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Li- Site and Metal-Site Ion Doping in Phosphate-Olivine $LiCoPO_4$ by First-Principles Calculation *

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We present a first-principles investigation of the crystal and electronic structure as well as the average insertion voltage of the Li-site (by Na and Cr) and metal-site (by isovalent Ni, Zn, Ca, Mg and Mn and aliovalent Cu, Al, In, Mo and Zr) doped $LiCoPO_4$. The results show that both the Li-site doping and metal-site doping may reduce the volume change of the material during Li extraction/reinsertion process. The metal doped at Li-site will block the path of Li ion diffusion. The doping by aliovalent transition metals will introduce defect levels in the energy band. It could influence the conductivity insertion voltage.

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Since the demonstration of reversible electrochemical Li insertion/extraction for $LiFePO_4$ in 1997,[1] Li transition metal phosphate with olivine structure $LiMPO_4$ (M=Fe, Mn and Co) has attracted much attention as potential cathode material for Li-ion batteries.[2−9] However, wide applications of these compounds were hindered by their inherent low electronic and ionic conductivity at room temperature. Since high electronic and ionic conductivities are prerequisites to maintain fast electrochemical reaction for high power batteries, many studies have been focused on improving their electrochemical performance by the carbon coating of particles[2] and the formation of a metal-phosphate (Fe_2P or Co_2P) layer along $LiMPO_4$ particle surface,[3,4] which did not improve the intrinsic electronic conductivity itself remarkably. One possible approach for improving the intrinsic electronic conductivity itself is to dope aliovalent and isovalent metals on Li sites or metal sites. For Li-site doping, a series of theoretical and experimental studies indicated that the electronic conductivity of $LiFePO_4$ can be increased by Cr^{3+} doping.[5,6] Recently, Ouyang *et al.* suggested that the Na ion doping also improves both the electronic and ionic conductivity of $LiFePO_4$, in comparison with the relative low ionic conductivity observed in the high valence transition metal ions doped sample.[7] For metal-site doping, Padhi *et al.*[1] have reported that the $Li(Mn_yFe_{1-y})PO_4$ solid solution system has a 4.1 V plateau (Mn^{3+}/Mn^{2+}) and the corresponding capacity increases as Mn content increases. Ni *et al.*[5] added a small amount of Mg^{2+}, Cu^{2+} and Zn^{2+} ions in $LiFePO_4$ by the route of co-precipitation, and found that these ions doping would improve its capacity delivery and cycle performance. The experimental investigation of Mn-doped[8] and Fe-doped[10] $LiCoPO_4$ have also shown that the capacity retention could be improved by the transition metal doping.

In this Letter, we theoretically investigate the crystal structure, electronic structure of the Li-site and Co-site doped $LiCoPO_4$, as well as the effect on the average insertion voltage. We choose isovalent Na^+ and high valence Cr^{3+} ions substituting Li ions and isovalent metal ions Ni^{2+}, Zn^{2+}, Mg^{2+}, Ca^{2+} and Mn^{2+} as well as aliovalent metal ions Al^{3+}, In^{3+}, Nb^{4+}, Mo^{4+} and Zr^{4+} substituting Co^{2+} ions.

The first-principles calculations based on density-functional theory are performed using the Vienna *ab initio* Simulation Package (VASP),[11] which has been successfully applied to calculate many complex systems. The electrons are described in the general gradient approximation (GGA) and the projector augmented wave method.[12] The doped systems are simulated by replacing Li and/or Co atoms with doping metal atoms in an 84-atoms super-cell at the corresponding concentration. The wave functions were expanded in plane waves with an energy cutoff of 450eV. Brillouin zone integration of band structure was performed with $2 \times 1 \times 4$ Monkhorst-Pack mesh. The formation energies are well converged with respect to k-points. Fermi level is smeared by the Gaussian method with a width of 0.1 eV.

The theoretical average Li insertion potential could be obtained through total energy calculations.[13] The average insertion voltage is given by

$$\bar{V} = -\Delta G_r/F, \tag{1}$$

where ΔG_r is the change of Gibbs free energy in the insertion reaction, and F is the Faraday constant. Since the contributions from the entropy are relative little, the Gibbs energy difference is approximated by the internal energy term ΔE at 0 K, supplied by our first-principles total-energy calculations as follows:

$$\Delta E = E_{\text{total}}[\text{lithiated}] - E_{\text{total}}[\text{delithiated}] - E_{\text{total}}[\text{Li}]. \tag{2}$$

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Here the cohesive energy of Li is calculated with its *bcc* structure, which corresponds to the structure phase of the Li anode.

The Li site doping: the sodium ion and high valence transition metal ions may substitute for Li ions of $LiCoPO_4$ and form the Li-site doped compound. It is expected that more Li ions are removed than the number of doped metal ions when high valence metal ions substitute Li sites. For example, two Li vacancies are formed around the doped Cr ion when one Li atom is replaced by one Cr atom in Li site Cr^{3+} doping. Actually, there are many possible configurations for the two Li vacancies around the doped Cr ion. Here the configuration of two Li vacancies located at both sides of the Cr ion along the *b* direction is adopted, which is energetically favoured as suggested by Shi *et al.*[14] The close configuration of Cr ion and two Li vacancies is consistent with the coulomb attraction between the positive charged Cr_{Li} defect and negatively charged Li vacancy defects.

Table 1. Lattice constants for pure and doped $LiCoPO_4$, as well as the calculated volume change during Li extraction/reinsertion.

	a (Å)	*b* (Å)	*c* (Å)	Volume (Å^3)	Volume change(%)
$LiCoPO_4$(cal)	9.816	5.869	4.691	270.29	11.42
$CoPO_4$	9.622	5.473	4.579	241.17	
$Li_{0.92}Na_{0.08}CoPO_4$	9.821	5.897	4.707	272.64	9.21
$Na_{0.08}CoPO_4$	9.687	5.527	4.623	247.52	
$Li_{0.75}Cr_{0.08}CoPO_4$	9.816	5.852	4.686	269.19	7.87
$Cr_{0.08}CoPO_4$	9.698	5.558	4.600	248.00	

The optimized crystal parameters for Na and Cr doped $LiCoPO_4$ are listed in Table 1, together with values for pure $LiCoPO_4$. When Na substituting Li atoms, the volume of the unit cell changes little (0.13%) due to the close ionic size of Na^+ (0.97 Å) and Li^+(0.68 Å). We find that the average Li-O bond length (2.120 Å) of Na-doped $LiCoPO_4$ is slightly greater than that of the undoped material (2.113 Å). It is indicated that the Na-doped $LiCoPO_4$ has a slightly wider Li ion pathway and weaker Li-O interactions, which may improve the ionic conductivity. For the high valence Cr doping, the relaxed volume and lattice parameters *b* and *c* are smaller than those of pure $LiCoPO_4$ while lattice parameter *a* does not change remarkably, as well as the average Li-O bond length decreases to 2.067 Å. This indicates a narrower pathway and a stronger interaction of Li-O bonds in the Cr doped $LiCoPO_4$, and thus a poorer ionic conductivity is expected. If the Li ions can be extracted entirely, the volume change of lithiated/delithiated phases for Na doped system and the high valence Cr-doped system are 9.21% and 7.87%, respectively, which are significantly smaller (by 11.43%) than that of the undoped phase. This suggests that the high valence Cr-doped and Na-doped structures are more stable than that of pure $LiCoPO_4$ during Li extraction/reinsertion process and then ensure a better reversibility and cycle life time of the cathode.[15]

The electronic structure may reflect the characteristic features of the cathode material in the discharge/charge phases. Figure 1 shows the total electronic density of states (DOS) for pure $LiCoPO_4$, as well as that of Na ion and Cr ion doped structures. All these DOS show a metallic character of the compounds. The Fermi level lies in a band, which is mainly formed by Co *d* states. From Fig. 1, we can see that there are no obvious changes for the total DOS of the Na doped system in comparison with that of pure $LiCoPO_4$. However, the bands of the high valence Cr ion doped system are expanded to the high energy region. The gaps between different bands become shallower due to the band broadening. This change could help to improve the electronic conductivity of the system, which is in agreement with the experimental results of electronic conductivity for the high-valence metal Li-site doping phosphate-olivine battery materials.[7]

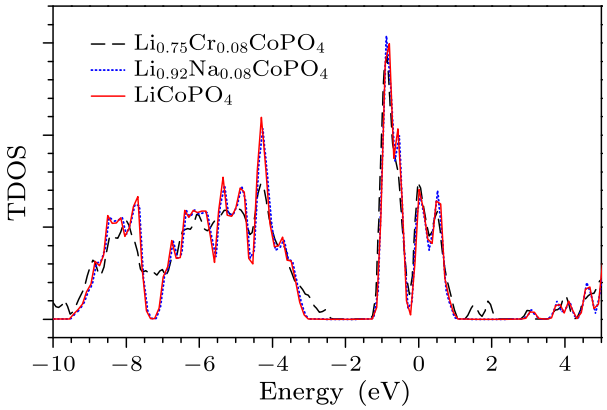

Fig. 1. Total density of states of pure $LiCoPO_4$ as well as Na- and Cr-doped $LiCoPO_4$. The Fermi level is set to be zero.

Table 2. Formation energy of Li vacancy or doped metal vacancy.

	Li(1)	Li(2)	Doped metal
$Li_{0.92}Na_{0.08}CoPO_4$	−1.664	−2.198	0.197
$Li_{0.75}Cr_{0.08}CoPO_4$	−1.785	−2.280	1.647

Since Li ions diffuse along a one-dimensional channel in $LiCoPO_4$, where the doped metal may reside, it is important to investigate the migration of Li and the doped metal ions in the doped system. Here we try to tackle the problem with the formation energy of their vacancies, i.e., the energy changes by removing them from the channel. There are two types of Li site in the doped $LiCoPO_4$. One is the Li ion located at the same tunnel with doped metal ion, denoted as Li(1) here. The other is located at a different tunnel with doped metal ion, denoted as Li(2). The energy required to remove a Li ion or the doped metal vacancy is listed in Table 2. It is indicated that both types of Li ions are very easy to be extracted, while $V_{Li}(2)$ is relative easier to form. However, when the doped metal ions are taken away from the one-dimension channel of the bulk compounds, it requires a huge energy especially for Cr ion. It is consistent with the earlier calculated

great migration energy barriers along Li ion transmission direction for Li ions and Cr ions, about 0.6 and 2.1 eV, respectively.[16] It is suggested that Li ions can be diffused along one-dimensional channel while Cr ions are not diffusible and only oscillate around their initial position. If all Li ions are extracted from the bulk compound, its theoretical capacity is about 167 mAh/g. However, the actual capacity is expected to be lower than the theoretical values since part of the Li ions are difficult to extract due to the block effect of the doped metal ions.

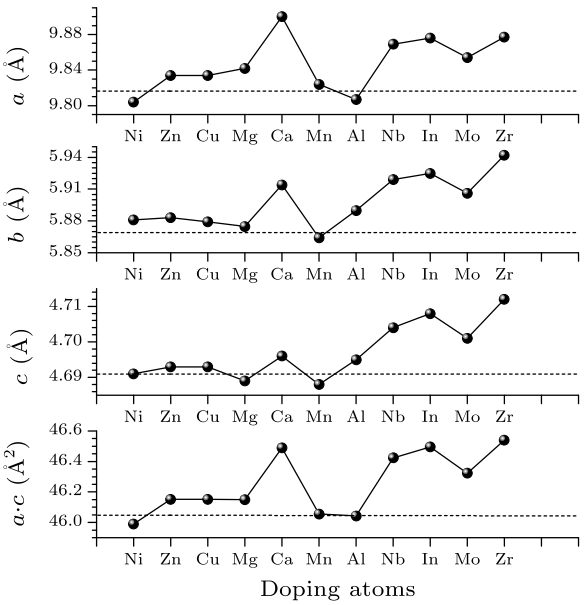

Fig. 2. Lattice parameters of Co-site metal doped $LiCoPO_4$ and the intercept area of Li ion diffusion path (dashed line represents the pure sample).

The metal site doping: In our investigation, we choose some bi-, tri-, and quad-valent metals to substitute for Co ion in $LiCoPO_4$ structures. The optimized crystal constants for the pure and metal-doped $LiCoPO_4$ are shown in Fig. 3. The results indicate that lattice parameters b and c of the doped structures increase except for the Ni, Mn and Al cases, while the change for the parameter c is not remarkable. The *ab initio* molecular dynamics study has proven that the Li ion diffusion channel is one-dimensional in phosphate-olivine materials.[17] In Fig. 2 we also show that the size of one-dimensional channel increases with the M-site doping of the studied metals except for those of Ni- and Al-doped cases. In addition, we find that the crystalline structure is clearly distorted due to metal ion doping. The Mn-doped distortion has also reported in $LiMn_yFe_{1-y}PO_4$ compound by Padhi *et al.*[1] It is well known that the distortion has a negative impact to the insertion and extraction performance of the cathode material. The structure changes of delithiated compounds is also remarkable when Co ion substituting by metal ions. The volume change of the doped systems for delithiated and lithiated phases is shown in Fig. 3. It is clear that, except for Al- and In-doped structures, the volume change of all other metal-doped systems decreases during Li extraction/reinsertion process. This indicates that the appropriate metal-site doping in $LiCoPO_4$ can enhance the structures stability of the materials during Li extraction/reinsertion process, thus the good reversibility and long cycle life time of cathode can be expected. The stability of structure is crucial to improve the capacity retention rate of the Li ion battery materials, and it has been suggested that the change of structure is responsible for the capacity fade observed in the experiments.[8,15]

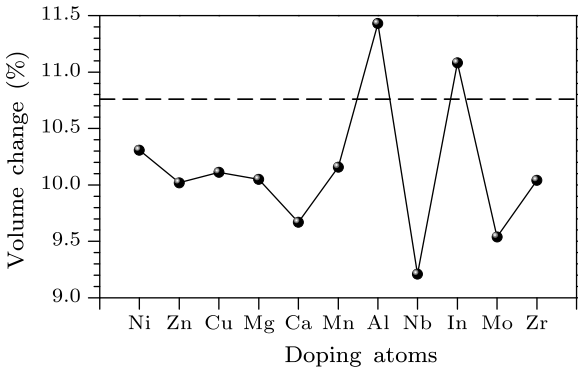

Fig. 3. Volume change of metal doped $LiCoPO_4$.

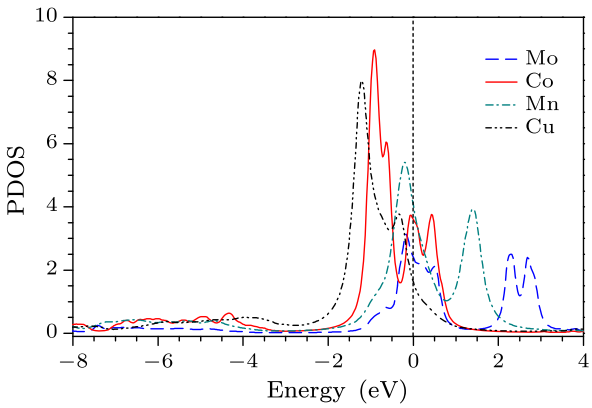

Fig. 4. PDOS of Co and metal-doped in $LiM_xCo_{1-x}PO_4$. The Fermi level is set to be zero.

In order to have an insight look of the characteristic features of the cathode material in the discharge/charge phases, the electronic structures of metal doped $LiCoPO_4$ are also studied. The partial density of states for doped aliovalent (Cu and Mo) and isovalent (Mn) metal ions and Co ion are shown in Fig. 4. It clearly shows that there is a hybridization between the doped-metal d states and Co $3d$ states. However, the $4d$ state of high valence Mo remarkably contributes to the bands around and above the Fermi level. Therefore, the high valence ion substituting for divalent Co ions may donate surplus electrons which may help to increase the electronic conductivity of the cathode material. For isovalent Mn doping, its d state has a remarkably contribution to the bands around and above the Fermi level, resembling the PDOS of doped high valence metals. The average total valence electrons within the Wigner–Seitz radius of Mn ions

are found to be reduced, which reflects that the increase of valence state of doped Mn ions. Meanwhile, it has been confirmed experimentally[8] that a Cu^{+1} ion substituting a Co^{2+} ion may form holes that increase the electronic conductivity of $LiCoPO_4$. Therefore, the aliovalent metal doping is expected to significantly affect the electronic properties of cathode materials.

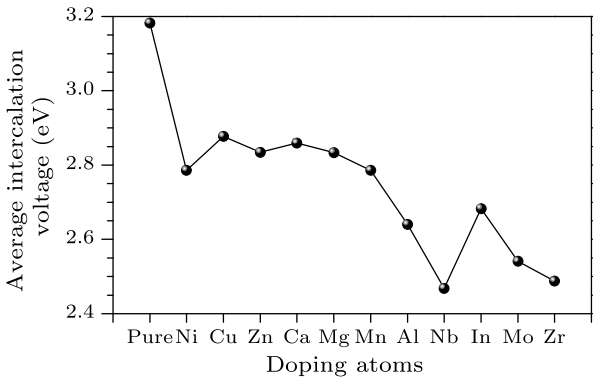

Fig. 5. Average intercalation voltage of $LiCoPO_4$ for different atoms.

The Li insertion potential plays an important role for applications in the cathode material of rechargeable Li ion batteries. The calculated average insertion voltages of the pure and metal-doped $LiCoPO_4$ are shown in Fig. 5. Our results for pure $LiCoPO_4$ are in good agreement with the GGA result by Bacq *et al.*[18] The results indicate that the GGA calculated average insertion voltage is underestimated by about 1.5 eV with respect to the experimental values. It is clear that the GGA results reflect the correct trend of the voltage change in Mn-doped $LiCoPO_4$, although the LDA+U calculated value are more consistent with experiments due to its better description on the strong correlation of d states. It is found that the calculated average insertion voltage of metal-doped sample is lower than that of the pure sample. Assuming the 1.5 eV difference between the theoretical and experimental average voltage for $LiCoPO_4$ is applicable to the doped systems, the real voltage of Co-site Ni, Cu, Zn, Ca, Mg, and Mn metal doped system are expected to be around 4.3–4.5 eV, which are in good agreement with available experimental results,[5] such as Mg, Mn, Ni doped samples. In addition, the substitution of Co-site by other metals (Al, Nb, In, Mo, and Zr) is expected to reduce the voltage to 3.95–4.2 eV. Although doping of these metals can reduce the average insertion voltage, the voltage is still higher than that of $LiFePO_4$. Usually, the ordinary electrolyte (1 M $LiPF_6$ dissolved in EC:DMC (1:1vol%)) can only work safely at the insertion voltage not higher than 4.8 V. It is obvious that reducing the average insertion voltage by the Co-site doping can make sure the doped $LiCoPO_4$ used as the cathode material and can avoid making the ordinary electrolyte decompose due to the higher average insertion voltage. This is a useful approach that can lower the voltage of $LiCoPO_4$ to match with other commercially used Li ion battery materials nowadays such as the ordinary electrolyte etc.

In summary, we have investigated the crystal and electronic structure as well as the average insertion voltage of the Li-site (by Na and Cr) and metal-site (by isovalent Ni, Zn, Ca, Mg and Mn and aliovalent Cu, Al, In, Mo and Zr) doped $LiCoPO_4$. Our results indicate that the volume change of the material is reduced by both Li-site doping and metal-site doping during Li extraction/reinsertion process. For Li-site substitution, it needs a rather great energy to remove the doped metal ions from $LiCoPO_4$. As a result, the Li-site doped metal will block the path of Li ion diffusion and decrease the Li ion diffusion in the Li battery material. For metal-site doping, when the transition metal with a different valence from that of Co ions, it will form aliovalent defects that contribute to electronic conductivity of the host material. In addition, the metal-site doping can decrease the average insertion voltage to a value avoiding decomposition of the widely used electrolyte. Hence, the metal doping is suggested to be a practical approach to influence the voltage of Li ion battery materials, such as $LiCoPO_4$.

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