In situ Raman spectroscopy of the electrochemical reduction of WO₃ thin films in various electrolytes

O. Pyper, A. Kaschner, C. Thomsen

Abstract

With in situ micro-Raman measurements during the electrochemical reduction of WO₃ thin films, the influence of the intercalated cation (H⁺/Li⁺) and an addition of water to the aprotic lithium electrolyte was investigated. The Raman spectra of lithium bronzes LiₓWO₃ show two main results: (i) the intercalation of hydrogen can be clearly distinguished in situ from the intercalation of lithium with this technique and (ii) even with an addition of 500 ppm of water to the lithium electrolyte no hydrogen intercalation was observed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: WO₃; H⁺/Li⁺ intercalation; Electrochromism; Electrochemical reduction; In situ micro-Raman spectroscopy

1. Introduction

Electrochromic devices with their tunable transmission for visible and infrared radiation will play an important role for architectural and automotive glazing in the future [1]. WO₃ is one of the most promising material for the working electrode [2,3] of these devices. WO₃ at room temperature is thermodynamically stable and has a slightly monoclinic distorted ReO₃-type structure, i.e. it is built from edge-sharing...
WO$_6$-octaeders with “lattice channels”. Through these small channels, monovalent cations such as H$^+$, Li$^+$ or Na$^+$ can be intercalated into the WO$_3$-framework. For charge compensation, this is accompanied with an electron-transfer [4] according to

$$xA^+ + xe^- + \text{WO}_3 \rightleftharpoons A_x\text{WO}_3.$$  

With this reversible, topotactic intercalation the structural distortion of the framework decreases with increasing $x$, and a strong color is observed. The coloration can be explained with the partial reduction of the WO$_3$-framework, resulting in W$^{5+}$ species in a background of W$^{6+}$ sites. In this situation, a low energy excitation (e.g. visible light) is needed to excite an electron to a neighboring site [5,6]:

$$W_a^{5+} + W_b^{6+} \xrightarrow{h\nu} W_a^{6+} + W_b^{5+}.$$  

Research on the intercalation chemistry of crystalline WO$_3$ is now almost two centuries old. Wöhler [7] discovered a gold-like appearance of Na$_x$WO$_3$ (with $x \approx 1$) in 1824, Glemser [8] performed intensive research on different species of H$_x$WO$_3$ (with $x$ up to 0.5) and Zhong et al. [9] reported different phases of Li$_x$WO$_3$ (with $x < 0.5$).

The kinetics of the intercalation and thus the speed of coloration is mainly determined by the movement of the cations from the electrolyte into the framework. The morphology and crystal structure of the thin films described here were investigated earlier with high-resolution transmission electron microscopy [10] (HTEM) and Raman spectroscopy [11]. The films were of nanocrystalline morphology when a curing temperature of 180$^\circ$C was used after the sol–gel process and had microcrystalline character after an additional curing at 400$^\circ$C. The films were monoclinic, i.e. they had the thermodynamically stable structure of WO$_3$, or they were orthorhombic with very similar lattice parameters. It was not possible to distinguish between both.

Many electrochromic systems are designed for the use of lithium as a mobile cation. However, several authors reported an increase in speed and depth of coloration with the addition of water to the non-aqueous lithium electrolyte. The mechanism is not well understood until now [12–14] because of the difficulties with the analysis of protons and lithium in the thin films. In situ X-ray diffraction measurements (XRD) have not been successful until now: (i) the structural changes of the tungsten framework are small, (ii) the peaks are broad because of the microcrystallinity of the material and (iii) the X-rays are not absorbed sufficiently by the thin film resulting in a weak signal/noise ratio. Raman spectroscopy has several advantages when analyzing structural properties and has already been used to study electrochromic WO$_3$ films [15–18] and electrochromic devices [19,20]. Dealing with wavelengths in the visible range, the construction of an in situ electrochemical cell is simple and allows micro-Raman measurements on the thin film with a good signal/noise ratio. Furthermore, the Raman spectra of monoclinic WO$_3$, H$_{0.1}$WO$_3$ and H$_{0.23}$WO$_3$ have already been reported [21]. There was an in situ Raman investigation on hydrogen bronzes; however, due to the potentialistic reduction of WO$_3$ the amount of hydrogen intercalated could not be measured [22].
In this work, we show results of in situ Raman measurements during the electrochemical reduction of WO$_3$ in hydrogen and lithium electrolytes, and the influence of addition water to the latter.

2. Experimental

The thin films were manufactured by a sol–gel spin coating process [10]: 3 g WOCl$_4$ were dissolved in 15.3 g 1-propanol (dried with 3 Å molecular sieve) and stirred overnight in a glove box. The soda-lime glass substrates (5 × 5 cm$^2$, with a sputtered SnO$_2$–In$_2$O$_3$ (ITO) coating) were cleaned with an aqueous EXTRAN-solution, 2-propanol and a UV/O$_3$ reactor. The coating process was performed in air by dropping the clear solution (a small amount of a grayish substance precipitated) onto the substrate through a 0.45 μm filter. The exceeding solution was spun off by accelerating the substrate from 3000 rpm/s to 750 rpm and holding this speed for 60 s, using a spin-coater KARL SUSS CT62. For curing (20 min), hotplates set to 200°C were used. To transform the nanocrystalline thin films to a microcrystalline structure, an additional curing at 400°C (1 h) was performed [10].

The film thickness was determined by etching away a part of the film with 1 mol/l of NaOH. The height of the resulting step was measured with a TENCOR a-STEP 200 profilometer. The variation of the film thickness was within a few nm only.

The cell for the measurements was built from polytetrafluorethylene (Teflon) without additional rubber sealings (Fig. 1): The sample was pressed by a steel clamp onto the electrolyte chamber with the thin film facing the electrolyte. After filling in the electrolyte (approx. 3 ccm) a lid with fitted counter and reference electrodes was mounted with the second clamp. Both of these electrodes were made from platinum for the proton electrolyte and from lithium mounted on platinum for the lithium electrolytes. The electrical contact to the thin film was performed with conducting glue outside the cell.

The Raman measurements were carried out in backscattering geometry with a triple-grating spectrometer equipped with a cooled charge coupled device detector. For excitation, the 488 nm line of an Ar$^+$/Kr$^+$ mixed-gas laser was used. The laser beam was focussed through the substrate and the ITO-coating on the thin film. Previous experiments showed only a slightly raised background signal between 450 and 600 cm$^{-1}$ for the substrate (glass + ITO) in the Raman spectra.

0.003 mol/l H$_2$SO$_4$ was used for the proton electrolyte and 1 mol/l LiCF$_3$SO$_3$/propylene carbonate solution for the lithium electrolyte. The latter was carefully dried with 3 Å molecular sieve and the water content was analyzed directly from the in situ cell with the Karl–Fischer technique. For handling the dry lithium electrolyte, an argon-filled glove box was used. The water content of the dry cell was below 10 ppm after filling the cell and 60 ppm after storing the cell for 20 h at ambient conditions. For measurements in mixed water/lithium electrolytes, the dry lithium electrolyte was mixed with water and analyzed again.

For the electrochemical reactions, the galvanostatic technique was chosen, using a precision current source. The potential of the cell was monitored between the sample
and the reference electrode to prevent side reactions of the electrolyte. For the Raman measurements the thin film was reduced within a few minutes with the desired charge transfer calculated from the active area, the thickness and the density of the thin film, the current and the time. Immediately after that, the Raman spectra were taken within a few minutes.

This sequential technique was chosen to prevent measurements on non-uniformly (during the measurement time) reduced material. On the other hand, the short time scale of both the electrochemical reaction and the measurement and the air tight cell prevented the bronzes from reoxidation during the measurement.

3. Results and discussion

3.1. Basic properties

The thin films obtained on glass showed a glossy surface and were clearly transparent. On close inspection with an optical microscope (magnification 1000), the surface was essentially homogeneous and structureless. However, a few distortions of approximately 1 \( \mu \text{m} \) in size were observed. The thickness of the thin films was 228 nm. The morphology was a dense packing of randomly oriented
micro-crystallites with a size of 40–100 nm [10]. XRD and Raman measurements confirmed the crystal structure of monoclinic WO₃ [11].

Electrochemical experiments with sintered bulk material were performed before the in situ measurements. For both electrolytes, lithium and hydrogen, galvanostatic and potentiostatic/cyclovoltammetric techniques were used, and the results found were independent of the technique chosen. The galvanostatic reduction of sintered pellets of WO₃ in H₂SO₄ (Fig. 2) showed a potential curve with two plateaus. From the phase diagram found by Glemser [8] and Dickens [23], one would expect four steps. However, the first plateau may be related to the formation of the orthorhombic hydrogen bronze in a two-phase reaction, and the second step, at its end, may be related to the formation of the cubic phase. This is supported by the purple color of the sample, which was observed after a charge transfer of 0.6 e⁻/f.u. The electronic isolation of pure WO₃ is the reason for the steep rise of the potential curve of the oxidation when using bulk material. On the other hand, the cyclovoltammetric curve of WO₃ in dry lithium electrolyte showed two clear reduction steps, which can be assigned to the known phase diagram [9] of lithium bronzes (Fig. 3, Table 1). Again, the oxidation was not as clear as the reduction.

3.2. In situ measurements in proton electrolyte

Fig. 4 shows Raman spectra of WO₃ in proton electrolyte for different oxidation states. All features differing from the ITO/glass background signal are shown. According to Refs. [17,18] the broad modes around 700 and 800 cm⁻¹ can be interpreted as W–O stretching modes. A relatively narrow line at 271 cm⁻¹ appears together with a weak signal at 329 cm⁻¹. We suggest bending vibrations δ(O–W–O) to be their origin. For large charge transfer a peak at 191 cm⁻¹ appears, which
probably arises from a ν(W–O–W) stretching mode. In none of our spectra, even for the deeply colored state of WO₃, a distinct mode around 950 cm⁻¹ originating from W=O stretching vibrations is observed. We suppose that structural disorder in our micro-crystalline samples leads to strong broadening, thus, does not allow the formation of a sharp peak. In the following we discuss the evolution of the observed peaks with the charge transfer.

The Raman spectra measured during the reduction in diluted H₂SO₄ can be divided into three groups: (i) up to −0.05 e⁻/f.u., the spectra are unchanged compared to that of unreduced WO₃, then (ii), up to −0.25 e⁻/f.u., only the peak at 811 cm⁻¹ remains, and (iii) from −0.35 e⁻/f.u., the weak peak at 191 cm⁻¹ as the only peak is detectable. The shift of the strongest peak from 801 to 811 cm⁻¹ can be interpreted as the shortening of W–O bonds [24], which corresponds to the slightly smaller cell parameters of H₀.₁WO₃ compared with WO₃, due to more negative charge between the tungsten atoms. The overall decrease of the number of peaks in the spectra is related to the increasing symmetry of the crystallographic cell from monoclinic to cubic. Due to the modulated background signal and the

Table 1
Comparison of the reported phases [9] of LiₓWO₃ with the phases found in this work (estimated relative error Δx = 10%)

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<td>Monoclinic</td>
<td>x&lt;0.04</td>
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<tr>
<td>0.078&lt;x&lt;0.12</td>
<td>Tetragonal</td>
<td>0.05&lt;x&lt;0.15</td>
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<tr>
<td>x&gt;0.21</td>
<td>Cubic</td>
<td>x&gt;0.15</td>
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Fig. 3. Cyclovoltammetric curves of polycrystalline (bulk) WO₃ in 1 mol/l LiCF₃SO₄/propylene carbonate: 43.7 mg sintered WO₃, contacted with Pt-wire, scan speed 0.05 mV/s. The first and the second cycle of a new sample are shown, the arrow denotes the start and the direction of the scans.

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non-symmetric shape of the peaks, the exact number of peaks was difficult to determine unambiguously. The maximum charge transfer applied for the reduction was $-0.68\text{e}^-$/f.u., at this point the sample was colored deep blue. The following reoxidation ended in the same spectrum as before reduction (Fig. 4, uppermost spectra), and the sample was colorless again. In another experiment with the same setup, a deep purple color of the sample was observed after reduction. At this point, the peak at 191 cm$^{-1}$ was not detectable anymore nor were other peaks. This purple color and the disappearance of the Raman peaks are expected for the extremely air sensitive cubic hydrogen bronze [8]. The evaluation of the spectra was hindered by the decreasing intensity of the peaks with increasing reduction: the coloring of the sample reduced the effective sample volume probed by the probe beam.

Fig. 4. Raman spectra of micro-crystalline WO$_3$ thin films, each taken after electrochemical reduction in 0.003 mol/l H$_2$SO$_4$. The charge transfers given describe the accumulated charge since the beginning of the experiment. The upper three spectra are measured during reoxidation. The spectra are vertically shifted for clarity.
3.3. *In situ measurements in lithium electrolytes*

The Raman spectra taken during the electrochemical reactions in lithium electrolytes were quite different from those measured in the proton electrolyte. This was observed with both dry (7 ppm water, Fig. 5) and wet (500 ppm water, Fig. 6) lithium electrolytes. Due to the propylene carbonate, these spectra showed an additional number of Raman peaks from the solvent. These modes [25] were eliminated from the evaluation, however, because of the overlap of some peaks with those of the lithium bronzes, some peaks of the latter might have remained unresolved.

For better comparison, the peak maxima of these measurements were determined and drawn into one graph, correlated to the charge transfer of the reduction (Fig. 7). Similar to the reduction in the proton electrolyte, the peak at 801 cm$^{-1}$ shifts towards

![Fig. 5. Raman spectra of micro-crystalline WO$_3$ thin films taken after electrochemical reduction in lithium electrolyte with 7 ppm water. The peak marked by an asterisk originates from propylene carbonate. The spectra are vertically shifted for clarity.](image-url)
810 cm$^{-1}$, but now this process is finished already at $-0.02 \text{e}^-$/f.u. This can be explained with the phase diagram of the lithium bronzes, where the first phase transition from WO$_3$ to Li$_x$WO$_3$ occurs at a much lower charge transfer than the one from WO$_3$ to H$_x$WO$_3$ (Tables 1 and 2). With charge transfers between 0.1 and 0.5 e$^-$/f.u., a characteristic mode was observed between 268 and 297 cm$^{-1}$ (shifting towards higher energy with increasing charge) and one around 170 cm$^{-1}$. The 271 cm$^{-1}$ mode in H$_x$WO$_3$ was assigned as $\delta$(O–W–O) vibration. The shift to higher energies can be due to lattice distortion resulting from lithium intercalation. The 170 cm$^{-1}$ mode only found in Li$_x$WO$_3$ may also originate from $\nu$(W–O–W) vibrations [18], but this assignment is not unambiguously clear. However, these two peaks appeared independent of the water content of the lithium electrolyte, and were not found in the measurements with proton electrolytes. Therefore, they can be used as fingerprint for lithium intercalation.

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Fig. 6. Raman spectra of micro-crystalline WO$_3$ thin films taken after electrochemical reduction in lithium electrolyte with 500 ppm water. The peaks marked by an asterisk originate from propylene carbonate. The spectra are vertically shifted for clarity.
3.4. Identification of the phases

In all electrolytes the reduction of WO$_3$ led to a shift in the Raman mode at 801 cm$^{-1}$ to higher energies. This is consistent with the shrinking of the W–O bond length with the beginning intercalation of small cations into the crystal lattice because of the negative charge introduced into the host lattice [24]. With ongoing reduction, a number of observed peaks disappear, which is consistent with the higher symmetry of the unit cell. In dry lithium electrolytes, the critical charge transfer during the reduction for a substantial change in the peak pattern is similar to that found by Zhong et al. [9] for the phase diagram of Li$_x$WO$_3$. The measurements with the wet lithium electrolyte were performed to test the theory of a possible transition from lithium to hydrogen intercalation, which could be the cause for faster coloring of “wetted” electrochromic systems. As the peak pattern during the reduction in the

![Graph showing Raman shift vs. charge transfer for different electrolytes.](image)

Fig. 7. Observed peak positions from Raman spectra of electrochemical reductions of WO$_3$ thin films in different electrolytes. Lines are a guide to the eye only.

<table>
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<th>This work</th>
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</thead>
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</tr>
<tr>
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<td>$0.1 &lt; x &lt; 0.25$</td>
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<tr>
<td>$0.15 &lt; x &lt; 0.23$</td>
<td>Tetragonal B</td>
<td>$x &gt; 0.25$</td>
</tr>
<tr>
<td>$0.33 &lt; x &lt; 0.5$</td>
<td>Tetragonal A</td>
<td></td>
</tr>
<tr>
<td>$x &gt; 0.5$</td>
<td>Cubic</td>
<td></td>
</tr>
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Table 2
Comparison of the reported phases [8,23] of H$_x$WO$_3$ with the phases found in this work (estimated relative error $\Delta x = 10\%$)
wet lithium electrolyte is comparable to the one in dry lithium electrolyte, we can assume that in this mixed Li⁺/H⁺-system also only lithium intercalation takes place. Thus, the kinetic effects of adding water to aprotic electrolytes might not be related to an intercalation of protons instead of lithium.

However, using diluted sulfuric acid as proton electrolyte we observed only three phases (four including the purple one, which we saw once), although Glemser [8] and Dickens [23] proved the existence of more phases in the phase diagram of HₓWO₃ (Table 2). This observation of missing phases was already seen in the potential curve of the electrochemical experiments with bulk WO₃ (Fig. 2) and might thus be related to the electrochemical method. Glemser and Dickens each used hydrogen in status nascendi for their synthesis.

4. Summary and conclusions

With this work we showed that micro-Raman technique is well suited for in situ measurements in electrochemical reactions. Especially with thin films, which are difficult to investigate with X-ray methods, micro-Raman technique can lead to new results. The in situ technique allowed measurements of the extremely air sensitive hydrogen bronzes.

We have shown data on lithium bronzes, which can be clearly distinguished from hydrogen bronzes. The addition of water to the lithium electrolyte did not change the peak pattern of the lithium bronzes to that of the hydrogen bronzes. This was interpreted such that in this mixed electrolyte lithium intercalation still takes place, although the water content is an important issue for the kinetics of the intercalation. Thus, the already known acceleration of coloring of electrochromic devices on wetting the lithium electrolyte cannot be explained by a transition from lithium to hydrogen intercalation, which can be expected to be faster because of its smaller ionic diameter. The water in the mixed electrolyte may play a catalytic role for the intercalation of lithium. To our knowledge, such was not observed before at electrochemical intercalation reactions.

Acknowledgements

The authors would like to thank S. Reich (Institut für Festkörperphysik, TU, Berlin) for fruitful discussions. This work was supported by the European Community (Brite Euram III, LANDSEC project, BE-96-3014). One of the authors (A.K.) would like to acknowledge an Ernst-von-Siemens-scholarship.

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