Thermodynamics of spinel Li$_x$TiO$_2$ from first principles

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Received 26 January 2005; accepted 4 May 2005
Available online 20 June 2005

Abstract

The thermodynamic and structural properties of Li$_x$TiO$_2$ spinel are investigated by means of a cluster expansion based on pseudopotential ground state energy calculations in the Generalized Gradient approximation (GGA). The cluster expansion enables a Monte Carlo simulation of configurational thermodynamics, giving the Li configurations, chemical potential and the insertion potential as function of Li composition at 300 K. For 1/2 < $x$ < 1 Li$_x$TiO$_2$ we find a two-phase region, consistent with what is found experimentally. The two coexisting phases differ in the sites occupied by Li: in Li$_{1/2}$TiO$_2$ and LiTiO$_2$ Li occupies the crystallographic 8a and 16c sites, respectively. This site occupation and the changes in the unit cell dimensions compare well with X-ray and neutron diffraction experiments. For $x$ < 1/2 in Li$_x$TiO$_2$ solid solution behavior is found and Li extraction can only occur at higher potentials. The potential step at Li$_{1/2}$TiO$_2$ is calculated to be 1.4 V, in good agreement with experiment, but considerably higher than in the comparable Co and Mn-spinel.

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Keywords: Lithium intercalation; Battery material; First principles; Spinel, Li$_x$TiO$_2$

1. Introduction

The growing demand for energy resources has led to the development of renewable energy sources, including photovoltaics (solar cells), solar thermal, wind, biomass and several others. To resolve the discrepancy between the moments of supply and demand of the energy produced, energy storage is required. For small scale applications one option is to store energy in rechargeable batteries. Rechargeable batteries convert chemical energy contained in the electrodes into electrical energy via electrochemical reactions. Transport of ions from one electrode to another through an electrolyte, causes an electrical current between the electrodes that can be used to power an application. In particular, lithium-ion batteries are very promising due to their stored energy/weight ratio [1]. During the last decades, three-dimensional framework spinel transition metal oxides have appeared to be a very promising class of lithium-ion electrode materials.

The use of spinel Li$_{1/2}$TiO$_2$ (often represented as Li$_1$Ti$_2$O$_4$) as electrode material is based on its ability to host an additional amount of Li leading to composition LiTiO$_2$ [2]. Other titanium oxide compounds studied in relation to Li intercalation include anatase, rutile and brookite (all TiO$_2$) [3–5]. In particular the anatase and the spinel structures have been found to be suitable anode materials. In the starting compound, spinel Li$_{1/2}$TiO$_2$, neutron diffraction indicates that Li resides on the tetrahedral 8a sites, whereas it occupies the octahedral 16c sites in LiTiO$_2$ [6]. The latter structure
can be indexed with the cubic Fd3m space-group. Colbow et al. cycled this material between about 3 and 1 V, leading to compositions between \( x = 0.4 \) and 1 for Li,TiO\(_2\). Between \( x = 1/2 \) and 1 the potential is constant around 1.34 V vs. Li/Li\(^+\), and Li can be reversibly cycled with little capacity loss [7]. Such a constant potential region is usually the result of a two phase equilibrium between the initial and final compositions. At higher potentials, between about 2.6 and 3 V, Li is extracted resulting in \( x = 0.4 \) at 3 V.

The spinel structure is an important phase for transition metal oxides applied in Li-ion battery materials. In particular spinel structures based on Mn have been, and still are, of considerable interest. Although the pure material, Li,MnO\(_2\), has an attractive theoretical capacity of 148 mAh/g at 4.1 V vs. Li/Li\(^+\), the material suffers from capacity fading upon cycling related to the cooperative Jahn–Teller distortion and Mn dissolution [8,9]. Partial substitution of Mn with other transition metals can resolve these problems. A first principle investigation has shown that the phase-behavior is mainly determined by the interactions of Li with the MnO\(_2\) host, and less influenced by the Jahn–Teller distortion [10]. In Li,MnO\(_2\) spinel calculations confirm the experimental two phase region between \( x = 1/2 \) and 1, and an ordered phase at \( x = 1/4 \). Similar calculations lead to very similar phase behavior for the Co-analogue of the spinel structure Li,CoO\(_2\) [11]. Apparently, most of the qualitative features of the phase behavior depend on the topology of the spinel structure, and not on the choice of transition metal. Therefore, the same features may also be expected in the present material, Li,TiO\(_2\). However, there is an important difference. The interaction of Li with the TiO\(_2\) host appears to be different, as is illustrated by the difference in potential vs. Li/Li\(^+\), about 1.34 V for Li,TiO\(_2\) and around 3 V for the Mn and Co spinel materials. As a result Li,TiO\(_2\) is more interesting for use as an anode, rather than as a cathode.

In this study we aim at calculating the thermodynamical behavior of Li,TiO\(_2\). The results will be compared to neutron diffraction data and electrochemical results. An attempt will be made to formulate a consistent picture of the electrochemistry, structure and electronic configuration. Additionally, the results will be compared to the structurally equivalent Li,CoO\(_2\) and Li,MnO\(_2\) materials. Such a comparison might shed light on the importance of various interactions that determine the performance of these materials as electrode materials in Li-ion batteries.

2. Methodology

At finite temperature, and away from the stoichiometry of very ordered compounds, there will be substantial disorder between vacant sites and those occupied by Li. Methods to study this have been outlined in previous work [12,13,11,10]. Typically, the procedure consist of calculating the energy of a number of ordered Li-vacancy arrangements and parameterizing a cluster expansion with the results. This cluster expansion can then be rapidly evaluated in a Monte Carlo simulation to accurately obtain the large number of possible Li-vacancy states with the proper thermal statistics. Using this procedure, it is possible to obtain the free energy of the system and hence the Li chemical potential. This free energy contains the energy component as well as the configurational entropy arising from the Li-vacancy disorder, but not the entropy from lattice vibrations and electronic excitations, unless these are explicitly included, which is rarely done for phase diagram calculations. The inclusion of the latter two entropy terms generally leads to some quantitative improvement in the order disorder transition temperatures [14], but they are neglected here. The cluster expansion is an effective tool to parameterize the configuration dependence of the ground state energy by extrapolating the first principles energy values calculated for a few ordered configurations [15]. Once a cluster expansion has been parameterized for a particular system, it can be used to predict the energy of any configuration in a relatively large super-cell. Monte Carlo simulations can then be used to probe configuration space and predict thermodynamic quantities. To describe the configurational energy with a cluster expansion, occupation variables \( \sigma_i \) are assigned to each Li site \( i \) which are +1 if Li occupies site \( i \) and −1 if the site is vacant. It can be shown that polynomials of the occupation variables, called cluster functions \( \phi \) and defined as the products of occupation variables belonging to different sites of clusters of sites (e.g. pair clusters, triplet clusters, etc.)

\[
\phi_x = \prod_{i \in z} \sigma_i,
\]

where \( z \) represents a set of Li sublattice sites within a cluster. These cluster functions then form a complete and orthonormal basis in configuration space [15]. Hence, the configurational energy can be expanded in terms of these basis cluster functions:

\[
E = C_0 + \sum_x C_x N_x \langle \phi_x \rangle,
\]

where the coefficients \( C_0 \) and \( C_x \) are the effective cluster interactions (ECI), \( \langle \phi_x \rangle \) represents the average value of symmetrically equivalent cluster functions and \( N_x \) is the multiplicity of the cluster. Once the ECI are known, this model for the energy describes the interactions of the Li atoms with each other and with the host structure. In practice, the cluster expansion in Eq. 2 can be truncated because the contribution to the total energy from clusters including many lattice sites, or well separated lattice sites can generally be neglected. The reduced
number of ECI can then be determined by fitting them to a sufficiently large number of first principles calculations on ordered configurations [16,17]. Truncating the cluster expansion introduces an additional inaccuracy, depending on the degree of convergence. It should be realized that a small (from a computational point of view) inaccuracy, of the order of a few meV, can lead to a considerable error in the transition temperature of phase and order disorder transitions.

The thermodynamic properties of interest include the phase diagram, site occupations and the electro-chemical potential as a function of composition, \( \mu(x) \), which is directly related to the open cell potential measured in equilibrium:

\[
V(x) = -\frac{\mu(x)_{\text{cathode}} - \mu(x)_{\text{anode}}}{Fz}.
\]

Here \( z \) is the electron charge transported by each Li-ion (for \( z = 1 \)) from the cathode to the anode or vice versa, and \( F \) is Faraday's constant. In Eq. 3 the cathode represents the material of interest and for convenience the anode is chosen to be Li-metal, which has a well known constant potential. A more comprehensive description of the method described can be found in [12].

In this contribution ground state energies needed to parameterize the cluster expansion were calculated using density functional theory (DFT) [18] in the generalized gradient approximation (GGA) (non-spin polarized) as implemented in the VASP plane wave pseudo-potential code [19]. The calculations were performed non-spin polarized, because spin polarized test calculations did not lead to significant energy differences. The energy calculations were performed on the primitive cell (12 ordered Li-vacancy configurations within spinel) and the conventional cubic unit cell (5 configurations) of the \( Fd\bar{3}m \) TiO\(_2\) structure, containing 6 Li sites and 24, respectively (1/3 8a sites and 2/3 16c sites). The energies of these 17 Li-vacancy arrangements were calculated and used to fit 10 ECI coefficients. During the calculations both the cell dimensions and the ionic positions were allowed to relax, without symmetry restrictions. The root mean square difference between the cluster expansion predicted energies and the DFT calculated energies was less than 5 meV per formula unit TiO\(_2\). Grand canonical Monte Carlo simulations were applied using the cluster expansion in order to predict the thermodynamic properties. Within these calculation thermodynamic equilibrium is reached in the Monte Carlo cell at a specified chemical potential by variation of the Li occupancies. The Monte Carlo cell contained 10,368 Li sites. Six thousand Monte Carlo passes per lattice site were performed for each temperature and chemical potential step, 2000 for equilibration and 4000 for averaging.

3. Results and discussion

3.1. Formation enthalpy

In Li\(_x\)TiO\(_2\) spinel there are two distinct crystallographic sites that can be occupied by Li, the tetrahedral 8a site and the octahedral 16c site. In the energy calculations only the Li occupancy over these sites is varied, whereas the occupation of Ti and O remains fixed (although they are allowed to relax). In Fig. 1 the formation enthalpy per formula unit Li\(_x\)TiO\(_2\) for the 17 calculated Li-vacancy arrangements are shown, illustrating the relative stability of the different configurations. We define the formation enthalpy as:

\[
E_{\text{Form}} = E - xE_{\text{LiTiO}_2} - (1-x)E_{\text{TiO}_2},
\]

where \( E \) is the energy of a specific Li-vacancy arrangement at a concentration \( x \), \( E_{\text{LiTiO}_2} \) is the energy with all octahedral 16c sites occupied and \( E_{\text{TiO}_2} \) is the energy of the empty TiO\(_2\) spinel host. Instead of the total energy, we consider the formation energy since it is the relevant quantity to study phase stability. The lines drawn in Fig. 1 give the convex hull, and connect the most stable structures as function of Li composition.

The cluster expansion based on the energies in Fig. 1 predicts that a single Li occupying a tetrahedral site in an otherwise empty host is more stable by 212 meV (per TiO\(_2\) unit) than Li occupying an octahedral site. The cluster expansion also predicts that the energy penalty of two Li occupying a nearest 8a–16c pair compared to the isolated positions (in an otherwise empty host) is 278 meV (per TiO\(_2\) unit), which is most likely due to the electrostatic repulsion between the nearby Li-ions. The octahedral 16c sites are located in the middle of two

![Fig. 1. Formation enthalpy for 17 Li-vacancy configurations. Squares indicate configurations with Li only at octahedral sites, triangles Li only at tetrahedral sites and spheres a combination of octahedral and tetrahedral site occupation (the solid sphere represents the empty primitive cell). The lines connect the most stable ground states that were found.](image-url)
connecting tetrahedral 8a sites. In the empty host the smallest 8a–16c distance is 1.82 Å, which is small compared to the smallest 8a–8a and 16c–16c distances, 3.64 and 2.97 Å, respectively.

3.2. Site occupation

With the grand canonical Monte Carlo simulation the site occupation of both tetrahedral and octahedral sites as function of Li content can be calculated. The result at 300 K is shown in Fig. 2. Based on the energy results shown above the behavior in Fig. 2 is not surprising. Insertion of Li first results in filling of the energetically more favorable tetrahedral sites. At \( x = 1/2 \), all tetrahedral sites are filled and additional Li has to be accommodated on the less favorable octahedral sites. However, this causes adjacent 8a and 16c sites to be occupied which is energetically unfavorable. In order to prevent this, Li ions at tetrahedral sites move to octahedral sites avoiding adjacent 8a–16c occupancy (there are twice as many octahedral sites as tetrahedral sites). This will cause a miscibility gap between \( x = 1/2 \) and 1, where two phases will coexist, a phase where Li occupies solely tetrahedral sites and a phase with solely Li at octahedral sites. These results are similar to those for Li\(_x\)CoO\(_2\) [11] and Li\(_x\)MnO\(_2\) [10] performed with the similar calculational methods.

In order to resolve the structure, and in particular to determine the Li-ion positions and occupancy, neutron diffraction was applied by Cava et al. [6] in addition to X-ray diffraction performed earlier by Murphy et al. [2]. Two compositions were studied with diffraction, \( x = 1/2 \) and 1. The cubic unit cell lattice parameter decreases on addition of Li, from 8.416 Å for \( x = 1/2 \) to 8.383 Å for \( x = 1 \) [2]. The GGA calculations slightly overestimate the cell size at \( x = 1 \), but the decrease in unit cell size is predicted quite well, 8.456 Å, for \( x = 1/2 \) to 8.372 Å for \( x = 1 \). For the two compositions measured, \( x = 1/2 \) and 1, neutron diffraction revealed that Li occupies the 8a (occupancy 1) sites and the 16c sites (occupancy 1) respectively [6]. This is correctly reproduced by the cluster expansion as is seen in Fig. 2. Calculation of the phase diagram, not shown, indicates that the two phase region is stable up to about 750 K.

3.3. Open cell potential

From the Monte Carlo calculated composition dependence of the chemical potential, the equilibrium open cell potential can be calculated with Eq. 3, leading to the result shown in Fig. 3. The voltage behavior is dominated by two regions. Below \( x = 1/2 \) the potential evolves smoothly indicating a solid solution, whereas above \( x = 1/2 \) the constant potential is indicative of a two phase equilibrium. The step at \( x = 1/2 \) is characteristic of spinel materials and is also observed experimentally and computationally in Li\(_x\)CoO\(_2\) and in Li\(_x\)MnO\(_2\). The step is due to the stability of Li\(_{1/2}\)TiO\(_2\) where all Li occupy the tetrahedral 8a sites. Experimentally, the voltage was measured between \( x = 0.4 \) and 1. The average voltage calculated here correctly predicts the main features of the experimental voltage curve. The calculation underestimates the voltage of the two phase plateau between compositions \( x = 1/2 \) and 1. Experimentally, the plateau is found at approximately 1.34 V [7], and here calculated to be approximately 1.0 V. It has recently been shown that this underestimation of the potential by LDA and GGA is due to the self-interaction in the d-orbitals of the transition metal [20]. The more localized the d-orbital the higher that self-interaction error. As a result the larger d-orbitals for Ti give less LDA/GGA error than the more localized orbitals in later transition metals such as Co and Ni [21]. DFT + U calculations seem to correct many of the voltage errors [22]. However, the step at \( x = 1/2 \) is predicted correctly, and has a calculated and experimentally measured value.
of approximately 1.4 V. This is larger than what was found for CoO$_2$ and MnO$_2$, which suggests that Li$_{1/2}$TiO$_2$ is relatively more stable. The plateau between $x = 1/2$ and 1 is due to the phase transition from Li$_{1/2}$TiO$_2$ (tetrahedral Li) towards LiTiO$_2$ (octahedral Li). The fact that at $x = 1/4$ (and possibly also at $x = 1/8$ and 3/8) in Fig. 1 the formation energy of a specific ordered configuration lies on the convex hull suggests that, at low enough temperature, there should be Li ordering at those compositions. Given that this ordering is not seen in our Monte Carlo simulations at 300 K, its order–disorder transition temperature is probably below room temperature.

### 3.4. Electronic structure

The total density of states (DOS) for three compositions is shown in Fig. 4. The energy scale is shifted such that the Fermi level is at zero. In the valence region the energy states are represented by three sets of bands assigned the s-bands, the p-bands and the d-bands, according to the dominant component in the band. The s-bands are dominated by the O-2s states, the p-bands by the O-2p states and the d-bands by the Ti-3d states. Due to the octahedral coordination of oxygen around Ti, the electrostatic field splits the latter bands into two components generally referred to as the $t_{2g}$ ($d_{xy}$, $d_{yz}$, $d_{zx}$) and $e_g$ ($d_{z^2}$ and $d_{x^2-y^2}$) states. Due to the covalent character of the bonds the real picture is more complicated. Orbital $\sigma$ overlap of the $d_{z^2}$ and $d_{x^2-y^2}$ states with O-2p states leads to anti-bonding states, $e_g'$ and bonding $e_g^*$ states. The bonding states are located in the overall p-band dominated by the O-2p states.

Hence the bonding $e_g^*$ states are predominantly of O-p character whereas the anti-bonding states, indicated as $d$-$e_g$ in Fig. 4, mainly consist of Ti-3d states. The $t_{2g}$ orbitals are non-bonding states.

The main bonding band in this material is the p-band which is dominated by O-2p states but has a considerable amount of Ti-3d admixture (in particular the bonding $e_g$ states mentioned above). Li insertion progressively leads to the narrowing of the p-bands indicating less energy dispersion of the energy levels participating in the bonding. In general covalent bonding leads to wider bands in the DOS [23]. Hence, bonding becomes more ionic in nature as more Li is inserted.

This is also apparent in the electron density. Figs. 5 and 6 show the difference of valence electron density before and after Li intercalation for two compositions Li$_{1/2}$TiO$_2$ (Li occupying tetrahedral sites) and LiTiO$_2$ (Li occupying octahedral sites), respectively. For this

![Fig. 4. Calculated density of states for TiO$_2$, Li$_{1/2}$TiO$_2$ (Li occupying tetrahedral 8a sites) and LiTiO$_2$ (Li occupying octahedral 16c sites). The spectra are aligned such that the Fermi level is at zero.](image1)

![Fig. 5. Difference in valence charge between Li$_{1/2}$TiO$_2$ (Li occupying tetrahedral 8a sites) and TiO$_2$. White indicates higher and black lower charge density. For the explanation of the symbols see text.](image2)

![Fig. 6. Difference in valence charge between LiTiO$_2$ (Li occupying octahedral 16c sites) and TiO$_2$. White indicates higher and black lower charge density. For the explanation of the symbols see text.](image3)
purpose the structures were calculated at the same lattice parameter with the same Ti and O positions, allowing for point by point subtraction of the electron density in real space. The electron density depletion at the Li-ions sites in Figs. 5 and 6 indicates that Li is fully ionized once intercalated. The electron charge initially carried by Li is donated to O and Ti. The shape of the electron density illustrates a density gain of Ti t_{2g}-like orbitals (lobes pointing away from oxygen). There is also charge depletion around Ti in d_{x^2-y^2}-like orbitals (lobes pointing towards the oxygen). The combinations of this charge depletion with the gain at the O atoms indicates that the e_g^0 orbitals become more ionic [13]. The more ionic character due to lithiation is also evident from the change in the distance between the p-band and the t_{2g} band, which increases as Li is inserted. The addition of electron density into the t_{2g} orbitals raises the energy of the other occupied t_{2g} orbitals, which causes the increase of the gap between the t_{2g} band and the p-band.

Figs. 5 and 6 show that in Li_{1/2}TiO_2 (Li on tetrahedral sites) relatively more charge density is transferred towards oxygen, compared to LiTiO_2 (Li on octahedral sites). Electrostatically, this favors Li occupation of the tetrahedral 8a sites being more effectively screened. This, in combination with the larger Li–Ti and Li–Li distances in Li_{1/2}TiO_2, explains the lower energy for Li occupying a tetrahedral site as was found with the cluster expansion.

Another, more subtle difference between Figs. 5 and 6 is that in the latter, electron density is observable in Ti d_{xy} type of orbitals with their lobes directed to the neighboring Ti atoms indicated by the dotted circle. Although the t_{2g} is mainly a non-bonding band, the bottom of the band has a Ti–Ti bonding character [24]. Li intercalation causes these levels to be occupied which leads to a stronger Ti–Ti bonding, and hence to shorter nearest Ti–Ti bond lengths, which most likely the origin of the smaller unit cell size of LiTiO_2 compared to Li_{1/2}TiO_2.

Despite the qualitative similarities between Li, TiO_2 and Li, CoO_2 and Li, MnO_2 in structure, the calculated potential of the two-phase plateau between x = 1/2 and 1 is considerably lower for Li, TiO_2, ~ 1 V, than that of Li, CoO_2 and Li, MnO_2, ~ 3 V. For the ~NaFeO_2 structure it has been shown that two aspects determine the potential of Li in an electrode material. (1) A smaller energy gap between the p-band and the d-bands raises the potential vs. Li/Li^+. (2) The potential is also raised if the charge transfer (of the charge compensating electron) is more towards the anion (in this case oxygen), which lowers the electrostatic energy upon Li extraction, and hence raises the potential [21]. Going from transition metal elements Ti towards Zn in the periodic table, the energy gap between the p-band and the d-band becomes smaller, and the charge transfer towards oxygen becomes larger, both raising the potential vs. Li/Li^+.

4. Concluding remarks

The cluster expansion based on the pseudopotential energy calculations correctly predicts the phase behavior of Li intercalation in TiO_2 and site occupation when compared to electrochemistry and diffraction experiments. Between x = 1/2 and 1 coexistence of two phases, Li_{1/2}TiO_2 (Li on tetrahedral 8a sites) and LiTiO_2 (Li on octahedral 16c sites), causes a flat potential vs. Li/Li^+.

Compared to similar calculations in CoO_2 spinel the potential for Li in TiO_2 vs. Li/Li^+ is lower, which appears consistent with the trend in heavier transition metal oxides with the ~NaFeO_2 structure [21]. Two factors play a role: a smaller energy gap between the O-2p band and the Ti-3d band for later transition metal elements leads to a higher intercalation potential. Also the larger charge transfer towards oxygen for later transition metal elements leads to a higher intercalation potential. The smaller charge transfer towards oxygen suggests that Li–Li interactions are stronger and range over larger distances in TiO_2 compared to CoO_2.
less phase stability, and vice versa, if only configurational stability is considered.

Acknowledgments

This work is a contribution from the Delft Institute for Sustainable Energy (DISE). Financial support from the Netherlands Organization for Scientific Research (NWO), VENI grant M.W., is gratefully acknowledged. The work at MIT was supported by the MRSEC program of the National Science Foundation under award number DMR 02-13282.

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