



Short communication

Stabilities and electronic properties of lithium titanium oxide anode material for lithium ion battery

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ABSTRACT

A theoretical study of the structural, elastic and electronic properties of spinel LiTi_2O_4 anode has been performed by density functional theory (DFT) plane-wave pseudopotential method. The independent elastic constants, shear modulus (G), bulk modulus (B), and Young's modulus (E) are evaluated, respectively. The results suggest that cubic LiTi_2O_4 is mechanically stable. The G/B ratio of 0.584 indicates the ductility of LiTi_2O_4 is good. The electron density difference of LiTi_2O_4 shows that the O_{2p} orbitals overlap effectively with Ti_{3d} ones, confirming the formations of strong covalent bonds between them, while Li is fully ionized in the lattice. The formation enthalpy for LiTi_2O_4 is calculated to be $-2070.723 \pm 1.6 \text{ kJ mol}^{-1}$. The strong covalent bonds between O and Ti atoms are not only responsible for the excellent mechanical stabilities but also very crucial for the thermodynamic stability of LiTi_2O_4 compound. Furthermore, in $\text{Li}_2\text{Ti}_2\text{O}_4$ compound, the full occupation of 16(c) sites by Li^+ not only leads to a smaller C_{12} value but also leads to a much larger C_{44} one. Therefore, the plasticity and ductility of the $\text{Li}_2\text{Ti}_2\text{O}_4$ become poor in comparison to LiTi_2O_4 , while the thermodynamic stability of $\text{Li}_2\text{Ti}_2\text{O}_4$ can be further improved after the Li^+ intercalation of LiTi_2O_4 .

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1. Introduction

There is a strong and ever-growing demand for renewable energy resources, reliable energy storage, and conversion devices in order to replace the traditional fossil fuels. Rechargeable batteries are considered as the most successful tried and true technologies that can repeatedly generate clean electricity from stored materials and convert reversely electric energy into chemical energy [1]. Undoubtedly, lithium-ion batteries (LIBs) are the most popular rechargeable batteries because of the efficiency, lightweight, and high energy density. One of the key safety issues in LIBs as power battery would be the dendritic lithium growth on the anode surface at high charging current because the conventional carbonous materials approach almost 0 V versus Li/Li^+ at the end of Li insertion [2]. Developing anode materials with high safety is one of the key challenges for lithium-ion batteries. Spinel lithium titanium oxides have been considered as one of the promising alternatives for the commercial carbon-based anode materials due to its unique properties. The poor electric conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ limits its high rate application, but LiTi_2O_4 anode materials have advantages in

electric conductivity facilitating high rate performance [3,4]. Recently, rapid advances in computing technology have made it possible to perform predictions of the properties of materials based on density functional theory (DFT) [5]. The electronic structure and crystal parameters of LiTi_2O_4 has been reported according to the first principle [6]. W. Ra et al. [7] reported that the electronic structural changes of electrochemically reacted LiTi_2O_4 by first principles calculations. L. Benco et al. [8] reported the average intercalation voltages of LiTi_2O_4 as cathode materials for lithium-ion batteries calculated from first principles using the LAPW method. Besides the electronic properties, the elastic properties are also of particular interest as they determine the mechanical response of a material to external stress and the macroscopic mechanical stability. To our knowledge, no theoretical study on the mechanical stability of LiTi_2O_4 has been reported. In this paper, it is our target to contribute understanding towards the relationship among electronic structure, thermodynamic and mechanical stabilities.

2. Theory and computation details

The present calculations were performed in the density functional theory (DFT) framework [9] implemented in the CASTEP package [10]. The exchange and correlation effects are treated with the Perdew–Wang functional in the generalized gradient approximation scheme (GGA-PW91) [11]. All computations

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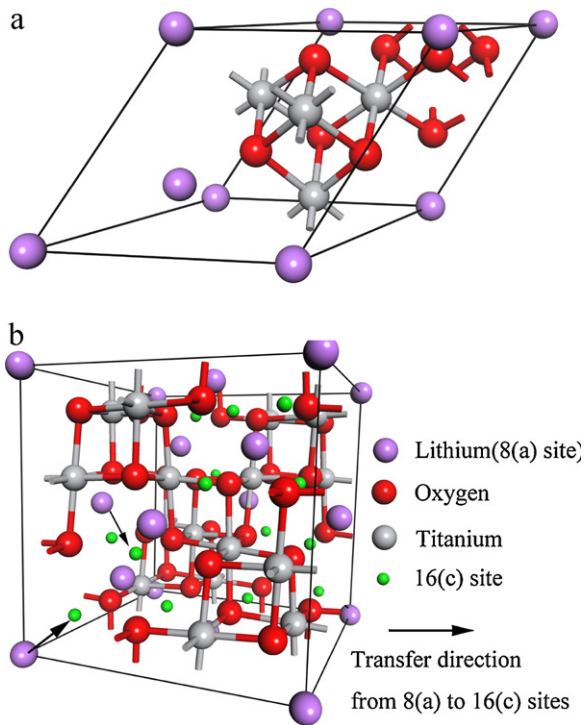


Fig. 1. Perspective view for LiTi_2O_4 crystal: (a) primitive cell (2 LiTi_2O_4 units) and (b) conventional cell (8 LiTi_2O_4 units). The small green spheres represent the 16(c) sites. $\text{Li}_{1-x}\text{Ti}_2\text{O}_4$ can be formed when foreign and 8(a) site lithium ion transfer to 16(c) sites. For $\text{Li}_2\text{Ti}_2\text{O}_4$, all 16(c) sites were occupied by Li^+ . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

were performed with a plane-wave energy cutoff of 450 eV, and the sampling over Brillouin zone was treated by a $(5 \times 5 \times 5)$ Monkhorst–Pack mesh. This set of parameters ensures that the total energy of system can be accurately evaluated, and the energy convergence is within 5.0×10^{-7} eV atom $^{-1}$. The primitive and conventional cells for LiTi_2O_4 crystal are shown in Fig. 1, in which the 16(c) sites and the Li^+ transfer direction were also depicted. In the following calculations, the periodic boundary condition is employed.

3. Results and discussion

Mechanical stability of materials mainly reflects the structural stability under a particular deformation condition. According to DFT calculations combined with a linear elastic theory, all mechanical parameters of single crystal materials can be calculated accurately. Elastic constants of a solid, which reflect the relationship between stress and strain, are very important because they are related to various fundamental solid-state properties such as interatomic potentials, equation of states (EoS), and phonon spectra [12]. It is well known that a cubic crystal has only three independent elastic constants C_{11} , C_{12} and C_{44} . Therefore, a set of three equations is required to determine all the elastic constants [13].

The calculated elastic constants (C_{11} , C_{12} and C_{44}) are listed in Table 1. According to the elastic constants, the shear modulus (G) [14], bulk modulus (B) [14], and Young's modulus (E) [15,16] can be derived by the following expressions:

$$B = \frac{C_{11} + 2C_{12}}{3} \quad (1)$$

$$G = \frac{C_{11} - C_{12} + 3C_{44}}{5} \quad (2)$$

$$E = \frac{(C_{11} - C_{12})(C_{11} + 2C_{12})}{C_{11} + C_{12}} \quad (3)$$

For a cubic crystal, the mechanical stability requires that all the independent elastic constants should satisfy the following criterions [17–20]:

$$C_{11} + 2C_{12} > 0 \quad (4)$$

$$C_{44} > 0 \quad (5)$$

$$C_{11} - C_{12} > 0 \quad (6)$$

$$C_{11} > 0 \quad (7)$$

Furthermore, the bulk modulus B should also satisfy an additional criterion [17–20]:

$$C_{12} < B < C_{11} \quad (8)$$

The results clearly suggested that under elastic strain perturbations cubic LiTi_2O_4 is mechanically stable. To further elucidate the mechanical properties, the G/B ratio, which is now widely accepted as a predictor in first-principles materials design, is introduced. Pugh [21] concluded that G/B ratio reflects the ductility of the materials. The smaller the G/B ratio is, the more ductile the materials are. From the calculated G and B values, the G/B ratio is calculated to be 0.584. The critical value which distinguishes ductile and brittle characteristics was about 0.571 [22]. In our work, the G/B ratio of 0.584 is rather close to the critical value, indicating the ductility of cubic LiTi_2O_4 is good. Besides the G/B ratio, it was recently reported that the $(C_{11} - C_{12})$ also plays an important role in the mechanical properties of materials [23]. The smaller the $(C_{11} - C_{12})$ is, the lower the Young's modulus is, and the better the plasticity is. In present work, the calculated $(C_{11} - C_{12})$ is 117.21 GPa, which indicate the Young's modulus is relatively high and the plasticity of the LiTi_2O_4 is relatively poor. As the mechanical properties are representations of microscopic bondings of systems, to bridge the relationship between them, the electronic structures were discussed in detail.

Fig. 2 depicts the electron density difference diagram for cubic LiTi_2O_4 . Due to the formation of covalent bonds, the electron distribution is changed, and the positive (in blue) or negative (in red) regions indicate, respectively where the electron density is enriched or depleted. From Fig. 2, it can be identified that covalent bonds between Ti and O atoms are formed, leading to some electron transformation from Ti to O atoms. And lithium exists in the crystal lattice as pure ions. According to the electron redistribution characteristics, it can also be confirmed that O atoms take sp^3 hybridizations, and the hybrid orbits overlap effectively with the 3d ones of three nearest neighbor Ti atoms. The formations of Ti–O covalent bonds are very crucial for the aforementioned mechanical properties. As the Ti–O bonds are evenly distributed in three dimensional framework, the mechanical properties thus show isotropic natures (i.e. $E_x = E_y = E_z$). Moreover, the strength of Ti–O bonds is expected to determine the resistance of materials against uniaxial tensions in the three directions. The stronger the bond is, the larger the Young's modulus is. The data listed in Table 1 clearly suggested that Ti–O bonds are rather strong and the Young's modulus possesses a large value (152.08 GPa). Besides the Young's modulus, the bulk modulus, which reflects the resistance of a material against volume change under hydrostatic pressure, is also very large (125.11 GPa). On the basis of Eq. (1), it can be figured out that C_{11} plays an important role in determining the bulk modulus. Therefore, the bonding between Ti and O atoms is also important for the bulk modulus. Although the Ti–O bonds are rather strong, the C_{44} ($C_{44} = C_{55} = C_{66}$) value is however a little bit small. In comparison to the Young's modulus, the shear deformation is smaller. Hence, the theoretical shear stress will be reached before the stress of crack tip exceeds the theoretical tensile stress. This can be deduced that the $(100)(001)$, $(010)(001)$, $(100)(010)$,

Table 1
Calculated elastic constants and modulus (all in GPa) of $\text{Li}_{1-x}\text{Ti}_2\text{O}_4$ ($x=0, 1$).

	C_{11}	C_{12}	C_{44}	$E_x = E_y$	E_z	B	G	G/B
$\text{LiTi}_2\text{O}_4^a$	203.25	86.04	82.78	152.08	152.08	125.11	73.11	0.584
$\text{Li}_2\text{Ti}_2\text{O}_4^b$	204.22	69.29	104.30	169.11	169.11	114.27	89.57	0.784

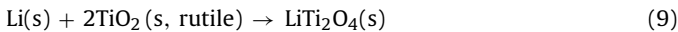
^a Li^+ occupies the 8(a) sites. The optimized lattice constant is 8.489 Å. The error for modulus is restricted to ± 4.854 GPa.

^b Li^+ occupies all the 16(c) sites. The lattice constant after geometry optimization is 8.412 Å. The error for modulus is restricted to ± 4.473 GPa.

$\langle 001 \rangle$, $\langle 010 \rangle$, $\langle 100 \rangle$, $\langle 001 \rangle$, $\langle 100 \rangle$ slip systems may be very active in LiTi_2O_4 compounds. The slips of $\langle 100 \rangle$, $\langle 010 \rangle$, and $\langle 001 \rangle$ crystal plane are expected to be prior to the cleavage process of the Ti–O bonds, and it may be the origin for the good ductility of LiTi_2O_4 .

Moreover, it should be emphasized that there is an intercalation process of Li^+ into the spinel host structures during realistic applications, and the mechanical properties should reflect such structural changes. According to the previous report [24], the foreign and 8(a) site Li^+ will transfer to the 16(c) sites (Fig. 1(b)), and finally all 16(c) sites were occupied by Li^+ to achieve a $\text{Li}_2\text{Ti}_2\text{O}_4$ formula. Table 1 also lists the corresponding elastic constants and moduli of $\text{Li}_2\text{Ti}_2\text{O}_4$. Based on the criterion aforementioned, $\text{Li}_2\text{Ti}_2\text{O}_4$ compound is mechanical stable. In comparison to LiTi_2O_4 , the C_{44} value increases to a very large extent, and this means that the occupation of 16(c) sites by Li^+ is unfavorable to the slip systems. The slips of $\langle 100 \rangle$, $\langle 010 \rangle$, and $\langle 001 \rangle$ crystal planes become more difficult and the shear modulus (G) thus increases to 89.57 GPa. In contrast, the C_{12} value decreases as the 16(c) sites are fully occupied by Li^+ , and this behavior not only leads to a smaller bulk modulus but also results in a larger ($C_{11}-C_{12}$) value. Therefore, both the plasticity and ductility of the $\text{Li}_2\text{Ti}_2\text{O}_4$ become poor as the Li^+ intercalation process is further considered.

The bonding of systems also significantly affects the thermodynamic properties. To obtain the formation enthalpy, the molar reaction enthalpy ($\Delta_f H_m$) is derived from the crystal energies first. Relying on the thermodynamic cycle described below



$\Delta_f H_m$ can be calculated by,

$$\begin{aligned} \Delta_f H_m &= \Delta_f H_m(\text{LiTi}_2\text{O}_4) - \Delta_f H_m(\text{Li}) - 2\Delta_f H_m(\text{TiO}_2(\text{rutile})) \\ &= E(\text{LiTi}_2\text{O}_4) - E(\text{Li}) - 2E(\text{TiO}_2(\text{rutile})) \end{aligned} \quad (10)$$

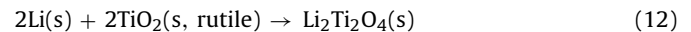
where $E(\text{Li})$, $E(\text{TiO}_2)$ (s, rutile), and $E(\text{LiTi}_2\text{O}_4)$ represent the total energies of lithium (-190.18902954715 eV), titanium oxide (-2483.2406419855 eV), and LiTi_2O_4 crystals (-5158.56640998375 eV). According to the DFT algorithm,

the molar reaction enthalpy ($\Delta_f H_m$) is calculated to be $-182.723 \text{ kJ mol}^{-1}$. Because the absolute value of formation enthalpy is unable to determine, some experimental data is needed to derive the formation enthalpy for LiTi_2O_4 . According to the thermodynamic data for substances, the $\Delta_f H_m$ value for TiO_2 (s, rutile) is $-944.0 \pm 0.8 \text{ kJ mol}^{-1}$ [25]. On the basis of the following equation:

$$\Delta_f H_m(\text{LiTi}_2\text{O}_4) = \Delta_f H_m + \Delta_f H_m(\text{Li}) + 2\Delta_f H_m(\text{TiO}_2, s, \text{rutile}) \quad (11)$$

The formation enthalpy of LiTi_2O_4 ($\Delta_f H_m$) is finally determined to be $-2070.723 \pm 1.6 \text{ kJ mol}^{-1}$. The formation enthalpy of $\text{Li}_2\text{Ti}_2\text{O}_4$ is obviously lower than that of LiCoO_2 ($-142.54 \pm 1.69 \text{ kJ mol}^{-1}$ [26]), LiNiO_2 ($-56.21 \pm 1.53 \text{ kJ mol}^{-1}$ [26]) and LiMn_2O_4 ($-1380.9 \pm 2.2 \text{ kJ mol}^{-1}$ [27]). Hence, $\text{Li}_2\text{Ti}_2\text{O}_4$ has a higher thermodynamic stability than that of LiCoO_2 , LiNiO_2 and LiMn_2O_4 .

The thermodynamic cycle of $\text{Li}_2\text{Ti}_2\text{O}_4$ described below



$\Delta_f H_m$ can be calculated by,

$$\Delta_f H_m = E(\text{Li}_2\text{Ti}_2\text{O}_4) - 2E(\text{Li}) - 2E(\text{TiO}_2(\text{rutile})) \quad (13)$$

where $E(\text{Li})$, $E(\text{TiO}_2)$ (s, rutile), and $E(\text{Li}_2\text{Ti}_2\text{O}_4)$ represent the total energies of lithium, titanium oxide, and $\text{Li}_2\text{Ti}_2\text{O}_4$ crystals (-5349.6273012625 eV). The molar reaction enthalpy ($\Delta_f H_m$) is calculated to be $-267.080 \text{ kJ mol}^{-1}$. On the basis of the following equation:

$$\Delta_f H_m(\text{Li}_2\text{Ti}_2\text{O}_4) = \Delta_f H_m + 2\Delta_f H_m(\text{Li}) + 2\Delta_f H_m(\text{TiO}_2, s, \text{rutile}) \quad (14)$$

The formation enthalpy of LiTi_2O_4 ($\Delta_f H_m$) is finally determined to be $-2155.08 \pm 1.6 \text{ kJ mol}^{-1}$. Hence, it can be concluded that the thermodynamic stability of $\text{Li}_2\text{Ti}_2\text{O}_4$ can be further improved after

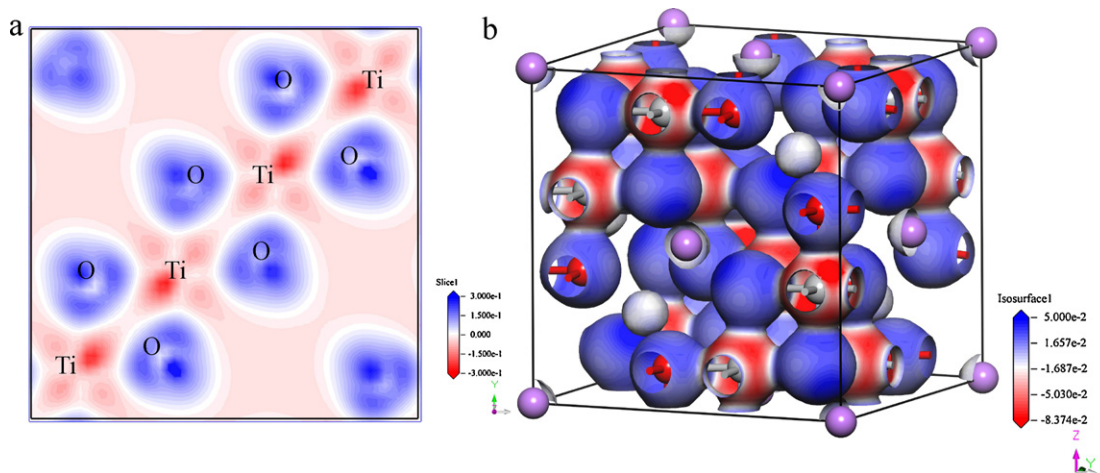


Fig. 2. Electron density difference diagram for LiTi_2O_4 : (a) view for $\langle 001 \rangle$ crystal plane and (b) three-dimensional view.

the Li^+ intercalation of LiTi_2O_4 . The high thermodynamic stability and good ductility of LiTi_2O_4 are expected to show a potential commercial application on power lithium-ion battery.

4. Conclusions

In present paper, we have carried out systematic investigation of the mechanical and thermodynamic stability of spinel LiTi_2O_4 anode material. The three elastic constants (C_{11} , C_{12} and C_{44}) and mechanical parameters, such as shear modulus G , bulk modulus B , and Young's modulus E of LiTi_2O_4 are calculated. Furthermore, the effect of electronic structures on thermodynamic and mechanical properties is also addressed. The calculated results suggest that the cubic compound LiTi_2O_4 is mechanically stable. The calculated G/B ratio of 0.584 indicates a good ductility of the LiTi_2O_4 , while ($C_{11}-C_{12}$) suggests the plasticity of the LiTi_2O_4 is relatively poor. The formation enthalpy of LiTi_2O_4 shows that it has a good thermodynamic stability. In $\text{Li}_2\text{Ti}_2\text{O}_4$ compound, the full occupation of 16(c) sites by Li^+ leads to a poor plasticity and ductility, while the thermodynamic stability of $\text{Li}_2\text{Ti}_2\text{O}_4$ can be further improved after the Li^+ intercalation of LiTi_2O_4 . The new approach presented in this work is promising for predicting the stability of electrode materials. It can be concluded that the first-principles approach can be useful to better understand the stability mechanisms of electrode materials and it will contribute to the development of safe and stable electrode materials.

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