Oxygen vacancy in LiTiPO$_5$ and LiTi$_2$(PO$_4$)$_3$: A first-principles study

Li-Juan Chen [a], Yu-Jun Zhao [a,*], Jia-Yan Luo [b], Yong-Yao Xia [b]

[a] *Department of Physics, South China University of Technology, Guangzhou 510640, China*
[b] *Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 2004339, China*

A R T I C L E   I N F O

A B S T R A C T

The structures of LiTiPO$_5$ and LiTi$_2$(PO$_4$)$_3$, as well as the possibility of oxygen vacancies formation in the systems are studied by first-principles calculations. It is found that oxygen vacancies can be formed in LiTiPO$_5$ and LiTi$_2$(PO$_4$)$_3$ under oxygen poor condition. The formation of oxygen vacancies introduce a defect band within their band gaps, which is expected to improve the electronic conductivity of LiTiPO$_5$ and LiTi$_2$(PO$_4$)$_3$ significantly. Meanwhile, a great concentration of oxygen vacancies may increase the discharge voltage of LiTiPO$_5$ and LiTi$_2$(PO$_4$)$_3$.

1. Introduction

Phosphate-based materials have generated considerable interest as potential cathode materials for secondary lithium batteries. This is primarily attributed to their competitive energy-density storage and better thermal properties than traditional cathode materials such as LiCoO$_2$, LiMn$_2$O$_4$ spinel, and V$_2$O$_5$ [1–6]. These materials take advantage of a relatively high lithium ion mobility and benefit from the inductive effect generated by their polyanionic groups, which increase the operating voltage in comparison with the simple oxides [1,2]. Recently, much attention has been focused on the phospho-olivine LiMPO$_4$ (M = Mn, Fe, Co and Ni) family of materials [3,6–12]. Good electrochemical performance has been reported for LISICON-type and NASICON-type materials such as A$_{1+x}$M$_2$(PO$_4$)$_3$ (A = Li, Na, M = Fe, V, Ti, Nb) [13–26]. Lithium transition metal phosphates suffer from low electrical conductivities and slow Li-ion diffusions that limit their rate capability. Past attempts to improve rate capability by increasing electrical conductivity have focused on coating particles with conductive carbons [27,28]. It is reported that the performance of many cathode materials are sensitive to the oxygen partial pressure during the sample preparation. For example, Wolfenstine et al. recently investigated the effect of heat-treatment under different oxygen partial pressures (pure oxygen, air, high-purity argon) on the discharge capacity of LiCoPO$_4$ and found that the samples heat-treated under low oxygen partial (high-purity argon) pressure exhibit a higher discharge capacity over the cycle range test compared to those prepared under air or pure oxygen [29]. The reason for the impact of oxygen partial pressure is not clear, although it was suggested due to formation of cobalt phosphides in LiCoPO$_4$, and titanium phosphides in LiTi$_2$(PO$_4$)$_3$ [29]. It is well known in metal oxides that oxygen vacancies are easy to form under oxygen poor condition and have critical roles in their electronic properties. Here we attempt to study the possibility of oxygen vacancy formation and its impact on the physical properties in LiTiPO$_5$ and LiTi$_2$(PO$_4$)$_3$, as the important Li battery cathode materials.

In this Letter, the crystal and electronic structure of LiTiPO$_5$ and LiTi$_2$(PO$_4$)$_3$, as well as the possibility of oxygen vacancy formation are investigated by the first-principles calculations. We find that in both LiTiPO$_5$ and LiTi$_2$(PO$_4$)$_3$, low oxygen partial pressure introduces oxygen vacancies in the crystals. These defects generate a defect band in both LiTiPO$_5$ and LiTi$_2$(PO$_4$)$_3$, which is expected to improve their conductivity significantly.

1.1. Computational details

The theoretical studies are conducted in the framework of density-functional theory combined with the generalized gradient approximation (GGA). All the calculations are done with the pseudopotential plane wave method [30] with the PW91 formulae [31], and the projector augmented wave (PAW) potentials, as implemented in the VASP code [32]. The charge density is obtained with an energy cut-off of 400.0 eV, and Γ-centered $4 \times 4 \times 4$ and $2 \times 2 \times 1$ k meshes for LiTiPO$_5$ and LiTi$_2$(PO$_4$)$_3$, respectively, following the Monkhorst–Pack **k**-space integration method [33]. In the structure optimization, all the internal structural parame-
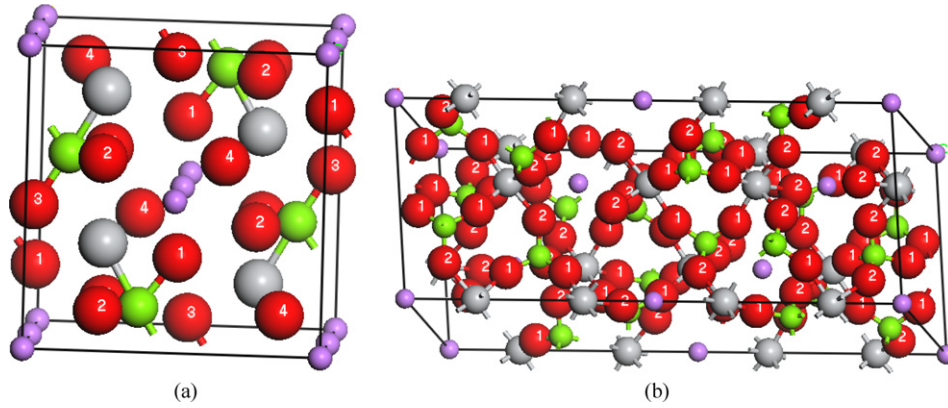
Fig. 1. Crystal structure of LiTiPO$_5$ (a) and LiTi$_2$(PO$_4$)$_3$ (b). The O, P, Ti, Li atoms are colored by red, green, gray, and orchid, respectively. (For interpretation of the references to color in this figure, the reader is referred to the web version of this Letter.)
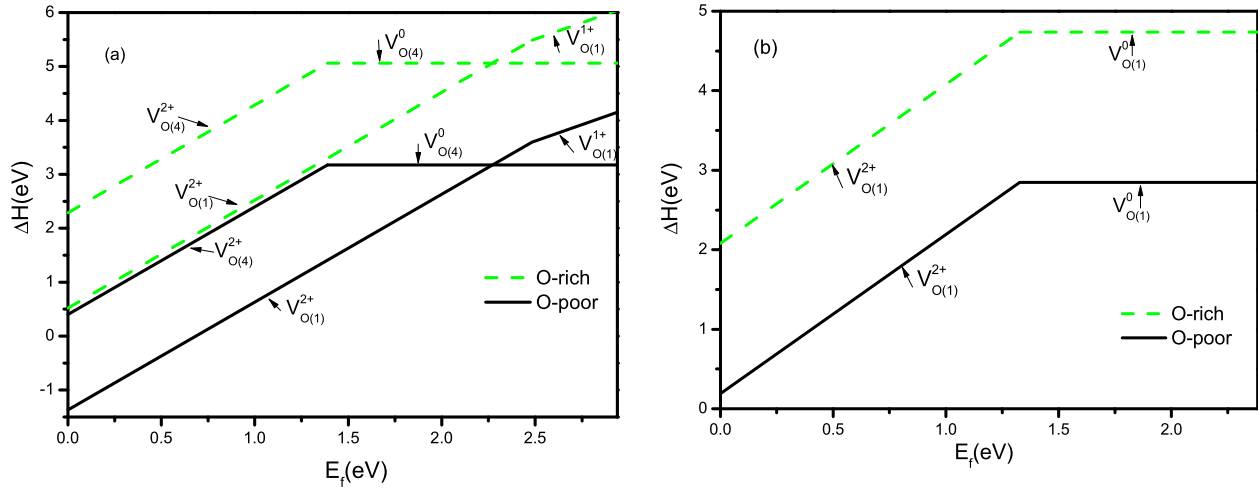

Fig. 2. The formation energy ΔH vs Fermi level for LiTiPO$_5$ (a) and LiTi$_2$(PO$_4$)$_3$ (b). $\Delta\mu_O$ is set to zero for O-rich condition while it is set to -1.89 eV for O-poor condition (corresponding to $T = 1000$ K, $p = 10^{-8}$ Pa).

ters are fully relaxed with the force convergence criterion of less than 0.02 eV/Å, while the lattice parameters are optimized with an energy criterion of less than 0.01 eV per molecular formula for LiTiPO$_5$ and LiTi$_2$(PO$_4$)$_3$. The density of states of the ideal and defected LiTiPO$_5$ and LiTi$_2$(PO$_4$)$_3$ are obtained with a Γ-centered $6 \times 6 \times 6$ and $4 \times 4 \times 2$ meshes, respectively.

2. Results and discussion

2.1. Crystal structure of LiTiPO$_5$ and LiTi$_2$(PO$_4$)$_3$

From X-ray diffraction studies [21] it is known that LiTiPO$_5$ has an oxotitanate cell, whose space group is Pnma (No. 62) and experimental lattice parameters are $a = 7.406$ Å, $b = 6.379$ Å, and $c = 7.238$ Å. The unit cell of LiTiPO$_5$ [shown in Fig. 1(a)] contains four formula units. All Li, Ti, and P atoms are equivalent respectively from the point view of symmetry, while there are four types of O atoms. For convenience, the four types of O ions are labeled as 1, 2, 3, and 4 in Fig. 1(a), respectively. LiTi$_2$(PO$_4$)$_3$ is isostructural with NaZr$_2$(PO$_4$)$_3$ [34] and adopts the well-known NASICON type structure consisting of a three-dimensional network made up of tetrahedra sharing all their corners with octahedra and vice versa to form the so-called "lantern" units, all oriented in the same direction along the **c**-axis. It is known that LiTi$_2$(PO$_4$)$_3$ is in the space group of $R\bar{3}C$ (No. 167) [23], whose experimental lattice parameters are $a_{hex} = 8.511$ Å, $c_{hex} = 20.843$ Å. The unit cell [shown in Fig. 1(b)] contains four formula units. All the Li, Ti, and P atoms are equivalent respectively in LiTi$_2$(PO$_4$)$_3$, while there are two types of O ions from the point view of symmetry. For convenience, the two types of O atoms are marked with 1 and 2 in Fig. 1(b). The lithium content will have a strong impact on the electrochemical behavior during Li insertion. The theoretical optimized lattice constants for LiTiPO$_5$ and LiTi$_2$(PO$_4$)$_3$ are listed in Table 1 along with the experimental values. Our theoretical results are in excellent agreement with the experiment data with errors of less than 1.3% for the lattice volume.

2.2. Possibility of oxygen vacancy formation in LiTiPO$_5$ and LiTi$_2$(PO$_4$)$_3$

In order to investigate the possibility of oxygen vacancy formation, we calculate the formation enthalpies (ΔH) of O vacancy in LiTiPO$_5$ and LiTi$_2$(PO$_4$)$_3$ (shown in Fig. 2) according to the formula [35,36]

$$\Delta H_f^{(D,q)} = E(D, q) - E(0) + \sum_\alpha n_\alpha \left(\Delta\mu_\alpha + \mu_\alpha^{Solid} \right)$$
$$+ q(E_{VBM} + E_F) \tag{1}$$

Table 1
Optimized and experimental lattice parameters for LiTiPO$_5$ and LiTi$_2$(PO$_4$)$_3$.

	a (Å)	b (Å)	c (Å)	Volume (Å^3)
LiTiPO$_5$ (Calc.)	7.356	6.403	7.229	340.489
LiTiPO$_5$ (Expt.) [24]	7.406	6.379	7.238	341.944
LiTi$_2$(PO$_4$)$_3$ (Calc.)	8.534	8.534	20.457	1290.321
LiTi$_2$(PO$_4$)$_3$ (Expt.) [26]	8.511	8.511	20.843	1307.53