PEDOT:PSS-\(\text{V}_2\text{O}_5\) 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 \(\text{V}_2\text{O}_5\), 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 (\(\text{V}_2\text{O}_5\) wt%). Films thicknesses varied from hundred of nms to few \(\mu\text{ms}\). As-deposited films colors range from blue for PEDOT:PSS to orange for \(\text{V}_2\text{O}_5\). PEDOT:PSS-\(\text{V}_2\text{O}_5\) films exhibit significant electrochromic properties associated with a good electrochemical stability. In the series, the hybrid film with 90 wt%–10 wt% PEDOT:PSS-\(\text{V}_2\text{O}_5\) shows a reversible behavior with significant reflectance modulation (\(\Delta R\approx20.5\%\) at 550 nm) in lithium based electrolyte and a good contrast (\(\Delta E^* > 30\)). The maximum contrast was reached for 3.7 \(\mu\text{m}\) 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, \(\text{V}_2\text{O}_5\), color tuning, bar coating, hybrid materials

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 \(\text{WO}_3\) and \(\text{IrO}_x\) or \(\text{NiO}\) (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 ($V_2O_5$) 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, multicolor 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 Fe$_2$O$_3$ in a PEDOT:PSS ink allowed to achieve a color modulation from bluish to reddish, while in first approximation Fe$_2$O$_3$ alone appears to be electrochemically inactive (Levasseur et al., 2019). Pursuing this hybrid approach herein, the electrochromic properties of bar coated opaque films, from mixture of electrochemically active V$_2$O$_5$ to commercial PEDOT:PSS ink, are investigated. V$_2$O$_5$ was preferentially used as it can be bring a larger color range to the PEDOT:PSS film. Indeed, other cathodic oxides such a Nb$_2$O$_5$ (Mjejri et al., 2018b) or WO$_3$ (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-V$_2$O$_5$ 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 V$_2$O$_5$ 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 V$_2$O$_5$ 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 V$_2$O$_5$ powders synthesized by polyl 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 V$_2$O$_5$ weight percentages were calculated from the PEDOT:PSS paste mass. Seven premixes were prepared: weight ratio of (PEDOT:PSS paste)/(V$_2$O$_5$) = (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-V$_2$O$_5$ paste and 60 wt% of ethanol. The various hybrid inks with different weight ratio between PEDOT:PSS, V$_2$O$_5$ 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% V$_2$O$_5$ as 100%, 85 wt%–15 wt% PEDOT:PSS-V$_2$O$_5$ as 15%, 90 wt%–10 wt% PEDOT:PSS-V$_2$O$_5$ as 10%, 95 wt%–5 wt% PEDOT:PSS-V$_2$O$_5$ as 5%, 99 wt%–1 wt% PEDOT:PSS-V$_2$O$_5$ 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, 1.127. The coatings were done on ITO-coated (In$_2$O$_3$: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 \times 2.5 \text{cm}^2 \) ITO-coated glass substrates. The thickness of the PEDOT:PSS-V\textsubscript{2}O\textsubscript{5} 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, PANalytical X’Pert instrument, 20 range from 10\textdegree to 50\textdegree and Cu K\alpha 1 \= 0.154056 \text{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-V\textsubscript{2}O\textsubscript{5} 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\textsubscript{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\textsuperscript{−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-V\textsubscript{2}O\textsubscript{5} 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\textdegree/D65 configuration (Konica Minolta Sensing Europe B.V), allowing the direct determination of colorimetric parameters of the CIE (L\textsuperscript{*}a\textsuperscript{*}b\textsuperscript{*}) color space.

## RESULTS AND DISCUSSION

### Structural and Morphological Properties of PEDOT:PSS-V\textsubscript{2}O\textsubscript{5} Hybrid Films

To optimize the electrochromic performance of the hybrid PEDOT:PSS-V\textsubscript{2}O\textsubscript{5} films, the weight ratio between PEDOT:PSS and V\textsubscript{2}O\textsubscript{5} 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\textsuperscript{*}, a\textsuperscript{*}, b\textsuperscript{*} chromaticity parameters, defined by the CIE LAB. A significant color gradient in relationship with the decrease of the V\textsubscript{2}O\textsubscript{5} weight percentages is visible.

From 100 wt% V\textsubscript{2}O\textsubscript{5} yellow-orange film, the hybrid mixture remains close to the appearance of pure V\textsubscript{2}O\textsubscript{5} till 10 wt%. The color turns greenish for 5 wt% V\textsubscript{2}O\textsubscript{5}, and for the 1 wt% V\textsubscript{2}O\textsubscript{5}, 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 V\textsubscript{2}O\textsubscript{5} wt% content has a strong influence on the film thickness. Overall, the thickness of hybrid films increases with increasing V\textsubscript{2}O\textsubscript{5} wt%.

If a low thickness increase is measured up to 5 wt% of V\textsubscript{2}O\textsubscript{5}, a first jump is observed for 10 wt% and 15 wt% while pure V\textsubscript{2}O\textsubscript{5} reaches thickness of 7 \textmu m already for bar n = 3. Using the bar (n = 3) corresponding to Figure 1, the thicknesses of the films vary from 0.6 \textmu m for pure PEDOT:PSS and 1 wt% V\textsubscript{2}O\textsubscript{5}, 0.8 \textmu m for 5 wt% V\textsubscript{2}O\textsubscript{5}, 2.5 \textmu m for 10 wt% and 15 wt% V\textsubscript{2}O\textsubscript{5} up to 7.2 \textmu m for pure V\textsubscript{2}O\textsubscript{5}. 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 V\textsubscript{2}O\textsubscript{5} a first peak of V\textsubscript{2}O\textsubscript{5} can be identified with a very weak signal associated with a low content (Figure 3b). For the 5 wt% V\textsubscript{2}O\textsubscript{5} hybrid film, the peaks intensities increase with the appearance of a second peak (Figure 3c). With the film containing 10 wt% V\textsubscript{2}O\textsubscript{5}, all the peaks can be indexed as V\textsubscript{2}O\textsubscript{5} (Space Group:Pmmm) (Figure 3d) revealing an agreement between color and crystallinity. 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 (V\textsubscript{2}O\textsubscript{5}, PEDOT:PSS and hybrid films PEDOT:PSS-V\textsubscript{2}O\textsubscript{5}) (Figure 4) demonstrates that...
the films morphology changes with the amount of V$_2$O$_5$. The PEDOT:PSS film appears smooth and homogenous (Figure 4a). The SEM micrograph of the hybrid composite film 99 wt%–1 wt% PEDOT:PSS-V$_2$O$_5$ (Figure 4b), 5 wt% V$_2$O$_5$ (Figure 4c), 10 wt% V$_2$O$_5$ (Figure 4d) shows a homogenous dispersion of the V$_2$O$_5$ particles in the PEDOT:PSS ink. Not surprisingly, the higher is the amount of V$_2$O$_5$, the rougher is the surface and the more particles are visible. The V$_2$O$_5$ film appears homogenous and resembles to a collection of the sub-micronic particles (100 nm) of V$_2$O$_5$ (Figure 4e). The V$_2$O$_5$ particles seem to form bigger aggregate especially when the vanadium oxide amount increases.

The Electrochromic Properties of PEDOT:PSS-V$_2$O$_5$ Hybrid Films

The electrochromic activity of the hybrid PEDOT:PSS-V$_2$O$_5$ films was recorded in a lithium-based ionic liquid electrolyte. Figure 5 shows the cyclic voltammograms of single V$_2$O$_5$, single PEDOT:PSS and hybrid PEDOT:PSS-V$_2$O$_5$ 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% V$_2$O$_5$ (Figure 5A). A small amount of V$_2$O$_5$ 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 V$_2$O$_5$ thin films (Benmoussa et al., 2002). These changes in the electrochemical behavior do not have a strong impact for film with a V$_2$O$_5$ amount lower than 1 wt%. The comparison of the CV intensities indicates lower performances for hybrid films, PEDOT:PSS-V$_2$O$_5$ as compared to pure V$_2$O$_5$ 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% V$_2$O$_5$, 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) 100% PEDOT:PSS. (b) film hybrid 99 wt%–1 wt% PEDOT:PSS-V$_2$O$_5$. (c) film hybrid 95 wt%–5 wt% PEDOT:PSS-V$_2$O$_5$. (d) film hybrid 90 wt%–10 wt% PEDOT:PSS-V$_2$O$_5$. (e) 100 wt% V$_2$O$_5$ film.

FIGURE 5 | (A) Cyclic Voltammograms (CVs) of various wt% hybrid films PEDOT:PSS-V$_2$O$_5$ cycled in PEDOT:PSS-V$_2$O$_5$/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 V$_2$O$_5$, inset CV of the 99%–1% PEDOT:PSS-V$_2$O$_5$ with a thickness of 0.5 µm.

FIGURE 6 | (A) Chronoamperograms (CA) of wt% hybrid PEDOT:PSS-V$_2$O$_5$ 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 ($\Delta E^*$) can be deduced from these three chromaticity parameters thanks to equation (1)

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

(1)

Where $L_{\text{red}}^*$, $a_{\text{red}}^*$, $b_{\text{red}}^*$ represent the chromaticity parameters in reduced state and $L_{\text{ox}}^*$, $a_{\text{ox}}^*$, $b_{\text{ox}}^*$ 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 $\mu$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 $V_2O_5$ the film resistance increases also, which is in agreement with a longer color switching time.

In order to minimize the amount of $V_2O_5$ 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-$V_2O_5$ 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-$V_2O_5$**

A more detailed study focusing on the 90 wt%–10 wt% PEDOT:PSS-$V_2O_5$ 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 $\mu$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 $\mu$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%$V_2O_5$ (in ochre) and a 90 wt%–10 wt% PEDOT:PSS-$V_2O_5$ (in orange). The hybrid PEDOT:PSS-$V_2O_5$ and pure $V_2O_5$ 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 $E = +1.5 \text{ V}$ and reduced state at $E = -1 \text{ V}$ with (A) parameter $a^*$, (B) parameter $b^*$, (C) parameter $L^*$ for 100 wt% $V_2O_5$, 10 wt% $V_2O_5$, and 0 wt% $V_2O_5$.

FIGURE 10 | Visual comparison between the colors in the oxidized and reduced states for 0 wt% $V_2O_5$, 100 wt% $V_2O_5$, and 90 wt%–10 wt% PEDOT:PSS-$V_2O_5$ vs. thickness (µm) during CA after three cycles and contrast value $\Delta E^*$. 
Hybrid Electrochromic Systems

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-V$_2$O$_5$.

FIGURE 12 | Illustration of the memory-effect by comparison between the standard PEDOT:PSS and 90 wt%–10 wt% PEDOT:PSS-V$_2$O$_5$ 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 (Rox) to the reflectance at the reduced state (Rred) as shown on the Equation 2.

\[ \Delta OD = \log(\text{Rox}/\text{Rred}) \]  

(2)

A \( \Delta OD \) 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.

\[ \text{CE} = \frac{\Delta OD}{Q} \]  

(3)

In this case, \( Q = 1.85 \text{ C.cm}^{-2} \) and CE obtained equals to 0.29 cm\(^2\).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-V\(_2\)O\(_5\) Film**

Figure 12 gathers the chromaticity parameters of the 0 wt% V\(_2\)O\(_5\) and the 90 wt%–10 wt% PEDOT:PSS-V\(_2\)O\(_5\) 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, V\(_2\)O\(_5\) shows a strong memory effect (Mjèri et al., 2018a). After 3 months, if the chromaticity parameters exhibit different values as compared to the first applied voltage at \( E = -1 \) V they also display a big difference with the initial data. From a blue-green film at \( E = -1 \) V, a green film is visible after 3 months. The mixture of 10 wt% V\(_2\)O\(_5\) 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 V\(_2\)O\(_5\) synthesized by the polyl 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-V\(_2\)O\(_5\) hybrids was studied via electrochemical techniques and surface morphology. The introduction of 10 wt% V\(_2\)O\(_5\) with a film thickness of 3.7 \( \mu \)m is sufficient to mimic the behavior of pure V\(_2\)O\(_5\) change of color with a faster reversible color change from oxidized to reduced states. Indeed 10 wt% V\(_2\)O\(_5\) 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 V\(_2\)O\(_5\) 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.

**FUNDING**

This activity included in the SUPERSMART project has received funding from the European Institute of Innovation and Technology (EIT) (Grant Agreement: 17161). This body of the European Union receives support from the European Union’s Horizon 2020 Research and Innovation Program. RF wishes to thank the financial support of Luquet-Duranton.

**ACKNOWLEDGMENTS**

The authors wish to thank Eric Lebraud for the XRD measurements.

**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

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., Manceriu, 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., Osterholm, 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., Mjeiri, I., Rolland, T., and Rougier, A. (2019). Color tuning by oxido addition in PEDOT:PSS-based electrochromic devices. *Polymers* 11:179. doi: 10.3390/polym11010179

Mjeiri, 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

Mjeiri, 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

Mjeiri, 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/acsena.8b00386

Mjeiri, I., Grocassan, R., and Rougier, A. (2018b). Enhanced coloration for hybrid niobium-based electrochromic devices. *ACS Appl. Energ. Mater.* 1, 4359–4366. doi: 10.1021/acsena.8b00967

Mjeiri, I., Manceriu, L. M., Gaudon, M., Rougier, A., and Sediri, F. (2016). Nanovanadium 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/acsena.8b02041

Qingyi, L., Xu, Z., Wanan, C., Yan, W., Caiyu, Y., Ye, C., et al. (2019). Donor-acceptor conjugated polymers containing isoidingo 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. J., 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. I. (2014). Nanostructured electrochromic smart windows: traditional materials and NIR-selective plasmonic nanocrystals. *Chem. Commun.* 50, 10555–10572. doi: 10.1039/C4CC03109A

Tashitouch, 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/jkps.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.

**Copyright © 2020 Futsch, Mjeiri, Rakotosafo and Rougier. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.**