

STRUCTURE AND ELECTROCHEMISTRY OF THE SPINEL OXIDES LiTi_2O_4 AND $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$

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Summary

LiTi_2O_4 is metallic, has the cubic spinel structure and is known to react with one further lithium atom to form $\text{Li}_2\text{Ti}_2\text{O}_4$. We find that the related spinel $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$, which is electrically insulating, also reacts reversibly with one lithium atom. Both $\text{Li}/\text{LiTi}_2\text{O}_4$ and $\text{Li}/\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ cells cycle reversibly with little capacity loss for over 100 cycles, but have subtle differences in their voltage profiles. We interpret the differences in cell behaviour using arguments based on the band structure of $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$.

Introduction

The spinel oxides LiTi_2O_4 and $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ are the end members of the solid solution series $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ for $0 \leq x \leq 1/3$. The two compounds exhibit completely different properties. LiTi_2O_4 is a dark-blue, metallic compound, whereas $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ is white and insulating. However, both materials react reversibly with lithium at room temperature in electrochemical cells [1]. Here we discuss the structure and electrochemistry of these spinel oxides.

A unit cell of the ideal face-centered-cubic (f.c.c.) spinel structure of LiTi_2O_4 consists of a cubic-close-packed array of 32 oxygen atoms occupying sites 32e of space group $Fd\bar{3}m$. One-eighth of the 64 tetrahedral holes per unit cell (sites 8a) and one-half of the 32 octahedral holes per unit cell (sites 16d) are filled by the cations Li and Ti, respectively. Figure 1 shows half a unit cell of the spinel structure. The resultant unit cell contains eight formula units of LiTi_2O_4 . Lithium substitutes for titanium in octahedral titanium sites in the $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ phase [1]. Both materials are stable in air.

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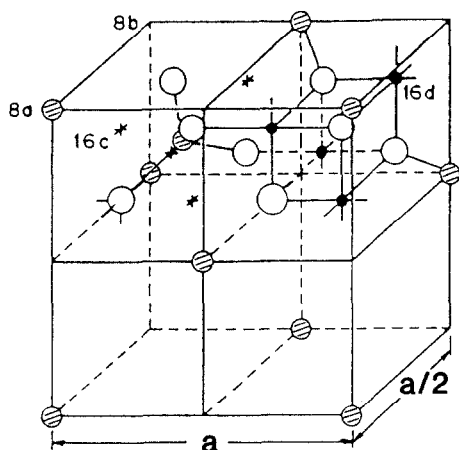


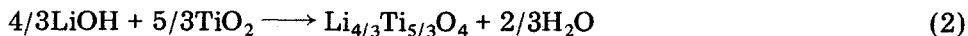
Fig. 1. Half a unit cell of the spinel structure showing the position of 8a (⊗) and 16d (●) cations, some of the 32e oxygens (○); 8b (•) and 16c (*) interstitial sites of one quarter (two octants) of the unit cell.

Experimental

Our purest samples of $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ were obtained by one of two methods. In the first, the following one-step reaction was used.



Stoichiometric quantities of the starting materials were ground together to a fine uniform powder which was pressed into pellets at 15 000 psi. The pellets were fired in an alumina boat, at 900 °C, in air, for 20 h, after which they were quenched in air to room temperature. The lattice constant of our $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ was $a = 8.367 \pm 0.002$ Å. Harrison *et al.* [2] report a value of $a = 8.358$ Å, which is smaller than the value we obtained. The rutile form of TiO_2 was present as an impurity of approximately 10% in the product. In the second method, the reaction



was used. This reaction was carried out, in alumina crucibles lined with nickel-foil, under a helium atmosphere at 800 °C. The helium was closed to the outer atmosphere but the escape of any excess gas pressure was allowed through an oil bubbler. Unlike many crucibles, nickel-foil was found to be inert to reaction with the materials involved in these reactions and thus made an excellent lining for the reaction vessels. Pellets of the LiOH/TiO_2 mixture were pressed prior to firing. The product of this reaction is substantially pure and gives lattice constants equal to those of $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ prepared from Li_2CO_3 .

The synthesis of LiTi_2O_4 is considerably more dependent on the reaction conditions. Our most successful method involves a two-step reaction



Powdered mixtures of lithium carbonate and titanium dioxide (anatase) were fired in an alumina boat, at 750 °C in air, for approximately 16 h. The starting materials for the preparation of LiTi_2O_4 were sifted together (180 μm) and sealed under vacuum (50 mT) in a quartz tube. The tube was then heated, at a rate of 150 °C h^{-1} , to a temperature of 850 °C, at which temperature the reaction mixture remained for 16 h. X-ray diffraction showed no apparent impurities in the LiTi_2O_4 product, but the walls of the quartz tube were clouded by their reaction with lithium. The lattice constant was $a = 8.416 \pm 0.002$ Å. Harrison *et al.* [2] report a value of $a = 8.405$ Å which, again, is smaller than our value.

Both LiTi_2O_4 and $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ are known to react with one further lithium atom to form $\text{Li}_2\text{Ti}_2\text{O}_4$ and $\text{Li}_{7/3}\text{Ti}_{5/3}\text{O}_4$, respectively [1]. Figures 2 and 3 show the voltage, $V(x)$, for an $\text{Li}/\text{Li}_{1+x}\text{Ti}_2\text{O}_4$ cell and an $\text{Li}/\text{Li}_{4/3+x}\text{Ti}_{5/3}\text{O}_4$ cell at 21 °C, for $0 \leq x \leq 1$, respectively. Both curves were obtained at discharge rates of 30 h for $\Delta x = 1$. For an ideal cell during a phase transition, the surface concentration of lithium remains fixed while the phase boundary moves through the crystal. This means that the chemical potential of Li in the cathode, μ_c , is constant, and from the equation

$$V(x) = [\mu_a - \mu_c(x)]/e \quad (5)$$

the voltage in a two-phase region is also constant. Thus, the plateaux in the $V(x)$ curves indicate the co-existence of $\text{LiTi}_2\text{O}_4/\text{Li}_2\text{Ti}_2\text{O}_4$ and of $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4/\text{Li}_{7/3}\text{Ti}_{5/3}\text{O}_4$ respectively. *In situ* X-ray diffraction confirmed the two-phase co-existence for LiTi_2O_4 and revealed that there is a slight decrease, from 8.416 Å to 8.380 Å [3], in the size of the unit cell on addition of lithium. In the case of $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$, the a lattice parameter increases slightly, from 8.36 Å to 8.37 Å, upon the addition of lithium. The average plateau voltages at 21 °C are 1.338 V for the $\text{Li}/\text{LiTi}_2\text{O}_4$ cell and 1.562 V for the $\text{Li}/\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ cell.

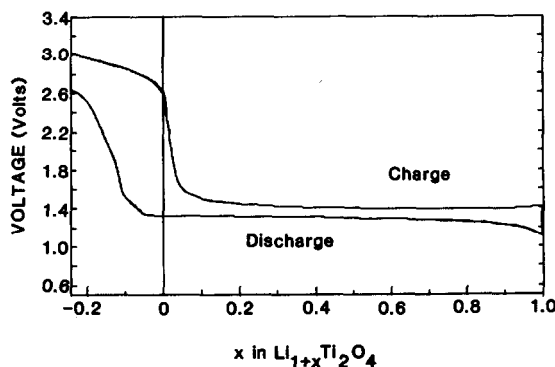


Fig. 2. $V(x)$ for $\text{Li}/\text{Li}_{1+x}\text{Ti}_2\text{O}_4$ cells at 21 °C and discharge rate of 30 h for $\Delta x = 1$.

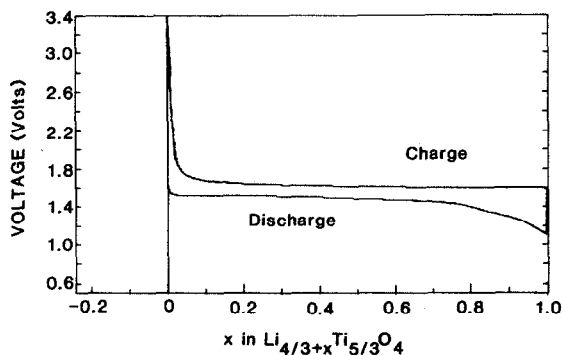


Fig. 3. $V(x)$ for $\text{Li}/\text{Li}_{4/3+x}\text{Ti}_{5/3}\text{O}_4$ cells at 21 °C and a discharge rate of 30 h for $\Delta x = 1$.

Discussion

$\text{Li}/\text{LiTi}_2\text{O}_4$ cells cycle reversibly through the flat portion of the voltage curve with little capacity loss for 100 cycles, as shown in Fig. 4. Figure 5 shows a similar curve for $\text{Li}/\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$. It is surprising that $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ cells are able to cycle at all as this material is electrically insulating and no graphite or other additive has been added to these cells to improve the conductivity. $\text{Li}_{7/3}\text{Ti}_{5/3}\text{O}_4$ is a dark-blue material that forms a conducting phase at the cathode surface on discharge of an $\text{Li}/\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ cell. However, it is not clear how the recharge of the cell works, since the cathode surface would then be an insulating $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ phase.

It has been reported [1] that Li can be removed from LiTi_2O_4 . Figure 2 shows that there is some reversible cell capacity near 2.8 V. Since new $\text{Li}/\text{LiTi}_2\text{O}_4$ cells have open circuit voltages near 2.0 V, this high voltage capacity corresponds to removing Li from the spinel host. By contrast, Fig. 3 shows that $\text{Li}/\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ cells do not show any capacity at high voltage that would correspond to a similar removal of Li from the $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ host material.

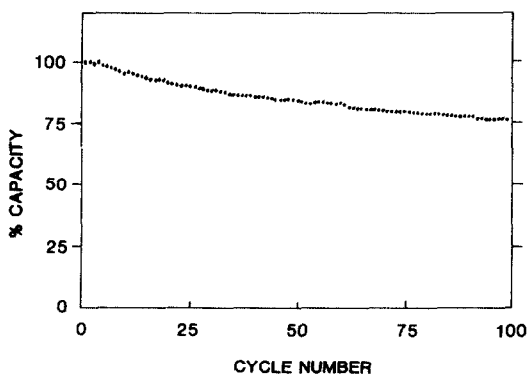


Fig. 4. Percent. cell capacity *vs.* cycle number for $\text{Li}/\text{Li}_{1+x}\text{Ti}_2\text{O}_4$ cells.

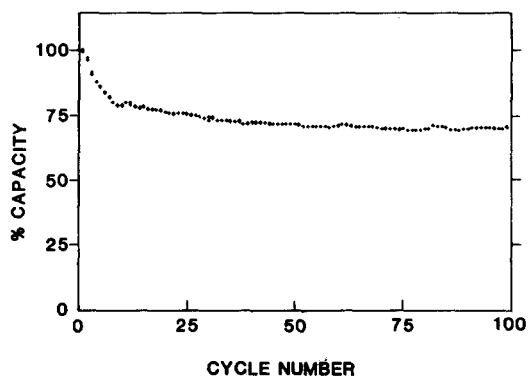


Fig. 5. Percent. cell capacity vs. cycle number for $\text{Li}/\text{Li}_{4/3+x}\text{Ti}_{5/3}\text{O}_4$ cells.

Figure 6 shows, schematically, the band structure for (a) LiTi_2O_4 and (b) $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ [2]. In LiTi_2O_4 , the $\text{Ti}:t_2$ band contains one electron per formula unit, corresponding to the mixed-valence states $\text{Ti}^{4+} + \text{Ti}^{3+}$. Removal of Li^+ ions from LiTi_2O_4 must be accompanied by the loss of an electron to maintain charge neutrality. The existence of such electrons in the t_2 band of

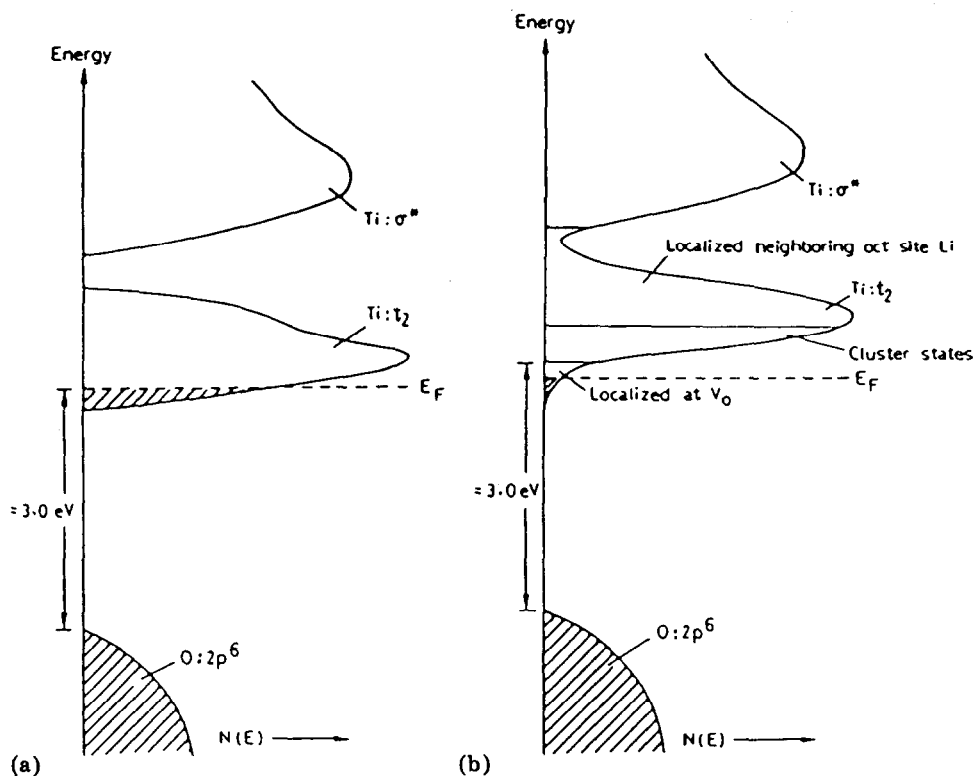


Fig. 6. Semi-empirical energy vs. density of states diagram for (a) LiTi_2O_4 and (b) $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$. (After Harrison *et al.* [2].)

LiTi_2O_4 allows such a removal to take place (Fig. 2). For $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ the Ti:t_2 band is unoccupied, so removal of Li^+ ions is not possible due to the lack of the necessary electrons to maintain charge neutrality. The energy band gap of approximately 3.0 eV between the Ti:t_2 band and the O:2p^6 band is apparently too large for the electrochemical removal of Li^+ ions from the host structure.

Conclusions

LiTi_2O_4 and $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ can be prepared from cheap starting materials. Cells employing these materials as cathodes show good reversibility and rate capability. As a result, it would be possible to use these cathode materials in practical cells for the 1.5 V rechargeable battery market.

Acknowledgements

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References

- 1 D. W. Murphy, R. J. Cava, S. M. Zahurak and A. Santora, *Solid State Ionics*, 9&10 (1983) 413 - 418.
- 2 M. R. Harrison, P. P. Edwards and J. B. Goodenough, *Philos. Mag. B*, 52 (1985) 679.
- 3 D. W. Murphy, M. Greenblatt, S. M. Zahurak, R. J. Cava, J. V. Waszczak, G. W. Hull and R. S. Hutton, *Rev. Chim. Mineral.*, 19 (1982) 441.