A study of lithium insertion in two tetragonal tungsten bronze type phases, (M = Nb and Ta), has been carried out. The electrochemical insertion of up to 20 lithium atoms per formula unit in Nb$_8$W$_9$O$_{47}$ (Li:2M = 1:2) proceeds through a reversible reaction with several singlephase and one two-phase domains, while in Ta$_8$W$_9$O$_{47}$ the reversibility of lithium insertion is limited to 15 atoms (Li:2M = 0.9). Structural changes on Nb$_8$W$_9$O$_{47}$ as a function of the number of lithium atoms inserted have been studied by X-ray powder diffraction.

Introduction

The study of the chemistry of tungsten bronzes and related phases has attracted considerable attention because of their potential use as electrodes, catalysts and in optical displays. Additionally, these phases were found to present interesting optical and ferroelectric properties. In this context and continuing with work started recently in our research group on insertion reactions in some niobium–tungsten mixed oxides,\(^5\) a study of lithium insertion in two tetragonal tungsten bronze (TTB) type phases of general formula M$_8$W$_9$O$_{47}$ (M = Nb and Ta), has been carried out. From the solid state chemistry point of view, the Nb$_8$W$_9$O$_{47}$/Ta$_8$W$_9$O$_{47}$ systems behave in a fairly similar way in the region rich in WO$_6$ Phases containing between 50 and 80 wt% of WO$_6$ present a structure similar to the so-called tetragonal tungsten bronze (TTB). These phases consist in a framework of MO$_6$ octahedra sharing corners, linked in such a way that three, four- and five-sided tunnels are formed. Decreasing oxygen-to-transition metal ratio (3 in WO$_6$ vs. 2.76 in M$_8$W$_9$O$_{47}$) is achieved in these TTB type phases by filling a certain number of five-sided tunnels with oxygen and metal atoms thus forming the so-called pentagonal columns (PCs) for short.\(^5\) A MO$_6$ pentagonal bipyramid sharing equatorial edges with five MO$_6$ octahedra. In Nb$_8$W$_9$O$_{47}$ (Fig. 1) one third of the pentagonal tunnels are occupied in this way.\(^5\) Cation sites with pentagonal bipyramidal coordination are preferentially occupied by niobium while in the corner sharing metal-oxygen octahedra, metal atoms are on average (0.4 Nb ± 0.6 W). While only one polymorph for Nb$_8$W$_9$O$_{47}$ has been reported to exist, two have been found for Ta$_8$W$_9$O$_{47}$, a low (tetragonal) and a high temperature form (orthorhombic), both exhibiting TTB type structures, although only in the high temperature one (1400 °C) it is possible to observe threefold TTB-type superstructure.\(^5\) A similar cation distribution to that found for the niobium-tungsten mixed phases was also proposed here. It is important to point out that although M$_8$W$_9$O$_{47}$ is the ideal composition, a small range of non-stoichiometry may exist in both niobium and tantalum TTB type phases, due to disorder in the tunnels occupancy. Compounds presenting structures containing PCs as main building units, such as W$_8$O$_{47}$, have been already studied as host materials for reversible lithium insertion reactions.\(^6\) In this work a study of the electrochemical lithium insertion in M$_8$W$_9$O$_{47}$ has been carried out. In order to evaluate the influence of lithium insertion on the structure of the parent oxide, some lithiated phases were synthesised by indirect chemical reaction and characterised by X-ray powder diffraction experiments. As the main difference between both mixed tungsten oxides is the presence of Nb\(^{4+}\) instead of Ta\(^{4+}\), it would be interesting to compare their behaviour versus lithium insertion reactions. No attempt is made in this work on testing M$_8$W$_9$O$_{47}$ as cathode materials in lithium ion batteries.

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Fig. 1 Idealised structure of Nb$_8$W$_9$O$_{47}$. When joining the different polyhedra, five-, four- and three-sided tunnels are formed where additional ions can be inserted.
Experimental

Preparation and characterisation of pristine materials, Nb₉W₂O₅

The tantalum-tungsten and niobium-tungsten mixed oxides used in this study were synthesised by solid state reaction. The starting materials, WO₃ (Alrich Chem. Co, 99 ++ %), Nb₂O₅ (Alfa Products 99.9%), and Ta₂O₅ (Alrich Chem. Co, 99.99%), were weighed in the appropriate stoichiometric ratio (4 M₉O₁₈:9 WO₃) and thoroughly mixed by grinding in an agate mortar using Analar grade acetone. Powders were then pressed into 10 mm diameter pellets, placed in a platinum crucible and fired at 1250 °C in an electrical furnace. During firing samples were periodically extracted from the furnace and ground to favour reaction before being finally quenched at room temperature. Phase identification was carried out by X-ray powder diffraction in a Siemens D-5000 diffractometer using Cu-Kα radiation (λ = 1.5418 Å). A typical diffraction experiment for determining cell parameters was run with a step size of 0.12° min⁻¹ using KCl as internal standard.

Electrochemical lithium insertion

Electrochemical experiments were carried out with a multi-channel potentiostatic-galvanostatic system MacPile II using a Swagelok™ type cell with metal lithium acting simultaneously as negative and reference electrode. Positive electrodes were prepared by mixing the phase being tested, Nb₉W₂O₅ or Ta₉W₂O₅, with carbon black and a binder, (0.5%) ethylene-propylene-diene terpolymer, EPDM, in cyclo-hexane) either in an 89:10:1 ratio (wt.%) for niobium containing samples or in a 59:40:1 ratio for the tantalum compound (Nb material is not a good electronic conductor so a larger proportion of carbon has to be used). The electrolyte used was a 1 mol dm⁻³ solution of LiClO₄ in a previously dried 50:50 mixture of ethylene carbonate (EC) and diethoxyethane (DEE). Cell assemblage was carried out in a MBraun glove box under an argon atmosphere with continuous purge of water vapour and oxygen ensuring an inside concentration for DEE. Cell assemblage was carried out in a MBraun glove box under an argon atmosphere with continuous purge of water vapour and oxygen ensuring an inside concentration for DEE. Cell assemblage was carried out in a MBraun glove box under an argon atmosphere with continuous purge of water vapour and oxygen ensuring an inside concentration for DEE.

Lithium chemical insertion

Lithium insertion was also carried out by chemical reaction of Nb₉W₂O₅ with an appropriate reducing agent, n-butyllithium in n-hexane. A given volume of this reagent (1.6 mol dm⁻³) was added to a known weight of host material previously placed in a glass reaction vessel. The mixture was stirred for 7 days. Reaction products were thoroughly washed with n-hexane, dried and stored in the glove box. Lithium content in LiₓNb₉W₂O₅ was analysed by AAS using a Varian SpectrAA spectrometer after extraction of the inserted ions using concentrated nitric acid. Phase identification was carried out by X-ray powder diffraction as described above. Although lithium inserted Nb₉W₂O₅ proved to be stable at least during the time of observation, intercalated samples were covered by a polyethylene film while recording data on the diffractometer to prevent sample oxidation.

Results and discussion

Electrochemical lithium insertion in Nb₉W₂O₅

Electrochemical lithium insertion in Nb₉W₂O₅ was carried out by discharging a cell with the following configuration: Li|LiClO₄ in (50% DEE:50% EC)|Nb₉W₂O₅. Results obtained from SPECS experiments run down to 1.1 V vs. Li⁺/Li using ±10 mV (2 h)⁻¹ potential steps, are shown in Fig. 2 as an E vs. composition (x in LiₓNb₉W₂O₅) plot. As can be seen in this graph, Nb₉W₂O₅ can reversibly incorporate up to 20 lithium atoms per formula unit which correspond to about 1.2 Li per metal atom. Almost all lithium atoms inserted are removed after completing a charge–discharge cycle. The main features of this plot are two plateaux, A and B, of approximately constant E values around 2.1 and 1.7 V vs. Li⁺/Li separating three regions where a continuous variation of E with composition is observed. In order to determine the existence of continuous transformations or to multiphase regions, potentiostatic experiments were analysed in more detail. Representing these results as Q vs. E, Fig. 3, it is possible to see that the electrochemical lithium insertion in this material goes really through three very well defined reduction steps labelled here as A, B and C. The electrochemical lithium extraction from LiₓNb₉W₂O₅ follows a similar mechanism and three analogous steps, labelled as A’, B’ and C’, are also present.

It was observed that the nature of the first step (labelled as A and A’) was always better defined on oxidation and second
voltage region where the reduction peak labelled in Fig. 3 as A making for a second oxidation peak A

Thus, it could be assumed that the first reduction step A which corresponds to the first plateaus (at higher E values) also labelled as A in Fig. 2, can be associated with a multiphase domain separating two solid solution regions, I and II. The phase I–phase II equilibrium potential can be given as the intercept at the slope extrapolations at zero current, i.e. 2.12 V. Fig. 5 shows the evolution of the cell voltage versus composition obtained when cycling a similar cell to the one described elsewhere in this work, between 3 and 1.75 V vs. Li+/Li. As can be seen in this graph, phase I transformation to phase II is a reversible process with all the atoms initially incorporated being extracted after completing a charge-discharge cycle. Since potentiostatic experiments run at \( \pm 10 \text{ mV (2 h)} \) potential steps did not reveal unambiguously the exact nature of reduction steps labelled in Fig. 3 as B and C and their corresponding oxidation steps B' and C', it was necessary to run experiments at much lower scan rates [\( \pm 10 \text{ mV (2 h)} \)] potential steps. The voltage region where the reduction peak labelled in Fig. 3 as B was found, is shown in Fig. 6. In this case, the monotonic tendency towards I–0 observed in the current decay vs. time plot, can be associated with a continuous transformation. In homogeneous solutions and assuming that there is no ion–ion interaction, the system behaves in a similar way independently of the amount of lithium atoms inserted. A similar behaviour of the current decay versus time is observed on the third reduction peak labelled in Fig. 3 as C making for a second continuous transformation between 1.3 and 1.6 V vs. Li+/Li on lithium insertion in Nb\(_2\)W\(_6\)O\(_{17}\).

A confirmation of these observations is presented in Fig. 7 which shows a comparison between two voltamperograms obtained when running SPECS experiments \( \pm 10 \text{ mV (2 h)} \) potential steps the voltage range where peak B was observed. A similar behaviour of the current decay versus time is observed on the third reduction peak labelled in Fig. 3 as C making for a second continuous transformation between 1.3 and 1.6 V vs. Li+/Li on lithium insertion in Nb\(_2\)W\(_6\)O\(_{17}\).

A confirmation of these observations is presented in Fig. 7 which shows a comparison between two voltamperograms obtained when running SPECS experiments \( \pm 10 \text{ mV (2 h)} \) potential steps the voltage range where peak B was observed.
Lithium insertion reaction reversibility in this material can be better appreciated in Fig. 8 where results obtained after completing three charge-discharge cycles in a cell configured as mentioned above are presented. Cycling is carried out with minimal capacity losses. Data shown were obtained from a galvanostatic experiment run at a cycling rate greater than C/76 (C/76 corresponds to a charge or a discharge within 76 h).

According to the structure shown in Fig. 1, a total of 26 different tunnels are found in a unit cell of this phase which will also contain two formula units of Nb₈W₉O₄₇. These cavities are distributed as follows: 8 five-sided tunnels; 6 four-sided and 12 three-sided channels. In order to be able to accommodate 40 lithium atoms (20 per formula unit) in 26 cavities is not possible to give a filling sequence of these cavities. An attempt was made to prepare lithiated phases by chemical reaction using KCl as internal standard. Powder patterns showed a gradual change in position and intensity of some reflections as the insertion reaction proceeded. Results are shown in Table 1.

Electrochemical lithium insertion in Ta₈W₉O₄₇

A preliminary study of the electrochemical lithium insertion in Ta₈W₉O₄₇, an isostructural phase with Nb₈W₉O₄₇, containing tantalum instead of niobium, was carried out by discharging a similar cell to the one described above. Results obtained from a SPECS experiment run at ±10 mV (2 h)−¹ potential steps. are shown in Fig. 9 as the evolution of cell voltage versus composition (x in LiₓTa₈W₉O₄₇). Only slight slope changes are observed with apparently no existence of voltage plateaux indicating multiphase regions. As can be seen in this plot, Ta₈W₉O₄₇ incorporates a larger number of lithium atoms per formula unit (27. Li/ΣM = 1.6) than its niobium analogue (20 Li/formula unit) between 3.1 and 1.1 V. However, almost 17% of those atoms remained in the structure after completing a charge-discharge cycle showing therefore the existence of larger structural changes on insertion. Fig. 10 shows the evolution of the cell voltage versus composition for a similar cell to the one described above but cycled up to 1.85 V showing therefore the existence of larger structural changes on insertion. Results are shown in Table 1.

Chemical lithium insertion in Nb₈W₉O₄₇

In order to study the influence of lithium insertion on the structure of the parent oxide, different inserted compositions included in the solid solution regions detected during the electrochemical study, were prepared by chemical reaction of Nb₈W₉O₄₇ and n-butyllithium. Inserted materials prepared were characterised as previously described and results in the following compositions: Liₓ₋₀.₂ Nb₈W₉O₄₇ Liₓ₋₀.₄ Nb₈W₉O₄₇ and Liₓ₋₁.₆ Nb₈W₉O₄₇. Phase characterisation was carried out by X-ray powder diffraction using KCl as internal standard. Powder patterns, which are shown in Fig. 11, were indexed using the same orthorhombic cell described in the literature for the starting material by using a least-squares cell refinement program. Results are shown in Table 1.

Powder patterns showed a gradual change in position and intensity of some reflections as the insertion reaction proceeded which can be related with small displacements of the atoms in Nb₈W₉O₄₇ in order to accommodate the lithium ions. The most important changes are observed between diffraction patterns b and c which correspond to phase I transition to phase II. A colour change for these materials was observed as the number of lithium atoms incorporated increased, going from pale yellow for the pristine phase to black for phase II which corresponds to an increase in the electronic conductivity of Nb₈W₉O₄₇ as the insertion reaction
proceeds. Powder patterns obtained after Li removal were very similar to those of the pristine phase confirming the reversibility of this reaction.

Conclusions
A study of lithium insertion in M₆W₉O₄ₓ (M = Nb and Ta), a tetragonal tungsten bronze type phase (TTB) has been carried out. The electrochemical insertion of up to 20 lithium atoms per formula unit of Nb₆W₉O₄ₓ (Li/2M = 1.2) is a reversible reaction which proceeds through three reduction steps: a first order transition at around 2.12 V and two continuous transformations at around 1.70 and between 1.40 and 1.50 V vs. Li/Li⁺. These transformations originated at least two solid solution regions of general formula LiₓNbₓW₉O₄ₓ with the following approximate composition limits: I: 0 < x < 1.2; II: 6 ≤ x ≤ 20. Two incremental capacity peaks observed at 1.70 V (11 < x < 12) and between 1.40 and 1.50 V probably indicate the existence of a tendency to local ordering in phase II. These results are supported by X-ray diffraction data of inserted materials which show important changes on the transition from phase I to II with additional variations as the number of lithium atoms inserted increased. In order to accommodate such a number of lithium atoms and taking into account the number of tunnels available per unit cell, multiple lithium occupancy has to be considered in some cavities.

Electrochemical lithium insertion was also studied in Ta₆W₉O₄ₓ, where the reaction seems to follow a different mechanism confirming that the second transition metal in these TTB type structures (Nb and Ta) plays an important role in the insertion reaction. Lithium insertion reversibility in Ta₆W₉O₄ₓ was observed for a smaller number of atoms than in its niobium analogue (Li/2M = 0.9).

Acknowledgements
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References

Table 1 Cell parameters and cell volume values obtained from X-ray powder diffraction data for LiₓNbₓW₉O₄ₓ.

<table>
<thead>
<tr>
<th>Compound</th>
<th>a/Å</th>
<th>b/Å</th>
<th>c/Å</th>
<th>Cell volume/Å³</th>
</tr>
</thead>
<tbody>
<tr>
<td>W₉Nb₂O₁₉</td>
<td>36.92</td>
<td>12.191</td>
<td>3.945</td>
<td>1764.65</td>
</tr>
<tr>
<td>W₉NbO₁₉</td>
<td>36.67(8)</td>
<td>12.186(2)</td>
<td>3.9447(8)</td>
<td>1763.0 ± 0.7</td>
</tr>
<tr>
<td>Li₁₋ₓNbₓW₉O₄ₓ</td>
<td>36.71(1)</td>
<td>12.20(1)</td>
<td>3.942(1)</td>
<td>1766.1 ± 0.9</td>
</tr>
<tr>
<td>LiₓNbₓW₉O₄ₓ</td>
<td>36.9(1)</td>
<td>12.28(5)</td>
<td>3.941(1)</td>
<td>1790.0 ± 12.7</td>
</tr>
</tbody>
</table>

*Ref. 5.

Fig. 11 X-Ray powder diffraction patterns of (a) Nb₆W₉O₄ₓ, (b) Li₁₋ₓNbₓW₉O₄ₓ, (c) LiₓNbₓW₉O₄ₓ, and (d) LiₓNbₓW₉O₄ₓ.