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## **RECENT PROGRESS IN SOL-GEL DERIVED ELECTROCHROMIC DEVICES**

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### **Abstract**

The future energy saving requirements placed on modern buildings will require that windows will have to meet higher standards, including: being able to reduce heat-loss while avoiding overheating of the building and gaining solar energy while assuring comfortable daylighting. These conflicting demands can be satisfied by using switchable or “smart” windows, the optical properties (transmittance and reflectance), of which can be varied between low and high transmitting states. This could be done either manually or automatically by the building’s own energy management system. We report our progress towards making electrochromic devices for switchable “smart” window applications. The future development of the next generation of switchable windows is addressed.

### **INTRODUCTION**

Heating, cooling and lighting account for the largest proportion of the total energy budget consumed in commercial and residential buildings. If the building of the future is to be “sustainable” in terms of energy consumption, then a step towards this will be the

use of active solar collector systems integrated into well designed energy management systems. Modern collector water-heating systems employ selective absorbers possessing a high efficiency for photothermal conversion. Selective absorbers, characterised by high solar absorptance ( $a_s$ ) and low thermal emittance ( $e_T$ ) - depressing total radiation losses, provide a net gain in solar conversion of more than 20 % compared to non-selective absorbers. This is because the working temperatures of selective absorbers are always higher. For example, in a domestic water-system the temperature difference at a working temperature of 40 °C is between 15 - 20 °C, when selective absorbers are used.

In Europe the annual requirement for glazed solar collectors with selective absorbers is estimated at 500000 m<sup>2</sup>. The market is currently dominated by the electroplating industry: Black chrome and MTI in the USA, Batek in the Netherlands and GIBO in Germany. Ni-pigmented anodised aluminium absorbers are produced by Tecknoterm in Sweden, Metalux in Germany, Showa in Japan and Fenis in Turkey, while black nickel coated absorbers are produced by Maxorb in the United Kingdom. Electroplating is a highly developed technique but is increasingly under attack because of its high environmental impact.

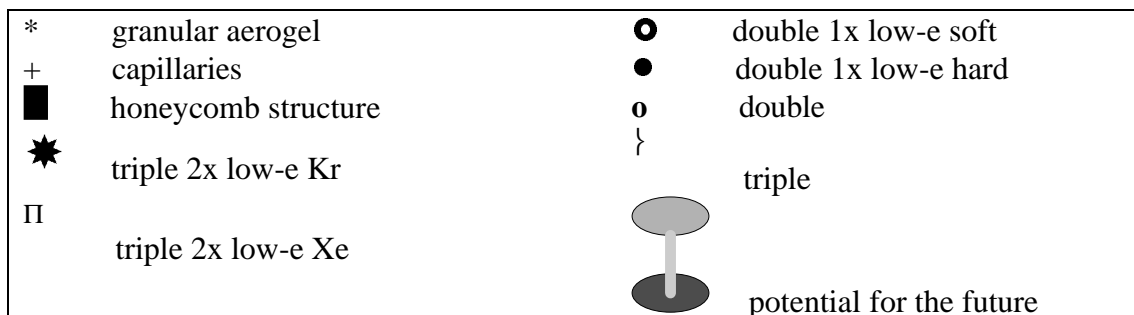
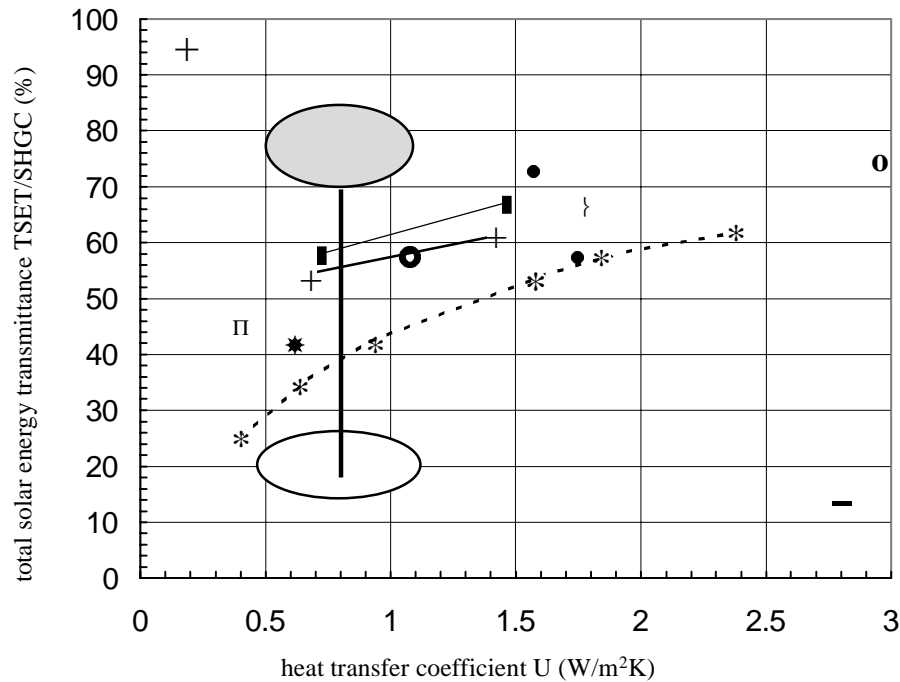
More advanced technologies are being used including: reactive evaporation for making Ti-oxynitride coatings (TINOX, Germany) and reactive sputtering to make Cr-oxynitride coatings (Fraunhofer Institute for Solare Energiesysteme in Freiburg , Germany). These advanced vacuum techniques require sophisticated and expensive equipment resulting in high production costs. These are compensated for, or at least in part, by the high selectivity of the absorber coatings. Sol-gel Crystal Black coatings (Thermafin Manufacturing, L.C., USA) must also be mentioned, since by using sol-gel technology it is possible to make high quality coatings with high spectral selectivity more cheaply than by vacuum deposition.

Selective unglazed solar hot-air absorbers mounted on the facade represents a significant step forward towards reducing the total energy needs of a building. It is expected, that

solar facades could save approximately 2.5 % of the total energy budget, which is equivalent to approximately  $1.2 \times 10^{10}$  m<sup>3</sup> of CO<sub>2</sub> per year. Unglazed solar absorbers suitable for building facades are yet to reach the market. This is because there are at present no selective coatings durable to assure a long exploitation period - at least fifteen years. Solar facades must be aesthetically pleasing; the unglazed solar facade is the colour of the solar absorber, which is an unacceptable black. Since no satisfactory alternatives exist, the major challenge to material science research is to produce coloured selective absorbers with high solar absorptance ( $a_s > 0.93$ ) and low thermal emittance ( $e_T < 0.1$ ) [1].

It is also possible to reduce the heating demands of a building by improving thermal insulation, while a saving in the amount of energy needed for cooling a building can be achieved by increasing its mass and/or installing efficient ventilation systems. Both approaches - if not applied properly - might lead to a reduced thermal and visual comfort, adding to the phenomena known as “sick building syndrome”. In hotter climates, the higher influx of the solar radiation through the windows can result in the overheating of the building interior. Alternatively, in colder climates the internal environment of highly thermally insulated buildings with small windows, may not provide adequate illumination. The amount of heat lost through a window depends on the material from which the window-frame is made, details of edge sealing and the ratio between the frame and the glazed areas. For modern buildings with extensive glazing heat-loss can be high. This heat-loss is expressed quantitatively in terms of the overall heat transfer coefficient (U-value in W/m<sup>2</sup>K) [2]. Usually, the U-value of double glazed windows is between 2 - 3 W/m<sup>2</sup>K, almost 10 times higher than the heat lost through the walls (Fig. 1). Modern windows with advanced glazing, with hard or soft low-emitting (low-e) coatings and filled with an inert gas, have a lower overall heat loss coefficient (1.5 - 2 W/m<sup>2</sup>K), but their total solar energy transmittance (TSET) and visible light transmittance ( $T_{vis}$ ) are rarely above 60 %. Windows employing monolithic aerogel, transparent insulation (e.g. capillary polycarbonate or honey comb materials) and vacuum glazing are alternatives to double and triple glazed windows with low e-coatings and an

inert gas (Kr, Xe) filling. These windows, with low U-values, can not respond “in-situ” to the variation in intensity of incoming solar radiation. By incorporating switchable



**Fig. 1** Solar energy transmission TSET versus the centre-of-glass U-value ( $\text{W}/\text{m}^2\text{K}$ ) for different windows (adapted from ref. [2]).

windows, the transmittance can be varied continuously between dark (low transmitting) and bleached (high transmitting) states, making it possible to avoid overheating during the day. This will reduce the amount of energy required for cooling in the summer, and

allow large area windows, with a high TSET to be incorporated into the building design without increasing the heating costs during the winter. In addition, switchable windows prevent the major visual discomfort caused by excessive glare.

Various switchable “smart” windows exist:

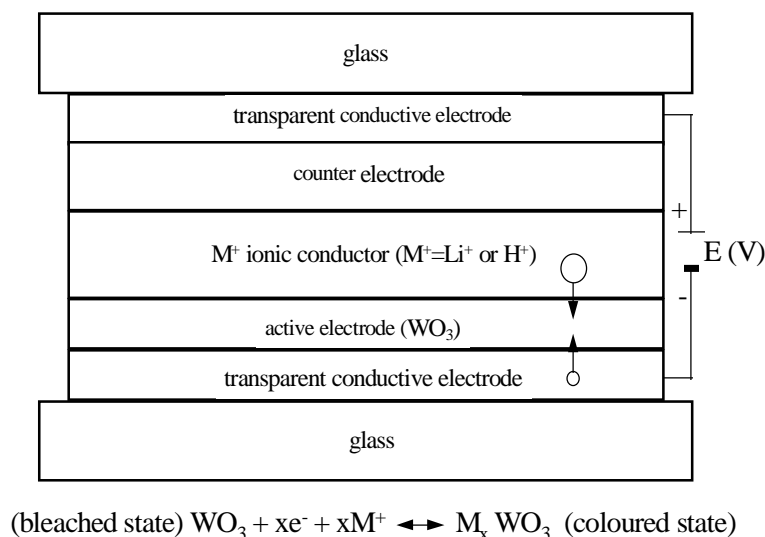
- Photochromic windows: transmittance change is a function of the irradiation dose.
- Thermochromic windows: transmittance change responds to the temperature variation of the glazing.
- Thermotropic windows: TSET decreases with increased scattering of the visible light at certain temperatures.
- Electrochromic windows: optical properties change under the action of a voltage or current pulse.

At present electrochromic (EC) windows are the best option, because they allow the transmittance to be varied either manually or automatically by the building’s energy management system.

In this report we present our own progress towards making EC devices for “smart” window applications. This will include a brief description of sol-gel processing, the dip-coating technique and the most promising films and materials. The properties of the “all sol-gel” EC devices, regarding their colour change and overall spectral characteristics, will be discussed in greater depth. The future development of the next generation of switchable windows will also be addressed.

## RESULTS

Within the frame-work of the Pilkington plc “Smartglass” project [3] our aims were to synthesise novel materials and films using sol-gel processing and dip-coating deposition and to manufacture an “all sol-gel” EC device (Fig. 2) with the following characteristics: a transmittance in the bleached (uncharged) state above 65 %, transmittance in the coloured state below 10 %, a switching speed less than 10 min and a cycling stability greater than 3000 cycles. In addition, the colour of the EC device in the charged state must offer alternative colours (dark neutral colours) other than blue, which is characteristic of charged  $\text{WO}_3$  films.



**Fig. 2** Basic design of EC device. Transport of positive ions to obtain coloured state of the device is indicated.

An “all sol-gel” EC device is one in which all three internal layers, including the ionic conductor, are processed by the sol-gel route. Sol-gel processing exhibits many advantages over traditional techniques for the preparation of advanced and functional coatings with optical, chemical, electrooptical and mechanical properties [4]. By using the sol-gel method a high degree of homogeneity of the film is achieved, since the starting materials are mixed on a molecular level, i.e. in solution. The relatively low-cost of the precursors and the simplicity of the dip-coating process means that the potential

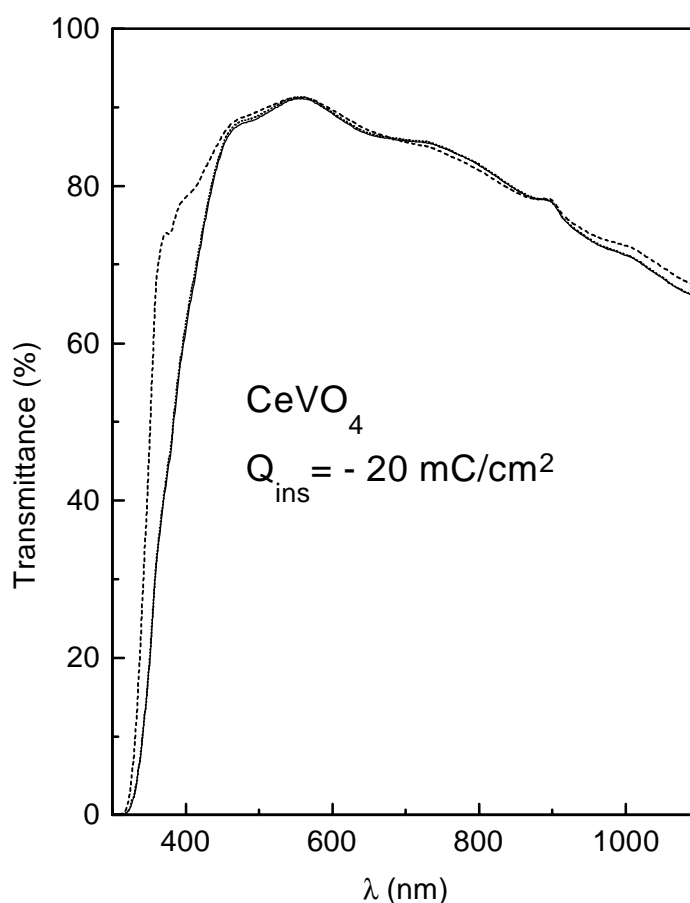
application of the sol-gel route is high. By using sol-gel processing a variety of dopants can be introduced to the initial sols in varying concentrations, yielding doped or mixed oxide films with much improved properties. In the frame of this project many different precursors and sol-gel routes were applied for manufacturing anodic/cathodic electrochromic and ion-storage films (Table 1).

**Table 1** Thin films made by sol-gel route in our laboratory ( for electrochromic and gasochromic device applications)

<b><i>Cathodic electrochromics</i></b>		<b>References</b>
• WO <sub>3</sub>	peroxo sol-gel route	5,6
• Nb <sub>2</sub> O <sub>5</sub>	amorphous (300°C)	7
	pseudohexagonal TT-phase (520°C)	8
• Li <sub>0.4</sub> Nb <sub>2</sub> O <sub>5.2</sub> , Li <sub>0.2</sub> Nb <sub>2</sub> O <sub>5.1</sub>	pseudohexagonal TT-phase (520°C)	9
• PWA/TiO <sub>2</sub>	amorphous xerogel	10,11
<b><i>Anodic electrochromics</i></b>		
• Ni - oxide		12, 13
• Ni(Si) - oxide, Ni(La) - hydroxide		14,15
• Li <sub>x</sub> NiO <sub>2</sub>	layered	16
• Co <sub>3</sub> O <sub>4</sub>	spinel	17
• Co(Al,Si) - oxide	amorphous	18
• LiCoO <sub>2</sub>	layered	16
• γFe <sub>2</sub> O <sub>3</sub>	maghemite	20
• Fe - oxide	amorphous	
<b><i>Ion - storage films</i></b>		
• CeO <sub>2</sub>	crystalline (cerianite)	21
• CeO <sub>2</sub> - TiO <sub>2</sub>	crystalline	22,23
• CeO <sub>2</sub> - SnO <sub>2</sub>		24,25
• Mo: CeO <sub>2</sub> , Si:CeO <sub>2</sub> , Si:Mo:CeO <sub>2</sub>		26
• CeVO <sub>4</sub>	crystalline	27,28,29
• SnO <sub>2</sub>	cassiterite	30,31
• Sb:SnO <sub>2</sub> , Mo: Sb:SnO <sub>2</sub> , Mo:SnO <sub>2</sub>		32,33
• Ce:Sb:SnO <sub>2</sub>		
• V/Ti - oxide, V/Ti/Zr - oxide,		34
• V/Ti/Ce - oxide		
• Nb/Fe - oxide	amorphous	35
• Fe/V - oxide	amorphous	
• Fe/Ti - oxide		36
• V <sub>2</sub> O <sub>5</sub>	amorphous	37,38
<b><i>Gasochromic films</i></b>		
• WO <sub>3</sub>	amorphous	39,40,41,42

### Counter-electrode films

We have concentrated a large part of our efforts into developing improved ion-storage counter-electrode films. The counter-electrode must have a high transmittance for visible light in the charged and discharged state and a ion-storage capacity exceeding  $20 \text{ mC/cm}^2$ . This ion-storage capacity is necessary if there is to be a sufficient number of ions to produce a deep coloration of the  $\text{WO}_3$  active electrochromic film and for the device to remain stable. Our research shows that, between all the materials tested,  $\text{CeVO}_4$  and V/Ti-oxide were the most efficient (Table 1).



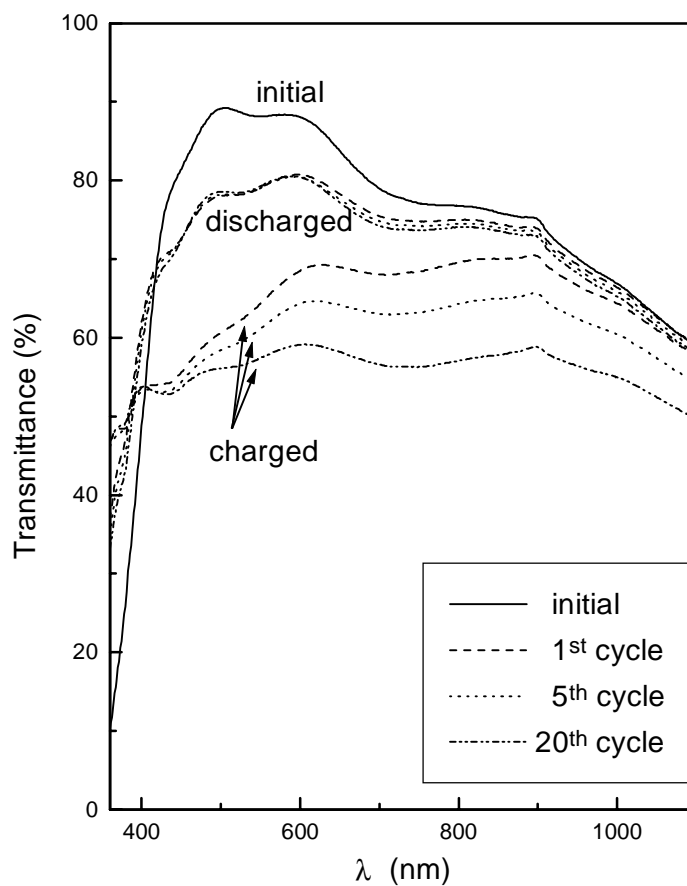
**Fig. 3** In-situ UV-VIS spectroelectrochemical response of  $\text{CeVO}_4$  films charged at  $-1.6 \text{ V}$  and  $1.6 \text{ V}$  vs.  $\text{Ag/AgCl}$ : (—) as deposited, (-----) charged and (.....) discharged states [27].



Cerium vanadate [27] exhibits an ion-storage capacity greater than  $20 \text{ mC/cm}^2$  and a high (90 %) transmittance in the visible region. The transmittance of the as-deposited and discharged states of the films are practically identical. The transmittance of charged and discharged states is marginal above 450 nm while below this wavelength the films bleach with charging (Fig. 3). The spectral coloration efficiencies ( $\eta$ ) are calculated according to the equation  $\eta = \log(T_O/T_R)/\Delta Q$  [7], where  $T_O$  and  $T_R$  are the spectral transmittance of oxidised ( $T_O$ ) and reduced ( $T_R$ ) films between 350 - 1100 nm and  $\Delta Q$  represent inserted or extracted charge. The  $\eta$  of  $\text{CeVO}_4$  in the visible region is less than  $2 \text{ cm}^2/\text{C}$  and positive, whilst relatively strong negative coloration efficiencies ( $\eta$ ) values are up to  $-40 \text{ cm}^2/\text{C}$  are observed in the near UV ( $\lambda < 450 \text{ nm}$ ). The coloration efficiency of  $\text{CeVO}_4$  films is the lowest among all known counter-electrode films. The excellent optical passiveness, together with high ion-storage capacity rank  $\text{CeVO}_4$  films among the most promising counter-electrode materials for EC device applications.

Sol-gel derived V/Ti-oxide films with amorphous structure [34] exhibit even higher ion-storage capacity ( $30 \text{ mC/cm}^2$ ) as compared to  $\text{CeVO}_4$  which - combined with high cyclic stability (few 1000 cycles), rank V/Ti-oxide films among the most promising counter electrodes. The quality of sol-gel films is comparable to the sputtered ones made in Pilkington plc. Sputtered V/Ti-oxide films are currently used in EC devices made by Pilkington plc and are coming to the market.

Films behave as optically passive counter electrodes (Fig. 4). The variation of films transmittance in bleached and coloured state is only 10 % which is still acceptable for the counter electrode with an optically passive response. The main drawback is relatively low transmittance of the cycled films in bleached state which is 10 % lower than that of the pristine films. In this respect V/Ti-oxide films are not as good as  $\text{CeVO}_4$  films which beside higher transmittance in the bleach state also do not exhibit yellowish-green colour typical of the V/Ti-oxide films. This influences the colour of the EC windows (see below).



**Fig. 4** In-situ UV-VIS spectroelectrochemical response of V/Ti-oxide films charged at -1.5 V and 1.5 V vs. Ag/AgCl [34].

### Ionic conductors

The functioning of the EC device requires a  $\text{Li}^+$  or  $\text{H}^+$  ionic conductor serving as an electrolyte. At the same time the function of the ionic conductor is to laminate the active colouring and counter electrode layers together (laminated EC device).

Due to the low reaction temperatures, sol-gel synthesis offers many possibilities to introduce organic molecules into inorganic polymeric matrices. This can lead to the

synthesis of a large number of novel inorganic-organic hybrid materials with varying properties. Generally, hybrid materials depending on the nature of the chemical bonding between the organic and inorganic constituents can be divided into two classes [5]:

- Class I materials: only weak bonds exist between the organic and inorganic components (van der Waals, hydrogen, ionic bonds).
- Class II materials: covalent chemical bonds bind both parts together.

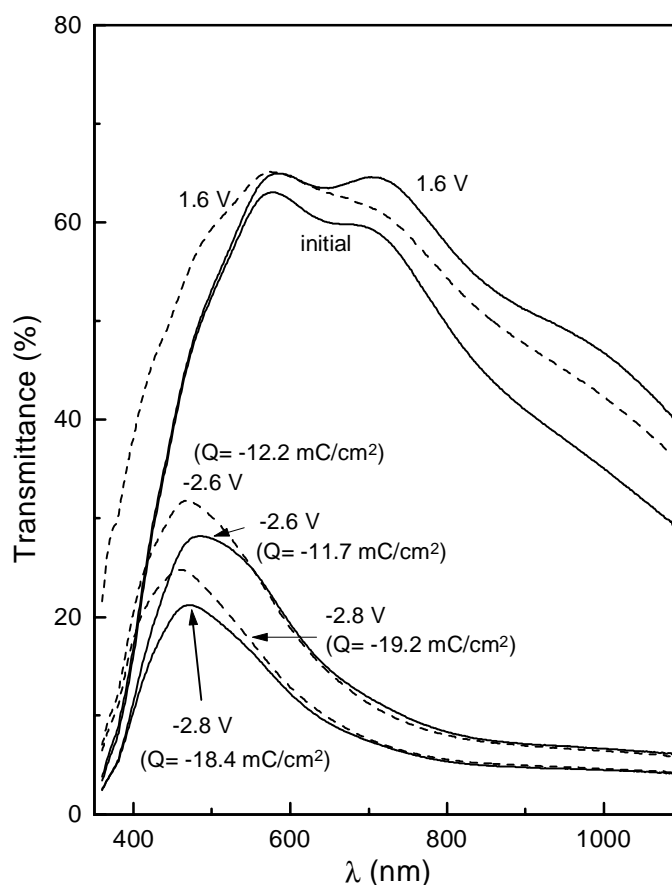
Organically modified electrolytes (ormolytes) present a good example of inorganic-organic hybrids. By varying several parameters in the sol-gel processing of the ormolyte we are able to obtain an ionic conductor with optimal properties, such as an ionic conductivity of  $10^{-4}$  -  $10^{-5}$  S/cm, dimensional stability and good flexibility. The present ormolyte is best described as a mixed class I - class II hybrid material where both weak physical bonds and covalent chemical bonds exist linking the silica network to the organic modifiers [5].

### **“All sol-gel” EC devices**

The basic concept of an “all sol-gel” device is not new and consists of laminating two pieces of glass - each coated with an electrochromic (mostly cathodic) and counter electrode film, with a transparent polymeric  $H^+$  or  $Li^+$  ionic-conductor. In 1982 Randin [43] described the use of a poly(AMPS)  $H^+$  ionic-conductor as a laminate for making  $WO_3$ -based EC devices. Later (1989), Granqvist *et. al.*, [44] successfully laminated sputtered  $WO_3$  and  $V_2O_5$  electrodes using a gel-type polymethyl-metacrylate (PMMA)  $Li^+$  ionic-conductor.

An attempt to make a true "all sol-gel" EC device was reported by Judeinstein and Livage in 1988 [45], who succeeded to laminate a device consisting of a  $SnO_2$  counter electrode and a sol-gel derived  $WO_3$  with a  $TiO_2$ -gel ionic-conductor. Unfortunately, the  $SnO_2$  counter electrode exhibited irreversible coloration. Özer *et. al.*, [46] used a sol-gel

made ITO counter-electrode and electro-chromically active  $\text{TiO}_2$  but used a  $\text{Li}^+$  doped polymeric electrolyte to laminate the device. The colouring/bleaching changes are good ( $\Delta T \sim 80 - 40 \%$ ) but the response time (50 s), is longer than that of a  $\text{WO}_3$  EC devices made using the sol-gel route. It was Macêdo and Aegerter [47] who made the first "all sol-gel" EC device with a  $\text{WO}_3 | \text{TiO}_2 \text{ gel} | \text{CeO}_2 / \text{TiO}_2$  configuration. The optical transmission changes of the device during the first cycle was  $60 \% < T < 20 \%$  and the response time was in the order of a few seconds. This is comparable to EC devices obtained by other techniques, although, the delamination of the device was observed during extended cycling .

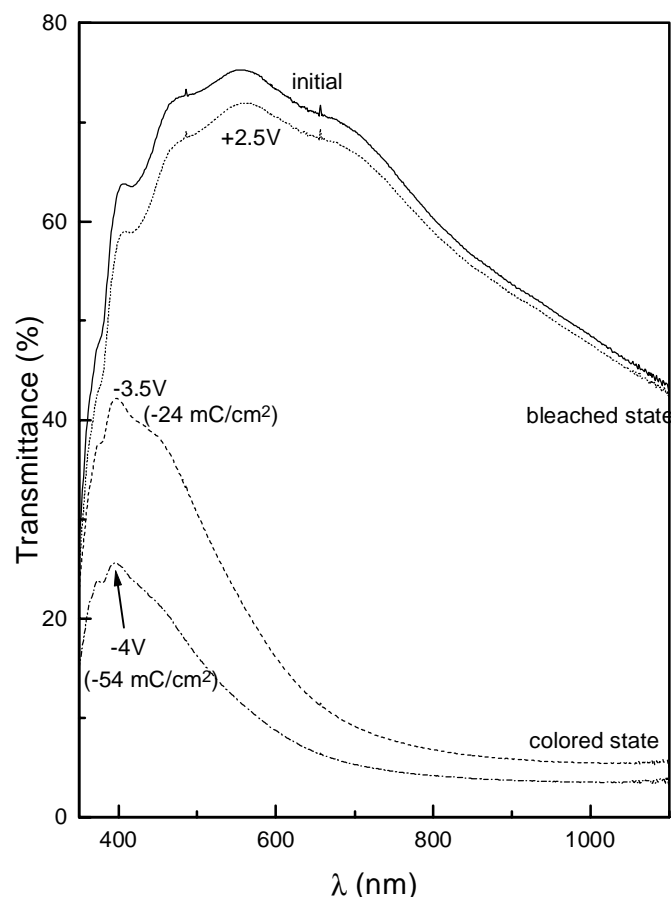


**Fig. 5** Transmittance spectra of  $\text{WO}_3 | \text{ormolyte} | \text{Nb/Fe - oxide}$  EC device after ( — ) 10<sup>th</sup> and ( ..... ) 2000<sup>th</sup> cycle [35].

Further discussion of the “all sol-gel” EC devices will be limited to their optical properties, since they demonstrate the advances made in developing the counter electrode films:  $\text{CeVO}_4$  [27],  $\text{SnO}_2/\text{Mo}/\text{Sb}$  [33], V/Ti-oxide [34] and Nb/Fe-oxide [35], used in EC devices.

The  $\text{WO}_3$  |ormolyte |Nb/Fe-oxide device [35] (Fig. 5) when charged at 1.6 V exhibits a maximum transmittance of approximately of 60 %, but at -2.6 V the transmittance drops to 25 %. Lower transmittance values, below 20 %, can be easily obtained by applying higher negative potentials i.e. -2.8 V, but this results in a reduction in the cycling stability. The reason of lower cycling stability is the small ion-storage capacity (18 - 20  $\text{mC}/\text{cm}^2$ ) of the Nb/Fe-oxide counter electrode, which when reversing the potential is not able to store all the charge coming across the electrolyte from the  $\text{WO}_3$  film. The deterioration of the electrolyte results from the accumulation of charge at the Nb/Fe-oxide/counter-electrode interface. Another problem is the low transmittance of device below 500 nm, caused by the low transmittance of the Nb/Fe-oxide counter electrode in charged state.

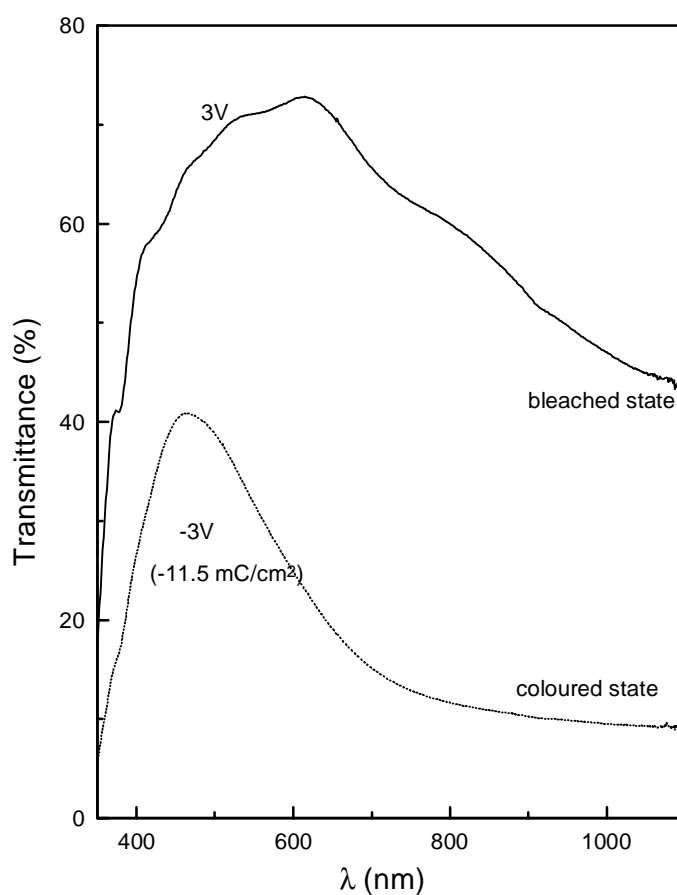
The  $\text{WO}_3$  |ormolyte | $\text{SnO}_2/\text{Mo}/\text{Sb}$  device [5] (Fig. 6) is a better option than using a similar device containing a Nb/Fe-oxide counter electrode, since the  $\text{SnO}_2/\text{Mo}/\text{Sb}$  counter-electrode has a higher spectral transmittance in the visible region. This is particularly noticeable for the transmittance which the device exhibits in bleached state below 500 nm. Here the counter electrode transmits more radiation than Nb/Fe-oxide films. Conversely, the higher transmittance and better optical passiveness of the  $\text{SnO}_2/\text{Sb}/\text{Mo}$  counter electrode means that the EC device does not colour to such a low transmittance value. This is obvious in the near UV. Similar to the previous EC device, the transmittance in the coloured state can be enhanced by applying higher cathodic potentials to the  $\text{WO}_3$  film. However, this also leads to an increase in the instability of the device. This demonstrates the importance of having a sufficiently high ion-storage capacity of the counter electrode.



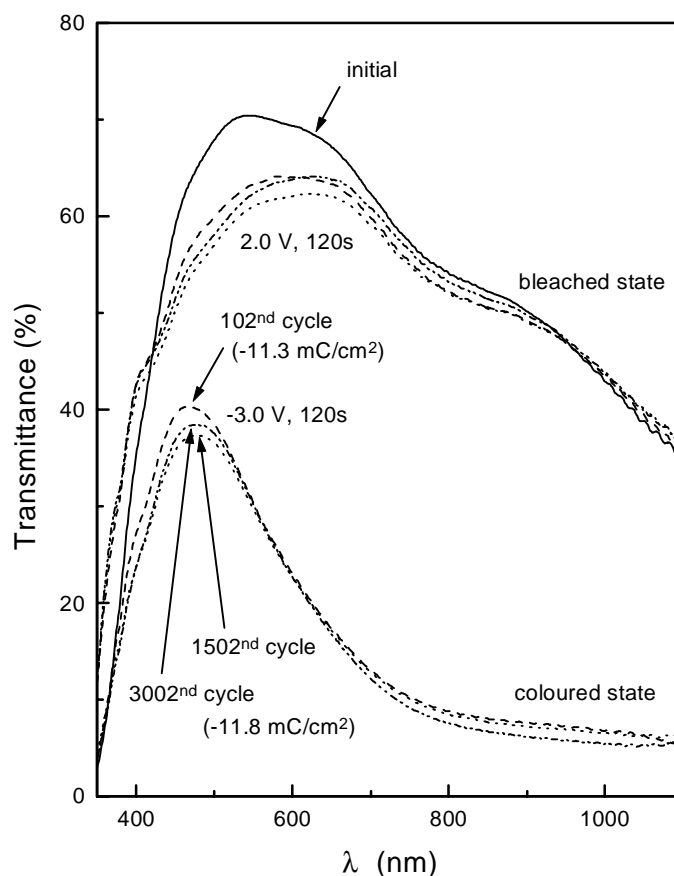
**Fig. 6** Transmittance spectra of  $\text{WO}_3 | \text{ormolyte} | \text{SnO}_2 / \text{Sb} / \text{Mo}$  EC device. Spectra of initial (—), coloured (---), bleached (····) and irreversibly coloured (- · - ·) states are shown.

$\text{WO}_3 | \text{ormolyte} | \text{CeVO}_4$  (Fig. 7) [27,28] and  $\text{WO}_3 | \text{ormolyte} | \text{V} / \text{Ti-oxide}$  devices (Fig. 8) [34] represent the state-of-art regarding cycling stability and optical properties. The latter device, which is being manufactured by Pilkington plc, uses V/Ti-oxide films deposited using the sputtering technique. The switching characteristics of the complete “all sol-gel” EC device, assembled with sol-gel derived V/Ti-oxide [34] and  $\text{CeVO}_4$  [27,28] counter-electrodes, are represented in Figs. 7 and 8. It is apparent that the transmittance of both types of devices in the bleach state is high, equivalent to the transmittance of the  $\text{WO}_3 | \text{ormolyte} | \text{SnO}_2 / \text{Mo} / \text{Sb}$  device. However, there is a distinctive, albeit relatively weak absorption of V/Ti-oxide films below 550 nm, which

has the detrimental effect of changing the colour of the film from yellow to a greenish-brown when charged. The optically passive response of the  $\text{CeVO}_4$  counter-electrode film (Fig. 3) means that the final EC device (Fig. 7) remains transparent in the bleached state while the colour of the device in low transmitting states retains characteristic blue colouration of  $\text{WO}_3$ .



**Fig. 7** Transmittance spectra of  $\text{WO}_3$  | ormolyte |  $\text{CeVO}_4$  EC device in bleached and coloured states are shown. Charging was performed for 110 s at -3.0 V and discharging at 3.0 V vs. counter electrode.



**Fig. 8** Transmittance spectra of  $\text{WO}_3$  | electrolyte | V/Ti-oxide EC device. Charging was performed for 120 s at -3.0 V and discharging at 2.0 V vs. counter electrode.

## CONCLUDING REMARKS

Electrochromic switchable windows are now commercially available but efforts to improve existing materials and to development of new electrochromic devices with improved properties are in progress.  $\text{WO}_3$  will continue to be the main active colouring film in the next generation of devices. Alternatives do exist and the  $\text{Nb}_2\text{O}_5$  films prepared in our laboratory [7] exhibit a more neutral dark coloration, while hydrated Ni-oxide [15] and Co-oxide films [17] are viable options for EC devices using proton electrolytes.



Anodic  $\text{LiCoO}_2$  or  $\text{LiNiO}_2$  films can be used as counter electrodes in combination with lithium based electrolytes. These films colour simultaneously with the active  $\text{WO}_3$  film and a transmittance below 10 % is obtainable.

New sol-gel ion-conductors for EC device application need to be developed because they can be applied using dip-coating deposition. This will mean that less demanding technologies for assembling EC devices, for example vacuum pressing can be applied.

The EC device is not the only option for making switchable windows. Thermotropic windows have already been marketed in car sun-roof applications, but because they cause blurring of the light in the low transmitting state they remain limited to specific building applications. Switchable windows can also be made utilising a process known as gasochromism [40,48]. This involves controlling the optical modulation of a catalytically active tungsten oxide film coated on the inside of a double glazed window. The film is then coloured by exposure to diluted hydrogen and bleached using “cleaned” air. The advantage of a gasochromic switchable window is in its simplicity, requiring only a single layer of  $\text{WO}_3$ .

New building regulations demand ever higher standards of efficient energy usage and management, in which switchable windows will play an increasingly important role. The search for novel materials for use in new and better switchable devices remains a fertile ground for research for the foreseeable future.

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**Povzetek**

Zahteve po energijskem varčevanju postavljajo vse višje standarde zasteklitve. V modernih stavbah moramo zmanjšati toplotne izgube oz. preprečiti pregrevanje preko oken, hkrati pa moramo zagotoviti primerno osvetlitev prostorov. Inteligentna okna predstavljajo nove rešitve, ki zadoščajo zgornjim zahtevam in so sposobna prilagajati svoje optične lastnosti (transmisijo in refleksijo) trenutnemu sončnemu sevanju. Do sedaj so bili odkriti štiri načini, ki omogočajo optično modulacijo: fotokromizem, termokromizem, termotropizem in elektrokromizem. V članku opisujemo napredek, ki smo ga naredili v našem laboratoriju na področju elektrokromnih oken, pripravljenih po sol-gel postopkih in s tehniko potapljanja. Zaključujemo s predlogi, ki naj bi v bodočnosti izboljšali učinkovitost inteligentnih oken.