DALTON
FULL PAPER

Cathodic insertion of ions in tungsten(VI) oxide from aqueous media

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Electrochemical insertion of ions in monoclinic tungsten(VI) oxide from aqueous solutions was investigated at room temperature. The solutions were nitric acid and solutions of Group I and II nitrates. In all the performed insertions, except with lithium nitrate, the obtained intercalates had the composition H_xWO_3 ($0.07 < x < 0.84$). Within this compositional range two types of hydrogen intercalated materials were obtained, both with tetragonal symmetry. For low degrees of insertion ($0.07 < x < 0.17$) the lattice constants were $a = b = 5.225(2)$ and $c = 3.884(4)$ Å. For high degrees of insertion ($0.50 < x < 0.84$) the lattice constants were $a = b = 5.358(2)$ and $c = 3.749(5)$ Å. With lithium nitrate as electrolyte solution intercalates with composition Li_xWO_3 were obtained. After exposure to air the lithium intercalated compounds were tetragonal with lattice constants $a = b = 5.1996(2)$ and $c = 3.8402(1)$ Å. The processes where barium nitrate was used as electrolyte were studied in detail, and the electrochemical processes were determined. The intercalates were characterized using X-ray powder diffraction, and Rietveld refinements of the structures of $H_{0.12}WO_3$ and Li_xWO_3 were performed.

Introduction

Insertion of ions in tungsten(VI) oxide has been studied by a variety of methods: electrolytic reduction of melts,[1,2] electrochemical insertion from water-free media,[3] solid state reactions,[4] reduction with organic compounds[5] and reduction on Jones reductors.[6] The electrochemical insertion of Li^+ ions in amorphous and crystalline thin films of tungsten(VI) oxide from water-free solutions of lithium salts has been studied extensively.[7]

The crystal structure of WO_3 is monoclinic at room temperature with unit-cell dimensions: $a = 7.306$, $b = 7.540$, $c = 7.692$ Å and $\beta = 90.881°$.[8] It is related to the cubic ReO_3 type with corner connected WO_6 octahedra. When intercalating small amounts of *e.g.* lithium or sodium ions in WO_3 the structure transforms to tetragonal symmetry with the ions located at interstitial sites.[3,9]

The present paper reports a study of electrochemical insertion at room temperature (22 °C) of H^+ and Li^+ in bulk amounts of WO_3 from aqueous solutions of Group I and II nitrates using an electrolysis cell.

Experimental

The insertion method

The cathode consisted of a stainless steel bar pressed against a plug of WO_3 soaked in an aqueous nitrate solution. A small amount of graphite served as contact between the steel bar and the WO_3. The anode was a platinum plate. The cell scheme can be written as follows: Cathode: Stainless steel bar | Graphite | WO_3 | Solution of M^{n+} nitrate | Pt: Anode. During the insertion experiments a constant current of 5.00 mA passed through the cell. In all the experiments where solutions of nitrates were used the anode process was as in eqn. (1). With lithium nitrate and with nitric acid as electrolyte solution the cathode process was as in eqns. (2) and (3). With barium nitrate as electrolyte solution the cathode process was as in eqn. (4).

$$x\,H_2O(l) \longrightarrow 2x\,H^+(aq) + \tfrac{1}{2}\,O_2(g) + 2x\,e^- \qquad (1)$$

$$x\,H^+(aq) + WO_3(s) + x\,e^- \longrightarrow H_xWO_3(s) \qquad (2)$$

$$x\,Li^+(aq) + WO_3(s) + x\,e^- \longrightarrow Li_xWO_3(s) \qquad (3)$$

$$x\,Ba^{2+}(aq) + (2 + x)\,WO_3(s) + x\,H_2O + 2x\,e^- \longrightarrow 2\,H_xWO_3(s) + x\,BaWO_4(s) \qquad (4)$$

Fig. 1 shows the arrangement of the cathode. A glass tube (8 mm inner diameter) ending in a G4 sintered disk was filled with 400 mg WO_3 (carefully compacted in the tube). On top of the WO_3 a small amount of graphite was placed. The tube was then filled, to the top, with electrolyte solution. The solution was pressed through the glass tube with a stainless steel bar (with an O-ring at the end) until the steel bar was in contact with the graphite/WO_3. A beaker with 100 ml electrolyte solution was placed on a magnetic stirrer. The platinum anode was placed in the solution, and the glass frit end of the cathode tube was dipped into the solution. The anode and cathode were connected to a potentiostat. During the insertion experiments a constant current of 5.00 mA was passed through the cell for a definite time. A short time after the current was started a blue layer of intercalate could be seen at the steel cylinder/WO_3 junction. The front of this layer progressed to the end of the tube during the experiment. At the end of the experiment the entire column conducts electrons. Therefore cathodic reduction of oxonium ions to hydrogen takes place. At this time the current was switched off.

The electrolyte solutions used in the experiments were mainly 0.06 and 0.6 M nitric acid, 1 M lithium nitrate, 0.08 and 0.33 M barium nitrate. Three experiments were made with 1 M potassium nitrate, beryllium nitrate or magnesium nitrate as electrolyte solution. All solutions were made from analytical grade chemicals. In experiments with barium nitrate solutions as electrolyte the materials obtained were a mixture of H_xWO_3

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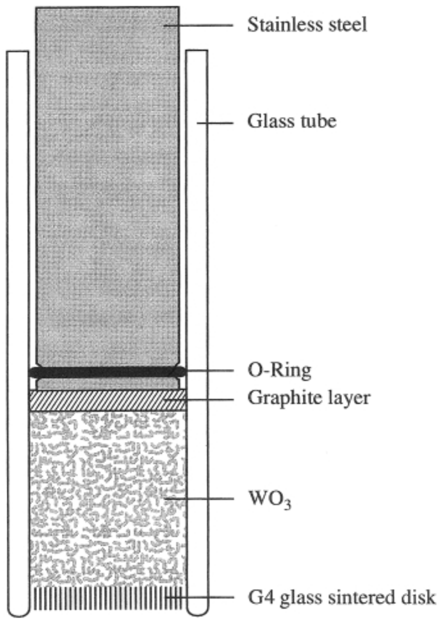

Fig. 1 The arrangement of the combined steel/graphite/WO_3 cathode.

Table 1 Lattice constants for H_xWO_3 materials. For $0.07 < x < 0.17$ each entry is the average of lattice constants obtained in 5 insertion experiments. For $0.50 < x < 0.84$ each entry is the average obtained in 2 insertion experiments. Standard deviations are given in parentheses

H_xWO_3	$a = b$/Å	c/Å	V/Å^3
$0.07 < x < 0.17$	5.225(2)	3.884(4)	106.0(2)
$0.50 < x < 0.84$	5.358(2)	3.749(5)	107.6(2)

Table 2 The amount (g) of $BaSO_4$ determined gravimetrically and that calculated from the Coulombs that passed through the cell. In the latter calculation it was assumed that the cathode process was: $x\,Ba^{2+}(aq) + (2 + x)\,WO_3(s) + x\,H_2O + 2x\,e^- \longrightarrow 2\,H_xWO_3(s) + x\,BaWO_4(s)$

Calculated $BaSO_4$	Gravimetrically determined $BaSO_4$
0.0252	0.0245
0.0447	0.0452
0.0763	0.0773

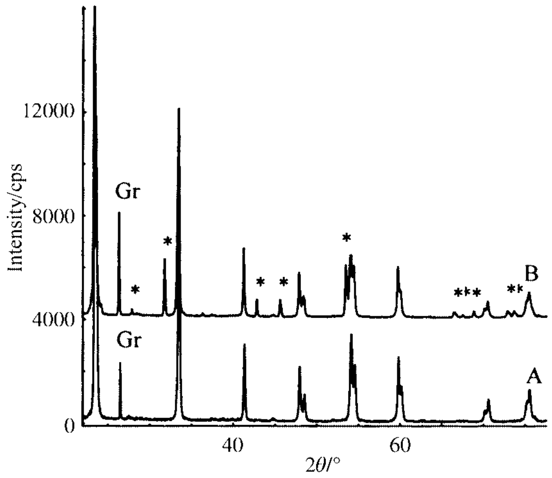

Fig. 2 X-Ray powder diffraction patterns of electrochemically prepared hydrogen intercalates of WO_3. (A) $H_{0.50}WO_3$ prepared with 0.6 M nitric acid as electrolyte. (B) $H_{0.50}WO_3$ prepared with saturated $Ba(NO_3)_2$ as electrolyte solution. The intensity scales have been adjusted so that the intensities of the main peaks of the intercalates are nearly equal. Gr, reflections from graphite; *, reflections from $BaWO_4$.

and $BaWO_4$ [see eqn. (4)]. Also small amounts of graphite, $Ba(NO_3)_2$ solution and in some experiments WO_3 were found. The $Ba(NO_3)_2$ solution was removed from the samples by elution with water under suction until the eluate was free of Ba^{2+} ions (tested with 0.5 M H_2SO_4). Then the $BaWO_4$ was removed by elution with 0.5 M HCl. In this eluate the amount of Ba^{2+} ions was determined gravimetrically as $BaSO_4$.

At the end of the insertion experiments with metal nitrate solutions as electrolyte the amount of oxonium ions formed according to eqn. (1) was determined by titration of the electrolyte solution with 0.1008 M sodium hydroxide. The quantity of oxonium ion found was equivalent to the total Coulombs that passed through the cell. From this amount the degree of intercalation was calculated. In experiments where barium nitrate was used as electrolyte solution the solids obtained were mixtures of hydrogen inserted tungsten oxide (H_xWO_3) and barium tungstate (see above). In the calculation of the degree of hydrogen insertion the amount of barium wolframate formed was taken into account [eqn. (4)].

Characterization

Immediately after an experiment was finished the electrolyte solution was sucked out of the solid in the cathode. The paste of intercalate with the remaining electrolyte was loaded into a sample holder and covered with Parafilm to avoid contact with air. X-Ray powder diffraction patterns of the intercalates were recorded with a Siemens D5000 diffractometer equipped with a primary germanium monochromator (Cu-Kα_1 radiation, $\lambda = 1.5406$ Å). The data were recorded in reflection geometry from 20 to 100° in 2θ with a step length of 0.02 and a counting time of 3 seconds per step. The patterns were indexed using the auto-indexing program TREOR 90[10] and the lattice parameters refined using CELLKANT.[11]

Results and discussion

H_xWO_3 intercalates

In all the insertion experiments, except when $LiNO_3$ solution was used, the materials obtained were of two types. When the insertion degree was low, light blue materials with the composition $H_{0.07 < x < 0.17}WO_3$ were formed. When it was high, dark blue materials $H_{0.50 < x < 0.84}WO_3$ were formed. The two types of material display tetragonal symmetry with significantly different lattice constants (Table 1). In some experiments mixtures of the two kinds of materials were obtained. However, the lattice constants for each component of such mixtures matched the values reported in Table 1. When solutions of potassium, beryllium and magnesium nitrate were used as electrolyte the intercalates had the composition $H_{0.1}WO_3$. Also for these compounds the lattice constants were in agreement with the values in Table 1. We assume that the cathode process also includes formation of tungstates [as in eqn. (4)], and that the tungstates formed are soluble.

In Fig. 2 X-ray powder diffraction patterns for two preparations of $H_{0.50}WO_3$ are shown. The lower pattern (A) is for a material where 0.6 M nitric acid was used as electrolyte. The upper pattern (B) is for a material where saturated aqueous $Ba(NO_3)_2$ solution was used as electrolyte. In B there are reflections (marked with *) stemming from $BaWO_4$. However, WO_3 does not form $BaWO_4$ when treated with $Ba(NO_3)_2$ at room temperature. The formation of $BaWO_4$ must therefore be part of the electrochemical process. Further evidence for this was supplied from three experiments where the amount of $BaWO_4$ formed was determined gravimetrically as $BaSO_4$ (see above). The results of these determinations are reported in Table 2, where amounts of $BaSO_4$ expected from the Coulombs that passed through the cell and the amounts experimentally found are given. It is clearly seen that these are in 1 : 1 proportion.

Table 3 Crystallographic data for the Rietveld refinements of the structures of $H_{0.12}WO_3$ and Li_xWO_3. Values in square brackets for $H_{0.12}WO_3$ and Li_xWO_3 are from Magnéli[9] and Zhong *et al.*,[3] respectively

Formula	$H_{0.12}WO_3$	Li_xWO_3
Formula weight	231.85	≈232.54
$a = b$/Å	5.2242(2) [5.248]	5.1996(2) [5.203]
c/Å	3.8853(2) [3.895]	3.8402(1) [3.844]
V/Å^3	106.039(11) [107.2]	103.825(9) [104.1]
Z	2	2
μ/mm^{-1}	98.51	100.60
Crystal system	Tetragonal	Tetragonal
Space group	$P4/nmm$ (no. 129)[a]	$P4/nmm$ (no. 129)[a]
T/K	298	298
Number of reflections	32	34
$R(F^2)$	0.0800	0.0530
R_{wp}	0.1893	0.1820
R_p	0.1440	0.1250

[a] Origin at $2/m$.

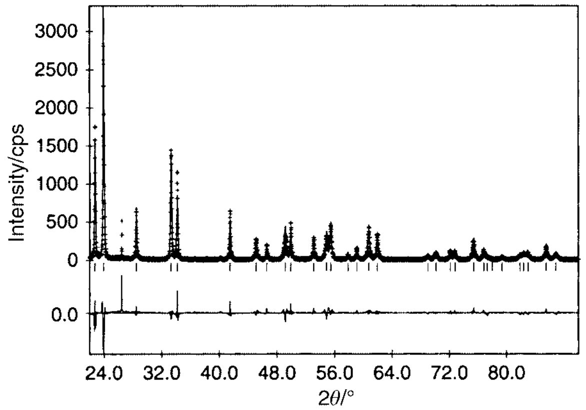

Fig. 3 Observed (crosses) and calculated (full lines) profiles for the Rietveld refinement of $H_{0.12}WO_3$. The lower curve is the difference between observed and calculated profiles. A small region around 26° was excluded from the refinements. At this position the strongest reflection of graphite is situated.

Rietveld refinement of $H_{0.12}WO_3$

The lattice constants of H_xWO_3 materials with a low degree of insertion ($0.07 < x < 0.17$) were similar to those reported by Magnéli[9] for $Na_{0.10}WO_3$. The systematic absences in the indexed powder pattern were compatible with the space group $P4/nmm$ (no. 129), used by Magnéli.[9]

A Rietveld refinement was performed for $H_{0.12}WO_3$, obtained using $Ba(NO_3)_2$ solution as electrolyte. $BaWO_4$ was removed from the sample as described above. The sample was dried over P_2O_5 and not covered with Parafilm during the data collection. The data were collected as described above and those from 7 separate scans were summed to obtain better statistics.

Initially, background parameters, profile parameters and lattice parameters were fitted using the Le Bail[12] method in GSAS.[13] Then the atom positions from Magnéli[9] for $Na_{0.10}WO_3$ were used as starting model for Rietveld refinements[14] in GSAS. Other than the before mentioned parameters, 2 positional parameters and 3 isotropic thermal parameters were refined. The final Rietveld refinement of the structure converged to $R(F^2) = 0.08$, $R_{wp} = 0.19$, and $R_p = 0.14$. The results are reported in Tables 3 and 4 and the difference plot is shown in Fig. 3. The general agreements between observed and calculated profiles shows that the arrangement of W and O atoms in $H_{0.12}WO_3$ and $Na_{0.10}WO_3$ are similar.

Li_xWO_3 intercalates

The materials obtained with $LiNO_3$ solutions as electrolyte were different from all the other materials prepared in this study. The lithium intercalated materials were mixtures of tetragonal and cubic phases. Since the structure of most tungsten oxide intercalates have unit cells with axes around 3.7, 3.7√2 and multiples thereof, unscrambling of lattice constants from diagrams of mixtures is difficult. Zhong *et al.*[3] found that mixtures of tetragonal and cubic phases of Li_xWO_3 exist for $0.11 < x < 0.36$. It may also be noted that the Li_xWO_3 samples are much more stable in air than the H_xWO_3 samples.

Table 4 Fractional coordinates and isotropic displacement factors (Å^2) for $H_{0.12}WO_3$ with standard deviations in parentheses. Values in square brackets are from Magnéli[9]

Atom	x	y	z	U_{iso}/Å^2
W	$\frac{1}{4}$	$\frac{1}{4}$	0.4309(3) [0.435]	0.014(6)
O1	$\frac{1}{4}$	$\frac{1}{4}$	0.980(4) [0.935]	0.041(5)
O2	$\frac{1}{2}$	0	$\frac{1}{2}$	0.071(4)

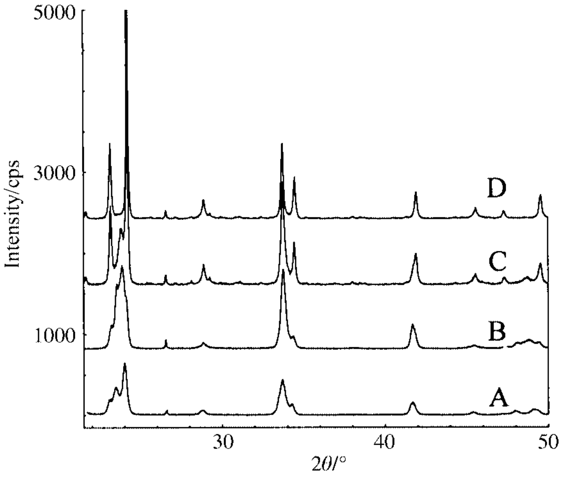

Fig. 4 The change with time of the X-ray powder diffraction patterns of a $Li_{0.3}WO_3$ sample. The pattern (A) was recorded during 7 hours on a wet sample covered with Parafilm. Patterns (B), (C), and (D) were recorded after the material had been exposed to air for 13, 160, and 223 hours respectively.

Fig. 4A shows the powder diffraction pattern of a material with mean composition $Li_{0.3}WO_3$. The diffraction pattern was recorded (during 7 hours) on a wet sample (covered with Parafilm) immediately after the insertion was finished. It shows peaks compatible with a mixture of cubic and tetragonal phases. Fig. 4B, 4C and 4D show the change in diffraction pattern with time of a washed and dried $Li_{0.3}WO_3$ sample exposed to air for 13, 160 and 223 hours, respectively. The pattern in Fig. 4D shows reflections from tetragonal Li_xWO_3 but also a few very weak reflections. A data set collected at this time was used in the refinement of the structure of Li_xWO_3. The change with time is in all probability a result of oxidation

Table 5 Fractional coordinates and isotropic displacement factors (Å^2) for Li_xWO_3 with standard deviations in parentheses. Values in square brackets are from Zhong *et al.*[3]

Atom	x	y	z	U_{iso}/Å^2
W	$\frac{1}{4}$	$\frac{1}{4}$	0.4366(4) [0.432]	0.007(1)
O1	$\frac{1}{4}$	$\frac{1}{4}$	0.9715(6) [0.932]	0.10(1)
O2	$\frac{1}{2}$	0	$\frac{1}{2}$	0.045(4)

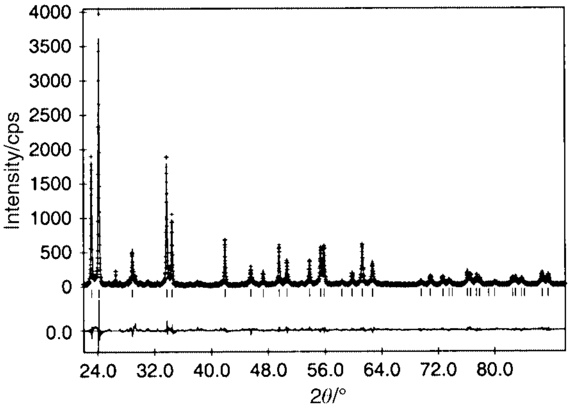

Fig. 5 Observed (crosses) and calculated (full lines) profiles for the Rietveld refinement of Li_xWO_3. Details as in Fig. 3.

of the intercalate. After a long time (weeks) the material changes to monoclinic WO_3.

Rietveld refinement of Li_xWO_3

The lattice constants obtained for Li_xWO_3 were similar to those reported by Zhong *et al.*[3] for a material with composition $Li_{0.09}WO_3$. The systematic absences in the indexed pattern are compatible with the space group *P*4/*nmm* (no. 129) used by Zhong *et al.* in their structure determination. However, our material is a decomposition product and we do not know the exact composition. The atomic positions for W and O from Zhonq *et al.*[3] were used as starting model for the Rietveld refinement which was performed as described above for $H_{0.12}WO_3$. The final Rietveld refinement of the structure converged to $R(F^2) = 0.05$, $R_{wp} = 0.18$, and $R_p = 0.12$. The results are reported in Tables 3 and 5 and the final difference plot is shown in Fig. 5.

Conclusion

We have shown that electrochemical cathodic insertion at room temperature of ions in tungsten(VI) oxide from aqueous solutions of Group I and II nitrates in general leads to formation of intercalates of composition H_xWO_3. Simultaneously tungstates are formed [eqn. (4) above]. An exception to this general behavior is insertion from aqueous lithium nitrate solution. In such insertions Li_xWO_3 is formed [eqn. (3)].

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