Making Smart Windows Smarter: Improving Optical Efficiency and Intercalation Rates in Sol-Gel Derived Tungsten Trioxide

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Electrochromic materials have been shown to alter their optical properties upon application of an external voltage or current.\(^1\) In the case of WO\(_3\), the shift occurs from a transparent, or bleached, state to dark blue upon reduction. This phenomenon is currently being harnessed for such applications as energy conserving “smart” windows and glare attenuators for car rearview mirrors. Widespread implementation of this technology in windows will save an estimated $11-20 billion in heating and cooling costs annually.\(^2\)

The mechanism behind the color change follows equations 1 and 2:\(^3\)

\[
xe^- + xM^+ + WO_3 \rightarrow M_xWO_3
\]

\[
W_6^{6+} + W_5^{5+} \rightarrow W_6^{5+} + W_5^{6+}
\]

W\(^{6+}\) is reduced to W\(^{5+}\) by injected electrons, balancing the charge with either H\(^+\) or Li\(^+\). Due to the ionic nature of the W-O bonds, all of the electron density is located on the oxygen atoms. Additional electrons enter the conduction band, which is located on the tungsten atoms. These additional electrons polarize the adjacent lattice to form polarons. Incident photons are absorbed by the polarons, which move from one site to another.

For smart window technology to become commonplace, it will be necessary to develop cheap and efficient methods of generating WO\(_3\) thin films are required. Sol-gel processing is not only less expensive than sputtering or chemical vapor deposition, it allows for finer control of stoichiometry and microstructure.\(^4\) Increasing the porosity of the electrochromic material allows a greater surface area for Li\(^+\) to enter the film. In addition, insertion of additives into the WO\(_3\) lattice is possible with sol-gel processing.\(^5\)

To determine the kinetics of lithium intercalation, the diffusion coefficients of sol-gel derived WO\(_3\) were measured by means of galvanostatic titration.\(^4\) As more lithium was added to the system, the diffusion coefficient increased almost two orders of magnitude from Li\(_{0.05}\)WO\(_3\) to Li\(_{0.37}\)WO\(_3\). Doping the sol with 5% by weight LiCF\(_3\)SO\(_4\) gave similar results but at a higher initial rate.

Electrochemical impedance spectroscopy revealed no Warburg dependence on the Li\(^+\) diffusion and an increased charge capacity over the undoped films.\(^6\) This result indicates that Li\(^+\) distorts the lattice upon intercalation but in a favorable manner to accommodate more Li\(^+\).

With this motivation, Deepa et al. prepared a series of WO\(_3\) sols that were modified by addition of 0-5% by weight oxalic acid dihydrate (OAD).\(^7\) Oxalic acid dihydrate is known to prevent coagulation of WO\(_3\) and thus addition of differing
concentrations of OAD affect the microstructure of the film.\textsuperscript{8} The coloration efficiency (CE) is given by equation 3.\textsuperscript{7}

\[ CE = \log\left(\frac{T_b}{T_c}\right)/(q/A) \]  

(3)

where \( T_b \) and \( T_c \) are the transmissions of the bleached and colored states respectively, \( q \) is the charge, and \( A \) is the area of the electrode. The coloration efficiency depends on the amount of OAD added: the maximum coloration efficiency was 81 cm\(^2\)C\(^{-1}\) for 3\% OAD. For a 250 nm thick film, coloration occurred in 190 s and bleaching took 28 s. In comparison, current commercial films have a coloration efficiency in the single digits and take over five minutes to color at room temperature.\textsuperscript{9}

Despite preliminary success, OAD doped WO\(_3\) films have a number of shortcomings. During the first five cycles, cyclic voltammetry shows pronounced changes in observed currents at the same potential.\textsuperscript{10} The authors believe this to be the result of naturally occurring substoichiometric phases of tungsten oxide. The initial enhanced rate of intercalation is caused by W\(^{4+}\) states transferring polarons to W\(^{5+}\) in a similar manner as described in eqn. 2. After five cycles, the voltammogram is stable, which indicates that all of the W\(^{4+}\) has become W\(^{5+}\), which only transfers polarons to W\(^{6+}\) atoms.

Commercially available smart windows are expected to be used five times a day on average and should have a lifespan of three years.\textsuperscript{7} The OAD doped films can withstand 1000 cycles with minimal change in efficiency but drastically succumb to fatigue before 1500 cycles.\textsuperscript{11}

Fully crystalline WO\(_3\) is not employed in current smart glass applications due to its slow diffusion rate and inferior coloration efficiencies.\textsuperscript{12} On the other hand, crystalline states have been shown to be able to withstand a greater number of cycles.\textsuperscript{13} Using a block copolymer assisted sol-gel preparation, Sallard, Brezensink and Smarsly fabricated a porous, crystalline film. Coloration efficiencies and kinetics (Table 1) are comparable to the OAD doped films but the crystalline films are more robust.\textsuperscript{14} The properties of both films exceed those of current commercial electrochromic products.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bleaching Time (s)</th>
<th>Coloration Time (s)</th>
<th>Coloration Efficiency (cm(^2)C(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 % OAD</td>
<td>28</td>
<td>192</td>
<td>81</td>
</tr>
<tr>
<td>Fully Crystalline</td>
<td>50</td>
<td>22</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 1. Coloration properties of interest of the 3\% OAD and crystalline films


9. SageGlass® Representative, personal communication


