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Optical Properties of Thin Films and Electrochromic Devices

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Electrochromic devices (ECDs) are electrochemical cells composed of thin films and electrolyte that have a property to change the color of transmitted light upon applied potential and, consequently, altering their transmittance and reflectance. This property is useful not only for the display industry but also for windows in buildings because it can promote savings of energy spent on air conditioning and lighting. ECDs are composed of two electrodes (ITO coated glasses), an electrochromic layer (WO_3, Nb_2O_5, Prussian blue thin film etc.), a counter electrode (CeO_2-TiO_2 thin film), and an electrolyte that can be liquid, solid, or gel. As electrolyte the most interesting is gel because of its semi-solid state, volume and shape flexibility, good ionic conductivity, and in most cases simplicity in preparation. Gels can be obtained from synthetic and natural macromolecules such as polysaccharides, proteins, and DNA. These macromolecules can be used in their natural form or can be subjected to chemical or physical modifications such as crosslinking or plasticization processes. Different thin films and ECDs, beside the electrochemical characterization, were tested for their optical properties. It was found that the transmittance of thin films depends strongly on their composition. That of ECDs depends of both thin films and the electrolyte. For example, a 40.2% change between the colored and discolored states was observed for the ECD with gelatin-$LiClO_4$ and 35.2% for the ECD with agar-$Eu(CF_3SO_3)$

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electrolyte. The results show that the thin films and electrolytes are equally important parts of ECDs. Their composition and properties influence the device optical performance. Therefore they need to be more deeply investigated.

Keywords: thin films, electrochromism, electrochromic devices

1. INTRODUCTION

Electrochromic materials possess the property of color change when subjected to the application of potential in an electrochemical cell or when current passes through them. This color change may be gradual or continuous and must be reversible when the applied potential is inverted [1].

The interest in these materials is due to the development of new and modern devices [2]. Among several research fronts for the application of these devices there are electrochromic rear-view mirrors for cars [3], available in the market for more than 20 years. Their main function is to provide to drivers a comfort during the night, since this type of device darkens when a strong beam of light is detected [4]. Another applications tested in practice are the transparent surfaces for constructions, as well as for vehicles, trains and aircrafts. The latter were announced in 2007 along with the presentation of the new model of Boeing 787 called Dream Liner [5]. The purpose of these applications is the possibility of controlling the passage of light and reduction of the energy consumption spent by using air conditioners. This is done by controlling the quantity of light and heat that enter through the windows [1,6].

The all solid state electrochromic devices (ECDs) are composed of different thin layers/films and may have various configurations. In general, an electrochromic device can be defined as an electrochemical cell with a sandwich structure, as shown in Fig. 1a. The ECD can be composed of thin films deposited on substrate that is an electronic conductor, i.e. glass coated with indium tin oxide (ITO) or fluorine tin oxide (FTO), for example. These thin films are transition metal oxides such as WO_3 or Nb_2O_5, which are electrochromic and CeO_2-TiO_2 counter electrode, which usually is a transparent coating. The electrochromic and counter electrode films are deposited on the opposing sides and are separated by the electrolyte, which may be liquid, solid, or gel. As mentioned above for the device to work it is necessary to apply the electric current or potential, which causes the reversible change of coloration, from transparent to blue or from blue to transparent. Fig. 1 illustrates the ECD in three different stages: transparent (Fig. 1a), partially dimed (Fig. 1b), and totally dimed (Fig. 1c).

The components of the ECDs may vary, so the comparison of known devices, described in the literature, is quite difficult. However, some data of

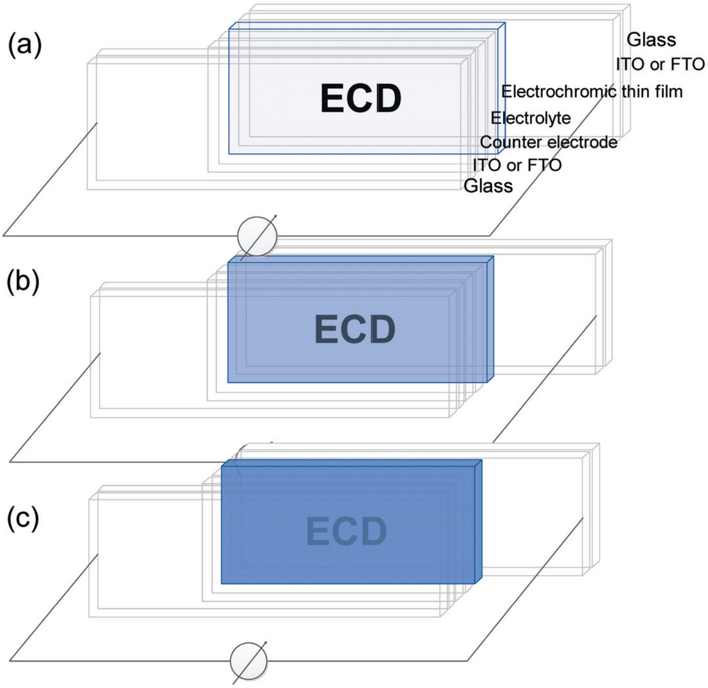

FIGURE 1
Electrochromic device (ECD) in bleached (a), slightly (b), and fully colored (c) states.

size, transmittance, reflectance, number of cycles of diming/bleaching of the devices developed between 1998 and 2001 can be found in the publications of Granqvist et al [7], Heusing and Aegerter [8], or Monk *et al* [1].

The main advantage of the ECDs is their ability to change the color, and so alter their optical properties; however, these devices have thin films and electrolytes in their configuration which can strongly influence the ECD's optical properties. Therefore, the present contribution aims to present some insights how thin films and gel electrolytes influence the optical properties of the electrochromic devices.

2. THIN FILMS

Electrochemical devices (EDs) can be assembled in different ways and using different materials, but they always have two electrodes and electrolyte between them. For example, electrochromic devices, shown in Fig. 1, can be assembled with liquid, gel, or solid electrolytes, but the gel and solid ones seem to be the best choice for practical application because they are easy to handle, don't leak when the device is broken, and provide good contact with electrodes, specially the gel electrolytes.

The electrodes of electrochemical devices can also be made from different materials that conducts current. Therefore, several metals or conducting ceramics can be used. Nowadays, the most used for modern EDs development, are the already mentioned ITO and FTO thin films deposited on glass or on poly(ethylene terephthalate) (PET) substrates. However, in some application these films can suffer ion injection, which alter their conductivity and transparency properties [9], so they are covered by protecting thin films as for example, the cerium dioxide (CeO_2) thin film. The CeO_2 compound is electrochemically active but optically passive. It was studied over the last twenty years for use as passive electrode in EDs [10,11]. Its function is the ion storage and the compensation of charges exchanged during an electrochemical reaction [12]. However, the CeO_2 thin films although their high optical transparency, in the visible region, and open structure, that allows an easy passage of ions during their intercalation and de-intercalation [9], they exhibit a slowest reaction rate compared to other materials [13,14]. It also traps the ions, resulting in a decrease of the ion storage capacity over the time [15]. To solve this problem, Baudry *et al* [16] developed CeO_2:TiO_2 thin films that were more stable electrochemically than pure CeO_2. Krasovec *et al* [17] proposed $CeVO_4$ thin films that showed slight color change, resulting in color efficiency of about 0.1 to 0.5 cm^2 C^{-1}. Masetti *et al* [14] synthesized mixed cerium-vanadium oxides that showed a total charge of 60 mC cm^{-2} during a reversible electrochemical cycling in the 1 to 5 V potential range versus Li. Malini and Sanjeeviraja [18] also reported on vanadium-cerium mixed oxides with a passive optical behavior and a good charge capacity. As other alternatives, CeO_2:ZrO_2 thin films were also studied [9,19]. These films are transparent, but their storage capacities are lower than that CeO_2:TiO_2. Addition of ZrO_2 to CeO_2-TiO_2 resulted in CeO_2-TiO_2-ZrO_2 thin films that had the charge density lower than CeO_2-TiO_2, but higher than CeO_2:ZrO_2 thin films. Moreover, these films remained transparent upon redox reactions [20].

Tungsten trioxide (WO_3) thin film is not only the most studied electrochromic material due to its reversible color change [1,21] but also the best candidate for all-solid electrochromic device applications. WO_3 thin films are synthesized in many laboratories, mostly by vacuum and wet deposition methods [1]. Because of their well-established characteristics, they are also commonly applied in electrochemical devices such as electrochromic windows [22,23], in energy storage devices [24], and chemical sensors [25,26]. Besides that, over the last 40 years WO_3 is also investigated as a catalyst [27,28]. The main characteristic of WO_3 is its property of color change under an electrochemical condition from transparent to blue [29]. After application of -1.0 V the transparent film dims by acquiring a blue color. Application of a reverse potential of +1.0 V restores the 70% of transparency of this film in the 550 to 1000 nm wavelength range. In the same wavelength range the blue

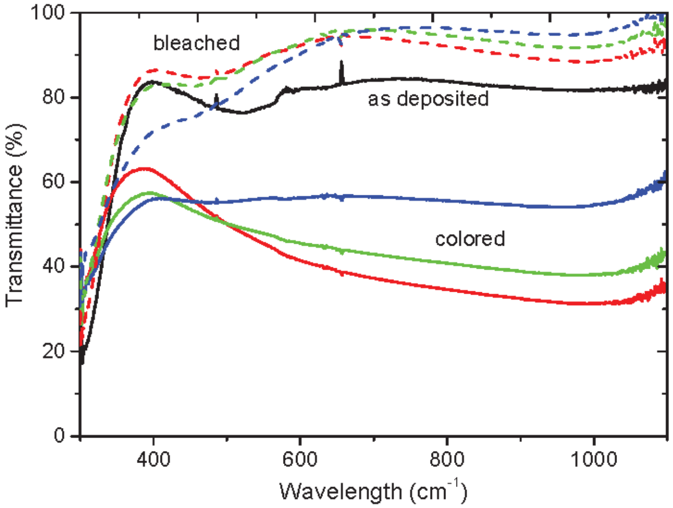

FIGURE 2
UV-Vis spectra of WO_3 thin film as deposited (——), colored at -1.5 V for 15 s (——), 30 s (——), and 60 s (——) and bleached at 1.5 V for 15 s (——), 30 s (——), and 60 s (——) states. The applied potentials were of ±1.0 V.

color state WO_3 transmits about 10% of light. Thus, the transmission change ΔT at 550 nm is of 52%. The only 70% of transmittance in bleached state could influence the whole device optical properties. A change of deposition condition promotes a decrease of ΔT. It is 44%, 42%, and 29% at 550 nm for potential of -1.5 V applied for 15, 30, and 60 s; respectively (Fig. 2). Additionally, the bleached films are more transparent than the deposited ones.

The vanadium pentoxide (V_2O_5) is a transition metal oxide with redox properties that can be used in different electrochemical devices as, for example, lithium ion battery or gas sensors among the others [1,30]. Similarly to tungsten trioxide and niobium pentoxide V_2O_5 changes reversibly color from brown-yellow to pale blue when a voltage or current is applied [31]. This electrochromic property is due to its favorable structure, which facilitates the ion intercalation [32]. However, similar to CeO_2, it shows some drawbacks such as low conductivity, lack of electrochemical stability, and low redox reversibility [33-35]. This limits its practical use. Again, aiming at improving these limitations its doping with other transition metal oxides, as for example Nb_2O_5 [36] or MoO_3 [37], was proposed. In both cases, 5 mol% Nb_2O_5 and MoO_3 doped V_2O_5 films revealed an increase of charge densities from about 70 mC cm^{-2} for pure V_2O_5 film to 82 mC cm^{-2} for V_2O_5:Nb_2O_5 [36] and 132 mC cm^{-2} for V_2O_5:MoO_3 [37]. The doping also promoted changes in their UV-Vis transmittance spectra in the wavelength range from 350 to 1110 nm (Fig. 3 and 4). The transmittance values, measured at 633 nm, varied between 45 and 86% for V_2O_5 (Fig. 3a) and between 38 and 85% for V_2O_5:Nb_2O_5 5 mol%. (Fig. 3b).

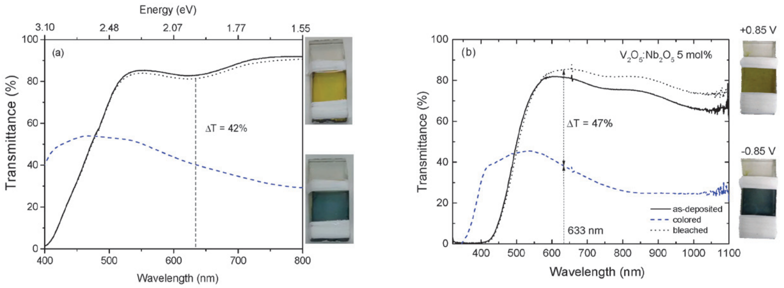

FIGURE 3
UV-Vis transmission spectra and pictures of V_2O_5 (a) and V_2O_5:Nb_2O_5 5 mol% (b) thin films in yellow and blue colored states. Adapted from [36].

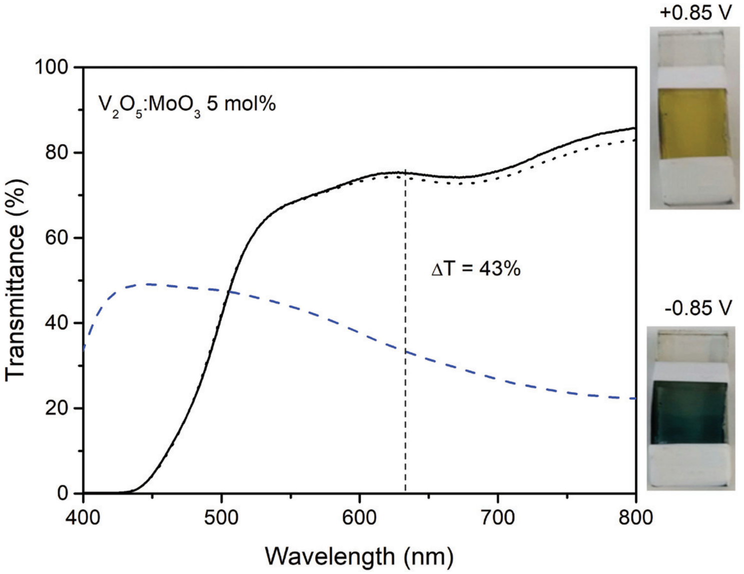

FIGURE 4
UV-Vis spectra and pictures of V_2O_5:MoO_3 5 mol% in yellow and blue colored states. Adapted from [37].

This gives a transmission variation of ΔT = 41 and 47% for undoped and doped V_2O_5 films, respectively, so an increase of ΔT = 6% at 633 nm.

The transmittance spectra, measured at 633 nm, for V_2O_5:MoO_3 5 mol% film show 43% of color change between the yellow (bleached) and the blue (colored) states (Fig. 4). It proves an excellent electrochromic performance of these films too. However, due to the yellow color of the film at bleached state its transmittance is rising from 60 % at 500 nm to about 85 % at 800 nm.

Figures 3 and 4 show also the films exhibit different light transmission modulations below 500 nm. In yellow color state the films are completely opaque at 400 nm, while in blue colored states there are 20% transparent for V_2O_5:Nb_2O_5 and almost 40% for V_2O_5 and V_2O_5:MoO_3, respectively. Therefore, because they transmit less than 40% of light in their blue color state, they are capable to control up to 80% of the daylight transmission [38]. Besides that, a comparison between those films reveals that V_2O_5:Nb_2O_5 and V_2O_5:MoO_3 5 mol% films show lower transmittances in the visible range than V_2O_5, which makes them better for blocking the visible light.

A summary of characteristics of some different thin films used in electrochemical devices and their colors at original state and upon cathodic as well as anodic reactions are gathered in Table 1. However, there are many scientific articles published over the last two decades that describe thin films for electrochemical devices, their synthesis and optical and electrochemical properties. The ones listed in Table 1 are only few of them.

3. ELECTROCHROMIC DEVICES

Besides many articles and at least two books [1,45] already published on electrochromic devices there is still not many practical applications available.

TABLE 1
Some solid thin film electrodes for ECDs and their color at original state, during cathodic reduction and anodic oxidation.

Electrochromic electrode	Color at original state and upon anodic oxidation	Color upon cathodic reduction	Reference
WO_3	Colorless	Blue	[1]
V_2O_5	Yellow	Blue	[36,37]
V_2O_5:Nb_2O_5	Yellow	Blue	[36]
V_2O_5:MoO_3	Yellow	Blue	[37]
TiO_2	Transparent	Blue	[39]
CeO_2-TiO_2	Light yellow	Light yellow	[40]
CeO_2-ZrO_2	Transparent	Transparent	[9,19]
CeO_2:V_2O_5	Yellowish	Light green Transparent	[17,18] [14]
CeO_2- TiO_2 -ZrO_2	Transparent	Transparent	[20]
NiO	Brown	Transparent	[41,42]
NiO:V_2O_5	Brown	Transparent	[42]
Nb_2O_5	Colorless	Blue	[43]
Nb_2O_5:TiO_2	Colorless	Blue	[44]
Prussian Blue	Blue	Transparent	[1]

This is because the ECDs manufacturing processes are very complex and this results in very high prices that are accessible only to high technology products. Two companies Gentex [46] and Pilkington are known to be active in this field. Recently a new company Ynvisible [47] has started the development activities in the domain of electrochromism. There is also Pleotint [48], but it makes products based on thermochromic materials. Probably there are others too, but not advised yet. Nowadays, the research remains very active and different systems are proposed. For example, John Reynolds group proposed polymer electrochromic materials for more than a decade. In a patent [49] they claim assembly process of the double electrochromic window that can change between more than two colors. Their ECD was composed of two working electrodes on external sides and a double-faced electrode in the middle, which has a sandwich type structure like CG|WE_1|E|IS|CG|IS|E|WE_2|CG where CG is a conducting glass, WE is a working electrode, E is an electrolyte, and IS is an ion storage or complimentary coloring electrode. The innovation is that these two electrodes (WE_1 and WE_2) can work independently; therefore, switch between different colors. The final effect is the color addition (RGB - abbreviation of red, green, blue). Additionally, this device can be made with more than two working electrodes, where the electrochromic materials used are mainly polymers such as poly (3,4-ethylenedioxythiophene):poly (styrene sulfonate) (PEDOT:PSS), poly (3,4-propylenedioxypyrrole) (Pprodop), and dihexyl substituted poly(3,4-propylenedioxythiophene) (PProDOT-Hx2), among many others. Because of addition of colors these devices can display a wide variety of them. For example, PEDOT:PSS and PProDOP layers deposited electrochemically give a blue coloration with color parameters of L* = 64, a* = - 5, b* = - 38 in color scale CIE LAB 1976 and orange with L* = 76, a* = 31, b* = 75, respectively. Addition of these colors produces a red/brown one with values of L* = 59, a* = 25, and b* = 50 [49]. CIE LAB 1976 is a colorimetric scale that defines colors perceived by the human eye [50]. It was developed because the human eye is more sensitive in the violet than in the green region. Therefore, to make the chromaticity diagram more uniform and colors comparable there were proposed three axes: white-black (L*), red-green (a*) and yellow-blue (b*).

In 2005, Kobayashi *et al* [51] described on organic electrochromic materials that showed vivid color change to yellow, cyan, or magenta because of electrochemical reactions of phthalate derivatives such as the biphenyl dicarboxylic acid diethyl ester (PCE; yellow color), diacetyl benzene (DAB; cyan color), and dimethyl terephthalate (DMT; magenta color). The authors constructed also the sandwich-type electrochemical cells, which were tested upon over 500 coloring and bleaching cycles and showed no color intensity decay. Furthermore, they have assembled flexible ECDs with gel polymer electrolyte and PET-ITO flexible electrodes as shown in Fig. 5a and a passive matrix (PM with 8 x 8 pixels) three-layered electrochromic device, shown in Fig. 5b. This displayed seven different colors: black, magenta, cyan, yellow,

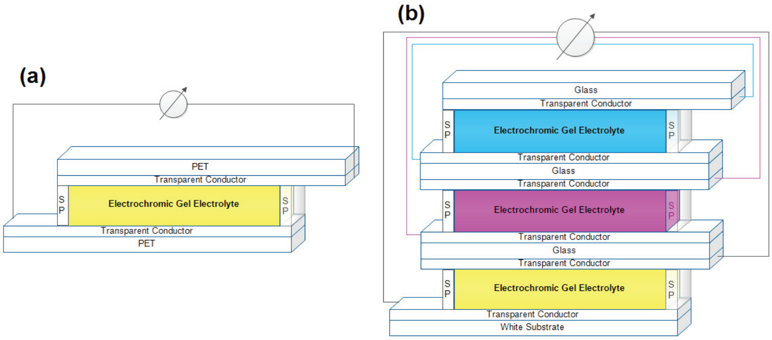

FIGURE 5
Flexible electrochromic device (a) and three-layered electrochromic device (b). Inspired by Figs. 5 and 6 of ref. [51].

blue, red, and green because of independent application of 2.6 V potential to the parts of this sandwich (Fig. 5b).

In 2007, Kobayashi *et al* [52] have described other flexible electrochromic device (ECD) with a subtractive color mixing. Similarly to the previous one, this device was made with a gel electrolyte that contained poly(vinyl buthyrate) (PVB), ferrocene (Fc), N-methylpyrrolidone (NMP), tetra-n-butylammonium perchlorate (TBAP), and either diacetyl benzene (DAB), dimethyl phthalate (DMT), or diethyl ester of dicarboxylic biphenyl (DEB). The device was made by injecting the above electrolyte in between two flexible electrodes of ITO/PET (indium tin oxide/poly(ethylene terephtalate)). As a result, due to electrochemical reactions of those molecules present in gel electrolyte, the ECD showed three primary subtractive colors: cyan (DAB), magenta (DMT), and yellow (DEB). However, a drawback of this device was its short color memory of 80 s in an open circuit and some side reactions during 120 cycles of coloration that resulted in a decrease of ECD absorbance from 0.45 to 0.35.

More recently, Assis *et al* [53,54] proposed the first reflective electrochromic device for camouflage purposes. This ECD showed a real time color change between green and yellow by using two colors subtractive mixing method. The device was built with Prussian blue (PB) electrodeposited coating as electrochromic blue-color layer and yellow-color gel electrolyte. The green color was achieved by subtractive mixing of blue colored PB and the yellow dyed electrolyte layer, in which LiI/I_2 was dispersed. The open circuit color of the device was green and its change to yellow was obtained by applying cathodic potentials, i.e., when PB became transparent. Application of anodic potential promoted oxidation of PB and the device blue coloration. The value of applied potentials between -2 and 2 V permitted a modulation of the intensity of green-yellow as shown in Fig. 6.

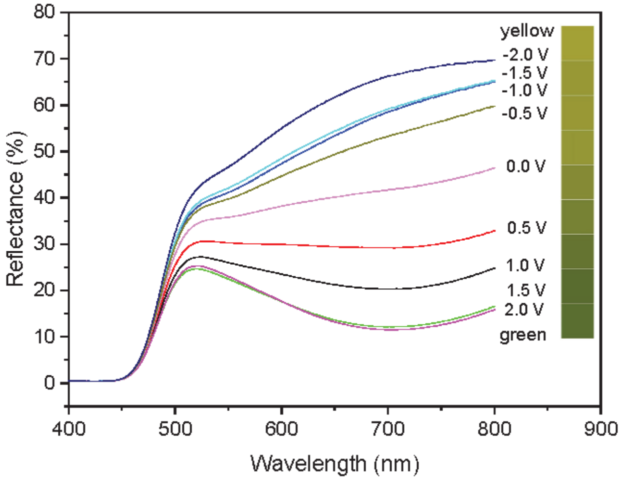

FIGURE 6
Reflectance spectra of the ECD with glass|ITO|PB|PVB-electrolyte|CeO_2–TiO_2|ITO|glass configuration after application of potentials ranging from -2.0 to 2.0 V. Adapted from [53].

The glass|ITO|PB|PVB-electrolyte|CeO_2–TiO_2|ITO|glass device was also subjected to CIE LAB 1976 or CIELAB analysis. This analysis confirmed a change of color, induced by application of different potentials, from deep green, characterized by CIELAB parameters of L* = 52.96, a* = –23.96, b* = 49.12, to yellow, characterized by CIELAB parameters of L* = 73.59, a* = –2.89, b* = 76.65. These data were very similar to CIELAB parameters of deep green (L* = 60, a* = –23, b* = 12) and blue (L* = 84, a* = –4, b* = –6), registered for electrochromic film of SprayDOT^{TM}-Green 145 and suggested as suitable for electrochromic double window with CG|WE_1|E|IS|CG|IS|E|WE_2|CG configuration [49,55].

Many different all-solid ECDs are described in the literature. As mentioned above, they differ in electroactive coatings and polymer electrolytes. Among them, there are devices with electrolytes based on natural macromolecules doped either with inorganic salts, acids, or ionic liquids. For example, the ECD with glass|ITO|WO_3|gelatin1[C2mim][SCN] |CeO_2-TiO_2|ITO|glass configuration, where [C_2mim][SCN] is the ionic liquid 1-ethyl-3-methylimidazolium thiocyanate, was assembled and tested by Leones *et al* [56]. Considering that during the daylight the eye sensitivity is maximum at 550 nm [57], this device, for its 10th color/bleaching cycle, had the maximum transmittance difference ($\Delta T=T_{bleached}-T_{colored}$) of 24% at 600 nm. At 500 nm this difference was 14% (Fig. 7). At 640th cycle, ΔT was 5% for both wavelengths. Thus, the optical density (OD=-log ($T_{colored}/T_{bleached}$)) at 600 nm was 0.432 and 0.059 for 10th and 640th cycles, respectively. At 500 nm, OD was 0.251 (OD = 0.61 at 550 nm) and 0.085 for 10th and 640th cycles, respectively.

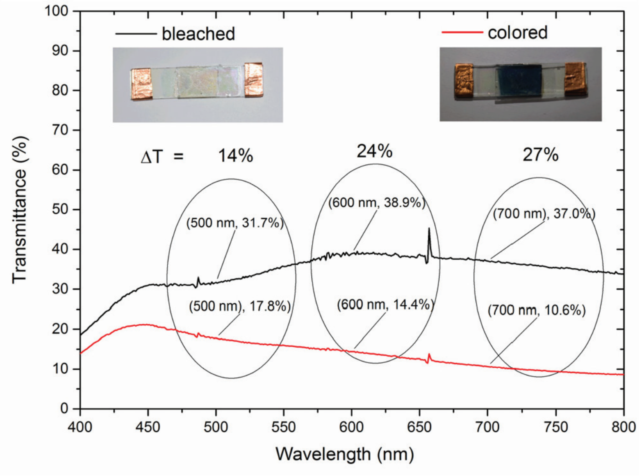

FIGURE 7
Transmittance of an ECD with glass|ITO|WO_3|gelatin$_1$[C_2mim][SCN]|CeO_2-TiO_2|ITO|glass configuration. Pictures of ECD in bleached and colored states in inset. Reproduced from [56].

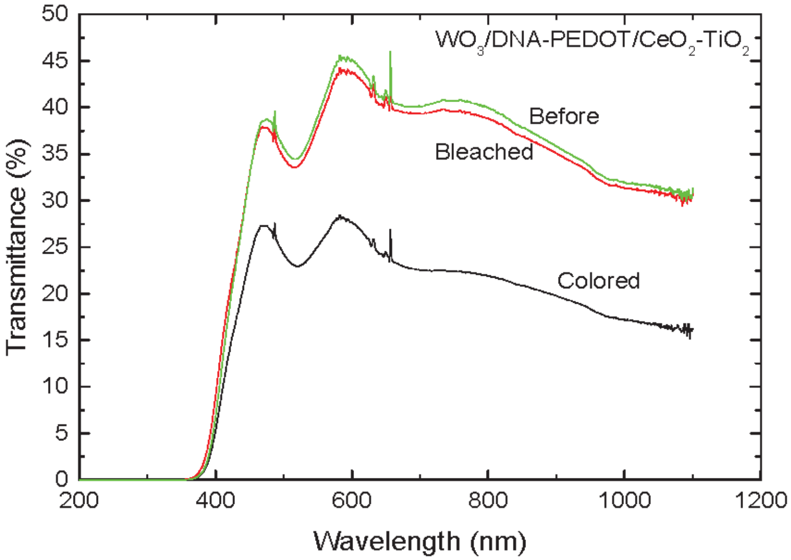

FIGURE 8
UV-Vis spectra of ECD with WO_3|DNA–PEDOT:PSS|CeO_2–TiO_2 configuration. The applied potentials were of −2.5 and 2.0 V. Reproduced from [23].

This ECD also showed the color efficiency (CE) of 23.19 and 20.16 $cm^2\ C^{-1}$ at 600 and 500 nm, respectively. Again, due to the electrochromic coating and mainly to the used electrolyte, the transmittance of this ECD was very low

TABLE 2
Selected electrochromic devices and their reduction and oxidation potentials and difference between colored and bleached states (ΔT).

ECD configuration	Reduction Potential (V)	Oxidation Potential (V)	ΔT_{550nm} (%)	Ref.
PB|HPC-electrolyte|CeO$_2$-TiO$_2$	-2.6	2.0	10	[62]
PB|PVB-electrolyte|CeO$_2$-TiO$_2$	-1.5	1.5	-	[53]
PB/PMMA-LiClO$_4$/WO$_3$	-0.5	1.0	-	[63]
PB/succinonitrile-LiBF$_4$/PBV	-1.0	0.7	65^*	[64]
PB or WO$_3$|chitosan-Tm(CF$_3$SO$_3$)$_3$|CeO$_2$-TiO$_2$	-2.8	2.8	4	[65]
WO$_3$|agar-CH$_3$COOH or LiClO$_4$|CeO$_2$-TiO$_2$	-2.5	2.0	24	[66]
WO$_3$|PAN-LiTFSI|CeO$_2$-TiO$_2$	-1.25	-0.40	29	[67]
WO$_3$|PMMA-succinonitrile|PB	-2.0	1.8	44	[68]
WO$_3$|starch-LiClO$_4$-glicerol|CeO$_2$-TiO$_2$	-2.0	2.0	16	[59]
WO$_3$|starch-LiClO$_4$-ethylene glycol|CeO$_2$-TiO$_2$	-3.0	3.0	37	[59]
WO$_3$|gelatin-CH$_3$COOH-glycerol|CeO$_2$-TiO$_2$	-1.5	1.5	15-20	[60]
WO$_3$|gelatin-glycerol|NiO	-1.1	1.8	63	[69]
WO$_3$|DNA–PEDOT:PSS|CeO$_2$–TiO$_2$	–2.5	2.0	15	[23]
WO$_3$|gelatin$_1$[C$_2$mim][SCN]|CeO$_2$-TiO$_2$	-2.8	3.0	14	[56]
WO$_3$|PVB electrolyte|Ni$_{1-x}$O|ITO	-2.0	2.0	65.8	[58]
PANI:DBSA|PVdF-HFP|ITO	-2.9	2.9	4	[70]

Prussian blue; HPC - hydroxypropyl cellulose; PVB – poly(vinyl butyrate); PAN – poly(acrylonitrile); PMMA – poly(methyl methacrylate); PANI – polyaniline; DBSA – dodecylbenzenesulfonic acid; ITO – indium tin oxide; PBV - poly(butyl viologen); HFP - * - at 650 nm.

(between 30 and 40% in the 550 – 800 nm range) in its transparent state. Nevertheless, a change from transparent to blue color was clearly visible and registered by picture (insets in Fig. 7).

Zhang *et al* [58] have assembled, through glass laminating method and high-pressure autoclave with high temperature to final assembly, 5 cm × 5 cm electrochromic device with glass|ITO|WO$_3$|PVB electrolyte|Ni$_{1-x}$O|ITO|glass configuration. The optical modulation and coloration efficiency of this device were of 65.8% and 175.34 cm^2 C^{-1}, respectively and its performance was almost constant during 300 color cycling tests.

Finally, several ECDs with natural polymer-based electrolytes have been proposed and among them there are those with DNA-based ionically conducting membranes [23]. UV–vis spectra of such ECD, in the 200–1100 nm range, for bleached and colored states are shown in Fig. 8. The results reveal the best transmittance change of 15% at the wavelength of 550 nm, which

FIGURE 9
Jim Grote giving invited talk at the dedicated him4th International Workshop on Nano and Bio-Photonics (IWNBP2017) held in Vogué, France, September 2017.

continue the same up to 1100 nm. This result is comparable to the ECD WO_3|starch-glycerol|CeO_2-TiO_2 that had the best transmittance change of 16% between colored and bleached states and starch-lithium salt-based electrolyte [59] or ECD WO_3|gelatin-glycerol|CeO_2-TiO_2, which transmittance between colored and bleached states varied between 15 and 20% at 550 nm [60]. ECDs with other polymeric electrolytes and listed in Heusing and Aegerter [61] paper have similar ΔTs.

A summary of selected ECDs and their reduction and oxidation potentials are gathered in Table 2.

FIGURE 10
From left: Jim Grote, Agnieszka Pawlicka, Isabelle Ledoux-Rak and François Kajzar visiting the Ardèche canyon on excursion organized by the IWNB2017 workshop.

4. CONCLUSIONS

Optical properties of thin solid films and electrochromic devices are important for display and smart windows applications because they can promote savings of energy spent with air conditioning and lighting. ECDs are composed of thin films where two electrodes usually are ITO coated glasses, an electrochromic layer which can be WO_3, Nb_2O_5, a Prussian blue thin film, a counter electrode which can be CeO_2-TiO_2 thin film, and a polymer gel electrolyte. Thin films and ECDs, beside the electrochemical characterization, were tested for their optical properties. It was found that the transmittance of thin films depends strongly on their composition. Those of ECDs depends of both the thin films and the electrolytes. For example, a 40.2% transmission change between the colored and discolored states was observed for the ECD with gelatin-$LiClO_4$ and 35.2% for agar-$Eu(CF_3SO_3)$ electrolytes. In summary, the results show that thin films and electrolyte are important part of ECDs and their composition influence the device optical performances. Therefore, they need to be more deeply investigated.

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