Mechanism of Li-insertion into spinel-structured $Li_{0.5}TiO_2$

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First-principles calculations of Li-insertion into spinel-structured titanate $Li_{0.5}TiO_2$ reveal a mechanism underlying the intercalation behaviour of this material. A key factor is the accommodation of charge density transferred to the host lattice upon lithium insertion. The strong coupling between the electronic degrees of freedom and structural deformations is responsible for the observed two-phase intercalation behaviour in spinel-structured titanate.

Introduction

Spinel-structured Li titanates are among the few oxide materials that intercalate Li to high concentrations at relatively low constant potential (1.34–1.56 eV[1–7]). The members of this series ($Li_{1+y}Ti_{2-y}O_4$, $0 \leq y \leq 1/3$) are formed upon substitution of a fraction of Ti-ions by Li-ions in cubic spinel $LiTi_2O_4$.[8,9] Up to now only the properties of the end members of the series have been studied using various experimental and theoretical techniques.[1–12] It has been established that, despite having a very similar crystal structure, these materials exhibit different conducting and thermodynamic properties.[1,6] While $LiTi_2O_4$ is metallic and superconducting below 13.7 K,[8] $Li_{4/3}Ti_{5/3}O_4$ is an insulator. Nevertheless, their Li-intercalation behaviour appears to be very similar.[1–7] In both cases, upon intercalation a stable Li-rich phase is adopted, with a cubic rock-salt structure and cell parameters very close to those of the parent material.[5,6,13] The structural changes observed upon Li-insertion into spinel are only minor so their cyclability in electrochemical cells[1–7] is excellent. Lithium is soluble in these materials only to very low concentrations to form homogeneous phases of $Li_{1+x}Ti_2O_4$ and $Li_{4/3+x}Ti_{5/3}O_4$ with their lattice slightly expanded.[6,7] At higher x, insertion proceeds at a constant potential (1.56 V[4–6] and 1.34–1.38 V[1,2] *vs.* Li for $Li_{4/3}Ti_{5/3}O_4$ and $LiTi_2O_4$ respectively) and the lattice contracts slightly.[7,8] In both cases the change of volume does not exceed 1%. As there are only minor structural changes on cycling, it is still unclear which mechanism is responsible for the phase separation.

First-principles simulations have played an important role in developing an atomistic picture of the processes underlying Li-insertion in various oxide materials as they provide reliable thermodynamics and invaluable information on the changes in electronic structure and local geometry.[14–21] First-principles calculations were applied to study the band structure of $Li_{0.5}TiO_2$ in order to shed light on the origin of its high T_c superconductivity.[10,11] Investigation of the thermodynamics and structural aspects of Li-intercalation into $Li_{0.5}TiO_2$ spinel has been attempted by means of a cluster-expansion technique based on first-principles calculations.[12] This technique has been used with success to predict the phase diagram and the equilibrium voltage profile for Li-intercalation into various materials.[22] However, the applicability of this approach is limited by an implicit assumption that Li–Li interactions can be reliably represented as a cluster hierarchy and thus are fundamentally independent of Li-ion concentration. This is clearly not the case for titanium-dioxide-based materials, where electronic and structural degrees of freedom are strongly coupled and in fact interaction may change with concentration from effective repulsion to effective attraction.[14,15] Therefore, examination of a few model structures of titanates is insufficient to predict the intercalation behaviour of $Li_{0.5}TiO_2$ spinel. The correct prediction of the two-phase equilibrium of the $Li_{0.5}TiO_2$ and $LiTiO_2$ phases[12] using the cluster expansion technique is not surprising as the end members were known and well-defined structures, which were analyzed correctly. For other concentrations the reliability of the results of Wagemaker *et al.*[12] is questionable, since only the smallest possible unit cell ($Li_xTi_4O_8$) was considered in the majority of calculations, a fraction of possible interstitial sites (5 out of 10) and configurations were included in the cluster expansion and the concentration dependence of interactions was neglected.[12] This is manifested by, for example, the predicted homogeneous delithiation[12] of $Li_{0.5}TiO_2$ spinel to TiO_2, which has not been observed experimentally.[23]

For an accurate description of intercalation in Li titanates, configurations have to be examined directly for a wide range of insertion concentrations in first-principles calculations.[13,14] Additionally, information on the structure and the electronic structure at various Li-ion concentrations provides insight into the mechanisms underlying intercalation, which cannot be obtained to the full extent using the cluster approach.

In the present paper, direct first-principles calculations are applied to pinpoint the mechanism underlying Li-intercalation into $Li_{0.5}TiO_2$ spinel and its phase transformation to $LiTiO_2$ rock salt.

Details of the calculations

All calculations were performed using CASTEP software within the pseudopotential plane-wave formalism.[24,25] Electron exchange and correlation effects were treated within the spin polarized generalized gradient approximation[26] with

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ultrasoft pseudopotentials used to replace the Ti (1s,2s,2p), O(1s) and Li(1s) core orbitals.[27] Reciprocal space was sampled on a regular net with a consistent spacing of 0.05 $Å^{-1}$. A plane wave cut-off energy of 380 eV was found to converge the total energy to 0.01 eV per formula unit. The size and shape of the cell and all internal degrees of freedom were fully relaxed with respect to the total energy. Ionic charges were calculated using Mulliken population analysis, which provides an accurate description of changes in distribution of electron density in a row of similar compounds. Most computations were performed on a conventional cubic unit cell of spinel containing 8 formula units of $LiTi_2O_4$.

Results and discussion

Spinel-structured $Li_{0.5}TiO_2$ has a cubic structure ($Fd\bar{3}m$ space group). The cell parameter and the fractional coordinates are compared with the experimental values in Tables 1 and 2. A unit of the face-centred-cubic (fcc) cell consists of an approximately cubic-close-packed array of 32 oxygen atoms, with one-eighth of the 64 tetrahedral holes (8a, 8b and 48f sites) and one-half of the 32 octahedral holes (16c and 16d sites) filled by cations. The Ti-ions are located at 16d sites; the O-ions are located at 32e sites, which are not fixed by symmetry, but are described by an internal parameter u. The ideal value of this parameter is 0.25,[28] while in $Li_{0.5}TiO_2$ spinel u = 0.26[13] (calculated value 0.26). Each TiO_6 octahedron shares three pairs of opposite edges (six in total) as shown in Fig. 1. Multiple edge sharing results in distortion of all O–Ti–O angles from their regular value of 90° due to repulsion of the Ti^{4+}-ions across the shared edges with half of the angles being 96° and their adjacent angles being 84° (calculated values 98° and their adjacent angles 82°). This brings the separation between O-ions forming the shared edge to 2.67 Å. Compared to rutile TiO_2,[17] where one pair of opposite edges is shared, the deviations of the O–Ti–O angles from 90° are smaller and not sufficient to screen the repulsions between pairs of Ti-ions across the shared edges efficiently without an elongation of Ti–O bonds from the value typical for tetravalent Ti (1.94–1.97 Å) to 2.06 Å, a typical value for trivalent Ti (2.05–2.1Å)[29] with a concomitant reduction of the charge on titanium ions and increase of the charge on oxygen ions.

Table 1 Cell parameters of spinel $Li_{0.5}TiO_2$ and rock-salt $LiTiO_2$

Structure	Calc. a/Å	Exp.[13] a/Å
$Li_{0.5}TiO_2$	8.40	8.41
$LiTiO_2$	8.36	8.37

Table 2 Fractional coordinates of Li-, Ti- and O-ions in $Li_{0.5}TiO_2$ and rock-salt $LiTiO_2$/Å

Structure	Ion	Calc.	Exp[13]
$Li_{0.5}TiO_2$	Li	0.125	0.125
	Ti	0.5	0.5
	O	0.262	0.263
$LiTiO_2$	Li	0	0
	Ti	0.5	0.5
	O	0.247	0.245

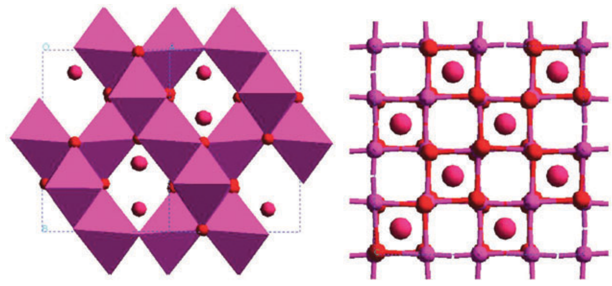

Fig. 1 The structure of $Li_{0.5}TiO_2$ spinel. A—side view in polyhedral representation. B—top view.

Therefore, Li-ions on sites belonging to the spinel structure, which will be further referred to as framework lithium ions, play an essential role in the structural stability of the $Li_{0.5}TiO_2$ spinel. Their charge donated to the lattice (−0.86 e per Li-ion) is distributed between O- and Ti-ions (approximately, in the proportion 2 : 1) to stabilise the elongation of the Ti–O bonds. The charge donated to Ti-ions is accommodated in hybridized t_{2g} orbitals with their main lobes pointing into open O–Ti–O angles (Fig. 2) to minimize repulsion with the valence charge density as discussed in ref. 17. This gives rise to a significant density of states at the Fermi energy (Fig. 3) and a tendency to instability including a superconducting transition at 13.7 K.[8,9] Increased disorder of Li-positions at high temperatures (T = 840 °C) results in a phase transformation to the ramsdellite $Li_{0.5}TiO_2$ phase,[30] which is metastable with respect to spinel at 0 K by 0.075 eV. When a fraction (up to 25%) of the framework Li-ions is removed from $Li_{0.5}TiO_2$, Ti-ions take their place.[23] An attempt to delithiate $Li_{0.25}TiO_2$ further was unsuccessful,[23] and to our knowledge the spinel-structured TiO_2 phase has not been observed.

As the framework Li-ions occupy only 1/8 of the tetrahedral sites (8a sites), both vacant octahedral (16c sites) and tetrahedral sites (8b sites) are potentially available for Li-intercalation. The latter have not been included in the cluster model discussed above.[12] The relative stability of these insertion sites

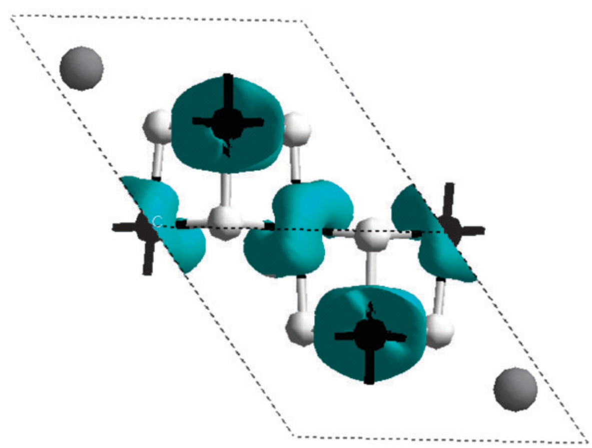

Fig. 2 The primitive unit cell of $Li_{0.5}TiO_2$ in rhombohedral representation together with an isosurface of the electron charge density.

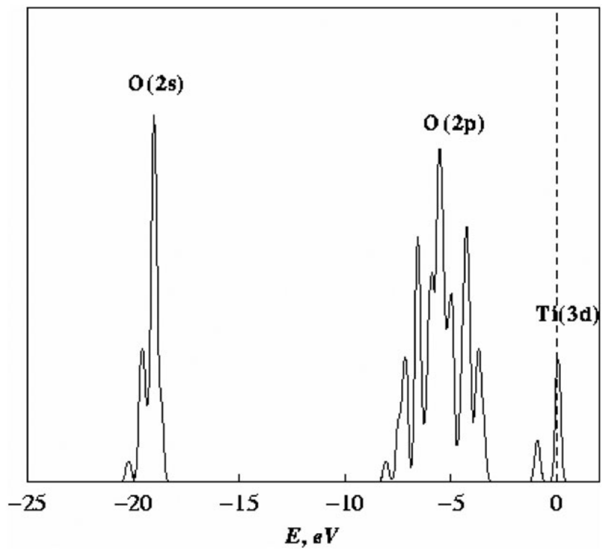

Fig. 3 Density of states for $Li_{0.5}TiO_2$ spinel. The Fermi level is shown as a vertical dashed line.

is determined by the local geometry of the neighbouring TiO_6 octahedra. In $Li_{0.5}TiO_2$, the distortions of the O–Ti–O angles described above create an ideal geometry for a Li-ion in a tetrahedral site with four Li–O contacts at 2.00 Å, which is a typical Li^+O^{2-} distance,[31] while the neighbouring octahedral sites are too spacious (offering Li–O contacts at 2.20 Å or more) and they are therefore unfavourable for Li occupancy. As a result, the framework Li-ions are distributed over tetrahedral sites to form a regular net with a Li–Li separation of at least 3.57 Å (compared to a typical Li–Li distance in Li-intercalated TiO_2 of around 3 Å), so that their interactions are efficiently screened.

Upon intercalation of Li-ions (with the formation of $Li_{0.5+x}TiO_2$, $x < 0.5$), strong coupling between electronic and structural degrees of freedom results in additional local distortions of the TiO_6 octahedra, which reverses the relative stability of tetrahedral and octahedral sites. Note the cluster model of Wagemaker *et al.*[12] does not account for such a reversal of stability. The hybridised t_{2g} orbitals displayed in Fig. 2 accommodate the electron density donated by both the framework and the intercalated Li-ions. This is in contrast to rutile, where the donated charge is localized first on the d_{yz} and subsequently on the d_{xy} orbitals leading to strong elongation of the corresponding Ti–O bonds.[13] As the charge is delocalized, no such elongation occurs in spinel. Although all Ti–O distances increase, they stay within the range typical values of Ti^{3+}–O^{2-} bonds[29] (from 2.06 Å in $Li_{0.5}TiO_2$ to 2.1 Å in $LiTiO_2$).

The extra charge has an important effect on the O–Ti–O angles. There are at least two factors that contribute to the gradual opening of the smaller angles at the expense of the adjacent larger angles: repulsion between the valence charge and the donated charge within the smaller angles, and increased repulsion between more negative oxygen ions forming a shared edge. This deformation causes the tetrahedral sites to close (Li–O at less than 1.80 Å) so that they become unsuitable for Li-ions while the octahedral sites become more favourable

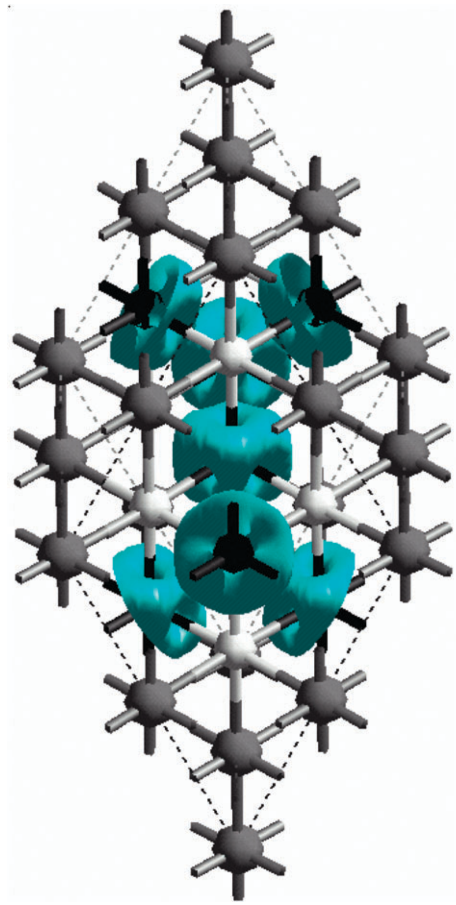

Fig. 4 Isosurface of the charge density in $LiTiO_2$ rock salt.

as their new geometry allows for a six-fold Li–O-coordination at 2.00 Å. Additionally, interactions of the less ionized octahedral Li-ions (donating −0.76 *e* in octahedral sites rather than −0.86 *e* in tetrahedral sites) are screened more rapidly allowing for shorter Li–Li distances. Therefore, a stable Li-rich phase with a highly regular, cubic, rock-salt-like structure will be formed (Fig. 4) in which all O–Ti–O angles are close to 90°, and all Li-ions occupy the centre of octahedral sites, *i.e.* a two-phase Li-insertion mechanism which is in fact observed in Li-intercalated spinel.[1–7] A slight decrease in the unit cell volume can be expected upon intercalation as more regular octahedra can be better packed.

First-principles calculations of supercells containing Li_n-$Ti_{16}O_{32}$, n = 8–16, confirm the above picture of Li-intercalation into $Li_{0.5}TiO_2$ spinel and provide a more detailed insight into the process. The intercalation of Li-ions proceeds immediately into octahedral sites as the tetrahedral sites are unstable with respect to the motion of the Li-ions to a neighbouring octahedral site. Occupation of an octahedral site has a strong influence on the framework Li-ions in tetrahedral sites. Each octahedral site has two framework Li-ions in neighbouring tetrahedral sites at a distance of only 2.3 Å (compared to a typical Li–Li distance in Li-intercalated TiO_2 of around 3 Å). The strong repulsion with the octahedral Li-ions pushes these neighbouring tetrahedral ions away from their crystallographic positions. This results in one of the neighbouring tetrahedral Li-ions migrating to a neighbouring

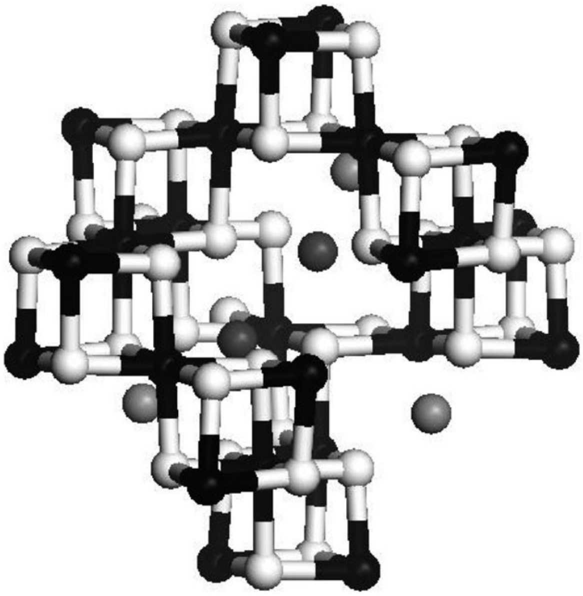

Fig. 5 A fragment of the lowest energy configuration of $Li_9Ti_{16}O_{32}$. Ti-ions are shown in black, O-ions in white, tetrahedral Li-ions in light grey and octahedral Li-ions in dark grey.

octahedral site leaving the tetrahedral site vacant as shown in Fig. 5. There is a small barrier associated with this displacement (0.04 eV), which decreases as the concentration of Li-ions grows. In the resulting geometry both the intercalated and displaced framework Li-ions reside in off-centre positions within the octahedral sites in order to reduce the repulsive interaction with the remaining neighbouring tetrahedral Li-ions. The enforced depopulation of the local tetrahedral site has a consequence for further Li-insertion. Such insertion proceeds into octahedral sites neighbouring both the tetrahedral vacancy and the octahedral Li-ions, which is more favourable than intercalation into an isolated octahedral site by 0.06 eV. The occupancy of neighbouring sites by Li-ions rather than sites with maximum separation can be interpreted as an effective attraction between Li-ions and can be seen as the local mechanism which results in the formation of the particularly stable rock-salt-like Li-rich phase. Up to a composition of $Li_{0.6875}TiO_2$ (3 Li-ions added to a conventional cubic cell of $Li_8Ti_{16}O_{32}$) the octahedral Li-ions reside in off-centre positions and gradually shift towards the centre as the number of occupied neighbouring Li-positions increases and the O–Ti–O angles become more regular. At $Li_{0.75}TiO_2$ (4 Li-ions added) the predicted homogeneous phase is different with all Li-ions occupying distorted tetrahedral sites in favour of a mixture of octahedral sites (inserted and neighbouring framework Li) and tetrahedral sites (other framework Li) predicted at smaller concentrations. This occurs because of the strong repulsions between the Li-ions in tetrahedral and octahedral sites. As a result it might be expected that ions move back into tetrahedral sites but a comparison of the total energies shows that single-state configurations at these concentrations are metastable with respect to coexistence of the $Li_{0.5}TiO_2$ and $LiTiO_2$ phases, in which all 16c octahedral sites are occupied by the Li-ions (by 0.08 eV for $Li_{0.75}TiO_2$). It is therefore unlikely that the $Li_{0.75}TiO_2$ phase will be achieved in practice. In $Li_{0.875}TiO_2$ and higher concentrations all Li-ions occupy the centre of octahedral sites, all O–Ti–O angles adopt a value close to 90°, and the expected stable rock-salt-like structure is adopted. As expected upon formation of the rock-salt structure, a small decrease in the cell parameters is observed in both computed and experimental structures (see Table 1). The computed energies imply that intercalation will proceed through a two-phase equilibrium of the $Li_{0.5}TiO_2$ and $LiTiO_2$ phases and are in agreement with the observed shape of the equilibrium voltage profile.[1,2] The equilibrium voltage estimated from the relative energies of these structures is 1.48 eV which is also in excellent agreement with the measured value (1.34–1.5 eV[2,3]). The concentration dependence of the barrier for the displacement of the framework Li-ions from tetrahedral to octahedral sites upon Li-intercalation suggests that at very low concentration and low temperatures these Li-ions may remain tetrahedral, which would delay the nucleation of the Li-rich phase by making further Li-intercalation into neighbouring octahedral sites energetically unfavourable. This leads to a small increase in the lattice parameter (0.5% at $x = 0.0625$), which may explain the small increase of the cell parameter at very low Li-concentrations reported for $Li_{0.5}TiO_2$[7] and $Li_{4/3}Ti_{5/3}O_4$.[6]

Conclusions

It has been demonstrated that intercalation behaviour of $Li_{0.5}TiO_2$ is dominated by a strong coupling between electronic and structural degrees of freedom and can be successfully predicted from its lattice morphology. Structural distortions associated with the accommodation of the charge donated upon intercalation in hybridized t_{2g} states, which are partly occupied in undoped $Li_{0.5}TiO_2$, create a new low-energy site for Li-ions. As a result, a particular stable Li-rich rock-salt-structured phase is formed and intercalation proceeds through a two-phase equilibrium at a constant potential. The predicted intercalation behaviour of the $Li_{0.5}TiO_2$-based spinel is in excellent agreement with experimental observations.

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