

ELECTROCHEMISTRY OF ANATASE TITANIUM DIOXIDE IN LITHIUM NONAQUEOUS CELLS*

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Summary

The electrochemical behavior of anatase TiO_2 ($>10^8$ ohm cm) was examined in 1M LiClO_4 -propylene carbonate/tetrahydrofuran solution at 30 °C.

The Li/anatase TiO_2 cell showed a stable working voltage of 1.780 ± 0.005 V under a low continuous drain below 20 mA g^{-1} . The high rate performance (ca. 700 mA g^{-1}), without the addition of any conductive binders, was also demonstrated in laboratory cells.

The reaction mechanism of anatase TiO_2 in lithium nonaqueous cells is discussed, in terms of topotactic lithium insertion into the anatase TiO_2 matrix up to 1 Fr mole $^{-1}$, using X-ray diffraction, *in situ* optical and electrochemical data.

1. Introduction

Titanium dioxides (TiO_2 s), especially anatase TiO_2 , have been of great interest to battery researchers and electrochemists since the application of anatase TiO_2 as a cathode-active material for lithium nonaqueous cells was indicated in 1979 [1].

In titanium dioxides, of whatever crystal structure, the Ti^{4+} ion is surrounded by six O^{2-} ions to form a unit octahedron. Different combinations of unit octahedra make different crystal structures, such as rutile, anatase, etc. Different types of TiO_2 s show remarkable differences in the ability to depolarize in lithium nonaqueous cells [1, 2]. In addition, pure TiO_2 s are inherently insulators and white in color because the Ti^{4+} ion has no d-electrons. Such an active material has not been known in the field of batteries based on aqueous solution.

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The interesting nature of anatase TiO_2 stimulated us to investigate it in more detail. In this paper we report on the re-examination of data on the electrochemical behavior of anatase TiO_2 in lithium nonaqueous cells, and discuss possible reaction mechanisms from X-ray diffraction, and *in situ* optical and electrochemical data.

2. Experimental

2.1. Materials

Titanium dioxides were prepared by the heat-treatment of metatitanic acid (H_2TiO_3) obtained from Teikoku Kako Co., Ltd. Metatitanic acid suspension was predried at *ca.* 100 °C for several days. Predried TiO_2 samples were heated at several temperatures for 4 h in air to attain the crystal growth of anatase TiO_2 . The crystal structure of the samples was identified using a Shimadzu X-ray diffractometer, type XD-3A, both with copper $K\alpha$ radiation filtered with nickel and with iron $K\alpha$ radiation filtered with manganese. BET surface areas and water contents of the samples were also examined using a Monosorp, type SA-1000 (Shibata Scientific Co., Ltd.), and a Karl Fischer automatic titrator, type MK-AS (Kyoto Electronic Co., Ltd.), respectively.

2.2. Electrochemical cell

The experimental cells consisted of a lithium anode (15 mm × 15 mm) and a TiO_2 cathode (15 mm × 20 mm) separated by a sheet of polypropylene nonwoven cloth (FT-330, Bylean Japan).

The cathodes were prepared by (i) pressing dry TiO_2 powder onto a screen; (ii) pasting TiO_2 dispersed in distilled water onto a screen; (iii) putting a dry TiO_2 pellet (11 mm dia., 10^3 kg cm^{-2} forming pressure) onto a stainless steel (SUS 304) screen (Dainippon Screen Co., Ltd.) with a 0.2 mm dia. stainless steel terminal wire spot-welded to the screen. Conductive binders such as acetylene black, carbon black or graphite, were not used except for special purposes. Cathodes were dried under vacuum at 150 °C before use.

The anodes were prepared by pressing a lithium sheet onto a stainless steel screen reinforced with 1 mm thick nickel plate. The lithium sheet was made by pressing a slice cut from a rod (99.9% purity, Rare Metallic Co., Ltd.).

After the cathodes had been wrapped in a nonwoven polypropylene bag, the anode and cathode were placed in a 3-ply (polyethylene/aluminum foil/polyethylene) flexible cell and 0.3 - 0.4 ml of electrolyte was introduced. The electrodes were placed under slight pressure by means of a commercial double clip. The cell was then sealed. All procedures were carried out in a dry box.

2.3. In situ optical measurement

In situ optical absorption measurements were carried out using a UV-visible spectrophotometer, model UV-240 (Shimadzu Corp.), in a cell of the type $\text{Li}/\text{electrolyte}/\text{TiO}_2/\text{In}_2\text{O}_3$ -coated glass as described previously [3].

The electrolyte used was 1M LiClO₄-propylene carbonate/tetrahydrofuran (1:1) solution containing less than 100 mg l⁻¹ of water. All electrochemical measurements were carried out at 30 °C. Other sets of experimental conditions are described in the Results section.

3. Results

3.1. Characterization of TiO₂ samples

The prepared samples were characterized by BET surface area, water content, and X-ray diffraction measurements. The results are summarized in Table 1. The water contents were obtained by a direct Karl Fischer method and the average of five runs is given.

The samples heat-treated below 500 °C showed ill-defined anatase peaks in the X-ray diffraction data, *i.e.*, no (1, 0, 3), (0, 0, 4) and (1, 1, 2) split, and no (1, 0, 5) and (2, 1, 1) split, etc. Higher heating temperatures reduced the surface area and the water content of samples and then the crystal structure of anatase was converted to rutile at 1000 °C. Of these samples, that heat treated at 700 °C was the most active and reliable material for the lithium nonaqueous cell. The cells using samples heat treated below 500 °C showed some lithium electrode deterioration after a week of storage at 60 °C and did not show a stable working voltage. On the other hand, the cells employing samples heat treated above 800 °C showed a lower activity than those with the sample heat treated at 700 °C. Therefore, the samples heat treated at 700 °C, which were well-defined anatase, were used hereafter.

3.2. Continuous discharge curves at low rate

Figure 1 shows the continuous discharge curve of the Li/anatase TiO₂ cell at a low rate (below 20 mA g⁻¹ of anatase TiO₂). The weight of TiO₂

TABLE 1
Characterization of prepared TiO₂ samples

Temp.* (°C)	Surface area** (m ² g ⁻¹)	Water content*** (wt.%)	Observation in XRD
200	191	3.80	ill-defined anatase
300	167	2.82	ill-defined anatase
400	121	2.01	ill-defined anatase
500	66	1.24	ill-defined anatase
600	39	0.78	well-defined anatase
700	21	0.58	well-defined anatase
800	7.5	0.29	well-defined anatase
900	4.3	0.14	well-defined anatase
1000	3 >	0.06	well-defined rutile

*Heating of metatitanic acid (H₂TiO₃) for 4 h.

**Monosorp method.

***Karl Fisher method.

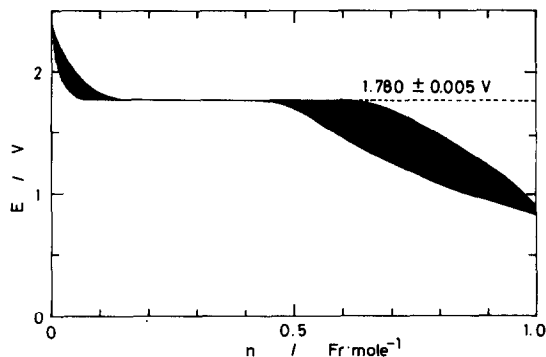


Fig. 1. Continuous discharge curve of a Li/anatase TiO_2 cell at a low rate (below 20 mA g^{-1}). No conductive binder in the cathode.

was varied from 10 to 100 mg. The degree of reduction, n , in Fr mole^{-1} , was calculated from the discharge capacity and the moles of TiO_2 used. Over 100 discharge curves of Li/ TiO_2 cells are shown in Fig. 1. The blocked-in area indicates the scattering of the results.

As can be seen, the Li/anatase TiO_2 cell shows a stable working voltage of $1.780 \pm 0.005 \text{ V}$ and the anatase TiO_2 is able to be reduced up to 1.0 Fr mole^{-1} in a lithium nonaqueous cell.

3.3. Pulse-discharge curve at high rate

In order to examine whether or not anatase TiO_2 is a suitable active material for heavy duty use, a high current pulse was applied to a Li/anatase TiO_2 cell. The result is shown in Fig. 2. The open circuit voltage curve in Fig. 2 agreed well with the low rate discharge curve in Fig. 1.

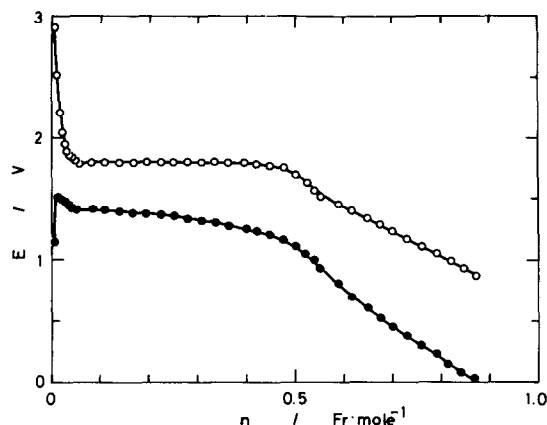


Fig. 2. Pulse-discharge curve (10 s current on, 320 s off) of a Li/anatase TiO_2 cell. Cathode: anatase TiO_2 , 29.5 mg (no conductive binder); current: $20 \text{ mA}/3 \text{ cm}^2$ (corresponding to 680 mA g^{-1}).

As is demonstrated in Fig. 2, anatase TiO_2 can be used in a lithium nonaqueous cell for heavy duty use.

3.4. Reversibility test

Although the reversibility of anatase TiO_2 in lithium nonaqueous cells has been reported [2 - 4], the reversibility was re-examined using a different method in order to obtain an understanding of the 1.780 ± 0.005 V level observed in discharge curves. For these tests, conductive binder and organic binder were used to give sufficient transmission lines and mechanical strength to the cathode and to minimize electrical isolation of active material during the charging process. Cells were discharged with a 6 mA pulse (10 s current on, 80 s off) to certain depths of discharge and then charged with a 3 mA pulse (10 s on, 80 s off). The results reported in Fig. 3 show that the open circuit voltage curves obtained in the discharge and charge processes are on either side of 1.78 V, indicating that an observed voltage plateau at 1.780 ± 0.005 V is close to the equilibrium voltage of the reaction taking place in the Li/anatase TiO_2 cell.

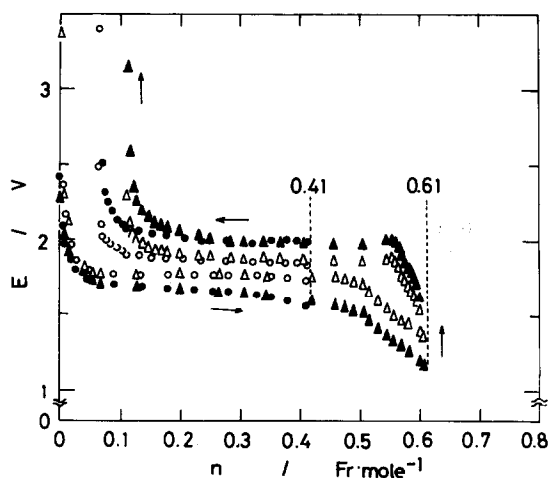


Fig. 3. Reversibility test results of a Li/anatase TiO_2 cell. Cathode mix: TiO_2 65 wt.%, acetylene black/graphite (1:1) 19 wt.% and Teflon 16 wt.%. Current pulse (10 s on, 80 s off); 6 mA for discharge and 3 mA for charge.

3.5. Ex situ X-ray diffraction measurements

In order to examine the crystal structure change of anatase TiO_2 during discharge, X-ray diffraction measurements of the discharge product at several depths of discharge were carried out using iron $K\alpha$ radiation filtered with manganese. To avoid the reaction with wet, polyethylene film was used to protect the discharge product. Anatase TiO_2 s for X-ray diffraction measurements were discharged to several depths at a low rate (20 mA g^{-1}) with monitoring of cell voltage. The results are shown in Fig. 4.

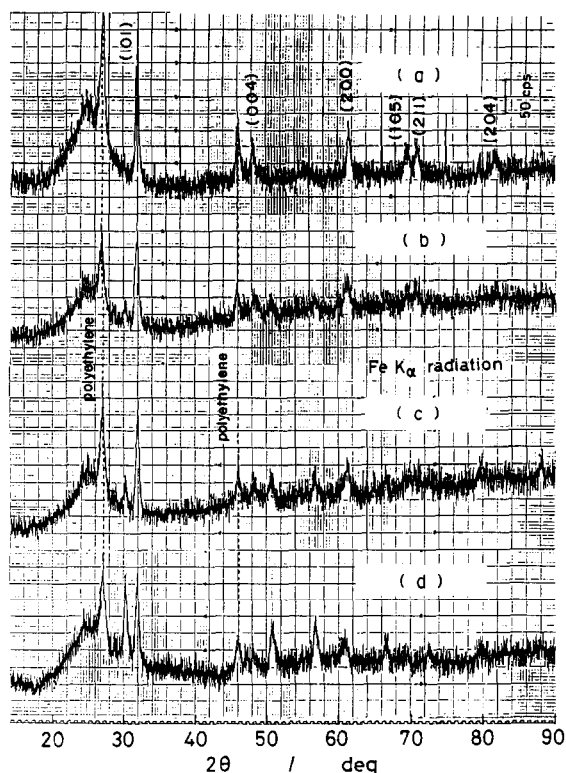


Fig. 4. *Ex situ* X-ray diffraction data on the reduction product of anatase TiO_2 in a lithium nonaqueous cell. (a) 0.25 Fr mole^{-1} degree of reduction (at 1.78 V), (b) 0.50 Fr mole^{-1} (at 1.78 V), (c) 0.75 Fr mole^{-1} (at 1.32 V) and (d) 1.00 Fr mole^{-1} (at 0.91 V).

At 0.25 and 0.5 Fr mole^{-1} of reduction, almost every diffraction line of anatase TiO_2 is still observed. On further reduction every diffraction line seems to split into two lines except (h, h, l) lines, suggesting the orthorhombic distortion of tetragonal anatase TiO_2 . Indices (h, k, l) for all the diffraction lines observed from the reduction product at 0.75 Fr mole^{-1} and 1.0 Fr mole^{-1} may be assigned assuming an orthorhombic unit cell having $a = 4.08$, $b = 3.82$, and $c = 9.05$ Å, as shown in Table 2. Since agreement between all the observed d values from $\text{Li}_{0.75}\text{TiO}_2$ and $\text{Li}_{1.0}\text{TiO}_2$ and the calculated d values was obtained, we have concluded that the reduction product of anatase TiO_2 in a lithium nonaqueous cell is a crystal compound having an orthorhombic unit cell with $a = 4.08$, $b = 3.82$ and $c = 9.05$ Å.

The original anatase TiO_2 was recovered from the reduction product at all levels of reduction after these products were electrochemically or chemically oxidised.

3.6. In situ optical measurement

Figure 5 shows the optical spectra of (a) fresh TiO_2 , (b) the reduced form at 1.50 V, and (c) the reoxidised form at 2.00 V. The color change is

TABLE 2

Analysis of X-ray diffraction data on the reduction product of anatase TiO_2 in a lithium nonaqueous cell

(Orthorhombic: $a = 4.08$, $b = 3.82$, $c = 9.05$ Å.)

(h, k, l)	d_{cal} (Å)	d_{pb}^* (Å)	d_{pb}^{**} (Å)
(1, 0, 1)	3.720	3.723	3.721
(0, 1, 1)	3.519	3.529	3.536
(1, 0, 3)	2.426	2.429	2.423
(0, 1, 3)	2.368	} 2.373	} 2.373
(1, 1, 2)	2.374		
(0, 0, 4)	2.263	2.266	2.264
(2, 0, 0)	2.040	2.043	2.039
(0, 2, 0)	1.910	1.936	1.912
(2, 1, 1)	1.765	1.763	1.759
(1, 2, 1)	1.699	—	1.696
(0, 1, 5)	1.636	—	} 1.635
(1, 0, 5)	1.655	—	
(2, 0, 4)	1.515	1.513	1.510
(0, 2, 4)	1.460	1.459	1.460
(2, 2, 0)	1.394	1.392	1.394

*Reduction product at 0.75 Fr mole^{-1} reduction ($\text{Li}_{0.75}\text{TiO}_2$).

**At 1.0 Fr mole^{-1} reduction ($\text{Li}_{1.0}\text{TiO}_2$).

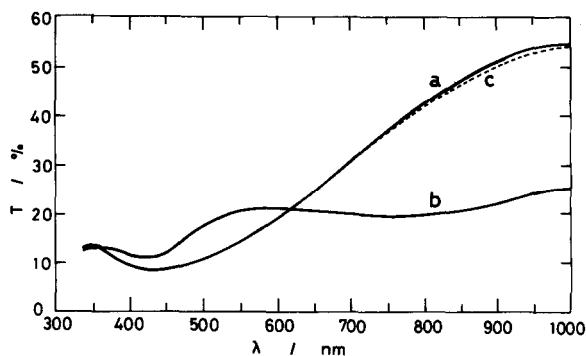


Fig. 5. Optical spectra of (a) fresh anatase TiO_2 , (b) reduced form at 1.50 V, and (c) reoxidized form at 2.00 V.

reversible even between 1.00 and 3.00 V [3], and thus the optical measurements also confirm the full reversibility of the electrochemical reaction of anatase TiO_2 .

In order to obtain the absorbance at 850 nm as a function of the degree of reduction, *in situ* optical absorbance measurements were carried out. The results are shown in Fig. 6. The absorbance at 850 nm initially decreased following the initial voltage decay from the open circuit voltage to the stable

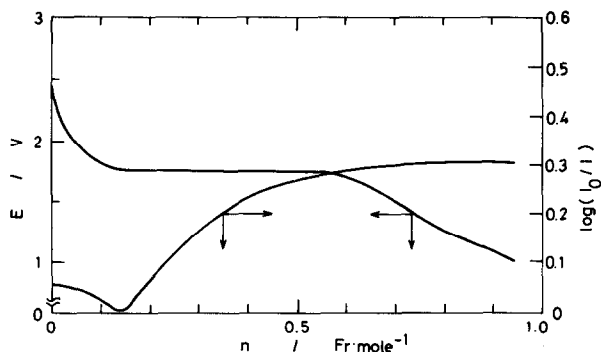


Fig. 6. *In situ* optical absorption at 850 nm as a function of degree of reduction. Current, $21.7 \mu\text{A cm}^{-2}$; TiO_2 , 182 mC cm^{-2} (based on one electron transferred per molecule).

working voltage at *ca.* 1.78 V. After the working voltage reached *ca.* 1.78 V, the absorbance at 850 nm continuously increased, but it was not a linear function of the degree of reduction. Thus, some correlation between optical absorption and the electrochemical data was obtained.

3.7. Performance of laboratory cells

The above experimental results indicate that the Li/anatase TiO_2 couple can be used for the development of the 1.5 volt class of lithium cells. In order to confirm this, cells having 100 - 300 mA h capacities were examined. An example of the results is shown in Fig. 7.

The cells consisted of two lithium anodes ($15 \text{ mm} \times 20 \text{ mm}$) and a TiO_2 cathode ($15 \text{ mm} \times 15 \text{ mm}$). The cathodes were prepared by pressing a dry TiO_2 powder on a 100 mesh stainless steel screen with a frame of titanium

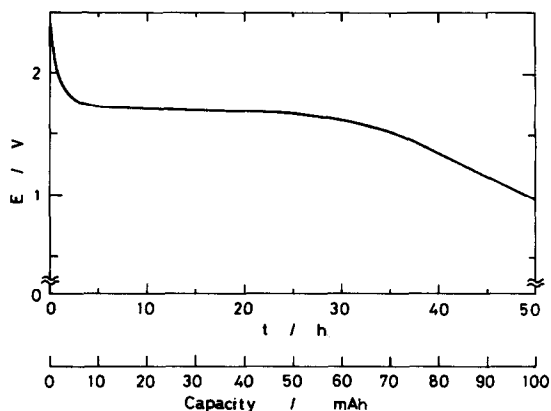


Fig. 7. Discharge curve of a Li/anatase TiO_2 cell at 2 mA. Lithium anodes: $15 \times 20 \text{ mm}^2$ ($\times 2$); cathode: $15 \times 15 \text{ mm}^2$; active material: 0.425 g of anatase TiO_2 (no conductive binder); electrolyte: 0.5 ml.

(0.5 - 2 mm thick, 4 mm wide) having a spot-welded terminal wire. The amount of electrolyte used was 0.5 ml.

As can be seen in Fig. 7, the Li/anatase TiO_2 cell without conductive binder works reasonably well. Other cells having 0.645 g or 1.064 g of anatase TiO_2 showed 190 mA h and 295 mA h discharge capacity, respectively, using the same discharge conditions as described in Fig. 7, when the cells were cut off at 1.0 V.

Thus, we have concluded that the Li/anatase TiO_2 couple can be used as a 1.5 V class of lithium cell.

4. Discussion

4.1. On the electrochemical behavior of anatase TiO_2 in a lithium nonaqueous cell

According to our results, anatase TiO_2 can be reduced up to 1 Fr mole^{-1} in a lithium nonaqueous cell, which agreed well with previous observations [1, 3, 4]. Although the initial open circuit voltage of the Li/anatase TiO_2 cell is relatively high (ca. 2.7 - 2.8 V), it has a stable working voltage of 1.780 ± 0.005 V, which corresponds to an energy density of 550 W h kg^{-1} based on the electrode couple.

In battery engineering, conductive binders such as acetylene black, carbon black or graphite, are almost always used to make the cathode. The reasons for the use of conductive binders are mainly:

- (i) to provide sufficient electronic conductivity throughout a cathode because the active material is insufficiently conducting;
- (ii) to provide sufficient free space in the cathode to include an electrolyte.

On the other hand, conductive binders do not produce electrical energy. They reduce the tap density of the cathode. Consequently, they reduce the ampere-hour capacity and the watt-hour energy density of the cell [5]. The use of a conductive binder may cause high voltage characteristics in the initial discharge stage of the 1.5 V lithium cell [2, 6]. Thus, cells not having conductive binders seem to be ideal. Although the starting material, anatase TiO_2 , is an insulator, Li/anatase TiO_2 cells do not require any conductive binder for cathode construction because the anatase TiO_2 reduction product produces effective transmission lines within the cathode when reduction begins, as discussed previously [7]. Such a characteristic of the active material may be of advantage when considering the Li/anatase TiO_2 cell as a 1.5 V-class lithium cell.

4.2. Reaction mechanism

The optical spectra in Fig. 5, which are typical for mixed valence compounds [8, 9], and the reversible electrochemical character, suggest that the electrochemical reaction of anatase TiO_2 is a topotactic (single phase) reaction.

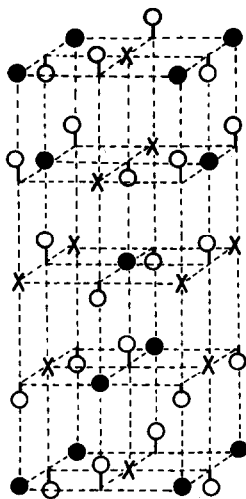
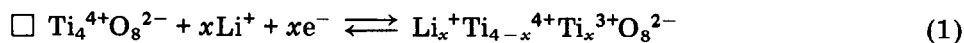


Fig. 8. Schematic illustration of anatase TiO_2 . ○, ●, and × signs denote oxygen ions (8e sites) titanium ions (4a sites) and vacant octahedral (4b sites), respectively.

The structure of anatase TiO_2 has the tetragonal space group $I4_1/amd$ with Ti^{4+} ions (octahedral sites) at positions 4(a) and O^{2-} ions at positions 8(e). The octahedral sites at the 4(b) positions are vacant with respect to cations, and may accommodate cations having almost the same ionic radii as Ti^{3+} (0.67 Å) and Ti^{4+} (0.61 Å), as illustrated in Fig. 8. The monovalent ions which may be accommodated at 4(b) sites seem to be Li^+ ions only (0.74 Å) because others are fairly large compared with Ti^{3+} and Ti^{4+} , e.g., Na^+ (1.16 Å), K^+ (1.51 Å), Rb^+ (1.49 Å) and Cs^+ (1.70 Å).

When electrons are inserted in Ti^{4+} ions (d^0) at positions 4(a), Ti^{3+} ions (d^1) are formed at the same positions. Electrons on Ti^{3+} ions may travel along 4(a) sites with the aid of thermal energy (hopping mechanism) [8] and an external electric field. Excess charges may be compensated by the accommodation of foreign ions (Li^+ ion in this case) at 4(b) sites in the anatase TiO_2 matrix. Li^+ ions may also be mobile along 4(b) sites (3-dimensional channel). Thus, the partially reduced anatase TiO_2 is both an electronic and an ionic conductor. This may be the reason why conductive binders are not required in the construction of cathodes for lithium nonaqueous cells.

The process discussed above corresponds to the reduction process. The oxidation process is the reverse of this. Since the numbers of 4(a) and 4(b) sites are equal, a hypothetical topotactic reaction of anatase TiO_2 can be represented as



(4b) (4a) (8e) (soln) (metal) (4b) (4a) (4a) (8e)

where □ denotes vacant sites.

The formulation of eqn. (1) is based on the structural unit (4TiO_2) of anatase TiO_2 . If a hypothetical topotactic reaction took place in $0 < x < 4$, the reduction product at 1 Fr mole⁻¹ may still have a tetragonal symmetry because 8(e) coordinates, *i.e.*, $(000: \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) + (00z, 00\bar{z}, 0\frac{1}{2}\frac{1}{4} + z, 0\frac{1}{2}\frac{1}{4} - z)$ only have a parameter z . The analysis of X-ray diffraction data on the reduction product ($\text{Li}_{0.75}\text{TiO}_2$ and $\text{Li}_{1.0}\text{TiO}_2$), however, indicates that the reduction product has orthorhombic symmetry ($a = 4.08$, $b = 3.82$, and $c = 9.05$ Å).

An orthorhombic reduction product of anatase TiO_2 was observed in an $\text{Li}_{0.5}\text{TiO}_2$ sample by Murphy *et al.* [10] who prepared it by the n-BuLi method. X-ray diffraction patterns observed by Bi *et al.* [4], who prepared the sample by electrochemical reduction of anatase TiO_2 in LiClO_4 -propylene carbonate solution, also seem to be those of an orthorhombic crystal. On the other hand, the X-ray diffraction data of $\text{Li}_{0.3}\text{TiO}_2$ and $\text{Li}_{0.6}\text{TiO}_2$ observed by Bonino *et al.* [2] do not show any orthorhombic crystal signals. Thus there are some disagreements between our results and those of Bonino *et al.* [2] in regard to X-ray diffraction data.

According to our experimental results, shown in Fig. 4, orthorhombic distortion of the cell seems to begin at about 0.5 Fr mole⁻¹, where half of the available 4(b) octahedral sites are occupied by Li^+ ions, and such a structural distortion seems to be reflected in the electrochemical data (see Figs. 1 - 3). Since the determined orthorhombic cell ($a = 4.08$, $b = 3.82$ and $c = 9.05$ Å: $V = 141$ Å³) is very close to the anatase TiO_2 cell (tetragonal; $a = 3.785$ and $c = 9.514$ Å: $V = 136$ Å³), the cell should contain 4Ti and 8O. In order to confirm any orthorhombic distortion, two possibilities were considered. One was the displacement of titanium ions in the matrix, and the other was the accommodation of lithium ions at tetrahedral sites in the anatase TiO_2 matrix.

Almost every possible displacement of titanium ions based on the anatase TiO_2 matrix was examined. Of these, one of interest is illustrated in Fig. 9. If the ideal displacement of the titanium ions illustrated in Fig. 9 took place during the electrochemical reduction of anatase TiO_2 , cubic spinel LiTi_2O_4 [11] having an $Fd\bar{3}m$ space group ($a = 8.391$ Å: $V = 591$ Å³) would be formed. As illustrated in Fig. 9, the unit cell volume of spinel LiTi_2O_4 is about four times greater than that of anatase TiO_2 . Such an ideal displacement, however, was not observed in our X-ray diffraction studies. Neither could the X-ray diffraction data in Table 2 be explained from considerations of other types of displacement of titanium ions in the anatase TiO_2 matrix. Therefore, we may conclude that the displacement of titanium ions did not take place during the electrochemical reduction of anatase TiO_2 in the lithium nonaqueous cell.

The other possibility is an orthorhombic distortion due to the occupation of tetrahedral sites by lithium ions without destruction of the unit octahedra linkage in the anatase TiO_2 matrix. In order to determine whether or not the anatase TiO_2 skeleton structure may survive, preliminary calculations of integrated intensities were carried out. The results are shown in Table 3. In calculating the intensities, equivalent atomic positions with

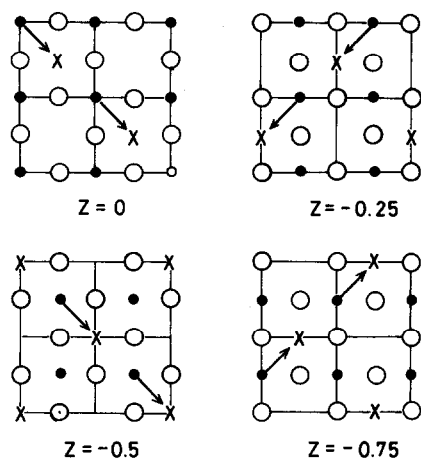


Fig. 9. An ideal displacement of titanium ions to form cubic spinel LiTi_2O_4 from the anatase TiO_2 matrix. ●, and ○ denote titanium and oxygen ions, respectively.

TABLE 3

Comparison between observed integrated intensities and calculated intensities assuming topotactic lithium insertion into anatase TiO_2 solid matrix

(h, k, l)	$I_{\text{cal}}^{\text{a}}$	$I_{\text{cal}}^{\text{b}}$	I_{ob}^{c}	I_{ob}^{d}
(1, 0, 1)	100	100	25	90
(0, 1, 1)	90	85	100	100
(1, 0, 3)	30	5	15	20
(0, 1, 3)	25	5	} 30	} 30
(1, 1, 2)	5	10		
(0, 0, 4)	70	25	35	70
(2, 0, 0)	50	30	30	70
(0, 2, 0)	35	25	55	60
(2, 1, 1)	20	20	15	35
(1, 2, 1)	20	15	—	30
(0, 1, 5)	10	15	—	} 25
(1, 0, 5)	10	15	—	
(2, 1, 3)	10	3>	—	—
(2, 0, 4)	30	15	20	30
(1, 2, 3)	10	3>	—	—
(0, 2, 4)	30	10	10	10
(2, 2, 0)	25	15	25	20

^a Calculation made using equivalent atomic positions with anatase TiO_2 ($D_{4h}^{19} - I_{41}/amd$) with $z = 0.25$.

^b Calculation made using equivalent atomic positions with anatase TiO_2 ($D_{4h}^{19} - I_{41}/amd$) with $z = 0.207$.

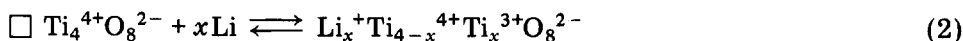
^c Reduction product at 0.75 Fr mole⁻¹ ($\text{Li}_{0.75}\text{TiO}_2$).

^d Reduction product at 1.0 Fr mole⁻¹ ($\text{Li}_{1.0}\text{TiO}_2$).

anatase TiO_2 ($z = 0.25$ and 0.207) were used. As can be seen in Table 3, the integrated intensities of diffraction lines are satisfactorily explained. Therefore, we have concluded that the skeleton structure of anatase TiO_2 survives even at 1.0 Fr mole^{-1} of reduction.

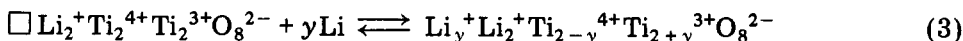
Tetrahedral sites for the accommodation of lithium ions are available, for example, at 16(f) positions in anatase TiO_2 . For 0 to 0.5 Fr mole^{-1} of reduction, lithium ions are accommodated at 4(b) positions (octahedral sites) as was previously discussed. For further reduction, *i.e.*, $0.5 - 1.0 \text{ Fr mole}^{-1}$, some lithium ions begin to occupy the tetrahedral sites in a statistical manner (for example, 16(f) sites). Statistically distributed lithium ions at tetrahedral sites (ionic radius 0.59 \AA) may distort the position of titanium ions at 4(a) sites due to electrostatic repulsion between lithium and titanium ions. Consequently, orthorhombic distortion may take place at about 0.5 Fr mole^{-1} of reduction. The occupation of the octahedral and tetrahedral sites by lithium ions may be reflected in the electrochemical data in Figs. 1 - 3 because of the different energy required.

From these considerations, we propose the following topotactic (one phase) reaction mechanism for the electrochemical reaction of anatase TiO_2 in lithium nonaqueous cells.



$$(0 < x < 2)$$

$$E_0 = 1.780 \pm 0.005 \text{ (at } 30 \text{ }^\circ\text{C)}$$



$$(0 < y < 2)$$

where (tetra) denotes tetrahedral sites such as 16(f) positions and the positions are given in space group $I4_1/amd$.

Further investigations, such as the determination of the space group, the atomic parameters and the location of the lithium ions, are now under way, together with research on the possibility of the specific Jahn-Teller distortion of the $[\text{Ti}^{3+}\text{O}_6^{2-}]$ unit octahedron.

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