

Novel Electrochromic Materials and Devices

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ABSTRACT

We review a number of recently discussed electrochromic devices for modulating optical transmittance and emittance. Data are given on all-solid-state devices as well as on polymer laminated devices, with and without self-powering by integrated solar cells. We then turn to a specific, flexible polyester-based device incorporating electrochromic W oxide and Ni oxide and discuss, among other things, some critical manufacturing aspects. They include gas treatments for precharging of the individual electrochromic films in order to make them ready for easy device assembly, and enhancements of the bleached-state transmittance through addition of Al or Mg to the Ni oxide.

INTRODUCTION

Electrochromic materials are able to change their optical properties upon charge insertion/extraction. When thin films of such materials are integrated in devices, it becomes possible to regulate the transmittance T , reflectance R , absorbance A , and emittance E between widely separated extremes [1-3]. A standard electrochromic design embodies five superimposed layers on one substrate or positioned between two substrates in a laminate configuration. Normally the substrates are made of glass or flexible polyester foil. The central part of the five-layer construction is a pure ion conductor (electrolyte) that can be inorganic (often based on an oxide film) or organic (an adhesive polymer). The ions should be small in order to be mobile; protons (H^+) or lithium ions (Li^+) are preferred. This ion conductor bounds on an electrochromic film (WO_3 being a typical example) capable of conducting electrons as well as ions. On the other side of the ion conductor is a film serving as an ion storage, ideally with electrochromic properties complementary to those of the first electrochromic film. This central three-layer structure is positioned between electrically conducting transparent films; the best material in terms of optical and electrical properties is $In_2O_3:Sn$ (known as Indium Tin Oxide, ITO), while films of $SnO_2:F$ are less costly and readily available on large area substrates. When a voltage of the order of one volt is applied between the transparent electrical conductors, ions can be shuttled between the ion storage film and the electrochromic film. The electrons injected from the transparent conductors then alter the optical properties. A reversal of the voltage, or short-

circuiting, brings back the original properties. The coloration can be stopped at any intermediate level, and the device exhibits open-circuit memory.

Electrochromism can lead to numerous applications. A few of these – such as architectural “smart windows”, rear-view mirrors for cars, and some display devices – are presently (early 2003) available on the market. More products are likely to appear in the future, especially when practical manufacturing techniques and more durable products become better established. Among the many possibilities, one can mention “smart labels”, variable-transmittance sunroofs for automobiles, and variable-emittance surfaces for temperature control of spacecraft.

SURVEY OF SOME RECENT ELECTROCHROMIC DEVICES

Below we present data for a selection of electrochromic devices concerning the modulation range for T , R , and E .

Work on a number of devices backed by a single glass or polyester substrate has been supported by industries in different parts of the world [4-7]. Optical modulation has been effected by H^+ transport as well as Li^+ transport. High values of luminous and solar transmittance, and a large modulation range, are noteworthy for devices incorporating NiO and IrO_2 ; these materials exhibit anodic electrochromism (color under charge extraction) and are complementary to WO_3 , which has cathodic electrochromism (colors under charge insertion).

Laminated devices represent another option [8-10]. Among those operating with H^+ transport, the electrolytes have been based on polyethylene oxide (PEO), a copolymer of sodium vinylsulfonic acid and 1-vinyl-2-pyrrolidinone and poly-2-acrylamido-2-methyl-propane sulfonic acid. The counter electrodes were IrO_2 , $K_3Fe(CN)_6$ (known as “Prussian Blue”), polyaniline, or a mixture of the latter two. The modulation range for visible light can be large. Laminated devices with Li^+ transport and inorganic counter electrodes have been subject to many detailed investigations [11-17]. The electrolytes were based on poly methyl methacrylate copolymerized with propylene carbonate or polypropylene glycol, polypyrrole, silane, glycidylxypropyl trimethoxysilane copolymerized with

tetraethylene glycol, ormolyte (inorganic-organic hybrid electrolyte), polyethylene glycol methacrylate copolymerized with PEO, or polyvinylidene fluoride; the polymers were made ion conducting by the addition of an appropriate Li salt. The counter electrodes were based on V_2O_5 , TiO_2 with or without additions of ZrO_2 or CeO_2 , SnO_2 doped with Mo and Sb, CoO deposited with Li, and NiO deposited with or without Li. A large range of optical modulation, together with durability and reasonable color/bleach response times, were observed in several cases.

Modulation of the optical properties requires the application of a DC voltage of a magnitude that is conveniently obtained from solar cells. These cells can be external to the electrochromic device. Alternatively, if semitransparent cells are used, they can be integrated in a multilayer design comprising a superimposed solar cell and electrochromic tandem configuration. A number of such designs have been discussed [18]. The solar cells investigated thus far have been of two types: dye sensitized nanocrystalline ones and doped amorphous $SiC:H$. All of the solar-cell-powered tandem devices exhibit a small range of optical modulation, and most of them have a low transmittance in the bleached state, which gives a limitation for several uses.

Electrochromic devices for modulating the thermal emittance have been studied recently [19-21]. Most of the devices exploit the fact that crystalline tungsten oxide is able to modify its infrared reflectance upon charge insertion/extraction. This surface must be exposed to the ambience either directly or via an infrared-transparent substrate such as CaF_2 , Si , or $ZnSe$. Charge is introduced via a grid electrode, normally of Al or Au , with a large open fraction. The counter electrode can be normal “amorphous” WO_3 , NiO , or a polymer electrolyte.

AN ELECTROCHROMIC FOIL: SPECIFIC DESIGN FEATURES AND PROPERTIES

This section discusses in some detail the preparation of a flexible electrochromic device. Particular attention is given to practical manufacturing technology and to optimization of the bleached-state transmittance. More details on this novel electrochromic device can be found elsewhere [3,22].

Deposition of thin films

Electrochromic films of WO_3 and NiO were made by DC magnetron sputtering onto 0.175-mm-thick polyester foil, precoated with an ITO layer having a resistance/square of 40 to 60 Ω , using a large box-type coater with 50x12.5 cm^2 targets [23]. For research purposes we also employed a smaller coater with 5-cm-targets [24] and prepared films on glass plates with ITO layers having a resistance/square of 15 Ω . The targets were plates of W, Ni, Mg, $NiV_{0.08}$, and $NiAl_{0.56}$ with purities between 99.95 and 99.99%. The additions to the Ni target rendered it non-magnetic and hence convenient for magne-

tron sputtering. Carbon substrates were used for compositional determinations using Rutherford Backscattering Spectrometry (RBS). Sputtering took place in Ar/O_2 or $Ar/O_2/H_2$ with optimized mixing ratios. The target-substrate distance lay between 13 cm for the small deposition unit and 20 to 25 cm for the large unit, and the total gas pressure was in the 30 to 40 mTorr range. Typical deposition rates and film thicknesses were 0.4 nm/s and 200 to 300 nm, respectively. Specifics on the depositions can be found elsewhere [22,24-26].

With regard to manufacturing, it is preferable to be able to deposit the films under conditions that make them ready for device lamination, or to have convenient processes for making the as-deposited films prepared for this. In the case of W oxide, one can carry out the deposition in $Ar/O_2/H_2$ according to principles described in the literature [27]. The hydrogen produces a blue color for the as-deposited films, and the key issue with regard to optimizing the gas mixture is to incorporate hydrogen into the film without creating oxygen deficiency. In practice, the optimization of the WO_3 films can be made by measuring their color in the as-deposited state. Color properties are conveniently specified by use of chromaticity coordinates – corresponding to red, blue and green primaries, respectively – using the CIE Colorimetric System [28]. Color neutrality is represented by $x = y = z = 0.333$. Figure 1 illustrates the spectral transmittance for a film made in an optimized mixture of $Ar/O_2/H_2$.

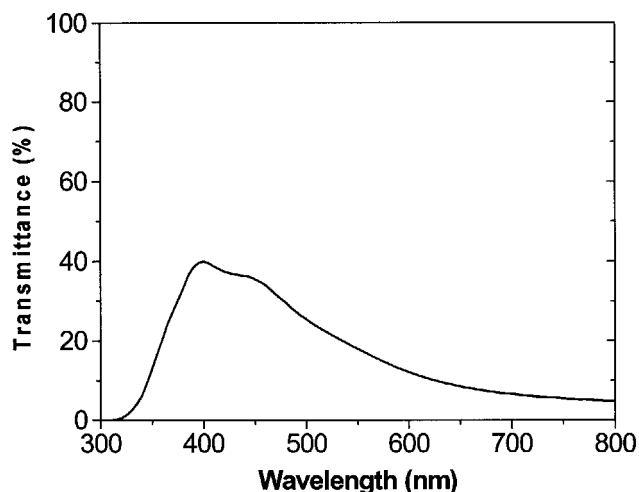


Figure 1: Spectral transmittance of a 300-nm-thick W oxide film produced by sputtering in $Ar/O_2/H_2$ under conditions making it ready for device lamination.

Transmittance enhancement of Ni oxide films

A number of recent electrochromic device designs include NiO films operating in conjunction with WO_3 , as mentioned before. This combination of materials is favorable with regard to electrochemical potentials and the option for achieving chemical compatibility to the electrolyte [29]. A long-standing problem with NiO , however, has been the residual optical

absorption in the $400 < \lambda < 500$ nm wavelength interval, which has precluded a fully transparent state and therefore has been detrimental to architectural applications. As shown next, the absorption in Ni oxide and Ni-V oxide can be significantly lowered by an addition of Al or Mg.

The study on the electrochemical and optical properties used cyclic voltammetry in a KOH electrolyte. Typical data were obtained with a lower (bleaching) potential of -0.5 V and an upper (coloring) potential, denoted U_{col} , of 0.6 V. Specifically, normal T and near-normal R were measured, and spectral absorbance was evaluated from $A(\lambda) = 1 - T(\lambda) - R(\lambda)$. Figure 2 compares bleached-state data on $A(\lambda)$ in the $300 < \lambda < 800$ nm wavelength range for films of $\text{NiAl}_{0.56}\text{O}_q$ (part a), $\text{NiMg}_{0.8}\text{O}_{2.4}$ (part b), and $\text{NiV}_{0.08}\text{Mg}_{0.5}\text{O}_{2.4}$ (part c). Absorbance is also shown for analogous films lacking Al or Mg, i.e., NiO_q and $\text{NiV}_{0.08}\text{O}_q$, where q signifies that the oxygen content has not been determined. With the films in their states of maximum transmittance, the absorbance is found to be significantly smaller for the films containing Al or Mg across the full spectral range. The difference is particularly large at $\lambda < 500$ nm. The strong absorbance at $\lambda < 350$ nm is due to the semiconductor band-gap, which appears to be widened as a consequence of the addition of Al or Mg. Similar beneficial effects were found for Mg addition to electrochromic IrO_2 [29].

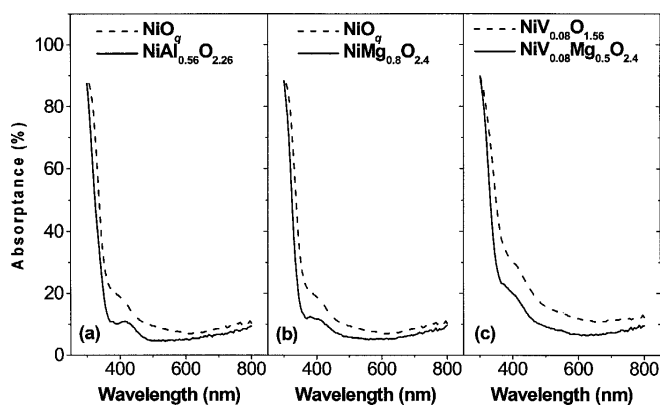


Figure 2: Spectral absorbance for 200-nm-thick Ni-oxide-based films of the shown compositions. The films were in their states of maximum transmittance. q denotes an unknown amount of oxygen.

Corresponding data on $T(\lambda)$ are shown in Figure 3 for the films of $\text{NiAl}_{0.56}\text{O}_q$ and $\text{NiV}_{0.08}\text{O}_q$. The transmittance-enhancing effect of the Al is apparent once again. The latter film has a luminous transmittance (T_{lum}) of 82% and chromaticity coordinates equal to (0.347,0.347,0.306), whereas the Al-containing film is characterized by $T_{\text{lum}} = 85\%$ and chromaticity coordinates being (0.334,0.339,0.328). An analogous analysis for the data in Figure 2(b) yielded that the films of NiO_q and $\text{NiMg}_{0.8}\text{O}_{2.4}$ have chromaticity coordinates (0.339,0.342,0.319)

and (0.337,0.336,0.327), respectively. It is thus clear that the addition of Al or Mg alters the visual appearance toward a more color-neutral state primarily by increasing the contribution from the blue part of the spectrum.

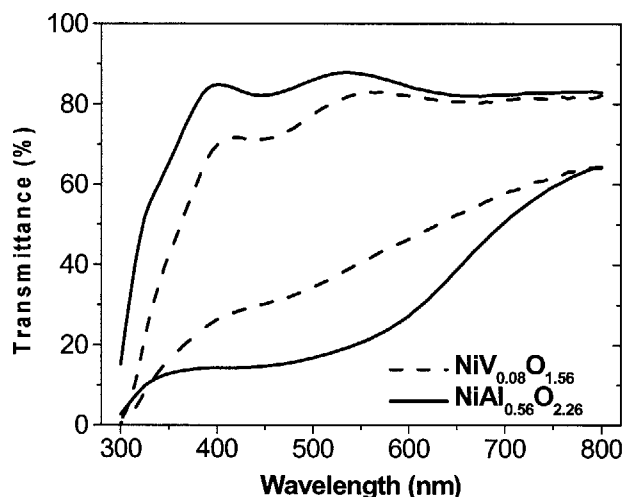


Figure 3: Spectral colored-state and bleached-state transmittance for 200-nm-thick Ni-oxide-based films made by sputtering from $\text{NiAl}_{0.56}$ and $\text{NiV}_{0.08}$ targets. Coloration and bleaching were accomplished in 1 M KOH at 0.6 and -0.5 V vs. Ag/AgCl, respectively. The coloration charges were 15 and 12 mC/cm^2 for the two films; this difference accounts for part of the difference in the optical performance.

The charge capacity – and hence the electrochromism – is influenced by the potentiodynamic range, particularly the magnitude of U_{col} . This effect was studied with regard to $\text{NiV}_{0.08}\text{Mg}_{0.5}\text{O}_{2.4}$ and $\text{NiV}_{0.08}\text{O}_q$, i.e., the films reported on in Figure 2, for $0.45 < U_{\text{col}} < 0.65$ V vs. Ag/AgCl. It was found that similar charge capacities could be obtained provided that U_{col} was set at a potential that was 0.05 to 0.1 V higher when Mg is present. This shift is insignificant for electrochromic device applications.

Pre-assembly charge balancing and device lamination

WO_3 films can be made dark (i.e., charge inserted) by sputtering in the presence of hydrogen [27], as mentioned above. If these films are to operate in conjunction with NiO films, the latter, ideally, should be made so that they are prepared for charge insertion prior to device assembly. Such discharged films are dark. However, the NiO films normally are transparent in their as-deposited state and hence require pre-treatment before device lamination. Charge insertion via an electrochemical procedure is possible, in principle, but obviously unwieldy and not suited for practical fabrication. An alternative method for discharging was developed in earlier work of ours [31]. Essentially, this new method employs exposure to ozone obtained by ultraviolet irradiation of the film in the presence of oxygen.

Figure 4 displays the decrease of T_{lum} as a function time when a conventional ozone photo-reactor was used to illuminate a 220-nm-thick $NiV_{0.08}$ oxide film. The transmittance drops by some 50% during a few minutes, and a further decrease takes place for extended exposure times. Figure 5 illustrates a typical spectral transmittance plot for this film prior to device lamination.

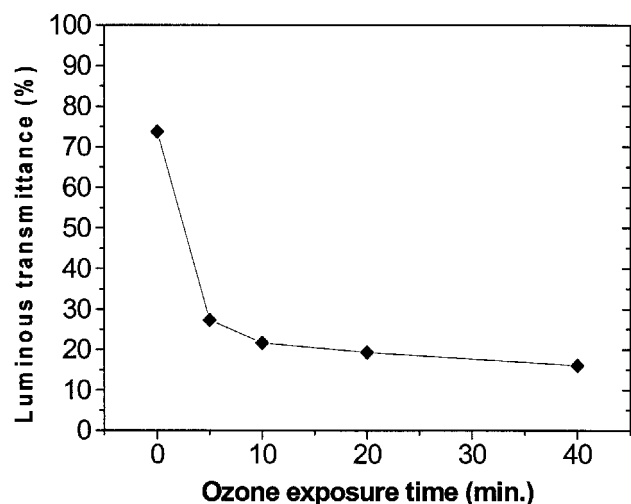


Figure 4: Luminous transmittance vs. post-deposition ozone exposure time for 220-nm-thick Ni-V oxide films produced by sputtering in $Ar/O_2/H_2$.

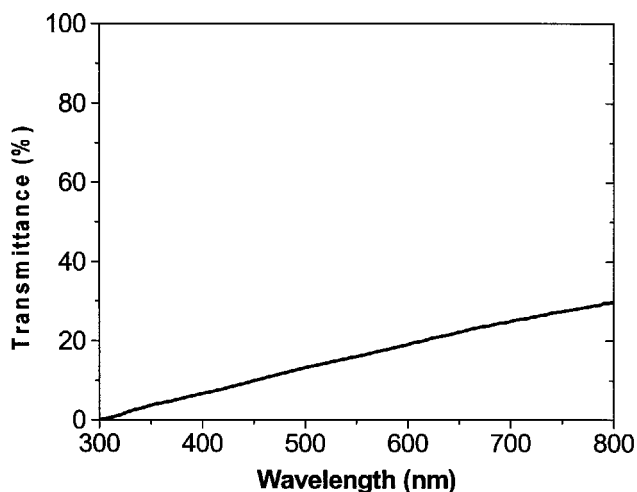


Figure 5: Spectral transmittance of a 220-nm-thick Ni-V oxide film produced by sputtering in $Ar/O_2/H_2$ and post-treated in ozone under conditions making it ready for device lamination.

Polyester-based foils – one with a WO_3 film colored by sputtering in the presence of hydrogen (cf. Figure 1) and another with a NiO film colored by post-deposition ozone exposure (cf. Figure 5) – were laminated together by a PMMA-based electrolyte using roll-pressing at a temperature of $80^\circ C$. The edges of the double foil were then sealed, electrical

contacts were attached, and the electrochromic device was ready for testing and use.

Device tests

Devices of the type described above were cycled between colored and bleached states using trapezoidal voltage pulses between -1.6 and $+1.5$ V, respectively. Figure 6 shows transmittance at three different wavelengths for cycling with one full color-bleach cycle each 200 s. The optical modulation is pronounced, especially for mid-luminous and red light. Most of the changes take place within a few tens of seconds after application of the pulse, but the coloration has not reached saturation even after several minutes. Figure 7 reports on the transmittance in fully colored and bleached states after cycling in the same way as in Figure 6. The foils are seen to change between a high level of about 70% and a low level of 35 to 40% at a wavelength of 550 nm, which is in agreement with the data in Figure 6. The span between the colored and bleached states remains practically unaltered for at least 5000 cycles. Lower transmittance levels, down to 25% or less in the colored state, could be reached for longer coloration times. It should be noted that the possibility of increasing T_{lum} by adding Al or Mg to the Ni oxide has not yet been implemented for the investigations reported on in this section; however, such work is currently under way.

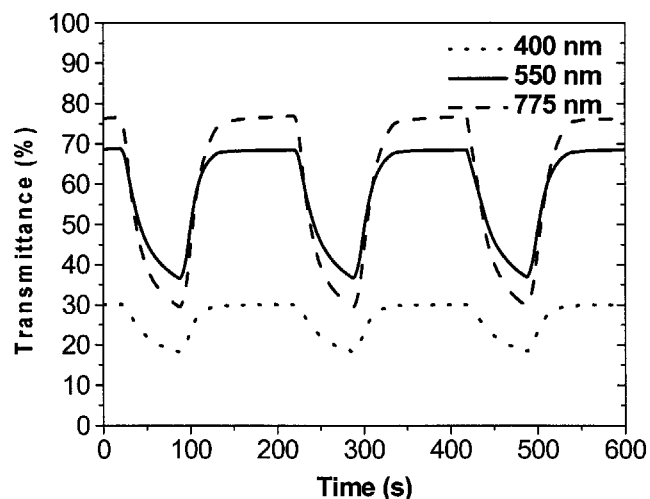


Figure 6: Transmittance at three wavelengths vs. time for electrochromic switching of a laminated device described in the main text.

The devices have open circuit memory, which is an asset because electrical power must be drawn only to effect changes in the optical properties. For example, it was found that the transmittance at a wavelength of 550 nm for a device colored to a transmittance equal to 20% increased only up to about 30% after a time as long as 160 h. Keeping the device in the colored state for an extended time influenced the bleaching time, and a device with an initial bleaching time of about one

minute attained a bleaching time of some 20 minutes after being maintained in the colored state for 160 h.

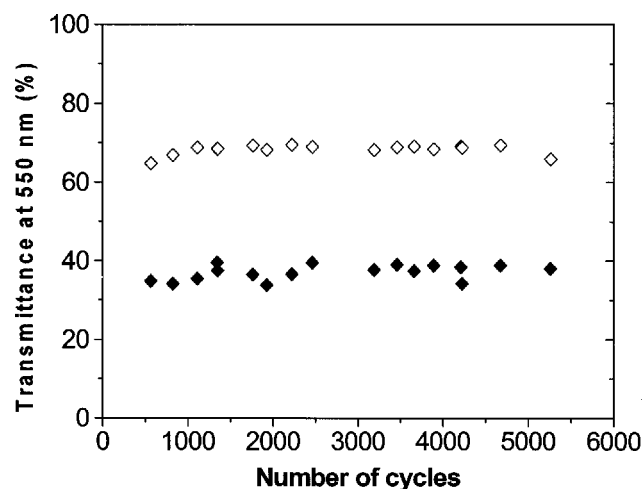


Figure 7: Transmittance at a wavelength of 550 nm vs. number of color/bleach cycles for a laminated electrochromic foil device in colored and bleached states.

The work reported above has demonstrated techniques to make flexible electrochromic foils with sufficient optical modulation range, dynamics, and durability for making them interesting for a range of applications. Easy manufacturing was found to be possible by a combination of different technologies, and the potentially cumbersome pre-lamination treatments of the films were avoided by sputtering the WO_3 film in the presence of hydrogen and by post-deposition treatment of the NiO film in ozone for a few minutes. New materials were developed for enhancing the bleached-state transmittance, specifically employing additions of Al or Mg to Ni oxide. The electrochromic foils can be used to achieve smart windows with large energy efficiency, provided that their control strategy is adequate. In particular, the window in a room should be set for minimum/maximum transmittance, when this room is unoccupied, if the building is dominated by space cooling/heating [32].

Another application concerns electrochromic foils in variable-transmittance visors for motorcycle helmets. Driving or riding safety requires different transmittance levels for varying lighting conditions, and properties such as those illustrated in Figures 6 and 7 are excellent for these applications.

CONCLUSION

In the first part of this paper we briefly reviewed a large number of electrochromic devices for modulating transmittance and emittance. Some data were given on all-solid-state devices as well as on polymer laminated devices, with and

without self-powering by integrated solar cells. A number of designs were found capable of large optical modulation, as well as dynamics and durability sufficient for applications. It should be realized that no listing of this kind can be expected to be complete. For example device-like constructions incorporating hydride-based switchable mirrors [33,34] and variable-electroplating-based systems were not included. The second part of the paper considered a specific, flexible polyester-based device incorporating electrochromic W oxide and Ni oxide and discussed, among other things, gas treatments for precharging of the individual electrochromic films in order to make them ready for facile device assembly, and enhancements of the bleached-state transmittance through additions of Al or Mg to the Ni oxide.

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