Electrochemical lithium insertion in TiO$_2$ with the ramsdellite structure

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Abstract

The electrochemical insertion of lithium in the ramsdellite polymorph of titanium dioxide, TiO$_2$ (R), is studied by electrochemical methods. At room temperature the maximal Li uptake under constant current densities of 0.1, 0.5 and 1.0 mA cm^{-2} is 0.85, 0.8 and 0.7 Li/Ti, respectively. Between 2.3 and 1.3 V versus lithium, the specific capacity achieved is as high as 285 A h kg^{-1} at 0.5 mA cm^{-2}. This corresponds to 85% of the maximum theoretical capacity (336 A h kg^{-1}), which may be reached by incorporation of one lithium per titanium under equilibrium conditions. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium insertion; Titanium dioxide; Ramsdellite; Lithium batteries; Electrode material

1. Introduction

Three stable crystalline polymorphs of TiO$_2$ are known: the well studied rutile TiO$_2$ (r) and anatase TiO$_2$ (a) forms besides the less known brookite TiO$_2$ (b). Furthermore, a high pressure form, TiO$_2$ II, was obtained by treating the above mentioned polymorphs under a pressure of 40 kbar at 450°C [1]. More recently, three other forms of TiO$_2$ have been synthesised. Monoclinic TiO$_2$ (B), isostructural with the bronze of composition Na$_{0.20}$TiO$_2$ [2,3], is prepared by a soft chemistry route [4]. Tetragonal TiO$_2$ (H) [5] is obtained by complete removal of lithium from the bronze of nominal composition K$_{0.13}$TiO$_2$ [2,6]. Finally, orthorhombic TiO$_2$ (R) with the ramsdellite structure is synthesised in a two-step route: single crystals of composition Li$_{0.5}$TiO$_2$ are formed by heating lithium metal with titanium dioxide at high temperature [7] and slowly cooling down, which upon exposure to air at room temperature or by soft-chemistry lead to the lithium-free TiO$_2$ (R) [8]. Recently, an alternative way to the ramsdellite Li$_{0.5}$TiO$_2$ has been described [9], which allows the preparation of pure powder sample to be investigated for application in electrochemical cells. The well-known spinel phase LiTi$_2$O$_4$ [10], prepared by ceramic methods, transforms to ramsdellite at high temperature.

Johnston [11] reported more than 20 years ago that this spinel phase was not stable above 1000°C, and a conversion to a ramsdellite structure took place, which presents unit cell parameters similar to that of orthorhombic Li$_2$Ti$_3$O$_7$ [12].

The three latter polymorphs are metastable. Both TiO$_2$ (B) and TiO$_2$ (H) are first transformed into the anatase polymorph when heated above 550 and 410°C, respectively [4,5], which is finally converted to rutile at higher temperature. On the other hand, TiO$_2$ (R) undergoes conversion to brookite by heating upon 367°C [8]. A second transformation, evidenced by DTA measurements, has not further been investigated.

In all these oxides, titanium is octahedrally coordinated by oxygen. The Ti-O$_6$ octahedra share vertices and edges to build up the three-dimensional framework of the oxide, leaving empty sites available for lithium insertion. For the ramsdellite structure [13], M-O$_6$ octahedra link up with adjacent octahedra by sharing opposite edges and thereby building up columns. Adjacent pairs of columns share edges to build up double columns, leading to a rather open framework structure with tunnels, which are partly occupied by lithium in the case of Li$_x$TiO$_2$ [7] (see Fig. 1), Li$_2$Ti$_3$O$_7$ [14] or Li$_2$MgSn$_3$O$_8$ [15]. In other cases, such as TiO$_2$ (R) [7] or γ-MnO$_2$ [12] the tunnels are lithium-free.

Titanium(IV) oxides are among the few transition metal oxides that can be reduced upon lithium intercalation at low voltage. This makes these oxides candidates for studying their behaviour and possible application as the anode in

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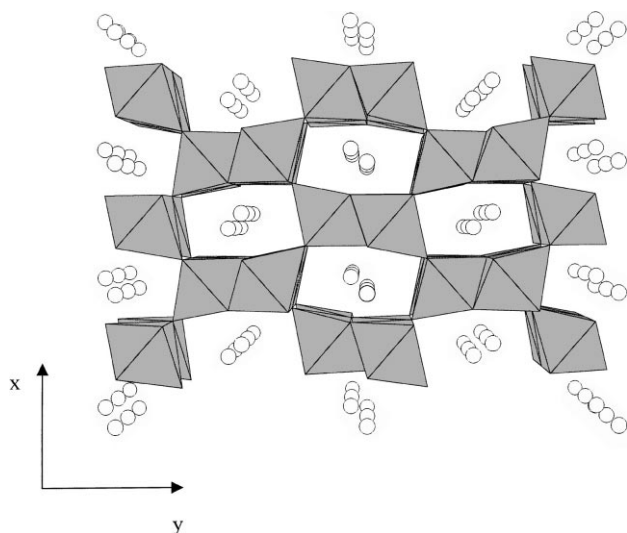*E-mail address*: akuhn@ceu.es (A. Kuhn).

Fig. 1. Perspective view of the structure of $Li_{0.5}TiO_2$ down the *c*-direction (after Akimoto et al., from [7]).

rechargeable lithium batteries, and so, in this connection, numerous articles have been published up today.

Lithium insertion has been reported for most of the TiO_2 polymorphs, although the ramsdellite form has not yet been investigated for the above mentioned purpose in detail. The quantity of inserted lithium, specific capacity and average voltage obtained for each polymorph are summarised in Table 1. Only small amounts of lithium can be inserted into rutile and brookite. For rutile 0.1 and 0.15 Li/Ti have been found at room temperature both chemically [16] and electrochemically [17,18], whereas at higher temperature the maximal lithium uptake reaches 0.5 Li/Ti [18], although no information about reversibility of the insertion process was given.

Anatase is able to accept reversibly 0.5 Li/Ti at a constant low voltage (close to 1.8 V versus Li) at room temperature [18,19], whereas for higher lithium uptake a steadily declining curve is observed [19]. At elevated temperature the lithium uptake was found to be 0.82 [18]. The additional

Li is inserted at 1.56 V versus Li, but the authors did not indicate whether this process including the higher lithium uptake is reversible or not. Reports on lithium insertion in TiO_2 (B) range from 0.5 [18] at both room temperature and 120°C [18] to 0.75 [20,21] at 100°C with electrochemical methods-although no information about cyclability behaviour has been facilitated-and 0.85 [4] Li/Ti by chemical lithiation with *n*-butyl lithium.

In the case of TiO_2 (H), discharge of electrochemical cells leads to the reversible incorporation of 0.75 Li/Ti, and a steadily declining potential curve from 2.3 to 0.5 V is observed during the insertion reaction [22].

Regarding applications the specific reversible capacities obtained are negligible for rutile (44 A h kg^{-1}), but can be improved using TiO_2 (a) and TiO_2 (B) (168 A h kg^{-1}), whereas the hollandite form develops a considerable specific capacity of about 250 A h kg^{-1}, although its use as electrode is questionable as the insertion processes occurs over a rather wide potential range (see above). Higher specific capacities at a constant low voltage have been recently reported for compounds within the ternary lithium–titanium–oxygen system. Examples are the recently reported ramsdellite $Li_2Ti_3O_7$ [23] and the spinel $Li_4Ti_5O_{12}$ [24–26], with specific capacity values of 235 and 168 A h kg^{-1}, respectively. In both oxides, titanium is in its highest oxidation state, Ti^{4+}, and reduction to the trivalent state takes place upon lithium insertion. However, no additional energetic advantage can be taken of the lithium already present in the structure, as lithium extraction would involve oxidation of the titanium cations, which are already in its highest oxidation state. Therefore, these lithium ions remain electrochemically inactive occupying potentially useful tunnel sites and lead hence to a loss of theoretical capacity raised by the increasing formula weight.

Recently, a synthesis route to ramsdellite-type TiO_2 has been reported. Thermal treatment of the superconducting spinel $LiTi_2O_4$ at high temperature yields the compound $Li_{0.5}TiO_2$ with the ramsdellite structure [9]. Lithium can be chemically removed to get a lithium-free compound that keeps the parent structure, i.e. ramsdellite TiO_2 [8].
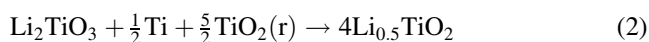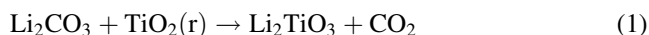
Table 1
Electrochemical data for Li insertion in the different TiO_2 modification

Modification	x_{max} in Li_xTiO_2	Experimental conditions		C_s (A h kg^{-1})	Potential range (V)	References
		Cell configuration	Temperature			
TiO_2 (r) Rutile	0.13	Li/LiClO$_4$, PC, TiO$_2$	RT	44	1.5	[18]
	0.5	Li/LiAsF6, PC/TiO$_2$	120°C	168	1.34	[18]
TiO_2 (a) Anatase	0.5	Li/LiAsF6, PC/TiO$_2$	RT	168	1.815	[18]
	0.5	Li/LiClO$_4$, PC/TiO$_2$	RT	168	1.780	[19]
	0.82	Li/LiCF$_3$SO$_3$, PEO/TiO$_2$	120°C	275	1.80 (0.5 Li) 1.56 (0.82 Li)	[18]
TiO_2 (B)	0.5	Li/LiAsF6, PC/TiO$_2$	25°C	168	1.8	[18]
	0.5	Li/LiCF$_3$SO$_3$, PEO/TiO$_2$	120°C	168	1.8	[18]
	0.75	Li/LiCF$_3$SO$_3$, PEO/TiO$_2$	100°C	252	1.3	[20,21]
TiO_2 (H)	0.75	Li/LiClO$_4$, EC+DEE/TiO$_2$	RT	252	1.5	[22]

In this paper, we present the study of the electrochemical lithium insertion into the TiO_2 (R) polymorph. Note that the insertion of lithium to reduce all the Ti(IV) ions to Ti(III) would give a high maximal theoretical specific capacity of 336 A h kg^{-1}, a value which is close to those reported for graphite (370 A h kg^{-1}) and much higher than the corresponding value of petroleum coke (186 A h kg^{-1}). Although the maximal theoretical specific capacity is not reached for any of the polymorphs listed in Table 1 we found that in the case of TiO_2 (R) this value is almost reached at room temperature, [33].

2. Experimental

A two-step synthesis was followed involving Li_2TiO_3, Ti and TiO_2.

$$Li_2CO_3 + TiO_2(r) \rightarrow Li_2TiO_3 + CO_2 \tag{1}$$

$$Li_2TiO_3 + \tfrac{1}{2}Ti + \tfrac{5}{2}TiO_2(r) \rightarrow 4Li_{0.5}TiO_2 \tag{2}$$

In order to minimise the loss of Li_2O during heat treatment, the synthesis of a stable lithium-containing precursor was chosen [11]. Li_2CO_3 (99%) and TiO_2 (rutile) (99.99%) were predried at 500 and 1000°C, respectively, for at least 12 h, mixed in the appropriate ratios, ground under acetone in an agate mortar and fired in an alumina crucible at 750°C in air for 18 h. Ramsdellite Li_xTiO_2 was prepared by heat treatment of a mixture containing the appropriate amounts of Li_2TiO_3, Ti metal (99.98%) and TiO_2 (rutile). The mixture was intimately ground and transferred afterwards to a quartz ampoule, which was then sealed under vacuum, slowly heated to 950°C and held there for 24 h before quenching the sample to room temperature.

We observed that the walls of the quartz ampoule were attacked probably due to their reaction with lithium. However, X-ray diffraction showed no apparent impurities in the black Li_xTiO_2 product. The X-ray phase purity was determined on a Philips X'Pert diffractometer using Cu Kα radiation. Unit cell parameters were indexed using the Fullprof program [27] by means of Rietveld profile fit [28,34].

Determination of the Li content was performed by means of inductive-coupled-plasma spectrometry (ICP) on a Perkin-Elmer instrument. A solution of lithium nitrate served as standard.

The electrochemical lithium uptake was evaluated by both constant current discharge/charge and chronoamperometric experiments in Swagelok test cells with the following configuration

$$Li(-)/LiPF_6 \, (1 \, M) \, in \, EC + DMC \, (1:1)/Li_xTiO_2$$
$$+ \, carbon \, black + binder(+)$$
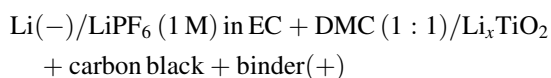
The liquid electrolyte was the commercial battery electrolyte solution Selectipur LP30® (Merck). Kynarflex® used as a binder was kindly provided by Elf-Atochem.

Lithium metal acted as the negative electrode. The positive electrode was prepared as pellets consisting of 85% (w/w) oxide, 10% (w/w) carbon black and 5% (w/w) binder. The amount of oxide was approximately 15–20 mg in each pellet. The cells were controlled using a MacPile II system [29]. Typical galvanostatic runs were performed applying 0.1–1.0 mA cm^{-2} current densities. In potentiostatic mode, the potential step was set to ± 10 mV and the system was allowed to stay for 30 min between two consecutive steps.

For studying the Li intercalation in a Li-free TiO_2 compound, each cell was previously fully charged up to 3 V versus lithium in order to get TiO_2 (R). Cells were afterwards studied during discharge–charge cycling between 3 and 1 V.

3. Results and discussion

3.1. Structural and chemical characterisation

The X-ray diffraction pattern of Li_xTiO_2, obtained following the procedure described in Section 2, was fully indexed using the primitive orthorhombic unit cell of ramsdellite with space group Pbnm (no. 62). Refined cell parameters are a=5.0199(4) Å; b=9.5672(10) Å, c=2.9581(2) Å. Our values are slightly different from those reported for $Li_{0.5}TiO_2$ [8,9]. Akimoto et al. showed that the dimension of the ramsdellite unit cell depends on the Li content [8]. Taking into account the data from these authors, our sample should have a lithium content lower than 0.5 Li/Ti (see Table 2). This has been confirmed by determining Li by means of ICP. We found that our oxide has a composition of $Li_{0.30(2)}TiO_2$. The present data support that some lithium is lost and so the observed reaction of quartz is due to the presence of lithium as a reactant. This would explain the lower lithium content found for our ramsdellite phase. In any case this is not a problem for electrode application as much as we will have to extract lithium completely before discharging the cell in order to get a higher specific capacity.

$Li_{0.3}TiO_2$ seems to be fairly reactive in air, obviously due to the presence of unstable Ti^{3+} ions. After exposure to air for few hours the initial black colour has changed to grey. The corresponding X-ray diffractogram can be indexed on

Table 2
Crystallographic data of Li_xTiO_2 compounds (this work and from [8])

x value in Li_xTiO_2	a (Å)	b (Å)	c (Å)
0.45[a]	5.0356(6)	9.6377(8)	2.9484(7)
0.41[a]	5.0311(9)	9.6113(11)	2.9488(10)
0.16[a]	4.9794(10)	9.5613(13)	2.9551(12)
0.14[a]	4.9732(13)	9.5425(16)	2.9586(16)
0[a]	4.9022(14)	9.4590(12)	2.9585(14)
0.3[b]	5.0199(4)	9.5672(10)	2.9581(2)
0[b]	4.8979(7)	9.4618(14)	2.9640(4)

[a] From [8].
[b] This work.

the base of two ramsdellite phases. Cell parameters of phase I: $a=5.020$, $b=9.567$, $c=2.958$ Å are coincident with those of black $Li_{0.3}TiO_2$, whereas the cell parameters of phase II $a=4.8979$, $b=9.4618$, $c=2.9640$ Å are in good agreement with those reported for the white Li-free TiO_2 [9]. The transformation of phase I ($Li_{0.3}TiO_2$) into phase II (TiO_2) is completed after exposing the same sample at $100°C$ over a larger time interval. The oxidation reaction of Li_xTiO_2 with water molecules of the atmosphere should produce, besides the rasmdellite polymorph of TiO_2, lithium hydroxide and molecular hydrogen:

$$Li_xTiO_2 + xH_2O \rightarrow TiO_2 + xLiOH + \frac{x}{2}H_2$$
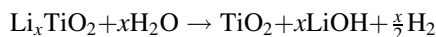
3.2. Electrochemical behaviour of ramsdellite TiO_2

Fig. 2 shows the variation of voltage versus composition when the cell Li/electrolyte/$Li_{0.3}TiO_2$ (R) is charged up to 3 V. In this figure charging curves obtained by application of a constant current density of 0.1 mA cm^{-2} (nearly equilibrium conditions) and 1.0 mA cm^{-2} are represented. It can be seen that under 0.1 mA cm^{-2} and for the maximal voltage reached it is possible to extract almost all lithium ions from $Li_{0.3}TiO_2$, obtaining hereby the quasi lithium-free $Li_{0.075}TiO_2$ (R). Alternatively, TiO_2 (R) can be obtained by chemical extraction using oxidising agents, such as bromine or nitronium tetrafluorborate, in acetonitrile solution. Lattice parameters of the as-obtained compound are given in Table 2. However, in this work we only present the results for the quasi lithium-free compound obtained in situ by electrochemical oxidation. Effects of the lithium extraction from Li_xTiO_2 (R) on the structure have been reported previously [8].

Lithium insertion has been performed by discharging cells Li/electrolyte/TiO_2 (R) under different experimental conditions. About 0.8 Li/Ti can be reversibly inserted at constant
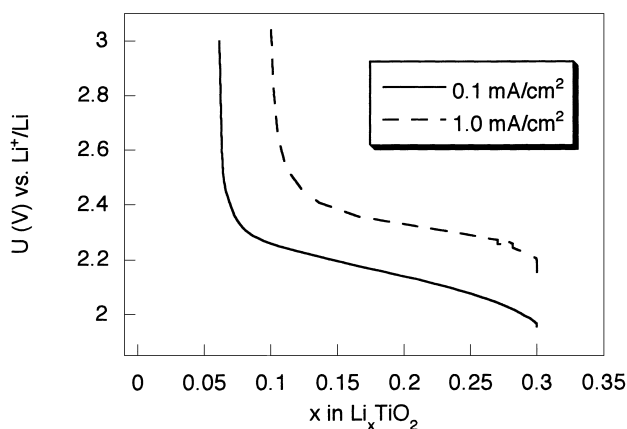
current densities ranging from 0.1 to 0.5 mA cm^{-2}, as it can be seen in Fig. 3b and c. The quantity of reversibly inserted lithium represents a specific capacity of about 290 A h kg^{-1}, approximately 80% of the maximal theoretical specific capacity expected for this material (336 A h kg^{-1}). This maximal value is almost reached under nearly equilibrium conditions used in the experiment shown in Fig. 3a (cutoff voltage was set to 1.2 V versus lithium). Applying a higher current density of 1.0 mA cm^{-2} (see Fig. 3d) 0.7 Li/Ti are now inserted reversibly into TiO_2, corresponding to a capacity of 235 A h kg^{-1}.

Cells built up using TiO_2 (R) as the positive electrode are able to sustain high currents while keeping a great part of the reversible capacity over a large number of cycles. Cycles performed at 0.5 mA cm^{-2} current density show a good cyclability and low polarisation (Fig. 4a). For a 1.0 mA cm^{-2} current density the cyclability is still acceptable (Fig. 4b), although polarisation increases significantly.

The voltage–composition plot also shows that the first 0.5 Li/Ti are inserted over a wide potential range from 2.3 to 1.3 V, with an average value of 1.8 V, similar to that described for TiO_2 (H) [22]. The additional Li is inserted at a low, almost constant voltage of 1.3 V, that resembles the Li insertion in anatase TiO_2 [18] and ramsdellite $Li_2Ti_3O_7$ [23]. This latter compound was proposed as candidate for anode material in view of its relatively high maximal theoretical specific capacity (235 A h kg^{-1}) and its low intercalation voltage (1.5 V). In the case of TiO_2 (R), a higher capacity can be obtained (336 A h kg^{-1}) but its usefulness as an anode is more limited since half of its capacity is developed at a higher average voltage. The difference in the intercalation voltages seems unexpected since in both ramsdellites the process taking place is the reduction of Ti^{4+} to Ti^{3+} in an octahedral coordination. Although both compounds crystallise in the ramsdellite structure they are locally different. In $Li_2Ti_3O_7$ part of the titanium positions are, depending on the adopted model, either vacant or occupied by lithium atoms [30]. The latter possibility is considered as the best approximation to the structure [30–32]. In any case, part of the lithium ions present in the parent $Li_2Ti_3O_7$ occupy tunnel positions, while in the case of TiO_2 (R) the tunnels are empty.

For $Li_2Ti_3O_7$ it has been proposed that the Li ions occupy two different kinds of tetrahedral sites in the tunnel, named T1 (or Li1) and T2 (or Li2) [15,31]. Furthermore, it has been indicated that the T1 sites are more stable from an energetic point of view, because the corresponding LiO_4 tetrahedron does not share faces to any (Li, Ti)O6 framework octahedron [15]. In fact, lithium ions located in the tunnels are distributed as follows: 60% over the more stable so-called T1 and 40% over the less stable so-called T2 site [31]. In the case of $Li_{0.5}TiO_2$ [7], as well as for the series Li_xTiO_2 ($0 \leq x \leq 0.5$) [8], only the T1 tetrahedral site is occupied by lithium ions up to a maximum of 50% as reported for $Li_{0.5}TiO_2$ [7]. It has been shown that the occupancy decreases gradually upon lithium extraction [8].

Fig. 2. Charging curves of cells Li/electrolyte/$Li_{0.3}TiO_2$ obtained by applying a constant current density of 0.1 mA cm^{-2} for 30 min with intermittent relaxation of 60 min to get nearly equilibrium conditions (solid line), and a constant current density of 1.0 mA cm^{-2} (dashed line).
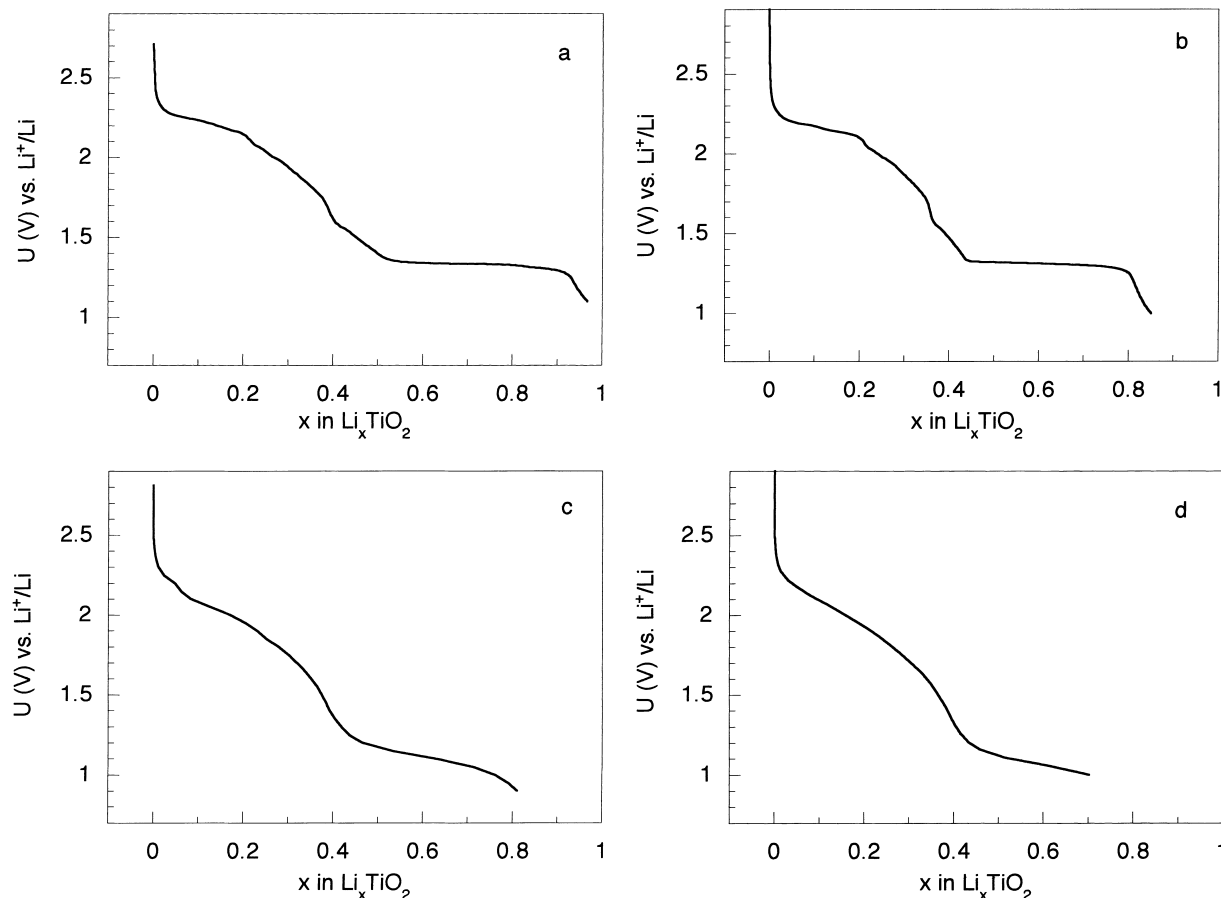
Fig. 3. Discharging curves of cells Li/electrolyte/TiO$_2$ under the following experimental conditions: (a) galvanostatic intermittent run, 0.1 mA cm^{-2} current density was applied for 30 min and the system was allowed to relax for 60 min. In addition, experiments have been performed applying the following constant current densities; (b) 0.1 mA cm^{-2}; (c) 0.5 mA cm^{-2} and (d) 1.0 mA cm^{-2}.

In order to perform the assignment of the experimental intercalation curve obtained for our sample to possible tunnel positions, the following suppositions have been made:

- The distribution of the lithium tunnel ions in Li$_{0.3}$TiO$_2$ over possible tetrahedral sites is the same as in Li$_x$TiO$_2$ [7], and according to the chemical composition, with an 30% occupation over the more stable T1 site, exclusively. On the other hand, the T2 sites remain empty.
- Once the lithium is completely removed chemically or electrochemically from the T1 tunnel site, it will enter again this more stable site upon the following lithium intercalation step. To summarise, reversible extraction from and insertion of lithium ions into Li$_{0.3}$TiO$_2$ takes place in the T1 position.

From the voltage–composition curve of TiO$_2$ (R) obtained under quasi-equilibrium conditions (Fig. 3a) several electrochemical processes, separated by more or less pronounced voltage drops, are detected. Taking into account that there are four formulae of TiO$_2$ per unit cell, approximate compositional limits corresponding voltage ranges

and maximum site occupation can be extracted from Fig. 5 and are summarised in Table 3.

Lithium insertion can be roughly divided into two regimes which are characterised by distinct voltage ranges. Insertion of the first half of Li ions takes place over a wide voltage window, in an almost steadily declining manner, whereas insertion of the second half is achieved at a low constant voltage.

The final lithium uptake within the first part of the voltage–composition curve is reached at 1.4 V, being the higher composition Li$_{0.48}$TiO$_2$ close to that described for single-crystals [7]. Several authors coincide that the maximum site occupation of the tetrahedral site T1 in both Li$_2$Ti$_3$O$_7$ and Li$_x$TiO$_2$ cannot exceed 50% due to very short distances between the centres of adjacent face-sharing LiO$_4$ tetrahedron in the tunnel [7,15,31]. For contents higher than 0.5 Li ions/Ti, occupation of the still empty tetrahedral T2 site should occur. This could be the origin of a nearby constant voltage–composition curve (see Fig. 5), which is developed at quite low voltage (1.35 V). The quantity of lithium inserted during this plateau would account for the filling of almost 50% of the T2 sites. Not surprisingly, a practically identical behaviour is observed in the case of
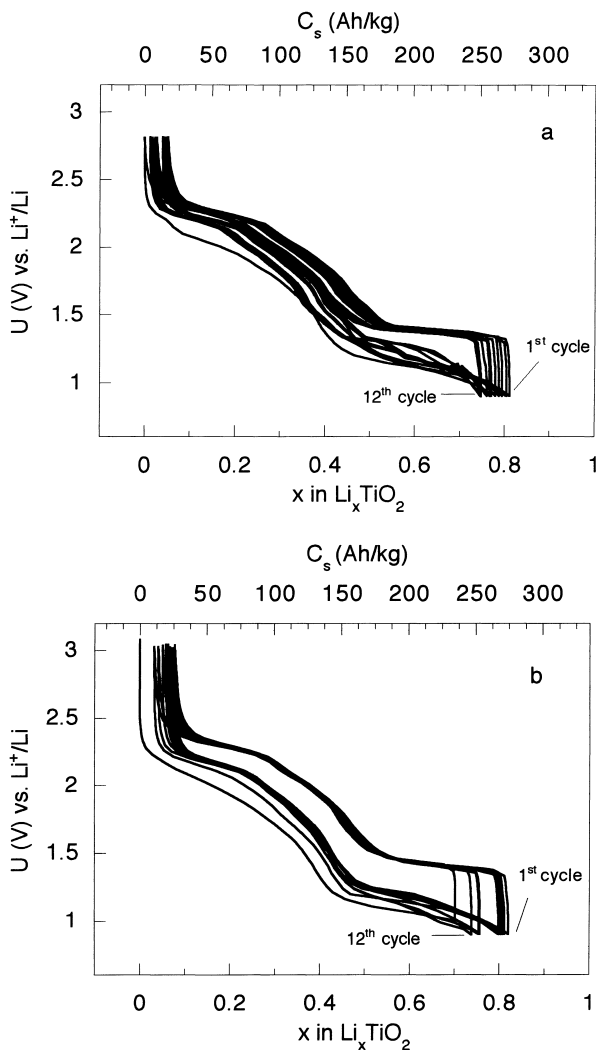
Fig. 4. Cycling behaviour of TiO_2 under the following constant current densities: 0.5 mA cm^{-2} (a); 1.0 mA cm^{-2} (b).

Fig. 5. Voltage–composition plot obtained under quasi-equilibrium conditions normalised to four formulae of TiO_2. The different supposed compositional limits are indicated (after Table 3).

$Li_2Ti_3O_7$, where the low-voltage regime (centred at 1.5 V) has been interpreted in terms of filling of half of the T2 site [23].

In any case, a detailed structural work on the complete Li_xTiO_2 system remains to be done to clarify the different behaviour of the voltage during the filling of T1 tetrahedral sites as well as checking the validity of the filling schema proposed above.
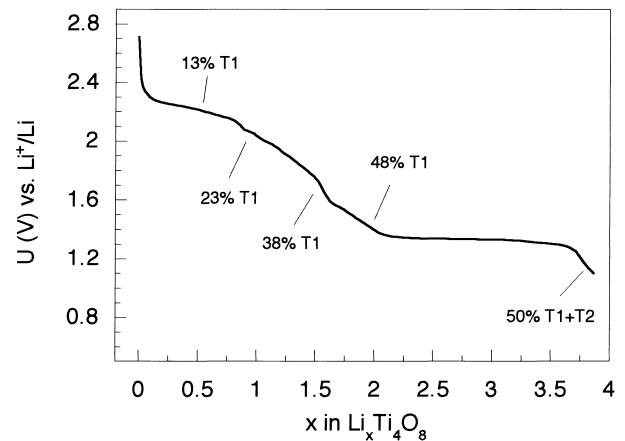
4. Conclusions

The electrochemical study of Li_xTiO_2 allows us to propose it as an electrode material. In comparison to $Li_4Ti_5O_{12}$ and $Li_2Ti_3O_7$ which intercalate lithium at a low average potential of 1.3 V, Li_xTiO_2 is able to intercalate much more lithium giving rise to a higher theoretical capacity of 336 A h kg^{-1}. Intercalation into TiO_2 (R) can be roughly divided into two potential ranges. Intercalation of the first 0.5 Li per formula takes place in a steadily declining voltage–composition curve with an average potential of 1.8 V, which could limit thereby its use as the anode. The additional lithium ions are inserted at lower potential. The Li/ramsdellite TiO_2 cell shows a stable working voltage of 1.3 V and the ramsdellite TiO_2 is able to be reduced up to one Li/TiO_2 in a lithium cell, making the compound useful as anodic material.

Table 3
Approximate compositional limits and voltage ranges for $Li_xTi_4O_8$

Compositional limits	Li$_{max}$ per formula TiO_2	Voltage range (V)	maximum site occupation (%)
Ti_4O_8–$Li_{0.52}Ti_4O_8$	0.13	2.8–2.3	13 (T1)
$Li_{0.52}Ti_4O_8$ to $Li_{0.92}Ti_4O_8$	0.23	2.3–2.1	23 (T1)
$Li_{0.92}Ti_4O_8$ to $Li_{1.52}Ti_4O_8$	0.38	2.1–1.7	38 (T1)
$Li_{1.52}Ti_4O_8$ to $Li_{1.92}Ti_4O_8$	0.48	1.7–1.4	48 (T1)
$Li_{1.92}Ti_4O_8$ to $Li_{3.68}Ti_4O_8$	0.92	1.4–1.2	∼50 (T1)+50 (T2)

Note added in proof:

The data in this paper points in the same direction as the results reported in a paper entitled "Investigation of ramsdellite titanates as possible new negative electrode materials for Li batteries" by R.K.B. Gover, J.R. Tolchard, H. Tukamoto, T. Murai and T.S. Irvine, which appeared in the Journal of Electrochemical Society, vol. 146 (12) pp. 4348–4353 (1999). The results reported in that paper cover the complete solid solution $Li_{1+x}Ti_{2-2x}O_4$ from $LiTi_2O_4$ to $Li_2Ti_3O_7$.

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