weight loss above 250 °C is related to volatilization of glucose. The DTA curve shows a small endothermic peak at 521.5 °C, which is related to transformation of crystalline material [23]. The TG curve almost keeps a constant value above 600 °C till 800 °C. Therefore, the calcined temperature should be higher than 520 °C.

Fig. 2 shows the XRD patterns of the LiFePO_4/C and $\text{LiFe}_{0.95}\text{M}_{0.05}\text{PO}_4/\text{C}$ ($\text{M} = \text{Sm}, \text{Eu}, \text{Yb}$) compounds. As shown in the Fig. 2, the dominant diffraction peaks can be indexed as the orthorhombic LiFePO_4 phase with space group $Pmnb$ (62). The XRD result suggests that LiFePO_4/C and $\text{LiFe}_{0.95}\text{M}_{0.05}\text{PO}_4/\text{C}$ ($\text{M} = \text{Sm}, \text{Eu}, \text{Yb}$) composites are well-crystallized and agree well with the olivine structure. There is no impurity phase to

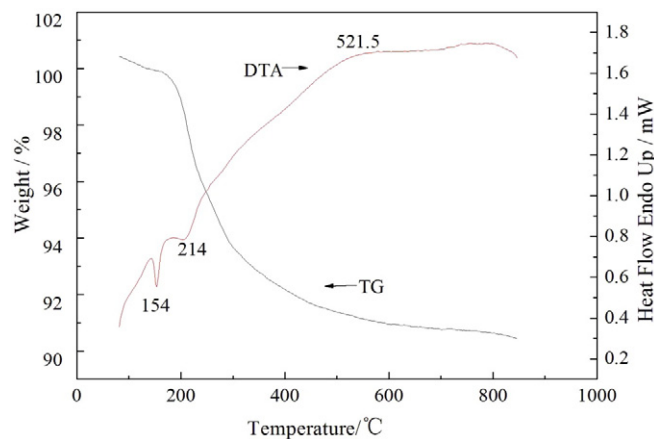


Fig. 1. TG-DTA curves of $\text{LiFePO}_4/\text{glucose}$ before heat treatment.

be detected in the as-prepared samples. It has implied that doping rare earth ion in LiFePO_4 does not change the lattice structure of LiFePO_4 synthesized via hydrothermal route. Moreover, there is no obvious diffraction response of carbon because of its low content and amorphous state.

However, doping rare earth ion affects the intensity ratio of $I(200)/I(020)$. The doped composites particles prepared via hydrothermal route have a random crystal orientation. The intensity of (020) plane seemingly becomes weaker and the intensity ratio of $I(200)/I(020)$ becomes larger with doping rare earth ion. The phenomenon mentioned above may be related to the fact that a part of rare earth ions occupies Fe site (M_2) into LiFePO_4/C , the rest would form solid solution with LiFePO_4 [17].

SEM images of LiFePO_4/C and $\text{LiFe}_{0.95}\text{M}_{0.05}\text{PO}_4/\text{C}$ ($\text{M} = \text{Sm}, \text{Eu}, \text{Yb}$) composites are shown in Fig. 3. The stick-shaped particles with about dimension 490 nm × 150 nm are smaller than particles with μm level scale produced by conventional solid-phase method. The doping rare earth ion into the LiFePO_4/C doesn't make its particle fine further. Actually, doping supervalent rare earth ion would create some defect, leading to the improvement of the electrochemical performance of LiFePO_4/C [24]. Another important feature of the SEM is that some particles of 10–30 nano scale level adhere to the surface of doped particles.

EDS image showed in the Fig. 4 indicates that the rare earth element has been doped in LiFePO_4/C . Wagemaker [24] reported that low levels of dopants were indeed soluble in the olivine lattice up to the extent of 3 mol%. According to the EDS we have reason to infer that the supervalent ions have occupied Fe^{2+} site in the LiFePO_4/C or have been dissolved into LiFePO_4/C to form solid solution [17].

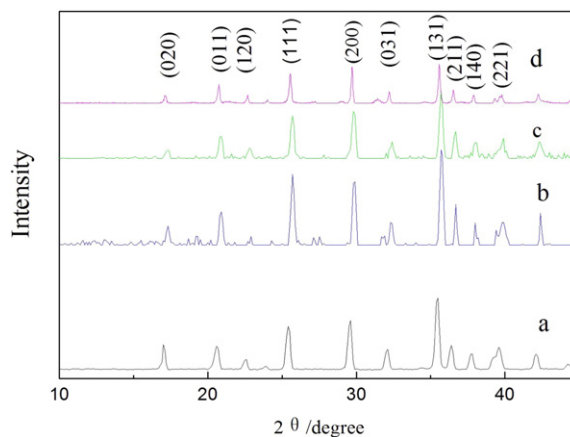


Fig. 2. XRD pattern for LiFePO_4/C and $\text{LiFe}_{0.95}\text{M}_{0.05}\text{PO}_4/\text{C}$ ($\text{M} = \text{Sm}, \text{Eu}, \text{Yb}$) composite. a LiFePO_4/C b $\text{LiFe}_{0.95}\text{Sm}_{0.05}\text{PO}_4/\text{C}$ c $\text{LiFe}_{0.95}\text{Eu}_{0.05}\text{PO}_4/\text{C}$ d $\text{LiFe}_{0.95}\text{Yb}_{0.05}\text{PO}_4/\text{C}$.

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