The effect of Cr doping on Li ion diffusion in LiFePO$_4$ from first principles investigations and Monte Carlo simulations

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C Y Ouyang[1,2]**, S Q Shi**[1]**, Z X Wang**[1]**, H Li**[1]**, X J Huang**[1] **and L Q Chen**[1]

[1] Laboratory for Solid State Ionics, Institute of Physics, Chinese Academy of Science,
PO Box 603, Beijing 100080, People's Republic of China
[2] Physics Department, Jiangxi Normal University, Nanchang 330027, People's Republic of China

Abstract
Using the adiabatic trajectory method, the migration energy barriers for the migration of Li ions and Cr ions along the one-dimensional diffusion pathway in pure and Cr doped LiFePO$_4$ are obtained from first principles calculations. The results show that while Li ions can diffuse along the diffusion pathway easily, Cr ions do not easily diffuse away from their initial positions. This means that the heavy Cr ions will block the one-dimensional diffusion pathway of the material. Monte Carlo simulations are performed to evaluate the influences of the blocking behaviours on the electrochemical performance of LiFePO$_4$ cathode material for Li ion secondary batteries. The results show that the evaluated capacity is highly sensitive to the amount of the dopant, the size of the super-cell being used for simulation (particle size of the powder cathode material) and the Monte Carlo steps for statistics (charge–discharge current density).

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Among typical Li secondary battery cathode materials such as LiCoO$_2$, LiMn$_2$O$_4$ and LiFePO$_4$, LiFePO$_4$ of the phospho-olivine family proposed by Goodenough *et al* [1] has attracted particular attention due to the high energy density, low cost and good environmental compatibility of its basic constituents. However, this cathode may be affected by a loss of capacity with increasing charge/discharge current density, associated with its fundamentally low electronic and ionic conductivity [1, 2]. This limitation should be less serious in a high-temperature application. Elevated temperatures will enhance not only the lithium diffusion rate but also the electronic conductivity, and could therefore increase the reversible capacity at higher current densities. However, it is not only the Li diffusion rate which increases at
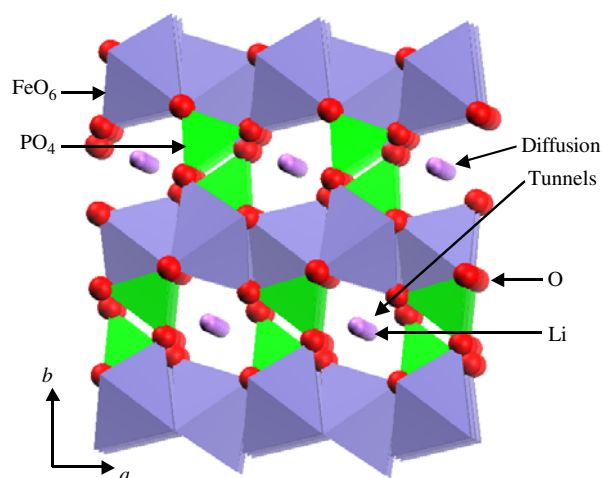
Figure 1. The standard olivine structure of a LiFePO$_4$ crystal.

higher temperatures; a number of other less desirable reactions will also be enhanced at the same time, and these reactions are hindrances to the enhancement of the reversible capacity [3].

Chung *et al* [4] showed experimentally that the electronic conductivity of LiFePO$_4$ could be increased enormously by substituting a 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 enhanced electronic conductivity does not improve the electrochemical performance as expected.

Later, we have successfully shown from *ab initio* molecular dynamics studies [6] that the Li diffusion in LiFePO$_4$ is one-dimensional. This one-dimensional diffusion behaviour is directly observed in the studies, and the Li ions can only be diffused along the *c*-axis direction.

In this paper, we intend to show why the enhanced electronic conductivity from the substitution of a small amount of high valence metal ions for lithium ions did not lead to improved electrochemical performance as expected. We will prove that the Cr ions in the Li site can block the diffusion motion of Li ions along the one-dimensional diffusion pathway from density functional theory (DFT) based first principles calculations. After this, we will evaluate how much the doped Cr ions in the LiFePO$_4$ crystal affect the electrochemical performance from Monte Carlo (MC) simulations.

2. Crystal structure and structural optimization

LiFePO$_4$ has the ordered olivine structure with space group *Pnma* [1]. Figure 1 shows its crystal structure schematically. As is shown in figure 1, the Li atoms occupy chains of edge-shared octahedra running parallel to the *c*-axis in alternate *a*–*c* planes, whereas the Fe atoms occupy zigzag chains of corner-shared octahedra running parallel to the *c*-axis in the other *a*–*c* planes. The *a*–*c* planes containing the Li atoms are bridged by PO$_4$ tetrahedra. The one-dimensional diffusion pathways [6], running along the *c*-axis direction and perpendicular to the paper sheet plane, are exhibited clearly in figure 1.

We have performed *ab initio* DFT based calculations using the Vienna *ab initio* simulation package VASP [7, 8]. This code solves the Kohn–Sham equations within the pseudopotential approximation [9] whereby the electrons are described in the local-density approximation (LDA) by ultrasoft pseudopotentials [10]. The valence electrons are expanded in a plane wave
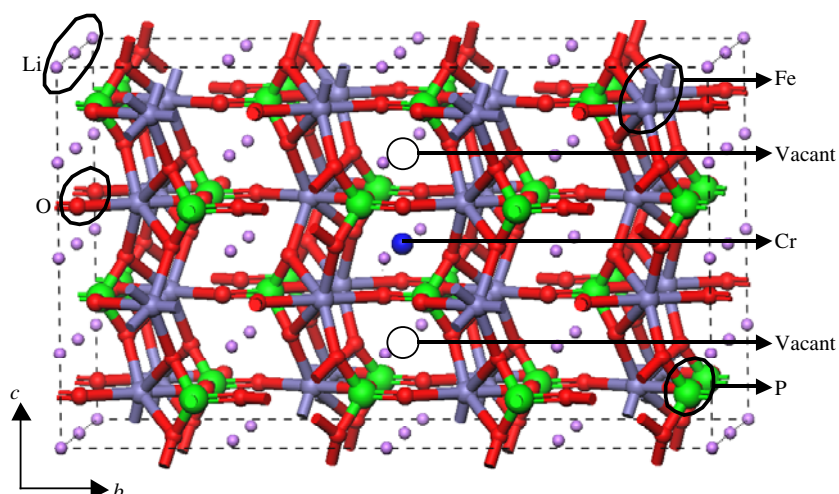
Figure 2. Optimized configuration for Li$_{29/32}$Cr$_{1/32}$FePO$_4$; the two vacancies and the Cr ion lie in a line along the c-axis direction.

Table 1. The relaxed structure for pure and Cr doped LiFePO$_4$.

Configurations	Lattice vectors (Å)		
	a	b	c
LiFePO$_4$	4.710	10.333	5.982
LiFePO4 (Exp)	4.693	10.334	6.008
Li$_{29/32}$Cr$_{1/32}$FePO$_4$	4.625	9.837	5.738

basis set and the effect of the core states on the valence electrons is treated with ultrasoft pseudopotentials.

The structural energy minimization was performed for pure LiFePO$_4$ and Li$_{29/32}$Cr$_{1/32}$FePO$_4$ in a $2 \times 2 \times 2$ super-cell. The Monkhorst–Pack scheme [11] with $7 \times 3 \times 5\,k$ point sets was used for the integration in the irreducible Brillouin zone. The energy cut-off for the plane waves was chosen to be 600 eV. This set of parameters assures a total energy convergence of 2 meV and was used for all the calculations in this work. In the structure optimization, partial occupancy at the Fermi level was treated according to Methfessel and Paxton [12]. In the case of Li$_{29/32}$Cr$_{1/32}$FePO$_4$, as shown in figure 2, there are two Li vacant sites in the super-cell; the optimized configuration is that the two vacancies lie nearby the Cr ions along the c-axis direction. The optimized configuration is obtained through the following: place the Cr ion in one Li site and change the locations of the two vacancies to construct new configurations. For each configuration the total energy is calculated after relaxation has been done. The configuration with lowest total energy is considered to be the optimized one. Table 1 shows the results of the optimized crystal constant. The calculated parameters are in very good agreements with the experimental values [1].

3. The migration energy barriers for Li and Cr ions

In order to figure out the migration energy barriers of the Li and Cr ions in the LiFePO$_4$ crystal, we employed the so-called 'adiabatic trajectory method' [13, 14] after structural optimization.
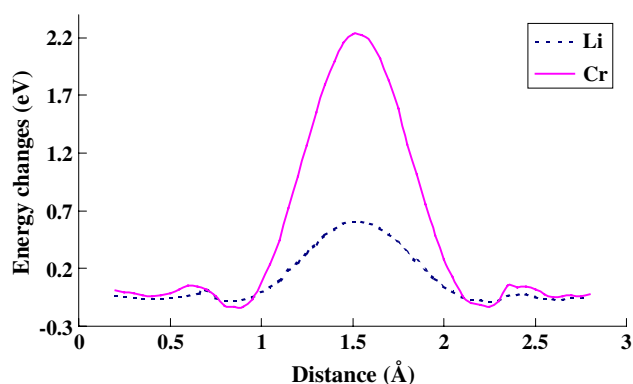
Figure 3. Migration energy barriers of Li and Cr ions in the LiFePO$_4$ crystal along the one-dimensional diffusion pathway.

With this method Meunier *et al* [15] have successfully studied Li diffusion in carbon nanotubes. In this method, a chosen migration ion is pushed to move with a small, constant speed in a specifically given direction, and all other atoms are relaxed continuously in response to the migration ion's motion. The energy barrier is obtained conveniently through monitoring the changes of the total energy.

In the present study, the migration energy barrier is only considered as the migration of a Li ion from one occupied site to a nearby vacant site. When we are considering the migration of one Li ion, we have already 'created' one vacant site in front of the moving Li ion. This is the same for the migration of the Cr ions with the vacancies pair (three vacancies in all). This is most possibly the fact for the diffusion of Li ions in the cathode materials. With the 'adiabatic trajectory method', the migration energy barriers are calculated as follows. The objective ion (Li or Cr ions in the present paper) in the $2 \times 2 \times 2$ super-cell is pushed to move along the one-dimensional diffusion pathway (*c* direction) to its nearest neighbouring sites with constant speed. The nearest neighbouring ion in front of the moving one is moved away beforehand to avoid blocking the way of the approaching migration ion. Figure 3 presents the migration energy barriers obtained by monitoring the total energy changes during the movement of the migration ions. It can be seen from the figure that the migration energy barriers along the *c* direction for Li ions and Cr ions are about 0.6 and 2.1 eV, respectively. The different migration energy barriers for Li ions and Cr ions indicate clearly that Li ions can be diffused along the *c* direction while Cr ions are not diffusible and can only be kept oscillating at their initial positions.

It is therefore understandable that the enhanced electronic conductivity due to the substitution of a small amount of high valence metal ions for lithium ions does not lead to improved electrochemical performance. The reason lies in the blocking of the one-dimension pathways by the heavy high valence metal ions in the Li sites. The positive contributions due to the enhanced electronic conductivity are (partially) offset by the negative blocking effect of the Cr ions.

4. Monte Carlo simulations

The Cr ions have been shown to be unable to migrate in the crystal, and this in turn leads to poorer electrochemical properties. But to what extent does the Cr doping affect the electrochemical properties, and how does the amount of the dopant influence the diffusive
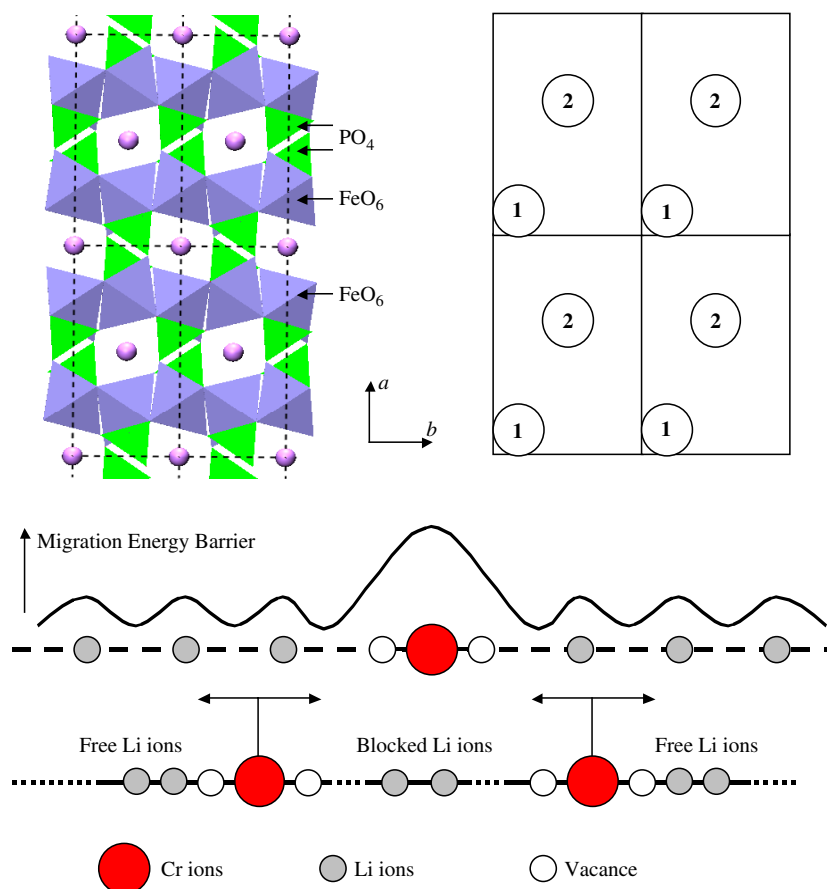
Figure 4. Schematic figure of the two tubes in one unit cell view from the *ab* plane. The two tunnels in each unit cell are denoted as 1 and 2 in the figure. In each tunnel, the Li sites are separated by Cr ions.

properties and even the capacity? To answer these questions, further numerical evaluations are necessary. The remainder of this paper reports on the Monte Carlo (MC) simulations we carried out.

We performed MC simulations based on the one-dimensional diffusion pathway conclusion [6]. The above relaxed structure shown that the crystal lattice parameters are $a = 4.710$ Å, $b = 10.333$ Å and $c = 5.982$ Å. Now if we choose a $1000 \times 1000 \times 1000$ super-cell as our objective, the crystal size will be $471 \times 1033 \times 598$ nm^3, which is of the same order as the real particle size of the powder cathode material. Since the Li ions can only migrate along the *c*-axis direction, the Li sites in the super-cell can then be divided into bundles of one-dimensional tubes. In each unit cell two tubes can be seen viewing from the *ab* plane, as shown in figure 4. Along one tunnel, the diffusion energy barrier is also schematically shown in figure 4. In each tube, the Li sites are separated by Cr ions, and it is understandable that the Li ions in the inner positions are less likely to be extracted out since they need to overcome the blocking effect of the heavy Cr ions. The outer ions will have more freedom of motion.

The purpose of the MC simulations is to find out how and to what extent the Cr doping effect influences the capacity of the material. This can be done by comparing the migration rates of Li ions in the pure and doped material in a given simulation step/time. In this sense,

Table 2. Simulated relative capacity of Cr doped LiFePO$_4$.

	Relative capacity		
MC steps	LiFePO$_4$	Li$_{0.97}$Cr$_{0.01}$FePO$_4$	Li$_{0.85}$Cr$_{0.05}$FePO$_4$
5 000	1	0.683	0.293
10 000	1	0.709	0.394
20 000	1	0.856	0.475
50 000	1	0.892	0.557
100 000	1	0.910	0.611

we are concerned to see if the Li ion migrates or not, and how difficult it is to migrate in these two kinds of material. So the lattice gas model has been used. The migration rate of the Li ions is controlled by the Metropolis Algorithm [16, 17], according to which the migration probability is proportional to $\exp(-\Delta E/k_B T)$, where ΔE is the migration energy barrier, K_B is the Boltzmann constant, and T the temperature. Details can be found in [18]. In each elementary jump, the occupied site and the hopping direction are randomly chosen. If the neighbouring site is occupied, then hopping is rejected and the hopping probability is 0. If the neighbouring site is vacant, then hopping is possible and the hopping probability is governed by the Metropolis method. One complete Monte Carlo step is carried out before all available occupied sites had been considered, whether the Li jumped or not. The initial state is that the Li ion stays in the occupied site, and the final state can be regarded as a saddle point. But the Li ion at a saddle point is very unstable, and it will easily jump to the neighbouring vacant site. Although it is also possible for the Li ion to jump back to the initial site with 50% possibility, as the only concern is to compare the migration rate for pure and doped materials, we might also assume it will not jump back. In this sense, the final state can be regarded as the Li having jumped to its neighbouring vacant site, leaving a vacancy in its initial site. For a Li ion to pass through a Cr occupied site, the migration energy barrier is the sum of that of the Cr ions and Li ions. Furthermore, in the present simulation, the boundary conditions are specifically defined as follows: assume that all the Li ions can be transported away from the interface area in time, so when the inner Li ions arrive at the interface, if they can overcome the energy barrier, they will disappear from the interface immediately. With these assumptions, MC steps are performed to evaluate the capacity of the Cr doped LiFePO$_4$ material. The results are compared to that of the undoped pure LiFePO$_4$ material. The temperature is important for the diffusive properties and will eventually influence the capacity. But the temperature is also an important factor for the electronic conductivity. So the influence of temperature is very complex, and in our present work we did not take it into consideration. The temperature was chosen to be 300 K for all the simulations. For convenience purposes, in the following simulations all the capacity values are scaled to the case of pure LiFePO$_4$, for which the capacity was chosen to be 1.

The relative capacity for the Cr doped LiFePO$_4$ after different MC steps is shown in table 2. The super-cell used here for simulation is $1000 \times 1000 \times 1000$. Although it is difficult to find out the numerical relationship between the charge/discharge intensity and the MC steps, it is still noticeable that more MC steps corresponds to charge/discharge with smaller current density while fewer MC steps corresponds to charge/discharge with higher current density. It can be seen from the table that the relative capacity of the 1% doped samples is much higher than that of the 5% doped samples. The capacity of the 5% doped sample is more sensitive to the number of MC steps (charge/discharge current density) than the 1% doped sample. Since the capacities we evaluated from the present MC simulation only take the influences of the diffusive properties into consideration, it is difficult for us to compare them quantitatively with the experimental results.
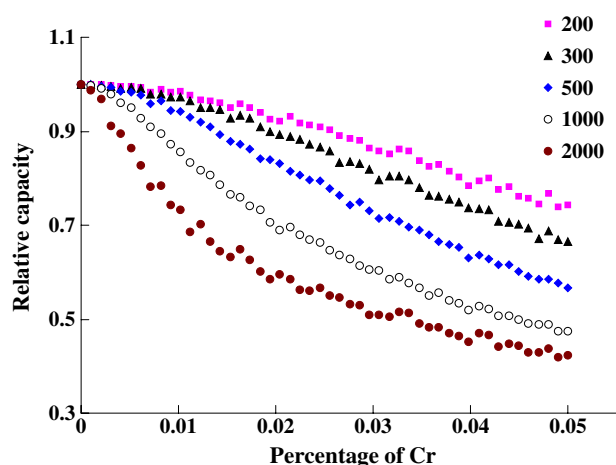
Figure 5. Variation relation of the simulated capacity with the dopant amount and super-cell size. The numbers 200, 300, 500, 1000 and 2000 refer to thee size of the super-cell being used.

The variation relation of the simulated capacity with the amount of the dopant for different size of the super-cell (particle size of the powder cathode material) is shown in figure 5. All the values of the capacity are calculated after 20 000 MC steps. It can be seen that the capacity decreases when increasing dopant amount is added. The different lines denote different sizes of the super-cell. With the size of the super-cell enlarged, the capacities for all values of dopant amount are enormously decreased. This gives instructive guidance to the applications of this material; that is to say, the capacity can be enhanced greatly by reducing the particle size of the powder cathode material.

5. Summary and conclusions

In summary, our first-principles calculation explains well that the enormously enhanced electronic conductivity through Li site doping does not improve the electrochemical performance as expected for LiFePO$_4$ cathode material. The migration energy barrier for Li ions and Cr ions in LiFePO$_4$ are about 0.6 and 2.1 eV respectively. This shows that Cr ions will block the one-dimensional diffusion pathways for the migration of the Li ions, leading to a negative effect on the electrochemical performance. Monte Carlo simulations show that the capacity loss due to the Cr ion doping is very sensitive to the amount of the dopant and the particle size. Both larger amount of dopant and larger particle size are disadvantageous factors to the reversible capacity.

Acknowledgments

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