Effect of C doping on the structural and electronic properties of $LiFePO_4$: A first-principles investigation*

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Using first-principles calculations within the generalized gradient approximation (GGA) $+U$ framework, we investigate the effect of C doping on the structural and electronic properties of $LiFePO_4$. The calculated formation energies indicate that C doped at O sites is energetically favored, and C dopants prefer to occupy O_3 sites. The band gap of the C doped material is much narrow than that of the undoped one, indicating better electronic conductive properties. To maintain charge balance, the valence of the Fe nearest to C appears as Fe^{3+}, and it will be helpful to the hopping of electrons.

Keywords: $LiFePO_4$, C doping, electronic structure, first-principles calculations

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1. Introduction

Low cost, nontoxicity, and better thermal stability make the olivine $LiFePO_4$ family become one of the most promising cathode materials for the next generation of lithium-ion batteries.[1−3] However, $LiFePO_4$ suffers from poor rate capability at high rates due to low electrical conductivity and poor electrochemical performances at low temperatures. Efforts to increase conductivity of the materials have focused on doping, [4] coating the particle surface,[5,6] and minimizing the particle size.[7] A remarkable jump in electrical conductivity of $LiFePO_4$ was reported after doping. Chung *et al.*[8] suggested that doping with supervalent ions into Li sites can increase the conductivity of $LiFePO_4$ by p-type and n-type conductions. Moreover, similar conclusions have been made by studying metal ions doped at Fe site.[9−11] Unfortunately, in many cases, doping decreases the electrical conductivity and does not produce any significant benefit.[12,13] Thus, it remains unclear how the electrical conductivity of $LiFePO_4$ can be increased. First-principles calculations are advantageous in understanding the electronic structure of the doping $LiFePO_4$. Shi *et al.*[14] found that the electronic conduction of $LiFePO_4$ can be significantly improved when a few portion of Li^+ are replaced by Cr^{3+}. Liu *et al.*[15] have investigated N doped $LiFePO_4$ using the first-principles calculations, and found that the valence of Fe nearest to N appears as Fe^{3+}, which will be favorable for the hopping of electrons. Coating the surface of the cathode material with a layer of different substances is the most successful scheme to enhance electrical conductivity.[16,17] In our previous work,[6] the effect of amorphous silicon film on the electrochemical performance of LiFePO4@C cells was investigated, and it is found that the amorphous silicon film on the electrode surface could remarkably improve the electrochemical performance at high charge/discharge rate. In some cases, a combination of surface coating with carbon and transition metal doping has been attempted.[18] However, the underlying mechanisms are controversial and reveal a lack of fundamental understanding. It has been argued that a significant increase of electrical conduction does not result from the carbon coating but the smaller size of the particle.[19] Delacourt *et al.* proposed that the improved conductivity did not rely on the lattice doping, while being attributed to the conductive layer on the particle surface consisting of metal elements, C, Si, O, and P.[20]

Though many interesting experimental results

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have been obtained, the inherent reasons of the enhanced electronic properties have not been systematically clarified. Our study was motivated by the notion that if the surface modification of $LiFePO_4$ is implemented by coating with carbon, the carbon atoms might be introduced into $LiFePO_4$ to substitute O atoms. In this paper, we study mainly the electronic structures of C-doped $LiFePO_4$ by means of the first-principles calculations. Moreover, their structural stability and electronic conductivity are discussed.

2. Methods

The calculations are performed using the Vienna *ab initio* simulation package (VASP) in the framework of the projector augmented-wave method.[21−23] The generalized gradient approximation (GGA) is employed for the exchange correlation potential.[11,24] To describe the Coulomb interaction among Fe-3d electrons, a Hubbard parameter U is added in the GGA (GGA+U) using the method of the rotationally invariant approach proposed by Liechtenstein *et al.*[25] Here, the Coulomb interaction U and exchange interaction J are set to be 5.3 eV and 1.0 eV respectively. Similar values of U and J are found in Ref. [26], where the self-consistent calculations through the linear regression method were proposed by Cococcioni and de Gironcoli.[27]

All calculations are performed with a unit cell that contains four formula units. The convergence tests of the total energy with respect to the $\boldsymbol{k}$-points sampling and cut-off energy have been carefully examined, which ensures that the total energy is converged to within 10^{-4} eV per formula unit. The Monkhorst–Pack scheme[28] 3×5×6 $\boldsymbol{k}$-point sampling is used for the integration in the irreducible Brillouin zone. Energy cut-off for the plane waves is chosen to be 600 eV. Before the calculation of the electronic structure, the lattice parameters and the ionic positions are fully relaxed, and the final forces on all the relaxed atoms are less than 0.01 eV/Å. In all the calculations, spin polarizations are considered because the magnetic atoms play an important role in the electronic properties. The antiferromagnetic (AFM) ordering in all calculations was taken for the magnetic states of $LiFePO_4$, which has been determined experimentally to be AFM within the approximately simply square lattices formed by the planes of transitional metal cations in the olivine structure.[29] The calculation of the density of states (DOS) is smeared by the Gaussian smearing method with a smearing width of 0.03 eV.

3. Results and discussion

3.1. The properties of pure $LiFePO_4$

To verify the computational approach, we calculated the structural parameters of pure $LiFePO_4$. The calculated results are listed in Table 1. Here, the related experimental data and the calculated results are cited. From the table, it is found that the calculated structural parameters of $LiFePO_4$ are consistent with the experimental results. Moreover, it could be also observed that the calculated results of $LiFePO_4$ with high-spin Fe^{2+} in GGA are close to those in GGA+U with deviation lower than 5%. This phenomenon is in agreement with the result reported by Zhou *et al.*[31]

Table 1. Lattice parameters of $LiFePO_4$.

	$LiFePO_4$ GGA	$LiFePO_4$ GGA+U	$LiFePO_4$ Other cal.	$LiFePO_4$ Exp.[a)]
a/Å	10.397	10.445	10.487[a)], 10.45[b)]	10.332
b/Å	6.042	6.056	5.915[a)], 6.05[b)]	6.011
c/Å	4.745	4.754	4.748[a)], 4.74[b)]	4.692
V/Å^3	298.12	300.81	294.521[a)], 299.54[b)]	291.400
Li(4a)	(0, 0, 0)	(0, 0, 0)	(0, 0, 0)[a)]	(0, 0, 0)
Fe(4c)	(0.282, 0.25, 0.978)	(0.282, 0.25, 0.974)	(0.282, 0.25, 0.975)[a)]	(0.280, 0.25, 0.991)
P(4c)	(0.096, 0.25, 0.423)	(0.095, 0.25, 0.419)	(0.095, 0.25, 0.418)[a)]	(0.095, 0.25, 0.420)
O_1(4c)	(0.096, 0.25, 0.748)	(0.097, 0.25, 0.743)	(0.097, 0.25, 0.743)[a)]	(0.095, 0.25, 0.751)
O_2(4c)	(0.458, 0.25, 0.206)	(0.457, 0.25, 0.208)	(0.457, 0.25, 0.206)[a)]	(0.449, 0.25, 0.209)
O_3(8d)	(0.168, 0.045, 0.290)	(0.166, 0.046, 0.286)	(0.166, 0.046, 0.285)[a)]	(0.169, 0.046, 0.280)

The atomic coordinates are given in units of (a, b, c).

[a)]Ref.[14], [b)]Ref.[30].

It has been well known that $LiFePO_4$ has orthorhombic structure (space group *Pnma*), with the lattice constants of $a = 10.332$ Å, $b = 6.011$ Å, and $c = 4.692$ Å.[14] The unit cell contains 4 $LiFePO_4$ formulas, including 28 atoms. There are three types of O atoms in the $LiFePO_4$ crystal, which are labeled as O1, O2, and O3, respectively, as shown in Fig. 1. P atom coordinates with O atoms to form PO_4 tetrahedra, Fe and Li atoms bond with O atoms to form FeO_6 and LiO_6 octahedra. The FeO_6 octahedra is interconnected via corner sharing along the *bc* plane, and having two common edges with the LiO_6 octahedra and PO_4 tetrahedra, as shown in Fig. 1.

In order to show how the electrons are distributed in $LiFePO_4$, many groups have reported the electronic structures of $LiFePO_4$. However, the calculated results exhibit a dependence on the calculation methods, especially the band gap, ranging from 0.22 eV (GGA method)[32] to 3.7 eV (GGA+U method).[26] Figures. 2(a)–2(c) show the total and partial density of states (DOS) of the perfect $LiFePO_4$, respectively. From Fig. 2(a), we can see that pure $LiFePO_4$ is a semiconductor with energy gap of 0.22 eV according to the GGA calculation. This is similar to the result reported previously.[32] However, using GGA+U method, the calculated band gap of pure $LiFePO_4$ is 3.72 eV, as shown in Fig. 2(b), which is in good agreement with the experimental[14] and the calculated results.[26]

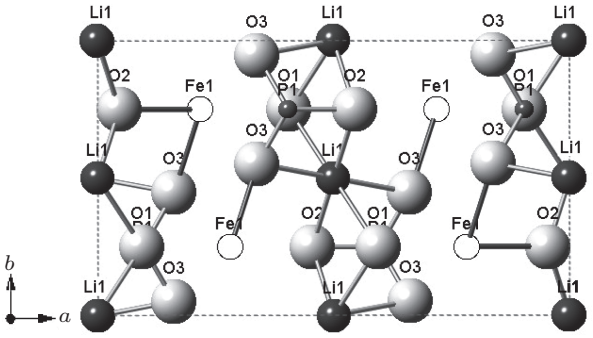


Fig. 1. Schematic drawing of the crystal structure of $LiFePO_4$.

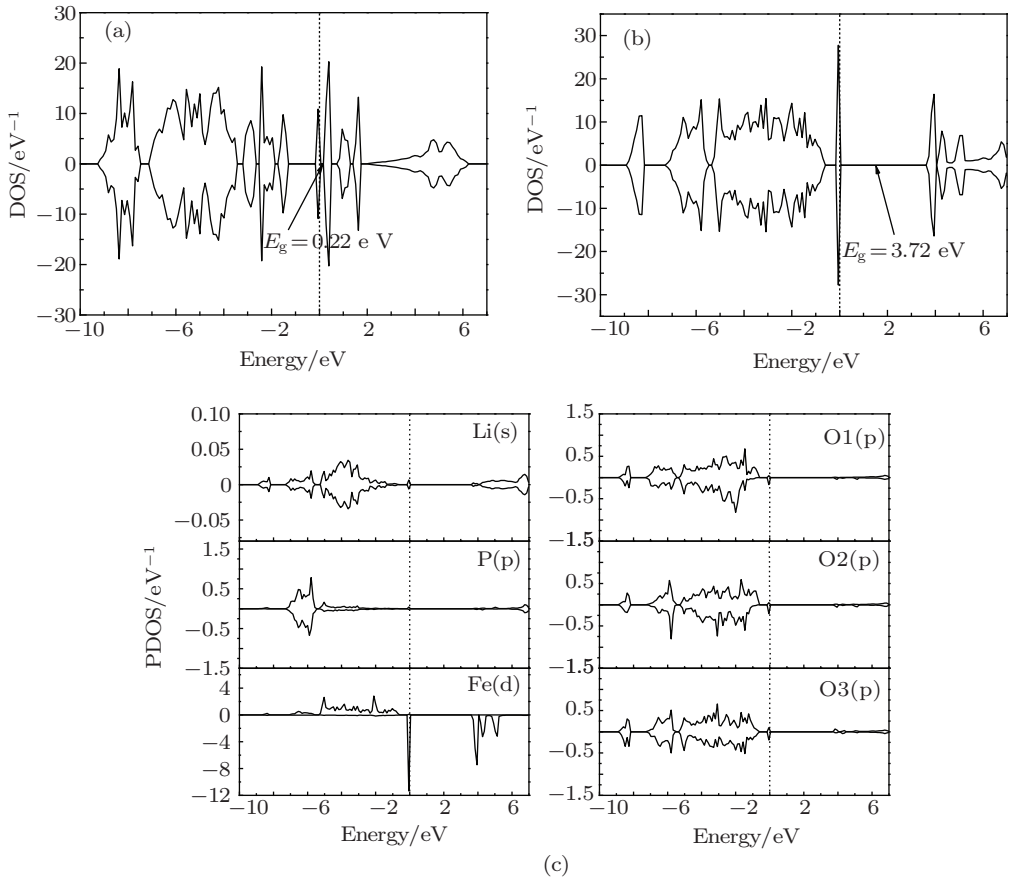


Fig. 2. (a) Total DOS of pure $LiFePO_4$ with GGA, (b) total DOS of pure $LiFePO_4$, and (c) projected DOS of pure $LiFePO_4$ with GGA+U. The Fermi level is set to be zero.

Figure 2(c) has shown the partial density of states (PDOS) of pure $LiFePO_4$ obtained using the GGA+U method. It is obvious that the electronic states near the Fermi level result mainly (almost all) from the contributions of Fe-3d and O-2p orbitals. The spin-up and spin-down parts are significantly split around the Fermi level of Fe-3d orbital. The spin-up orbital has been fully occupied. In $LiFePO_4$, for the spin-down orbital part, just a peak at 0.054 eV below the Fermi level, the others are empty. Since the Fe site is in an approximately octahedral environment surrounded by the neighboring O ions, the 3d states are split into states of t_{2g} (d_{xy}, d_{yz} and d_{xz}) and e_g ($d_{x^2-y^2}$ and d_{z^2}) symmetries. In any case, the PDOS results indicate that Fe ion exhibits +2 valence, which is consistent with the results of X-ray absorption near-edge structure (XANES) and Mössbauer spectrum.[33,34]

3.2. Doping effect

The effect of C-doping on the structure of $LiFePO_4$ was explored. There are three nonequivalent O atoms in $LiFePO_4$. One O atom of a unit cell of $LiFePO_4$ was substituted with one C atom, and then the doped structure was fully relaxed. Table 2 summarizes the relaxed parameters and formation energy for C doped at O sites in $LiFePO_4$. It can be seen that the crystal with C doped at O_3 site has the lowest formation energy with the value of 1.86 eV. In the cases of the other two doped models, the formation energies are much higher, indicating that C dopants prefer to occupy O_3 sites. The results above are consistent with those of N doped at O sites in $LiFePO_4$.[15] From Table 2, it can be also seen that the volumes of the doped materials for three C doped models are larger than that of the pure $LiFePO_4$. The increased volumes provide more open Li ions diffusion channels, which would lower the activation energy during the intercalation and deintercalation of Li ions. Thus, the electrochemical properties of $LiFePO_4$ will be improved.

Table 2. The relaxed parameters and formation energy for C-doped $LiFePO_4$.

Configurations	a/Å	b/Å	c/Å	V/Å^3	d_{Fe-C} /Å	Δd/%	Formation energy/eV
Pure $LiFePO_4$	10.445	6.056	4.754	300.81	–	–	–
C-doped at the O_1 site	10.354	6.052	4.855	304.20	2.030	–8.80%	3.22
C-doped at the O_2 site	10.519	6.063	4.777	304.66	2.001	–6.63%	3.09
C-doped at the O_3 site	10.412	6.088	4.756	301.43	2.057	–0.82%	1.86

C doping causes the local distortions of the lattice. The distortions of the Fe–O octahedron for three C doped models are shown in Figs. 3(a)–3(d), respectively. For $LiFePO_4$, the lengths of the Fe–O bonds for the O_1, O_2, and O_3 sites are 2.226, 2.143, and 2.074 Å, respectively. As O atoms at the O_1, O_2, and O_3 sites are replaced by C atom, the lengths of the Fe–C bonds are reduced to 2.030, 2.001, and 2.057 Å, respectively. The decrease percentages are respectively 8.80%, 6.63%, and 0.82%, because the atomic radius of C is smaller than that of O. The significant distortion of the Fe–O(C) octahedron causes the expansion and relative high formation energy. In the case of C doped at O_3 site, compared with the initial Fe–O bond, it is found that the Fe–C bond is reduced by only 0.017 Å (from 2.074 Å to 2.057 Å), which means that there exists little effect on the cell volume. This may be the main reason why C doped at O_3 site has the lowest formation energy, as seen in Table 2.

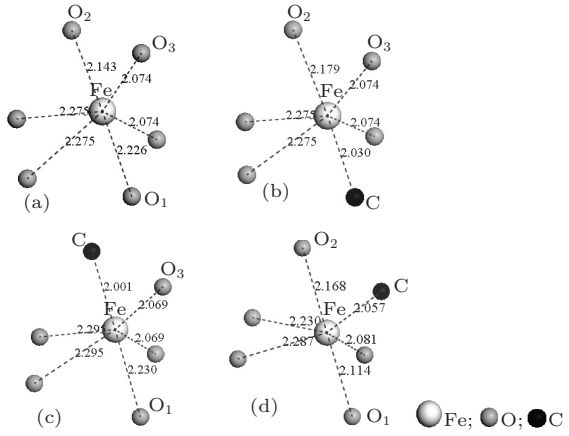


Fig. 3. The distortions of the Fe–O octahedral caused by C doping. (a) Fe–O octahedral, (b) distortion of the Fe–O octahedral when O_1 site is replaced by C doping, (c) distortion of the Fe–O octahedral when O_2 site is replaced by C doping, and (d) distortion of the Fe–O octahedral when O_3 site is replaced by C doping.

To further analyze the impact of C doping on the properties of $LiFePO_4$, we have also calculated the electronic structures of $LiFePO_4$ with C doping. Fig-

ures 4–6 show the DOS and PDOS of Li-2s, P-3p, O-2p, C-2p, and Fe-3d in C doped $LiFePO_4$, respectively. In Figs. 4–6, the labeled Fe4 is the iron atom nearest neighbor to the doped C atom, and Fe1 is the iron atom which does not bond with the doped C atom. From the figures, it can be found that the gap states around the Fermi level are mostly attributed to C-2p and Fe-3d states for C doped $LiFePO_4$, although there is little contribution of the O-2p state. According to Figs. 4–6, the band gaps of C doped at O_1, O_2, and O_3 sites in $LiFePO_4$ are narrower than that of pure $LiFePO_4$, which suggests that the C-doped materials may exhibit higher electronic conduction than the pure $LiFePO_4$. A similar conclusion was drawn from the investigation results of Liu *et al.*[15] It is found that the electronic conductivity and the mobility of Li ion in $LiFePO_{3.75}N_{0.25}$ were increased.

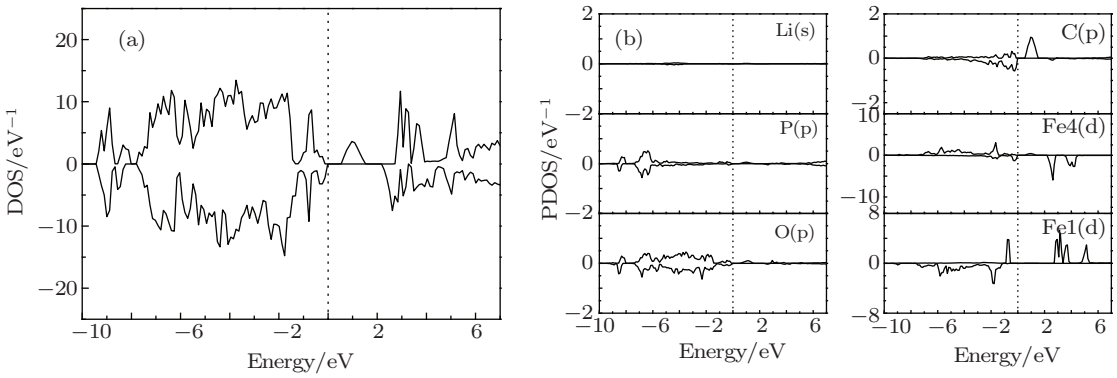


Fig. 4. DOS of $LiFePO_{3.75}C_{0.25}$: (a) total DOS, (b) projected DOS of C doped at the O_1 site in $LiFePO_4$. Fe4 is the nearest to C, and Fe1 is an Fe not bonded with C.

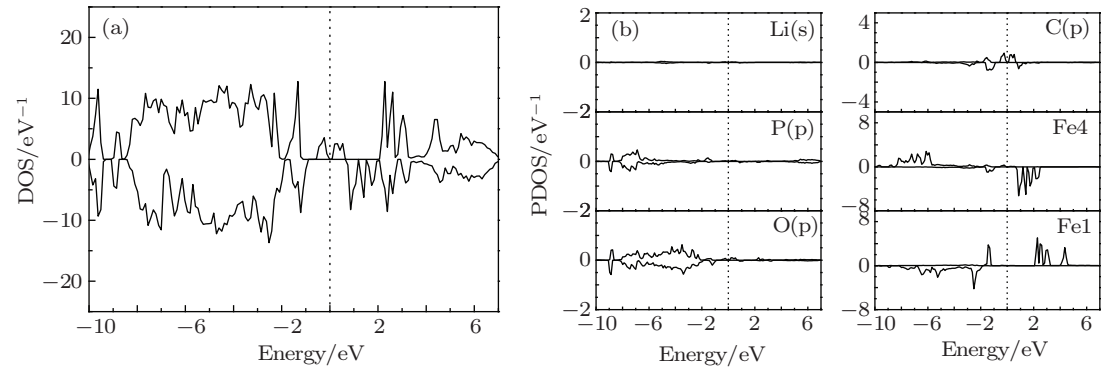


Fig. 5. DOS of $LiFePO_{3.75}C_{0.25}$: (a) total DOS, (b) projected DOS of C doped at the O_2 site in $LiFePO_4$. Fe4 is the nearest to C, and Fe1 is an Fe not bonded with C.

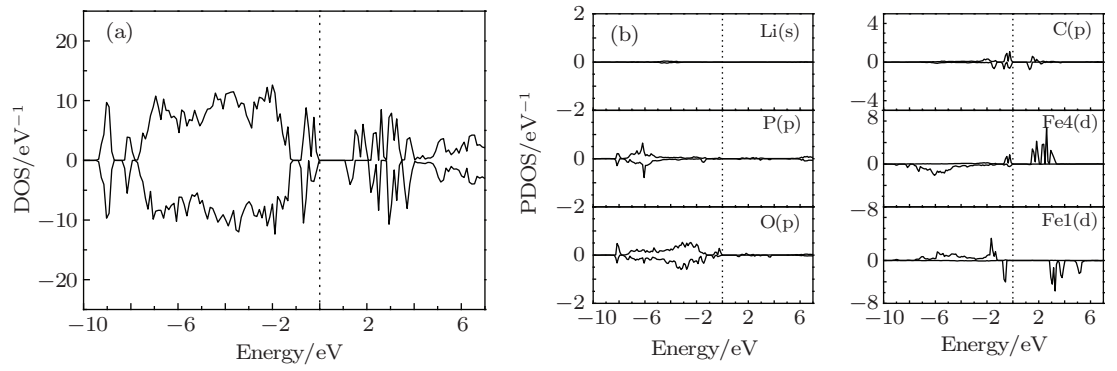


Fig. 6. DOS of $LiFePO_{3.75}C_{0.25}$: (a) total DOS, (b) projected DOS of C doped at the O_3 site in $LiFePO_4$. Fe4 is the nearest to C, and Fe1 is an Fe not bonded with C.

The difference of the charge densities for the doped and undoped crystals is compared in order to study the effect of C doping on the charge transfer. For the purpose of analyzing the difference in the charge densities, both $LiFePO_{3.75}C_{0.25}$ and pure $LiFePO_4$ are calculated in the same geometry with the relaxed $LiFePO_4$ so that the charge densities can be subtracted point by point. Aydinol *et al.* firstly proposed such a treatment for a charge difference plot.[35] Figure 7 shows the positive 0.02 $e/Å^3$ isosurface for the charge-density difference ($\Delta\rho = \rho_{LiFePO_{3.75}C_{0.25}} - \rho_{LiFePO_4}$). It should be noted here that the charge-density difference ($\Delta\rho$) is the negative value of electron-density difference (Δe), so that a positive value of $\Delta\rho$ means a depletion of electrons. The charge density distribution on the Fe–C line for C doped at O_3 site in $LiFePO_4$ is shown in Fig. 8. Here, the charge density distribution on the Fe–O(O_3) line in pure $LiFePO_4$ is also shown for comparison. It can be seen from Figs. 7 and 8 that Fe and C are not completely ionized. The Fe–C bonding is covalent like. Moreover, it can be found that the Fe ion nearest to C atom loses more electrons than other Fe atoms. The positive isosurface shape is the characteristic of a t_{2g} orbital, which confirms that the valence state of Fe ion nearest to C atom is changed from Fe^{2+} ($t_{2g}^4\,e_g^2$) into Fe^{3+} ($t_{2g}^3\,e_g^2$). C doping induces Fe^{3+} states, and electron hopping can be realized through the [–Fe^{3+}–C–Fe^{2+}–O–] chain. A small polaron hopping conducting mechanism in $LiFePO_4$ is generally accepted.[15,38] Fe^{3+} site is necessary for the electron polaron hopping. However, for the Fe ions far from the C atom in $LiFePO_{3.75}C_{0.25}$ and pure $LiFePO_4$, there exists no charge transfer. Therefore, all Fe atoms are in a valence state of 2+. Thus, the electron hopping is limited. Thermal excited electrons are extremely rare due to the large band gap of 3.72 eV, so pure $LiFePO_4$ shows poor electron conductivity. When C is doped, Fe^{3+} is induced and the electron–hole hopping along the Fe–C–Fe chains may occur. This might lead to the better electron mobility.

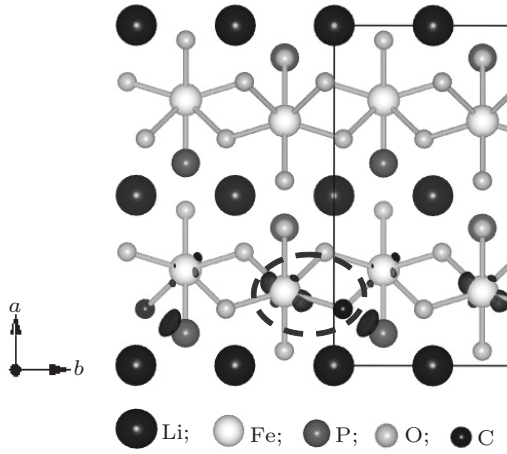


Fig. 7. The positive 0.02 $e/Å^3$ isosurface of the difference between charge densities between $LiFePO_{3.75}C_{0.25}$ and pure $LiFePO_4$ ($\rho_{LiFePO_{3.75}C_{0.25}} - \rho_{LiFePO_4}$). View along [001], rending using VESTA. [36,37]

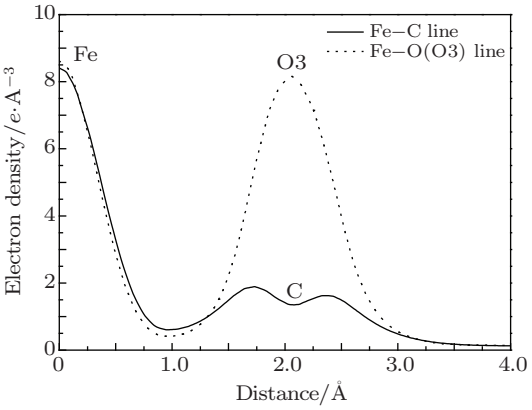


Fig. 8. Electron density distribution on the Fe–C line for C doped at O_3 site in $LiFePO_4$.

Based on the results and discussion above, the formation energies of C doped at O sites are energetically favored, even though C dopants prefer to occupy O_3 sites. Furthermore, the analysis of the atomic and electronic structures of $LiFePO_{3.75}C_{0.25}$ suggests that change of the Fe–O(C) bond causes the increasing of the volume and the narrowing of the band gap, accordingly improving the electrochemical performance of $LiFePO_4$. In other words, doping C at the O site is an effective way to improve the electrochemical performance of $LiFePO_4$.

4. Conclusions

In conclusion, we have investigated the effects of C doping on the structural and electronic properties of $LiFePO_4$. It is found that C doped at O sites is energetically favored, and doped C atom prefers to occupy O_3 sites. A much narrower gap near the Fermi level is predicted. The Fe–C bonding is covalent like. We predict that the coexistence of Fe^{2+} and Fe^{3+} ions will benefit the electron conductivity, and doping C at the O site is an effective way to improve the electrochemical properties of $LiFePO_4$.

References

[1] Padhi A K, Nanjun daswamy K S and Goodenough J B 1997 *J. Electrochem. Soc.* **144** 1188

[2] Yamada A, Chung S C and Hinokuma K 2001 *J. Electrochem. Soc.* **148** A224

[3] Ong S P, Chevrier V L and Ceder G 2011 *Phys. Rev.* B **83** 075112

[4] Yamada A, Takei Y, Koizumi H, Sonoyama N, Kanno R, Itoh K, Yonemura M and Kamiyama T 2006 *Chem. Mater.* **18** 804

[5] Sides C R, Croce F, Young V Y, Martin C R and Scrosati B 2005 *Electrochem. Solid-State Lett.* **8** A484

[6] Lin Y B, Yang Y M, Lin Y, Zeng B Z, Zhao G Y and Huang Z G 2011 *Electrochim. Acta* **56** 4937

[7] Choi D and Kumta P N 2007 *J. Power Sources* **163** 1064

[8] Chung S Y, Bloking J T and Chiang Y M 2002 *Nat. Mater.* **1** 123

[9] Lin Z P, Zhao Y M and Zhao Y J 2011 *Chin. Phys.* B **20** 018201

[10] Ouyang X F, Shi S Q, Ouyang C Y, Jiang D Y, Liu D S, Ye Z Q and Lei M S 2007 *Chin. Phys.* **16** 3042

[11] Zhang H, Tang Y H, Shen J Q, Xin X G, Cui L X, Chen L J, Ouyang C Y, Shi S Q and Chen L Q 2011 *Appl. Phys.* A **104** 529

[12] Lala S M, Montoro L A, Lemos V, Abbate M and Rosolen J M 2005 *Electrochim. Acta* **51** 7

[13] Molenda J, Marzec J, Swierczek K, Ojczyk W, Ziemnicki M, Molenda M, Drozdek M and Dziembaj R 2004 *Solid State Ionics* **171** 215

[14] Shi S Q, Liu L J, Ouyang C Y, Wang D S, Wang Z X, Chen L Q and Huang X J 2003 *Phys. Rev.* B **68** 195108

[15] Liu Z J, Huang X J and Wang D S 2008 *Solid State Commun.* **147** 505

[16] Wang L, Huang Y D, Jiang R R and Jia D Z 2007 *J. Electrochem. Soc.* **154** A1015

[17] Doeff M M, Wilcox J D, Yu R, Aumentado A, Marcinek M and Kostecki R 2008 *J. Solid State Electrochem.* **12** 995

[18] Zhang B, Wang X J, Liu Z J, Li H and Huang X J 2010 *J. Electrochem. Soc.* **157** A285

[19] Gaberscek M, Dominko R and Jamnik J 2007 *Electrochem. Commun.* **9** 2778

[20] Delacourt C, Wurm C, Laffont L, Leriche J B and Masquelier C 2006 *Solid State Ionics* **177** 333

[21] Kresse G and Furthmüller J 1996 *Phys. Rev.* B **54** 11169

[22] Xu G G, Wu Q Y, Chen Z G, Huang Z G, Wu R Q and Feng Y P 2008 *Phys. Rev.* B **78** 115420

[23] Weng Z Z, Zhang J M, Huang Z G and Lin W X 2011 *Chin. Phys.* B **20** 027103

[24] Perdew J P, Chevary J A, Vosko S H, Jackson K A, Pederson M R, Singh D J and Fiolhais C 1992 *Phys. Rev.* B **46** 6671

[25] Liechtenstein A I, Anisimov V I and Zaanen J 1995 *Phys. Rev.* B **52** R5467

[26] Zhou F, Kang K, Maxisch T, Ceder G and Morgan D 2004 *Solid State Commun.* **132** 181

[27] Cococcioni M and de Gironcoli S 2005 *Phys. Rev.* B **71** 035105

[28] Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188

[29] Rousse G, Rodriguez-Carvajal J, Patoux S and Masquelier C 2003 *Chem. Mater.* **15** 4082

[30] Maxisch T and Ceder G 2006 *Phys. Rev.* B **73** 174112

[31] Zhou F, Cococcioni M, Marianetti C A, Morgan D and Ceder G 2004 *Phys. Rev.* B **70** 235121

[32] Yamada A, Hosoya M, Chung S C, Kudo Y, Hinokuma K, Liu K Y and Nishi Y 2003 *J. Power Sources* **232** 119

[33] Deb A, Bergmann U, Cairns E J and Cramer S P 2004 *J. Phys. Chem.* B **108** 7046

[34] Prince A A M, Mylswamy S, Chan T S, Liu R S, Hannoyer B, Jean M, Shen C H, Huang S M, Lee J F and Wang G X 2004 *Solid State Commun.* **132** 455

[35] Aydinol M K, Kohan A F, Ceder G, Cho K and Joannopoulos J 1997 *Phys. Rev.* B **56** 1354

[36] Momma K and Izumi F 2008 *J. Appl. Crystallogr.* **41** 653

[37] Chevrier V L, Ong S P, Armiento R, Chan M K Y and Ceder G 2010 *Phys. Rev.* B **82** 075122

[38] Maxisch T, Zhou F and Ceder G 2006 *Phys. Rev.* B **73** 104301