PHYSICAL REVIEW B **69**, 104303 (2004)

First-principles study of Li ion diffusion in $LiFePO_4$

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(Received 12 November 2003; revised manuscript received 16 December 2003; published 30 March 2004)

The diffusion mechanism of Li ions in the olivine $LiFePO_4$ is investigated from first-principles calculations. The energy barriers for possible spatial hopping pathways are calculated with the adiabatic trajectory method. The calculations show that the energy barriers running along the c axis are about 0.6, 1.2, and 1.5 eV for $LiFePO_4$, $FePO_4$, and $Li_{0.5}FePO_4$, respectively. However, the other migration pathways have much higher energy barriers resulting in very low probability of Li-ion migration. This means that the diffusion in $LiFePO_4$ is one dimensional. The one-dimensional diffusion behavior has also been shown with full *ab initio* molecular dynamics simulation, through which the diffusion behavior is directly observed.

DOI: 10.1103/PhysRevB.69.104303 PACS number(s): 66.30.Dn, 31.15.Ar, 71.15.Pd, 84.60.−h

Among the typical Li secondary battery cathode material such as $LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$, etc., $LiFePO_4$ of the phospho-olivine family proposed by Goodenough *et al.* appears particularly interesting due to their high-energy density, low cost, and the environmental compatibility of its basic constituents.[1] However, this cathode may be affected by a loss of capacity with increasing charge-discharge current density, associated with its intrinsic low electronic and ionic conductivity. It is generally accepted that $LiCoO_2$ possesses a two-dimension diffusion plane[2] while $LiMn_2O_4$ possesses three-dimensional diffusion channels.[3] Therefore, an interesting question arises, how about the diffusion channel(s) in $LiFePO_4$? This paper is intended to find out the answer to this question.

Chung *et al.*[4] showed experimentally that the electronic conductivity of $LiFePO_4$ could be increased enormously by substituting small amount of high valence metal ions for lithium ions. Their conclusion was later confirmed experimentally and theoretically in our group.[5] However, it seems that the improved electronic conductivity did not improve the battery performance as expected. Prosini *et al.*[6] have determined the diffusion coefficient of lithium in $LiFePO_4$ as a function of the lithium concentration using the galvanostatic intermittent titration technique (GITT) and ac impedance method. They found that the diffusion coefficients are about 1.8×10^{-14} and 2.2×10^{-16} cm^2/s for $LiFePO_4$ and $FePO_4$, respectively. While the experiments are able to measure the total diffusion coefficient, it is generally very difficult to understand the microscopic diffusion mechanism. Therefore, theoretical studies are extremely important in understanding these issues.

To investigate these questions, we performed *ab initio* density functional-based total energy calculations using the Vienna *ab initio* simulation package VASP.[7,8] We use this code to solve the Kohn-Sham equations within the pseudopotential approximation[9] whereby the electrons are described in the local-density approximation (LDA) or generalized gradient approximation (GGA) and ultrasoft pseudopotentials.[10] The valence electrons are expanded in a plane wave basis set and the effect of the core states on the valence electrons is treated with ultrasoft pseudopotentials.

Since the chemical diffusion coefficient is sensitive to the Li content in the $Li_\delta FePO_4$ material,[6] three typical Li concentrations are thus calculated: $\delta=1$, 0.5, and 0. For each Li concentration, the ionic positions, lattice parameters and cell volume are relaxed with the conjugate gradient method using forces and stresses. In most of the calculations, the LDA have been used. However, to test the reliability of the LDA in the Fe-olivine system, nonlocal or gradient-corrected functional [GGA-PW91 (Ref. 11)] has also been applied for the case of $\delta=1$. For $\delta=0.5$ in a $2\times2\times2$ supercell, there are 16 Li ions in the lattice while 32 Li cites available. Therefore, the initial configurations need to be figured out beforehand. Seven configurations for the case of $\delta=0.5$ have been considered, including four ordered structures and three disordered structures. For the four ordered structures, two configurations are constructed by taking away all of the Li ions at y or $z=0.25$ and 0.75 sites in the lattice, and was denoted as b2575 and c2575, respectively. The other two denoted as b05 and c05 are formed by taking away all of the Li ions at y or $z=0$ and 0.5 sites in the lattice. x, y, and z are the fractional coordinates of the Li ion cites. ($x=0.25$ and 0.75 sites are equal to $y=0.25$ and 0.75 sites while $x=0$ and 0. 5 sites are equal to $y=0$ and 0. 5 sites for the olivine LiFePO4 structure.) The three disordered structures denoted as ran1, ran2, and ran3 are constructed by putting the 16 ions randomly in the 32 sites.

Table I presents the optimized structure after the ionic relaxation with conjugate gradient method. It can be seen that configuration c2575 possesses the lowest total energy for the case of $\delta=0.5$, indicating a most favorable configuration and will be chosen as the objective of the following calculations for the case of $\delta=0.5$.

Figuring out the diffusion pathways is always crucial in understanding the microscopic diffusion mechanism. In order to calculate the diffusion pathways for the Li ions, we have employed the so-called "adiabatic trajectory method"[12,13] after the structural optimization. With this method Vincent Meunier *et al.*[14] have studied Li diffusion in carbon nanotubes successfully. In this method, one chosen Li ion is pushed to move with a small, constant speed in a given direction, and all other atoms are relaxed continuously in

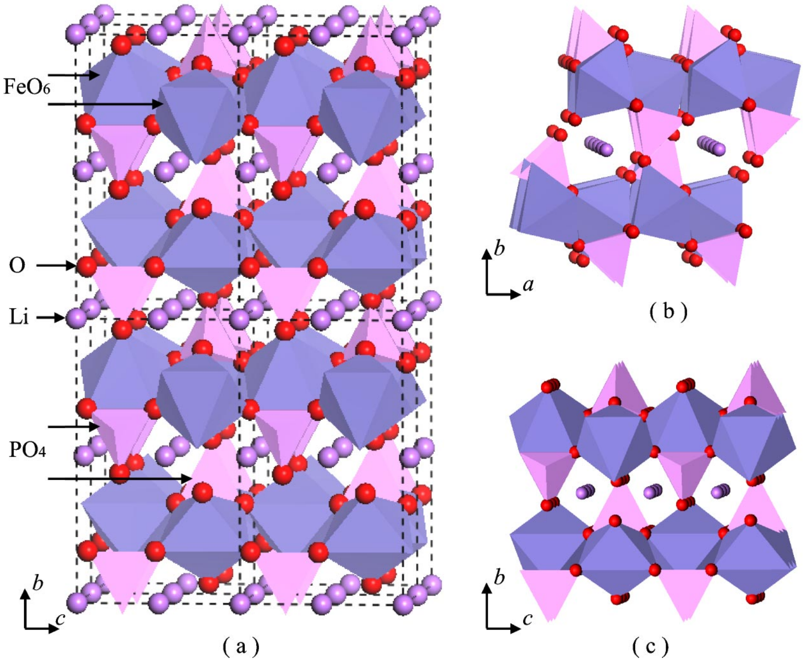
TABLE I. The relaxed structure for different objective configurations, for the case of $\delta=1$, the relaxation have been performed with both LDA and GGA.

Configurations		Lattice vectors (Å) a	b	c	Total energy (eV)
$\delta=1$	LDA	4.710	10.333	5.982	−1596.7452
	GGA	4.698	10.229	6.011	−1601.6685
	Exp [1]	4.6922	10.3324	6.0105	
$\delta=0$		4.775	9.831	5.797	−1427.4171
$\delta=0.5$	b2575	4.690	9.962	5.885	−1527.9571
	c2575	4.777	9.935	5.885	−1533.4018
	b05	4.694	9.966	5.884	−1528.3274
	c05	4.778	9.931	5.886	−1533.1688
	ran1	4.741	9.922	5.885	−1530.4069
	ran2	4.737	9.924	5.889	−1530.7824
	ran3	4.739	9.922	5.886	−1530.6100

response to the Li ion motion. The energy barrier can be obtained conveniently through monitoring the changes of the total energy. This method has been found to be a viable alternative to a costly point-by-point determination of the potential energy surface. Calculations are carried out with a grid spacing corresponding to an effective energy cutoff of 297 eV with a single Γ point.

As shown in Fig. 1, $LiFePO_4$ has the ordered olivine structure.[1] The Li atoms occupy chains of edge-shared octahedral running parallel to the c axis in an alternate a-c planes whereas the Fe atoms occupy zigzag chains of corner-shared octahedral running parallel to the c axis in the other a-c plains. The a-c planes containing the Li atoms are bridged by PO_4 tetrahedral. This crystal structure provides two spatial diffusion tunnels, running parallel to the c axis and a axis, respectively, as shown in Figs. 1(b) and 1(c).

With the ''adiabatic trajectory method,'' the diffusion energy barriers are calculated as the following. The Li ion in the center of the $2\times2\times2$ super cell, with fractional coordinates (0.5, 0.5, 0.5), is pushed to move along the two tunnels to its nearest neighboring sites with a constant speed. The nearest neighboring Li ion in front of the moving one is removed beforehand to avoid blocking the way of the coming Li ion. Figure 2 presents the energy barriers obtained by monitoring the total energy changes of different Li concentration configurations. For comparison purpose, the Li ion was also pushed to move along the b direction, though there is no spatial tunnel in this direction. It can be seen from the



(a) (b) (c)

FIG. 1. (Color online) (a) Crystal structure of $LiFePO_4$ viewed along the a axis and the two possible spatial diffusion tunnels for Li ions running along the (b) c axis and (c) a axis.

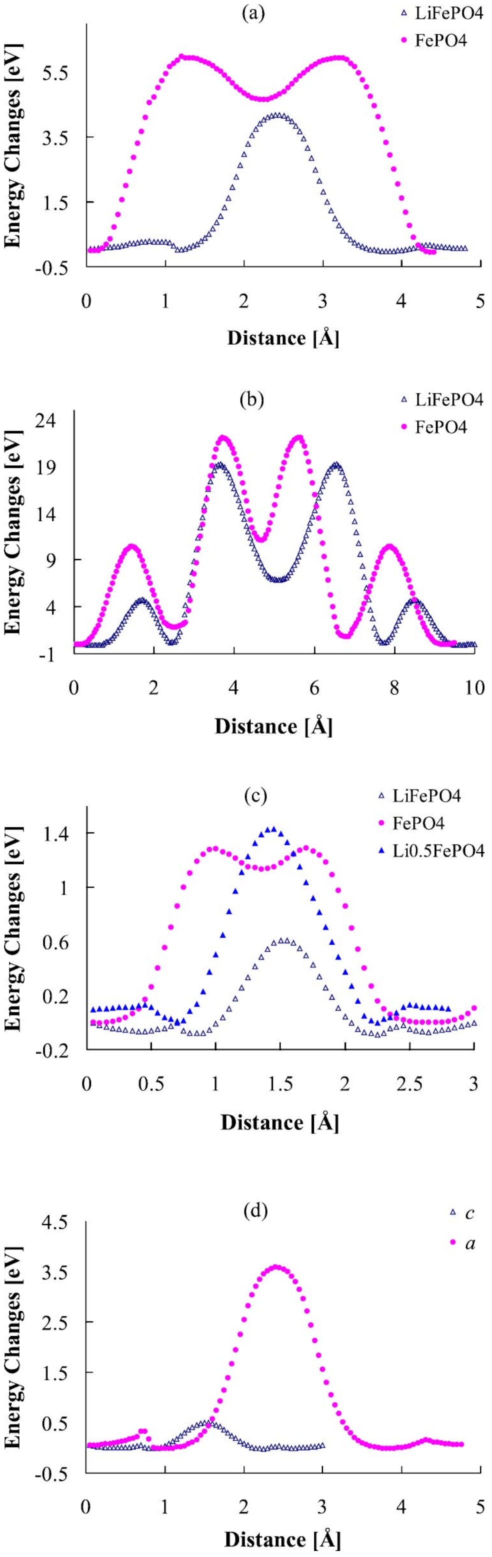


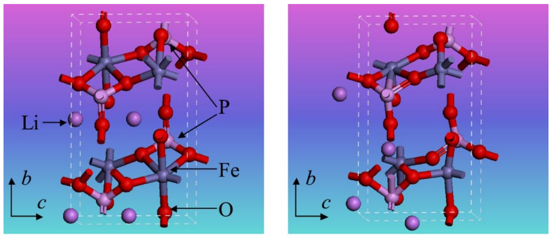
FIG. 2. (Color online) Energy barriers of three different diffusion pathways (a)–(c) are for the migrating direction running along the *a*, *b*, and *c* axis, respectively. (d) shows the energy barriers along *a* and *c* directions in $LiFePO_4$ obtained from GGA.

Fig. 2(c) that the energy barriers along the *c* direction is about 0.6, 1.2 and 1.5 eV for $LiFePO_4$, $FePO_4$, and $Li_{0.5}FePO_4$ respectively. The different energy barriers for the three species are mainly due to the different atomic surroundings of the diffusion pathway, including the different ionic position and bonding length (lattice vector), which is the direct result of the different Li concentration. However, the energy barriers along the other two directions are much higher that prohibits the diffusion occurs along these two directions, as shown in Figs. 2(a) and 2(b). This means that the diffusion in $LiFePO_4$ is one dimensional. As the energy barrier along *c* direction for $LiFePO_4$ is lower than that of $FePO_4$ and $Li_{0.5}FePO_4$, the diffusion coefficient will be higher, which is consistent with Prosini's experimental results.[6] To test the reliability of the LDA obtained energy barriers, Fig. 2(d) shows the GGA results of $LiFePO_4$ when the Li ion is pushed to move along the. It can be seen that the energy barriers are about 3.60 and 0.51 eV for *a* and *c* axis directions, respectively, which are a little lower than the LDA results (4.2 and 0.6 eV). However, the energy barrier along *c* axis direction is also much higher than that of *a* axis direction. The conclusion of the one-dimensional diffusion mechanism is unchanged.

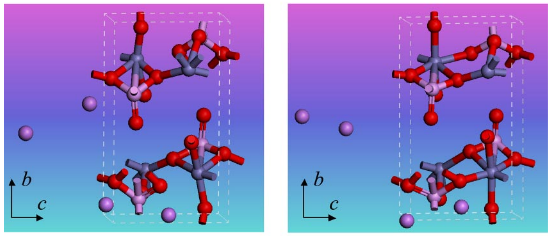
Upon that it is understandable that the enhanced electronic conductivity due to the substitution of small amount of high valence metal ions for lithium ions does not lead to improved battery performance. As the heavy high valence metal ions in the Li sites will block the one-dimensional diffusion pathways, the ionic conductivity is decreased, which is certainly harmful to the battery performance. It is also reasonable that c2575 configuration is the most favorable configuration for the case of $Li_{0.5}FePO_4$. Since the motion of Li ions is only free to move in one dimension, with the Coulomb interaction among the Li ions, they will distribute as far away as possible, which finally leads to the c2575 configuration.

The above considerations are all based on the constrained motion of singleLi ions within the $LiFePO_4$ crystal. In practice, however, it is known that diffusion is a complex process involving the concerted motion of many different Li atoms. It is therefore highly desirable to study Li diffusion with full *ab initio* molecular dynamics (MD) simulations. Unfortunately, as the ensemble average is always required, such simulations are currently computational very expensive. As a compromise, we have therefore opted to carry out dynamical simulations with a relatively small system and short time scale.

In the present work, we perform the full MD simulation with the CASTEP simulation packages,[15] which is also plane-wave pseudopotential DFT based. The equations of motion are integrated using the Verlet[16] algorithm and the integration time step Δt is set to be 1 fs. Simulations are carried out using the NVT ensemble with the temperature controlled with a Nosé-Hoover thermostat.[17] After local relaxations have been finished, simulation begins with $T = 273$ K, and no obvious diffusion happed within the time scale of 1 ps. Then we change the temperature to 1273 K, and we observed that the Li ions diffuse significantly. Figure 3 shows the evolution of the trajectory of the diffusion Li ions in $LiFePO_4$ at T



(a) $t = 0$ (b) $t = 0.5$ps



(c) $t = 1$ps (d) $t = 1.5$ps

FIG. 3. (Color online) The evolution of the diffusion trajectory in one unit cell at $T = 1273$ K.

$= 1273$ K. We observed two Li ions hopped from the initial sites to their neighboring sites along c direction while the other two keep oscillating around their initial sites. This proves that the Li diffusion is one dimensional.

Figure 4 displays the mean square displacements (MSD) of the four species in $LiFePO_4$ crystal as a function of time. As it can be seen from Fig. 4(a), when the temperature is 273 K, all the species are keeping oscillating around their original sites. However, when the temperature is increased to 1273 K, while Fe, P, O are oscillating around their original sites, Li shows a remarkable diffusion behavior [Fig. 4(b)]. To shed more light on the diffusion direction of Li ions, Fig. 4(c) shows the mean square displacements of Li ions projected at the a, b, and c directions at 1273 K. It shows clearly that the component along the c direction is much higher than those of along the a and b directions which fluctuates around a certain relatively small value. This indicates again that Li ions only diffuse along c direction.

In summary, our first principle calculations show that Li diffusion in olivine $LiFePO_4$ is one dimensional, which explains why the enhanced electronic conductivity through Li site doping did not improve the electrochemical performance for $LiFePO_4$ as cathode material. The diffusion energy barrier in $FePO_4$, a little lower than in $Li_{0.5}FePO_4$, is about two times higher than in $LiFePO_4$, which agrees well with the experiments. The directly observed diffusion trajectory from full *ab initio* MD simulations confirmed the one-dimensional diffusion pass way.

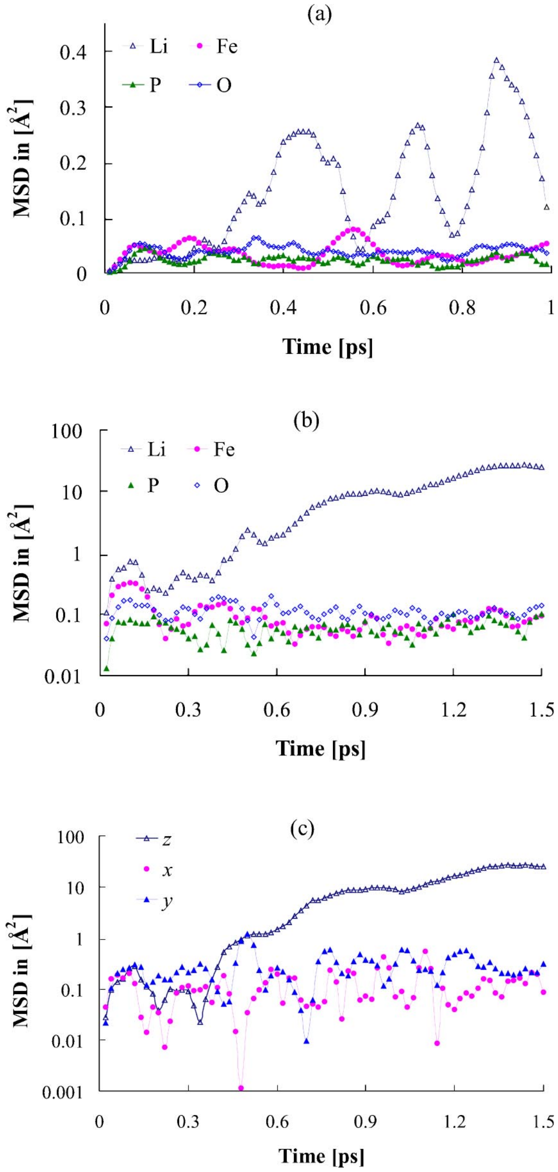


FIG. 4. (Color online) Mean square displacements of the four species at (a) 273 K and (b) 1273 K. (c) shows the mean square displacements of Li ions projected in the three axes at 1273 K.

This work was supported by National Science Foundation of China (NSFC) (Grant No. 59972041); National 863 key program (Grant No. 2001AA32301), and National 973 key program (Grant No. 2002CB211802) of China.

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