Electrochromism in Materials Prepared by the Sol-Gel Process

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Abstract. Electrochromism is defined as the persistent but reversible optical change (usually transmission) produced electrochemically. The preparation by the sol-gel process of thin films made of amorphous or crystalline nanoparticles of WO₃, V₂O₅, Nb₂O₅, TiO₂, CeO₂, Fe₂O₃ and mixed compounds such as WO₃-TiO₂, CeO₂-TiO₂, CeO₂-SnO₂, have opened remarkable new opportunities for obtaining electrochromic layers exhibiting large optical transmission variation in the UV, visible or infrared range and acceptable kinetics under H⁺ or Li⁺ insertion. In this paper we give an overview of what has been recently achieved in this field, with emphasis for cathodic electrochromic coatings of Nb₂O₅ and TiO₂ composition. Finally we stress the future developments in this fast growing field.

Keywords: electrochromism, coating, nanoparticle, sol-gel material, WO₃, Nb₂O₅, TiO₂, CeO₂, Fe₂O₃, mixed compound

1. Introduction

A wide class of materials, called chromogenic materials, change in a persistent but reversibly way their optical properties (transmission, absorption, reflectance and/or emittance) in response to a change in ambient conditions [1]. Technologically, electrochromism, defined as the persistent but reversible optical change produced electrochemically by the passage of electronic and ionic currents through them is the most promising effect. These materials may be crystalline or amorphous and very often are porous to provide an open network for a rapid ionic diffusion. A common feature of such materials, unlike the liquid-crystals used in displays, is that once they are colored, the applied voltage can be switched off and the color retained making electrochromic devices (EC) more energy efficient.

Various EC systems have been already commercialized such as hearing aid battery powered electrochromic sunglasses, automobile rear and side view mirrors (more than one million sold in 1993), automotive sunroofs [2, 3], etc. These developments are the first steps towards the realization of large area devices for application in architectural glazing with active optical response to change in environmental conditions, saving cooling and lighting energy and providing glare control and improved thermal comfort [4, 5].

2. Materials for Electrochromic Devices

Electrochromism is known since 1953 when Kraus [6] discovered that a WO₃ vapor layer deposited on a semitransparent metal layer (Cr, Ag) was intensively blue colored when cathodically polarized in 0.1 N H₂SO₄. However, world wide research started only after the fundamental works of Deb [7, 8] on the same material two decades later. Today several inorganic oxides (mostly of transition metals to which we shall restrict this review), and organic materials are known to exhibit this property [9, 10]. Their coloration and bleaching under cathodic or anodic polarization or for a few of them under both states is usually described by

\[ \text{MeO}_n + x\text{I}^+ + xe^- \leftrightarrow \text{I}_x\text{MeO}_n \]  

(1)

where Me is a metal atom, I⁺ is a singly charged ion usually H⁺ or Li⁺, e⁻ is an electron and n depends on the particular type of oxide.
All electrochromic materials have been originally prepared by non sol-gel methods. However the sol-gel process [11–13] is most promising to prepare better oxide coatings and even coatings which can not be obtained conventionally and for which a careful control of their texture and structure may lead to tailored electrochemical properties [14, 15]. Table 1 lists most of the sol-gel materials already tested for this purpose.

In the following we briefly review the most recent results obtained with sol-gel EC materials that the authors believe as promising for use in commercial devices such as WO₃, V₂O₅, CeO₂, Fe₂O₃ and some mixed compounds with emphasis on TiO₂ and Nb₂O₅. More details will be found in [79] and [80].

**WO₃ and Related Compounds.** WO₃ is the most studied and best electrochromic material for EC applications. Its color changes from transparent or yellow to deep blue with a large optical modulation when it is reduced under cathodic polarisation. Several sol-gel routes have been developed for its preparation [18–29, 31, 36].

Cronin et al. [3, 17] have recently developed new WO₃ sol by reacting metallic W with a mixture of hydrogen peroxide and acetic or propionic acid. The resulting W-peroxy acid was then esterified by reacting with low boiling 1 to 3 carbon alcohol to produce a peroxyster-W derivative (PTE). Electrochromically active coatings with optical transmission varying from 85% to less than 15% in a matter of seconds have been obtained by removing the volatile organics by firing at temperatures as low as 100°C, an important parameter for industrial application. Higher firing temperatures only increase the film density, toughness and resistance to scratching. The method can be extended to other transition metals such as Mo, Mn, Cr, Rh, Ir, Ni, etc.

Denesuk et al. [32] reported on WO₃ films from the above sol preparation with additions of oxalic acid dihydrate. The films were inhomogeneous amorphous/crystalline hybrid structure containing small (~5 nm) regions of increased electron density. The intercalation capacity and the dynamic optical efficiency of these hybrid films are much larger and essentially independent of cycling.

In the mixed compound WO₃-TiO₂, the number of tungsten active sites is reduced and the coloration efficiency diminishes from about 70 cm²/C (undoped film) to 35 cm²/C, with 33% Ti doping [33].

**Table 1.** Inorganic electrochromic materials prepared from sol-gel process: (a) amorphous, (b) crystalline, (*) for counter electrode.

<table>
<thead>
<tr>
<th>Material</th>
<th>State</th>
<th>Color</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO₃</td>
<td>a, c</td>
<td>Blue</td>
<td>[3, 16–32]</td>
</tr>
<tr>
<td>WO₃-TiO₂</td>
<td>a</td>
<td>Blue</td>
<td>[33]</td>
</tr>
<tr>
<td>WO₃-MoO₃</td>
<td></td>
<td></td>
<td>[34]</td>
</tr>
<tr>
<td>MoO₃</td>
<td>a, c</td>
<td></td>
<td>[35, 36]</td>
</tr>
<tr>
<td>CeO₂</td>
<td>UV</td>
<td></td>
<td>[33, 37, 38]</td>
</tr>
<tr>
<td>CeO₂-SnO₂</td>
<td></td>
<td></td>
<td>[38]</td>
</tr>
<tr>
<td>CeO₂-TiO₂</td>
<td>c, *</td>
<td>UV</td>
<td>[37, 39-47]</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Grey</td>
<td></td>
<td>[48-54]</td>
</tr>
<tr>
<td>TiO₂-Al₂O₃</td>
<td>Blue</td>
<td></td>
<td>[48]</td>
</tr>
<tr>
<td>TiO₂-Cr₂O₃</td>
<td>Blue</td>
<td></td>
<td>[48]</td>
</tr>
<tr>
<td>TiO₂-WO₃</td>
<td></td>
<td></td>
<td>[52, 55, 56]</td>
</tr>
<tr>
<td>TiO₂-viologen</td>
<td></td>
<td></td>
<td>[53]</td>
</tr>
<tr>
<td>Nb₂O₅</td>
<td>a, c</td>
<td>a-brown, c-blue</td>
<td>[39, 50, 51]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[57-66, 67]</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td></td>
<td></td>
<td>[68-70]</td>
</tr>
<tr>
<td>Fe₂O₃-TiO₂</td>
<td></td>
<td></td>
<td>[69, 70]</td>
</tr>
<tr>
<td>SnO₂</td>
<td></td>
<td></td>
<td>[61]</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>c</td>
<td>Green, yellow, red</td>
<td>[36, 49, 54]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[71-74]</td>
</tr>
<tr>
<td>V₂O₅-Nb₂O₅</td>
<td></td>
<td></td>
<td>[75, 76]</td>
</tr>
<tr>
<td>V₂O₅-TiO₂</td>
<td>Powder</td>
<td>Grey</td>
<td>[77]</td>
</tr>
<tr>
<td>V₂O₅-Nb₂O₅</td>
<td>Powder</td>
<td>Grey</td>
<td>[77]</td>
</tr>
<tr>
<td>V₂O₅-TiO₂</td>
<td>a</td>
<td>Blue, green, yellow reddish-brown</td>
<td>[78]</td>
</tr>
</tbody>
</table>

**TiO₂ and Related Compounds.** Coatings have been prepared from classical [48–51] and modified (acetic acid) alkoxo routes [54]. In both cases the electrochromic properties of the coatings are similar, but their color was found either grey or blue respectively as the presence of impurities or organic groups modifies the ligand field around the Ti and alters the cosmetic aspect of the film after ion insertion. This may be a tool to adjust the color of the coating.

A new approach has been proposed by Hagfeldt et al. [53] who prepared thick coatings (3.5–4 μm) of nanocrystalline TiO₂ particles by spreading a paste of 15 nm size colloidal TiO₂ particles on conducting glass. After autoclaving at 200°C and firing at 450°C in air during 30 min, the films were found crystalline (anatase) and highly porous. The Li intercalation is reversible (0.11 C/cm²) and is accompanied by an intense color change from transparent to dark blue and with
reasonable color kinetics (≈25 s) (Fig. 1). Stability tests show a decline of the cathodic wave of ≈25% during the first three cycles but no other change has been observed up to 110 cycles. This behavior contrasts with that of anatase films prepared by conventional methods which are unable to intercalate Li ions to any significant extent. Apparently the nanoporous morphology of the coating with unique morphology and surface structure greatly facilitates the reversible Li intercalation.

TiO₂ mixed with Al₂O₃ or Cr₂O₃ [48] also changes the color of the coating after Li insertion. Stangar et al. [55] have also incorporated phosphotungstic acid H₅PW₁₂O₴₀ · xH₂O (PWA) to TiO₂ xerogel with a ratio PWA/Ti = 0.07. The optical density change in the visible range is only about 40% due to a large structureless UV band. The maximum amount of H⁺ inserted was 25 mC/cm² and the kinetics was slow. This compound is attractive as protons are already present in the structure and there is no need for an additional ion conductive material in close contact with the electrochromic material; its strong acidity and solubility in water and some organic solvents should limit its use.

Hagfeld et al. [53] proposed another interesting approach by attaching viologen molecules (having low redox potential and significant reversibility) to TiO₂ nanoparticles and this combines the effect of the large nanosize particles active area with the good electrochromic properties of viologen. Such systems exhibit a high coloration efficiency (85 cm²/C) in the UV-Vis spectral range but stability tests indicate a gradual decrease of the charge exchanged (≈25%) up to 100 cycles (Fig. 2).

V₂O₅ and Related Compound. V₂O₅ coatings are yellow in the bleached state and their transmission is not as large as in WO₃. They are proposed mainly as electrodes for ion or energy storage [73]. The reversibility and kinetic for Li⁺ ions is good in crystalline V₂O₅ [74] and the insertion occurs at rather well defined sites leading to a green color typical of intercalation transfers between V⁴⁺ and V⁵⁺. Thick films (about 10 μm) show multiple color turning red to yellow to green. The electrochromism in mixed V₂O₅-TiO₂ coatings [78] prepared from a stabilized mixture of V and Ti alkoxides in isopropanol depends on the atomic ratio x = Ti/(V + Ti) and the calcination temperature.

Nb₂O₅. Sol-gel Nb₂O₅ films are very promising candidates to substitute WO₃ coatings and have been prepared using different sol precursors [57–59, 62–65]. The preparation of chloroalkoxides by dissolving NbCl₅ in butanol and glacial acetic acid under ultrasonic agitation is a simple recipe to obtain precursors leading to colloidal particles (≈70 nm size) [66]. Coatings obtained with these sols present good microstructure with no cracks and defects even at microscopic scale. Figure 3 shows X-ray diffraction patterns of Nb₂O₅ precipitate obtained with a sol prepared with chloroalkoxides heat treated between 400 and 600°C.
in air for 10 min [66]. The material is amorphous up to 400°C and becomes essentially crystalline only at ~600°C (TT phase). After Li⁺ insertion the color of the amorphous coating is brown while it is deep blue when crystalline, similar to WO₃. The color of these coatings can be therefore continuously changed from brown to blue by adjusting their crystalline structure. Figure 4 shows typical optical spectra obtained with 100 nm thick amorphous and crystalline coatings (1 and 2 dips). Variation of the optical transmission from 80% to less than 20% in the 400–1200 nm range can be observed. The color efficiency, defined as $Q/(OD)$ is 22 cm²/C at 600 nm for a 300 nm thick crystalline coating [66]. This value is larger than that reported by Lee et al. [57] (6 cm²/C), comparable to that obtained by Ohtani et al. [67], but smaller than 167 cm²/C reported for WO₃ [67]. The electrochemical properties are fully reversible and stable. Figure 5 shows typical cycle dependences of the maximum Li⁺

Figure 3. X-ray diffraction of Nb₂O₅ precipitate heat treated between 400 and 600°C in air for 10 min, showing the TT structure.

Figure 4. UV-VIS spectrum observed during electrochromic switching of Nb₂O₅ films before and after polarization at -1.8 V: one layer (~100 nm thick) calcinated at 400°C (--) and one and three layers calcinated at 600°C (---).

Figure 5. Cyclic dependence of Li⁺ charge inserted (or extracted) during full voltametry cycles between +2 V and -1.8 V measured at a rate of 50 mV/s for Nb₂O₅ coatings heat treated 2 h in O₂ atmosphere: (●) 560°C (crystalline), (⋄) 500°C (partly crystalline) and (■) 400°C (amorphous).
charge densities inserted at $-1.8$ V (vs Ag/AgCl) or extracted at $+2$ V measured up to 2000 full voltammetry cycles. For crystalline coatings, no changes are observed. The kinetics of coloring and bleaching are fast (Fig. 6). The amount of charge which can be inserted depends on the structure, the heat treatment and the thickness of the coatings (Fig. 7). $H^+$ can also be inserted but the lifetime of the coatings is short due to corrosion problem at the interface EC layer-electrolyte.

**CeO$_2$ and Related Compound.** Pure and doped CeO$_2$ coatings are excellent materials for passive ion storage electrode, as they only color below 370 nm. Homogeneous, crack free coatings with particulate texture have been obtained from sols prepared by thermal decomposition of $(NH_4)_2$ Ce(NO$_3$)$_6$, to which was added H$_2$O$_2$ [37]. The films heat treated at 520°C are crystalline but exhibit a more amorphous structure at lower temperatures. The electrochemical process is highly reversible for Li$^+$ insertion with a storage capacity of $9 \text{ mC/cm}^2$.
(250 nm thick coating). 20 mC/cm² for (280 nm thick film) have been reported for films made with the same sols precipitated by adding NH₄ OH (pH = 9) followed by HNO₃ peptization [38].

CeO₂·TiO₂ coatings, first reported by Baudry et al. [40, 41-46], show better electrochemical properties. 20 mC/cm² can be inserted reversibly in equimolar mixed oxide films fired at 450°C [40, 46]. The coatings are composed of small CeO₂ crystallites (~1 to 5 nm) imbedded in an amorphous and porous TiO₂ matrix which acts as a continuous structure for the Li⁺ ions to reach the surface of each crystallite. Similar coatings have also been prepared by dissolving CeCl₃ in titanium isopropoxide but their overall electrochemical properties are inferior [37, 38].

SnO₂ doped CeO₂ coatings also do not color in the visible region and charge transfer up to 22 mC/cm² has been reported for a 280 nm thick film with 17 mol% SnO₂. The value however decreases with cycling.

**Fe₂O₃ and Related Compounds.** The preparation of Fe₂O₃ electrochromic coatings has been reported using either ferric nitrate-ethyl acetate solution [68] or precipitation of FeCl₃·6H₂O with (NH₃)₃H₂O followed by peptization of the precipitate with glacial acetic acid [69, 70]. Amorphous Fe₂O₃ films obtained at 300°C show anodic coloration properties under Li⁺ ion insertion (T = 60% at 300 nm) and the presence of OH—and small size particles is fundamental. Their transformation into Fe₂O₃ at 500°C make them inactive. The adherence of the films to ITO coating is poor and the mechanical stability deteriorates with cycling. Coatings obtained by doping with nonabsorbing Ti and Sn oxide [69, 70] color and bleach in a narrower spectral range (300-400 nm) with a smaller transmission variation (15-30%). They exhibit, however, large charge intercalation (up to 60 mC/cm²) higher than most of the known electrochromic coating, making them interesting for ion reservoir.

3. **Future Developments and Conclusion**

Recent sol-gel processing of oxide coatings for EC devices is reported. The research definitively indicates that excellent coatings for H⁺ and Li⁺ intercalation can be obtained with nanoparticles linked together by some adequate thermal treatment. These coatings present a high surface area which can bind high amount of ions to their active sites. A high porosity allows fast diffusion of the ions and the small thickness (μm) and nanoscale size of their constituents give these coatings adequate optical appearance and properties.

The future of the sol-gel process for the preparation of EC or related coatings (e.g., for solar cells) is bright and, at short term, interesting all solid state devices such as rear view mirrors for automobile, etc., will be on the market. Large scale devices such as smart windows still require considerable research in order to overcome the technical difficulties encountered during the scale-up development.

**Acknowledgment**

Research sponsored by Fapesp, CNPq and FINEP (Brazil).

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