Formation of new tungsten bronzes: electrochemical zinc insertion in \(\text{WO}_3\)

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New tungsten bronzes have been synthesised by electrochemical zinc insertion in monoclinic \(\text{WO}_3\). Through 'electrochemical spectroscopy' we have detected that zinc insertion proceeds by a three-step reduction process. X-ray diffraction shows that these steps are associated with the formation of different single phases of variable composition \(\text{Zn}_x\text{WO}_3\) monoclinic for \(x = 0.001\), tetragonal for \(x = 0.05–0.09\) and cubic for \(x = 0.2–0.3\).

Introduction

Bronzes have been widely studied owing to their interesting chemical, electrical and optical properties. ⁵ The tungsten bronzes, with general formula \(\text{M}_x\text{WO}_3\), are the compounds most extensively studied in this family. The common structural feature of these materials is that of \(\text{WO}_3\), which is derived from the well known \(\text{ReO}_3\) structure, and consists of octahedra with shared corners. These structural arrangements provide empty tunnels, running parallel to the \(b\)-axis, where ions can be accommodated. Distortions from the major ideal type occur as a function of the inserted ion content. This is the case for monoclinic \(\text{WO}_3\) (m-WO₃) where a gradual insertion of M ions parallels the structural transformation taking place when \(\text{WO}_3\) is heated. As the concentration of inserted ion increases, distortions from the cubic ideal symmetry (\(\text{ReO}_3\)) tend to disappear. This happens, for example, when sodium is inserted. The different \(\text{Na}_x\text{WO}_3\) compositions that are formed are, firstly monoclinic, then orthorhombic, afterwards tetragonal and, finally cubic, as \(x\) is increased from 0 to 0.93.⁶

Although a large variety of bronzes formed using monovalent ions has been studied, bronzes containing divalent ions as for example \(\text{Zn}^{2+}\) have not been so widely studied. In this work we present a study of the formation of zinc tungsten bronzes. Among the different preparative routes for the synthesis of tungsten bronzes, we have selected electrochemical insertion reactions to carry out the synthesis of \(\text{Zn}_x\text{WO}_3\). The main advantage in using this technique is that the redox potential, rate of insertion and stoichiometry can all be controlled while discharging the appropriate cell, allowing intermediate phases, \(\text{Zn}_x\text{WO}_3\), to be prepared. Using 'step potential electrochemical spectroscopy'⁷ we have detected both single-phase regions (solid solutions) and two-phase domains formed during the insertion reaction from which we could select the \(\text{Zn}_x\text{WO}_3\) sample to be obtained and studied by X-ray diffraction. Usually, structural rearrangements associated with guest-host matrix interactions can be studied by X-ray diffraction, which is the case for the \(\text{Zn}_x\text{WO}_3\) samples studied here.

Experimental

The zinc insertion study was carried out by electrochemical methods in \(\text{ZnSO}_4\) type cells² containing \(\text{WO}_3\) (Merck, 99.9%).

Results and Discussion

The X-ray diffraction pattern of the commercial oxide mainly corresponded to m-WO₃, the most stable polymorph at room temperature. Since the triclinic to monoclinic transition occurs at 17 °C, we were not surprised that some weak reflections of the triclinic polymorph were also detected. We used the commercial oxide directly as the active material in our electrochemical cells since the intensities of the triclinic reflections were very weak.
Fig. 1 shows the voltage–composition plot obtained from the first charge-discharge cycle of a cell containing m-WO₃ as the active material in the cathode. It can be observed that electrochemical zinc insertion and deinsertion is feasible in m-WO₃. The reaction proceeds through different processes as can be deduced from the evolution of the cell voltage with x in Zn₃WO₃; different regions labelled as I, II, III, A and B are observed. The regions where a continuous variation of the potential with composition is observed correspond to single-phase regions (I, II and III) whereas the voltage plateaus, A and B, are assigned to two-phase regions which are bounded by points of inflection at definite changes in slope of the potential–composition curve.

In order to check our first interpretation we analysed the potentiostatic experiment in more detail, observing the current relaxation with time at each voltage step. Fig. 2 shows these data for the discharging curve. For high potential values, between 1.25 and 0.6 V, only small currents are detected and the cell exhibits a low capacity. For low potential values, below 0.6 V, the current increases reaching a maximum value at 0.55 V vs. Zn⁰⁺-Zn²⁺. In this region, peak A (Zn₃WO₃; 0.01 < x < 0.05), the behaviour of current with time is far from a t⁻¹/² law. Hence we deduced that the diffusion of the zinc ions is not the process that rules the insertion reaction. When a different scan rate was used, peak A shows a noticeable change of shape, see Fig. 3. This behaviour confirms that the system is crossing a two-phase domain. In this case, the shape of the peak A in the E-t diagram is asymmetrical with a linear slope whose intercept with the zero current is at the open-circuit two-phase equilibrium value. On the basis of the different experiments carried out, this equilibrium value is approximately 0.58 V vs. Zn⁰⁺-Zn²⁺. For potentials below 0.38 V, in the B peak, the current vs. time plot exhibits a clear anomalous behaviour that indicates that the system is again crossing another two-phase domain with an equilibrium value of 0.43 V vs. Zn⁰⁺-Zn²⁺. The corresponding compositions of this region are ZnₓWO₃ with 0.09 < x < 0.2.

On the basis of the experiment above described, we can conclude that zinc insertion in m-WO₃ proceeds through successive steps that involve the existence of single- and two-phase regions. The single phase domains correspond to the abrupt drops of the potential in the E-x plot (regions labelled as I, II and III) and with regions of minimum current in the I-t plot. On the other hand, plateaus in the voltage-composition plot and maxima of current in the I-t plot, where the behaviour of current with time does not follow a t⁻¹/² law, correspond to two-phase domains. In both cases, the system shows a very slow reaction undoubtedly due to the double positive charge of zinc ions.

(b) Structural characterisation

In order to characterise the detected phases ZnₓWO₃ (x = 0–0.01, 0.05–0.09 and 0.2–0.3) we have carried out a structural study. We have synthesised by electrochemical methods and characterised by X-ray diffraction several samples with composition ZnₓWO₃, where x corresponds to compositions belonging to different regions of the E–composition plot (I, II, III, A and B). Following the procedure described in the experimental section, several cells with configuration Zn/(Zn(CF₃SO₂)₂) in PC–DMSO (1:4) were discharged at predetermined values of x.

The starting structure (WO₃ structure) is built up of apex-linked WO₆ octahedra forming an infinite tridimensional network of interconnecting tunnels typical of the WO₃-type structure. At room temperature WO₃ is not cubic as is the ideal ReO₃, but monoclinic. However, as insertion proceeds, distortions from the ReO₃ cubic ideal symmetry tend to disappear.

Fig. 4 shows the X-ray diffraction patterns of samples ZnₓWO₃ where x = 0–0.005, 0.02, 0.06, 0.1 and 0.3. At low values of zinc concentration, x < 0.01 [see e.g. x = 0.005, Fig. 4(a)], the monoclinic WO₃ matrix is maintained although a certain loss of crystallinity is observed. Note that this sample corresponds to a region where a continuous variation of the potential with composition is detected (single phase assigned to region I in Fig. 1 and 2). As insertion proceeds a second abrupt change of potential is detected for a slight variation in composition (region II in Fig. 1 and 2). In this case study by X-ray diffraction showed that, for samples with composition within this region [see e.g. x = 0.06, Fig. 4(c)], a new phase, with variable composition and tetragonal symmetry, is formed. Between these solid solution regions the system, as proposed from the electrochemical results, should consist of a two-phase domain (region A in Fig. 1 and 2); indeed, we can see in Fig. 4(b) that the sample corresponding to this region, x = 0.02, is mainly formed by a mixture of monoclinic and tetragonal phases.
Paper electrochemical and structural data

Fig. 5 A Zn-WO$_3$ phase diagram built from the combination of both electrochemical and structural data

<table>
<thead>
<tr>
<th>Range of existence</th>
<th>Phase</th>
<th>Cell parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-WO$_3$</td>
<td></td>
<td>$a=7.31(1), b=7.53(4)$, $c=7.63(1)$</td>
</tr>
<tr>
<td>0 ≤ x ≤ 0.01</td>
<td>monoclinic</td>
<td>$a=7.32(1), b=7.52(7)$, $c=7.70(6)$</td>
</tr>
<tr>
<td>0.01 &lt; x ≤ 0.05</td>
<td>monoclinic + tetragonal</td>
<td>$a=7.32(1), c=3.87(9)$</td>
</tr>
<tr>
<td>0.05 &lt; x ≤ 0.09</td>
<td>tetragonal</td>
<td>$a=7.22(6), c=3.87(9)$</td>
</tr>
<tr>
<td>0.09 &lt; x ≤ 0.2</td>
<td>tetragonal + cubic</td>
<td>$a=3.76(1)$</td>
</tr>
<tr>
<td>0.2 &lt; x ≤ 0.3</td>
<td>cubic</td>
<td>$a=3.76(1)$</td>
</tr>
</tbody>
</table>

For a sample with composition $x=0.005$ 
For a sample with composition $x=0.3$

so-called electrochemical spectroscopy, to satisfactory characterise an insertion system.

(c) Other properties

The electrical properties of Zn-WO$_3$ samples reflect the classical behaviour of tungsten bronzes in relation with the amount of ions inserted. Thus, when zinc is inserted in WO$_3$ (an insulator) its electrical conductivity increases by up to four orders of magnitude (for Zn$_{0.3}$WO$_3$). In the same way the colours of zinc tungsten bronzes show a dramatic change. Thus, as reaction proceeds the insertion compounds, originally green–yellow, develop different colours: initially sky blue, later deep blue and, finally blue violet for Zn$_{0.3}$WO$_3$. This latter colour is related to 0.6 electron/formula transfer between guest and host. The same colour is reported for Na$_{0.3}$WO$_3$, where the electron transfer is to the same extent.

Finally it should be mentioned that samples Zn$_{0.3}$WO$_3$ are unstable to air. After exposing them to the atmosphere they lose their colour reverting to the initial colour of the parent compound, i.e. green–yellow m-WO$_3$.

Conclusions

Zinc insertion in m-WO$_3$ has been studied and the existence of three single phases Zn$_x$WO$_3$, where $x=0.001$, 0.015-0.09 and 0.2-0.3 has been found. The transformation of the first to the second, and the second to the third, proceeds in both cases through a two-phase region. Different compositions in the whole range Zn$_x$WO$_3$ have been studied by X-ray diffraction, and the corresponding results perfectly correlate with the electrochemical characterisation. The first phase is monoclinic, the second tetragonal and the third cubic. For the whole range of composition, the system reacts slowly and this is likely to be due to the double positive charge of zinc ions.

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References


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