



Improving the electrochemical kinetics of lithium manganese phosphate via co-substitution with iron and cobalt



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ARTICLE INFO

Article history:

Received 7 November 2014

Received in revised form 29 January 2015

Accepted 6 February 2015

Available online 13 February 2015

Keywords:

Lithium manganese phosphate

Solid-state reaction

Substitution

Cathode material

ABSTRACT

High Mn content multicomponent olivine phosphate $\text{LiMn}_{0.9}\text{Fe}_{0.1-x}\text{Co}_x\text{PO}_4/\text{C}$ ($x = 0, 0.05$ and 0.1) are synthesized by two-step solid-state method and characterized by X-ray powder diffraction, FTIR spectra, XPS, electron microscopy and electrochemical measurements. Upon substitution, the cell volume decrease as a result of the smaller ionic radii of Fe^{2+} and Co^{2+} compared to Mn^{2+} . Structural analysis demonstrates that Fe and/or Co substitution decrease the Mn–O and P–O bond length and increase the Li–O bond length, leading to enhanced physical stability and expanded Li diffusion channels. The Fe^{2+} and/or Co^{2+} substituted LiMnPO_4 is found to have improved kinetics, lithium storage performance, and electronic conductivity during electrochemical reaction. In particular, $\text{LiMn}_{0.9}\text{Fe}_{0.05}\text{Co}_{0.05}\text{PO}_4/\text{C}$ delivers a capacity of 145 mA h g^{-1} at a current of 0.05 C and exhibits enhanced capacity retention compared to that of unmodified LiMnPO_4/C . The enhanced electrochemical performance of co-substituted LiMnPO_4 is attributed to the enhanced physical stability, the favorable delithiation/lithiation induced by previous redox reaction of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Co}^{2+}/\text{Co}^{3+}$ and the improved electric/ionic transport properties.

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1. Introduction

Olivine LiMPO_4 ($M = \text{Mn, Fe, Co}$ and Ni) have attracted much attention as promising alternative cathodes for the conventional layered lithium transition metal oxide LiMO_2 due to their excellent thermal stability induced by the strong covalency of the P–O bond [1]. Among them, the LiFePO_4 cathode has been successfully developed and commercially produced for application in plug-in hybrid electric vehicles and electric vehicles [2]. Nevertheless, its relatively low discharge potential (3.4 V vs. Li/Li^+) limits its energy density. The higher redox potential of LiMnPO_4 (4.1 V vs. Li/Li^+) makes the theoretical energy density about 1.2 times larger than that of LiFePO_4 [3,4]. Furthermore, the mild voltage of LiMnPO_4 is compatible with most of the commercial electrolytes used in lithium ion batteries, while LiCoPO_4 (4.8 V vs. Li/Li^+) and LiNiPO_4 (5.1 V vs. Li/Li^+) are not easily compatible with these present electrolytes [5]. However, LiMnPO_4 suffers from poor Li^+ intercalation/deintercalation kinetics caused by the intrinsically low ionic and electronic conductivity from the heavy polaronic holes localized on the Mn^{3+} sites, and the interface strain between the LiMnPO_4 and

MnPO_4 phase [6–8]. In response, strategies including particle-size minimization, electrically conductive coating, forming $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$ solid solutions and substitutional doping have been applied in efforts to improve the electrochemical performance [9–11]. Despite the combined advantages of relative high electrical conductivity of LiFePO_4 and relative high voltage of LiMnPO_4 , the overall energy density of Mn–Fe solid solutions decreases with the increase of Fe content owing to the lower equilibrium potential of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox potential. On the other hand, metal doping such as Mg^{2+} , Zn^{2+} and Cu^{2+} enhances the electrochemical activity of LiMnPO_4 with compromising on energy density as most dopants are inactive during electrochemical lithiation [12,13].

Multicomponent olivine compounds such as binary, ternary, or even quaternary systems containing Fe, Mn, Co and Ni have been investigated as cathode materials for the combined advantages of single olivine phases. Recently, combined first-principle calculations and experimental study have been reported on the feasibility to drive the well-established two-phase insertion process of a single-component olivine into a single-phase for multi-component olivine [14]. Meanwhile, the redox reaction of transition metal in multicomponent is significantly modified by local environment change for the occupation of other transition metal [15]. Moreover, compared with the compromising on energy density brought by inactive dopant, the capacity of multicomponent olivine can retain

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a high theoretical capacity of 170 mA h g^{-1} as each transition metal actively participates in electrochemical reaction within a reasonable voltage range.

In this study, we report modifying LiMnPO_4 via Mn site substitution with Fe^{2+} and/or Co^{2+} to enhance its electrochemical performance and evaluate the effect of substitution. To achieve 4.0 V potential, high Mn content $\text{LiMn}_{0.9}\text{Fe}_{0.05}\text{Co}_{0.05}\text{PO}_4/\text{C}$ (denoted as LMFCP), $\text{LiMn}_{0.9}\text{Co}_{0.1}\text{PO}_4/\text{C}$ (denoted as LMCP), $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4/\text{C}$ (denoted as LMFP) and LiMnPO_4/C (denoted as LMP) samples were synthesized by a two-step high-energy ball-milling-assisted solid-state reaction. The physicochemical properties and electrochemical performance were studied using X-ray diffraction, FTIR spectra, electron microscopy, X-ray photo electron spectrometry and electrochemical measurements. The presence of Fe^{2+} and Co^{2+} was found to improve the physical stability of the crystal and enhance the kinetics during electrochemical delithiation/lithiation.

2. Experimental

2.1. Materials preparation

$\text{LiMn}_{0.9}\text{Fe}_{0.1-x}\text{Co}_x\text{PO}_4$ ($x = 0, 0.05$ and 0.1) were synthesized by a two-step solid-state reaction. In a typical synthesis, Li_2CO_3 , $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, and $\text{NH}_4\text{H}_2\text{PO}_4$ in stoichiometric proportion of $\text{LiMn}_{0.9}\text{Fe}_{0.1-x}\text{Co}_x\text{PO}_4/\text{C}$ ($x = 0, 0.05$ and 0.1) and 10 wt% acetylene black were mixed in ethanol. The precursors were milled for 1 h at a speed of 500 rpm in a stainless steel jar on a high-energy milling machine, with a balls (steel) to material of 10–1. This mixture after milling was dried at 120°C for several hours to remove the ethanol completely and then was annealed at 350°C for 10 h in a flowing of Ar. The decomposed mixture was ball-milled again for 5 h in ethanol with 10 wt% sucrose. Further, the mixture was heat-treated again at 600°C for 10 h to crystallize $\text{LiMn}_{0.9}\text{Fe}_{0.1-x}\text{Co}_x\text{PO}_4$ in flowing of Ar. For comparison, the unsubstituted LiMnPO_4 was also prepared by the same process without the addition of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

2.2. Materials characterization

Crystalline phase of the as-prepared materials were identified by X-ray diffraction (XRD, D/max-rB, Rigaku, Japan) measurements using $\text{Cu K}\alpha$ radiation in the 2θ range of $10\text{--}70^\circ$. The GASA Rietveld program was used to analyze the diffraction patterns. Particle morphologies were observed by scanning electron microscopy (SEM, SPA400 Seiko Instruments) and field-emission transmission electron microscopy (TEM, JEOL 2100F). The carbon content in composites was measured by a carbon-sulfur analyzer (CS-902, Wanlianda Xinke, Beijing, China). X-ray photoelectron spectra (XPS) studies were performed using a Kratos AXIS Ultra DVD (Kratos Analytical Ltd.). XPS spectra analysis was done using XPS Peak-fit software.

2.3. Electrochemical measurements

The electrochemical performance of the as-prepared composite was evaluated using CR2032 coin-type cells. To prepare the working electrodes, the active materials, acetylene black, and poly(vinylidene fluoride) were mixed at a weight ratio of 80:13:7 in N-methyl pyrrolidone. The mixed viscous slurry was uniformly spread on an Al foil current collector with loading mass of active materials fixed about 2 mg cm^{-2} . The working electrodes were fabricated by dispersing active materials, carbon black, and poly(vinylidene fluoride) in N-methyl pyrrolidone to form a slurry, which was uniformly spread on an Al foil current collector. The electrodes dried under vacuum at 120°C for 12 h were subsequently assembled into cells in glove box filled with argon using Li metal foil as anode and a polypropylene micro-porous film as separator. Then, 1 M LiPF_6 dissolved in a mixture of ethylene carbonate and dimethyl carbonate (1:1 volume proportion) was used as the electrolyte. The cells were tested in a voltage range of 2.5–4.8 V (vs. Li^+/Li) using a constant-current protocol at various rates ($1 \text{ C} = 170 \text{ mA g}^{-1}$) on a battery testing system (Neware BTS-610). The two electrode cells activated were subjected to electrochemical impedance spectroscopy (EIS) with a sinusoidal voltage signal (5 mV) over a frequency range from 10^3 to 10^{-2} Hz.

3. Results and discussion

3.1. Structure and morphological characterization

Fig. 1 shows the XRD patterns of LMP, LMFP, LMCP and LMFCP. All the diffraction peaks could be indexed to crystalline LiMnPO_4 which belongs to the Pmnb space group (JCPDS card no.

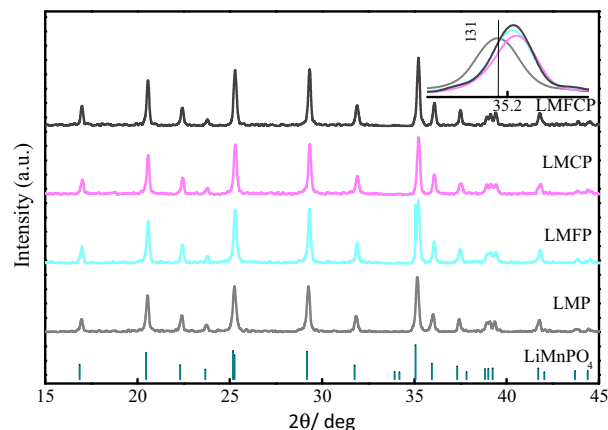


Fig. 1. XRD patterns of LMP, LMFP, LMCP and LMFCP. The insert shows the magnified section of the 131 reflection peaks to highlight the shift of the reflections.

74-0375) with an orthorhombic structure. No typical diffraction peaks of carbon or other impurity phase are observed, which indicated that carbon exists in amorphous form and $\text{Fe}^{2+}/\text{Co}^{2+}$ is completely doped into the lattice of LMP or that the Fe/Co content is too low to be tested. As shown in the insert of Fig. 1, the reflections of the doped samples regularly shift to higher angles, indicating the shrinkage of the cell volume.

The XRD patterns of the samples were further analyzed by Rietveld refinements. The Rietveld refinements of X-ray diffraction patterns for the four samples are shown in Fig. 2 and the refined lattice parameters and bond length for all samples are shown in Tables 1 and 2 respectively. The structural refinements were carried out by the presumption of Fe/Co occupied at the Mn site corresponding to the stoichiometric composition of the precursors. The reliability factors R_{wp} are less than 4.5%, R_p are less than 3.6%, suggesting that the refinement results are credible. The decrease of lattice parameters after Fe^{2+} and/or Co^{2+} substitution is consistent with the fact that the ionic radius of Fe^{2+} and Co^{2+} (0.76 \AA and 0.74 \AA vs. 0.80 \AA for Mn^{2+}) is smaller than that of Mn^{2+} in octahedral coordination [16,17]. The differences in lattice constants and reliable factors of the refinements demonstrate that the Fe^{2+} and/or Co^{2+} have been successfully doped into the LMP phase [18]. Compared with LMP, the average lengths of the Mn–O for doped samples become shorter, indicating that the compositions modified by Fe^{2+} and/or Co^{2+} substitution have a more stable structure for the delithiation/lithiation reaction, and consequently

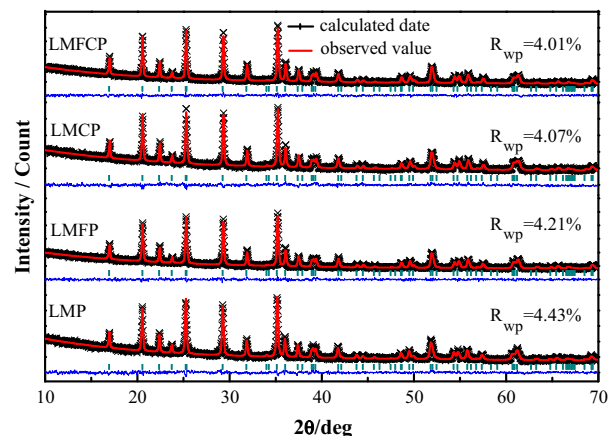


Fig. 2. Rietveld refinement plots of the XRD patterns for the LMP, LMFP, LMCP and LMFCP.

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