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Effect of Zn doping on the performance of LiMnPO₄ cathode for lithium ion batteries

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ABSTRACT

In this work, effect of Zn doping on the performance of LiMnPO₄ is revisited. Samples of pure and Zn-doped LiMnPO₄ are synthesized by a new solid-state method, and their structure, morphology and electrochemical behavior are characterized and compared. The results reveal that a small amount of Zn doping (2 at.%) is highly beneficial for the performance of LiMnPO₄ due to the reduced charge transfer resistance, the increased lithium ion diffusion and phase conversion, but this effect is remarkably traded off at a high level of Zn doping (10 at.%). Compared with LiMnPO₄, LiMn_{0.98}Zn_{0.02}PO₄ has a much higher capacity and a much better rate capability. After 2 at.% Zn doping, the discharge capacity increases from 101 to 139 mAh g⁻¹ at 0.1 C and 56 to 105 mAh g⁻¹ at 2 C.

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1. Introduction

Lithium ion batteries are widely used in portable electronic devices, but the commercial cobalt-containing cathode materials are expensive, unsafe and toxic, which largely limit their applications in portable power tools, power supplies and hybrid electric vehicles. Therefore, developing low-cost, safe and nontoxic cathode materials to substitute cobalt-containing cathodes is highly desired for the lithium ion batteries community. Among various researched cathode materials, the cheap and environment-friendly LiMnPO₄ olivine appears to be quite attractive due to its high potential plateau of 4.1 V which is compatible with that of the present cobalt-containing cathode materials [1,2]. Despite low electrochemical activity reported in the early literature owing to its low electronic conductivity and slow lithium ion diffusion [3-5], the performance of LiMnPO₄ has recently been significantly improved by the approaches including carbon coating [6–9], particle size reduction [10-13] and cation doping or substitution [14-21].

For cation doping or substitution, most works focused on the Mn-site doping or substitution, and various cations such as Fe²⁺,

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 Mg^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ca^{2+} , Ti^{4+} , Zr^{4+} and their combination have been attempted [14-21]. Among these cations, negative effect of Zn substitution (10 at.%) on the performance of LiMnPO₄ was reported by Chen et al. [14] and Wang et al. [18]. However, this result is more or less out of expectation according to the mechanism of substitute effect proposed by Chen et al. [14]. In fact, Chen et al. [14] pointed out that there was some unidentified impurity present in their Zn-substituted sample which might influence the activity of the material and thus mask the effect of Zn doping. They also pointed out that the impurity formation resulted from the limit of synthesis reaction rather than the limit of solid solubility [14]. This is the case since 10 at.% Zn doping could be completely incorporated into the lattice of LiMnPO₄ by a solid-state reaction according to the report by Wang et al. [18]. These results indicate the importance of the synthesis method for cation doping or substitution. In addition, as an electrochemically inactive ion, the Zn doping level of 10 at.% in their experiments may be a little bit high [14,18]. Take electrochemically inactive Mg doping for example, the optimum doping level is less than 5 at.%, and further increase will worsen the electrochemical performance of LiMnPO₄ [16,19]. More recently, an interesting paper was published on $LiMn_{0.95}Zn_{0.05}PO_4/C$ electrode material which exhibited better electrochemical performance as compared to LiMnPO₄/C [22]. This result suggested a positive effect of Zn doping on the electrochemical behavior of LiMnPO₄.

In the present work, to clarify the effect of Zn doping, Zn doped LiMnPO₄ materials with low (2 at.%) and high (10 at.%) level were

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Fig. 1. XRD patterns and cell volumes of LiMnPO₄, LiMn_{0.98}Zn_{0.02}PO₄ and LiMn_{0.9}Zn_{0.1}PO₄.

prepared by a new method and the effect of Zn doping on the electrochemical performance was revisited. Our electrochemical results demonstrate that the performance of LiMnPO₄ could be significantly improved by a small amount of Zn doping, but a too high level of Zn doping would reduce the reversible capacity of the material.

2. Experimental

LiMnPO₄, LiMn_{0.98}Zn_{0.02}PO₄ and LiMn_{0.9}Zn_{0.1}PO₄ were synthesized by a new solid-state method which was recently developed for synthesizing LiMn_{0.9}Fe_{0.05}Mg_{0.05}PO₄ in our group [21]. Chemicals of LiH₂PO₄, MnC₄H₆O₄·4H₂O, H₂C₂O₄·2H₂O and ZnO was mixed with 14 wt.% of sucrose by ball-milling for 6 h. The milled mixture was dried and then heated at 700 °C for 10 h under an Ar atmosphere.

The obtained samples were identified by X-ray diffraction (XRD) utilizing Cu K_{α} radiation to identify the crystalline phase. Lattice parameters were refined using Rietica program. The morphology and particle size of the samples were observed by scanning electron microscopy (SEM, XL30, Philips) equipped with energy-dispersive spectrometry (EDS, Phoenix). The particle size distribution is measured by a laser particle size analyzer. The chemical compositions of the resulting material were determined using an atomic absorption spectroscopy (AAS). The specific surface areas of the samples were determined by Brunauer–Emmett–Teller (BET) method with nitrogen as adsorption gas.

Electrochemical measurement was conducted by assembly of 2025 coin-type cell with a lithium metal anode. The cathode was made by mixing active material, Super P and polyvinylidene fluoride (PVDF) in a weight ratio of 8:1:1. The typical loading of cathode with a diameter of 1.3 cm was about 2.2 mg of active materials. The electrolyte was 1 M LiPF₆ in EC/DMC (1/1) solution. All cells were assembled in an Ar-filled glove box. For rate test, the cells were charged in a constant current–constant voltage (CC–CV) mode (charged at 0.1 C to 4.5 V, held at 4.5 V until the current decreased to 0.01 C) and then discharged at various rates to 2.0 V at 25 °C. The rate of 1 C is equal to a current density of 150 mA g⁻¹ or 0.25 mA cm⁻². Electrochemical impedance spectroscopy (EIS) was carried out in a frequency range from 0.1 Hz to 100 kHz with an AC signal of 5 mV.

3. Results and discussion

XRD patterns of LiMnPO₄, LiMn_{0.98}Zn_{0.02}PO₄ and LiMn_{0.9}Zn_{0.1}PO₄ are shown in Fig. 1a. All samples have a similar pattern which can be fully indexed into an orthorhombic structure with a space group of *Pmnb*. The absence of carbon peak in the patterns indicates the amorphous nature of the carbon pyrolyzed from sucrose. As the ionic radius of Zn²⁺ (0.74 Å) is

smaller than that of Mn^{2+} (0.80 Å), the Zn doping causes an obvious lattice contraction. As shown in Fig. 1b, the change of the cell volume with the amount of Zn dopant is approximately linear and follows Vergard's law. These observations prove that the doped Zn was successfully incorporated into the Mn-site of the lattice to form LiMn_{0.98}Zn_{0.02}PO₄ and LiMn_{0.9}Zn_{0.1}PO₄ solid solutions. The AAS measurement shows that the atomic ratio of Li:Mn:Zn is 1:0.968:0.02 for LiMn_{0.98}Zn_{0.02}PO₄ and 1:0.888:0.097 for LiMn_{0.9}Zn_{0.1}PO₄, which are much closer to the nominal values.

Fig. 2 shows SEM images of LiMnPO₄, LiMn_{0.98}Zn_{0.02}PO₄ and LiMn_{0.9}Zn_{0.1}PO₄, and EDS mappings of carbon for LiMn_{0.98}Zn_{0.02}PO₄ and zinc for LiMn_{0.98}Zn_{0.02}PO₄ and LiMn_{0.9}Zn_{0.1}PO₄. The SEM images at low magnification (not shown) exhibit that no significant differences in particle size and morphology are observed for the three samples, and the particles are mainly secondary particles composed of primary particles. These observations are validated by the particle size distribution measurement. The agglomerated particles of the three samples all showed a bimodal particle size distribution. The first peak is sharp and located at around $1.4 \,\mu$ m, while the second peak is broad and located at around 6.4 µm. Fig. 2a-c shows SEM images at high magnification and it is seen that the primary particles of all samples are submicron crystals with an average size around 200 nm. EDS mappings (Fig. 2d-f) indicate a uniform distribution of C and Zn in the doped sample. The EDS mapping of Zn for LiMn_{0.9}Zn_{0.1}PO₄ is more dense than that for LiMn_{0.98}Zn_{0.02}PO₄, indicative of a higher content of Zn in the $LiMn_{0.9}Zn_{0.1}PO_4$ sample. In addition, the specific surface area determined by BET measurement is estimated to be $42.9 \text{ m}^2 \text{ g}^{-1}$ for LiMnPO₄, $44.5 \text{ m}^2 \text{ g}^{-1}$ for LiMn_{0.98}Zn_{0.02}PO₄ and $42.0\,m^2\,g^{-1}$ for LiMn_{0.9}Zn_{0.1}PO_4. From the SEM observation, particle size distribution and BET measurements, we can conclude that the particle morphology and size are unaffected by Zn doping, consistent to what was observed by Wang et al. [22].

To evaluate the effect of Zn doping, the electrochemical behavior of LiMnPO₄, LiMn_{0.98}Zn_{0.02}PO₄ and LiMn_{0.9}Zn_{0.1}PO₄ was measured and compared using 2025 coin-type cells. Fig. 3 shows electrochemical impedance spectra of LiMnPO₄, LiMn_{0.98}Zn_{0.02}PO₄ and LiMn_{0.9}Zn_{0.1}PO₄ recorded at the fully discharged state after 5 cycles at 0.2 C (1 C equal to a current density of 150 mAg^{-1}). The spectra of the three samples have a similar profile composed of a semicircle in a high-to-medium frequency region and an inclined line in the low frequency region. The semicircle is approximately related to the charge transfer process. Clearly, reduced semicircles were observed for the two Zn doped LiMnPO₄ samples, which indicates decreased charge transfer resistances after Zn doping. However, it is noted that the semicircle of the $LiMn_{0.9}Zn_{0.1}PO_4$ lies between those of LiMnPO₄ and LiMn_{0.98}Zn_{0.02}PO₄. In other words, the charge transfer resistance of LiMn_{0.9}Zn_{0.1}PO₄ is larger than that of the LiMn_{0.98}Zn_{0.02}PO₄, but smaller than that of LiMnPO₄. The inclined line of the spectra is attributed to the Warburg impedance



Fig. 2. SEM images of (a) LiMnPO₄, (b) LiMn_{0.98}Zn_{0.02}PO₄ and (c) LiMn_{0.9}Zn_{0.1}PO₄; EDS mappings of (d) carbon for LiMn_{0.98}Zn_{0.02}PO₄, zinc for (e) LiMn_{0.98}Zn_{0.02}PO₄ and (f) LiMn_{0.9}Zn_{0.1}PO₄.

associated with the lithium ion diffusion in bulk of the electrode materials, which is evidenced by linear relationship between Z'and $\omega^{-1/2}$ in the low frequency region as shown in the inset of Fig. 3 [23]. According to the Warburg behavior in the low frequency, lithium ion diffusion coefficient can be roughly determined (calculation equation and related parameters description can be found elsewhere [23]). In the present work, the effective surface area used for calculating diffusion coefficient is taken as one-third of the total surface area because there is only one-dimensional channel for lithium diffusion for LiMnPO₄ based materials [24]. In addition, Li concentration used for calculation is $0.022 \text{ mol cm}^{-3}$. On the basis of calculation equation, the diffusion coefficient is estimated to be 1.69×10^{-15} cm² s⁻¹ for LiMnPO₄, 1.94×10^{-14} cm² s⁻¹ for $LiMn_{0.98}Zn_{0.02}PO_4$ and $2.64 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ for $LiMn_{0.9}Zn_{0.1}PO_4$. The above observations demonstrate that the Zn doping can facilitate charge transfer and lithium ion diffusion, but this effect is remarkably traded off at a high level of Zn doping.

Coupled with the results of EIS and the mechanism of substitute effect proposed by Chen et al. [14], improved electrochemical performance of Zn-doped LiMnPO₄ is highly expected, which is confirmed by the rate performance as shown in Fig. 4. For rate test, cells were charged at 0.1 C to 4.5 V, held at 4.5 V until the



Fig. 3. Impedance spectra of LiMnPO₄, LiMn_{0.98}Zn_{0.02}PO₄ and LiMn_{0.9}Zn_{0.1}PO₄ recorded at the fully discharged state after 5 cycles at 0.2 C (1 C equal to a current density of 150 mA g⁻¹ or 0.25 mA cm⁻²). Inset: the relationship between Z' and $\omega^{-1/2}$ in the low frequency region.

current decreased to 0.01 C and then discharged at various rates to 2.0 V. Fig. 4a shows typical charge and discharge curves of LiMnPO₄, LiMn_{0.98}Zn_{0.02}PO₄ and LiMn_{0.9}Zn_{0.1}PO₄ cycled at 0.1 C. As shown in Fig. 4a, flat voltage plateaus around 4.1 V observed in all curves indicate that the charge and discharge reaction proceeds in a two-phase manner. Fig. 4b exhibits rate capability of LiMnPO₄, LiMn_{0.98}Zn_{0.02}PO₄ and LiMn_{0.9}Zn_{0.1}PO₄. It is evident that the LiMn_{0.98}Zn_{0.02}PO₄ sample has a much better rate capability as compared to the LiMnPO₄ sample. At 0.1 C, the discharge capacity can reach 139 mAh g^{-1} for LiMn_{0.98}Zn_{0.02}PO₄, while only a capacity of 101 mAh g⁻¹ is observed for LiMnPO₄. More importantly, as the discharge rate increases from 0.1 to 2 C, the LiMn_{0.98}Zn_{0.02}PO₄ sample shows a much slower decrease in capacity. At 2C, the discharge capacity is 56 mAh g^{-1} for LiMnPO₄ and 105 mAh g^{-1} for LiMn_{0.98}Zn_{0.02}PO₄, which results in correspondingly a capacity retention of 55% and 76%, respectively. Therefore, the electrochemical performance of LiMnPO₄ could be significantly enhanced by a small amount of Zn doping, which is clearly different from the observations reported by Chen et al. [14] and Wang et al. [18], and confirms the positive effect of Zn doping reported by Wang et al. [22].

However, we should note that the Zn doping level was 10 at.% in the experiments reported by Chen et al. [14] and Wang et al. [18], which is higher than that (5 at.%) used by Wang et al. al. [22]. To address the question whether the too high level of the inactive Zn doping causes the worsened electrochemical performance of LiMnPO₄, the electrochemical performance of LiMn_{0.9}Zn_{0.1}PO₄ was also measured and comparatively shown in Fig. 4. It is seen that the discharge capacities of LiMn_{0.9}Zn_{0.1}PO₄ decrease dramatically as compared with those of LiMn_{0.98}Zn_{0.02}PO₄ but still higher than those of LiMnPO₄ especially at high rates. This demonstrates that a too large amount of Zn doping will degrade the reversible capacity due to the inactive nature of Zn doping, which is similar to the result observed for inactive Mg doping [16,19]. Wang et al. [18] reported that 10 at.% Zn substitution led to a discharge capacity decrease of more than 20 mAh g⁻¹ at all rates. For example, the discharge capacity at 0.1 C decreased from 95 to 62 mAh g⁻¹ after 10 at.% Zn substitution. It is noted that the performance of our LiMnPO₄ is roughly similar to that reported by Wang et al. (a precise comparison is difficult because the carbon content in the composite, the cathode fabrication and the cell test condition



Fig. 4. (a) Typical charge/discharge curves of LiMnPO₄, LiMn_{0.98}Zn_{0.02}PO₄ and LiMn_{0.9}Zn_{0.1}PO₄ cycled at 0.1 C and (b) rate capability of LiMnPO₄, LiMn_{0.98}Zn_{0.02}PO₄ and LiMn_{0.9}Zn_{0.1}PO₄. Cells were charged at 0.1 C to 4.5 V, held at 4.5 V until the current decreased to 0.01 C and then discharged at various rates to 2.0 V.

are different) [18], but our LiMn_{0.9}Zn_{0.1}PO₄ exhibits much higher capacities at all rates as compared with their LiMn_{0.9}Zn_{0.1}PO₄. We speculate that such a difference may be highly due to the different method used for preparation of Zn doped LiMnPO₄. In addition, it is interesting that the discrepancy of the discharge capacity between LiMn_{0.98}Zn_{0.02}PO₄ and LiMn_{0.9}Zn_{0.1}PO₄ became smaller when the discharge current density became larger. This behavior may possibly be understood by the mechanism proposed by Chen et al. [14]. Similar to Mg doping, the presence of Zn ion may create a more favorable boundary between the two phases for increased conversion of lithiated phase to delithiated phase, and thus may enhance the electrochemical kinetics and improve the electrochemical performance of LiMnPO₄. From this mechanism, LiMn_{0.9}Zn_{0.1}PO₄ may have a higher conversion rate of lithiated phase to delithiated phase than LiMn_{0.98}Zn_{0.02}PO₄, and then the increased phase conversion of LiMn_{0.9}Zn_{0.1}PO₄ may partly or completely counterbalance its increased charge transfer resistance and reduced lithium ion diffusion as revealed by EIS. As a result, the $LiMn_{0.9}Zn_{0.1}PO_4$ still has a good rate performance. Anyway, the above electrochemical results prove that a proper amount of Zn doping is highly beneficial for the electrochemical performance of LiMnPO₄.

4. Conclusions

Zn doped LiMnPO₄ was synthesized by a new solid-state reaction method, and we demonstrated that the electrochemical performance of LiMnPO₄ can be significantly improved by a small amount of Zn doping due to the reduced charge transfer resistance, the increased lithium ion diffusion and phase conversion. The results are of great importance to the performance promotion of LiMnPO₄ and helpful to further understanding of the effect of cation doping.

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References

- A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, Journal of the Electrochemical Society 144 (1997) 1188.
- [2] G.H. Li, H. Azuma, M. Tohda, Electrochemical Solid-State Letters 5 (2002) A135.
- [3] A. Yamada, Y. Kudo, K.Y. Liu, Journal of the Electrochemical Society 148 (2001) A1153.
- [4] A. Yamada, M. Hosoya, S.C. Chung, Y. Kudo, K. Hinokuma, K.Y. Liu, Y. Nishi, Journal of Power Sources 119–121 (2003) 232.
- [5] C. Delacourt, P. Poizot, M. Morcrette, J.M. Tarascon, C. Masquelier, Chemistry of Materials 16 (2004) 93.
- [6] S.K. Martha, B. Markovsky, J. Grinblat, Y. Gofer, O. Haik, E. Zinigrad, D. Aurbach, T. Drezen, D. Wang, G. Deghenghi, I. Exnar, Journal of the Electrochemical Society 156 (2009) A541.
- [7] S.M. Oh, S.W. Oh, C.S. Yoon, B. Scrosati, K. Amine, Y.K. Sun, Advanced Functional Materials 20 (2010) 3260.
- [8] Z. Bakenov, I. Taniguchi, Electrochemistry Communications 12 (2010) 75.
- [9] S.M. Oh, S.W. Oh, S.T. Myung, S.M. Lee, Y.K. Sun, Journal of Alloys and Compounds 506 (2010) 372.
- [10] N.H. Kwon, T. Drezen, I. Exnar, I. Teerlinck, M. Isono, M. Graetzel, Electrochemical Solid-State Letters 9 (2006) A277.
- [11] T. Drezen, N. Kwon, P. Bowen, I. Teerlinck, M. Isono, I. Exnar, Journal of Power Sources 174 (2007) 949.
- [12] D.Y. Wang, H. Buqa, M. Crouzet, G. Deghenghi, T. Drezen, I. Exnar, N.H. Kwon, J.H. Miners, L. Poletto, M. Grätzel, Journal of Power Sources 189 (2009) 624.
- [13] D.W. Choi, D.H. Wang, I.T. Bae, J. Xiao, Z.M. Nie, W. Wang, V.V. Viswanathan, Y.J. Lee, J.G. Zhang, G.L. Graff, Z.G. Yang, J. Liu, Nano Letters 10 (2010) 2799.
- [14] G.Y. Chen, J.D. Wilcox, T.J. Richardson, Electrochemical Solid-State Letters 11 (2008) A190.
- [15] S.K. Martha, J. Grinblat, O. Haik, E. Zinigrad, T. Drezen, J.H. Miners, I. Exnar, A. Kay, B. Markovsky, D. Aurbach, Angewandte Chemie International Edition 48 (2009) 8559.
- [16] T. Shiratsuchi, S. Okada, T. Doi, J.I. Yamaki, Electrochimica Acta 54 (2009) 3145.
- [17] J. Kim, D.H. Seo, S.W. Kim, Y.U. Park, K. Kang, Chemical Communications 46 (2010) 1305.
- [18] D.Y. Wang, C.Y. Ouyang, T. Drézen, I. Exnar, A. Kay, N.H. Kwon, P. Gouerec, J.H. Miners, M.K. Wang, M. Grätzel, Journal of the Electrochemical Society 157 (2010) A225.
- [19] Z. Bakenov, I. Taniguchi, Journal of the Electrochemical Society 157 (2010) A430.
- [20] J.W. Lee, M.S. Park, B. Anass, J.H. Park, M.S. Paik, S.G. Doo, Electrochimica Acta 55 (2010) 4162.
- [21] C.L. Hu, H.H. Yi, H.S. Fang, B. Yang, Y.C. Yao, W.H. Ma, Y.N. Dai, Electrochemistry Communications 12 (2010) 1784.
- [22] Y.R. Wang, Y.F. Chen, S.Q. Cheng, L.N. He, Korean Journal of Chemical Engineering 28 (2011) 964.
- [23] H. Liu, C. Li, H.P. Zhao, L.J. Fu, Y.P. Wu, H.Q. Wu, Journal of Power Sources 159 (2006) 717.
- [24] D. Morgan, A. Van der Ven, G. Ceder, Electrochemical Solid-State Letters 7 (2004) A30.