



The doping effect on the crystal structure and electrochemical properties of $\text{LiMn}_x\text{M}_{1-x}\text{PO}_4$ (M = Mg, V, Fe, Co, Gd)

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ARTICLE INFO

Article history:

Received 16 August 2010

Received in revised form

14 December 2010

Accepted 19 January 2011

Available online 26 January 2011

Keywords:

Lithium secondary batteries

Cathode material

Doping effect

Electrochemical performance

ABSTRACT

To substitute minor Mn^{2+} by the transition metal ion M = Mg^{2+} , V^{3+} , Fe^{2+} , Co^{2+} , or Gd^{3+} , $\text{LiMn}_{0.95}\text{M}_{0.05}\text{PO}_4$ samples are synthesized by a solid-state reaction route. The interpretation of doping effects is complicated by the interrelations between doping microstructure and morphology, because the crystal structure would be affected by the doped elements. The lattice structure and deviation of Li–O bond lengths of the doped LiMnPO_4 are refined by XRD refinement. All the samples present a couple of oxidation and reduction peaks in cyclic voltammetry, corresponding to a redox $\text{Mn}^{3+}/\text{Mn}^{2+}$ reaction coupled with the extraction/reinsertion process of Li^+ in LiMnPO_4 structure. During charge/discharge process, the electron flowing and Li^+ cation diffusion in the various doped LiMnPO_4 samples should be different thermodynamic and kinetic process. For further studying which step in thermodynamic and kinetic process would affect or control the electrochemical performance, the initial charge/discharge capacities and cycleability of doped LiMnPO_4 samples are obtained under different voltage range (from 2.7 to the upper cut-off voltage 4.4, 4.6 and 4.8 V, respectively) and different environment temperatures (0, 25, and 50 °C). At relative higher measuring temperature, the discharge capacity of Co-doped LiMnPO_4 shows 151.9 mAh g^{-1} .

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1. Introduction

Lithium transition-metal phosphates LiMPO_4 (M = Mn, Fe, Co and Ni) have recently attracted much attention due to their lower toxicity, lower cost, higher electrochemical and thermal stabilities [1–3]. LiMnPO_4 become another very promising cathode material for lithium ion batteries beside LiFePO_4 [5–7]. LiMnPO_4 should be a more ideal substitute for LiCoO_2 because the working potential (about 4.1 V) is very close to that of LiCoO_2 [5–9]. However, poor charge/discharge capacity and cycle performance of LiMnPO_4 even at a reasonably low current density, have limited their practical application in high power batteries. Till date only an acceptable discharge capacity has been achieved at low current densities and under trickle charge mode tests. The poor electrochemical performance of LiMnPO_4 is mostly for the intrinsically low electronic conductivity and/or slow diffusion of Li-ion through LiMnPO_4 particles [10–12].

To overcome such short-comings of LiMnPO_4 in recent years, one such synthetic approach for improving the electrochemical performance of LiMnPO_4 is to minimize the particle size and obtain uniform particle size distribution with preferential morphology [7–9,13–18]. For instance, Wang et al. synthesized particles of LiMnPO_4 as small as 100 nm, and reported a reversible capacity of 70 mAh g^{-1} at 0.05C rate [8]. Delacourt et al. synthesized 100 nm diameter particles of LiMnPO_4 by precipitation method, which enhanced the reversible capacity to 70 mAh g^{-1} compared with only 35 mAh g^{-1} for 1 μm diameter particles [16]. Kwon et al. [9] reported LiMnPO_4 with a size of 130 nm synthesized by sol–gel route showing a reversible capacity of 134 mAh g^{-1} at 0.1C. Recently, Wang et al. reported platelet-like LiMnPO_4 with a thickness of 35 nm successfully synthesized by polyol method. The as-synthesized platelet-like LiMnPO_4 showed an improved reversible capacity of 159 mAh g^{-1} (C/10) at elevated temperature (50 °C) [7,12]. The good electrochemical performance of LiMnPO_4 was attributed to the constituent nanoparticle morphology since it reduced the diffusion path length for lithium ions and further created a large contact area with conductive additives such as carbon.

Carbon coating has been verified to be another efficient way which can mainly decrease the boundary resistance of crystals and thereby improve the electrochemical performance of the materials. However, minimizing the particle size and carbon coating cannot resolve the low lattice electronic conductivity or chemical diffu-

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sion ability of lithium ion within the crystal structure. The third approach involves doping transition metal cations in the lattice of LiMnPO_4 to improve the diffusion ability of Li^+ ions and ionic conductivity. Metal cation doped LiMnPO_4 is considered to reduce the availability of the $\text{Mn}^{3+}/\text{Mn}^{2+}$ redox couple, and enhances its cathode performance [19–21]. Nie et al. showed the Jahn–Teller effects in Li_xMnPO_4 using first principles calculation. The existence of Mn^{3+} ions in Li_xMnPO_4 was further shown to be not conducive to the stability of the material during the charge/discharge process. In other words, the J–T effect induced volume and cell distortion of the electrode, would finally lead to rapid mechanical degradation of the capacity [22]. The density functional theory-based calculations on LiMPO_4 ($M = \text{Fe}, \text{Mn}, \text{Co}, \text{and Ni}$) moreover showed that the lowest Li migration energy for the nonlinear pathway along the (0 1 0) channel is a curved trajectory between Li sites. Consequently with such a one-dimensional pathway for Li migration, the lattice distortion by J–T effect in LiMnPO_4 might block the long-range Li conduction and thereby decrease the electrochemical performance [4].

In this work, we substitute minor Mn^{2+} by alkali-, transition-, and inner transition-metal ions, like $M = \text{Mg}^{2+}$ (alkali metal ion), V^{3+} , Fe^{2+} , Co^{2+} (transition metal ions) and Gd^{3+} (inner-transition metal ions) to synthesize $\text{LiMn}_{0.95}\text{M}_{0.05}\text{PO}_4$ doped samples. The synthesized materials have been thoroughly characterized using XRD, cyclic voltammetry (CV), and their charging/discharging capacities have been tested at various cut-off voltages and different testing temperatures. The interpretation of doping effects, in relation to the lattice structure and the electrochemical performance are discussed in detail.

2. Experimental

2.1. Preparation of LiMnPO_4 and doped samples

A stoichiometric ratio of lithium acetate, manganese acetate, and citric acid are mixed and dissolved in water at room temperature. Citric acid is used here as a carbon source. The added doping precursor includes $\text{Mg}(\text{NO}_3)_2$, V_2O_5 , $\text{Co}(\text{CH}_3\text{COO})_2$, FeC_2O_4 , Gd_2O_3 . Aqueous $\text{NH}_4\text{H}_2\text{PO}_4$ is added into the above mixture according to the mole ratio of $\text{LiMn}_{0.95}\text{M}_{0.05}\text{PO}_4$ ($M = \text{Mg}, \text{V}, \text{Fe}, \text{Co}, \text{Gd}$). The mixture is stirred for 1 day and dried at 60°C . The obtained powder is pressed into pellets at the pressure of 5 MPa, and then decomposed at 350°C in N_2 atmosphere for 10 h. The pre-heated precursor is ball-milled for 10 h in a planetary-type ball miller, and pressed into pellets under the pressure of 5 MPa. The pellet is reacted at 700°C for 20 h in N_2 atmosphere in a tube furnace. The obtained products have been referred to as LMMgP, LMVP, LMFeP, LMCoP, LMGDp according to the dopant $\text{Mg}(\text{NO}_3)_2$, V_2O_5 , $\text{Co}(\text{CH}_3\text{COO})_2$, FeSO_4 , Gd_2O_3 , respectively. For comparison, LiMnPO_4 without dopant is also prepared using the same procedure, and simply named as LMP.

2.2. Structural and morphological characterization

The crystal structure of the as-prepared samples is measured using a Rigaku diffractometer with $\text{Cu K}\alpha$ radiation operating at 40 kV and 30 mA. The diffraction data are collected for 4 s at each 0.02° step width over 2θ ranging from 10 to 80° . The lattice parameters of the as-synthesized samples are refined by Rietveld analysis using the General Structure Analysis System (GSAS) [23]. The morphology is characterized using scanning electron microscope (SEM, Hitachi-X650 microscope, 20 kV). The particle size distribution is determined by the optical particle size analyzer (Mastersizer 2000, England). Elemental composition (Li:Mn) of the doped LiMnPO_4 samples is determined by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometer) (Plasma-400).

2.3. Electrochemical tests

Cyclic voltammeteries (CVs) are conducted on a PARSTAT2273 electrochemical workstation. In a potential range of 2.7–4.8 V (vs Li^+/Li), the CV profiles for the above test cells are recorded at a scan rate of 0.1 mV s^{-1} at 25°C . A lithium foil acts as both the counter electrode and reference electrode.

Electrochemical charge–discharge performance of the samples is evaluated in model CR2016 coin cells. The as-prepared sample $\text{LiMn}_{0.95}\text{M}_{0.05}\text{PO}_4$ ($M = \text{Mg}, \text{V}, \text{Fe}, \text{Co}, \text{and Gd}$) is mixed with acetylene black and Teflon powder in the weight ratio 80:15:5. Lithium foil is used as the anode, and 1 M LiPF_6 in EC:DMC = 1:1 is used as the electrolyte. The separator is Celgard 2300 membrane. Cells are assembled in an argon-filled glove box. Cycling and charge–discharge performances of the testing cells are carried out on Land CT2001A. The cut-off voltage is controlled at the range of 2.7–4.4 V, 2.7–4.6 V, and 2.7–4.8 V vs Li/Li^+ , respectively. The cell testing is performed under the surrounding temperature of 0, 25, and 50°C , respectively. The temperature is controlled using Huber ministat240 (accuracy $\pm 0.1^\circ\text{C}$). For the entire cell testing, we adopt the constant current–constant voltage (CC–CV) in charging and constant current (CC) in discharging process. The cells are charged with a C/20 rate to the upper cut-off voltage, kept at the upper voltage until the C/100 rate, and then discharged to 2.7 V at C/20 = 8.5 mAh g^{-1} rate ($1\text{C} = 170 \text{ mAh g}^{-1}$). The electrochemical capacity of the samples is calculated on the amount of the active material.

3. Results and discussion

Fig. 1 shows the XRD patterns of the LiMnPO_4 and $\text{LiMn}_{0.95}\text{M}_{0.05}\text{PO}_4$ ($M = \text{Mg}, \text{V}, \text{Fe}, \text{Co}, \text{and Gd}$) that are synthesized at 700°C for 20 h in nitrogen atmosphere. All patterns are clearly indexed as orthorhombic structure of LiMnPO_4 with $Pnma$ space group, and no other impurity phases are detected. All doped LiMnPO_4 samples by the various transition metal elements reveal a single-phase with a well-ordered olivine structure of LiMnPO_4 . Compared with the detailed XRD patterns of the minor doped samples, only Fe- and Gd-doped LiMnPO_4 present a little shift (as shown in Fig. 1).

The scanning electron microscope (SEM) images of LiMnPO_4 and $\text{LiMn}_{0.95}\text{M}_{0.05}\text{PO}_4$ ($M = \text{Mg}, \text{V}, \text{Fe}, \text{Co}$ and Gd) are shown in Fig. 2. LiMnPO_4 is relatively more agglomerated than the other doped samples. The Co- and Gd-doped LiMnPO_4 samples show relatively narrow size distribution (around 100–300 nm) of nanoparticles. All the samples present common irregular and agglomerated particles. The similarity in morphology and crystal size of all the doped samples could be indicated that there is no more effect by the doping elements, because all the doped samples are synthesized under the same reaction conditions. Fig. 3 shows the particle size distribution of doped- LiMnPO_4 samples. The geometric mean diameter is dependent on the minor doped transition metal elements. Most of the doped LiMnPO_4 samples present two part of particle size distribution, and the relatively large size might be due to the agglomerations of the nanoparticles. Compared with the geometric mean diameter of pure LiMnPO_4 particles, the average particle size of Fe-doped sample presents a big value, but the others present relative smaller values. The geometric mean diameter of LiMnPO_4 , Mg, V, Fe, Co and Gd-doped samples are 397.2, 356.8, 341.2, 424.9, 305.9 and 342.8 nm. The small nanoparticle size and narrow size distribution of Co-doped LiMnPO_4 will be benefit for the electrochemical properties.

The XRD patterns of the doped LiMnPO_4 samples by various transition metal elements are refined by Rietveld analysis. The best refinement model is chosen from a $Pnma$ space group. The refine-

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