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Durability of Electrochromic Switching Devices for Glazings

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ABSTRACT

Electrochromic device testing and durability is discussed in this study. This work begins with a discussion of performance criteria for switchable glazings used in building applications. This is followed by device design of several common electrochromic device types. The types are distinguished by structure and electrolyte type. A number of test methods are used for the analysis of electrochromic devices. Device lifetime and degradation covers considerable work on amorphous tungsten oxide. Some degradation and ageing modes are identified for electrochromic devices during static and cyclic testing. The degradation modes are film dissolution, transparent conductor etching, gas generation, humidity dependence, secondary reactions and photoreactions. Many of these mechanisms are specific to the materials, device design, and the operating conditions used. Overall, future of electrochromic devices looks very promising, but there are many issues in this study that designers need to take into consideration for electrochromic glazings.

1. INTRODUCTION

There is growing interest in the development of materials and devices that can be used for chromogenic optical switching of large-area glazings[1]. Optically switchable glazings will benefit future building, automotive, aircraft and marine glazings. Dynamic glazings or "Smart Windows" can offer interactive control of light and solar energy. Transmission control can be useful to reduce lighting, heating and cooling energy loads. Also other advantages such as privacy and glare control are important. One of the leading chromogenic technologies for large-area optical switching devices for glazings is electrochromism.[2,3]

However, electrochromism with its great potential has its share of technical uncertainties and problems. A few prominent effects are seen in many different device types and structures, namely residual coloration, reduction of dynamic range and lowering of charge capacity during long term cyclic switching. The origins of the effects are only partially understood at this time. Also, it is very important to note that these effects are dependent upon the conditions of testing and in some cases are temporary. Even though it is early to discuss these problems while the research on devices moves forward, it is important to be aware of the issues. This study covers selected aspects of performance, test methods and device stability of electrochromic devices along with solutions to many of the shortcomings. Further details on test methods can be found in a companion study [4].

2. PERFORMANCE CRITERIA

Before we can fully understand the issues of stability we must define the performance criteria and discuss the design of electrochromic devices. The potential performance of an electrochromic device is shown in the following:

SPECTRAL RESPONSE

Solar Transmittance, T_S	T_S (Bleached) = 50-70% T_S (Colored) = <10-20%
Visible Transmittance, T_P	T_P (Bleached) = 50-70% T_P (Colored) =<10-20%

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Near-IR Reflectance (Only Certain Devices)	R_{nir} (Bleached)=10-20% R_{nir} (Colored) =>70%
SWITCHING VOLTAGE	1-5 Volts
MEMORY	1-24 Hours
SWITCHING SPEED	1-60+ Seconds
CYCLIC LIFETIME	>10K-1M Cycles
LIFETIME	5-20 Years
OPERATING TEMPERATURE	-30 to 70 C 0-70 C, If Protected

These performance criteria was obtained from discussions with several researchers and by best estimates of the necessary requirements for a building window glazing. The actual application of the switching device may vary from these idealized values. For example, in automotive applications an electrochromic device is expected to operate at higher temperatures than for a building application. A sunroof for a car might experience higher temperatures and UV exposure, but have a lower required lifetime than a building window. An aircraft window would see even greater exposure.

The bleached transmission properties are limited by the optical properties of the transparent conductor and substrate material. Two transparent conductors on glass without the electrochromic layers can drop the maximum solar transmittance to about 72-56% depending on the material [5]. Because of this, improvements in transparent conductors are also important to the performance of electrochromic devices. Furthermore, for large-area application transparent conductors must have very low sheet resistances to overcome resistive power loss and slow switching time.

3. DEVICE DESIGN

To obtain a practical electrochromic device one must consider device design carefully. In the current state of technology we now probably know more about the electrochromic layer than the entire device, including its various dependencies and characteristics. Even though several device designs exist and are represented by a variety of commercial and prototype devices, there is still a lot of room for improved device design. So far electrochromic materials occur in two phases, liquids and solids; a gas phase electrochromic has not been noted yet. Solid materials can contain water either free or bound or occurring as a hydroxide. The electrochromic material can be organic or inorganic. The structural form of the electrochromic material can range from amorphous to crystalline and in some cases be polymeric. The typical inorganic electrochromic layer can be amorphous or crystalline tungsten oxide, a-WO_3 or c-WO_3, iridium oxide, IrO, or nickel oxide, NiO. The most used material is a-WO_3. Devices generally rely on at least 3-5 layers of materials to be functional. Electrochromic devices color by the reversible injection/ejection of both electrons and ions in/out of an electrochromic material. A typical cathodic electrochromic reaction is : a-WO_3 $+xH^+ +e^-$ <-> a-M_xWO_3 , $M = Li^+, H^+, Na^+, K^+$ etc., where WO_3 is transparent and M_xWO_3 is blue colored. A typical anodic coloration reaction is: $Ni(OH)_2$ <-> NiOOH + $H^+ + e^-$, where $Ni(OH)_2$ is transparent and NiOOH is bronze colored. Devices are designed in such a way as to store ions and shuttle them back and forth into the electrochromic layer with applied potential. All electrochromic devices require an electron delivery system. Also, all electrochromic devices require an ion delivery and storage system. For transmissive devices the electrical conductor layers are usually highly doped semiconductors, such as SnO_2:F or In_2O_3:Sn. The sheet resistance of this layer is typically in the range of 1-30 Ω /square. Also, antireflected metals, metal grids and partially transparent metals can be used with some reduction in transmittance. In large devices (>30 cm^2) the switching response time is controlled by the conductivity of the transparent conductors. The

ion delivery materials require an electrolyte or an ion conductor and ion storage layer. The ion conductor typically has ionic conductivity 10^{-3}-10^{-6} $(\Omega\ cm)^{-1}$. Transport of ions in the electrochromic reaction is also a limiting process for the switching time of the device. Also the ease of ion injection and ejection is dependent on the morphology and structure of the electrochromic material and the ion size. Typical ionic radii are [6] Li^+ = 0.60Å, Na^+=0.95Å, K^+=1.33Å, and the proton is considerably smaller. The thermal dependencies of the device is dictated by the thermal dependency of ionic transport from the storage medium to the electrochromic material, and vice versa. The low temperature switching speed of the device is determined by this factor. Ion storage media may have electrochromic or non-electrochromic characteristics as long as they are complementary to the active electrochromic material. It is important that the ion storage material has ion storage characteristics (charge capacity) that the active electrochromic material matches.

A typical device construction begins with the transparent electronic conductor usually applied to a substrate of glass or plastic. If the transparent conductor is an oxide then its thickness is about 0.3-0.6 µm; if it is a metal layer then the thickness is about 10-20 nm. The second layer is the electrochromic layer. It has both ionic and electronic conduction. The thickness of the electrochromic layer is 0.1-0.5 µm. The third layer can be an ion conductor or an electrolytic material. This layer exhibits ionic conduction. The fourth layer is the counter electrode material. Its thickness is about that of the electrochromic layer. When an electrolyte is used, with sufficient ion storage, the fourth layer is not needed. In another type, the fourth layer is a combined electronic conductor and ionic storage medium, thus eliminating the fifth layer. The fifth layer is the second electronic conduction layer, similar to the first layer. Another type is known as the complementary device structure, where the counter electrode and working electrode are both electrochromic materials, one coloring anodically and the other cathodically. In such a design they color together and bleach together. By use of two electrochromic materials one can increase the optical density of the device over that of the single material. For example this is done in the Nissan device[7]. In this device cathodic a-WO_3 and anodic Prussian Blue, $(Fe_4(Fe(CN))_6)_3$, are coupled together. However by doing so they introduce an electrochemical imbalance and to make a practical device another electrode must be added to periodically adjust for the charge imbalance in the device. A successful complementary device is based on anodic IrO_2 or $Ir(OH)_2$ and cathodic a-WO_3. An example of this device has been made by EIC Labs[8]. Examples of devices are shown in Table 1.

Table 1. Examples of Electrochromic Devices

Device Structure	Example Group	Reference
ITO/a-WO_3/$LiClO_4$+Redox/ITO,Metal	Asahi	9-11
SnO_2/a-WO_3/$LiClO_4$+PC/ $LiWO_3$/SnO_2	Zenith	13
ITO/a-WO_3/$LiClO_4$+PC/Metal	Zenith	13, 14
SnO_2/a-WO_3/$LiClO_4$+PC/ Prussian Blue/SnO_2	Nissan	7
ITO/a-WO_3/Poly-AMPS/a-IrO_2/ITO	EIC	8
SnO_2/a-WO_3/Poly-AMPS/Carbon	American Cyanamid	15
SnO_2/a-WO_3/Electrolyte/Metal	Ebauches, GMRL	16-18
ITO, SnO_2/a-WO_3/MgF_2,LiF/Au	Chalmers, Fujitsu	19-22
ITO/a-WO_3/a-SiO_2/Au	Latvian State U.	20, 24
ITO,SnO_2/$Ni(OH)_2$/Electrolyte/Pt,SnO_2,ITO	LBL, Chalmers	25-29
ITO/Viologen/Metal	Toshiba	30

4. CHARACTERIZATION AND TEST METHODS FOR ELECTROCHROMIC DEVICES

A number of test methods are used for the analysis of electrochromic devices. All of the methods known are not standardized for the testing of electrochromic devices[4]. The type of methods used are: (1) cyclic voltammetry cycling-accelerated test; (2) square wave cycling-accelerated test; (3) solar and outdoor exposure; and (4) accelerated UV and Weather-O-Meter exposure. Cyclic voltammetry is a measure of the cyclic current and voltage response of the device. A triangle potential is used as the driving potential (usually under ±2V) and a reference electrode is used to help correlate potentials to known electrochemical standards. Cyclic voltammetry is very good for determination of chemical changes in the electrode as it cycles. In general, a d.c. voltage is used to drive actual devices. Square wave cycling is used to simulate an accelerated cyclic d.c. potential response. However since electrochromism is actually a current controlled phenomenon, fixed voltage sources with controlled current have also been used for testing.[15] Accelerated UV exposure is accomplished by the use of specialized high intensity lamps.[31,32] Care must be taken not to thermally effect the device when this test is performed. All of these methods are coupled with standard tests of spectral transmittance, reflectance and integrated optical properties. Examples of idealized responses for cathodic and anodic type electrochromic devices are shown respectively in Figs. 1 and 2.

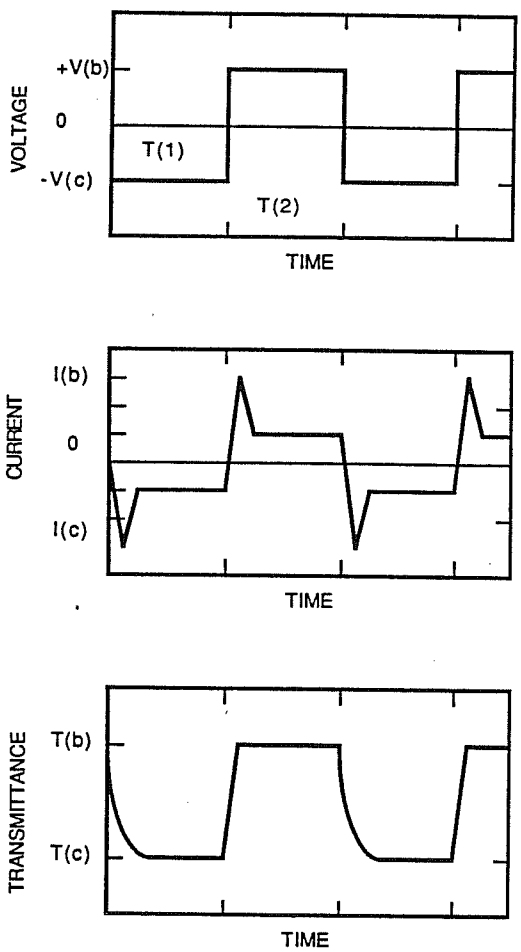

Fig. 1. Response of an idealized electrochromic tungsten oxide switching device. Shown are the driving potential and current with resulting transmittance response.

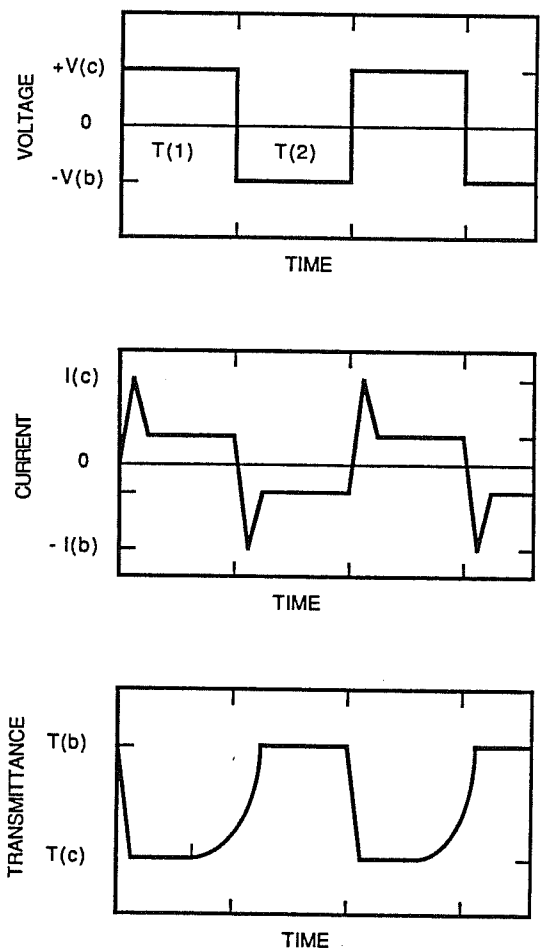

Fig. 2. Response of an idealized electrochromic nickel oxide switching device. Shown are the driving potential and current with resulting transmittance response.

Monochromatic coloration efficiency, CE(λ), is a common performance parameter, expressed as cm^2/C per change in optical density. To obtain CE(λ), total injected/ejected charge as a function of unit area must be known.along with the change in optical density at a selected wavelength. This information can be obtained by integration of voltammetry data or by the use of a coulometer and a spectrophotometer or laser. In many cases a 550 nm wavelength is used. Unfortunately CE is a wavelength dependent property, but few investigators treat it as such. Therefore a better parameter for CE would be an integrated spectral value, weighted to the solar or luminous spectral distribution. Information on the amount of charge required for coloration compared to bleaching will also give the efficiency of each half cycle. The change in surface density of charge, mC/cm^2 (also many authors refer to this quantity as charge, charge capacity or charge per unit area) is monitored during cyclic testing. The maximum surface density of charge is used to compare charge storage characteristics of different electrochromic materials. The maximum surface density of charge is determined from chronopotentiometry. In some cases coloration and bleaching cycles require different amounts of charge to give the same change in optical density. Also, the rates at which a device colors and bleaches are usually different due to changes in conductivity and ionic transport conditions.

The change in optical density, $\Delta OD(\lambda)$ can be obtained from the relationship between injected charge, Q, and the coloration efficiency: $\Delta OD(\lambda)=Q/CE(\lambda)$. Where both CE(λ) and OD(λ) are wavelength, λ dependent quantities. Also, optical density can be obtained by $\Delta OD(\lambda)=\log(T_b(\lambda)/T_c(\lambda))$, where $T_b(\lambda)$ is the bleached transmittance and $T_c(\lambda)$ is the colored transmittance. Also, for transparent devices the absolute values of optical density need to be given, defined as: $OD=\log(T_o/T_x)$, where T_o is the incident or reference transmittance and T_x is the measured transmittance value of the device. For visible and solar applications, both spectral and integrated data should be reported. Frequently in device studies, only contrast ratios or the change in optical density are given.

5. DEVICE DURABILITY

5.1 Cyclic Stability

Cyclic stability is one of the most important properties of electrochromic devices. Typically during cycling, the larger the change in coloration is, the shorter the lifetime of the device. Experimentally derived results are shown in Fig. 3, after work done at RCA on a-WO_3 display devices.[33] This mechanism of degradation is not fully understood, but it appears fundamental in many devices. But the degree of degradation is very dependent on electrolyte type and operating conditions. From the RCA work, if a device is to last 10^6 cycles then its contrast ratio must be within the range of 2:1 to 4:1 ratio. The contrast ratio is defined in the RCA study as the ratio of reflectances compared to a white background as: $CR(\lambda) = R_b(\lambda)/R_c(\lambda)$, where $R_b(\lambda)$ is the reflectance in the bleached state and $R_c(\lambda)$ is the reflectance in the colored state. Work on protonic devices has suggested that cyclic degradation is an extension of the dissolution process or voltage enhanced corrosion.[18] In protonic devices that have been cycled for many thousands of cycles and dissembled, the a-WO_3 film has been found to be granular and is less adherent to the substrate.[16] It is suspected that the film has suffered mechanically from hydrogen embrittlement. The most obvious change during cycling is the gradual reduction of charge per unit area during bleaching and coloration of the film. This results in a decline of the change in the film's optical density.

In aprotic (non-aqueous) devices, a-WO_3 corrosion is slowed by two processes: low ionizability of large organic molecules, and inhibited tungsten ion formation. For a-WO_3 electrodes cycled in $LiClO_4$- propylene carbonate (PC) after 10,000 cycles of coloration and bleaching, a decrease in injected charge density is noted. The charge density began at 5-6 mC/cm^2 and dropped to 4-1 mC/cm^2 after $5x10^5$ cycles. An example of this is shown in Fig. 4. Only an electrochemical emf change was noted in the film. After cycling, lithium ions were found bound into the film structure and were judged responsible for the emf shift but not active in coloration. After cycling, the film in the bleached state becomes more ion conductive as the

result of lithium incorporation.[9-12,14] There appear to be two active sites for lithium ions one for coloration: a-WO_3+ xLi^++xe^- ↔ a-Li_xWO_3 and another for ion exchange according to: W-O-H+Li^+ ↔ W-O-Li+H^+. Also the O/W ratio increased during cycling. This result may mean that the a-WO_3 may form a metatungstate structure $(M^+)_6(W_{12}O_{39})$ where M = H, Li, etc., which can serve as an ion exchange site.[9] A decay factor of two in charge has been noted after 100 hours of cycling ($9x10^4$ cycles) of a a-WO_3/$LiClO_4$-Propylene Carbonate /Li_xWO_3 device.[13] It was found that by irradiating the cell with UV light while applying a bleaching voltage the decline in the charge injection level was reduced.[13]

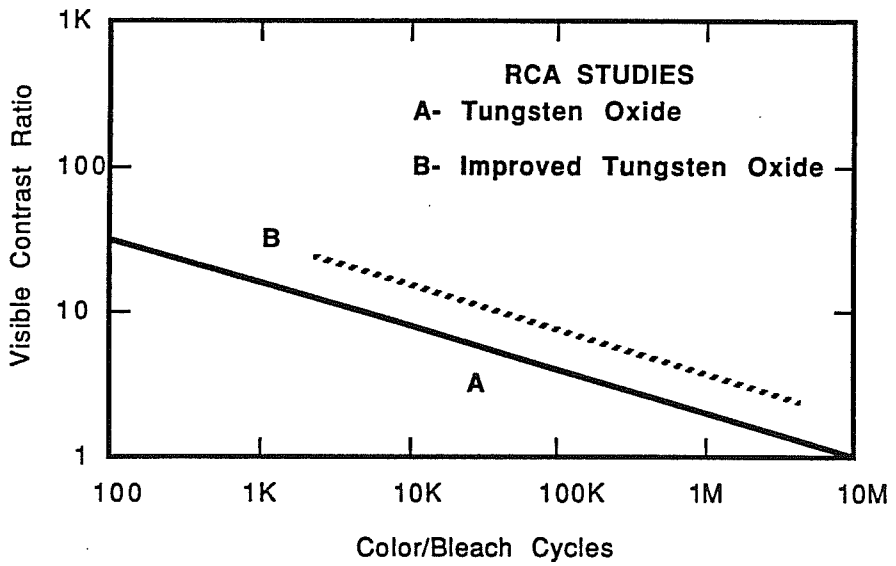

Fig. 3. Relationship between contrast ratio and lifetime for a tungsten oxide electrochromic device (ITO/a-WO_3/ electrolyte /metal). Two device responses are shown: (A) standard vacuum evaporated film and (B) films produced by an improved process. From the RCA work.[33]

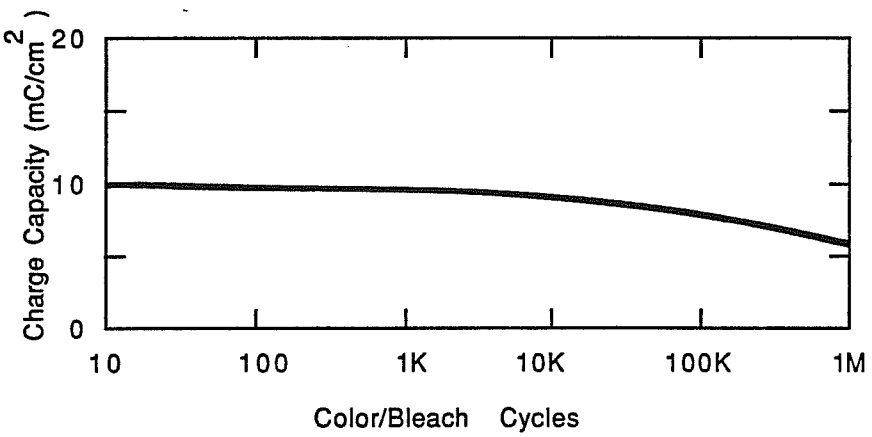

Fig. 4. Long term cycling of tungsten oxide devices (ITO/a-WO_3/polymer-$LiClO_4$+RedOx/ITO). The decline in charge capacity (charge per unit area) and hence optical density can be seen after long cycling. This effect is seen in many device types. After Asahi Glass work[9-12].

Depending on how electrochromic $Ni(OH)_2$ is prepared, the film may require precycling before a steady-state response is obtained. Studies on sputtered electrochromic $Ni(OH)_2$ has shown only a small change in the transmittance after 10^4 cycles.[25] An investigation of cathodic electrochemically deposited $Ni(OH)_2$ has shown early residual coloration after cycling.[26] But work on anodically deposited $Ni(OH)_2$ films and devices has shown good stability.[27-29]

5.2 Thermal Dependence and Decomposition

The thermal dependence of cyclic switching is important to the lifetime of the electrochromic device. A device consisting of Glass/ITO/a-WO_3/polymer-$LiClO_4$- Redox/ITO/glass have been studied for thermal ageing.[11,12] As depicted in Fig. 5, color/bleaching cycles were carried out using a d.c. potential of 1.0V or -1.0V for a 1 minute interval. Over 10^5 cycles were performed on the device. Cells were cycled for over 30 days under different temperatures of, room temperature (RT), 50, 60, 90 C.

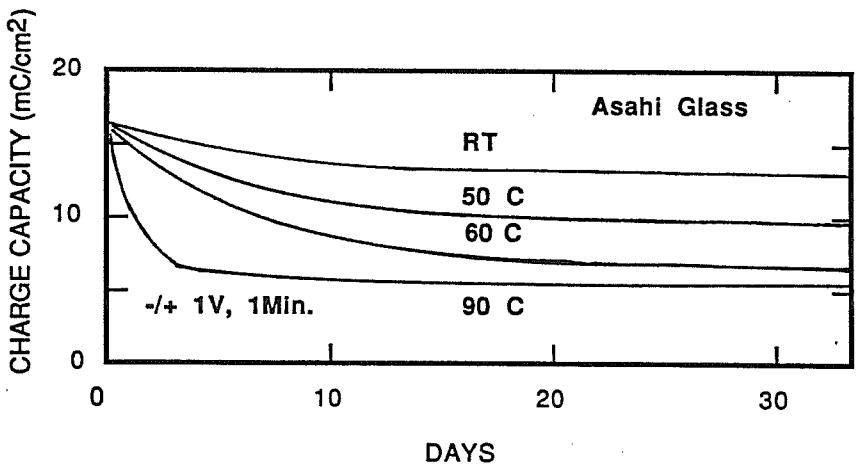

Fig. 5. The decline in charge capacity (charge per unit area) with time and temperature for a tungsten oxide electrochromic device (ITO/a-WO_3/polymer-$LiClO_4$+RedOx /ITO). This device was cycled at ± 1V potential for 1 minute intervals over the period of testing. After Asahi Glass.[9-12]

The effect of higher temperature caused the device to slow down and decline in charge injection levels. After a few days a constant charge injection level was achieved. The injected charge per unit area starts at about 16 mC/cm^2 and drops to 14 mC/cm^2 at RT. At 90 C the injected charge drops and becomes constant at 6 mC/cm^2.

Thermal stability is important for devices with polymer electrolytes. Studies have been performed on the $LiClO_4$-PC electrolyte.[7] Decomposition was noted at 10^3 hours at 60 C, $3x10^2$ hours at 70 C , $2x10^2$ hours at 80 C and 15 hours at 90 C. It is also common for gas bubbles to form in the device during decomposition.

6. DEGRADATION MODES

A few degradation and ageing modes have been identified in electrochromic devices. The modes are film dissolution, cyclic electrochemical instability, transparent conductor etching, gas generation, humidity dependence, secondary reactions and photoreactions. Many of these modes are enhanced by defects in the films. In certain cases a film defect causing shorting of layers can result in device failure. Some of the modes identified are specific to the materials, device design, and the operating conditions used. The most is known about amorphous tungsten oxide because of its development for small display devices during in the

1970's. Many of the degradation modes identified can be avoided or controlled by proper design and operating conditions. But, one must be careful when applying those findings to transparent devices with new counter-electrodes, larger areas and slower switching requirements.

6.1 Electrochromic Film Dissolution

One effect that has been noted by many authors is the dissolution of a-WO_3 films in water and to some degree in acidic environments, following the reaction: a-WO_3 -> W^{+6}(solution) +$6e^-$ + $3/2O_2$. The dissolution of c-WO_3 is considerably slower. The dissolution rate of a-WO_3 in water has been estimated as 2.5 μm/day.[16] The dissolution rate (R) is a function of the electrolyte pH. For example the rate is 1μm/yr at pH=0 and and 10^3 μm/yr at pH=6, following the equation $R= k_1 10^{0.33pH}$. At higher pH values the rate increases, for a pH=9 the rate is 10^4 μm/yr, following the equation $R= k_2 10^{0.66pH}$. These values were obtained for a flowing electrolyte.[33] For a static sealed electrolyte these rates decreased by an order of magnitude to 2-2.5 nm/day at 50 C in a glycerin-H_2SO_4.[16] This effect can pose a shelf-life problem for these devices. It is thought that a-WO_3 films are in the form of trimeric clusters which are weakly bound to each other with water bridge bonds. This results in a very open microstructure and high proton mobilities, giving higher switching speeds. This structure has been identified as the xerogel structure, consisting of a highly porous low density oxide.[17] Unfortunately this structure is subject to dissolution and cyclic erosion. When the film dissolves it forms metatungstate or polytungstate ions.[18] To reduce this problem, alkali salts in aprotic electrolytes have been used, but the drawback is that the device response is decreased and sealing becomes critical.

6.2 Transparent Conductor Etching and Ion Trapping

Another degradation effect occurs when the electrolyte chemically etches the transparent conductor layer . The transparent conductor In_2O_3:Sn (ITO) has some of the best optical and conduction properties is sensitive to etching in acids. ITO has a reduction potential of -1.0 V to -2.5V (SCE) depending on the pH of the electrolyte.[12] ITO in acidic electrolytes can go through dissolution by $In_2O_3 + 6H^+ \rightarrow 2In^{+3} + 3H_2O$ and electrochemical reduction by: $In_2O_3 + 6H^+ + 6e^- \rightarrow 2In + 3H_2O$, and $In \rightarrow In^{+3} + 3e^-$. Doped SnO_2 has much better etch resistance, but does not have as good optical and electrical properties as ITO [5] However, in strong acids doped SnO_2 can go through electrochemical reduction by[16]: $SnO_2 \rightarrow Sn^{+4} + O_2 + 4e^-$. In the SnO_2/a-WO_3/P-AMPS/C device, the reduction of SnO_2 is seen at potentials above 1.0V. To cure this problem a protective cover can be used for areas in direct contact with the acidic electrolyte.[15] Another problem with the ITO is that there is evidence from the Tufts University group that it traps lithium which degrades the electrical properties of the ITO. This problem is solved by using tin oxide transparent conductors.

6.3 Gas Formation

Internal generation of gas is a very serious device degradation effect and usually results in device failure. For a-WO_3 devices there is a danger of generating H_2 gas if the voltage across the device is too high. Also, if the a-WO_3 film is colored to H_xWO_3 beyond $x \approx 0.28$, then an electrode-electrolyte interface reaction can occur causing dissolution of H_xWO_3 and formation of H_2 gas.[33] Also, gas can form from the decomposition of a polymer electrolyte, under high potentials or temperature. In ITO/ a-WO_3 /IC/Au devices it has been concluded that water in the device is dissociated at the Au interface during coloration. During bleaching gas bubbles are observed at the Au interface during application of a -1V potential.[19] For electrochromic TiO_2 the coloration peak occurs after the oxygen evolution potential. This makes TiO_2 impractical for use with water based electrolytes because of gas generation.

6.4 Water and Humidity Dependency

Another important effect occurs in ITO/ a-WO_3 /IC/Au devices. These devices have been reported to be very dependent upon ambient humidity. Experiments have shown that weight changes occur during coloration and bleaching which correspond to adsorption and desorption of water in the cell and its surroundings. Mass spectrometer measurements have shown that O_2 left the cell during coloration and H_2 left the cell during bleaching. Also, coloration does not occur until a threshold voltage (which corresponds to the electrolysis of water) is reached across the insulating layer. This electric field disassociates the water in the insulating layer thereby providing the necessary protons for coloration.[20,34,21]

The coloration and bleaching process was studied in a ITO/a-WO_3 /a-SiO_2/Au device.[23,24] The gold interface serves as a surface for catalytic dissociation of water. When the device voltage exceeds 1.3V, a hydroxide layer is formed on the gold surface following: $Au + 3OH^- \rightarrow Au(OH)_3 + 3e^-$. At this stage coloration takes place in the a-WO_3 layer. Above 1.6V the threshold for oxygen discharge is reached. On the negative current cycle, at 0.8 V the reduction of gold hydroxide occurs and bleaching begins. At -0.1V water is reformed. Final bleaching of the a-WO_3 film is observed at -0.4V. At -3V oxygen evolution occurs. The presence of water in this device is important to its operation and the gold layer serves as a catalytic surface.

6.5 Photoreactions

It is known that a-WO_3 is photochromic when exposed to UV radiation.[31,32] The photocurrent rises dramatically for wavelengths below 400 nm. Also, for annealed films the photocurrent rises between 400-480 nm.[31] It has been observed in a-WO_3 that under UV irradiation (at 253 nm in vacuum) the reaction, $W^{+6} \rightarrow W^{+5}$ occurs.[32] This means that an electrochromic device based on a-WO_3 will have its bleaching and coloration kinetics slowed down by the effect of photochromism. This is one reason why indoor and outdoor tests give different rate kinetics.[11] After 100 hours of UV irradiation in a Weather-O-Meter at 63 C, the injected charge dropped from 13 to 8 mC/m^2.

Photochromism can be used to regenerate aged a-WO_3 devices. After long cycling the electrochromic layer or electrolyte contains trapped charge, which causes the charge injection levels to fall, and an emf shift is noted of -170mV. A contrast ratio of 4:1 was seen before cycling. The peak current density was 4 mA/cm^2 bleached and -5 mA/cm^2 colored. After 100 hrs ($9x10^4$ cycles) the peak current was 1 mA/cm^2 bleached and -4 mA/cm^2 colored. After UV regeneration the bleaching current became 2 mA/cm^2 and -5 mA/cm^2 colored. By irradiation and biasing the device in the bleached state the energy of UV light freed trapped charge and partially restored the dynamics of the uncycled device.[13] Other UV photoreactions can take place in polymer electrolytes, so in designing a device care must be made to protect the electrolyte if it is sensitive to UV degradation.

6.6 Secondary Reactions

The organic viologen system has always been attractive for switching devices because its absorption spectrum can be adjusted at any visible wavelength, it has high charge efficiency (2.5x better than WO_3) and switches fast. The problem with the viologens is that they show unexpected secondary irreversible reactions with use.[30] These reactions is are seen in conjunction with liquid electroytes, there is a possibility of suppression with solid electroytes.[35]

7. CONCLUSIONS

This study has assembled information about the durability of electrochromic materials and devices. There are several highlights that are important for consideration. They are that better standards are needed to test electrochromic devices. Especially for coloration efficiency. Currently coloration efficiency it is reported as a single value for a single wavelength. For glazings work this must be changed to a solar or luminous weighted value. For determination of device durability the monitoring of surface density of charge with optical response is the most favored. Film dissolution is a serious effect for WO_3 in acidic liquids. This problem is controlled by using polymer or aprotic electrolytes. Cyclic stability appears to be related to the intensity of coloration. This is not well understood and further work may help explain this effect. Transparent conductors undergo etching and trapping of lithium ions. Gas generation is seen in devices operating at too high a potential, also gas can be generated as a byproduct of decomposition of the electrolyte, usually at extreme temperatures. Devices based on the tungsten oxide/ion conductor/metal structure are sensitive to humidity. Although in the future with more device testing secondary reaction will become important to assure long term stability. Currently secondary reaction are only noted for the viologen electrochromics. UV Photoreaction are seen in tungsten oxide and are significant to polymer electrolyte stability. UV absorbers are used to reduce this effect. In the few devices that have been tested, thermal dependence on reduction of charge capacity was significant. Further testing is required to see if this effect is device structure or materials dependent.

8. ACKNOWLEDGMENTS

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