Electrochromism in Materials Prepared by the Sol-Gel Process

MICHEL A. AEGERTER,* CESAR O. AVELLANEDA, AGNIEZSKA PAWLICKA† AND MOHAMED ATIK
Instituto de Física de São Carlos, Universidade de São Paulo, Caixa Postal 369, 13560-970, São Carlos, SP, Brasil

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 WO_3, V_2O_5, Nb_2O_5, TiO_2, CeO_2, Fe_2O_3 and mixed compounds such as WO_3-TiO_2, CeO_2-TiO_2, CeO_2-SnO_2, 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 Nb_2O_5 and TiO_2 composition. Finally we stress the future developments in this fast growing field.

Keywords: electrochromism, coating, nanoparticle, sol-gel material, WO_3, Nb_2O_5, TiO_2, CeO_2, Fe_2O_3, 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 emitance) 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 WO_3 vapor layer deposited on a semitransparent metal layer (Cr, Ag) was intensively blue colored when cathodically polarized in $0.1N$ H_2SO_4. 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

$$\mathrm{MeO}_n + x\mathrm{I}^+ + xe^- \leftrightarrow \mathrm{I}_x\mathrm{MeO}_n \qquad (1)$$

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.

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[*] Present address: Institut für Neue Materialien, Im Stadtwald, Gebäude 43, D 66-123 Saarbrücken, Germany.

[†] Instituto de Quimica de São Carlos, Universidade de São Paulo, Cx. Postal 780, 13560-970 SP (Brazil).

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 WO_3, V_2O_5, CeO_2, Fe_2O_3 and some mixed compounds with emphasis on TiO_2 and Nb_2O_5. More details will be found in [79] and [80].

WO_3 and Related Compounds. WO_3 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].

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

Material	State	Color	References
WO_3	a, c	Blue	[3, 16–32]
WO_3-TiO_2	a	Blue	[33]
WO_3-MoO_3			[34]
MoO_3	a, c		[35, 36]
CeO_2		UV	[33, 37, 38]
CeO_2-SnO_2			[38]
CeO_2-TiO_2	c, ∗	UV	[37, 39–47]
TiO_2		Grey	[48–54]
TiO_2-Al_2O_3		Blue	[48]
TiO_2-Cr_2O_3		Blue	[48]
TiO_2-WO_3			[52, 55, 56]
TiO_2-viologen			[53]
Nb_2O_5	a, c	a-brown, c-blue	[39, 50, 51] [57–66, 67]
Fe_2O_3			[68–70]
Fe_2O_3-TiO_2			[69, 70]
SnO_2			[61]
V_2O_5	c	Green, yellow, red	[36, 49, 54] [71–74]
V_2O_5-Na_2O			[75, 76]
V_2O_5-Ta_2O_5	Powder	Grey	[77]
V_2O_5-Nb_2O_5	Powder	Grey	[77]
V_2O_5-TiO_2	a	Blue, green, yellow reddish-brown	[78]

Cronin et al. [3, 17] have recently developed new WO_3 sol by reacting metalic 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 peroxyester-W derivative (PTE). Electrochromically active coatings with optical transmission varying from 85% to less then 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 WO_3 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 WO_3-TiO_2, the number of tungsten active sites is reduced and the coloration efficiency diminishes from about 70 cm^2/C (undoped film) to 35 cm^2/C, with 33% Ti doping [33].

TiO_2 and Related Compounds. Coatings have been prepared from classical [48–51] and modified (acetic acid) alkoxy 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 Hagfeld et al. [53] who prepared thick coatings (3.5–4 μm) of *nanocrystalline* TiO_2 particles by spreading a paste of 15 nm size colloidal TiO_2 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/cm^2) and is accompanied by an intense color change from transparent to dark blue and with

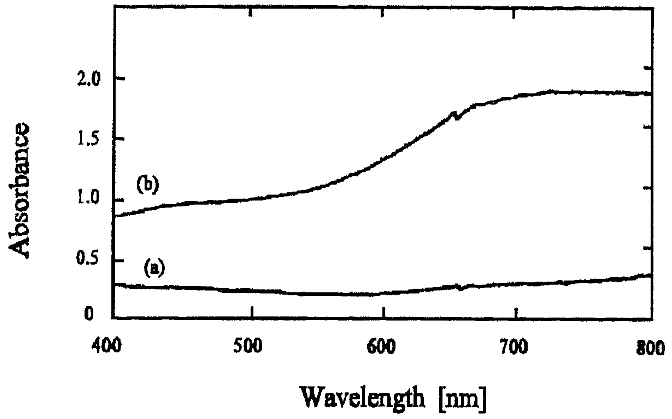

Figure 1. UV-VIS spectrum observed during electrochromic switching of nanocrystalline TiO_2 (a) bleached state (−0.64 V vs Ag/AgCl) and (b) colored state after polarizing to −1.64 V vs Ag/AgCl for 10 s. $1M$ $LiClO_4$ in acetonitrile, film thickness 3.5 μm. The observed background absorption in the bleached state is due to light scattering. 10 seconds after applying the potential step the absorbance increases to a value above one in the whole visible region with a broad maximum of absorbance close to 2 in a wavelength interval of 660–880 nm. Charge passed is 0.10 C/cm^2 [from 53].

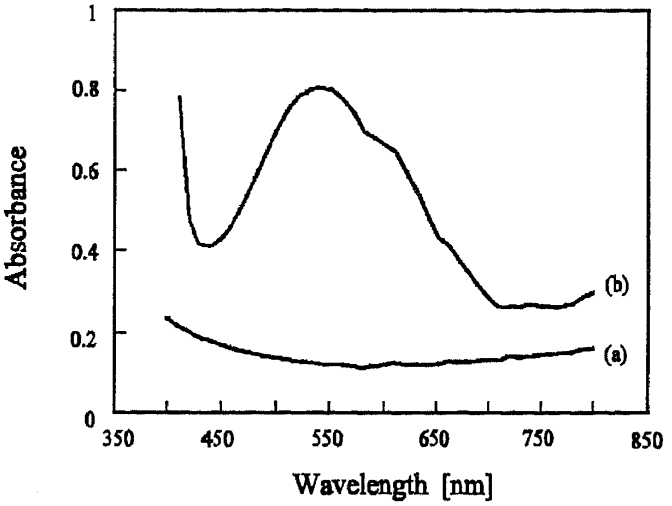

Figure 2. UV-VIS spectrum observed during electrochromic switching of a viologen coated nanocrystalline TiO_2 electrode: (a) bleached state under open circuit condition (b) colored state after polarizing to −0.86 V. $0.1M$ $TPAClO_4$ in propylene carbonate is used as electrolyte and the electrode area is 1.0 cm^2. The observed background absorption in the bleached state is due to light scattering. Charge passed during coloration is 8.0 mC/cm^2 [from 53].

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.

TiO_2 mixed with Al_2O_3 or Cr_2O_3 [48] also changes the color of the coating after Li insertion. Stangar et al. [55] have also incorporated phosphotungstic acid $H_3PW_{12}O_{40} \cdot xH_2O$ (PWA) to TiO_2 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/cm^2 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 TiO_2 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 cm^2/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).

V_2O_5 and Related Compound. V_2O_5 coatings are yellow in the bleached state and their transmission is not as large as in WO_3. They are proposed mainly as electrodes for ion or energy storage [73]. The reversibility and kinetic for Li^+ ions is good in crystalline V_2O_5 [74] and the insertion occurs at rather well defined sites leading to a green color typical of intervalence transfers between V^{4+} and V^{5+}. Thick films (about 10 μm) show multiple color turning red to yellow to green. The electrochromism in mixed V_2O_5-TiO_2 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.

Nb_2O_5. Sol-gel Nb_2O_5 films are very promising candidates to substitute WO_3 coatings and have been prepared using different sol precursors [57–59, 62–65]. The preparation of chloroalkoxides by dissolving $NbCl_5$ 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 Nb_2O_5 precipitate obtained with a sol prepared with chloroalkoxides heat treated between 400 and 600°C

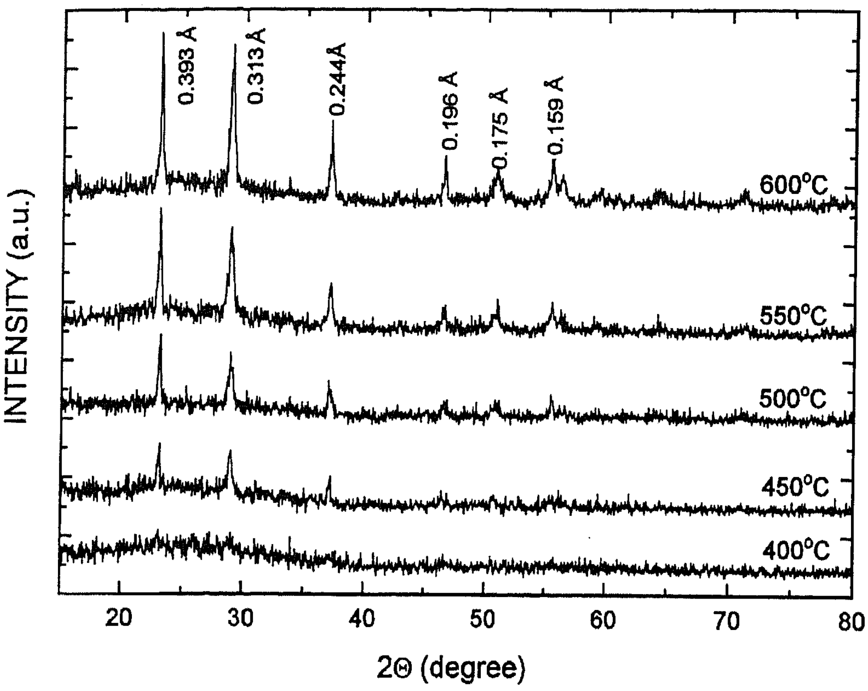

Figure 3. X-ray diffraction of Nb_2O_5 precipitate heat treated between 400 and 600°C in air for 10 min, showing the TT structure.

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 WO_3. 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 cm^2/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 cm^2/C), comparable to that obtained by Ohtani et al. [67], but smaller than 167 cm^2/C reported for WO_3 [67]. The electrochemical properties are fully reversible and stable. Figure 5 shows typical cycle dependences of the maximum Li^+

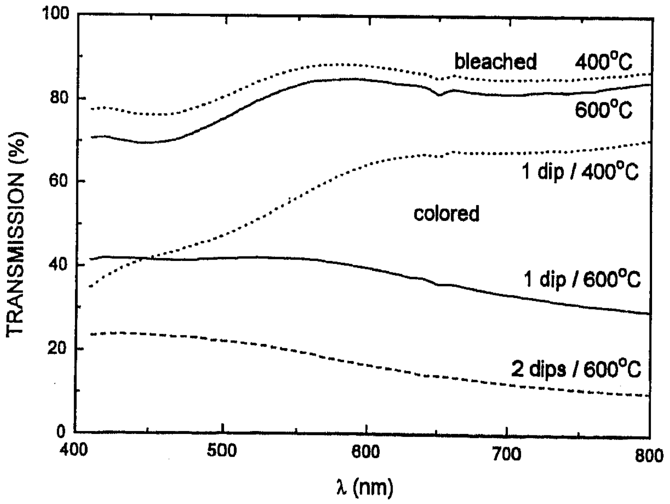

Figure 4. UV-VIS spectrum observed during electrochromic switching of Nb_2O_5 films before and after polarization at −1.8 V; one layer (~100 nm thick) calcinated at 400°C (- - -) and one and three layers calcinated at 600°C (—).

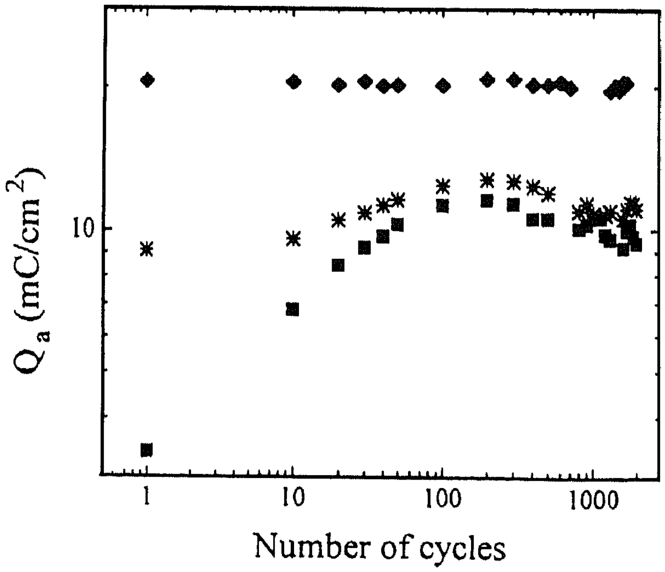

Figure 5. Cyclic dependence of Li^+ charge inserted (or extracted) during full voltametry cycles between +2 V and −1.8 V measured at a rate of 50 mV/s for Nb_2O_5 coatings heat treated 2 h in O_2 atmosphere: (✱) 560°C (crystalline), (♦) 500°C (partly crystalline) and (■) 400°C (amorphous).

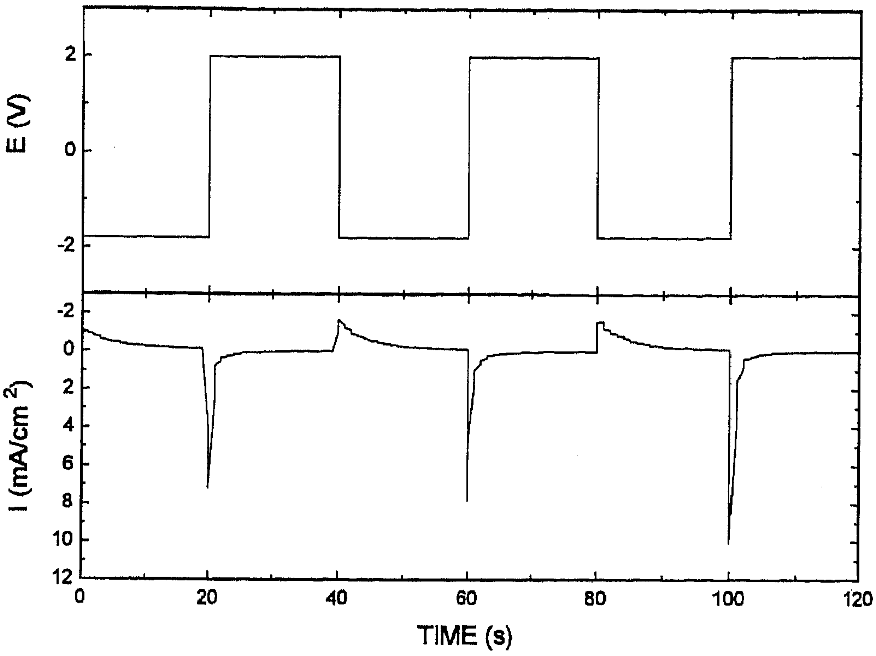

Figure 6. Chronoamperometry of Nb_2O_5 coating with potential steps of −1.8 V and 2 V at every 20 s interval.

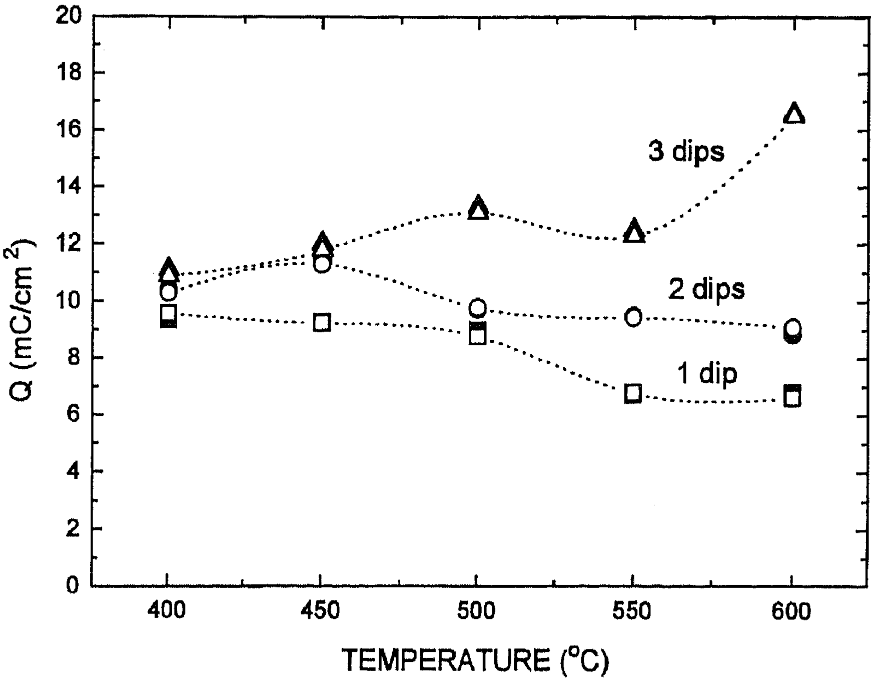

Figure 7. Charge densities for 1, 2 and 3 layers of crystalline Nb_2O_5 coatings calcinated at different temperatures. The full and empty symbols refer to the insertion and extraction process, respectively.

charge densities inserted at −1.8 V (vs Ag/AgCl) or extracted at +2 V measured up to 2000 full voltametry 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 $(NH_4)_2Ce(NO_3)_6$, to which was added H_2O_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 mC/cm^2

(250 nm thick coating). 20 mC/cm^2 for (280 nm thick film) have been reported for films made with the same sols precipitated by adding NH_4OH (pH = 9) followed by HNO_3 peptization [38].

CeO_2-TiO_2 coatings, first reported by Baudry et al. [40, 41–46], show better electrochemical properties. 20 mC/cm^2 can be inserted reversibly in equimolar mixed oxide films fired at 450°C [40, 46]. The coatings are composed of small CeO_2 crystallites (~1 to 5 nm) imbedded in an amorphous and porous TiO_2 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 $CeCl_3$ in titanium isopropoxide but their overall electrochemical properties are inferior [37, 38].

SnO_2 doped CeO_2 coatings also do not color in the visible region and charge transfer up to 22 mC/cm^2 has been reported for a 280 nm thick film with 17 mol% SnO_2. The value however decreases with cycling.

Fe_2O_3 and Related Compounds. The preparation of Fe_2O_3 electrochromic coatings has been reported using either ferric nitrate-ethyl acetate solution [68] or precipitation of $FeCl_3 \cdot 6H_2O$ with $(NH_3)_{aq}$ followed by peptization of the precipitate with glacial acetic acid [69, 70]. Amorphous Fe_2O_3 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 $-Fe_2O_3$ 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 Si 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/cm^2) 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.

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