PAPER

Check for updates

Tuning polaronic redox behavior in olivine phosphate†

Yue Gu,‡ Mouyi Weng,‡ Gaofeng Teng, Hua Zeng, Jianshu Jie, Weiji Xiao,
Jiaxin Zheng* and Feng Pan ID *

In order to understand and improve the conductivity of LiFePO$_4$, lots of attempts have been made both experimentally and theoretically. Here we performed hybrid density functional theory calculations to systematically investigate the electronic structures with polaronic redox behavior of polyanionic intercalation compounds similar to LiFePO$_4$, such as in XMPO$_4$ (X = Li, Na; M = Mn, Fe, Co, Ni). It is proved that the replacement of Li ions does not eliminate the polaronic redox behavior of Fe ions during delithiation and hence does not lead to a significant improvement in electronic conductivity. By contrast, replacing Fe with Mn, Co or Ni can tune the polaronic redox behavior during delithiation by varying degrees. For Ni, the polaronic redox behavior has almost disappeared, and band gaps disappear during delithiation, indicating a better electronic conductivity. For Mn or Co, the polaronic redox behavior is still obvious with little improvement in the electronic conductivity. This study provides important clues to improve the electronic conductivity of LiFePO$_4$-like cathode materials.

Introduction

With the rapid development of transportation applications, including hybrid electric vehicles, plug-in hybrid electric vehicles (PEVs) and pure electric vehicles (EVs), lithium-ion batteries (LIBs) with high power density are urgently demanded. The rate capability (charge and discharge rate), as one of the most important factors affecting the power density of LIBs, has been a key issue that researchers are committed to improve.[1,2] The rate capability of LIBs depends mainly on the electronic and ionic conductivity. As a safer LIB cathode, LiFePO$_4$ (LFP) has been intensively studied in the past decade,[3] whose rate capability was found to be surprisingly decoupled from its low intrinsic diffusion coefficient of lithium (about 3.6×10^{-10} cm^2 s^{-1})[4] and electronic conductivity (about 10^{-9} S cm^{-1}).[5] It is now widely believed that the covalent character of polyanion frameworks in LiFePO$_4$ is a key factor that limits its electronic conductivity. Over the past twenty years, in order to improve the conductivity of LiFePO$_4$, a large number of attempts have been made. Early research mostly focused on reducing the particle size.[6–9] Then, many studies began to concentrate on nanocoating LiFePO$_4$ with a conductive medium, such as carbon,[10–12] a conductive polymer[13] or conductive metal phosphides.[14,15] However, these methods do not change the intrinsic low electronic conductivity of LiFePO$_4$

School of Advanced Materials, Peking University, Shenzhen Graduate School, Shenzhen 518055, People's Republic of China. E-mail: zhengjx@pkusz.edu.cn, panfeng@pkusz.edu.cn

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8cp06083e

‡ These authors contributed equally to this work.

itself. Another strategy is doping with other elements.[5,16–21] For example, the experimental work by Chung *et al.*[5] claimed that low-level doping with a range of aliovalent ions (Mg^{2+}, Al^{3+}, Ti^{4+}, Zr^{4+}, and Nb^{5+}) increased the electronic conductivity by a factor of 1×10^8, though the actual mechanism is controversial.

The quasiparticle formed by the electron and its self-induced distortion is called a small polaron as the range of the lattice distortion is of the order of the lattice constant. Experimental and theoretical work[22–25,35–38] reported that excess charge carriers form small polarons in Li$_x$FePO$_4$ and some similar structures, and the conductivities of these materials are reduced to varying degrees. These studies showed that the mechanism of polaron hopping strongly inhibits the electronic conductivity of Li$_x$FePO$_4$ during delithiation. From this perspective, electronic conduction in structurally similar cathode materials may be *via* a similar mechanism. Recently, one of the hot topics to improve the performance of LiFePO$_4$ batteries is to replace Fe ions in LiFePO$_4$ materials with adjacent Mn,[26] Co,[27] and Ni[28] ions, or use ions which have relatively similar physical and chemical properties to lithium ions (such as Na[29]) to undertake the role of Li ions during charging/discharging process. Thus, it is necessary to systematically examine the existence of small polarons in these structures.

Note that the generalized gradient approximation (GGA) and GGA+U, which are frequently used in *ab initio* calculations, cannot easily predict the polaronic state during delithiation. GGA cannot correct the self-interaction errors (SIEs) for transition metal atoms. For GGA+U, it can correct the SIEs for transition metal atoms, but the value of parameter U is affected by too many factors, such as the structure type, atomic species, and atomic

valence; therefore, it is very troublesome to use GGA+U in a system that will change valences. In previous work, the creation of a hole polaron involves removing an electron from the valence-band maximum (VBM), however, this method does not work well with the actual situation. During the actual charge and discharge process, the lithium ions will affect the surrounding structure and further affect the charge distribution. If the redox behaviors of materials are judged only by removing an electron, the effect of removing lithium ions will not be fully evaluated, and some misjudgment may occur. Therefore, this work calculated the materials' redox behaviors by removing lithium ions, and strived to obtain results that are more similar to the actual ones. The magnetic moment values of the transition metal ions are also given here as a reference for their valences. In this work, we first studied the polaronic redox behavior in LiMPO$_4$ (M = Mn, Fe, Co, Ni) without defects, which has been metioned in previous work, and then we further studied the polaronic redox behavior in defectless NaMPO$_4$ and LiMPO$_4$ with antisite defects. Our work was all based on hybrid density functional theory[30] calculations. The exact Hartree–Fock (HF) exchange energy is introduced to correct the error from the spurious self-interaction of electrons, which is expected to provide a more accurate prediction of electronic structures than GGA+U with standard parameters. Our results proved that the replacement of Li does not eliminate the polaronic redox behavior of Fe during delithiation. By contrast, replacing Fe with Mn, Co or Ni can tune polaronic redox behavior during delithiation by varying degrees.

Calculation method

In this work, the theoretical study was performed with the Vienna *Ab initio* Simulation Package (VASP)[31,32] using projector-augmented wave (PAW)[33] pseudopotentials and the exchange–correlation functionals parametrized by Perdew–Burke–Ernzerhof for the generalized gradient approximation (GGA-PBE).[33] The cutoff energy was set as 520 eV. All calculations are spin-polarized with an antiferromagnetic configuration (specific settings can be seen in Fig. S1, ESI†). All the atomic positions and cell parameters are fully relaxed until the force on each atom is smaller than 0.03 eV Å^{-1} and energies are converged to within 1×10^{-5} eV per atom. For hybrid density functional theory calculations, the HSE06[30] method was used, the HFSCREEN value was set to 0.25, and k-points was set to a $2 \times 2 \times 1$ grid. This HFSCREEN value is the default value of the HSE06 method, and generally, the result from this value is trustworthy.

In this work, all structures are based on the LiFePO$_4$ structure of the *Pnma* space group. Each cell contains 4 Fe ions (or transition metal (M), such as Mn, Co, or Ni ions), which are labeled M-I, M-II, M-III, and M-IV, respectively. The 4 Li ions in the cell were labeled Li1, Li2, Li3, and Li4 in the order of delithiation (as shown in Fig. 1).

Results and discussion

Fig. 1 shows the crystal structure of olivine-type LiFePO$_4$. This structure consists of PO$_4$ tetrahedra, the divalent M ions occupy
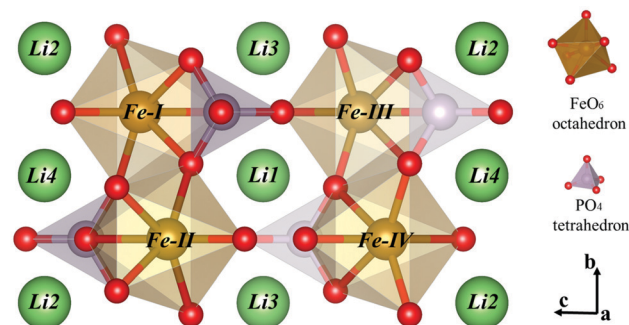

Fig. 1   Crystal structure of LiFePO$_4$: projection of a 3D model on the *ac* plane.

the shared octahedral position, and Li ions are located in the chains of the edge-sharing octahedra. An advantage of this structure is that the P–O covalent bonds in PO$_4{}^{3-}$ are very strong, stabilizing the structure during charging and discharging, and preventing the release of oxygen at high voltage. It was reported to crystallize in the orthorhombic space group *Pnma* with $a = 4.6950$, $b = 6.0112$ and $c = 10.3377$ Å.[34] The calculated lattice parameters of LiFePO$_4$ are $a = 4.749$, $b = 6.083$ and $c = 10.457$ Å, in satisfactory agreement with the above experimental values.

Polaronic redox behavior of Li$_x$FePO$_4$

In Li$_x$FePO$_4$, since the density of states (DOS) near the Fermi level is basically all composed of d orbitals of Fe ions and p orbitals of O ions, the partial density of states (PDOS) of Fe-3d and O-2p is given directly in Fig. 2. The absolute values of magnetic moments of Fe ions in these structures are also shown in Fig. 2. For the case of $x = 1$, the valence band maximum (VBM) and the conduction band minimum (CBM) are all basically composed of 3d orbitals of Fe. The DOS shows that the band gap of LiFePO$_4$ is about 3.76 eV (experimental data give about 3.8–4.0 eV[34]), indicating a poor conductivity. For the case of complete delithiation ($x = 0$), it can be found that the CBM is nearly invariant, but the VBM varies obviously: the sharp peak of Fe-3d disappears completely. This indicates that during delithiation, the charge-compensating electrons are mainly contributed by Fe ions. The band gap of FePO$_4$ is about 3.43 eV, which is still a large value, and the conductivity has not been significantly improved. For Fe^{2+} in LiFePO$_4$ and Fe^{3+} in FePO$_4$, the calculated magnetic moments are about 3.7 and 4.3 μ_B, respectively. These results show that Fe^{2+} exhibits a high spin t$_{2g}$($\downarrow$)t$_{2g}^3$($\uparrow$)e$_g^2$($\uparrow$) configuration and Fe^{3+} exhibits a high spin t$_{2g}^3$($\uparrow$)e$_g^2$($\uparrow$) configuration.[22]

In the case of $x = 0.75$, Li1 (one of the four equivalent Li ions) was removed. It can be found that the peaks of Fe-I, Fe-III, and Fe-IV (named in Fig. 1) at the VBM shifted slightly relative to the case of $x = 1$, and are still below the Fermi level. However, the peak of Fe-II at the VBM shifted to the position above the Fermi level and caused a significant reduction in the bandgap value. For the case of $x = 0.5$, Li1 and Li2 were removed. The peak of Fe-IV at the VBM also shifted to the position above the Fermi level and basically overlapped with the peak of Fe-II. At the same time, the peaks of Fe-I and Fe-III at the VBM also basically
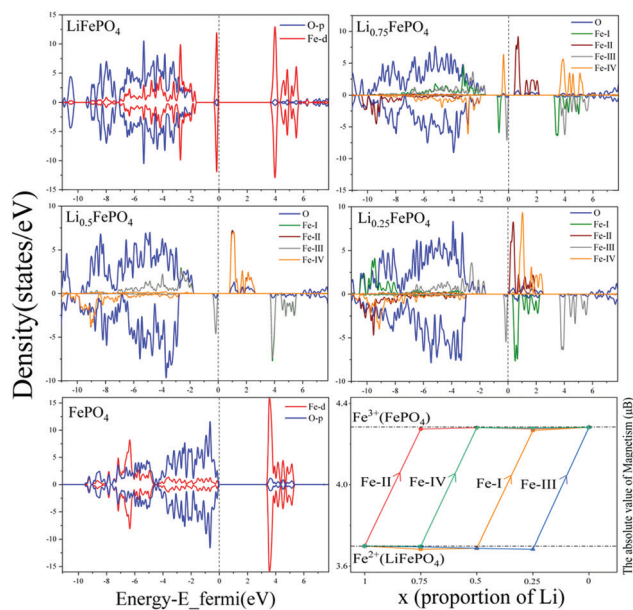
Fig. 2 The HSE06 calculated partial density of states (PDOS) of Li_xFePO_4 and the absolute value of the calculated magnetic moments of four Fe ions in Li_xFePO_4 (x = 1, 0.75, 0.5, 0.25, 0).

coincided. For the case of x = 0.25, Li1, Li2 and Li3 were removed. The peak of Fe-I at the VBM shifted to the position above the Fermi level and the peaks of Fe-I, Fe-II and Fe-IV at the CBM do not overlap. From the above analysis, we can find that whenever a Li ion is removed, there will be an Fe ion whose peak at the VBM is shifted to the position above the Fermi level, while the peaks of the other three Fe are not substantially changed. Finally, in the case of x = 0, the peaks of all Fe ions at the VBM almost completely disappeared. The above results show that there is a clear polaronic redox behavior in the delithiation process of $LiFePO_4$. Therefore, although the band-gap value of Li_xFePO_4 is significantly reduced during the delithiation process, this does not mean that the conductivity in the delithiation process will be improved. From the absolute value of the magnetic moment in Fig. 2, we can see that whenever one of the four Li ions in the unit cell is removed, there will be one Fe ion whose magnetic moment (absolute value) jumps from around 3.7 μ_B to about 4.3 μ_B. This indicates that Fe ions do not transfer electrons at the same time during the delithiation process. Instead, they jump from divalent to trivalent one by one and exhibit polaronic redox behavior. Therefore, we can clearly observe the polaronic redox behavior of Li_xFePO_4 during delithiation based on HSE06 calculations. Our results are in line with previous experimental and theoretical studies,[22–25] which lays a good foundation for the next step to expand the scope of the analysis.

Polaronic redox behavior of $NaFePO_4$

We next present the PDOS of $NaFePO_4$ and $Na_{0.75}FePO_4$ in Fig. 3. The magnetic moments of Fe ions in these structures are given in Table S1 (ESI†). Referring to Fig. 2, we can find that replacing lithium with sodium has little effect on the DOS.
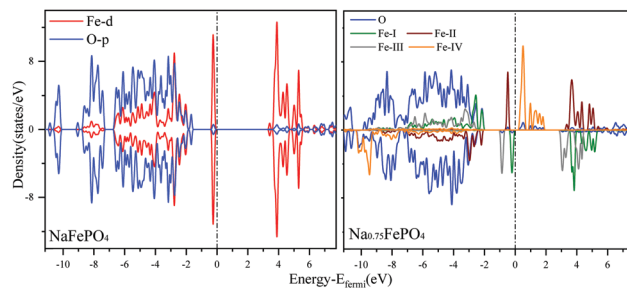

Fig. 3 The HSE06 partial density of states (PDOS) of $NaFePO_4$ and $Na_{0.75}FePO_4$.

It is shown that in $NaFePO_4$, when one Na ion is removed, the peak of Fe-IV at the VBM shifted to the position above the Fermi level, while the peaks of Fe-I, Fe-II, and Fe-III at the VBM shifted slightly relative to the case of $NaFePO_4$. From Table S1 (ESI†), we can see that when one Na ion is removed, the absolute value of the magnetic moment of Fe-IV jumps from around 3.7 μ_B to about 4.3 μ_B, just like the situation in $LiFePO_4$. By comparing $NaFePO_4$ with $LiFePO_4$, it is found that whether the polaronic redox behavior exists is based on Fe ions. In addition, the band gap of $NaFePO_4$ does not change much with respect to $LiFePO_4$. Therefore, from the perspective of the values of the bandgap, replacement of Li ions has little effect on the conductivity.

Polaronic redox behavior of Li_xMPO_4 (M = Mn, Co, Ni)

The PDOS of Li_xMPO_4 (M = Mn, Co, Ni; x = 1, 0.75) are shown in Fig. 4 and 5, and the PDOS of MPO_4 are shown in Fig. S2 (ESI†). The absolute values of the magnetic moments of TM ions in these structures (x = 1, 0.75, 0.5, 0.25, 0) are given in Fig. 6. In $LiMPO_4$, the calculated magnetic moments of Mn^{2+}, Co^{2+} and Ni^{2+} are about 4.6, 2.7 and 1.8 μ_B. Combined with Fig. 4, we can see that all of Mn^{2+}, Co^{2+} and Ni^{2+} show high-spin states. For MPO_4, the calculated magnetic moments of Mn^{3+}, Co^{3+} and Ni^{3+} are about 3.8, 3.2 and 0.9 μ_B, corresponding to Mn^{3+} and Co^{3+} in high-spin states, and Ni^{3+} in a low-spin state, respectively. It is worth noting that in Fig. 4, we can find that when M = Mn, Fe or Co, the peak of $LiMPO_4$ at the VBM is separated from the
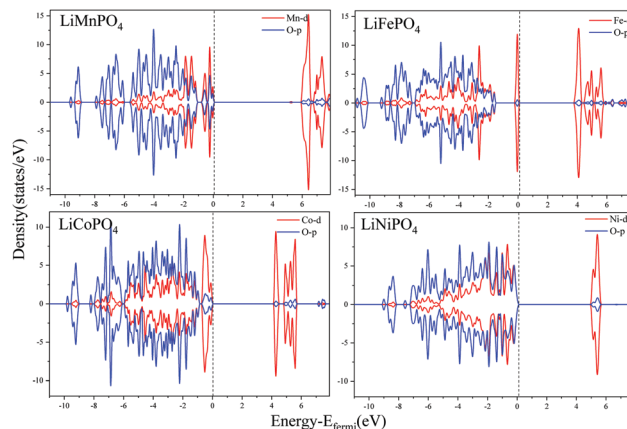

Fig. 4 The HSE06 calculated partial density of states of $LiMPO_4$ (M = Mn, Fe, Co, Ni).
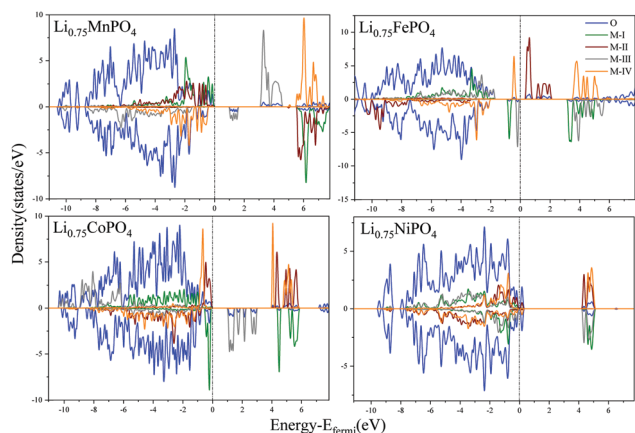
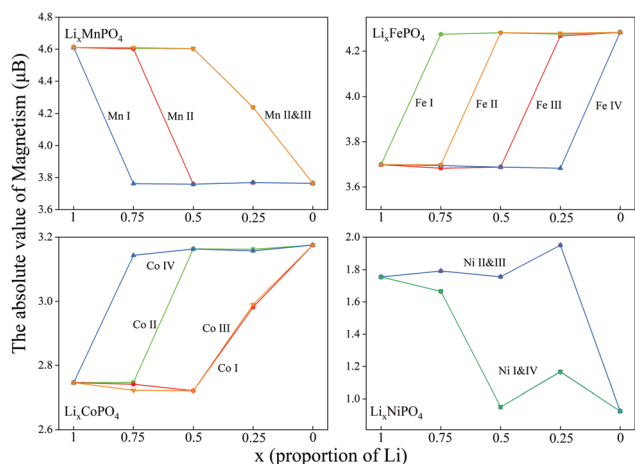Fig. 5 The HSE06 calculated partial density of states of $Li_{0.75}MPO_4$ (M = Mn, Fe, Co, Ni).

Fig. 6 The absolute value of the calculated magnetic moments of four transition metal ions in Li_xMPO_4 (x = 1, 0.75; M = Mn, Fe, Co, Ni).

rest of the valence band, while in the case of M = Ni, the contributions of Ni and O to the peak at the VBM are very similar, and the peak here is not separated from the lower part. This phenomenon can be attributed to the fact that the Ni–O bond is more covalent than the other M–O bonds.

From Fig. 5, it can be interestingly found that, in the case of M = Mn or Co, the PDOS shows a similar change to the case of M = Fe, while the case of M = Ni is very different. In $LiMnPO_4$ or $LiCoPO_4$, when one Li ion is removed, the peak of one Mn or Co ion at the VBM shifted to the position above the Fermi level, while the peaks of the other three Mn or Co ions at the VBM just shifted slightly. However, in $LiNiPO_4$, for the four Ni ions, when one Li ion is removed, the variation of their DOS near the Fermi level is very close. Moreover, the contribution of Ni-3d does not show a clear advantage with respect to the contribution of the O-2p orbital; this is very different from the situation of M = Mn, Fe and Co.

Therefore, it can be concluded that there is still obvious polaronic redox behavior in $Li_{0.75}MnPO_4$ and $Li_{0.75}CoPO_4$, and the polaronic redox behavior in $Li_{0.75}NiPO_4$ is very weak.

As a verification, we show the change of the magnetic moments of transition metal ions in the whole delithiation process (x = 1, 0.75, 0.5, 0.25, 0) in Fig. 6. We can find that when one Li ion is removed, the magnetic moments of the four Ni ions in $LiNiPO_4$ have changed into two pairs of values. While in $LiMnPO_4$ and $LiCoPO_4$, when the first or second Li ion is removed, one Mn or Co ion shows the greatest change, its magnetic moment jumps from the magnetic moment of the bivalent state to the magnetic moment of the trivalent state, and the other three Mn or Co ions change little. However, when the third or last Li ion is removed, there is a case where the magnetic moments of two transition metal ions change together. Thus, polaronic redox behavior also exists in $LiMnPO_4$ and $LiCoPO_4$, but may be weaker than that in $LiFePO_4$. In addition, due to the Jahn–Teller effect, the effective mass of the polaron in $LiMnPO_4$ may be larger, which also increases the influence of polaronic redox behavior. The weak polaronic redox behavior in $LiNiPO_4$, combined with the disappearing bandgap in Fig. 5, indicates better electrical conductivity in Li_xNiPO_4 compared with $LiFePO_4$. The above difference between Ni and Fe (Mn, Co) can be attributed to the more covalent nature of the Ni–O bond in $LiNiPO_4$, as discussed in Fig. 4, which makes the polaronic redox behavior in $LiNiPO_4$ drastically weakened.

In addition, we calculated the case of $LiFe_{0.5}Mn_{0.5}PO_4$. For this case, we tested various arrangements of Fe and Mn ions in antiferromagnetic conditions, and then took the structure with the lowest energy for the next calculations (see Fig. S3 for the specific structure, ESI†). The calculation results show that the Fe or Mn ions jump from divalent to trivalent one by one (after all Fe ions are changed, Mn ions change) and exhibit obvious polaronic redox behavior (see Fig. S4, ESI†).

Polaronic redox behavior of Li_xMPO_4 (M = Mn, Co, Ni) with antisite defects

Further, we briefly examined the effect of antisite defects (common in olivine cathode materials) on the polaronic redox behavior by exchanging the position of a Li and an M ion in the $LiMPO_4$ (M = Mn, Fe, Co, Ni) structure. The absolute values of the magnetic moments of TM ions in these structures (x = 1, 0.75, 0.5, 0.25) are given in Fig. 7. The case of Li0 wasn't considered since the removal of the antisite Li is impossible during in real electrochemical cycling.

After the introduction of the antisite defect, it can be found that the change in the magnetic moments of the transition metal ions shows no obvious difference to before and so the polaronic redox behaviors do not change in the case of M = Mn, Fe, Co. But, for M = Ni, the magnetic moments of the three Ni ions including the antisite Ni are substantially unchanged, and the magnetic moments of the Ni ions closest to the antisite Li ion in the three normal positions are significantly changed. From this result, $LiNiPO_4$ may exhibit a slight polaronic redox behavior under the influence of the antisite defect.

Here, we calculated the formation energy of an antisite defect with an M/Li exchange pair in $LiMPO_4$ (M = Mn, Fe, Co, Ni). It can be seen that the formation energies are 0.72,
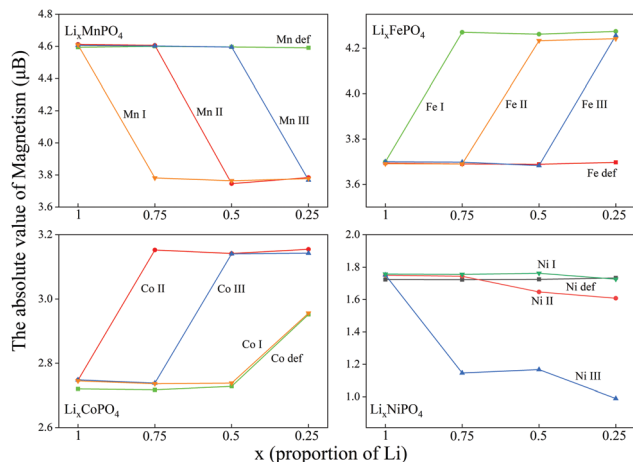
Fig. 7 The absolute value of the calculated magnetic moments of four transition metal ions in Li_xMPO_4 (x = 1, 0.75; M = Mn, Fe, Co, Ni) with antisite defects.

0.63, 0.34 and 0.30 eV in the order M = Mn, Fe, Co, Ni. For M = Mn, Fe, Co, antisite defects have little effect on the change of polaronic redox behavior. However, for $LiNiPO_4$, the antisite defect energy is the lowest, and it can be considered that $LiNiPO_4$ may have more antisite defects. Since $LiNiPO_4$ may exhibit a slight polaronic redox behavior under the influence of the antisite defect, we believe that $LiNiPO_4$ would show obvious polaronic redox behavior in the actual situation with the largest degree of antisite defects, so that its rate capability would not be significantly improved compared with $LiFePO_4$, which is also consistent with the experimental results.[28] In order to improve this situation, it may be necessary to reduce the number of antisite defects in $LiNiPO_4$.

Conclusions

In this work, HSE06 hybrid functional investigations have been performed on $XMPO_4$ systems (X = Li, Na, and M = Mn, Fe, Co, Ni). By analyzing the PDOS and magnetic moments of TM ions, polaronic redox behavior is clearly found for $LiFePO_4$ during the delithiation. When Li ions are replaced by Na ions, the polaronic redox behavior remains unaffected, with little effect of replacing Li on improving the conductivity. When Fe is replaced by Mn or Co, the polaronic redox behavior also exists, while when Fe is replaced by Ni, the polaronic redox behavior almost disappears. In combination with the substantial reduction in the bandgap during delithiation, it is believed that the electronic conductivity of $LiNiPO_4$ may be greatly improved during delithiation. For $LiMnPO_4$ and $LiCoPO_4$, it is judged that the electronic conductivity should not be greatly improved since the polaronic redox behavior is still obvious. The difference between Ni and Mn, Fe and Co can be attributed to the more covalent nature of the Ni–O bond in $LiNiPO_4$, so that the polaronic redox behavior in $LiNiPO_4$ is greatly weaker. For the cases with antisite defects, our results indicate that the polaronic redox behaviors do not change in the case of M = Mn, Fe, Co.

But $LiNiPO_4$ may exhibit a slight polaronic redox behavior under the influence of the antisite defect. The low antisite defect energy of $LiNiPO_4$ makes the number of antisite defects increase, so that $LiNiPO_4$ may also exhibit polaronic redox behavior in the actual situation. This work shows that in olivine structural materials like $LiFePO_4$, polaronic redox behavior does not necessarily exist, and replacement of Fe can play a role in tuning this behavior.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

1 Z. Yang, J. Zhang, M. C. W. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon and J. Liu, *Chem. Rev.*, 2011, **111**(5), 3577–3613.
2 B. Dunn, H. Kamath and J. Tarascon, *Science*, 2011, **334**(6058), 928–936.
3 A. K. Padhi, K. S. Nanjundaswamy and J. B. Goodenough, *J. Electrochem. Soc.*, 1997, **144**(4), 1–7.
4 J. Sugiyama, H. Nozaki, M. Harada, K. Kamazawa, O. Ofer, M. Månsson, J. H. Brewer, E. J. Ansaldo, K. H. Chow and Y. Ikedo, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **84**(5), 1–9.
5 S. Y. Chung, J. T. Bloking and Y. M. Chiang, *Nat. Mater.*, 2002, **1**(2), 123–128.
6 K. Saravanan, M. V. Reddy, P. Balaya, H. Gong, B. V. R. Chowdari and J. J. Vittal, *J. Mater. Chem.*, 2009, **19**(5), 605–610.
7 S. Lim, C. S. Yoon and J. Cho, *Chem. Mater.*, 2008, **20**(12), 4560–4564.
8 C. M. Doherty, R. A. Caruso, B. M. Smarsly, P. Adelhelm and C. J. Drummond, *Chem. Mater.*, 2009, **21**(21), 5300–5306.
9 Y. Wang, Y. Wang, E. Hosono, K. Wang and H. Zhou, *Angew. Chem., Int. Ed.*, 2008, **47**(39), 7461–7465.
10 S. L. Bewlay, K. Konstantinov, G. X. Wang, S. X. Dou and H. K. Liu, *Mater. Lett.*, 2004, **58**(11), 1788–1791.
11 K. Zaghib, K. Striebel, A. Guerfi, J. Shim, M. Armand and M. Gauthier, *Electrochim. Acta*, 2004, **50**(2–3 Spec. Iss.), 263–270.
12 N. Ravet, Y. Chouinard, J. F. Magnan, S. Besner, M. Gauthier and M. Armand, *J. Power Sources*, 2001, **97–98**, 503–507.
13 D. Lepage, C. Michot, G. Liang, M. Gauthier and S. B. Schougaard, *Angew. Chem., Int. Ed.*, 2011, **50**(30), 6884–6887.
14 P. S. Herle, B. Ellis, N. Coombs and L. F. Nazar, *Nat. Mater.*, 2004, **3**(3), 147–152.

15 C. Hu, H. Yi, H. Fang, B. Yang, Y. Yao, W. Ma and Y. Dai, *Mater. Lett.*, 2011, **65**(9), 1323–1326.

16 X. J. Chen, G. S. Cao, X. B. Zhao, J. P. Tu and T. J. Zhu, *J. Alloys Compd.*, 2008, **463**(1–2), 385–389.

17 H. H. Chang, C. C. Chang, C. Y. Su, H. C. Wu, M. H. Yang and N. L. Wu, *J. Power Sources*, 2008, **185**(1), 466–472.

18 H. C. Shin, S. Bin Park, H. Jang, K. Y. Chung, W. Il Cho, C. S. Kim and B. W. Cho, *Electrochim. Acta*, 2008, **53**(27), 7946–7951.

19 W. S. Yoon, K. Y. Chung, K. W. Nam, J. McBreen, D. Wang, X. Huang, H. Li, L. Chen and X. Q. Yang, *J. Power Sources*, 2008, **183**(1), 427–430.

20 J. Xu, G. Chen, Y. J. Teng and B. Zhang, *Solid State Commun.*, 2008, **147**(9–10), 414–418.

21 Z. Liu, X. Huang and D. Wang, *Solid State Commun.*, 2008, **147**(11–12), 505–509.

22 T. Maxisch, F. Zhou and G. Ceder, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2006, **73**(10), 1–6.

23 B. Ellis, L. K. Perry, D. H. Ryan and L. F. Nazar, *J. Am. Chem. Soc.*, 2006, **128**(35), 11416–11422.

24 Y. Sun, X. Lu, R. Xiao, H. Li and X. Huang, *Chem. Mater.*, 2012, **24**(24), 4693–4703.

25 M. D. Johannes, K. Hoang, J. L. Allen and K. Gaskell, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2012, **85**, 115106.

26 C. Delacourt, P. Poizot, M. Morcrette, J. M. Tarascon and C. Masquelier, *Chem. Mater.*, 2004, **16**(1), 93–99.

27 K. Amine, K. Yasuda and M. Yamachi, *Electrochem. Solid-State Lett.*, 2000, **3**(4), 178–179.

28 J. Wolfenstine and J. Allen, *J. Power Sources*, 2005, **142**(1–2), 389–390.

29 S. M. Oh, S. T. Myung, J. Hassoun, B. Scrosati and Y. K. Sun, *Electrochem. Commun.*, 2012, **22**(1), 149–152.

30 J. Heyd, G. E. Scuseria and M. Ernzerhof, *J. Chem. Phys.*, 2003, **118**(18), 8207–8215.

31 G. Kresse and J. Furthmüller, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **54**(16), 11169–11186.

32 G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**(1), 15–50.

33 D. Joubert, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**(3), 1758–1775.

34 G. Rousse, J. Rodriguez-Carvajal, S. Patoux and C. Masquelier, *Chem. Mater.*, 2003, **15**(21), 4082–4090.

35 H. D. Luong, T. D. Pham, Y. Morikawa, Y. Shibutaniac and V. A. Dinh, *Phys. Chem. Chem. Phys.*, 2018, **20**, 23625–23634.

36 J. X. Zheng, G. F. Teng, J. L. Yang, M. Xu, Q. S. Yao, Z. Q. Zhuo, W. L. Yang, Q. H. Liu and F. Pan, *J. Phys. Chem. Lett.*, 2018, **9**(21), 6262–6268.

37 K. M. Bui, V. A. Dinh, S. Okada and T. Ohno, *Phys. Chem. Chem. Phys.*, 2015, **17**, 30433–30439.

38 M. D. Johannes, K. Hoang, J. L. Allen and K. Gaskell, *ECS Trans.*, 2012, **41**(29), 35–42.

This journal is © the Owner Societies 2019

Phys. Chem. Chem. Phys., 2019, **21**, 4578–4583 | **4583**