Electronic and Atomic Structures of LiMPO₄ 
(M = Fe, Fe₁/₄Mn₁/₄Co₁/₄Ni₁/₄): A DFT Study

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Electronic and atomic structures of LiFe₁₄Mn₁₄Co₁₄Ni₁₄PO₄ and LiFePO₄ were investigated by using the first-principles density functional theory. Our calculations demonstrate that doping Mn, Co and Ni atoms at Fe sites of LiFePO₄ enhances the electron localization at Fe sites, which leads to the metallic characteristics of LiFe₁₄Mn₁₄Co₁₄Ni₁₄PO₄. Thus, the electronic conductivity of LiFe₁₄Mn₁₄Co₁₄Ni₁₄PO₄ may be improved. The doped material is expected to be promising cathode material for rechargeable lithium-ion batteries.

Keywords: Cathode Materials, Structural Prediction, Band Gap, Lithium-Ion Batteries.

1. INTRODUCTION

Rechargeable lithium-ion batteries (LIBs) have been used widely in mobile phones, laptop computers, digital cameras, electrical vehicles and hybrid electrical vehicles. In rechargeable LIBs, the cathode material is a key component mainly relating to the performance of the batteries. Recently, lithium transition metal phosphates with ordered olivine-type structures, LiMPO₄ (where M = Fe, Mn, Ni, and Co), and lithium iron silicate (Li₂FeSiO₄) have attracted great attention as lithium insertion cathode materials for the next generation of rechargeable LIBs. The potential of the ordered olivine-type structures, LiFePO₄ (~3.0–5.1 V). Also, Mn and Fe in the solid solution LiFePO₄-FePO₄ with a voltage plateau at 3.4 V. Wang et al. reported LiFe₁₄CoPO₄ solid solutions keep a rather high capacity during 20 cycles, retaining 88.4% of the original capacity for LiFe₆Co₃PO₄, 86.3% for LiFe₂Co₃PO₄, and 88.1% for LiFe₃Co₃PO₄. Chen et al. synthesized successfully the ternary solid solution LiFeₓ/₄Mn₁/₄Co₁/₄PO₄ by the hydrothermal reaction with the lattice parameters of a = 10.337 Å, b = 6.008 Å, c = 4.717 Å, and volume = 292.95 Å³. A quaternary solid solution LiFeₓ/₄Mn₁/₄Co₁/₄Ni₁/₄PO₄ with lattice parameters smaller than LiFePO₄ and larger than LiCoPO₄ has further been prepared, where there are three redox couples of Fe<sup>3+</sup>/Fe<sup>2+</sup>, Mn<sup>2+</sup>/Mn<sup>3+</sup> and Co<sup>3+</sup>/Co<sup>2+</sup> at ~3.6, 4.2 and 4.7 V. Also, Mn and Fe in the solid solution display high electrochemical activity in a voltage range of 3.0–5.1 V.

The above studies show that the ionic substitution with Mn, Co and Ni at Fe sites of LiFePO₄ improves electrochemical performance. However, the detailed electronic and atomic structures of LiFe₁₄Mn₁₄Co₁₄Ni₁₄PO₄ still open, which is useful to consider physical background of the compound and find ways for further improvement of the electrochemical performance. In this study, the structural performance of LiFeₓ/₄Mn₁/₄Co₁/₄Ni₁/₄PO₄ including the lattice parameters and the electronic densities of states was quantitatively analyzed using the first-principles density functional.
theory (DFT) compared to LiFePO₄. This is because DFT is a useful tool to realize the above goal.²¹–²⁹

### 2. COMPUTATIONAL METHOD

All the calculations in this work were carried out using the DMol³ package based on the first-principles DFT.³⁰,³¹ We used the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functionals and Double Numerical plus d-functions (DND) atomic orbitals as basis set.³² In the meantime, we also used the local density approximation (LDA) with the Perdew-Wang (PWC) exchange-correlation functionals.³³ The first-principles DFT semicore pseudopotentials (DSPP) treatment was implemented for relativistic effects, which replaces core electrons by a single effective potential.³⁴ Li 2s, Fe 3d and 4s, Mn 3d and 4s, Co 3d and 4s, Ni 3d and 4s, P 3s and 3p, and O 2s and 2p were regarded as the valence electrons, and all the others were regarded as the core electrons.

To study the doping effect, the calculations of the 1 × 2 × 1 expanded supercell (56 atoms) for LiFe₁/₄Mn₁/₄Co₁/₄Ni₁/₄PO₄ and LiFePO₄ were performed, while the latter calculation was made for comparison purpose. The Brillouin zone of the supercell was sampled by 4 × 4 × 4 k-points within the Monkhorst-Pack scheme.³⁵ Full structural optimizations were obtained with symmetry constraints using a convergence tolerance of energy of 2.0 × 10⁻⁵ hartree (1 hartree = 27.2114 eV), a maximum force is 0.004 hartree/Å and a maximum displacement of 0.005 Å. The orbital cutoff was set to be global, and smearing was 0.005 Ha.

In order to demonstrate the validity of our computational method, structural optimizations of LiFePO₄ were performed based on the bulk crystal structure observed experimentally.³⁶ The structural optimizations of LiFe₁/₄Mn₁/₄Co₁/₄Ni₁/₄PO₄, Fe₁/₄Mn₁/₄Co₁/₄Ni₁/₄PO₄ and FePO₄ are based on the optimized LiFePO₄. The olivine-type crystal structures of LiFe₁/₄Mn₁/₄Co₁/₄Ni₁/₄PO₄ and LiFePO₄ in the 1 × 2 × 1 expanded supercell (56 atoms) are orthorhombic (space group Pnma), and shown in Figure 1. As shown in Figure 1(a), one unit cell of LiFePO₄ contains four groups of three cation-centered polyhedrons; a PO₄ tetrahedron, a LiO₆ octahedron and a FeO₆ octahedron. As shown in Figure 1(b), one unit cell of LiFe₁/₄Mn₁/₄Co₁/₄Ni₁/₄PO₄ contains four groups of three cation-centered polyhedrons; the first group consists of a PO₄, a LiO₆ and a FeO₆. 2nd to 4th have the same two formers, while the third are MnO₆, CoO₆ and NiO₆, respectively. The calculated lattice parameters and atomic coordinates for LiFePO₄ and FePO₄ are listed in Table I, and compared with experimental values of LiFePO₄.³⁶ As seen in Table I, in the GGA calculations, the lattice parameters ‘a’ and ‘b’ of LiFePO₄ decrease by 2.7% and 2.9% compared with the experimental values, respectively, and ‘c’ increases by 0.4% and the calculated volume decreases by 5.1%. We have also used LDA calculations, the obtained lattice parameters ‘a’, ‘b’ and ‘c’ of LiFePO₄ decrease by 6.3%, 6.9% and 1.8%, respectively, and the calculated volume decreases by 14.4%. Thus, GGA has better calculation accuracy and thus is used in this work. Note that the lattice parameters of FePO₄ in Table I are similar to those in LiFePO₄, indicating the structural stability of LiFePO₄ when Li de-intercalation occurs, which confirms that LiFePO₄ as a cathode material for rechargeable LIBs gains a long cycling lifetime.

### 3. RESULTS AND DISCUSSION

The calculated lattice parameters and atomic coordinates for LiFe₁/₄Mn₁/₄Co₁/₄Ni₁/₄PO₄ and Fe₁/₄Mn₁/₄Co₁/₄Ni₁/₄PO₄ are listed in Table I. As seen in Table I, ‘a’ and ‘b’ of LiFe₁/₄Mn₁/₄Co₁/₄Ni₁/₄PO₄ decrease by 0.2% and 0.2% compared with the experimental values, respectively, and ‘c’ increases by 1.3% and the calculated volume increases by 0.9%. Thus, two structures are very similar. In addition, this is also the case between Fe₁/₄Mn₁/₄Co₁/₄Ni₁/₄PO₄ and LiFe₁/₄Mn₁/₄Co₁/₄Ni₁/₄PO₄, indicating the structural stability of the latter when Li de-intercalation occurs, which confirms that LiFe₁/₄Mn₁/₄Co₁/₄Ni₁/₄PO₄ as a cathode material for LIBs should benefit for a long cycling lifetime.

The corresponding average bond lengths and the bond angles of atoms in LiFePO₄ and FePO₄, LiFe₁/₄Mn₁/₄Co₁/₄Ni₁/₄PO₄ and Fe₁/₄Mn₁/₄Co₁/₄Ni₁/₄PO₄ are calculated, which are also shown in Table I. In LiFePO₄ when Li de-intercalation occurs, the transition metal Fe is oxidized from Fe²⁺ to Fe³⁺ valence states, and the average bond length of Fe–O decreases by 4.4%, and P–O increases by 0.3%, and the average bond angles of O–Fe–O and O–P–O increase by 2.4% and 1.7%, respectively. In the case of LiFePO₄, Mn–O, Co–O, Ni–O and P–O decrease by 5.4%, 8.0%, 9.0%, 4.0% and 0.7%, respectively, and the average bond angles of O–Fe–O, O–Mn–O, O–Co–O, O–Ni–O and
O–P–O increase by 1.8%, 4.4%, 5.1%, 2.4% and 1.2%, respectively. It is obvious that FeO$_6$ and NiO$_6$ octahedra are less distorted than MnO$_6$ and CoO$_6$ octahedra. The distortion in O–Mn–O angle would not seem to be a result of Mn doping into the LiFePO$_4$ host, but rather reflect Jahn-Teller distortion for octahedral coordination. This distortion in O–Mn–O angle also occurs on Li delithiation from Li$_{0.875}$Mn$_{1.125}$SiO$_4$ to Li$_{0.875}$Fe$_{0.875}$Mn$_{0.125}$SiO$_4$.

As a comparison, our calculated average bond lengths are in accordance with the experimental results. Thus, as for LiFePO$_4$ and LiFe$_{1/4}$Mn$_{1/4}$Co$_{1/4}$Ni$_{1/4}$PO$_4$ when Li de-intercalation occurs, the decreases in the average bond lengths of Fe–O, Mn–O, Co–O and Ni–O are due to the so-called rehybridization shift, which occur in the transition metal ligand bond at high levels of oxidation in order to reduce the effect of valent change on the transition metal site. However, the average bond lengths of P–O are almost unchanged, implying the bonding nature between P and O atoms remains unchangedable during the delithiation-liithiation process. Thus, it is obvious that both LiFe$_{1/4}$Mn$_{1/4}$Co$_{1/4}$Ni$_{1/4}$PO$_4$ and LiFePO$_4$ show little structural distortions during Li de-intercalation, and this structural stability is actually the consequence of a strong covalent P–O bond.

The electron density difference diagrams of (001) surfaces of FePO$_4$, LiFePO$_4$, Fe$_{1/4}$Mn$_{1/4}$Co$_{1/4}$Ni$_{1/4}$PO$_4$, and LiFe$_{1/4}$Mn$_{1/4}$Co$_{1/4}$Ni$_{1/4}$PO$_4$ are shown in Figure 2. The gray balls denote Fe atoms. The red and blue regions denote the electron accumulation and loss. As shown in Figure 2, for Fe$_{1/4}$Mn$_{1/4}$Co$_{1/4}$Ni$_{1/4}$PO$_4$ and FePO$_4$, the change of the electron density near Fe atoms occurs obviously when Li intercalation, and the electron accumulation around Fe sites by the Li intercalation happens, which is accompanied by the transformation of Fe atoms from the Fe$^{3+}$ ($t_{2g}^3 e_g^2$) to the Fe$^{2+}$ ($t_{2g}^4 e_g^2$). Oppositely, Li de-intercalation in LiFePO$_4$ and LiFe$_{1/4}$Mn$_{1/4}$Co$_{1/4}$Ni$_{1/4}$PO$_4$ implies a systematic depletion of electron in the $t_{2g}$ band.

The density of states (DOS) and partial density of states (PDOS) for LiFePO$_4$, FePO$_4$ and Fe-3d states calculated are shown in Figure 3. As shown in Figure 3, LiFePO$_4$
possesses a band gap \( (E_g) \) of 1.06 eV around the Fermi level \( E_F \), being larger than calculated \( E_g = 0.53 \) eV \(^{40} \) and close to calculated \( E_g \) of 1.08 eV.\(^{41} \) Therefore, LiFePO\(_4\) is a semiconductor with low electronic conductivity (our experimental value is \( 5.86 \times 10^{-3} \) S cm\(^{-1}\)),\(^{14} \) being much lower than that of commercial LiCoO\(_2\) (\( 10^{-3} \) S cm\(^{-1}\)) cathode material.\(^{42} \) This decreases the discharge capacity upon cycling, as observed by us earlier for LiFePO\(_4\), where the discharge capacity loss over the first 30 cycles is \( \sim 15\% \).\(^{7} \) As for LiFePO\(_4\), the valence band lies in the range from \(-11.85 \) to 0.00 eV formed by hybridization of Fe 3d-states, P 3p-states and O 2p-states. The conduction bands are mainly made up from Fe-3d states and the two bands are separated by \( E_F \) around \( E_F \). The PDOS of Fe-3d states demonstrates that the narrow bands near \( E_F \) can be assigned to Fe-3d bands. We observed the two main bands, one is from 1.26 to 2.71 eV corresponding to the conduction band with an \( e_g \) characteristics, and the other is from \(-1.66 \) to 0.00 eV, relating to the valence band with a \( t_{2g} \) characteristic. The above results show a typical Fe\(^{2+} \) state in LiFePO\(_4\).

The bonding nature for Li-intercalation into the host structures can be studied by comparing DOS of delithiated-lithiated phases. Since there is a strong bonding among Fe-3d, P-3p and O-2p states of FePO\(_4\), some metallic characteristics are present. When Li is intercalated, P-3p and O-2p states are shifted to the left with respect to \( E_F \), leading to hybridization among Li-2s, P-3p and O-2p states. Fe-3d states are shifted left compared with \( E_F \). Thus, the Li intercalation into the host structures is responsible for the metal-semiconductor transition of FePO\(_4\).

DOS and PDOS for LiFe\(_{1/4}\)Mn\(_{1/4}\)Co\(_{1/4}\)Ni\(_{1/4}\)PO\(_4\), Fe\(_{1/4}\)Mn\(_{1/4}\)Co\(_{1/4}\)Ni\(_{1/4}\)PO\(_4\), and related Fe-3d, Mn-3d, Co-3d and Ni-3d states are shown in Figure 4. There is a strong bonding among Fe-3d, Mn-3d, Co-3d, Ni-3d, P-3p and O-2p states in Fe\(_{1/4}\)Mn\(_{1/4}\)Co\(_{1/4}\)Ni\(_{1/4}\)PO\(_4\), showing metallic characteristics. When Li is intercalated, the P-3p and O-2p states are shifted left with respect to \( E_F \), resulting in hybridization among Li-2s, P-3p and O-2p states. Fe-3d and Ni-3d states are shifted left too. Mn-3d, Co-3d and Ni-3d states form a band localized within the band gap, which is formed by Fe-3d states located below and above \( E_F \), also displaying metallic characteristics of LiFe\(_{1/4}\)Mn\(_{1/4}\)Co\(_{1/4}\)Ni\(_{1/4}\)PO\(_4\). Note that Mn-3d states play a key role in them.

4. CONCLUSIONS

Electronic and atomic structures of LiFe\(_{1/4}\)Mn\(_{1/4}\)Co\(_{1/4}\)Ni\(_{1/4}\)PO\(_4\) and LiFePO\(_4\) were investigated by using the first principles DFT. It is found that LiFePO\(_4\) is a semiconductor with a band gap of 1.06 eV while LiFe\(_{1/4}\)Mn\(_{1/4}\)Co\(_{1/4}\)Ni\(_{1/4}\)PO\(_4\) displays a metallic characteristic by filling the band gap with Mn-3d, Co-3d and Ni-3d states, implying an improvement in the electronic conductivity of LiFe\(_{1/4}\)Mn\(_{1/4}\)Co\(_{1/4}\)Ni\(_{1/4}\)PO\(_4\). The doped material is expected to be promising cathode material for rechargeable LIBs.
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References and Notes


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