

# A novel layered lithium niobium titanate as battery anode material: Crystal structure and charge-discharge properties



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## ABSTRACT

LiTi<sub>2</sub>NbO<sub>7</sub> was synthesized from CsTi<sub>2</sub>NbO<sub>7</sub> by direct Cs<sup>+</sup>/Li<sup>+</sup> ion exchange and subsequent thermal decomposition of the hydrated form. Neutron powder diffraction data were collected at high-resolution (ILL, France) and analyzed by Rietveld refinements and Fourier difference techniques, revealing a layer-like crystal structure (orthorhombic *Pbnm*, *a* = 9.2476(6), *b* = 16.955(2), *c* = 3.7542(2) Å) partly similar to that of monoclinic LiTi<sub>3</sub>O<sub>7</sub>. Lithium is tetrahedrally coordinated and bridges adjacent layers of (Ti,Nb)O<sub>6</sub> octahedra. Nb atoms are strongly ordered in one of the three independent sites available for Ti/Nb, thus compensating for the unbalance of negative charge from the surrounding O atoms. Electrochemical measurements were performed on a LiTi<sub>2</sub>NbO<sub>7</sub> electrode vs. Li/Li<sup>+</sup> couple. Overlapping Ti<sup>4+</sup>/Ti<sup>3+</sup> and Nb<sup>5+</sup>/Nb<sup>4+</sup> redox processes occur around 1.4 V, with a specific charge of 245 mAh/g (about 2.8 electrons per f.u.) in the 2.30 to 1.15 V range. Charge-discharge cycling results show a reversible and stable specific capacity of 220 mAh/g at low current density, indicating that this material is a promising alternative to Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> spinel for reversible anode applications in lithium batteries.

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## 1. Introduction

The standard LiC<sub>6</sub> anode of lithium batteries is well known to raise serious safety issues. These are mainly related to possible growth of lithium dendrites, which may produce short-circuits with risk of firing the carbonate electrolyte [1,2]. Thus, on searching for alternative anode materials a lot of research efforts have been focused on transition metal oxides with cathodic potentials around 1.0–1.5 V vs. Li/Li<sup>+</sup>, which can be used as anode materials vs. high-voltage (4.0 to 5.0 V) oxide cathodes and still provide an interesting electric power [3–5]. In this respect, a number of lithium titanium oxide materials have been investigated because of the suitable Ti<sup>4+</sup>/Ti<sup>3+</sup> reduction potential, which is observed to range around 1.5 V against lithium [6]. Some significant examples are TiO<sub>2</sub> [7], LiTi<sub>2</sub>O<sub>4</sub> in the anatase [8] and spinel-like [8,9] modifications, and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> with spinel structure [9–11]. The latter material, in particular, shows a quite good reversibility in charge-discharge operation, and it is already liable to industrial applications. Also niobium oxides were investigated as anode materials, since the Nb<sup>5+</sup>/Nb<sup>4+</sup> potential is similar to that of the titanium couple, but lower niobium oxidation states are also available for further redox reaction steps: thus, in principle a larger capacity per atom could be attained [12–14].

Quite recently, the research was extended to the mixed titanium-niobium oxide TiNb<sub>2</sub>O<sub>7</sub>, which showed very satisfactory properties of lithium intercalation. A reversible capacity of 285 mAh/g was demonstrated in the 1.0 to 2.0 V range [15–17], corresponding to insertion of

3.6 Li atoms per formula unit (f.u.), and even better performances could be obtained by use of nanomaterial fabrication techniques [18–22]. The mechanism of Li intercalation into this material was also elucidated by determining the lithium atom distribution in the perovskite-related crystal structure of Li<sub>x</sub>TiNb<sub>2</sub>O<sub>7</sub>, and by analyzing its electronic properties [23]. Lithium was successfully inserted electrochemically also in the LiTiNbO<sub>5</sub> compound [24] with a completely different layer-like structural topology.

We thus decided to explore the atomic arrangement and electrochemical behaviour of other compounds in the Li,Ti,Nb,O system, focusing on the LiTi<sub>2</sub>NbO<sub>7</sub> material. This was reported to have been synthesized from CsTi<sub>2</sub>NbO<sub>7</sub> by double ion exchange (Cs<sup>+</sup> to H<sup>+</sup> to Li<sup>+</sup>) in water solution [25], but its chemical and physical properties were not characterized in detail. The orthorhombic crystal structure of the caesium compound, on the other hand, was determined [26], and despite the different symmetry it shows a similar layer-like configuration as that of monoclinic Li<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> [27]. An investigation of LiTi<sub>2</sub>NbO<sub>7</sub> was therefore undertaken, with the aims of (i) finding a simpler synthesis route by direct ion exchange from CsTi<sub>2</sub>NbO<sub>7</sub>, (ii) determining the crystal structure and lithium location by high-resolution neutron diffraction, and (iii) assessing the ability of the material to intercalate lithium atoms reversibly against a Li anode, so as to operate successfully as an electrode in rechargeable batteries.

## 2. Experimental

### 2.1. Synthesis, X-ray and neutron diffraction

The  $\text{Nb}_2\text{O}_5$  reagent was prepared by thermal treatment of the commercial (Sigma-Aldrich) orthorhombic product at 1200 °C for 24 h [12], so as to get the more reactive monoclinic phase, then it was quenched in liquid  $\text{N}_2$ .  $\text{Cs}_2\text{CO}_3$  was dried at 350 °C for 1 h and then mixed with  $\text{TiO}_2$  and  $\text{Nb}_2\text{O}_5$  in 1:4:1 M ratio. The ground and pelletized powder was annealed at 1050 °C for 20 h in a Pt crucible and subsequently quenched in air. The obtained sample proved to be pure orthorhombic  $\text{CsTi}_2\text{NbO}_7$  by X-ray diffraction analysis (Bruker D8 Advance equipment,  $\text{CuK}\alpha$  radiation):  $a = 9.326$ ,  $b = 18.412$ ,  $c = 3.798$  Å, space group  $Pnam$ .

Ion exchange was performed on  $\text{CsTi}_2\text{NbO}_7$  in a 4 M solution of  $\text{LiNO}_3$  at 50 °C for 8 days, changing solution every 2 days. By atomic emission flame photometry the alkali composition  $\text{Li}_{0.98}\text{Cs}_{0.02}$  was determined for the compound obtained; the small amount of residual caesium will be neglected henceforth. The fresh product and that kept in air for 12 h were analyzed by thermogravimetry to measure the water content (Fig. 1). After the initial removal of different amounts of superficial water below 60 °C, in both cases a weight loss of about 5.0% is observed in the 200 to 270 °C thermal range. This corresponds to  $n = 0.91$  in the chemical formula  $\text{LiTi}_2\text{NbO}_7 \cdot n\text{H}_2\text{O}$ , indicating the presence of approximately one structural  $\text{H}_2\text{O}$  molecule per formula unit.

X-ray diffraction patterns (PANalytical diffractometer,  $\text{CuK}\alpha$  radiation) were recorded both on fresh  $\text{LiTi}_2\text{NbO}_7 \cdot \text{H}_2\text{O}$  and on the dehydrated sample obtained by annealing at 350 °C for 1 h (Fig. 2). In both cases protection against water absorption was assured by kapton film covering of the specimens. The pattern of the hydrated compound is similar to that of the parent caesium salt; its unit-cell was refined to  $a = 9.277(1)$ ,  $b = 18.228(3)$ ,  $c = 3.7616(5)$  Å, confirming the  $Pnam$  space group [25,26]. Anhydrous  $\text{LiTi}_2\text{NbO}_7$ , on the other hand, shows a significantly different diffractogram, which could not be indexed correspondingly. By use of the DICVOL indexing code [28], and taking into account the systematic absences of reflections, the lattice parameters  $a = 9.263(4)$ ,  $b = 16.948(8)$ ,  $c = 3.757(1)$  Å were obtained with  $Pbnm$  symmetry. It appears that, on dehydration, the  $a$  and  $c$  constants change little, but the  $b$  one is shortened very much as a consequence of the inter-layer water removal.

Neutron diffraction measurements for  $\text{LiTi}_2\text{NbO}_7$  were performed on the high-resolution ( $\Delta d/d = 5 \times 10^{-4}$ ) D2B powder diffractometer at the reactor source of the Institut-Laue-Langevin (Grenoble, France). A primary beam monochromator set at  $\lambda = 1.5957$  Å was employed.

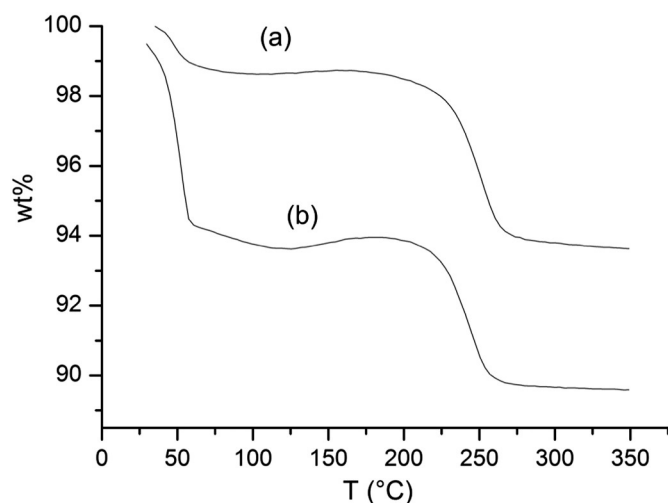


Fig. 1. Thermogravimetric analysis of  $\text{LiTi}_2\text{NbO}_7 \cdot n\text{H}_2\text{O}$ : (a) fresh sample obtained by ion exchange of  $\text{CsTi}_2\text{NbO}_7$ ; (b) after 12 h in air.

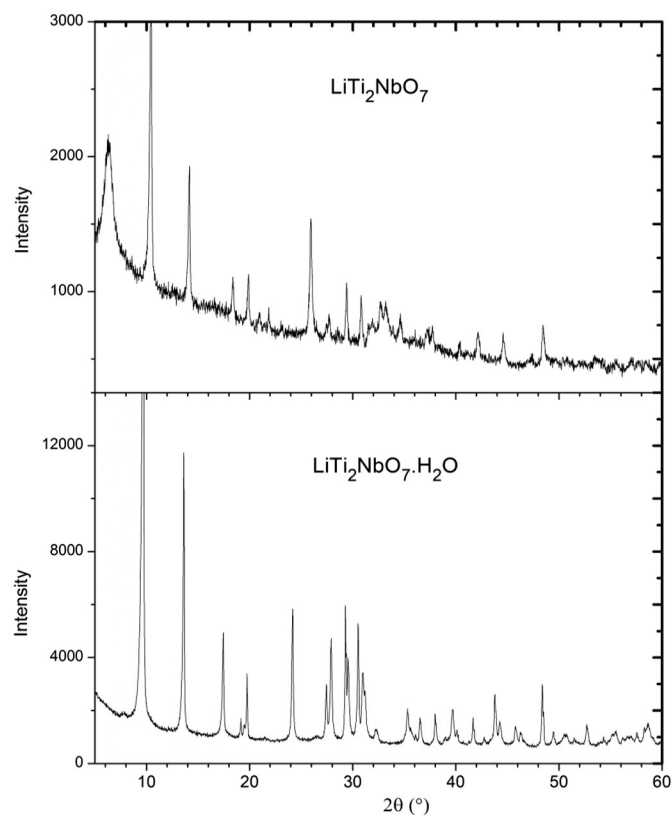


Fig. 2. X-ray powder patterns ( $\text{CuK}\alpha$  radiation) of the fresh hydrated (below) and dehydrated (above) samples of lithium dititanium niobium oxide.

The sample was put in a vanadium can, sealed with indium wire in Ar atmosphere for protection against hydration. Measurements were carried out in the 5–160°  $2\theta$  range.

The GSAS computer code [29] was employed for analyzing the diffraction data and performing the Rietveld refinements of the crystal structure. The Bragg peak was modelled by a pseudo-Voigt function (linear combination of Gaussian and Lorentzian components, with  $\sigma$  and  $\gamma$  half-widths, respectively). The  $\sigma$  and  $\gamma$  coefficients depend on  $\theta$  according to  $\sigma = (U \tan^2 \theta + V \tan \theta + W)^{1/2}$  and  $\gamma = X / \cos \theta + Y \tan \theta$ ; the  $U$ ,  $V$  and  $W$  parameters come from the instrumental resolution function,  $X$  is the Scherrer coefficient for Lorentzian particle size broadening, and  $Y$  represents the particle strain broadening. The full width and the mixing coefficient of the pseudo-Voigt function vary with  $\sigma$  and  $\gamma$  according to literature relationships [30].

### 2.2. Electrochemistry

Active material electrodes were fabricated by mixing  $\text{LiTi}_2\text{NbO}_7$  (70%), PVDF binder (15% Solvay 8020 polyvinylidene difluoride) and conductive carbon black (15%, Super P MMM Carbon). The mixture was dispersed in *n*-methyl-pyrrolidone (NMP) to obtain a dense slurry which was casted on copper foil and dried at 90 °C for 2 h. The active material load was around 1–3  $\text{mg}/\text{cm}^2$ . Measurements were performed using CR2032 coin half cells equipped with metallic lithium foils as counter electrode (all potentials are reported versus the couple  $\text{Li}^+/\text{Li}$ ). The electrolyte was a commercial electrochemical grade solution of 1 M  $\text{LiPF}_6$  in dimethylcarbonate:diethylcarbonate 1:1 supported by a porous polypropylene foil. Cells were assembled in an argon filled glove box ( $[\text{O}_2] < 1$  ppm). The measurements were carried out at room temperature using a Biologic VMP3 multi-channel battery tester.

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