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Preparation and electrochemical properties of $Li_3V_{1.8}Mn_{0.2}(PO_4)_3$ doped via different Mn sources

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HIGHLIGHTS

- Mn-doped LVP composites (LVMP) synthesized using various manganese sources.
- Manganese with valences +3 and +4 successfully inserted $Li_3V_2(PO_4)_3$ without impurity.
- LVMP doped by MnOOH delivers 137 mAh g^{-1} near theoretical capacity and remains 98% after 50 cycles.
- MnOOH is a prefer dopant to improve the electrochemical properties of LVP.

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ABSTRACT

This work attempts to substitute V of $Li_3V_2(PO_4)_3$ (LVP) by the doped ion of manganese with the valence of +2, +3 and +4 and various ionic radiuses. A series of Mn-doped LVP composites (LVMP) by different manganese sources are synthesized by sol–gel and heat-treatment. Manganese ion with the valences of +3 and +4 have been successfully inserted into the lattice of $Li_3V_2(PO_4)_3$ to form a stable solid-solution even the substitution mole ratio reaches to 0.2, except the impurity phase of $LiMnPO_4$ in LVMP when manganese ions with the valence of +2 involve in the substitution. Mn^{2+} exists in all three samples as expected, but the main valence state of Mn ions in LVMP-A, LVMP-B and LVMP-C are Mn^{4+}, Mn^{3+} and Mn^{2+}, respectively. LVMP-B (MnOOH as dopant) delivers the highest capacity of 137 mAh g^{-1}, than LVMP-A (MnO_2 as dopant) 125 mAh g^{-1} and LVMP-C (Mn_3O_4 as dopant) 123 mAh g^{-1}. LVMP-B shows the best cycle performance, remaining 98% of the initial capacity after 50 cycles in range 3.0–4.3 V. Mn source of MnOOH properly substituted the structure of LVP enhances the lithium diffusion ability and stability of LVP during charge/discharge.

1. Introduction

Numerous efforts have been made on the development of framework materials based on the phosphate polyanion. Monoclinic $Li_3V_2(PO_4)_3$ (LVP) with both mobile Li^+ cations and redox-active metal sites located within a rigid phosphate framework, become attractive candidates owning to its high theoretical discharge capacity of 197 mAh g^{-1} (3.0–4.8 V) and characteristics three-dimensional pathways for Li^+ extraction and re-insertion [1,2]. The strong P–O bonds and three-dimensional (3D) solid framework in $(PO_4)^{3-}$ anions can guarantee both the dynamic and thermal stability required to fulfill the safety features in high power applications, such as electric vehicles (EVs) and hybrid electric vehicles (HEVs) [3].

However, the critical disadvantage of poor electronic and ionic conductivities limit the application fields of $Li_3V_2(PO_4)_3$ [4–6]. Improvements of poor conductivity have been achieved, such as synthesizing nanoparticles, forming electrically conductive coating on materials, and doping cations in the Li or V site to improve electrochemical properties. Metal ion doping is a convenient way to improve the electrochemical performance of $Li_3V_2(PO_4)_3$. A lot of cations have been employed to dope $Li_3V_2(PO_4)_3$, and some positive impacts are reported on its electrochemical performance. V^{3+} has been partially substituted with isovalent or aliovalent metal ions, such as Nb^{5+} [7], Ti^{4+} [8], Zr^{4+} [9], Fe^{3+} [10], Al^{3+} [11,12], Ce^{3+} [13], Cr^{3+} [14], Sc^{3+} [15], Y^{3+} [16], Mg^{2+} [17,18], Mn^{2+} [19,20], Co^{2+} [21]

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and Na^+ [3]. The modified NASICON structure and the electro chemical performance of LVP are quite dependent on the doping elemental structure besides doping content.

Manganese is an interesting substitute in NASICON structure of LVP, because Mn-based materials, such as $LiMnO_2$, Li_2MnO_3, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, have been widely studied as cathode materials for lithium batteries [22–26]. M. Bini et al. [20] reported that a solubility limit ($x = 0.124$) was determined for Mn(II) doped LVP via sol–gel route, generating the smaller irreversible capacity for LVP. In the previous work, the ionic radius of various doping elements is an important factor to the crystal structure and electrochemical properties [15,27,28]. But the doping structure and electrochemical properties of LVP are unknown after the precursor of the doped ion manganese with valence of +2, +3, and +4, respectively.

In this work, we attempt to substitute V by the doped ion of manganese with the valence of +2, +3 and +4 and various ionic radiuses. $(CH_3COO)_2Mn \cdot 4H_2O$ and MnO_2 as +2 and +4 manganese sources are commercial, and MnOOH and Mn_3O_4 as +3 and +2/+3 manganese source are synthesized before as doping precursors. A series of Mn-doped $Li_3V_2(PO_4)_3$ composites by different manganese sources are synthesized and their electrochemical properties are discussed in detail.

2. Experiment

2.1. Synthesis of MnOOH nanorods

MnOOH was prepared via a facile hydrothermal treatment as the previous work. $KMnO_4$ was first fully dissolved in deionized water under room temperature, and then ethanol added. After vigorous stirring for 30 min, the suspension was transferred into Teflon-lined stainless steel autoclave. The sealed autoclave was heated in an oven at 140 °C for 24 h. The product was centrifuged, washed with deionized water and absolute alcohol. MnOOH was obtained after drying at 80 °C in vacuum.

2.2. Synthesis of Mn_3O_4 nanoparticles

6 mmol $MnCl_2 \cdot 4H_2O$ (1.2 g) added into 60 mL ethanol amine (ETA), the mixture was operated in a 600 W ultrasonic reactor for 4 h [29]. Then 100 mL distilled water was added into the resulting colloid solution. After constantly stirred at room temperature for 5 h, the clear brown mixture turned to a dark brown suspension. The suspension was centrifuged at 8000 rpm for 5 min and washed repeatedly with H_2O to remove the residual ETA until the pH of the filtrate was neutral. The Mn_3O_4 nanoparticles were dried at 80 °C in vacuum, and collected as a dark brown powder.

2.3. Synthesis of $Li_3V_{1.8}Mn_{0.2}(PO_4)_3$

The $Li_3V_{1.8}Mn_{0.2}(PO_4)_3$ composites (LVMP) were prepared by a sol–gel method [1]. All chemicals used in this work were of analytical grade. V_2O_5, $NH_4H_2PO_4$, Li_2CO_3, MnO_2, $(CH_3COO)_2Mn \cdot 4H_2O$ and oxalic acid were used as raw materials. First, V_2O_5 and oxalic acid in a stoichiometric ratio of 1:3 were dissolved in deionized water under magnetic stirring at 80 °C until a clear blue solution was formed. Oxalic acid was used both as a chelating agent and reducing agent. Then a mixture of stoichiometric $NH_4H_2PO_4$, MnO_2 (or MnOOH, Mn_3O_4, $(CH_3COO)_2Mn \cdot 4H_2O$) and Li_2CO_3 was added to the solution, and this batch was vigorously stirred for 10 min at 80 °C. Citric acid was then added to the mixed solution. The mixture was stirred to evaporate the water for several hours until homogenous gel was formed. The gel was dried at 100 °C after it was aged overnight. The dried precursor was decomposed at 350 °C under nitrogen atmosphere for 4 h. The preheated precursor was grounded and reacted at 800 °C for 8 h under nitrogen atmosphere. The samples produced are simply named as LVMP-A, LVMP-B, LVMP-C and LVMP-D according to the doping reagents of MnO_2, MnOOH, Mn_3O_4 and $(CH_3COO)_2Mn \cdot 4H_2O$, respectively.

2.4. Characterization

All X-ray studies are done on a done on a Rigaku diffractometer (Dmax-2200) with Cu Kα radiation at 30 kV and 30 mA. The diffraction data are collected for 4 s at each 0.02° step from 10 to 80°. The morphology is investigated by field emission scanning electron microscope (FE-SEM, SIGMA, ZEISS).

2.5. Electrochemical measurement

The electrochemical characterizations were carried out using coin cell (CR2016). The composite cathode was formulated with active materials (80 wt%), Super P (10 wt%) and poly (vinylidene fluoride) (10 wt%) mixed in N-methyl-2-pyrrolidone. After stirred overnight, the slurry was cast onto Al foil by using a doctor blade, and dried at 120 °C for 12 h under vacuum. The weight loading of the cathode electrode is about 4 mg cm^{-2}. The coin cells were assembled in an argon-filled glove box using lithium metal as the negative electrode, Celgard 2500 as the separator, and 1 M $LiPF_6$ (dissolved in ethylene carbonate, dimethyl carbonate and ethylmethyl carbonate with a 1:1:1 volume ratio) as the electrolyte. The galvanostatic charge and discharge experiments were made at room temperature (25 °C) by using LAND CT2001A (Wuhan, China) within the voltage range 3.0–4.3 V (1 C = 133 mAh g^{-1} *vs.* Li^+/Li), and 3.0–4.8 V (1 C = 197 mAh g^{-1} *vs.* Li^+/Li), respectively. Cyclic voltammetry (CV) was conducted on PARSTAT2273 electrochemical workstation at the scanning rate of 0.1 mV s^{-1} in the potential ranges of 3.0–4.5 V and 3.0–4.8 V (*vs.* Li^+/Li), respectively. A lithium foil acted as both the counter electrode and reference electrode. Electrochemical impedance spectroscopy (EIS) measures were carried out at the fresh state on PARSTAT2273 electrochemical workstation with sinusoidal signal of 5 mV over a frequency range from 100 kHz to 10 mHz.

3. Results and discussion

3.1. Structure and morphology characterization

In this work, MnO_2, MnOOH, Mn_3O_4 and $(CH_3COO)_2Mn \cdot 4H_2O$ are selected to be the manganese ion donor. The SEM images of MnO_2, MnOOH and Mn_3O_4 are shown in Fig. 1. As presented in Fig. 1A–C, the as-prepared MnOOH (Fig. 1B) mainly exist in the form of thin rod compared with the regular spheres of MnO_2 (Fig. 1A) and Mn_3O_4 nanoparticles (Fig. 1C). The XRD pattern of as-prepared MnOOH (shown in Fig. 1D) can be readily indexed to a monoclinic phase (space group: $P2_1/c$) with lattice constants $a = 0.530$ nm, $b = 0.527$ nm, $c = 0.530$ nm, compatible with literature values (PDF 41-1379). The characteristic peaks of Mn_3O_4, as labeled in Fig. 1D, are in good agreement with space group $I4_1/amd$ (JCPDS no. 80-0382), and no other impure crystalline phases is observed.

Fig. 2 shows the XRD patterns of manganese-doped LVP by different manganese sources. The XRD patterns of LVMP-A and LVMP-B are well indexed with the monoclinic $Li_3V_2(PO_4)_3$ (JCPDS PDF no. 80-1517, the space group of $P2_1/n$). There are no impurity peaks corresponding to the characteristic Mn-contained phase. Manganese ion with the valences of +3 and +4 have been successfully inserted into the lattice of $Li_3V_2(PO_4)_3$ to form a stable