

H. P. Heim¹, A. Desjean²*

¹Institute for Materials Engineering – Polymer Technology, University of Kassel, Kassel, Germany

²Daimler AG, Sindelfingen, Germany

Climatic Ageing of Components of Polymer Based Electrochromic Devices

Combining a shading function and a polycarbonate window displays an attractive alternative to the currently employed glass roof in vehicles. However, the ageing of such a device must be investigated before any application. Therefore, our investigations focus on the ageing of the components of a polycarbonate based electrochromic device. The optical, electrical, mechanical and electrochemical properties of the ion storage layer as well as the substrate will be assessed after storage in a climate with a high humidity and high temperature level.

1 Introduction

Vehicles are equipped with more and more glass windows to improve the comfort and spatial atmosphere for the customers. Drawbacks of this trend are the overheating of the interior and glaring effects. An attractive solution to avoid these problems while simultaneously reducing the weight of the vehicle, is to combine an electrochromic shading function and a polycarbonate window.

An electrochromic device can be fabricated from 7 layers (or less) constituted of two transparent conductive electrodes (as Indium Tin Oxide (ITO) for instance), coated onto a substrate (usually glass), an electrochromic layer, an electrolyte and an ion storage layer.

Electrochromic systems have been studied for years and are already commercialized for some applications such as rear view mirrors (Heuer et al., 2002; Heusing and Aegerter, 2006). The main advantages of electrochromic devices are that they require a small electrical voltage to change the transparency of the window and that power is required only during switching. Many devices use metal oxides as electrochromic material but have a slow switching speed and high production costs (Heuer et al., 2002; Heusing and Aegerter, 2006).

Some organic conductive polymers like Poly(3,4-ethylenedioxythiophene) – Poly(styrene sulfonate) PEDT/PSS display electrochromic properties with faster switching rates and enable easy processing (Heuer et al., 2002).

In this study, the objective is the examination of the ageing of an electrochromic device based on a polycarbonate (PC)

substrate. The main focus is the ageing of the components of such a device. The thermal ageing of PC, PC/ITO (Indium Tin Oxide) and different types of ion storage layer materials on PC/ITO substrate at 80 °C, while exposed to a relative humidity of 75 % for a time period of 1 000 h are investigated.

2 Experimental

Two different titanium oxides are used as ion storage layers. One of these materials, amorphous TiO₂, is sputtered on PC/ITO at the University of Kassel, Institute for Nanostructure Technologies and Analytics, Germany. The other layer Ti₂O₃ is obtained by means of electron beam vapor deposition from the company Vakuumtechnik Dresden, Germany.

The titanium oxide layers have a thickness of 100 nm, and are applied on 60 × 80 mm and 10 × 80 mm PC/ITO sheets. The surface of the PC/ITO sheets is previously activated by 20 min exposure to UV-Ozon. The PC/ITO sheet (Lexan 9030, Sabic) is sputtered with an ITO layer of Elamet C from GfO AG.

First, samples are stored 16 h at 35 °C before initial measurements are carried out. The different specimens are placed on small wooden rods for 1 000 h, in order to have a homogeneous warmth repartition. The wooden rods are placed on 15 × 20 cm glass plates in the middle of an environmental chamber VC 7034 with temperature and humidity control from Vötsch Industrietechnik GmbH. The temperature is set at 80 °C and the relative humidity at 75 %. Transmission and sheet resistance are measured every 250 h on five 60 × 80 mm samples, while the bending and electrochemical behavior is characterized each time on three 10 × 80 mm samples before and after storage in the chamber.

Transmission measurements are performed using the UV-VIS-NIR Shimadzu spectrometer Solidspec3700.

Sheet resistance measurements are carried out with the aid of the 4-point probe method with the Loresta-EP resistivity meter from Mitsubishi Chemicals. Four point probes are placed on the layer to be measured. A constant current flows between the two external probes, while the voltage is measured using the two inner probes to determine the resistance. Sheet resistance of the thin films is obtained by multiplying the measured resistance and the resistivity correction factor.

The effects on the mechanical properties are determined by assessing the density of cracks according to the bending strain

* Mail address: Aline Desjean, Daimler AG, PWT/VWK, X376, 71049 Sindelfingen, Germany
E-mail: aline.desjean@daimler.com

using a self-made device (Fig. 1). The device is built according to the German Norm EN ISO 178 to carry out a three-point flexural test. Different flexural strains are applied using screws of different lengths to adjust the deflection.

The crack density is characterized by using an optical microscope.

Electrochemical properties are evaluated using a potentiostat SP 200 from BioLogic Science Instruments. Measurements are performed at 25 °C in a three electrode cell.

A potential is applied on the working electrode, where electrochemical changes occur. In voltammetry measurements, the current changes are recorded as a function of the potential applied at the working electrode. The potential at the reference electrode is measured by the difference in potential between the working electrode and a reference electrode. A counter

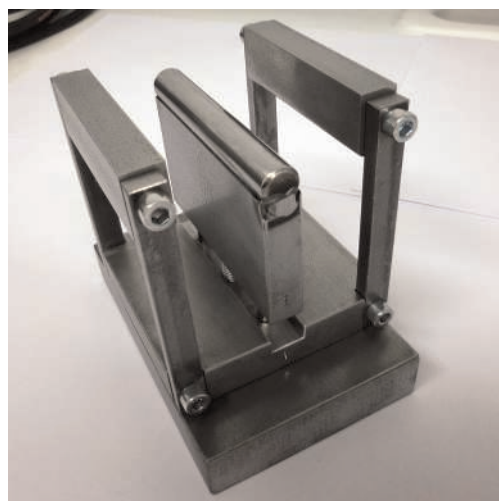


Fig. 1. Self-made device for applying flexural test

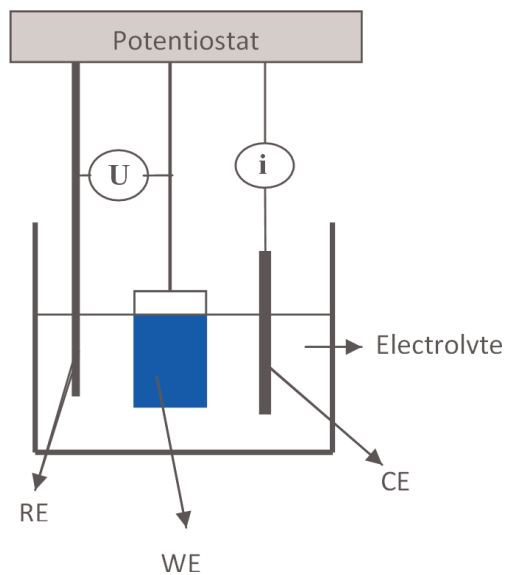


Fig. 2. Three electrode cell for voltammetry measurements (Monk et al., 1995)

electrode is used to complete the circuit, enabling the current flow (Fig. 2).

In this study, the working electrode is the sample, the counter electrode is platinum, the reference electrode is a Ag/Ag⁺ non-aqueous reference electrode, containing a solution of 0,1 M TBAP and 0,01 M AgNO₃ in Acetonitrile (+0,48 V vs NHE (Tung and Ho, 2003)). The electrolyte is a solution of 0,1M LiCF₃SO₃ Poly(ethyleneglycol)methylether.

Open circuit measurements are performed on the assemblies, followed by cyclic voltammetric experiments. In order to have reproducible measurements, data resulting from the 5th voltammogram are analysed. After this measurement, chrono-amperometric experiments are carried out: A potential is applied for 2 min and the current response is recorded against the time. These measurements are conducted at -1.0 V and +0.5 V (vs. reference electrode), where electrochemical activities of titanium oxides are observed.

3 Results and Discussion

3.1 Optical Properties

The transmission of PC, PC/ITO and titanium oxide specimens displays no noticeable change in the visible range (380 to 800 nm) after ageing.

A strong augmentation of the transmission in the IR range occurs for the PC/ITO samples and titanium oxide layers coated onto PC/ITO (Table 1). Nevertheless, TiO₂ shows less transmission change (Fig. 3). The main degradation in the visi-

ΔT (%)	PC	PC + ITO	PC + ITO + TiO ₂	PC + ITO + Ti ₂ O ₃
380–800 nm	-1.2	1.5	1.0	-0.1
1820 nm	-0.8	17.0	7.9	14.4

Table 1. Difference of transmission after and before storage

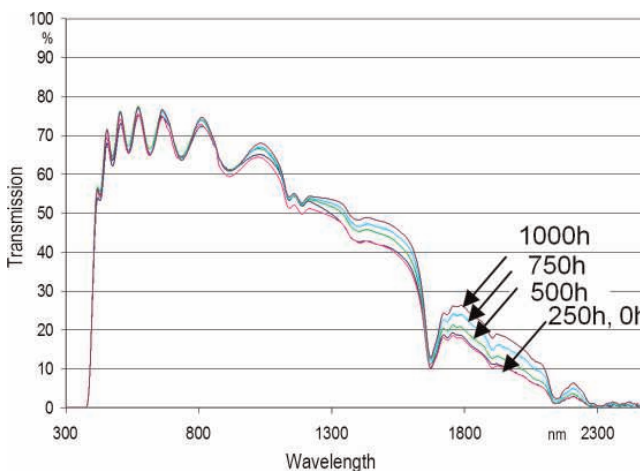


Fig. 3. Transmission of PC/ITO/TiO₂ at different ageing time

ble and IR range occurs during the first 250 h to 500 h of storage (Fig. 4).

As the degradation occurs only in the IR range, it indicates a chemical modification of the layers.

After ageing, cracks are visible on the titanium oxide and ITO layers (Fig. 5). Specimens coated with TiO₂ show the strongest surface degradation. Some small spots display an absence of coating.

This degradation could be due to the difference in coefficients of thermal expansion of the various layers. The same specimens (PC, PC/ITO, PC/ITO/TiO₂ and Ti₂O₃) were stored for 1000 h at 80 °C. No delamination could be seen for all the samples (Heim and Desjean, 2012). The difference in coefficients of thermal expansion cannot explain the cracks.

The two titanium oxide samples were also exposed at 75 % rH, 25 °C for 1000 h. Again no delamination could be seen.

Absorption of water during storage at 80° C, 75 % rH could be quantitatively observed using the area of the water peak at 1900 nm. Here, polycarbonate absorbs water combined with the thermal expansion. The delamination could then be explained by this absorption coupled to the difference of thermal coefficients with the layers above.

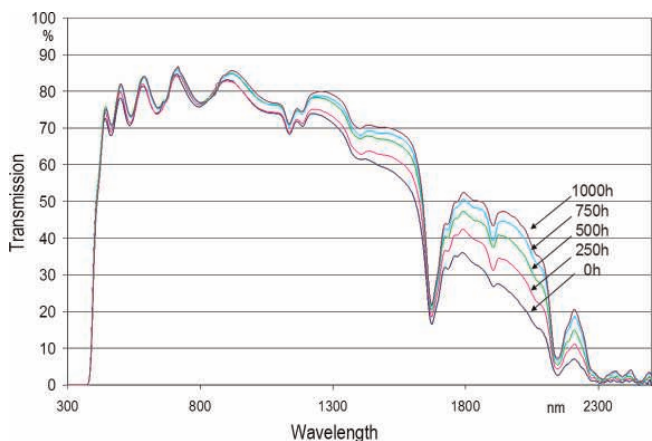


Fig. 4. Transmission of PC/ITO at different ageing time



Fig. 5. Degradation at the TiO₂ surface (magnification: x21)

3.2 Electrical Properties

The sheet resistance of ITO, TiO₂ and Ti₂O₃ increases during storage, most strongly for ITO (up to $2.6 \times 10^5 \Omega/\text{sq}$) and Ti₂O₃ (up to $4.0 \times 10^5 \Omega/\text{sq}$). The augmentation mainly occurs during the first 250 h (Fig. 6).

Oxidation of the ITO layer has been reported causing an increase of the sheet resistance (Kim et al., 2004) due to the diminution of oxygen vacancies in the layer. It explains the sheet resistance increases for the oxides layers, as the conductivity is based on oxygen vacancies. Such an oxidation could cause structural modification and therefore explain the observed increase in the IR range.

3.3 Mechanical Properties

Specimens are bent at a strain from 0.2% to 4% (from 0.5% to 2% at intervals of 0.5% and then at intervals of 1%). After each bending the crack density of the layers is evaluated via microscopy (Fig. 7).

No alteration due to ageing could be detected for PC. Cracks are observable at the surface of ITO, the crack density after ageing is the same as the crack density of samples without ageing bent at about 2% strain.

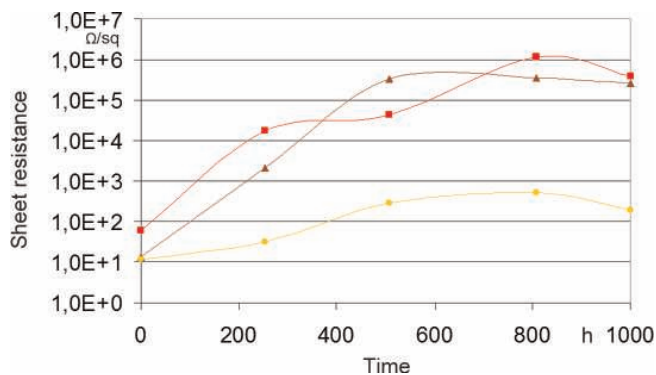


Fig. 6. Sheet resistance vs time (▲: PC/ITO, ■: PC/ITO/Ti₂O₃, ●: PC/ITO/TiO₂)



Fig. 7. Example of cracks on ITO layer without bending (after ageing), 200x

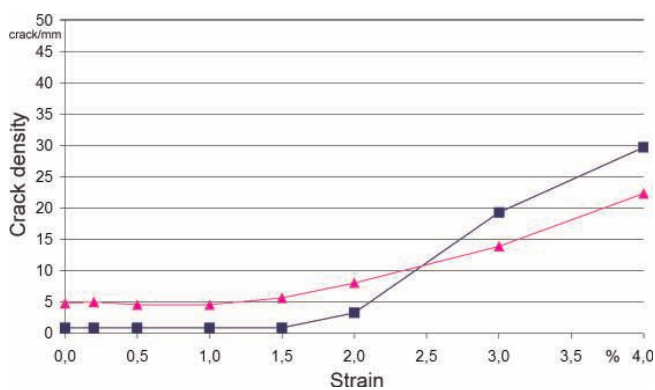


Fig. 8. Crack density vs bending strain for TiO_2 layers (■: without ageing, ▲: after ageing)

A delamination of the titanium layers occurs due to ageing. The crack density of the titanium layers after ageing is the same as the crack density of samples without ageing bent at 2% strain for TiO_2 (Fig. 8) and 2.2% for Ti_2O_3 .

3.4 Electrochemical Properties

Cyclic voltammograms of unaged PC/ITO/ TiO_2 and PC/ITO/ Ti_2O_3 samples exhibit anodic peaks (respectively -0.9 V and $+0.3$ V), which indicate oxidation of the layers. The response time is analysed with chronoamperometry curves. The response time is the time difference between 90% and 10% decrease of the current intensity (Fig. 9). PC/ITO/ TiO_2 displays a faster response time than Ti_2O_3 (Table 2). After climatic storage of 1 000 h, PC/ITO/ Ti_2O_3 samples exhibit almost no more

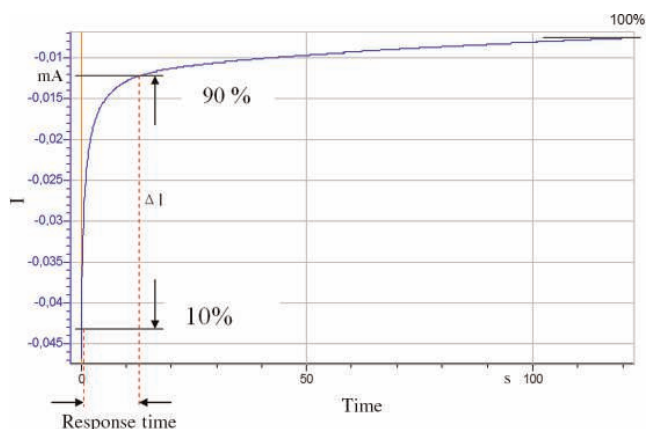


Fig. 9. Response time calculation with current vs time curve

Response time (s)	PC/ITO/ TiO_2	PC/ITO/ Ti_2O_3
-1.0 V	1.5	1
$+0.5$ V	2	8

Table 2. Response time of specimens without ageing

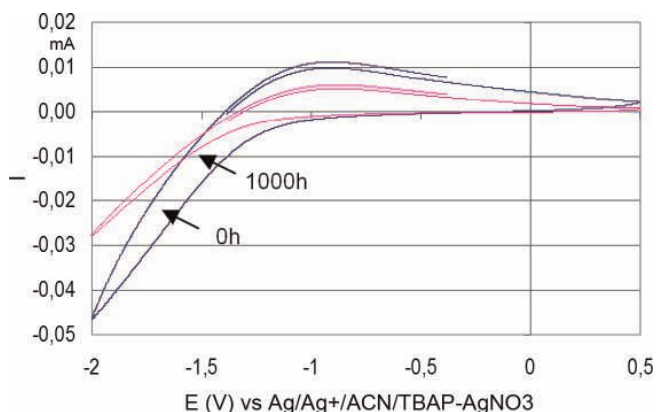


Fig. 10. Cyclic voltammogram from PC/ITO/ TiO_2 with and without ageing (scan rate: 50 mV/s)

electrochemical activity, only a third of the samples exhibit a really slight electrochemical response with low current intensity.

A third of the PC/ITO/ TiO_2 samples still display electrochemical activity, with the same response time as samples without ageing. The current intensity on cyclic voltammograms is lower than without ageing (Fig. 10). This means that the amount of intercalated ions in the layer is lower after ageing, due to degradation of the titanium layer.

4 Conclusion

After thermal ageing in a climate with high humidity, transmission measurements show a strong increase in the IR range for PC/ITO and PC/ITO/ Ti_2O_3 . A transmission increase as well as a surface deterioration occurs for the PC/ITO/ TiO_2 specimens.

The sheet resistance increases strongly during the first 500 h of storage, especially for Ti_2O_3 and ITO. This phenomenon could be related to the transmission increase in the IR range.

As the degradation occurs only in the IR range, it indicates a chemical modification of the layers. Oxidation of the ITO layer has been reported, causing an increase of the sheet resistance (Kim et al., 2004). This could explain the increases in transmission and sheet resistance for ITO and the TiO_x layers.

No change of the mechanical properties is identifiable for PC and PC/ITO. Both titanium layers exhibit strong damage and delamination after storage. The delamination is attributed to the absorption of water of PC and the differences in the coefficients of thermal expansion.

After analysis of the electrochemical properties, TiO_2 appears to be more stable than Ti_2O_3 , although it still shows degradation effects.

In addition, water absorption on the surface of TiO_x (Caputo et al., 2008; Södergren et al., 1997) has been reported. This microstructural change could contribute to the increases in transmission and sheet resistance and the loss of the electrochemical properties, as well as delamination effects.

References

- Caputo, G., Nobile, C., Buonsanti, R., Kipp, T., Manna, L., Cingolani, R., Davide Cozzoli, P., Athanassiou, A., "Determination of Surface Properties of Various Substrates Using TiO₂ Nanorod Coatings with Tunable Characteristics", *J. Mater. Sci.*, **43**, 3474–3480 (2008), DOI:10.1007/s10853-007-2335-x
- Heim, H. P., Desjean, A., "Characterization of the Thermal Ageing of Electrochromic Devices", E-MRS Spring Conference, Symposium Q (2012)
- Heuer, H., Wehrmann, R., Kirchmeyer, S., "Electrochromic Windows Based on Conducting Poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate)", *Adv. Funct. Mater.*, **12**, 89–94 (2002), DOI:10.1002/1616-3028(20020201)12-2<89::AID-ADFM89>3.0.CO;2-1
- Heusing, S., Aegerter, M. A., "Stand der Anwendung der Elektrochromie in der Architektur", www.inm-gmbh.de (2006)
- Kim, Y.-N., Park, J. H., Shin, H. G., Song, J. K., Lee, H. S., "Fabrication of Thin Film Using Nanosized Indium Tin Oxide (ITO) Powder and Its Degradation Characteristics", *Materials Science Forum*, **449–452**, 285–288 (2004)
- Monk, P. M. S., Mortimer, R. J., Rosseinsky, D. R.: *Electrochromism, Fundamentals and Applications*, VCH, Weinheim (1995)
- Södergren, S., Siegbahn, H., Rensmo, H., Lindström, H., Hagfeldt, A., Lindquist, S. E., "Lithium Intercalation in Nanoporous Anatase TiO₂ Studied with XPS", *J. Phys. Chem. B.*, **101**, 3087–3090, (1997), DOI:10.1021/jp9639399
- Tung, T.-S., Ho, K.-C., "A Complementary Electrochromic Device Containing Poly(3,4-ethylenedioxythiophene) and Prussian Blue", *The Electrochemical Society, Proceedings Volumes 17*, 254–266 (2003)

Date received: June 05, 2012

Date accepted: March 05, 2013

Bibliography
DOI 10.3139/217.2657
Intern. Polymer Processing
XXVIII (2013) 3; page 256–260
© Carl Hanser Verlag GmbH & Co. KG
ISSN 0930-777X

You will find the article and additional material by entering the document number **IPP2657** on our website at www.polymer-process.com