



PEDOT:PSS-V₂O₅ Hybrid for Color Adjustment in Electrochromic Systems

Romain Futsch, Issam Mjejri, Harena Rakotozafy and Aline Rougier*

CNRS, Univ. Bx, Bx INP, ICMCB, UMR 5026, Pessac, France

Electrochromism is known as a modulation of the optical properties under an applied voltage. Used in various applications, aside to the commercialized smart windows based on transmissive electrochromic devices (ECDs), the opaque systems have received significant interest for displays purposes. Herein, in a novel approach to adjust color, electrochromic oxides with high EC performance were chosen as additives to commercialized conductive and electrochromic polymer ink. More precisely opaque films were deposited (using Bar Coater) from mixtures of V₂O₅, synthesized by polyol process, with poly(3,4-ethylenedioxythiophene, polystyrene sulfonate) PEDOT:PSS commercial ink in different weight percentages (wt%) ranging from 0 to 100 (V₂O₅ wt%). Films thicknesses varied from hundred of nms to few μms. As-deposited films colors range from blue for PEDOT:PSS to orange for V₂O₅. PEDOT:PSS-V₂O₅ films exhibit significant electrochromic properties associated with a good electrochemical stability. In the series, the hybrid film with 90 wt%–10 wt% PEDOT:PSS-V₂O₅ shows a reversible behavior with significant reflectance modulation ($\Delta R \approx 20.5\%$ at 550 nm) in lithium based electrolyte and a good contrast ($\Delta E^* > 30$). The maximum contrast was reached for 3.7 μm thick layer. Our results indicate that the hybrid film, combining the benefit of mixing inorganic and organic materials, are promising materials for enhancing electrochromic devices color and hybrid electrochromic materials processability on large scale.

Keywords: electrochromism, PEDOT:PSS, V₂O₅, color tuning, bar coating, hybrid materials

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*Correspondence:

Aline Rougier
aline.rougier@icmcb.cnrs.fr

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INTRODUCTION

Electrochromic materials that undergo reversible color change under an applied voltage (Lang et al., 2019) have received great interest due to their potential applications, such as smart windows (Runnerstrom et al., 2014; Nunes et al., 2019), information storage and displays (Mjejri et al., 2018b; Qingyi et al., 2019). Electrochromism occurs in a number of organic (Hu et al., 2018; Han et al., 2019), inorganic (Danine et al., 2014; Mjejri et al., 2016), and hybrid materials (Rodrigues et al., 2009) both in the visible and IR regions. Smart windows mature technology is typically based on combination of WO₃ and IrO_x or NiO (Granqvist et al., 2019). Optimizing both materials and devices architectures is interesting to develop the technology and target more application (Jung et al., 2004; Varghese et al., 2018; Danine et al., 2019). In particular, focusing on display applications, our interest in reflective devices increases with the need of enhancing the range of colors developed in ECDs. For inorganic materials, multi-electrochromism (e.g., materials

displaying different colors depending on the voltage applied) is observed when vanadium oxide (V₂O₅) is deposited as a micrometric thick film. This material switch colors from blue, to green and orange depending on the voltage applied. Vanadium oxides offer several advantages: (i) they show both anodic and cathodic colorations (ii) their abundance and layered structure facilitate the exchange of a large amount of Li cations, and (iii) the existence of several oxidation states leading to the possibility of obtaining multicolor displays (Chu et al., 2016; Mjejri et al., 2019). The modulation of color may also be achieved by introducing new concepts of devices changing color independently on each side. In 2017, our group (Mjejri et al., 2017) reported for the first time a double-sided electrochromic device based on Metal-Organic Frameworks (MOFs) switching from light to dark blue on one side and from yellow to brownish on the other side. Integrating organic and inorganic materials into a hybrid material provides an opportunity to combine their advantages and explore new design. While transition metal oxides (TMOs) present generally a good redox activity they suffer, among other things from a too low electrical conductivity and a poor switching frequency. On the contrary, polymer-based electrochromic films are characterized by rapid kinetics, multi-color electrochromism, easy-processability using conventional printing technique (doctor blade, screen-printing, inkjet...), sufficient electrically conductivity while they typically suffer from shorter lifetime range and are highly sensitive to the working environment (Byker, 2001). To counter balance the pros and cons of both polymer and inorganic materials, hybrid systems are investigated. Recently, several groups have synthesized hybrid films by combining oxide and conductive polymer showing a better charge injection for a higher contrast for electrochromic displays (Lee et al., 2011) and better efficiency for solar cells (Lee et al., 2014). Following this path, we recently reported that the addition of low content of Fe₂O₃ in a PEDOT:PSS ink allowed to achieve a color modulation from bluish to reddish, while in first approximation Fe₂O₃ alone appears to be electrochromically inactive (Levasseur et al., 2019). Pursuing this hybrid approach herein, the electrochromic properties of bar coated opaque films, from mixture of electrochromically active V₂O₅ to commercial PEDOT:PSS ink, are investigated. V₂O₅ was preferentially used as it can be bring a larger color range to the PEDOT:PSS film. Indeed, other cathodic oxides such a Nb₂O₅ (Mjejri et al., 2018b) or WO₃ (Danine et al., 2014) will only intensify the blue color of the PEDOT:PSS reduced state.

The preparation of oxide inks remains a big challenge for an easy film processability. A poor control of thickness and morphology is generally achieved with traditional coating techniques. Mixing a commercial PEDOT:PSS ink with oxides allows to promote higher quality film. Indeed, with the mixture of PEDOT:PSS-V₂O₅ presented in this paper, industrial technique such as screen-printing can be used for the layer deposition at room temperature and baked at the temperature applied for PEDOT:PSS (e.g., 120°C for 5 min). Another advantage consists in reducing the amount of V₂O₅ used to obtain a film as the oxide will only be added in small quantity in the PEDOT:PSS ink which can be beneficial for cost reason as this oxide requires expensive vanadium precursors. Vanadium oxide is generally deposited

using vacuum techniques for good film quality, which are not suitable for large-scale display production. Other deposition techniques have been developed lately such as inkjet printing (Costa et al., 2012) or atomic layer deposition (Blanquart et al., 2013) and can be interesting for further study on V₂O₅ electrochromic properties. With our approach, a conductive layer is obtained thanks to the presence of PEDOT:PSS conductive polymer which can possibly reduce the number of layers needed for building the electrochromic display (Tashtoush and Kasasbeh, 2013). In summary, the goal of this study was to investigate a win-win strategy based on the polymer good processability and conductivity and the large color palette brought by the oxide.

MATERIALS AND METHODS

Hybrid Inks Formulation

The hybrid electrochromic inks were formulated from the mixture of the commercial PEDOT:PSS ink Agfa Orgacon EL-P5015 and V₂O₅ powders synthesized by polyol process (Mjejri et al., 2018a). The commercial PEDOT:PSS ink characterized by high-viscosity commercial paste (>100,000 mPa·s) developed for screen printing was first homogenized with a three-roll mill and then diluted with ethanol to lower the viscosity. PEDOT:PSS was chosen thanks to its printing properties, its conductivity and it shows a very different reversible change of color from oxidized to reduced states making it suitable for electrochromism display fabrication (Andersson, 2006). The V₂O₅ weight percentages were calculated from the PEDOT:PSS paste mass. Seven premixes were prepared: weight ratio of (PEDOT:PSS paste)/(V₂O₅) = (100-x)/x, with x = 0.01%, 0.1%, 1%, 5%, 8%, 10%, 15%. These preparations were then diluted with ethanol with a mixing ratio of 40 wt% of PEDOT:PSS-V₂O₅ paste and 60 wt% of ethanol. The various hybrid inks with different weight ratio between PEDOT:PSS, V₂O₅ and ethanol were stirred for 15 min at room temperature, then dispersed using an ultrasonic bath for 30 min at room temperature and stirred again for 24 h.

To simplify the readability of the study, the ink formulation will be mentioned as the weight percentage of the vanadium oxide in the PEDOT:PSS as followed: 100 wt% V₂O₅ as 100%, 85 wt%–15 wt% PEDOT:PSS-V₂O₅ as 15%, 90 wt%–10 wt% PEDOT:PSS-V₂O₅ as 10%, 95 wt%–5 wt% PEDOT:PSS-V₂O₅ as 5%, 99 wt%–1 wt% PEDOT:PSS-V₂O₅ as 1% and PEDOT:PSS as 0%.

On the figures, 100% have been drawn in ochre, 15% in green, 10% in orange, 5% in purple, 1% in red, and 0% in blue. All percentages correspond to the wt%.

Hybrid Film Deposition and Characterization

The films were deposited with a bar coater (K control from RK Print Coat Instruments, Erichsen) with jointed whorl bars, noted from 1 to 8 with the following whorl diameters (mm): 0.08, 0.15, 0.31, 0.51, 0.64, 0.76, 1, 1.27. The coatings were done on ITO-coated (In₂O₃:Sn) glass substrates (commercialized by SOLEMS with a resistance of 30 Ω/sq) and then dried at 120°C/5 min on a hot plate. Depositions were made on

5*2.5 cm² ITO-coated glass substrates. The thickness of the PEDOT:PSS-V₂O₅ films were measured using a Veeco Dektak 6M Stylus Profilometer (Veeco Instruments Inc., New York, NY, United States). For the identification of the crystal phases of the hybrid films, X-ray diffraction (XRD, Philips PW 1820, PANalyticalX'Pert instrument, 2 θ range from 10° to 50° and Cu K α 1 λ = 0.154056 nm) was used. The layer morphology was investigated with a JEOL JSM-840 (operating at 15 kV) scanning electron microscope (JEOL JSM-840, JEOL SAV-Europe, Croissy sur Seine, France).

Electrochromic Measurements

Electrochemical measurements of hybrid films PEDOT:PSS-V₂O₅ deposited on ITO/glass were carried out in a three electrodes cell configuration using a BioLogic SP50 potentiostat/galvanostat apparatus. The counter electrode and reference electrode consisted of a platinum foil and saturated calomel electrode, SCE ($E_{SCE} = 0.234$ V/ENH), respectively. The operating voltage was controlled between -1.0 V and +1.5 V at a scan rate of 20 mV s⁻¹, in lithium-based electrolyte, namely, lithium bis-trifluoromethanesulfonimide (LiTFSI, Solvionic, purity N 99.99%) in 1-ethyl-3 methylimidazolium bis(trifluoromethanesulfonyl)-imide (EMIM-TFSI, purity N 99.99%) with a corresponding molar ratio of 1:9 (LiTFSI:EMIM-TFSI). All the electrochemical measurements were performed at room temperature. The *ex-situ* optical reflectance of PEDOT:PSS-V₂O₅ hybrid films were measured using a Varian Cary 5000 UV-vis-NIR spectrophotometer between 300 and 800 nm. Colorimetry analysis was carried out using a Konica Minolta CM-700D spectrophotometer with SCE 10°/D65 configuration (Konica Minolta Sensing Europe B.V), allowing the direct determination of colorimetric parameters of the CIE (L*a*b*) color space.

RESULTS AND DISCUSSION

Structural and Morphological Properties of PEDOT:PSS-V₂O₅ Hybrid Films

To optimize the electrochromic performance of the hybrid PEDOT:PSS-V₂O₅ films, the weight ratio between PEDOT:PSS

and V₂O₅ was investigated. **Figure 1** shows the photographs of the various films deposited by bar coater using the same bar ($n = 3$) in association with the L*, a*, b* chromaticity parameters, defined by the CIE LAB. A significant color gradient in relationship with the decrease of the V₂O₅ weight percentages is visible.

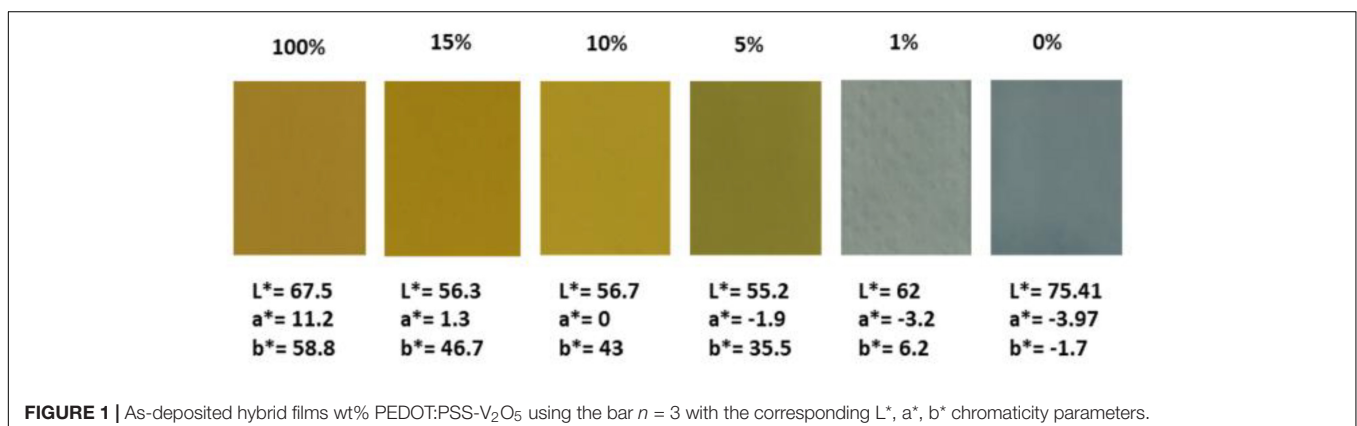
From 100 wt% V₂O₅ yellow-orange film, the hybrid mixture remains close to the appearance of pure V₂O₅ till 10 wt%. The color turns greenish for 5 wt% V₂O₅, and for the 1 wt% V₂O₅, the hybrid film adopts a light blue-gray aspect while the PEDOT:PSS films appear blue.

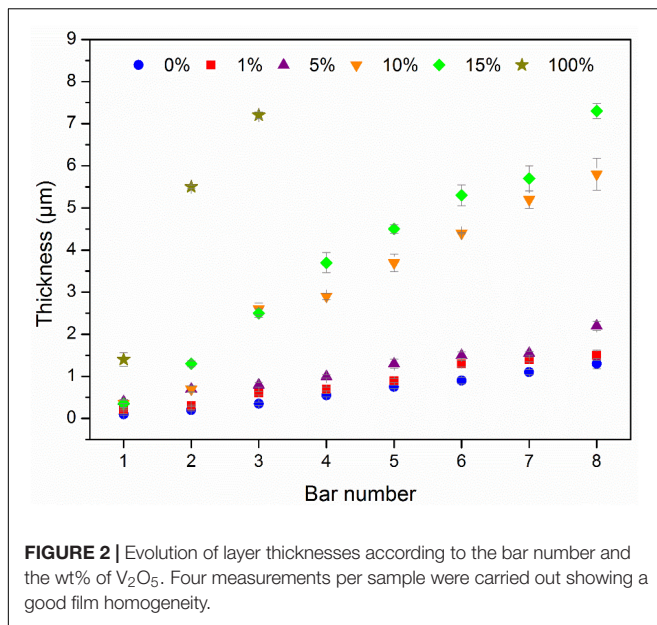
As displayed in **Figure 2**, using any bars (from $n = 1$ to 8), the V₂O₅ wt% content has a strong influence on the film thickness. Overall, the thickness of hybrid films increases with increasing V₂O₅ wt%.

If a low thickness increase is measured up to 5 wt% of V₂O₅, a first jump is observed for 10 wt% and 15 wt% while pure V₂O₅ reaches thickness of 7 μ m already for bar $n = 3$. Using the bar ($n = 3$) corresponding to **Figure 1**, the thicknesses of the films vary from 0.6 μ m for pure PEDOT:PSS and 1 wt% V₂O₅, 0.8 μ m for 5 wt% V₂O₅, 2.5 μ m for 10 wt% and 15 wt% V₂O₅ up to 7.2 μ m for pure V₂O₅. The aspect and the chromaticity parameters of the films deposited with the bar $n = 3$ are relatively similar to the bar with a higher whorl diameter as the chromaticity parameters of the as-deposited state remain quite similar even when the film thicknesses increase.

The crystallinity of the hybrid films was studied by X-ray diffraction analysis (**Figure 3**). The PEDOT:PSS layer (**Figure 3a**) shows an amorphous behavior, whereas for the hybrid film with 1 wt% of V₂O₅ a first peak of V₂O₅ can be identified with a very weak signal associated with a low content (**Figure 3b**). For the 5 wt% V₂O₅ hybrid film, the peaks intensities increase with the appearance of a second peak (**Figure 3c**). With the film containing 10 wt% V₂O₅, all the peaks can be indexed as V₂O₅ (Space Group:Pmmm) (**Figure 3d**) revealing an agreement between color and cristallinity. Indeed, the d-spacing values of all diffraction peaks match the ones of the orthorhombic crystalline phase (JCPDS# 85-0601) and of the ITO substrate (JCPDS # 44-1087).

The SEM analysis of the hybrid films (V₂O₅, PEDOT:PSS and hybrid films PEDOT:PSS-V₂O₅) (**Figure 4**) demonstrates that

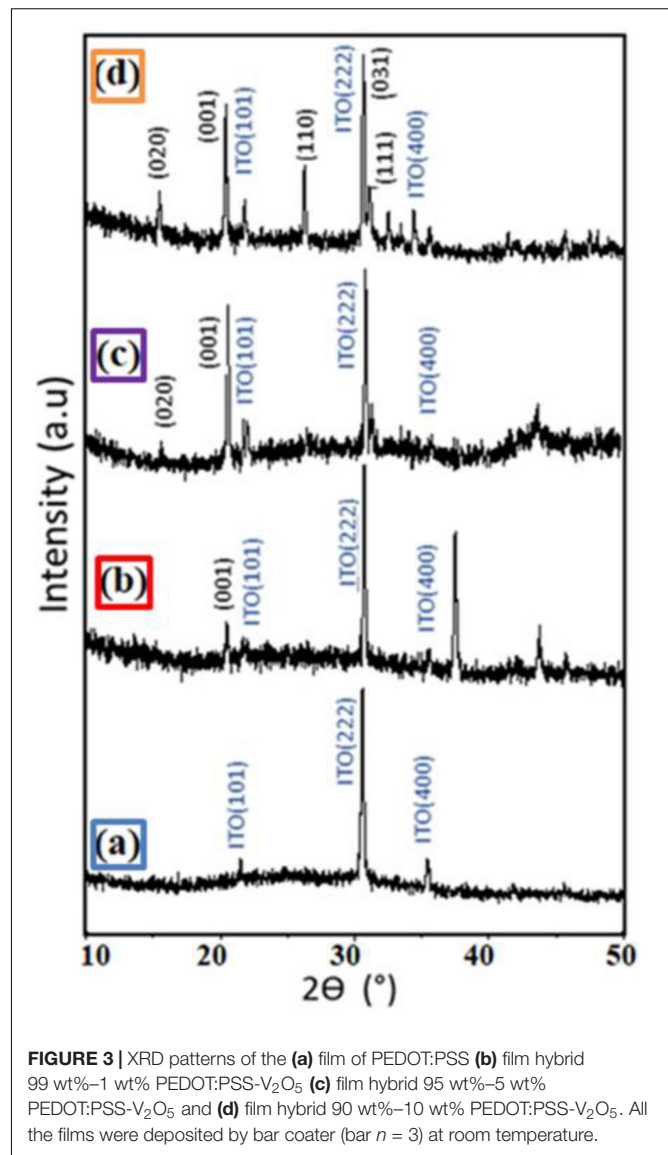




the films morphology changes with the amount of V₂O₅. The PEDOT:PSS film appears smooth and homogenous (Figure 4a). The SEM micrograph of the hybrid composite film 99 wt%–1 wt% PEDOT:PSS-V₂O₅ (Figure 4b), 5 wt% V₂O₅ (Figure 4c), 10 wt% V₂O₅ (Figure 4d) shows a homogenous dispersion of the V₂O₅ particles in the PEDOT:PSS ink. Not surprisingly, the higher is the amount of V₂O₅, the rougher is the surface and the more particles are visible. The V₂O₅ film appears homogenous and resembles to a collection of the sub-micronic particles (100 nm) of V₂O₅ (Figure 4e). The V₂O₅ particles seem to form bigger aggregate especially when the vanadium oxide amount increases. The 10 wt% V₂O₅ and the 100 wt% V₂O₅ films surfaces appear very similar. For the 10% hybrid film, the oxide particles seem to be embedded in the PEDOT:PSS which has an impact on the chromatic parameters as it will be mentioned later in the paper.

Electrochromic Properties of PEDOT:PSS-V₂O₅ Hybrid Films

The electrochromic activity of the hybrid PEDOT:PSS-V₂O₅ films was recorded in a lithium-based ionic liquid electrolyte. Figure 5 shows the cyclic voltammograms of single V₂O₅, single PEDOT:PSS and hybrid PEDOT:PSS-V₂O₅ films deposited onto ITO and cycled, at a scan rate of 20 mV s⁻¹ between -1 V and +1.5 V, in a three electrodes cell using ionic liquid based LiTFSI:EMIM-TFSI (1:9) as a supporting electrolyte and SCE as reference electrode, for thickness of 1.5 μm. The shape of the cyclic voltammograms adopts significant changes as soon as the addition of 0.1 wt% V₂O₅ (Figure 5A). A small amount of V₂O₅ induces a high reactivity associated with strong increase in current and featured CV illustrated by the presence of redox peaks both in anodic and cathodic sweeps (Figure 5B). Higher peak resolution is achieved by cycling thinner films as reported in Figure 5B inset. The CV shape of a 1 wt% submicron film of 500 nm displays a specific signature with both anodic and



cathodic distinguishable peaks. Such signature recalls the one observed for crystallized sputtered V₂O₅ thin films (Benmoussa et al., 2002). These changes in the electrochemical behavior do not have a strong impact for film with a V₂O₅ amount lower than 1 wt%. The comparison of the CV intensities indicates lower performances for hybrid films, PEDOT:PSS-V₂O₅ as compared to pure V₂O₅ film alone.

Figure 6 shows the chronoamperograms recorded for 30 s at +1.5 V (Figure 6A) and for 30 s at -1 V (Figure 6B). The CA was applied for five cycles, the second cycle is drawn for a film thickness of 1.5 μm. Starting from 1 wt% V₂O₅, the switching time increases with a higher current density. This trend well agrees with the faster kinetic reported for electrochromic conductive polymers as compared to oxides (Thakur et al., 2012).

In order to evaluate the electrochromic properties, the chromaticity parameters L^* , a^* , b^* were measured during chronoamperometry cycles. These three parameters defined by

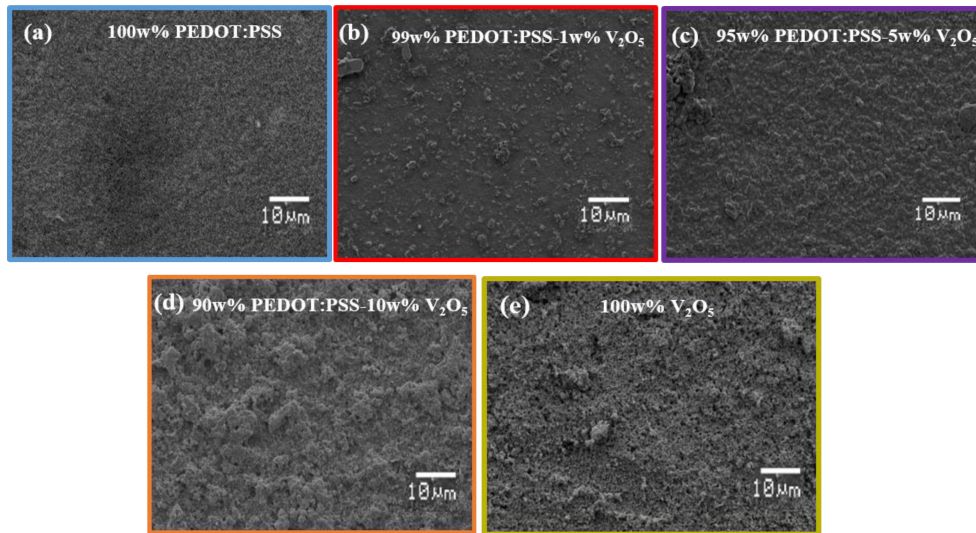


FIGURE 4 | SEM of the (a) 100wt% PEDOT:PSS, (b) film hybrid 99 wt%–1 wt% PEDOT:PSS-V₂O₅, (c) film hybrid 95 wt%–5 wt% PEDOT:PSS-V₂O₅, (d) film hybrid 90 wt%–10 wt% PEDOT:PSS-V₂O₅, (e) 100 wt% V₂O₅ film.

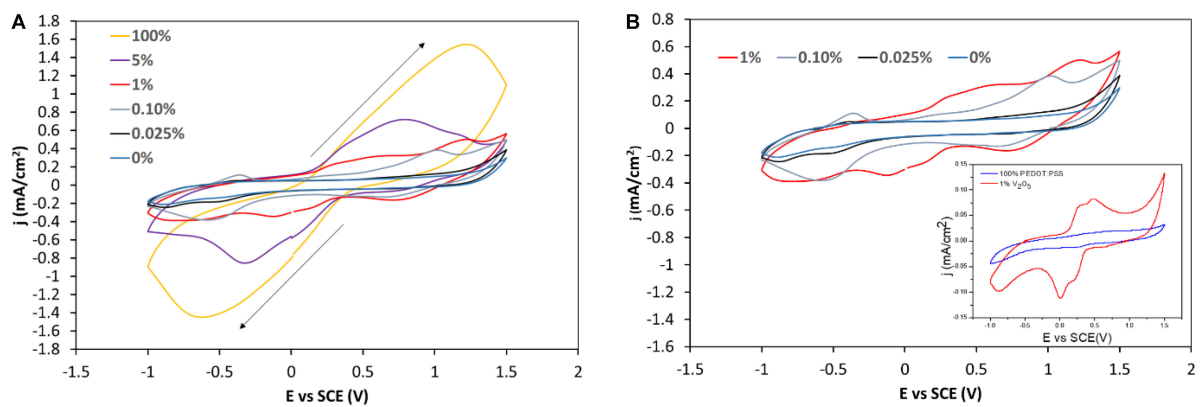


FIGURE 5 | (A) Cyclic Voltammograms (CVs) of various wt% hybrid films PEDOT:PSS-V₂O₅ cycled in PEDOT:PSS-V₂O₅/Li-electrolyte/Pt vs. SCE using a 20 mV/s scan rate. (B) Zoom on the CVs of the film containing 1 wt% or less V₂O₅, inset CV of the 99%–1% PEDOT:PSS-V₂O₅ with a thickness of 0.5 μm.

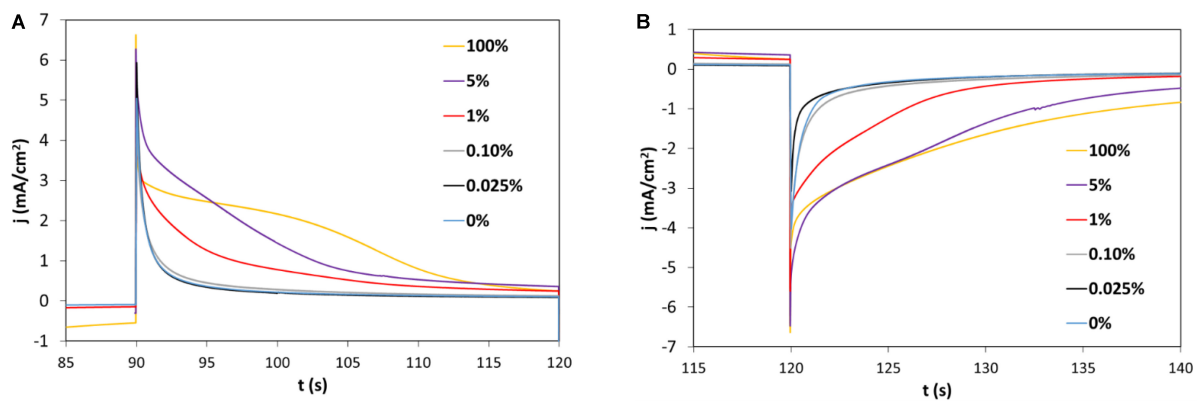
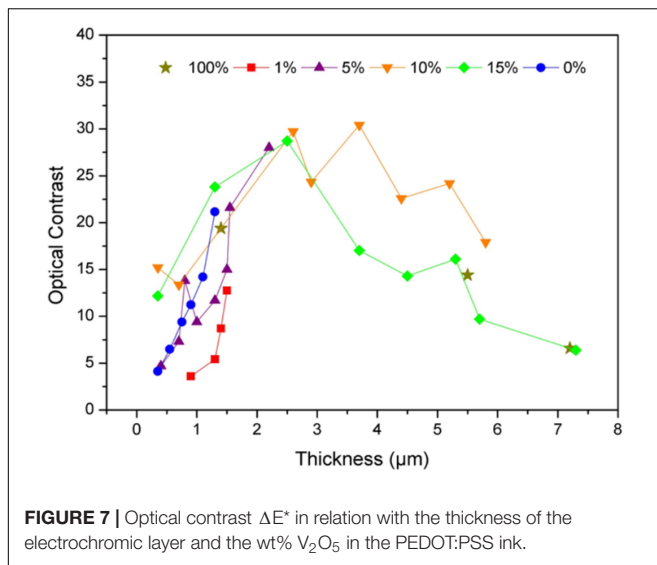


FIGURE 6 | Chronoamperograms (CA) of wt% hybrid PEDOT:PSS-V₂O₅ cycled in LiTFSI:EMIM-TFSI (1:9) electrolyte/Pt vs. SCE with (A) the oxidation at E vs. SCE = +1.5 V and (B) the reduction at E vs. SCE = -1 V (second cycle is represented).



the CIE colorimetric space, are used to define and compare quantitatively the colors. The optical contrast (ΔE^*) can be deduced from these three chromaticity parameters thanks to equation (1)

$$\Delta E^* = \sqrt{(L_{\text{red}}^* - L_{\text{ox}}^*)^2 + (a_{\text{red}}^* - a_{\text{ox}}^*)^2 + (b_{\text{red}}^* - b_{\text{ox}}^*)^2} \quad (1)$$

Where L_{red}^* , a_{red}^* , b_{red}^* represent the chromaticity parameters in reduced state and L_{ox}^* , a_{ox}^* , b_{ox}^* the ones in oxidized state, at a voltage of -1 V and $+1.5$ V for 30 s for each cycle, respectively. The optical contrast is determined for each film after two cycles of CA. **Figure 7** displays the evolution of the optical contrast vs. the layer thickness for each wt%. A certain thickness is required to obtain a good change of color from the oxidized to the reduced state.

However, over a thickness of $4 \mu\text{m}$, contrast decrease for all the films containing at least 10 wt% of vanadium oxide. The decrease in contrast for a thick layer may illustrate a limitation in the redox

process that does not occur only on the surface of the film but remain limited to a certain thickness. For a high oxide amount (above 10 wt%) layer for the mixture between PEDOT:PSS and V₂O₅ the film resistance increases also, which is in agreement with a longer color switching time.

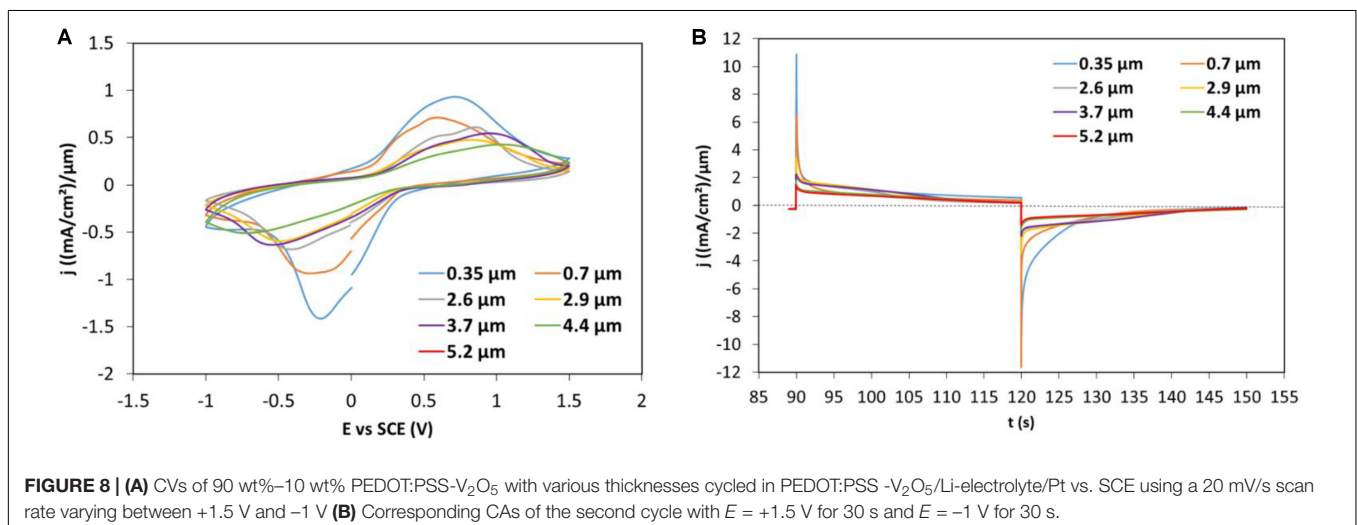
In order to minimize the amount of V₂O₅ for cost reason and to obtain a similar contrast value as for pure vanadium oxide, the ink formulation with 90 wt%–10 wt% PEDOT:PSS-V₂O₅ was chosen as the best candidate for a satisfying color change and a good thickness control.

Electrochromic Properties of 90 wt%–10 wt% PEDOT:PSS-V₂O₅

A more detailed study focusing on the 90 wt%–10 wt% PEDOT:PSS-V₂O₅ was then carried out to evaluate the impact of the thickness on the electrochromic performance. **Figure 8** shows the CVs for various thicknesses, the electrochemical behavior of a submicron film is very different from the behavior of a film with a thickness of $2.5 \mu\text{m}$ and more (**Figure 8A**). The current density value does not evolve much for films over this thickness. The same observation can be deduced from the CA curves (**Figure 8B**) with furthermore, a shift toward higher current density value for layers above $2.5 \mu\text{m}$ for both oxidation and reductions parts after 20 s. This change in slope may indicate a different redox reaction on the surface of the film that may change with the amount of vanadium oxide.

Figure 9 displays the evolution of the chromaticity parameters vs. thickness for the initial (i.e., as-deposited), oxidized ($+1.5$ V) and reduced (-1 V) states of 100 wt% PEDOT:PSS (in blue), 100 wt%V₂O₅ (in ochre) and a 90 wt%–10 wt% PEDOT:PSS-V₂O₅ (in orange). The hybrid PEDOT:PSS-V₂O₅ and pure V₂O₅ exhibit similar trend with only a small shift toward lower values of the L^* parameter for the three states (**Figure 9A**), more than five points lost for the a^* parameter (**Figure 9B**) and again a shift toward lower values for the b^* parameter (**Figure 9C**).

The presence of PEDOT:PSS, responsible of a slightly darker color, has a definitive impact on the b^* parameter. The shift



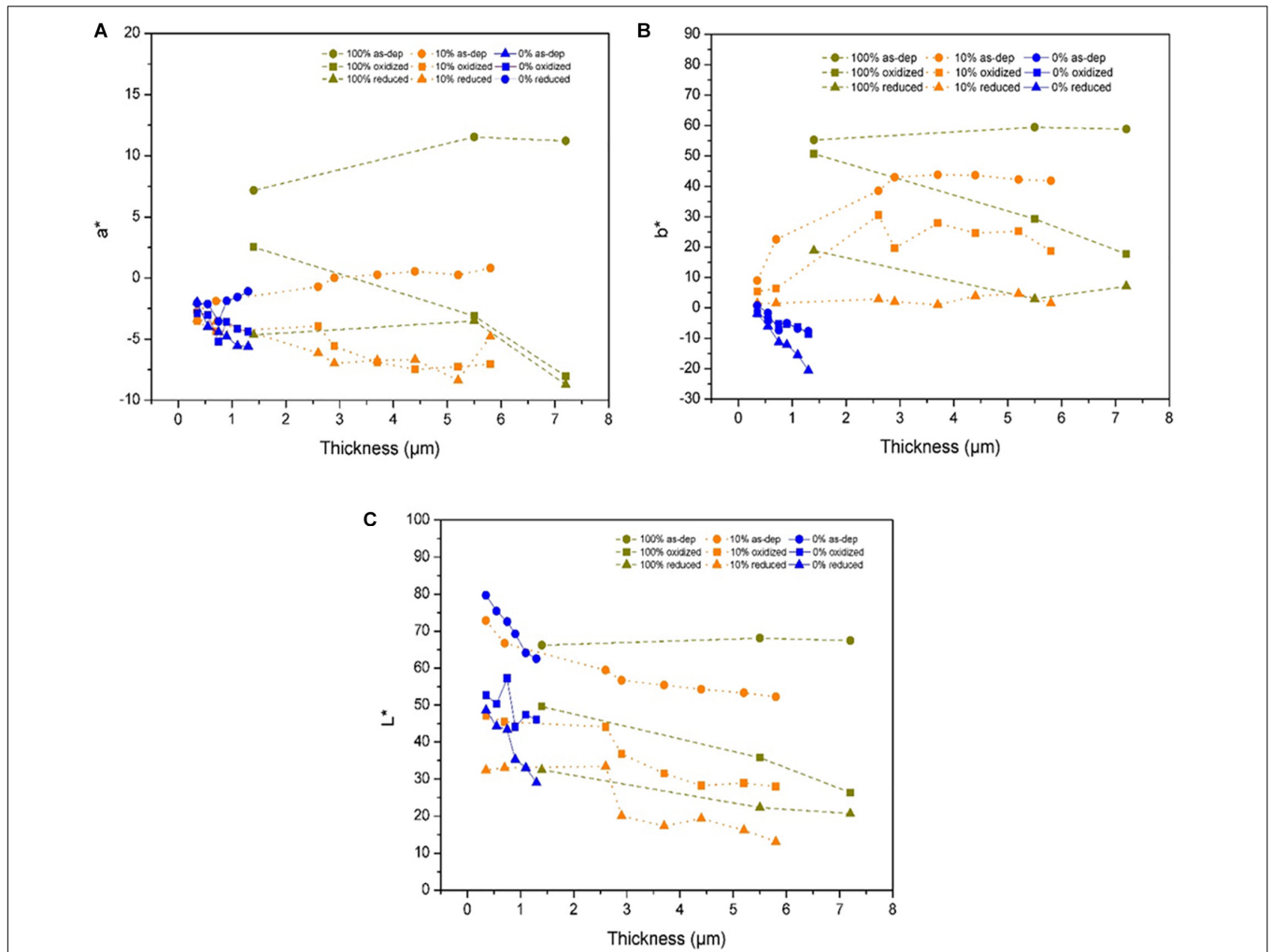


FIGURE 9 | Comparison of the chromaticity parameters between initial, oxidized state at $E = +1.5$ V and reduced state at $E = -1$ V with **(A)** parameter a^* . **(B)** parameter b^* . **(C)** parameter L^* for 100 wt% V₂O₅, 10 wt% V₂O₅, and 0 wt% V₂O₅.

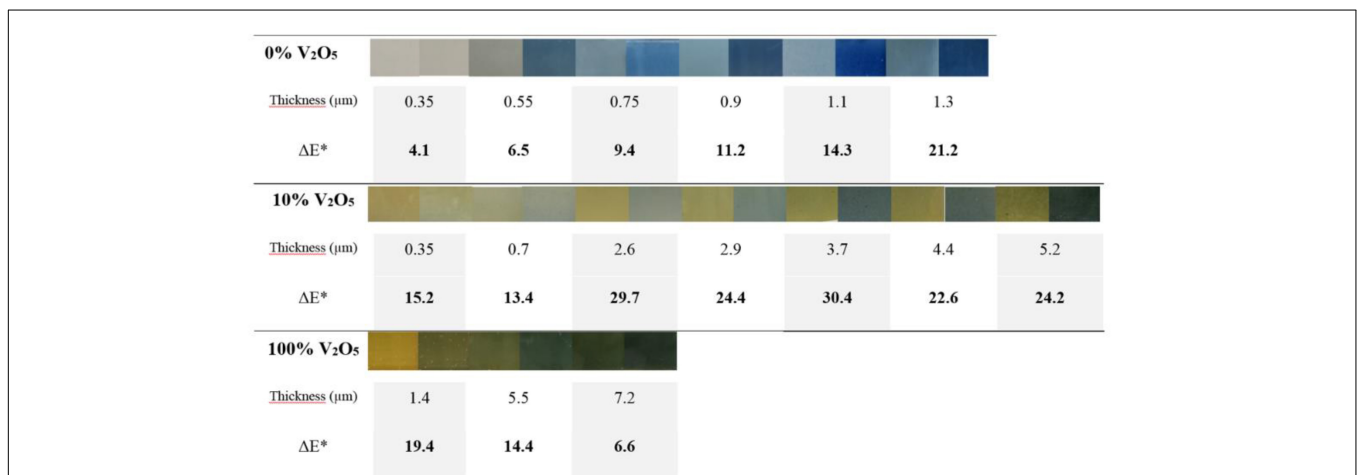


FIGURE 10 | Visual comparison between the colors in the oxidized and reduced states for 0 wt% V₂O₅, 100 wt% V₂O₅, and 90 wt%–10 wt% PEDOT:PSS-V₂O₅ vs. thickness (μm) during CA after three cycles and contrast value ΔE*.

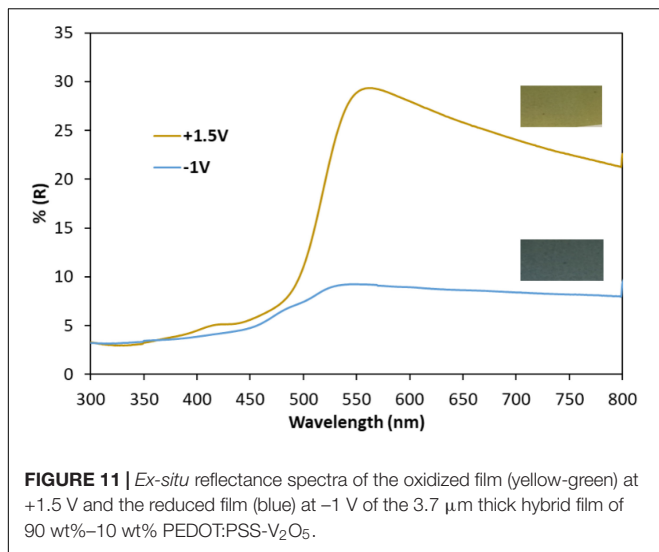


FIGURE 11 | *Ex-situ* reflectance spectra of the oxidized film (yellow-green) at +1.5 V and the reduced film (blue) at -1 V of the 3.7 μm thick hybrid film of 90 wt%–10 wt% PEDOT:PSS-V₂O₅.

toward darker and more bluish films may be correlated to the SEM micrographs on the **Figure 4**, in which V₂O₅ appears embedded in PEDOT:PSS.

Initially, the corresponding curve follows the same trend and gives to the mixture a bluer color for low thickness especially in the reduced state. However, and as already observed on the electrochemical behavior, for film above 2.5 μm the V₂O₅ behavior takes the lead and has the strongest impact on the chromaticity parameters.

On the **Figure 10** are gathered, the colors in oxidized and reduced states of the 0 wt% V₂O₅, 100 wt% V₂O₅ and 90 wt%–10 wt% PEDOT:PSS-V₂O₅ films for various thicknesses. For a

given thickness, the left picture illustrated the oxidized state ($E = +1.5$ V) and the right one the reduced state ($E = -1$ V). The pictures together with the chromaticity parameters were recorded during CA measurements. In agreement with the **Figure 8B**, the thicker is the layer, the harder the current density is driven to a value close to 0. Therefore after few cycles, the greenish layer of the surface is correlated with an irreversible reaction from V⁵⁺ to V⁴⁺ with the Li⁺ insertion.

When comparing the CA curves (not shown here) between 0 wt% V₂O₅, 100 wt% V₂O₅, and 90 wt%–10 wt% PEDOT:PSS-V₂O₅, it could be noticed that the 0 wt% V₂O₅ corresponds to a very fast kinetic with less than 1 s for color change. 10 wt% V₂O₅ adopts a visual change in 5 s while it takes at least 15 s to observe a change of color from the oxidized to the reduced state for 100 wt% V₂O₅. As expected the changing color mechanism for PEDOT:PSS is much faster than the one of crystallized V₂O₅. Besides the presence of the polymer helps to reduce the time necessary to change the color from oxidized to reduced states (and vice-versa) without affecting the optical contrast when only 10%wt V₂O₅ is added to the polymer ink.

Aiming at a better investigation of the optical properties, the reflectance spectra was recorded on the film with the highest contrast between the oxidized and reduced states for the mixture 90 wt%–10 wt% PEDOT:PSS-V₂O₅ (e.g., a film thickness of 3.7 μm) (**Figure 11**). The reversible color changes of hybrid composite films between the two states are associated with reflectance values of about 8.3% for the reduced state and 28.9% for the oxidized state at 550 nm, respectively, leading to an optical reflectance modulation, ΔR , of 20.6%.

The electrochromic performance are characterized thanks to the optical density (OD) which can be calculated directly from the reflectance spectra and represents the logarithm of the ratio

0% V ₂ O ₅	Initial	E = -1V	3 months	Initial	E = -1V	3 months	Initial	E = -1V	3 months
Thickness (μm)		0.9			1.1			1.3	
L*	69.2	35.34	63.2	64.2	33.1	56.8	62.57	29.1	55.97
a*	-4.79	-1.88	-3.09	-5.54	-1.56	-3.18	-5.6	-1.11	-3.91
b*	-5.08	-12.1	-5.29	-6.85	-15.5	-7.32	-7.72	-20.6	-9.76
10% V ₂ O ₅	Initial	E = -1V	3 months	Initial	E = -1V	3 months	Initial	E = -1V	3 months
Thickness (μm)		2.9			3.7			4.4	
L*	55.41	20.08	31.89	54.3	17.3	24.5	53.3	19.33	25.4
a*	0.27	-6.97	-5.34	0.54	-6.74	-8.5	0.25	-6.68	-9.2
b*	43.81	2.04	17.5	43.7	1.01	21.7	42.22	3.89	16.7

FIGURE 12 | Illustration of the memory-effect by comparison between the standard PEDOT:PSS and 90 wt%–10 wt% PEDOT:PSS-V₂O₅ with chromaticity parameters taken at the initial stage, at $E = -1$ V and after 3 months after applying first $E = -1$ V, leaving the samples rest at room temperature and ambient atmosphere without any cycle in between.

of the reflectance at the oxidized state (R_{ox}) to the reflectance at the reduced state (R_{red}) as shown on the Equation 2.

$$\Delta OD = \log(R_{ox}/R_{red}) \quad (2)$$

A ΔOD of 0.54 is estimated at 550 nm. The color efficiency (CE) can be calculated with the charge transferred per unit area (Q) deduced from the CA curves.

$$CE = \Delta OD/Q \quad (3)$$

In this case, $Q = 1.85 \text{ C}\cdot\text{cm}^{-2}$ and CE obtained equals to $0.29 \text{ cm}^2\cdot\text{C}^{-1}$. This rather low value may be explained by a measurement of the capacity in chronoamperometry mode rather than in dynamic mode using cyclic voltammetry. Besides, there is a lack of comparison with other hybrid systems mixing two electrochromic materials as a single layer.

Memory Effect of 90 wt%–10 wt% PEDOT:PSS-V₂O₅ Film

Figure 12 gathers the chromaticity parameters of the 0 wt% V₂O₅ and the 90 wt%–10 wt% PEDOT:PSS-V₂O₅ films for different thicknesses recorded as initial state, in reduced state (−1 V), and after resting the film for 3 months. No voltage was applied meanwhile and films were stored at ambient atmosphere and room temperature. The PEDOT:PSS film goes back to its most stable state exhibiting no memory effect with a very low value difference between initial and 3 months values. On the contrary, as reported by our group in a prior work, V₂O₅ shows a strong memory effect (Mjeiri et al., 2018a). After 3 months, if the chromaticity parameters exhibit different values as compared to the first applied voltage at $E = -1 \text{ V}$ they also display a big difference with the initial data. From a blue-green film at $E = -1 \text{ V}$, a green film is visible after 3 months. The mixture of 10 wt% V₂O₅ in the PEDOT:PSS induced a memory-effect.

CONCLUSION

In this paper, hybrid composite films with different compositions between a polymer ink of PEDOT:PSS and V₂O₅ synthesized by the polyol process were successfully deposited with a bar coater technique. The influence of the film thickness according to the amount of vanadium oxide in PEDOT:PSS-V₂O₅ hybrids was studied via electrochemical techniques and surface morphology.

REFERENCES

- Andersson, P. (2006). *Electrochromic Polymer Devices: Active-Matrix Displays and Switchable Polarizers*. Licentiate Thesis, Linköping University, Sweden.
- Benmoussa, M., Outzourhit, A., Bennouna, A., and Ameziane, E. L. (2002). Electrochromism in Sputtered V₂O₅ thin films: structural and optical studies. *Thin Solid Films* 405, 11–16. doi: 10.1016/S0040-6090(01)01734-5
- Blanquart, T., Niinistö, J., Gavagnin, M., Longo, V., Heikkilä, M., Puukilainen, E., et al. (2013). Atomic layer deposition and characterization of vanadium oxide thin films. *RSC Adv.* 3, 1179–1185. doi: 10.1039/C2RA22820C
- Byker, H. (2001). Electrochromics and polymers. *Electrochim. Acta* 46, 2015–2022. doi: 10.1016/S0013-4686(01)00418-2

The introduction of 10 wt% V₂O₅ with a film thickness of 3.7 μm is sufficient to mimic the behavior of pure V₂O₅ change of color with a faster reversible color change from oxidized to reduced states. Indeed 10 wt% V₂O₅ are sufficient to gain color tuning, significant optical contrast and memory-effect suggesting that there is no need to mix further inorganic material in the polymer. Our approach is a promising route to improve the electrochromic properties including the tuning of color of displays based on PEDOT:PSS-based ink in a very simple way, combining advantages of V₂O₅ inorganic and PEDOT:PSS polymer materials. The memory-effect was also improved for hybrid films as compared to single PEDOT:PSS. Furthermore, dispersing the vanadium oxide in a polymer ink reduces the overall toxicity, the cost, improves the process control and allows the use of the hybrid in industrial technique such as screen-printing which is promising for developing large-scale electrochromic displays.

DATA AVAILABILITY STATEMENT

All datasets generated for this study are included in the article/supplementary material.

AUTHOR CONTRIBUTIONS

RF, IM, and HR conducted the investigation and methodology. AR supervised the project. RF wrote the original draft.

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- Chu, J., Kong, Z., Lu, D., Zhang, W., Wang, X., Yu, Y., et al. (2016). Hydrothermal synthesis of vanadium oxide nanorods and their electrochromic performance. *Mater. Lett.* 166, 179–182. doi: 10.1016/j.matlet.2015.12.067
- Costa, C., Pinheiro, C., Henriques, I., and Laia, C. A. T. (2012). Electrochromic properties of inkjet printed vanadium oxide gel on flexible Polyethylene Terephthalate/Indium Tin oxide electrodes. *ACS Appl. Mater. Interf.* 4, 5266–5275. doi: 10.1021/am301213b
- Danine, A., Cojocaru, L., Faure, C., Olivier, C., Toupance, T., Campet, G., et al. (2014). Room temperature UV treated WO₃ thin films for electrochromic devices on paper substrate. *Electrochim. Acta* 129, 113–119. doi: 10.1016/j.electacta.2014.02.028
- Danine, A., Mancieru, L., Faure, C., Labrugère, C., Penin, N., Delattre, A., et al. (2019). Toward simplified electrochromic devices using silver as counter

- electrode material. *ACS Appl. Mater. Interf.* 11, 34030–34038. doi: 10.1021/acsami.9b12380
- Granqvist, C. G., Arvizu, M. A., Qu, H., Wen, R., and Niklasson, G. A. (2019). Advances in electrochromic device technology: multiple roads towards superior durability. *Surf. Coat. Technol.* 357, 619–625. doi: 10.1016/j.surfcoat.2018.10.048
- Han, Y., Lin, Y., Sun, D., Xing, Z., Jiang, Z., and Chen, Z. (2019). Poly(Aryl Amino Ketone)-based materials with excellent electrochromic and electrofluorochromic behaviors. *Dyes Pigments* 163, 40–47. doi: 10.1016/j.dyepig.2018.11.045
- Hu, C. H., Yamada, Y., and Yoshimura, K. (2018). Poly(3,4-Alkylenedioxythiophenes): PxDOTs Electrochromic Polymers as Gasochromic materials. *Solar Energ. Mater. Solar Cells* 187, 30–38. doi: 10.1016/j.solmat.2018.07.022
- Jung, Y., Lee, J., and Tak, Y. (2004). Electrochromic mechanism of IrO₂ prepared by pulsed anodic electrodeposition. *Electrochem. Solid State Lett.* 7, H5–H8. doi: 10.1149/1.1634083
- Lang, A. W., Osterhölml, A. M., and Reynolds, J. R. (2019). Paper-based electrochromic devices enabled by nanocellulose-coated substrates. *Adv. Funct. Mater.* 29:1903487. doi: 10.1002/adfm.201903487
- Lee, J. S., Choi, Y. J., Park, H. H., and Pyun, J. C. (2011). Electrochromic properties of Poly(3,4-Ethylenedioxythiophene) Nanocomposite Film Containing SiO₂ Nanoparticles. *J. Appl. Polym. Sci.* 122, 3080–3085. doi: 10.1002/app.34130
- Lee, S., Kim, H. P., Yusoff, A. R. M., and Jang, J. (2014). Organic photovoltaic with PEDOT:PSS and V₂O₅ mixture as hole transport layer. *Solar Energ. Mater. Solar Cells* 120, 238–243. doi: 10.1016/j.solmat.2013.09.009
- Levasseur, D., Mjejri, I., Rolland, T., and Rougier, A. (2019). Color tuning by oxide addition in PEDOT:PSS-based electrochromic devices. *Polymers* 11:179. doi: 10.3390/polym11010179
- Mjejri, I., Doherty, C. M., Rubio-Martinez, M., Drisko, G. L., and Rougier, A. (2017). Double-sided electrochromic device based on metal–organic frameworks. *ACS Appl. Mater. Interf.* 9, 39930–39934. doi: 10.1021/acsami.7b13647
- Mjejri, I., Gaudon, M., and Rougier, A. (2019). Mo addition for improved electrochromic properties of V₂O₅ thick films. *Solar Energ. Mater. Solar Cells* 198, 19–25. doi: 10.1016/j.solmat.2019.04.010
- Mjejri, I., Gaudon, M., Song, G., Labrugère, C., and Rougier, A. (2018a). Crystallized V₂O₅ as oxidized phase for unexpected multicolor electrochromism in V₂O₃ thick film. *ACS Appl. Energ. Mater.* 1, 2721–2729. doi: 10.1021/acsam.8b00386
- Mjejri, I., Groccassan, R., and Rougier, A. (2018b). Enhanced coloration for hybrid niobium-based electrochromic devices. *ACS Appl. Energ. Mater.* 1, 4359–4366. doi: 10.1021/acsam.8b00967
- Mjejri, I., Mancieru, L. M., Gaudon, M., Rougier, A., and Sediri, F. (2016). Nano-vanadium pentoxide films for electrochromic displays. *Solid State Ionics* 292, 8–14. doi: 10.1016/j.ssi.2016.04.023
- Nunes, S. C., Saraiva, S. M., Pereira, R. F. P., Pereira, S., Silva, M. M., Carlos, L. D., et al. (2019). Sustainable dual-mode smart windows for energy-efficient buildings. *ACS Appl. Energ. Mater.* 2, 1951–1960. doi: 10.1021/acsam.8b02041
- Qingyi, L., Xu, Z., Wanan, C., Yan, W., Caiyu, Y., Ye, C., et al. (2019). Donor-acceptor conjugated polymers containing isoindigo block for novel multifunctional materials for electrochromic, resistance memory, and detector devices. *Solar Energ. Mater. Solar Cells* 200:109979. doi: 10.1016/j.solmat.2019.109979
- Rodrigues, L. C., Barbosa, P. C., Silva, M. M., Smith, M. J., Gonçalves, A., and Fortunato, E. (2009). Application of hybrid materials in solid-state electrochromic devices. *Opt. Mater.* 31, 1467–1471. doi: 10.1016/j.optmat.2009.02.004
- Runnerstrom, E. L., Llordés, A., Lounis, S. D., and Milliron, D. J. (2014). Nanostructured electrochromic smart windows: traditional materials and NIR-selective plasmonic nanocrystals. *Chem. Commun.* 50, 10555–10572. doi: 10.1039/C4CC03109A
- Tashtoush, N., and Kasasbeh, O. (2013). Optical properties of vanadium pentoxide thin films prepared by thermal evaporation method. *Jordan J. Pharmaceut. Sci.* 6:1. doi: 10.31257/2018/jkp/100101
- Thakur, V. K., Ding, G., Ma, J., Lee, P. S., and Lu, X. (2012). Hybrid materials and polymer electrolytes for electrochromic device applications. *Adv. Mater.* 24, 4071–4096. doi: 10.1002/adma.201200213
- Varghese, H. R., Yang, J., and Zheng, L. (2018). Flexible electrochromic materials based on CNT/PDA hybrids. *Adv. Colloid Interf. Sci.* 258, 21–35. doi: 10.1016/j.cis.2018.07.003

Conflict of Interest: RF was employed by the company Luquet-Duranton.

The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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