

All sol–gel electrochromic system for plate glass

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Abstract

The development on an all sol–gel electrochromic system for large area devices is described. Previously developed syntheses routes for tungsten oxide, WO_3 , coating sols and cerium oxide–titanium oxide sols, $\text{CeO}_2\text{–TiO}_2$, were employed, which enabled large substrates ($35 \times 35 \text{ cm}^2$) to be coated homogeneously and without visible cracking. Optoelectrochemical measurements were employed to determine the variation of the electrochromic properties (change in optical density, ΔOD , and switching times) of WO_3 layers, investigated as a function of coating parameters, such as chamber humidity and the temperature of heat treatment. A novel composite electrolyte system, based on organically modified silanes, was developed, which has an ionic conductivity of $\sim 10^{-5} \text{ S cm}^{-1}$ at 25°C . Cells were constructed in two formats: $10 \times 15 \text{ cm}^2$ and $35 \times 35 \text{ cm}^2$. Switching times less than one minute were achieved for the smaller format with a change in transmission from 75% to 20% (at $\lambda = 0.633 \mu\text{m}$).

1. Introduction

In recent years there has been a research and development effort in the area of electrochromic (EC) devices [1] due to the multitude of potential applications for these devices. Progress has been made in applications and small area electrochromic devices such as sunglasses and automobile rearview mirrors are already available, commercially. Large area devices for automobile or architectural glazing, for example, have a number of problems associated with them: the prohibitive cost of preparing the electrochromic layer and the ion-storage layer by physical deposition methods (sputtering or thermal evaporation), the technical difficulties in sputtering large surfaces, and the loss of performance over

large areas associated with the limiting surface resistance of the optically transparent electrodes [2], normally ITO (indium tin oxide) or FTO (fluorine doped tin oxide) coated glass.

There also several problems connected with the type of electrolyte, which may be employed. Small area devices can be constructed, which either contain a liquid or semi liquid electrolyte, sufficient reliability with respect to the sealing of the units being a prerequisite, so that there is no problem in relation to safety. Thin films of hydrated oxides have also been employed for this purpose, for example tantalum oxide, Ta_2O_5 [3]. Although the latter functions excellently in small area devices the coating of large areas with such thin films without defects is problematic. Polymer electrolytes offer a reasonable alternative but tend to exhibit an insufficient longterm UV-stability.

Large area coating by sol–gel is an interesting alternative, particularly as wet-chemical coating

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techniques are relatively inexpensive. However, the electrochromic properties of WO_3 -layers are sensitive to preparation conditions, for example water concentration in the sol and thermal treatment, requiring careful control of coating parameters and thorough knowledge characterization of preparation dependent effects. In addition, the coating sol should be stable and easy to handle.

The approach we followed was therefore to employ a modified peroxotungstic acid route to prepare a tungsten oxide sol, which was stable for several weeks. Optoelectrochemical measurements were then used to investigate the affects of coating parameters, e.g., chamber humidity, temperature of heat treatment, on the kinetics of coloration and bleaching, as a function of the number of cycles. The optimized WO_3 -coatings were then incorporated in complete EC-cells.

Sol-gel prepared cerium oxide-titanium oxide, CeO_2 - TiO_2 , was selected as an ion storage layer due to its lack of coloration, as first proposed by Baudry and Aegerter [4].

A solid Li^+ conducting composite electrolyte, which is described elsewhere [5], based on organically modified silanes, avoids safety problems of leakage associated with liquid electrolytes. Apart from possessing a conductivity, $\sim 10^{-5} \text{ S cm}^{-1}$ at 25°C , the electrolyte also fulfills an important secondary role as a binder between glass panes.

2. Experimental

2.1. Syntheses

The synthesis routes have already been described in detail elsewhere [5] and thus will only be briefly described here.

Stable tungsten oxide coating sols were synthesized using a route based on the dissolution of tungsten metal powder in an excess of hydrogen peroxide solution (30%), in the presence of ethanol and glacial acetic acid, to give peroxotungstic acid. The CeO_2 - TiO_2 -sol was synthesized using cerium (III) nitrate hexahydrate, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and titanium isopropylate, $\text{Ti}(\text{O}^i\text{Pr})_4$, as precursors, in an equimolar ratio.

Glass substrates with an ITO layer (Donnelly Applied Films, $12 \Omega/\square$) or an FTO layer (Libbey-Owens-Ford, $10 \Omega/\square$) were coated by dip coating under controlled conditions of relative humidity and temperature. Tungsten oxide layers 250 nm thick and CeO_2 - TiO_2 layers 140 nm could be obtained in a single coating step [5]. Substrates up to $35 \times 35 \text{ cm}^2$ in size have been coated in this way.

The solid ionic conductor system, which had been previously developed [5], is based on glycidoxypolytrimethoxysilane (GPTS), tetraethoxysilane (TEOS), LiClO_4 , $\text{Zr}(\text{O}^n\text{Pr})_4$ and tetraethylene glycol (TEG).

2.2. Optoelectrochemical measurements

Optoelectrochemical measurements were conducted on individual WO_3 -coated ITO's to determine the affects of sol-gel coating parameters (chamber humidity, heating temperature and duration) on electrochromic properties such as the change in optical density, ΔOD , and the coloring and bleaching times. Measurements were carried out also on the complete EC cells.

In order to study the coloration and bleaching kinetics of the WO_3 -layers, WO_3 -coated ITO-substrates were placed in three electrode cells containing liquid electrolyte (LiClO_4/PC) and switched at a variety of potentials as referenced against a Ag/AgClO_4 electrode. Complete cells were poled between $+2.5$ and -2.5 V . On switching, the average transmission over the wavelength range 380–800 nm was measured as a function of time, employing a multichannel UV-VIS spectrometer (Zeiss Specord S10). Coloring times were defined as the time between 90% of the initial transmission, T_0 , and 110% of the final transmission, T_x , bleaching times were similarly defined. The change in optical density, ΔOD , was also taken as an important criterion for assessing the electrochromic layers, whereby

$$\Delta\text{OD}_x^{(380-800 \text{ nm})} = \log\left(T_0^{(380-800 \text{ nm})}/T_x^{(380-800 \text{ nm})}\right). \quad (1)$$

The variation in ΔOD and in the switching times were investigated as function of the number of cycles.

3. Results

3.1. Optoelectrochemical measurements on WO_3 -layers

Coatings were prepared at two different chamber humidities (20% and 40%), with heating at 120°C or 240°C for either 1 or 2 h. The former temperature was chosen as being sufficient to remove physically adsorbed water, but not chemically bound water with the expectation that a lower heating temperature would facilitate faster kinetics. The second heating temperature was selected to be as high as possible without leading to complete crystallization of the layers.

A small effect from the chamber humidity was observed but only for layers heated at 120°C and only during the first switching cycle, with layers drawn in 40% relative humidity showing faster coloration and bleaching. The duration of the heat treatment had no effect. The heating temperature had the largest effect on the properties as shown in Figs. 1 and 2.

Fig. 1 shows the variation in ΔOD for WO_3 -layers heated at 120 and 240°C as a function of the number of switching cycles (positive values of ΔOD correspond to coloring and negative values represent bleaching). It can be seen from the figure that the WO_3 -films heated at only 120°C had a gradual de-

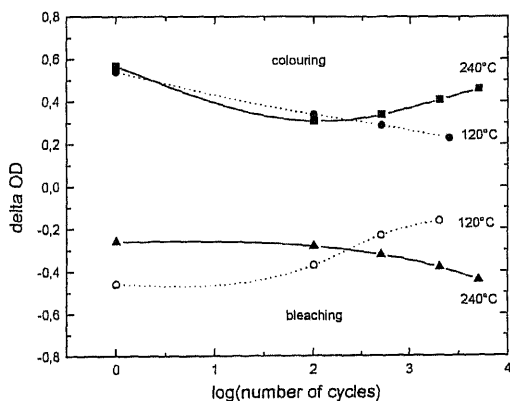


Fig. 1. ΔOD plotted against the logarithm of the number of cycles for WO_3 -layers heated at 120°C and 240°C. Each value is an average from measurements on eight different samples, whereby the variation in the samples lies within $\pm 10\%$. The drawn lines are a guide for the eye.

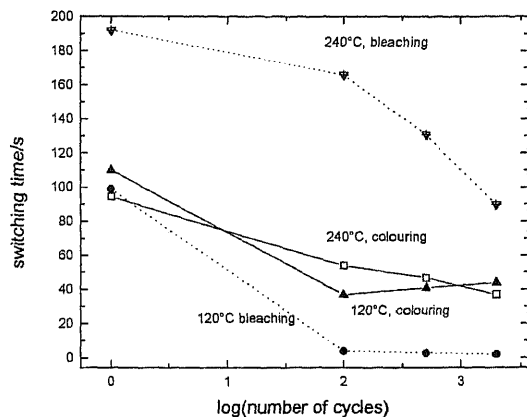


Fig. 2. Switching times as a function of the number of cycles and the temperature of heating, the values are averages composed from four different samples, whereby the variation in between the different samples lies within $\pm 10\%$. The plotted lines are a guide for the eye.

crease in ΔOD with an increasing number of cycles, whereas those layers heated at 240°C, after an initial decrease in ΔOD , had an increase in ΔOD as a function of the number of cycles.

Fig. 2 shows the variation in switching times of the WO_3 -layers heated at 120 and 240°C as a function of the number of switching cycles. The bleaching times are less for the layers heated at 120°C. However, the intensity of the coloration decreases for these layers at the same time. All of the layers tend to shorter switching times with increasing number of cycles.

3.2. Results for complete cells

The optoelectrochemical properties were also determined for cells of the format: $10 \times 15 \text{ cm}^2$, constructed with WO_3 -layers, which had been heat treated at 240°C for 1 h. Fig. 3 shows the change in the average transmission on coloration after successively larger numbers of cycles, up to a maximum of 2000 cycles. It is obvious from the plots that the coloration intensifies and the switching time is reduced through repeated cycling. The tests on the smaller cells gave a constant change in optical density of 0.6 or a change in transmission from 75 to 20% ($\lambda = 0.633 \mu\text{m}$) in a switching time of less than 60 s, after the initial conditioning of the cells. The

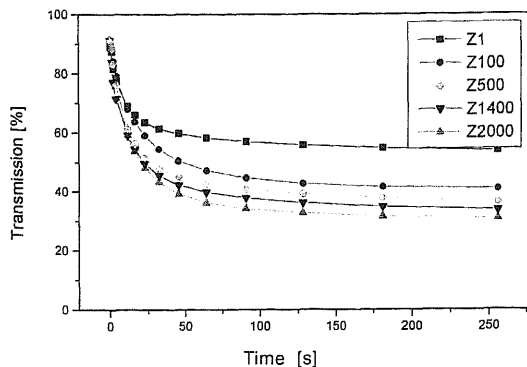


Fig. 3. Time dependence of the transmission, averaged over the range 380–800 nm, as a function of the number of cycles for an all sol-gel electrochromic cell ($10 \times 15 \text{ cm}^2$). Lines are drawn as guides for the eye. Error in the measured transmission is less than $\pm 1\%$.

cells were colored potentiostatically at -2.5 V . The lifetime of the cells is currently between 10^4 and 10^5 cycles, however, further optimization of the switching parameters and the sealing of the cells may extend the lifetime beyond 10^5 cycles. The coloration of the cells remained homogeneous on scaling to the larger format.

4. Discussion

The gradual decrease in ΔOD with an increasing number of cycles for the WO_3 -films heated at only 120°C is due to the poor chemical resistance of the layers to the electrolyte medium, especially as traces of water are present. Such behavior has been reported previously by other authors [1]. The behavior seen after the 1st cycle, for the layers heated at 240°C , represents the conditioning of the layers. We have speculated that such behavior is due to the permanent incorporation of a fraction of the lithium ions in the WO_3 -layer, which do not lead to coloration. Indeed, investigations with electrochemical quartz microbalances seem to confirm that lithium ions are incorporated irreversibly [6], but other such

studies have indicated that due to the variety of mobile species, that the actual mechanism leading to conditioning is probably more complicated [7]. Another consequence of conditioning is the decrease in switching times. The ΔOD observed in the initial cycle is probably due to residual water in the WO_3 -layers.

Measurements on complete cells also show a dependence of properties on the number of cycles.

5. Conclusions

Sol-gel technology can be exploited to prepare electrochromic cells with properties acceptable for commercial applications. The coloration of the cells remained homogeneous on scaling to the larger format.

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