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Advances in Electrochromic Device Technology: Multiple Roads towards Superior Durability

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ABSTRACT

Most electrochromic (EC) devices must have a service lifetime of many years, and this is particularly so for "smart windows" in buildings with good energy efficiency and indoor comfort. The central part of oxide-based EC devices contains thin films based on W oxide and Ni oxide together with an interposed electrolyte. Depending on operating conditions, these films may show degradation at a slower or faster pace, and means to prevent or reverse this phenomenon, or as a minimum allow reliable lifetime prediction, have been sought ever since the beginnings of EC technology. Here we survey recent endeavors related to EC films of W oxide and Ni oxide and show that (*i*) *electrochemical pretreatment* of films in a liquid electrolyte can significantly improve durability, (*ii*) *electrochemical posttreatment* in a liquid electrolyte can rejuvenate degraded films, (*iii*) *mixed oxides* can have better durability and optical performance than corresponding pure oxides, and (*iv*) *lifetime prediction* is possible.

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1. Introduction

Oxide-based electrochromic (EC) devices typically consist of a W-oxide-based film separated from a Ni-oxide-based film by a solid electrolyte and also include surrounding films serving as transparent electrical conductors [1–4]; this configuration is illustrated in Fig. 1. The entire five-layer structure is either deposited sequentially onto a single glass or polymer substrate [5,6] or consists of two such substrates, each with a double-layer coating, connected by a polymer electrolyte [7]. The mobile ions should be small, and protons (H^+) or Li^+ ions are commonly used. The optical transmittance is changed when a voltage is applied between the transparent electrical conductors and shuttles ions from the electrolyte, as well as charge-balancing electrons from the transparent conductors, between the W-oxide-based and Ni-oxide-based films. The films' coloration is referred to as "cathodic" (darkening under ion insertion) and "anodic" (darkening under ion extraction), respectively. It is preferable that both types of films are porous on the nanometer scale, and it appears that the surface of the film is very important for Ni-oxide-based films in contact with Li-ion-conducting electrolytes [8]. Clearly, the EC device can be viewed as a thin-film electrical battery whose optical absorption is governed by its charging state. And, just as for batteries, the performance of the EC device tends to decline with time.

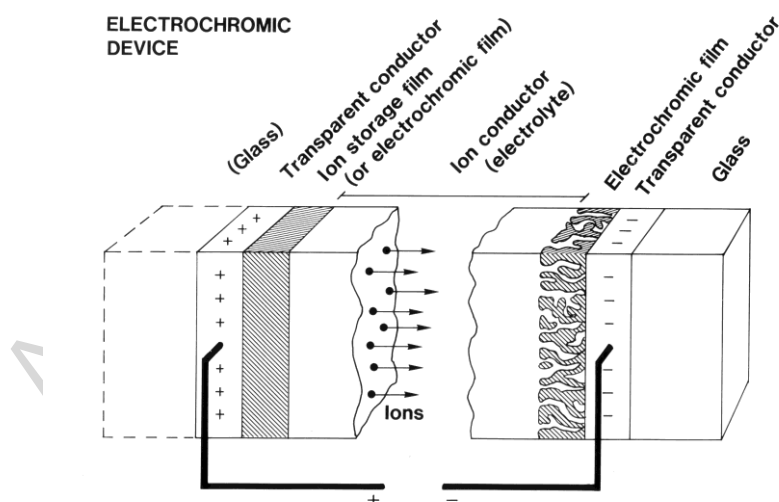
Fig. 1. Generic EC device configuration showing a multilayer structure on a single substrate (monolithic design) and, alternatively, such a structure interposed between two substrates (polymer laminate design). The substrate(s) can be of glass or polymer. Arrows illustrate the transport of positive ions in an electrical field caused by a voltage supplied between two transparent conductors.

EC devices have many current and forthcoming applications in modern technology. The largest one, at least in terms of surface areas, is in variable-transmittance glazing for energy-efficient buildings with good indoor comfort [2,9]. Other applications regard non-emissive information displays and surfaces with variable visible reflectance or thermal emittance. The required service lifetime depends on the intended application but should be decades in the case of EC glazing. Today's EC technology is indeed adequate for the mentioned applications, but enhanced durability nevertheless is of great interest since it will allow larger and faster optical transmittance modulation. Durability issues have been investigated ever since the inception of EC technology: Early work focused on etching of W oxide films in strongly acidic electrolytes [10,11], but this problem was evaded by the use Li-ion-conducting electrolytes such as polymers [12,13] which became available as by-products of battery-related research and development. Subsequent work has often been focused on full EC devices, and results can be found in numerous publications [14–20]. It should be noted that durability and degradation are multifaceted phenomena and also include aspects such as degree of crystallinity, mechanical failure during repeated ion insertion/extraction, and parasitic electrochemical reactions.

The present paper surveys several recent endeavors to understand and model degradation of EC thin films based on W oxide and Ni oxide and to use this knowledge in order to create films which are superior to those in current use. Specifically, we investigate four approaches: (*i*) a novel technique to boost the EC performance of WO_3 films through *electrochemical pretreatment* in an Li-ion-conducting electrolyte, (*ii*) *electrochemical posttreatment* of electrochemically cycled and degraded W-oxide-based and Ni-oxide-based films in a Li-ion-conducting electrolyte to remove trapped ions and thereby rejuvenate the EC films, (*iii*) the use of *oxidic admixtures* to improve WO_3 films, and (*iv*) *lifetime prediction* for W-oxide-based and Ni-oxide-based films. The EC films were deposited by reactive dc magnetron sputtering onto transparent conducting layers of In_2O_3:Sn (ITO) backed by glass. Electrochemical operations were performed in a glove box with water content below 0.5 ppm. We refer to detailed reports, cited below, for further details.

2. Enhanced durability of WO_3 films by electrochemical pretreatment

We very recently discovered that WO_3 films could achieve greatly improved electrochemical cycling durability by immersing them in an electrolyte comprised of $LiClO_4$ together with propylene carbonate (PC) and applying a voltage of 6 V vs. a conventional

Li/Li$^+$ counter electrode for several hours (this counter electrode was used throughout our studies); the polarity of the voltage assured Li$^+$ expulsion [21]. Fig. 2 shows the evolution of the current density and of the optical transmittance at a mid-luminous wavelength of 550 nm when the voltage was applied during a 24-h period. The current density displays an initial sharp decrease followed by a distinct broad peak after ~4 h and a final slow decrease after ~6 h, whereas the transmittance remains high and almost unchanged throughout the electrochemical treatment.
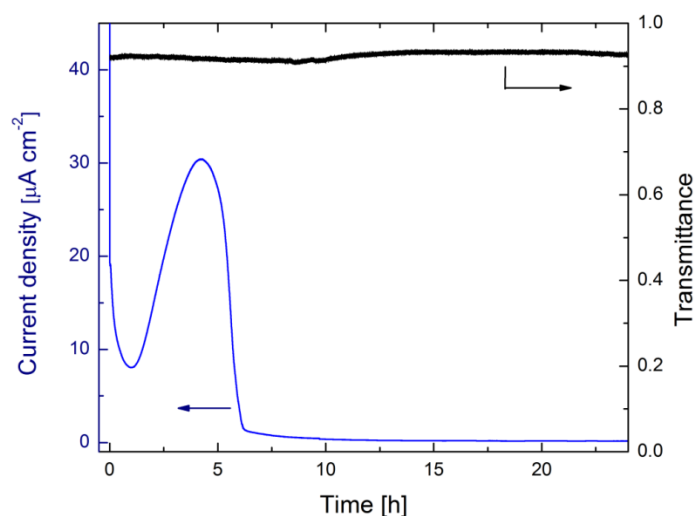

Fig. 2. Current density (left-hand scale) and optical transmittance at 550 nm (right-hand scale) for a ~300-nm-thick WO$_3$ film in an electrolyte of LiClO$_4$–PC. Data show property evolution upon potentiostatic treatment. The weak transmittance minimum after 9 h may be spurious. Arrows indicate applicable scale. From Ref. 21.

Electrochemical cycling and concurrent optical transmittance measurements at a wavelength of 550 nm were conducted on as-deposited and electrochemically pretreated WO$_3$ films; data are reported in Fig. 3. Specifically, Figs. 3a and 3b show results from cyclic voltammetry (CV) performed in LiClO$_4$–PC. The voltage applied to the EC film was swept repeatedly between two endpoints while the current density was recorded. The voltage range was chosen to be 1.5–4.0 V and the sweep rate s was 20 mV s^{-1}; this range is significantly wider than in most prior work on the EC properties of WO$_3$ immersed in LiClO$_4$–PC and was employed in order to enable durability studies within reasonably short time spans. The areas encircled by consecutive voltage sweeps in the positive and negative directions in the CV data, denoting charge capacity, shrink very rapidly upon extended cycling for the as-deposited film (Fig. 3a), whereas the decline is seen to be almost nil for the potentiostatically pretreated film

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(Fig. 3b). Analogous results on the optical transmittance display a dramatic decrease of the optical modulation range for the as deposited film (Fig. 3c) while the pretreated film conspicuously maintained its modulation range almost unaltered (Fig. 3d). The reason for the striking durability enhancement through electrochemical pretreatment is currently under investigation, and preliminary data indicate that carbonaceous surface layers as well as atomic intermixing at WO_3/ITO and ITO/glass interfaces play significant roles.
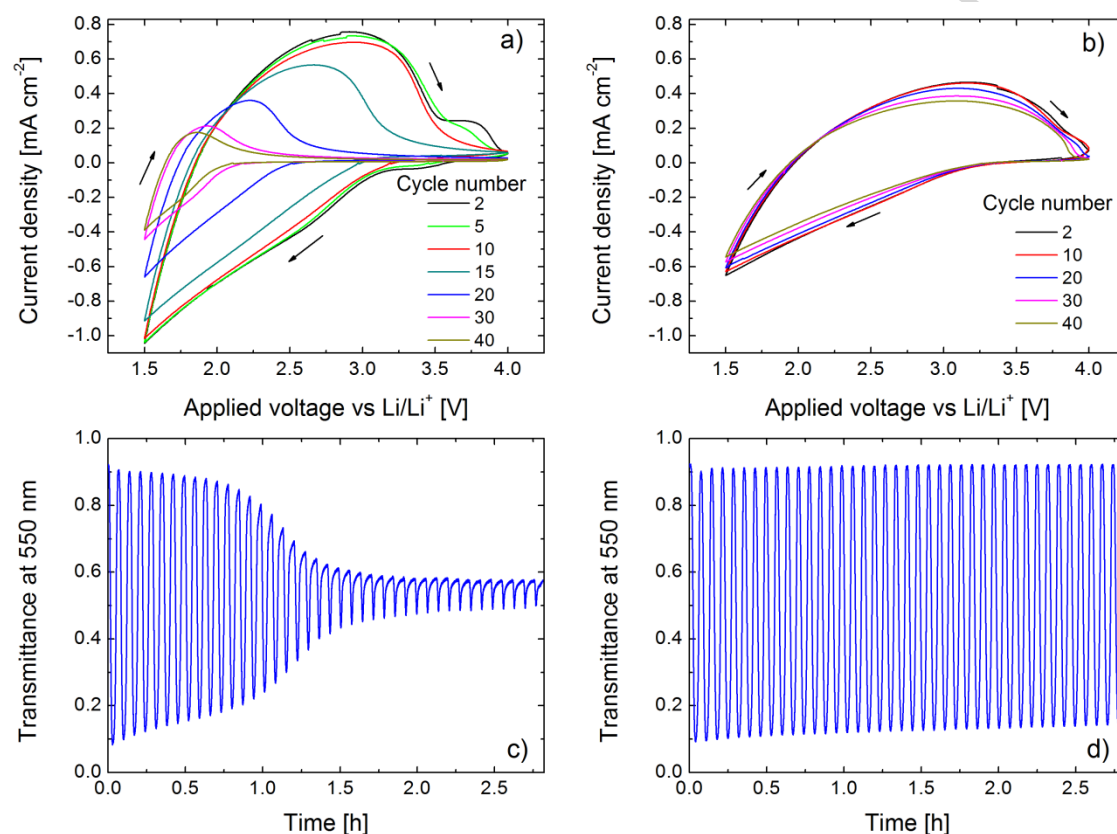

Fig. 3. Time-dependent evolution of cyclic voltammograms (panels a and b) and corresponding optical transmittance at 550 nm (panels c and d) for a ~300-nm-thick WO_3 film in as-deposited state (panels a and c) and after potentiostatic pretreatment in an electrolyte of $LiClO_4$–PC (panels b and d). Arrows indicate voltage sweep direction. It may be noted that the encircled areas in the voltammograms (panels a and b) are not the same for the initial cycle, which implies that the colorations efficiencies are different and actually significantly higher for the pretreated film. From Ref. 21.

3. Rejuvenation of degraded W-oxide-based and Ni-oxide-based films by electrochemical posttreatment

It was found a few years ago that EC films, which had been degraded through excessive voltage cycling in electrolytes on $LiClO_4$–PC, could be rejuvenated and regain their initial properties through electrochemical treatment in the same kind of electrolyte. Initial work was

performed on WO$_3$ films subjected to galvanostatic posttreatment in which a constant current with a density of 10^{-5} A cm^{-2} was run through the sample for several hours [22]. The degradation–rejuvenation process could be repeated several times with only minor loss in efficiency [23] and analogous galvanostatic rejuvenation was subsequently demonstrated also for cathodically coloring EC films of TiO$_2$ [24] and MoO$_3$ [25].

Rejuvenation of degraded WO$_3$ films can be accomplished also by potentiostatic posttreatment as illustrated in Fig. 4 [26]. The experiment was performed as follows: A WO$_3$ film was first subjected to 10 CV cycles in the range of 2.0–4.0 V at s = 20 mV s^{-1}, followed by a resting period of 10 min. Subsequent to this conditioning of the sample, it went through 20 harsh CV cycles in the range of 1.5–4.0 V at s =10 mV s^{-1}. The transmittance modulation interval declined rapidly, which clearly is consistent with the data shown in Fig. 3a. A voltage of 5.55 V was then applied to the sample, which led to a current with a density that fell off rapidly at the beginning, then displayed a peak, and finally dropped to a low value. The current density evolution is principally similar to that for electrochemical pretreatment (cf. Fig. 2). The optical transmittance at 550 nm increased somewhat when the voltage was applied, then remained rather unchanged, and finally increased to the same value as for the uncycled film; this final change took place simultaneously with the appearance of the peak in the current density. At the end of the experiment, CV cycling was resumed for 2.0–4.0 V at s = 20 mV s^{-1} and it was found that the initial EC properties were recovered, i.e., the WO$_3$ film had been rejuvenated with regard to its electrochromism. Rejuvenation was possible only if the voltage exceeded ~5 V and occurred faster when the voltage was increased [26].

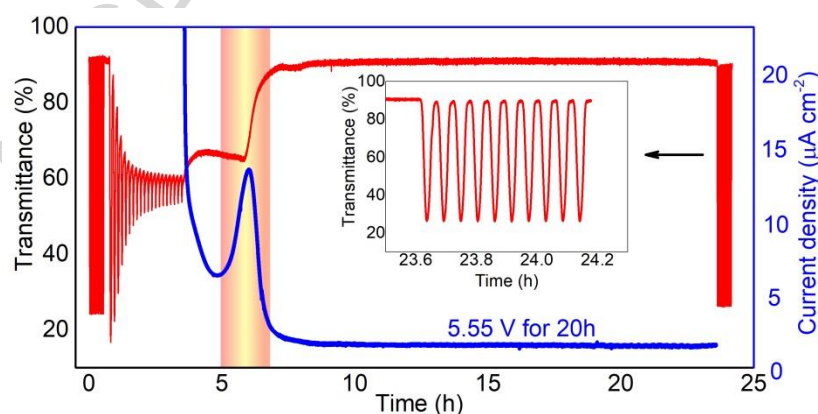**Fig. 4.** Time-dependent evolution of optical transmittance at 550 nm (red) and current density (blue) for a ~300-nm-thick WO$_3$ film subjected to a series of electrochemical operations in an electrolyte of LiClO$_4$–PC, as described in the main text. Inset shows time-resolved transmittance after the potentiostatic posttreatment. After Ref. 26.

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The degradation of the EC properties upon extended CV cycling may be assigned to trapping of Li ions by following notions asserting that amorphous WO_3 can be described as a network of connected sites with low inter-site barriers, and permitting rapid ion diffusion in the host material, and other sites with larger energy barriers which are able to serve as traps for diffusing ions [27–30]. In this picture, rejuvenation is associated with the release of these trapped ions by electrochemical treatment. Conclusive evidence in favor of this model was acquired by investigating the Li content—including its depth profile—by time-of-flight elastic recoil detection analysis (ToF-ERDA) [31] as well as time-of-flight secondary ion mass spectroscopy (ToF-SIMS) [32]. Fig. 5 reports data from a degraded WO_3 film subjected to galvanostatic detrapping of Li ions [31]. The main part of the figure shows that the optical transmittance modulation drops rapidly during harsh electrochemical cycling—in analogy with data in Figs. 3a and 4—until it reaches the point denoted II at which the Li content was investigated and found to be much greater than in the as-deposited film. Rejuvenation with a current density of 10^{-5} A cm^{-2} yielded an abrupt onset of high transmittance after ~9 h, which could be ascribed to Li ion detrapping as apparent from the absence of Li in the ToF-ERDA data pertaining to point III in Fig. 5.
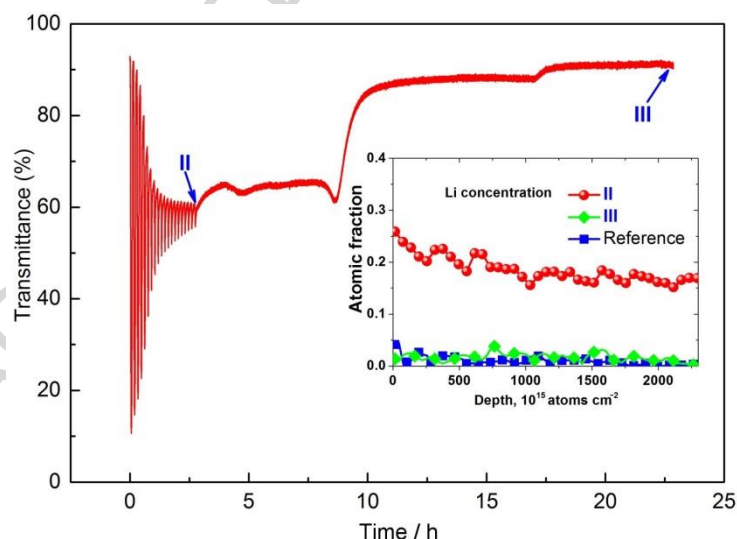

Fig. 5. Time-dependent evolution of optical transmittance at 550 nm of a ~300-nm-thick WO_3 film subjected to a series of electrochemical operations in an electrolyte of LiClO$_4$–PC, as described in the main text. Inset shows ToF-ERDA-based depth profiles for Li ions taken at points II and III and also for a reference sample that had been immersed in the electrolyte without posttreatment. From Ref. 31.

Electrochemical rejuvenation of EC properties is possible also in anodically coloring Ni oxide films immersed in $LiClO_4$–PC and involves not only Li ions but, interestingly, also Cl-based ones [33]. Fig. 6 reports optical transmittance modulation during CV cycling at 2.0–4.0 V at $s = 50$ mV s^{-1} during a period of ~11 h (500 CV cycles). The optical modulation interval dropped to about half of its initial value during this process. Potentiostatic posttreatment at 4.1 V was then performed for 20 h, followed by a 2-h resting period. Finally, the CV cycling was resumed and it was found that the original EC performance was regained, at least approximately.
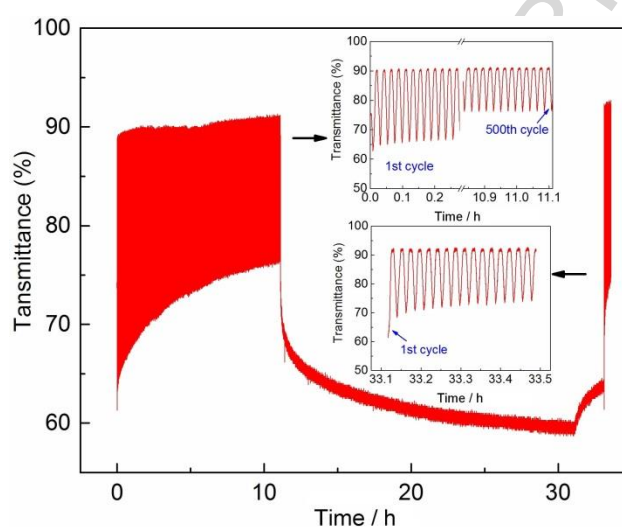

Fig. 6. Time-dependent evolution of optical transmittance at 550 nm of a ~300-nm-thick $NiO_{1.15}$ film subjected to a series of electrochemical operations in an electrolyte of $LiClO_4$–PC, as described in the main text. Selected time-resolved data, indicated by arrows, are shown in the insets. After Ref. 33.

4. Enhanced durability and optical properties by oxidic admixtures in WO₃ films

Mixed oxides can have better EC properties than their constituents, as has been realized for many years [34,35]. The optical performance can be improved as a consequence of intermixing of absorption bands in the individual oxides, and durability can be boosted as a result of chemical and electrochemical changes. Many binary oxide mixtures have been investigated during recent years and, for example, work has been reported on W oxide mixed with Ti, V, Nb, Mo, Ta, or Ti, and on Ni oxide mixed with Al, Ti, V, or Ir [2,36–39]. Several other binary oxides have been studied as well.

Fig. 7 illustrates the enhanced durability that can be achieved by adding Ti to WO_3 [36] and reports CV data taken for 1.5–4.0 V and at $s = 10$ mV s^{-1} but otherwise as stated above. A

decline in the current density upon extended CV cycling is apparent and signals degradation and loss of EC performance. This process is very fast for the WO_3 film (Fig. 7a) but much slower for the $W_{0.88}Ti_{0.12}O_3$ film (Fig. 7b), which proves the beneficial effect of the added Ti. Principally similar results have been reported in prior work [40–43].
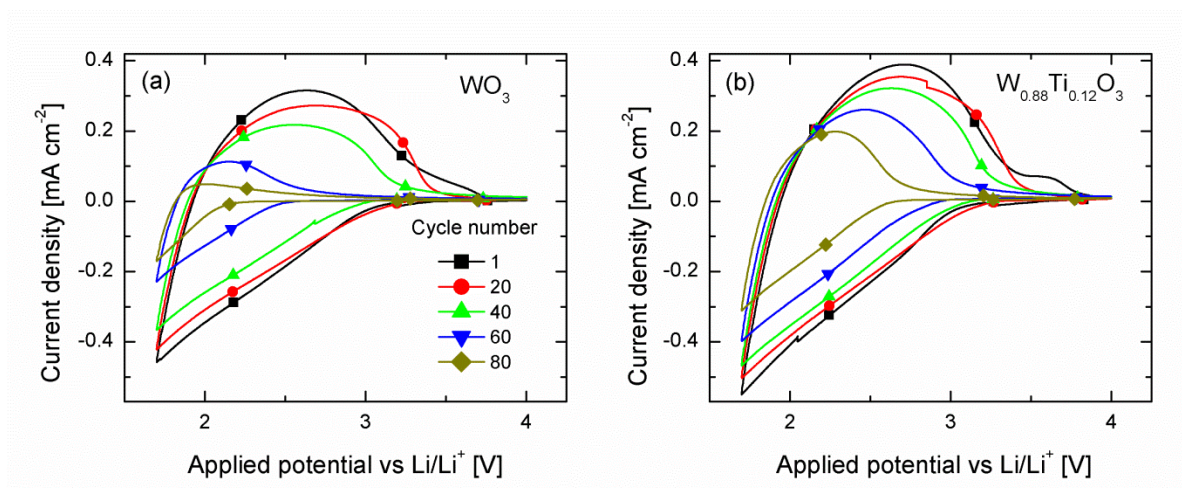

Fig. 7. Cyclic voltammograms for ~300-nm-thick films of the shown compositions in an electrolyte of $LiClO_4$–PC. Data are shown for the indicated number of CV cycles. After Ref. 36.

Further optimization of the EC performance can be achieved by going to ternary oxide mixtures, which again was demonstrated a long time ago [44]. Recent comprehensive work was devoted to films of $W_{1-x-y}Ti_xMo_yO_3$ with $x < 0.2$ and $y < 0.2$ [45]. Mo was added since it has a well-known propensity to improve the color properties of EC WO_3 films, especially their color neutrality [34,46,47]. Fig. 8 reports chromaticity coordinates (**x**, **y**) [48] for a number of ternary compositions with $x \approx 0.1$ and different magnitudes of y and shows that approximate color neutrality is achievable. Electrochemical durability was diminished at large Mo contents and it was appropriate to have $y < 0.06$.
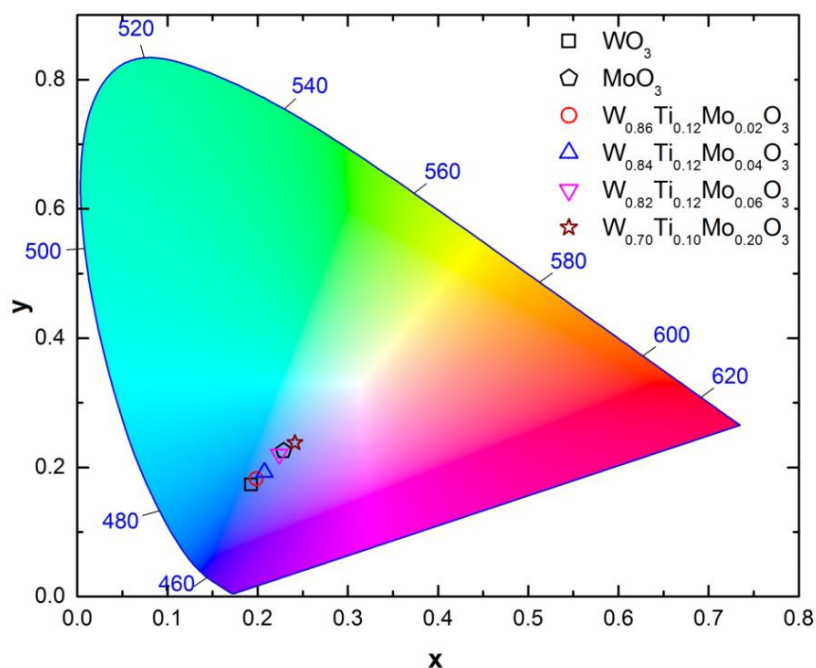
Fig. 8. CIE 1931 chromaticity diagram (daylight illuminant D65) for ~300-nm-thick $W_{1-x-y}Ti_xMo_yO_3$ films with the shown compositions. Numbers along the curve denote wavelengths in nm. White light corresponds to **x** = **y** = ⅓. From Ref. 45.

A companion study was performed on films of $W_{1-x-y}Ni_xTi_yO_3$ with $x < 0.4$ and $y < 0.2$ [49] and was motivated by the fact that Ni addition to WO_3 can give interesting EC properties [50]; it was found that $y \approx 0.17$ yielded improved durability whereas Ni addition was unable to provide any significant enhancement of the EC performance.

Complex Ni-oxide-based EC oxides have been investigated recently too, and data have been reported for oxides of Ni–W–Li [51], Ni–Al–Li [52], Ni–Zr–Li [53,54], Ni–Fe–C [55] and Ni–Ti–Li [56] as well as on Ni–LiPON [57].

5. Life-time modelling of W-oxide-based and Ni-oxide-based films

It was noted several times above that the charge capacity Q of W-oxide-based films tends to shrink upon CV cycling and that this effect occurs concurrently with a decrease of the optical modulation range. The decrease of Q is very fast when the voltage range is as large as 1.5–4.0 V (cf. Figs. 3a and 7a), but the same tendency prevails for CV cycling within narrower voltage ranges given that the cycle number x is large enough. This decline can be accurately modeled for W-oxide-based [58] and Ni-oxide-based films [59,60] as discussed next.

A detailed study of Q as a function of x was reported recently [58] for cycling of WO$_3$ films up to 5500 times in the voltage range of 2.0–4.0 V at $s = 20$ mV s^{-1}. Fig. 9a reports that the cyclic voltammograms shrink upon continued voltage sweeps and, strikingly, Q falls off according to a curved trajectory when x is plotted on a logarithmic scale (Fig 9b). The optical modulation range is also diminished, as shown in the inset in Fig. 9b; this effect is due to a rise in the dark-state transmittance, whereas the bleached-state appeared unaffected by the CV cycling (which is different from when harsher cycling was performed in the wider range of 1.5–4.0 V).
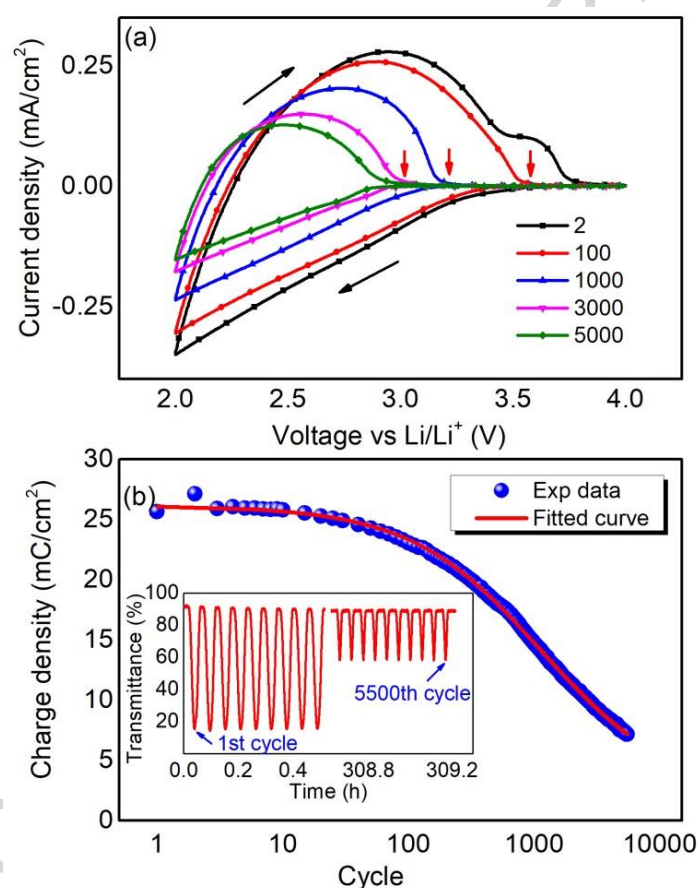

Fig. 9. Cyclic voltammograms (a) and charge density vs. cycle number (b) for a ~300-nm-thick WO$_3$ film in an electrolyte of LiClO$_4$–PC. Dots in panel (b) show experimental data, and the curve was drawn as a fit to Eq. (1) using parameters given in the main text. Selected time-resolved data, as indicated by arrows, are shown in the inset.

Ni oxide films were also investigated with regard to CV-cycle-dependent decline in charge capacity, and Fig. 10 reports data for a film immersed in LiClO$_4$–PC and cycled for up to 10,000 times in the voltage range of 2.0–4.1 V at $s = 50$ mV s^{-1}. Clearly the cyclic

voltammograms shrink upon continued cycling (Fig. 10a), and Q drops almost linearly when x is shown on a logarithmic scale. This decline does not approach zero charge capacity, as for W-oxide-based films, but excessive CV cycling made the Ni oxide films delaminate from the substrate and abruptly lose their charge capacity [60].
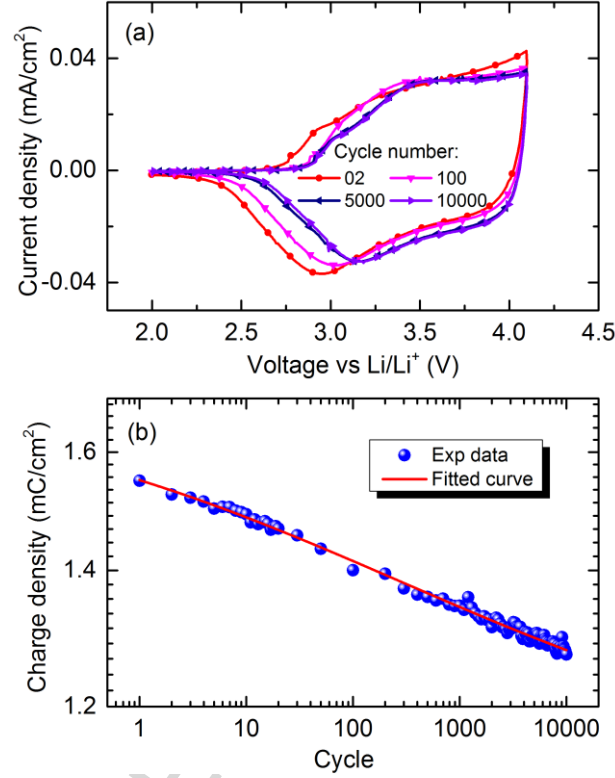

Fig. 10. Cyclic voltammograms (a) and charge density vs. cycle number (b) for a ~300-nm-thick Ni oxide film in an electrolyte of LiClO$_4$–PC. Dots in panel (b) show experimental data, and the curve was drawn as a fit to Eq. (1) using parameters given in the main text. From Refs. 4 and 59.

Various functional dependencies were employed in order to model the dependence of Q on x, and it was found that a power-law or, alternatively, a stretched-exponential expression could account for the data adequately [60]. Using the power-law, the relationship can be written

$$Q(x) = A_2 + \frac{A_1 - A_2}{1 + (\frac{x-1}{x_0})^p} \quad , \tag{1}$$

where A_1 and A_2 are the initial and final charge capacities, x_0 is the number of cycles at which Q has dropped to the average of its initial and final value, and p denotes a kinetic exponent. Specifically, the model data in Fig. 9b were obtained with $A_1 = 26.65$ mC cm^{-2}, $A_2 = 0$ and $p = 0.73$, whereas the model data in Fig. 10b were based on $A_1 = 1.59$ mC cm^{-2}, $A_2 = 1.20$ mC

cm^{-2} and p = 0.36. The power-law dependence—as well as the alternative stretched-exponential expression—can be reconciled with so-called dispersive chemical kinetics [61–65] that can account for a variety of diffusion-limited reactions. No fundamental justification for Eq. (1) is currently at hand, but the equation nevertheless can be used for empirical life-time prediction.

6. Conclusion

Electrochromic technology hinges on devices with sufficient durability for their intended applications, and the demands are particularly stringent in the case of smart windows for energy efficient glazing in buildings with good indoor comfort. These windows must last for decades, even under exposure to intense solar radiation and associated heating. Current technology for smart windows is adequate, but it can be improved if their durability becomes better so that the optical modulation range and speed can be enhanced. As shown in this survey paper, there are multiple roads towards device longevity and life-time prediction. These roads entail (*i*) *electrochemical pretreatment* of films in a liquid electrolyte and shows that their durability can be significantly improved, (*ii*) that *electrochemical posttreatment* of films in a liquid electrolyte can rejuvenate degraded films, (*iii*) that *mixed oxide* films can have better durability and optical performance than films of the corresponding pure oxides and, finally, (*iv*) that *lifetime prediction* is possible. Several of the mentioned techniques employ electrochemistry at "unusual" potentials, which means that reaction pathways and reaction products are currently unknown. This is an obvious obstacle to rapid progress but also—viewed from a different perspective—an incentive to take electrochemistry into a realm that today is mostly terra incognita. Our work therefore may serve as a sketchy road map for future work.

Finally, it should be emphasized that the work so far has dealt with individual electrochromic films with cathodic and anodic coloration and immersed in one particular lithium-ion-conducting electrolyte. Obviously what has been learnt for these systems has to be implemented for full electrochromic devices with two electrochromic films and with solid polymeric or inorganic electrolytes.

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Acknowledgments

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