

ANATASE AS A CATHODE MATERIAL IN LITHIUM-ORGANIC ELECTROLYTE RECHARGEABLE BATTERIES

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Summary

A preliminary investigation of anatase, TiO_2 , as a positive electrode material in secondary lithium-organic electrolyte batteries is reported.

Up to 0.6 lithium equivalents can react with 1 mole of TiO_2 . However, optimum cycling behaviour is obtained for regimes involving compositions between 0.15 and 0.45 Li/TiO_2 mole ratio.

Under these conditions, prolonged cycling at 0.25 - 0.5 mA cm^{-2} gives satisfactory results.

Introduction

Titanium dioxide is an attractive electrode material in lithium-organic electrolyte batteries because of its low cost, low solubility in typical organic electrolytes [1], and high theoretical energy density associated with the couple formed with lithium. A striking difference in behaviour between the two allotropic forms of TiO_2 , *i.e.*, rutile and anatase, as cathodes in lithium primary cells was observed by Ohzuku *et al.* [2], who examined the materials in lithium perchlorate (LiClO_4)-propylene carbonate (PC) electrolyte. While cells based on anatase gave flat discharge curves at about 1.8 V, those based on rutile indicated poorer performances. These differences were explained on the basis of the discharge mechanism [2], which implies the diffusion of lithium into the TiO_2 matrix in a first stage: the process may be easier for anatase than for rutile, because of different structural features. These results are in agreement with those obtained by Murphy *et al.* [3], who reported a lack of chemical incorporation of lithium by reaction with *n*-butyllithium (*n*-BuLi) in hexane at room temperature. By contrast, anatase consumed 0.6 equivalents of *n*-BuLi, forming a black compound [4].

Considering the whole of these results and the general intrinsic interest in lithium storage systems, it appeared to us to be worthwhile to study the lithium/anatase couple in terms of rechargeable behaviour. Preliminary results obtained in this investigation are reported here.

Experimental

Propylene carbonate (PC), a reagent grade Merck product, was purified by fractional distillation under reduced pressure. Lithium perchlorate, LiClO_4 , an Alpha product, was vacuum dried at 150°C .

Rutile and anatase TiO_2 were kindly supplied by Montedison, Research Center SIBIT, Spinetta Marengo, Italy. They were prepared *via* the sulphate process. The average particle size was $0.25\ \mu\text{m}$. The anatase used for most of the experiments had the following composition: TiO_2 , 99.46; ZnO , 0.1; K_2O , 0.19; P_2O_5 , 0.25 percent by weight (wt.%)*. The heat treatment of the samples was performed at $980 - 990^\circ\text{C}$. Samples with slightly different chemical composition and heat treatment were also tested. The results will be quoted in the next section.

The electrochemical cells for the cycling tests were prepared in a glove-box maintained under argon atmosphere, by placing a lithium disk, three glass wool separator disks soaked with a 1M LiClO_4 -PC solution and a pellet of the positive material into a Teflon container having nickel terminals. The pellet of positive material was obtained by compressing a powdered mixture of TiO_2 (90 wt.%), carbon black (6 wt.%) and powdered Teflon (4 wt.%) onto an inert metallic support. It was observed that a good reproducibility of the electrochemical results was obtained only when the pellets of cathode material were kept for at least two weeks in a glove-box (with a few ppm of H_2O) before use.

The cells had a surface area of $1.2\ \text{cm}^2$ and a volume of about $0.6\ \text{cm}^3$. An average amount of active material of 20 - 25 mg was used in each experiment.

Three electrode cells for the polarization tests were obtained in a similar way using, as counter and reference electrodes, two pieces, electrically isolated from each other, of a lithium pellet. The polarization curves were obtained at various sweep rates with a galvanostat driven by a function generator. Prolonged cycling tests were performed using polarity-reversing electronic timers.

The materials were characterized by X-ray powder patterns obtained using a JEOL diffractometer, Model JDX-8S, with $\text{Cu K}\alpha$ radiation.

*Zinc oxide is added to improve the photostability, while phosphorus and potassium oxides are relevant for the particle size.

Results and discussion

Cells of the type:



showed an open circuit voltage (OCV) of between 2.80 and 2.90 V at room temperature for anatase and about 2.50 V for rutile. The striking difference in discharge behaviour between the two forms, as observed by Ohzuku *et al.* [2], was confirmed. Typical discharge curves obtained at 0.5 mA cm^{-2} at room temperature are shown in Fig. 1. The cathodic utilization for anatase, based on a one electron mechanism and for a 1 V cut-off, is close to 60%; while that for rutile is much lower. Consequently, only the anatase form has been considered for further tests.

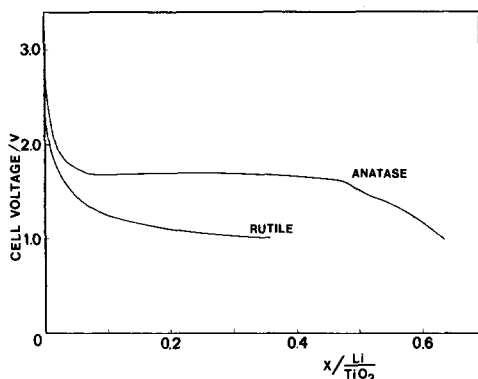


Fig. 1. Typical room temperature discharge curves of cell (1) with rutile and anatase as cathode materials. Current density: 0.5 mA cm^{-2} . X indicates the lithium equivalents discharged per mole of TiO_2 .

It is interesting to note that the maximum cathodic utilization observed for anatase is in agreement with the results obtained by Whittingham and Dines [4] for the incorporation of lithium by means of *n*-BuLi. The nature of the product formed has not yet been clarified. Indeed, we could not confirm the findings of Ohzuku *et al.* [2], who postulated the formation of LiTiO_2 as the final stage of a process, the beginning of which was the diffusion of lithium ions with the formation of a metastable incorporation product. Reflections which can be attributed to LiTiO_2 were absent in our X-ray powder patterns, but, together with those of unreacted anatase, a set of reflections of one or more unidentified phases appeared. In Fig. 2 schematic patterns of samples obtained after various depths of discharge (0.3 and 0.6 lithium equivalents per mole TiO_2) are presented. There is no definite indication of the formation of an intercalation product. It seems more likely that a new, stoichiometric phase is formed.

This conclusion may be indirectly supported by further experiments. We followed the OCV as a function of composition in the range 0.00 - 0.25

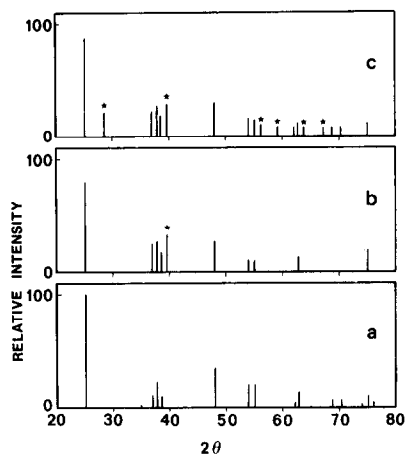


Fig. 2. Schematic X-ray diffraction patterns of samples after different discharge depths, compared with the starting material. Cu $K\alpha$. (a) Anatase; (b) after 0.3 equivalents of lithium discharged; (c) after 0.6 equivalents of lithium discharged. Unidentified reflections are marked with an asterisk.

equivalents of lithium per mole TiO_2 . The results reported in Fig. 3 show a practical constancy of OCV in the studied range*. This behaviour could be attributed to the attainment of equilibrium between two or more phases. The final voltage values are obtained quite slowly: in Fig. 4 a typical voltage recovery curve is shown after a 1 mA cm^{-2} pulse, corresponding to the discharge of 0.1 equivalents of lithium per mole TiO_2 . The shapes of the recovery curves are similar in all the studied ranges, though the attainment of a stable voltage was slower as the lithium content increased. These results give an indication of a rather slow diffusion of lithium into the cathode material.

The reversibility of anatase cathodes has been investigated by polarization tests using a lithium reference electrode. Cathodic and anodic polarization curves of Li_xTiO_2 at various degrees of discharge are also shown in Fig. 5. The results indicated that the reversibility of the electrode progressively increased, passing from $x_m = 0$ to $x_M = 0.2$, where x represents the lithium equivalent

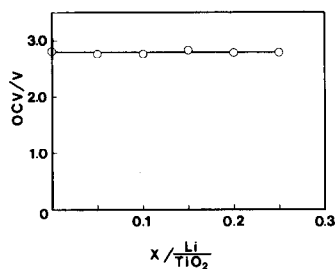


Fig. 3. Open circuit voltage (OCV) at room temperature of cell 1 as a function of cathode composition. Cathodic current density during discharge: 1 mA cm^{-2} .

*See 'Note added in proof', p. 269.

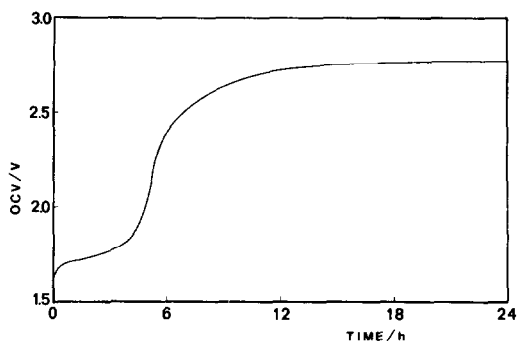


Fig. 4. Open circuit voltage (OCV) at room temperature of cell 1 as a function of time, after a discharge of 0.1 lithium equivalents at a current density of 1 mA cm^{-2} .

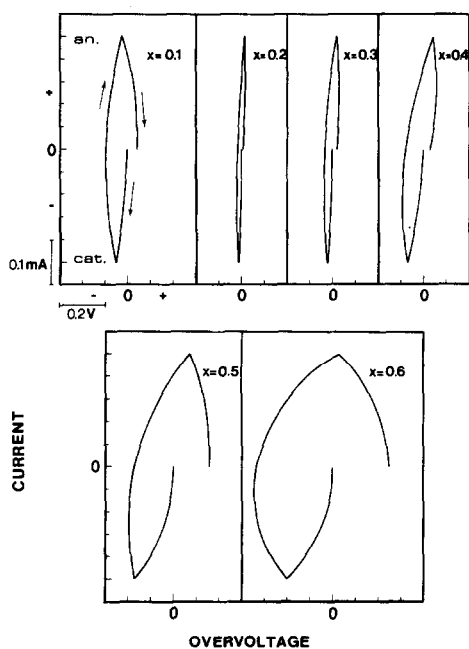


Fig. 5. Cathodic and anodic polarization scans of Li_xTiO_2 at different x values. Room temperature; sweep rate: $1 \mu\text{A s}^{-1}$.

per mole of TiO_2 and m and M the minimum and maximum values at the beginning and the end of the experiment, respectively. Polarization cycles on $\text{Li}_{0.2}\text{TiO}_2$, indeed, showed a practical absence of hysteresis and even under reasonably high currents, the anodic and cathodic scans remained linear.

The study of the recharge efficiency of the first cycle may add further information. These experiments were performed by discharging fresh cells to a known depth at constant current and then recharging at the same current density up to an arbitrarily chosen voltage value. Figure 6 shows a typical bell trend with a maximum efficiency corresponding to a composition of $x =$

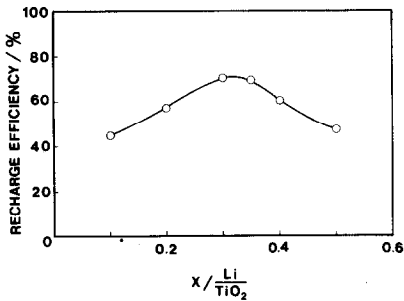


Fig. 6. Recharge efficiency in the first cycle for anatase. Room temperature; current density: 0.5 mA cm^{-2} .

0.30 - 0.35. The optimum range for recharge efficiency is between $x = 0.2$ and $x = 0.4$, which corresponds to the optimum range for the polarization cycles.

Further tests were devoted to the study of practical cyclability of materials having a lithium content in the optimum range. Thus a cell of the type:



was submitted to cycles involving the transference of lithium between $x_m = 0.13$ and $x_M = 0.20$. Typical results are reported in Fig. 7. Indication of cell deterioration, such as increase of cell resistance, progressively appeared from the 30th cycle. This, however, may be ascribed to the negative electrode, which suffers from non-uniform metal deposition. It is, in fact, known [5] that lithium presents a poor plating-stripping efficiency in the $\text{LiClO}_4\text{-PC}$

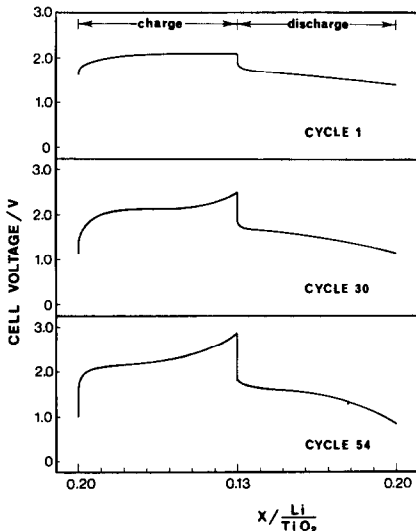


Fig. 7. Charge-discharge cycles of cell 2. Room temperature; current density: 1 mA cm^{-2} .

electrolyte. Indeed, massive lithium dendrite formation was noticed on the negative side of cell (2), when disconnected and opened after the 54th cycle.

In this respect (dendrite formation), current density could be a critical parameter as shown in Fig. 8, where the recharge-discharge curves after a large number of cycles at three different current densities are reported: the influence of the cycling rate on the charging overvoltage is evident.

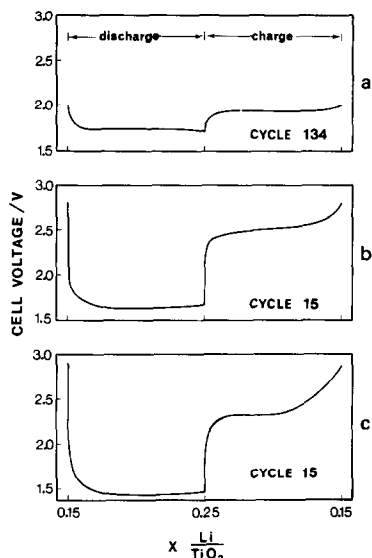


Fig. 8. Discharge-charge cycles at different current densities. Room temperature. (a) 0.25 mA cm^{-2} ; (b) 0.5 mA cm^{-2} ; (c) 1.2 mA cm^{-2} .

Depth of cycles is also an important factor, and it must be considered in relation to the lowest composition which is reached during the recharge. Indeed, we observed that when the recharge depth was such that the final composition was below $x_m = 0.1$, the recharge was characterized by high overvoltage, and subsequently the cycling behaviour tended to worsen rapidly. By contrast, when the lowest lithium content was $x_m = 0.15$, the cells could sustain cycle depths higher than 0.15 without any deterioration or substantial increase in overvoltage. In Fig. 9 an example is given of discharge curves of a cell, which, after having been submitted to 130 cycles of 0.05 depth at 0.25 mA cm^{-2} , was submitted to several cycles of 0.10 and 0.15 depth, respectively, passing from $x_m = 0.15$ progressively to $x_M = 0.20$, 0.25, and 0.30.

When lithium dendrite formation effects are limited by using sufficiently low cycling rates, cells based on anatase can be submitted to a very high number of cycles without any significant deterioration. As shown in Fig. 10, after the first 10 - 15 cycles, the discharge voltage attained stable values which are maintained under prolonged cycling tests.

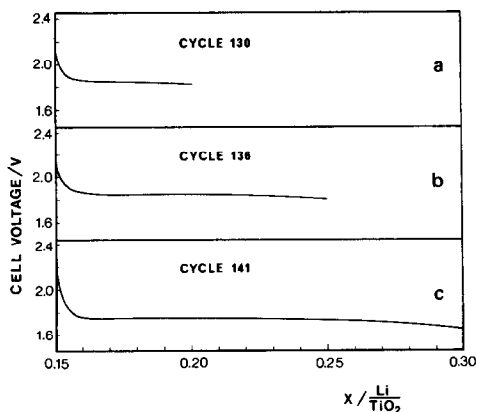


Fig. 9. Discharge curves of a cell of type 2 after extended cycling at different depths of discharge: (a) $\Delta x : 0.05$; (b) $\Delta x : 0.10$; (c) $\Delta x : 0.15$. Room temperature; current density: 0.25 mA cm^{-2} .

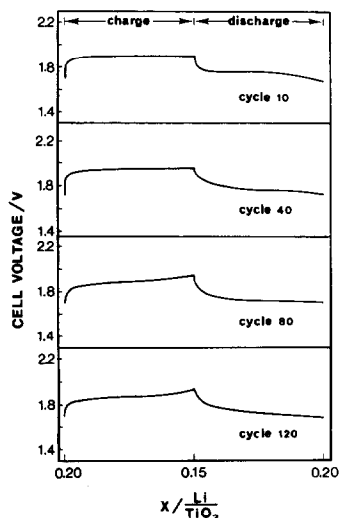


Fig. 10. Typical cycling behaviour of a cell of type 2. Room temperature; current density: 0.25 mA cm^{-2} .

A comparison was also made between materials characterized by a slightly different composition (lower ZnO content: 0.05 instead of 0.10 wt.%) or obtained at lower temperature (960 instead of 980 °C): no difference was observed as far as the cycling behaviour is concerned.

At this stage of the research no attempt was made to optimize the positive electrode performances by studying the influence of various relevant factors (additives, optimum cathode formulation, compaction pressure, type and number of separators).

Conclusions

The results reported confirm the interest in anatase as a potential cathode material in lithium secondary batteries. It is, indeed, characterized by a flat discharge curve and by a quite good cyclability. However, the latter feature is optimized in a range of compositions (approximately $0.15 < x < 0.40$). The low cost of commercial anatase (on which the present research was carried out) can stimulate further studies aiming to cell optimization.

The discharge mechanism is not yet fully clarified*, but various experimental facts (such as new reflections in X-ray diffraction patterns, trend of discharge curves, open circuit values as a function of discharge depth) are in favour of the reversible formation of a new phase in the composition range investigated.

Acknowledgements

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Note

When the work was about to be submitted, we became aware of a paper by Dhao-Zhi Bi, Ji-Qiang Wang and Yi-Hong Sun, having the title: *A study of $\alpha\text{-TiO}_2$ as cathode material for ambient temperature lithium secondary cells: typical charge and discharge characteristics of $\alpha\text{-TiO}_2$ in organic electrolytes*, to be presented at the 12th International Power Sources Symposium, Brighton, England, September 15 - 18, 1980. The conclusion reported in the abstract ("..... the electrochemical reaction of $\alpha\text{-TiO}_2$ in organic electrolytes is reversible. Therefore it is a possible cathode material in low voltage (1.5 to 1.8 V) low drain ambient temperature lithium secondary cells.") is in substantial agreement with the conclusion of the present paper.

*Note added in proof

On the basis of a model described in a recent paper [6], Voinov suggests that the discharge mechanism of Li/TiO_2 cells is the insertion of lithium in tetrahedral sites of ccp oxygen layers. According to this model, the open circuit voltage values dependence on the amount of intercalated lithium, may be described by the replacement of $p\pi$ Ti-O bonds by σ Li-O bonds. This would imply O.C.V. values almost constant up to about $x = 0.5$ in Li_xTiO_2 , as indeed we have observed in this work (see Fig. 3).

References

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