



# Electrochemical properties of V and Ti co-doping $\text{Li}_{1.02}\text{FePO}_4/\text{C}$ material prepared by solid-state synthesis route



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## ABSTRACT

V and Ti co-doping  $\text{Li}_{1.02}\text{Fe}_{1-2x}\text{V}_x\text{Ti}_x\text{PO}_4/\text{C}$  ( $X = 0.00, 0.01, 0.03, 0.05$ ) composites were synthesized via a simple high-temperature solid-state method using phloroglucinol as carbon sources. The  $\text{Li}_{1.02}\text{Fe}_{1-2x}\text{V}_x\text{Ti}_x\text{PO}_4/\text{C}$  materials were characterized by a variety of means, such as powder X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), galvanostatic charge–discharge test, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The results showed that the V and Ti co-doping samples didn't change the olivine structure of  $\text{LiFePO}_4$  and there was a carbon coating layer on the surface of the  $\text{Li}_{1.02}\text{Fe}_{1-2x}\text{V}_x\text{Ti}_x\text{PO}_4/\text{C}$  material. The adding of phloroglucinol as carbon source could increase the electrical conductivity and thus improve the electrochemical performance of  $\text{Li}_{1.02}\text{Fe}_{1-2x}\text{V}_x\text{Ti}_x\text{PO}_4/\text{C}$ . The co-doping of V and Ti ions could optimize the crystal microstructure, thereby decreasing the  $\text{Li}^+$  diffusion resistance and increasing the exchange current density, which could improve the electrochemical performance of  $\text{Li}_{1.02}\text{Fe}_{1-2x}\text{V}_x\text{Ti}_x\text{PO}_4/\text{C}$  material. The optimized  $\text{Li}_{1.02}\text{Fe}_{0.94}\text{V}_{0.03}\text{Ti}_{0.03}\text{PO}_4/\text{C}$  sample exhibited the superior electrochemical performance. The initial discharge capacities of  $\text{Li}_{1.02}\text{Fe}_{0.94}\text{V}_{0.03}\text{Ti}_{0.03}\text{PO}_4/\text{C}$  were 165 mA h/g, 164.5 mA h/g, 158 mA h/g and 154 mA h/g at 0.1C, 0.2C, 0.5C and 1C rate respectively. Meanwhile the  $\text{Li}_{1.02}\text{Fe}_{0.94}\text{V}_{0.03}\text{Ti}_{0.03}\text{PO}_4/\text{C}$  sample keeps 99% discharge capacity after 100 cycles.

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## 1. Introduction

Lithium-ion batteries have been playing an important role in many applications such as digital products, electric vehicles, hybrid electric vehicles and energy storage systems [1,2]. As an important part of the lithium-ion batteries, cathode material has been developed rapidly in recent years. Olivine-structured  $\text{LiFePO}_4$  as one of the most promising cathode materials for lithium-ion batteries has attracted tremendous interests [3–7].  $\text{LiFePO}_4$  as cathode material has many advantages such as low cost, high security, excellent cycle life, high thermal stability [8–10]. Nevertheless it should be noted that there are two inherent weak points of  $\text{LiFePO}_4$ : poor electronic conductivity and lower Li-ion diffusivity [11].

In order to overcome these demerits, different fabrication

approaches have been put forward by researchers. Carbon coating as one of the effective approach has been used to improve the electronic conductivity and Li-ion diffusivity of  $\text{LiFePO}_4$  [12–16]. As carbon coating could stop the growth of the crystal particles and improve the electronic conductivities, thus many chemical compounds have been used to carbon coating, such as glucose, sucrose, citric acid etc. Moreover cation doping was also an effective method to modify the property of  $\text{LiFePO}_4$ , which could control the particle size of  $\text{LiFePO}_4$  and make the particle size homogeneous without agglomeration [17,18]. As high metal ions could enter into the crystal lattice of  $\text{LiFePO}_4$  and increase the cationic vacancy defects, thus the performance of  $\text{LiFePO}_4$  material was improved. Wang and Jiao [19] have synthesized  $\text{LiFePO}_4$  with rare earth ions doping via a solid-state reaction method. The results exhibited that the specific discharge capacities of the material doped with 1%  $\text{Ce}^{3+}$  could reach 128.9 mA h/g at 1C. Cao and Luo [20] have also synthesized  $\text{LiFePO}_4/\text{C}$  with Nb doping via a solid-state reaction method. The optimized  $\text{LiFe}_{0.99}\text{Nb}_{0.01}\text{PO}_4/\text{C}$  cathode displayed a discharge specific capacity 160.5 mA  $\text{hg}^{-1}$  at 0.1C discharge rate 136.0 mA  $\text{hg}^{-1}$  at 5C discharge rate and maintained 134.8 mA  $\text{hg}^{-1}$  after 50cycles. Liu and Huang

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[21] studied the multi-doped LiFePO<sub>4</sub>/C from spent electroless nickel plating solution. The charge–discharge tests demonstrate that the multi-doped LiFePO<sub>4</sub>/C gives outstanding capacity of 160.1, 152.4 and 146.6 mA h/g at 0.1, 0.5 and 1C, and the cycle efficiency retain 99.0% at 1C after 50 cycles. There are many methods for synthesizing LiFePO<sub>4</sub> cathode materials, such as sol–gel, spray pyrolysis, hydrothermal and solid-state reaction. Compared with other methods, solid-state method is often simple and can be easily extended to industrial production [22,23].

In this paper, V<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> modified V-Ti-LiFePO<sub>4</sub>/C cathode materials were synthesized by solid-state reaction. The effects of V and Ti co-doping to the structure, electrochemical properties and Li<sup>+</sup> diffusion were studied in detail. At the same time, phloroglucinol as carbon source joined in the mixture when ball milling. Through this method, the materials of Li<sub>1.02</sub>Fe<sub>1-2x</sub>V<sub>x</sub>Ti<sub>x</sub>PO<sub>4</sub>/C (x = 0.00, 0.01, 0.03, 0.05) with good electrochemical performance and cycle performance were prepared.

## 2. Experimental

The stoichiometric amounts of Lithium dihydrogen phosphate (LiH<sub>2</sub>PO<sub>4</sub>, 99.5%, Sichuan Lithium materials co., LTD), Lithium Acetate (LiAc, 99.5%, Sichuan Lithium materials co., LTD), Ferrous oxalate (FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, 99.5%, Hubei haoyuan material technology co., LTD), Vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>, 99.9%, Shanghai Jingchun biological technology co., LTD), Titanium dioxide (TiO<sub>2</sub>, 99.9%, Shanghai Jingchun biological technology co., LTD) and Phloroglucinol (C<sub>6</sub>H<sub>6</sub>O<sub>3</sub>·2H<sub>2</sub>O) were mixed in ethanol and ball milled at the speed of 300r/min for 4 h, and the weight ratio of Phloroglucinol is 10 g/mol Li<sub>1.02</sub>Fe<sub>1-2x</sub>V<sub>x</sub>Ti<sub>x</sub>PO<sub>4</sub>/C. Then the mixture was dried at 80 °C in the oven for 5 h. After drying, the mixture was calcined at 450 °C for 4 h and 700 °C for 4 h under N<sub>2</sub> (the purity of 99.99%) atmosphere, the heating rate was 3 °C/min. The vacuum tube furnace (HEFEI KEJING materials technology co. LTD) was used for the preparation of composite electrode material.

The purity and structure of the material were detected with X-ray diffraction (XRD, U1timal IV, Rigaku) using Cu Kα radiation and at step of 0.02° per 10s in the range of 10–80°. Scanning electron microscopy (SEM, Inspect S50 FEI) was used to observe the particle size and particle morphology. Carbon coating effects of the materials were examined by transmission electron microscope (TEM, JEOL, JEM-2010F).

To evaluate the electrochemical properties of the materials, Li<sub>1.02</sub>Fe<sub>1-2x</sub>V<sub>x</sub>Ti<sub>x</sub>PO<sub>4</sub>/C, poly vinylidene fluoride (PVDF) binder and acetylene black were mixed with mass ratio of 90: 5: 5 and with the addition of suitable amount of N-methyl-2-pyrrolidinone (NMP). The mixture was stirred to slurry and then spread uniformly over an aluminum foil. The coated electrode was dried in vacuum oven for 10 h at 120 °C. The aluminum foils coated with cathode materials were cut into wafer with the diameter of 14 mm. The quality of the active material was 4–6 mg and the thickness of the electrode was about 0.1 mm. The electrolyte was 1 mol/L LiPF<sub>6</sub> in ethylene carbonate (EC)/diethyl carbonate (DEC)/ethyl methyl carbonate (EMC) (1:1:1 in volume ratio). Coin-type half cells (CR2032) were assembled in an argon-filled glove box (Super1220/750), Mikrouna, Germany). The cell consisted of the as-prepared working electrode, microporous polypropylene membrane (Celgard 2400, Celgard Inc., USA) as separator and Metallic lithium wafer as counter electrode.

Cyclic voltammogram (CV) and Electrochemical impedance spectroscopy (EIS) measurements were performed using CHI660D electrochemical workstation (Chenhua Instrument Inc., Shanghai, China). EIS were operated at open potential in the frequency range of 0.05 Hz to 100 kHz at the first cycle and half charged state. CV measurement was carried out at a voltage range of 2.4–4.2 V at

room temperature while the scanning speed was 0.01 mV/s. Galvanostatic charge and discharge experiments were carried out on an automatic galvanostatic charge/discharge unit (Land 2001A, Wuhan, China) Between 2.4 and 4.2 V at room temperature.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of Li<sub>1.02</sub>Fe<sub>1-2x</sub>V<sub>x</sub>Ti<sub>x</sub>PO<sub>4</sub>/C (x = 0.00, x = 0.01, x = 0.03, x = 0.05) composite material with different content of Ti and V. From Fig. 1, it can be seen that the XRD patterns of V and Ti co-doping samples are similar to the standard diffraction peaks of LiFePO<sub>4</sub> (PDF#40-1499). In the Figure the peaks of V and Ti were not found, which maybe due to its low content in the composites. The diffraction peak of carbon does not appear in the XRD diffraction, which identified that the carbon generated by pyrolysis was amorphous carbon.

Fig. 2(a)–(d) shows the SEM picture of Li<sub>1.02</sub>FePO<sub>4</sub>/C and different content of V and Ti composite materials. From Fig. 2(a) it can be seen that the Li<sub>1.02</sub>FePO<sub>4</sub>/C composite has a larger particle size with irregular particles. At the same time the V and Ti codoping composite materials in the Fig. 2(b)–(d) have relatively normal particle size. With the increasing content of V and Ti, the particle size gradually become smaller and more homogeneous distribution, which indicates that the V and Ti codoping can affect the particle size of the materials. When the content of V and Ti reached to 0.03, the particle size became smallest and most uniform. With the content of V and Ti reached to 0.05, the particle size became slightly bigger. It showed that V and Ti codoping can effectively inhibit the crystal growth, and at the same time was found that the Li<sub>1.02</sub>Fe<sub>0.94</sub>V<sub>0.03</sub>Ti<sub>0.03</sub>PO<sub>4</sub>/C has the least particle size and well uniform size distribution. With the particle size reduced, the mass-transfer resistance decreased, the Li<sup>+</sup> ions diffusion became easier, and the electrochemical properties of the material would be improved.

Carbon-coating can improve the electrochemical properties of the LiFePO<sub>4</sub> cathode material. Theoretically, carbon should be uniformly coated over the cathode material in the process of carbon coating in order to improve the current density. In order to carry out further research about the state of carbon over the surface of the particles. HR-TEM was used to study the Li<sub>1.02</sub>Fe<sub>0.96</sub>V<sub>0.03</sub>Ti<sub>0.03</sub>PO<sub>4</sub> and Li<sub>1.02</sub>Fe<sub>0.96</sub>V<sub>0.03</sub>Ti<sub>0.03</sub>PO<sub>4</sub>/C composite electrode materials.

Fig. 3 shows further characterization images taken from the Li<sub>1.02</sub>Fe<sub>0.94</sub>V<sub>0.03</sub>Ti<sub>0.03</sub>PO<sub>4</sub> (a) and Li<sub>1.02</sub>Fe<sub>0.94</sub>V<sub>0.03</sub>Ti<sub>0.03</sub>PO<sub>4</sub>/C (b, c, d). The TEM images (Fig. 3(d)) clearly reveal that an amorphous carbon layer with a thickness of approximately 5 nm covered the surface of Li<sub>1.02</sub>Fe<sub>0.94</sub>V<sub>0.03</sub>Ti<sub>0.03</sub>PO<sub>4</sub>/C. From Fig. 3(a) and (b) it can be seen that the particle size becomes smaller after carbon coating, which

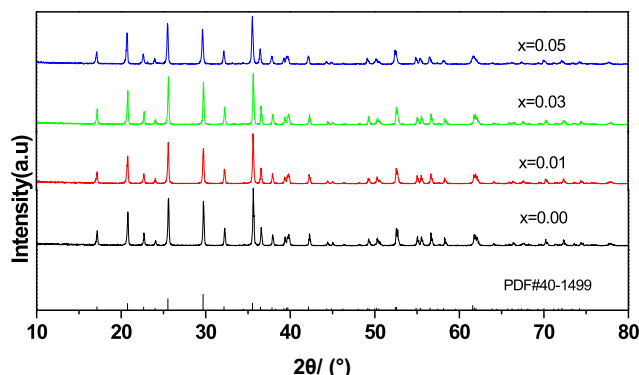


Fig. 1. XRD patterns of Li<sub>1.02</sub>Fe<sub>1-2x</sub>V<sub>x</sub>Ti<sub>x</sub>PO<sub>4</sub>/C (x = 0.00, x = 0.01, x = 0.03, x = 0.05).

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