Oxygen vacancy in LiTiPO₅ and LiTi₂(PO₄)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

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 LiCoO₂, LiMn₂O₄ spinel, and V₂O₅ [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 other materials [3,6–12]. Good electrochemical performance has been reported for LISICON-type and NASICON-type materials such as A₁₋ₓMₓ(PO₄)₃ (A = Li, Na, M = Fe, V, Ti, Nb) [13–26]. 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 LiTiPO₅ and LiTi₂(PO₄)₃, as the important Li battery cathode materials.

In this Letter, the crystal and electronic structure of LiTiPO₅ and LiTi₂(PO₄)₃, as well as the possibility of oxygen vacancy formation are investigated by the first-principles calculations. We find that in both LiTiPO₅ and LiTi₂(PO₄)₃, low oxygen partial pressure introduces oxygen vacancies in the crystals. These defects generate a defect band in both LiTiPO₅ and LiTi₂(PO₄)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 × 4 × 4 and 2 × 2 × 1 k meshes for LiTiPO₅ and LiTi₂(PO₄)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\textsubscript{5} (a) and LiTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{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 $\Delta H$ vs Fermi level for LiTiPO\textsubscript{5} (a) and LiTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} (b). $\Delta \mu_{\text{O}}$ 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\textsubscript{5} and LiTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}. The density of states of the ideal and defected LiTiPO\textsubscript{5} and LiTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} are obtained with a $\Gamma$-centered $6 \times 6 \times 6$ and $4 \times 4 \times 2$ meshes, respectively.

2. Results and discussion

2.1. Crystal structure of LiTiPO\textsubscript{5} and LiTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}

From X-ray diffraction studies [21] it is known that LiTiPO\textsubscript{5} has an oxotitanate cell, whose space group is Pnma (No. 62) and experimental lattice parameters are $a = 7.406 \ \text{Å}$, $b = 6.379 \ \text{Å}$, and $c = 7.238 \ \text{Å}$. The unit cell of LiTiPO\textsubscript{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\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} is isostructural with NaZr\textsubscript{2}(PO\textsubscript{4})\textsubscript{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 e-axis. It is known that LiTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} is in the space group of $\text{R}3\text{c}$ (No. 167) [23], whose experimental lattice parameters are $a_{\text{hex}} = 8.511 \ \text{Å}$, $c_{\text{hex}} = 20.843 \ \text{Å}$. The unit cell [shown in Fig. 1(b)] contains four formula units. All the Li, Ti, and P atoms are equivalent respectively in LiTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{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\textsubscript{5} and LiTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{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\textsubscript{5} and LiTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}

In order to investigate the possibility of oxygen vacancy formation in LiTiPO\textsubscript{5} and LiTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} (shown in Fig. 2) according to the formula [35,36]

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

Table 1: Optimized and experimental lattice parameters for LiTiPO\textsubscript{5} and LiTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}.

<table>
<thead>
<tr>
<th></th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>Volume (Å\textsuperscript{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiTiPO\textsubscript{5} (Calc.)</td>
<td>7.356</td>
<td>6.403</td>
<td>7.229</td>
<td>340.489</td>
</tr>
<tr>
<td>LiTiPO\textsubscript{5} (Expt.) [24]</td>
<td>7.406</td>
<td>6.379</td>
<td>7.238</td>
<td>341.944</td>
</tr>
<tr>
<td>LiTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} (Calc.)</td>
<td>8.534</td>
<td>8.534</td>
<td>20.457</td>
<td>1280.321</td>
</tr>
<tr>
<td>LiTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} (Expt.) [26]</td>
<td>8.511</td>
<td>8.511</td>
<td>20.843</td>
<td>1307.53</td>
</tr>
</tbody>
</table>
where $E(D,q)$ and $E(0)$ are the total energies of the supercell with and without defect $D$. Here $(\Delta \mu_{\alpha} + \mu_{\alpha}^{\text{Solid}})$ is the absolute value of the chemical potential of atom $\alpha$. Also $n_{\alpha}$ is the number of atoms for each defect; $n_{\alpha} = -1$ if an atom is added, while $n_{\alpha} = 1$ if an atom is removed. $E_{\text{VBM}}$ represents the energy of the valance band maximum (VBM) in the defect-free system and $E_F$ is the Fermi energy relative to the $E_{\text{VBM}}$. The Fermi level could be self-consistently determined when all the defects are involved at a given growth condition. However, we only focus on the oxygen defects in this work, and thus the Fermi level is actually only a parameter between VBM and the conduction-band minimum (CBM) reflecting various samples prepared at different growth condition ($E_F \leq E_{\text{VBM}} \leq E_{\text{CBM}}$). The atomic structure was fully relaxed in our calculations.

The surrounding O2 atmosphere is regarded as an ideal-gas-like reservoir. The temperature and pressure dependence for the chemical potential of oxygen, $(\Delta \mu_{\alpha} + \mu_{\alpha}^{\text{Solid}})$, may be expressed as following [37]

$$\mu_{\alpha}(T, p) = \mu_{\alpha}(T, p^0) + \frac{1}{2} k T \ln \left( \frac{p}{p^0} \right).$$  

(2)

The detailed numerical relation between $T$ and $\mu_{\alpha}$ is discussed in Ref. [37]. Under the O rich condition, $\Delta \mu_{\alpha}$ is set to zero and $\mu_{\alpha}^{\text{Solid}} = 1/2 \Delta \mu_{O}^{\text{total}} = \mu_{O}(0 \text{ K}, p^0)$. The dependence of the formation enthalpy on the Fermi level is shown in Fig. 2 for oxygen vacancies in LiTiPO$_3$ and LiTi$_2$(PO$_4$)$_3$ under O-rich and O-poor conditions. Here O-poor condition is exemplified at $T = 1000 \text{ K}$ and $p = 10^{-8}$ Pa, a typical O-poor sample growth condition. From Fig. 2 we find that under the O-poor condition, O vacancies are able to form in both LiTi$_2$(PO$_4$)$_3$ and LiTiPO$_5$, especially in LiTiPO$_5$. The formation enthalpy of oxygen vacancies can be as low as 0.2 eV for LiTi$_2$(PO$_4$)$_3$, and even lower for LiTiPO$_5$ when the Fermi level is near VBM. When the Fermi level is close to CBM, oxygen vacancies are hard to form as the formation enthalpies are around 3.0 eV for both LiTi$_2$(PO$_4$)$_3$ and LiTiPO$_5$ even under O-poor condition. The O vacancies are mostly neutral charged when $E_F$ is close to the CBM, and they favor +2 charge state below mid-gap. In LiTiPO$_5$, the oxygen vacancies are relatively easy to form at O(1), O(2), or O(3) sites except that $E_F$ is near the CBM. The O-vacancy formation energies at O(2) and O(3) sites are not shown in Fig. 2 since they are similar to that of O(1). In LiTi$_2$(PO$_4$)$_3$, the formation energy of oxygen vacancy is always lower at the O(1) site when $E_F$ changes within the band gap. The stability of $V_{\alpha}^{2+}$ is understandable since O-vacancies are expected to be a donor when $E_F$ is close to the VBM.

2.3. Influence of oxygen vacancy on the discharge voltage

From the electronic densities of states (DOS) in Fig. 3(a), we find that the ideal LiTiPO$_5$ has a calculated band gap of 2.94 eV and the experimental band gap is expected to be remarkably greater than the calculated one due to the well-known demerit of LDA/GGA on band gap evaluation. LDA + U or GGA + U may improve the description of the band gap and electronic structures for most transition metal (TM) oxides, especially the late TM oxides. However, for the systems of LiTiPO$_5$ and LiTi$_2$(PO$_4$)$_3$, LDA + U or GGA + U turns out not to improve the band gap remarkably since Ti is an early TM. For example, we have calculated the band-gap with GGA + U (U = 2.5 eV, as typically adopted in Ref. [38]) to be 2.91 eV for the ideal LiTiPO$_5$, no remarkable changes from the value obtained from GGA calculation. Thus GGA is still employed in this work. The obvious band gap indicates that the ideal LiTiPO$_5$ is expected to be an insulator, which will limit the electron mobility during the battery discharge. From Fig. 3(c), we find that the valence band around the Fermi level is mainly hybridized with titanium 3d states, phosphorus 3p states and oxygen 2p states, and the conduction bands are mainly made up by titanium 3d states in LiTiPO$_5$. By comparing the DOS of ideal LiTiPO$_5$ and defected LiTiPO$_5$, we observe that the defected LiTiPO$_5$ with O-vacancy has a band gap of 2.0 eV, which is significantly smaller than that of ideal LiTiPO$_5$. Fig. 3(b) shows the DOS of ideal LiTi$_2$(PO$_4$)$_3$ and defected LiTi$_2$(PO$_4$)$_3$. It indicates that LiTi$_2$(PO$_4$)$_3$ is an insulator with a calculated band gap of 2.38 eV in the ideal LiTi$_2$(PO$_4$)$_3$ and 1.94 eV in defected LiTi$_2$(PO$_4$)$_3$ with O-vacancy. In accordance with LiTiPO$_5$, O-vacancies significantly reduce the band gap of LiTi$_2$(PO$_4$)$_3$. Although the reduced band gap by O-vacancies in LiTiPO$_5$ and LiTi$_2$(PO$_4$)$_3$ will have no contribution for a better conductivity directly, it will increase the electron carriers by significantly reducing other possible donor levels. Our recent experiment also shows that the electronic conductivity of LiTi$_2$(PO$_4$)$_3$ is increased when the sample is heat-treated under N$_2$ atmospheres [39].

The discharge/charge voltage of the cathodic materials is controlled by the energy of active redox couple which varies from one material to another depending on two main factors [40]: (1) the electrostatic field at the cation position and (2) the covariant contribution to the cation–anion bonding. The discharge voltage, $V(x)$, actually depends on the value of $x$ in Li$_x$TiPO$_5$ or Li$_x$Ti$_2$(PO$_4$)$_3$ since the chemical potential of Li is a function of $x$, similarly to the case of Li$_x$MPO$_4$ discussed in Ref. [40]. The detailed expression for the discharge voltage can be written as following [41]

$$V(x) = \frac{1}{F} \left( \frac{\delta \Delta G(x)}{\delta x} \right)_{T,p},$$

(3)
where \( F \) is the Faraday constant and \( \Delta G(x) \) is the change in Gibbs's free energy for the intercalation reaction,

\[
\delta \text{Li} + \text{Li}_x \text{TiPO}_5 \rightarrow \text{Li}_{x+\delta} \text{TiPO}_5; \tag{4}
\]
or

\[
\delta \text{Li} + \text{Li}_x \text{Ti}_2(\text{PO}_4)_3 \rightarrow \text{Li}_{x+\delta} \text{Ti}_2(\text{PO}_4)_3. \tag{5}
\]

The detailed calculation of Gibbs's free energy as a function of \( x \) is complicated due to lack of practical ordering of Li ions at any value of \( x \), which requires a comprehensive Monte Carlo simulation. Fortunately, the calculation of the average intercalation voltage through first-principle has been proposed in Ref. [42]. Generally, Gibbs's free energy contributions from the volume changes and entropy associated with the intercalation are negligibly. Otherwise, the stability of the cathode materials will be a critical issue. Therefore, the average discharge voltage in a fully Li discharge procedure for LiTiPO\(_5\) or LiTi\(_2(\text{PO}_4)_3\) (cf. Eqs. (4)-(5)) can be deduced from the change of the internal energy \( \Delta E \) at 0 K, i.e.,

\[
\mathcal{V} \approx -\frac{\Delta E}{F}. \tag{6}
\]

Here \( \Delta E \) is given by the total energy difference between Li\(_2\)TiPO\(_5\) and the sum of LiTiPO\(_5\) and metallic lithium for LiTiPO\(_5\), while it is given by the energy difference between Li\(_2\)Ti\(_2(\text{PO}_4)_3\) and the sum of LiTi\(_2(\text{PO}_4)_3\) and metallic lithium for LiTi\(_2(\text{PO}_4)_3\). Experimentally, it is hard to realize the “lithium-stuffed” composition Li\(_2\)TiPO\(_5\) [21]. Therefore, we estimate its discharge voltage by inserting Li atoms into LiTiPO\(_5\) lattice.

The study of both factors can be properly accomplished on oxides formed by MO\(_6\) octahedra (M = transition metal cation) linked by tetrahedral polyoxoanions \( \text{SO}_4^{2-} = \text{PO}_4^{3-} = \text{AsO}_4^{3-} = \text{SO}_4^{2-} \) etc.) [41]. The calculated average voltage for Li/LiTiPO\(_5\) with O-vacancy free is 0.68 V, and it is increased by 1.5% to 0.78 V for the system with O-vacancy. In general, the GGA calculated voltage of delithium is lower than the experimental measurement. In Li/LiTiPO\(_5\) case, the experimental observed voltage of delithium is to be 1.51 V [21]. In our calculations, it is found that the lengths of two different Ti–O bonds next to the O-vacancy decreased with 11.1% and 3.7% in the system, respectively, compared to the corresponding bonds without O-vacancy in LiTiPO\(_5\). Experimentally, it is hard to realize the “lithium-stuffed” composition Li\(_2\)TiPO\(_5\) [21]. Therefore, we estimate its discharge voltage by inserting Li atoms into LiTiPO\(_5\) lattice.

This may result in the decrease of the total charge around Ti and the leads to the increase of the Ti redox voltage.  

3. Conclusion

In conclusion, by means of first-principles theory, we have calculated the crystal constants and volumes of ideal LiTiPO\(_5\) and LiTi\(_2(\text{PO}_4)_3\) systems, which are in good agreement with available experiment values. Our calculated results indicate that oxygen vacancies may be formed under extreme O-poor condition in LiTi\(_2(\text{PO}_4)_3\) and particularly in LiTiPO\(_5\). Their electronic conductivity is expected to increase in comparison with the ideal LiTiPO\(_5\) and LiTi\(_2(\text{PO}_4)_3\) respectively, since the band gaps of the systems are significantly reduced by the defect band introduced by oxygen vacancies. The discharge voltages of LiTiPO\(_5\) and LiTi\(_2(\text{PO}_4)_3\) may be increased due to possible large concentration of oxygen vacancies. It is expected that the impact of the defects to the electronic conductivity will stimulate further experimental research on the promising spinel and olivine structural cathode materials, such as LiTiPO\(_5\) and LiTi\(_2(\text{PO}_4)_3\).