Electrochromic Glazing with an Ion-Conducting PVB Interlayer

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Keywords

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Abstract

Smart windows with switchable light transmittance and reflectance are the windows of the future. Among the different possible technologies for smart windows electrochromism is the most promising candidate. We present a new laminated electrochromic glass consisting of two K glass panes coated with complementary electrochromic thin films and laminated together by use of an ion-conducting PVB sheet.

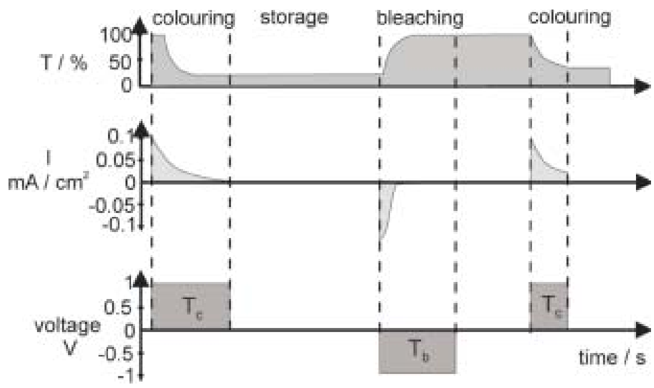
For the first time ion-conducting PVB films are used as a polymer electrolyte in electrochromic glazings. This has many advantages compared to other technologies for the preparation of polymer electrolytes such as the poured resin technology. Additionally, an electrochromic glass which combines the possibility of adjusting the light transmittance with the properties of a laminated safety glass becomes possible. The well known technologies for the production of conventional PVB interlayers and for the production of laminated safety glass can also be used for the manufacture of electrochromic glazing.

Introduction

Since more than 60 years plasticized PVB is in use as an interlayer material for laminated safety glass. This is because of its unique properties such as high, adjustable adhesion to glass, high optical transparency, excellent toughness and flexibility, high impact strength, light and temperature resistance. In addition to safety glass features, other functionalities have been included in the last decades, among them sound control [1], UV blocking, colours and others. By providing a new, ion conducting PVB sheet, the application potential of PVB is extended to the area of polymer electrolytes for electrochromic devices.

Electrochromic devices offer many advantages for the non-mechanical transmission change of smart glazing in future architectural and automotive applications. An important characteristic of electrochromic glazing is the switching of both, the visible light transmission and the overall energy transmission (g value) in response to changing weather conditions. Modern buildings with large area glazing require not only a low heat loss in winter (low U value) but also protection against overheating in summer (low g value) even in moderate climatic zones. However, a high g-value is necessary during winter months to realize solar energy gains. Because of the possibility of user controlled or automatic change the optical properties of electrochromic windows such systems can match very well these demands. Large energy savings up to 50 % due to lowering of the climatisation costs can be realized [2].

Figure 1: Electrical and optical switching behaviour of a battery-type electrochromic device



Electrochromism

Several technologies are discussed for the construction of switchable glazing devices, among them thermochromism, photochromism, electrochromism and the use of electro-optical field effects in liquid crystal or so-called suspended particle devices. Considering all advantages and drawbacks of the different concepts, the most advanced technology is electrochromism. Electrochromism is defined as the reversible change of the optical properties of a material induced by electrochemical oxidation and reduction due to an applied d.c. voltage.

Three different basic device constructions for electrochromic elements are possible:

a) electrochromic compound(s) dissolved in a liquid or gel-type electrolyte (used in automatic-dimming rear view mirrors produced e.g. by Gentex, USA)
b) electrochromic solid films joint together by an electrolyte, preferably a solid polymer electrolyte (battery type)
c) hybrid type devices with one solid electrochromic film and one dissolved redox-active substance in a liquid or gel-type electrolyte.

The first and third kind of electrochromic devices are self bleaching. A constant current flow has to be maintained to provide a constant coloration. Only the second kind of device has a memory effect and needs current flow only during switching [3]. Therefore, and because of gel-type or liquid electrolytes cannot be used in large area glazing only battery-type smart glazing can be used in architectural applications. The electrical and optical switching characteristics of such a battery-type electrochromic device are shown in figure 1.

Due to the application of a small d.c. voltage a current flow is induced which is accompanied by a change in optical transmittance of the glazing (coloration or charging). If the voltage is switched off the glazing retains its optical transmittance. By short circuiting or reversing the applied voltage a current in opposite direction flows and the glazing bleaches (discharging). A controlled gradual change of the light transmittance is possible. Figure 2 schematically shows the change in light transmittance of such an electrochromic system in the coloured and bleached state, which can be used to regulate the amount of light and heat radiation which enters a building through the glazing.

However, the application potential of electrochromic devices is not limited to smart windows in residential and commercial buildings. They can also be used for:

- glazings for means of transportation, e.g. automatic regulation of the light and heat transmittance of switchable glazing panels (in vehicles, trains, aircraft, ships) and for automatic-dimming rear view mirrors
- large area information displays (e.g. airports, train stations, advertising)
- fast switching sunglasses
- switchable filters for light and heat (for cameras, microscopes, spectrometers, etc).

Despite the large application potential, the many benefits of electrochromic glass and huge research efforts until today automatic-dimming rear-view mirrors are the only commercial product based on electrochromism. This can be explained by the drawbacks of previous development concepts for electrochromic devices: Vacuum deposition methods for electrochromic films are expansive and restricted to only a low number of electrochromic materials. Further disadvantages are the often proposed use of tungsten oxide as only one electrochromic film coupled with a so-called ion-storage layer, the use of the poured resin technology for the preparation of solid polymer electrolytes or even the use of non-solid electrolytes (gel-type or liquid) and many others.

Our new concept overcomes these drawbacks and provides a laminated electrochromic glazing with the potential for very high transmittance change, safety glass properties, moderate production costs and durability.

Figure 2:

Schematic drawing of the control of the transmission and reflection of electromagnetic radiation by use of an electrochromic device

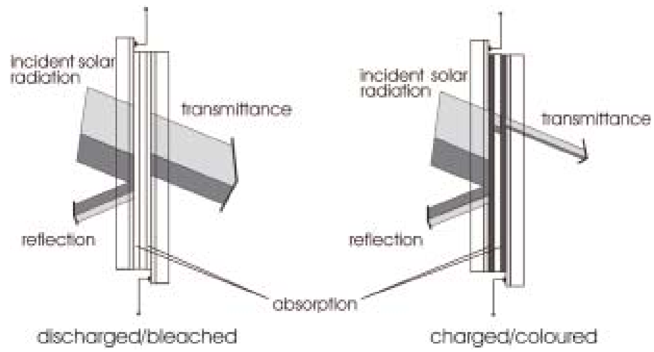


Figure 3:

Schematic drawing of the construction of the electrochromic glazing with the ion conducting PVB interlayer

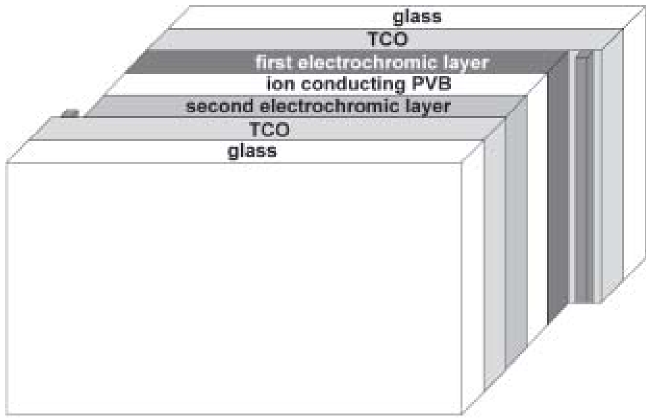
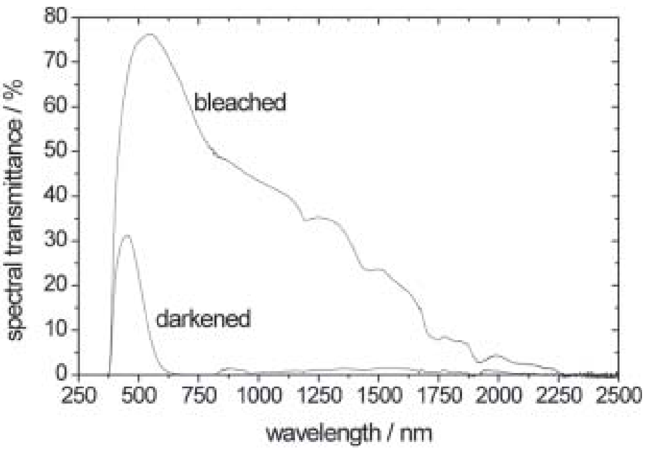


Figure 4:

Transmission spectra in the fully bleached and darkened state of the electrochromic glazing with ion conducting PVB interlayer and tungsten oxide



Electrochromic glazing with ion conducting PVB interlayer

For the first time ion-conducting PVB films are used as a polymer electrolyte in electrochromic glazing. This has many advantages compared to other technologies for the preparation of polymer electrolytes such as the poured resin technology. Additionally, an electrochromic glass which combines the possibility of adjusting the light transmittance with the properties of a laminated safety glass becomes possible. The well known technologies for the production of conventional PVB interlayers and for the production of laminated safety glass can also be used for the manufacture of electrochromic glazing.

The construction of an electrochromic glazing is shown in Figure 3. The applied glass can be either float glass or heat strengthened and it is coated with a FTO (Fluorine doped Tin Oxide) – so called K-Glass - or ITO (Indium doped Tin Oxide) layer. This layer is responsible to conduct the electrical current into the electrochromic layers. The connection to the direct-current supply (bus bar) is realized with metallic conductors printed directly to the edges of the glass.

The electrochromic layers themselves are coated electrochemically on the FTO layer. This technology implies lower costs for equipment installation and maintenance in comparison with vacuum coaters. One electrochromic layer is usually Tungsten trioxide (WO_3), the other can be an electrochromic inorganic complex compound (e.g. Prussian Blue PB: $[Fe^{III}Fe^{II}(CN)_6]^-$) or a polymeric layer system (e.g. Polyaniline, Polythiophene). The fact that a complementary electrochromic system is used, is a big advance: The difference in transmittance between the bleached and the coloured state is much bigger and the coloration rate is faster in comparison to existing electrochromic systems with only one electrochromic film and a so-called ion-storage layer. The transmittance in the visible T_L can be varied between 75% and 10% (in a range from 380 to 780 nm according to EN 410). But the shadowing does not only work in the visible, but also in the infrared. The energy transmission T_E is variable between 50% and 10% (in a range from 300 to 2500 nm according to EN 410). These values are valid for a system with WO_3/PB electrochromic layers. Figure 4 shows the transmittance versus the wavelength for such a system in the fully bleached and fully coloured situation.

The two glass panes are laminated with a ion conducting PVB interlayer. The ion conductivity realizes the ion transport between the electrochromic layers. The final product is an insulating glazing with the laminated electrochromic glazing as external pane and a low-e coated glass as inner pane.

The PVB film for electrochromic glazing uses a modified resin in combination with a special plasticizer system. To get a sufficient ion conductivity of the film, a conducting salt is added to the formulation. This salt is usually based on Lithium or Potassium. The conductivity of the film should be in a range of 5×10^{-6}

S/cm to 2 x 10^{-5} S/cm to get acceptable switch times. The switch times of an electrochromic glazing with such a PVB interlayer varies dependent on the size of the glazing between 5 and 20 min., which is absolutely satisfactory for architectural glazing. Figure 5 shows the transmittance vs. the wavelength for discrete time to bleach the glass, Figure 6 to darken it.

Why do we use PVB interlayer as a polymeric electrolyte for the electrochromic glazing ?

PVB film is used to produce laminated safety glass for more than five decades and it´s the most experienced material for this application. Adhesion to glass and ion conducting function is integrated in one material. So it is obvious to use PVB film in electrochromic glazing. It can be laminated under almost the same process conditions than standard PVB interlayer. The delivery form is also the same, either refrigerated or PE interleaved. The mechanical properties of the film give the laminate a satisfactory stability. The UV stability of the PVB film is excellent. There are no effects due to secondary induced polymerisation of free monomers or oligomeres as compared to poured resins.

The components for production of electrochromic glazing can be easily integrated in a standard laminating line. For the lamination itself standard operations are used (pre-niproller, autoclave). Figure 7 shows a scheme for the integration of electrochromic components to a laminating line.

What tests are necessary to verify the long term durability?

The continuous cycle test switches the electrochromic glazing incessantly between the bleached and coloured state. The test indicates the stability of the switching and possible interactions between the PVB film and the electrochromic layers. The objective is to reach at least 40,000 cycles, which is equivalent to an average of five switches a day over 20 years.

This test should be also done under more severe environmental conditions. The UV radiation, humidity test and high temperature storage according to EN 12543 Part 4 simulates different weather conditions. After the tests the samples are evaluated in terms of visual changes (e.g. discoloration, bubbles, delaminations, haze) and loss of transmittance ratio.

The only standard which is actually valid for the testing of electrochromic glazing is the ASTM E2141-02. This standard describes the exposition of electrochromic specimen to simulated solar irradiation in a temperature- and humidity-controlled chamber at selected temperatures ranging from 70°C to 105°C while the specimen are cyclically coloured and bleached. This procedure runs for 50.000 cycles, inspecting the samples every 4.000-10.000 cycles. The test is passed, if the transmission in the bleached state is more than 50% or the ratio between the transmission of the bleached and the coloured state is more than 4 at room temperature.

The insulating glass units should be tested according to prEN 1279 Part 2: Type test on airfilled insulating glass units. It describes a climate changing test of four weeks with temperatures between -18°C and +53°C in addition with a heat storage for another 7 weeks at 58°C. The relative humidity goes up to 95% including a condensing phase. The test is followed by a

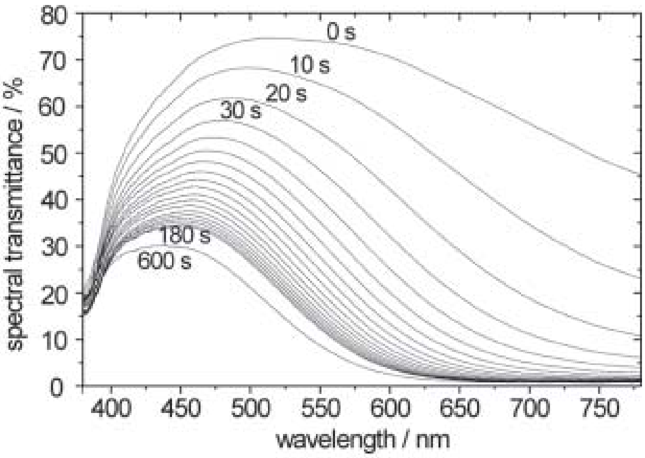


Figure 5:

Change of the transmittance of an electrochromic glass with ion conducting PVB between 380 and 780 nm during coloration: spectra recorded in steps of 10 seconds between 0 and 180 seconds and after 600 seconds

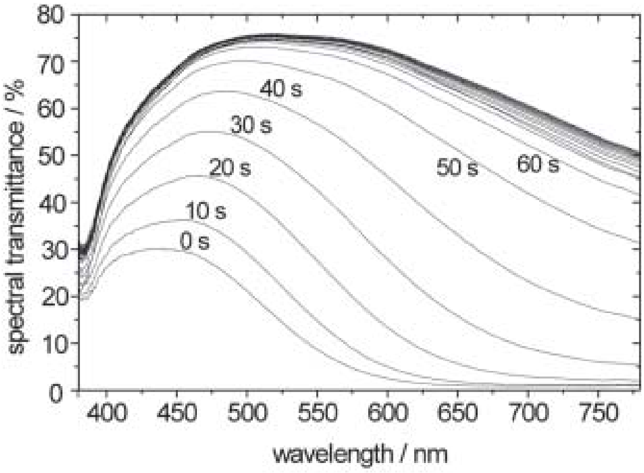


Figure 6 :

Change of the transmittance of an electrochromic glass with ion conducting PVB interlayer between 380 and 780 nm during bleaching: spectra recorded in steps of 10 seconds between 0 and 180 seconds and after 600 seconds

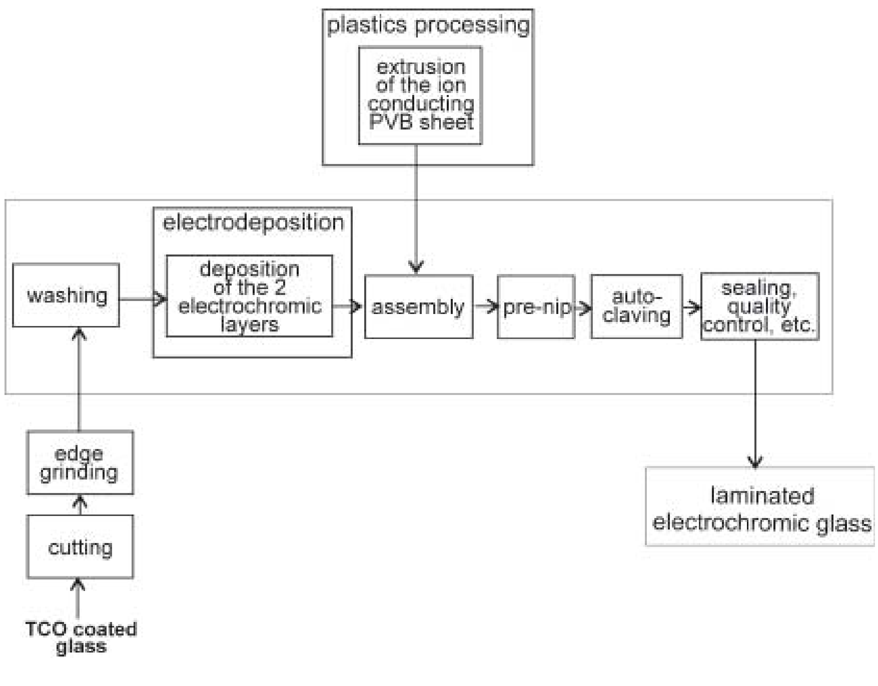


Figure 7:

Schematic drawing of the production process for the electrochromic glass with ion conducting PVB interlayer visuell inspection for defects and a measurement of the transmission ratio.

To verify the adhesion between the single layers of an electrochromic glazing, the compressive shear strength (CSS) test regarding patent DE 19756274 is a common method. Laminated samples of size 25.4 x 25.4 mm^2 are sheared under an angle of 45° until they are destroyed. The maximum force related to the sample area is the CSS in N/mm^2. So the construction will break at the weakest connection of the single layers. Typical values of laminates with standard PVB are between 8 and 20 N/mm^2. Figure 8 shows the CSS test apparatus.

The impact strength of the system can be determined according to EN 12600. A pendulum consisting a twin tire of 50 kg weight swings onto the laminate from a height of 190, 450 and 1200mm. The test counts as fulfilled at a certain height, when the glass does not break or if it breaks, the opening in the laminate is not bigger than 76 mm.

Figure 8:
Compressive shear strength test apparatus

Summary

Electrodeposition is a very cost effective way of producing electrochromic layers. It is much cheaper than other technologies like sputtering. The use of complementary electrochromic thin films allows for a bigger difference in light transmittance between the bleached and coloured state Electrochromic layers can be made from oxides, inorganic complex compounds or polymeric layer systems. This means bigger variety in materials and colours. The ion conducting PVB film as a polymeric electrolyte enables the use of standard laminating lines to produce electrochromic glazing and adds the benefit of safety and security to the system.

References

[1] U. Keller: Improved sound reduction with laminated glass, Glass Processing Days 2001, Conference Proceedings Book, pages 735-737

[2] H. Wittkopf: Electrochromics for architectural glazing applications, Glass Processing Days 1997, Conference Proceedings Book, pages 299-303

[3] K.-H. Heckner, A. Kraft: Similarities between electrochromic windows and thin film batteries, Solid State Ionics 152-153 (2002) 899-905