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Ab initio studies on n-type and p-type $Li_4Ti_5O_{12}$*

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This paper studies the structure and electronic properties of $Li_4Ti_5O_{12}$, as anode material for lithium ion batteries, from first principles calculations. The results suggest that there are two kinds of unit cell of $Li_4Ti_5O_{12}$: n-type and p-type. The two unit cells have different structures and electronic properties: the n-type with two 16*d* site Li ions is metallic by electron, while the p-type with three 16*d* Li ions is metallic by hole. However, the $Li_4Ti_5O_{12}$ is an insulator. It is very interesting that one n-type cell and two p-type cells constitute one $Li_4Ti_5O_{12}$ supercell which is insulating. The results show that the intercalation potential obtained with a p-type unit cell with one additional electron is quite close to the experimental value of 1.5 V.

Keywords: lithium ion batteries, $Li_4Ti_5O_{12}$ anode, intercalation potential, spinel structure

PACC: 7115A, 7115H, 7125, 7130

1. Introduction

Spinel $Li_4Ti_5O_{12}$ is the end member of the solid solution of $Li_{3+x}Ti_{6-x}O_{12}$ ($0 \leq x \leq 1$).[1] The compound has a cubic structure with a space group symmetry $Fd\bar{3}m$. Within the spinel structure, lithium atoms occupy all the 8*a* sites and 1/6 of the 16*d* sites, while the remaining 5/6 of the 16*d* sites are taken by Ti atoms and all the 32*e* sites are occupied with O atoms. So this structure is always denoted as $[Li_3]^{8a}[Li_1Ti_5]^{16d}O_{12}$.[2] At the end of the intercalation process, an additional 8 Li atoms are intercalated into one spinel unit cell and locate at the octahedral (16*c*) sites. At the same time, the tetrahedral (8*a*) Li atoms also transport to the octahedral (16*c*) sites. The structure is then denoted as $[Li_6]^{16c}[Li_1Ti_5]^{16d}O_{12}$. This structure provides a three-dimensional interstitial 8*a* tetrahedral and 16*c* octahedral space for the transport of the Li^+ ions. Normally, this material works between the delithiated state $Li_4Ti_5O_{12}$ and lithiated state $Li_7Ti_5O_{12}$, possessing very flat charge/discharge potential plateaus at about 1.5 V vs Li/Li^+.[3] At the same time, the spinel framework remains unchanged during the charge/discharge cycling, and the lattice parameters remain almost unchanged,[4] which earns $Li_4Ti_5O_{12}$ the name "zero-strain insertion material". Therefore, insertion and extraction of lithium are extremely reversible,[5] since lattice strain is one of the important causes of capacity losses during cycling of the lithium ion battery electrodes.

Because the 16*d* sites are randomly occupied by 1/6 Li atoms and 5/6 Ti atoms, the unit cell of $Li_4Ti_5O_{12}$ is non-stoichiometric. So the $1 \times 1 \times 3$ supercell should be constructed in order to satisfy the stoichiometry. However, the supercell is too large for common computational facilities. To save computational expenses, some cubic unit cell models are used to calculate the electronic structure, as can be found in the literature. Lippens *et al*[6] calculated the electronic structure of $Li_4Ti_5O_{12}$, Liu *et al*[7] studied the electronic structure of $Li_4Ti_5O_{12}$ and the Ti site transition metal doping effect on the electronic structure from first principles calculations. In both cases, the cubic spinel models do not satisfy the stoichiometry of $Li_4Ti_5O_{12}$, and the calculated electronic structures are metallic. In the present work, we aim to compare the electronic properties with the average intercala-

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tion potentials of the two kinds of non-stoichiometry unit cells. Our first principles calculation results give a positive prediction to the foreground of the "new" anode materials for lithium ion batteries.

2. Structural models and computational details

All the calculations in the present study are performed with the VASP (Vienna *ab initio* simulation package).[8,9] The electronic structure of the ground state is described within the density functional theory and the generalized gradient approximation and Perdew–Wang exchange-correlation functional (PW91),[10] with the projector augmented wave method,[11] which has wide applications in the calculation of electronic and magnetic properties of oxide compounds.[12,13] The convergence tests of the total energy with respect to the $\boldsymbol{k}$-points sampling and cut off energy have been carefully examined. All the final calculations in the present studies are performed by using $3 \times 3 \times 3$ Monkhorst–Pack[14] $\boldsymbol{k}$-points grid, and the cut off energy is chosen to be 580 eV. With these parameters, the total energy is converged to within 10^{-4} eV per formula unit. The equilibrium lattice constant is optimized by fitting the Murnaghan equation of state.[14,15] The positions of the ions are relaxed with the conjugated gradient method by using forces and stresses, and the final force on each atom is less than 0.05 eV/Å (1 Å = 0.1 nm). The calculation of the density of states (DOS) is smeared by the Methfessel–Paxton approach with a smearing width of 0.05 eV. As the material is non-magnetic, spin-polarizations are not included in all the calculations.

3. Results and discussion

3.1. Lattice parameters and crystal structures of n-type and p-type

In order to satisfy the stoichiometry of $Li_4Ti_5O_{12}$, a large supercell model containing 3 unit cells is required. As the 16*d* sites are randomly occupied by 1/6 Li atoms and 5/6 Ti atoms, so there are two kinds of non-stoichiometry unitcells of $Li_4Ti_5O_{12}$ with 2 or 3 Li atoms occupying the 16*d* sites. In our previous work, we have optimized the Li and Ti atoms distribution in one unit cell, with 2 or 3 Li atoms occupying the 16*d* sites.[16] In the present work, we denote those three configurations (O2-1, O2-2, and O2-3) with 2 Li atoms occupying 16*d* sites as n-type, and denote those four configurations (O3-1, O3-2, O3-3, and O3-4) with 3 Li atoms occupying 16*d* sites as p-type. Then one stoichiometry supercell can be seen as one n-type cell and two p-type cells configuration as it is shown in Fig.1.

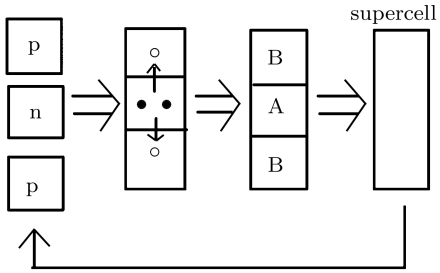


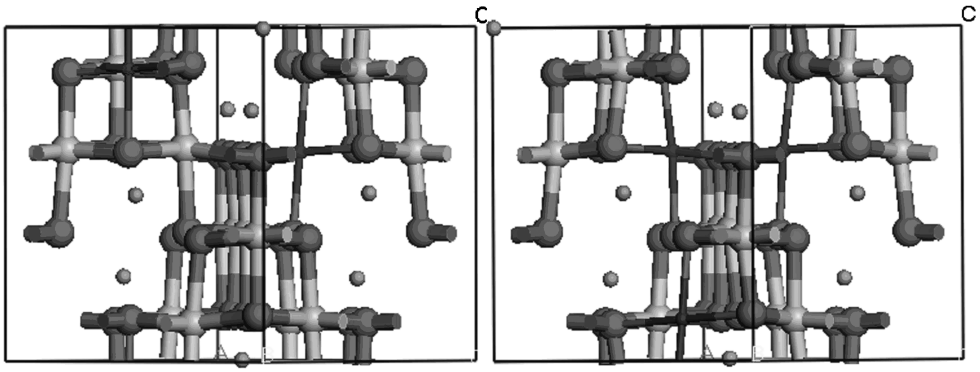
Fig.1. One n-type cell and two p-type cells constitute one $Li_4Ti_5O_{12}$ supercell.

Table 1. The configurations of n-type $Li_4Ti_5O_{12}$ and p-type $Li_4Ti_5O_{12}$.

$Li_4Ti_5O_{12}$	configurations	fractional Li positions at 16*d* sites
n-type	O2-1	(3/8, 3/8, 5/8) and (1/8, 1/8, 5/8)
	O2-2	(3/8, 3/8, 5/8) and (5/8, 7/8, 7/8)
	O2-3	(1/8, 1/8, 5/8) and (5/8, 5/8, 5/8)
p-type	O3-1	(3/8, 3/8, 5/8), (1/8, 1/8, 5/8) and (5/8, 5/8, 5/8)
	O3-2	(3/8, 3/8, 5/8), (3/8, 5/8, 3/8) and (5/8, 5/8, 5/8)
	O3-3	(3/8, 3/8, 5/8), (5/8, 7/8, 7/8) and (5/8, 5/8, 5/8)
	O3-4	(3/8, 3/8, 5/8), (3/8, 7/8, 1/8) and (5/8, 5/8, 5/8)

Figure 2 gives the schematic view of the relaxed atomic positions of n-type $Li_4Ti_5O_{12}$ and p-type $Li_4Ti_5O_{12}$ with the configurations O2-2 and O3-3, respectively. From Fig.2 we can see clearly that the TiO_6 octahedral

structures are not changed after lattice relaxation of both n-type and p-type. The blue color Li atoms are occupied 16*d* sites. In this paper all the calculated models use the structures in Fig.2.



(a) n-type (b) p-type

Fig.2. Schematic view of the atomic structure of $Li_4Ti_5O_{12}$: (a) n-type; (b) p-type. The largest red spheres are the O atoms, the middle-sized grey spheres indicate the Ti atoms, and the smallest spheres are lithium atoms.

3.2. Electronic structure

Figure 3 shows the total DOS of $Li_4Ti_5O_{12}$. The calculated electronic structures exhibit metallic properties, for both n-type $Li_4Ti_5O_{12}$ and p-type $Li_4Ti_5O_{12}$. However, as it is reported in Ref.[16], the electronic structure of $Li_4Ti_5O_{12}$ is insulating, and the band gap opens between the occupied O-2*p* states and empty Ti-3*d* states. This means that both n-type and p-type have better electron conductivity than single phase $Li_4Ti_5O_{12}$.

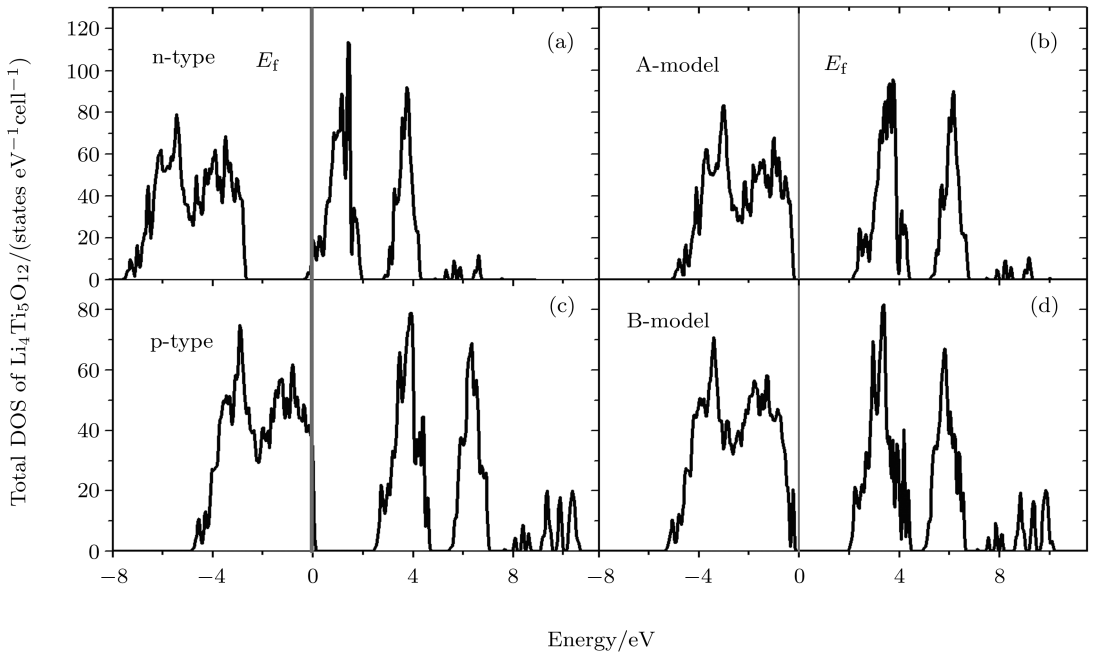


Fig.3. The total DOS of $Li_4Ti_5O_{12}$: (a) n-type; (b) n-type but removing two electrons; (c) p-type; (d) p-type but adding one electron. The Fermi level is aligned to 0.

Reference [16] has explained the reason for the metallic properties of the n-type: there are two more excess electrons in the unit cell that remain at the Ti-3*d* orbit. If we remove the two electrons from the n-type in the calculation the insulating electronic structure will appear as it is shown in Fig.3(b). But for the p-type the conductive mechanism is a little different. There are 11 Li atoms, 13 Ti atoms and 32 O atoms within one unit p-type cell. It is the same that each Li atom denotes 1 electron (Li^+), each Ti atom denotes 4 electrons (Ti^{4+}), and each O atom accepts 2 electrons (O^{2-}), then there will be one O-2*p* orbit empty resulting in the metallic properties, in other words there is one hole in the unit cell, so the Fermi level crosses the valance band. If we add one electron in the p-type unit cell in the calculation then the insulating electronic structure also appears again as it is shown in Fig.3(d). If we denote the structure of removing 2 electrons from the n-type as the A-model, and denote the structure of adding 1 electron into the p-type as the B-model, we can see that both the A-model and B-model are of the same electronic structures with the supercell $Li_4Ti_5O_{12}$.

3.3. Lithiated states and intercalation potentials

If we use n-type or p-type $Li_4Ti_5O_{12}$ as the anode material for lithium ion batteries, there is no doubt that the advantage is the better electronic conductivity than for the normal $Li_4Ti_5O_{12}$. Because of their same intercalation process, the Li ions occupying the 8*a* sites with the new intercalated Li atoms all transport to the octahedral (16*c*) sites, so the theoretical capacity of them are all about 175 mAh/g (charge/discharge between $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$). However, their intercalation potentials are different from each other. The average intercalation potential is calculated with the following formula:[17]

$$V_{\text{ave}} = -\Delta E/nF,$$

where ΔE is the calculated total energy difference given by the following formula:

$$\Delta E = E_{\text{tot}}[Li_7Ti_5O_{12}] - E_{\text{tot}}[Li_4Ti_5O_{12}] - xE_{\text{bcc}}[Li],$$

where $E_{\text{tot}}[Li_7Ti_5O_{12}]$ and $E_{\text{tot}}[Li_4Ti_5O_{12}]$ are the total energy of $Li_7Ti_5O_{12}$ and $Li_4Ti_5O_{12}$, and $E_{\text{bcc}}[Li]$ is the total energy of metallic lithium in a body centered cubic (bcc) unit cell.

The predicted intercalation potential results are given in Table 2. The calculated average intercalation potential from $Li_4Ti_5O_{12}$ to $Li_7Ti_5O_{12}$ is about 1.48 V,[17] but the intercalation potentials are 1.42 V and 2.00 V for n-type $Li_4Ti_5O_{12}$ and p-type $Li_4Ti_5O_{12}$, respectively. From Ref.[18] we notice that there is a single phase which from 2.00 V to 1.55 V in the discharge process, we think that this single phase process is the electron transporting process in the supercell and the 2.00 V voltage is caused by p-type $Li_4Ti_5O_{12}$. As it is mentioned above, the A-model is an n-type cell with 2 electrons removed, and the B-model is a p-type cell with 1 electron added. The calculated results of their intercalation potentials are 1.86 V and 1.46 V, and then the average intercalation potential of a supercell constructed by one A-model cell and two B-model cells from $Li_4Ti_5O_{12}$ to $Li_7Ti_5O_{12}$ is about 1.59 V. This is quite close to the result of 1.55 V in Ref.[18]. It implies that using an A-model and B-model unitcell to simulate the normal supercell in the calculation process is more reasonable than an n-type and p-type unitcell.

Table 2. The calculated lattice constant (in Å) and average intercalation potential (in V) of n-type, p-type, A-model and B-model $Li_4Ti_5O_{12}$.

system	unit cell	lattice constant	lithated states	intercalation potential
supercell	$Li_{32}Ti_{40}O_{96}$	8.315	$Li_{56}Ti_{40}O_{96}$	1.48
n-type	$Li_{10}Ti_{14}O_{32}$	8.315	$Li_{18}Ti_{14}O_{32}$	1.42
p-type	$Li_{11}Ti_{13}O_{32}$	8.312	$Li_{19}Ti_{13}O_{32}$	2.00
A-model	$Li_{10}Ti_{14}O_{32}$	8.315	$Li_{18}Ti_{14}O_{32}$	1.86
B-model	$Li_{11}Ti_{13}O_{32}$	8.312	$Li_{19}Ti_{13}O_{32}$	1.46

The differences of their intercalation potentials are attributed to the different total energies. We can see that the total DOS of lithiated states are nearly the same as that shown in Fig.4. But the Fermi levels are at different sites for the delithiated states. This means the ΔE will be different.

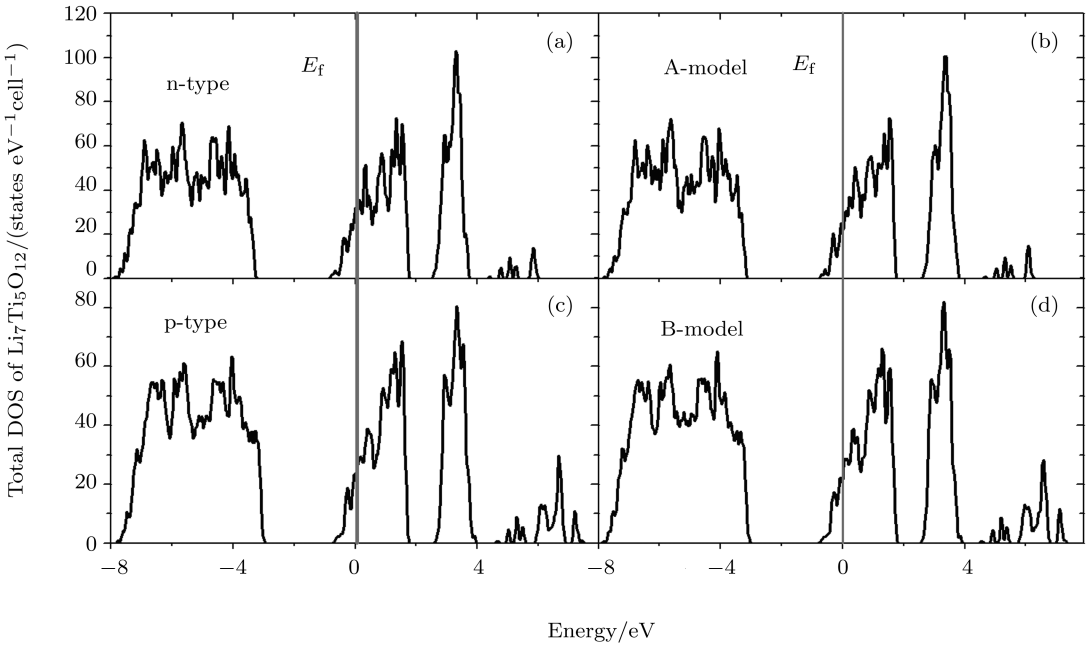


Fig.4. The total DOS of $Li_7Ti_5O_{12}$: (a) n-type; (b) n-type but removing two electrons; (c) p-type; (d) p-type but adding one electron. The Fermi level is aligned to 0.

4. Conclusions

In summary, results from our first principles calculations show that both n-type and p-type have the same lattice constants and the same capacities with the normal $Li_4Ti_5O_{12}$ supercell, but the electronic structures are different which determine their different electronic conductivity properties: n-type is metallic by electrons as majority carriers, p-type is metallic by hole as majority carriers, but the normal $Li_4Ti_5O_{12}$ is an insulator. The average intercalation voltages are calculated to be 1.42 V, 2.00 V, 1.86 V and 1.46 V (vs Li/Li^+) for the n-type, p-type, A-model and B-model, respectively. We can see that the results of the intercalation potentials of the n-type and B-model are quite close to the experimental value of 1.5 V, and the electronic structures of the A-model and B-model are similar to the normal supercell. On the other hand, we think that the single phase process whose voltage decreases from 2.00 V to 1.55 V is due to the excess electrons transporting process.

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