nature energy

ARTICLES

https://doi.org/10.1038/s41560-019-0332-3

Hybrid dynamic windows using reversible metal electrodeposition and ion insertion

Shakirul M. Islam[1], Tyler S. Hernandez[2,3], Michael D. McGehee[3] and Christopher J. Barile[1]*

Dynamic windows with electronically controlled transmission reduce glare without obstructing views while increasing the energy efficiency of buildings and automobiles via lighting, heating and cooling savings. Electrochromic materials, which change colour with voltage, are widely explored for use in dynamic windows, but they have not been extensively commercialized due to problems associated with colour, cost, switching speed and durability. Here, we develop a class of dynamic windows that combines reversible metal electrodeposition with ion insertion chemistry. These devices function through the reversible electroplating of Bi and Cu at the working electrode and Li^+ insertion in a nickel oxide counter electrode. In one minute, 100 cm^2 windows uniformly switch between a clear state with 75% transmission and a colour-neutral black state possessing 10% transmission, which represents a significant improvement over previous metal-based architectures. We demonstrate that these hybrid windows cycle at least 4,000 times without degradation and are compatible with flexible substrates. Lastly, we discuss how this approach can be used to design practical large-scale windows.

Dynamic windows, which possess electronically controlled tinting, increase both the energy efficiency and aesthetics of interior spaces in buildings and automobiles. In buildings, dynamic windows enable lighting, heating, ventilation and air conditioning (HVAC) energy savings that lead to an average reduction of 10% in energy consumption compared to static low-emissivity windows[1]. In automobiles, dynamic windows also lead to significant HVAC savings, which is particularly important in extending the driving range of battery-powered electric vehicles[2].

Over the past several decades, researchers have explored numerous dynamic window technologies. The majority of this research has focused on electrochromic materials, such as transition metal oxides, polymers and small organic molecules, which change colour upon application of a voltage[3–6]. It is difficult using these approaches, however, to simultaneously exhibit the fast switching times, colour-neutral tinting, long-term durability, and low cost needed to achieve widespread commercialization[7].

Recently, we started to explore reversible metal electrodeposition as a promising alternative to traditional electrochromic materials for dynamic windows. These windows possess minute-long switching times, a colour-neutral opaque state, cycle thousands of times without significant degradation, and represent a substantial improvement upon previous metal-based dynamic windows[8]. Dynamic windows using reversible metal electrodeposition function via the reversible electrochemical movement of metal between two electrodes. The electrolyte of these windows contains a colourless salt containing metal cations. Upon switching the device to the opaque state, electrochemical reduction of the metal cations to a solid thin film of elemental metal occurs at a transparent conducting cathode, such as tin-doped indium oxide (ITO) on glass. Pt nanoparticles appended to the ITO substrate via a self-assembled monolayer (SAM) serve as metal nucleation sites that allow metals to electrodeposit uniformly across 25 cm^2 electrodes[9]. Oxidation of a metal anode hidden behind the frame of the window balances the cathodic reaction.

A number of properties of metals make them excellent materials for use in dynamic windows. First, the high extinction coefficient of metals causes them to almost completely block visible and infrared light at thicknesses of 20–30 nm[10]. By comparison, thin films of electrochromic materials are usually 100–1,000 nm thick, which increases materials and deposition costs[11,12]. Furthermore, many metals are colour-neutral in their opaque state, as opposed to WO_3, the most common electrochromic material, which is blue when dark[13]. In addition, most metals are chemically inert, photostable, and can be electrodeposited from inexpensive and nontoxic aqueous electrolytes[14,15].

Despite these numerous promising attributes, the main challenge hindering the progress of metal-based dynamic windows is that it is difficult to electrodeposit metals uniformly over the metre-long dimensions required for practical windows. This difficulty arises in part from the fact that metal ions must diffuse laterally across great distances from the counter electrode frame to the centre of the window during electrodeposition (Fig. 1a). With this diffusion requirement, metal will preferentially electrodeposit on the edges of large-scale windows, or the switching speed of the window will have to be significantly decreased to achieve uniform tinting.

One strategy to reduce the ion diffusion lengths in metal-based dynamic windows is to incorporate a metal mesh counter electrode[16]. In this architecture, metal ions are removed from the metal mesh and electroplated onto the transparent conducting working electrode during window tinting. To ensure adequate transparency and minimize haze and diffraction patterns, the mesh lines must have a thickness of ~10 µm and a pitch of several hundred micrometres[17]. As the windows cycle, the mesh lines must grow and contract uniformly during device lightening and darkening, respectively. Furthermore, the dimensions of the initial mesh lines fabricated may limit the minimum achievable transmission of the devices.

To circumvent the complications arising from a metal mesh counter electrode, here we develop metal-based dynamic windows that harness a plane-parallel NiO counter electrode that facilitates transverse ion diffusion (Fig. 1b) via the insertion of Li ions. We

---

[1]Department of Chemistry, University of Nevada, Reno, Reno, NV, USA. [2]Department of Chemistry, Stanford University, Stanford, CA, USA. [3]Department of Chemical and Biological Engineering, University of Colorado, Boulder, CO, USA. *e-mail: cbarile@unr.edu

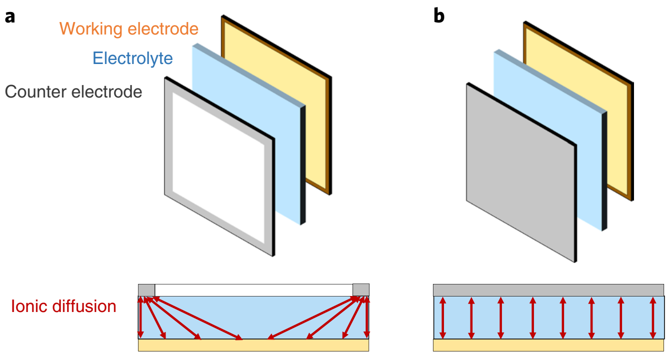

Fig. 1 | Metal-based dynamic window architectures. a,**b**, Schematic of reversible metal electrodeposition device architectures (expanded view at the top and side view at the bottom) with a metal frame around the device perimeter, which requires lateral metal ion diffusion to the centre of the window (**a**), and a plane-parallel counter electrode, which maintains constant transverse ion diffusion regardless of scale (**b**).

demonstrate that both the metal-based working electrode and the NiO counter electrode in these second-generation hybrid windows switch rapidly and uniformly between colourless and colour-neutral opaque states. Additionally, these hybrid windows are compatible with flexible substrates, cycle at least 4,000 times without degradation, and switch uniformly on the 100 cm^2 scale with an optical contrast of ~65% in one minute.

Selecting a compatible metal oxide counter electrode

Previously, we developed an aqueous electrolyte containing Cu and Bi that supports rapid and reversible electrodeposition and enables devices to switch between transparent and colour-neutral opaque states[18]. To construct a dynamic window that combines this metal-based electrolyte with the traditional insertion-based counter electrodes found in electrochromic devices, we first needed to select a counter electrode material that is compatible with the Cu–Bi electrolyte. We evaluated three different metal oxides for use in the counter electrode that are known to intercalate Li^+ in conventional electrochromic windows[12,19,20]. Using cyclic voltammetry, we assessed the durability of NiO, V_2O_5 and CeO_2 in the Cu–Bi electrolyte, which also contains a high concentration of LiBr that allows for Li^+ insertion. The voltammograms show that a thin film of CeO_2 degrades significantly within a few cycles of lithiation and delithiation (Supplementary Fig. 1a). A thin film of V_2O_5 is more stable, but still degrades substantially after 30 cycles (Supplementary Fig. 1b). In contrast, we find that thin films of NiO are stable with respect to lithiation and delithiation in the acidic (pH ~ 2) Cu–Bi electrolyte for at least 1,000 cycles (Supplementary Fig. 1c). It is known that oxides with less electronegative elements are more basic, which renders them less stable in the presence of acid[21]. The electronegativity of Ni, V and Ce follows the trend Ni > V > Ce, which directly correlates with the order of the durability of the oxides in the Cu–Bi electrolyte.

25 cm^2 hybrid dynamic windows

Having determined that NiO thin films are compatible with the Cu–Bi electrolyte, we constructed 25 cm^2 dynamic windows using ITO on glass modified with a SAM of Pt nanoparticles as the working electrode and an ITO on glass counter electrode coated with $LiNiO_x$ formed via electrodeposition. The ~200 nm-thick $LiNiO_x$ films are porous (see scanning electron micrograph/energy dispersive X-ray (SEM-EDX) data in Supplementary Fig. 2), allowing for rapid and sufficient Li^+ insertion. Thinner or thicker films produced less than optimal optical properties (Supplementary Fig. 3). These windows possess initial transparencies of about 65–75% across the visible spectrum (Fig. 2a, black line). This initial visible transparency is comparable to standard low-emissivity glass windows and higher than currently commercialized dynamic windows[22]. On applying −2.5 V to a device, the transmission of the window decreases to about 6% within 60 s and returns to its original transparency within 90 s when the voltage is switched to 0 V (Fig. 2b and Supplementary Fig. 4). The differences in cell potentials between the working and counter electrodes when the window is in its dark state establish a nonzero open-circuit potential, which allows for switching the device to clear to occur at 0 V. Importantly, after tinting the device using −2.5 V, the device can be held at any desired intermediate transparency by applying a voltage of −0.55 V, and the average amount of power required to keep the device at any tinted state is very low (2.7 $W m^{-2}$, Supplementary Fig. 5). Moreover, the transmission profile during switching is relatively flat over the visible part of the spectrum, which gives rise to an aesthetically pleasing clear-to-grey-to-black transition. Furthermore, the transmission spectra demonstrate that the windows also effectively modulate infrared light (Supplementary Fig. 6), which makes them useful for controlling the flow of heat in and out of spaces such as buildings and automobiles. Although smooth metal films have a mirror appearance, the windows appear black in their opaque state due to the morphology of the metal electrodeposits[18]. The electrodeposits consist of rough features on the nanometre scale, which by broadening plasmon absorption and promoting light trapping enhance absorption relative to reflection and result in a black opaque state. The performances of the windows using either a Cu–Bi liquid electrolyte (Supplementary Fig. 7) or a Cu–Bi gel-like electrolyte (Fig. 2) that contains hydroxyethylcellulose to increase solution viscosity (9.5 Pa-s) are similar, which is important because a viscous electrolyte is needed to manufacture practical, well-sealed dynamics windows.

We next assessed the durability of metal-based NiO hybrid dynamic windows. Supplementary Fig. 8 illustrates that the difference between the maximum and minimum transmission of a device during switching degrades over the course of 100 cycles from about 75% to about 60% due to side reactions of metal electrodeposition occurring on the counter electrode. During cycling, the transparency of the NiO-coated ITO counter electrode decreases, and the electrode visibly greys. When 0 V is applied to turn the window clear, lithiation of NiO occurs on the counter electrode, but some Cu and Bi electrodeposition also occurs on top of the NiO, as evidenced by SEM-EDX analysis (Supplementary Fig. 9), which diminishes the maximum transparency of the window during cycling.

To improve the durability of the hybrid dynamic windows, we developed a strategy to impede metal electrodeposition on the counter electrode. We explored using metal electrodeposition inhibitors, which bind to metal ions and decrease electrodeposition kinetics[23,24]. In particular, we spin-coated a ~450 nm-thick thin film of N_5-benzyl-1H-1,2,4-triazole-3,5-diamine (BTD) on the NiO counter electrode, since triazoles are well known to be potent Cu electrodeposition inhibitors[25]. We selected BTD (Fig. 3a) as the metal inhibitor to protect the NiO, since it is transparent, it forms a porous film (as shown in the SEM image in Supplementary Fig. 10) permeable to Li^+ ions, and its hydrophobic benzyl group renders it insoluble in the aqueous Cu–Bi electrolyte. Cyclic voltammetry data demonstrate that the addition of a BTD overlayer significantly increases the overpotential and decreases the current density for Cu and Bi electrodeposition on a NiO-coated ITO electrode (Fig. 3b). These results show that a BTD thin film decreases the kinetics of electrodeposition on NiO surfaces, and hence should limit the extent to which metal electrodeposition occurs as a side reaction on the NiO counter electrode in two-electrode systems, thus increasing the durability of hybrid dynamic windows (Fig. 3a). Indeed, metal-based dynamic windows containing BTD-coated NiO on ITO counter electrodes switch without significant change in contrast ratio over the course of 4,000 cycles (Fig. 3c).

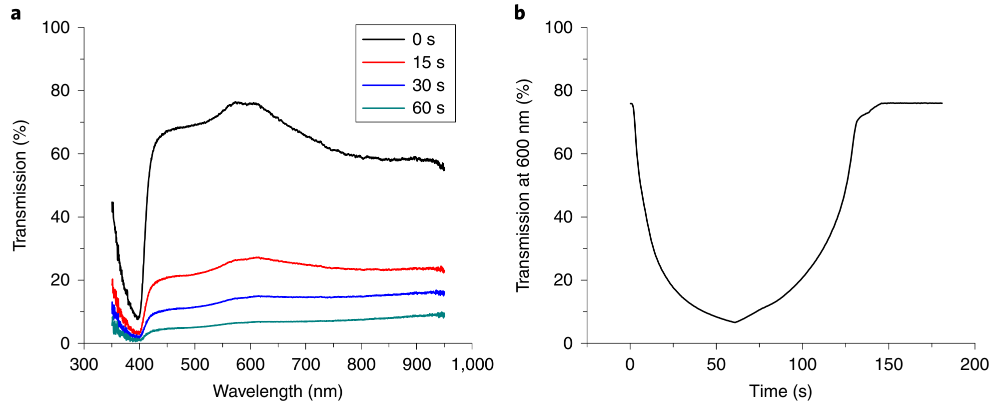

Fig. 2 | Transmission profile of 25 cm^2 hybrid dynamic window. **a**, Transmission of a 25 cm^2 dynamic window with a Pt-modified ITO on glass working electrode, a LiNiO$_x$ on ITO on glass counter electrode formed using electrodeposition, and a Cu–Bi gel electrolyte as a function of wavelength after 0 s (black), 15 s (red), 30 s (blue) and 60 s (teal) of window tinting at −2.5 V. **b**, Transmission of the same window at 600 nm during 60 s of metal electrodeposition at −2.5 V and 120 s of metal stripping at 0 V.

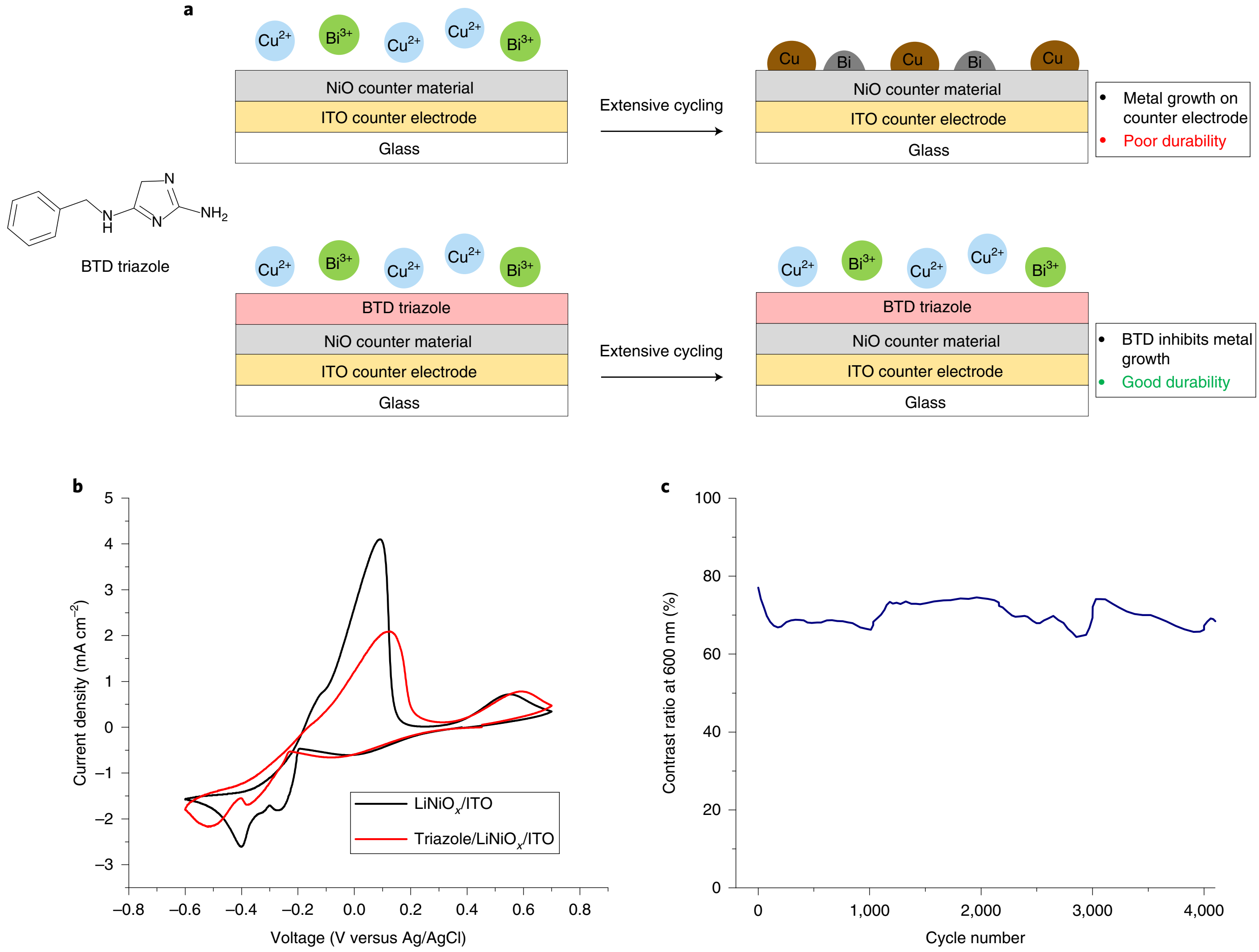

Fig. 3 | A metal inhibitor on LiNiO$_x$ improves device durability. **a**, Schematic of LiNiO$_x$ counter electrode in a metal-based dynamic window after extensive cycling. Cu^{2+} and Bi^{3+} metallic ions (blue and green, respectively) are reduced to Cu^0 and Bi^0 solid metal (brown and grey, respectively) on the surface of the unmodified LiNiO$_x$ (top). When the LiNiO$_x$ counter electrode is modified with BTD, a triazole-based metal inhibitor, metal deposition does not occur on the LiNiO$_x$, which improves device durability (bottom). **b**, Cyclic voltammograms of LiNiO$_x$ (black) and BTD-coated LiNiO$_x$ (red) on ITO on glass in a three-electrode cell with a Cu–Bi liquid electrolyte at a scan rate of 50 mV s^{-1}. **c**, Contrast ratio of dynamic window with a Pt-modified ITO on glass working electrode and a BTD-coated LiNiO$_x$ on ITO on glass counter electrode over the course of 4,000 cycles.

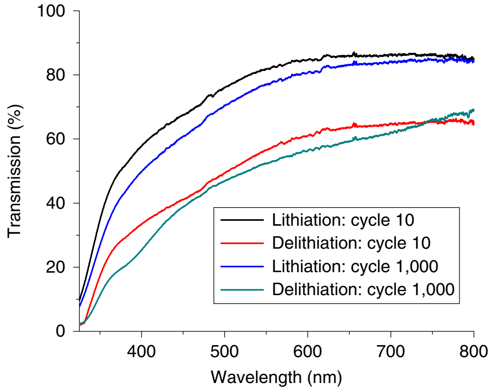

Fig. 4 | Transmission of LiNiO$_x$ during lithiation and delithiation. Transmission of a 200-nm-thick NiO film on an ITO on glass working electrode in a three-electrode cell using a 1 M LiBr electrolyte. A voltage of −0.01 V was applied for 180 s to lithiate the electrode and 0.67 V was applied for 60 s to delithiate the electrode.

As discussed previously, to develop large-scale windows in which metal ions diffuse transversely as opposed to laterally, the counter electrode must be oriented parallel to the plane of the working electrode. Previous approaches to achieving this orientation have relied upon the oxidation of Br^- to Br_3^- on a bare transparent conducting oxide as the counter electrode reaction[26]. However, this strategy is unsuitable with an aqueous electrolyte because Br_3^- causes the electrolyte to turn yellow during cycling (Supplementary Fig. 11). Hence, we predicted that the presence of a NiO thin film on the counter electrode could allow for Li^+ insertion to occur as a more suitable counter electrode reaction. NiO thin films have been previously shown to electrochromically cycle in Li-containing electrolytes through a two-step process[27–31]. The first step involves an initial 'activation' of the material followed by reversible Li insertion between bleached and coloured states.

$$\alpha \mathrm{Li}^+ + \alpha e^- + \mathrm{NiO}_x \rightarrow \mathrm{Li}_\alpha\mathrm{NiO}_x \quad (1)$$

$$\mathrm{Li}_\alpha\mathrm{NiO}_x \leftrightarrow \beta e^- + \beta \mathrm{Li}^+ + \mathrm{Li}_\gamma\mathrm{NiO}_x \quad (2)$$

where $\beta + \gamma = \alpha$ and $\mathrm{Li}_\alpha\mathrm{NiO}_x$ is the bleached state and $\mathrm{Li}_\gamma\mathrm{NiO}_x$ is the opaque state.

To determine the reaction occurring at the NiO counter electrode in our devices, we performed spectroelectrochemical measurements of NiO-coated ITO on glass electrodes in three-electrode cells, since NiO is an anodically-colouring material[12]. In other words, whereas reductive metal electrodeposition turns the working electrode dark, oxidative processes occur that simultaneously turn the NiO counter electrode dark. This complimentary-darkening counter electrode increases the contrast ratio of hybrid dynamic windows. When a NiO on ITO-coated glass electrode is switched in a LiBr electrolyte, its contrast ratio at 600 nm is ~15% (Fig. 4). Control experiments lithiating and delithiating a bare ITO electrode show that there is very little change in the transmission of the electrode (Supplementary Fig. 12). This experiment demonstrates that lithiation and delithiation of NiO is the chemistry that occurs during two-electrode device operation.

Additionally, the results of the half-cell measurements in Fig. 5 and cyclic voltammetry (Supplementary Fig. 13) show that the spectroelectrochemical behaviour of the NiO film does not change substantially over the course of 1,000 lithiation and delithiation cycles. Analogous experiments conducted with a BTD-coated NiO substrate are similarly durable (Supplementary Fig. 14), indicating that the BTD layer does not significantly perturb the lithiation and delithiation process during cycling.

Hybrid dynamic windows using NiO as a counter electrode enable the construction of devices on flexible polyethylene terephthalate (PET) substrates (Fig. 5). Flexible dynamic windows are useful for curved applications such as car sunroofs, sunglasses and displays, and they also allow inexpensive roll-to-roll manufacturing techniques to be used along with windows that can be cut to specified sizes. Although we electrodeposited NiO ITO-coated glass substrates to form the counter electrodes, this approach was not suitable for ITO-coated PET substrates due to nonuniform NiO electrodeposition that occurs as a result of the high sheet resistance (30 Ω sq^{-1}) and increased heterogeneity of the ITO on PET surfaces. Therefore, we deposited NiO on ITO-coated PET substrates using a low-cost, scalable chemical bath deposition technique modified from a literature procedure[32], which enables the construction of well-functioning flexible hybrid dynamic windows (Supplementary Fig. 15).

Large-scale hybrid dynamic windows

To test the scalability of the hybrid dynamic windows developed here, we constructed 100 cm^2 windows using a spray-coating process to deposit the NiO on the counter electrode. Photographs and transmission data recorded at the centre and edge of the device highlight that the window switches to its dark state uniformly (Fig. 6 and Supplementary Fig. 16). The uniform nature of device switching enables these windows to access any intermediate state of grey while maintaining an aesthetically pleasing view through the window. Strikingly, the transmission at 600 nm of a 100 cm^2 window decreases from about 75% to about 9% within 60 s (Fig. 6c). In comparison, the transmission at 600 nm of a 25 cm^2 window decreases to about 6% within 60 s (Fig. 2b). These results indicate that quadrupling the area of the window only slightly decreases the device switching speed. Previous dynamic windows using reversible metal electrodeposition that contain a metal frame counter electrode rely upon the lateral diffusion of metal ions across the length and width of the windows. In contrast, in hybrid metal-based windows, ions need to diffuse only across the thickness of the device during window operation. In short, this architecture enables 100 cm^2 windows to switch rapidly and uniformly.

Outlook and comparison to other dynamic windows

Currently, the most successful dynamic windows use transition metal oxides: typically WO_3 on the working electrode and other metal oxides such as NiO on the counter electrode[5]. We assert that the metal-based windows developed here are a promising alternative to these traditional electrochromic approaches. Whereas WO_3 switches between clear and blue, metals such as the mixture of Bi and Cu electrodeposited in this work are colour-neutral. Furthermore, the high extinction coefficients of metals allow metal-based dynamic windows to turn almost completely opaque (<0.1% transmission)[18], enabling them to be used for privacy applications. Additionally, we anticipate that the cost of these windows will be competitive with existing technologies. The windows contain an inexpensive aqueous-based electrolyte, and the optically active components of both electrodes are entirely solution-processed, which is advantageous over the expensive sputtering techniques often used for WO_3. We note that the organic components of these windows such as BTD will probably undergo degradation by ultraviolet sunlight over the 20–30 years needed for windows in many applications. Ultraviolet filters similar to those used in car windows could be used to protect the organic components of the window. Future work will focus on developing all-inorganic versions of this device architecture to enhance durability towards ultraviolet light.

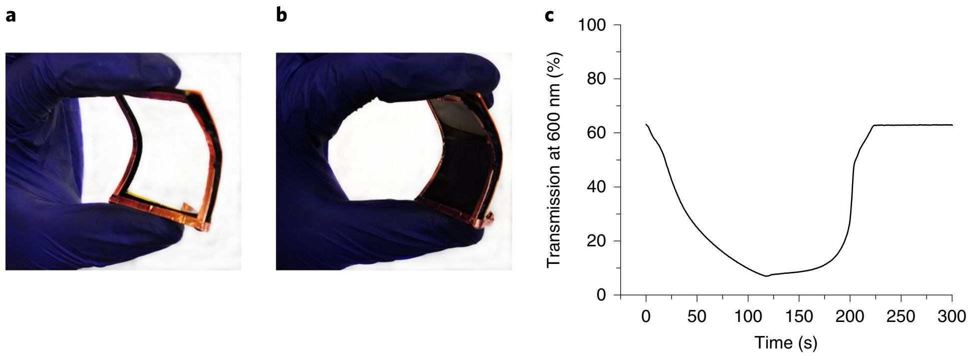

Fig. 5 | Flexible hybrid dynamic windows. a,**b**, Photographs of a 25 cm² flexible dynamic window after 0 s (**a**) and 120 s (**b**) of metal electrodeposition using a Pt-modified ITO on PET working electrode and a $LiNiO_x$ on ITO on PET counter electrode formed using a chemical bath deposition technique. **c**, Transmission at 600 nm of the window during 120 s of metal electrodeposition at -2.5 V and 180 s of metal stripping at 0 V.

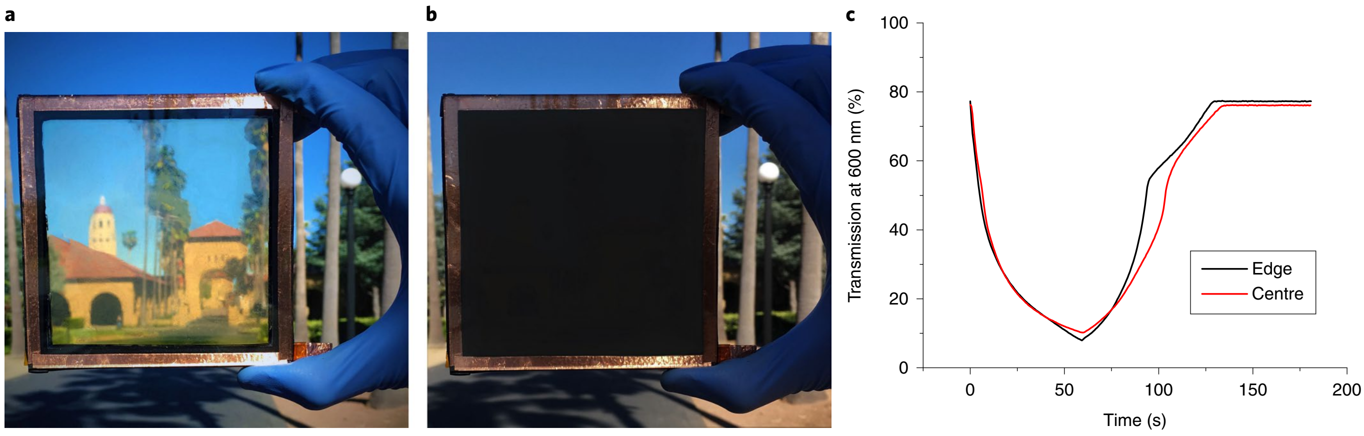

Fig. 6 | 100 cm² hybrid dynamic windows. a,**b**, Photographs of a 100 cm² dynamic window after 0 s (**a**) and 120 s (**b**) of metal electrodeposition using a Pt-modified ITO on glass working electrode and a $LiNiO_x$ on ITO on glass counter electrode. **c**, Transmission at 600 nm through the edge (black) and the centre (red) of the window during switching at −2.5 V for 60 s followed by 0 V for 120 s.

The development of robust large-scale dynamic windows has been an incredible challenge and ongoing quest by academia, and especially industry, for several decades[33]. One of the grand impediments to the commercialization of large dynamic windows is switching speed. By integrating Ohm's law over a two-dimensional electrode, it becomes clear that doubling the length of a dynamic window quadruples the voltage difference that exists between the centre and edge of the window. At large scales (for example, 1 m²), this voltage difference causes nonuniform tinting that can be avoided only by dramatically decreasing the device current such that switch speeds are 10–30 minutes. Kinestral Technologies, Inc. has recently developed patterned transparent conducting oxide electrodes for electrochromic windows that have variable resistance. They deliberately increase the voltage drop, but engineer the voltage to vary linearly across the electrodes in such a way that the voltage difference between the two electrodes is the same throughout the window[34]. The hybrid dynamic window architecture developed here is entirely compatible with these patterned electrodes and possesses the added benefits of neutral colour and high optical contrast associated with electrodeposited metals.

Conclusions

We describe a class of dynamic windows that combine reversible Bi and Cu electrodeposition with Li^+ insertion in a NiO counter electrode. This approach harnesses the advantageous optical properties of metals while facilitating transverse ion diffusion, which enables robust devices to be constructed on a large scale. We demonstrate that 100 cm² versions of these hybrid dynamic windows uniformly switch between clear and black states with ~65% optical contrast in one minute. Furthermore, the windows cycle at least 4,000 times without significant degradation when a small-molecule inhibitor of metal electrodeposition is used to prevent metal growth on the NiO counter electrode. Taken together, these results indicate that hybrid metal-based dynamic windows are a promising alternative to those based on traditional electrochromic materials.

Methods

Electrochemical methods. Chemicals were received from commercial sources and used without further purification. BTD was synthesized in two steps from benzylamine following a literature procedure[35]. Electrochemical studies were conducted using a VSP-300 Biologic potentiostat. For experiments using three electrodes, electrochemical potentials were measured and reported with respect to a 'no-leak' Ag/AgCl (3 M KCl) reference electrode (eDAQ) and used a Pt wire counter electrode. ITO electrodes (Xinyan Technology, 15 Ω sq⁻¹) were cleaned by successively sonicating in de-ionized H_2O with 5% Extran solution for 5 min and isopropanol for 5 min. The electrodes were subsequently dried under a stream of air. Pt nanoparticles (Sigma-Aldrich) used to modify the working electrodes had average diameters of 3 nm. After cleaning, the ITO substrates were immersed in a solution of 3-mercaptopropionic acid (10 mM in ethanol) for 24 h. The electrodes were next rinsed with ethanol and H_2O before they were immersed for at least 24 h in the Pt nanoparticle dispersion that was diluted 1:4 with H_2O. Lastly, ITO on glass substrates were annealed in air at 275 °C for 30 min before use.

Dynamic window assembly. Two-electrode 25 cm² dynamic windows were constructed using a Pt-modified ITO working electrode and a $LiNiO_x$ on ITO or a BTD-coated $LiNiO_x$ on ITO counter electrode. Two-electrode 100 cm^2 dynamic windows used fluorine-doped tin oxide (15 Ω sq^{-1}) electrodes prepared in the same manner as the ITO electrodes. The aqueous liquid Cu–Bi electrolyte consisted of 5 mM $BiCl_3$, 15 mM $CuCl_2$, 10 mM HCl and 1 M LiBr. The Cu–Bi gel electrolyte was made by adding 3.0% hydroxyethylcellulose by weight to the liquid electrolyte and has a viscosity of 9.5 Pa-s, as measured using a NDJ-5S viscometer. To make uniform electrical contact, Cu tape with conductive adhesive was applied across the perimeter of both the working and counter electrodes. Butyl rubber Solargain edge tape separated the two device electrodes with an interelectrode spacing of ~3 mm. For durability studies, for each cycle, −2.5 V was applied for 60 s to induce metal electrodeposition and 0 V was applied for 120 s for metal stripping.

Thin-film synthesis. To test the generality of NiO-based dynamic windows using reversible metal electrodeposition, thin films of $LiNiO_x$ were deposited using either electrodeposition, a chemical bath deposition method, or a spray-coating technique. To fabricate $LiNiO_x$ films using electrodeposition, a modified literature protocol was followed[36]. Chronoamperometry at +1 V for 30 minutes was performed in an aqueous solution of 500 mM $NiSO_4$ that was adjusted to pH 7.5 using 1 M KOH. The ITO substrates were subsequently rinsed with H_2O, dried under a stream of air, and annealed in air for 1 h at 300 °C. Next, the NiO_x films were lithiated using chronoamperometry at −1 V for 10 min in an aqueous solution of 1 M LiBr. The films were then rinsed with H_2O and dried under a stream of air. The thicknesses of the $LiNiO_x$ films were measured using a KLA Tencor D-100 Stylus Profilometer. Electrodes containing BTD were fabricated by spin-coating $LiNiO_x$ substrates at 4,000 rpm for 60 s using a solution of BTD in tetrahydrofuran (10 mg ml^{-1}). As measured by profilometry, the BTD films had an average thickness of ~450 nm. $LiNiO_x$ films were also fabricated using a chemical bath deposition method modified from the literature[32]. In this approach, an aqueous solution containing 500 mM $NiSO_4$, 94 mM $K_2S_2O_8$ and 3.1–3.5% ammonia was first formed by mixing the constituent chemicals together vigorously for 2–3 min. Next, the nonconductive side and edges of the ITO substrates were temporarily covered with Kapton tape, and the substrates were immersed in the chemical bath and mechanically shaken for 20 min at 80 r.p.m. using an American Rotator V Model R-4140 shaker. Finally, the electrodes were rinsed gently with H_2O, dried in a stream of air, and heated in air for 1.5 h at 300 °C. $LiNiO_x$ films on the 100 cm^2 substrates were prepared using a spray pyrolysis technique. The NiO precursor solution consisted of $Ni(NO_3)_2$ dissolved in water at a concentration of 50 mM. The precursor solution was sprayed onto ITO substrates, which were placed on a hot plate (300 °C), at a flow rate of 100 μl min^{-1} for 10 min. The spray-coated NiO substrates were then lithiated using chronoamperometry at −1 V for 40 min in an aqueous solution of 0.5 M LiBr. The films were then rinsed with H_2O and dried under a stream of N_2. CeO_2 thin films on ITO-coated glass were fabricated following a literature procedure[37]. V_2O_5 thin films were prepared by spin-coating a solution containing 14 μl vanadium(V) oxytriisopropoxide and 286 μl isopropanol on ITO-coated glass at 4,000 r.p.m. for 60 s. The thin films were subsequently annealed in air for 30 min at 275 °C.

Materials characterization. Most transmission spectra were measured with an Ocean Optics FLAME-S-VIS-NIR or an Ocean Optics FLAME-S-UV-VIS-ES spectrometer coupled with an Ocean Optics halogen light source (HL-2000-FHSA) or an Ocean Optics DH-mini UV-Vis-NIR light source. Optical data measured between 1,000–1,800 nm were measured using a Varian Cary 500 Scan UV-Vis-NIR spectrometer equipped with a Labsphere DRA-CA-5500 integrating sphere. Photographs of windows were taken with a Nikon D5000 Digital Camera. SEM and EDX spectra were obtained using a JEOL JSM-6010LA microscope operated at an accelerating voltage of 20 kV.

Data availability

Data that support the plots in this paper and other findings of this study are available from the corresponding author upon reasonable request.

Received: 21 August 2018; Accepted: 18 January 2019;

References

1. Lee, E. S., Yazdanian, M. & Selkowitz, S. E. *The Energy-savings Potential of Electrochromic Windows in the U.S. Commercial Buildings Sector* LBNL-54966 (Lawrence Berkeley National Laboratory, 2004).
2. Jeffers, M. A., Chaney, L. & Rugh, J. P. *Climate Control Load Reduction Strategies for Electric Drive Vehicles in Warm Weather* (SAE International, 2015).
3. Mortimer, R. J., Dyer, A. L. & Reynolds, J. R. Electrochromic organic and polymeric materials for display applications. *Displays* **27**, 2–18 (2006).
4. Runnerstrom, E. L., Llordes, A., Lounis, S. D. & Milliron, D. J. Nanostructured electrochromic smart windows: traditional materials and NIR-selective plasmonic nanocrystals. *Chem. Comm.* **50**, 10555–10572 (2014).
5. Granqvist, C. G. Electrochromics for smart windows: oxide-based thin films and devices. *Thin Solid Films* **564**, 1–38 (2014).
6. Nguyen, W. H., Barile, C. J. & McGehee, M. D. Small molecule anchored to mesoporous ITO for high-contrast black electrochromics. *J. Phys. Chem. C* **120**, 26336–26341 (2016).
7. Thakur, V. K., Ding, G., Ma, J., Lee, P. S. & Lu, X. Hybrid materials and polymer electrolytes for electrochromic device applications. *Adv. Mater.* **24**, 4071–4096 (2012).
8. Barile, C. J. et al. Dynamic windows with neutral color, high contrast, and excellent durability using reversible metal electrodeposition. *Joule* **1**, 133–145 (2017).
9. Alcaraz, G. K. A., Juarez-Rolon, J. S., Burpee, N. A. & Barile, C. J. Thermally-stable dynamic windows based on reversible metal electrodeposition from aqueous electrolytes. *J. Mater. Chem. C* **6**, 2132–2138 (2018).
10. Heavens, O. S. *Optical Properties of Thin Solid Films* (Dover Publications, New York, 1965).
11. Barile, C. J., Slotcavage, D. J. & McGehee, M. D. Polymer–nanoparticle electrochromic materials that selectively modulate visible and near-infrared light. *Chem. Mater.* **28**, 1439–1445 (2016).
12. Niklasson, G. A. & Granqvist, C. G. Electrochromics for smart windows: thin films of tungsten oxide and nickel oxide, and devices based on these. *J. Mater. Chem.* **17**, 127–156 (2007).
13. Wen, R. T., Granqvist, C. G. & Niklasson, G. A. Eliminating degradation and uncovering ion-trapping dynamics in electrochromic WO_3 thin films. *Nat. Mater.* **14**, 996–1001 (2015).
14. Gamburg, Y. D. & Zangari, G. *Theory and Practice of Metal Electrodeposition* (Springer, New York, 2011).
15. Jensen, J., Madsen, M. V. & Krebs, F. C. Photochemical stability of electrochromic polymers and devices. *J. Mater. Chem. C* **1**, 4826–4835 (2013).
16. Strand, M. T. et al. Factors that determine the length scale for uniform tinting in dynamic windows based on reversible metal electrodeposition. *ACS Energy Lett.* **3**, 2823–2828 (2018).
17. Tench, D. Morgan & Warren, L. F. Electrodeposition cell with high light transmission. European patent EP1071980A1 (2001).
18. Hernandez, T. S. et al. Bistable black electrochromic windows based on the reversible metal electrodeposition of Bi and Cu. *ACS Energy Lett.* **3**, 104–111 (2018).
19. Lu, Y. et al. Mechanism of electrochemical deposition and coloration of electrochromic V_2O_5 nano thin films: an in situ X-ray spectroscopy study. *Nanoscale Res. Lett.* **10**, 387–392 (2015).
20. Varsano, F., Decker, F. & Masetti, E. Optically passive cerium containing counter-electrodes for electrochromic devices. *Ionics* **5**, 80–85 (1999).
21. Greenwood, N. N. & Earnshaw, A. *Chemistry of the Elements* (Butterworth-Heinemann, Oxford, 1997).
22. *The Energy Benefits of View Dynamic Glass* (View Inc., accessed 30 November 2018); https://view.com/assets/pdfs/workplace-demo-room.pdf
23. Grujicic, D. & Pesic, B. Electrodeposition of copper: the nucleation mechanisms. *Electrochim. Acta* **47**, 2901–2912 (2002).
24. Kelly, J. J., Tian, C. & West, A. C. Leveling and microstructural effects of additives for copper electrodeposition. *J. Electrochem. Soc.* **146**, 2540–2545 (1999).
25. Leung, T. Y. B., Kang, M., Corry, B. F. & Gewirth, A. A. Benzotriazole as an additive for copper electrodeposition influence of triazole ring substitution. *J. Electrochem. Soc.* **147**, 3326–3337 (2000).
26. Araki, S., Nakamura, K., Kobayashi, K., Tsuboi, A. & Kobayashi, N. Electrochemical optical-modulation device with reversible transformation between transparent, mirror, and black. *Adv. Mater.* **24**, OP122–OP126 (2012).
27. Passerini, S. & Scrosati, B. The intercalation of lithium in nickel oxide and its electrochromic properties. *J. Electrochem. Soc.* **137**, 3297–3300 (1990).
28. Wen, R. T., Niklasson, G. A. & Granqvist, C. G. Electrochromic nickel oxide films and their compatibility with potassium hydroxide and lithium perchlorate in propylene carbonate: optical, electrochemical and stress-related properties. *Thin Solid Films* **565**, 128–135 (2014).
29. Liu, Q. et al. Electrolytes-relevant cyclic durability of nickel oxide thin films as an ion-storage layer in an all-solid-state complementary electrochromic device. *Sol. Energy Mat. Sol. C* **157**, 844–852 (2016).
30. Mihelčič, M. et al. Comparison of electrochromic properties of $Ni_{1-x}O$ in lithium and lithium-free aprotic electrolytes: from $Ni_{1-x}O$ pigment coatings to flexible electrochromic devices. *Sol. Energy Mat. Sol. C* **120**, 116–130 (2014).
31. Guo, J. et al. Mechanistic insights into the coloration, evolution, and degradation of NiO_x electrochromic anodes. *Inorg. Chem.* **57**, 8874–8880 (2018).
32. Xia, X. H. et al. Electrochromic properties of porous NiO thin films prepared by a chemical bath deposition. *Sol. Energy Mat. Sol. C* **92**, 628–633 (2008).
33. Granqvist, C. G. Electrochromic materials: out of a niche. *Nat. Mater.* **5**, 89–90 (2006).
34. Bergh, H. S. et al. Electrochromic multilayer devices with spatially coordinated switching. US patent US2016/0011481A1 (2016).
35. Li, Y., Tse, E. C. M., Barile, C. J., Gewirth, A. A. & Zimmerman, S. C. Photoresponsive molecular switch for regulating transmembrane proton-transfer kinetics. *J. Am. Chem. Soc.* **137**, 14059–14062 (2015).

36. Kondalkar Vijay, V. et al. Electrochromic performance of nickel oxide thin film: synthesis via electrodeposition technique. *Macromol. Symp.* **361**, 47–50 (2016).
37. Özer, N. Optical properties and electrochromic characterization of sol–gel deposited ceria films. *Sol. Energy Mat. Sol. C* **68**, 391–400 (2001).

Acknowledgements

This research was supported by Research and Innovation at the University of Nevada, Reno and also by the Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Building Energy Efficiency Frontiers in Innovation Technologies Program, Award Number DE-EE0008266/001. T.S.H. acknowledges a National Science Foundation Graduate Research Fellowship (No. NSF DGE-1656518). We acknowledge the Shared Instrumentation Laboratory in the Department of Chemistry at the University of Nevada, Reno (UNR). SEM-EDS analysis was performed in the Mackay Microbeam Laboratory at UNR, and we thank J. Desormeau for his kind assistance. We appreciate R. Kazemi and Dr. Alpuche's laboratory for assistance in profilometry measurements. We also acknowledge T. Hull for work with CeO_2 films, initial large-scale work by J. Jaurez-Rolon, and L. Postak from Quanex for providing the Solargain edge tape. We are grateful for fruitful discussions with M. Strand. We appreciate W. Scheideler, a post-doctoral student in R. Dauskardt's group at Stanford University, for help with preparing the NiO samples via spray pyrolysis.

Author contributions

All authors designed the experiments, discussed the results, and commented on the manuscript. S.M.I. and T.S.H. performed the experiments and analysed the data. M.D.M. and C.J.B. wrote the paper. C.J.B. conceived the project.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information is available for this paper at https://doi.org/10.1038/s41560-019-0332-3.

Reprints and permissions information is available at www.nature.com/reprints.

Correspondence and requests for materials should be addressed to C.J.B.