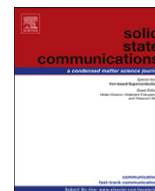




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A GGA+U study of lithium diffusion in vanadium doped LiFePO₄

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ARTICLE INFO

Article history:

Received 10 November 2011

Received in revised form

4 February 2012

Accepted 8 March 2012

by B.-F. Zhu

Available online 5 April 2012

Keywords:

A. LiFePO₄

A. Vanadium doping

D. Band structure

D. Ion diffusion

ABSTRACT

Recent experiments showed beneficial influence of vanadium doping on the electrochemical performance of lithium iron phosphate (LiFePO₄) cathode materials. First-principles calculations have been performed to investigate the stability, electronic structure and lithium diffusivity of vanadium-doped LiFePO₄ and to elucidate the origin of such improvement. It is found that vanadium prefers occupying Fe sites and leads to additional density of states within the intrinsic bandgap. By the nudged elastic band method, we show that the barrier of Li ions diffusion along the one dimensional channel in both LiFePO₄ and FePO₄ phases can be effectively reduced by vanadium doping. Structural analysis shows the lower diffusion barrier ties closely to a volumetric expansion of the diffusion channel.

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1. Introduction

Since its discovery by Padhi et al. [1] in 1997, the iron-based olivine-type LiFePO₄ has been widely investigated and evaluated as a viable Li-ion battery (LIB) cathode material. Due to its inexpensiveness, nontoxic nature, good thermal stability, high theoretical capacities (170 mA hg⁻¹) and high reversible voltage (3.5 V) [2], LiFePO₄ is considered to be a promising next generation LIB cathode. However, commercial applications of LiFePO₄ have been greatly hindered by its low electronic ($\sim 10^{-9}$ s cm⁻¹) and ionic conductivity (10^{-13} – 10^{-16} cm² s⁻¹) [3–5], which renders the material unsuitable for high power electric vehicle applications. Many synthesis and processing strategies have been developed to enhance the electrochemical performance of LiFePO₄, including coating of the grains with carbon [6] and metal powders [7], addition of conducting polymers [8], formation of submicron or nanometer size nanocrystalline particles [9], and doping with other elemental species [5]. 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 [10]. As a potential alternative approach, heterogeneous valence metallic ions have been employed as doping species to improve the electrochemical properties of pure LiFePO₄ [11–14]. Among the active dopants, vanadium (V) has attracted considerable attention due to its capability of reversibly intercalate lithium ions in multiple phases [15–19]. However, despite the observed electrochemical performance improvement of the doped phosphate materials, the valence states of vanadium in doped LiFePO₄ vary from different reports and the exact microscopic details such as the location of the dopant atoms and the origin of the vanadium promotion effect are yet not well understood. The inconsistency of vanadium doping in previous studies might arise due to different factors, such as synthesis methods, used precursors, or post-processing. Ab initio investigation of the stability, electronic structure and ionic diffusion of V doped LiFePO₄ can provide valuable atomistic scale information for understanding the vanadium doping effect in the electrochemical reactions. There have been substantial theoretical works on LiFePO₄ cathode material, including the study of its crystal structure and electronic property [20]. Using first principles calculations, Liu et al. found that nitrogen doped LiFePO₄ could enhance both the electronic conductivity and Li ion diffusion [21]. However, to our knowledge, a detailed mechanistic study of the effects of V doping on LiFePO₄ has not been reported.

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In this report, we investigated the structural stability, electronic structure and lithium ion diffusion properties of both pure and V-doped LiFePO_4 and FePO_4 using first-principles calculations. Due to the limitation of traditional local density approximation (LDA) and generalized gradient approximation (GGA) in accurately describing the electronic structures of transition-metal material [22,23], we apply a more reliable treatment of the correlated electron orbital in transition metal containing phosphates within GGA+U method, which has shown to give excellent agreement to experimental results [24]. Additionally, the nudged elastic band method has been used to determine the lithium ion minimum energy diffusion path to elucidate the impact of V doping on ionic diffusivity. Our results clarify the V doping effects in LiFePO_4 and would further stimulate the exploration of doping of LiFePO_4 for improved performance.

2. Methodology

First-principles calculations have been performed to investigate the structural, electronic properties and lithium ion diffusion of Olivine-type LiFePO_4 and its de-lithiated counterpart FePO_4 , as well as the V doped $\text{LiFePO}_4/\text{FePO}_4$. Perdew–Burke–Erzerhof (PBE) [25] exchange correlation functional are used with the projected augmented wave potentials (PAW) [26] as implemented in the Vienna Ab initio Simulation Package (VASP) [27], which shows good agreements with experimental structural properties for a number of cathode materials [21]. Plane waves with a cutoff energy of 500 eV are used to expand electron wave functions and an appropriate k -point mesh is used to sample the Brillion zone. The atomic coordinates are fully optimized until the force on each atom is converged to less than 0.02 eV/Å. GGA+U methods have been carried out in our calculations and the effective Hubbard-U parameters for iron and vanadium are set to 4.3 eV and 3.0 eV, respectively, in accordance with previous literatures [28]. To investigate the lithium ion diffusion property in Li_xFePO_4 ($x=0.1$), the nudged elastic band (NEB) [29] method is used to find the minimum energy path (MEP) between two local stable sites of Li along the (0 1 0) direction. To avoid image interactions due to periodic boundary condition, a supercell that contains eight formula cells has been utilized for the NEB calculation [30]. For activation energy calculations, a single Li ion vacancy is introduced in the pure(doped) LiFePO_4 unit cell while a single Li ion is added in pure(doped) FePO_4 to study the Li diffusion in lithiated/delithiated phase. Four intermediate images are constructed to interpolate the initial and final states along the Li diffusion path. By adding spring forces along the band between

images and projecting out the component of the perpendicular forces, we locate the transition states (TSs) and deduce the activation barrier from the energy difference between the TS and the initial state.

3. Results and discussions

Olivine-type LiFePO_4 is an orthorhombic crystal with $pnma$ space group and the unit cell is in the formula of $\text{Li}_4\text{Fe}_4\text{P}_4\text{O}_{16}$, whose structure is shown in Fig. 1(a). The structure framework consists of FeO_6 octahedra (yellow) and PO_4 tetrahedra (blue) with Li ion locating at the 1D channel along [0 1 0] direction. Fig. 1(b) and (c) indicate the possible doping sites of V atoms on either Fe or P atoms, with polyhedron that contains V highlighted in white. To investigate the stability of V substitution on different sites, the formation heats of V incorporation into either Fe or P sites are calculated by the following expressions:

$$Eh_{\text{Fe}} = (E_{\text{Li}_4\text{Fe}_3\text{VP}_4\text{O}_{16}} + E_{\text{Fe}}) - (E_{\text{Li}_4\text{Fe}_4\text{P}_4\text{O}_{16}} + E_{\text{V}})$$

$$Eh_{\text{P}} = (E_{\text{Li}_4\text{Fe}_4\text{VP}_3\text{O}_{16}} + E_{\text{P}}) - (E_{\text{Li}_4\text{Fe}_4\text{P}_4\text{O}_{16}} + E_{\text{V}})$$

where $E_{\text{Li}_4\text{Fe}_3\text{VP}_4\text{O}_{16}}$ and $E_{\text{Li}_4\text{Fe}_4\text{VP}_3\text{O}_{16}}$ imply the total energy of $\text{Li}_4\text{Fe}_3\text{VP}_4\text{O}_{16}$ and $\text{Li}_4\text{Fe}_4\text{VP}_3\text{O}_{16}$, E_{V} and E_{Fe} are the total energy of bulk Fe and V, respectively, in BCC structure, while E_{P} is the total energy of P in β structure [31]. A negative number of formation heat indicates the doping of V atom is energetically favorable. It is found the formation heat of V-doping on the Fe site is -1.29 eV per unit cell while doping on the P site has a positive formation heat (0.78 eV). It is thus expected that the V atoms prefer to substitute Fe sites rather than P sites in LiFePO_4 , and we focus on V doping on Fe sites in the following discussion. However, it has to be mentioned V doping at other sites or formation of other complex phases in real experiments might also occur due to the non-ideal and non-equilibrated processes involved during synthesis.

Structural stability and volumetric expansion are key factors in determining the long-term cyclability of LIB cathodes. To quantify these parameters for LiFePO_4 and V-doped LiFePO_4 , we tabulate (Table 1) the lattice constants, volume and volumetric change of these structures before and after Li intercalation with both GGA and GGA+U methods. The results show that the volume change between LiFePO_4 and FePO_4 is 4.2% by GGA+U method, which is in reasonable agreement to the experimental result of 6.5% [1]. Upon V doping into Fe sites, the volumetric change gets slightly increased to 4.5%. These small values suggest that LiFePO_4 and V-doped LiFePO_4 are likely to maintain structural stability during

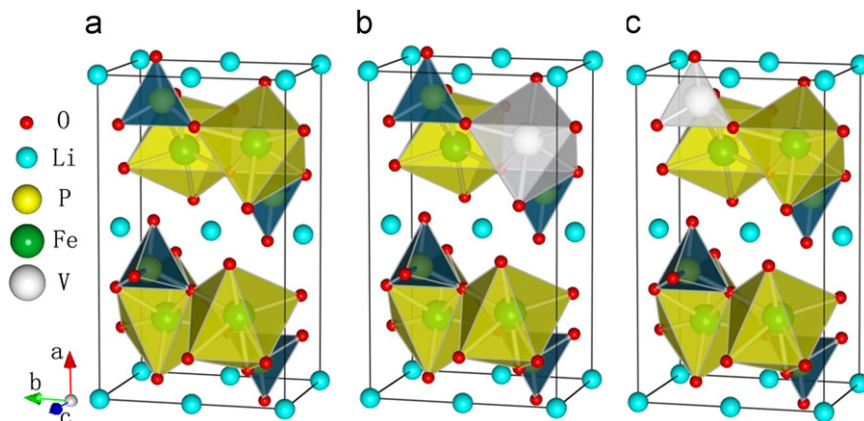


Fig. 1. (Color online) (a) Pure LiFePO_4 in unit cell, 25% vanadium doped into: (b) the Fe site and (c) the P site of LiFePO_4 .

Table 1
Structural parameters of Li_xFePO_4 and V-doped Li_xFePO_4 within GGA and GGA+U calculations.

	a (Å)	b (Å)	c (Å)	V (Å ³)	ΔV (Å ³)
LiFePO_4					
GGA	10.38	6.05	4.75	298.30	1.1%
GGA+U	10.41	6.08	4.75	300.64	4.2%
Exp. 1	10.33	6.01	4.69	291.39	6.5%
$\text{LiFe}_{0.75}\text{V}_{0.25}\text{PO}_4$					
GGA	10.40	6.05	4.74	298.24	2.0%
GGA+U	10.46	6.09	4.76	303.22	4.5%
Exp.					
FePO_4					
GGA	9.98	6.01	4.92	295.10	
GGA+U	9.97	5.93	4.87	287.92	
Exp. 1	9.82	5.79	4.79	272.36	
$\text{Fe}_{0.75}\text{V}_{0.25}\text{PO}_4$					
GGA	9.94	6.00	4.90	292.24	
GGA+U	10.00	5.92	4.89	289.49	
Exp.					

Table 2
Formation energies (eV) of Li_xFePO_4 and $\text{Li}_x\text{Fe}_{0.75}\text{V}_{0.25}\text{PO}_4$ with different concentrations.

x	0	0.25	0.5	0.75	1
Li_xFePO_4	0	0.10	0.14	0.13	0
$\text{Li}_x\text{Fe}_{0.75}\text{V}_{0.25}\text{PO}_4$	0	-0.09	0.09	-0.03	0

the charge/discharge process. Especially, the V-doped FePO_4 has larger volume than the pure counterpart that should contribute to an improvement of the Li ion diffusivity of Li_xFePO_4 during Li intercalation.

Besides volumetric expansion, it is well known that during the dynamic process of lithium intercalation, Li_xFePO_4 materials undergo phase separation into LiFePO_4 and FePO_4 phases, which results in the formation of phase boundary and hinders the lithium diffusion. To investigate the phase stability of V-doped Li_xFePO_4 ($x=0.25, 0.5, 0.75, 1$), we calculate the total energy difference of the compound with respect to its constituent fully lithiated and fully de-lithiated phases, as defined by the following equation [24]:

$$\Delta E_{\text{formation}}(\text{Li}_x\text{Fe}_{1-\delta}\text{V}_\delta\text{PO}_4) = E(\text{Li}_x\text{Fe}_{1-\delta}\text{V}_\delta\text{PO}_4) - xE(\text{Li}_x\text{Fe}_{1-\delta}\text{V}_\delta\text{PO}_4) - (1-x)E(\text{Fe}_{1-\delta}\text{V}_\delta\text{PO}_4)$$

where $E(\text{Li}_x\text{Fe}_{1-\delta}\text{V}_\delta\text{PO}_4)$ ($x=0.25, 0.5, 0.75, 1$, and $\delta=0, 0.25$) is the total energy of $\text{Li}_x\text{Fe}_{1-\delta}\text{V}_\delta\text{PO}_4$ per formula unit. A positive value of $\Delta E_{\text{formation}}(\text{Li}_x\text{Fe}_{0.75}\text{V}_{0.25}\text{PO}_4)$ ($x=0.25, 0.5, 0.75, 1$) means that it is energetically unfavorable to form a uniform single phase compound. The formation energies of Li_xFePO_4 and $\text{Li}_x\text{Fe}_{0.75}\text{V}_{0.25}\text{PO}_4$ ($x=0.25, 0.5, 0.75, 1$) have been listed in Table 2 and some basic information of the phase separation can be found by comparing the formation energy of $\text{Li}_x\text{Fe}_{0.75}\text{V}_{0.25}\text{PO}_4$ with that of Li_xFePO_4 which has been discussed previously [24]. It is interesting that the formation energy is lower for $\text{Li}_x\text{Fe}_{0.75}\text{V}_{0.25}\text{PO}_4$, which suggests the V-doped FePO_4 may have stronger phase stability in the charge/discharge process when used as LIB cathode.

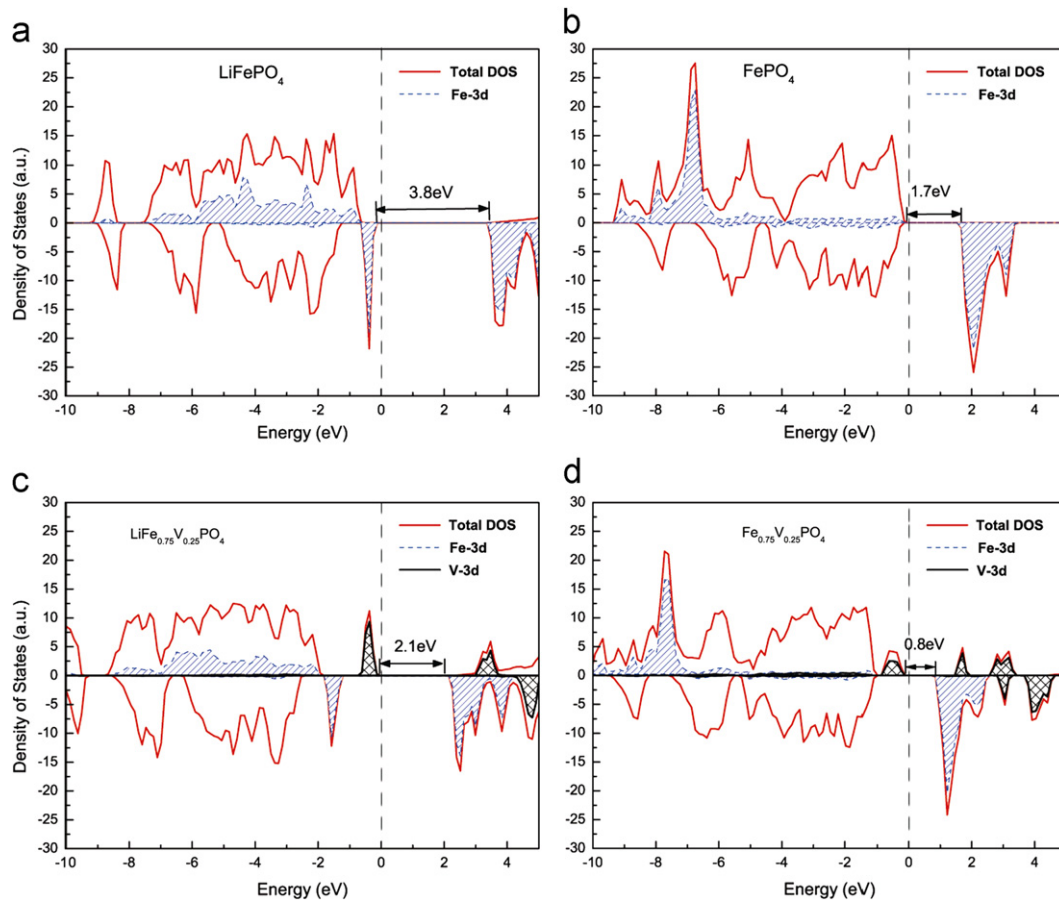


Fig. 2. (Color online) DOS of (a) LiFePO_4 , (b) FePO_4 , (c) $\text{LiFe}_{0.75}\text{V}_{0.25}\text{PO}_4$ and (d) $\text{Fe}_{0.75}\text{V}_{0.25}\text{PO}_4$, red lines mark the total spin-polarized DOS, dot lines and black lines indicate the projected DOS of 3d-electrons of Fe and V, respectively. The Fermi level is set to zero.

It is reported experimentally that the V-doped LiFePO_4 cathode exhibits remarkable enhancement in the electrochemical performance compared with pure olivine LiFePO_4 [13]. However, the origin of such improvement has not yet been clearly understood. To gain insight into the performance improvement, spin-polarized total density of states (DOS) of Li_xFePO_4 and $\text{Li}_x\text{Fe}_{0.75}\text{V}_{0.25}\text{PO}_4$ ($x=0, 1$) as well as projected DOS of $3d$ electrons of Fe and V atoms are presented in Fig. 2 within the GGA+U framework. The calculated bandgaps of pure LiFePO_4 and FePO_4 are 3.8 eV and 1.7 eV respectively, which are in good agreement with previous theoretical studies [20] and experiments [32]. In Fig. 2(a), it is found the $3d$ -electrons of Fe are the primary contributor to both the valence band maximum (VBM) and conduction band minimum (CBM) DOS. Thus the bandgap is effectively determined by the contributions of spin-down states of $3d$ -electrons of the Fe atoms. However, the bandgap of FePO_4 in Fig. 2(b) is found to be much smaller, which may be attributed to the different valent states of Fe in them. With a transition from Fe^{2+} to Fe^{3+} , the contribution to the VBM by spin-down states vanishes due to the loss of one $3d$ -electron. Thus the bandgap is determined by both $3d$ -electron of Fe and $2p$ -electron of O in FePO_4 . It is interesting that upon doping, an isolated impurity states caused by $3d$ -electron of V appears near the Fermi level and the bandgap of LiFePO_4 has been reduced as the vanadium resides the Fe site in Fig. 2(c). A similar picture can be found in V-doped FePO_4 from Fig. 2(d). Thus V doping clearly reduces the optical bandgap of both LiFePO_4 and FePO_4 , which might also contribute

to the increased electronic conductivity [15–18]. While it should be mentioned that some recent theoretical studies suggest that free polaron mechanism may accounts for the electronic conductivity [33,34], our analysis still provides valuable information on the electronic structure change due to V doping.

It had been thought that the electrochemical performance of LiFePO_4 derived compounds is primarily limited by the ameliorative electronic conductivity. However, some recent studies show that the Li ion diffusion also play an important role [16] and it is still unclear which step constitutes the rate determining step in the overall electrochemical cycles. Within the olivine type structure, Li ion prefers to transport through 1D-like tunnel along b axis in Li_xFePO_4 (as marked in Fig. 3(a)) [21,29]. NEB method has been used to calculate the Li ion diffusion properties and determine the MEP of Li diffusion along b axis in both pure and V-doped Li_xFePO_4 . Two limiting cases of Li concentrations in V-doped Li_xFePO_4 have been considered and the calculated minimum energy paths of Li diffusion along b axis are given in Fig. 3(b), which correspond to fully lithiated and fully de-lithiated phases in such system, respectively. For comparison, the results of pure Li_xFePO_4 are also shown in Fig. 3(b). It is found the Li diffusion path along b axis is an arch-like curve due to Pauling repulsion between Li ion and FeO_6 octahedra. It can be seen that the energy barriers of Li ion diffusion in fully lithiated and fully de-lithiated phase of pure Li_xFePO_4 are 0.55 eV and 0.24 eV, respectively. Since such energy barriers imply the mobility of Li ion along the tunnel, thus it is reasonable to expect that the

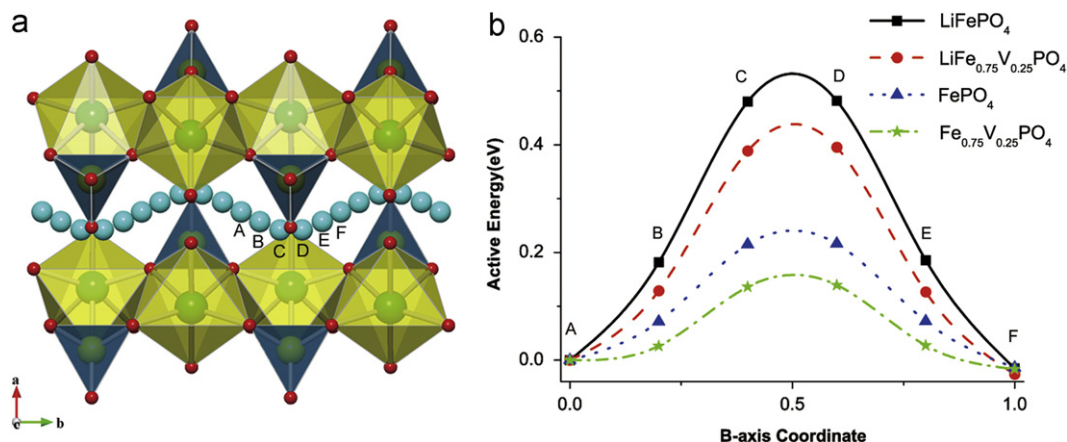


Fig. 3. (Color online) Minimum energy path of Li diffusing along the tunnel of b axis in pure and doped LiFePO_4 of fully lithiated and fully de-lithiated phases.

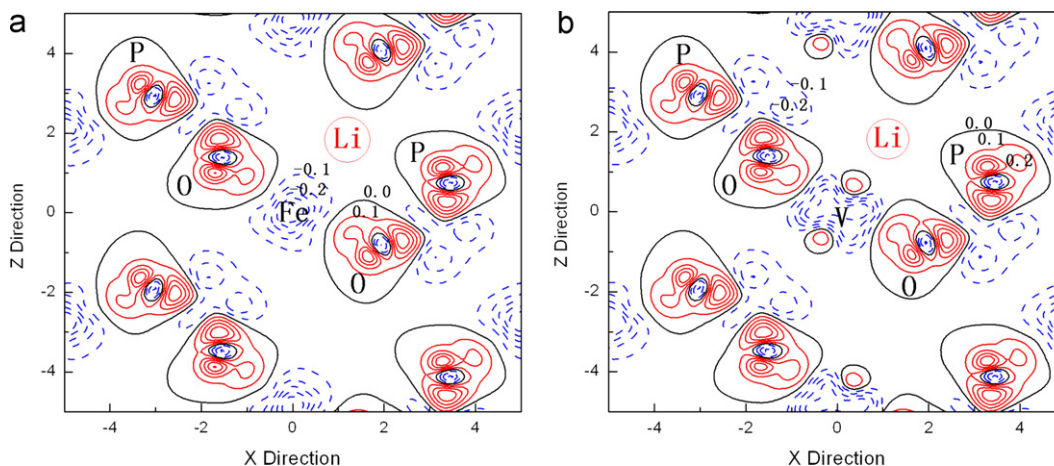


Fig. 4. (Color online) Differential charge density contours of (a) FePO_4 , (b) $\text{Fe}_{0.75}\text{V}_{0.25}\text{PO}_4$ on the (0 1 0) plane.

barrier of fully lithiated phase is higher than that of de-lithiated one because Li ions will hinder each other in diffusion process at high concentration. Upon V doping, the Li ion diffusion barriers decrease to 0.44 eV and 0.16 eV for $\text{LiFe}_{0.75}\text{V}_{0.25}\text{PO}_4$ and $\text{Fe}_{0.75}\text{V}_{0.25}\text{PO}_4$, respectively. The same trend holds that it is easier for Li diffusion in a lower concentration in V-doped Li_xFePO_4 . Moreover, comparing with pure Li_xFePO_4 , Li diffusion energy barriers are suppressed and Li intrinsic diffusion ability can be enhanced by vanadium doping. To better understand this effect, we did both structural and electronic structure analysis. As discussed above, the volume of V-doped system expands compared to the pure system, which means the free space for Li diffusion is larger in V-doped system. To further illustrate the impact on energy barriers caused by V-doping, charge difference contours of FePO_4 and $\text{Fe}_{0.75}\text{V}_{0.25}\text{PO}_4$ are plotted on (0 1 0) plane in Fig. 4(a) and (b). It should be mentioned that Li ion diffusion path is perpendicular to the (0 1 0) plane. It can be seen that there are some positive charge accumulation near the Fe site in Fig. 4(a), which accounts for the extra barrier hindering the Li ion diffusion along the tunnel, since positive charges repel each other. In contrast, it is clear from Fig. 4(b) that negative charge appears at the vanadium site, which would reduce the Li ion diffusive activate energies effectively. This leads to an effective widening up of the lithium diffusion channel. The lowered energy barrier suggests that the Li ion will exhibit higher carrier mobility and also contribute to the enhanced electrochemical performance.

4. Conclusion

In summary, we have performed a GGA+U study to investigate the structural, electronic and diffusion properties of LiFePO_4 and V-doped LiFePO_4 . It is found the vanadium likely dopes into the Fe site rather than P site in energy. The DOS calculation suggests the V-doping could introduce impurity states near Fermi level and reduce the bandgaps of LiFePO_4 and FePO_4 . Furthermore, Li diffusion barrier gets significantly lowered along the (0 1 0) tunnel upon V doping. Our findings provide a fundamental understanding on the performance enhancement of V-doped LiFePO_4 in previous experiments.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (Grant no.11004068 and 51101064) and Program for New Century Excellent Talents in University (NCET). Rong Chen would like to acknowledge the support from the Thousand Young Talents Plan, the Recruitment program of global experts. The authors acknowledge the Texas Advanced Computing Center (TACC) at The University of Texas at Austin (<http://www.tacc.utexas.edu>) for providing grid resources that have contributed to the research results reported within this paper.

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