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First principles investigation on the elastic and electronic properties of Mn, Co, Nb, Mo doped $LiFePO_4$

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ABSTRACT

In this work, the mechanical stability and electronic property of $LiFePO_4$ doped with Mn, Co, Nb and Mo studied using the first principles calculation. The doped $LiFePO_4$ has low defect formation energy and meets the criterion of mechanical stability, indicating that the doping of the four 3d transition metals can be stable. Band structure calculations depict half-metallic nature of the doping system. By calculating the Debye temperature and Poisson's ratio, it is found that the dopants can improve the mechanical stability of $LiFePO_4$. In addition, the study of the anisotropy of the material also shows that the doping of Co can make the material tend to be more isotropic. The above shows that the doping of Mn, Nb, Mo, especially Co, can improve the mechanical stability of the material and reduce the degree of anisotropy of the material, thereby reducing the risk of microcracking and shear deformation of the material.

1. Introduction

The olivine-type $LiFePO_4$ was put forward by Padhi [1] in 1997 firstly. It can be used as cathode material for Li ion second battery. It attracts much attention, because of its high theoretical capacity, good stability and safety, low cost and environmental friendly [2]. At present, this material is mainly used in Electric Vehicle (EV) and Hybrid Electric Vehicle (HEV), but the low ionic and electronic conductivity affects its cycling performance and restricts its further application on lithium batteries [3]. In order to improve its performance, many efforts have focused on particle size reduction, carbon coating and cation doping [4–8]. In these methods, the cation doping has attracted much attention as an effective method. Wang and co-workers [9], by first principles calculations and experiments, confirmed that the doping of Mo can enhance the electronic conductivity of materials. Chung et al. [10] have been observed that the electrochemical properties of $LiFePO_4$ were improved by doping Nb. All the above studies indicate that doping can effectively improve the partial performance of materials. However, current doping studies ignore the effect of material stability on battery performance. And the stability and safety of the battery materials are the basis of its application. At the same time, it will also greatly affect the performance of the material.

The unstable lattice vibration will cause phase transition of the material [11]. And external pressure may also lead to material deformation, resulting in material instability. Wang et al. [12] found that after 60 cycles, the charging and discharging curve of $LiFePO_4$ would have obvious slope characteristics. The polarization is increased upon cycling. In addition, flaws can be observed in some particles after 10 cycles, which should be a result from internal high strain during lithium extraction/insertion process. Maxish et al. [13] use the first principle to calculate the elastic properties of Li_xFePO_4. It is found that Li_xFePO_4 has a smaller shear modulus and a higher degree of anisotropy compared with other cathode materials, which leads to the decrease of the capacity of the $LiFePO_4$ and the poor cycle performance. Because the lattice structure symmetry of $LiFePO_4$ after doping will be changed, the structural stability of materials will also be changed. As a commercially available cathode material, $LiCoO_2$ also suffers from the breakdown of micro-structure due to internal strain [14]. At present, many studies have shown that the doping of metal cations in Co site can effectively protect the structural stability of $LiCoO_2$, inhibit the phase transition and improve the cycle performance of the material [15–17]. Therefore, the doping in Fe site may play a positive role in improving the structural stability of $LiFePO_4$ and improving its cycling performance.

To the best of our knowledge the change of $LiFePO_4$ stability after doping has not been investigated. In this work, four elements of transition group Mn, Co, Nb, and Mo are selected for substitution. By calculating the formation energy, elastic properties and anisotropy, the

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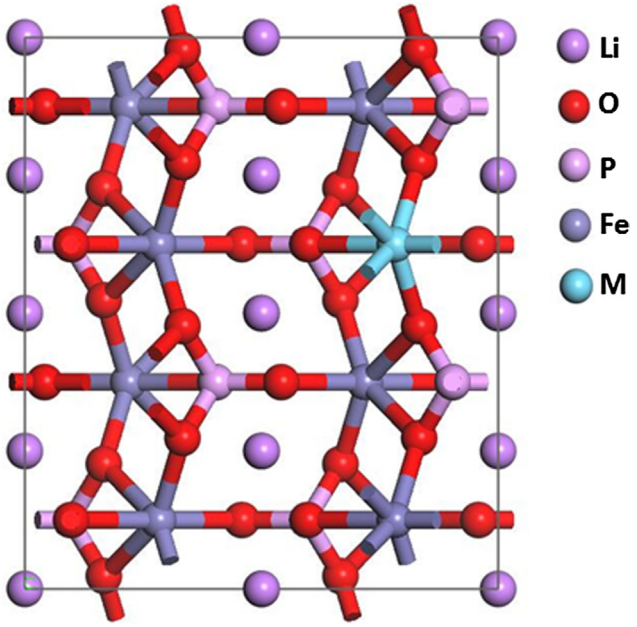

Fig. 1. Bulk model of M-doped $LiFePO_4$ (M = Mn, Co, Nb, Mo).

influence of different doping elements on the structure stability of the material is studied.

2. Computational details

All calculations are performed using the CASTEP in the framework of the density functional theory (DFT). The general gradient approximation (GGA) by Perdew and Wang (PW91) for the exchange-correlation was used. The configulation of Li-$1s^2$ $2s^1$, O-$2s^2$ $2p^4$, P-$3s^2$ $3p^3$, Fe-$3d^6$ $4s^2$, Co-$3d^7$ $4s^2$, Nb-$4s^2$ $4p^6$ $4d^4$ $5s^1$ are treated as the valence electrons for the Ultrasoft Pseudopotentials (USPP). Energy cut-off for the plane waves (380 eV) and a Monkhorst-Pack mesh (3 × 4 × 5) [11] were applied to ensure the total ground state energy convergence of 1.0×10^{-5} eV per atom. For the geometry optimization, Broyden – Fletcher – Goldfarb – Shanno (BFGS) algorithm was used. For all the calculations 1 × 2 × 1 supercell were used.

As shown in Fig. 1, the calculation model of $LiFePO_4$, space group is Pnma, has an orthorhombic olivine structure. Each cell contains four formula units and 28 atoms. The doping models were obtained by replacing a Fe atom in 1 × 2 × 1 supercell. And the doping concentration of all doped models is 1/8. In the crystal structure, each FeO_6 octahedron is connected by the corners shared. Meanwhile, FeO_6 octahedron linked to two LiO_6 octahedron and one PO_4 tetrahedron by the edge shared.

3. Results and discussion

3.1. Geometries, electronic property and formation energy

The lattice optimization results of the undoped system are basically consistent with those measured experimentally. We have carried out spin-polarized electronic structure calculations of $LiFePO_4$. The result is shown in Fig. 2. It can be seen an energy gap of 0.19 eV of the minority-spin bands. Our results are in good agreement with Yamada et al. [3]. It indicates that the models and parameters used in the calculation are reasonable.

The variation of the side length of the doped system is less than 1% in Table 1, indicating that the doping does not destroy the original lattice structure, and the doping concentration is more reasonable. The change of lattice volume after doping is consistent with the ionic radius

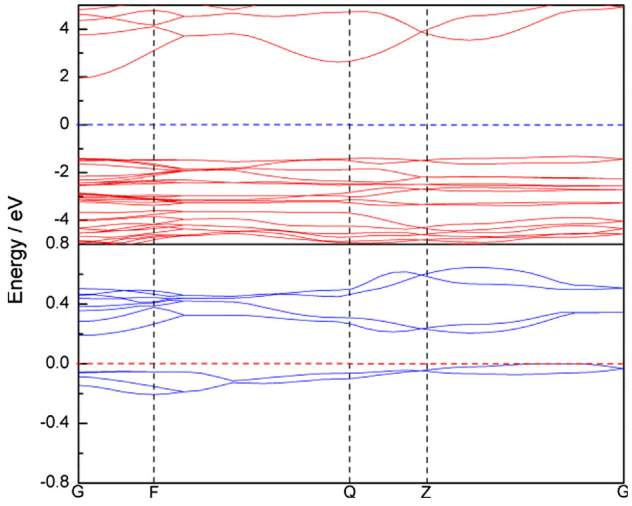

Fig. 2. Band structures of $LiFePO_4$. The red and blue lines represent majority-spin states and minority-spin states, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Lattice parameters of $LiFePO_4$ before and after doping.

		a (Å)	b (Å)	c (Å)	V (Å^3)
$LiFePO_4$	*Ours*:	10.35	12.06	4.72	589.16
	Expt. [18]:	10.33	12.02	4.69	582.34
	Calc. [19]:	10.49	11.83	4.75	589.46
$LiFe_{1-1/8}Mn_{1/8}PO_4$	*Ours*:	10.36	12.1	4.73	593.48
$LiFe_{1-1/8}Co_{1/8}PO_4$	*Ours*:	10.32	12.04	4.72	587.62
$LiFe_{1-1/8}Nb_{1/8}PO_4$	*Ours*:	10.43	12.11	4.73	597.41
$LiFe_{1-1/8}Mo_{1/8}PO_4$	*Ours*:	10.39	12.11	4.73	595.09

of doped elements. It is worth noting that the changes in lattice constants are only reflected in the changes in the values of a and b, and the size of the c value remains basically unchanged.

The band structure of Mn, Co, Nb, Mo doped is shown in Fig. 3. After Mn doping, the energy gap of the majority-spin is reduced from 3.29 eV to 3.04 eV, and the energy gap of minority gap is changed from 0.19 eV to 0.18 eV. It can be seen that an overlap of the minority-spin bands after the doping of Co and Nb, indicating that it's a half metal. After Mo doping, the energy gap of the majority-spin is reduced from 3.29 eV to 2.53 eV, and the energy gap of minority gap is changed from 0.19 eV to 0.13 eV.

The orbital contribution of dopants (Mn, Co, Nb and Mo) in the vicinity of the Fermi level is more clearly indicated by plotting the partial densities of states. It is not difficult to find from Fig. 4 that the d-orbitals of the dopants contributes to the density of states in the vicinity of and reduces the band gap. In addition, the more the number of the d band electrons of the dopants, the higher the peak near the Fermi level. The d-orbital of Nb goes through the Fermi level and causes the band gap of $LiFePO_4$ after doping to disappear. Therefore, the band gaps after doping of Mn, Co, Nb and Mo are decreased, which is beneficial to the transition of electrons and plays an important role in improving the electron mobility of $LiFePO_4$.

The defect formation energy E_f is an important concept used to characterize the degree of difficulty in the formation of a particular defect and the stability of its system. The smaller the energy is, the more stable it is. A formation energy greater than 0 indicates that the formation of the substance is endothermic, and less than 0 is exothermic. The formation energy of a defect or impurity M in charge state q is defined as [20]: