

First-principles study of structural, electronic and Li-ion diffusion properties of N-doped LiFePO₄ (010) surface



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ABSTRACT

The structural, electronic and Li-ion diffusion properties of N-doped LiFePO₄ (010) surface have been investigated by first-principles calculation under the DFT + U framework. The calculated results show that the substitution of nitrogen for oxygen on the (010) surface of the LiFePO₄ is energetically favored and N-substitution can significantly decrease the band gap of the LiFePO₄, indicating better electronic conductive properties. The nudged elastic band (NEB) method is used to calculate the activation energy for Li-ion diffusion. It is found that for pure LiFePO₄ (010) surface high intrinsic activation energy of Li-ion diffusion retards fast Li transport. However, this energy barrier can be effectively reduced by nitrogen surface modification. Our results imply that N doping on the LiFePO₄ (010) surface could improve its electron conductivity and ion diffusion properties.

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1. Introduction

Extensive research is currently under way to explore the atomic-scale physics of energy-related materials, aiming to improve their performance. Lithium iron phosphate (LiFePO₄) is one of the most promising cathode materials for the next-generation of lithium ion battery because of its high energy density, high safety, low cost, and environmental friendliness [1–3]. However, on the way to its practical application for power batteries, olivine-LiFePO₄ suffers from low electronic conductivity and poor ionic conductivity [4,5]. In order to overcome these drawbacks, various strategies have been implemented such as particle size reduction [6], coating with a conductive layer (e.g., carbon layer) [7], and aliovalent ion doping [8]. While surface coating and particle size reduction have shown to improve the power density, they are usually associated with lower tap density for the cathode material as the particle size decreases [9]. As a potential alternative approach, the anion doping has been employed to improve the electrochemical properties of LiFePO₄. Some preliminary works show that LiFePO₄ modified by halogen ions such as F[−] and Cl[−] exhibits good rate capability [10,11]. Liu et al. [12] investigated N-doped LiFePO₄ by first-principles calculation and expected that N doping into bulk LiFePO₄

could improve its electron conductivity and ion transport properties. However, the role of N-doping on the surface of LiFePO₄ is not fully understood.

The Li-ion mobility is the key parameter for battery applications with high energy density. Previously computational [13] and experimental [14] studies of LiFePO₄ indicated that Li-ion migration occurs preferentially via one-dimensional channels oriented along the [010] direction (b axis). Such one-dimensional diffusion inhibits its high-rate applications. In addition, Dathar et al. [15] reported that Li-ion surface diffusion has higher activation energy than bulk diffusion, which makes it the possible rate-limiting step in charge/discharge kinetics. Therefore, efforts to reduce the surface diffusion barrier are essential in order to optimize rate performance. Park et al. [16] reported that anion surface modification of LiFePO₄ can greatly improve the charge transfer kinetics and the charge/discharge performance owing to the stronger Li⁺ binding on the surface sites in the presence of nitrogen or sulfur on the surface of LiFePO₄. However, the origin of the improvement in terms of an electronic and ionic contribution is not yet well understood. Very recently, our theoretical investigation [17] showed that the activation energy of Li-ion diffusion on the (010) surface of LiFePO₄ could be effectively reduced by sulfur surface modification. Here, we chose the LiFePO₄ (010) surface as the target for the study since it is normal to the favored [010] diffusion pathway, which facilitates Li access to all the particle volumes.

In this work, we conduct DFT investigations on the structural, electronic and Li-ion diffusion properties of N-doped LiFePO₄ (010) surface and to explore the effects of N doping on the electronic conductivity and

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Li-ion diffusion. Our study is motivated by the notion that (i) surface modification of LiFePO_4 by nitrogen atoms enhances the electronic conductivity of LiFePO_4 – a desirable property for the electrode materials, and (ii) it also reduces the Li-ion diffusion activation energies at the surface – an important property needed for high-rate lithium ion batteries.

2. Method

Calculations in this work were performed in a plane wave basis set using the projector augmented wave (PAW) method [18] in the generalized gradient approximation (GGA) [19] as it is implemented in the Vienna ab initio simulation package (VASP) code [20]. PAW potentials have been widely used for battery materials and have shown good predictive capability [12,13,15–17]. GGA + U method [21] was used in our calculations and the effective Hubbard-U parameter with $U = 4.3$ eV [22] was set to describe the Fe-3d states. It has been shown that GGA + U is an appropriate method for predicting material properties of phosphates containing 3d transition metals [23]. The LiFePO_4 (010) surface was built by cleaving the optimized bulk crystal. The surface calculations were performed on a slab model [17,24]. Considering the efficiency of the computations, a smaller 1×1 surface supercell was used in this work. Convergence test with respect to the slab thickness was carried out with a 1×1 surface unit cell. It was found that a slab of 12.1 Å is sufficient to get a converged surface energy for the low energy (010) surface termination. And a vacuum layer of 10 Å is found to be enough to remove any spurious interaction between the periodically repeated slabs in the direction of the surface normal. For all calculations, a plane-wave basis with a kinetic energy cutoff of 500 eV was used. The Brillouin-zone integration was performed within the Monkhorst–Pack scheme using k meshes of $(3 \times 6 \times 1)$ and $(6 \times 12 \times 1)$ for the geometry relaxation and calculation of the electronic density of states, respectively. All calculations were performed with spin polarization and ferromagnetic spin ordering was initialized on the Fe ions. The optimized structures were obtained by relaxing all atomic positions until the interatomic forces were less than 0.01 eV/Å.

Activation energy calculations were performed with the climbing-image nudged elastic band (CI-NEB) method [25] in supercells containing $1 \times 2 \times 1$ unit cells. It is an efficient method for finding energy saddle points for the ion diffusion [17,25]. Five intermediate images were

constructed to interpolate the initial and final states along the Li-ion diffusion path. All lattice parameters were fixed, but all the internal degrees of freedom were relaxed during NEB calculation.

3. Results and discussion

3.1. Structural properties

Bulk LiFePO_4 has an ordered olivine structure with $Pnma$ space group and the unit cell accommodates four LiFePO_4 formula-units. The calculated lattice parameters of the fully relaxed bulk LiFePO_4 structure are $a = 10.427$ Å, $b = 6.057$ Å, and $c = 4.743$ Å, respectively, in good agreement with the experimental values [26] ($a = 10.332$ Å, $b = 6.011$ Å, and $c = 4.692$ Å) and the other calculated results [27]. The initial (010) surface structure was carved out of the fully relaxed bulk LiFePO_4 crystal. Wang et al. [28] reported that the low energy (010) surface termination in the [010] direction should cut through the LiO_6 octahedra but only cut the top of the FeO_6 octahedra, leaving threefold Li and fivefold Fe exposed on the surface. Fig. 1(a) shows the relaxed surface structure of the low energy (010) surface. Compared to the bulk LiFePO_4 , the lengths of the $\text{Fe}_{(1)}\text{-O}$ bonds for the $\text{O}_{(1)}$, $\text{O}_{(2)}$, $\text{O}_{(3)}$, $\text{O}_{(4)}$ and $\text{O}_{(5)}$ sites in the pure LiFePO_4 (010) surface [see Fig. 1(a)] are reduced to be 2.067 Å, 2.007 Å, 2.216 Å, 2.204 Å, and 2.159 Å, respectively. The distance between the $\text{Li}_{(2)}$ atom and the neighboring $\text{Fe}_{(1)}$ atom is 3.546 Å.

The surface bonding state characterized with TOF-SIMS by Park et al. [16] has indicated that nitrogen preferably substitutes for oxygen in the $(\text{PO}_4)^{3-}$ anions in the surface layer. We herein replaced the $\text{O}_{(1)}$ atom in the pure LiFePO_4 (010) surface with a nitrogen atom to simulate the N-doped LiFePO_4 (010) surface [N- LiFePO_4 (010)]. Fig. 1(b) shows the relaxed structure of the N- LiFePO_4 (010) surface. To investigate the stability of N substitution on $\text{O}_{(1)}$ site, the formation energy is calculated by the following expression [29,30]:

$$E_{\text{form}} = [E_{\text{N-LFP}(010)} - E_{\text{LFP}(010)} + N_N(E_{\text{O}} - E_{\text{N}})]/N_N \quad (1)$$

where $E_{\text{N-LFP}(010)}$, $E_{\text{LFP}(010)}$, E_{O} and E_{N} represent the DFT total energies of the N- LiFePO_4 (010), LiFePO_4 (010), and isolated O and N atoms, respectively; N_N is the number of N atoms in the supercell. The calculated

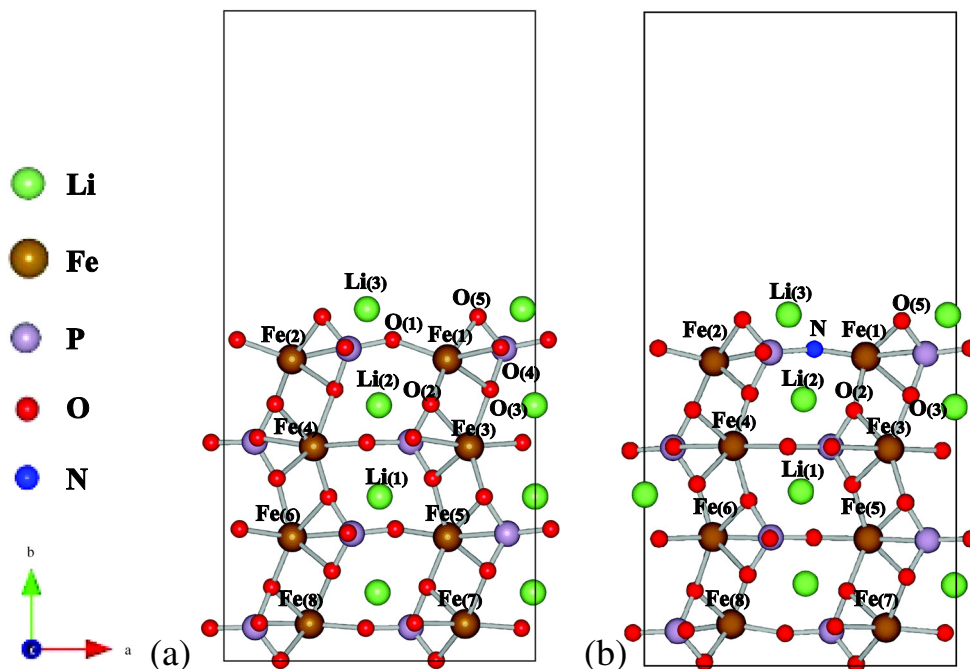


Fig. 1. The relaxed surface structures of (a) LiFePO_4 (010) surface and (b) N-doped LiFePO_4 (010) surface.

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