Solution-Deposited Solid-State Electrochromic Windows

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HIGHLIGHTS
Amorphous WO$_3$ and NiO$_x$ films are produced by a solution-deposition method.

The WO$_3$ and NiO$_x$ films are assembled into a solid-state electrochromic device.

The solid-state device exhibits state-of-the-art electrochromic performance.

Amorphous NiO$_x$ is a superior counter electrode material compared with crystalline NiO$_x$.

Cheng et al., iScience 10, 80–86, December 21, 2018 © 2018 The Authors. https://doi.org/10.1016/j.isci.2018.11.014
Solution-Deposited Solid-State Electrochromic Windows

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SUMMARY
Commercially available electrochromic (EC) windows are based on solid-state devices in which WO₃ and NiOₓ films commonly serve as the EC and counter electrode layers, respectively. These metal oxide layers are typically physically deposited under vacuum, a time- and capital-intensive process when using rigid substrates. Herein we report a facile solution deposition method for producing amorphous WO₃ and NiOₓ layers that prove to be effective materials for a solid-state EC device. The full device containing these solution-processed layers demonstrates performance metrics that meet or exceed the benchmark set by devices containing physically deposited layers of the same compositions. The superior EC performance measured for our devices is attributed to the amorphous nature of the NiOₓ produced by the solution-based photodeposition method, which yields a more effective ion storage counter electrode relative to the crystalline NiOₓ layers that are more widely used. This versatile method yields a distinctive approach for constructing EC windows.

INTRODUCTION
Electrochromic (EC) windows (also known as smart or dynamic windows) undergo changes in light transmittance in response to an applied voltage, enabling the dynamic control of daylight and solar heat passing through buildings (Granqvist, 2006, 2012a; Runnerstrom et al., 2014). This technology can provide both indoor thermal and visual comfort for building occupants while improving building energy efficiency by as much as 20% (Granqvist, 2012a). These features have prompted substantial investment into deploying EC windows at scale, but the high price of such windows ($1,000/m² c.f. ~$150/m² for a regular window (Smart windows cost, 2016)) has prevented their widespread use. A significant fraction of the cost is imbedded in the vacuum environment required to sputter EC window layers. This process can require a substantial capital outlay, and the long residence times needed to fabricate the key layers on rigid substrates also preclude rapid throughput (Garg et al., 2005). These factors present the impetus to develop solution-based deposition methodologies to reduce the costs associated with fabricating EC windows (Barile et al., 2017; Cai et al., 2016a; Llorde’s et al., 2016).

A conventional EC window consists of an EC layer, an electrolyte layer, and an ion storage counter electrode sandwiched between two transparent conducting layers (Figure 1). Thin films of WO₃ and NiOₓ are widely used as the respective EC and counter electrode layers in commercial EC windows (Gillaspie et al., 2010; Niklasson and Granqvist, 2006). Both of these layers contribute to reversible color switching in response to an electrical bias (Figure 1). The NiOₓ layers are lithiated to form LiₓNiOₓ before device assembly to provide a source of intercalating Li⁺ during reduction (coloration) of WO₃. A voltage applied to the assembled device drives coloration of both metal oxide layers as Li⁺ migrates into the WO₃ layer. The ion-conducting and electrically insulating electrolyte layer serves to shuttle Li⁺ between the metal oxide layers and prevent short circuiting of the device. Liquid electrolytes are common in academic studies, but solid polymer-based electrolytes are used in commercial systems to satisfy safety and sealing issues (Granqvist, 2012b; Thakur et al., 2012).

The EC behavior of these layers is exquisitely sensitive to impurities, film defects, thickness, porosity, and crystallinity (Cai et al., 2016b; Granqvist, 2014; Lee et al., 2006; Scherer and Steiner, 2013). These factors therefore impose very stringent conditions on how EC windows can be manufactured. Physical vacuum deposition has emerged as the most reliable and scalable method of producing uniform and optical-quality metal oxide films of variable thicknesses (Thumavichai et al., 2017). Notwithstanding, the metal oxide semiconductor industry teaches that manufacturing methods progressively transition from vacuum to solution-processing methods to reduce costs (Yu et al., 2016). The ability to solution process at ambient
temperatures and pressures offers the opportunity to reduce energy consumption and capital equipment while also reducing processing times (Llorde´ s et al., 2016). Moreover, the avoidance of high vacuum lessens the safety concerns associated with handling potentially hazardous materials (e.g., lithium-containing chemicals). There are several reports of solution-based methods for processing EC or counter electrode layers, including electrodeposition (Baeck et al., 2003; Cai et al., 2016b), chemical bath deposition (Ristova et al., 2002; Vidales-Hurtado and Mendoza-Galva´ n, 2008; Xia et al., 2008), sol-gel methods (Livage and Ganguli, 2001), and spray pyrolysis (Kamal et al., 2005; Tenent et al., 2010). However, none of these methods are well suited for synthesizing both WO3 and NiOx films. Consequently, these layers are evaluated in electrochemical half-cells or in devices in which the working or counter electrode is physically deposited (Jiao et al., 2003; Srivastava et al., 2005; Zhang et al., 2009). These observations motivated us to build an EC device wherein all layers are solution-processed.

We demonstrate herein the use of a “photodeposition” method (Cheng et al., 2018; Smith et al., 2013) to solution-process both the WO3 and NiOx EC layers of an EC device with a solution-deposited poly(methyl methacrylate) (PMMA)-based electrolyte. To our knowledge, this is the first report of a solid-state EC device containing internal layers that are fully solution-processable at low temperature. The performance of our laboratory-scale solid-state EC devices meets or exceeds current literature benchmarks in terms of optical modulation ($\Delta T_{633\ nm}$) measured as the difference in light transmittance between the fully colored and bleached states at $\lambda = 633\ nm$, switching time for coloration ($t_{\text{color}}$, defined by the time required to reach 90% of a transmittance change from the fully bleached to fully colored state) and bleaching ($t_{\text{bleach}}$, and

![Figure 1. Working Principles for an Electrochromic Device](image-url)

Scheme outlining the coloration and bleaching process of an EC device with a WO3 electrochromic layer and NiOx counter electrode layer sandwiched between two transparent conductive glass substrates. The pristine device is formed by transparent LiyNiOx and WO3 layers and an interstitial electrolyte. Applying a forward bias to the electrochromic layer of the device injects electrons into WO3, which are then compensated by Li+ migrating from the counter electrode through the electrolyte to yield colored LiyWO3. The simultaneous extrusion of Li+ from LiyNiOx enables the formation of colored Liy-zNiOx. The bleaching process is obtained by applying a reverse bias, yielding the initial LiyNiOx and WO3 transparent layers. The coloration and bleaching processes are summarized by the overall reversible reaction shown in the Scheme.
coloration efficiency (CE; the change in optical density acquired by injection of charge per unit area; Table 1). We also demonstrate the superior performance of amorphous thin film materials in EC windows by directly comparing amorphous and crystalline NiOx counter electrodes in the same device architecture and produce by analogous solution-based methods. This study presents an opportunity to harness low-cost solution-processing methods for the production of high quality EC devices.

RESULTS AND DISCUSSION
Electrode Synthesis and Device Assembly
Amorphous tungsten oxide (a-WO3) films were prepared using a photodeposition methodology known to yield amorphous metal oxide layers (Cheng et al., 2018; He et al., 2017; Smith et al., 2013). Briefly, a solution of WCl6 in 2-propanol was spin-cast onto a fluorine-doped tin oxide (FTO) substrate and the resultant precursor film was irradiated with UV light ($\lambda_{\text{max}} = 185 \text{ nm}$) to form a metal oxide film. Characterization of the films by top-view and cross-sectional scanning electron microscopy (SEM) was consistent with the successful formation of porous a-WO3 films of $\approx 600 \text{ nm}$ thickness (Figure S1). NiOx films were prepared following a similar procedure: aqueous solutions of 0.25 M NiCl2 were spin-cast onto an FTO substrate followed by UV irradiation ($\lambda_{\text{max}} = 185 \text{ nm}$) for 8 hr. The complete liberation of chlorine from the precursor film and the formation of NiOx was confirmed by X-ray fluorescence and X-ray photoelectron spectroscopy analyses (Figure S2). The X-ray diffraction (XRD) pattern of the as-prepared NiOx films showed a broad reflection centered at $2\theta = 18^\circ$ indexed to the (001) facets of $\alpha$-Ni(OH)2 (Smith et al., 2016), together with the reflections corresponding to the FTO substrate (Figure S3). This broad reflection was no longer observed, and no additional reflections appeared after annealing the NiOx films at 200°C for 1 hr, which denotes the successful formation of amorphous films (Figure S3). The thickness of a-NiOx films prepared by spin casting and UV treating five layers of NiCl2 precursor on the FTO substrate before the annealing step was determined to be 120 nm by cross-sectional SEM (Figure 2). Cross-sectional and top-view SEM images (Figures 2 and S4A) show that the NiOx films follow the contour of FTO and have smooth uniform surfaces. Crystalline NiOx (c-NiOx) films were also obtained by annealing the as-deposited NiOx films at 400°C for 1 hr. The resulting XRD pattern shows well-defined reflections corresponding to crystalline cubic NiO (Figure S3). Five-layer c-NiOx films show smooth uniform surfaces with a thickness of 105 nm (Figures S4B and S4C).

Solid-state EC devices with active areas of $\approx 2 \text{ cm}^2$ were assembled using a-WO3 films coated on FTO glass as the working electrode, either a- or c-NiOx films deposited on FTO glass as the counter electrode, and a PMMA-based gel as the electrolyte. NiOx counter electrodes were lithiated before device assembly by submerging the films in 1 M LiClO4 propylene carbonate and applying a potential of $-1.5 \text{ V (vs Ag/AgCl)}$ across the cell for 5 min. The PMMA-based gel electrolyte was drop-cast directly onto the a-NiOx electrode and contained within a silicone spacer with a thickness of 1 mm. The device was completed with the a-WO3 working electrode and sealed with epoxy glue.

Electrochromic Performance of Solid-State Devices
The EC performance of the full devices containing either a- or c-NiOx counter electrode was tested by using UV-Vis spectroscopy to measure the optical properties under applied potentials (Figure 3). The optical

### Table 1. Performance Parameters of Our Solid-State EC Devices in Comparison with That of Solid-State Devices Reported in the Literature

| Counter Electrode Material | Phase | Deposition Method | $\Delta T$ (%) | $t_{\text{color}}$ (s) | $t_{\text{bleach}}$ (s) | CE (cm$^2$/C) | Reference |
|----------------------------|-------|-------------------|----------------|----------------------|-------------------|---------------|-----------|
| NiO porous film            | Crystalline | Chemical bath deposition | 55            | 10                    | 20                | 87.2          | Zhang et al., 2009 a |
| NiO nanoparticle film      | Crystalline | Inkjet printing   | 75            | 10                    | 13                | 131.9         | Cai et al., 2016a b |
| NiOx film                  | Crystalline | Magnetron sputtering | 52            | 5                     | 2                 | -             | Liu et al., 2016 c |
| NiOx film                  | Amorphous | Photodeposition    | 60            | 4                     | 6                 | 141           | this work d |
| NiOx film                  | Crystalline | Photodeposition    | 26            | 78                    | 17                | 72            | this work d |

All devices use WO3 as the electrochromic layer, NiOx as the counter electrode, and a polymer-based electrolyte.

aMeasured at 633 nm over the $-2.5$ to $+2.5 \text{ V}$ potential range.
bMeasured at 550 nm over the $-2.5$ to $+2.5 \text{ V}$ potential range.
cMeasured at 550 nm over the $-1.8$ to $+1.8 \text{ V}$ potential range.
dMeasured at 633 nm over the $-2.1$ to $+2.1 \text{ V}$ potential range.
modulation ($\Delta T_{633\text{ nm}}$) was determined by recording the transmittance of the devices in either a fully colored or a fully bleached state at potentials of $-2.1$ or $+2.1$ V, respectively. EC devices with the a-NiO$_x$ counter electrode showed a $\Delta T_{633\text{ nm}}$ of 60%, compared with $\Delta T_{633\text{ nm}}$ of 26% for the device with c-NiO$_x$ counter electrode (Figure 3A) (c.f. 19% for devices in which the counter electrode was bare FTO [Figure S5]). Switching times from the fully colored to the fully bleached state ($t_{\text{bleach}}$), and the reverse ($t_{\text{color}}$), were measured by tracking the transmittance at $\lambda = 633$ nm in response to consecutive applied potentials of $+2.1$ and $-2.1$ V for 30 s each (Figure 3B). The device with the a-NiO$_x$ counter electrode showed rapid switching times of $t_{\text{bleach}} \sim 6$ s and $t_{\text{color}} \sim 4$ s, whereas the device with a c-NiO$_x$ counter electrode showed much slower $t_{\text{color}}$ and $t_{\text{bleach}}$ of 78 and 17 s, respectively.

CE, which measures the change in optical density acquired by injection of charge per unit area, was determined in accordance with Equations 1 and 2:

\[
CE = \frac{\Delta (\text{OD})}{\Delta Q} \quad \text{(Equation 1)}
\]

\[
\Delta (\text{OD}) = \log \left( \frac{T_b}{T_c} \right) \quad \text{(Equation 2)}
\]

where $\Delta (\text{OD})$ is the change in optical density and $\Delta Q$ is the charge density (C/cm$^2$) obtained from electrochemical measurements; $T_b$ is the maximum transmittance in the bleached state at a fixed wavelength (obtained from Figure 3B); and $T_c$ is the varying transmittance obtained during the coloration process at this same wavelength. The CE values were determined from the slope of the linear region of $\Delta (\text{OD})$ versus $\Delta Q$ (Figure 3C) were determined to be 141 cm$^2$/C for a device containing an a-NiO$_x$ counter electrode. This value is approximately twice that of the device with c-NiO$_x$ counter electrode (72 cm$^2$/C).

The differences in performance metrics of the EC devices containing either an a-NiO$_x$ or c-NiO$_x$ counter electrode demonstrate the superior EC performance of a-NiO$_x$ systems. It appears that the superior performance of a-NiO$_x$ is manifest in the superior ion-storage properties of the films given that a-NiO$_x$ is characterized by a charge capacity of 4.1 mC/cm$^2$ during the pre-lithiation process that is 2-fold higher than the value measured for c-NiO$_x$ (1.6 mC/cm$^2$). These findings are consistent with the higher ion storage capacity generally observed for amorphous materials (Ku et al., 2012; Lee et al., 2014). The improved ion storage performance that arises in amorphous materials is believed to be due to the larger interstitial spaces between more disordered atoms (Lee et al., 2014; Legrain et al., 2015; Llordés et al., 2016). These larger interatomic spaces can accommodate intercalated ions and facilitate the mobility of ions in materials. In the case of NiO$_x$ counter electrode materials in EC devices, the amorphous film is capable of balancing more charges during each EC cycle, thereby accommodating greater lithium insertion into the WO$_3$ during each coloration cycle and resulting in higher $\Delta T$. Furthermore, the enhanced ion mobility in a-NiO$_x$ yields faster switching times between bleach and colored states.

Table 1 lists the performance of our solid-state EC devices containing photodeposited NiO$_x$ counter electrodes along with other reported devices of similar sizes and configurations. The $\Delta T_{633\text{ nm}}$ of 60% reported here for the a-NiO$_x$ is in keeping with systems synthesized by other methods. The switching times ($t_{\text{bleach}}$ and $t_{\text{color}}$) of our device is among the fastest reported to date, exceeded only by $t_{\text{bleach}}$ for films made using high-vacuum sputtering methods. The CE of 141 cm$^2$/C exceeds all other known examples of devices based on WO$_3$ and NiO$_x$ materials, highlighting the excellent EC performance of our solution-processed
devices containing amorphous films. It is worth noting that the performance is also comparable with commercially available EC windows, which use sputtered WO3 and NiOx films and polymer-based electrolytes. These full-scale windows typically show an optical modulation of merely 45% over the visible light region and a switching time of 15–20 min (with the important caveat that the device sizes are different) (Range of products, 2018).

Performance Dependence on a-NiOx Thickness

The thicknesses of the a-NiOx films are controlled simply by spin casting and UV treating a variable number of NiCl2 precursor layers on the FTO substrate before annealing. NiOx films with thicknesses of 70, 120, 240, and 360 nm were prepared by 3, 5, 10, or 15 layers of deposition, respectively (Figures 2, S6, and S7). Amorphous NiOx films of increasing thicknesses (120, 240, and 360 nm) were assembled into EC devices as the counter electrode material (with all other parameters held constant) and similarly assessed for their optical properties in response to an applied voltage. Increasing thickness of a-NiOx from 120 nm to 360 nm caused a slight decrease in $D_{T633 \text{ nm}}$ from 60% to 56% (Figure S8). Switching times $t_{\text{bleach}}$ and $t_{\text{color}}$ also increased slightly reaching 11 and 13 s, respectively, for the thickest of the three a-NiOx films (Figure S8). The stability of the EC devices was also tested by tracking the transmittance change over time while continuously switching between the colored and bleached states. The thicker NiOx films exhibit enhanced cycling stability despite the loss in optical modulation and increase in switching times. SEM characterization showed that the 120-nm a-NiOx film was compromised during cycling, whereas the morphologies of the thicker films (240 and 360 nm) were mostly maintained (Figure S9). For the device with a 120-nm thickness of a-NiOx, 81% of the initial optical modulation value remained after 100 cycles (Figure 4A). The EC device with a 240-nm thickness of a-NiOx retained 90% of the initial $\Delta T_{633 \text{ nm}}$ after 100 cycles and 75% after 200 cycles (Figure 4B). Further increasing the thickness of the a-NiOx film to 360 nm enabled the device to retain nearly 100% of the initial $\Delta T$ after 400 cycles (Figure 4C). By contrast, solid-state devices using inkjet-printed WO3 and NiO nanoparticle electrodes retain only 80% $\Delta T_{633 \text{ nm}}$ after 100 cycles, with significant further degradation thereafter (Cai et al., 2016a).

Conclusion

Solution-based photodeposition of readily available metal precursors (WCl6 and NiCl2) can be used to synthesize both the working and counter electrode materials of EC windows. The exceptional performance of EC devices containing these materials is demonstrated here with amorphous WO3 and NiOx thin films assembled together with a PMMA-based gel electrolyte. The resulting solid-state systems exhibit optical modulations ($\Delta T_{633 \text{ nm}}$), switching times ($t_{\text{color}}$ and $t_{\text{bleach}}$), coloration efficiencies (CE), and cycling stabilities commensurate with the best reported devices to date, including those produced by expensive or specialized methods. We also show that this low-temperature process yields amorphous layers of NiOx that act as...
superior counter electrodes relative to crystalline NiOₓ, which we anticipate will trigger greater research efforts on the use of amorphous materials for EC devices. These collective results represent an opportunity to drive down the costs of energy-saving EC windows that have already attracted substantial commercial investment.

Limitations of the Study
This study demonstrates the ability to use photodeposition to make uniform EC nickel and tungsten oxide layers. The formation of the photodeposited a-NiOₓ films must be optimized to compete with sputtering at an industrial scale. Future investigations will also seek to resolve the factors that lead to the increases in transmittance of the bleached state during cycling (Figure 4C).

METHODS
All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION
Supplemental Information includes Transparent Methods and 9 figures and can be found with this article online at https://doi.org/10.1016/j.isci.2018.11.014.

ACKNOWLEDGMENTS
The authors are grateful to the Canadian Natural Science and Engineering Research Council (RGPIN 337345-13), Canadian Foundation for Innovation (229288), Canadian Institute for Advanced Research (BSE-BERL-162173), Canada Research Chairs, and Stewart Blusson Quantum Matter Institute for financial support. Additional thanks to the Center for High-Throughput Phenogenomics for access to SEM facilities. D.M.W. and C.P.B. also wish to acknowledge the generous and ongoing support of Peter Bradshaw.

AUTHOR CONTRIBUTIONS
C.P.B. supervised the project. W.C. designed and performed the experiments. M.M. carried out XRD measurements. D.J.D. conducted SEM analyses. K.H., C.K., and B.T. assisted with thin film preparation. W.C., D.M.W., and C.P.B. wrote the manuscript with input from all authors.

DECLARATION OF INTERESTS
The authors declare no competing interests.

Received: August 25, 2018
Revised: October 21, 2018
Accepted: November 6, 2018
Published: December 21, 2018
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Supplemental Information

Solution-Deposited Solid-State Electrochromic Windows

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Figure S1. SEM characterization of a-WO₃ films, Related to Figure 2. Top-view (left) and cross-sectional (right) SEM images of 5-layer WO₃ films produced by photodeposition followed by annealing at 100°C for 1 hr. Cross-sectional SEM images were acquired on fresh edges of cleaved samples at a tilt angle of 52 degrees.
Figure S2. Photodeposition of NiO$_x$ films, Related to Figure 2. (a) Schematic illustration showing UV light irradiation of spin-cast NiCl$_2$ precursor films on FTO glass leads to formation of NiO$_x$. (b) Content of Cl in precursor film determined by X-ray fluorescence (XRF) analyzer as a function of UV irradiation time. The chloride ions are completely removed by UV light illumination in 8 hrs. (c) XPS spectra of NiCl$_2$ precursor and as-formed NiO$_x$ in binding energy range corresponding to Cl 2p. No Cl 2p signal exists in as-formed NiO$_x$, confirming complete decomposition of chloride ions by UV irradiation. (d) XPS spectrum of NiO$_x$ in the binding energy range corresponding to Ni 2p, matching well with that of Ni$^{2+}$. 
Figure S3. XRD characterization, Related to Figure 2. XRD patterns of photodeposited NiO$_x$ films annealed at 100, 200, 300, and 400°C for 1 hr. Broad diffraction peak at labeled with ▲ symbol corresponds to (100) planes of α-Ni(OH)$_2$. The reflections denoted with * symbol correspond to cubic phase NiO (JCPDS 47-1049). All other reflections arising from the FTO substrate can be indexed to SnO$_2$ (JCPDS 41-1445).
Figure S4. SEM characterization of amorphous and crystalline NiO$_x$ films, Related to Figure 2. (a, b) Top-view and (c) cross-sectional SEM images of a- and c-NiO$_x$ films produced by photodeposition followed by annealing at 200 and 400°C for 1 hr, respectively. Cross-sectional SEM images were acquired on fresh edges of cleaved samples at a tilt angle of 52 degrees.

Figure S5. Optical modulation of an EC device with bare FTO counter electrode, Related to Figure 3. Transmittance spectra of EC device using bare FTO as the counter electrode in the colored and bleached states. The spectra were recorded after coloring at -2.1 V or bleaching at +2.1 V for 60 s. $\Delta T_{633\text{ nm}}$ was determined to be 19%.
Figure S6. SEM characterization of a-NiO$_x$ film, Related to Figure 2. (a, c) Top-view and (b, d) cross-sectional SEM images of 3-layer and 10-layer a-NiO$_x$ films produced by photodeposition followed by annealing at 200°C for 1 hr. Cross-sectional SEM images were acquired on fresh edges of cleaved samples at a tilt angle of 52 degrees.
Figure S7. Relation between film thickness and number of deposition layers, Related to Figure 2. A linear relation was found between the thickness of a-NiO$_x$ films determined from cross-sectional SEM images (see Figures 2 and S6) and the number of layers of a-NiO$_x$ coated on FTO substrates.
Figure S8. Thickness-dependent electrochromic performance, Related to Figures 3 and 4. Optical modulation and switching times of devices using a-NiO\textsubscript{x} films with thicknesses of (a, b) 120 nm, (c, d) 240 nm, and (e, f) 360 nm as counter electrode materials. The 360-nm a-NiO\textsubscript{x} film was made by 15 layers of coating and the thickness was calculated from the equation shown in Figure S7.
Figure S9. Influence of electrochromic cycling on the morphologies of a-NiO\textsubscript{x} films, Related to Figure 4. SEM images of a-NiO\textsubscript{x} films with different thicknesses before and after electrochromic cycling.
Transparent Methods

Materials
WCl₆ (99.99%), NiCl₂·6H₂O (99.9%), LiClO₄ (99.99%), PC (99.7%, anhydrous), 2-propanol (99.9%), and PMMA (Mₙ ~ 350000) purchased from Sigma-Aldrich were used directly without further purification. FTO-coated glass purchased from Hartford Glass (TEC7) was first cleaned by sequential ultrasonication in detergent solution (Extran 300, EMD), distilled water, acetone, and isopropanol, and then it was dried in N₂ flow and further subjected to UV-Ozone treatment for 30 min prior to use.

Film syntheses
In a typical synthesis of NiOₓ film, a 0.25 M NiCl₂ aqueous solution prepared by dissolving 0.24 g (1.0 mmol) NiCl₂·6H₂O in 4 ml distilled water was spin-coated on FTO glass at 3000 rpm for 60 s (Laurell model WS-650MZ-23NPP-Lite). The resultant precursor thin films were subjected to UV (Atlantic Ultraviolet G18T5VH/U; λₘₐₓ = 185 nm) irradiation until complete decomposition was confirmed by tracking the chlorine content by XRF analysis. To produce multi-layer thin films, the spin-coating and UV light irradiation steps were repeated multiple times. The as-deposited films were annealed in an oven (Ney Vulcan 3-550) in air at different temperatures for 1 hr using a ramping rate of 10 °C/min.

The same procedures were used for synthesis of a-WO₃ films, except that a 0.25 M WCl₆ solution in isopropanol was used as precursor solution and UV irradiation time was 5 min. The as-deposited films were annealed in air at 100°C for 1 hr. WO₃ films with 5 layers of deposition were prepared and used in all devices throughout this work.

Electrolyte preparation
LiClO₄ and PMMA were dried at 100°C overnight, while PC was dried using a molecular sieve type-3A with a w/v of 20% overnight. The molecular sieves were activated by annealing at 300°C overnight before use. 0.53 g LiClO₄ was dissolved in 10 ml dry PC to form a 0.5 M solution. 1.34 g PMMA was then added to the LiClO₄-PC solution under magnetic stirring. The mixture was stirred and heated at 60°C on a hot plate for 16 hrs to form a colorless transparent gel.

Device assembly
Prior to device assembly, NiOₓ films were prelithiated by electrochemical means using a conventional three electrode system with NiOₓ films on FTO glass as the working electrode, Ag/AgCl as the reference electrode, Pt wire as the counter electrode and 1 M LiClO₄-PC as electrolyte. The lithium ions were intercalated into the NiOₓ films by applying a potential of -1.5 V for 5 min.

Electrochromic devices were fabricated by placing a 2 × 2 cm square silicone rubber sheet (50 A, thickness = 1 mm; McMaster-CARR) with a centered hollow circle (diameter = 1.6 cm) on top of the prelithiated NiOₓ film on FTO glass that serves as the counter electrode. The LiClO₄-PC-PMMA gel electrolyte was then drop-cast into the hollow circle. The FTO glass coated with a-WO₃ films (working electrode) was then laid on top of the silicon spacer to form a closed cell. Epoxy glue was used to seal the cell. The assembled devices were then heated at 60°C overnight before measuring the electrochromic performance. The assembled device had an active area of 2.0 cm².
Physical methods
An XRF analyzer (Thermo Fisher Scientific) was used to track chlorine in thin films. XPS analyses were carried out on a Leybold MAX200 spectrometer using Al Kα radiation. The pass energy was 192 eV for the survey scan and 48 eV for the narrow scan. Grazing incidence X-ray diffraction (GIXRD) experiments were performed with a Rigaku Smartlab diffractometer in parallel beam mode using Cu Kα radiation. Data were collected with a scan step of 0.04°, an incidence angle of 0.3°, and a scan rate of 3° min⁻¹. SEM images were acquired in secondary electron mode at 1 kV accelerating voltage on a Helios NanoLab 650 Focused Ion Beam SEM. To obtain cross-sectional images, FTO substrates coated with a-NiOx films were cleaved in-house and the freshly broken edges were imaged at a tilt angle of 52°. The electrochromic properties of EC devices were measured with a PerkinElmer Lambda 35 UV-Vis spectrophotometer and a CHI660D potentiostat.