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EDITED BY
Zhen Wang,
Hainan University, China

REVIEWED BY
Wu Zhang,
University of Alberta, Canada
Xueqing Tang,
Suzhou Institute of Nano-Tech and Nano-Bionics (CAS), China

*CORRESPONDENCE
Michael D. McGehee,
michael.mcgehee@colorado.edu

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Gel polymer electrolyte for reversible metal electrodeposition dynamic windows enables dual-working electrodes for faster switching and reflectivity control

Yuchun Cai[1,2], Tyler S. Hernandez[1,3], Andrew L. Yeang[1], Michael T. Strand[1,4], F. Max Yavitt[1,5], Eldho Abraham[6] and Michael D. McGehee[1,7,8]*

[1]Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, CO, United States, [2]Department of Chemistry, University of Colorado Boulder, Boulder, CO, United States, [3]Department of Chemistry, Stanford University, Stanford, CA, United States, [4]Department of Materials Science and Engineering, Stanford University, Stanford, CA, United States, [5]BioFrontiers Institute, University of Colorado Boulder, Boulder, CO, United States, [6]Department of Physics, University of Colorado Boulder, Boulder, CO, United States, [7]Materials Science and Engineering Program, University of Colorado Boulder, Boulder, CO, United States, [8]National Renewable Energy Laboratory, Golden, CO, United States

Dynamic windows based on reversible metal electrodeposition are an attractive way to enhance the energy efficiency of buildings and show great commercial potential. Dynamic windows that rely on liquid electrolytes are at risk of short circuiting when two electrodes contact, especially at larger-scale. 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 is implemented into windows that exhibit comparable electrochemical and optical properties to windows using a liquid electrolyte. Furthermore, the GPE enables the fabrication of windows with dual-working electrodes (WE) and a metal mesh counter electrode in the center without short-circuiting. 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 building systems with greater control over the appearance and performance of the windows in a single device architecture.

KEYWORDS

dynamic window, reversible metal electrodeposition, gel polymer electrolyte, electrochromic, dual-working electrode, poly(vinyl alcohol)

1 Introduction

Dynamic windows tune visible light and heat flow while maintaining views, thereby saving 10%–20% of energy for buildings and vehicles over static low emissivity coatings (Eleanor et al., 2004; Sbar et al., 2012). In addition to energy savings, a study has shown that occupants in office buildings with dynamic windows will be healthier, happier and more productive (Hedge and Nou, 2018). By reducing glare and optimizing both the temperature and light flow in an indoor work environment, employee productivity can increase by up to 2% (Prnewswire, 2018). Currently there are many technologies using electrochromic oxides and organic molecules to tune the color and transmission of the window (Barile et al., 2017). 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 (Barile et al., 2017; Jeong et al., 2017; Hernandez et al., 2018; Strand et al., 2018; Hernandez et al., 2020; Eh et al., 2020; Kimura et al., 2020; Poh et al., 2021; Guo et al., 2022; Kimura et al., 2022; Song et al., 2022; Tao et al., 2022). These windows operate by the reversible electrodeposition of metals ions, e.g., 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 (Hernandez et al., 2018; Strand et al., 2018). Recently, we reported poly (vinyl) alcohol as a growth inhibitor to reversibly deposit metal films with more uniform morphology (Hernandez et al., 2020). Previously, the electrolyte implemented in these windows consisted of Bi^{3+} and Cu^{2+} ions in an liquid, aqueous ClO_4^- based electrolyte (Hernandez et al., 2020).

Though aqueous liquid electrolytes often have higher ionic conductivities than ones with high polymer content (Alesanco et al., 2018), dynamic windows with liquid electrolytes face problems including 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 electrodes to avoid short-circuiting (Luo et al., 2015; Alipoori et al., 2020). For this study, a crosslinked porous polyvinyl alcohol (PVA) gel polymer electrolyte (GPE) is synthesized as a physical separator where the polymer backbone provides mechanical structure. The pores are filled with BiCu ClO_4 liquid electrolyte which dictates ionic conductivity based on concentration. To build strong three-dimensional porous PVA frameworks to infill with aqueous electrolyte, physical crosslinking is induced by "freeze" (5°C) -thaw (25°C) phase separation cycles to form PVA gel crystallites (Hassan and Peppas, 2000; Lozinsky, 1998)' (Hyon et al., 1989). As previously demonstrated, dimethyl sulfoxide (DMSO) is an attractive choice as a cosolvent with H_2O to synthesize highly-transparent PVA gels due to its miscibility with water and distinct hydrogen bonding properties (Hassan and Peppas, 2000; Hou et al., 2015). When the weight ratio of DMSO: H_2O is over 2:1, 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 (Kanaya et al., 2012). As such, the optimized ratio used in our GPE windows was 4:1 DMSO: H_2O (weight percent ratio) which results in the highest transparency gel (98%) (Supplementary Figure S1). This high-transparent physically cross-linked PVA gel was implemented into RME dynamic windows (PVA GPE window), and the PVA GPE window can be tinted below 0.1% visible light transmittance, exhibits color-neutral transmittance, and has a comparable coloration efficiency to that of 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).

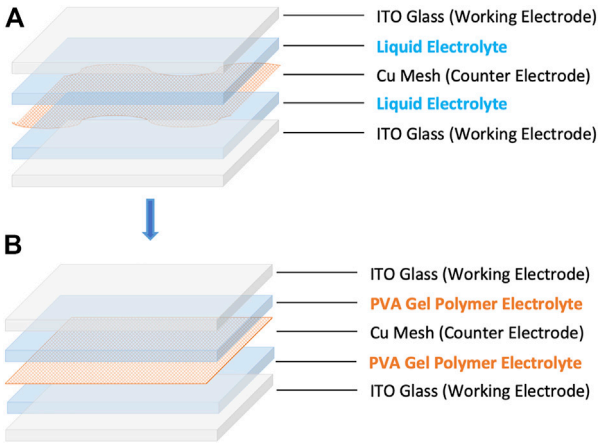

FIGURE 1
Schematic diagram of dual-working electrode windows with liquid electrolyte **(A)** and PVA gel polymer electrolyte **(B)**.

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 Figure 1A. Substituting the liquid electrolyte with GPE as the physical separator prevents short-circuiting without losing significant transmittance in this dual-WE device architecture (Figure 1B). With this new device architecture, we can plate metal on either sheet of ITO separately or tint both sheets of ITO simultaneously. Metal viewed through the ITO appears mirrorlike as the light encounters a smooth ITO-metal interface. 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 matte appearance (Strand et al., 2021). 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. Further, by tinting both sides of ITOs at the same time, dual-WE PVA GPE dynamic windows exhibit fast switching speed.

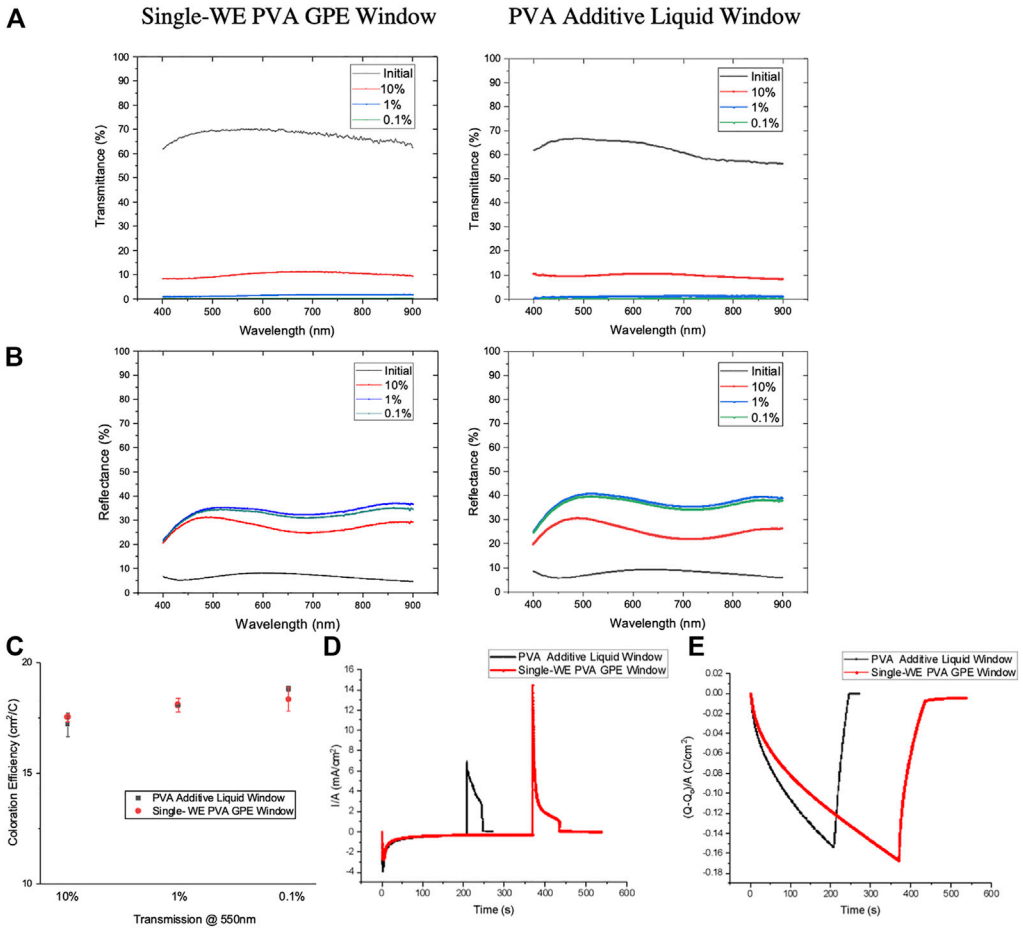

FIGURE 2
Comparison between liquid electrolyte window and single working electrode PVA GPE window. **(A)**, Transmission spectra of single-WE PVA GPE window (left) and liquid window (right). **(B)**, Specular reflection spectra single WE PVA GPE window (left) and liquid window (right). **(C–E)**, Coloration 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) and PVA GPE (red).

2 Materials and methods

2.1 Liquid electrolyte preparation

Chemicals were bought and used without purification. The electrolyte used for RME consisted of 10 mM $Cu(ClO_4)_2 \bullet 6H_2O$ (ACROS Organics), 10 mM $BiOClO_4 \bullet H_2O$ (GFS Chemicals), 10 mM $HClO_4$ (Alfa Aesar), 1 M $LiClO_4 \bullet 3H_2O$ (ACROS Organics) with 0.1 w/v% PVA (31,000–50,000 g/mol, 87% hydrolyzed, Aldrich) additive. PVA was added last and stirred at 1200 rpm and 60–70°C until dissolved, about 1 h.

2.2 PVA gel polymer electrolyte preparation

10 wt% 89–98 k PVA (99% hydrolyzed) was added to wt. 80: 20 DMSO: H_2O solvent, dissolved by stirring at 90°C for 2 h, 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 baths for 1h, and then soaked in DI water for another 24 h 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 the water in the hydrogel with enough liquid electrolyte to get PVA gel polymer electrolyte (GPE).

2.3 Pt-modified ITO working electrode preparation

Indium tin oxide (ITO) on glass substrates (Xinyan Technology Ltd., sheet resistance of 10 Ω $\square^{-1}$) were cleaned by sonication in 10% Extran in DI water solution, pure DI water, acetone, then isopropyl alcohol for 15 min each. After, the substrates were dried with N_2 then cleaned in a UV-Ozone cleaner for 15 min. The ITO was then placed in a 10 mM 3-mercaptopropionic acid in ethanol solution and placed on a shaker for 24 h. 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 h. The substrates were then rinsed with DI water, dried with N_2, then annealed at 250°C for 25 min before use.

2.4 RME dynamic window fabrication

PVA Additive Liquid Window: Two-electrode devices used Pt-modified ITO (5 cm^2 × 5 cm^2) on glass substrates (Pt-ITO) as a working electrode and a Cu 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 the 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 a 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 3 M tapes. Then the Cu mesh-glass with "free-standing GPE" and the ITO-glass (5 cm^2 × 5 cm^2) are "sandwiched" with small clamps. The pressure provided by the clamps avoids potential optical problems as the PVA GPE is compressed evenly in each direction, and the contact between PVA GPE and ITO-glass (5 cm^2 × 5 cm^2) 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.

PVA GPE Window (Device with Sealings for Durability Testing): First, the PVA gel is made in the half-device architecture with Cu mesh, rubber edge seals, and the backside glass through freeze-thaw cycling. And the half device is soaked in DI water and PVA additive liquid electrolyte in this order. The ITO-glass is then compressed onto the half device to seal by rubber edge seals. Silicone seals are used for additional secure sealing.

2.5 Electrochemical characterization

Electrochemical experiments were run using a BioLogic SP-50 or SP-150 potentiostat. Two-electrode devices were cycled at −0.7 V until the privacy state was reached for window tinting and +0.7 V until transparency was restored for window bleaching.

2.6 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 135 mm 819C Series Spectralon Collimated Beam integrating sphere. The 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.

2.7 Mechanical characterization

Hydrogels and GPEs 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/GPE plug were measured using calipers. Hydrogels/GPEs 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.

2.8 Other characterization

Scanning Electron Microscopy-Energy Dispersive Spectroscopy (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.

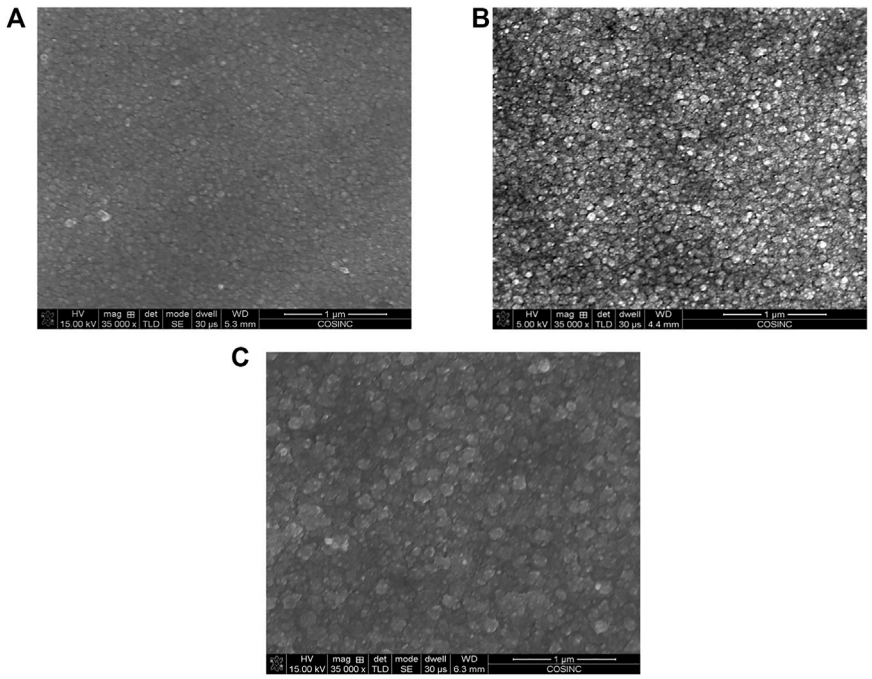

FIGURE 3
SEM images of Bi-Cu depositions on Pt-ITO at 10% **(A)**, 1% **(B)**, 0.1% **(C)** transmittance states for PVA GPE windows.

3 Results

3.1 Single-working electrode PVA gel polymer electrolyte window's performance

To synthesize a gel polymer electrolyte with acceptable haze, proper mechanical strength and ionic conductivity, we prepared nine PVA gels with varied PVA precursor molecular weights (31–50 k, 89–98 k, and 146–186 k) and varied PVA mass fractions in the DMSO: H_2O solutions (5 wt%, 10 wt%, and 20 wt%). Considering the solubility limit of PVA precursors in DMSO: H_2O solvent and gel formation, we chose three PVA gels for the exploration: 5 wt% 146–186 k, 10 wt%, 89–98 k, 20 wt% 31–50 k PVA gels (Supplementary Table S1).

To systematically evaluate the gels in windows, we assessed the optical and mechanical properties as well as ionic conductivity for 5 wt% 146–186 k, 10 wt% 89–98 k, 20 wt% 31–50 k PVA GPE. Considering 10 wt% 89–98 k PVA GPE has the largest Young's modulus (148 kPa), low haze (2.0%), and high ionic conductivity (liquid electrolyte filling 91%), it was chosen as the suitable material to be implemented into our windows. Details are noted in SI GPE choice section, including Supplementary Figures S2–S9.

After selecting the 10 wt% 89–98 k PVA GPE as the most suitable material, we implemented it into our RME dynamic window in a "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

To evaluate the selected GPE's performance, its optical and electrochemical behaviors were characterized and compared with liquid windows. The transmission and specular reflection spectra show the comparable optical behaviors of single-WE PVA GPE window and 0.1 wt% PVA additive liquid window (Figures 2A,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 Figures 2C–E. Single-WE PVA GPE window has similar coloration efficiency as the 0.1 wt% PVA additive liquid window depending on the desired contrast (Figure 2C), a further testament to the suitability of this gel in an RME dynamic window. The charge density vs. time curve (Figure 2E) shows that the tinting speed of single-WE PVA GPE windows is slower than PVA-additive liquid windows, which can be explained by the lower ionic conductivity of GPE compared with pure liquid electrolyte.

3.1.2 Morphologies of metal deposits

We used SEM to characterize the metal film morphology in a PVA GPE window at different tinting states. Figure 3

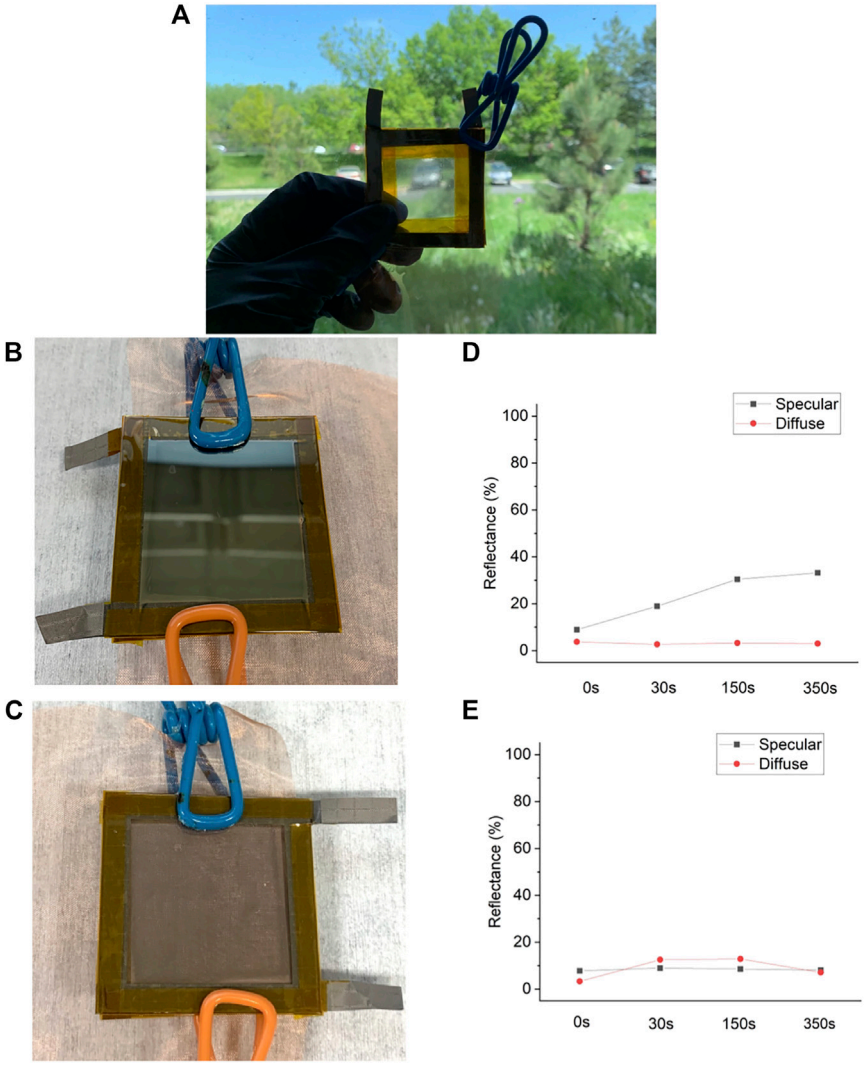

FIGURE 4
(A) Photo of a real dual-WE PVA GPE window. **(B,C)** If only one side is tinted, the tinted side is more reflective and the untinted side is more absorptive. Photograph of the window when it has 1% transmittance at 550 nm from the tinted **(B)** and untinted side **(C)**. Specular and diffuse reflectance from the tinted **(D)** and untinted side **(E)** at initial, 10%, 1%, 0.1% transmission states.

shows SEM images of Bi-Cu metal deposition on ITO at the state of 10%, 1%, 0.1% transmittance of a single-WE PVA GPE window. 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 (Supplementary Figure S10). Therefore, we infer that there is probably a thin layer of electrolyte 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 Figure 3.

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. Figure 4A 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. In fact, the

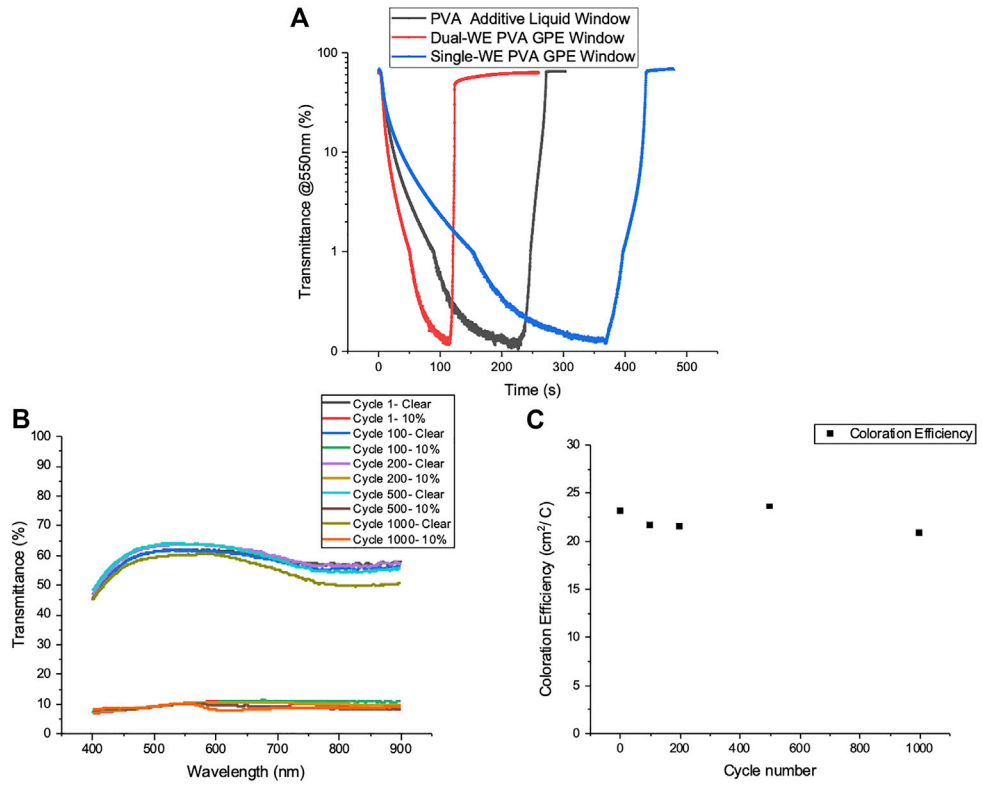

FIGURE 5
(A) Transmittance at 550 nm versus time curves for PVA additive liquid window, single-WE PVA GPE window, and dual-WE PVA GPE window with symmetric logarithmic scales. **(B,C)** Performance of a sealed dual-WE PVA GPE window over 1000 cycles. Transmission spectra of clear and 10% transmission states **(B)** and coloration efficiency **(C)**.

side of ITO tinted has a strong impact on the resulting visual effect. If the front side ITO is tinted, the front side of our window will appear more reflective (Figure 4B) (looking directly at the plated film), while the back side of the device is more absorptive (Figure 4C). If only the back side ITO is tinted, these visual effects will be switched. Figures 4D,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 proportion of diffuse reflectance in the total reflectance implies a more absorptive film.

3.2.2 Faster switching speed by tinting both sides of the GPE window and durability test

PVA additive liquid windows, single-WE PVA GPE windows, and dual-WE PVA GPE windows (both sides tinted) were tinted to privacy state (0.1% transmittance at 550 nm) to compare their switching speeds. Figure 5A shows the transmittance of these three windows at 550 nm vs. time curves of a privacy cycle, where it is clear the dual-WE GPE window switch the fastest. On average it takes liquid and single-WE PVA GPE windows 205 and 355 s, respectively, to reach privacy states. The single-WE PVA GPE window is 73% slower, due to the lower ionic conductivity in the gel polymer system. However, for the dual-WE PVA GPE window it takes only 106 s on average to reach the privacy state, which is double the tinting speed of liquid windows. Detailed transmission and reflection spectra of the dual-WE PVA GPE window at initial, 10%, 1%, and 0.1% transmittance states at 550 nm are illustrated in Supplementary Figure S11.

To test the durability of PVA GPE windows, a dual-WE PVA GPE 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 in Figures 5B,C, exhibiting the consistent electrochemical behaviors of these windows over 1000 cycles.

4 Discussion

In this manuscript we have shown that a physically cross-linked poly (vinyl 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. In addition, the gel circumvents failure due to hydrostatic pressure and leakage. We also showed that gels can be used as a separator to prevent short-circuiting for dual-working electrode windows with a copper mesh counter electrode in the middle. The dual working electrode windows switch approximately twice as fast. Furthermore, having two working electrodes enable a tinted window to achieve different optical properties: one with higher specular reflection or one with higher absorption and some diffuse reflection. Finally, we observed 1000 transmission cycles with a dual working electrode PVA gel polymer electrolyte window.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

Author contributions

YC: Writing–original draft, writing–review and editing, validation, conceptualization, investigation, methodology. TH: Writing–review and editing, validation, conceptualization, investigation, methodology. AY: investigation, validation, methodology, writing–review and editing. MS: Validation, methodology, writing–review and editing. FY: Investigation, writing–review and editing. EA: Investigation, writing–review and editing. MM: Writing–review and editing, conceptualization, funding acquisition, supervision, project administration.

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Conflict of interest

Authors TH, MS, and MM are cofounders of Tynt Technologies.

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.

Publisher's note

Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fnano.2022.1083247/full#supplementary-material

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