Electrochromic Safety Glass – from wet deposition processes to an all solid state product

M. Rottmann, A. Kraft
Gesimat GmbH, Berlin, Germany

Abstract

Electrochromic films of WO_3 and Prussian Blue were deposited on K-glass panes by wet based electrodeposition. For scaling up the deposition process we developed a specialized process procedure to obtain highly uniform EC-films on large substrates with relatively high sheet resistance. The lamination of two K-glass panes, coated with WO_3 and Prussian Blue thin films with an ion conducting PVB sheet enables the production of an all solid state electrochromic safety glass with especially advanced properties.

Keywords: electrochromics, smart windows, wet deposition

1. Introduction

Today sputter coating techniques are preferably used to produce large area multilayer coatings for energy efficient windows or sun protection glasses. Modern sputter coater enable the depositing of multilayer films subsequent within one deposition process with very good uniformity and less number of visible defects. The decrease of square meter costs by scaling up the deposition process to large area glass panes up to jumbo format 6x3.21m and a continuous process management with very high throughput support the present market success.

For production of so called smart windows which can switch the U- and g-value wet deposition processes are the method of the choice. Electrochromic layers which can switch the transmission of solar radiation in the visible and near infrared region have to be deposited on glass panes with transparent conducting oxide (TCO) coatings. The well known electrochromic tungsten oxide (WO_3) [1] can be deposited by vacuum [2] (because it is a simple inorganic oxide) and wet processes [3]. But there are a lot of other electrochromic substances which have much more complicated molecule structure than WO_3 which cannot be deposited by vacuum processes. The high energy at vacuum deposition would destroy every inorganic complex compound and organic polymer molecules.

Gesimat developed a wet deposition process which allows the large area and uniform electrodeposition of electrochromic films on surfaces with relatively high sheet resistance (e.g. K-glass). A well developed wet deposition process, applicable for most electrochromic substances (e.g. transition metal oxides, inorganic complex compounds, organic polymers) is introduced.

2. Wet electrodeposition of electrochromic layers

2.1 General description

The application of wet processes for thin film deposition of electrochromic layers has many important advantages:

1. The deposition of a wide variety of electrochromic layers becomes possible, e.g. inorganic oxides, complex compounds, organic polymers.
2. It is a very cheap deposition technique.
3. A nanoporous layer structure for ion movement during EC-switching is formed at deposition

Fig. 1 Wet processors for electrodeposition of electrochromic films on glass panes up to 1 sqm.

In contrast to coatings for windows with static light and heat transmission properties, electrochromic layers have to enable ion transport during switching the ec-system [4]. These ion insertion and extraction within the electrochromic layers require a nanoporous layer structure which can be built excellent by wet depositon processes.

Figure 1 shows typical wet processors for electrodeposition of tungsten oxide and Prussian Blue films on glass substrates. Shown vessels for deposition onto 1 sqm glass panes are very small and much more cheaper compared to vacuum coater systems. This wet processing technique is a development of Gesimat GmbH. The K-glass panes were coated with electrochromic layers in a batch process. Each deposition process takes about 30min.

Modern wet electroplating processes are very cost effective deposition processes which can achieve uniformity results of vacuum deposition and absolutely match every demand of environmental protection.

2.2 Electrodeposition of thin WO_3 films

The deposition of WO_3 is performed according equation

$$W_2O_{11}^{2-} + 2\ H^+ \rightarrow 2\ \mathbf{WO_3} + 2\ O_2 + H_2O \qquad (1)$$

from aqueous peroxy-tungstic acid solutions [3]. By applying a cathodic potential to a cleaned K-glass pane, a tungsten(III)oxide film is deposited on the electrical conducting K-glass surface. A corresponding anodic potential is applied to a Ti counter electrode. After intensive process developments by applying SPC methods we achieved uniformities of deposited WO_3 films on K-glass panes of less than ± 5% of mean (3δ) value (fig. 2, 3).

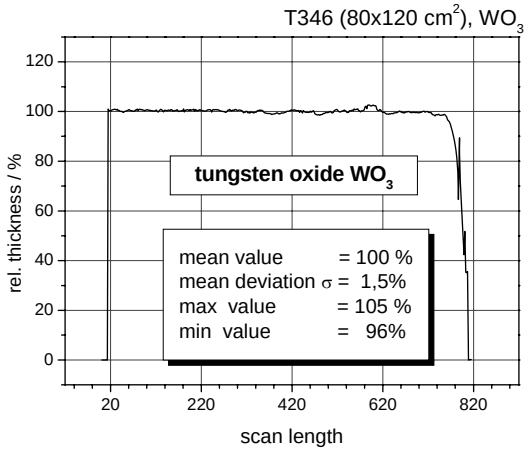

Fig. 2 Thickness profile of a thin WO_3 film on K-glass pane 800x1200mm.

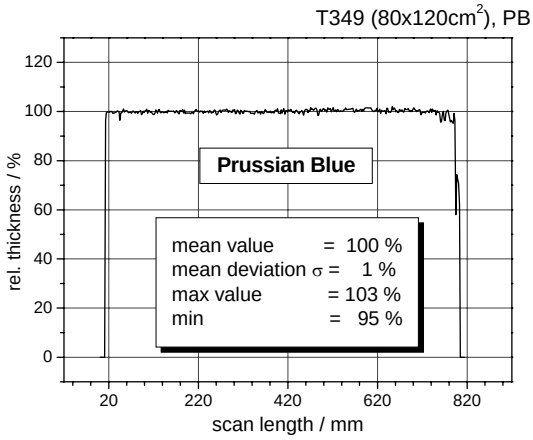

Fig. 3 Thickness profile of a thin PB film on K-glass pane 800x1200mm.

2.3 Electrodeposition of Prussian Blue thin films

Prussian Blue (PB) is a well known and widely studied electrochromic material. It shows complementary electrochromic properties to tungsten oxide with a blue coloured state at anodic and a fully bleached state at cathodic potentials. Prussian Blue thin films can be prepared by electrodeposition from aqueous ferric ferricyanide solutions [5] according equation (2)

$$Fe^{2+} + K^+ + [Fe(CN)_6]^{3-} \rightarrow \mathbf{K[FeFe(CN)_6]} \qquad (2)$$

in the same manner like WO_3 film deposition. Both processes are adapted to each other to use the same equipment.

PB is an inorganic complex compound with a high resistance against solar UV radiation. Although its suitability as counter electrode in WO_3 based electrochromic systems is known, no further developments of large area electrochromic devices containing WO_3 and PB are known. The reason is to be searched in the deposition technique which has to be applied to obtain PB thin film on glass substrates. Because of its complex molecule structure it isn't possible to deposit PB thin film by any vacuum processes. The high energy conditions at vacuum coating processes would destroy the complex molecule structure of PB.

Gesimat developed an electrodeposition process for preparing of PB thin films on large area K-glass panes with high thickness uniformity. As shown in figure 3 thickness profiles with a standard deviation of δ=1% can be achieved.

3. Electrochromic Safety Glass

3.1 Construction and preparation

General construction of our electrochromic safety glass is shown in fig. 4.

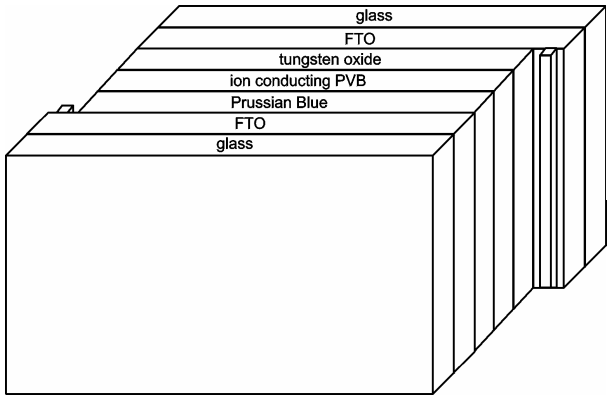

Fig. 4 scheme of electrochromic safety glass

Two coated K-glass panes are laminated together with an ion conducting PVB interlayer [6, 7]. The used electrochromic system consists of two complementary electrochromic layers. WO_3 at one K-glass pane is colouring at cathodic potentials, PB on the other K

-glass pane is colouring at anodic potentials. The resulting device is an all solid state product with especially advanced properties:

- very high switching range of more than 65% light transmittance between coloured and bleached states due to the use of a complementary electrochromic system [8]
- high coloration efficiency by use of two colouring electrochromic layers

- safety glass properties because of the use of a modified PVB interlayer as electrolyte [6]
- low cost/high volume product potential by application of wet electrodeposition processes (thin film deposition) and safety glass production techniques (lamination) [6]
- inorganic EC-system is highly resistant against environmental attacks [8]
- effective and sustainable protection against any danger of short circuits due to solid electrochromic layers are separated from each other by an ion conducting PVB sheet (0.02…0.8mm)

3.2 Switching Behaviour

The EC safety glass shows a gradual switching behaviour by applying a d.c. voltage. According to applied polarity a blue colouration appears or the system is bleached. Because of its construction the system shows battery like properties without self discharging phenomena. A reached colouration state will be retained after cut off the voltage. Only for colouration change a voltage apply is necessary. A whole switching process takes an energy amount of about 200Ws/sqm.

Colouring and bleaching of EC safety glass units is performed with a microprocessor control unit MM2. Between bleached and full coloured state 38 intermediate colouration states can be applied. The control unit realizes an automated switching control to desired colouration state with maximum acceleration.

Fig. 5 presents transmission spectra for a full colouration process of an EC device. Measurements were done using UV-VIS-NIR spectrophotometer (Perkin-Elmer Lambda 19) after interrupting the colouration process at given time steps. The light transmittance τ_V and the solar direct transmittance τ_e were calculated according to the European standard EN 410 using the spectrometer data. Due to the nature of the two complementary electrochromic layers our system achieves a very high switching range of more than 65% light transmittance, which is not matched by other developed EC-systems.

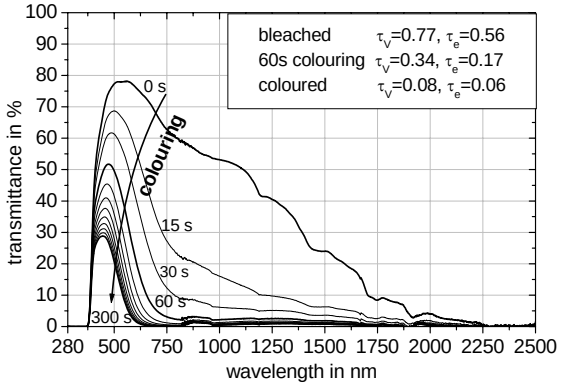

Fig. 5 Transmission spectra during colouration process

Fig. 6 shows current density – time dependence for 3 switched cycles. It can be observed that the bleaching is faster than colouring, because the EC device is discharged after 2/3 of colouring time.

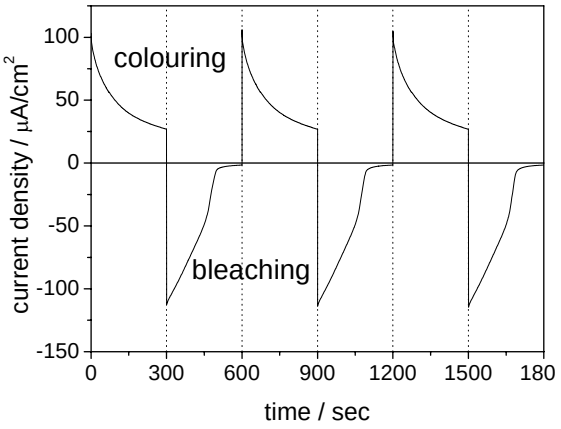

Fig. 6 current density curves of an EC device

One important parameter of an electrochromic device is the colouration efficiency CE. CE is calculated by a relationship between transmittance T and switched electrical charge density Q by equation (3)[9].

$$CE = \Delta OD/Q = \Delta[\log(To/T)]/Q \qquad (3)$$

Calculated data are plotted in fig.7. At 550nm our EC system achieves CE values of 67 cm²/C, which are higher than EC devices based only at WO_3 (40 cm²/C, [10]) Maximum values of 180 cm²/C were calculated in the spectral range of 710-740nm.

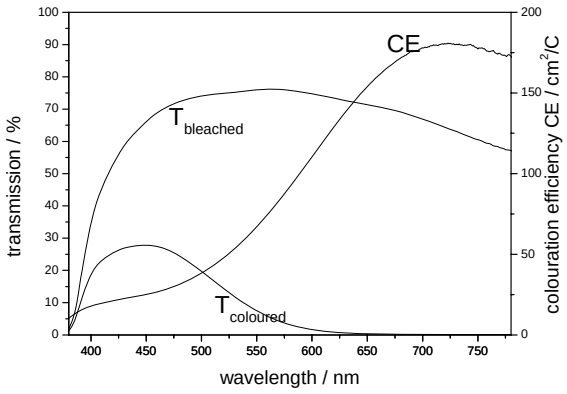

Fig. 7 Colouration efficiency in the visible spectral region.

3.3 Solar radiation control

The practical use of electrochromic windows is investigated by the Department of Applied Physics, Brandenburg University of Technology Cottbus. A test room façade consists of 3 electrochromic insulating glazing of 800x1200mm. The electrochromic windows were switched by computer controlled power supply. Outside and insight of the test room luminance measurements were performed during switching experiments. Up to now a lot

of data were collected for different day times, seasons and weathering conditions. Currently data analysis is running. Early first results can be given here. Fig. 8. presents results of luminance measurements outside and inside of the test room at 3 sunny days in August 2004. If electrochromic windows are fully bleached indoor illuminance rises up to 4,400lux and leads to sun glaring inside the test room over a long day period. At full coloured EC windows the indoor illuminance is diminished down to 550 lux. The recommended minimum value for indoor illuminance of workplaces, 500 lux, is reached only at high noon.

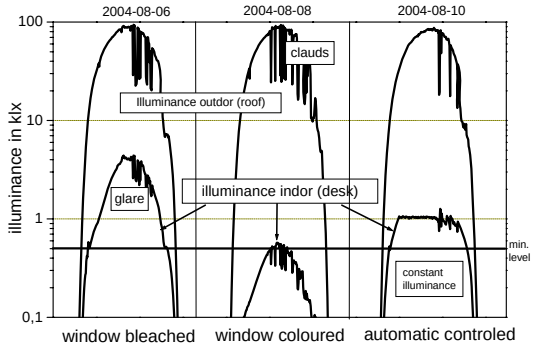

Fig. 8 Measured illuminance at a test room [11] with 3 800x1200mm EC windows of Gesimat, 3 sunny days in August 2004.

An optimum indoor illumination can be realised by computer controlled switching of EC-windows. Due to the deep colouring capability our electrochromic windows could be kept constant indoor illuminance at 1000lux over the whole day. By its high light transmittance of about 75%, the minimum indoor illuminance of 500lux is exceeded from 6am to 18 pm.

4. Conclusion

Wet coating processes were used to deposit thin electrochromic films on K-glass substrates. It could be shown, that our optimized wet electrodeposition processes match uniformity requirements for optical coatings on glass. Electrodeposition based wet coating is best coating method for electrochromic layers on glass panes because a nanoporous layer structure can be formed.

WO_3 and Prussian Blue are an optimum working complementary electrochromic systems. Gesimat solved scaling problems for wet electrodeposition of PB and WO_3 thin films on large area K-glass panes.

Because of their excellent switching behaviour electrochromic safety glass of Gesimat enables an optimum indoor illumination with day light and prevented sun glare insight a test room at every day time.

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