Gel Polymer Electrolyte for Reversible Metal Electrodeposition Dynamic Windows Enables Dual-Working Electrodes for Faster Switching and Reflectivity Control

AUTHOR NAMES

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ABSTRACT

Dynamic windows based on reversible metal electrodeposition are an attractive way to enhance the energy efficiency of buildings and show great commercial potential. When a liquid electrolyte is used to build dynamic windows, there is a risk for the two electrodes to touch and cause short-circuiting, especially in larger-scale formats. Here we developed a poly (vinyl alcohol) (PVA) gel polymer electrolyte (GPE) with 85 % transmittance that is sufficiently stiff to act as a separator. The GPE enabled the fabrication of windows with dual-working electrodes (WE) and a metal mesh counter electrode in the center without short-circuiting. With the GPE exhibiting comparable electrochemical and optical properties to liquid electrolyte. Our dual-WE PVA GPE window reaches the 0.1% transmittance state in 101 s, more than twice the speed of liquid windows with one working electrode (207 s). Additionally, each side of the dual-WE GPE window can be tinted individually to demonstrate varied optical effects (i.e., more reflective, or more absorptive),

providing users and intelligent buildings systems with greater control over the appearance and performance of the windows in a single device architecture.

1. Introduction

Dynamic windows can help tune visible light and heat flow while maintaining views, thereby saving 10-20% of energy for buildings and vehicles over static low emissivity coatings[1, 2]. In addition to energy savings, a study has shown that occupants in office buildings with dynamic windows will be healthier, happier and more productive[3]. By reducing glare and optimizing both the temperature and light flow in an indoor work environment, employee productivity can increase by up to 2%[4]. Currently there are many technologies using electrochromic oxides and organic molecules to tune the color and transmission of the window[5]. Compared with these technologies, dynamic windows based on reversible metal deposition (RME) have the advantage of potential low cost, neutral color, and great contrast ratio[5-13]. These windows operate by the reversible electrodeposition of metals ions, for example Bi^{3+} and Cu^{2+}, to their metallic form on a Pt-coated indium tin oxide (ITO) transparent electrode. A copper mesh works as a counter electrode to balance the metal ions in the electrolyte [7, 8]. Recently, we reported poly (vinyl) alcohol as a growth inhibitor to reversibly deposit metal films with more uniform morphology[6]. So far, the electrolyte currently implemented in these windows is a liquid, consisting of Bi^{3+} and Cu^{2+} ions in an aqueous ClO_4^- based electrolyte[14].

Though aqueous liquid electrolytes often have higher ionic conductivities than ones with high polymer content[15], dynamic windows with liquid electrolytes face problems such as leakage and short circuiting, especially for large-scale windows in fenestration applications. Polymer gel electrolytes are attractive due to their ability to act as a physical separator between the two

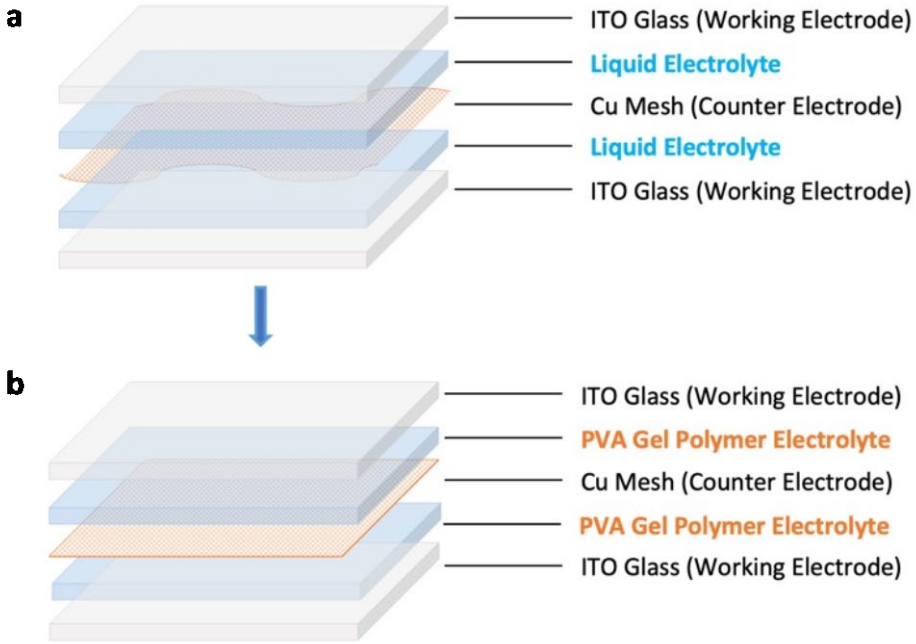

Figure 1. Schematic diagram of dual-working electrode windows with liquid electrolyte (a) and PVA gel polymer electrolyte (b).

electrodes to help avoid short-circuiting[16, 17]. For this study, a porous polyvinyl alcohol (PVA) gel polymer electrolyte (GPE) is synthesized as a physical separator where the polymer backbone provides the mechanical structure and the pores are filled with BiCu ClO_4 liquid electrolyte, which will strongly dictate the ionic conductivity of the porous GPE system. To build strong three-dimensional porous PVA frameworks to infill with aqueous electrolyte, physical crosslinking is induced by "freeze" (5^0C) -thaw (25^0C) phase separation cycles to form PVA gel crystallites[18, 19, 20]. To synthesize highly-transparent PVA gels, dimethyl sulfoxide (DMSO) is incorporated as a water-miscible cosolvent in addition to H_2O for PVA precursors as shown in other work[18]. DMSO is an attractive choice as a cosolvent as it is miscible with water and has different hydrogen bonding properties than water[21]. When the weight ratio of DMSO: H_2O is over 2:1 in the co-solvent, hydrogen bonds formed between DMSO and PVA limit the growth of PVA crystalline regions,

resulting in a small volume of crystallites and thus a very high transparency in gels[22]. As such, the ratio was varied and finally, we found 80 to 20 DMSO to H_2O gave the highest transparency gel (98%), which is the ratio used in our GPE windows (**Fig. S1**). This high-transparent physically cross-linked PVA gel was implemented into RME dynamic windows (PVA GPE window), and the PVA GPE window can readily be tinted to below 0.1% visible light transmittance, exhibits color-neutral transmittance, and has similar coloration efficiency with liquid windows (mean value: 18.4 cm^2/C for PVA GPE window, 18.8 cm^2/C for liquid window, to 0.1% transmission).

Importantly, the use of PVA GPE in windows provides opportunities for dual-working electrode (dual-WE) windows without short circuiting. Dual-WE windows are made by incorporating a second piece of ITO-glass and integrating the Cu mesh counter electrode within the electrolytic matrix to the center layer of the window**.** Compared with single-WE windows, dual-WE windows are more susceptible to short circuits because there is a higher potential for the middle free-standing mesh to touch the working electrodes, as shown in **Fig 1.a**. Substituting liquid electrolyte with GPE as the physical separator prevents short-circuiting without losing significant transmittance in this dual-WE device architecture (**Fig 1.b**). With this new device architecture, we can plate metal on either sheet of ITO separately or tint both sheets of ITO at the same time. If the metal is viewed through the ITO, the light encounters a smooth ITO-metal interface and looks like a mirror. If instead it is viewed from the other side, the light interacts with the rough top surface of the metal film, causing strong absorption and a less shiny appearance[23]. Thus, occupants can choose to tint either side of the dual-WE PVA GPE window to the same transmittance but get an absorptive or reflective visual effect according to their needs. By tinting both sides of ITOs at the same time, dual-WE PVA GPE dynamic windows shows fast switching speed.

2. Materials and methods

Liquid Electrolyte Preparation

Chemicals were bought and used without purification. The electrolyte used for RME consisted of 10 mM $Cu(ClO_4)_2 \cdot 6H_2O$ (ACROS Organics), 10 mM $BiOClO_4 \cdot H_2O$ (GFS Chemicals), 10 mM $HClO_4$ (Alfa Aesar), 1 M $LiClO_4 \cdot 3H_2O$ (ACROS Organics) with 0.1 w/v% PVA (31,000-50,000 g/mol, 97% hydrolyzed, Aldrich) additive. PVA was added last and stirred at 1200 rpm and 60-70°C until dissolved, about 1 hour.

PVA Gel Polymer Electrolyte Preparation

10wt% 89-98k PVA (99% hydrolyzed) was added to wt. 80:20 DMSO: H_2O solvent, dissolved by stirring at 90^0C for 2 hours, and processed under the two freeze-thaw cycles under vacuum to make PVA gels. After the freeze-thaw cycling, PVA gels are stirred in three separate fresh DI water bathes for 1h and then soaked in DI water for another 24h to remove extra DMSO to form PVA hydrogels. Then they were directly soaked in baths of BiCu ClO_4 with 0.1wt% PVA additive electrolyte for 24 h to replace water in the hydrogel with enough liquid electrolyte to get PVA gel polymer electrolyte (GPE)

Pt-modified ITO working electrode preparation

Indium tin oxide (ITO) on glass substrates (Xinyan Technology Ltd, sheet resistance of 10 $\Omega \square^{-1}$) were cleaned by sonication in 10% Extran in DI water solution, pure DI water, acetone, then isopropyl alcohol for 15 minutes each. After, the substrates were dried with N_2 then cleaned in a UV-Ozone cleaner for 15 minutes. The ITO was then placed in a 10 mM 3-mercaptopropionic acid in ethanol solution and placed on a shaker for 24 hours. The ITO substrates were then rinsed with ethanol then water before being placed in a Pt-nanoparticle solution (Sigma Aldrich) diluted 1:19

with DI water and placed on a shaker for 24-72 hours. The substrates were then rinsed with DI water, dried with N_2, then annealed at 250℃ for 25 minutes before use.

RME Dynamic Window Fabrication

PVA Additive Liquid Window：Two-electrode devices used Pt-modified ITO on glass substrates (Pt-ITO) as a working electrode and a metal counter electrode. Butyl rubber edge seal (Quanex: Solargain edge tape LP03, 1.5 mm thickness) separated the two electrodes and encapsulated the electrolyte between the Pt-ITO and back piece of glass. Conductive tape (Conducty Z22, ElectricMosaic) was used to make electrical contact with the working electrode.

PVA GPE Window (Sandwiched for Testing)：First, the "free-standing" PVA gel is made in a mold (made by rubber edge seal on glass substrate) and is peeled off after freeze-thaw cycling and then soaked in DI water and PVA additive liquid electrolyte in this order. The Cu mesh is adhered to the backside glass using 3M tape. Then the Cu mesh-glass with "free-standing GPE" and the ITO-glass are "sandwiched" with small clamps. The pressure provided by the clamps helps avoid potential optical problems as the PVA GPE is compressed evenly in each direction, and the contact between PVA GPE and ITO-glass will be more uniform (transmittance of the whole device ~70%). Furthermore, this method provides a convenient way to make windows. PVA gels can be cut into any size and shape fitting for different applications.

Electrochemical Characterization

Electrochemical experiments were run using a BioLogic SP-50 or SP-150 potentiostat. Three-electrode experiments used a Pt wire counter electrode and a "no-leak" Ag/AgCl (eDAQ) reference electrode. Two-electrode devices were cycled at -0.7 V until privacy state was reached for window tinting and +1.0 V until transparency was restored for window bleaching.

Optical Characterization

Ocean Optics OCEAN FX Miniature and Flame Miniature spectrometers were used in a standard configuration with an Ocean Optics halogen light source (HL-2000) for most transmission and specular reflection measurements.

Total Reflection measurements were conducted using a 135mm 819C Series Spectralon Collimated Beam integrating sphere. Remaining transmission measurements (total and diffuse transmission) were conducted using a Varian CARY 500 UV-Vis-NIR Spectrophotometer (Labsphere DRA-CA-5500) equipped with a 150 mm integrating sphere. The haze coefficient values, quantifying the amounts of scattered light, were calculated based on the total and diffused transmission measurements using the integrating sphere following the ASTM D1003 (Standard Test Method for Haze and Luminous Transmittance), commonly used for haze measurements in windows applications.

Mechanical Characterization

Hydrogels were formed at a thickness of 5 mm between glass slides and a plug was cut to a diameter of 5 mm with a biopsy punch. The diameter and height of each hydrogel plug was measured using calipers. Hydrogels were compressed to 30% strain at a rate of 10% strain/min (MTS Synergie 100). The compressive modulus (N=3) was measured from the slope of the linear region of the stress-strain curve from 10 to 15% strain.

Characterization

SEM-EDS was run using a HITACHI SU3500 scanning electron microscope operated at an accelerating voltage of 5/ 15 kV and equipped with an EDS detector.

3. Results

3.1 Single- Working Electrode PVA Gel Polymer Electrolyte Window's Performance

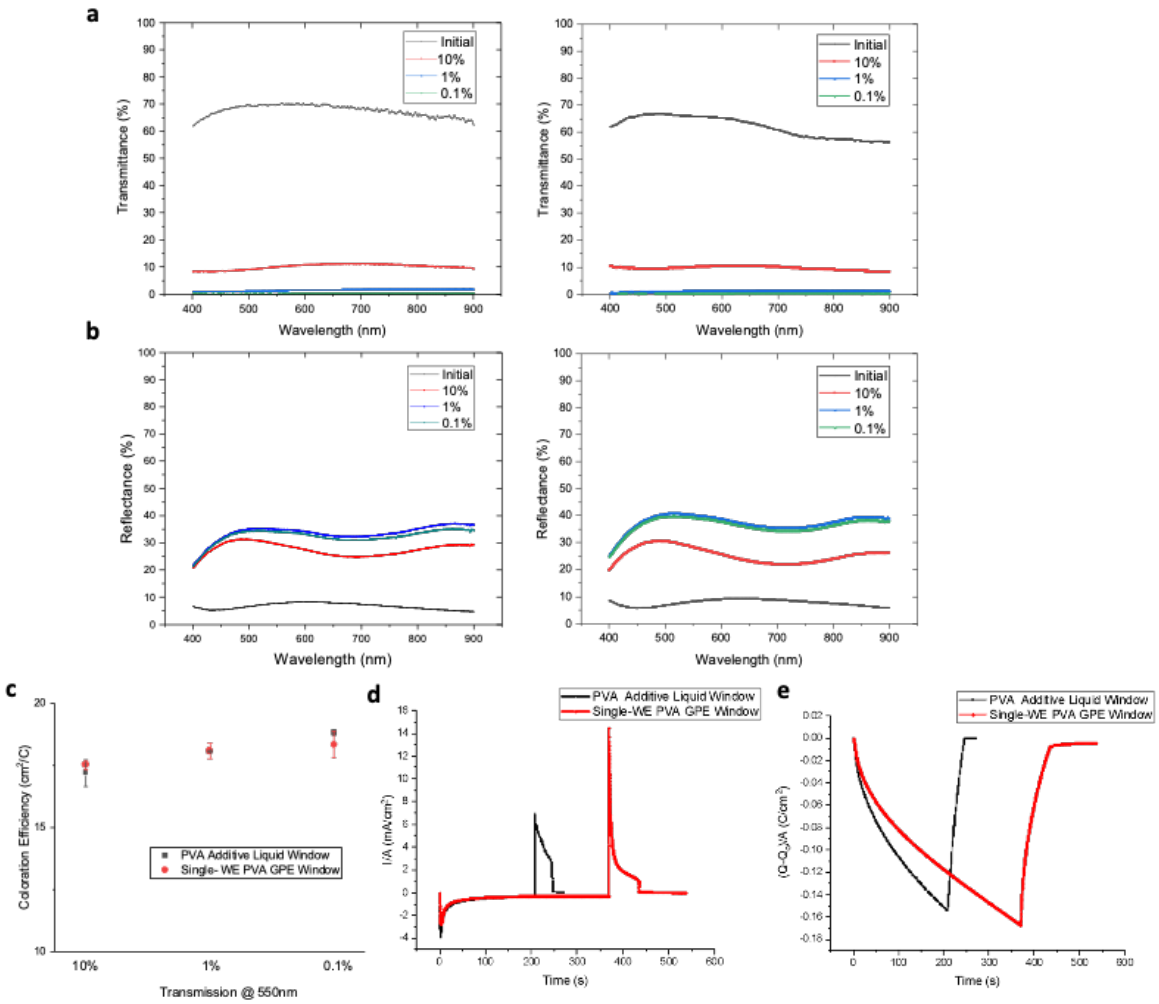

Figure 2. Comparison between liquid electrolyte window and single working electrode PVA GPE window. a, Transmission spectra of single WE PVA GPE window (left) and liquid window (right). b, Specular reflection spectra single WE PVA GPE window (left) and liquid window (right). c-e, Coloration efficiency at various window transmittance states(c), current density vs. time curve (d) and charge density vs. time curve (e) for windows using liquid electrolyte (black)

We prepared nine PVA gels with varied PVA precursor molecular weights (31-50k, 89-98k, and 146-186k) and varied PVA mass fractions in the DMSO: H_2O solutions (5wt%, 10wt%, and

20wt%) to understand the role of these variables on the GPE's properties. From the perspective of solubility of PVA precursors in DMSO: H_2O solvent and gel formation, three PVA gels are chosen for our exploration: 5wt% 146-186k, 10wt%, 89-98k, 20wt% 31-50k PVA gels (**Table S1**).

To systematically evaluate the gels in windows, we assessed the optical and mechanical properties as well as ionic conductivity for 5wt% 146-186k, 10wt% 89-98k, 20wt% 31-50k PVA GPE. Considering 10wt% 89-98k PVE GPE has the largest Young's modulus (148kPa), low haze (2.0%), and high ionic conductivity (liquid electrolyte filling 91%), it is chosen as the suitable material to be implemented into our windows. Details are noted in SI GPE choice section, including **Fig. S4-8**.

After selecting the 10 wt% 89-98k PVA GPE as the most suitable material, we implemented it into our RME dynamic window in the "sandwiched" way where freestanding PVA GPE is clamped between the two electrodes for testing.

3.1.1 Comparable Optical and Electrochemical Performance with Liquid Windows

The transmission and specular reflection spectra show the comparable optical behaviors of single-WE PVA GPE window and 0.1wt% PVA additive liquid window (**Fig. 2.a, b**, in each left as GPE windows and right as liquid windows). Coloration efficiency, current and charge density vs. time curves for the single-WE PVA GPE window are plotted in **Fig. 2.c, d, e**. Single-WE PVA GPE window has similar coloration efficiency as the 0.1wt% PVA additive liquid window depending on the desired contrast (**Fig. 2.c**), a further testament to the suitability of this gel in an RME dynamic window. The charge density vs. time curve (**Fig 2.e**) shows that the tinting speed of single-WE PVA GPW windows is slower than PVA-additive liquid windows, which can be explained by the lower ionic conductivity of GPE compared with pure liquid electrolyte.

3.1.1 Morphologies of Metal Deposits

Fig. 3 shows SEM images of Cu-Bi metal deposition on ITO at the state of 10%, 1%, 0.1% transmittance. The images show that the diameter of metal deposit particles gradually increases with increasing tinting time. The morphology of the metal films is similar with and without the polymer gel (**Fig. S10**). Therefore, we infer that there is probably a thin layer of electrolyte

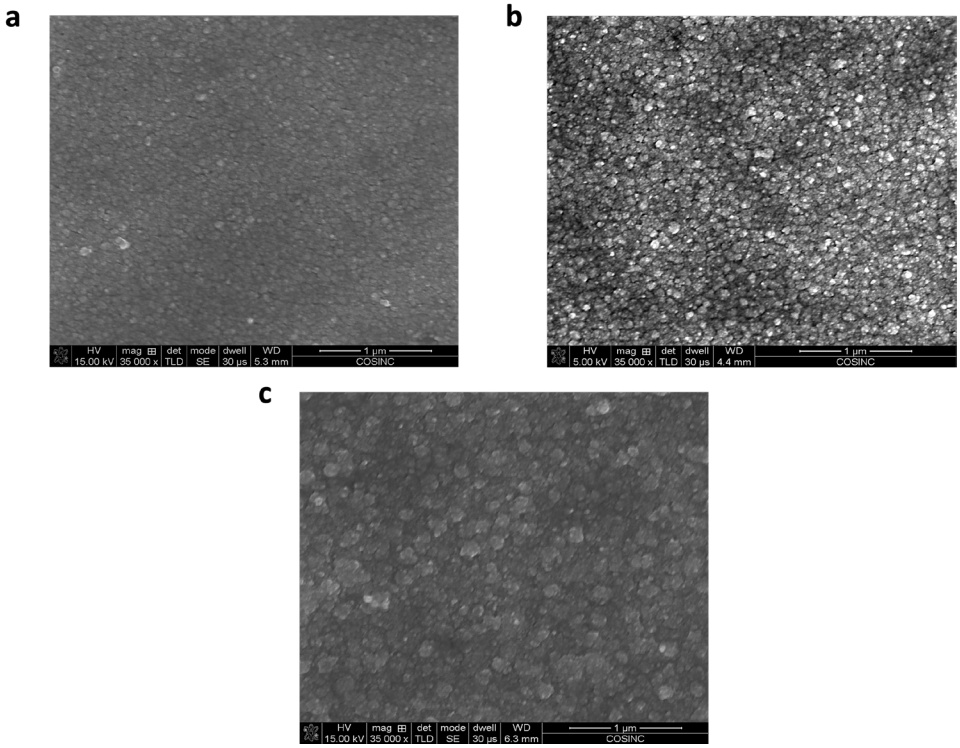

Figure 3. SEM images of Bi-Cu depositions on Pt-ITO at 10% (a), 1% (b), 0.1% (c) transmittance states for PVA GPE windows.

between the GPE and the ITO-glass electrode, which may be caused by the strong hydrophilicity of the PVA gel framework. If the metal only grows where the aperture of the GPE is in contact

with the ITO-glass, the metal deposition layer would not be as shown in the SEM image in **Fig. 3**.

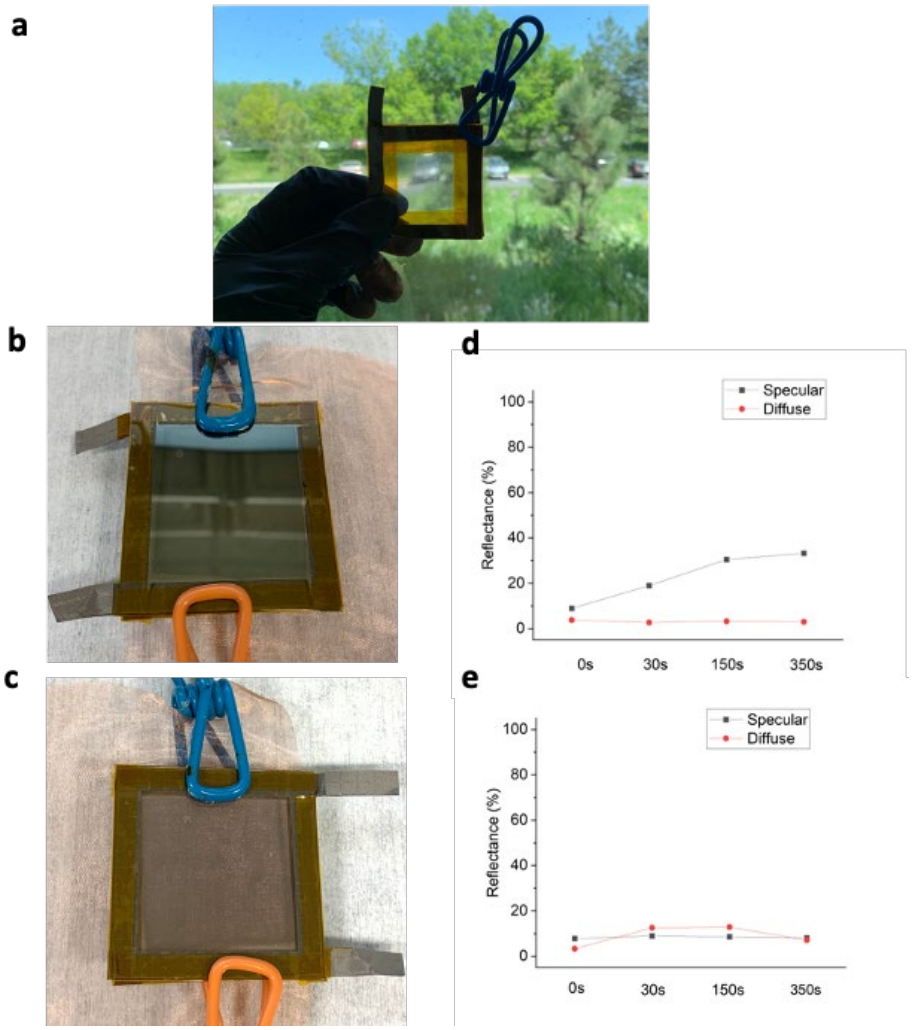

Figure 4. a, Photo of real dual-WE PVA GPE window. b, c, If only one side is tinted, the tinted side is more reflective and the untinted side is more absorptive. Photograph of the window when it has 1% transmittance at 550nm from the tinted (b) and untinted side (c). Specular and diffuse reflectance from the tinted (d) and untinted side (e) at initial, 10%, 1%, 0.1% transmission states.

3.2 Dual-Working Electrode PVA Gel Polymer Electrolyte Window's Performance

3.2.1 Different Optical Performance by Tinting One Side of the GPE Window

As stated above, substituting liquid electrolytes with GPE as the physical separator prevents short-circuiting in the dual-WE device architecture. **Fig. 4.a** shows a fully assembled dual-WE PVA GPE window with two pieces of ITO-glass working electrodes and one Cu mesh counter electrode in the middle. With this new device architecture, we can tint either side of ITO separately or tint both sides of ITO at the same time. By only tinting one side of the ITO, we can get different visual effects from two sides of the window. If the front side ITO is tinted, we can clearly see that the front side of our window is more reflective (**Fig. 4.b**) (looking directly at the plated film), while the back side of the device is more absorptive (**Fig. 4.c**). If the back side ITO is tinted only, the visual effects will be switched. **Fig. 4.d** and **Fig. 4.e** show the specular and diffuse reflectance of a dual-WE PVA GPE window from the front and the back side, respectively, with the front side ITO-glass tinted. The higher the proportion of diffuse reflectance in the total reflectance, it will be more absorptive.

3.2.2 Faster Switching Speed by Tinting Both Sides of the GPE Window and Durability Test

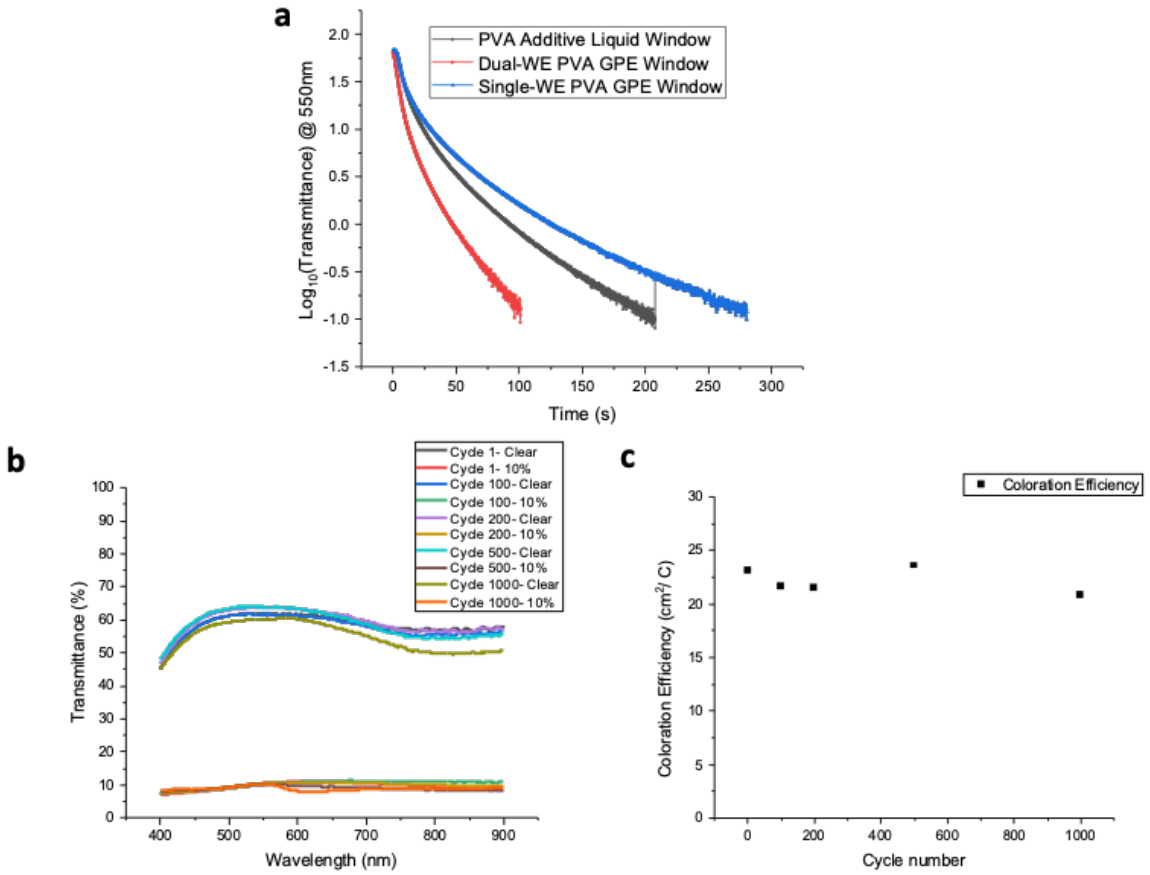

Figure 5. a, Log_{10}(transmittance) versus time curve for PVA additive liquid window, single-WE PVA GPE window and dual-WE PVA GPE window. b, c, Performance of a sealed dual-WE PVA GPE window over 1000 cycles. Transmission spectra of clear and 10% transmission states (a) and coloration efficiency (b).

Fig. 5.a shows these three windows' transmittance at 550 nm vs. time curves until they reach the privacy state, where we can see dual-WE GPE window switch the fastest. To reach the privacy (0.1% transmission) state, the liquid window takes 205 s, and the single-WE PVA GPE window takes 355 s in average, which is 73% slower. For dual-WE PVA GPE window, it takes only 106 s in average to reach the privacy state, which is double the tinting speed of liquid windows.

To test the durability of PVA GPE windows, dual-WE PVA Gel Window was sealed with rubber and silicone and cycled to 10% transmittance at 550 nm. Transmission spectra and coloration efficiency are plotted over cycling, as shown Fig. 5.c, showing the comparable electrochemical behaviors of these windows over 1000 cycles.

4 Discussion

In this manuscript we have shown that a physically cross-linked polyvinyl alcohol polymer gel can be used to improve dynamic windows based on reversible metal electrodeposition. Using the gel polymer instead of an aqueous electrolyte causes a minimal increase in haze and only slows down the window by a factor of approximately 1.7 due to the reduced conductivity of the metal ions in the polymer gel matrix compared to its fully liquid counterpart. The gel circumvents failure due to hydrostatic pressure and leakage. We also showed that gels can be used as a separator in order to fabricate a dual working electrode window with a copper mesh counter electrode in the middle to prevent short-circuiting. The dual working electrode windows switch approximately twice as fast. Furthermore, having two working electrodes enable a tinted window with two different optical properties: one with higher specular reflection or one with higher absorption and some diffuse reflection. Finally, we observed 1000 cycles with a dual working electrode PVA gel polymer electrolyte window.

ACKNOWLEDGEMENT

This research was funded by the National Science Foundation (NSF) under award number 2127308. The authors would like to thank Lori Postak from Quanex for providing the Solargain

butyl rubber edge tape. The authors would like to thank Isaac Gould and Jay Patel for assisting with the diffuse reflection experiments that are shown in Fig. 6.c, d.

This research was supported in part by the Colorado Shared Instrumentation in Nanofabrication and Characterization (COSINC): the COSINC-CHR (Characterization) and/or CONSINC-FAB (Fabrication), College of Engineering & Applied Science, University of Colorado Boulder. The authors would like to acknowledge the support of the staff (Tomoko Borsa) and the facility that have made this work possible.

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Competing Interests

Tyler Hernandez and Michael McGehee are cofounders of Tynt Technologies.

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