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Electrochemical behavior of a lithium titanium spinel compound synthesized *via* a sol–gel process

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The synthesis and the structural features of a mixed lithium titanium spinel $Li_{4/3}Ti_{5/3}O_4$ obtained *via* a sol–gel process in non-aqueous media are reported. Electrochemical lithium insertion occurs in one reduction process located at 1.550 V, and corresponds to the insertion of 1 Li per $Li_{4/3}Ti_{5/3}O_4$ (150 A h kg^{-1}) in octahedral sites. During cycling experiments performed at discharge–charge rates of $C/20$, a stabilization of the specific capacity around 105 A h kg^{-1} (0.7 F mol^{-1}) occurs after the 20th cycle.

So-called 'rocking-chair' rechargeable batteries that use lithium intercalation compounds for the positive and negative electrodes have been proposed as alternatives for batteries containing lithium metal.[1,2] Recent work has pointed to using the spinel $Li_{4/3}Ti_{5/3}O_4$ as a new cathodic intercalation material rechargeable for Li cells and also as a negative electrode for rocking-chair batteries.[3–6] From these results, such a cell reversibly inserts 0.7–1 Li per $Li_{4/3}Ti_{5/3}O_4$ at an average plateau voltage of 1.55 V, yielding a specific capacity of 120–150 A h kg^{-1} at the end of the 100th cycle.[4,5] This compound shows much better electrochemical properties than the spinel $LiTi_2O_4$,[4] at a lower working potential of only 1.34 V, owing to the lower ratio of Ti^{4+} ions in $LiTi_2O_4$ (50%) than in $Li_{4/3}Ti_{5/3}O_4$ (100%).

In previous work,[7–9] we pointed out the potential of the sol–gel process for the synthesis of new cathodic intercalation materials for Li cells. This method was originally developed as a fabrication technique for glasses or ceramics at low temperature. Owing to polymerisation in liquid solution, it offers many advantages compared to the conventional powder route, such as a better control of morphology, texture of materials and homogeneous final solids. We have shown that various V_2O_5-based compounds (bronzes and mixed oxides) as well as manganese oxides obtained through the sol–gel route exhibit attractive electrochemical performance especially when compared with that exhibited by closely related materials prepared by the solid-state reaction route.[7–9]

The purpose of this paper is to investigate electrochemical Li insertion in the spinel $Li_{4/3}Ti_{5/3}O_4$ synthesized *via* a sol–gel process.

Experimental

Synthesis of the spinel compound $Li_{4/3}Ti_{5/3}O_4$

Titania sol–gel synthesis has been developed from the hydrolysis and condensation of metal–organic precursors or metal alkoxides, $Ti(OR)_4$, which indicates they are the result of a direct combination of a metal M with an alcohol ROH. The reactions traditionally considered with these precursors are those of hydrolysis [eqn. (1)] and of polymerization–condensation by dehydration [eqn. (2)].[10–12]

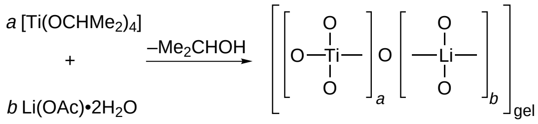
$$Ti(OR)_4 + H_2O \rightarrow Ti(OH)(OR)_3 + ROH \qquad (1)$$

$$\equiv Ti{-}OH + HO{-}Ti\equiv \rightarrow \equiv Ti{-}O{-}Ti\equiv + H_2O \qquad (2)$$

The process leads directly to a polymeric gel. Alternatively, for the synthesis of the spinel $Li_{4/3}Ti_{5/3}O_{12}$, the water molecules are generated *in situ* by the dissolution of a hydrated lithium salt in an alcoholic solvent.

Titanium isopropoxide, $Ti(OCHMe_2)_4$ (Aldrich) (25 ml, 0.082 mol) was added to a solution containing 6.75 g of $LiC_2H_3O_2{\cdot}2H_2O$ in 75 ml of ethanol. A yellow solution was obtained which became more and more viscous leading eventually to the formation of a white monolithic gel after 1 h. The gel was dried in air at 60 °C for one day.

This synthesis leads to an intimate mixture of lithium and titanium oxides and to formation of Ti—O—Li bonds in the solution according to eqn. (3).[10–14]



$$a\,[Ti(OCHMe_2)_4] + b\,Li(OAc){\cdot}2H_2O \xrightarrow{-Me_2CHOH} \left[\left[O{-}\overset{\displaystyle O}{\underset{\displaystyle O}{Ti}}{-}\right]_a O \left[{-}\overset{\displaystyle O}{\underset{\displaystyle O}{Li}}{-}\right]_b\right]_{gel} \qquad (3)$$

The samples obtained after calcination of the gel were characterized by X-ray diffraction, performed with a Inel diffractometer using the Cu-Kα radiation. Thermogravimetry was performed in air at heating rates of 10 °C min^{-1} using a Netszch STA 409 analyser with the simultaneous recording of mass losses (TG) and temperature variations (DTA).

Electrochemical measurements

The electrochemical measurements were performed in doubly distilled propylene carbonate obtained from Fluka. Anhydrous perchlorate was dried under vacuum at 200 °C for 12 h. The electrolytes were prepared under a purified argon atmosphere.

The stainless steel working electrode had a geometric area of 0.5 cm^2 on which the lithium titanium oxide (*ca.* 5 mg), mixed with graphite (20% by mass), was pressed. Lithium was used as the reference and auxiliary electrodes. Galvanostatic cycling experiments were performed in a two-electrode cell. This cell was prepared inside the dry box by placing a clean metal disk, a glass fiber separator soaked with the electrolyte solution, and the cathode pellet in a Teflon container with two stainless-steel terminals.

Results and Discussion

Structural properties of the spinel compound $Li_{4/3}Ti_{5/3}O_4$

The simultaneously recorded thermal analysis curves (TG and DTA) of the powder obtained after calcination of the gel at

60 °C for 1 day are shown in Fig. 1. The total mass loss was 38%. A first mass loss is recorded from 60 to 280 °C (15%), followed by a more substantial mass loss from 300 to 400 °C (23%). Two broad exothermic peaks located at 134.6 and 357.3 °C are associated with the removal of ethanol and then organic compounds as acetate or isopropoxide. A weak endothermic peak observed at 450 °C can be ascribed to the anatase–rutile transformation before formation of the spinel phase $Li_{4/3}Ti_{5/3}O_4$.

X-Ray diffraction experiments *vs.* temperature are shown in Fig. 2. At room temperature [Fig. 2(a)] the sample was amorphous. At 350 °C [Fig. 2(b)], the amorphous powder crystallised into anatase. As can be seen in Fig. 2(c), a mixture of rutile TiO_2 and the spinel $Li_{4/3}Ti_{5/3}O_4$ is obtained at 500 °C. At higher temperature [800 °C, Fig. 2(d)], the XRD pattern of the pure white spinel phase $Li_{4/3}Ti_{5/3}O_4$ is obtained. All the diffraction lines for this compound can be indexed on the basis of a cubic lattice with a parameter $a = 8.346$ Å which is smaller than the value obtained from the literature ($a = 8.35$–8.36 Å).[4,5] According to Colbow *et al.*,[4] the spinel phase $LiTi_2O_4$ consists of a cubic-close-packed array in which 32 oxygen atoms occupy 32e sites of space group *Fd*3*m*; one half of the octahedral 16d sites and one eighth of tetrahedral 8a sites are filled by metal ions (here titanium) and lithium, respectively.

In the case of $Li_{4/3}Ti_{5/3}O_4$ which has a higher Li/Ti ratio (0.8) than $LiTi_2O_4$ (0.5), substitution of titanium by lithium ions occurs in octahedral sites and Ohzuku *et al.* have suggested the following formula $Li^{8a}[Li^{16d}_{1/3}Ti^{16d}_{5/3}]O_4$.[4]

It should be remarked that the formation of the pure sol–gel spinel occurs at 800 °C over 2 h, *cf.* 800 °C over 12 h or even 900 °C over 20 h for the classical compound,[4,5] as a consequence of mixing at a molecular level in the gel of the precursors.

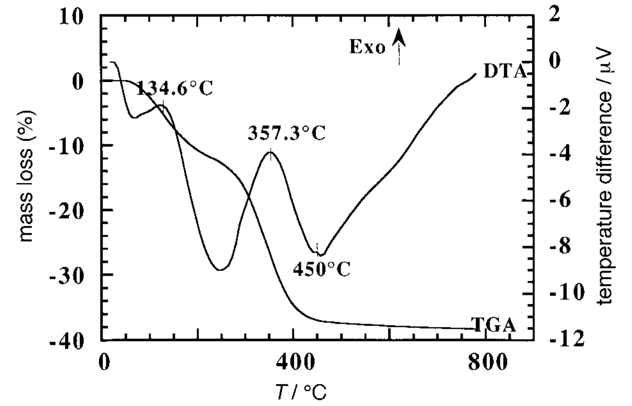


Fig. 1 Simultaneous thermal analysis (TG and DTA) of the Li/Ti xerogel

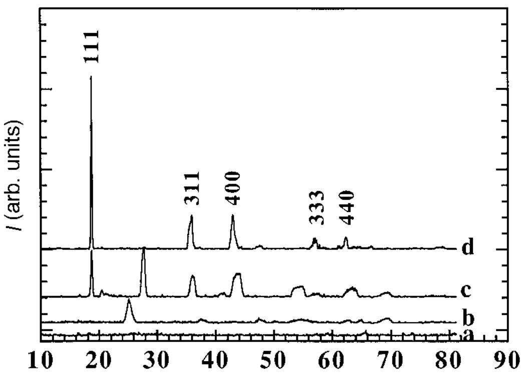


Fig. 2 Evolution of the X-ray diffraction patterns (Cu-Kα) of the xerogel at RT (a), heated at 350 °C for 5 h (b), 500 °C for 5 h (c) and 800 °C for 2 h (d)

Electrochemical properties of the spinel compound $Li_{4/3}Ti_{5/3}O_4$

Typical chronopotentiometry at *C*/60 for the reduction–oxidation processes of the sol–gel spinel $Li_{4/3}Ti_{5/3}O_4$ in 1 M $LiClO_4$ in propylene carbonate is shown in Fig. 3(a). One main process for Li insertion and extraction is evidenced in both galvanostatic and voltammetric curves. This step appears as a voltage plateau located at *ca.* 1.550 V, and corresponds to the insertion of 1 Li per $Li_{4/3}Ti_{5/3}O_4$ in octahedral sites. The accommodation of only 1 Li per mole of spinel, which corresponds to the reduction of 50% of titanium is due to the limited number of available 16c octahedral sites in the spinel structure. Of particular interest is the very close operating voltages (*ca.* 20–30 mV) during reduction and oxidation processes. This probably indicates similar kinetics for Li transport in the oxide for insertion and deintercalation as well as reversible behaviour. For instance, the chronopotentiometric curves obtained at *C*/60 are very close to the open circuit voltage data ($x = 0.2$, $E_{eq} = 1.567$ V; $x = 0.55$, $E_{eq} = 1.564$ V).

The influence of the current density on the discharge–charge curves of the sol–gel compound is shown in Fig. 3. No significant decrease in the total faradaic yield, *ca.* 0.8–0.95 F (mol oxide)$^{-1}$, is observed for different rates ranging from *C*/60 to *C*/5. An important decrease in the faradaic yield is only observed for higher discharge rates such as *C*/2 which may be explained by the electronically insulating character of the compound.[4] Whatever the current density applied, a slight capacity loss is observed during the charge process, indicating that *ca.* 0.06 Li ions are permanently trapped inside the host lattice.

Regarding the high specific capacity exhibited by the cathodic material (150 A h kg^{-1}) which corresponds to the accommodation of 1 Li^+ ion per Ti, and the interesting reversible behaviour of the Li insertion reaction found from galvanostatic studies, we have evaluated the cycling behaviour of $Li_{4/3}Ti_{5/3}O_4$ within cycling between 4 and 1.2 V at room temperature. Fig. 4 shows the evolution of the specific capacity as a function of the number of cycles for different discharge–charge rates (*C*/10, *C*/20 and *C*/60). An important variation of the cycling behaviour of the compound as a function of discharge–charge rate is observed. At *C*/10, from an initial value of 150 A h kg^{-1}, the specific capacity decreases rapidly to *ca.* 75 A h kg^{-1} after 20 cycles owing to a constant loss of *ca.* 0.02 Li ions during each oxidation process. At lower rates, the capacity fading is slower. For example at *C*/20, a stabilization of the specific capacity at *ca.* 105 A h kg^{-1}

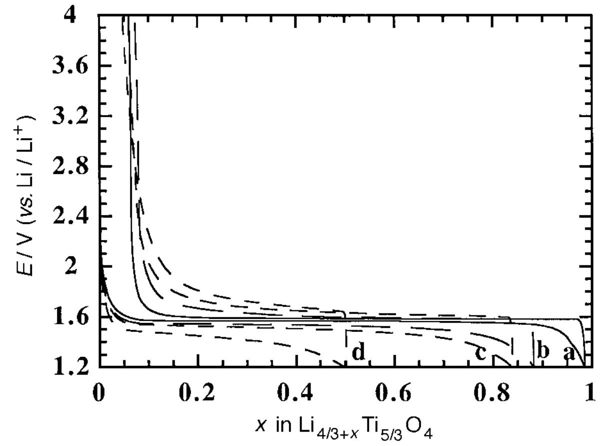


Fig. 3 Influence of the current density on the cyclic chronopotentiograms for a $Li_{4/3}Ti_{5/3}O_4$ electrode in 1 M $LiClO_4$/PC at RT. *C*/60 (a), *C*/10 (b), *C*/5 (c) and *C*/2 (d).

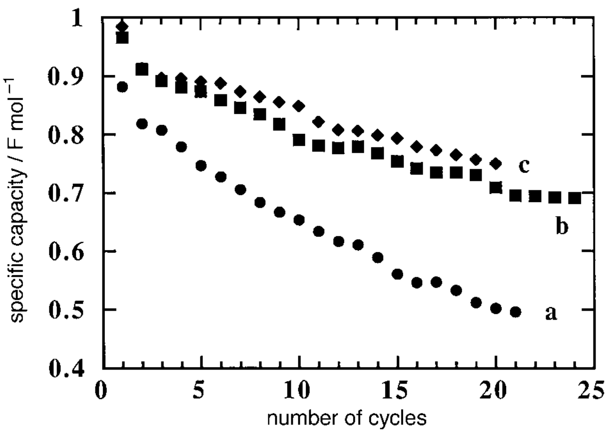


Fig. 4 Evolution of the specific capacity as a function of the number of cycles for differents discharge–charge rates. $C/10$ (a), $C/20$ (b) and $C/60$ (c).

(0.7 F mol^{-1}) occurs after the 20th cycle. In order to confirm whether or not the matrix is damaged by cycling we have performed XRD experiments for $Li_{4/3}Ti_{5/3}O_4$ after cycling. Typical lines of the spinel structure are observed and can be indexed on the cubic structure with cell parameters close to that of the parent oxide, *i.e.* the structure is well maintained even after extended cycling.

Recently, a better reversible behavior has been reported by Ohzuku *et al.* for this compound synthesized by solid state reactions in which 1 Li^+ was reversibly accommodated during 100 cycles.[5] However, the latter experiments have been performed at very low discharge–charge rates ($C/180$).

In summary, the presence of some Li ions trapped in the spinel structure are responsible for decline in the capacity while no significant structural changes occur. Such an inconsistency raises some questions and calls for deeper investigations on electrochemical and structural properties to understand and to solve this phenomenon. This work is in progress in our laboratory.

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