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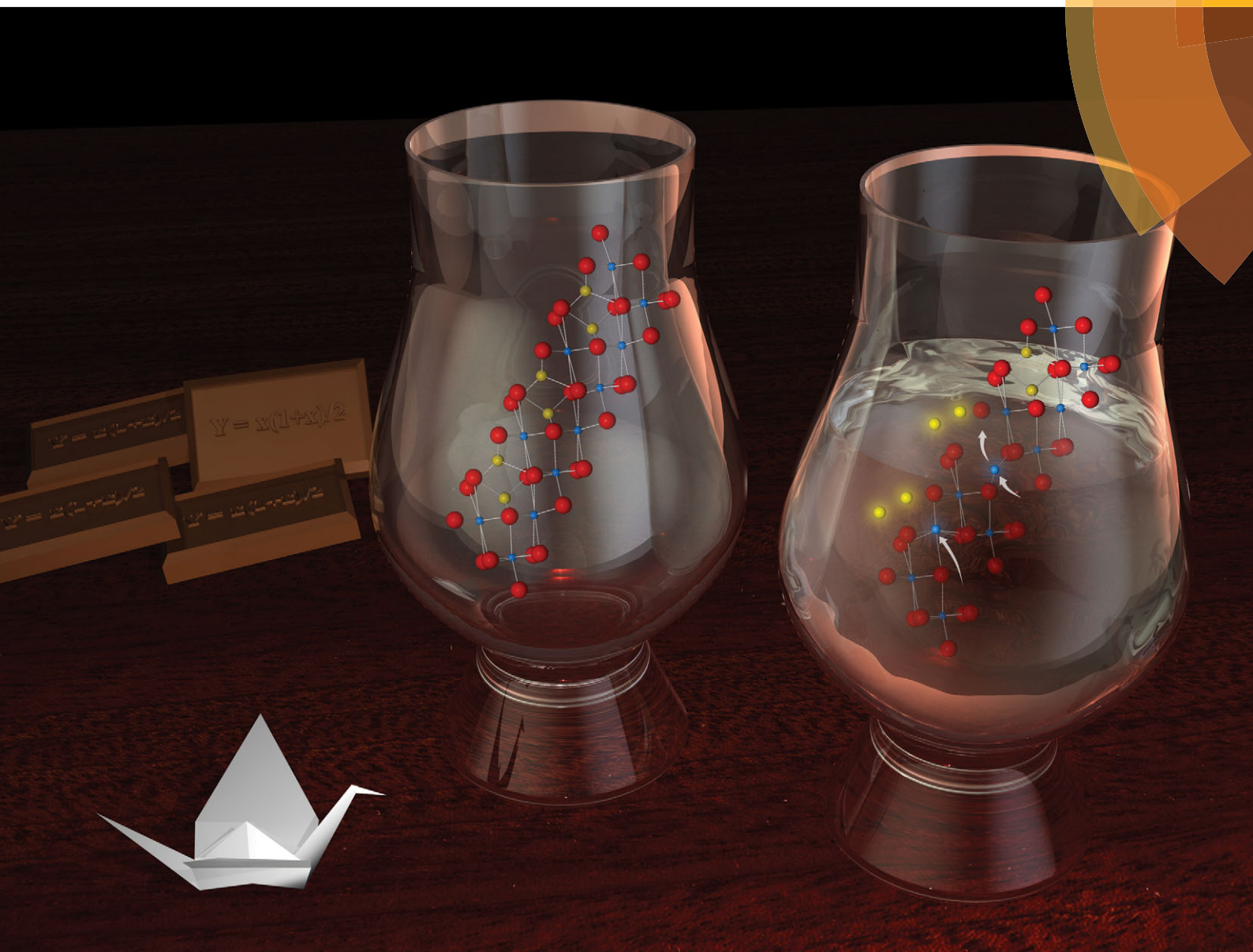
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## COMMUNICATION

# Titanium migration driven by Li vacancies in $Li_{1-x}Ti_2O_4$ spinel†

A. Kitada,[a] A. M. Arevalo-Lopez[b] and J. P. Attfield*[b]

Gentle oxidation of lithium titanate spinel ($LiTi_2O_4$) with water at room temperature gives Li-deficient $Li_{0.33}Ti_2O_4$. Combined X-ray and neutron Rietveld analysis shows that 28% of the Ti cations are displaced to alternative octahedral sites, in keeping with a proposed model based on Ti-migration limited by Li-vacancy concentration.

Lithium transition metal oxide spinels have important physical and electrochemical properties. $LiTi_2O_4$ spinel has been extensively studied as it displays superconductivity with a critical temperature of 11 K.[1–6] Lithium titanate spinels also have attractive properties as negative electrodes for lithium ion batteries such as a very flat potential and a relatively low volume change upon charging–discharging and with a good rate performance.[7–13]

The cubic spinel structure of $LiTi_2O_4$ consists of cubic-close-packed (ccp) oxide layers with Li cations occupying tetrahedral sites (with symmetry label 8a in the $Fd\bar{3}m$ space group) and Ti cations in 16d octahedral sites, and is written here as $(Li)_{8a}[Ti_2]_{16d}O_4$. Alternative 16c octahedral cation sites (marked 'X' on Fig. 1) close to the 8a sites are empty and define a three-dimensional network of channels through which lithium ions diffuse during electrochemical reactions. Intercalation of additional lithium into $LiTi_2O_4$ results in migration of Li cations from 8a to 16c sites, giving an ordered rocksalt type product denoted as $\{Li_2\}_{16c}[Ti_2]_{16d}O_4$.[5,8,14]

The structural consequences of delithiating $LiTi_2O_4$ to form $Li_{1-x}Ti_2O_4$ are less well understood. Electrochemical delithiation was found to be limited to a deficiency of $x \sim 0.3$ due to oxidative decomposition of the electrolyte[3] so chemical methods have mainly been used. An early study showed delithiation up to $x = 0.8$ could be achieved with iodine in acetonitrile. The product $Li_{0.2}Ti_2O_4$ was reported to be a cation-disordered defect rocksalt material (cubic, $a = 4.116$ Å) without spinel superstructure peaks,
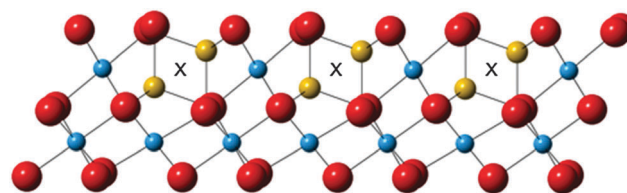


**Fig. 1** Structure of $LiTi_2O_4$ spinel showing cation sites between two successive close packed oxide layers. Li(8a)/Ti(16d)/O(32e) are shown as yellow/cyan/red spheres, and interstitial 16c sites between pairs of Li sites are marked by crosses. Lower/upper cation layers are labelled Layer 1/Layer 2 in the text.

indicating that 16c and 16d sites have equal cation occupancies.[8] A wide two-phase region between $x \approx 0.15$ and $x \approx 0.7$ has subsequently been reported.[6] Samples in the small-$x$ region maintain the spinel cation arrangement although a small amount of Ti migration was observed, e.g. 1.8% Ti migration from 16d to 16c sites at $x = 0.14$.[4] The $x \approx 0.7$ product was reported to have substantial Ti occupancy of the 16c octahedral sites and also the tetrahedral 8a sites.[6] However both oxidation methods used gave secondary phase impurities; oxidation by air introduced an amorphous carbonate impurity and $Br_2$ or $I_2$ treatments led to a non-spinel $Li_{1-y}Ti_{2-y}O_3$ secondary phase. A simple oxidation method to generate high purity material is thus needed to determine the structure and degree of cation migration in $Li_{1-x}Ti_2O_4$ accurately.

Here we report the preparation of lithium-deficient disordered spinel $Li_{0.33}Ti_2O_4$ by mild oxidation through immersion in water at room temperature (RT). The sample has been characterized by chemical and thermogravimetric (TGA) analysis, and combined powder X-ray and neutron structure refinement has been used to establish the cation distribution from which a likely migration mechanism is proposed.

The $LiTi_2O_4$ spinel precursor was prepared by a reported solid state method.[2] Immersion of $LiTi_2O_4$ in water for short periods of a few days was found to produce two-phase spinel samples like those reported previously.[6] To obtain the $x \approx 0.7$ phase, 0.1608 g of $LiTi_2O_4$ precursor was delithiated chemically

[a] Department of Materials Science and Engineering, Kyoto University, Yoshida-honmachi, Sakyo, Kyoto 606-8501, Japan

[b] Centre for Science at Extreme Conditions (CSEC) and School of Chemistry, University of Edinburgh, Edinburgh EH9 3FD, UK. E-mail: j.p.attfield@ed.ac.uk

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by reaction with distilled water (100.0 ml) in a capped flask for 2 weeks at RT. Bubbles were seen when the precursor was immersed due to evolution of $H_2$ and the solution became strongly basic (pH = 12). The reaction is;

$$LiTi_2O_4 + xH_2O \rightarrow Li_{1-x}Ti_2O_4 + (x/2)H_2 + xLiOH,$$
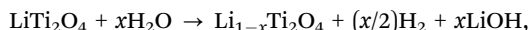
and the Li concentration in the solution after delithiation was measured using ICP-AES giving $x = 0.667$. The blue-black sample was filtered and dried at RT in a desiccator for a few days. TGA was performed by heating the product up to 1000 °C in air at 2 °C min$^{-1}$. Oxidation of $Li_{1-x}Ti_2O_4$ gave a 1.6% mass gain corresponding to $x = 0.67$, in excellent agreement with the ICP-AES result. The final TGA product was white, consistent with full oxidation of $Ti^{3+}$ to $Ti^{4+}$. Combustion analysis (by the Elemental Analysis Service of London Metropolitan University) revealed that the water-treated $Li_{1-x}Ti_2O_4$ sample contained <0.1% C and H. This rules out possible $Li^+/H^+$ ion exchange or water incorporation during deintercalation, and shows that LiOH or $Li_2CO_3$ impurities are not present. Hence, although many previous deintercalation studies have used dry non-aqueous solvents, water oxidation is found to be a useful method for preparation of $Li_{1-x}Ti_2O_4$.

Powder X-ray diffraction (PXRD) data from a Bruker D2 instrument using CuKα radiation displayed in Fig. 2 show only spinel peaks from the $Li_{0.33}Ti_2O_4$ sample with no secondary phases, unlike products in ref. 6. Substantial diffuse scattering in the background evidences disorder of the heavy Ti atoms within the spinel lattice. Rietveld fits showed that Ti is disordered over octahedral 16c and 16d sites, but did not give a significant improvement ($R_{wp}$ decreased slightly to 5.71 from 5.76%) when Ti was also allowed to occupy the tetrahedral 8a Li sites as proposed elsewhere,[6] so this possibility was not considered further.

Powder neutron diffraction (PND) data were collected from 0.1 g of the $Li_{0.33}Ti_2O_4$ sample on instrument D20 at ILL Grenoble with a neutron wavelength of 1.3029(4) Å. Combined fits to the PXRD and PND profiles using the GSAS package[15] were used to test further Li/Ti disorder models. The total lithium content was fixed to 0.33 in keeping with the ICP-AES and TGA results. Ti was found to be disordered over 16c and 16 d sites. Models where Li was allowed to occupy alternative 8b tetrahedral sites, or co-occupy octahedral 16c or 16d positions with Ti gave insignificant or negative Li occupancies at those sites. Hence we conclude that the average structure of the Li-deficient $Li_{1-x}Ti_2O_4$ spinel phase is best described by the model shown in Table 1, with Li at tetrahedral 8a sites only, and Ti at octahedral 16c and 16d sites with respective 28 and 72% occupancies for $Li_{0.33}Ti_2O_4$.[†] The Li–O distance is 1.867(2) Å and Ti(16c)–O and Ti(16d)–O distances are 2.113(2) and 2.019(1) Å. The predicted $Ti^{3.83+}$–O length of 1.983 Å based on ionic radii[16] is close to the Ti(16d)–O value, but the Ti(16c)–O distance is long and suggests that local rearrangement occurs around occupied 16c sites.

Substantial migration of Ti cations during a reaction at RT is surprising in view of the strength of Ti–O bonds, but this effect is consistently observed in $Li_{1-x}Ti_2O_4$ spinels, and a similar
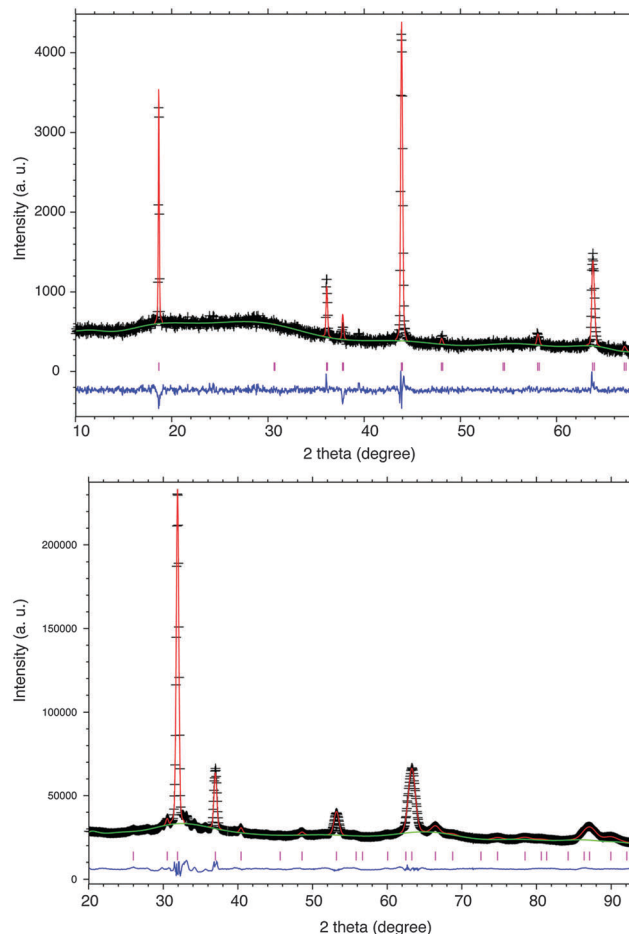


Fig. 2 Rietveld fits from the combined refinement of $Li_{0.33}Ti_2O_4$ against PXRD (upper, weighted profile residual $R_{wp}$ = 5.69%) and PND (lower, $R_{wp}$ = 2.06%) profiles at RT.

Table 1 Refined structural parameters for $Li_{0.33}Ti_2O_4$ in space group $Fd\bar{3}m$ (No. 227). The cubic cell parameter is $a$ = 8.259(3) Å

| Atom | Site | $x$ | $y$ | $z$ | Occupancy | $U_{iso}$ (Å$^2$) |
|---|---|---|---|---|---|---|
| Li(1) | 8a | 0.125 | 0.125 | 0.125 | 0.33 | 0.0442(8) |
| Ti(1) | 16d | 0.5 | 0.5 | 0.5 | 0.719(8) | 0.0442 |
| Ti(2) | 16c | 0 | 0 | 0 | 0.281 | 0.0442 |
| O(1) | 32e | 0.2557(2) | 0.2557 | 0.2557 | 1.00 | 0.0273(4) |

disorder was reported in delithiated $LiV_2O_4$ spinel with cation distribution $(Li_{0.28}V_{0.1})_{8a}\{V_{0.4}\}_{16c}[V_{1.5}]_{16d}O_4$.[17] Migration of V to tetrahedral 8a sites was attributed to $V^{5+}$ formation, but tetrahedral coordination of $Ti^{4+}$ is less likely and is not evidenced in our study for $Li_{0.33}Ti_2O_4$. It is evident that the hypothetical fully delithiated $[Ti_2]_{16d}O_4$ spinel form of $TiO_2$ is highly unstable. This has been explained through first principles calculations which confirm that the hypothetical $Fd\bar{3}m$ $[Ti_2]_{16d}O_4$ polymorph is much less stable than rutile, anatase, brookite, ramsdellite, or the high pressure α-PbO$_2$ forms of $TiO_2$.[18] In the case of manganese, by contrast, $[Mn_2]_{16d}O_4$ with $Fd\bar{3}m$ symmetry has been proven to be stable both experimentally and theoretically.[19–21] This shows that Ti cation size as well as charge is significant in destabilising $[Ti_2]_{16d}O_4$.

We note that a straightforward explanation for the migration of octahedral cations in delithiated $Li_{1-x}Ti_2O_4$ spinels can be given on the basis of the occupancy of octahedral sites between close-packed oxide layers. Several kinds of stacking are observed among stable $TiO_2$ polymorphs; rutile, ramsdellite and the $\alpha$-$PbO_2$ form are close to hexagonal close-packing (hcp), anatase has ccp, and brookite has a mixed ccp–hcp sequence.[5] $Ti^{4+}$ ions occupy half of the octahedral sites between each pair of oxide layers in all of these structures. This provides a key distinction from the hypothetical $[Ti_2]_{16d}O_4$ spinel polymorph. The $LiTi_2O_4$ spinel structure has two alternating types of layer in terms of cation occupancy as shown in Fig. 1. One type (labelled Layer 1) has 3/4 of the octahedral sites filled by Ti, while the other (Layer 2) has 1/4-filling of octahedral Ti sites plus half the tetrahedral sites occupied by Li. Complete delithiation to give $[Ti_2]_{16d}O_4$ would leave a 3 : 1 Layer 1 : Layer 2 ratio of occupied octahedral sites which is highly disfavoured due to cation–cation repulsions with respect to 1 : 1 distributions. The alternative 16c sites in spinel have a 1 : 3 Layer 1 : Layer 2 ratio, so migration from 16d to 16c sites is a mechanism for equalizing the filling of octahedral sites in the two layer types. The observed 16d and 16c Ti occupancies of 72 and 28% in our refinement of $Li_{0.33}Ti_2O_4$ are equivalent to a Layer 1 : Layer 2 octahedral Ti ratio of 0.61 : 0.39, showing that the populations are approaching equality.

To consider if there is any quantitative relationship between Li deficiency and the degree of Ti migration in $Li_{1-x}Ti_2O_4$, we write the cation distribution as $(Li_{1-x})_{8a}\{Ti_y\}_{16c}[Ti_{2-y}]_{16d}O_4$. The boundary conditions are $y = 0$ at $x = 0$, as no migration is observed in stoichiometric $LiTi_2O_4$, and $y = 1$ at $x = 1$ as cation–cation repulsions favour equal Layer 1 and Layer 2 populations as noted above (corresponding to a hypothetical $\{Ti\}_{16c}[Ti]_{16d}O_4$ disordered and defective rocksalt polymorph of $TiO_2$). The simplest relationship $y = x$ is in poor agreement with the observed $y = 0.56$ (twice the 16c occupancy) for $x = 0.67$ for our $Li_{0.33}Ti_2O_4$ sample. A better description requires consideration of interactions between Li and Ti cations where clustering leads to $y < x$. Each 16c site is only 1.79 Å from two 8a Li sites, so both of these tetrahedral sites have to be vacant for the 16c site to be occupied by Ti (see Fig. 1). Hence we propose that for small $x$, local defect clusters of two Li vacancies surrounding an interstitial Ti at 16c are formed. This assumption gives $y = x/2$ at small $x$. Combining this with the above boundary conditions gives a simple quadratic variation $y = (x/2)(1 + x)$, which provides an approximate description of greater degrees of clustering at high $x$. For our highly deficient $x = 0.67$ sample this equation predicts $y = 0.56$ (16c Ti occupancy = 0.28), in perfect agreement with the observed populations in Table 1. This indicates that Ti migration from 16d to 16c sites in highly Li-deficient $Li_{1-x}Ti_2O_4$ is limited by the distribution of remaining Li cations, with Li vacancies clustering around Ti cations on 16c sites.

For $Li_{0.86}Ti_2O_4$ which represents the distinct small Li-deficiency ($x < 0.15$) phase, the $y = 0.08$ value predicted by the clustering model is somewhat larger than the reported value of 0.04.[4] This suggests that defect clustering may drive the phase separation observed between $x \approx 0.15$ and $x \approx 0.7$ in the $Li_{1-x}Ti_2O_4$ system,[6] with very little Ti migration in the small-$x$ region, and a cascade effect above the $x \approx 0.15$ limit where Li vacancies and 16c Ti cations cluster in small areas with large $x \approx 0.7$.

Clustering of vacancies and cations is reported in many other solids and may be associated with electronic effects such as charge order or metal–metal bonding. For example, in $Na_{1-x}CoO_2$, redistribution of $Na^+$ into two prismatic sites between $CoO_2$ layers is accompanied by $Co^{3+}/Co^{4+}$ charge ordering,[22] while in $KNi_2Se_2$ Ni–Ni bonding is an electronic driving force for vacancy formation and Ni migration into adjacent K layers.[23] Hence Ti–Ti bonding[8] and local $Ti^{3+}/Ti^{4+}$ charge order may also play a part in the Ti migration in $LiTi_2O_4$.

In conclusion, water oxidation is demonstrated to be a useful method for obtaining Li-deficient $Li_{1-x}Ti_2O_4$ spinels without decomposition to other Ti oxide phases. Combined PXRD and PND refinement shows that $Li_{0.33}Ti_2O_4$ has Li at tetrahedral sites only, but Ti is disordered over two octahedral positions. This Ti migration acts as a mechanism for equalizing the filling of octahedral sites between close-packed oxide layers to minimize cation–cation repulsions. The wide immiscibility gap between $x \approx 0.15$ and 0.7 is driven by clustering of Li vacancies and 16c Ti cations. Further microstructural and computational investigations of defect clustering and phase segregation will be useful to add further insights.

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