

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

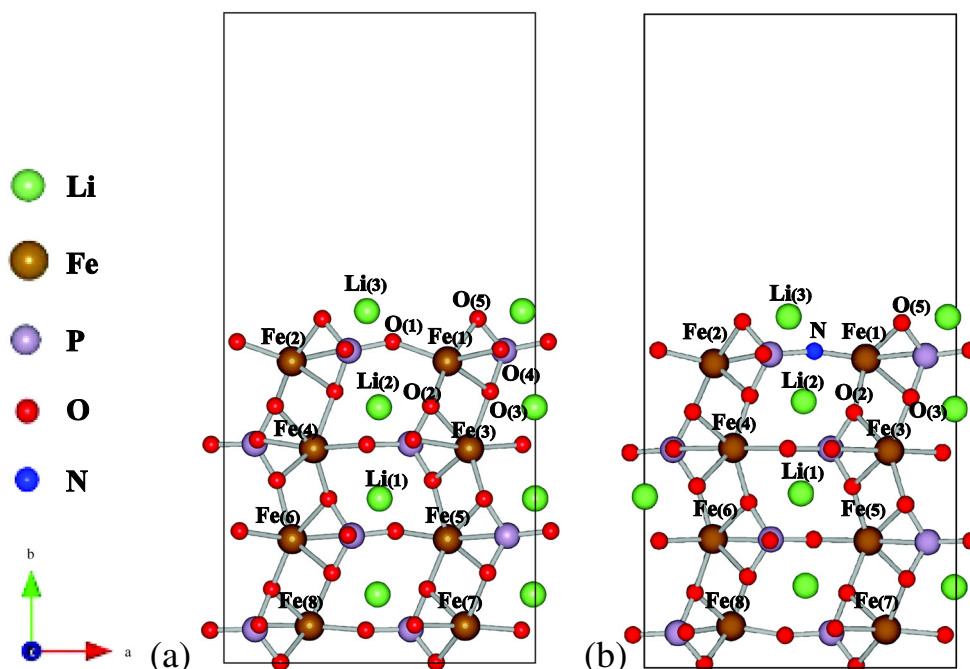


Fig. 1. The relaxed surface structures of (a) LiFePO_4 (010) surface and (b) N-doped LiFePO_4 (010) surface.

formation energy is 0.54 eV/atom. The low formation energy indicates that nitrogen substitution for oxygen in the $(\text{PO}_4)^{3-}$ anion is energetically favored. N doping induces the local geometric distortion to the surface. The length of P–N bond becomes slightly longer than the P–O₍₁₎ bond while the Fe₍₁₎–N bond is shorter than the Fe₍₁₎–O₍₁₎ bond. The N atom tends to be attracted to the neighboring Fe₍₁₎ atom so that the length of the Fe₍₁₎–N bond is reduced to be 1.966 Å. However, the length of the Fe₍₁₎–O₍₃₎ bond is noticeably increased from 2.216 Å to 2.504 Å after N doping. The increase percentage is about 13%. The distance between the Li₍₂₎ atom and the neighboring Fe₍₁₎ atom is increased from 3.546 Å to 3.577 Å, which would result in the weakening of the electrostatic repulsion between the Li ion and Fe ion.

3.2. Electronic structure

Bulk LiFePO₄ has been reported to be a semiconductor with large band gap of about 3.58–4.0 eV by computational and experimental methods [22,31–33]. Our calculated band gap for bulk LiFePO₄ using DFT + U is 3.58 eV [17], in good agreement with the reported results. The large band gap prevents the intrinsic generation of an electron or hole and thus leads to poor electron conductivity. Although previous theoretical work by Maxisch et al. [34] suggested that electron conductivity proceeds via hopping of small hole polarons in LiFePO₄, our analysis based on the relationship between the band gap and electronic conductivity still provides valuable information on the electronic conductivity change. Fig. 2 shows the density of states (DOS) of N-doped LiFePO₄ (010) surface. Our recent theoretical study reports that the band gap for the pure LiFePO₄ (010) surface is 1.38 eV [17]. From Fig. 2, it can be seen that the band gap is reduced to be 0.65 eV after N doping. The smaller band gap indicates that the N-doped LiFePO₄ (010) surface may exhibit better electronic conduction.

To further analyze the impact of N doping on the electronic structure and gain insight into the electronic conduction improvement, we have also calculated the spin-polarized partial density of states (PDOS) of P-2p, N-2p and Fe-3d of the N-LiFePO₄ (010) surface, as shown in Fig. 3. It can be seen from Figs. 2 and 3 that the spin-down states of 3d-electrons of the Fe atoms are the primary contributors to both the valence-band maximum (VBM) and conduction-band minimum (CBM) for the N-LiFePO₄ (010) surface. Our recent work [17] has shown that, for the pure LiFePO₄ (010) surface, Fe-3d states are also the primary contributors to both the VBM and CBM. For comparison, the partial DOS for pure LiFePO₄ (010) surface is also presented in Fig. 4. From Figs. 3 and 4, it is clear that N doping significantly affects the spin-down states of 3d-electrons of Fe atoms at different positions

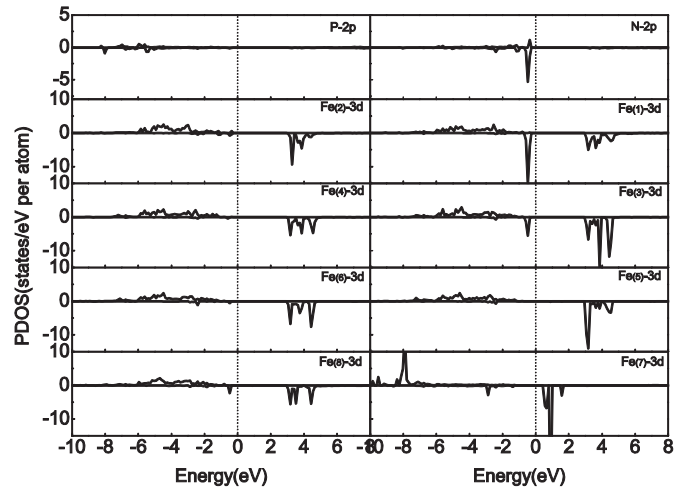


Fig. 3. The PDOS of P-2p, N-2p and Fe-3d of the N-LiFePO₄ (010) surface. The Fermi level is set to be zero.

in the LiFePO₄ (010) surface, leading to a large shift in the CBM (E_c) to the Fermi level (E_f) with the slight change in the VBM (E_v) and thus narrowing the band gap, as shown in Fig. 5. Fig. 5 shows clearly that N doping greatly reduces the band gap of LiFePO₄, which might also contribute to the increased electronic conductivity.

3.3. Li-ion diffusion

Considering the importance of Li-ion mobility in improving the rate capability of the charge/discharge of Li-ion batteries, we then investigated the Li-ion mobility with the calculation of activation energies by the NEB method. The Li-ion diffusion coefficient can be estimated by the following formula [35,36]:

$$D = a^2 \nu \exp(-E_{act}/k_B T) \quad (2)$$

where a is approximately 3 Å, corresponding to the distance of a hop along the [010] direction, ν is about 10^{13} Hz, which is generally in the range of phonon frequencies, and T is the temperature ($T = 300$ K). Once the activation energy E_{act} is known, the diffusion coefficient can be estimated. The activation energy for [010] Li-ion diffusion in bulk LiFePO₄ is calculated to be 0.32 eV [17]. The low activation energy corresponds to fast bulk Li-ion diffusion. The estimated Li-ion diffusion

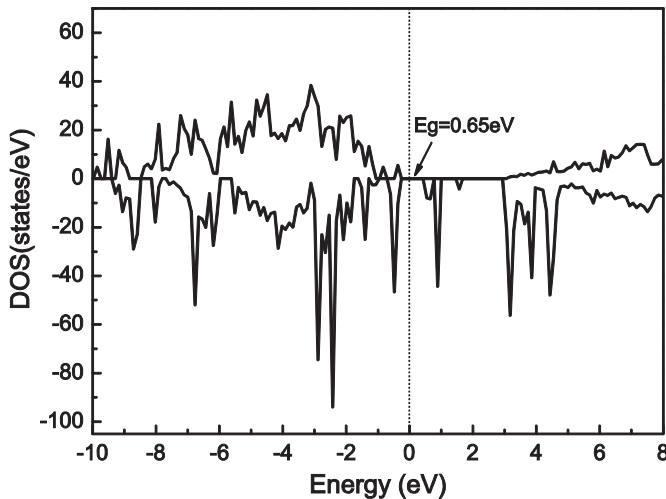


Fig. 2. Total density of states (DOS) of N-doped LiFePO₄ (010) surface. The Fermi level is set to be zero.

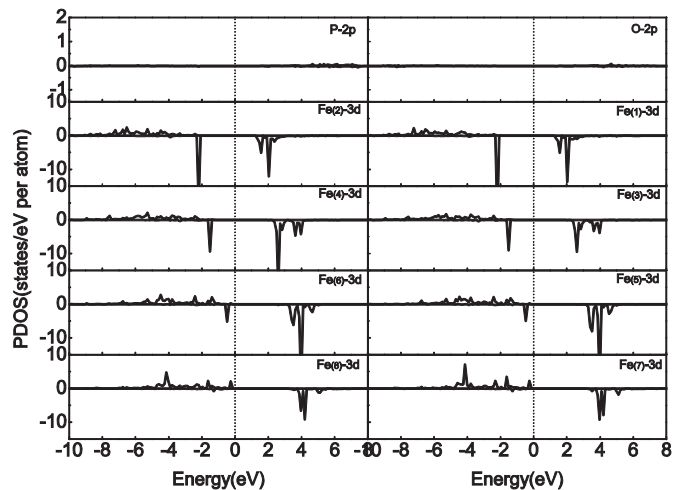


Fig. 4. The PDOS of P-2p, O-2p and Fe-3d of the pure LiFePO₄ (010) surface. The Fermi level is set to be zero.

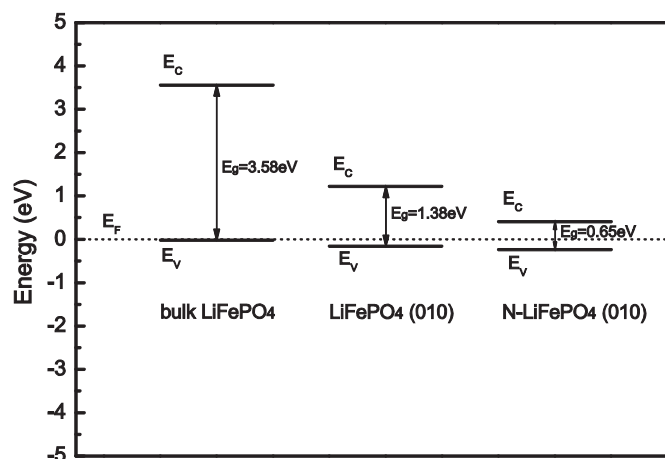


Fig. 5. Energy landscapes for bulk LiFePO₄, LiFePO₄ (010) surface, and N-LiFePO₄ (010) surface, respectively. E_c , E_v , and E_f represent the conduction-band minimum (CBM), the valence-band maximum (VBM), and the Fermi level, respectively. The Fermi level is set to be zero.

coefficient for bulk LiFePO₄ is 2.0×10^{-8} cm²/s at room temperature. However, it is found that the rate of Li-ion diffusion in bulk LiFePO₄ calculated from first principles is much faster than that observed in experiment (10^{-13} to 10^{-14} cm²/s) [37]. This discrepancy has been addressed by considering the different components of Li-ion diffusion in bulk and on the surface [15]. Fig. 6(a) gives Li-ion transport paths along the *b*-channel of the pure LiFePO₄ (010), and the corresponding activation energies are shown in Fig. 6(b) and (c). The activation energies are estimated to be 0.66 eV for Li-ion subsurface transport along the “path 1” (site1 to site2) and 0.64 eV for surface diffusion along the “path 2” (site2 to site3). These activation energies translate to diffusion coefficients in the range of 10^{-14} – 10^{-13} cm²/s at room temperature. Thus, Li-ion diffusivity towards the surface is expected to be slower by 6 orders of magnitude than that of bulk diffusion. Therefore, hopping through the surface is likely to be a rate-limiting step for Li mobility. Efforts should be made to reduce the surface diffusion barrier with proper surface modification in order to optimize rate performance.

Doping is one of the common methodologies to modify the electrochemical properties of electrode materials. Fig. 6(d) shows Li-ion transport paths along the *b*-channel of the N-LiFePO₄ (010) surface, and the

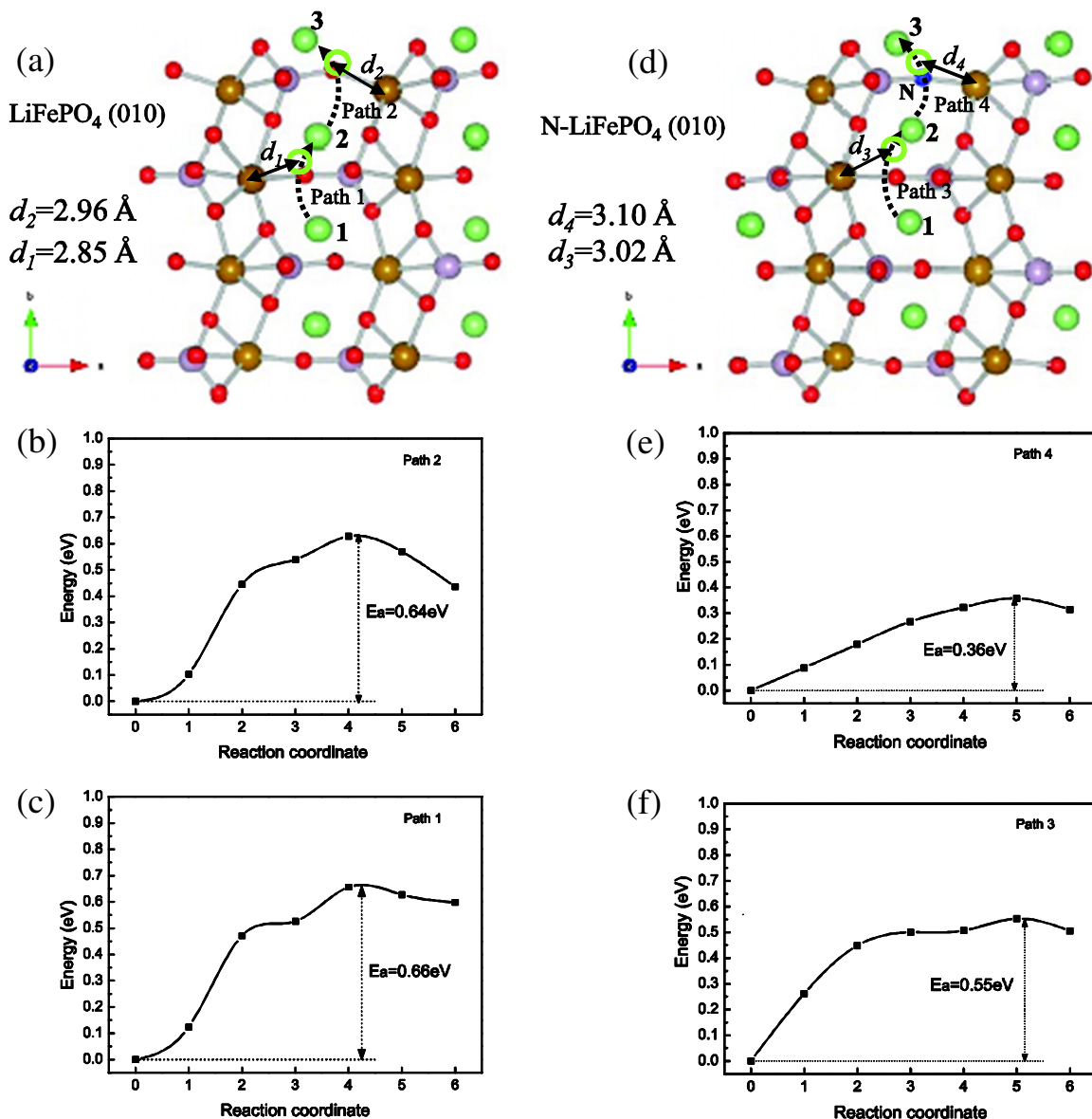


Fig. 6. Li-ion transport paths and corresponding activation energies for Li-ion diffusion along the *b*-channel of the pure and N-doped LiFePO₄ (010) surface, respectively. The open circles indicate the hopping Li-ions at the transition state along the minimum energy paths. The distances between the Li-ions and the neighboring Fe ions at transition state are also shown.

corresponding activation energies are shown in Fig. 6(e) and (f). The activation energies for Li-ion subsurface transport along the “path 3” (site1 to site2) and surface diffusion along the “path 4” (site2 to site3) are decreased to 0.55 eV and 0.36 eV, respectively. Compared to the pure LiFePO₄ (010) surface, N doping decreased activation energy by about 0.11 eV for Li-ion subsurface transport along the *b*-channel. It should be noted that, a reduction of activation energy of only 0.11 eV will increase the rate of Li-ion transport by a factor of 10² [$\exp(0.11\text{eV}/k_B T) \sim 10^2$] at room temperature. The improvement is more significant for Li-ion surface diffusion along the *b*-channel. The decrease of 0.28 eV in activation energy for Li-ion surface diffusion along the *b*-channel would result in the increase of diffusivity by a factor of 10⁴ [$\exp(0.28\text{eV}/k_B T) \sim 10^4$] at room temperature. Therefore, it can be expected that N doping on the LiFePO₄ (010) surface will improve Li-ion transport properties.

As shown in Fig. 6(a) and (d), the Li-ion diffusion paths along the *b*-channel are arch-like curves, due to electrostatic repulsion between Li ion and the neighboring Fe ion. Seo et al. suggested that electrostatic repulsion between the Li-ions and the neighboring transition metals (TMs) at transition state may account for the difference in activation barrier among the LiMBO₃ (M = Mn, Fe, and Co) and multicomponent olivine compounds [35,38], a similar mechanism is likely to affect the activation energy in the LiFePO₄. The hopping Li-ions at the transition state along the minimum energy paths (Path1, Path2, Path3 and Path4) are shown in Fig. 6 by marking open circles, and the distances (*d*₁, *d*₂, *d*₃, and *d*₄) between the Li-ions and the neighboring Fe ions at transition state are also shown. From Fig. 6, it can be seen that, after N doping, the distances between the Li-ions and the neighboring Fe ions at transition state for surface diffusion (along Path2 and Path4) and subsurface diffusion (along Path1 and Path3) are increased from 2.96 Å to 3.10 Å and from 2.85 Å to 3.02 Å, respectively. According to the general model adopted by Seo et al., the increase of the distance could result in the weakening of the electrostatic repulsion between the Li ion and the neighboring Fe ion at the transition state, which leads to a lower activation energy for Li-ion diffusion after N doping. Since the Li-ion mobility is inversely proportional to the exponential of the activation energy according to Eq. (2), a slight reduction of activation energy will result in a significant enhancement in the Li-ion transport property. This strongly implies that the kinetics of LiFePO₄ cathode can be improved by modifying the environment of Li-ion diffusion pathway through the introduction of nitrogen to the surface of the LiFePO₄ particles.

4. Conclusion

In conclusion, we have investigated the structural, electronic and Li-ion diffusion properties of the N-doped LiFePO₄ (010) surface with first-principles calculations under the DFT + U framework. The calculated low formation energy of 0.54 eV/atom indicated that nitrogen substitution for oxygen in the (PO₄)^{3−} anion is energetically favored. A much smaller band gap of the N-LiFePO₄ (010) surface as compared to pure LiFePO₄ (010) surface is predicted. The nudged elastic band method was used to calculate the activation energy for Li-ion diffusion. It is found that surface diffusion along the *b*-channel has a higher activation energy than bulk diffusion and hopping through the surface is likely to be a rate-limiting step for Li mobility. N doping reduces the Li-ion diffusion activation energies at the surface and improves Li-ion transport properties. The above results mean that the nitrogen surface-modified LiFePO₄ will exhibit higher electronic and ionic conductivity, which gives rise to the enhanced electrochemical performance.

Acknowledgments

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