

Improving electrochemical performance of LiMnPO₄ by Zn doping using a facile solid state method

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Abstract—Olivine structure LiMnPO₄/C as cathode materials for Li-ion batteries were synthesized via a simple solid-state reaction. Improvement of the electrochemical performance of LiMnPO₄/C cathode material was realized significantly by the method of doping Zn. The obtained LiMn_{0.95}Zn_{0.05}PO₄/C electrode material was studied by the measurements of X-ray diffraction pattern, scanning electronic microscopy, electrochemical impedance spectroscopy and electrochemical performance. The results indicate that the LiMn_{0.95}Zn_{0.05}PO₄/C materials exhibit discharge specific capacity of 140.2 mA h g⁻¹ at 0.02 C rate and better rate capability. These excellent results are elucidated by EIS test, which showed that there was the decrease of charge transfer resistance and faster lithium-ion diffusion in LiMnPO₄/C cathode materials after Zn doping.

Key words: Lithium Manganese Phosphates, Doping, Zinc, Lithium Ion Battery, Electrochemistry

INTRODUCTION

One of the most promising cathode materials for high power lithium ion batteries is the lithium transition metal phosphate LiMPO₄ with an olivine structure [1,2]. Among this class of materials, LiFePO₄ has been extensively investigated and is now used in commercial batteries for high power application [3,4]. Encouraged by the success of LiFePO₄, LiMnPO₄ is attracting increased attention due to the redox potential of 4.1V versus Li/Li⁺ [5,6], which is considered to be optimum for current electrolyte. The higher voltage implies that the theoretical energy density of LiMnPO₄ is larger than that of LiFePO₄. Nevertheless, there have been very few reports on the electrochemical investigation of LiMnPO₄ in contrast to an abundance of studies on the cathode properties of LiFePO₄, which is attributed to the slow phase transition [7,8], including the electric and ionic conductivities, the Jahn-Teller effect, interface strain between MnPO₄ and LiMnPO₄ and the metastable nature of the delithiated phase. So it is very difficult to obtain the high electro-active LiMnPO₄.

To improve the electrochemical performance of LiMnPO₄, many efforts have been made. The research results show high capacity, but have slow charge-discharge rates, which corresponds to longer than ten days charge and one week discharge times [9]. Recent research results indicate that the most effective approach is the use of small particles to improve its rate performance [10], which is largely stimulated by the belief that a decrease in the particle size yields a decrease in Li or electron transport length and an increase in the relative surface area. Solution-based methods are well known for their advantage in tailoring the size and morphology of the particles [11]. So the most common methods for obtained electro-active LiMnPO₄ are solution-based methods. By the precipitation of LiMnPO₄ from aqueous solution, a reversible capacity of 70 mA h g⁻¹ at 0.05 C

was observed [12]. Using a sol-gel synthesis, the cathode material of LiMnPO₄ with size of 130 nm could be obtained with a reversible capacity of 134 mA h g⁻¹ at 0.1 C [13]. Recently, the platelet-like LiMnPO₄ with a thickness of 30 nm was successfully synthesized by polyol method with demonstrated capacity of 141 mA h g⁻¹ at 0.1 C and with good capacity retention upon cycling [14].

To date, there are few reports on the synthesis of electro-active LiMnPO₄ by solid state method. In contrast to other methods, the solid state method simplifies the producing procedure and is easier to put into practical application. In the present work, a solid state reaction is selected for the synthesis of carbon-coated and cation-doped LiMnPO₄. The results demonstrated that LiMn_{0.95}Zn_{0.05}PO₄ could be synthesized via a simple solid state method. Moreover, the obtained LiMn_{0.95}Zn_{0.05}PO₄ composite materials showed excellent electrochemical characteristics.

EXPERIMENTAL

Zn-doped LiMnPO₄/C was synthesized by solid-state reaction combined with the addition of β-Cyclodextrin and cation doping. Li₂CO₃ (Shanghai Chemicals, 98.0%), Mn(CH₃COO)₂·4H₂O (Shanghai Chemicals, 99.0%), NH₄H₂PO₄ (Shanghai Chemicals, 99.0%), and ZnO (Shanghai Chemicals, 99.5%) with molar ratios of 1 : 1.9 : 2 : 0.1 were used as precursors. The required amounts of β-Cyclodextrin (β-Cyclodextrin : product LiMnPO₄ is 1 : 5 in weight) were added as carbon source. The starting materials in the appropriate amount of de-ionized water were thoroughly mixed and ground with a pestle. The mixture was heated in a tube furnace at 500 °C for 5 h under nitrogen gas to decompose the carbonate, acetate and ammonium, then calcinated at 700 °C for a few hours and cooled to room temperature. For comparison, undoped LiMnPO₄/C samples were prepared with the same procedures as that of the above-mentioned procedures except for not adding the doping reagent.

The crystalline phase of the prepared powders was identified by

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powder X-ray diffraction with a Shimadzu XRD-6000 diffractometer using Cu K α radiation ($\lambda=1.5418 \text{ \AA}$) scanned in 2θ range of 10–60°. The morphology of the prepared powders was observed by scanning electron microscopy (SEM) with Hitachi FEG SEM.

Composite electrodes containing the LiMnPO₄/C or LiMn_{0.95}Zn_{0.05}PO₄/C were prepared by the following procedure. A slurry of isopropanol was prepared by mixing active material (75 wt%), carbon (acetylene black; 20 wt%) and binder (polyethylenetetrafluoride; 5 wt%), then the slurry was compressed onto stainless steel foil current collectors. After drying at 120 °C overnight, the electrodes were punched into 10 mm Φ disks; the final electrodes had an active material loading of 6–7 mgcm⁻². The electrodes were subsequently assembled into Coin-type 2016 cells using metallic lithium as the anode with a micro-porous membrane separator (Celguard[®] 2325, American) and liquid electrolyte mixtures containing 1 mol L⁻¹ LiClO₄ and a solvent mixture of ethylene carbonate and dimethyl carbonate (1 : 1, v/v). The cells were assembled in a glove box filled with pure argon.

The electrochemical properties of the composite cathodes were measured by a program-controlled battery test system (Land[®], Wuhan, China). The charge and discharge characteristics of the cathodes were evaluated at various currents (C/50, 0.05 C, 0.1 C rates) in the voltage range of 2.4–4.5 V vs. Li^{+/}Li⁰ at room temperature. The electrochemical capacity of the samples was evaluated on account of the active material. Electrochemical impedance spectroscopy (EIS) was performed in a three-electrode cell with lithium foil as counter and reference electrodes by using a CHI 660C Electrochemical Workstation (Chenghua, Shanghai, China) at room temperature. In EIS measurement, the excitation voltage applied to the cells was 5 mV and the frequency range was 100 kHz to 0.1 Hz.

RESULTS AND DISCUSSION

X-ray diffraction patterns of the synthesized LiMnPO₄/C and Zn-doped LiMnPO₄/C are shown in Fig. 1. For comparison, the XRD pattern of standard LiMnPO₄ (Card 33-804) is shown below that of the synthesized cathode materials. From Fig. 1, it can be seen that all diffraction peaks of the synthesized LiMnPO₄/C and Zn-doped

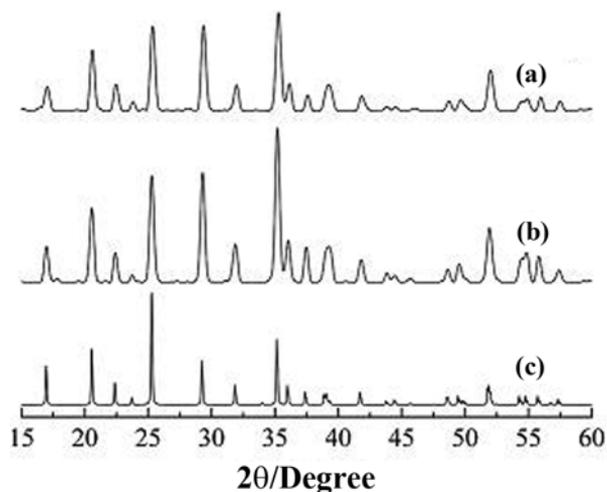


Fig. 1. XRD patterns of samples: (a) LiMnPO₄/C, (b) Zn-doped LiMnPO₄, and (c) Standard LiMnPO₄ (Card 33-803).

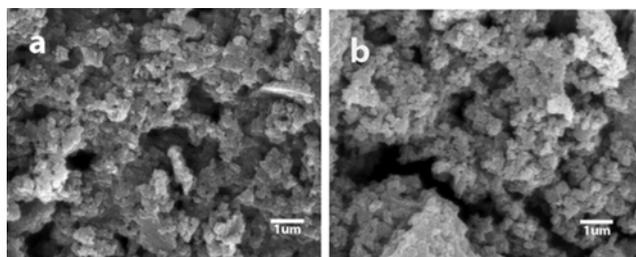


Fig. 2. SEM photograph of (a) LiMnPO₄/C and (b) LiMn_{0.95}Zn_{0.05}PO₄/C.

LiMnPO₄/C are in good agreement with that of standard LiMnPO₄. No noticeable impurities (as reported in the literature [15]) are observed. This result demonstrates that these two samples are both pure phase LiMnPO₄ with olivine structure indexed in Pnma of orthorhombic system. Zn doping did not destruct the lattice structure of LiMnPO₄. It was also noticed that the relative intensity of diffraction peaks was changed in contrast to that of standard LiMnPO₄. This difference was caused by the synthesized condition, which was related to the morphology [16]. No diffraction response of the coating carbon appears in the diffraction pattern, which indicates that the carbon generated from β -Cyclodextrin is amorphous carbon and its presence does not affect the structure of LiMnPO₄.

The SEM images of the LiMnPO₄/C and LiMn_{0.95}Zn_{0.05}PO₄/C are shown in Fig. 2. As shown, the morphology and size of the particles are very similar. This is mainly attributed to the similar synthesis condition. Generally speaking, the particle size is mainly affected by the reaction temperature, added carbon species and reactant concentration. From the SEM observation, the crystal size of these sample particles is about hundreds of nanometers and of uniform distribution, although there is slight agglomeration. The uniform morphology and small size are due to the admixing of carbon source in the starting material. The addition of β -Cyclodextrin into as-prepared materials plays an important role in reducing particle size to hinder the growth of LiMnPO₄/C particles during heating [17]. This provides better electrical contact between particles, and thereby enhances the surface electronic conductivity.

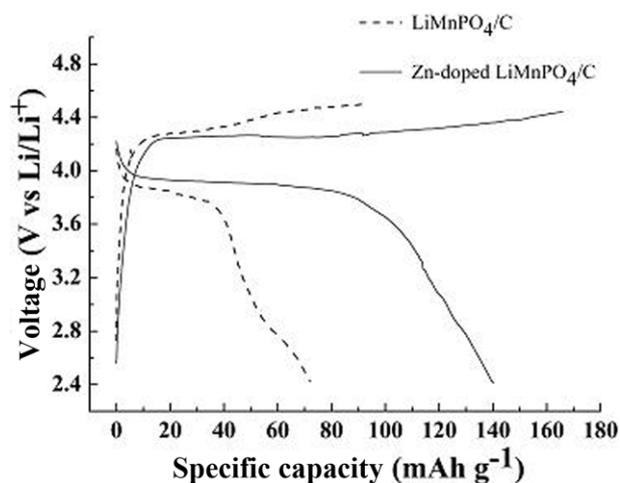


Fig. 3. Initial charge-discharge curves of (a) LiMnPO₄/C and (b) Zn-doped LiMnPO₄/C at 0.02C.

The electrochemical properties of these two materials were evaluated as cathode materials for Lithium batteries at room temperature. Coin cells constructed with an active cathode and a lithium anode were galvanostatically charged and discharged between 2.4 V and 4.5 V. The initial charge/discharge curves of LiMnPO_4/C and Zn-doped LiMnPO_4/C at discharge current density of 0.02 C are presented in Fig. 3. As can be seen, after Zn doping, the discharge capacity of LiMnPO_4/C increased from 71.9 mAh/g to 140.2 mAh g^{-1} at 0.02 C rate. The capacity of Zn-doped LiMnPO_4/C was twice that of LiMnPO_4/C . The dramatic increase of discharge capacity is very interesting. Because, as is well known, olivine LiMnPO_4 material is characterized by poor electronic conductivity and limited lithium-ion diffusion; its rate capability is very poor. Electro-active LiMnPO_4 cathode materials are very difficult to prepare by solid state method. To obtain a higher capacity, many efforts have been made. It is found that one effective way is to reduce the particle size and adopt slow charge-discharge rates such as 0.01 C, which corresponds to longer than four days charge/discharge times. In this paper, a facile solid state method is used to synthesize LiMnPO_4 and a faster charge/discharge current is adopted. The electrochemical test of Zn-doped LiMnPO_4 showed an excellent charged/discharge performance. Furthermore, when the cell was assembled with Zn-doped LiMnPO_4/C composite electrode and charged/discharged at 0.02 C, the plateau was obvious in charge and discharge curves at potential of 4.1 V (versus Li^+/Li), which was the typical redox potential of $\text{Mn}^{3+} \leftrightarrow \text{Mn}^{2+}$ in olivine LiMnPO_4 . However, when the cell was assembled with LiMnPO_4/C composite electrode and charged/discharged at the same current, the plateau of the charge curve became higher and the plateau of the discharge curve became lower. Meanwhile, the length of the plateau was shortened. This clearly showed that Zn-doped sample had smaller electrochemical polarization, and it also further suggested that better electrochemical performance of Zn-doped LiMnPO_4/C was induced by the doping. The above results demonstrate that cation doping is a very effective method for improving the electrochemical performance of LiMnPO_4 and the solid state reaction is a promising method for synthesizing the excellent electrochemical performance of LiMnPO_4 .

Because of the characteristics of LiMnPO_4 , more attention has been paid to its rate capability. To evaluate its rate capability, a test

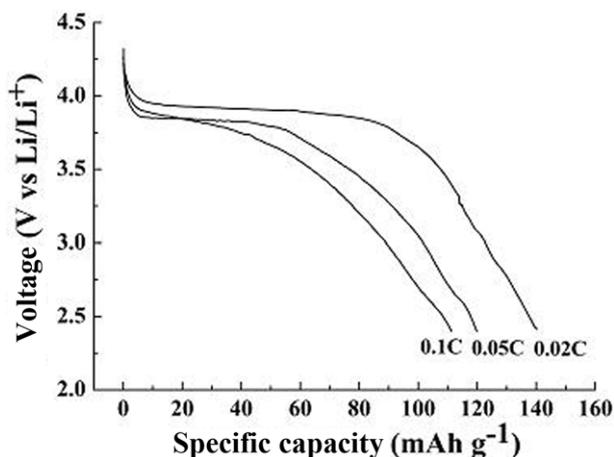


Fig. 4. Initial discharge curves of $\text{LiMn}_{0.95}\text{Zn}_{0.05}\text{PO}_4/\text{C}$ at different discharge current.

at different discharge current was conducted for $\text{LiMn}_{0.95}\text{Zn}_{0.05}\text{PO}_4$. Fig. 4 shows the initial discharge curves of $\text{LiMn}_{0.95}\text{Zn}_{0.05}\text{PO}_4/\text{C}$ at 0.02 C, 0.05C and 0.1 C. All the charge processes of the cell were fulfilled with the same current of 0.02 C between 2.4 and 4.5 V (versus Li/Li^+), to insure the identical initial conditions for each discharge. The electrode is able to deliver a specific capacity of 140.2 mAh g^{-1} at 0.02 C rate, with a voltage plateau at about 4 V (versus Li/Li^+). When the discharge current was set at 0.05 C, 0.1 C, the discharge capacity of the $\text{LiMn}_{0.95}\text{Zn}_{0.05}\text{PO}_4/\text{C}$ cathode was 119.8 mAh g^{-1} and 111.3 mAh g^{-1} , respectively, which is a better value reported for this material. The rate discharge performance indicated that the $\text{LiMn}_{0.95}\text{Zn}_{0.05}\text{PO}_4/\text{C}$ composite synthesized by the method introduced in this work was promising to be put into practical use as cathode material for lithium batteries. The excellent electrochemical performance could be attributed to the high phase purity, small and uniform particle size, and improved conductivity through cation doping and carbon coating. The obvious factor that affected the electrochemical performance of LiMnPO_4 is Zn doping. Although there is some controversy about the enhanced mechanism of the conductivity, cation doping is still an effective way to improve the rate capability of olivine-type LiFePO_4 [18,19]. The results in this paper indicate that cation doping is also suitable for improving the electrochemical performance of olivine-type LiMnPO_4 .

EIS can reflect the electrochemical characteristics and inner structure more accurately [20]. To investigate the difference of electrochemical performance of these two samples, the electrochemical impedance spectroscopy of both samples was measured in the frequency range from 0.1 to 100 kHz in a three-electrode cell with lithium foil as counter and reference electrodes. Fig. 5 shows typical Nyquist plots of LiMnPO_4/C and Zn-doped LiMnPO_4/C composite electrodes. Both profiles exhibit a semicircle in the high frequency region and a straight line in the low-frequency region. Interpretation of the impedance spectra was based on the equivalent circuit in the inset of Fig. 5. The symbols R_e , R_{ct} , CPE, and Z_w , denote the solution resistance, charge-transfer resistance, capacitance of the double layer, and Warburg impedance, respectively. An intercept at the Z' axis in high frequency corresponded to the ohmic resistance (R_e), which represented the resistance of the electrolyte. The numerical value of the diameter of the semicircle on the Z'' axis is approxi-

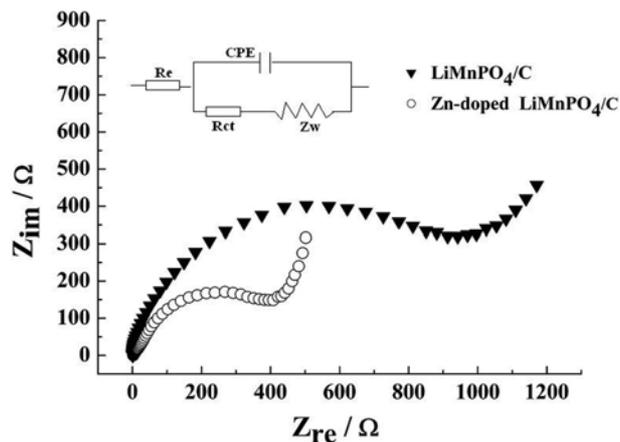


Fig. 5. Nyquist plots of LiMnPO_4/C and Zn-doped LiMnPO_4/C composite electrodes.

mately equal to the charge transfer resistance (R_{ct}) [21]. We fitted these impedance data with the equivalent circuit shown in the inset of Fig. 5 to estimate the charge transfer resistance, R_{ct} . The calculated values of these two samples are 485.5 Ω and 963.7 Ω , respectively, which indicates that there is a remarkable decrease in R_{ct} after Zn doping. As is well known, a low R_{ct} means a large exchange current density (i^0). So Zn doping could enhance the electrochemical activity of LiMnPO₄/C. In other words, Zn doping is more favorable for the insertion and de-insertion of lithium ions during the charge and discharge process. The inclined line in the low frequency represents the Warburg impedance (Z_w), which is associated with lithium-ion diffusion in the active cathode material [22]. As can be seen from Fig. 5, the slope of the impedance of Zn-doped LiMnPO₄/C composite is bigger than that of LiMnPO₄/C, indicating that Zn doping is able to enhance the electrochemical activity of LiMnPO₄. According to the above analysis, it can be concluded that the improved electrochemical performance results from the decrease of charge transfer resistance and faster lithium-ion diffusion, which is induced by Zn doping.

As is well known, stability is very important for battery materials, but there are very few reports on the electrochemical stability of LiMnPO₄ [7]. To date, there is considerable debate about the stability of LiMnPO₄. On one hand, the three-dimensional framework of LiMPO₄ is stabilized by strong covalent bonds, and one can expect the good cycle life exemplified by LiFePO₄. On the other, a Jahn-Teller (JT) distortion is predicted to be unavoidable in Mn(III)[d₄: t_{2g}³e_g¹] of MnPO₄ [23]. The devastating impact of JT distortion on durability is known from other systems [24]. To make out the stability of LiMn_{0.95}Zn_{0.05}PO₄/C, the cycling performance for LiMn_{0.95}Zn_{0.05}PO₄/C at 0.1C was investigated when cycled between 2.4 V and 4.5 V at room temperature, as shown in Fig. 6. The capacity faded slowly at the first several cycles, and then the capacity had very little change. Except for the first several cycles, LiMn_{0.95}Zn_{0.05}PO₄/C presented a good cycling stability. To reduce the influence of solvent decomposition, a lower cut-off voltage (4.5 V) was selected for the cathode materials in our experiments. This may be the reason for the good cycling stability of LiMn_{0.95}Zn_{0.05}PO₄/C. But the stability of LiMn_{0.95}Zn_{0.05}PO₄/C is not comparable with that of LiFePO₄. To find a clear explanation of the stability of LiMnPO₄, much practical and theoretical research is still necessary.

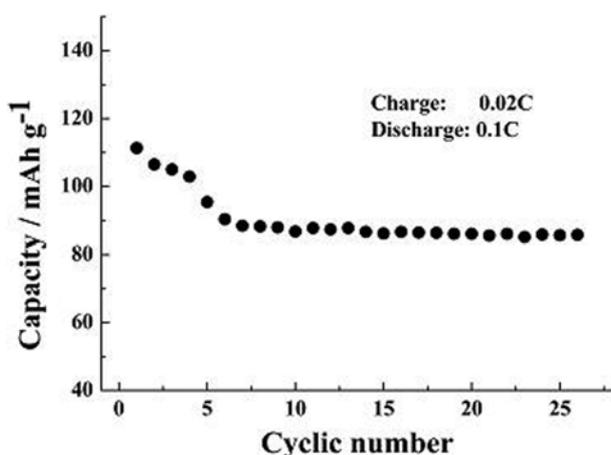


Fig. 6. Cycling performance of LiMn_{0.95}Zn_{0.05}PO₄/C at 0.1C.

CONCLUSIONS

LiMnPO₄/C and Zn-doped LiMnPO₄/C cathode materials were synthesized by the simple solid-state method. The particle size of Zn-doped LiMnPO₄/C is similar to that of undoped LiMnPO₄/C, which implies that the particle size is independent of the doping. The electrochemical tests demonstrated that there was an obvious melioration in electrochemical performance for LiMnPO₄/C cathode materials after Zn doping. Zn-doped LiMnPO₄/C electrode materials exhibited a specific capacity of 140.2 mAh g⁻¹ at 0.02C, 119.8 mA h g⁻¹ at 0.05C and 111.3 mA h g⁻¹ at 0.1C, which is a better result reported for this material. The good performance is ascribed to the decrease of charge transfer resistance and faster lithium-ion diffusion in LiMnPO₄/C cathode materials after Zn doping, which was confirmed by EIS test. The excellent results demonstrate that it is promising to improve the electrochemical performance of olivine structure LiMnPO₄ by cation doping using a facile solid state method.

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