

Electrochemical properties of iron substituted lithium manganese phosphate prepared by sol-gel method

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Keywords: Iron substituted lithium manganese phosphate, Sol-gel, Lithium ion battery.

Abstract: Olivine $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ (LMFP) materials were synthesized by the modified sol-gel method with the addition of sucrose as an additional carbon source. Electrochemical properties of LMFP were advanced. The materials doped possess high reversible capacity of $107.4 \text{ mAh}\cdot\text{g}^{-1}$ at 0.2 C-rate and excellent cycling stability (the capacity retention of 85.8% via 50 cycles), exhibiting the improved electrochemical properties.

Introduction

Currently, energy and environment are the most important topics. One of the greatest challenges is how to make use of Green Energy according to the strategy of sustainable development and the replacement of fossil fuels [1]. During the past decades, lithium ion batteries (LIBs) have dominated the portable electronic market and been applied to electric vehicles (EVs), hybrid EVs (HEVs) and smart grids, due to their high energy density and safety [2, 3].

All the time, lithium transition metal oxides are used as the main cathode active materials. However, these materials have some limitations for the intrinsic drawbacks, such as a poor thermal stability [4]. For this reason, the olivine- LiMPO_4 ($\text{M} = \text{Mn, Fe, Co, Ni}$) compounds are drawing more and more interests owing to their low cost, environmentally benign nature, high capacity and thermal stability. As a promising candidate, lithium manganese phosphate LiMnPO_4 is expected for its high energy density (700 Wh/kg) and abundant resource [5]. Unfortunately, LiMnPO_4 is being affected by the actual defect, such as slow lithium diffusion kinetics, low electronic and polaronic conductivity. In addition, the high structural strain at the phase boundary between charged and discharged phase and the instable structure due to Jahn-Teller distortion of Mn^{3+} ion limit its application [6, 7, 8]. Hence, many efforts have been conducted to improve its properties.

Recently, partial substitution by transition metal in LiMnPO_4 is employed to achieve high energy density and stability. Indeed, some researches demonstrate an increase in kinetics when some of the Mn ions are replaced with Fe to form the solid solution $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$ [9]. Therefore, the solid solutions with an olivine structure is regarded as a promising material. What is more, the partial substitution of Mn ions by Fe ions can effectively improve the specific and rate capabilities, which may be attributed to the excellent contact area between active materials and electrolyte [10, 11].

In this work, we synthesize the LMFP utilizing Fe substitution by sol-gel method and investigate improved performance of LMFP, principally. LiMnPO_4 sample is prepared as a comparison, as well. The results indicate that iron substituted lithium manganese phosphate exhibits distinctly improved electrochemical properties, compared to the simple lithium manganese phosphate.

Experimental

$\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ was prepared by the modified sol-gel method, reported in a previous study [12]. All reagents were analytical grade. LiH_2PO_4 , $\text{FeC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$, $\text{Mn}(\text{COOCH}_3)_2\cdot 4\text{H}_2\text{O}$ were dissolved in deionized water in the correct stoichiometric ratios to get a mixed solution, and a critic

acid solution was added to the preceding solution. Sucrose was added as an additional carbon source. After placed in oil bath at 80 °C for 10 h, the mixture was dried at 100 °C for 12 h in a vacuum oven. Finally, the gel was calcined at 700 °C for 10 h to obtain the composite.

The structure was characterized by powder X-ray diffraction (XRD, Rint-2000, Rigaku, Japan) using Cu-K α radiation over the 2 θ range of 10°-80°.

Electrochemical tests were performed by the coin cells (2032 type) that were assembled in an argon glove box. The cathode materials were formed from the active materials, a poly (tetrafluoroethylene) binder and acetylene black in 80:10:10 weight ratio. 1 M LiPF₆ dissolved in a mixture of ethylene carbonate and dimethyl carbonate (1:1 vol. %) was used as the electrolyte between the lithium metal anode and the cathode. The capacities and cycle performances of the cells were carried out on a LAND CT2001A tester (Wuhan, China) in the voltage range of 2.5-4.5 V. Electrochemical impedance spectroscopy (EIS) was conducted over a frequency range of 10 kHz to 10 mHz, with a 5 mV a.c. input signal by CHI660C (Shanghai, China).

Results and discussion

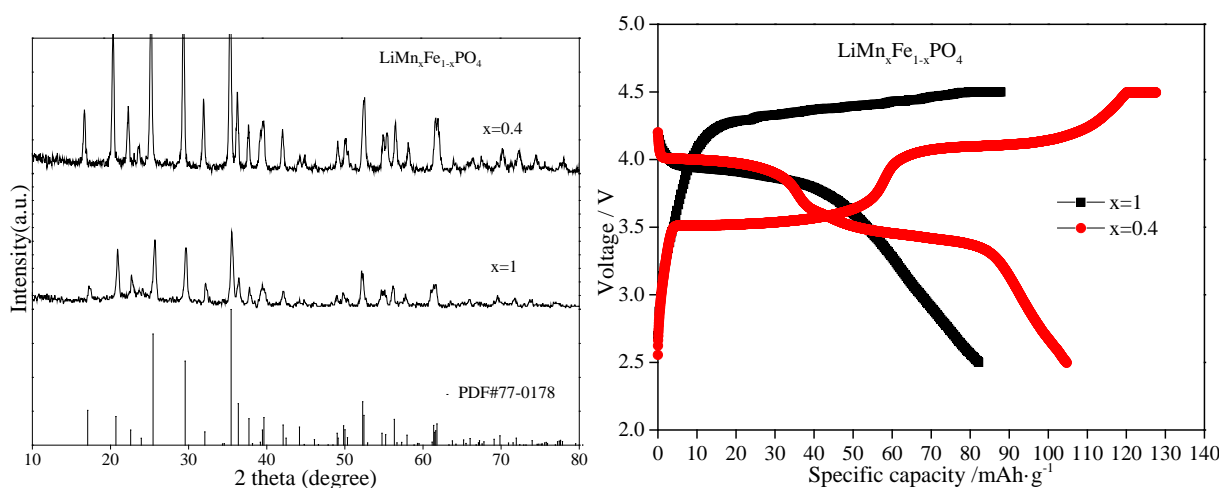


Fig.1 X-ray diffraction patterns of the samples. Fig.2 Initial charge-discharge curves of the samples

The XRD patterns are shown in Fig.1. The crystal structure of the samples are consistent with a highly ordered orthorhombic olivine structure (compared with the PDF card No. 77-0178). The peak intensity of the sample with Fe substitution increases, compared with simple LiMnPO_4 , which arises from Fe^{2+} improving the crystallinity likely. There are not impurity phases in the patterns, which indicates that the modified sol-gel process could obtain the pure $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ materials.

Fig.2 presents the initial charge-discharge curves of the cell with LMFP cathodes at the rate of 0.2 C. The composites incorporating 60% iron deliver initial discharge specific capacity of $107.4 \text{ mAh}\cdot\text{g}^{-1}$, which is higher than that of LiMnPO_4 ($82.7 \text{ mAh}\cdot\text{g}^{-1}$). Fig.3a shows the charge-discharge plateaus of LiMnPO_4 at 4.2 and 3.95 V. However, the charge curve of LMFP exhibits two distinct plateaus at 3.51 and 4.15 V, corresponding to the extraction of lithium ions at the voltage regions of $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Mn}^{3+}/\text{Mn}^{2+}$ couples in Fig.3b. Alike, the discharge plateaus at 4.0 and 3.49 V correspond to lithium ion insertion into the Fe and Mn sites. Moreover, the incorporation of Fe corroborates the curves because of the solid solution. Clearly, the improvement of the sample results from the doping iron.

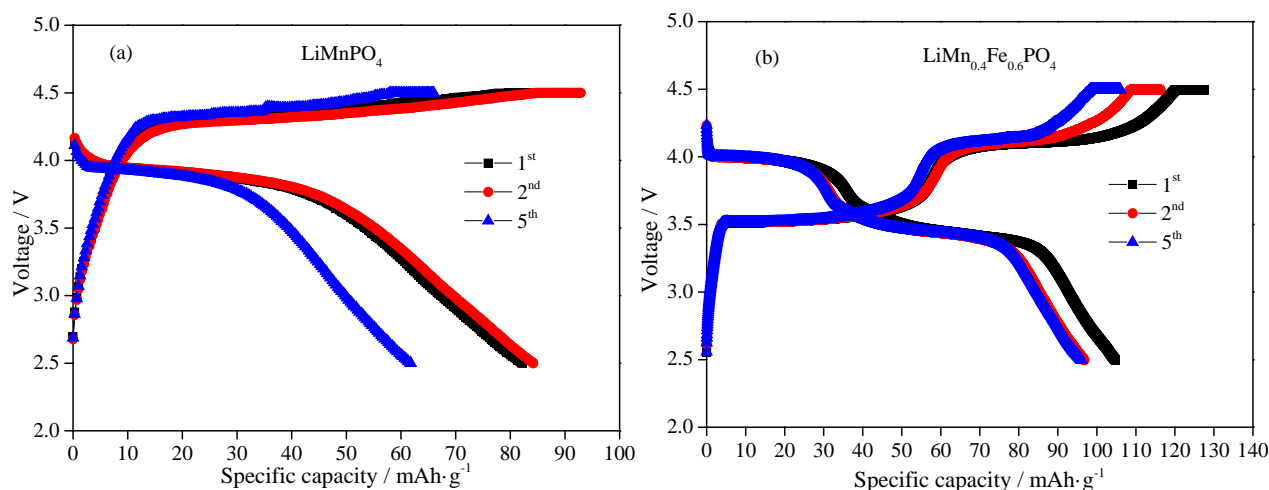


Fig.3 First, second and fifth cycle charge-discharge curves of LiMnPO_4 and $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ (a, b)

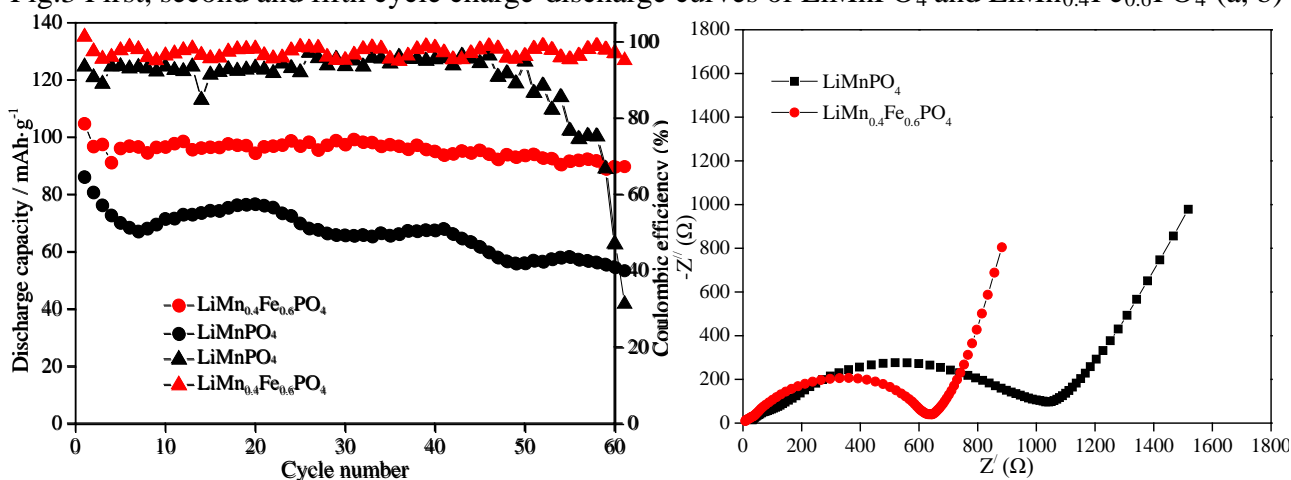


Fig.4 Cycle performances of the samples

Fig.5 EIS plots of the samples after first cycle

The cycle performances and coulombic efficiencies of the samples at 0.2 C-rate are presented in Fig.4. It reveals that LiMnPO_4 shows declined and instable cycle performance, while LMFP exhibits excellent cyclic stability. Across 60 cycles, LiMnPO_4 delivers a lower capacity retention of 67.4% ($55.4 \text{ mAh}\cdot\text{g}^{-1}$) than LMFP (85.8%, $89.9 \text{ mAh}\cdot\text{g}^{-1}$). In addition, the coulombic efficiencies of the samples show a stable tendency from the third cycle, with end of the cells activation. However, the efficiency of LiMnPO_4 decreases dramatically, while LMFP remains stable after 50 cycles. The promoted remarkably cycle property is attributed to doping iron inhibiting the dissolution of Mn.

The impedance spectra of the samples are presented in Fig.5. It shows a merged semicircle at high-frequency region and a straight line at low-frequency region. The semicircle corresponds to the charge-transfer resistance, and the line is related to the diffusion of lithium ions [13]. For $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$, the resistance is smaller obviously, which suggests that Fe substitution makes a positive influence on the properties of the active reaction process and the diffusion of lithium ions.

Conclusion

A doping $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ composite cathode material was synthesized by the modified sol-gel process successfully. The material showed a higher discharge capacity of $107.4 \text{ mAh}\cdot\text{g}^{-1}$ at 0.2 C-rate and more excellent cycle stability with capacity retention of 85.8% after 60 cycles, relative to the simple LiMnPO_4 . Incorporation of Fe can facilitate lithium ion diffusion and electron conduction and improve the electrochemical properties efficiently.

Acknowledgments

The authors are grateful to the University Scientific Research Foundation of Gansu Province (Grant no. 2014A-034) and the Student Innovation Training Program (no. Y510151132) for

financially supporting this work.

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