Chapter

Perspective Chapter: Electrochromic Efficiency in $Ti_xMe_{(1-x)}O_y$ Type Mixed Metal-Oxide Alloys

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Abstract

Energy-effective smart windows, mirrors, display devices, and automobile sunroofs have been considered as applications of electrochromic materials. This chapter focuses on the electrochromic behavior of Ti-based mixed metal oxides. Transition metal oxides such as Titanium oxide (TiO_2) have been used as promising electrochromic material for this purpose since a smart window contains solid electrolyte and electrochromic material layers (commonly metal oxide layers) sandwiched between transparent conductive layers. However, relatively few publications studied the possible advantages (higher colorization efficiency) of the mixtures of different metal oxides as electrochromic material. This chapter aims to assess the results of investigations of Ti-based multicomponent materials (TiO_2-WO_3, TiO_2-V_2O_5, TiO_2–MoO_3, TiO_2–SnO_2) showing enhanced electrochromic properties compared to the pure TiO_2.

Keywords: mixed metal oxides, reactive sputtering, electrochromic materials, coloration efficiency, TiO_2

1. Introduction

Air conditioning, heating, and ventilation in buildings account for 30–40% of the world's energy consumption [1]. Improving the thermal and optical properties of windows can reduce a building's energy deficit by up to 40% [2]. Therefore, it is important to develop technologies that dynamically control the transparency of windows to reduce energy consumption in buildings. Electrochromic windows are among the favorable solutions to this problem, as they change their light-transmitting properties when exposed to DC bias [3–5]. Dynamic control of sunlight transmission provides an opportunity to reduce energy and lighting costs by 20–50% for commercial buildings [1, 6, 7]. The active components of such electrochromic window technologies are metal oxide layers or organic films [3, 8–11] that display electrochromism, a phenomenon where a material changes its optical properties upon charge injection or

extraction. There are many types of such as Titanium Dioxide (TiO_2), Chromium Oxide (CrO), Niobium Pentoxide (Nb_2O_5), Tin Oxide (SnO_2), Nickel Oxide (NiO), Iridium Oxide (IrO_2), Tungsten Trioxide (WO_3), Molybdenum Trioxide (MoO_3), and Vanadium Oxide (V_2O_5) [12–19].

The color change caused by applied direct electric current (DC) is the definition of electrochromic phenomena. Transition metal (Tungsten and Molybdenum) oxide films are the most widely investigated materials for this purpose. The solid-state electrochromic device consists of the electrochromic, charge storage, and electrolyte layers sandwiched between transparent conducting electrodes (TCO).

Electrochromic properties, mainly coloration efficiency, kinetics of the coloration-bleaching process, and cyclic durability of metal oxides strongly depend on its compositional morphological, structural, and characteristics. It is important to study the effect of deposition techniques and growth parameters. Important parameter for EC films is the coloration efficiency (CE) which refers to the optical density change (ΔOD) at a certain wavelength induced when a unit area is injected with charge (Q_d). The CE is calculated using the following equation, and ΔOD is equal with the change of transmittance according to the Beer–Lambert law:

$$\mathrm{CE}(\lambda) = \Delta\mathrm{OD}/\mathrm{Qd} = \log(T_b/T_c/Q_d \quad (1)$$

where T_b is the transmittance of the bleached state, T_c is the transmittance of the colored state, and Q_d is the density of the charge inserted into or extracted from the electrochromic material (cm^2/C, square centimeter per Coulomb). CE has been calculated by specific absorption wavelength (λ) and the transmittances (T_b and T_c) have been dependent on this wavelength. The coloring process evaluated the power requirements by CE and the CE was clear about the electronic efficiency of the ECDs. The result of the CE was presented by a plot of optical change vs. charge density which fitted the linear part of the graph, or alternatively, the relative transmission vs. input charge curves were plotted and CE values can be determined from the fitted exponential curves, see **Figure 1** [20].

Due to possible electron transitions between two sets of electrons, the EC effect can be more pronounced in mixed oxides. Despite this, only a small number of studies can be read about the possible optimization of the EC parameters in mixed oxide-type films. The purpose of this review is to summarize the results of such investigations on Ti-based mixed oxide layers.

2. "Pure" metal oxides

2.1 Tungsten oxide (WO_3)

The most widely studied EC oxide is Tungsten oxide (WO_3), and films of this material have been prepared by several different methods. "Traditional" thin film-making methods include for instance: chemical methods (spin-coating, sol–gel deposition, chemical bath deposition, Langmuir–Blodgett technique, etc.), chemical and physical vapor deposition, electrochemical methods (anodization, plating), see Ref. [10] and references therein. Examples of physical vapor deposition: sputtering [20–22], thermal evaporation [23–27], and pulsed laser deposition [28, 29].

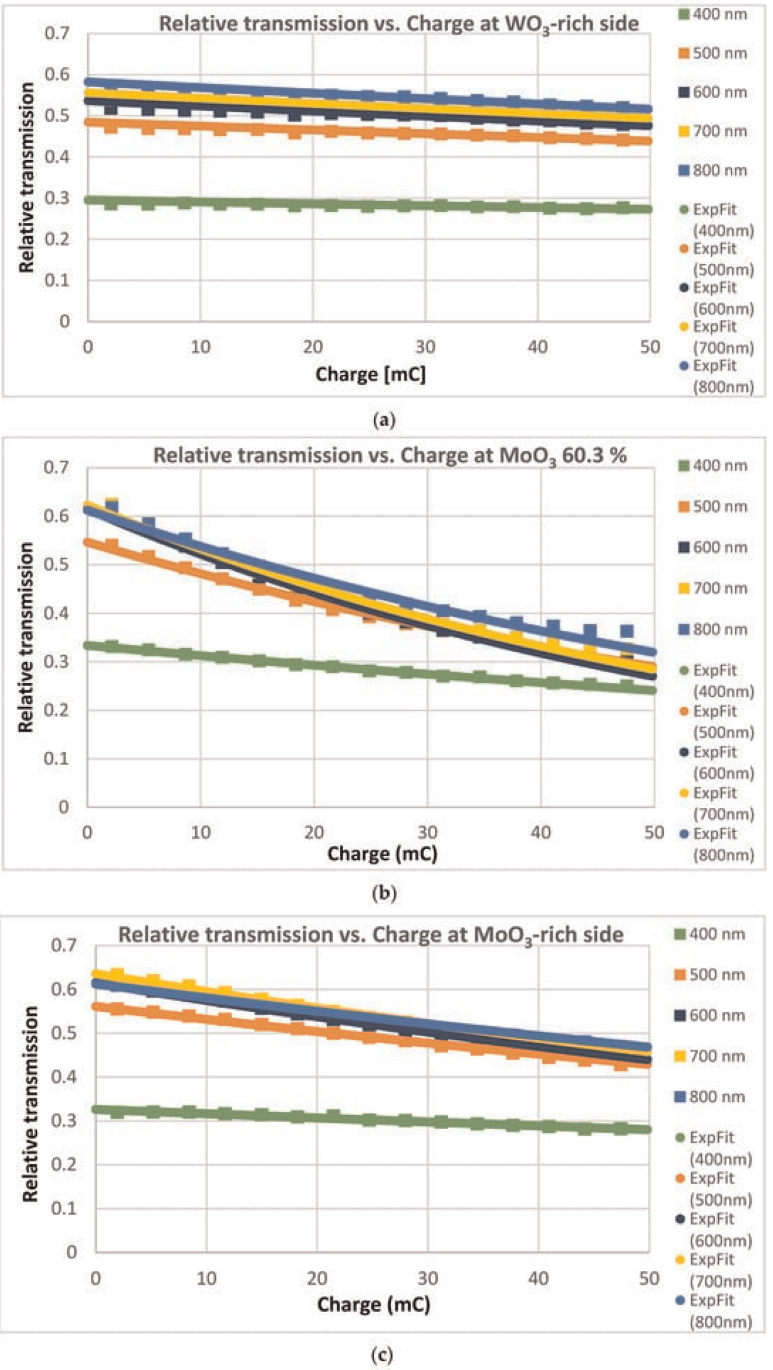

Figure 1.
Relative transmission vs. input charge curves at five wavelengths for a pure WO3 sample (a), for a WO3-MO3 (Mo-60.3%) mixed sample (b), and for a pure MoO3 sample (c). CE values were determined from the fitted exponential curves (ExpFit). From Ref. [20].

Specific examples of chemical methods are the following: chemical vapor deposition [30–32] and related spray pyrolysis [33–37], and many investigations based on chemical methods to make W oxide films [38–40]. Other researchers used electrodeposition [40, 41], anodization [42–45], and electrophoretic deposition [46]. The CE was found to be more than 60 cm^2/C in the red region in most cases [10, 47].

2.2 Molybdenum oxide (MoO_3)

Electrochromic Mo oxide (MoO_3) shows similar behavior to W oxide, and widespread studies used films prepared by evaporation [48, 49], chemical vapor deposition [50], wet chemical techniques [51, 52], and electrodeposition [53]. CE was measured 34 cm^2/C at 630 nm [49].

2.3 Titanium oxide (TiO_2)

EC properties of Ti oxide (TiO_2) were also extensively studied prepared by the following methods: sputtering [54], chemical vapor deposition [55], and spray pyrolysis [56, 57], various wet chemical techniques [58–60], and anodization [61–63]. The CE was $\sim$25 cm^2/C for reactive DC magnetron sputtering deposited TiO_2 films. TiO_2 films have been also deposited by different chemical techniques and those films were used to determine the CE values, and verified that such films can show the same values of CE [54].

Different deposition methods as radio frequency (RF) reactive sputtering technique [64] and thermionic vacuum arc method have been reported for TiO_2 [65].

3. Mixed oxides

3.1 TiO_2-WO_3

TiO_2 and WO_3 core/shell nanorod arrays were prepared by the combination of hydrothermal and electrodeposition methods, in the work of Cai et al. [66]. The deposition solution was prepared by dissolving Na_2WO_4 salt in deionized water (concentration: 12.5 mM) and adding hydrogen peroxide to the solution maintaining a concentration ratio of 3 with sodium tungstate. Fluorine-doped tin oxide (FTO) glass coated with TiO_2 nanorod array was used as the deposition electrode. Remarkable enhancement of the electrochromic properties was found in the nano-array films. Significant optical modulation (57.2% at 750 nm, 70.3% at 1800 nm, and 38.4% at 10 μm), excellent cycling performance (65.1% after 10,000 cycles) and high CE (67.5 cm^2 C − 1 at 750 nm), fast switching speed (2.4 s and 1.6 s), have been achieved for the core/shell nanorod arrays. Since a larger surface area for charge-transfer reactions was available for ion diffusion, the improved electrochromic properties were mainly attributed to the core/shell structure and the porous space among the nanorod arrays. The presented data made the TiO_2 and WO_3 core/shell nanorod arrays a promising material for practical electrochromic purposes.

Patil et al. [67] have used spray pyrolysis technique at 525°C to deposit TiO_2-doped WO_3 thin films onto FTO coated conducting glass substrates. Tungsten trioxide (WO_3) and titanyl acetylacetonate ($C_{10}H_{14}O_5Ti$) were used as base materials for the deposition of TiO_2-doped WO_3 thin films. The WO_3 powder was dissolved in liquid ammonia at 80°C to obtain an ammonium tungstat solution. The titanyl acetyl acetonate powder ($C_{10}H_{14}O_5Ti$) was mixed with methanol separately at room

temperature. The two solutions were stirred in different volume % to form a homogeneous 100 ml precursor solution, at pH = 9. Volume percentage of the dopant varied between 13% and 38% v/v of TiO_2. (For greater than 38% doping percentage of TiO_2 in WO_3 homogeneous solution could not be formed and precipitation dominates.) The thin film samples were uniform, transparent, and strongly adhesive to the substrates. With the help of chronoamperometry (CA), cyclic voltammetry (CV) and chronocoulometry (CC) techniques, electrochromical properties of TiO_2-doped WO_3 thin films have been studied. They concluded that within the studied range, TiO_2 doping enhances the electrochromic performance of WO_3 and samples exhibited increasingly high reversibility with TiO_2 doping concentrations.

Dhandayuthapani et al. [68] reported a low-temperature making of WO_3/TiO_2 films via a combined chemical bath deposition and nebulized spray deposition method. The WO_3 layer influenced the compositional, morphological, structural, and electrochemical properties of TiO_2 films. The layered WO_3 nanoplates on the TiO_2 layer significantly improved the current density of the TiO_2 films. The electrochemical investigation of the annealed WO_3/TiO_2 films displayed a CE of 128.3 cm^2C^{-1}, optical modulation (ΔT) of 78%, and reversibility of 77.2%. Excellent durability for 1000 cycles was exhibited with a fast response of 6 s for coloration and bleaching. This enhancement could be explained by the interconnected nanoplate bundles which accommodate more charges and facilitate faster charge transport. The complementarity of the WO_3–TiO_2 layers leads to efficient electrochromic character [68].

In a recent work, Ashok Reddy et al. [69] investigated the preparation of Titanium dioxide (TiO_2) nanorods/Tungsten oxide (WO_3) hybrid thin films and the effect of nanostructures on the electrochromic characteristic of the films. They deposited WO_3 thin films at the substrate temperature of 400°C. The partial pressures of oxygen were varied. Tungsten nanorods were prepared on FTO coated glass sheets by hydrothermal process. Optimized WO_3 layers were deposited on the TiO_2 nanorod film by sputter deposition. They performed electrochemical, optical, and material analysis on the films using CV, UV–visible spectrometry, x-ray diffraction (XRD), Raman, and x-ray photoelectron spectroscopy (XPS). The enhanced CE of the optimized WO_3 films was attributed to the big active surface area which favored H^+ ions intercalation in the layers. The TiO_2 nanorods/WO_3 hybrid films showed a good electrochemical property in terms of the diffusion coefficient of 1.8×10^{-7} cm^2/s better than those of pure WO_3 (0.6×10^{-7} cm^2/s) and TiO_2 nanorods (0.4×10^{-7} cm^2/s).

Nah et al. [70] demonstrated that homogeneous and well-ordered arrays of $TiO_2 - WO_3$ nanotubes can be layered by anodization of Ti alloys in an ethylene glycol/fluoride-based electrolyte under special electrochemical conditions. They grew nanotube films on different substrates [Ti, Ti-0.2 at% W (Ti-0.2 W), and Ti-9 at% W (Ti-9 W)] by anodization at 120 V in a solution of ethylene glycol with 0.2 Mol HF. The growth time was controlled to achieve a comparable thickness of the layers. Ordered oxide nanotube layers were obtained with a thickness of 1.1–1.2 μm and 85–95 nm tube diameter. These aligned mixed oxide nanotube structures are very good for enhanced electrochromic reactions. It was shown that only small amounts of WO_3 (such as 0.2 at %) can drastically improve the electrochromic properties (cycling stability, contrast, onset potential) of nanotube layer-based devices, see **Figure 2**.

3.2 $Ti_{0.50}V_{0.50}O_x$

Burdis et al. [71] used RF sputtering from metallic targets for deposited thin films of $V_{0.50}Ti_{0.50}O_x$. They used this film as a potential counter electrode in investigating

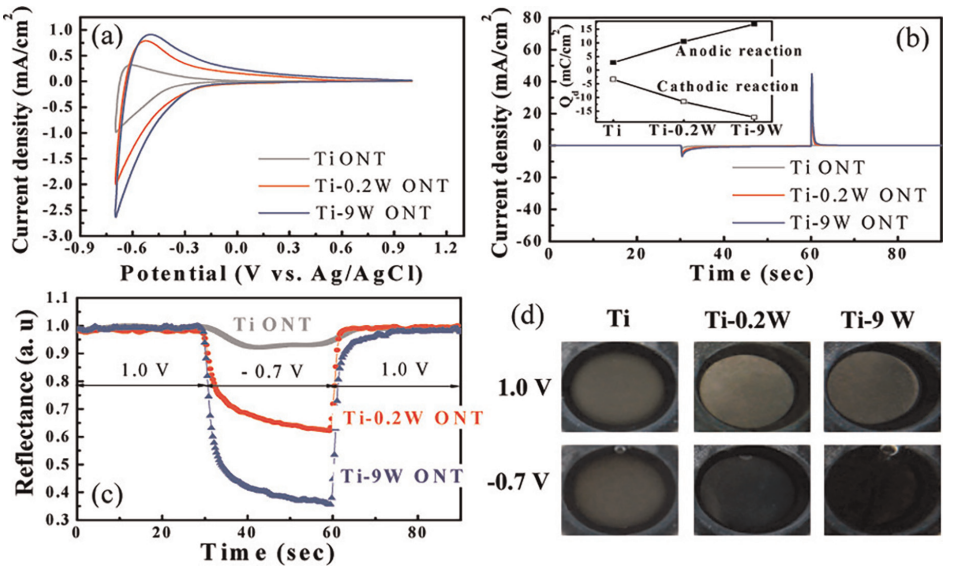

Figure 2.
(a) Cyclic voltammograms of the oxide nanotube (ONT) layers on Ti, Ti-0.2 W, and Ti-9 W performed between −0.7 and 1.0 V with a scan rate of 50 mV in 0.1 Mol $HClO_4$ electrolyte; (b) current density − time curves acquired by pulse potential measurement applied between −0.7 and 1.0 V with 30 s duration; (c) in situ reflectance curves of Ti, Ti-0.2 W, and Ti-9 W ONTs obtained during potential pulsing applied between 1.0 and − 0.7 V; and (d) optical images of the electrochromic effect of the different nanotube surfaces during polarization cycling between 1 and − 0.7 V. The inset of (b) shows integrated charge density (Q_d) for the samples. Reprinted (adapted) with permission from Ref. [70]. Copyright 2008 American Chemical Society.

electrochromic device behavior. They concluded that the film can reversibly store relatively large amounts of charge and it is slightly yellow-looking in transmission, while showing acceptably low electrochromic CE. The electrochemistry of $V_{0.50}Ti_{0.50}O_x$ is found to be simple, in fact rather the same as that of WO_3, for those reasons, they found that this material was considered almost exemplary to use in such a variable transmission device. Charge capacities were measured to 60 mC/cm^2 for 300 nm film thickness. The authors planned to characterize further the electrochromic coloration of these films up to high levels of charge insertion and to determine the effect of repeated charging and discharging on the lifetime of such films.

Marcel et al. [72] used the lamination of two tungsten and vanadium-titanium oxide thin films to reduce the blue absorption of vanadium oxide prepared by roll-to-roll radiofrequency sputtering technique. To produce flexible devices adaptable for eyewear applications, an ITO-coated mylar substrate was used. The working electrode has been set as Tungsten oxide, while the counter-electrodes that were examined vanadium-titanium oxide mixtures. The electrolyte used to assemble both electrodes was a polymer gel lithium ionic conductor constituted of a lithium bis(trifluoro-methanesulfonyl)imide (LiTFSI, LiC2F6NO4S2) lithium salt dissolved in propylene carbonate (PC) and incorporated within a photopolymerized acrylate matrix. They investigated the electrochromic properties of the counter electrode at four different atomic ratios of titanium in the (0–100%) range increased at 25% steps. A blue shift effect in the transmittance spectra of as-deposited films was first observed as the titanium amount was increased. In situ, optical behavior was investigated while the potential range for cycling was (1.5-4 V), and the sample with equal proportion of vanadium and titanium displayed a noteworthy neutrality of coloration. Complete

devices were prepared with different Ti/V ratios of 0, 1:3, 1:1, and 3:1 in the counter electrode. The film thickness of tungsten oxide has been fixed to 300 nm, and the thickness of vanadium-titanium oxide films has been set based on their respective electrochemical capacity. The obtained electrochromic performances together with their cycling lifetimes and response times were evaluated to find the optimal vanadium-titanium composition.

3.3 TiO_2: MoO_3

Shrestha et al. [73] fabricated self-organized TiO_2–MoO_3 composite oxide nanotubes with tunable characteristics by anodization of a Ti-Mo alloy and these nanotube layers exhibited a considerably enhanced electrochromic color contrast compared with simple TiO_2 nanotubes. They prepared self-organized binary oxide nanotube layers: a single phase Ti-Mo (7 wt%) alloy sheet was polished to a mirror finish, and it was used as a working electrode in a classical anodization assembly. This consists of a traditional 3-electrode system with an Ag/AgCl (3 Mol KCl) reference electrode and a Pt mesh as a counter electrode. The color contrast in terms of reflectivity for the amorphous Ti-Mo-nanotubes is 2.5-fold higher than that of the amorphous TiO2-nanotubes for the same charge density.

Ezhilmaran and Bhat [74] prepared a bilayer electrode with nanoparticulate TiO2 in the bottom layer and randomly oriented MoO3 nanostructures as the top layer to obtain electrochromic device. The TiO_2, MoO_3, and TiO_2/MoO_3 films were prepared using simple solution methods by spin-coating the precursor solutions on conducting FTO substrates. After the spin-coating, the samples were dried and annealed. The heterojunction film was prepared by spin-coating MoO_3 precursor solution on the TiO_2 film. The electrode showed a superior behavior in terms of higher current density and charge storage capacity as well as rate capability as compared to the similar reports in the literature. A color contrast of 38%, switching response of ~2 s and high CE of 72.5 cm2/C were obtained.

To enhance the CE, Ismaeel et al. [75] have performed electrochromic measurements to the full composition range of reactive magnetron sputtered mixed Titanium oxide and Molybdenum oxide (TiO_2-MoO_3). Spectroscopic ellipsometry (SE) has been used to determine and map the composition and optical parameters. To check the results of SE, scanning electron microscopy (SEM) with energy-dispersive x-ray spectroscopy (EDS) has been used. Ti and Mo targets were put separately from each other (see **Figure 3a**), and the indium-tin-oxide (iTO) covered glass sheets and Si-probes on a glass holder (30 cm × 30 cm) were moved under the two separated targets (Ti and Mo) in a reactive argon-oxygen (Ar-O_2) gas mixture, as it can be seen in **Figure 3**. After one sputtering process, all the compositions (from o to 100) % have been achieved by using this combinatorial process, in the same sputtering chamber. Transmission electrochemical cell has been used to determine the CE (the change of light transmission for the unit electric charge) for the mixed metal oxides (TiO_2-MoO_3) that are deposited, see **Figures 3** and **4**. The two maximums in CE (see **Figure 4**) can be explained by the fact that the Ti-rich side was at a much more higher temperature during the deposition process, so the Ti-rich oxide is polycrystalline while the Mo-rich side remains amorphous or nanocrystalline [75]. CE has been considered an important parameter in this study. The maximum value of the CE is 22.2 $cm^2\ C^{-1}$ (at λ = 600 nm) at ~60–40% Ti-Mo ratio on the Ti-rich polycrystalline material, while CE is 19.8 $cm^2\ C^{-1}$ (at λ = 600 nm) at ~20% - 80% Ti-Mo ratio on the Mo-rich amorphous (or nanocrystalline) material.

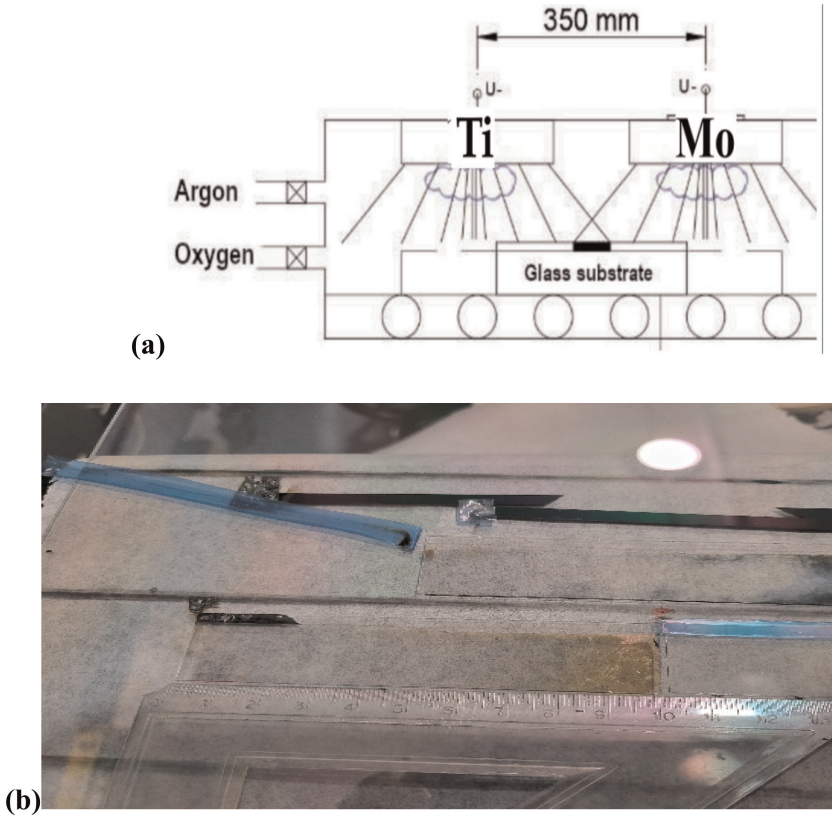

Figure 3.
(a) Schematic of the two targets' arrangements in a closer position (35 cm from each other) and the chamber for the DC magnetron sputtering device; (b) TiO_2-MoO_3 layers on ITO-covered glasses after-electrochromic-experiments. From Ref. [75].

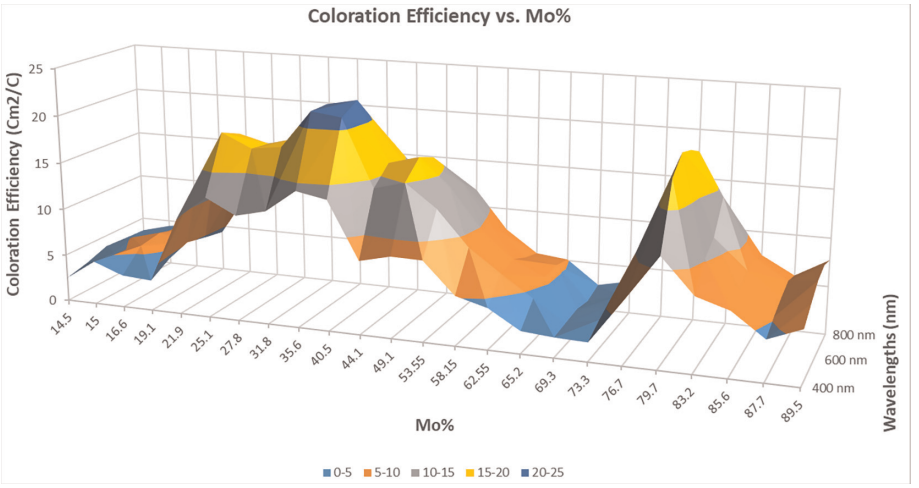

Figure 4.
CE vs. Mo% for wavelengths from (400–800) nm of TiO_2-MoO_3. From Ref. [75].

These results are concordant with the results of Habashyani et al. [76] which are published in a recent paper. Using radio frequency magnetron sputtering (RFMS), the authors have grown undoped and Ti-doped vertical nanowall structured MoS_2 thin films and thermally oxidized these films to α-MoO_3 using the following deposition parameters: 45 min oxidation at 380°C under 500 sccm of O_2 gas ambient. Sample names' labeling was the following: undoped MoO_3 - > MBO, Ti:MoO_3 with 20 W RF-power - > MTO_{20}, Ti:MoO_3 with 30 W RF-power - > MTO_{30}, Ti:MoO_3 with 40 W RF-power - > MTO_{40}.

Ti has led to denser nanowall formations. Optical modulation (OM) in the visible region was enhanced with increasing Ti concentration within the coloring potential range of −0.2 to −0.45 V. This is relatively low working voltage, which makes the signals energy efficient in electrochromic materials. The highest Ti-doped MoO_3 (MTO_{40}) and undoped (MTO) samples showed 52.2% and 37.6% OM at λ = 700 nm (47.8% and 25.7%, respectively, at λ = 550 nm) under −0.45 V applied potential. On the other hand, the coloring times for MBO, MTO_{20}, MTO_{30}, and MTO_{40} were 4.7, 4.1, 6.2, and 2.9 s, respectively, while the bleaching durations were 3.1, 1.4, 1.1, and 1.2 s for samples. MBO sample is the undoped while the Mo/Ti ratio in sample MTO_{20} is 79.5, in MTO_{30} is 17.0, in MTO_{40} is 6.7 (highest Ti-doped).

Although the nanowall structure of the highest Ti-doped thin film (MTO_{40}) was destroyed, this thin film showed the best coloring response time and OM at the visible wavelengths. MTO_{20} and MTO_{30} samples, on the other hand, have performed better at longer wavelengths with higher OM and CE. As a result, Ti-doping has a beneficial effect on the electrochromic behavior such as OM, CE, and response times during coloring and bleaching of the MoO_3. These Ti-doped MoO_3 electrochemical characteristics demonstrate the suitability of these materials for device applications.

3.4 TiO_2: SnO_2

Ismaeel et al. [77] determined the optimal composition of reactive magnetron-sputtered combinatorial mixed layers of titanium oxide and tin oxide (TiO_2-SnO_2) for electrochromic purposes. SE was used to obtain the thickness and composition maps of the sample. They also compared the performance of different optical models, such as 2-Tauc–Lorentz multiple oscillator model (2 T–L) or the Bruggeman effective medium approximation (BEMA) to map the sample parameters. To check the results of SE, SEM, with EDS was used. It was shown that in the case of molecular-level mixed layers, 2 T–L is better than an EMA-based optical model. By using SE, the

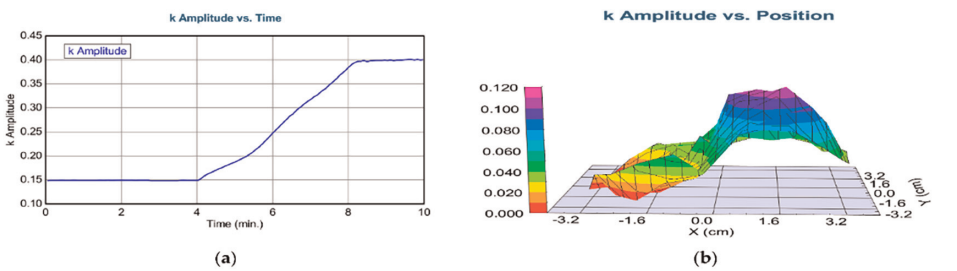

Figure 5.
(a) The imaginary part of the refractive index (k Amplitude) as a function of time for highly conductive Si in the liquid cell during coloration (time-scan, simple 2-layer Cauchy model). From 0 to 4 min, there is low absorption, however, from 4 to 8 min, there is a growing absorption; and (b) Map of the k parameter after coloration (simple 1-layer Cauchy model). From Ref. [77].

X(cm)	k Amplitude (Error ± 0.005)
−3.5	0.0002
−3	0.0025
−2.5	0.044
−2	0.004
−1.5	0.015
−1	0.025
−0.5	0.056
0	0.041
0.5	0.092
1	0.105
1.5	0.075

Table 1.
k Amplitude vs. Position at the center line after the colorization in the dry state. From Ref. [77].

electrochromic efficiencies of mixed metal oxides (TiO_2-SnO_2) deposited by reactive sputtering were also mapped, too, see **Figure 5**.

The coloration process was followed in situ by SE at the center point of the mixed metal oxide – highly conductive Si sample. They could map the colorized layer using a simple one-layer Cauchy dispersion optical model after the coloration ±process. For the Cauchy model, the k Amplitude (extinction) parameter has been considered a good indicator of the CE, as it is shown in **Figure 5b**. The maximum k value exhibits that the optimal composition is at (30%) TiO_2– (70%) SnO_2. See **Table 1**.

4. Conclusions

Many binary oxides were studied as potentially promising EC materials. However, most of the studies have investigated only a few compositions. Some of them studied only the role of adding a single percentage of a secondary material, emphasis of research was put on studying the effects of doping. Only a few examples can be found where a comprehensive investigation spanning the full compositional range between the component oxides was made. Note, that in most cases the mixed metal oxides showed better EC properties than the pure oxides. For example, Ismaeel et al. [75] found a fourfold enhancement of CE in Titanium-Molybdenum oxide mixed films. Therefore, in order to enhance the EC performance of materials further focus should be put on studying properties of mixed oxide materials in the full (0–100%) composition range. Combinatorial sputtering techniques offer a feasible way to prepare samples for this purpose.

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