**Nora Zikulnig**

# Reflective and Transmittive Organic Electrochromic Devices

## MASTER THESIS

For obtaining the academic degree
Diplom-Ingenieurin

Diploma Programme of
Technical Physics

Graz University of Technology

**Graz University of Technology**

Supervisor:

Univ.-Prof. Dipl.-Ing. Dr. techn. Günther Leising

Institute of Solid State Physics

Graz, October 2010

# Acknowledgement

This work was carried out within cooperation of austriamicrosystems and the Institute of Solid State Physics TU Graz.

I address special thanks to my supervisor Univ.-Prof. Dipl.-Ing. Dr. techn. Günther Leising for his advice and support. And I thank my study colleagues and the stuff from the institute particularly Dipl.-Ing. BSc Christian Gruber, Dipl.-Ing. BSc Andreas Hirzer, Harald Kerschbaumer, Robert Krauss, Birgit Kunert, “Sternchen” Elisabeth Stern.

Many thanks to austriamicrosystems, especially to Dipl.-Ing. Mario Manninger for his kind support. Further I wish to address thanks to Jan Enenkel, Dipl.-Ing. Karl Ilzer, Dipl.-Ing. Dr.-techn. Manfred Pauritsch, Dipl.-Ing. Peter Trattler and Stefanie Tscherntschitsch.

Last but not least I owe sincere gratitude to my family. I am grateful to my mum for her help. Special thanks are also due to my husband: He stood by me day and night and never complained about being neglected.

# Table of contents

# 1. Introduction

If we imagine a weekday, we will recognize that we look at displays the whole day through. It can start in the morning with the digital clock, the coffee machine, following with the electric toothbrush. On the way to our work we meet displays at the bus stop and displays in the tramway. If we go by car, we are informed of speed, fuel gauge, fuel consumption, mileage, temperature, and we use our GPS. At work we operate computers, maybe measuring instruments. Washing machine, tumble drier, electric cooker, dishwasher, microwave help us with our housework. A big deal in our life is entertainment electronics such as TV, DVD-recorder, hi-fi system, mp3 player, notebook, gaming console, digital camera, etc.

Nearly everybody is lost without a mobile phone. The capabilities of smart phones are far beyond making just a phone call.

So every day humans come in contact with consumer goods, which communicate with human by visual effects. In these cases visual effects work as interface between human and machine. An electrical signal can be transformed in a visual signal, which can be noticed by human and then recorded as visual information. Symbols, figures, icons, writing, and so on are used for man-machine-interaction. Depending on the rate of complexity there is a need of black and white images or of colour images. With colour images very complex picture alterations are possible and so complex information can be visualized. The change of colour can also be used as an element of design. For simple information, e.g. function display on/off, black and white images or two colour images are satisfactory.

Many consumer goods described above have indicators for the operating status, state of charge, ready to receive status, etc. Such control indicators can be realized by simple displays, which change colour and/or shape, instead of using multicoloured high resolution displays. Electrochromic devices are a good choice, since they can change between different coloured states and persist in the wanted state with nearly no further input of power (memory effect).

# 2. Fundamentals electrochromism

Crystals with imperfections can show colour centres, induced for example by influence of radiation. Przibram reported the migration of the colour centres – and the colour – in a coloured potassium bromide crystal under the influence of an electric field toward the point of lowest potential. With this movement a well-defined edge of the colour was visible [1].

Based on this observation Dreyer filed a patent for an application: “light modulation device employing a scotophoric light valve”.
“This invention relates to devices and methods for modulating light. In particular, this invention relates to light modulation devices and methods employing a scotophor as a light valve, and to such light valves.
A scotophor, as the term is used herein, is a material which is tenebrescent. Tenebrescence is the property possessed by certain natural and synthetic materials of reversibly darkening and bleaching under suitable irradiation (cf. H. Leverence, “Luminescence of Solids,” John Wiley & Sons, New York, 1950).” [2].

However the nomination “electrochromism” was first introduced by Platt: “…the absorption and emission spectra of certain dyes may be shifted by hundreds of angstroms upon application of a strong electric field. This effect could be called “electrochromism”, in analogy to “thermochromism” and “photochromism” which describe changes of color produced by heat and by light.” [3].

## 2.1. Electrochromic effect

If the colour of a substance changes with electrochemical oxidation and reduction, it is a matter of electrochromism. This means there is an electrochromic substance with an intrinsic transmittance at a given wavelength. Over electrical control, for example upon application of a voltage, the transmittance gets changed. If this change in transmittance occurs in the visible region (400 nm to 800 nm) human can observe it as a change in colour.

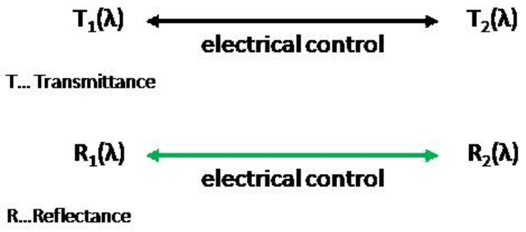


**Fig. 2.1. Illustration of the electrochromic effect: change in transmittance and/or reflectance in an electrochromic substance over electrical control**

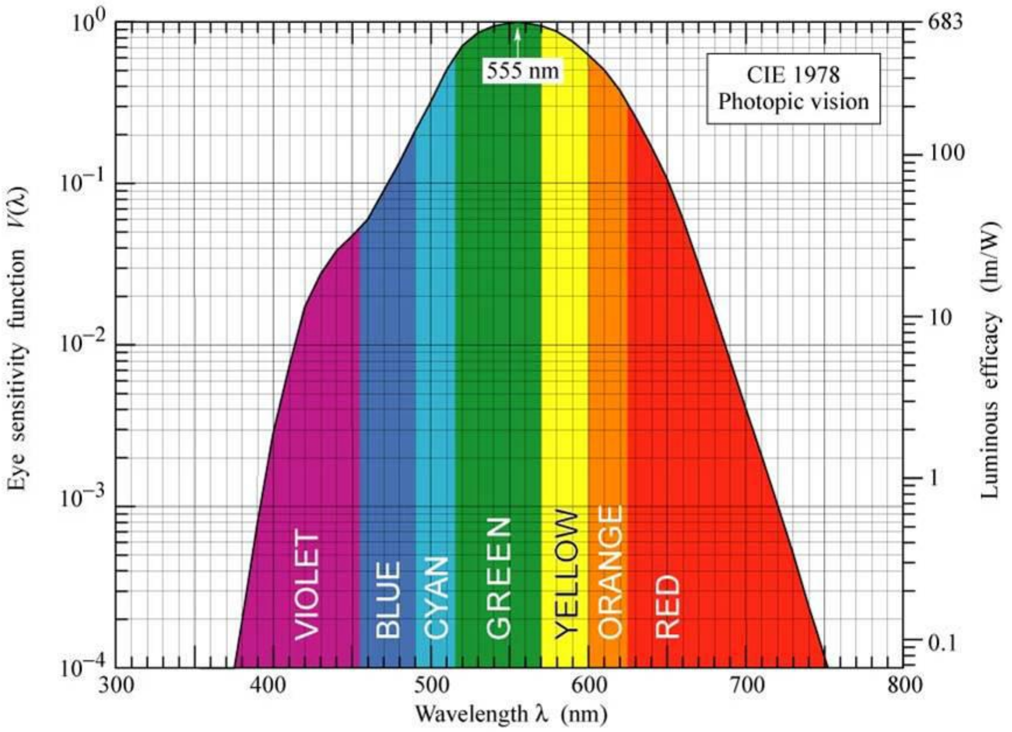


**Fig. 2.2. Eye sensitivity function, *V*(λ), (left ordinate) and luminous efficacy, measured in lumens per Watt of optical power (right ordinate). *V*(λ) is greatest at 555 nm. Also given is a polynomial approximation for *V*(λ) (after 1978 CIE data).**

The change in transmittance and in colour of an electrochromic substance is usually due to a “redox” process within the electrochromic substance [4].

For this “redox” process, with accompanied change of the transmittance and/or reflectance, only a small electric current at low DC potentials of the order of a fraction of volts to a few volts is required. When the colour has changed, then this new redox state persists in the so called “memory effect” with theoretically no further input of power. In reality small refreshing charges are necessary [5,6].

### 2.1.1. Electrical properties

Electrical properties can be divided into intrinsic properties and extrinsic or forced properties.

#### 2.1.1.1. Intrinsic properties

Every electrochromic substance has a characteristic band structure in its neutral state. The energy gap $E_g$ between its highest occupied molecular orbital (HOMO), known as valence band, and its lowest unoccupied molecular orbital (LUMO), known as conduction band, is responsible for the absorbance/transmittance. Therefore it determines the intrinsic optical properties and colour impression [7].

$$\boldsymbol{E_g = |E_{LUMO} - E_{HOMO}| = h \cdot \nu = \frac{h \cdot c}{\lambda}}$$

$\boldsymbol{E_g}$…energy (band) gap
$\boldsymbol{E_{LUMO}}$...energy level of the lowest unoccupied molecular orbital (LUMO)
$\boldsymbol{E_{HOMO}}$...energy level of the highest occupied molecular orbital (HOMO)
$\boldsymbol{h}$…plank constant ($h = 6{,}6260688 \cdot 10^{-34}\ Js$)
$\boldsymbol{\nu}$…frequency
$\boldsymbol{c}$...speed of light ($c = 2{,}99792458 \cdot 10^{8}\ m/s$)
$\boldsymbol{\lambda}$...wavelength

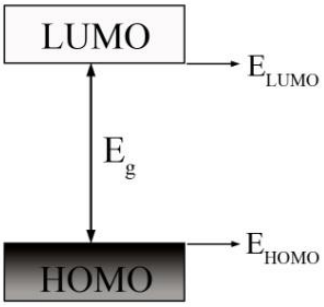


**Fig. 2.3. Illustration of a band gap transition between the valence band (VB) – HOMO and the conduction band (CB) – LUMO**

### 2.1.1.2. Extrinsic and forced properties (oxidation-reduction)

As mentioned before an electrochromic substance can change its transmittance at a given wavelength over electrical control and this happens due to the “redox” process within the electrochromic substance. Depending on applied voltage the electrochromic substance gets reduced or oxidised. Reduction describes the gain of electrons or a decrease in oxidation number and oxidation describes the loss of electrons or an increase in oxidation number. Figure 2.4 shows the three redox states of viologens (bipyridiliums).

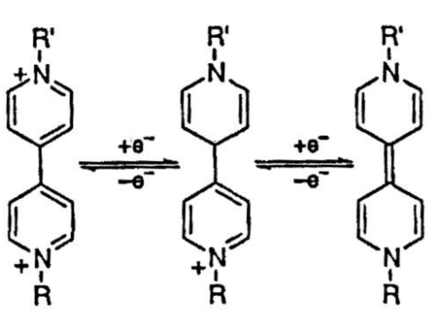


**Fig. 2.4. The three common redox states of viologens, showing the two successive electron transfer reactions (Mortimer, R. J.; Dyer, A. L.; Reynolds, J. R. Displays 27 (2006) 2)**

Oxidation or reduction of an electrochromic substance is usually accompanied by an inflow and outflow of counterions, which we will name “dopants” [4].

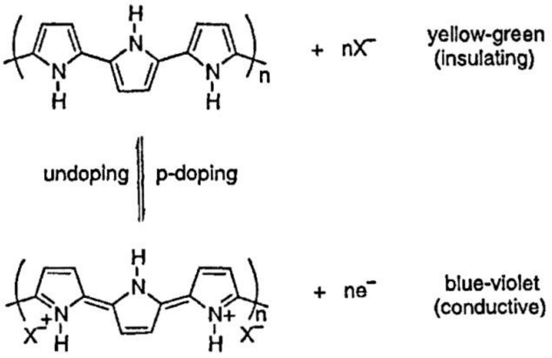


**Fig. 2.5. Electrochromism in polypyrrole thin films. The yellow-green (undoped) form undergoes reversible oxidation to the blue-violet (conductive) form, with insertion of charge-compensating anions ($X^-$) (Mortimer, R. J.; Dyer, A. L.; Reynolds, J. R. Displays 27 (2006) 2)**

Upon electrochemical “doping”, “p-doping” for oxidation and “n-doping” for reduction, the band structure of the neutral electrochromic substance is modified, generating lower energy intraband transitions [6]. Figure 2.6 shows the band structures and possible energetic transitions for an “undoped” state and the oxidised – p-doped – states of a conjugated polymer.

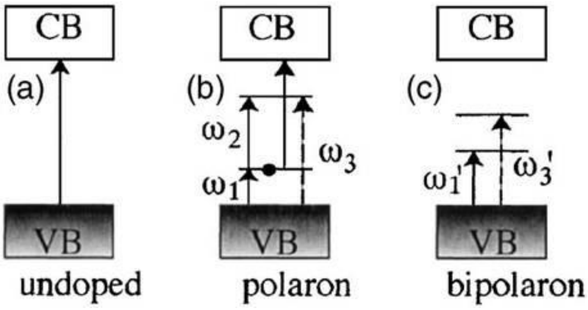


**Fig. 2.6. Band structures and energy transitions for an undoped state (a) and the oxidised – p-doped – states (b, c) of a conjugated polymer (VB…valence band; CB…conduction band) (Holt, A. L.; Leger, J. M.; Carter, S. A. J. Chem. Phys. 123 (2005) 044704)**

Initial oxidation – p-doping – generates polarons along the polymer chain. The polaron creates two energy levels inside the band gap and thus new transitions are possible. Upon complete electrochemical oxidation bipolarons are created, with localized energy states further from the band edges than the polaron states [6,8].

A polaron is a quasiparticle: It describes the appearance of a crystal electron and the deformation, which is produced from the crystal electron, in the crystal-lattice. If electrons are moving through a lattice, they will generate a polarisation in their neighbourhood because of their electrical charge. The neighbouring electrons will be forced aside and the atomic cores will be attracted. This polarisation cloude will be carried along with the electron. Electron hole-polarons (“hole-polarons”) were also found [9].
A bipolaron is a bound pair of two polarons.

### 2.1.1.2.1. Cyclovoltammetry

An important measurement method for investigation of electrochromic substances is cyclovoltammetry. By cyclovoltammetry voltage cycling accompanied by current measurement is done.

As already mentioned, oxidation or reduction of an electrochromic substance is usually accompanied by an inflow and outflow of counterions. So there is an ion transport within the electrochromic cell, and this "slow" process is responsible for the characteristic appearance of cyclovoltammograms from electrochromic substances. The current contains an ionic component and an electronic component.

Figure 2.7 shows an example for a measurement result of cyclvoltammetry.

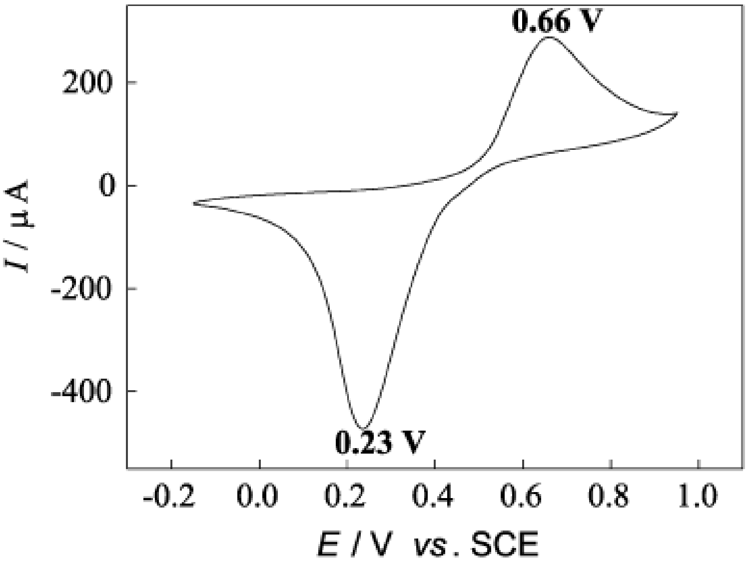


**Fig. 2.7. Cyclic voltammogram of the carbon paste electrode modified with *N,N*-ethylene*bis*(salicylideneiminato)-oxovanadium(IV) complex in 0.10 mol $L^{-1}$ KCl solution, at a potential scan rate of 25 mV $s^{-1}$ between -0.15 and 0.95 V *vs.* SCE. (Teixeira, M. F. S.; Cavalheiro, E. T. G.; J. Braz. Chem. Soc. 15 (2004) 803)**

By following the curve shape clockwise, starting at 0 V, a very small increase of the current can be recognised until ~0,45 V are reached, and then a steep increase follows. This steep increase indicates the start of the oxidation of the electrochromic substance and the start of the ion transport. At 0,66 V the maximal current is reached and with increasing voltage the current decreases. This is a sign that nearly the whole electrochromic substance is oxidised. Following the curve further it can be seen that on the way back at about 0,425 V a steep decrease of the current starts. This decrease indicates the start of the reduction of the electrochromic substance and again the start of the ion transport in opposite direction. When the whole electrochromic substance is reduced the current approaches 0 µA again. Going on the curve leads back to the starting point (0 V).

The flow of the ions is responsible for the curve shape of the cyclovoltammogram. If the curve is closed the reversibility of the process is proofed.

### 2.1.2. Optical properties

Every electrochromic substance has in its neutral and oxidised and reduced state characteristic transmission spectra and reflection spectra. The spectra of the neutral state result from electron transitions between the valence band (HOMO) and the conduction band (LUMO). As mentioned before upon electrochemical doping (oxidation or reduction), the band structure of the neutral electrochromic substance is modified, generating lower energy intraband transitions which result in new transmission and reflection spectra.
Figure 2.8 shows absorbance spectra of PProDOT-$Et_2$ at different applied potentials.

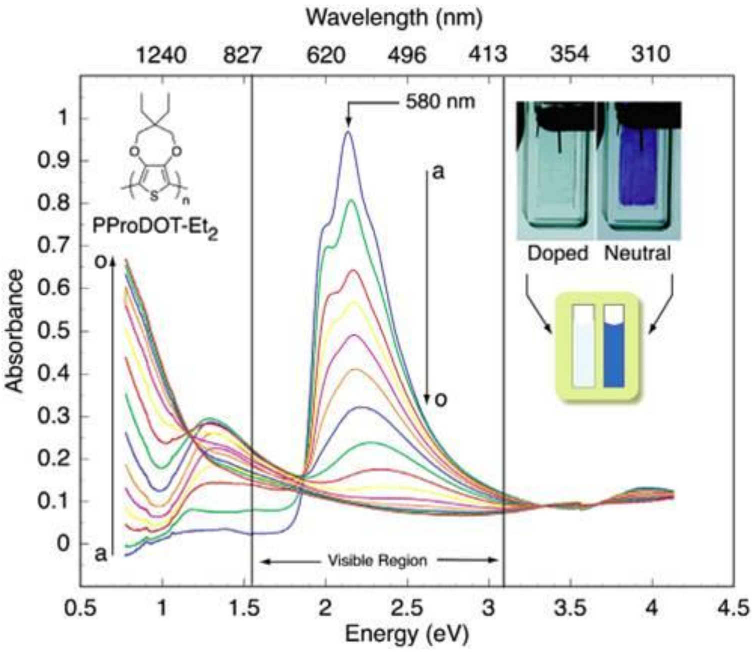


**Fig. 2.8. Spectroelectrochemistry of a PProDOT-$Et_2$ film on ITO/glass at applied potentials between (a) -0.1 V and (o) +0.9 V vs Ag/$Ag^+$ with 50 mV increments. The inset shows photographs of the polymer film in its doped and neutral states. Below the photographs are shown the CIE 1931 Yxy color swatches of the corresponding states measured by in situ colorimetry. (Argun, A. A.; Aubert, P. H.; Reynolds, J. R. Chem. Mat. 16 (2004) 4401)**

The diagram offers a peak in the visible region for the neutral state. Initial oxidation – p-doping – results in a new peak in the near infrared at the cost of the peak in the visible region. This absorption peak in the near infrared is attributed to polarons. Upon complete electrochemical oxidation bipolarons are created and this results in a peak in the near-IR beyond the range of the spectrophotometer. The absorption peak in the visible region disappears [6,10].

So the absorption peak shifts to lower energy parts of the spectrum during oxidation – p-doping. If the electrochromic substance has in its neutral – undoped – state a band gap $E_g$ greater than 3 eV (~400 nm), it is colourless and transparent in the undoped form, and it is coloured in the doped form, since the absorption peak shifts from the UV-sector to the visible region. An energy gap $E_g$ equal to or less than 1,5 eV (~800 nm) leads to absorption in the visible region and therefore the electrochromic substance is coloured in its neutral form and gets bleached and colourless during oxidation – p-doping, as the absorption peak is transferred to the near infrared. Electrochromic substances with intermediate energy band gaps (1,5 eV < $E_g$ < 3 eV) possess a coloured undoped state and a distinct coloured p-doped state [7].

For example PProDOT-$Et_2$, the electrochromic substance represented in figure 2.8, is blue-coloured in its neutral state and transparent (“bleached”) in its totally oxidised (p-doped) state. Besides the electrochromic substances, which change between a coloured and a bleached state, there are also examples, which change between two coloured states and lack a transparent state. Polyelectrochromic or multicolour-electrochromic substances possess more than two redox states and therefore exhibit more than two colours [5,6].

### 2.2. Electrochromic systems

There are different systems of electrochromic substances: First the organic systems, where it can be distinguished between conjugated molecules, conjugated oligomers and conjugated polymers. Second the inorganic systems, especially metal oxides.

Furthermore there are the intermediate systems (hydrocarbon metal complexes – e.g. phthalocyanines), and the hybrid systems, which will not be explained closer here.

### 2.2.1. Organic systems

Organic chemistry is defined as the chemistry of hydrocarbons and their derivatives [11].

Examples for electrochromic conjugated molecules are bipyridiliums (viologens), carbazoles, quinones. Representatives of electrochromic conjugated oligomers are several oligothiophenes. Derivatives of poly(thiophene) (PTh), poly(pyrrole) (PPy) and poly(aniline) (PANI) are widely used as electrochromic conjugated polymers [6,12].

### 2.2.1.1. Electrochromic (conjugated) polymers

All conjugated polymers can be electrochemical oxidised and/or reduced. This redox process is accompanied by a change of the transmission spectra and therefore all conjugated polymers are electrochromic.

A huge number of conjugated polymers are available, and by changing the side chains the properties can be modified. So there are many options to create conjugated polymers with different electrochromic behaviour.

Most conjugated polymers have specific colours in their neutral states. Figure 2.9 shows structural formulas of conjugated polymers and below the formulas the colours of the conjugated polymers in their neutral states and next to that the colours of the reduced (n-doped) states and/or the colours of the oxidised (p-doped) states. In some cases an intermediate colour lies between the neutral and oxidised (p-doped) state, and few polymers have p-doped and n-doped states. There is a wide range of colours available.

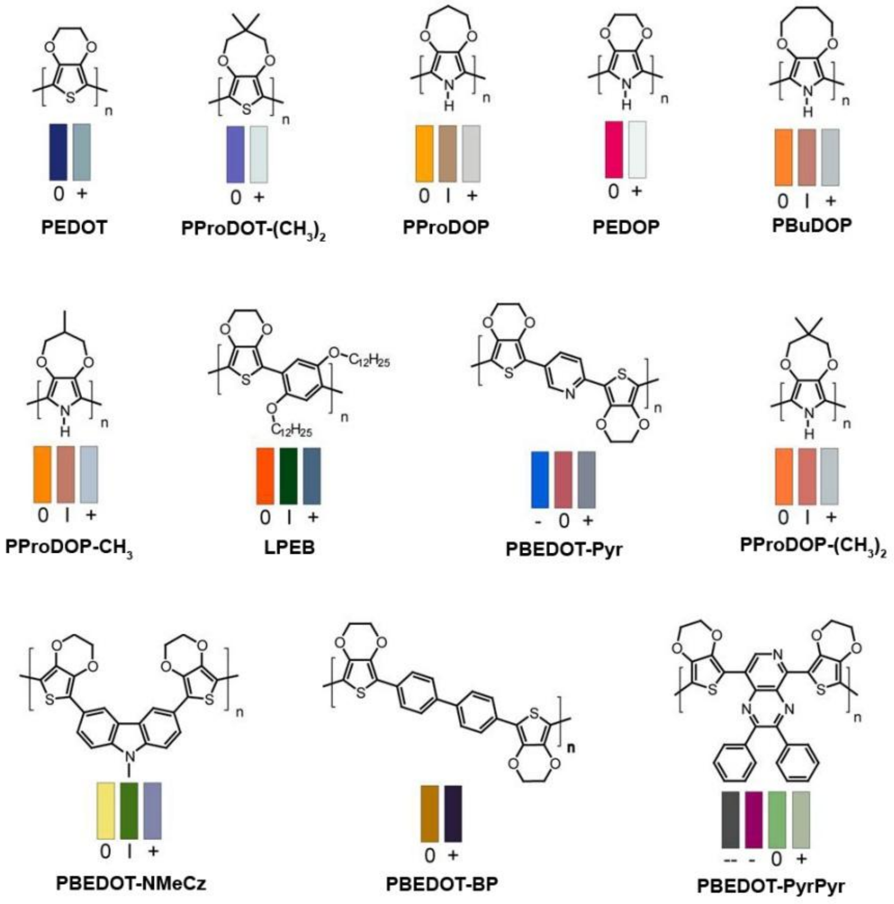


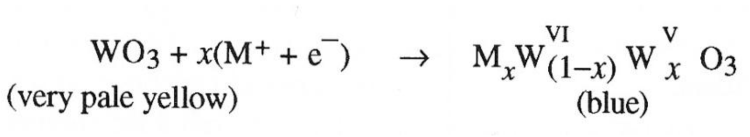
**Fig. 2.9. Structural formulas and colours of conjugated polymers in their neutral (0), oxidized (p-doped) (+), reduced (n-doped) (-, --) and intermediate (I) state (adapted from: Argun, A. A.; Aubert, P. H.; Reynolds, J. R. Chem. Mater. 16 (2004) 4401. Thompson, B. C.; Schottland, P.; Zong, K.; Reynolds, J. R. Chem. Mater. 12 (2000) 1563.)**

### 2.2.1.2. Applications

Organic electrochromic substances are used in electrochromic displays.
Another application of organic electrochromic substances are electrochromic sunglasses.

### 2.2.2. Inorganic systems

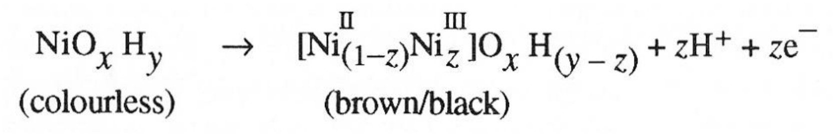
The most well known example for an inorganic electrochromic substance is tungsten trioxide. The “redox” reaction is shown in figure 2.10. Tungsten trioxide is very pale yellow in its neutral state and the oxidation number is six. By the inflow of electrons and metal- or hydrogen cations the tungsten gets reduced. The oxidation number of several tungsten atoms is now five. The reduced state is blue [12].
Tungsten trioxide is a cathodically colouring substance since it forms colour when it is reduced at a cathode [12].



$$\underset{\text{(very pale yellow)}}{WO_3 + x(M^+ + e^-)} \rightarrow \underset{\text{(blue)}}{M_x\overset{\text{VI}}{W}_{(1-x)}\overset{\text{V}}{W}_x O_3}$$

**Fig. 2.10. “Redox” reaction of tungsten trioxide $WO_3$; x…fractional insertion coefficient, M…Metal (usually lithium) or hydrogen (“Electrochromism – Fundamentals and Applications” by P. M. S. Monk; R. J. Mortimer; D. R. Rosseinsky, VCH, Weinheim, 1995)**

An example for an inorganic anodically colouring substance, which forms colour when it is oxidised at an anode, is nickel oxide. Nickel oxide is colourless in its neutral state and gets brown/black after oxidation. The “redox” reaction is shown in figure 2.11 [12].



$$\underset{\text{(colourless)}}{NiO_x H_y} \rightarrow \underset{\text{(brown/black)}}{[\overset{\text{II}}{Ni}_{(1-z)}\overset{\text{III}}{Ni}_z]O_x H_{(y-z)}} + zH^+ + ze^-$$

**Fig. 2.11. “Redox” reaction of nickel oxide; x,y,z…fractional insertion coefficient (“Electrochromism – Fundamentals and Applications” by P. M. S. Monk; R. J. Mortimer; D. R. Rosseinsky, VCH, Weinheim, 1995)**

There are many other metal oxides with electrochromic properties available: cobalt oxide, iridium oxide, molybdenum trioxide, etc [12].

Another example for an inorganic electrochromic substance apart from metal oxides is prussian blue (PB, ferric ferrocyanide or iron(III)hexacyanoferrate(II)) [5,12].

### 2.2.2.1. Applications

High volume applications of inorganic systems are auto-dimming rearview mirrors.

Inorganic electrochromic substances are used in smart windows.

# 3. *Electrochromic Devices (ECD)*

There are two different types of electrochromic devices: Reflective ECDs and transmittive ECDs. Figure 3.1 shows the basic operating principle for a reflective electrochromic device (a) and for a transmittive electrochromic device (b).

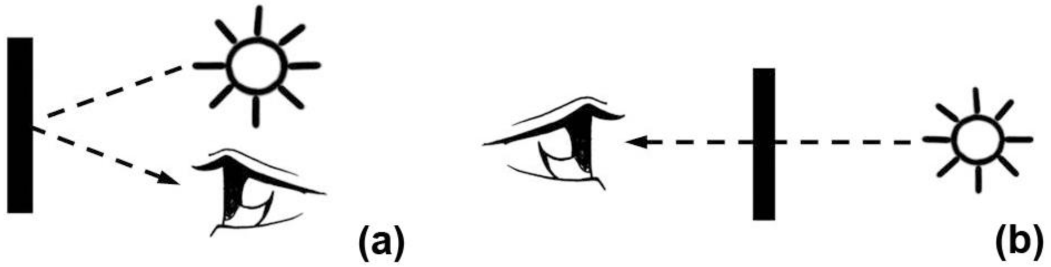


**Fig. 3.1. Basic operating principle for a reflective ECD (a) and for a transmittive ECD (b)**

Both electrochromic device types consist of two electrodes, an ionically conductive electrolyte as well as an electrochromic layer.

Figure 3.2 presents a scheme of the simplest form of an (electrochemical) electrochromic setup.

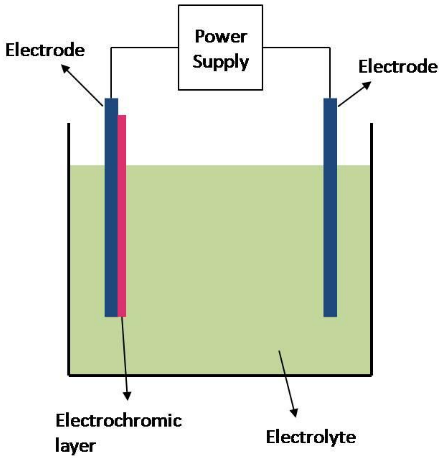


**Fig. 3.2. Scheme of an electrochromic setup**

There is a beaker with electrolyte and two electrodes, which are immersed in the electrolyte. The two electrodes are connected to a power supply. One electrode is coated with an electrochromic layer. Depending on the applied voltage the electrochromic substance gets reduced or oxidised. Therefore the transmission and reflection spectra change.

Electrochromic devices, transmittive or reflective respectively, are usually fabricated in a sandwich form, where the electrolyte (gel or solid) is enclosed between the two electrodes. Often both electrodes are coated with electrochromic layers. Two electrochromic layers offer more options to intensify or to vary the colour effect of the electrochromic device or to improve the functionality.

In the next subchapters schematic diagrams of a transmittive and a reflective ECD are shown and described.

## 3.1. Transmittive ECD

In figure 3.3 a schematic diagram of a transmittive electrochromic device is shown.

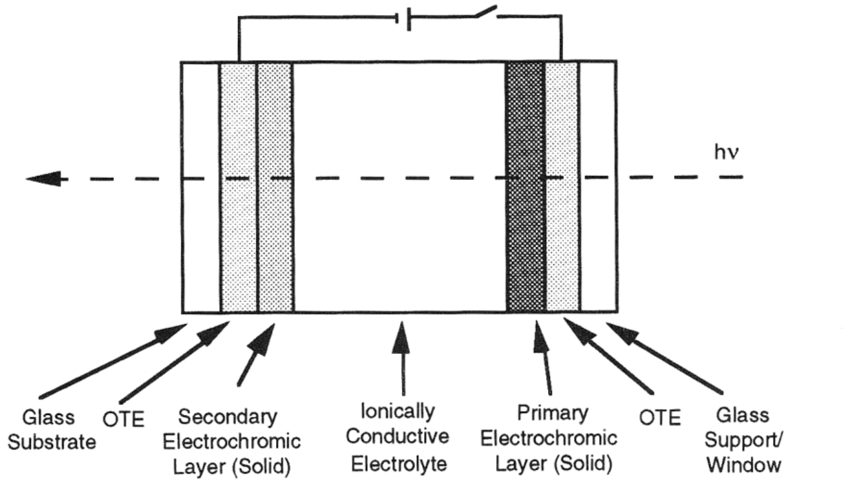


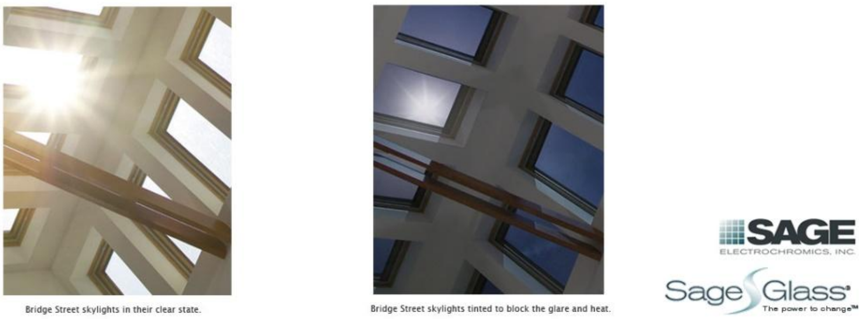
**Fig. 3.3. Schematic diagram of a transmittive ECD ("Electrochromism – Fundamentals and Applications" by P. M. S. Monk; R. J. Mortimer; D. R. Rosseinsky, VCH, Weinheim, 1995)**

For transmittive electrochromic devices optically transparent electrodes (OTE), for example indium tin oxide (ITO), on transparent supports, for example glass slides, are used. The light beam enters the electrochromic device at one side and first passes a transparent support and an optically transparent electrode. Then it goes through an electrochromic layer, passes an ionically conductive electrolyte and arrives at the next electrochromic layer. Before the beam of light comes out of the electrochromic device it again crosses an optically transparent electrode (OTE) and a transparent support.

As mentioned before two electrochromic layers improve the operational sequence.

### 3.1.1. Examples and applications

Applications of transmittive electrochromic devices are electrochromic windows. Figure 3.4 shows elctrochromic windows from SAGE: left in their clear state and right in their tinted state to block the glare and the heat.


Bridge Street skylights in their clear state.

Bridge Street skylights tinted to block the glare and heat.

**Fig. 3.4. Electrochromic windows from SAGE in their clear state (left) and in their tinted state (right)**

Electrochromic sunglasses are another example for transmittive electrochromic devices. In figure 3.5 electrochromic sunglasses from ASHWIN in different electrochromic states are shown.

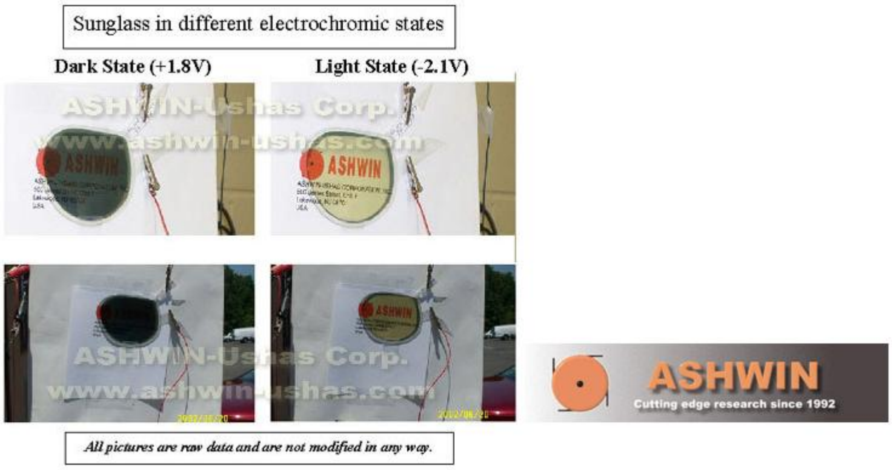


**Fig. 3.5. Electrochromic sunglasses from ASHWIN in different electrochromic states**

### 3.2. Reflective ECD

A schematic diagram of a reflective electrochromic device is shown in figure 3.6.

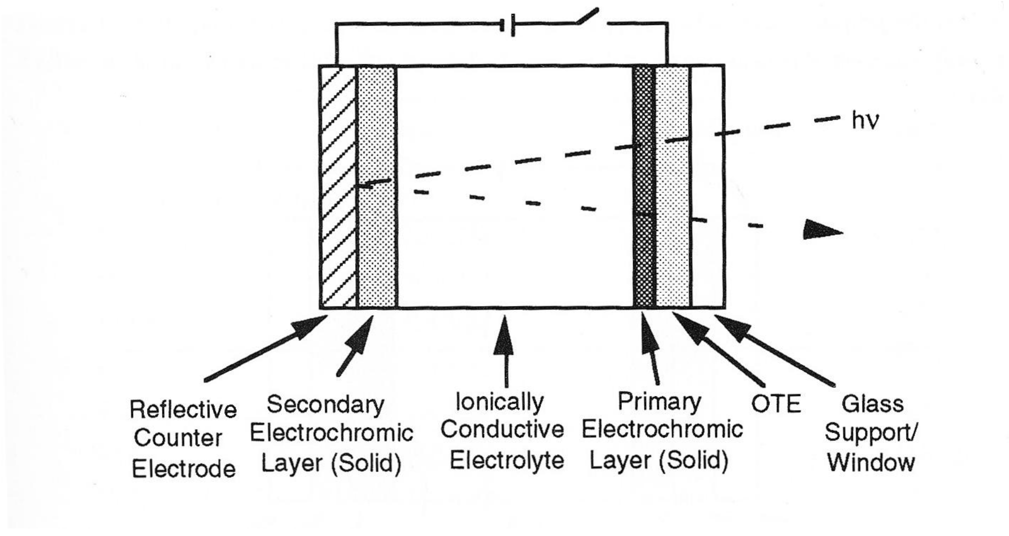


**Fig. 3.6. Schematic diagram of a reflective ECD ("Electrochromism – Fundamentals and Applications" by P. M. S. Monk; R. J. Mortimer; D. R. Rosseinsky, VCH, Weinheim, 1995)**

The beam of light first passes a transparent support, for example a glass window, and an optically transparent electrode (OTE), for example indium tin oxide (ITO). Then there is the primary electrochromic layer. Next, the light beam goes through the ionically conductive electrolyte and the secondary electrochromic layer. At the surface of the reflective counter electrode the light beam is reflected and crosses all layers in opposite direction.

As mentioned before two electrochromic layers improve the operational sequence.

### 3.2.1. Examples and applications

High volume applications of reflective electrochromic devices are auto-dimming rearview mirrors. For the construction of auto-dimming-rearview mirrors inorganic electrochromic systems are used. Figure 3.7 shows an auto-dimming rearview mirror from GENTEX.

**Fig. 3.7. Auto-dimming rearview mirror from GENTEX**

Another example for an application of reflective electrochromic devices are reflective electrochromic displays. Figure 3.8 shows a flexible reflective electrochromic display from Siemens.

**Fig. 3.8. Flexible reflective electrochromic display from SIEMENS**

# 4. Laboratory samples of electrochromic devices

Two laboratory samples of transmittive electrochromic devices and two laboratory samples of reflective elechtrochromic devices were provided by Ciba (now part of BASF). Furthermore the essential components of the electrochromic devices were received, again provided by Ciba.

## 4.1. Transmittive ECD

One transmittive ECD arrived at austriamicrosystems on the 29.7.2009. So it was termed: “Transmittive Device (29.7.2009)” (figure 4.1)

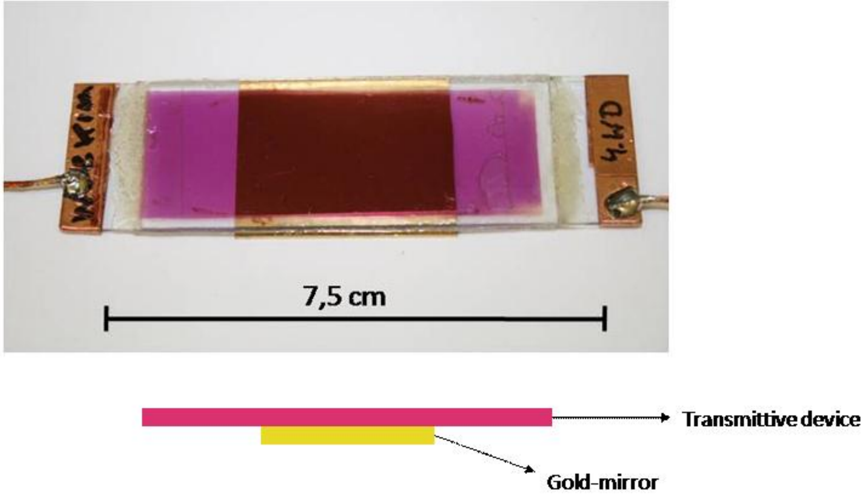


**Fig. 4.1. “Transmittive Device (29.7.2009)” with a gold mirror as background and with white paper as background**

The second transmittive ECD arrived at austriamicrosystems on the 5.8.2009. So it was termed: “Transmittive Device (5.8.2009)” (figure 4.2)

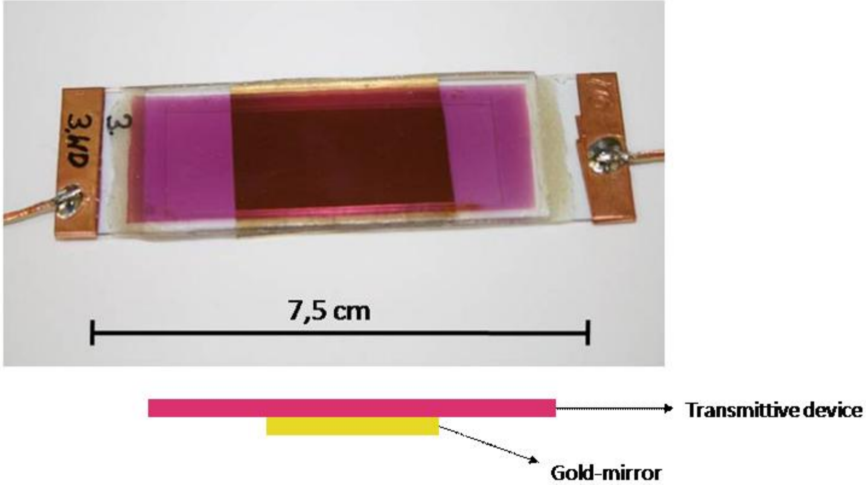


**Fig. 4.2. “Transmittive Device (5.8.2009)” with a gold mirror as background and with white paper as background**

The structure of these transmittive devices is shown in figure 4.3.

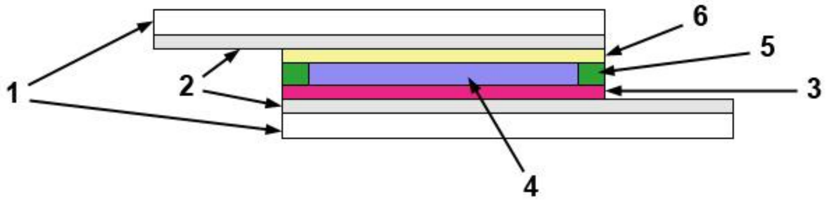


**Fig. 4.3. Schematic longitudinal section of the transmittive ECDs from Ciba (now part of BASF): 1…Glass slide; 2 ITO (indium tin oxide) layer; 3…Cathodically colouring polymer; 4…Gel electrolyte; 5…Polyester spacer; 6…Non colouring polymer**

The gel electrolyte is composed of “propylene carbonate” and “poly methyl methacrylate” and “ionic liquid – 1-butyl-3-methylimidazolium trifluoromethanesulfonate”.

In the following subchapters the essential components of the transmittive electrochromic devices, gratefully provided by Ciba (now part of BASF), are presented.

### 4.1.1. ITO coated glass slides

Figure 4.4 shows the packed ITO coated glass slides and a single one (length: 76 mm, width: 26 mm). The thickness of the ITO coated glass slides was measured with a micrometer (digitrix II, 0-25 mm, 0,001 mm): 1,096 mm. It is allowed to equal it with the thickness of the glass slides, since the order of magnitude of the ITO layer thickness is nanometre. The resistance of the ITO layer was measured for 1 cm measuring distance (ohmmeter: FLUKE 12 Multimeter): $R_{ITO} = 28\ \Omega$

**Fig. 4.4. ITO coated glass slides (thickness: 1,096 mm; $R_{ITO} = 28\ \Omega$) packed (left) and a single one unpacked (right)**

### 4.1.2. Magenta polymer (cathodically colouring polymer)

Figure 4.5 shows the magenta polymer in a small bottle with screw cap, as received from Ciba. The magenta polymer was weighed with an automatic weighing-machine: 0,2167 g

**Fig. 4.5. Magenta Polymer (0,2167 g)**

### 4.1.3. Clear polymer (non colouring polymer)

The clear polymer in a small bottle with screw cap is shown in figure 4.6. The clear polymer was weighed with an automatic weighing-machine: 0,1923 g

**Fig. 4.6. Clear Polymer (0,1923 g)**

### 4.1.4. Gel electrolyte

Figure 4.7 shows Poly Methyl Methacrylate (PMMA) in a bottle with screw cap. PMMA was provided by Ciba for the production of the gel electrolyte.

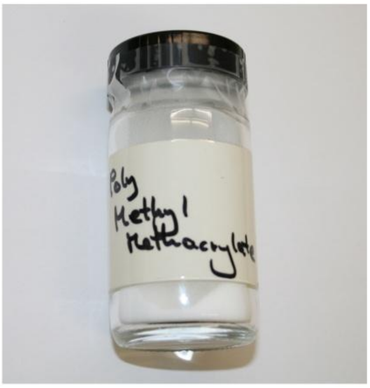


**Fig. 4.7. Poly Methyl Methacrylate (PMMA)**

### 4.1.5. Clear polyester panels (polyester spacer)

Figure 4.8 shows the packed polyester panels for the production of the polyester spacer.
The thickness of a polyester panel was measured at five different measuring points with a micrometer (digitrix II, 0-25 mm, 0,001 mm). The average thickness was (166 ± 2) µm.
In addition the thickness of six further polyester panels was measured, each at one measuring point close to a corner, with the same micrometer (digitrix II, 0-25 mm, 0,001 mm). Average thickness of all measured panels: (166 ± 5) µm

**Fig. 4.8. Packed polyester panels (thickness: (166 ± 5) µm)**

### 4.1.6. Cu tape

A coil of Cu tape, which is used for the contacting of the transmittive devices, is shown in figure 4.9.

**Fig. 4.9. Coil of Cu tape**

## 4.2. Reflective ECD

Both laboratory samples of reflective electrochromic devices arrived at austriamicrosystems on the 13.7.2009. They were termed: “Reflective Device (13.7.2009 – Nr.1)” (figure 4.10 / left) and “Reflective Device (13.7.2009 – Nr.2)” (figure 4.10 / right).

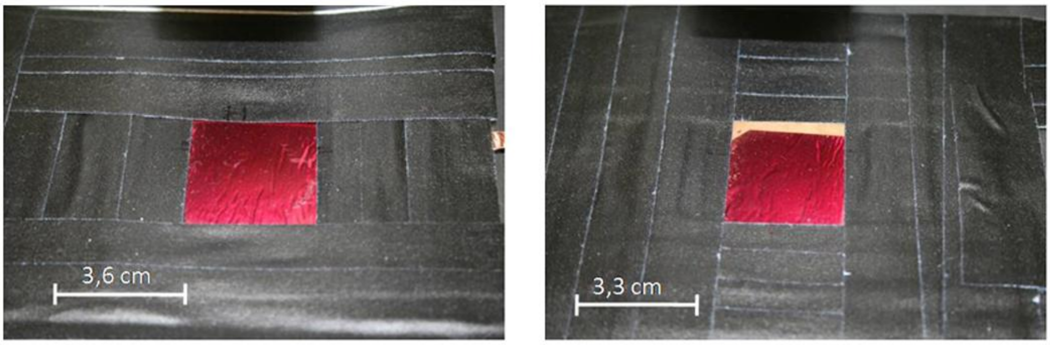


**Fig. 4.10. “Reflective Device (13.7.2009 – Nr.1)” (left) and “Reflective Device (13.7.2009 – Nr.2)” (right)**

The structure of these reflective devices is shown in figure 4.11.

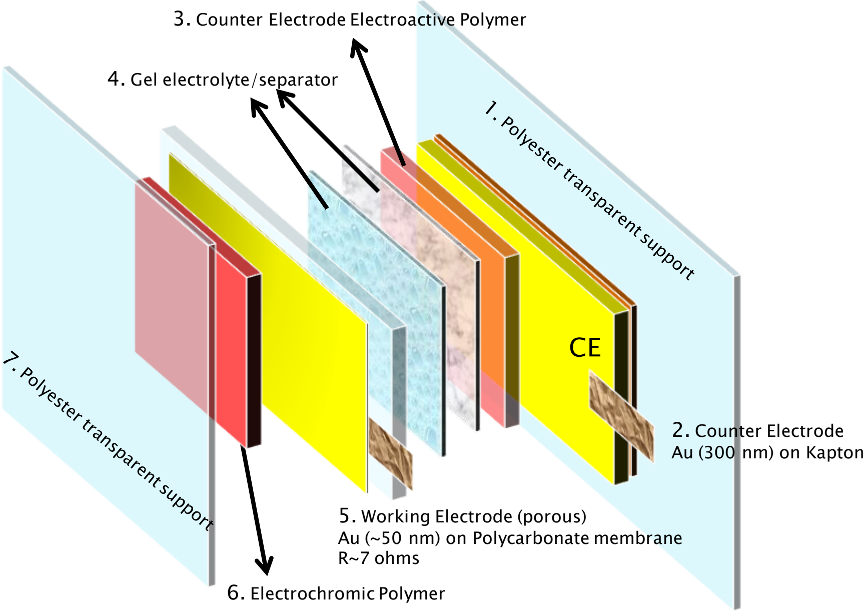


**Fig. 4.11. Schematic structure of the reflective ECDs from Ciba (now part of BASF) (Graphic by Ece Unur)**

The gel electrolyte is composed of “propylene carbonate”, “ethylene carbonate”, “poly methyl methacrylate”, “tetrabutylammonium tetrafluoroborate”.

In the following subchapters the essential components of the reflective electrochromic devices, gratefully provided by Ciba (now part of BASF), are presented.

### 4.2.1. Polyester transparent support

Figure 4.8 shows the packed polyester panels, which are used for the transparent support of the reflective electrochromic devices.

### 4.2.2. Au (300 nm) on kapton (counter electrode)

As counter electrode a piece of Au coated kapton is used. On top of the Au layer there is the polymer layer.
Ciba sent two pieces of Au coated kapton with magenta polymer layer on top of the Au layer. A piece of Cu tape is attached for the connecting. (Figure 4.12)

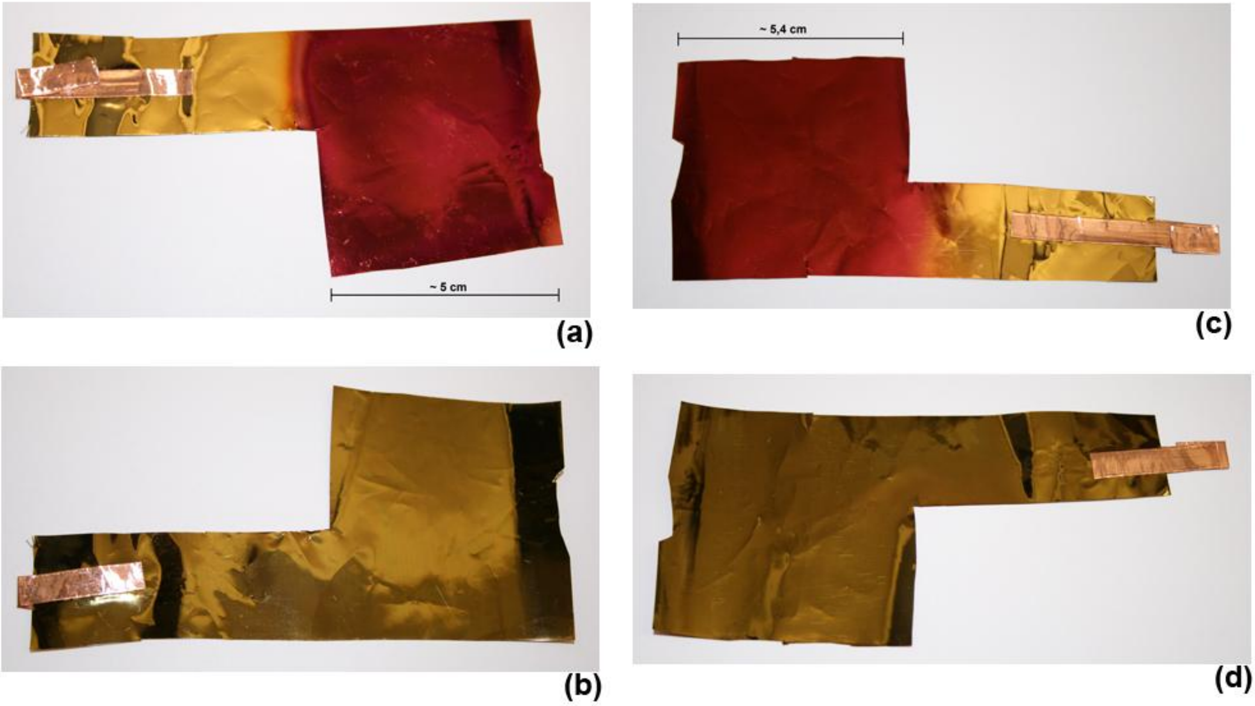


**Fig. 4.12. Two pieces of Au coated kapton with magenta polymer layer: 1.piece (a, b): magenta polymer layer on top (a), kapton layer on top (b); 2.piece (c, d): magenta polymer layer on top (c), kapton layer on top (d)**

### 4.2.3. Counter electrode electroactive polymer (magenta polymer)

Figure 4.5 shows the magenta polymer in a small bottle with screw cap, as received from Ciba. The magenta polymer was weighed with an automatic weighing-machine: 0,2167 g

### 4.2.4. Gel electrolyte / separator

Figure 4.7 shows Poly Methyl Methacrylate (poly MMA) in a bottle with screw cap. Poly MMA was provided by Ciba, for the production of the gel electrolyte.
As separator two pieces of coffee filters are used.

### 4.2.5. Au (~50 nm) on polycarbonate membrane (working electrode)

As working electrode a piece of Au coated polycarbonate membrane is used. On top of the Au layer there is the polymer layer.

Ciba sent two pieces of Au coated polycarbonate membrane with magenta polymer on top of the Au layer. A piece of Cu tape is attached for the connecting. (Figure 4.13)

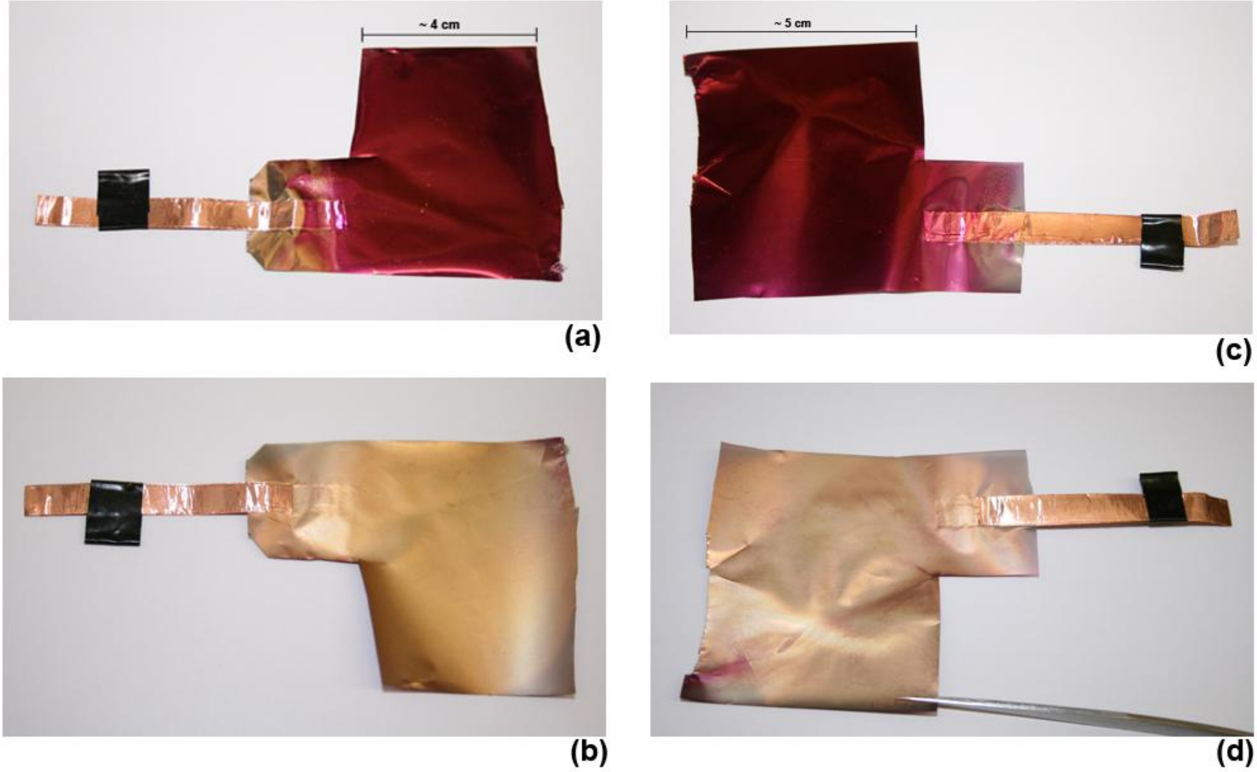


**Fig. 4.13. Two pieces of Au coated polycarbonate membrane with magenta polymer layer: 1.piece (a, b): magenta polymer layer on top (a), polycarbonate membrane layer on top (b); 2.piece (c, d): magenta polymer layer on top (c), polycarbonate membrane layer on top (d)**

From the Au coated polycarbonate membrane two small triangles were cut off and then attached to a SEM-holder with conductive silver. Figure 4.14 shows the SEM-holder with the two fixed triangles. The triangle on the left side is fixed with the Au layer on top, and the triangle on the right side is fixed with the polycarbonate membrane on top.

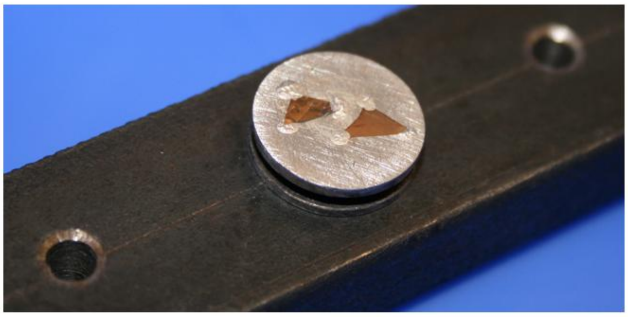


**Fig. 4.14. Two triangles of Au coated polycarbonate membrane fixed on a SEM-holder with conductive silver: Triangle on the left side – Au layer on top; triangle on the right side – polycarbonate layer on top**

These triangles have been investigated first with an optical microscope (Olympus BX51) (figure 4.15) and second with a scanning electron microscope SEM (FEI Quanta 200) (figure 4.16).

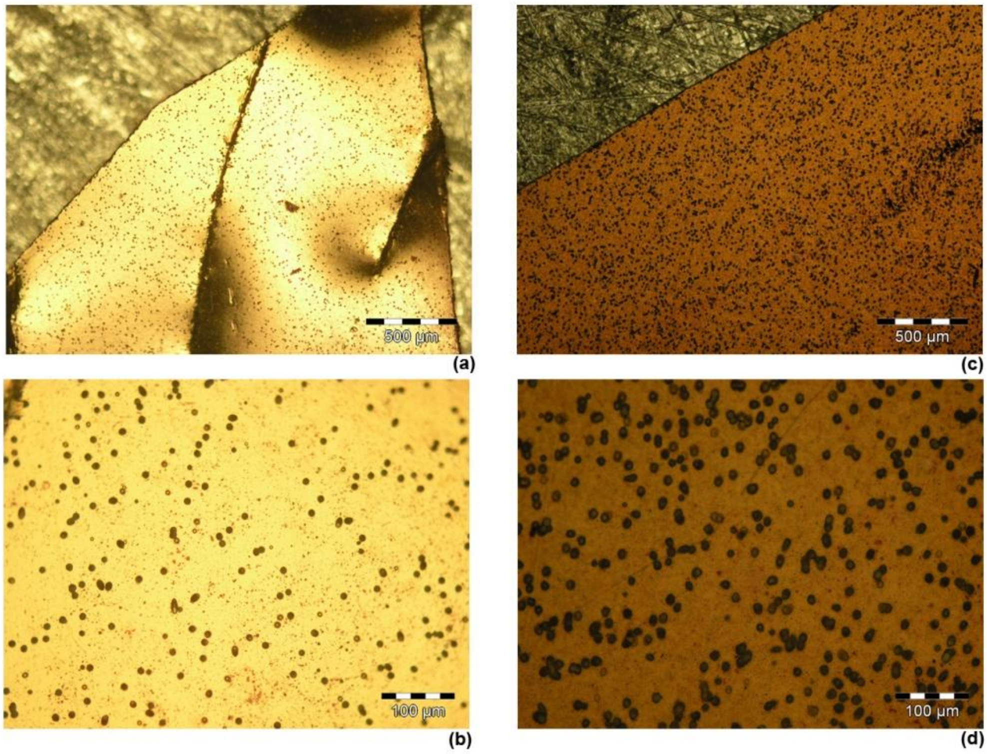


**Fig. 4.15. Au coated polycarbonate membrane investigated with an optical microscope (Olympus BX51): Au layer on top (a, b); polycarbonate membrane layer on top (c, d)**

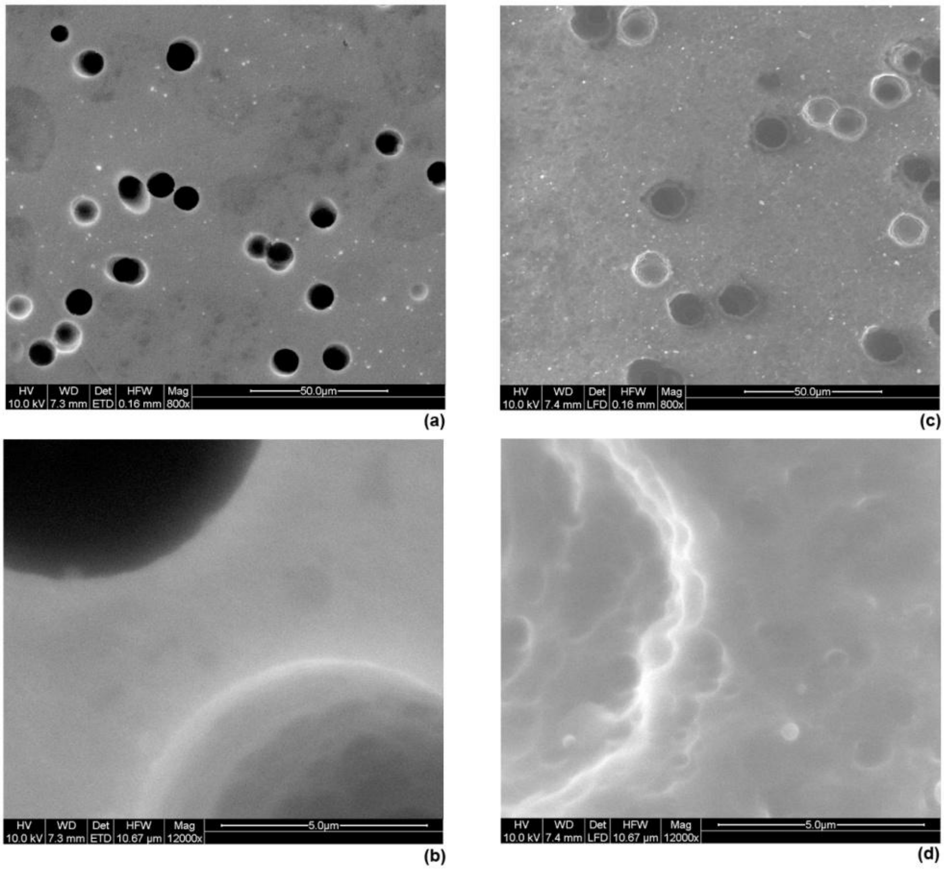


**Fig. 4.16. Au coated polycarbonate membrane investigated with a SEM (FEI Quanta 200): Au layer on top (a, b); polycarbonate membrane layer on top (c, d)**

### 4.2.6. Electrochromic polymer (magenta polymer)

Figure 4.5 shows the magenta polymer in a small bottle with screw cap, as received from Ciba. The magenta polymer was weighed with an automatic weighing-machine: 0,2167 g

### 4.2.7. Cu tape

Cu tape is used for the contacting of the counter electrode and the working electrode of reflective electrochromic devices. Figure 4.9 shows a coil of Cu tape, gratefully provided by Ciba.

# 5. Experimental part

There are different ways for investigation of ECDs. In the following subchapters different measurement methods are described and measurement results are presented.

The two reflective electrochromic devices (“Reflective Device (13.7.2009 – Nr.1)” and “Reflective Device (13.7.2009 – Nr.2)” – see chapter 4.2) and the two transmittive electrochromic devices (“Transmittive Device (29.7.2009)” and “Transmittive Device (5.8.2009)” – see chapter 4.1) from Ciba (now part of BASF) have been investigated.
Magenta polymer is a cathodically colouring substance since it forms colour when it is reduced at a cathode (see chapter 2.2.2).
In most of the following experiments the magenta polymer coated electrode of the transmittive devices and the working electrode of reflective devices respectively were connected to the minus output of the voltage source. So the ECDs got coloured, whenever the voltage source displayed a positive voltage, and bleached, whenever the voltage source displayed a negative voltage. If they were connected to the plus output of the voltage source, the ECDs got bleached, whenever the voltage source displayed a positive voltage, and coloured, whenever the voltage source displayed a negative voltage.

## 5.1. Cyclovoltammograms (Cyclovoltammetry)

Cyclovoltammetry is an important measurement method for investigation of electrochromic substances. The process of voltage cycling accompanied by current measurement is described in detail in chapter 2.1.1.2.1.
During cyclovoltammetry investigations of the optical properties of the electrochromic devices were done. On the one hand photos were made, on the other hand reflection spectra were measured, both at different voltage values.

### 5.1.1. Setup for measurements

The setup is composed of an electrical assembly and a setup for optical measurements.

#### 5.1.1.1. Circuit diagram

Figure 5.1 shows a schematic circuit diagram for cyclovoltammetry. The electrochromic device is connected to the source measure unit (Keithley 236 source measure unit). The source measure unit does voltage cycling and current measurement. A photo of the source measure unit is shown in figure 5.1.

**Fig. 5.1. Schematic circuit diagram for cyclovoltammetry (a); KEITHLEY 236 source measure unit (b)**

The source measure unit is connected to a computer in order to control the run of the cyclovoltammetry by an installed program (“UI_measure_vers4”, created with LabVIEW).
In our case the cyclovoltammograms started at 0 V. At first the voltage was increased (or decreased) until a selectable “high level” was reached. Then the voltage was decreased (or increased) until a chosen “low level”. On its way back the voltage went through 0 V. From the “low level” the voltage was increased (or decreased) again until the starting point (0 V) was reached to finish one cycle.
In addition to the “high level” and “low level” also the “step size” and the “delay time” had to be set. The voltage didn´t change continuously but stepwise. The “step size” set the voltage size of the steps. The “delay time” is the period of time of each voltage step. Last but not least the number of the cycles (“loops”) had to be set.

### 5.1.1.2. Setup for optical measurements

During cyclovoltammetry optical investigations with a CCD spectrometer and visual investigations with a camera were made. The two setups are described in the following subchapters.

#### 5.1.1.2.1. Investigation with a CCD spectrometer

Figure 5.2 shows a photo of the setup for optical measurements. The construction in the centre, which was termed “Reflectometer”, is composed of a base plate, a z-shifter and a 20 degree-reflection-base plate.
Organic electrochromic devices were placed on the base plate. A gold mirror served as background for the transmittive devices. With the z-shifter it is possible to change the distance between the base plate and the 20 degree-reflection-base plate to adjust the device in reflection position (figure 5.2).
The 20 degree-reflection-base plate has two drilled holes, where a mini lamp with lens and a focusing lens are attached. As light source-supply a constant current source (Voltcraft 4005; set to 0,400 A) is used. The light beam from the mini lamp is reflected at the electrochromic device and goes through the focusing lens and the optical fiber to a S1000 CCD spectrometer, where the reflected intensity at each wavelength is measured.

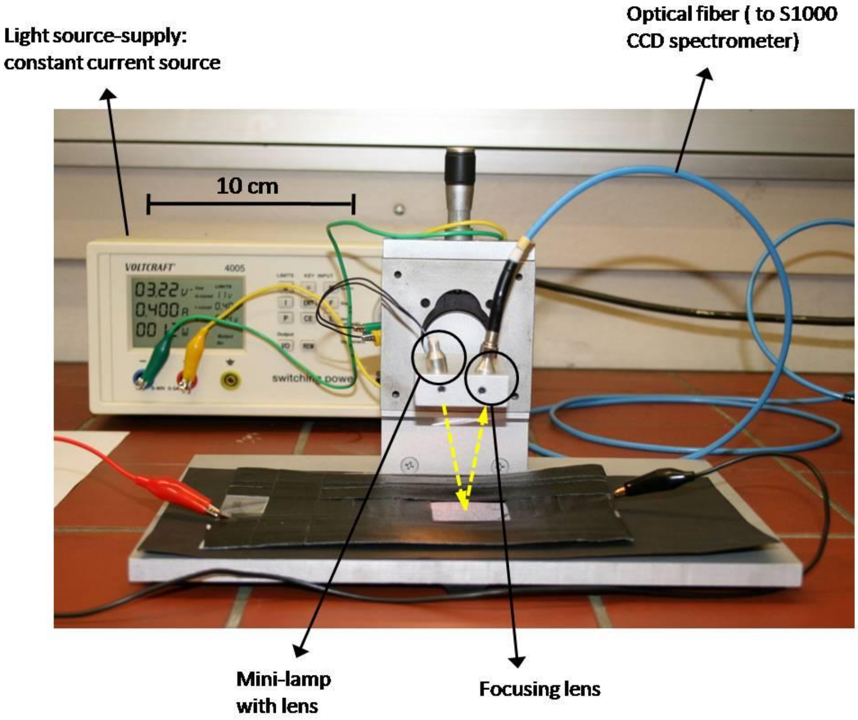


**Fig. 5.2. Setup for investigation with a CCD spectrometer during cyclovoltammetry**

### 5.1.1.2.2. Investigation with a camera

A photo of the setup for visual investigation with a camera is shown in figure 5.3. The reflective electrochromic device lies in such a way on the base plate of the “Reflectometer”, that no shadow of the 20 degree-reflection-base plate is visible on the photos. To archive, that the reflective device is lying in a planar position, a small piece of metal is put under the device next to the base plate. At the front of the photo is the camera tripod.

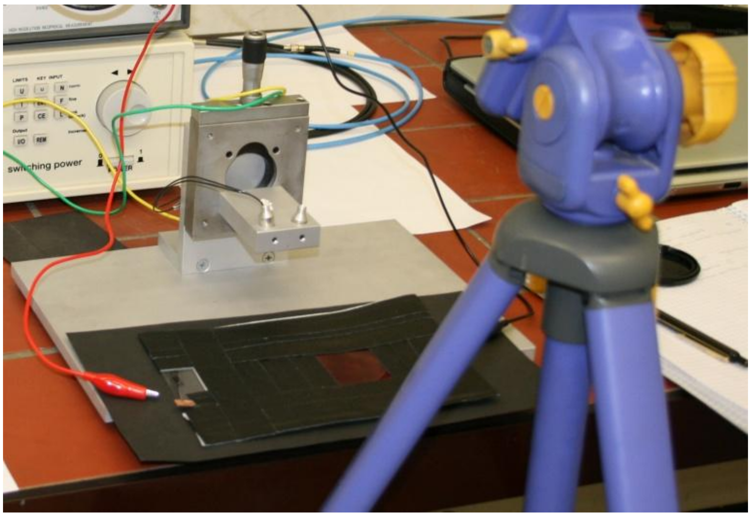


**Fig. 5.3. Setup for visual investigation with a camera during cyclovoltammetry**

### 5.1.2. Photos

During cyclovoltammetry at different voltage values photos of the electrochromic devices were made.

In the first cyclovoltammetry experiments with the two reflective electrochromic devices it was noticed, that after storage of the devices for about 16 hours the devices didn´t bleach completely during the first cyclovoltammogram. So it was assumed that the devices need a “preconditioning” after storage to reach the complete bleaching of the device.

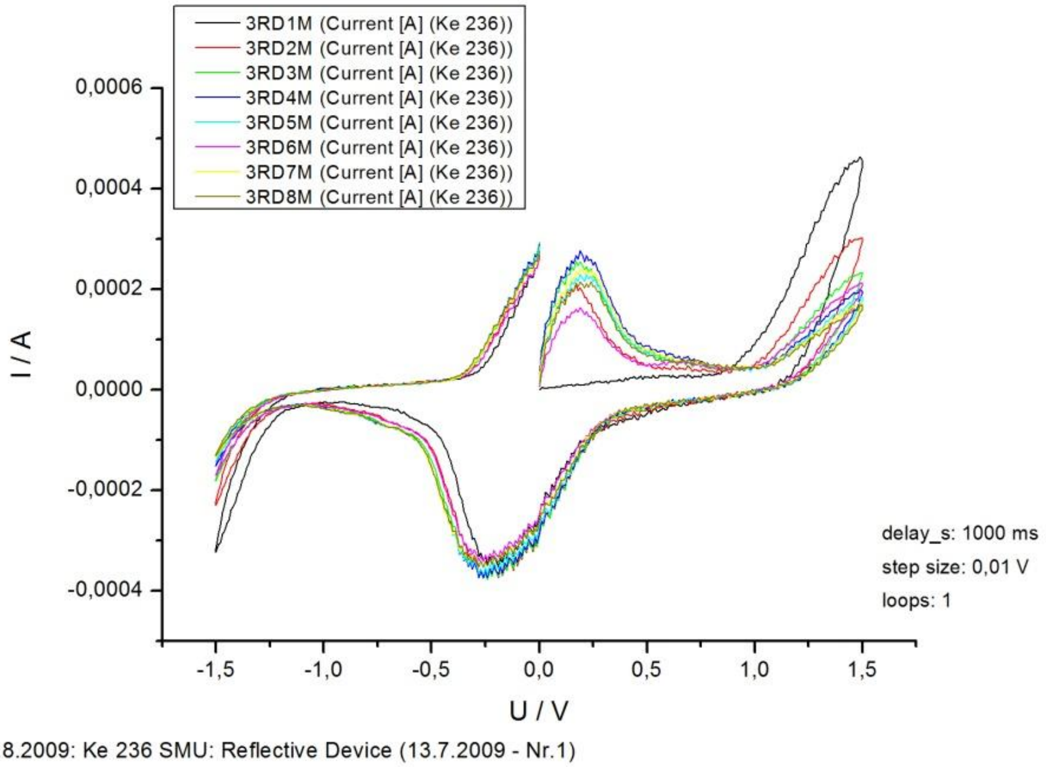
It was decided to run as many cyclovoltammograms until the maximum colouration and bleaching was reached. Immediately after that, another cyclovoltammogram was started in order to take photos at different voltage values.

*Investigation of the “Reflective Device (13.7.2009 – Nr.1)” from figure 5.4 to figure 5.6:*

On the 28.8.2009 cyclovoltammograms with the “Reflective Device (13.7.2009 – Nr.1)” were made (see figure 5.4).

The working electrode of the reflective electrochromic device was connected to the minus output of the source measure unit and therefore the ECD got coloured, if the source measure unit displayed a positive voltage, and bleached, if the source measure unit displayed a negative voltage.

For all cyclovoltammograms in figure 5.4 the same settings were used. As “high level” +1,5 V and as “low level” -1,5 V were chosen. The step size was 0,01 V and the delay time was set to 1000 ms. With each cyclovoltammogram one cycle was run and took about 10 minutes.



28.8.2009: Ke 236 SMU: Reflective Device (13.7.2009 - Nr.1)

**Fig. 5.4. Cyclovoltammograms of the “Reflective Device (13.7.2009 – Nr.1)” measured on the 28.8.2009**

The interval between the end of a cycovoltammogram and the start of the following:

- 1st (3RD1M) to 2nd (3RD2M): 2 min 1 sec
- 2nd (3RD2M) to 3rd (3RD3M): 55 sec
- 3rd (3RD3M) to 4th (3RD4M): 35 sec
- 4th (3RD4M) to 5th (3RD5M): 4 min 1 sec
- 5th (3RD5M) to 6th (3RD6M): 35 min 35 sec
- 6th (3RD6M) to 7th (3RD7M): 50 sec
- 7th (3RD7M) to 8th (3RD8M): 5 min 20 sec

At the fourth (3RD4M), the fifth (3RD5M) and the seventh (3RD7M) cyclovoltammogram photos were made. A photo series taken during the seventh cyclovoltammogram is presented in figure 5.6. Figure 5.5 shows the positions in the cyclovoltommogram, where the photos were taken.

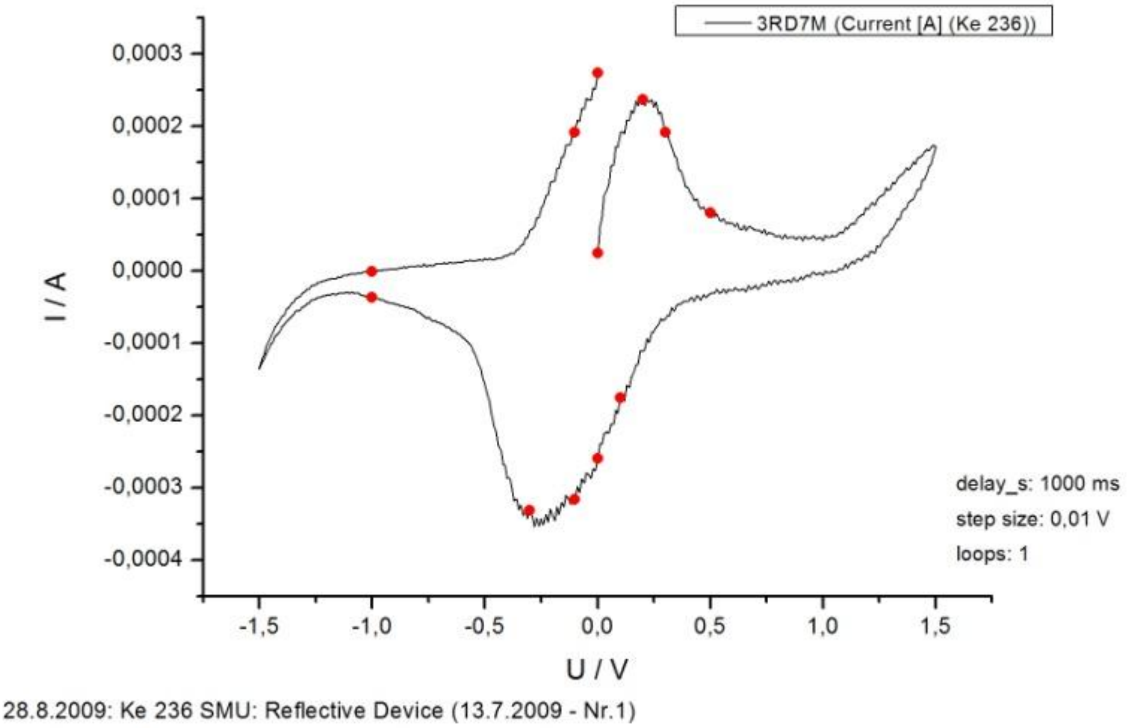


**Fig. 5.5. Cyclovoltammogram “3RD7M” of the “Reflective Device (13.7.2009 – Nr.1)” measured on the 28.8.2009; voltage positions are marked, where the photos shown in figure 5.6 have been taken**

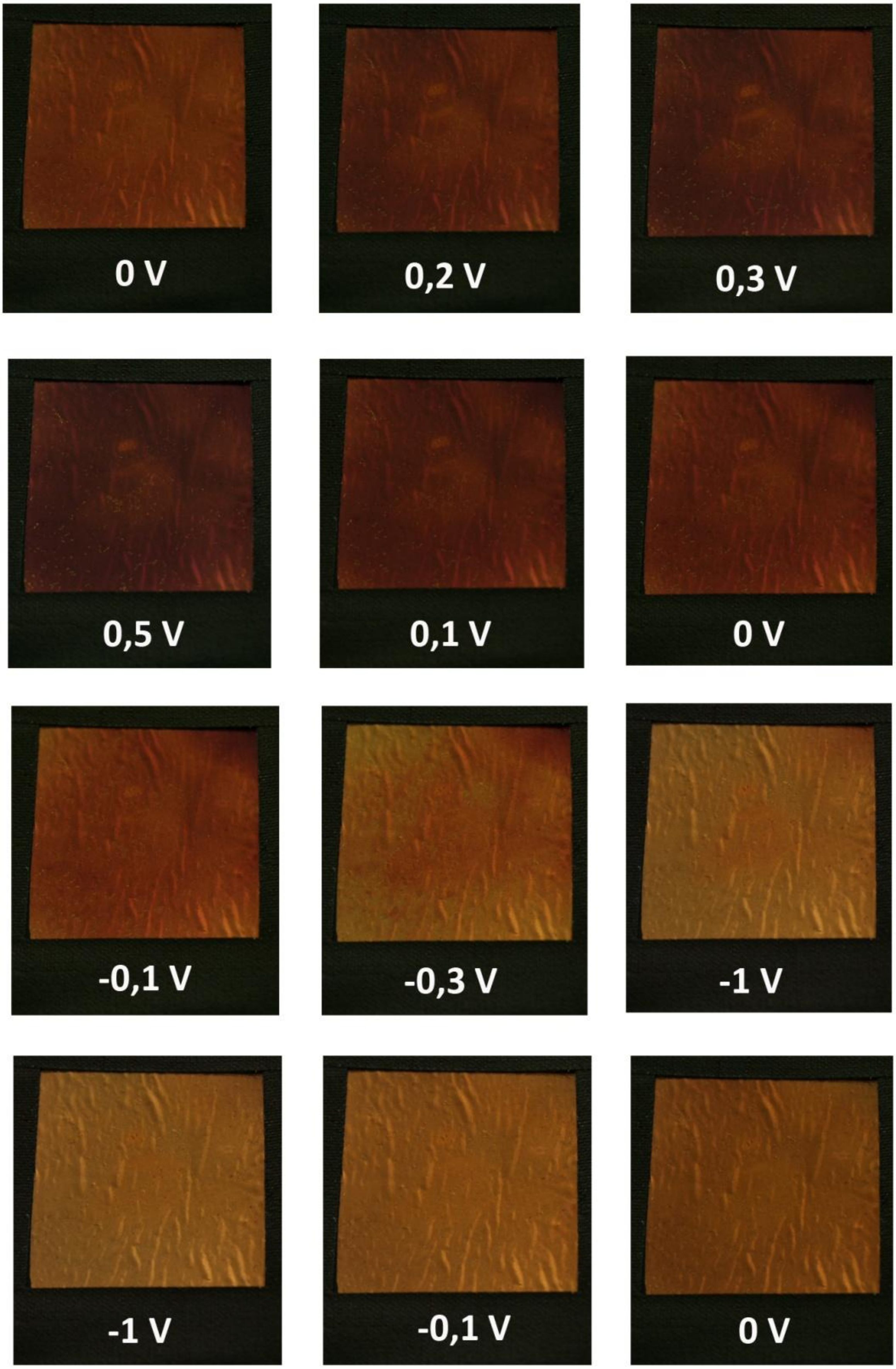


**Fig. 5.6. Photo series of the “Reflective Device (13.7.2009 – Nr.1)” taken at different voltage values during the cyclovoltammogram “3RD7M” on the 28.8.2009**

*Investigation of the "Reflective Device (13.7.2009 – Nr.2)" from figure 5.7 to figure 5.9:*

Figure 5.7 shows cyclovoltammograms of the "Reflective Device (13.7.2009 – Nr.2)". "High level" was set to +1,5 V and "low level" to -1,5 V. A "step size" of 0,01 V and a "delay time" of 1000 ms were chosen. With each cyclovoltammogram one cycle was run and took about 10 minutes.
The reflective electrochromic device coloured, if the source measure unit displayed a positive voltage, and bleached, if the source measure unit displayed a negative voltage.

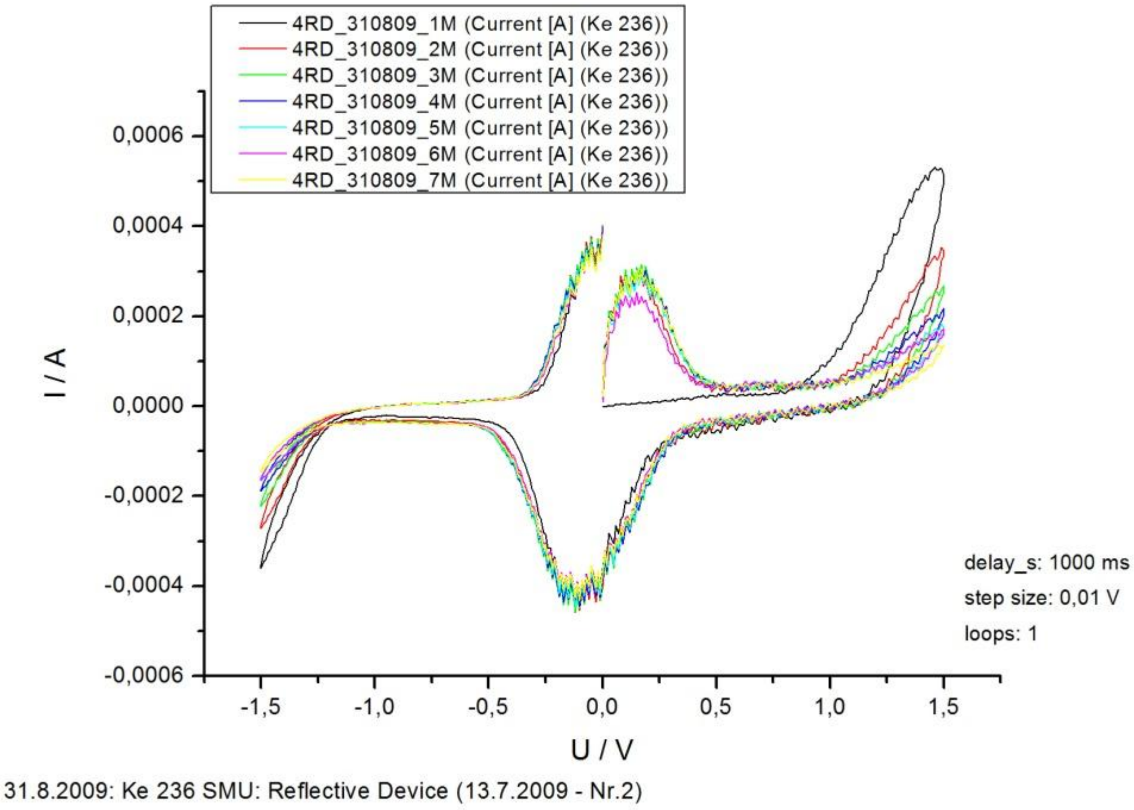


**Fig. 5.7. Cyclovoltammograms of the "Reflective Device (13.7.2009 – Nr.2)" measured on the 31.8.2009**

The interval between the end of a cycovoltammogram and the start of the following:

- 1st (4RD_310809_1M) to 2nd (4RD_310809_2M): 35 sec
- 2nd (4RD_310809_2M) to 3rd (4RD_310809_3M): 1 min 10 sec
- 3rd (4RD_310809_3M) to 4th (4RD_310809_4M): 2 min 10 sec
- 4th (4RD_310809_4M) to 5th (4RD_310809_5M): 3 min 35 sec
- 5th (4RD_310809_5M) to 6th (4RD_310809_6M): 4 min 40 sec
- 6th (4RD_310809_6M) to 7th (4RD_310809_7M): 1 min

During the third cyclovoltammogram of the 31.8.2009 (4RD_310809_3M) photos were taken (see figure 5.9). The corresponding voltage positions in the cyclovoltammogram are marked in figure 5.8.

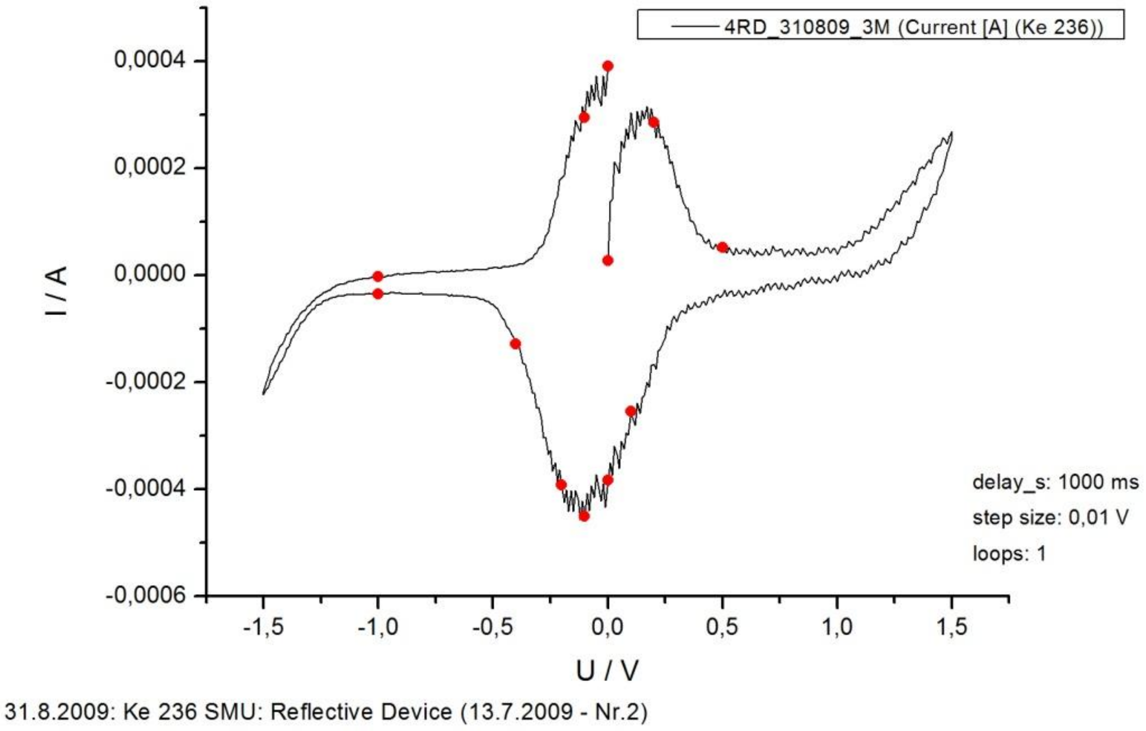


**Fig. 5.8. Cyclovoltammogram "4RD_310809_3M" of the "Reflective Device (13.7.2009 – Nr.2)" measured on the 31.8.2009; voltage positions are marked, where the photos shown in figure 5.9 have been taken**

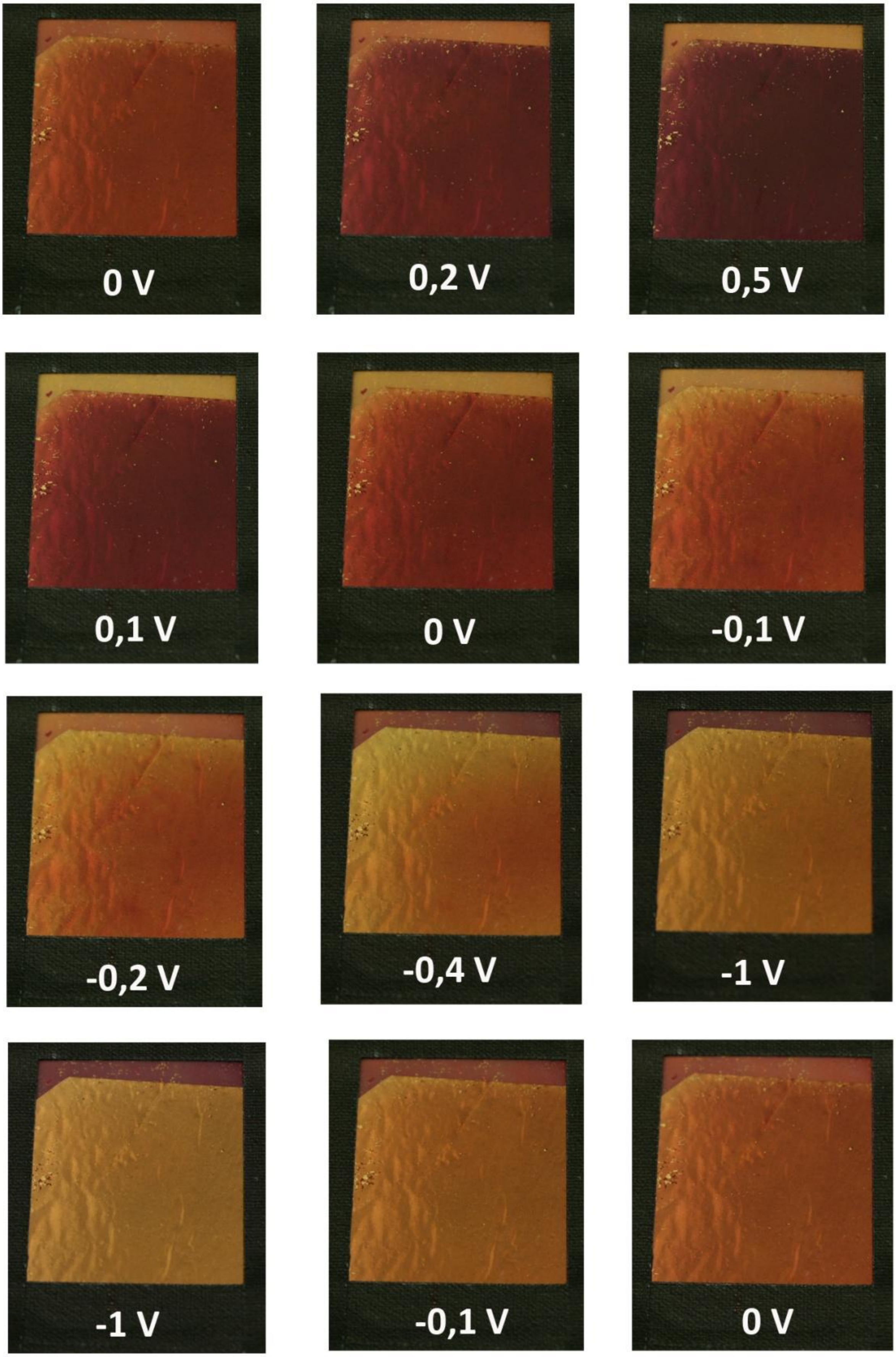


**Fig. 5.9. Photo series of the "Reflective Device (13.7.2009 – Nr.2)" taken at different voltage values during the cyclo-voltammogram "4RD_310809_3M" on the 31.8.2009**

*Investigation of the "Transmittive Device (5.8.2009)" from figure 5.10 to figure 5.12:*

On the 1.9.2009 cyclovoltommograms of the "Transmittive Device (5.8.2009)" were run (see figure 5.10). The settings for these cyclovoltammograms were: "high level" +1,5 V, "low level" -1,5 V, "step size" 0,01 V, "delay time" 1000 ms. One cycle was run with each cyclovoltammogram and took about 10 minutes.

The magenta polymer coated electrode of the transmittive device was connected to the minus output of the source measure unit and therefore the ECD got coloured, if the source measure unit displayed a positive voltage, and bleached, if the source measure unit displayed a negative voltage.

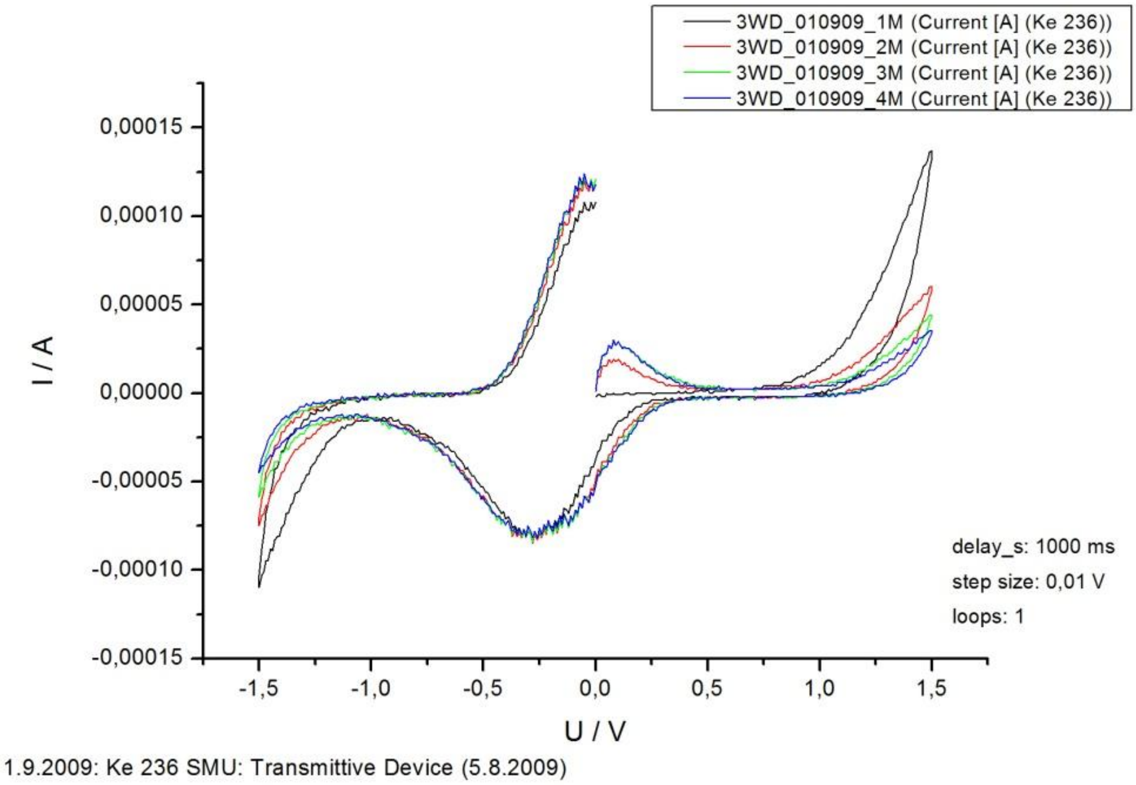
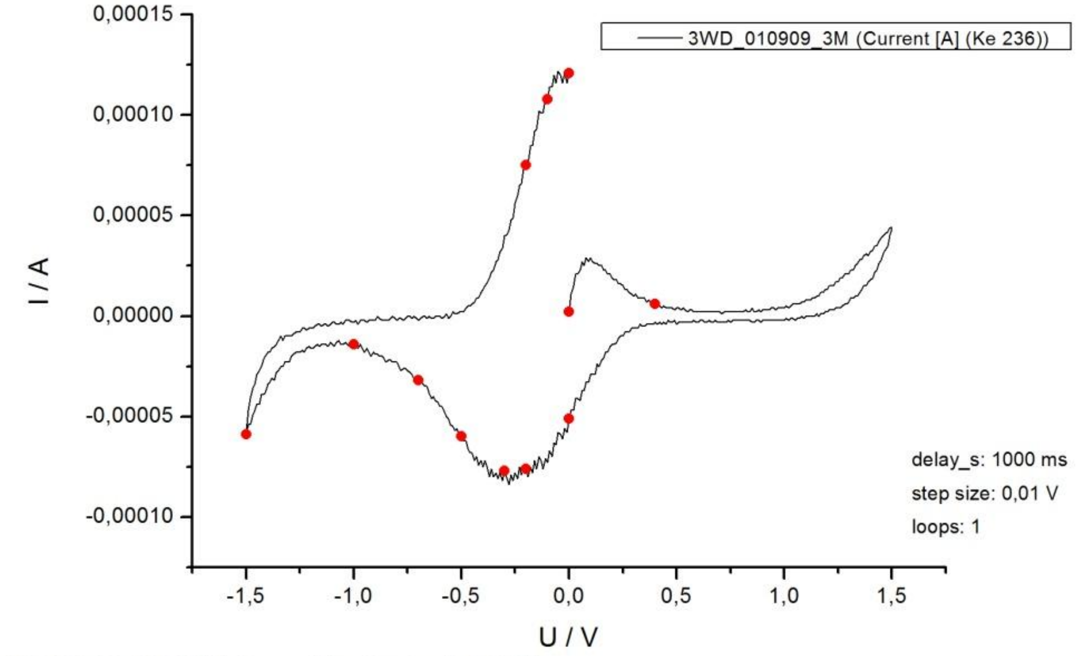


**Fig. 5.10. Cyclovoltammograms of the "Transmittive Device (5.8.2009)" measured on the 1.9.2009**

The interval between the end of a cycovoltammogram and the start of the following:

- 1st (3WD_010909_1M) to 2nd (3WD_010909_2M): 1 min 10 sec
- 2nd (3WD_010909_2M) to 3rd (3WD_010909_3M): 1 min 20 sec
- 3rd (3WD_010909_3M) to 4th (3WD_010909_4M): 3 min 28 sec

Photos were taken during the third cyclovoltammogram (3WD_010909_3M).



1.9.2009: Ke 236 SMU: Transmittive Device (5.8.2009)

**Fig. 5.11. Cyclovoltammogram “3WD_010909_3M” of the “Transmittive Device (5.8.2009)” measured on the 1.9.2009; voltage positions are marked, where the photos shown in figure 5.12 have been taken**

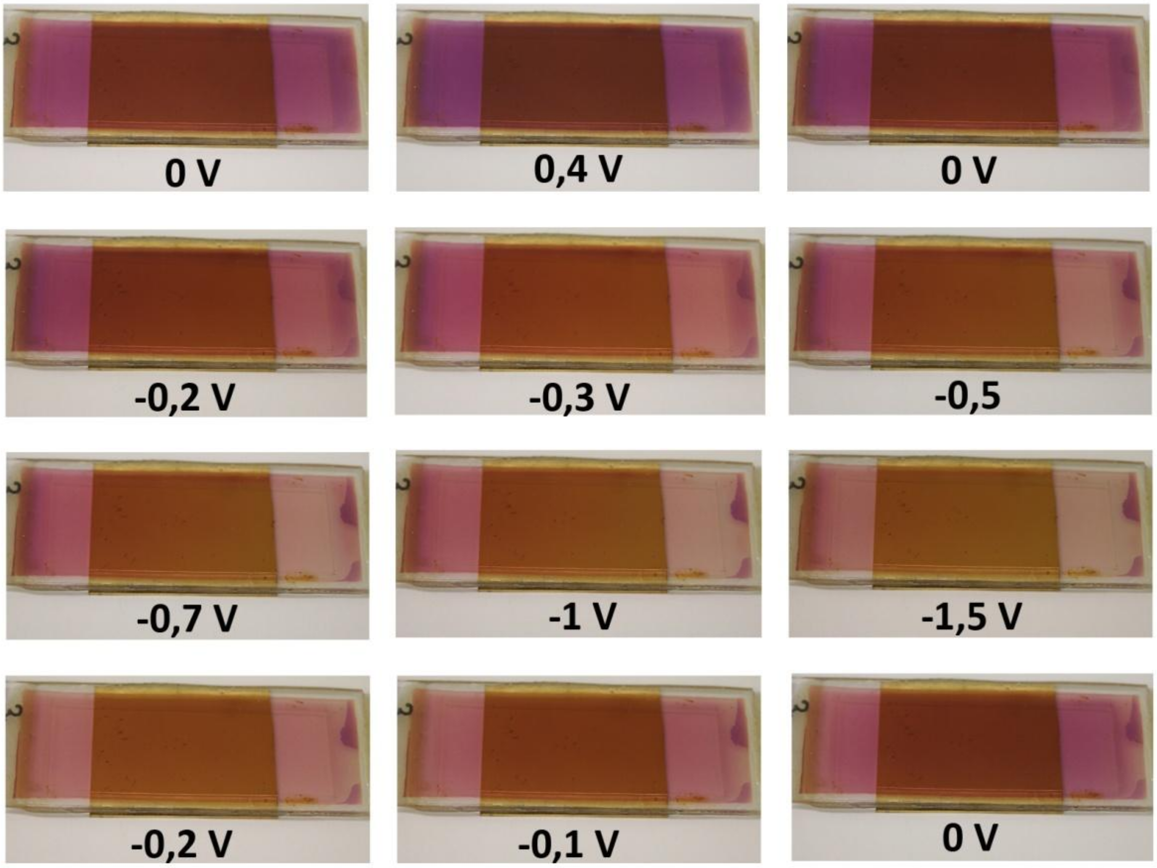


**Fig. 5. 12. Photo series of the “Transmittive Device (5.8.2009)” taken at different voltage values during the cyclo-voltammogram “3WD_010909_3M” on the 1.9.2009**

*Investigation of the "Transmittive Device (29.7.2009)" from figure 5.13 to figure 5.15:*

Figure 5.13 shows cyclovoltammograms of the "Transmittive Device (29.7.2009)". The settings for these five cyclovoltammograms were: "high level" +1,5 V, "low level" -1,5 V, "step size" 0,01 V, "delay time" 1000 ms. With each cyclovoltammogram one cycle was run and took about 10 minutes.

The transmittive electrochromic device coloured, if the source measure unit displayed a positive voltage, and bleached, if the source measure unit displayed a negative voltage.

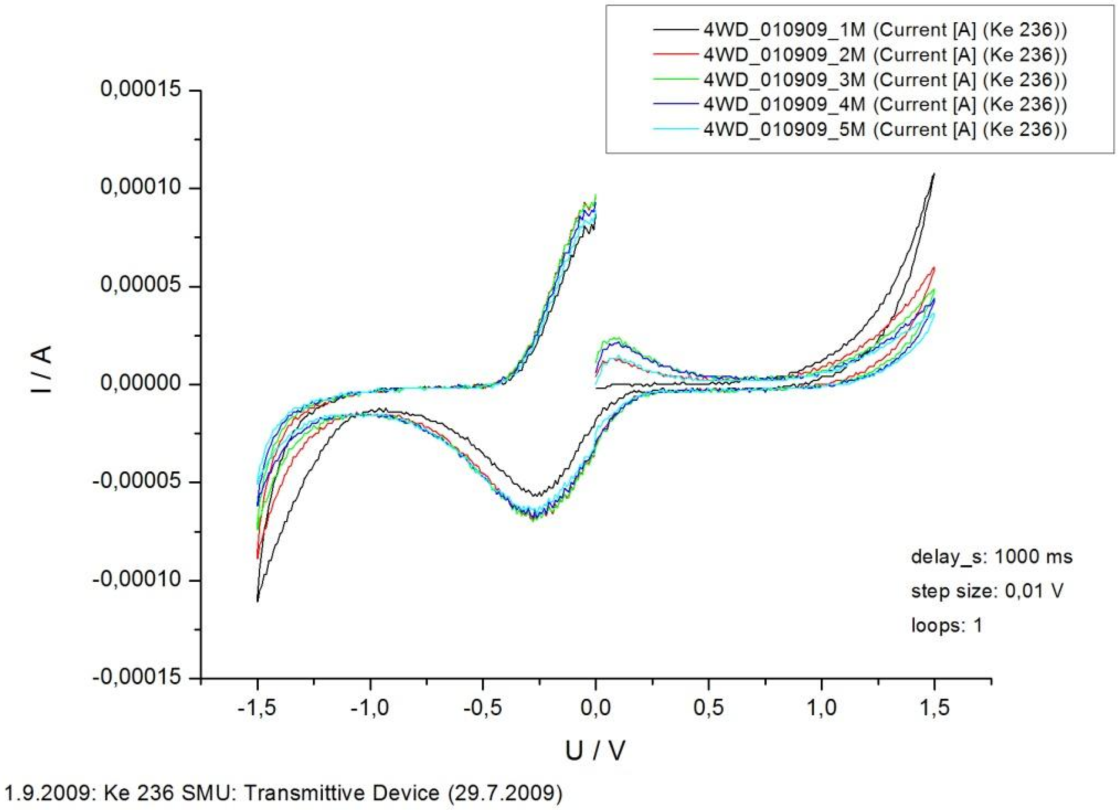


**Fig. 5.13. Cyclovoltammograms of the "Transmittive Device (29.7.2009)" measured on the 1.9.2009**

The interval between the end of a cycovoltammogram and the start of the following:

- 1st (4WD_010909_1M) to 2nd (4WD_010909_2M): 45 sec
- 2nd (4WD_010909_2M) to 3rd (4WD_010909_3M): 26 sec
- 3rd (4WD_010909_3M) to 4th (4WD_010909_4M): 45 sec
- 4th (4WD_010909_4M) to 5th (4WD_010909_5M): 3 min 31 sec

Photos were taken during the fourth cyclovoltammogram (4WD_010909_4M).

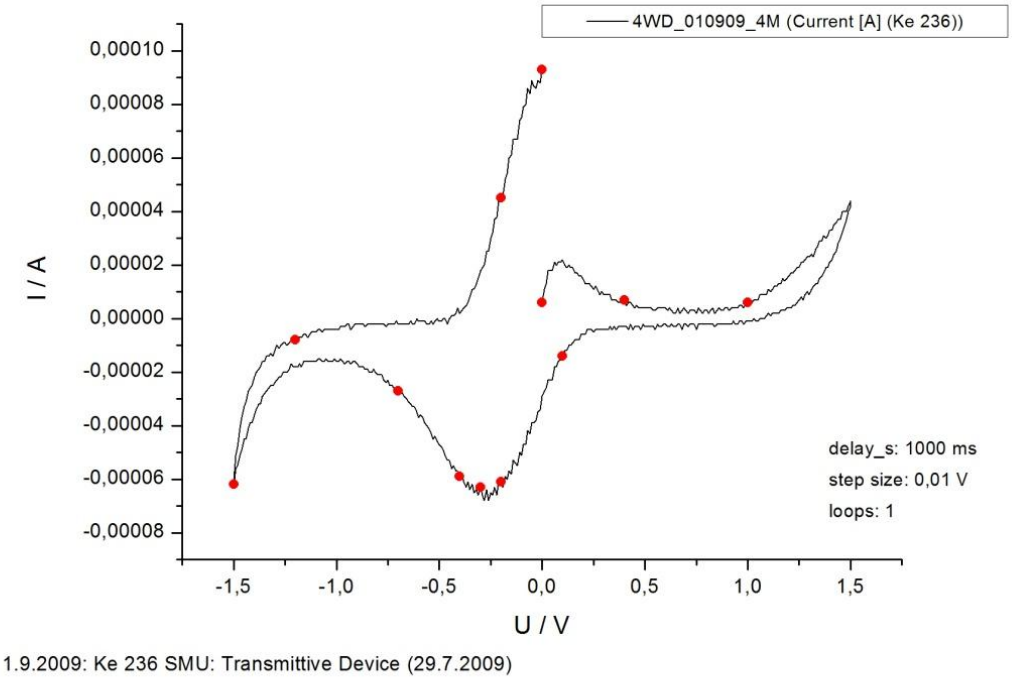


**Fig. 5.14. Cyclovoltammogram "4WD_010909_4M" of the "Transmittive Device (29.7.2009)" measured on the 1.9.2009; voltage positions are marked, where the photos shown in figure 5.15 have been taken**

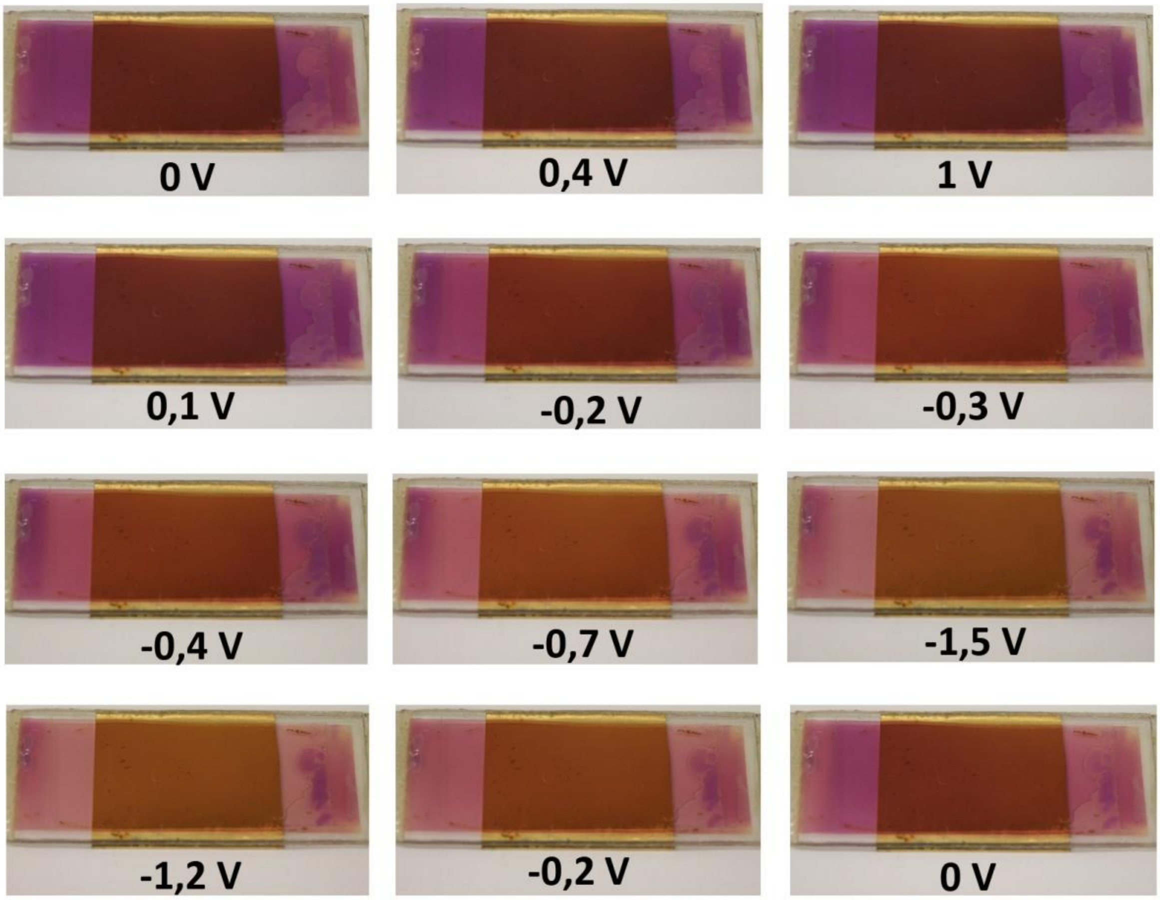


**Fig. 5.15. Photo series of the "Transmittive Device (29.7.2009)" taken at different voltage values during the cyclovoltammogram "4WD_010909_4M" on the 1.9.2009**

### 5.1.3. Reflection spectra (CCD spectrometer)

During cyclovoltammetry at different voltage values reflection spectra of the electrochromic devices were measured with the CCD spectrometer.

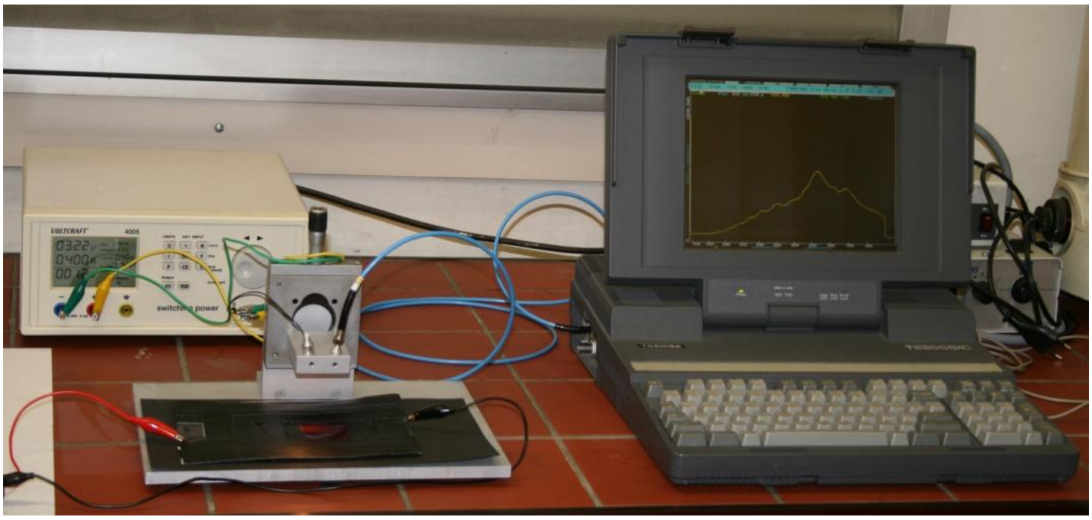


**Fig. 5.16. Investigation of the electrochromic devices with the CCD spectrometer during cyclovoltammetry**

*Measurement results of the "Reflective Device (13.7.2009 – Nr.1)" from figure 5.17 to figure 5.24:*

On the 11.8.2009 cyclovoltammograms with the "Reflective Device (13.7.2009 – Nr.1)" were made (see figure 5.17, 5.18) after storage for a few days.
For the two cyclovoltammograms in figure 5.17 the same settings were used. As "high level" +1,5 V and as "low level" -1,5 V were chosen. The step size was 0,01 V and the delay time was set to 1000 ms. With each cyclovoltammogram one cycle was run and took about 10 minutes.
With the cyclovoltammogram shown in figure 5.18 two cycles were run for about 10 minutes, and the settings were: "high level" +1,5 V, "low level" -1,5 V, "step size" 0,02 V, "delay time" 1000 ms.
The working electrode of the reflective electrochromic device was connected to the minus output of the source measure unit and therefore the ECD got coloured, if the source measure unit displayed a positive voltage, and bleached, if the source measure unit displayed a negative voltage.

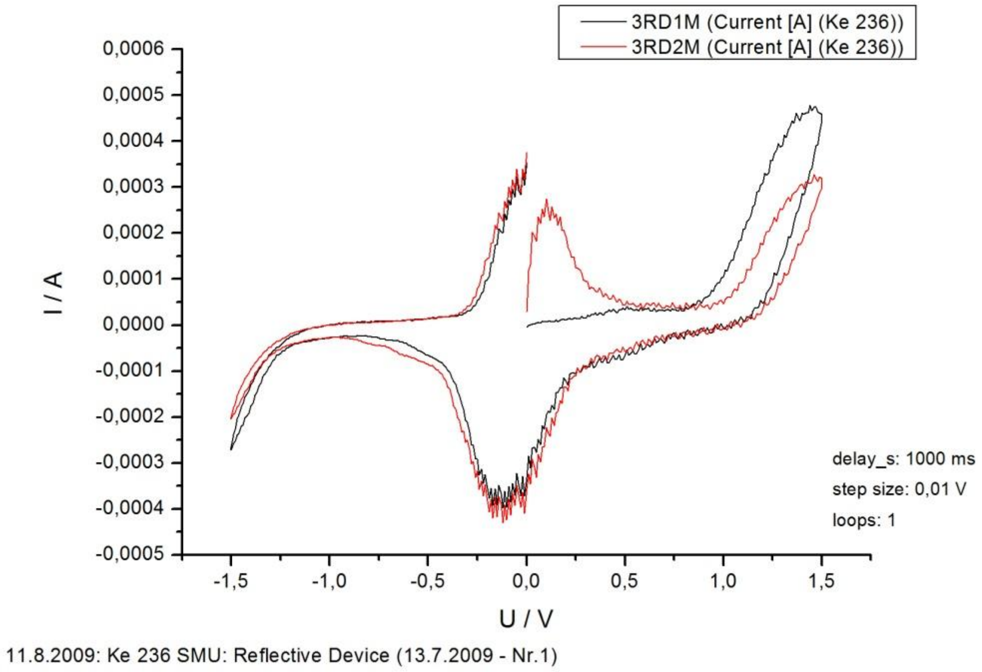


**Fig. 5.17. Cyclovoltammograms of the "Reflective Device (13.7.2009 – Nr.1)" measured on the 11.8.2009**

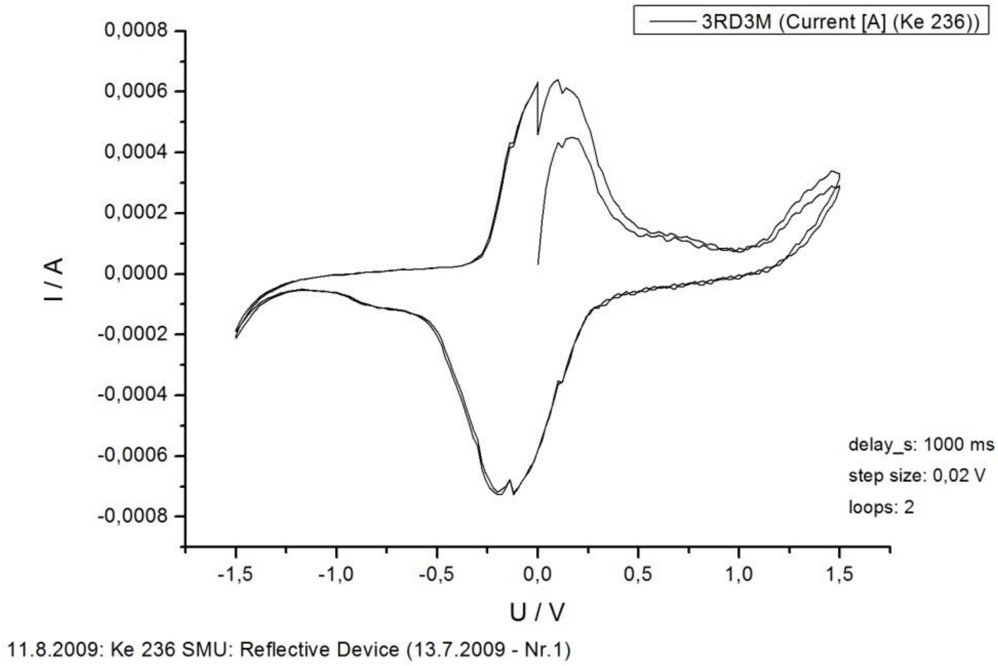


**Fig. 5.18. Cyclovoltammogram of the "Reflective Device (13.7.2009 – Nr.1)" measured on the 11.8.2009**

The interval between the end of a cycovoltammogram and the start of the following:

- 1st (3RD1M) to 2nd (3RD2M): 35 sec
- 2nd (3RD2M) to 3rd (3RD3M): 40 sec

During the first (3RD1M) and the second (3RD2M) cyclovoltammogram reflection spectra were measured (see figure 5.20, 5.22). The corresponding voltage positions in the cyclovoltammograms are marked in figure 5.19, 5.21.

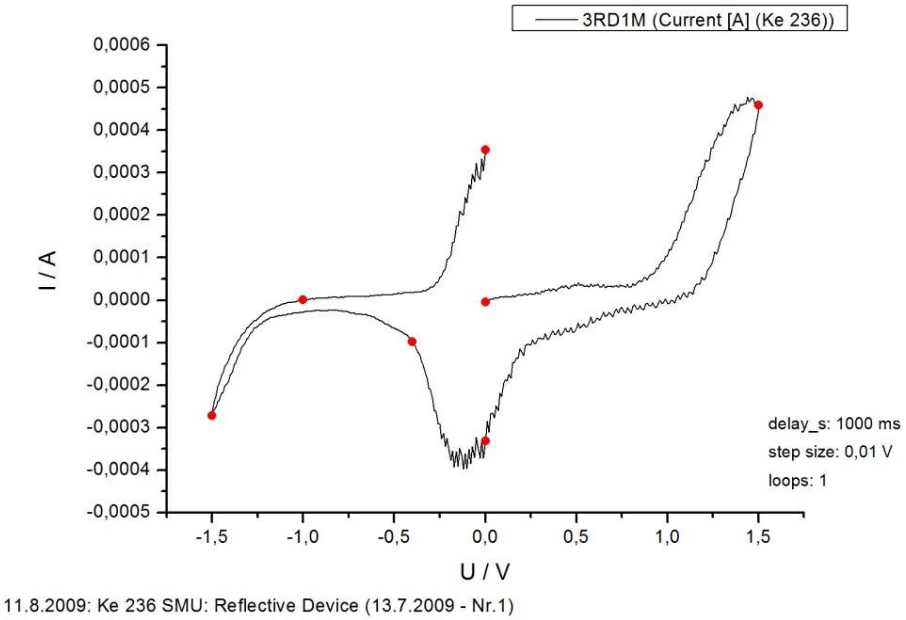


**Fig. 5.19. Cyclovoltammogram "3RD1M" of the "Reflective Device (13.7.2009 – Nr.1)" measured on the 11.8.2009; voltage positions are marked, where the reflection spectra shown in figure 5.20 have been measured**

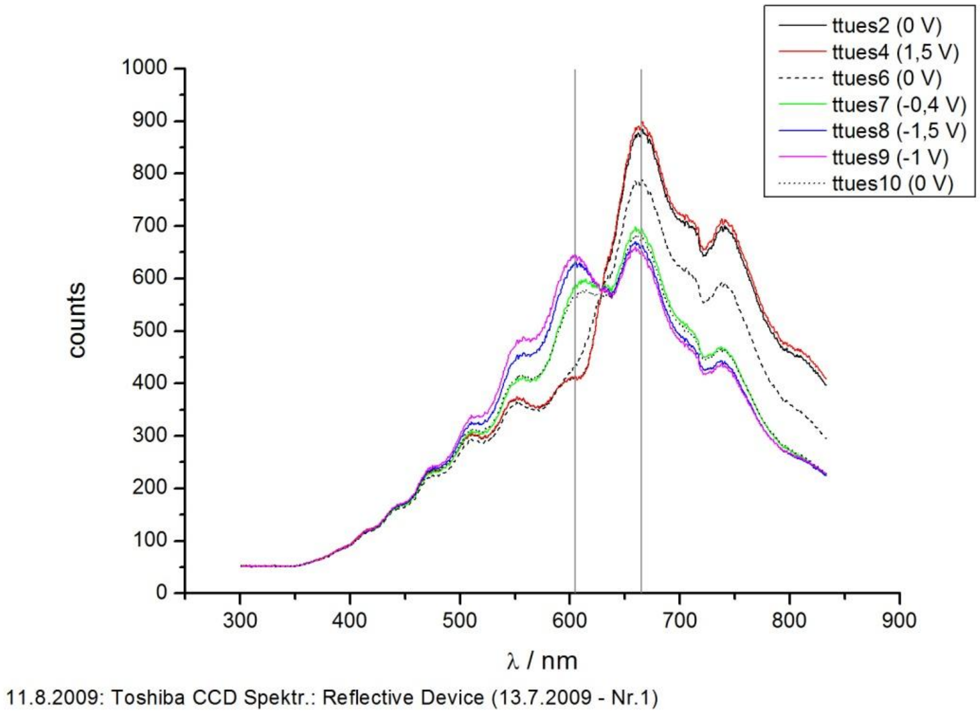


**Fig. 5.20. Reflection spectra of the "Reflective Device (13.7.2009 – Nr.1)" measured at different voltage values during the cyclovoltammogram "3RD1M" on the 11.8.2009**
**Vertical lines: chosen wavelengths for the calculation of colour modulation (table 5.1)**

Reflection spectra measured with the CCD spectrometer:

x – axis: unit nm; calibrated and controlled using mercury line spectrum (PEN RAY LAMP, B-73818; LOT ORIEL GROUP)

y – axis: raw spectra in arbitrary units; to get absolute reflection spectra the raw reflection spectra had to be corrected. As alterations were relevant, raw spectra were sufficient.

To express colour modulation the colouring range between a spectrum with maximum counts value and a spectrum with minimum counts value at wavelengths with a high difference of counts values is given in percent.

To calculate the colour modulation either the spectrum with maximum counts value or minimum counts value at a chosen wavelength was set to 100 %. Two suitable wavelengths were chosen.
For example in figure 5.20 the chosen wavelengths are 605 nm and 665 nm. The maximum counts values and the minimum counts values were read out:
605 nm → maximum: 646 counts (“ttues9”), minimum: 414 counts (“ttues4”)
665 nm → maximum: 895 counts (“ttues4”), minimum: 651 counts (“ttues9”)
The reflection spectrum “ttues9” was set to 100 % (see table 5.1).

**Table 5.1. Colour modulation at 605 nm and 665 nm calculated from the reflection spectra “ttues9” and “ttues4” of the “Reflective Device (13.7.2009 – Nr.1)” (see figure 5.20)**

| | ttues9 | | ttues4 | | Colour modulation |
|---|---|---|---|---|---|
| | counts | % | counts | % | % |
| 605 nm | 646 ± 5 | 100 | 414 ± 5 | 64 ± 1 | 36 ± 1 |
| 665 nm | 651 ± 5 | 100 | 895 ± 5 | 137 ± 1 | 37 ± 1 |

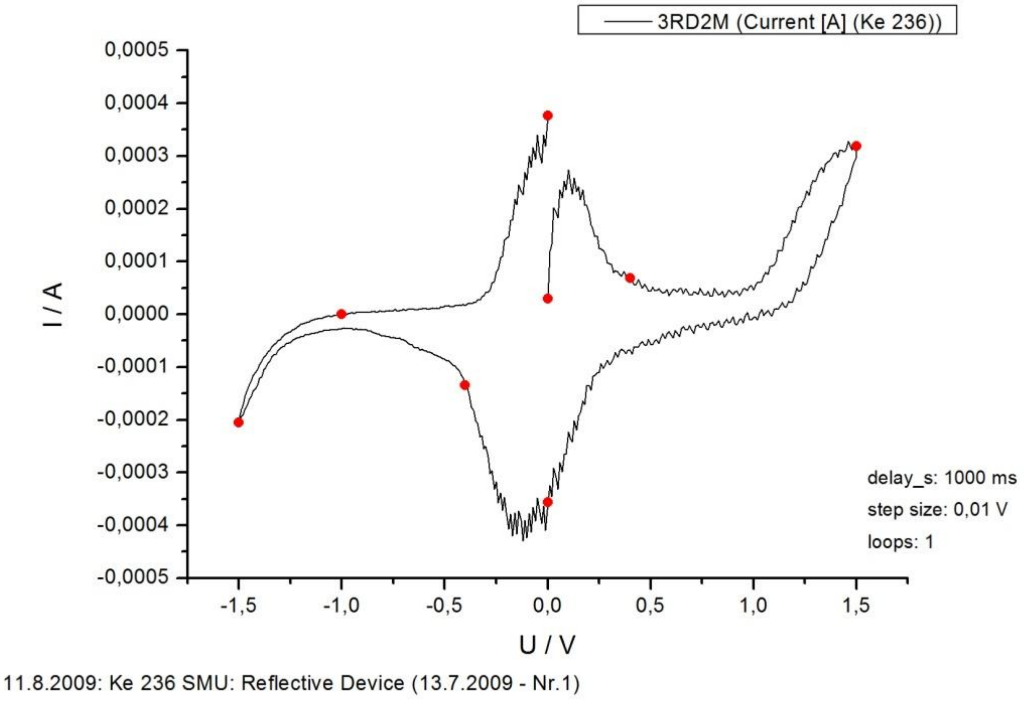


**Fig. 5.21. Cyclovoltammogram “3RD2M” of the “Reflective Device (13.7.2009 – Nr.1)” measured on the 11.8.2009; voltage positions are marked, where the reflection spectra shown in figure 5.22 have been measured**

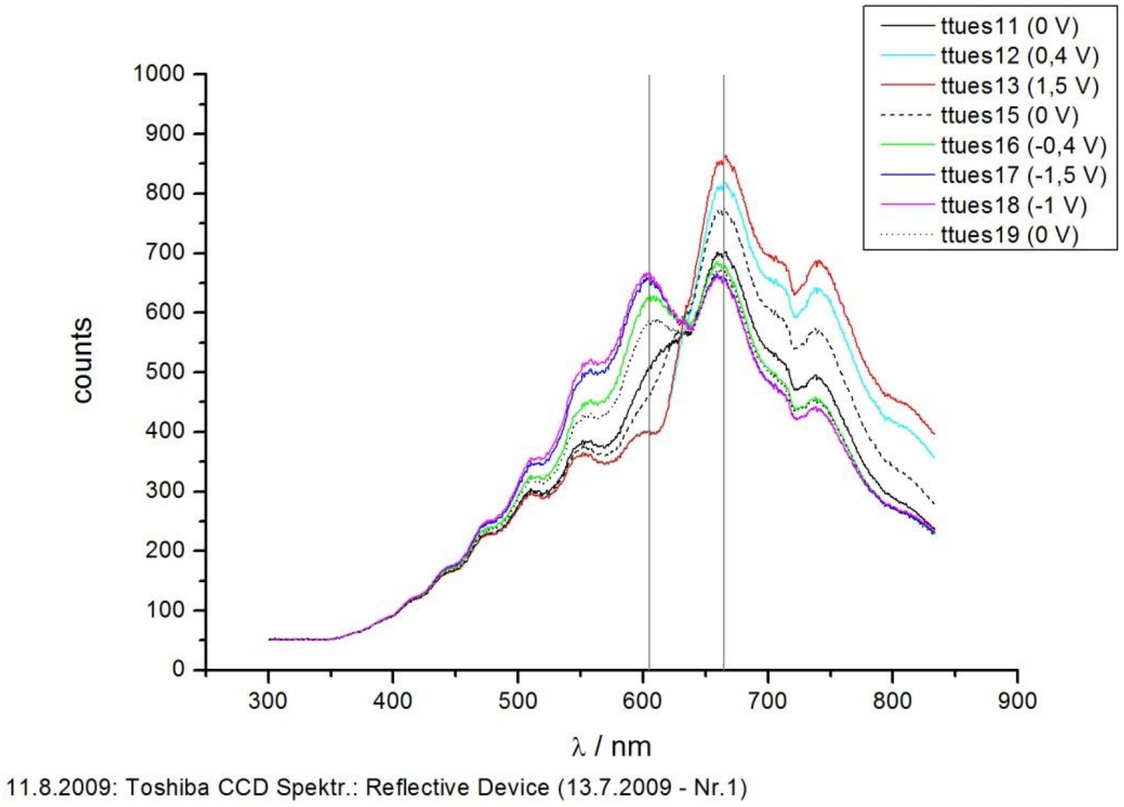
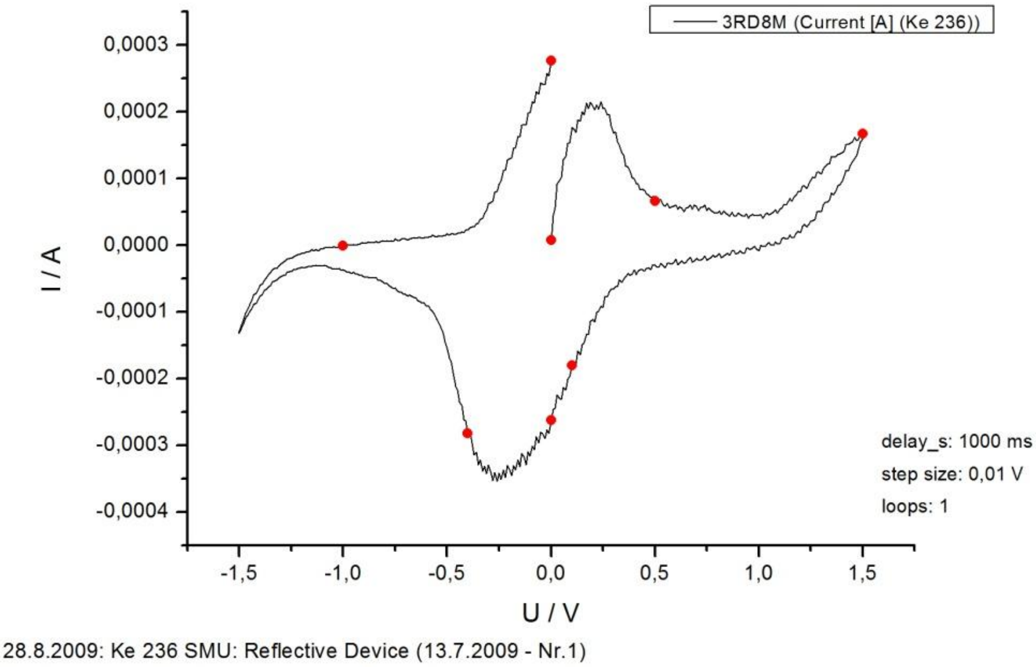


**Fig. 5.22. Reflection spectra of the “Reflective Device (13.7.2009 – Nr.1)” measured at different voltage values during the cyclovoltammogram “3RD2M” on the 11.8.2009**
**Vertical lines: chosen wavelengths for the calculation of colour modulation (table 5.2)**

**Table 5.2. Colour modulation at 605 nm and 665 nm calculated from the reflection spectra “ttues18” and “ttues13” of the “Reflective Device (13.7.2009 – Nr.1)” (see figure 5.22)**

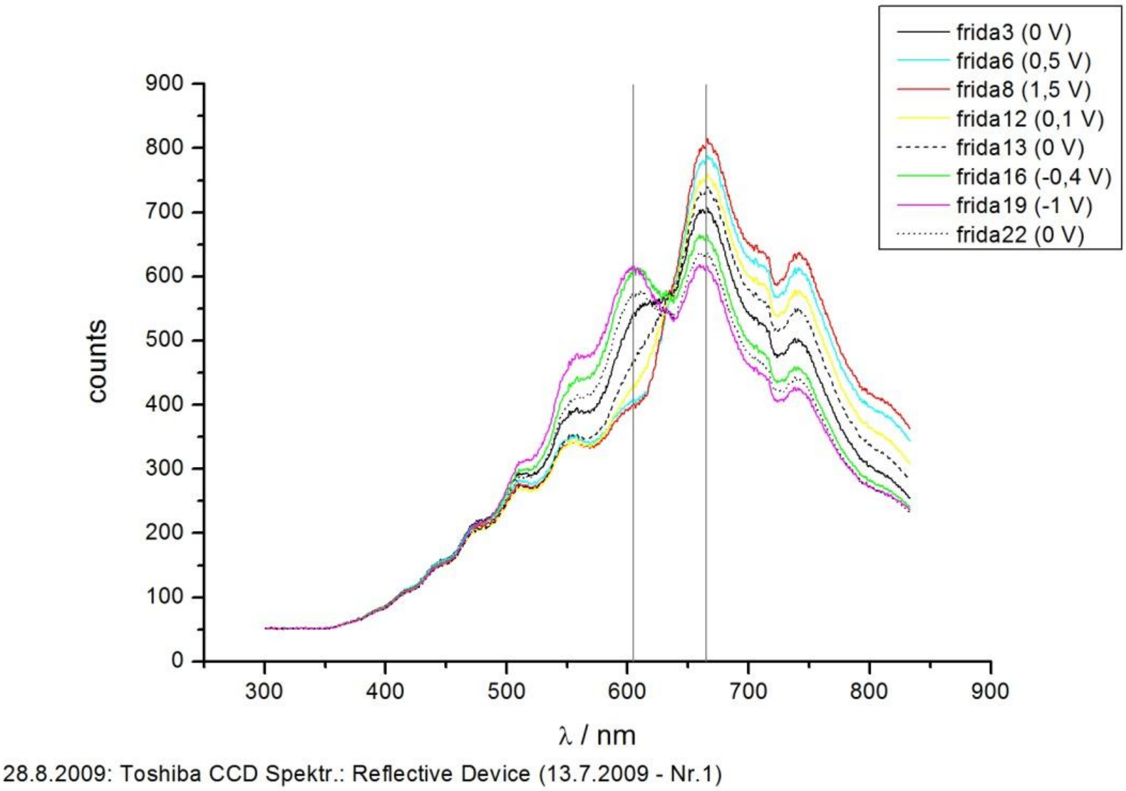
| | ttues18 | | ttues13 | | Colour modulation |
|---|---|---|---|---|---|
| | counts | % | counts | % | % |
| 605 nm | 667 ± 5 | 100 | 401 ± 5 | 60 ± 1 | 40 ± 1 |
| 665 nm | 655 ± 5 | 100 | 860 ± 5 | 131 ± 1 | 31 ± 1 |

On the 28.8.2009 reflection spectra of the “Reflective Device (13.7.2009 – Nr.1)” were measured during the eighth (3RD8M) cyclovoltammogram (see figure 5.4).



28.8.2009: Ke 236 SMU: Reflective Device (13.7.2009 - Nr.1)

**Fig. 5.23. Cyclovoltammogram "3RD8M" of the "Reflective Device (13.7.2009 – Nr.1)" measured on the 28.8.2009; voltage positions are marked, where the reflection spectra shown in figure 5.24 have been measured**



28.8.2009: Toshiba CCD Spektr.: Reflective Device (13.7.2009 - Nr.1)

**Fig. 5.24. Reflection spectra of the "Reflective Device (13.7.2009 – Nr.1)" measured at different voltage values during the cyclovoltammogram "3RD8M" on the 28.8.2009**
**Vertical lines: chosen wavelengths for the calculation of colour modulation (table 5.3)**

**Table 5.3. Colour modulation at 605 nm and 665 nm calculated from the reflection spectra “frida19” and “frida8” of the “Reflective Device (13.7.2009 – Nr.1)” (see figure 5.24)**

| | frida19 | | frida8 | | Colour modulation |
|---|---|---|---|---|---|
| | counts | % | counts | % | % |
| 605 nm | 617 ± 5 | 100 | 400 ± 5 | 65 ± 1 | 35 ± 1 |
| 665 nm | 614 ± 5 | 100 | 809 ± 5 | 132 ± 1 | 32 ± 1 |

*Measurement results of the “Reflective Device (13.7.2009 – Nr.2)” from figure 5.25 to figure 5.32:*

Cyclovoltammograms with the “Reflective Device (13.7.2009 – Nr.2)” were made (see figure 5.25, 5.26) after storage for a few days on the 11.8.2009.
The settings for the two cyclovoltammograms in figure 5.25 were: “high level” +1,5 V, “low level” -1,5 V, “step size” 0,01 V, “delay time” 1000 ms. With each cyclovoltammogram one cycle was run and took about 10 minutes.
With the cyclovoltammogram shown in figure 5.26 two cycles were run and the settings were: “high level” +1,5 V, “low level” -1,5 V, “step size” 0,02 V, “delay time” 1000 ms. Again it took about 10 minutes.
The reflective electrochromic device coloured, if the source measure unit displayed a positive voltage, and bleached, if the source measure unit displayed a negative voltage.

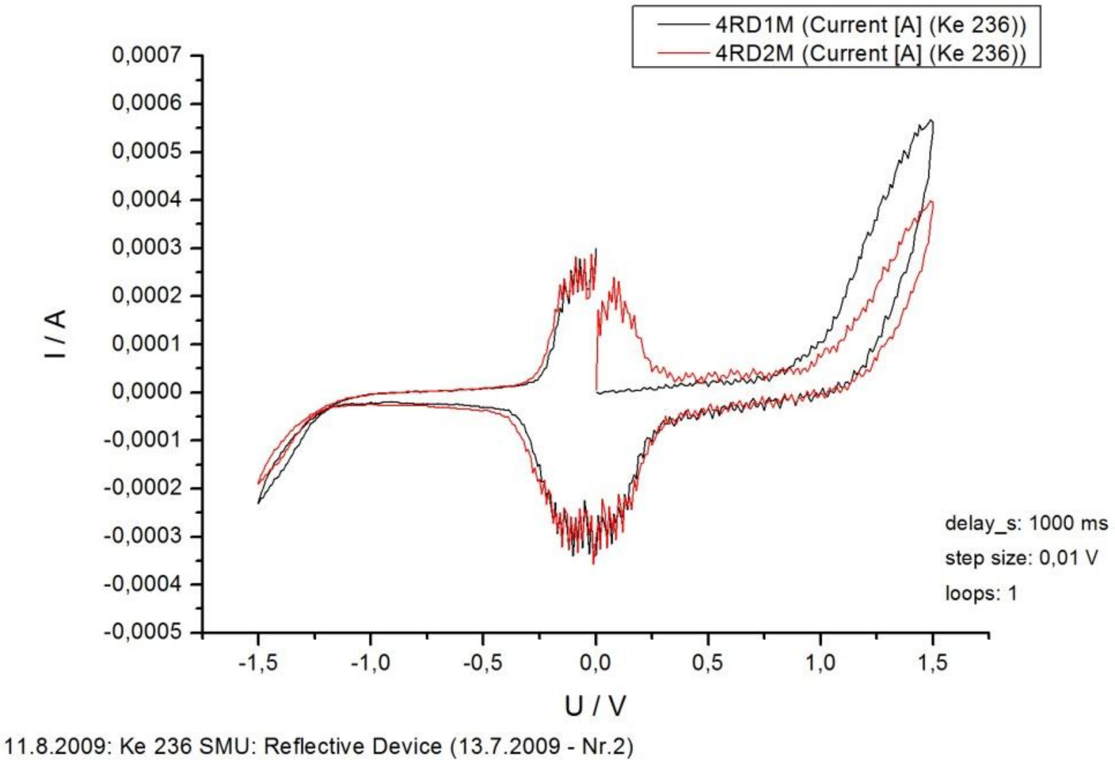


**Fig. 5.25. Cyclovoltammograms of the “Reflective Device (13.7.2009 – Nr.2)” measured on the 11.8.2009**

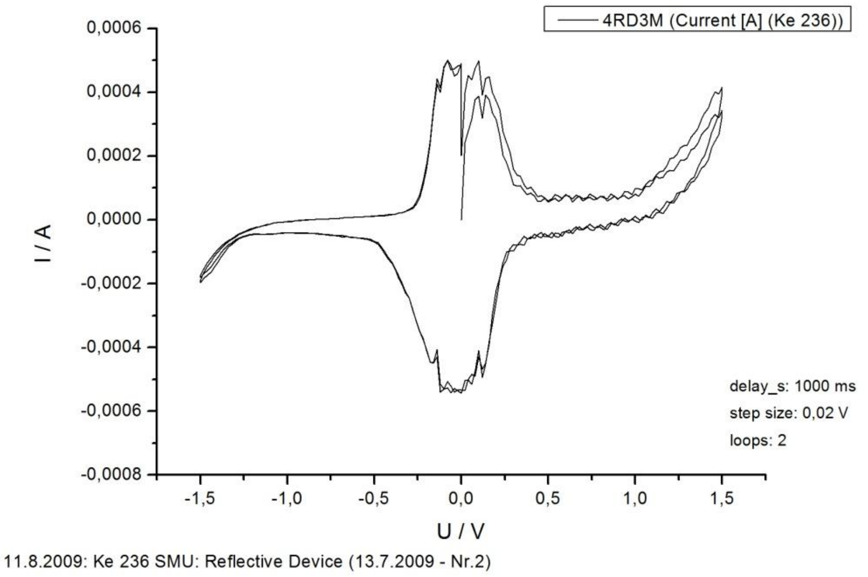


**Fig. 5.26. Cyclovoltammogram of the “Reflective Device (13.7.2009 – Nr.2)” measured on the 11.8.2009**

The interval between the end of a cycovoltammogram and the start of the following:

- 1st (4RD1M) to 2nd (4RD2M): 40 sec
- 2nd (4RD2M) to 3rd (4RD3M): 50 sec

Reflection spectra measured during the first (4RD1M) and the second (4RD2M) cyclovoltammogram are presented in figure 5.28, 5.30. Figure 5.27 and 5.29 show the positions in the cyclovoltommograms, where the reflection spectra were measured.

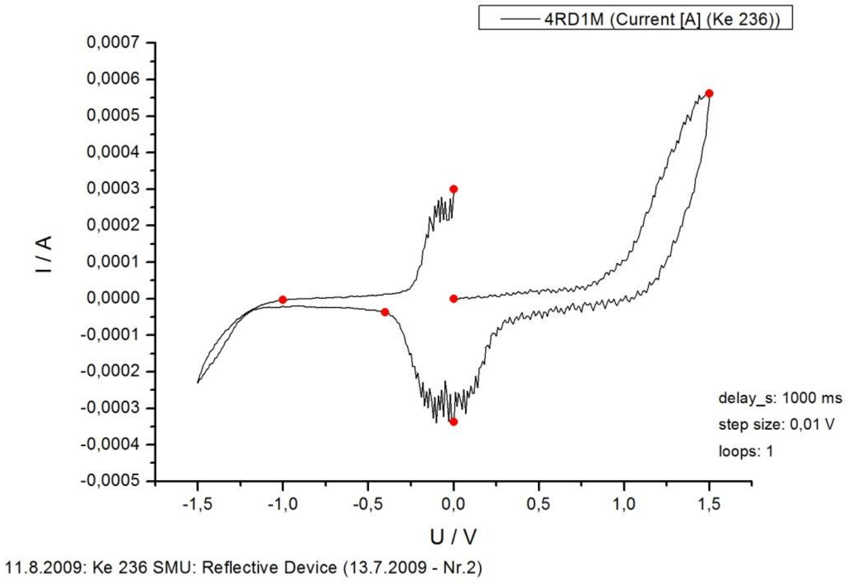
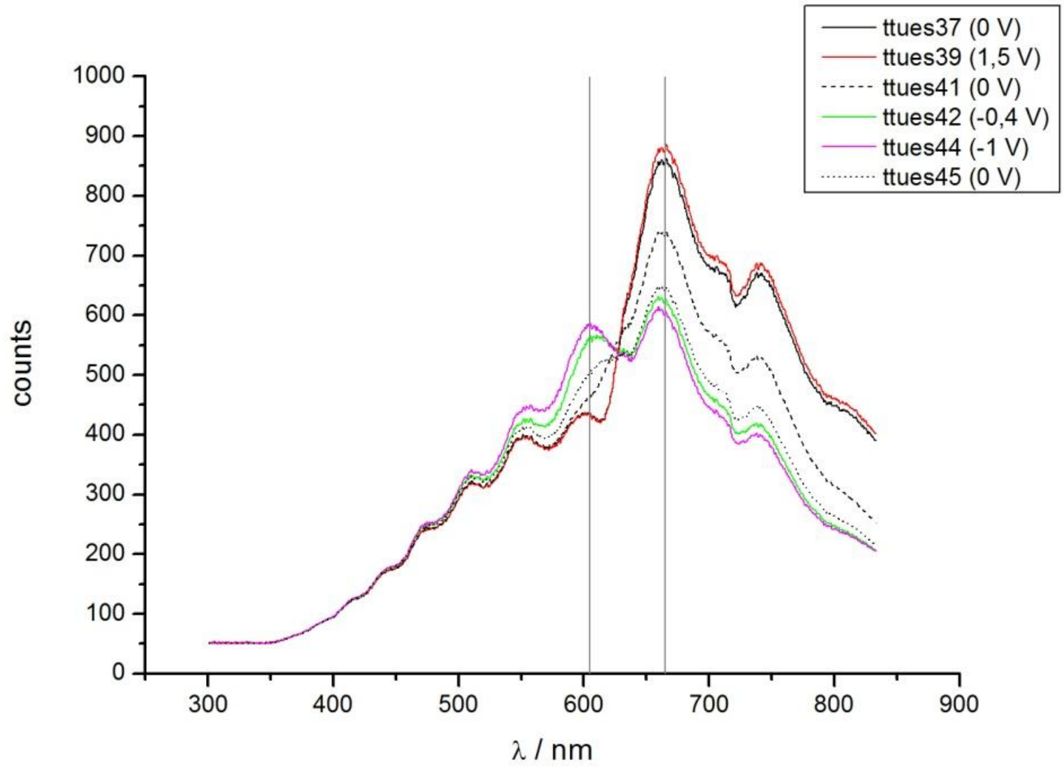


**Fig. 5.27. Cyclovoltammogram “4RD1M” of the “Reflective Device (13.7.2009 – Nr.2)” measured on the 11.8.2009; voltage positions are marked, where the reflection spectra shown in figure 5.28 have been measured**



11.8.2009: Toshiba CCD Spektr.: Reflective Device (13.7.2009 - Nr.2)

**Fig. 5.28. Reflection spectra of the "Reflective Device (13.7.2009 – Nr.2)" measured at different voltage values during the cyclovoltammogram "4RD1M" on the 11.8.2009**
**Vertical lines: chosen wavelengths for the calculation of colour modulation (table 5.4)**

**Table 5.4. Colour modulation at 605 nm and 665 nm calculated from the reflection spectra "ttues44" and "ttues39" of the "Reflective Device (13.7.2009 – Nr.2)" (see figure 5.28)**

| | ttues44 | | ttues39 | | Colour modulation |
|---|---|---|---|---|---|
| | counts | % | counts | % | % |
| 605 nm | 587 ± 5 | 100 | 434 ± 5 | 74 ± 1 | 26 ± 1 |
| 665 nm | 606 ± 5 | 100 | 883 ± 5 | 146 ± 1 | 46 ± 1 |

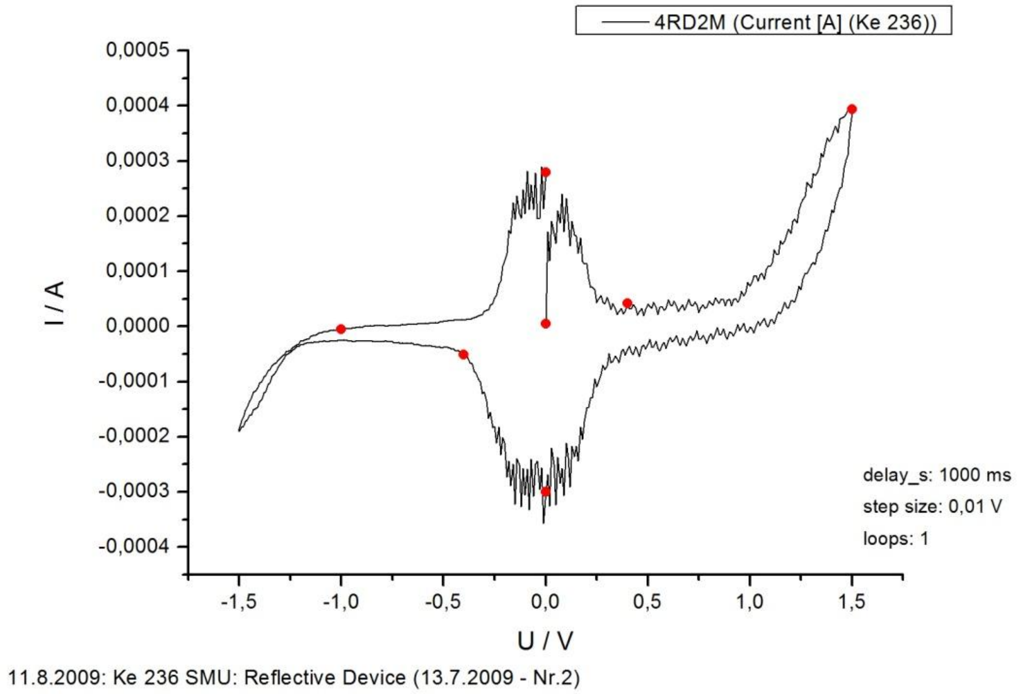


**Fig. 5.29. Cyclovoltammogram "4RD2M" of the "Reflective Device (13.7.2009 – Nr.2)" measured on the 11.8.2009; voltage positions are marked, where the reflection spectra shown in figure 5.30 have been measured**

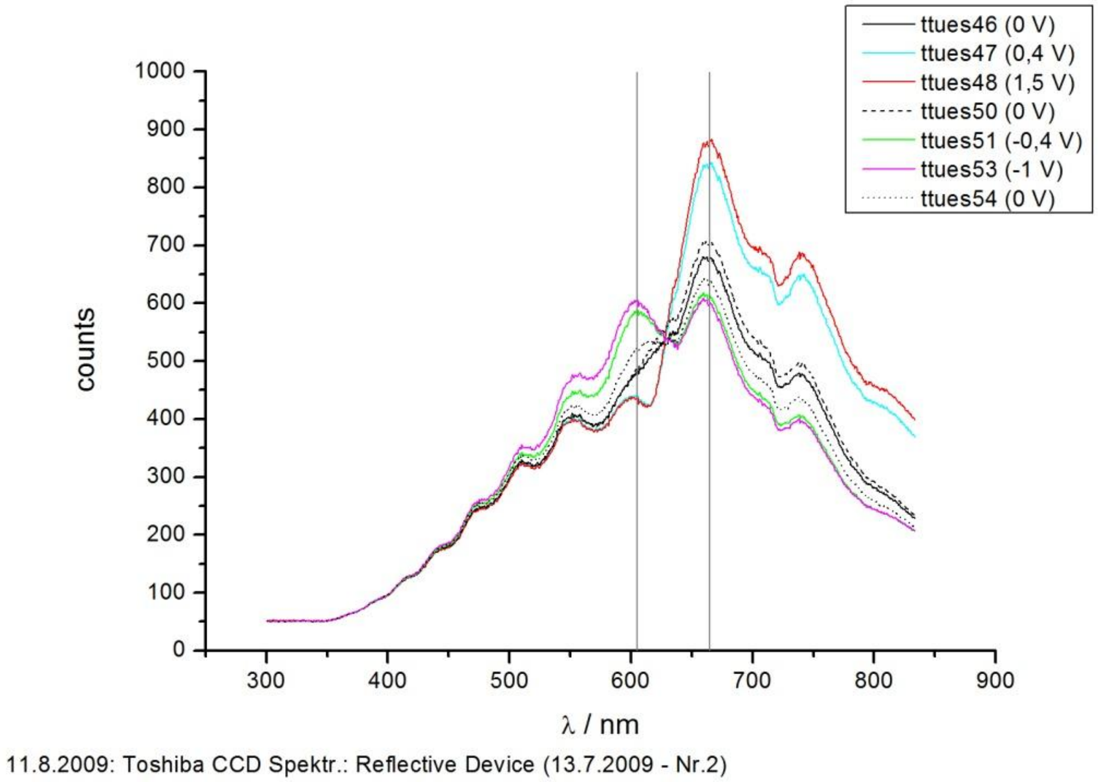


**Fig. 5.30. Reflection spectra of the "Reflective Device (13.7.2009 – Nr.2)" measured at different voltage values during the cyclovoltammogram "4RD2M" on the 11.8.2009**
**Vertical lines: chosen wavelengths for the calculation of colour modulation (table 5.5)**

**Table 5.5. Colour modulation at 605 nm and 665 nm calculated from the reflection spectra “ttues53” and “ttues48”of the “Reflective Device (13.7.2009 – Nr.2)” (see figure 5.30)**

| | ttues53 | | ttues48 | | Colour modulation |
|---|---|---|---|---|---|
| | counts | % | counts | % | % |
| 605 nm | 605 ± 5 | 100 | 436 ± 5 | 72 ± 1 | 28 ± 1 |
| 665 nm | 600 ± 5 | 100 | 878 ± 5 | 146 ± 1 | 46 ± 1 |

Another reflection spectrum series of the “Reflective Device (13.7.2009 – Nr.2)” was measured on the 31.8.2009 during the seventh (4RD_310809_7M) cyclovoltammogram (see figure 5.7).

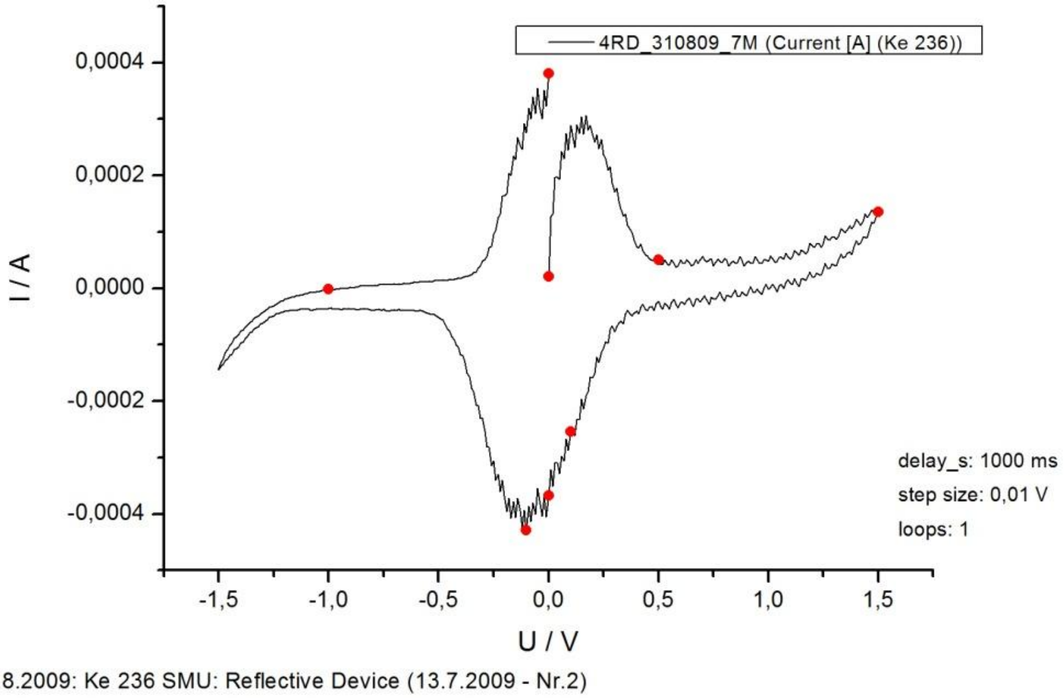


**Fig. 5.31. Cyclovoltammogram “4RD_310809_7M” of the “Reflective Device (13.7.2009 – Nr.2)” measured on the 31.8.2009; voltage positions are marked, where the reflection spectra shown in figure 5.32 have been measured**

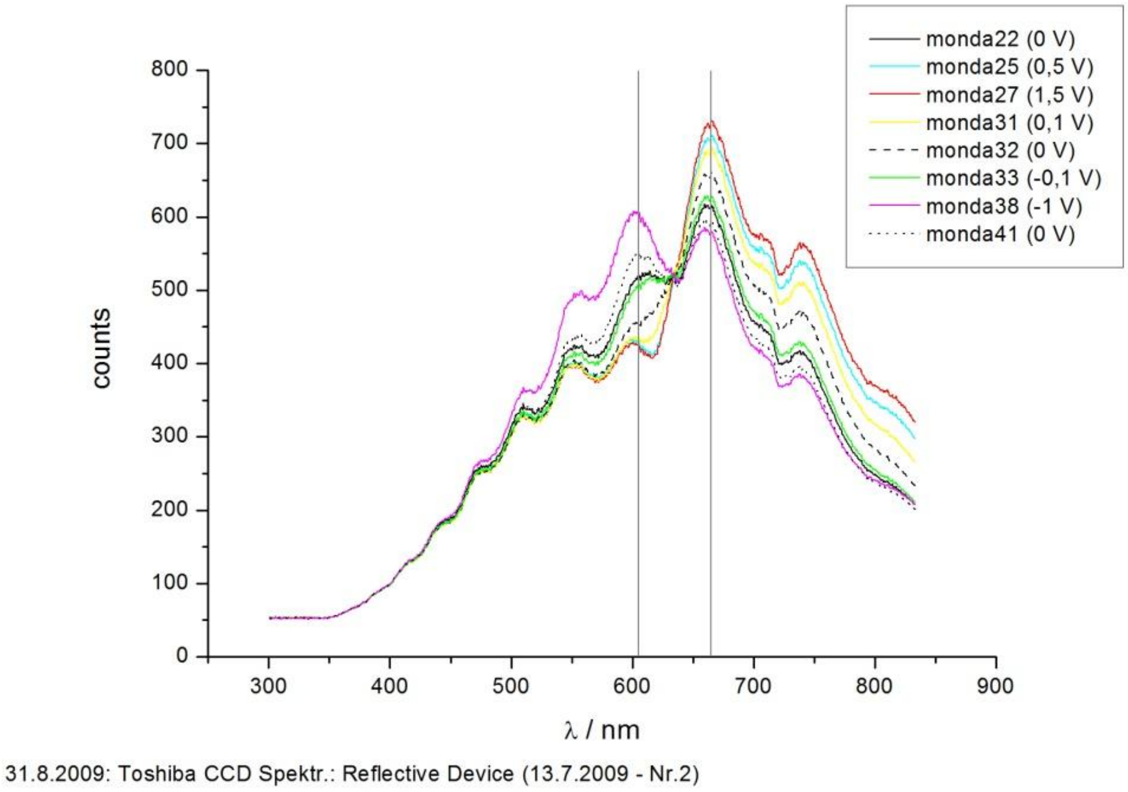


**Fig. 5. 32. Reflection spectra of the "Reflective Device (13.7.2009 – Nr.2)" measured at different voltage values during the cyclovoltammogram "4RD_310809_7M" on the 31.8.2009**
**Vertical lines: chosen wavelengths for the calculation of colour modulation (table 5.6)**

**Table 5.6. Colour modulation at 605 nm and 665 nm calculated from the reflection spectra "monda38" and "monda27" of the "Reflective Device (13.7.2009 – Nr.2)" (see figure 5.32)**

| | monda38 | | monda27 | | Colour modulation |
|---|---|---|---|---|---|
| | counts | % | counts | % | % |
| 605 nm | 607 ± 5 | 100 | 425 ± 5 | 70 ± 1 | 30 ± 1 |
| 665 nm | 581 ± 5 | 100 | 729 ± 5 | 125 ± 1 | 25 ± 1 |

*Measurement results of the "Transmittive Device (5.8.2009)" from figure 5.33 to figure 5.40:*

On the 11.8.2009 cyclovoltommograms of the "Transmittive Device (5.8.2009)" were run (see figure 5.33, 5.34) after storage for a few days.

For the two cyclovoltammograms in figure 5.33 the same settings were used. As "high level" +1,5 V and as "low level" -1,5 V were chosen. The step size was 0,01 V and the delay time was set to 1000 ms. With each cyclovoltammogram one cycle was run and took about 10 minutes.

With the cyclovoltammogram shown in figure 5.34 two cycles were run for about 10 minutes, and the settings were: "high level" +1,5 V, "low level" -1,5 V, "step size" 0,02 V, "delay time" 1000 ms.

The magenta polymer coated electrode of the transmittive device was connected to the plus output of the source measure unit and therefore the ECD got bleached, if the source measure unit displayed a positive voltage, and coloured, if the source measure unit displayed a negative voltage.

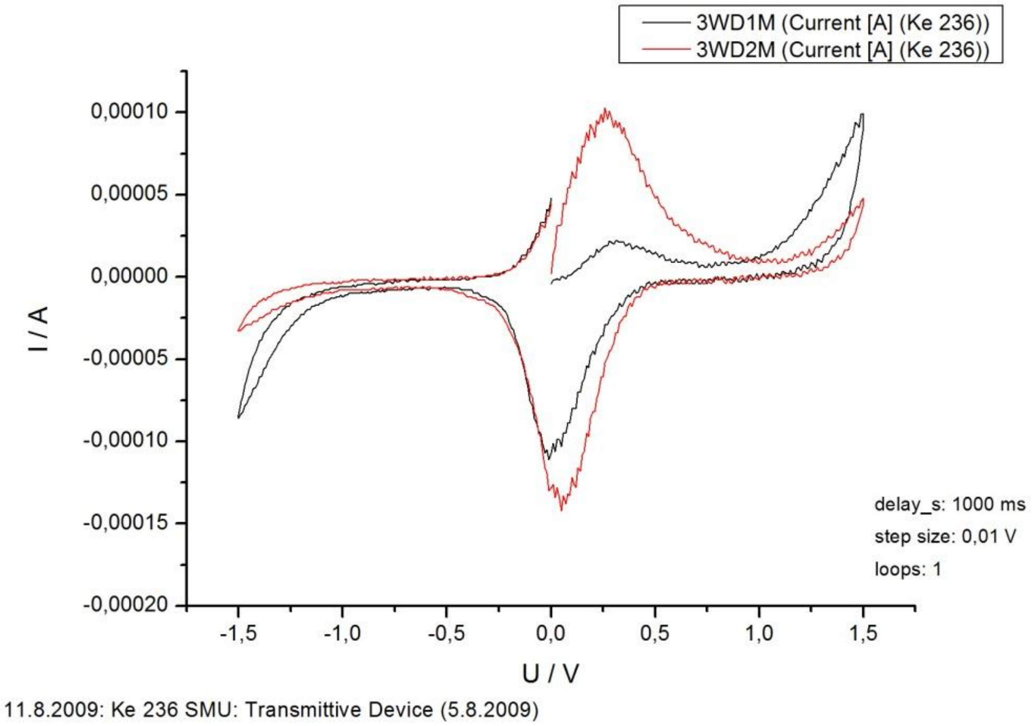


**Fig. 5.33. Cyclovoltammograms of the "Transmittive Device (5.8.2009)" measured on the 11.8.2009**

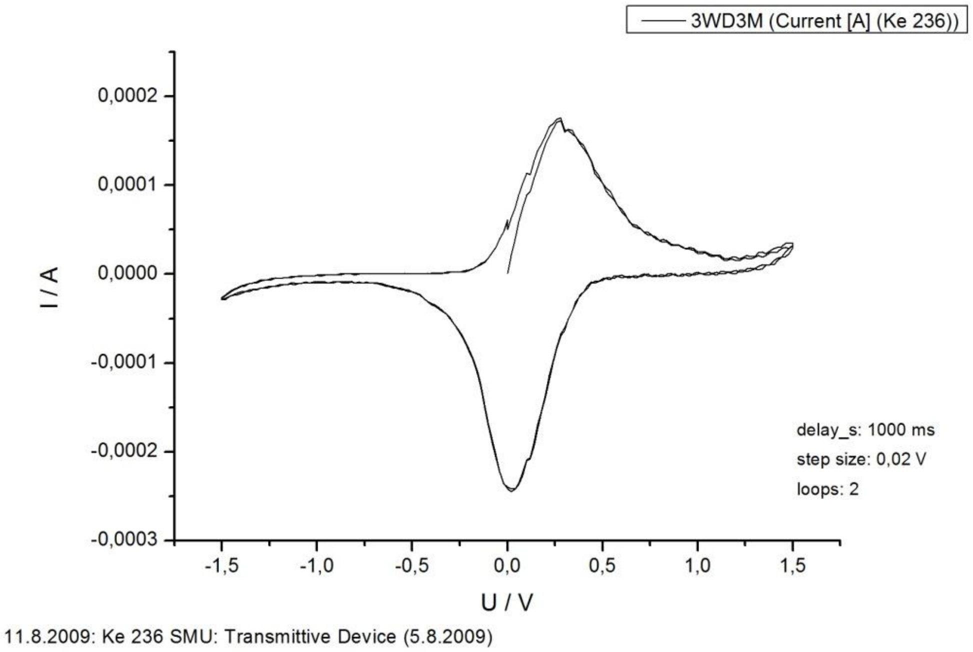


**Fig. 5.34. Cyclovoltammogram of the "Transmittive Device (5.8.2009)" measured on the 11.8.2009**

The interval between the end of a cycovoltammogram and the start of the following:

- 1st (3WD1M) to 2nd (3WD2M): 43 sec
- 2nd (3WD2M) to 3rd (3WD3M): 1 min 5 sec

Reflection spectra were measured during the first (3WD1M) and the second (3WD2M) cyclo-voltammogram.

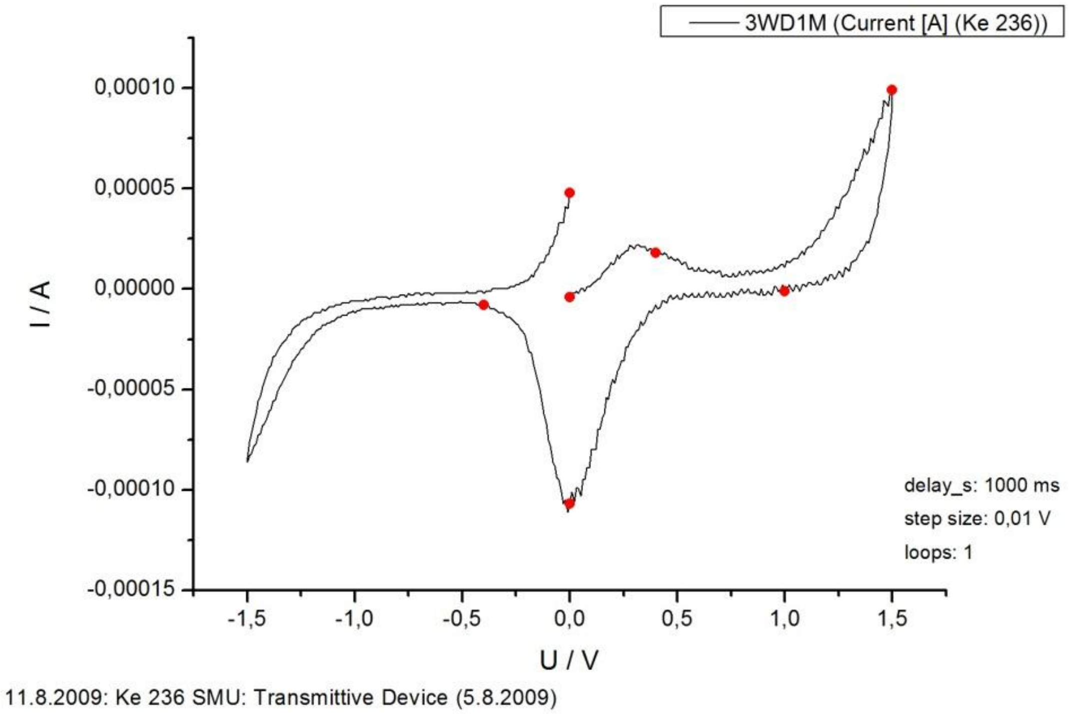
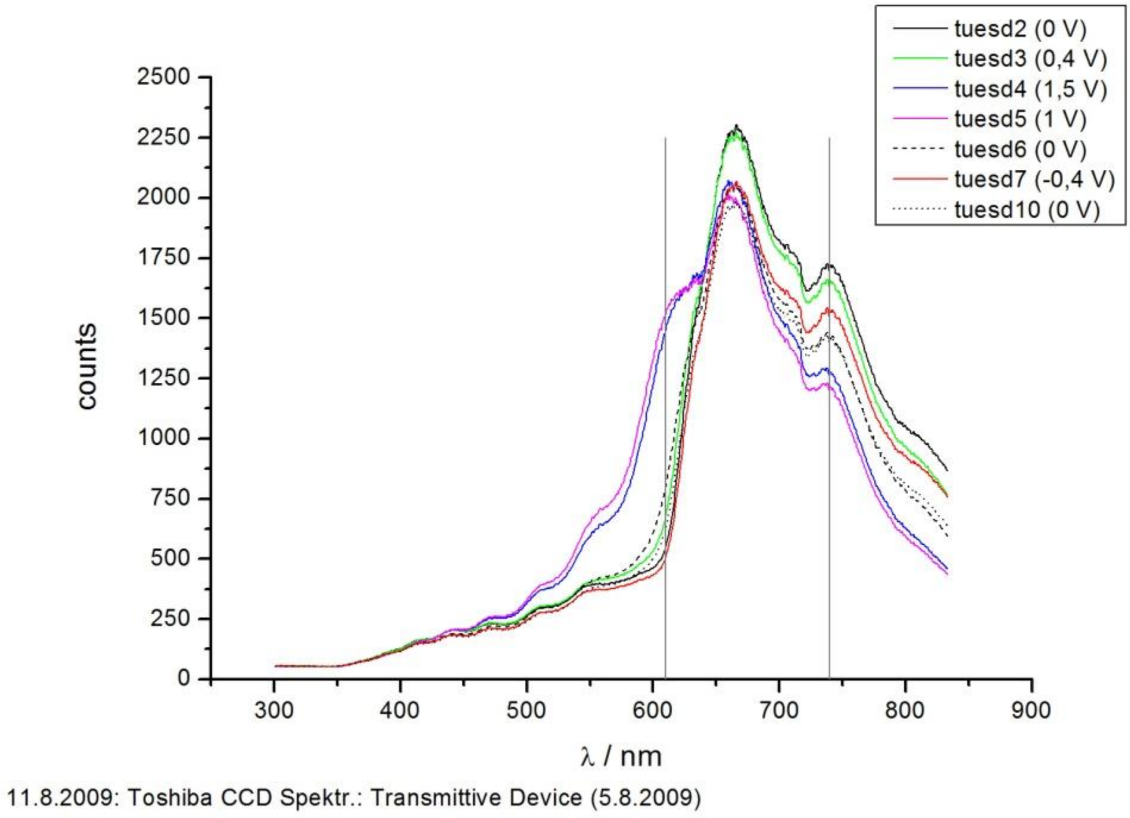


**Fig. 5.35. Cyclovoltammogram "3WD1M" of the "Transmittive Device (5.8.2009)" measured on the 11.8.2009; voltage positions are marked, where the reflection spectra shown in figure 5.36 have been measured**



11.8.2009: Toshiba CCD Spektr.: Transmittive Device (5.8.2009)

**Fig. 5.36. Reflection spectra of the “Transmittive Device (5.8.2009)” measured at different voltage values during the cyclovoltammogram “3WD1M” on the 11.8.2009**
**Vertical lines: chosen wavelengths for the calculation of colour modulation (table 5.7)**

**Table 5.7. Colour modulation at 610 nm and 740 nm calculated from the reflection spectra “tuesd5” and “tuesd7” of the “Transmittive Device (5.8.2009)” (see figure 5.36)**

| | tuesd5 | | tuesd7 | | Colour modulation |
|---|---|---|---|---|---|
| | counts | % | counts | % | % |
| 610 nm | 1515 ± 12 | 100 | 508 ± 12 | 34 ± 1 | 66 ± 1 |
| 740 nm | 1214 ± 12 | 100 | 1529 ± 12 | 126 ± 1 | 26 ± 1 |

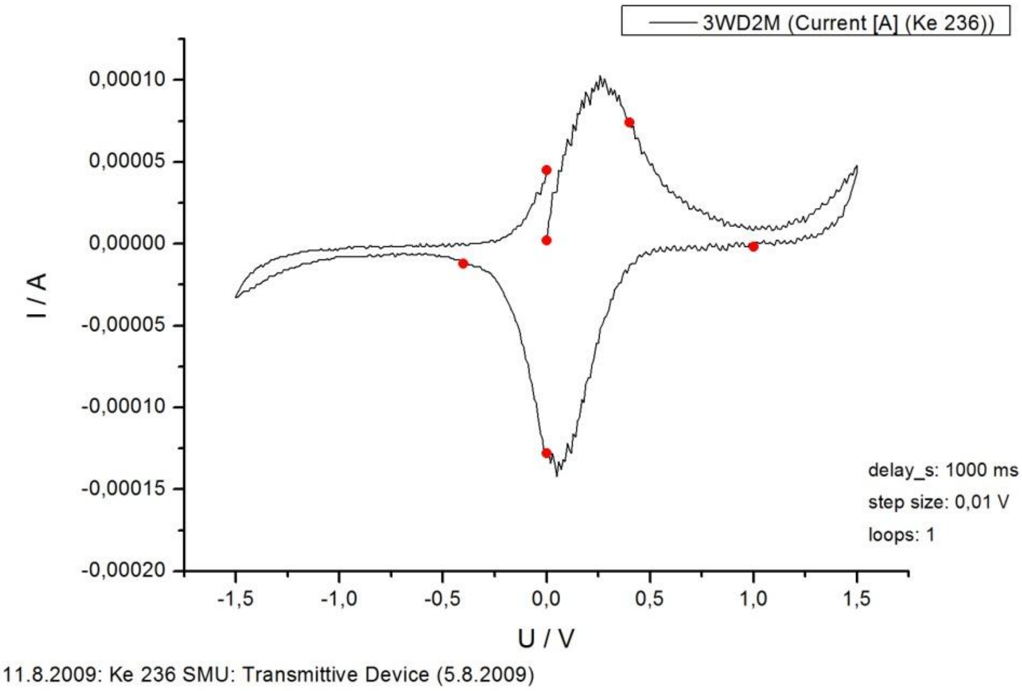


**Fig. 5.37. Cyclovoltammogram "3WD2M" of the "Transmittive Device (5.8.2009)" measured on the 11.8.2009; voltage positions are marked, where the reflection spectra shown in figure 5.38 have been measured**

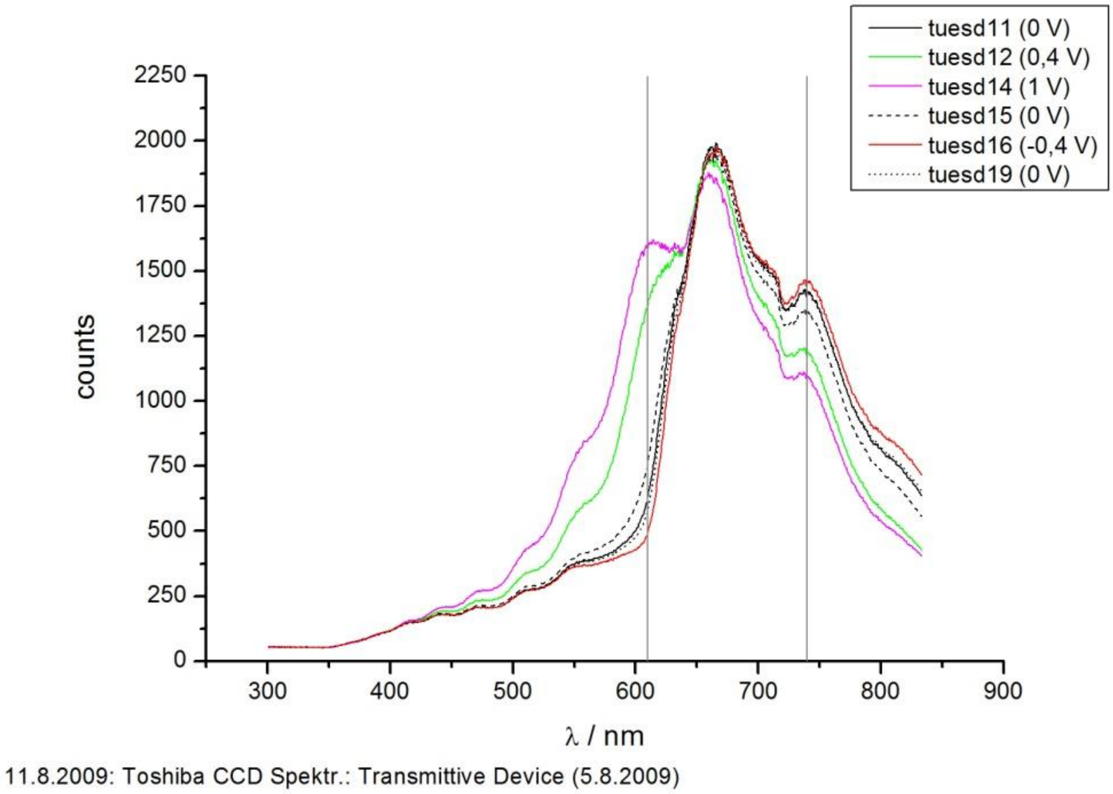


**Fig. 5.38. Reflection spectra of the "Transmittive Device (5.8.2009)" measured at different voltage values during the cyclovoltammogram "3WD2M" on the 11.8.2009**
**Vertical lines: chosen wavelengths for the calculation of colour modulation (table 5.8)**

**Table 5.8. Colour modulation at 610 nm and 740 nm calculated from the reflection spectra “tuesd14” and “tuesd16” of the “Transmittive Device (5.8.2009)” (see figure 5.38)**

| | tuesd14 | | tuesd16 | | Colour modulation |
|---|---|---|---|---|---|
| | counts | % | counts | % | % |
| 610 nm | 1588 ± 12 | 100 | 496 ± 12 | 31 ± 1 | 69 ± 1 |
| 740 nm | 1094 ± 12 | 100 | 1458 ± 12 | 133 ± 1 | 33 ± 1 |

More reflection spectra of the “Transmittive Device (5.8.2009)” were measured on the 1.9.2009 during the fourth (3WD_010909_4M) cyclovoltammogram (see figure 5.10).

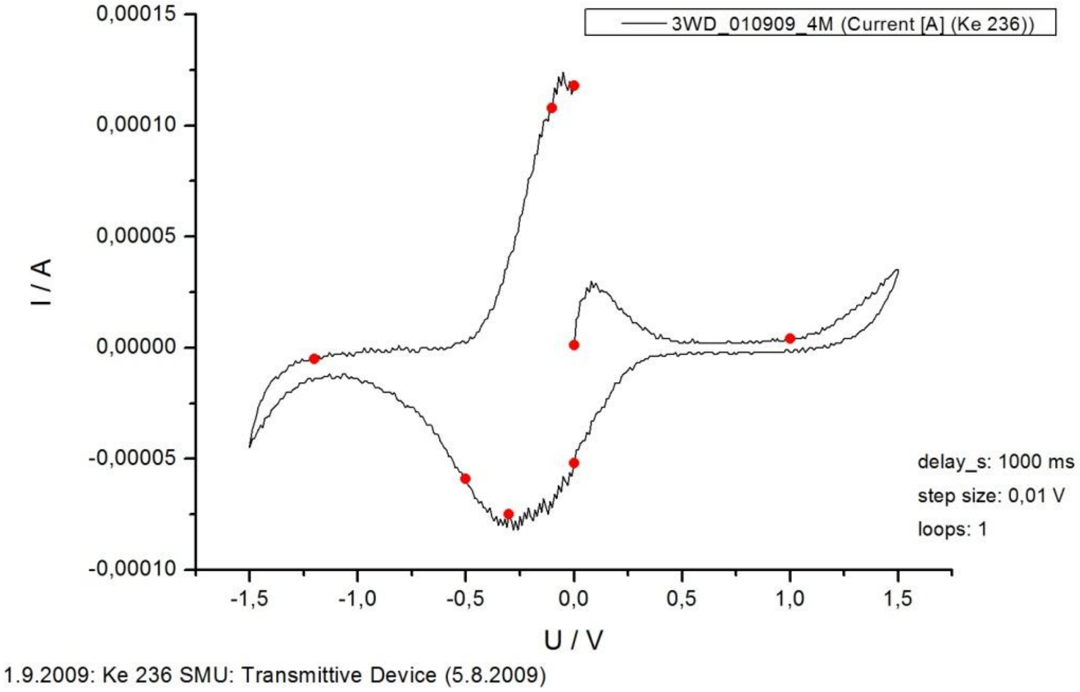
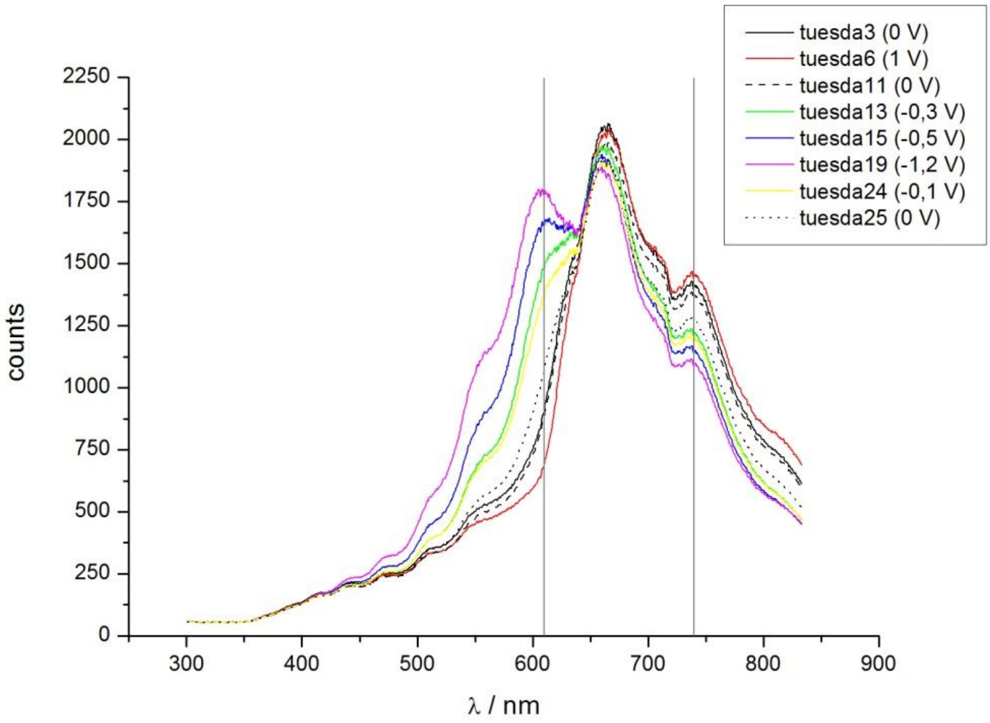


**Fig. 5.39. Cyclovoltammogram “3WD_010909_4M” of the “Transmittive Device (5.8.2009)” measured on the 1.9.2009; voltage positions are marked, where the reflection spectra shown in figure 5.40 have been measured**



1.9.2009: Toshiba CCD Spektr.: Transmittive Device (5.8.2009)

**Fig. 5.40. Reflection spectra of the "Transmittive Device (5.8.2009)" measured at different voltage values during the cyclovoltammogram "3WD_010909_4M" on the 1.9.2009**
**Vertical lines: chosen wavelengths for the calculation of colour modulation (table 5.9)**

**Table 5.9. Colour modulation at 610 nm and 740 nm calculated from the reflection spectra "tuesda19" and "tuesda6" of the "Transmittive Device (5.8.2009)" (see figure 5.40)**

| | tuesda19 | | tuesda6 | | Colour modulation |
|---|---|---|---|---|---|
| | counts | % | counts | % | % |
| 610 nm | 1775 ± 12 | 100 | 692 ± 12 | 39 ± 1 | 61 ± 1 |
| 740 nm | 1098 ± 12 | 100 | 1455 ± 12 | 133 ± 1 | 33 ± 1 |

*Measurement results of the "Transmittive Device (29.7.2009)" from figure 5.41 to figure 5.48:*

Cyclovoltammograms with the "Transmittive Device (29.7.2009)" were made (see figure 5.41, 5.42) after storage for a few days on the 11.8.2009, too.
The settings for the two cyclovoltammograms in figure 5.41 were: "high level" +1,5 V, "low level" -1,5 V, "step size" 0,01 V, "delay time" 1000 ms. With each cyclovoltammogram one cycle was run and took about 10 minutes.
With the cyclovoltammogram shown in figure 5.42 two cycles were run and the settings were: "high level" +1,5 V, "low level" -1,5 V, "step size" 0,02 V, "delay time" 1000 ms. As well it took about 10 minutes.
The transmittive electrochromic device bleached, if the source measure unit displayed a positive voltage, and coloured, if the source measure unit displayed a negative voltage.

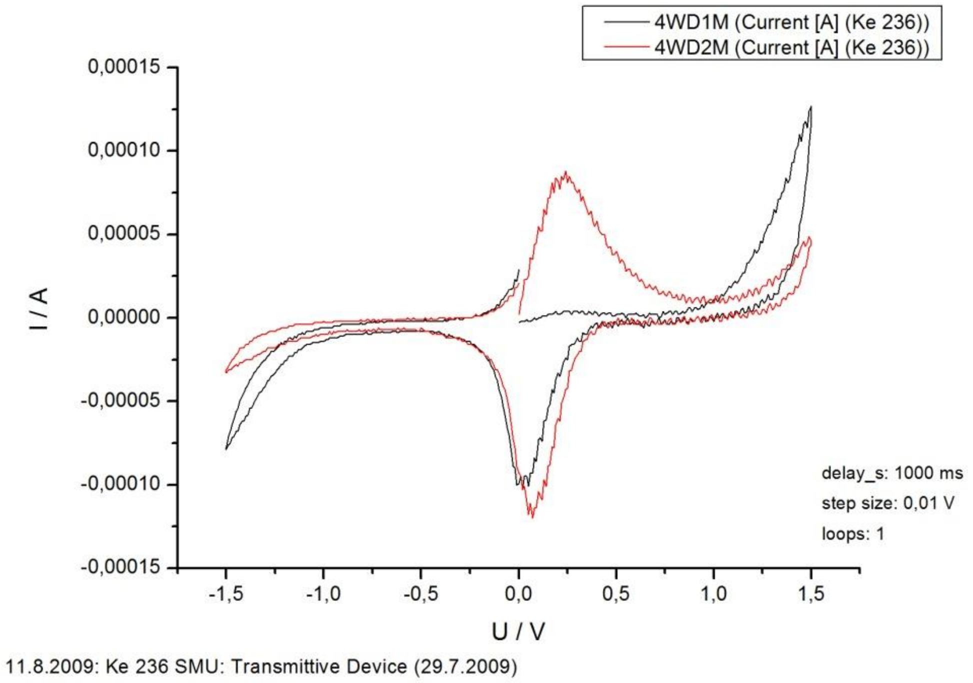


**Fig. 5.41. Cyclovoltammograms of the “Transmittive Device (29.7.2009)” measured on the 11.8.2009**

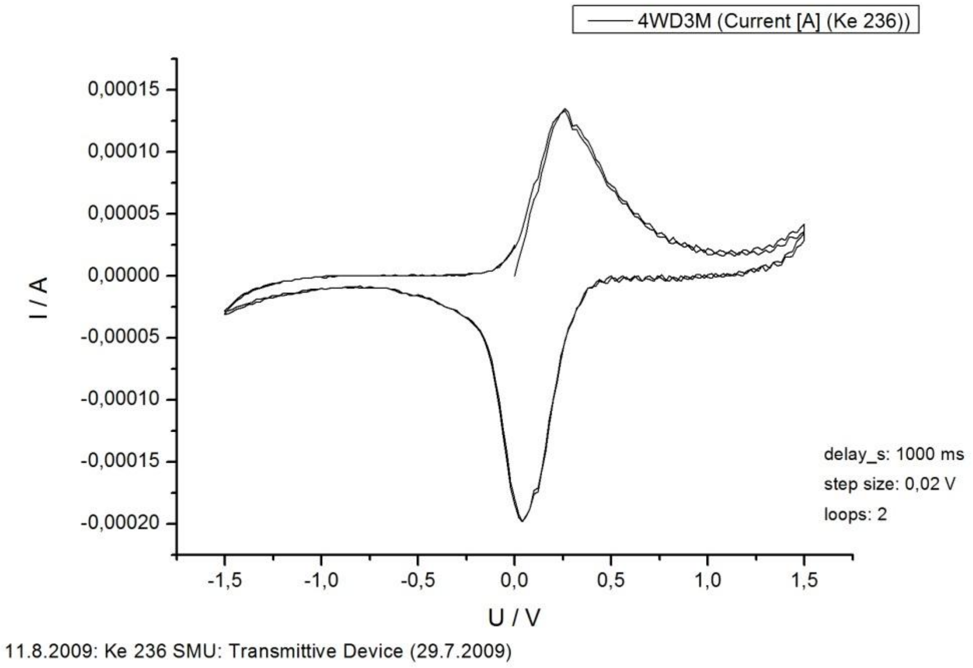


**Fig. 5.42. Cyclovoltammogram of the “Transmittive Device (29.7.2009)” measured on the 11.8.2009**

The interval between the end of a cycovoltammogram and the start of the following:

- 1st (4WD1M) to 2nd (4WD2M): 40 sec
- 2nd (4WD2M) to 3rd (4WD3M): 55 sec

Reflection spectra series taken during the first (4WD1M) and the second (4WD2M) cyclovoltammogram are presented in figure 5.44, 5.46. The corresponding voltage positions in the cyclovoltammograms are marked in figure 5.43, 5.45.

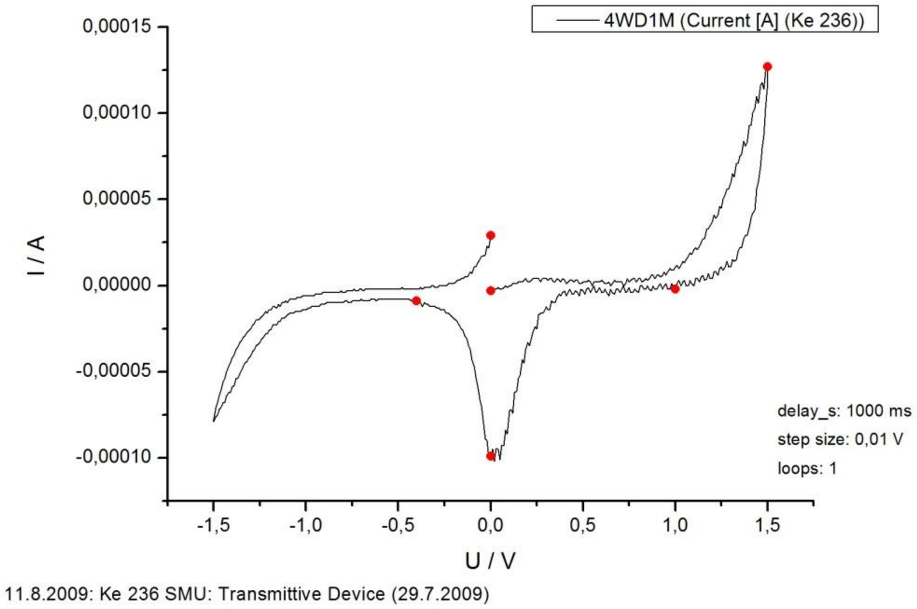


**Fig. 5.43. Cyclovoltammogram "4WD1M" of the "Transmittive Device (29.7.2009)" measured on the 11.8.2009; voltage positions are marked, where the reflection spectra shown in figure 5.44 have been measured**

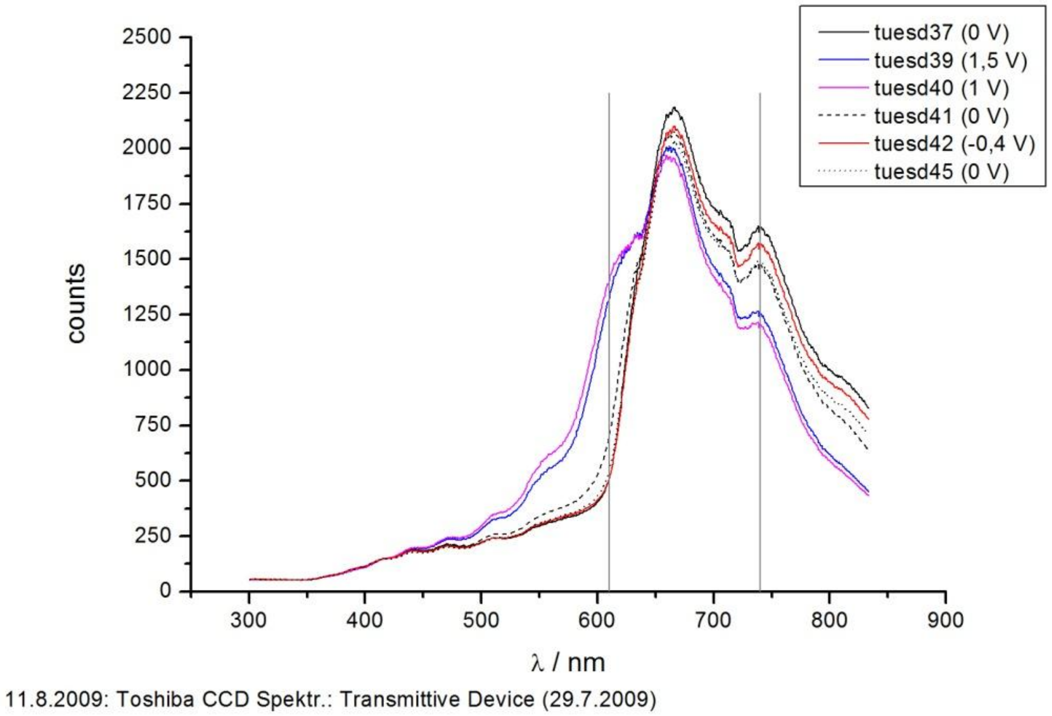


**Fig. 5.44. Reflection spectra of the "Transmittive Device (29.7.2009)" measured at different voltage values during the cyclovoltammogram "4WD1M" on the 11.8.2009**
**Vertical lines: chosen wavelengths for the calculation of colour modulation (table 5.10)**

**Table 5.10. Colour modulation at 610 nm and 740 nm calculated from the reflection spectra "tuesd40" and "tuesd42" of the "Transmittive Device (29.7.2009)" (see figure 5.44)**

| | tuesd40 | | tuesd42 | | Colour modulation |
|---|---|---|---|---|---|
| | counts | % | counts | % | % |
| 610 nm | 1400 ± 12 | 100 | 511 ± 12 | 37 ± 1 | 63 ± 1 |
| 740 nm | 1202 ± 12 | 100 | 1564 ± 12 | 130 ± 1 | 30 ± 1 |

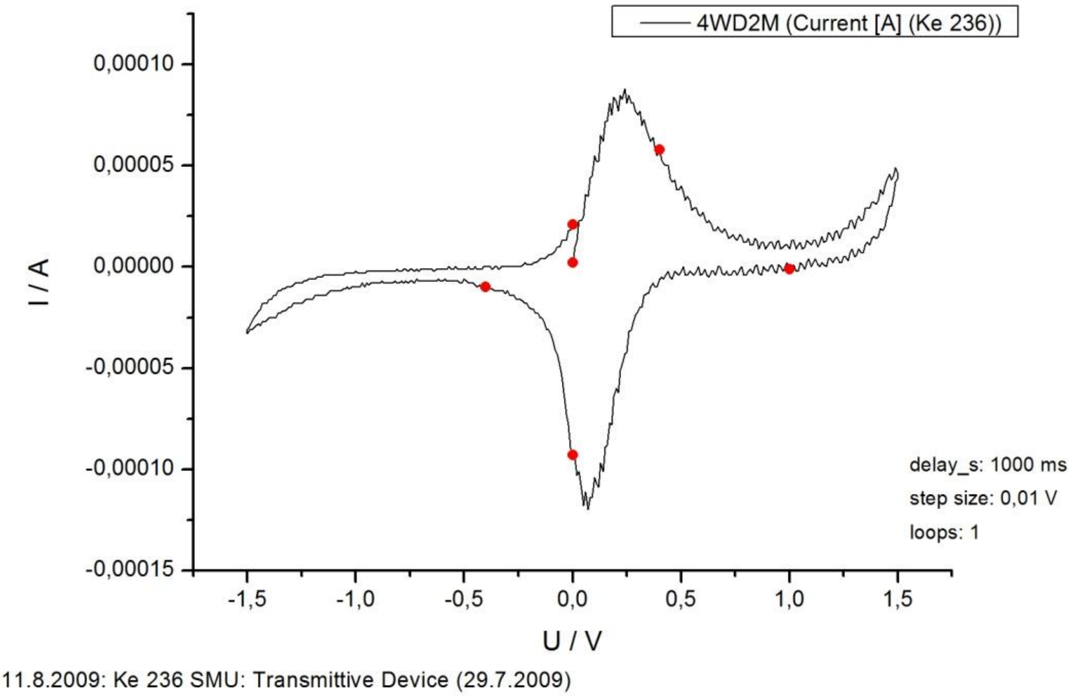
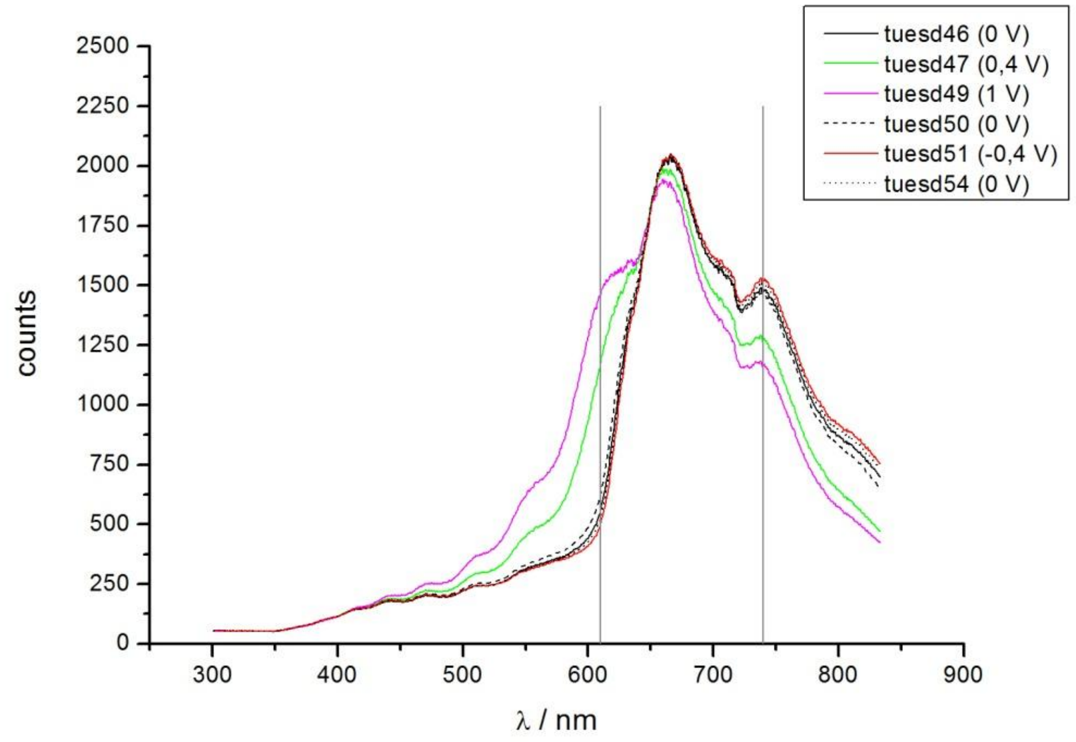


**Fig. 5.45. Cyclovoltammogram "4WD2M" of the "Transmittive Device (29.7.2009)" measured on the 11.8.2009; voltage positions are marked, where the reflection spectra shown in figure 5.46 have been measured**



11.8.2009: Toshiba CCD Spektr.: Transmittive Device (29.7.2009)

**Fig. 5.46. Reflection spectra of the "Transmittive Device (29.7.2009)" measured at different voltage values during the cyclovoltammogram "4WD2M" on the 11.8.2009**
**Vertical lines: chosen wavelengths for the calculation of colour modulation (table 5.11)**

**Table 5.11. Colour modulation at 610 nm and 740 nm calculated from the reflection spectra "tuesd49" and "tuesd51" of the "Transmittive Device (29.7.2009)" (see figure 5.46)**

| | tuesd49 | | tuesd51 | | Colour modulation |
|---|---|---|---|---|---|
| | counts | % | counts | % | % |
| 610 nm | 1459 ± 12 | 100 | 503 ± 12 | 34 ± 1 | 66 ± 1 |
| 740 nm | 1170 ± 12 | 100 | 1527 ± 12 | 131 ± 1 | 31 ± 1 |

On the 1.9.2009 reflection spectra of the "Transmittive Device (29.7.2009)" were measured during the fifth (4WD_010909_5M) cyclovoltammogram (see figure 5.13).

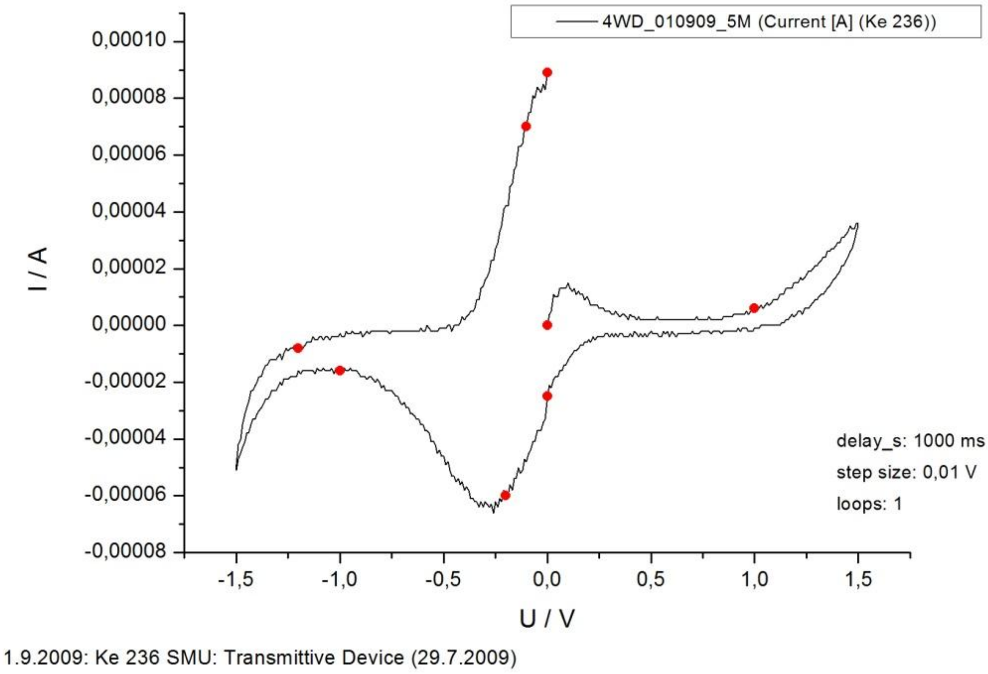


**Fig. 5.47. Cyclovoltammogram "4WD_010909_5M" of the "Transmittive Device (29.7.2009)" measured on the 1.9.2009; voltage positions are marked, where the reflection spectra shown in figure 5.48 have been measured**

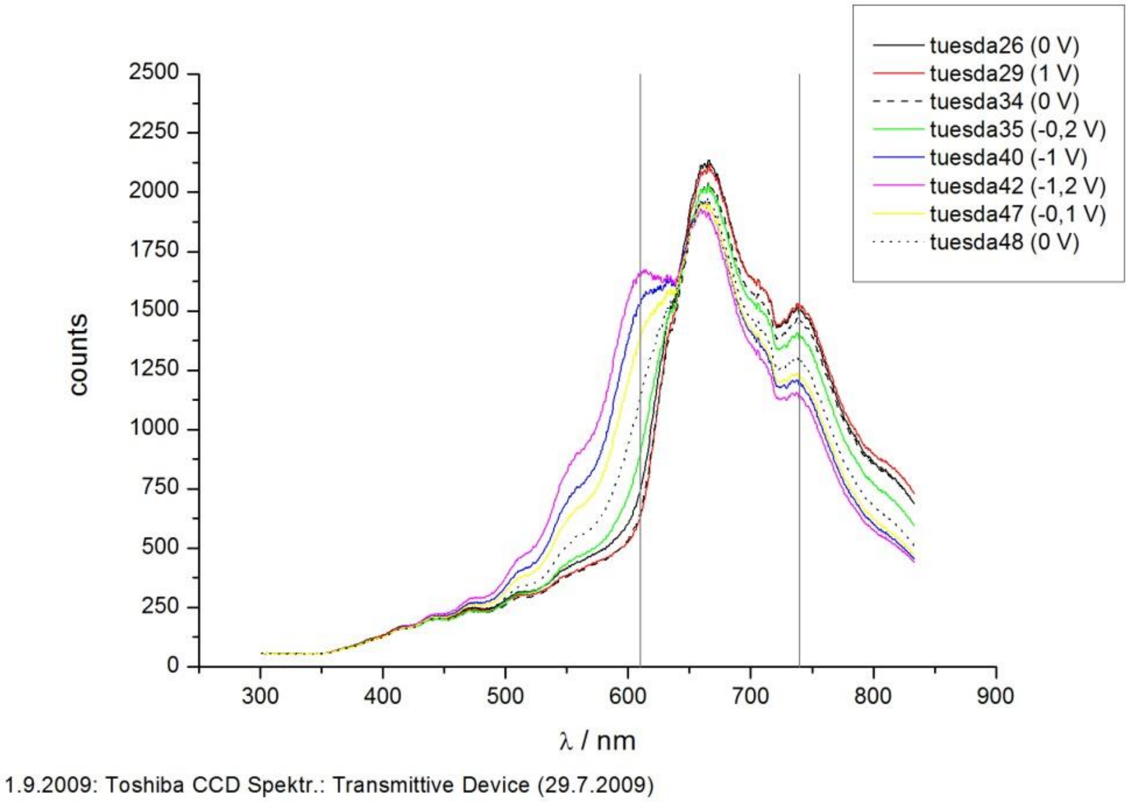


**Fig. 5.48. Reflection spectra of the "Transmittive Device (29.7.2009)" measured at different voltage values during the cyclovoltammogram "4WD_010909_5M" on the 1.9.2009**
**Vertical lines: chosen wavelengths for the calculation of colour modulation (table 5.12)**

**Table 5.12. Colour modulation at 610 nm and 740 nm calculated from the reflection spectra "tuesda42" and "tuesda29" of the "Transmittive Device (29.7.2009)" (see figure 5.48)**

| | tuesda42 | | tuesda29 | | Colour modulation |
|---|---|---|---|---|---|
| | counts | % | counts | % | % |
| 610 nm | 1644 ± 12 | 100 | 634 ± 12 | 39 ± 1 | 61 ± 1 |
| 740 nm | 1140 ± 12 | 100 | 1521 ± 12 | 133 ± 1 | 33 ± 1 |

## 5.2. DC voltage-pulse-operation

Another way to investigate electrochromic devices is to observe their behaviour during DC voltage-pulse-operation. For it a defined positive voltage value and a defined negative voltage value were set alternatively, each for the same period of time.

### 5.2.1. Setup for measurements

The setup is composed of an electrical assembly and a setup for optical measurements.

#### 5.2.1.1. Circuit diagram

A schematic circuit diagram is shown in figure 5.49. The electrochromic device is connected to a programmable pulse generator (OOR-X; Model 550 – 50 MHZ; Programmable Pulse Generator). For counting the pulses a universal counter (TTi; TF 830; 1.3 GHz; Universal Counter), which is connected to the "sync out" exit of the programmable pulse generator, is used. An oscilloscope (GW Cursor Readout Oscilloscope GOS-625) is integrated in the electrical setup to display the voltage.

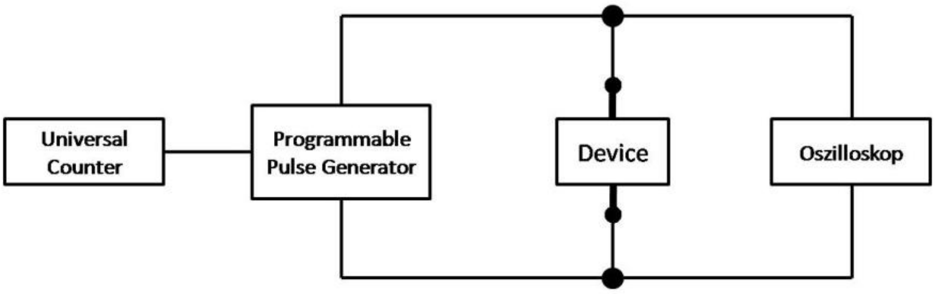


**Fig. 5.49. Schematic circuit diagram for DC-voltage pulse operation**

### 5.2.1.2. Setup for optical measurements

For the case of DC voltage-pulse-operation two ways of optical investigation were used: First visual investigation with photos and second investigation with a Si-photodiode. The two setups are described in the following subchapters.

#### 5.2.1.2.1. Investigation with a camera

The setup for visual investigation with a camera is the same as described in chapter 5.1.1.2.2.

#### 5.2.1.2.2. Investigation with a Si-photodiode

Figure 5.50 shows the setup for investigation with a Si-photodiode. In the centre of the photo is the “Reflectometer” (chapter 5.1.1.2.1) with a transmittive device lying on the base plate (with a gold mirror as background). The focusing lens is connected to a Si-photodiode, which is connected to a voltmeter (Keithley 175 Autoranging Multimeter).
As light source-supply a constant current source (Voltcraft 4005; set to 0,320 A) is used.

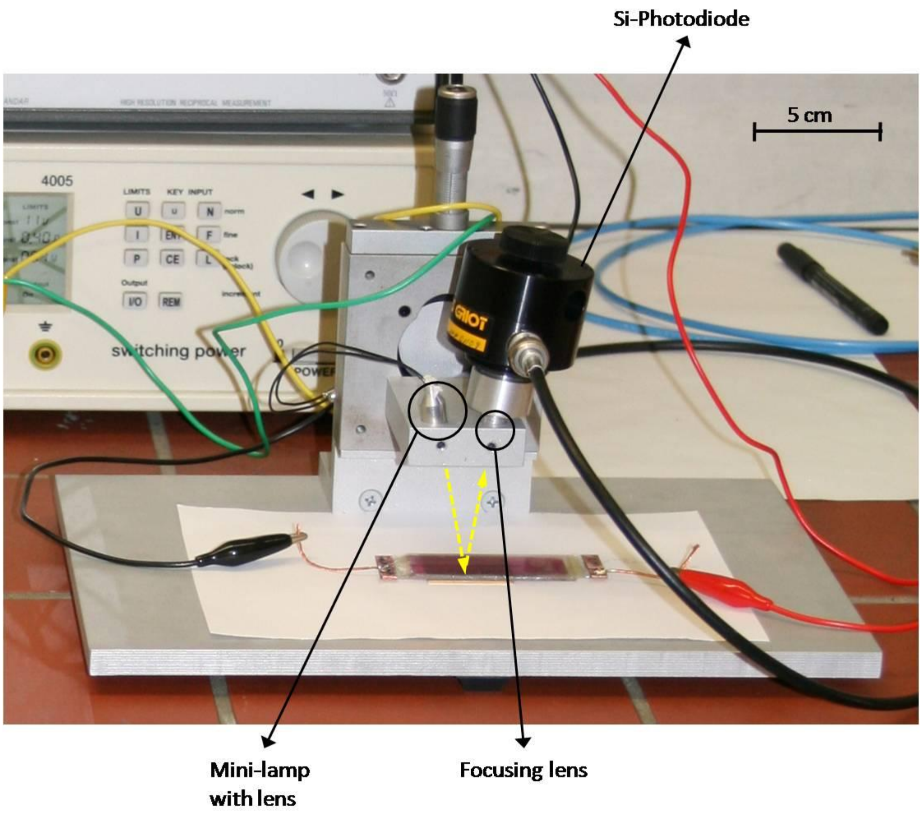


**Fig. 5.50. Setup for investigation with a Si-photodiode during DC voltage-pulse-operation**

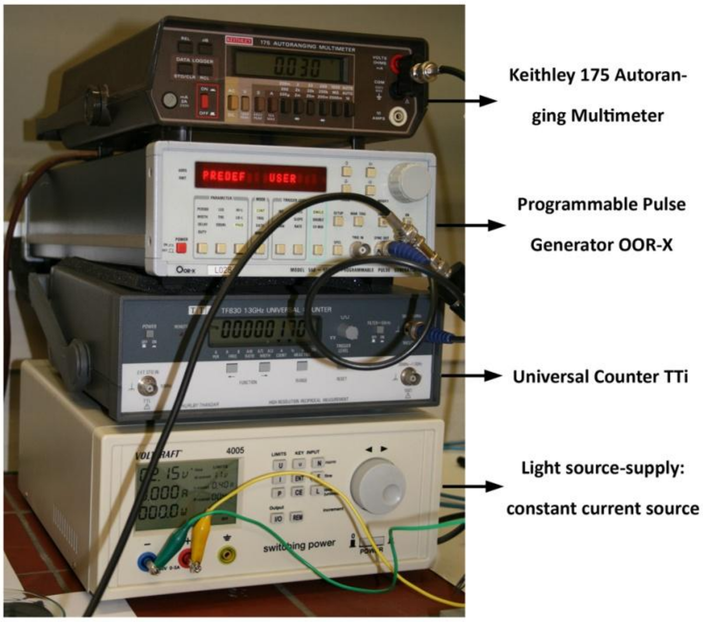


**Fig. 5.51. Instruments used for DC voltage-pulse-operation**

## 5.2.2. Influence of the pulse history for the electrochromic effect

During DC voltage-pulse-operation at different pulse numbers photos of the electrochromic devices were made on the one hand, the intensity of the light reflected by the electrochromic device were measured with a Si-photodiode on the other hand. In both cases the electrochromic devices had been in storage for one or more days before the experiments were carried out.

For all experiments the same settings of the programmable pulse generator were used:

[Period: 8000.0 ms, Width: 4000.0 ms, Delay: 0.0 ns, duty cycle off, LEE=TRE: 10.0 ms, LEE=TRE: 10.0 ms, EDGES EQ ON, HI-LEV: +0,75 V, LO-LEV: -0,75 V, PREDEF: USER, Mode: Cont, Pulse: Signal.]

During each pulse the voltage was first set to +1,5 V for 4000 ms and second to -1,5 V for again 4000 ms. The voltage was increased/decreased to +1,5 V/-1,5 V within 10 ms and then kept the same for the remaining time (3990 ms). So the duration of one pulse was 8000 ms.

Pulse histories of about hundreds or more consecutive pulses were carried out. The influence of the pulse history on the electrochromic effect was observed.

### 5.2.2.1. Photos

During DC voltage-pulse-operation at different pulse numbers photos of the electrochromic devices in the coloured and the bleached states were made. The electrochromic devices had been in storage for one or more days before.

*On the 7.9.2009 photos at different pulse numbers of the “Reflective Device (13.7.2009 – Nr.1)” were made (see figure 5.52).*

The working electrode of the reflective electrochromic device was connected to the minus output of the programmable pulse generator and therefore the ECD got coloured, if the programmable pulse generator supplied a positive voltage, and bleached, if the programmable pulse generator supplied a negative voltage.

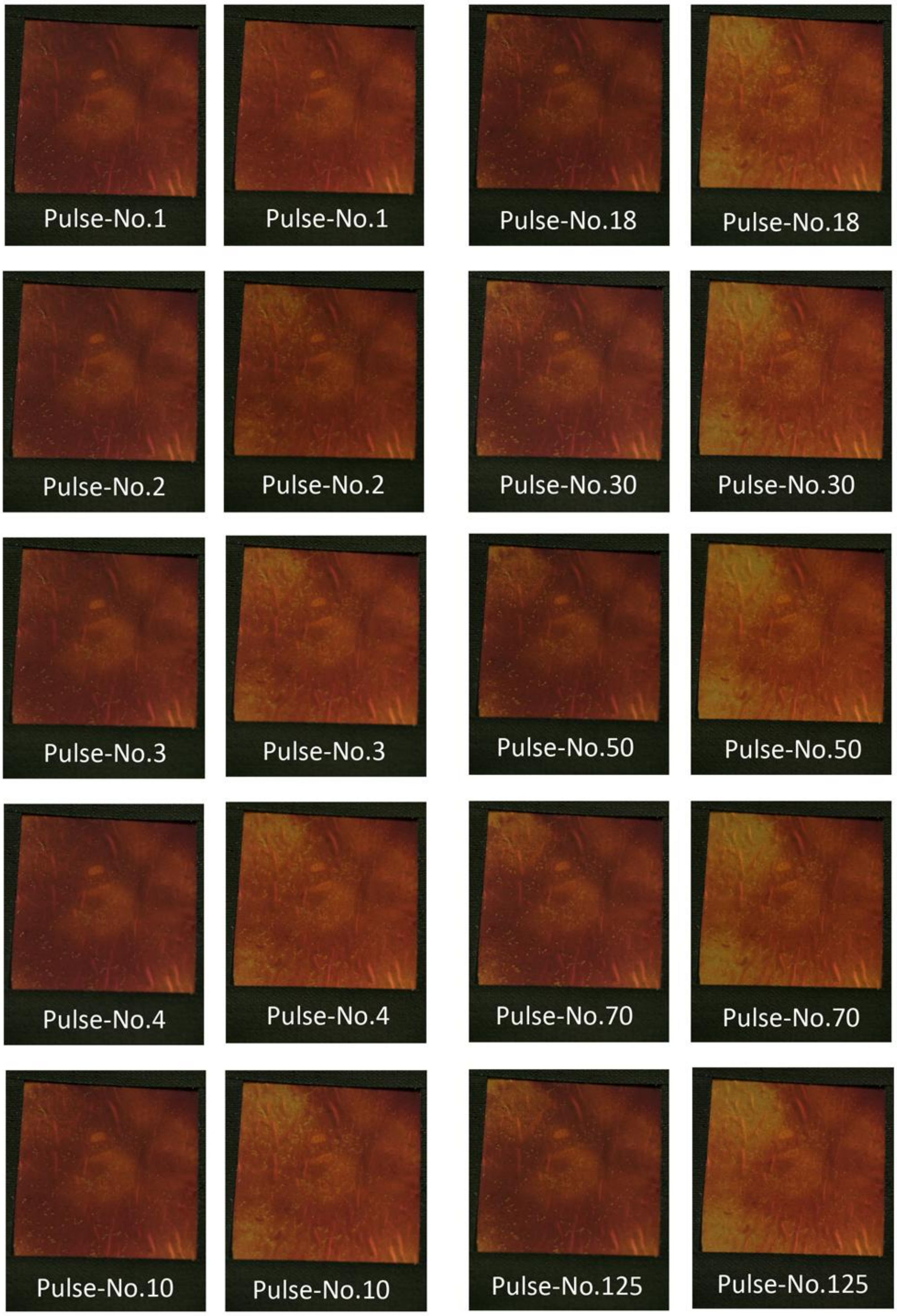


**Fig. 5.52. Photo series of the “Reflective Device (13.7.2009 – Nr.1)” taken at different pulse numbers during the DC voltage-pulse-operation on the 7.9.2009**
**left: coloured state**
**right: bleached state**

The bleaching of the “Reflective Device (13.7.2009 – Nr.1)” increased slowly over the pulse history but didn´t reach the maximum bleaching observed during cyclovoltammetry on the 28.8.2009 (see figure 5.6).
The colouration became less intensive and also didn´t reach the maximum colouration observed during cyclovoltammetry on the 28.8.2009.

*Figure 5.53 shows a photo series of the “Reflective Device (13.7.2009 – Nr.2)” taken at different pulse numbers during DC voltage-pulse-operation on the 7.9.2009.*

The reflective electrochromic device coloured, if the programmable pulse generator supplied a positive voltage, and bleached, if the programmable pulse generator supplied a negative voltage.

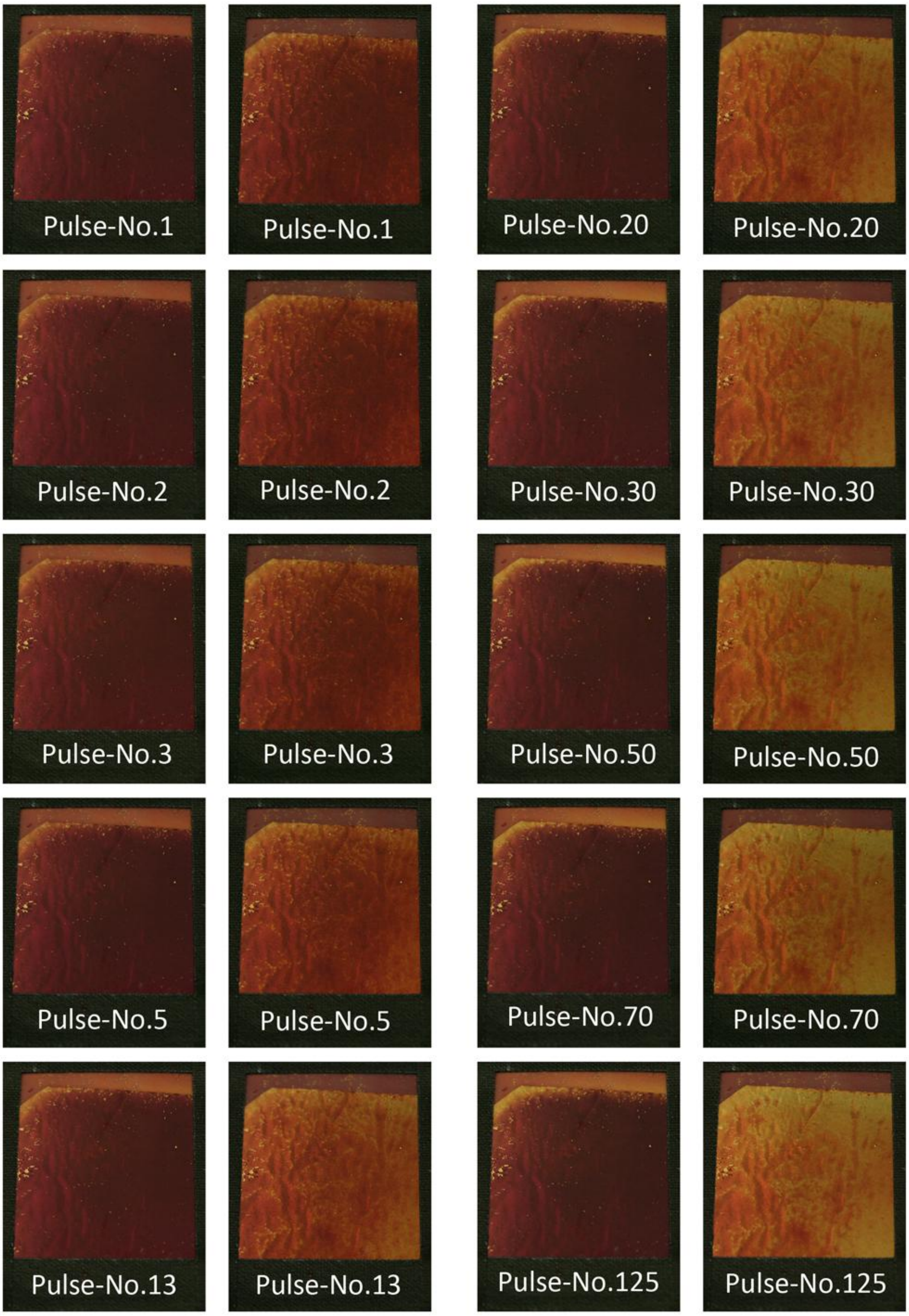


**Fig. 5.53. Photo series of the “Reflective Device (13.7.2009 – Nr.2)” taken at different pulse numbers during the DC voltage-pulse-operation on the 7.9.2009**
**left: coloured state**
**right: bleached state**

The bleaching of the “Reflective Device (13.7.2009 – Nr.2)” increased clearly over the first 50 pulses and then stayed almost the same. The bleached state didn´t reach the maximum bleaching observed during cyclovoltammetry on the 31.8.2009 (see figure 5.9).

The colouration stayed almost the same during the whole pulse history and was as intensive as on the 31.8.2009 during cyclovoltammetry.

*On the 10.9.2009 photos of the "Transmittive Device (5.8.2009)" at different pulse numbers were taken (see figure 5.54).*

The magenta polymer coated electrode of the transmittive device was connected to the minus output of the programmable pulse generator and therefore the ECD got coloured, if the programmable pulse generator supplied a positive voltage, and bleached, if the programmable pulse generator supplied a negative voltage.

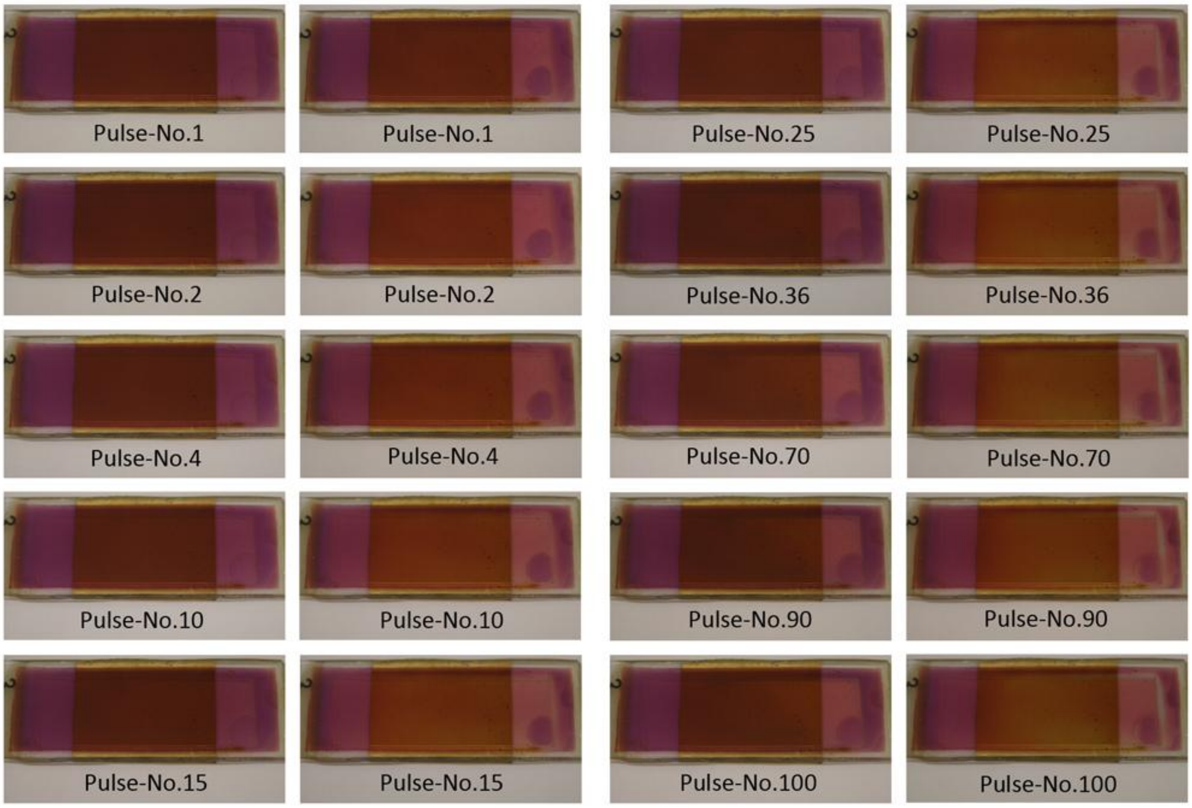


**Fig. 5.54. Photo series of the "Transmittive Device (5.8.2009)" taken at different pulse numbers during the DC voltage-pulse-operation on the 10.9.2009**
**left: coloured state**
**right: bleached state**

The bleaching of the "Transmittive Device (5.8.2009)" increased slowly over the pulse history and was by far not as strong as the maximum bleaching observed during cyclovoltammetry on the 1.9.2009 (see figure 5.12).
The coloured state was for the first few pulses as intense as the maximum colouration observed during cyclovoltammetry on the 1.9.2009, but became weaker and weaker over the remaining pulse history.

In figure 5.54 an air bubble in the right hand lower corner of the "Transmittive Device (5.8.2009)" is visible. This air bubble came into being only after photos had been taken on the 1.9.2009 (see figure 5.12, cyclovoltammetry: no air bubble noticeable).
Maybe the electrochromic device wasn´t hermetically sealed.

*Photos of the "Transmittive Device (29.7.2009)" were taken at different pulse numbers on the 10.9.2009. A photo series is shown in figure 5.55.*

The transmittive electrochromic device coloured, if the programmable pulse generator supplied a positive voltage, and bleached, if the programmable pulse generator supplied a negative voltage.

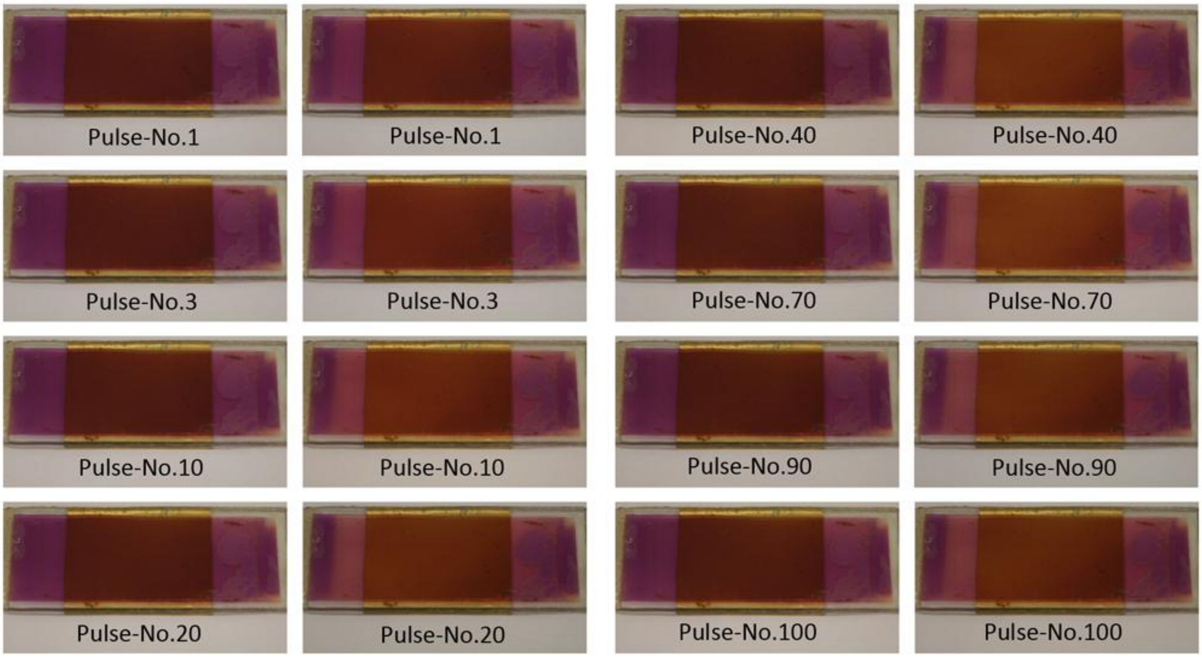


**Fig. 5.55. Photo series of the "Transmittive Device (29.7.2009)" taken at different pulse numbers during the DC voltage-pulse-operation on the 10.9.2009**
**left: coloured state**
**right: bleached state**

Until the first 20 pulses the bleaching of the "Transmittive Device (29.7.2009)" increased slowly, then it stayed almost the same over the remaining pulse history.
The state of maximum bleaching observed during cyclovoltammetry on the 1.9.2009 (see figure 5.15) by far wasn´t reached.
The colouration over the first few pulses was as intensive as on the 1.9.2009 during cyclovoltammetry. Over the remaining pulse history the colouration became just a little weaker.

The air bubble on the right hand side of the "Transmittive Device (29.7.2009)" in figure 5.55 was larger than on the photos taken on the 1.9.2009 (see figure 5.15).
Probably this electrochromic device, too, has not been airtight.

### 5.2.2.2. Si-photodiode

The intensity of the light reflected by the electrochromic device was measured with a Si-photodiode. Therefore the Si-photodiode was connected to a voltmeter (Keithley 175 Autoranging Multimeter), and during DC voltage-pulse-operation at different pulse numbers the measured voltage value of the coloured state and the bleached state respectively were read from the multimeter display.

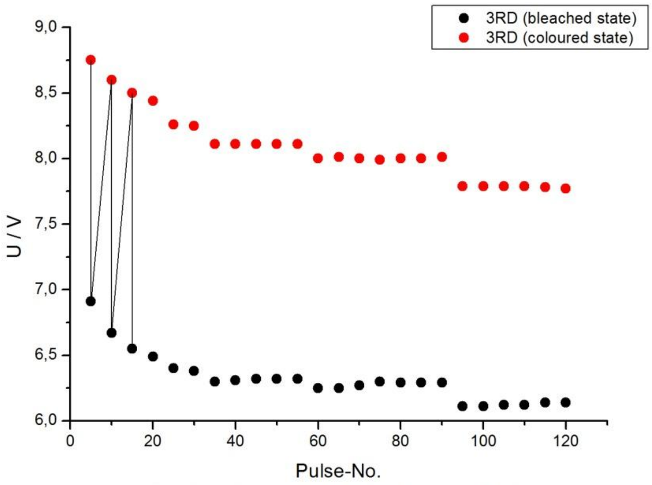
These experiments were carried out with the two reflective electrochromic devices, “Reflective Device (13.7.2009 – Nr.1)” and “Reflective Device (13.7.2009 – Nr.2)”. The reflective electrochromic devices had been in storage for one or more days before the experiments were carried out.

*The measurement results of the “Reflective Device (13.7.2009 – Nr.1)” from the 17.9.2009 are presented in table 5.13 and figure 5.56.*

The working electrode of the reflective electrochromic device was connected to the minus output of the programmable pulse generator and therefore the ECD got coloured, if the programmable pulse generator supplied a positive voltage, and bleached, if the programmable pulse generator supplied a negative voltage.

**Table 5.13. Voltage values of the Si-photodiode at different pulse numbers measured during DC voltage-pulse-operation of the “Reflective Device (13.7.2009 – Nr.1)” with a multimeter on the 17.9.2009.**

| Pulse-No. | Voltage U / V ΔU = ± 0,05 V | | Pulse-No. | Voltage U / V ΔU = ± 0,05 V | |
|---|---|---|---|---|---|
| | Coloured state | Bleached state | | Coloured state | Bleached state |
| 5 | 8,75 | 6,91 | 65 | 8,01 | 6,25 |
| 10 | 8,60 | 6,67 | 70 | 8,00 | 6,27 |
| 15 | 8,50 | 6,55 | 75 | 7,99 | 6,30 |
| 20 | 8,44 | 6,49 | 80 | 8,00 | 6,29 |
| 25 | 8,26 | 6,40 | 85 | 8,00 | 6,29 |
| 30 | 8,25 | 6,38 | 90 | 8,01 | 6,29 |
| 35 | 8,11 | 6,30 | 95 | 7,79 | 6,11 |
| 40 | 8,11 | 6,31 | 100 | 7,79 | 6,11 |
| 45 | 8,11 | 6,32 | 105 | 7,79 | 6,12 |
| 50 | 8,11 | 6,32 | 110 | 7,79 | 6,12 |
| 55 | 8,11 | 6,32 | 115 | 7,78 | 6,14 |
| 60 | 8,00 | 6,25 | 120 | 7,77 | 6,14 |



17.9.2009: Pulshistorie mit Photodiode u. Keithley 175: Reflective Device (13.7.2009 - Nr.1)

**Fig. 5.56. Voltage value of the Si-photodiode in dependence on the pulse number (“Reflective Device (13.7.2009 – Nr.1)”, 17.9.2009):**
**red dots: coloured state**
**black dots: bleached state**

The voltage lift between the coloured state and the bleached state was calculated for each pulse listed in table 5.13.

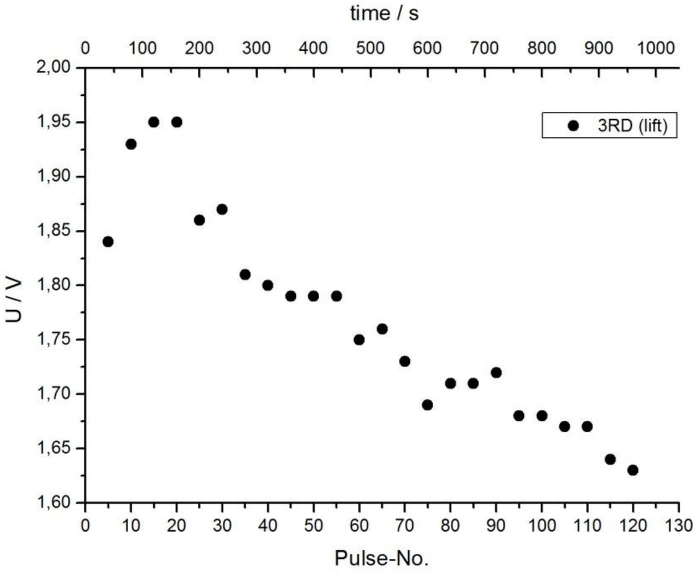
$$\boldsymbol{U_{lift} = U_{coloured} - U_{bleached}}$$

$\boldsymbol{U_{lift}}$...voltage lift between the coloured and the bleached state
$\boldsymbol{U_{coloured}}$...voltage value of the Si-photodiode in the coloured state
$\boldsymbol{U_{bleached}}$...voltage value of the Si-photodiode in the bleached state

The calculated values of the voltage lift for each pulse listed in table 5.13 of the "Reflective Device (13.7.2009 – Nr.1)" are presented in table 5.14 and figure 5.57.

**Table 5.14. Voltage lift $U_{lift}$ between the coloured and the bleached state of the "Reflective Device (13.7.2009 – Nr.1)", calculated from the voltage values of the Si-photodiode at the coloured and the bleached state presented in table 5.13 and figure 5.56.**

| Pulse-No. | $\boldsymbol{U_{lift}}$ / V<br>$\Delta U_{lift}$ = ± 0,1 V | Pulse-No. | $\boldsymbol{U_{lift}}$ / V<br>$\Delta U_{lift}$ = ± 0,1 V |
|---|---|---|---|
| 5 | 1,84 | 65 | 1,76 |
| 10 | 1,93 | 70 | 1,73 |
| 15 | 1,95 | 75 | 1,69 |
| 20 | 1,95 | 80 | 1,71 |
| 25 | 1,86 | 85 | 1,71 |
| 30 | 1,87 | 90 | 1,72 |
| 35 | 1,81 | 95 | 1,68 |
| 40 | 1,80 | 100 | 1,68 |
| 45 | 1,79 | 105 | 1,67 |
| 50 | 1,79 | 110 | 1,67 |
| 55 | 1,79 | 115 | 1,64 |
| 60 | 1,75 | 120 | 1,63 |



17.9.2009: Pulshistorie mit Photodiode u. Keithley 175: Reflective Device (13.7.2009 - Nr.1)

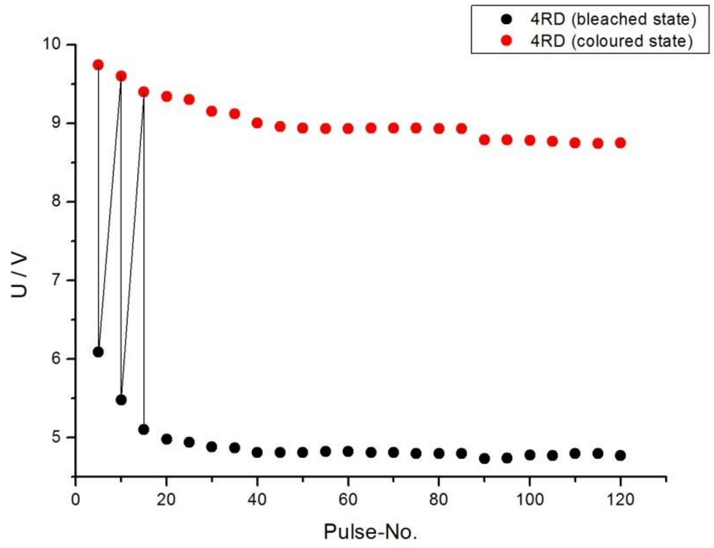
**Fig. 5.57. Voltage lift between the coloured and the bleached state of the "Reflective Device (13.7.2009 – Nr.1)" in dependence on the pulse number and the time**

*The measurement results of the "Reflective Device (13.7.2009 – Nr.2)" from the 17.9.2009 are presented in table 5.15 and figure 5.58.*

The reflective electrochromic device coloured, if the programmable pulse generator supplied a positive voltage, and bleached, if the programmable pulse generator supplied a negative voltage.

**Table 5.15. Voltage values of the Si-photodiode at different pulse numbers measured during DC voltage-pulse-operation of the "Reflective Device (13.7.2009 – Nr.2)" with a multimeter on the 17.9.2009.**

| Pulse-No. | Voltage U / V<br>ΔU = ± 0,05 V | | Pulse-No. | Voltage U / V<br>ΔU = ± 0,05 V | |
|---|---|---|---|---|---|
| | Coloured state | Bleached state | | Coloured state | Bleached state |
| 5 | 9,74 | 6,09 | 65 | 8,94 | 4,81 |
| 10 | 9,60 | 5,48 | 70 | 8,94 | 4,81 |
| 15 | 9,40 | 5,10 | 75 | 8,94 | 4,80 |
| 20 | 9,34 | 4,98 | 80 | 8,93 | 4,80 |
| 25 | 9,30 | 4,94 | 85 | 8,93 | 4,80 |
| 30 | 9,15 | 4,88 | 90 | 8,79 | 4,73 |
| 35 | 9,12 | 4,87 | 95 | 8,79, | 4,74 |
| 40 | 9,00 | 4,81 | 100 | 8,78 | 4,78 |
| 45 | 8,96 | 4,81 | 105 | 8,77 | 4,77 |
| 50 | 8,94 | 4,81 | 110 | 8,75 | 4,80 |
| 55 | 8,93 | 4,82 | 115 | 8,74 | 4,80 |
| 60 | 8,93 | 4,82 | 120 | 8,75 | 4,77 |



17.9.2009: Pulshistorie mit Photodiode u. Keithley 175: Reflective Device (13.7.2009 - Nr.2)

**Fig. 5.58. Voltage value of the Si-photodiode in dependence on the pulse number ("Reflective Device (13.7.2009 – Nr.2)", 17.9.2009):**
**red dots: coloured state**
**black dots: bleached state**

The calculated values of the voltage lift for each pulse listed in table 5.15 of the "Reflective Device (13.7.2009 – Nr.2)" are presented in table 5.16 and figure 5.59.

**Table 5.16. Voltage lift $U_{lift}$ between the coloured and the bleached state of the "Reflective Device (13.7.2009 – Nr.2)", calculated from the voltage values of the Si-photodiode at the coloured and the bleached state presented in table 5.15 and figure 5.58.**

| Pulse-No. | $U_{lift}$ / V $\Delta U_{lift}$ = ± 0,1 V | Pulse-No. | $U_{lift}$ / V $\Delta U_{lift}$ = ± 0,1 V |
|---|---|---|---|
| 5 | 3,65 | 65 | 4,13 |
| 10 | 4,12 | 70 | 4,13 |
| 15 | 4,30 | 75 | 4,14 |
| 20 | 4,36 | 80 | 4,13 |
| 25 | 4,36 | 85 | 4,13 |
| 30 | 4,27 | 90 | 4,06 |
| 35 | 4,25 | 95 | 4,05 |
| 40 | 4,19 | 100 | 4,00 |
| 45 | 4,15 | 105 | 4,00 |
| 50 | 4,13 | 110 | 3,95 |
| 55 | 4,11 | 115 | 3,94 |
| 60 | 4,11 | 120 | 3,98 |

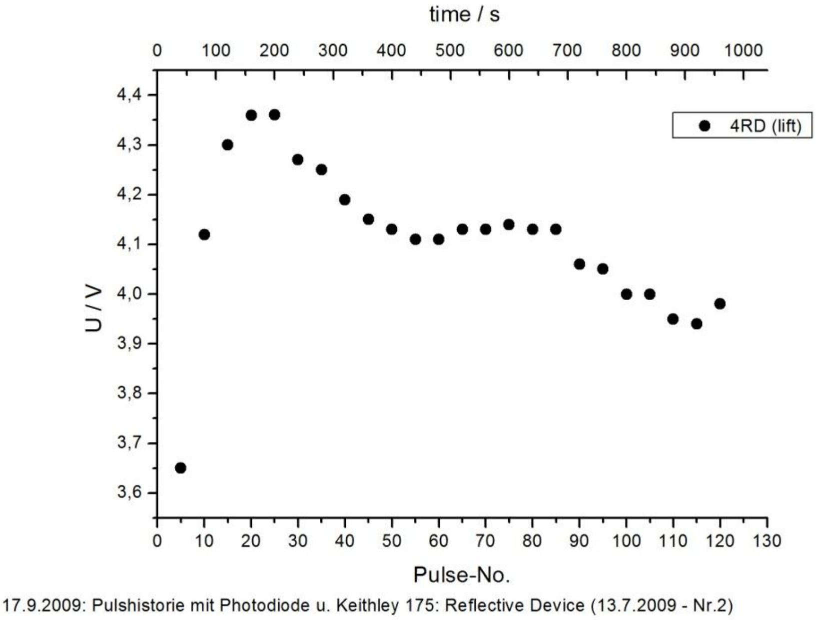


**Fig. 5.59. Voltage lift between the coloured and the bleached state of the "Reflective Device (13.7.2009 – Nr.2)" in dependence on the pulse number and the time**

## 5.3. Operation with DC voltage-pulse-packets

This method of investigation of electrochromic devices is similar to the DC voltage-pulse-operation: A defined positive voltage value and a defined negative voltage value are set alternatively for a given time. In contrast to the DC voltage-pulse-operation only pulse-packets, for example 5 consecutive pulses, are observed, not the whole pulse history.

### 5.3.1. Setup for measurements

The setup is composed of an electrical assembly and a setup for optical measurements.

#### 5.3.1.1. Circuit diagram

Figure 5.60 shows a schematic circuit diagram: The Keithley 236 source measure unit is used as a pulse voltage source. $R_I$ is a current sense resistor (12,4 Ω). For these measurements an oscilloscope (UEI; Handyscope HS4) was used. "CH U" is the first channel of the oscilloscope and "CH I" is the second channel of the oscilloscope.

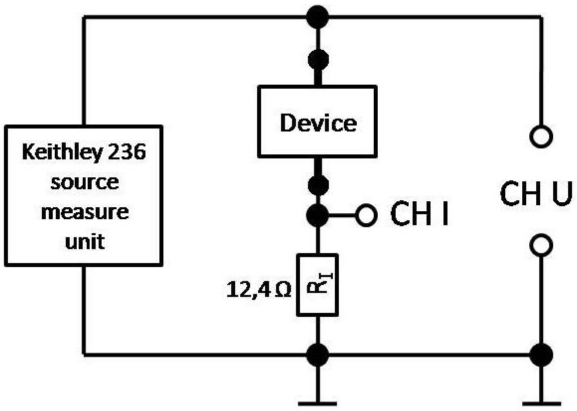


**Fig. 5.60. Schematic circuit diagramm for operation with DC voltage-pulse-packets**

#### 5.3.1.2. Setup for optical measurements

Figure 5.61 shows the setup for optical measurements. In the centre of the photo is the "Reflectometer" with a transmittive device lying on the base plate with a gold mirror as background. The focusing lens is connected to a Si-photodiode, which is connected to the third channel ("CH Si") of the oscilloscope.

The oscilloscope is linked via USB to a computer and the monitor of the computer serves as display for the oscilloscope.

The light source-supply (constant current source – Voltcraft 4005) was set to 0,400 A.

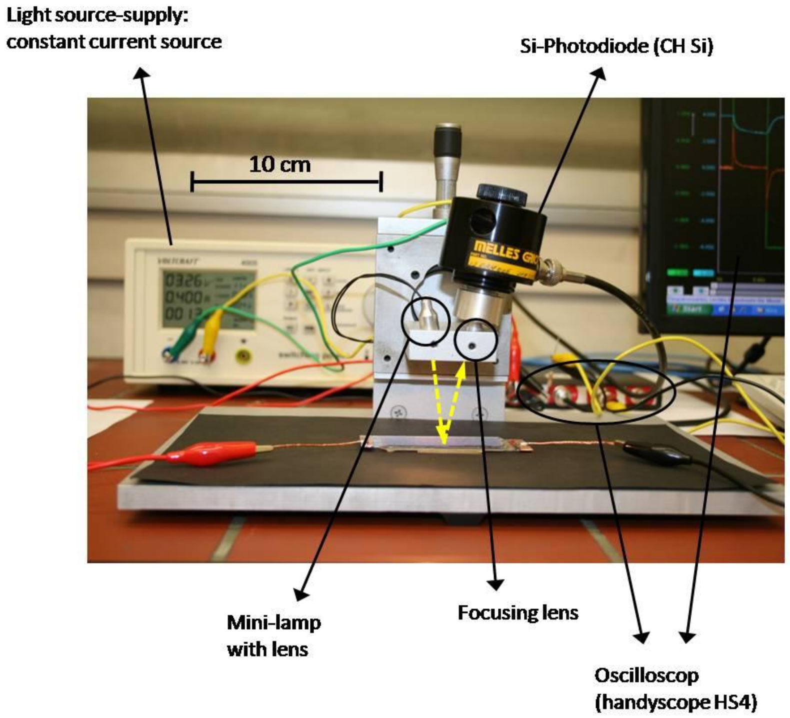
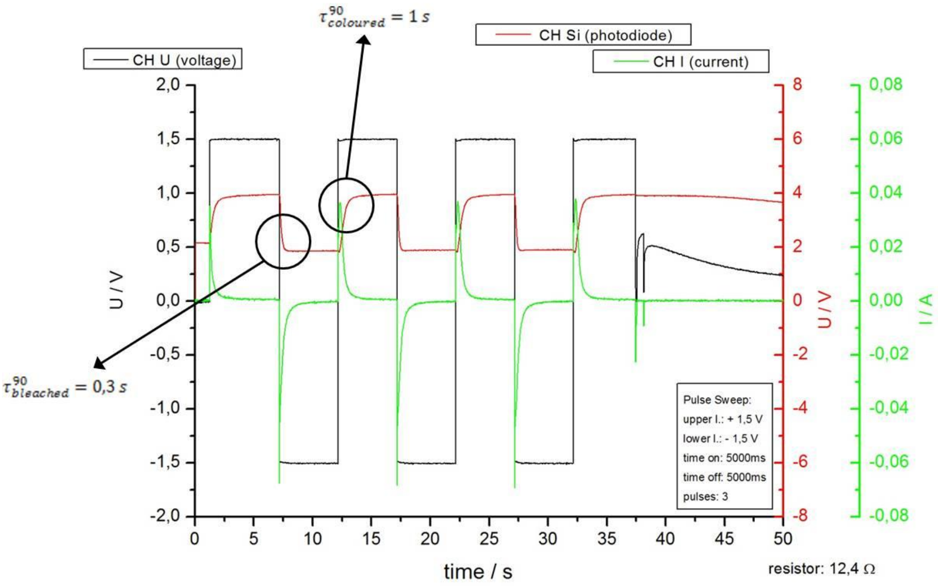


Fig. 5.61. Setup for optical measurements during operation with DC voltage-pulse-packets

## 5.3.2. Measurement results

*The first experiments were done with the “Reflective Device (13.7.2009 – Nr.1)”.*

The working electrode of the reflective ECD was connected to the minus output of the source measure unit.



7.8.2009: Oszilloskop [SN #17013]: Reflective Device

Fig. 5.62. Voltage, current and Si-photodiode signal in dependence on the time for the “Reflective Device (13.7.2009 – Nr.1)” measured on the 7.8.2009 – pulses: 5000 ms; with “preconditioning”

The black curve in figure 5.62 describes a voltage pulse sequence with upper level +1,5 V and lower level -1,5 V. The upper level has maintained for 5 seconds before the voltage changed to the lower level. The period of time for the lower level has been 5 seconds.
The first and the last upper voltage level of the sequence has maintained for more than 5 seconds. This effect was caused by the source measure unit.

The source measure unit doesn´t apply voltage to the reflective electrochromic device anymore as soon as the voltage pulse sequence is finished. Nevertheless a positive voltage was still registered by the oscilloscope.
Probably a charge balancing process in the electrochromic device is responsible for this behaviour: The shape of the curve shows a steep increase of voltage followed by a slow decrease of voltage. The short disturbances at 38 seconds (x-axis) can be attributed to the source measure unit.
The green curve shows the behaviour of the current: when the voltage switches a sharp current peak occurs, and after about 2 seconds the current is virtually zero.
The red curve shows the colour modulation of the "Reflective Device (13.7.2009 – Nr.1)". If the voltage from the Keithley 236 is on the upper level (+1,5 V), the reflective electrochromic device is in its coloured state, if it is on the lower level (-1,5 V), the ECD is bleached. In both states saturation appeared.
The switching times, where 90 % of the full effect is reached, were calculated: For the coloured state the switching time was 1,0 s ($\tau_{coloured}^{90} = 1{,}0\ s \pm 0{,}1\ s$) and for the bleached state the switching time was 0,3 s ($\tau_{bleached}^{90} = 0{,}3\ s \pm 0{,}1\ s$).
After the completed voltage pulse sequence the signal of the Si-photodiode slowly decreased.

Further measurement results of the "Reflective Device (13.7.2009 – Nr.1)" are shown in figure 5.63 to figure 5.68. Always the voltage values were set to +1,5 V and -1,5 V. The time of the pulses was varied.

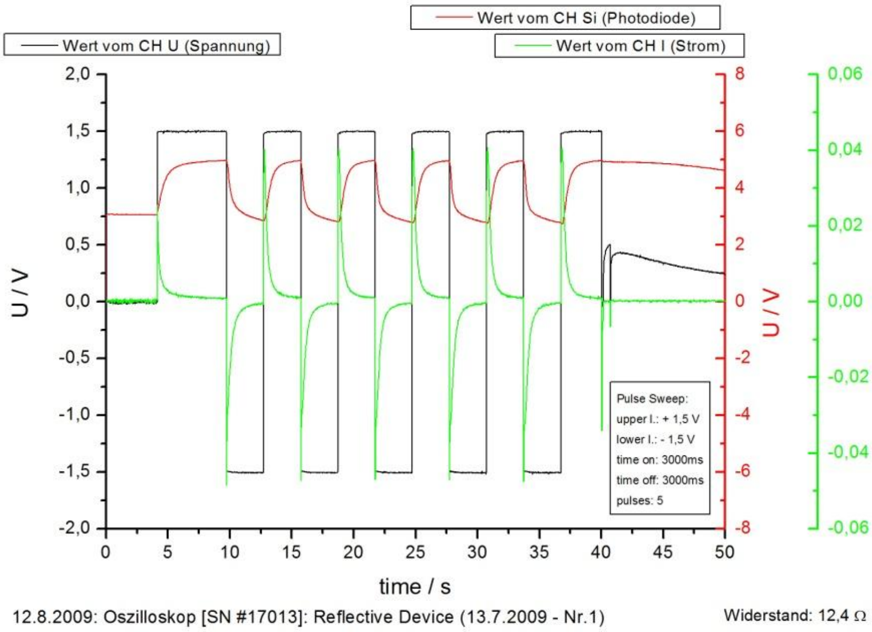


**Fig. 5.63. Voltage, current and Si-photodiode signal in dependence on the time for the "Reflective Device (13.7.2009 – Nr.1)" measured on the 12.8.2009 – pulses: 3000 ms; with "preconditioning"**

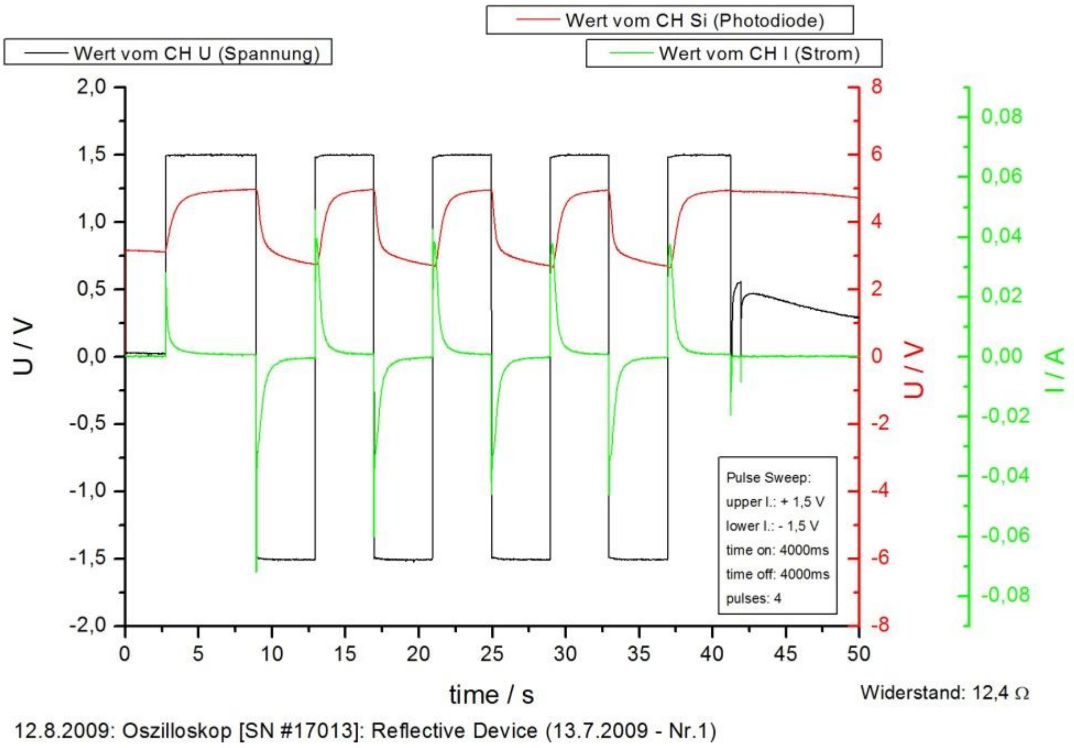


**Fig. 5.64. Voltage, current and Si-photodiode signal in dependence on the time for the “Reflective Device (13.7.2009 – Nr.1)” measured on the 12.8.2009 – pulses: 4000 ms; with “preconditioning”**

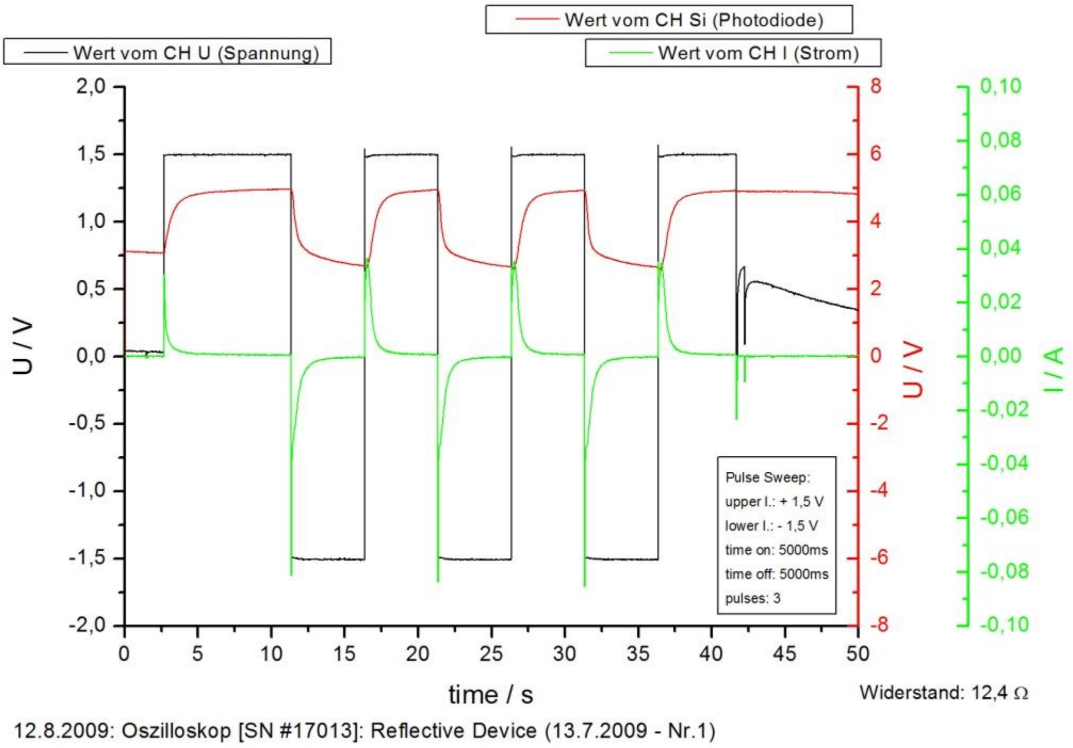


**Fig. 5.65. Voltage, current and Si-photodiode signal in dependence on the time for the “Reflective Device (13.7.2009 – Nr.1)” measured on the 12.8.2009 – pulses: 5000 ms; with “preconditioning”**

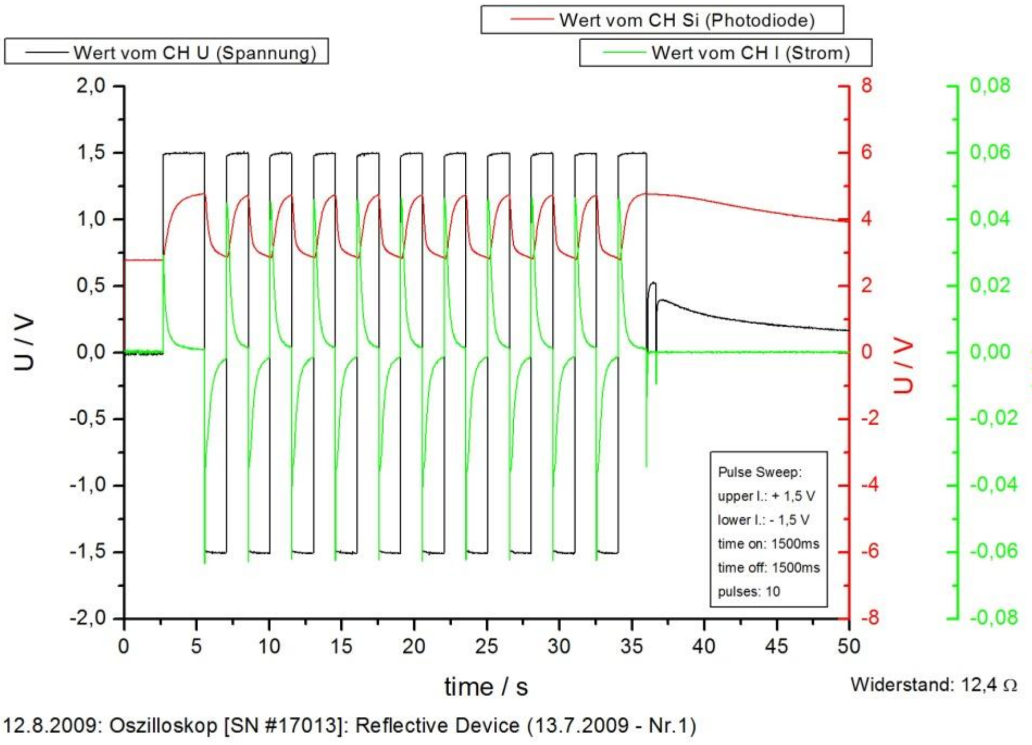


**Fig. 5.66. Voltage, current and Si-photodiode signal in dependence on the time for the "Reflective Device (13.7.2009 – Nr.1)" measured on the 12.8.2009 – pulses: 1500 ms; with "preconditioning"**

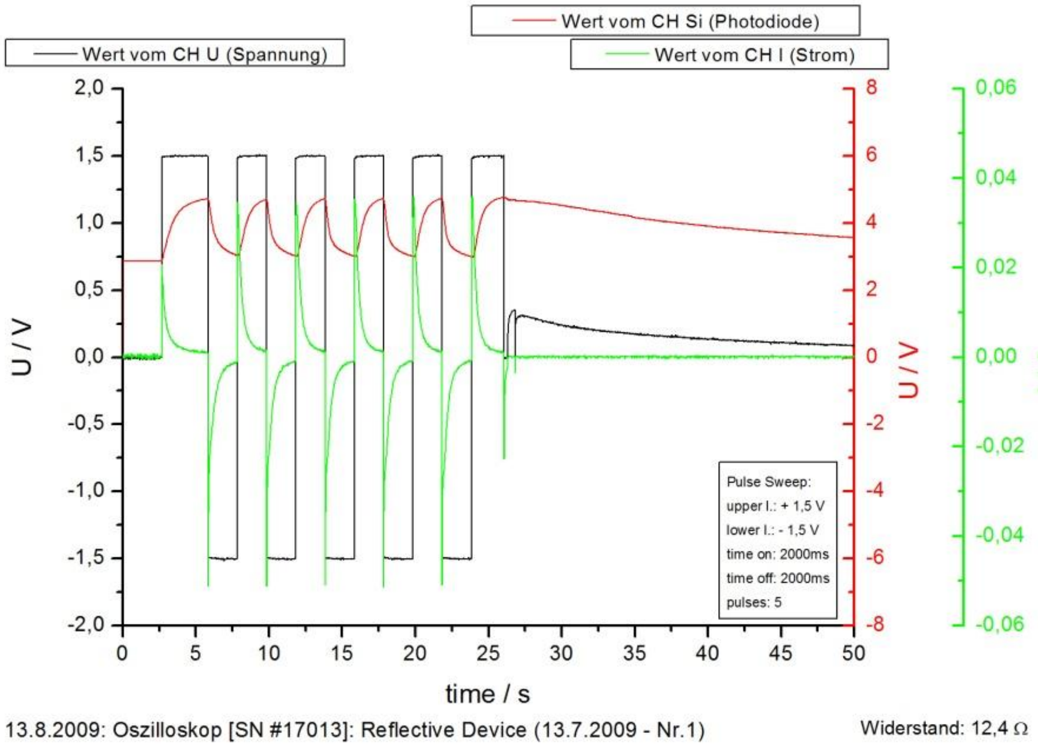
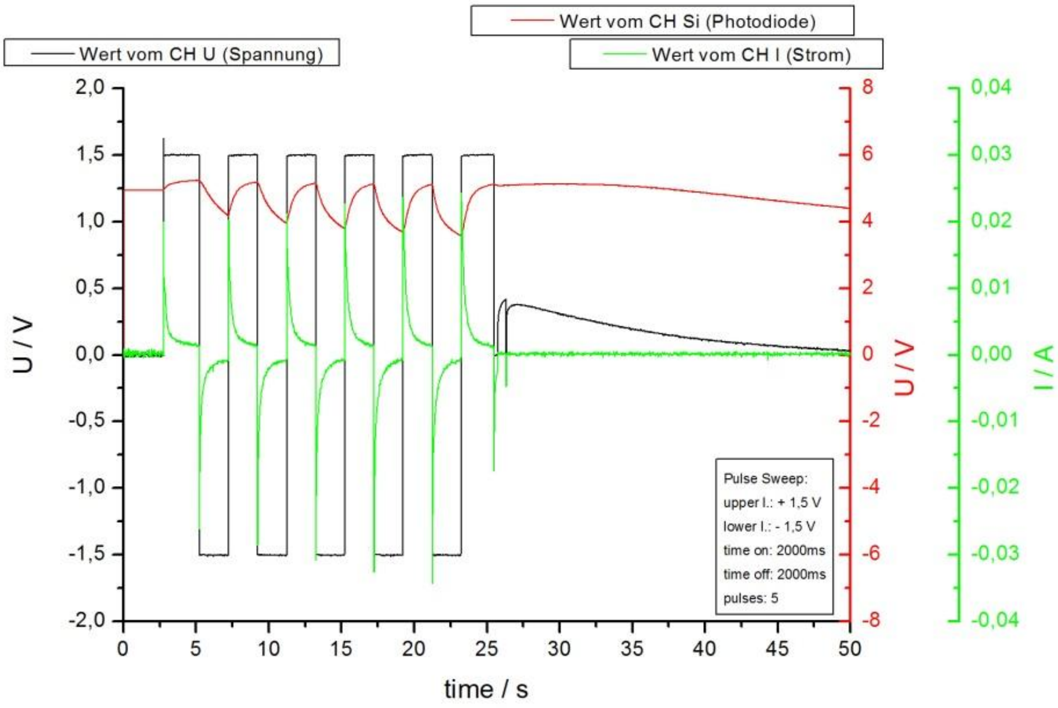


**Fig. 5.67. Voltage, current and Si-photodiode signal in dependence on the time for the "Reflective Device (13.7.2009 – Nr.1)" measured on the 13.8.2009 – pulses: 2000 ms; with "preconditioning"**



Pulse Sweep:
upper l.: + 1,5 V
lower l.: - 1,5 V
time on: 2000ms
time off: 2000ms
pulses: 5

14.8.2009: Oszilloskop [SN #17013]: Reflective Device (13.7.2009 - Nr.1)

Widerstand: 12,4 Ω

**Fig. 5.68. Voltage, current and Si-photodiode signal in dependence on the time for the "Reflective Device (13.7.2009 – Nr.1)" measured on the 14.8.2009 – pulses: 2000 ms; without "preconditioning"**

The saturation, which had appeared in the measurement result of the 7.8.2009 (see figure 5.62), wasn´t reached anymore in the experiments on the following days. Perhaps this is an aging phenomena or a sign of degeneration of the "Reflective Device (13.7.2009 – Nr.1)".
The measurement shown in figure 5.67 was done after "preconditioning" via cyclovoltammetry. A measurement with the same settings was done after storage (for about 23 hours) and is shown in figure 5.68. If no "preconditioning" was carried out, more than 5 pulses were needed until a constant colour modulation appeared.

*Measurement results of the "Reflective Device (13.7.2009 – Nr.2)" are shown in figure 5.69 to figure 5.74.*

The working electrode of the reflective electrochromic device was connected to the minus output of the source measure unit and therefore the ECD got coloured, if the source measure unit displayed a positive voltage, and bleached, if the source measure unit displayed a negative voltage.
Always the voltage values were set to +1,5 V and -1,5 V. The time of the pulses was varied.

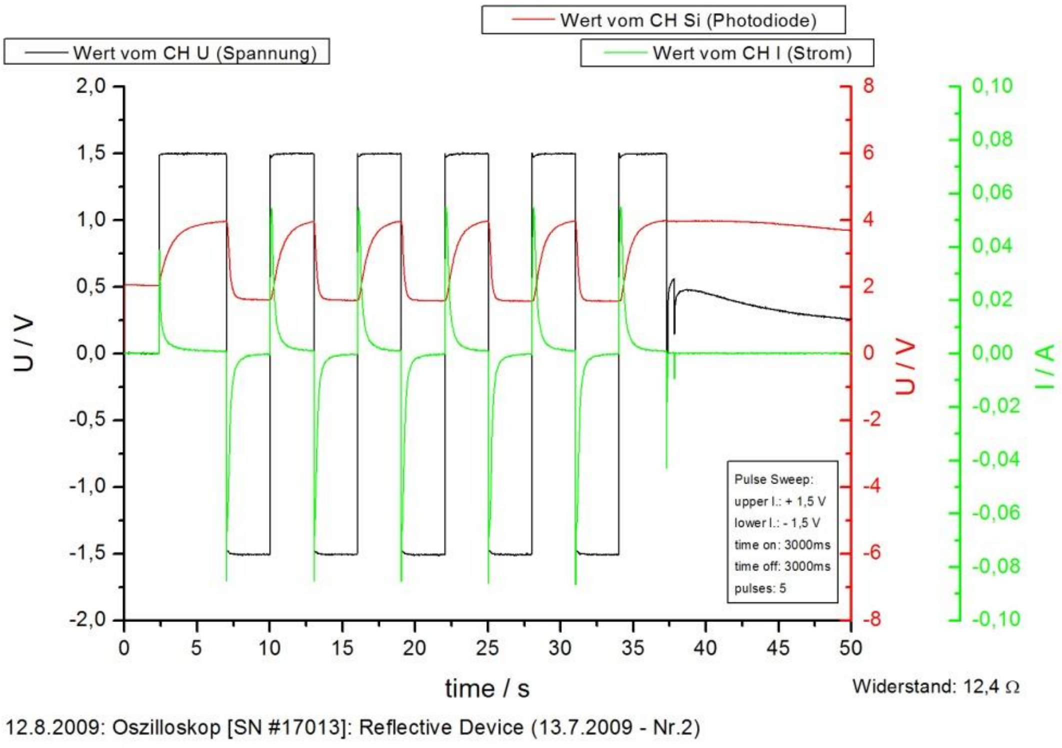


**Fig. 5.69. Voltage, current and Si-photodiode signal in dependence on the time for the "Reflective Device (13.7.2009 – Nr.2)" measured on the 12.8.2009 – pulses: 3000 ms; with "preconditioning"**

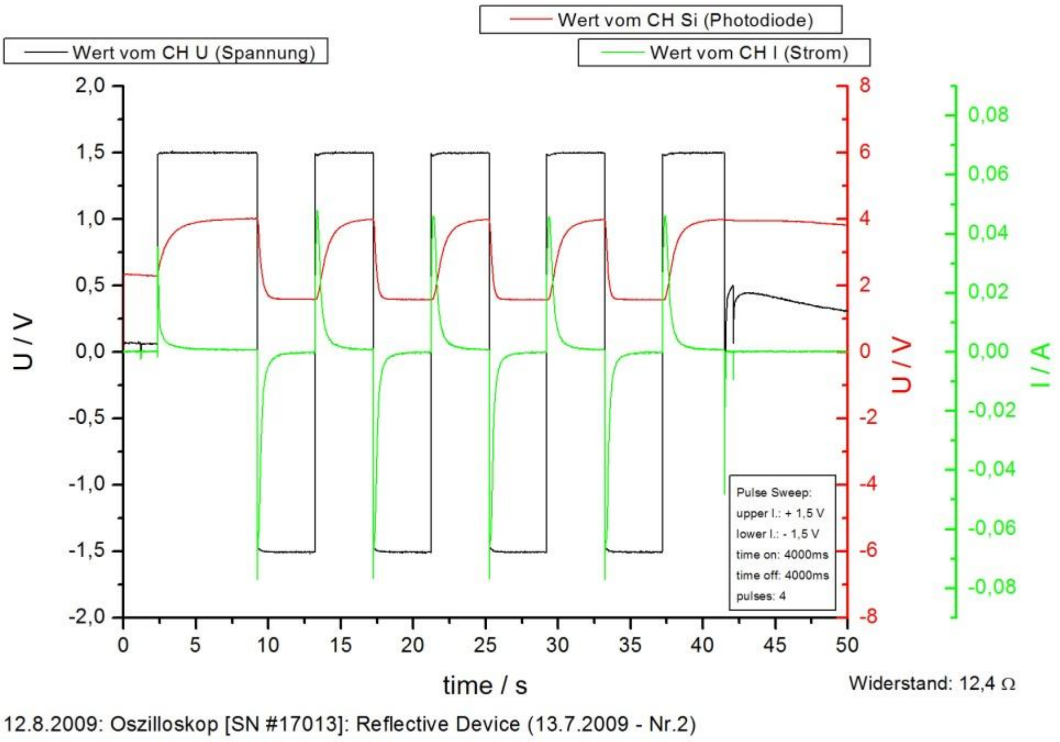


**Fig. 5.70. Voltage, current and Si-photodiode signal in dependence on the time for the "Reflective Device (13.7.2009 – Nr.2)" measured on the 12.8.2009 – pulses: 4000 ms; with "preconditioning"**

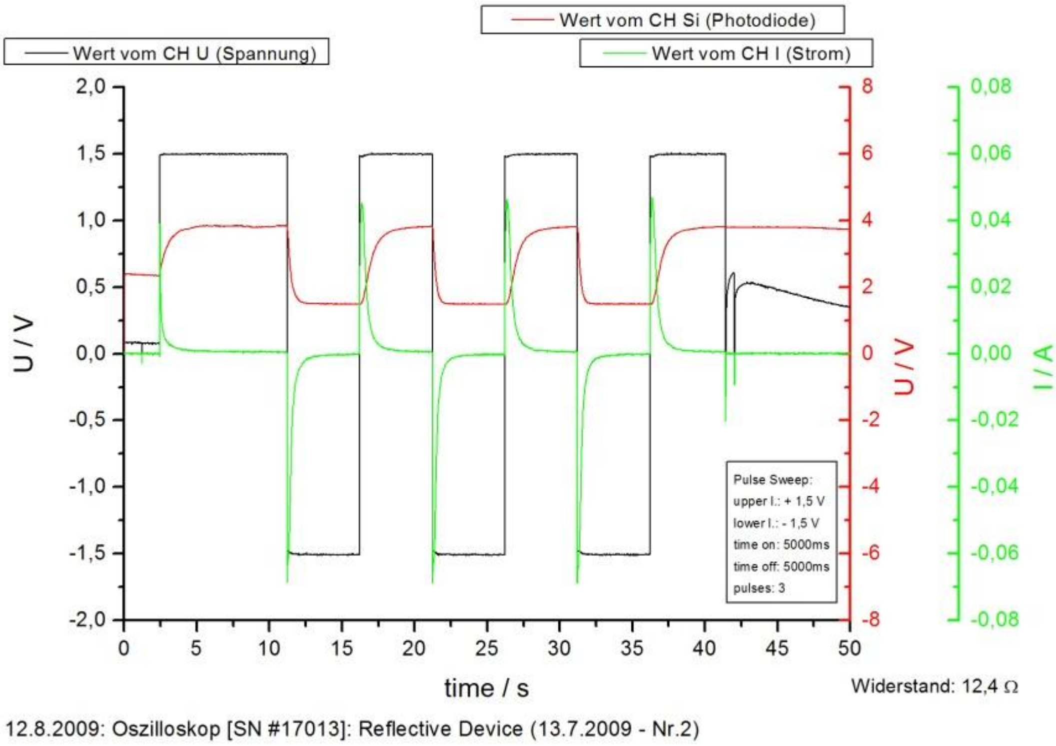


**Fig. 5.71. Voltage, current and Si-photodiode signal in dependence on the time for the "Reflective Device (13.7.2009 – Nr.2)" measured on the 12.8.2009 – pulses: 5000 ms; with "preconditioning"**

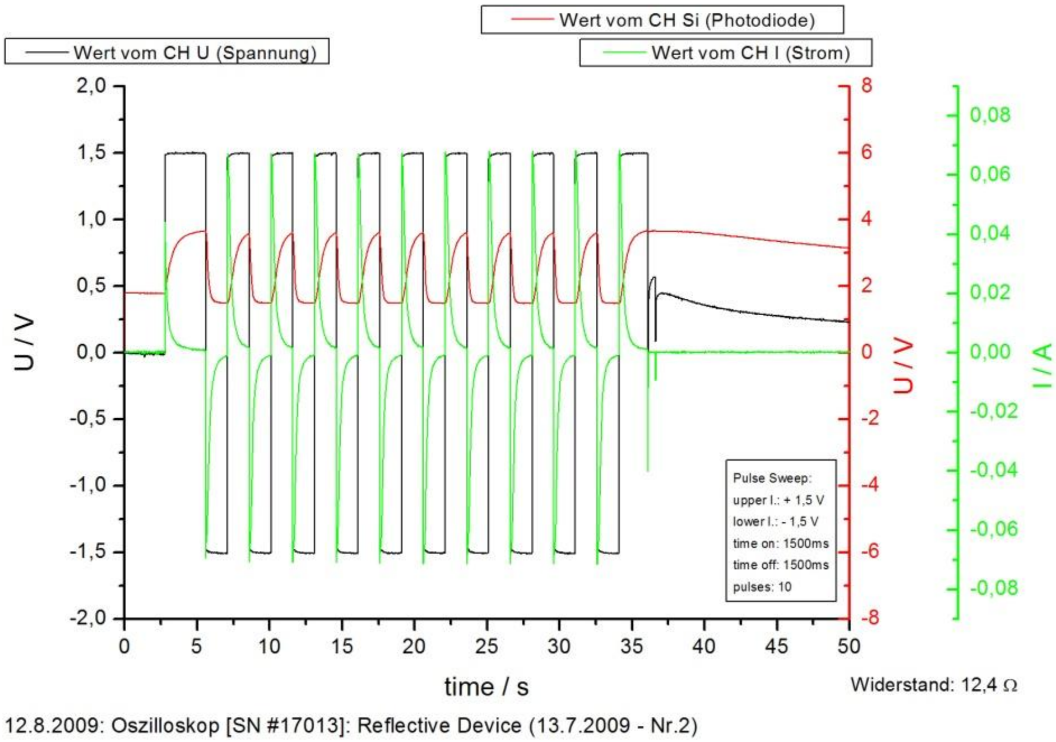


**Fig. 5.72. Voltage, current and Si-photodiode signal in dependence on the time for the "Reflective Device (13.7.2009 – Nr.2)" measured on the 12.8.2009 – pulses: 1500 ms; with "preconditioning"**

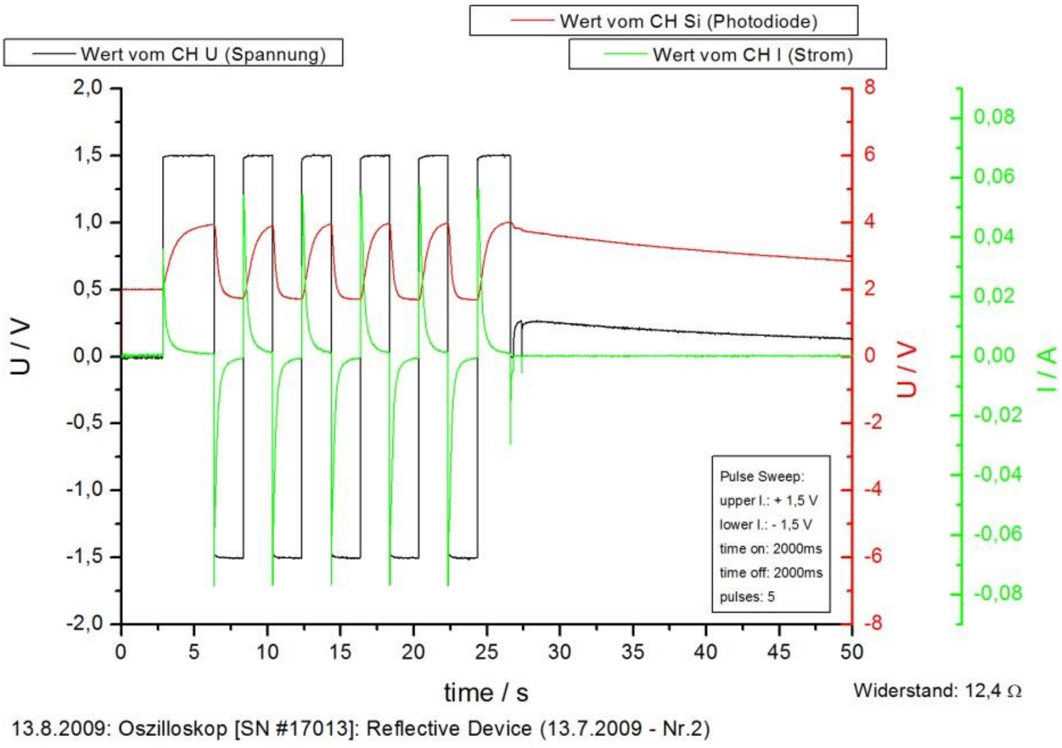


**Fig. 5.73. Voltage, current and Si-photodiode signal in dependence on the time for the "Reflective Device (13.7.2009 – Nr.2)" measured on the 13.8.2009 – pulses: 2000 ms; with "preconditioning"**

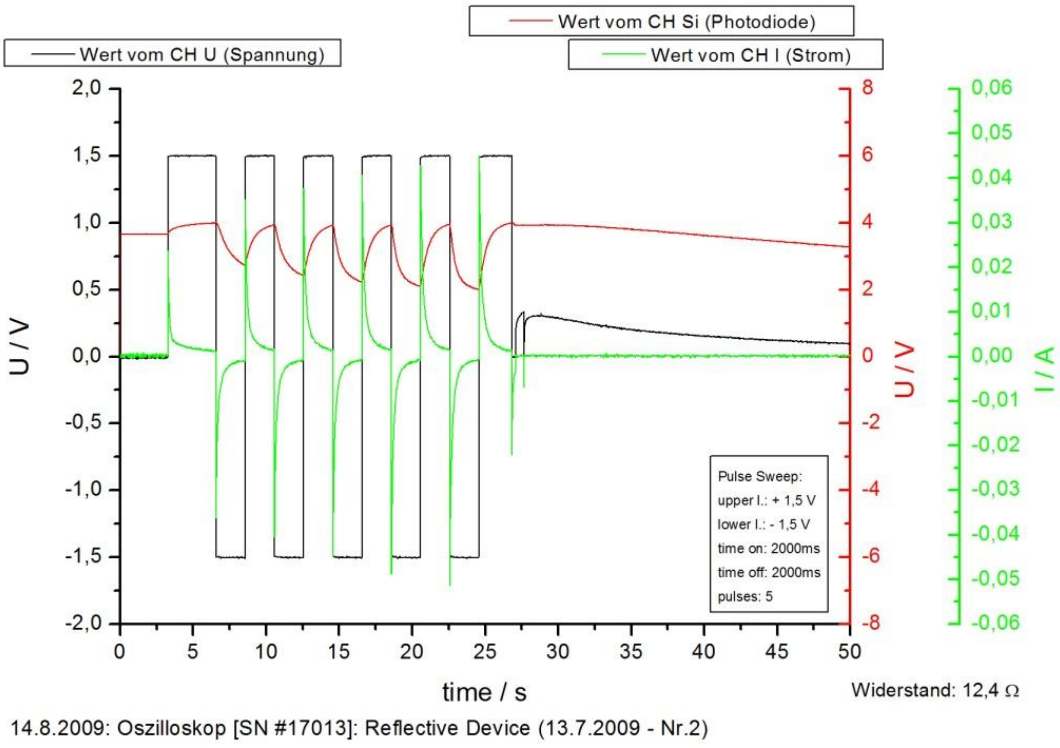


**Fig. 5.74. Voltage, current and Si-photodiode signal in dependence on the time for the "Reflective Device (13.7.2009 – Nr.2)" measured on the 14.8.2009 – pulses: 2000 ms; without "preconditioning"**

In figure 5.69 to figure 5.73 saturation of the bleached state appeared. In these cases “preconditioning” of the electrochromic devices had been done. Saturation of the coloured state appeared in figure 5.71, the period of time of the pulses was 5 seconds.
The switching times, where 90 % of the full effect is reached, were calculated from the measurement results shown in figure 5.71: For the coloured state the switching time was 1,8 s ($\tau_{coloured}^{90} = 1{,}8\ s \pm 0{,}1\ s$) and for the bleached state the switching time was 0,5 s ($\tau_{bleached}^{90} = 0{,}5\ s \pm 0{,}1\ s$).
The measurement shown in figure 5.73 was done after “preconditioning” via cyclovoltammetry. A measurement with the same settings was done after storage (for about 23 hours) and is shown in figure 5.74.

Figure 5.70 and figure 5.71:
For the first seconds the voltage value was not zero. Probably a charge balancing process in the electrochromic device was responsible. There was an interim period of about 50 s between these measurements and the preceding measurements, where a positive voltage value of about 0,25 V was still registered by the oscilloscope at the end of the measurement.

*Measurement results of the “Transmittive Device (5.8.2009)” are shown in figure 5.75 to figure 5.79.*

The magenta polymer coated electrode of the transmittive device was connected to the minus output of the source measure unit and therefore the ECD got coloured, if the source measure unit displayed a positive voltage, and bleached, if the source measure unit displayed a negative voltage.
Always the voltage values were set to +1,5 V and -1,5 V. The time of the pulses was varied.

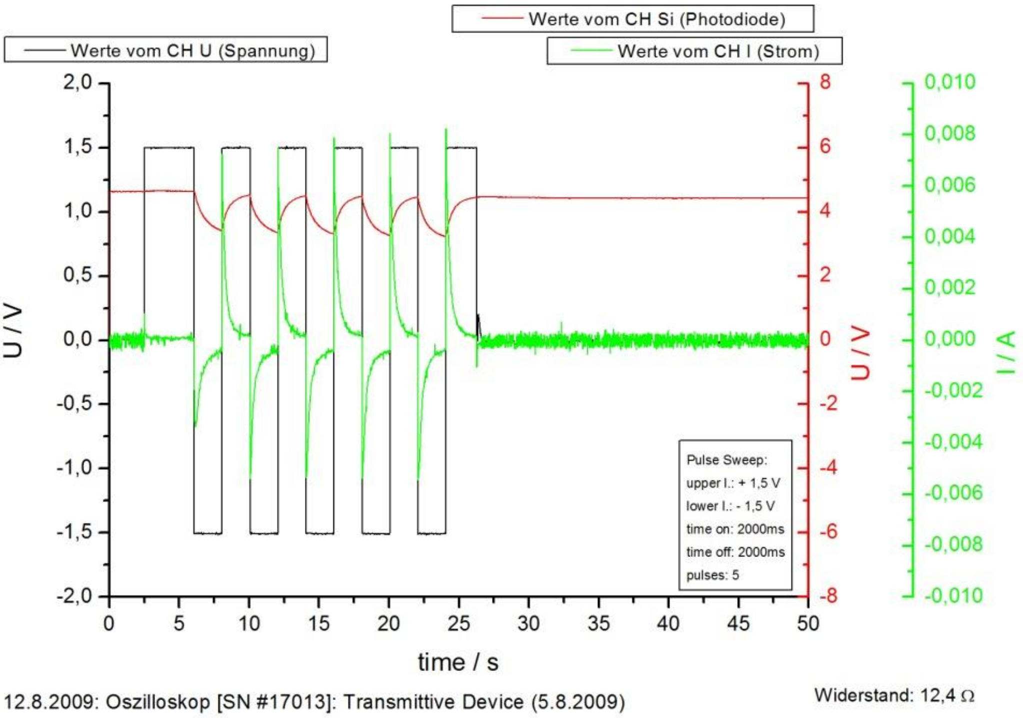


**Fig. 5.75. Voltage, current and Si-photodiode signal in dependence on the time for the “Transmittive Device (5.8.2009)” measured on the 12.8.2009 – pulses: 2000 ms; without “preconditioning”**

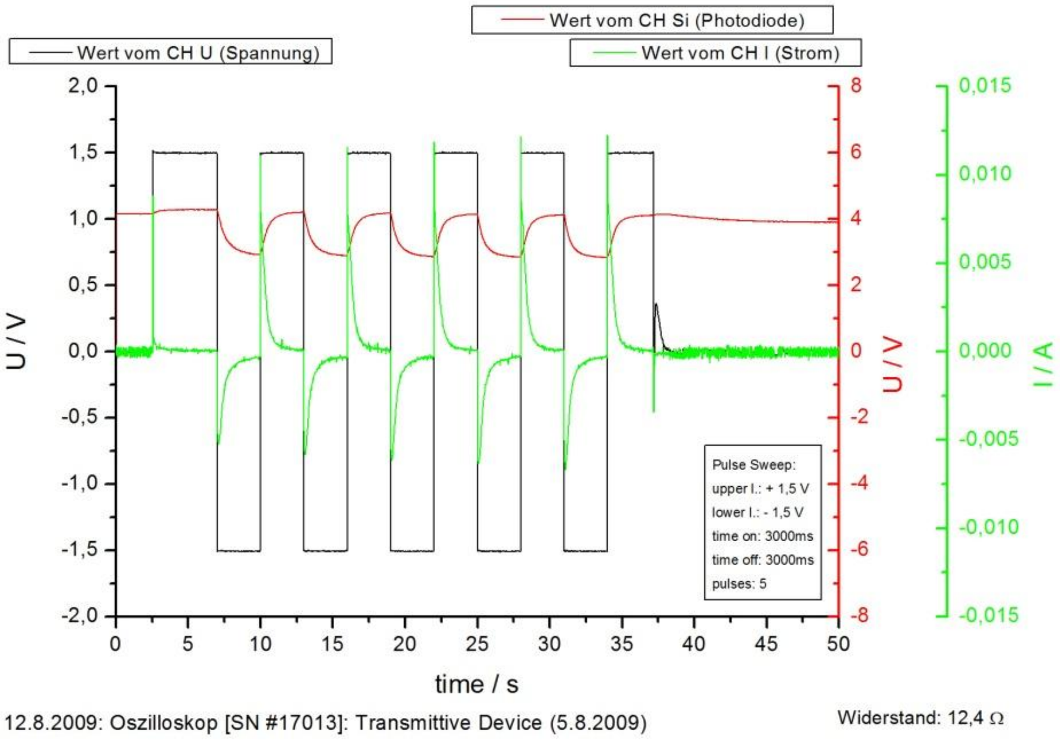


**Fig. 5.76. Voltage, current and Si-photodiode signal in dependence on the time for the "Transmittive Device (5.8.2009)" measured on the 12.8.2009 – pulses: 3000 ms; with "preconditioning"**

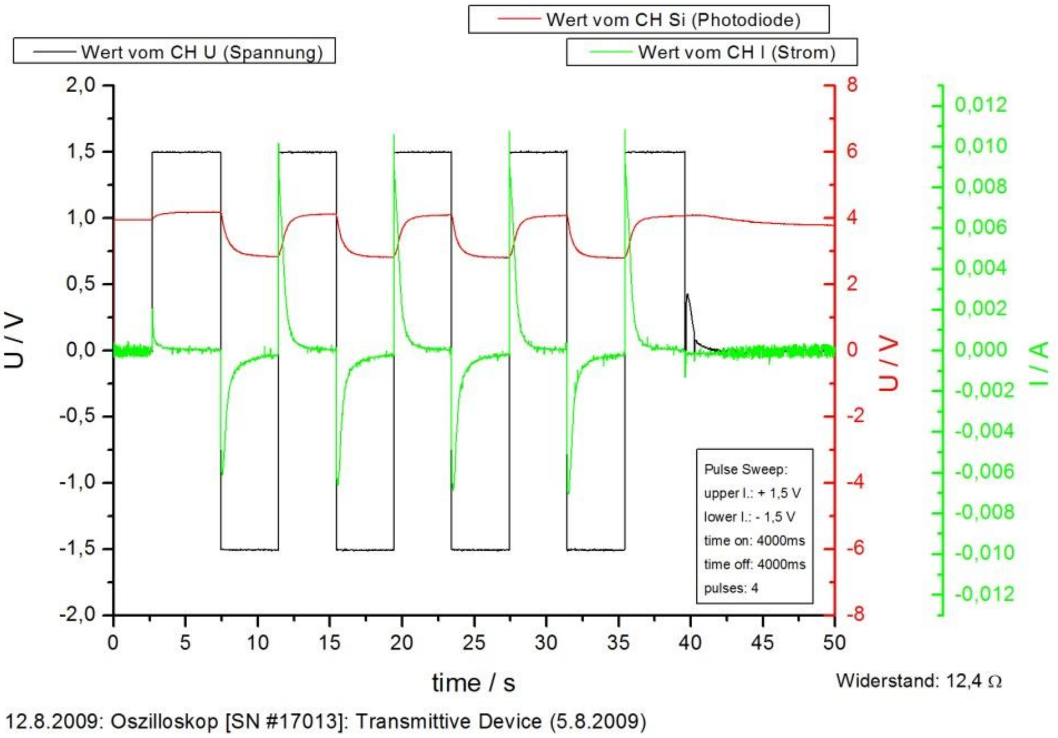
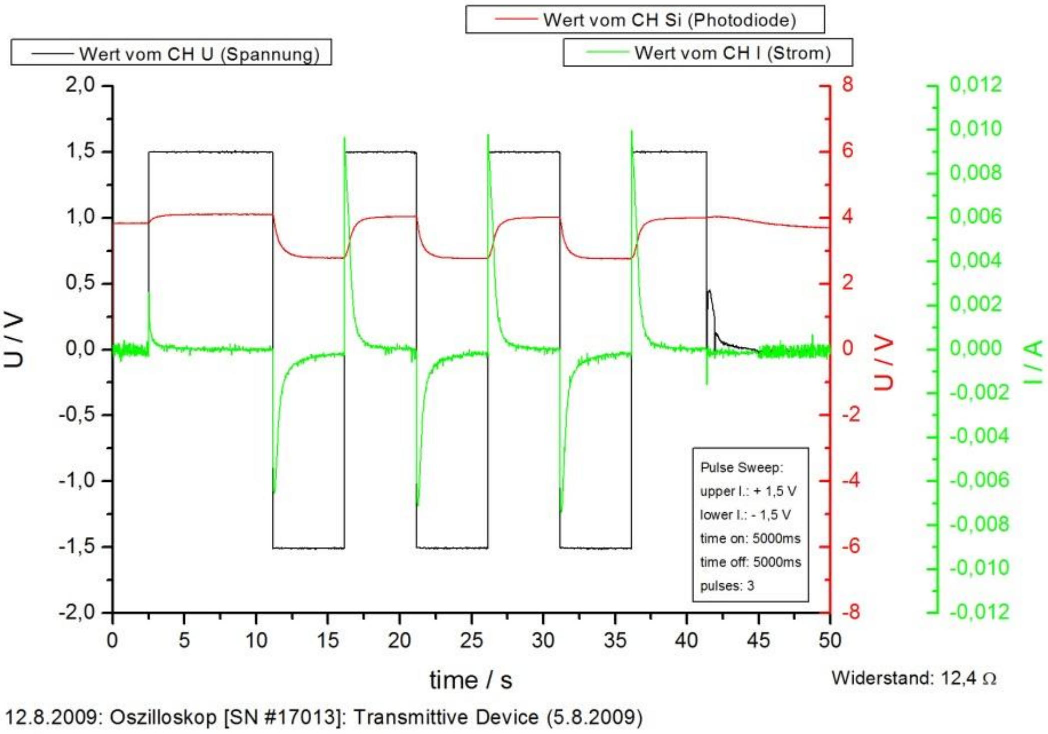
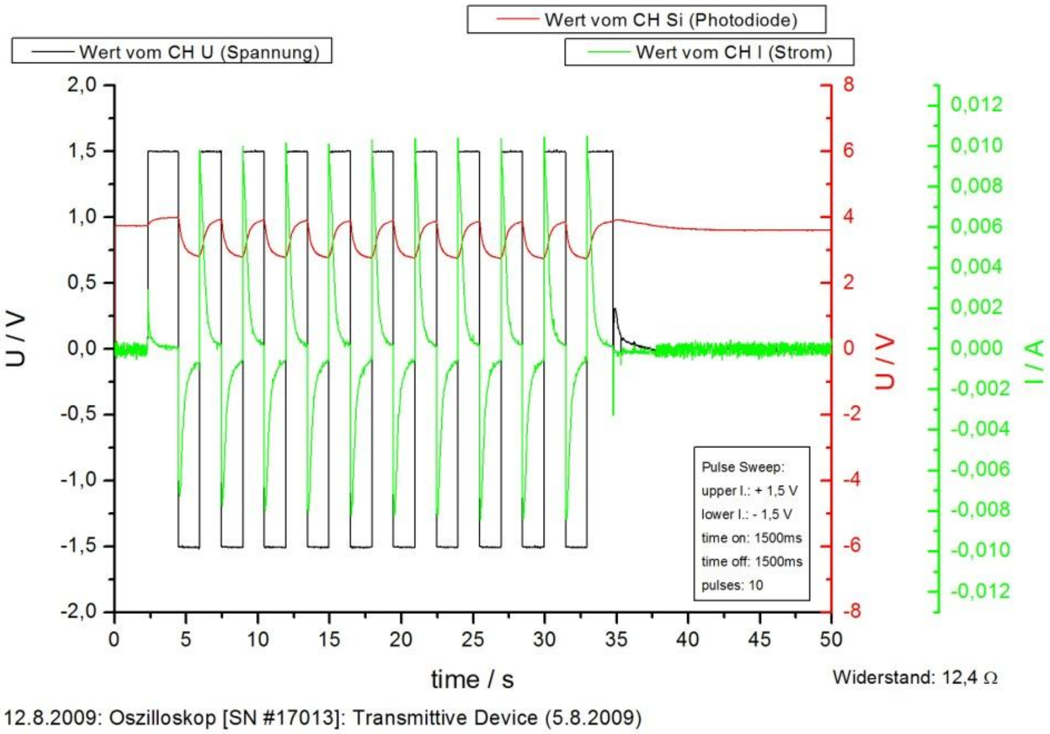


**Fig. 5.77. Voltage, current and Si-photodiode signal in dependence on the time for the "Transmittive Device (5.8.2009)" measured on the 12.8.2009 – pulses: 4000 ms; with "preconditioning"**



12.8.2009: Oszilloskop [SN #17013]: Transmittive Device (5.8.2009)

**Fig. 5.78. Voltage, current and Si-photodiode signal in dependence on the time for the "Transmittive Device (5.8.2009)" measured on the 12.8.2009 – pulses: 5000 ms; with "preconditioning"**



12.8.2009: Oszilloskop [SN #17013]: Transmittive Device (5.8.2009)

**Fig. 5.79. Voltage, current and Si-photodiode signal in dependence on the time for the "Transmittive Device (5.8.2009)" measured on the 12.8.2009 – pulses: 1500 ms; with "preconditioning"**

Saturation in the coloured and in the bleached state appeared in figure 5.77 and 5.78.
The switching times, where 90 % of the full effect is reached, were calculated from the measurement results shown in figure 5.78: For the coloured state the switching time was 1,2 s ($\tau^{90}_{coloured} = 1{,}2\ s \pm 0{,}1\ s$) and for the bleached state the switching time was 1,0 s ($\tau^{90}_{bleached} = 1{,}0\ s \pm 0{,}1\ s$).
The measurement shown in figure 5.75 was done after storage (for about 22 hours). In figure 5.76 to 5.79 following measurements are shown. The period of time between these measurements and the preceding measurements was about one minute.

*Measurement results of the "Transmittive Device (29.7.2009)" are shown in figure 5.80 to figure 5.84.*

The transmittive ECD got coloured, if the source measure unit displayed a positive voltage, and bleached, if the source measure unit displayed a negative voltage.
Always the voltage values were set to +1,5 V and -1,5 V. The time of the pulses was varied.

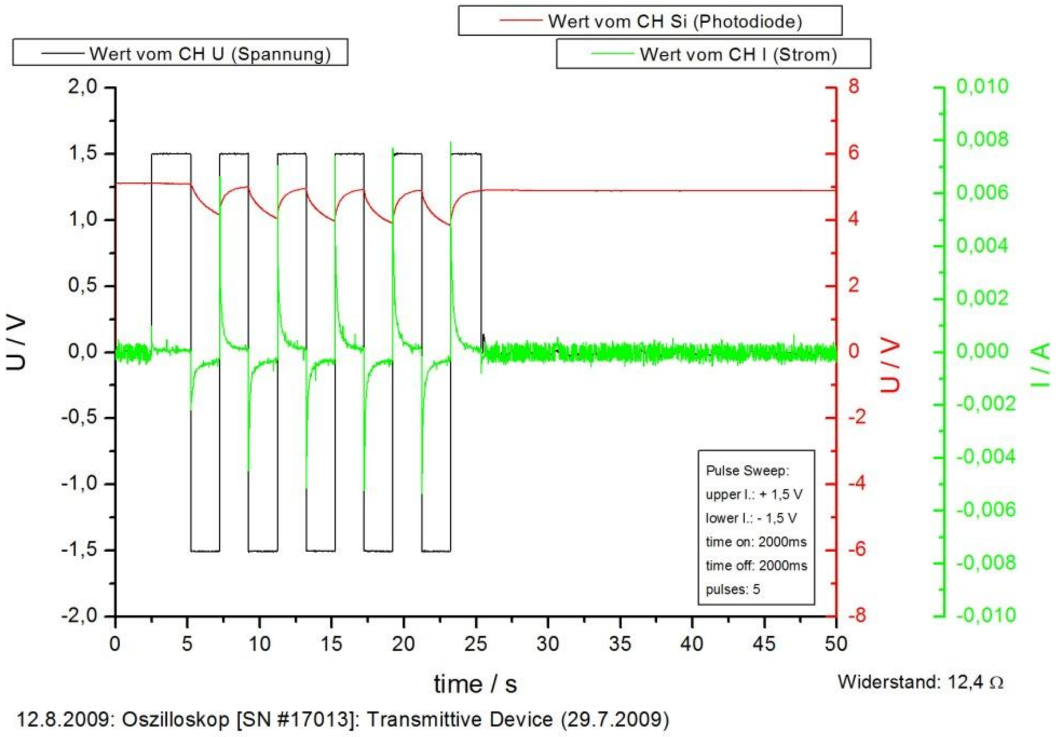


**Fig. 5.80. Voltage, current and Si-photodiode signal in dependence on the time for the "Transmittive Device (29.7.2009)" measured on the 12.8.2009 – pulses: 2000 ms; without "preconditioning"**

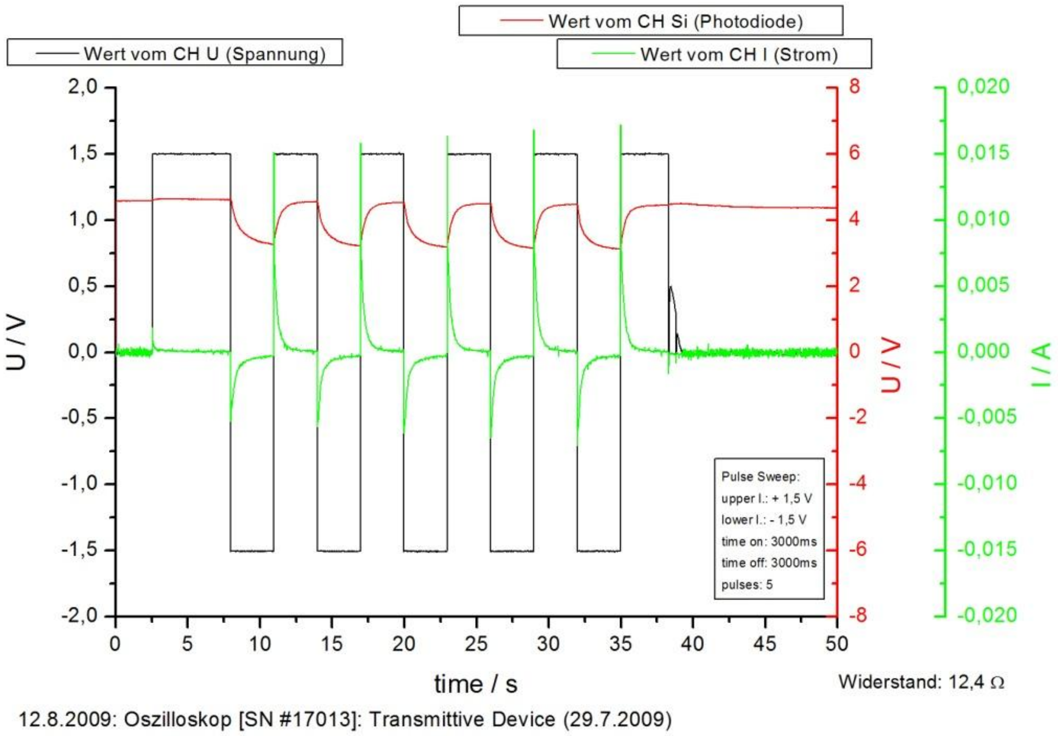


**Fig. 5.81. Voltage, current and Si-photodiode signal in dependence on the time for the "Transmittive Device (29.7.2009)" measured on the 12.8.2009 – pulses: 3000 ms; with "preconditioning"**

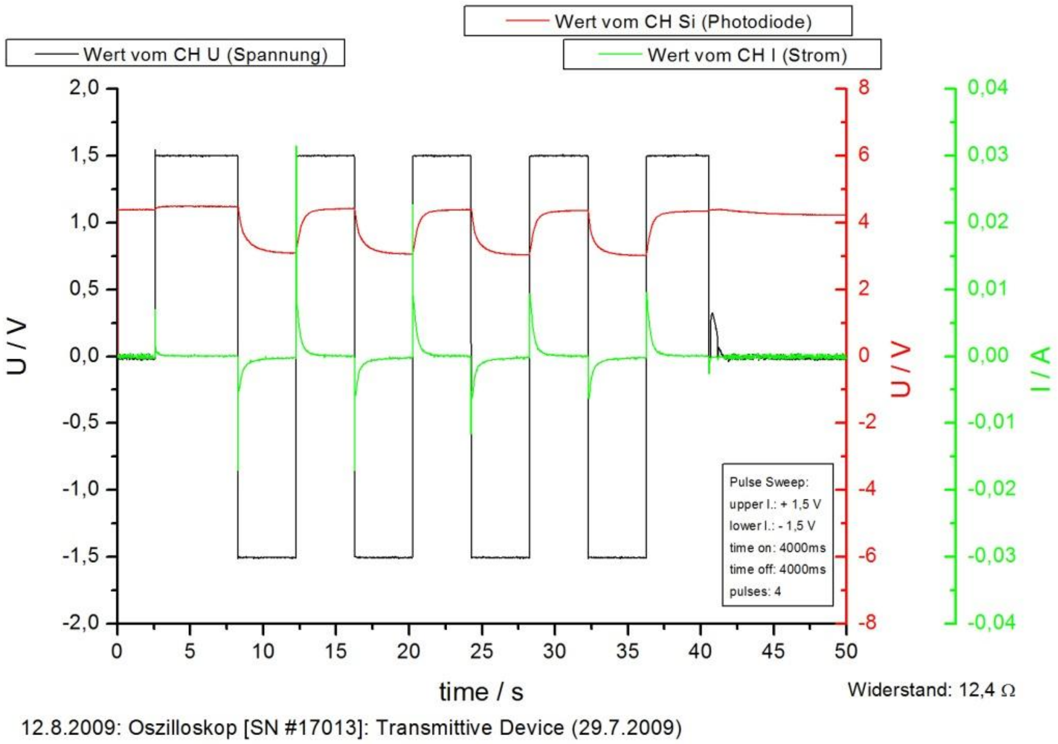


**Fig. 5.82. Voltage, current and Si-photodiode signal in dependence on the time for the "Transmittive Device (29.7.2009)" measured on the 12.8.2009 – pulses: 4000 ms; with "preconditioning"**

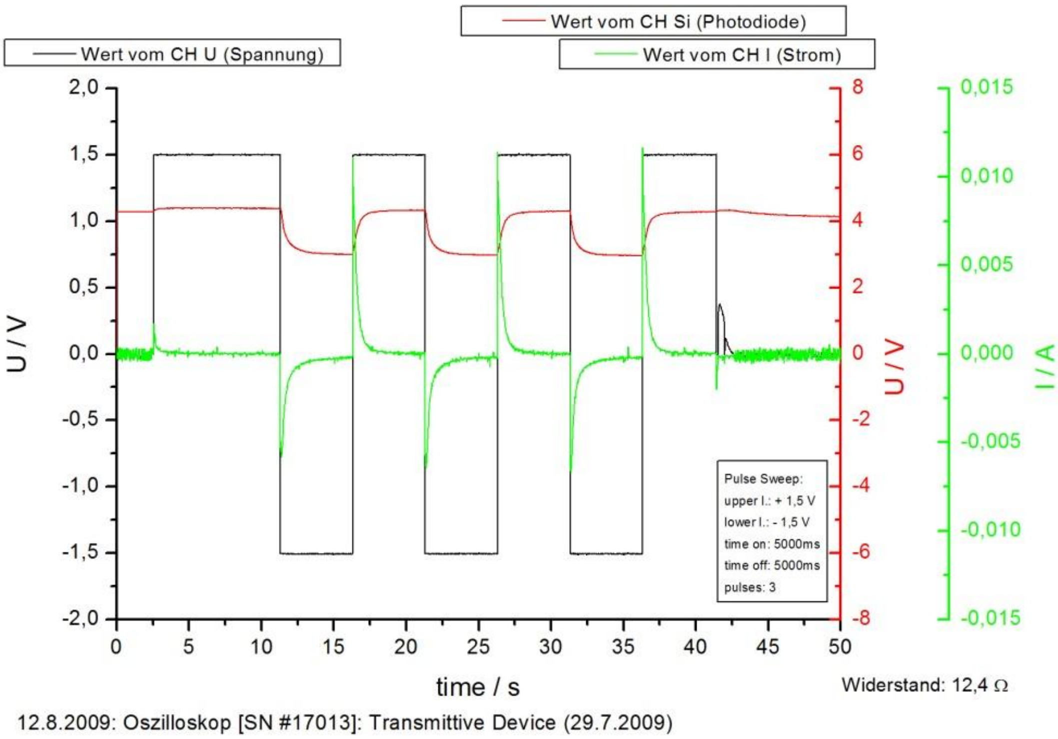


**Fig. 5.83. Voltage, current and Si-photodiode signal in dependence on the time for the "Transmittive Device (29.7.2009)" measured on the 12.8.2009 – pulses: 5000 ms; with "preconditioning"**

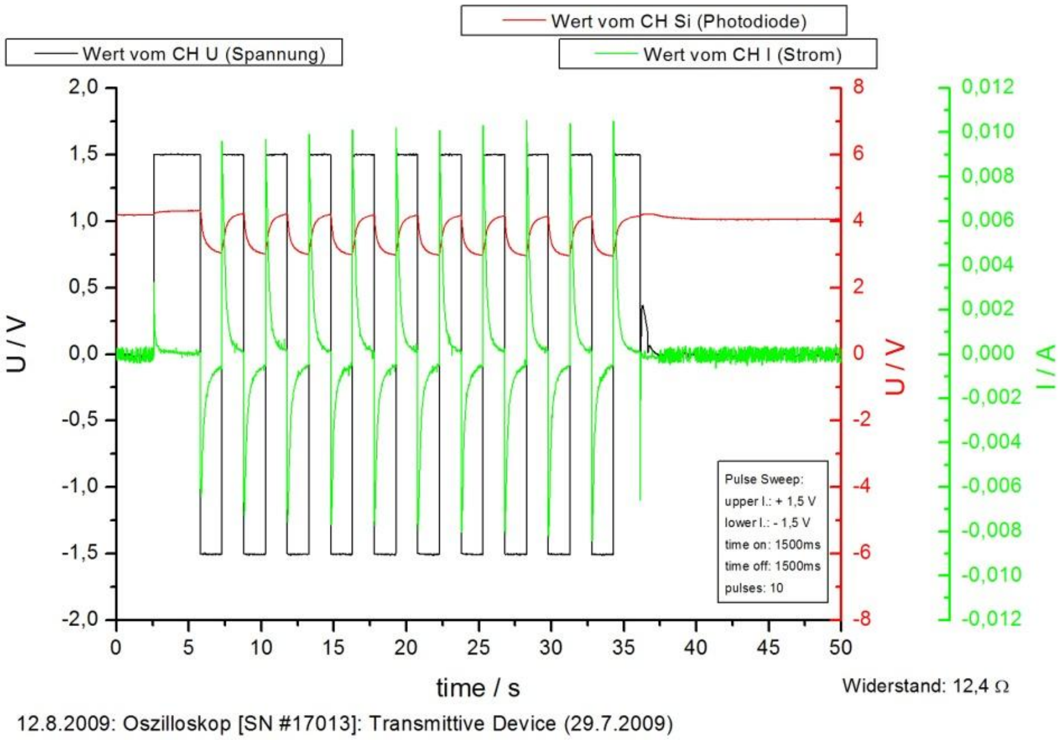


**Fig. 5.84. Voltage, current and Si-photodiode signal in dependence on the time for the "Transmittive Device (29.7.2009)" measured on the 12.8.2009 – pulses: 1500 ms; with "preconditioning"**

In figure 5.83 saturation in the coloured and in the bleached state appeared. In figure 5.82 the saturation appeared at least in the coloured state.

The switching times, where 90 % of the full effect is reached, were calculated from the measurement results shown in figure 5.83: For the coloured state the switching time was 0,9 s ($\tau_{coloured}^{90} = 0{,}9\ s \pm 0{,}1\ s$) and for the bleached state the switching time was 1,0 s ($\tau_{bleached}^{90} = 1{,}0\ s \pm 0{,}1\ s$).

The measurement shown in figure 5.80 was done after storage (about 22 hours). In figure 5.81 to 5.84 following measurements are shown. The period of time between these measurements and the preceding measurements was about one minute.

## 5.4. Colour-stability-points

A colour-stability-point is a voltage value, where the colour of the electrochromic device is stable.

To find possible colour-stability-points the cyclovoltammograms were differentiated to get the gradient values. The voltage values with a gradient of zero were investigated for their colour stability.

### 5.4.1. Setup for measurements

The setup is composed of an electrical assembly and a setup for optical measurements.

#### 5.4.1.1. Circuit diagram

A schematic circuit diagram is shown in figure 5.1. The electrochromic device is connected to the Keithley 236 source measure unit. For the purpose of preconditioning cyclovoltammetry was performed. Afterwards special voltage values were set manually with the Keithley 236 source measure unit to investigate possible colour-stability-points. The voltage was continuously increased and decreased respectively until the wanted voltage value was reached.

#### 5.4.1.2. Setup for optical measurements

The optical setup is the same as described in chapter 5.1.1.2.1.

### 5.4.2. Measurement results

These experiments were carried out with the two reflective electrochromic devices (“Reflective Device (13.7.2009 – Nr.1)” and “Reflective Device (13.7.2009 – Nr.2)”).

First, cyclovoltammograms of the two reflective devices were differentiated and smoothed over the following equation:

$$\frac{dy_i}{dx_i}=\frac{1}{7}\left(\frac{y_{i+4}-y_{i+3}}{x_{i+4}-x_{i+3}}+\frac{y_{i+3}-y_{i+2}}{x_{i+3}-x_{i+2}}+\frac{y_{i+2}-y_{i+1}}{x_{i+2}-x_{i+1}}+\frac{y_{i+1}-y_i}{x_{i+1}-x_i}+\frac{y_i-y_{i-1}}{x_i-x_{i-1}}+\frac{y_{i-1}-y_{i-2}}{x_{i-1}-x_{i-2}}+\frac{y_{i-2}-y_{i-3}}{x_{i-2}-x_{i-3}}\right)$$

$\frac{dy_i}{dx_i}$...average differential quotient – average gradient

$y_i$...current values (I)

$x_i$...voltage values (U)

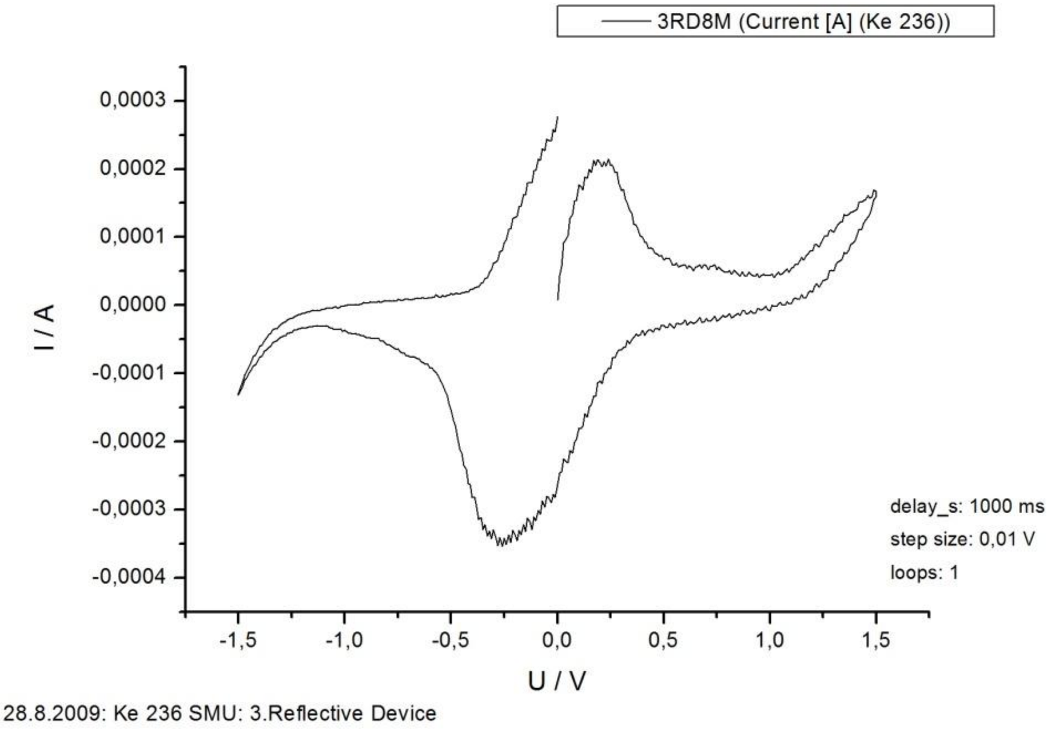


**Fig. 5.85. Cyclovoltammogram "3RD8M" of the "Reflective Device (13.7.2009 – Nr.1)" measured on the 28.8.2009; working electrode connected to the minus output of the source measure unit (see chapter 5.1.2)**

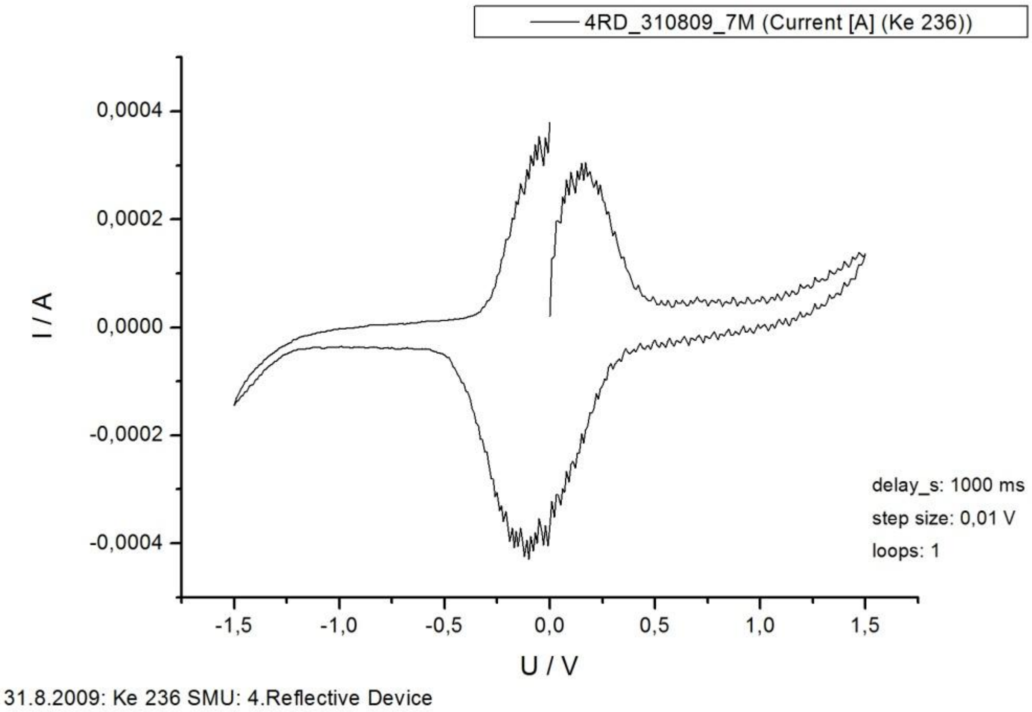


**Fig. 5.86. Cyclovoltammogram "4RD_310809_7M" of the "Reflective Device (13.7.2009 – Nr.2)" measured on the 31.8.2009; working electrode connected to the minus output of the source measure unit (see chapter 5.1.2)**

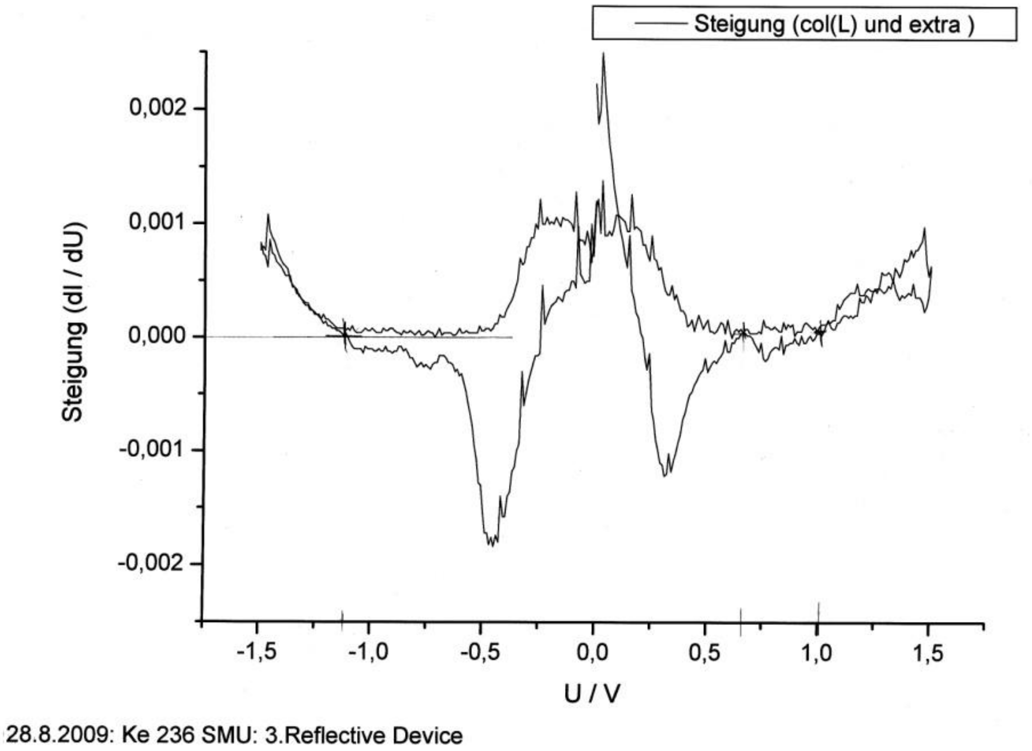


**Fig. 5.87. Average gradient in dependence on the voltage of the cyclovoltammogram from figure 5.85 of the "Reflective Device (13.7.2009 – Nr.1)"**

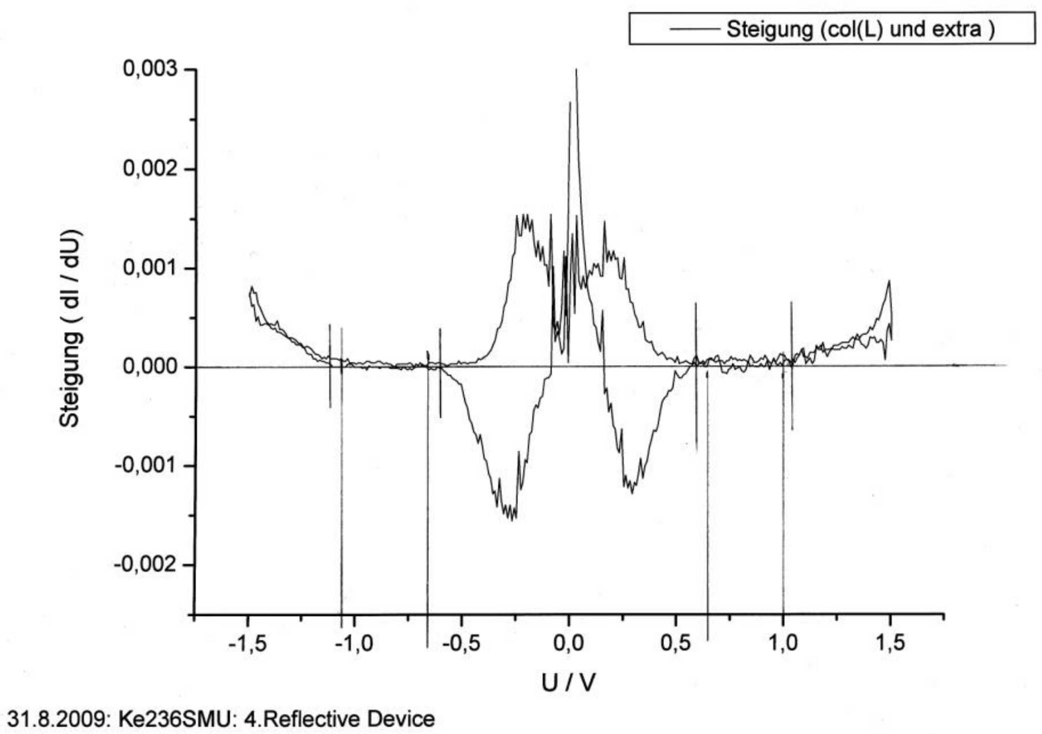


**Fig. 5.88. Average gradient in dependence on the voltage of the cyclovoltammogram from figure 5.86 of the "Reflective Device (13.7.2009 – Nr.2)"**

Possible colour-stability-points with a gradient of zero are marked in figure 5.87 and figure 5.88.

Possible colour-stability-points of the "Reflective Device (13.7.2009 – Nr.1)" (working electrode connected to the minus output of the source measure unit):

- 1.point at -1,12 V
- 2.point at +0,66 V
- 3.point at +1,00 V

Possible colour-stability-points of the "Reflective Device (13.7.2009 – Nr.2)" (working electrode connected to the minus output of the source measure unit):

- 1.point at -1,06 V
- 2.point at -0,66 V
- 3.point at +0,64 V
- 4.point at +1,00 V

These voltage values were investigated for their colour stability.

The working electrodes of the reflective electrochromic devices were connected to the minus output of the source measure unit and therefore the reflective ECDs got coloured, if the source measure unit displayed a positive voltage, and bleached, if the source measure unit displayed a negative voltage.

“Preconditioning” via cyclovoltammetrie was done until the maximum colouration and the maximum bleaching were reached.

Afterwards the voltage was manually and continuously (by 0,01 V steps) increased and decreased respectively from 0 V until the voltage value of the possible colour-stability-point was reached.

The voltage value was hold for about one hour and reflection spectra were measured with the S1000 CCD spectrometer. The first reflection spectrum was measured directly (few seconds) after the voltage value of the possible colour-stability-point was reached. If the following measured spectra were of the same shape, the set voltage value was proved to be a colour-stability-point.

*Figure 5.89 to 5.91 show the measurement results for the “Reflective Device (13.7.2009 – Nr.1)”.*

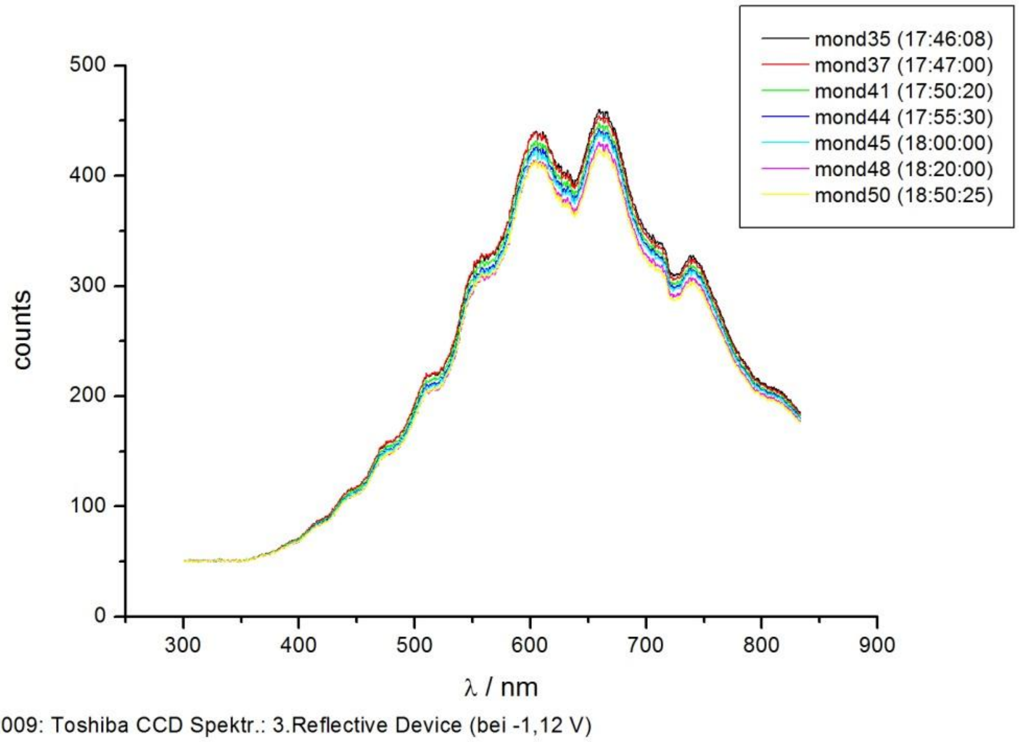
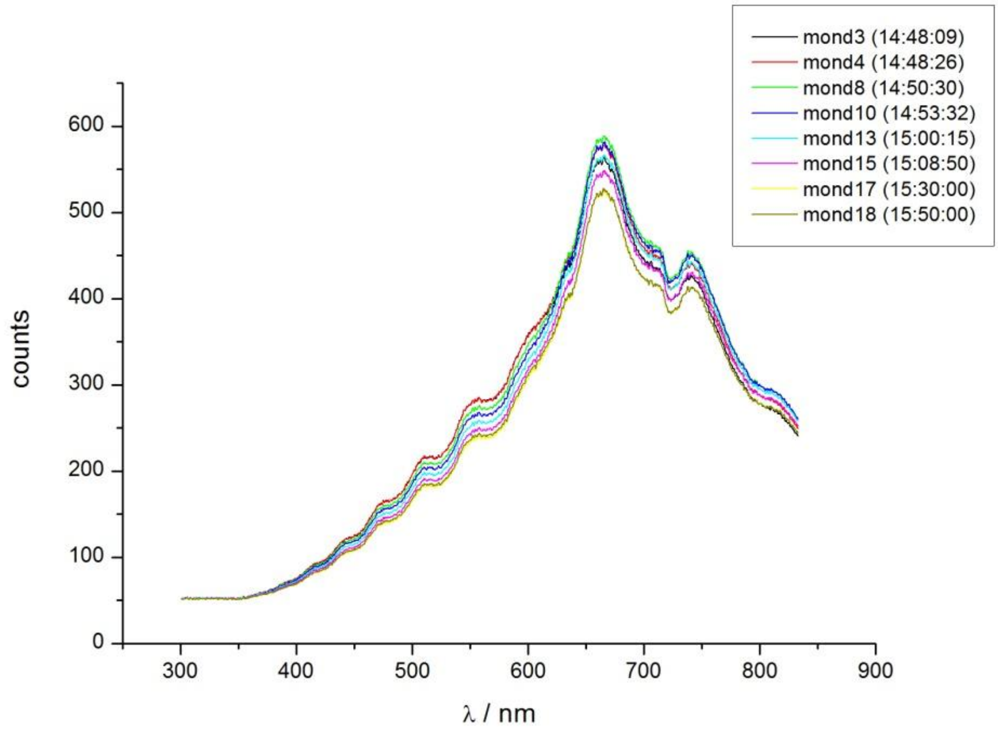
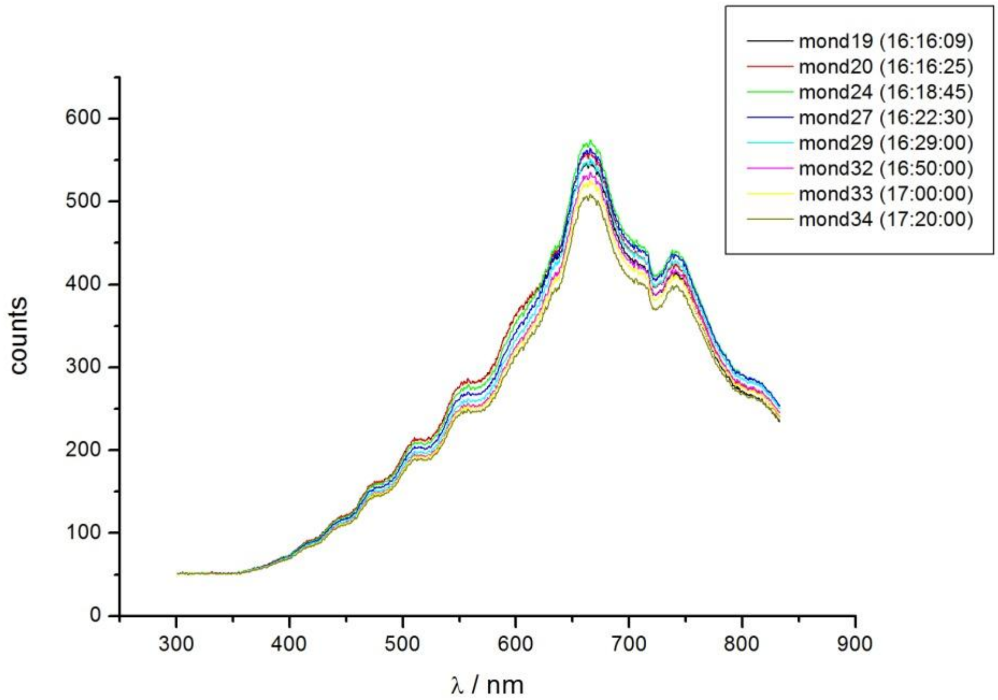


**Fig. 5.89. Reflection spectra of the “Reflective Device (13.7.2009 – Nr.1)” at the voltage value -1,12 V measured at different times on the 28.9.2009**



28.9.2009: Toshiba CCD Spektr.: 3..Reflective Device (bei +0,66 V)

**Fig. 5.90. Reflection spectra of the "Reflective Device (13.7.2009 – Nr.1)" at the voltage value +0,66 V measured at different times on the 28.9.2009**



28.9.2009: Toshiba CCD Spektr.: 3.Reflective Device (bei +1,00 V)

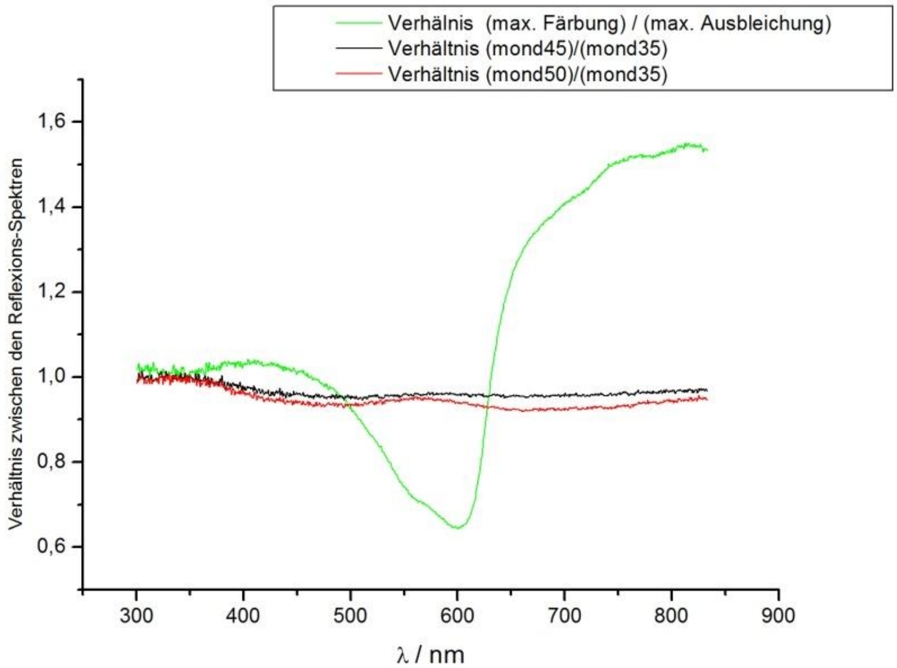
**Fig. 5.91. Reflection spectra of the "Reflective Device (13.7.2009 – Nr.1)" at the voltage value +1,00 V measured at different times on the 28.9.2009**

As shown in figure 5.89, the reflection spectra at -1,12 V kept their shape, only the number of counts, the intensity, decreased.

At +0,66 V (figure 5.90) and at +1,00 V (figure 5.91) the reflection spectra changed a little bit during the first two and a half minutes:

+0,66 V → modulation at 660 nm: 25 counts
absolute counts at 660 nm: 583 counts
+1,00 V → modulation at 660 nm: 23 counts
absolute counts at 660 nm: 567 counts

The ratio between the first reflection spectrum and each following spectrum was calculated and some of the results are presented in figure 5.92 to figure 5.94. As comparison the ratio between the maximum colouration and the maximum bleaching was added. For this calculation the reflection spectra “frida8” (maximum colouration) and “frida19” (maximum bleaching), measured on the 28.8.2009 during cyclovoltammetry (see chapter 5.1.3 – figure 5.24), were used.



28.9.2009: Toshiba CCD Spektr.: 3.Reflective Device (bei -1,12 V)

**Fig. 5.92. Ratios between the reflection spectra of the “Reflective Device (13.7.2009 – Nr.1)” measured at the voltage value -1,12 V on the 28.9.2009. (For the ratio between maximum colouration and maximum bleaching reflection spectra of the “Reflective Device (13.7.2009 – Nr.1)”, taken during cyclovoltammetry on the 28.8.2009, were used: “frida8” – maximum colouration; “frida19” – maximum bleaching)**

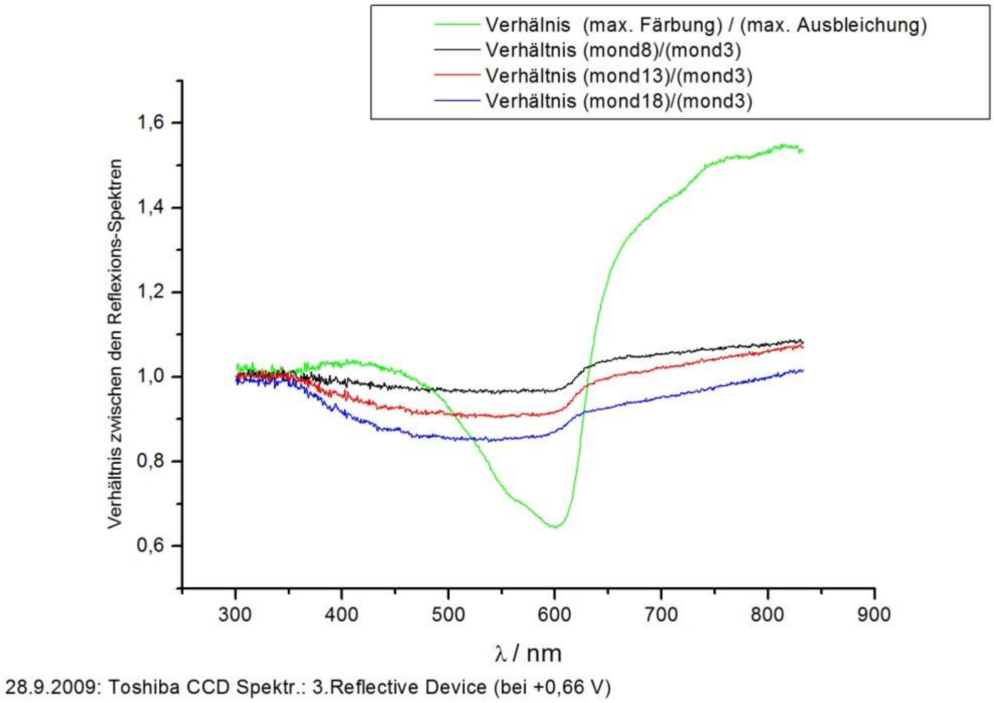


**Fig. 5.93. Ratios between the reflection spectra of the "Reflective Device (13.7.2009 – Nr.1)" measured at the voltage value +0,66 V on the 28.9.2009. (For the ratio between maximum colouration and maximum bleaching reflection spectra of the "Reflective Device (13.7.2009 – Nr.1)", taken during cyclovoltammetry on the 28.8.2009, were used: "frida8" – maximum colouration; "frida19" – maximum bleaching)**

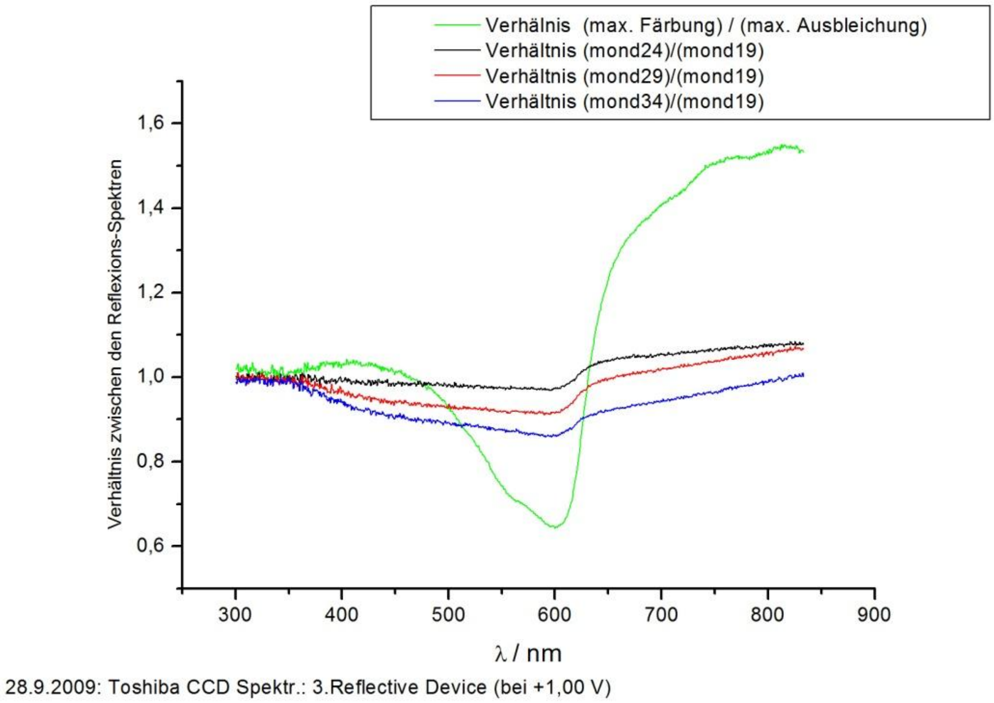


**Fig. 5.94. Ratios between the reflection spectra of the "Reflective Device (13.7.2009 – Nr.1)" measured at the voltage value +1,00 V on the 28.9.2009. (For the ratio between maximum colouration and maximum bleaching reflection spectra of the "Reflective Device (13.7.2009 – Nr.1)", taken during cyclovoltammetry on the 28.8.2009, were used: "frida8" – maximum colouration; "frida19" – maximum bleaching)**

All three points (-1,12 V; +0,66 V; +1,00 V) were confirmed being colour-stability-points of the “Reflective Device (13.7.2009 – Nr.1)”, since the shapes of the reflection spectra are decisive for the colour impression.

*The measurement results for the “Reflective Device (13.7.2009 – Nr.2)” are shown in figure 5.95 to 5.98.*

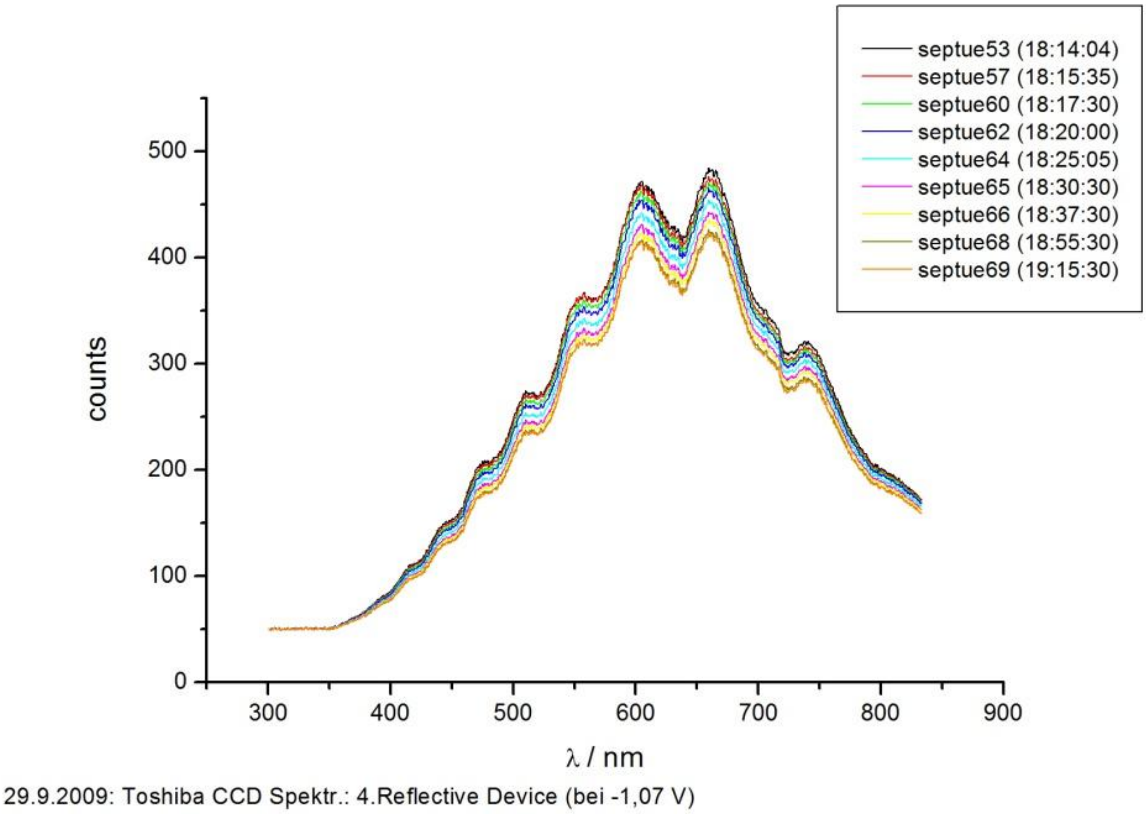


**Fig. 5.95. Reflection spectra of the “Reflective Device (13.7.2009 – Nr.2)” at the voltage value -1,07 V measured at different times on the 29.9.2009**

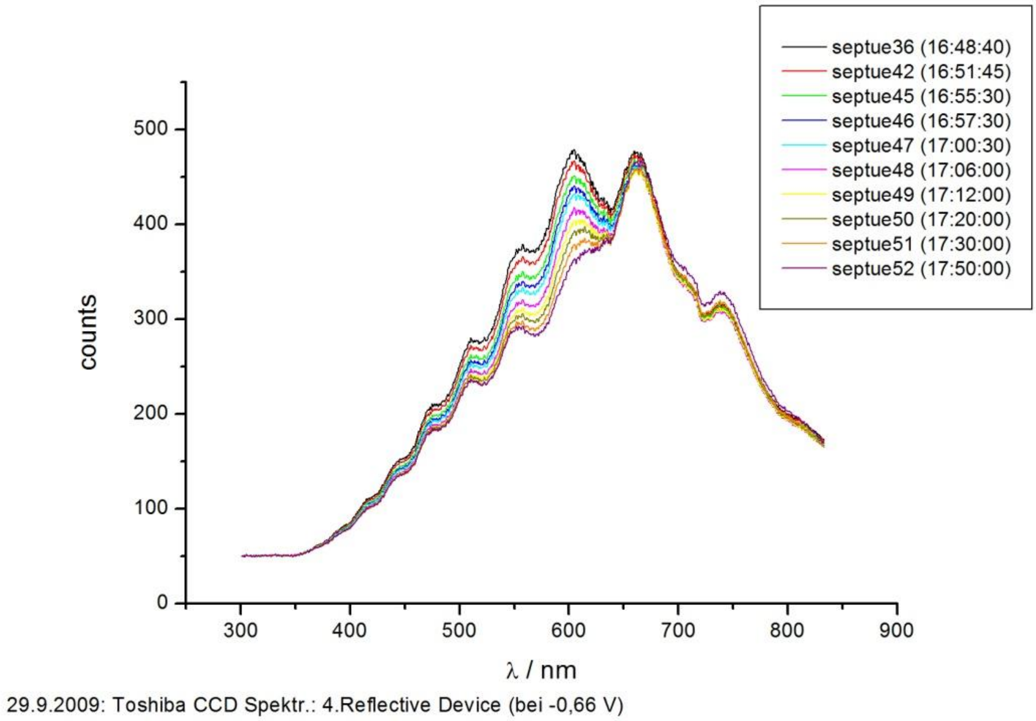


**Fig. 5.96. Reflection spectra of the "Reflective Device (13.7.2009 – Nr.2)" at the voltage value -0,66 V measured at different times on the 29.9.2009**

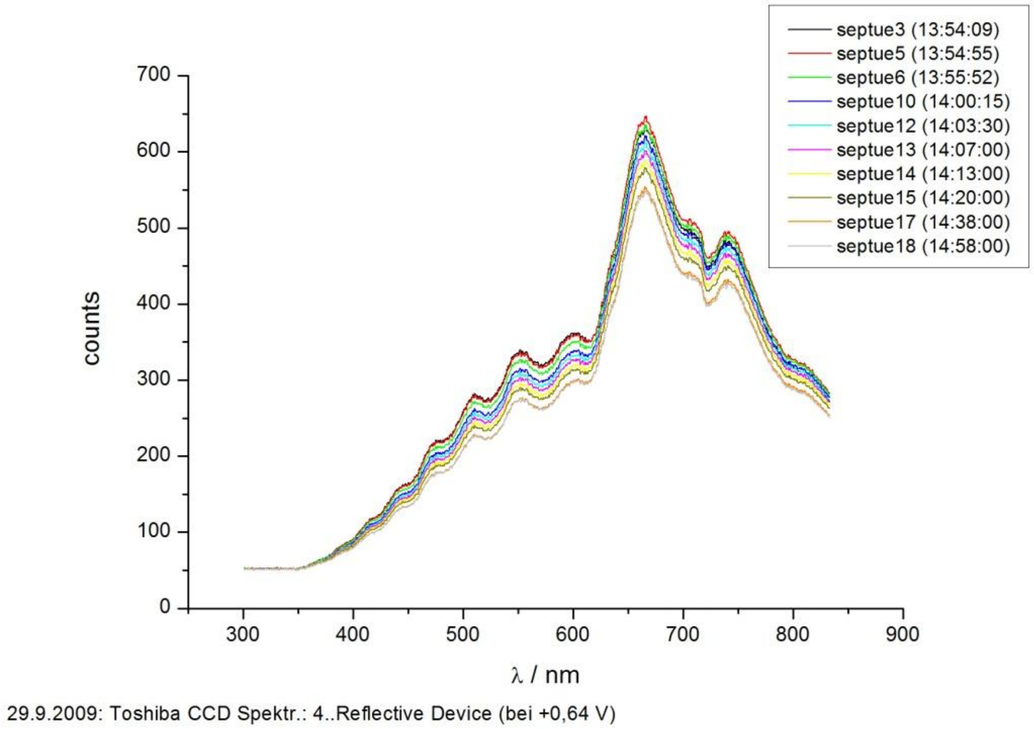


**Fig. 5.97. Reflection spectra of the "Reflective Device (13.7.2009 – Nr.2)" at the voltage value +0,64 V measured at different times on the 29.9.2009**

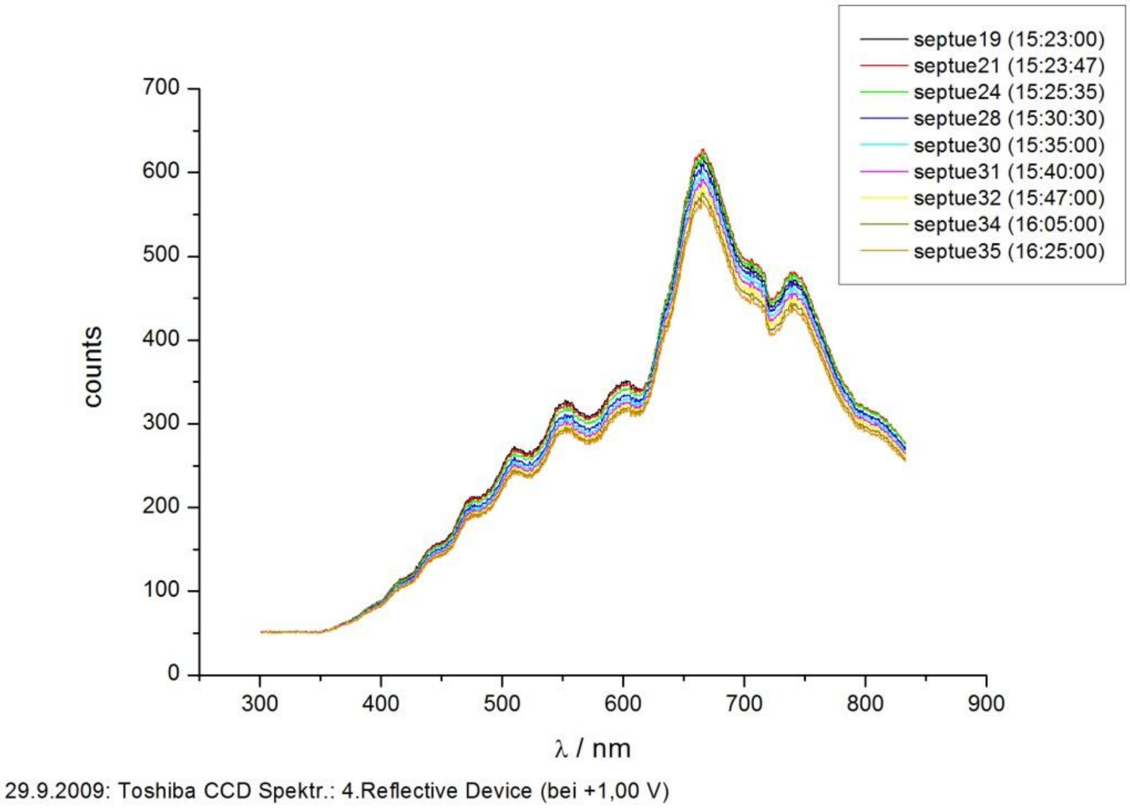


**Fig. 5.98. Reflection spectra of the “Reflective Device (13.7.2009 – Nr.2)” at the voltage value +1,00 V measured at different times on the 29.9.2009**

At -1,07 V the reflection spectra remained in their shape, the number of counts, the intensity, decreased (see figure 5.95).

As shown in figure 5.96, the appearance of the reflection spectra at -0,66 V changed continuously the whole measurement time (about one hour) through. It was expected that the number of counts decreased too, as this happened at each of the voltage values during the other measurements.

At +0,64 V (figure 5.97) and at +1,00 V (figure 5.98) the reflection spectra changed a little bit during the first minute:

+0,64 V → modulation at 660 nm: 14 counts
absolute counts at 660 nm: 635 counts
+1,00 V → modulation at 660 nm: 11 counts
absolute counts at 660 nm: 616 counts

Ratios between the reflection spectra are presented in figure 5.99 to figure 5.102. For the calculation of the ratio between the maximum colouration and the maximum bleaching reflection spectra “monda27” (maximum colouration) and “monda38” (maximum bleaching) of the “Reflective Device (13.7.2009 – Nr.2)”, taken during cyclovoltammetry on the 31.8.2009 (see chapter 5.1.3 – figure 5.32), were used.

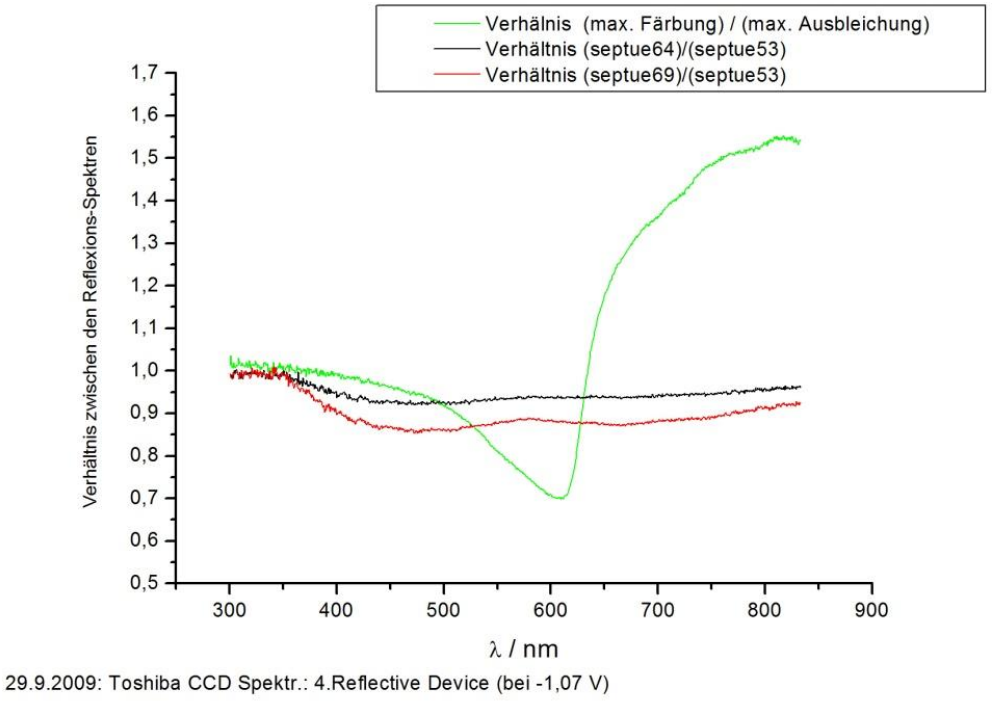


**Fig. 5.99. Ratios between the reflection spectra of the "Reflective Device (13.7.2009 – Nr.2)" measured at the voltage value -1,07 V on the 29.9.2009. (For the ratio between maximum colouration and maximum bleaching reflection spectra of the "Reflective Device (13.7.2009 – Nr.2)", taken during cyclovoltammetry on the 31.8.2009, were used: "monda27" – maximum colouration; "monda38" – maximum bleaching)**

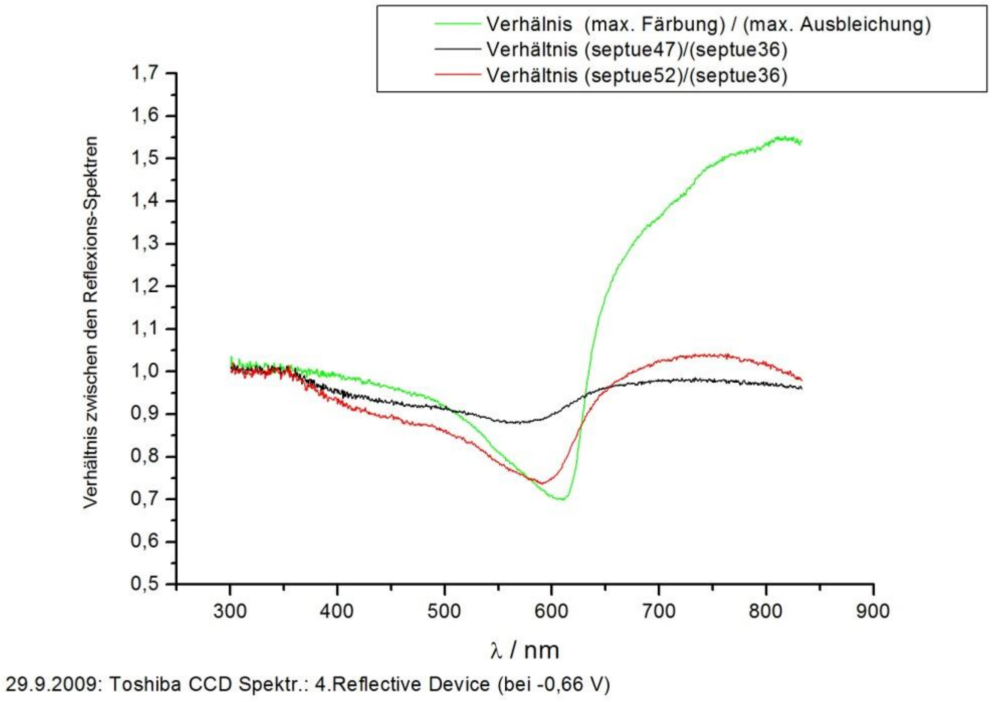
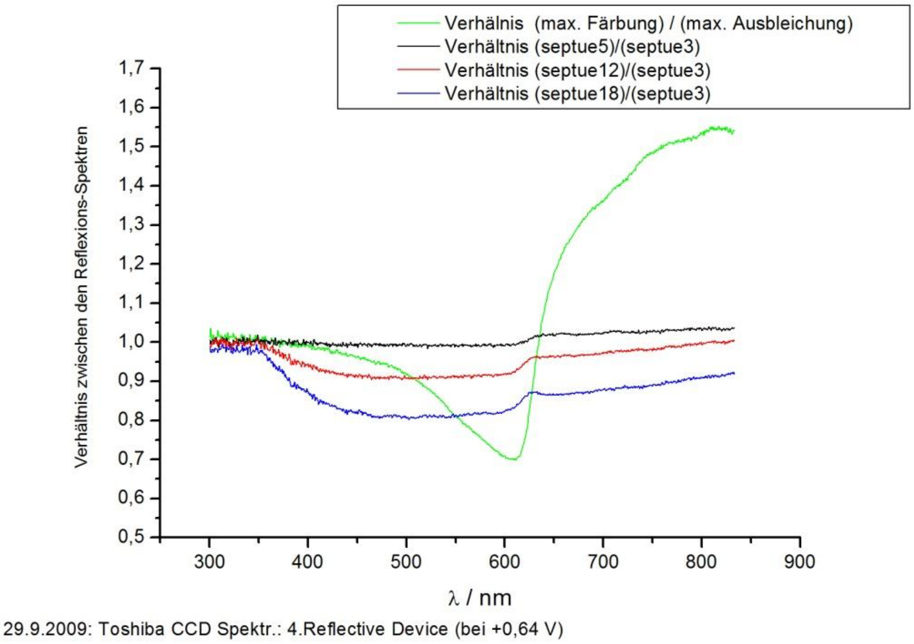
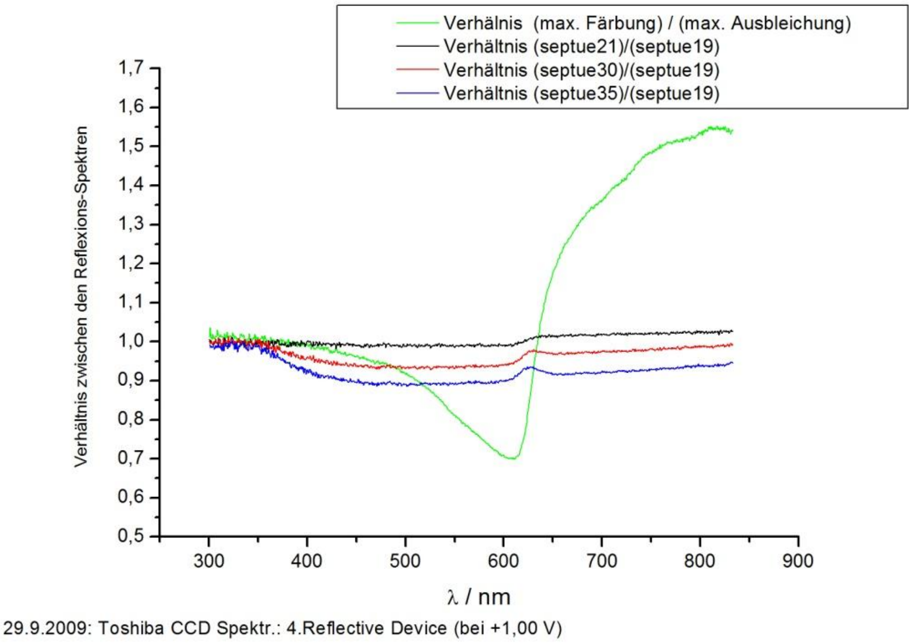


**Fig. 5.100. Ratios between the reflection spectra of the "Reflective Device (13.7.2009 – Nr.2)" measured at the voltage value -0,66 V on the 29.9.2009. (For the ratio between maximum colouration and maximum bleaching reflection spectra of the "Reflective Device (13.7.2009 – Nr.2)", taken during cyclovoltammetry on the 31.8.2009, were used: "monda27" – maximum colouration; "monda38" – maximum bleaching)**



29.9.2009: Toshiba CCD Spektr.: 4.Reflective Device (bei +0,64 V)

**Fig. 5.101. Ratios between the reflection spectra of the "Reflective Device (13.7.2009 – Nr.2)" measured at the voltage value +0,64 V on the 29.9.2009. (For the ratio between maximum colouration and maximum bleaching reflection spectra of the "Reflective Device (13.7.2009 – Nr.2)", taken during cyclovoltammetry on the 31.8.2009, were used: "monda27" – maximum colouration; "monda38" – maximum bleaching)**



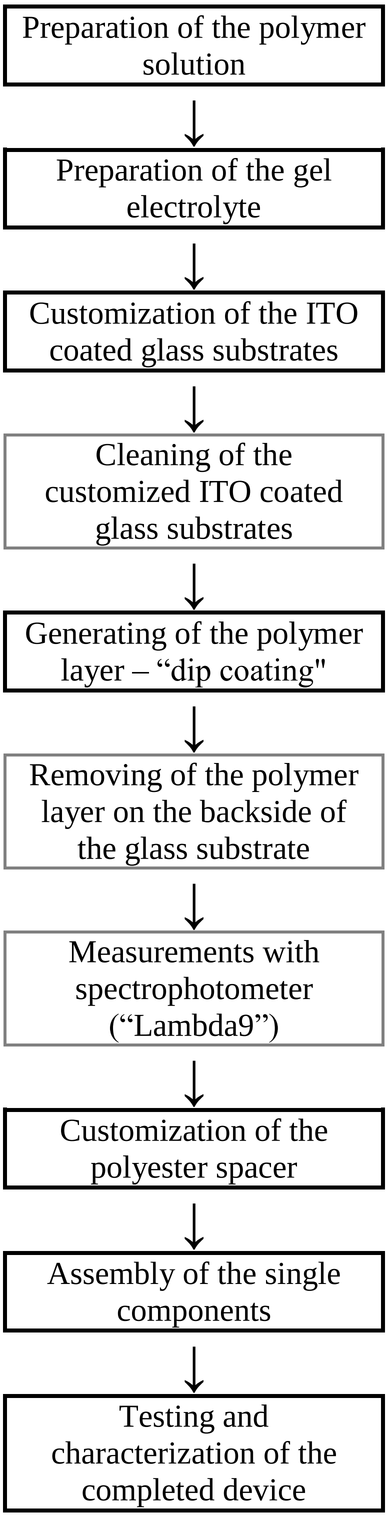
29.9.2009: Toshiba CCD Spektr.: 4.Reflective Device (bei +1,00 V)

**Fig. 5.102. Ratios between the reflection spectra of the "Reflective Device (13.7.2009 – Nr.2)" measured at the voltage value +1,00 V on the 29.9.2009. (For the ratio between maximum colouration and maximum bleaching reflection spectra of the "Reflective Device (13.7.2009 – Nr.2)", taken during cyclovoltammetry on the 31.8.2009, were used: "monda27" – maximum colouration; "monda38" – maximum bleaching)**

Corresponding to the results, -1,07 V, +0,64 V, +1,00 V have been found to be colour-stability-points of the "Reflective Device (13.7.2009 – Nr.2).

# 6. Fabrication and characterization of electrochromic devices – demonstrator

Organic electrochromic devices were made and investigated. Below an overview of the fabrication process is shown.



For sample compartments: 50 ml gas tight glass vials (DURAN)

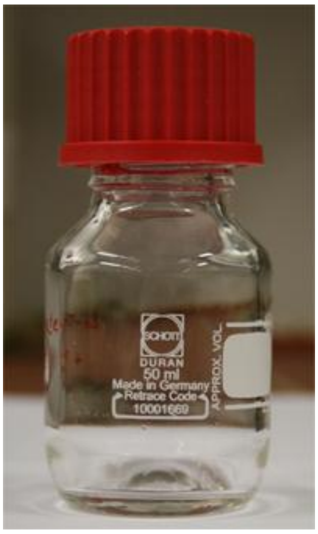


**Fig. 6.1. 50 ml gas tight glass vials (DURAN)**

## 6.1. Preparation of the polymer solutions

Three polymer solutions with different polymers were prepared. For that the following polymers were dissolved in toluene: “magenta polymer”, “clear polymer” (“non colouring polymer”), both gratefully provided by Ciba (now part of BASF), and “regioregular P3HT” (“regioregular poly(3-hexylthiophene-2,5-diyl)”).

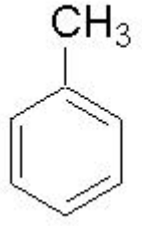


**Fig. 6.2. Structural formula of toluene**

### 6.1.1. Magenta polymer solution

First 20 ml of 0,5 % weight toluene solution (solution of the polymer in toluene) was prepared.
To calculate the needed amount in gram of the magenta polymer 10 ml toluene was translated into gram ($m = V \cdot \rho$) with the density of toluene ($\rho = 0{,}8669\ g/cm^3 = 0{,}8669\ g/ml$): 10 ml toluene is equivalent to 8,669 g toluene. Now the 8,669 g were set 99,5 % weight.
For the further calculation in this work 99,5 % weight was allowed to be 100 % weight, since the accuracy is satisfying. Accordingly 0,5 % weight is 0,043345 g. This means 0,043345 g magenta polymer was needed to prepare 10 ml 0,5 % weight toluene solution and 0,08669 g for 20 ml 0,5 % weight toluene solution.

Solution 1:

20 ml toluene (Sigma-Aldrich: Cat.: 34866; Toluene chromasolv (for high performance liquid chromatography); min 99,9%) was put into a 50 ml gas tight glass vial (DURAN), and magenta polymer (0,0867 g) was added. To dissolve the magenta polymer in the toluene a magnetic stir bar (length: 20 mm; diameter: 6 mm) was put into the 50 ml gas tight glass vial (DURAN), and then the vial was placed on a magnetic stirrer (300 turns per minute) at room temperature.

Solution 2:

After some experiments the concentration of the magenta polymer – toluene solution was increased to about 1 % weight. For that 0,0865 g magenta polymer was added to solution 1.

Solution 3:

Later more solution was needed and therefore 5 ml toluene (Aldrich: Cat.: 17,996-5; Toluene; reagent plus$^{TM}$; 99%) and the rest of the magenta polymer (~0,04 g) were put into solution 2. At that time a higher quantity of the polymer was not available.

Solution 4:

A few days later 5 ml toluene (Aldrich: Cat.: 17,996-5; Toluene; reagent plus$^{TM}$; 99%) was put into solution 3.

The solutions 1 to 4 were used for dip coating experiments (see chapter 6.4.). During dip coating the concentration of the magenta polymer – toluene solution changes slightly since toluene is a volatile solvent. There is no importance to know the exact concentration as the thickness of the polymer layer was calculated from the optical density (see detailed chapter 6.4).

### 6.1.2. Clear polymer (non colouring polymer) solution

First 20 ml of 0,2 % weight toluene solution was made. Same calculation as in chapter (6.1.1.) resulted in an amount of 0,017338 g clear polymer to prepare 10 ml of 0,2 % weight toluene solution and 0,034676 g for 20 ml 0,2 % weight toluene solution.

So 20 ml toluene (Sigma-Aldrich: Cat.: 34866; Toluene chromasolv (for high performance liquid chromatography); min 99,9%) was put into a 50 ml gas tight glass vial (DURAN), and 0,0346 g clear polymer was added. To dissolve the clear polymer a magnetic stir bar (length: 20 mm; diameter: 6 mm) was put into the bottle, and then the vial was placed on a magnetic stirrer (300 turns per minute) at room temperature.

After the first experiments with the magenta polymer it was decided to increase the concentration of the clear polymer – toluene solution. For that the rest of the clear polymer (~0,16 g) was put into the polymer solution. Since 25 ml polymer solution was needed for the dip coating container, 5 ml toluene (Aldrich: Cat.: 17,996-5; Toluene; reagent plus$^{TM}$; 99%) was added to the clear polymer – toluene solution in the 50 ml gas tight glass vial (DURAN), and the vial was again put on the magnetic stirrer (150 turns per minute) until the whole clear polymer was dissolved (room temperature). Now the concentration of the clear polymer – toluene solution was ~0,9 % weight.

With this ~0,9 % weight clear polymer – toluene solution dip coating experiments were carried out.

### 6.1.3. Regioregular P3HT solution

The quantity of 0,3087 g of regioregular P3HT (Aldrich: Cat.: 669067; poly(3-hexylthiophene-2,5-diyl); regioregular; electronic grade; 99,995% trace metal basis; average $M_n$ ~17500) was put into a 50 ml gas tight glass vial (DURAN). 15 ml toluene (Aldrich: Cat.: 17,996-5; Toluene; reagent plus$^{TM}$; 99%) and a magnetic stir bar (length: 20 mm; diameter: 6 mm) were added, and then the vial was put on a magnetic stirrer (450 turns per minute) for about 18 hours (room temperature). Afterwards 20 ml toluene (Aldrich: Cat.: 17,996-5; Toluene; reagent plus$^{TM}$; 99%) was added to the regioregular P3HT – toluene solution, and the vial was again put on the magnetic stirrer (150 turns per minute) for about 3 hours (room temperature).

The target was to prepare a high concentrated solution, since the drawing process can be speeded up with the increase of the concentration (see figure 6.33).

Only, the used quantity regioregular P3HT didn´t dissolve completely in 35 ml toluene. Small dark grains of the polymer were among the regioregular P3HT – toluene solution. So it was not possible to determine the concentration of the regioregular P3HT – toluene solution. These grains had an effect on the appearance of the regioregular P3HT polymer layers (details see chapter 6.4).

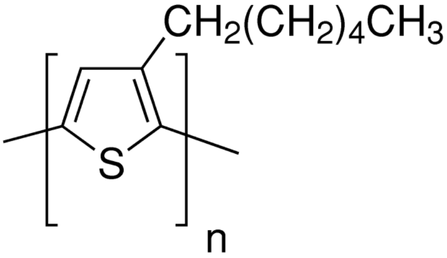


**Fig. 6.3. Structural formula of poly(3-hexylthiophene-2,5-diyl) – P3HT**

## 6.2. Preparation of the gel electrolyte

The gel electrolyte is composed of “propylene carbonate” and “poly methyl methacrylate” (gratefully provided by Ciba) and “lithium triflate”.

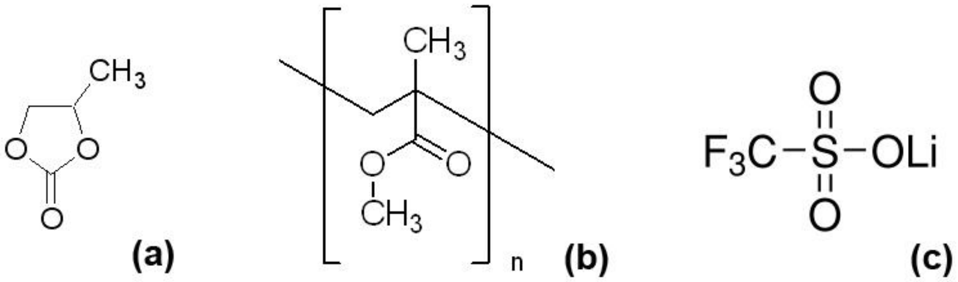


**Fig. 6.4. Structural formulas of propylene carbonate – PC (a), poly methyl methacrylate – PMMA (b) and lithium triflate (c)**

Poly methyl methacrylate (2,2957 g) was put into a 50 ml gas tight glass vial (DURAN) and then 10 ml propylene carbonate (FLUKA: Cat.: 82227; Propylene carbonate; selectophore®;

≥99,0%(GC)) was added. To dissolve the poly methyl methacrylate in the propylene carbonate a magnetic stir bar (length: 20 mm; diameter: 6 mm) was put into the 50 ml gas tight glass vial (DURAN), and then the vial was placed on a heated magnetic stirrer (300 turns per minute; ~100 °C). The solution was so viscous that the magnetic stir bar didn´t twist but only wobbled. First the solution was cloudy and became clear after one and a half hour. When the 50 ml gas tight glass vial (DURAN) was put off the heated magnetic stirrer the solution cooled down and got solid. So 10 ml propylene carbonate was added, and the 50 ml gas tight glass vial (DURAN) was put on the heated magnetic stirrer again to get a gel like consistence in the cooled state (room temperature) too. This basic solution was deairated in a vacuum system and then flooded with argon.

Lithium triflate (1,5610 g) was put into a 50 ml gas tight glass vial (DURAN) (Aldrich: Cat.: 481548; Lithium trifluoromethanesulfonate; 99,995%; trace metals basis). Propylene carbonate (dried with molecular sieve, pore size 10Å; VACUUM GENERATORS) was bubbled with argon. 2 ml of this degassed propylene carbonate was added to the lithium triflate in the 50 ml gas tight glass vial (DURAN) by an injection with injection-filter. Since the lithium triflate didn´t dissolve in this amount of propylene carbonate (PC) again 2 ml of propylene carbonate was added. A magnetic stir bar (length: 20 mm; diameter: 6 mm) was put into the 50 ml gas tight glass vial (DURAN) with the Li-triflate – PC solution, and the vial was put on a magnetic stirrer (450 turns per minute) and was flooded with argon during the stirring until the whole Li-triflate was dissolved at room temperature.

Then the Li-triflate – PC solution was added to the 50 ml gas tight glass vial (DURAN) with the poly methyl methacrylate – PC solution, and the vial was put on a magnetic stirrer (450 turns per minute) and first flooded with argon and then bubbled with argon during the stirring at room temperature.

The completed gel electrolyte consists of 24 ml propylene carbonate, 2,2957 g poly methyl methacrylate and 1,5610 g lithium triflate.

## 6.3. Customization of the ITO coated glass substrates

Two types of ITO coated glass were used:

“ITO-CG 1” → thickness: 1,100 mm; $R_{ITO}$ = 38 Ω
“ITO-CG 2” → thickness: 0,698 mm; $R_{ITO}$ = 390 Ω

The thickness of the ITO coated glass slides was measured with a micrometer (digitrix II, 0-25 mm, 0,001 mm). It is allowed to equal the measured thickness to the thickness of the glass slides, since the order of magnitude of the ITO layer thickness is nanometre. The resistance of the ITO layer was measured for 1 cm measuring distance (ohmmeter: FLUKE 12 Multimeter).

The dimensions of the ITO coated glass substrates for the first experiments with the dip coater were approximately 50 mm in length and 20 mm in width. The substrates were cut out of larger pieces of ITO coated glass (only one side of the glass has an ITO layer) with a diamond cutter.

For the first fabricated devices, which served for study purpose, the dimensions of the single ITO coated glass substrates were approximately 55 mm in length and 20 mm in width.

The dimensions of the ITO coated glass substrates for the demonstrator were determined and limited by the plastic casing with an acrylic plastic window (details see figure 6.92, 6.93) and the available dip coating container (details see figure 6.8 b). Substrates with 45 mm width and 60 to 65 mm length were cut out.

After some dip coating experiments the way of cleaning was decided:
The customized ITO coated glass substrates were put into a beaker with technical isopropanol and then the beaker was placed into the ultrasonic bath for a few minutes. After that both sides of the ITO coated glass substrates were cleaned with cotton sticks and isopropanol (Sigma-Aldrich: Cat.: 15,497-0; 2-propanol; ACS spectrophotometric grade; ≥99,5%).

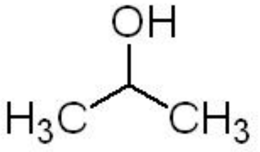


**Fig. 6.5. Structural formula of 2-propanol**

## 6.4. Generating of the polymer layer – “dip coating”

A dip coater (“NANO DIP – ND-0407”, SDI Company) was used to apply the polymer on the ITO coated glass substrate.
The dip coater is composed of a mechanical drawing device and a control unit with touch screen (see figure 6.6). The drawing device consists of a base plate, where the container with the solution can be placed, an “upper and lower” driving part with a motor and a gripper arm, which is fixed on the “upper and lower” driving part. The wanted starting position of the gripper arm can be adjusted manually with two screws on the backside. The smaller screw is for fixation and with the large screw the whole “upper and lower” driving part with motor and gripper arm can be driven up and down. The drawing process itself is done automatically with the motor under control of the control unit. The drawing speed and the drawing path length can be set and the current status of the drawing process (remaining drawing path length, current speed and remaining time) is presented at the screen of the control unit.

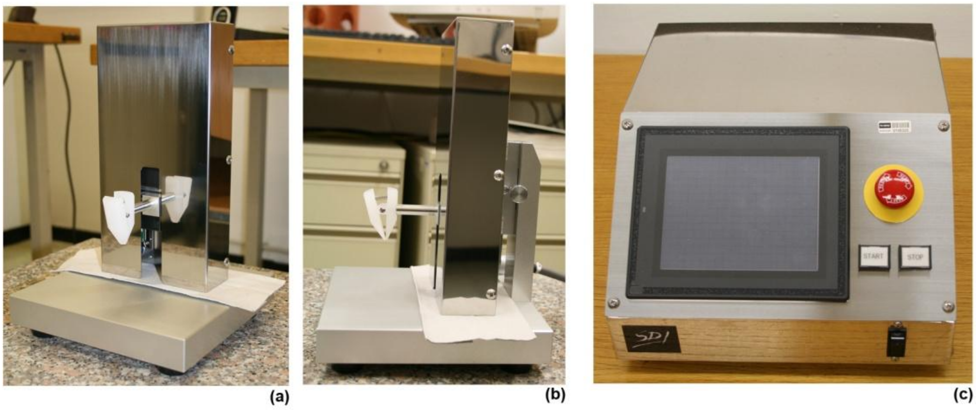


**Fig. 6.6. Mechanical drawing device (a, b) and control unit (c) of the dip coater (“NANO DIP – ND-0407”, SDI Company)**

Dip coating process:

The substrate is fixed with the gripper arm. The container, filled with the solution, is positioned on the base plate of the drawing device right under the hanging substrate. With the touch screen of the control unit the drawing speed and the drawing path length can be set. The substrate can be immersed manually or automatically in the solution of the coating substance. With the start button on the control unit the extraction of the immersed substrate can be started. The extraction is carried out at a constant speed. During this pull out process a thin polymer layer deposits on the surface of the substrate. The evaporation of the volatile solvent toluene starts immediately.

After the dip coating process the substrates with the polymer layers were stored enclosed in petri dishes at room temperature for a few days before further processing.

The thickness of the layer depends on the drawing speed and the concentration of the polymer solution. The influence of other factors like atmosphere, temperature, etc. was not investigated in this work.

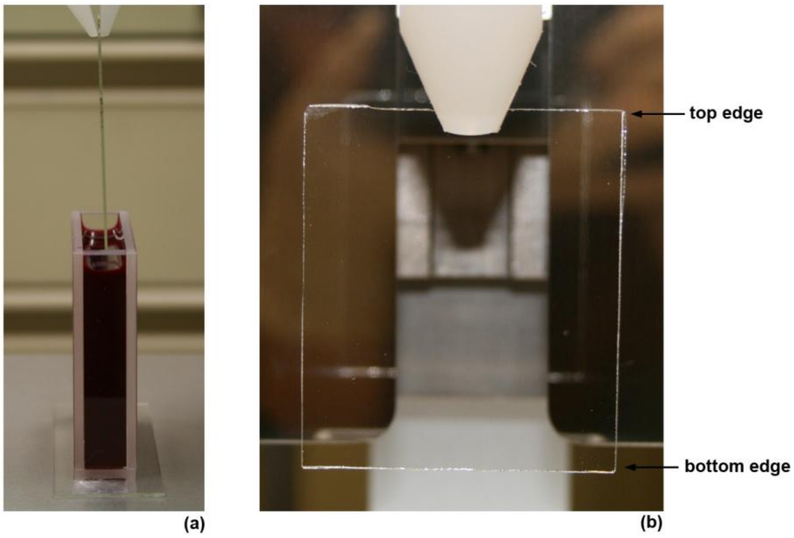


**Fig. 6.7. With polymer solution filled container (cuvette: inner dimensions: height: 52,5 mm; width: 50 mm; depth: 10 mm) placed on the base plate right under the hanging substrate – side view (a). Fixed substrate (length: 52 mm, width:45 mm) from the front view (b)**

The concentration of the polymer – toluene solution changes slightly during the dip coating experiments, since toluene is a volatile solvent and for that evaporates during the pull out process.

Since the available quantity of polymer solution was limited, it was important to use suitable containers, which were big enough, to fit to the ITO coated glass substrates, but on the same time the volume had to be small enough to use as little as possible of polymer solution.

With the first experiments the dimensions of the ITO coated glass substrates were approximately 50 mm in length and 20 mm in width. Short side first the substrates were dived into the container and the lengths of the polymer-layers had to be about 20 mm. A cuvette (outer dimensions: height: 45,4 mm; width: 32 mm; depth: 12 mm; inner dimensions: height: 43,7 mm; width: 30 mm; depth: 10 mm) was used as container for the polymer solution in these cases (see figure 6.8).

The ITO coated glass substrates for the demonstrator were larger (length: 60 to 65 mm; width: 45 mm) and the polymer layers had to be approximately 45 mm in length. (Again short side first the ITO coated glass substrates were dived into the container.) As container for the polymer solution a

cuvette with outer dimensions of 55 mm height, 55 mm width, 15 mm depth and inner dimensions of 52,5 mm height, 50 mm width, 10 mm depth was used (see figure 6.8).
Figure 6.8 shows the two cuvettes, which served as container for the polymer solution during the dip coating processes. To improve the stability of the cuvettes, they were fixed on a slide with double faced adhesive tape.

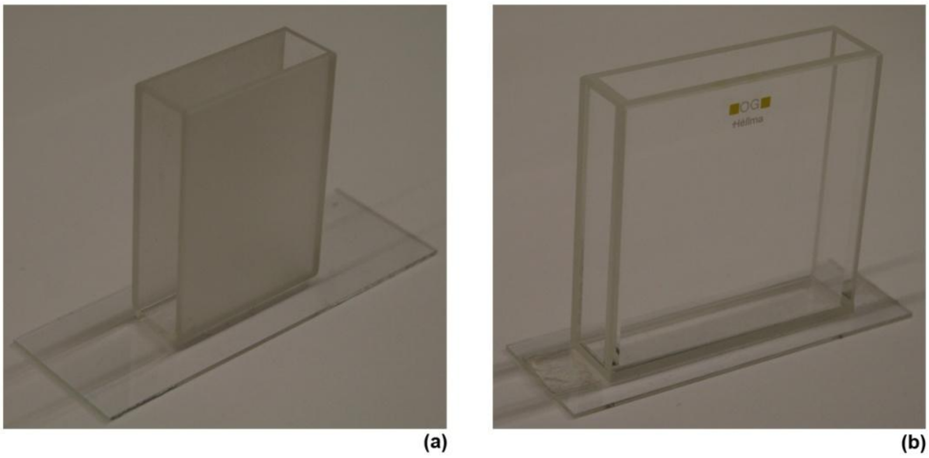


**Fig. 6.8. Containers for the dip coating process – cuvettes fixed on base plates (slides: length: 76 mm, width: 26 mm): (a)…inner dimensions: height: 43,7 mm; width: 30 mm; depth: 10 mm; (b)...inner dimensions: height: 52,5 mm; width: 50 mm; depth: 10 mm**

For all dip coating experiments ITO coated glass substrates (only one side of the glass had an ITO layer) were used.

After the dip coating process the polymer layers on the ITO coated glass substrates were investigated with an optical microscope (Olympus BX51) and/or a spectrophotometer “Lambda9” (PERKIN-ELMER – Lambda9 – UV/VIS/NIR Spectrophotometer). The polymer layers on the “backside” (side without ITO layer) of the ITO coated glass substrates were removed with cotton sticks and toluene (Aldrich: Cat.: 17,996-5; Toluene; reagent plus$^{TM}$; 99%).

The first dip coating experiment was done with magenta polymer solution (0,5 % toluene solution) on the 5.11.2009. Drawing speed was set to 5 µm/s and the drawing path length to 20000 µm. The mechanical drawing device was placed on a desk. Used ITO coated glass: ITO-CG 1. Figure 6.9 demonstrates the polymer layer on the ITO coated side, investigated with an optical microscope (Olympus BX51).

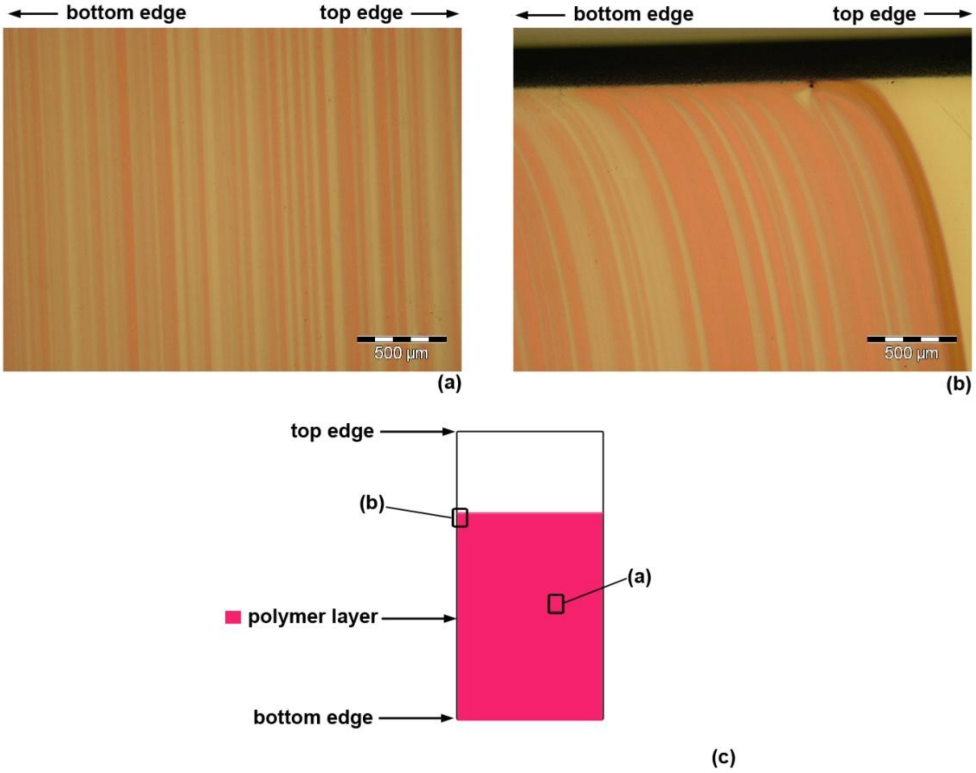


**Fig. 6.9. Magenta polymer layer on the ITO coated side of the "Dip coated substrate (5.11.2009)" investigated with an optical microscope (Olympus BX51): (a), (b) photos; (c) scheme**

The photos in figure 6.9 show an inhomogeneous polymer layer. To see, if vibrations were the reason for the stripes, the second dip coating experiment was carried out with the drawing device placed on a special desk to prevent vibrations. Stripes didn´t occur, so the special desk was used for the further experiments.

On the 6.11.2009 the second dip coating experiment was done. The same magenta polymer solution was taken and the same drawing speed (5 µm/s) and drawing path length (20000 µm) were chosen as on the 5.11.2009. Used ITO coated glass: ITO-CG 1. Figure 6.10 shows photos of the polymer layer on the ITO coated side of the glass substrate.

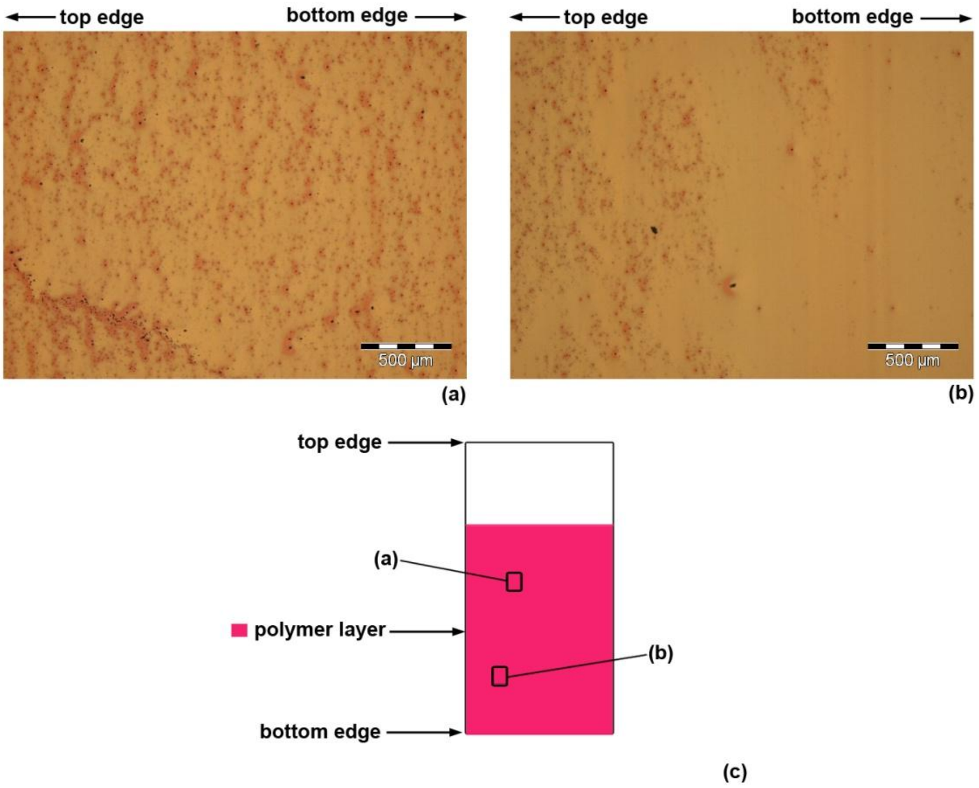


**Fig. 6.10. Magenta polymer layer on the ITO coated side of the "Dip coated substrate (6.11.2009)" investigated with an optical microscope (Olympus BX51): (a), (b) photos; (c) scheme**

The photo (a) in figure 6.10 shows an inhomogeneous part of the polymer layer. An investigation of the polymer free part of the "Dip coated substrate (6.11.2009)" with the optical microscope showed parts with particles of dirt and clean parts.

From that it was concluded that the black points on the photos were particles of dirt and that this filth was responsible for the inhomogeneous appearance of the magenta polymer layer. Photo (b) in figure 6.10 shows an extract of the polymer layer with homogenous parts.

The ITO coated glass substrates, used for the first and this second dip coating experiment, were dived completely into toluene in a beaker for cleaning. Further the second glass substrate in the beaker filled with toluene was placed into the ultrasonic bath for three minutes.

For all the other experiments the ITO coated glass substrates were cleaned with cotton sticks and isopropanol (Sigma-Aldrich: Cat.: 15,497-0; 2-propanol; ACS spectrophotometric grade; ≥99,5%) before running the dip coating process.

The next dip coating experiment was done on 9.11.2009. The same magenta polymer solution as in the previous experiments was used, and again the drawing speed was 5 µm/s and the drawing path length was 20000 µm. This time, before the ITO coated glass substrate (ITO-CG 1), fixed on the gripper arm, was immersed in the polymer solution, the surface was blown over with $CO_2$. And during the dip coating process a plastic bucket was put over the drawing device to prevent disturbances caused by air circulations. The magenta polymer layer on the ITO coated side of the glass substrate was investigated with an optical microscope (Olympus BX51) (see figure 6.11).

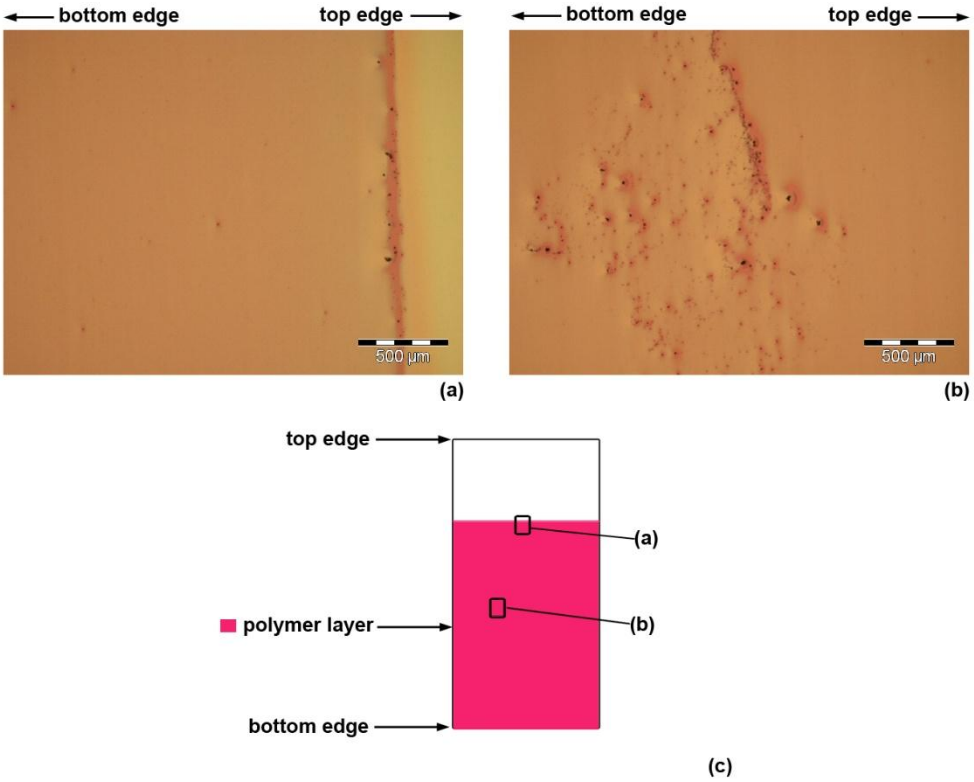


**Fig. 6.11. Magenta polymer layer on the ITO coated side of the "Dip coated substrate (9.11.2009)" investigated with an optical microscope (Olympus BX51): (a), (b) photos; (c) scheme**

Except of two small areas of about 1,5 mm in diameter the whole magenta polymer layer on the ITO coated side of the "Dip coated substrate (9.11.2009)" was homogeneous (see figure 6.11) and the whole polymer layer on the "backside" was homogenous.

This dip coated substrate was investigated with the "Lambda9". The transmission of the "Dip coated substrate (9.11.2009)" was measured at three different places: first with polymer layer on both sides of the "Dip coated substrate (9.11.2009)" and again after removing the magenta polymer from the "backside". Figure 6.12 shows photos of the used sample-holder for the measurements in the "Lambda9", and figure 6.13 and 6.14 show the three different measuring positions of the "Dip coated substrate (9.11.2009)" in the sample-holder.

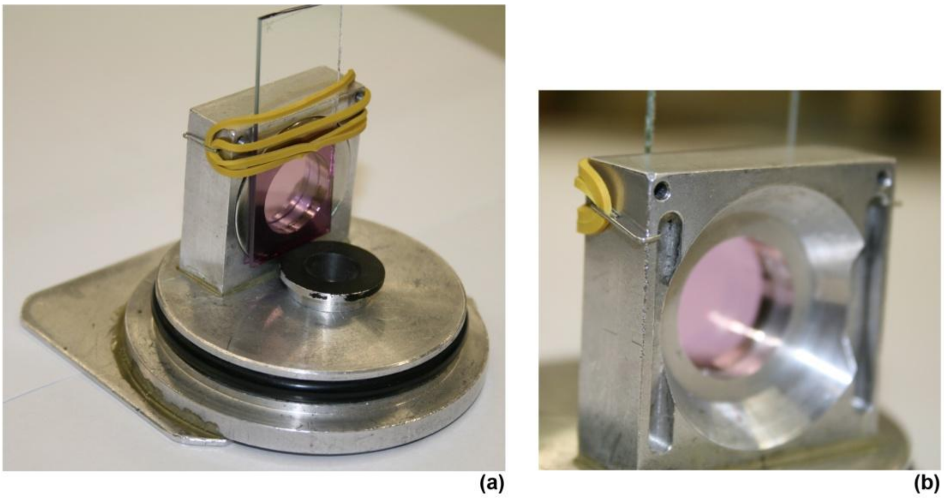


**Fig. 6.12. Sample-holder of the "Lambda9" with fixed "Dip coated substrate (9.11.2009)". (a)…front view; (b)…back view**

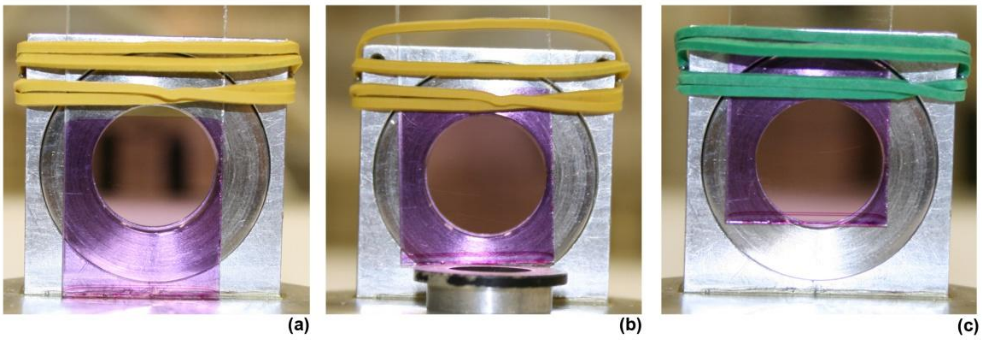


**Fig. 6.13. “Dip coated substrate (9.11.2009)” fixed on the sample-holder for the transmission measurements (three different measuring positions) in the “Lambda9” – polymer layer on both sides of the substrate.**
**(a)…dc9nov1M (figure 6.15)**
**(b)…dc9nov2M (figure 6.15)**
**(c)…dc9nov3M (figure 6.15)**

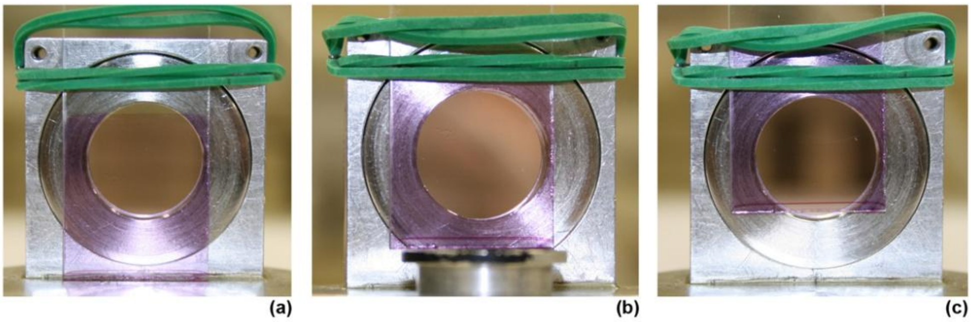


**Fig. 6.14. “Dip coated substrate (9.11.2009)” fixed on the sample-holder for the transmission measurements (three different measuring positions) in the “Lambda9” – polymer layer only on the ITO coated side of the glass substrate.**
**(a)…dc9nov4M (figure 6.15)**
**(b)…dc9nov5M (figure 6.15)**
**(c)…dc9nov6M (figure 6.15)**

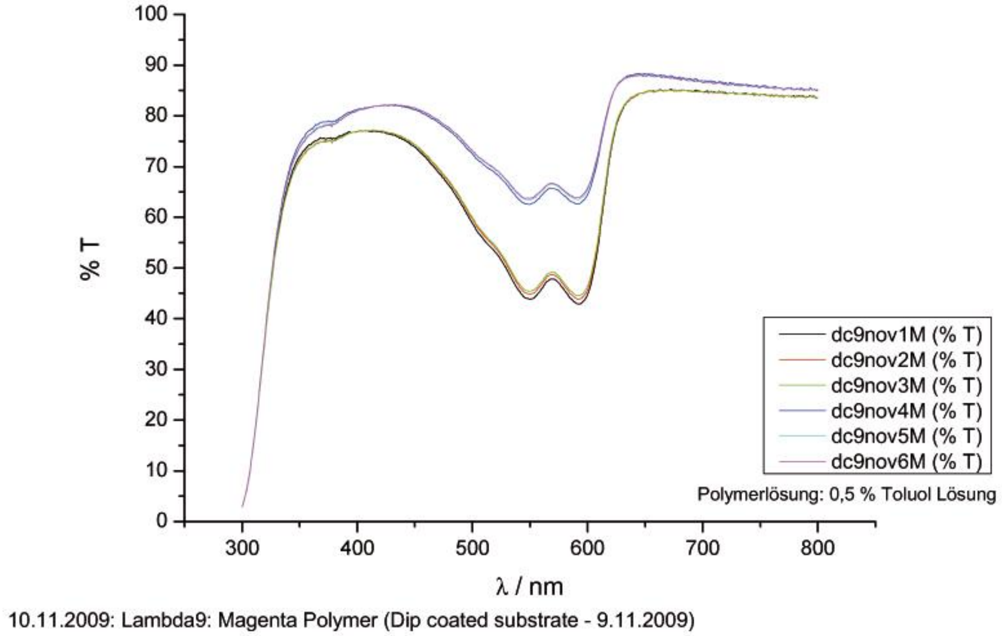


**Fig. 6.15. Transmission spectra of the “Dip coated substrate (9.11.2009)” measured with the “Lambda9” (three different measuring positions). Polymer layer on both sides of the substrate: dc9nov1M, dc9nov2M and dc9nov3M; polymer layer only on the ITO coated side of the glass substrate: dc9nov4M, dc9nov5M and dc9nov6M**

On the 11.11.2009 the dip coating process was carried out in the same way as on the 9.11.2009 except the drawing speed, which was set to 2,5 µm/s. After the dip coating process was finished the magenta polymer layers on the ITO coated glass substrate (ITO-CG 1) were investigated with an optical microscope (Olympus BX51) and the “Lambda9” (see figures 6.16, 6.17, 6.18).

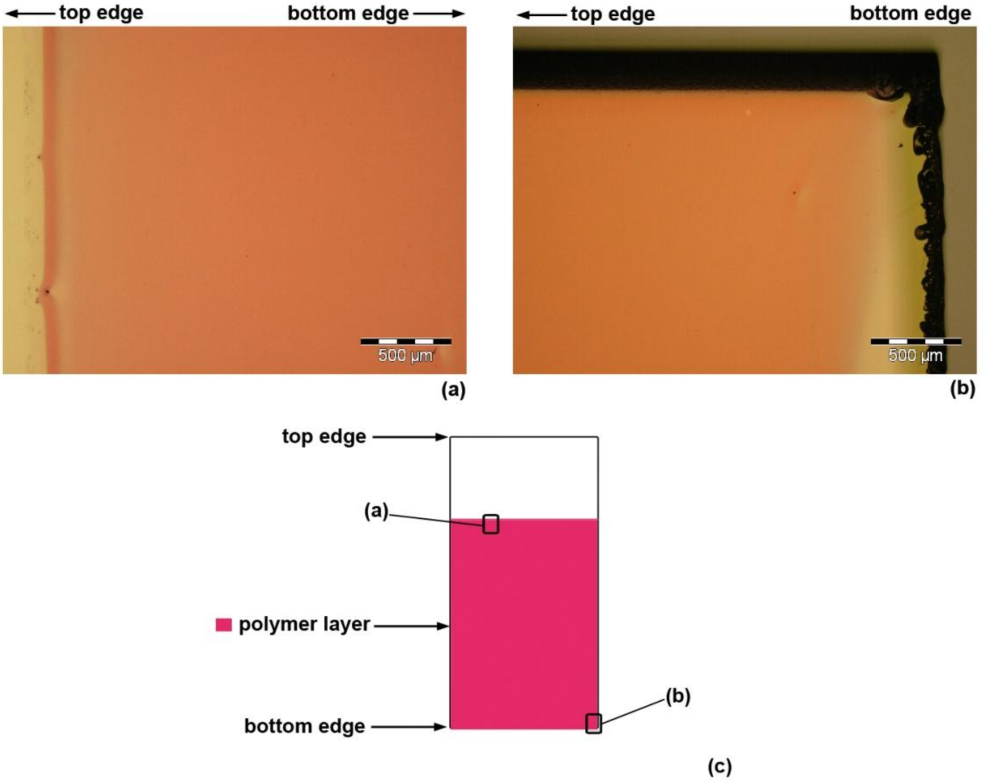


**Fig. 6.16. Magenta polymer layer on the ITO coated side of the “Dip coated substrate (11.11.2009)” investigated with an optical microscope (Olympus BX51): (a), (b) photos; (c) scheme**

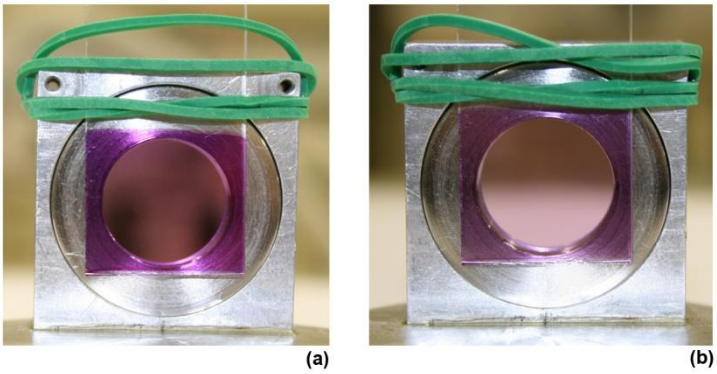
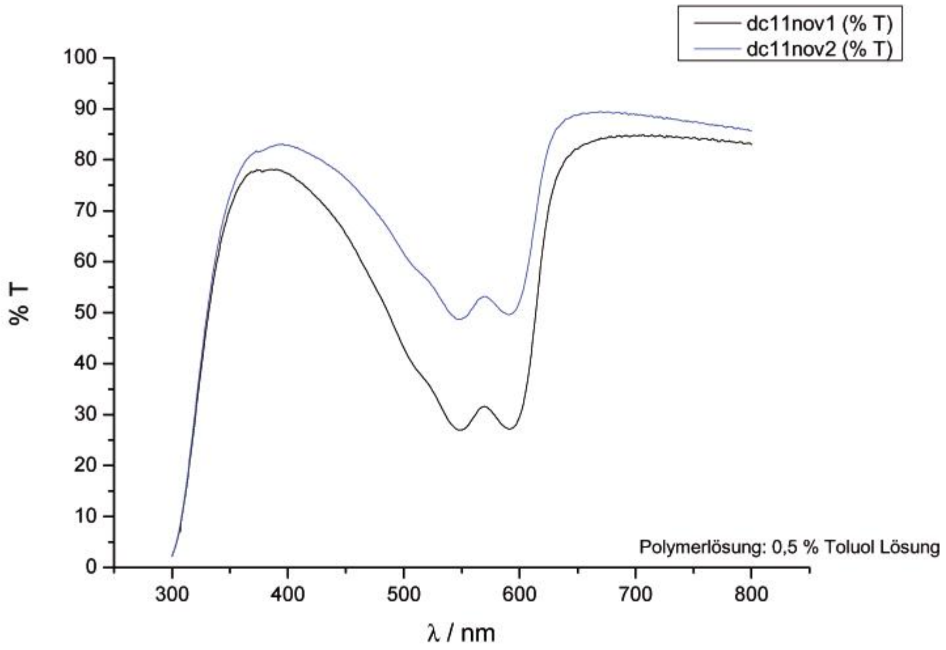


**Fig. 6.17. “Dip coated substrate (11.11.2009)” fixed on the sample-holder for the transmission measurements in the “Lambda9”. (a)…polymer layer on both sides of the substrate; (b)…polymer layer only on the ITO coated side of the glass substrate**



Polymerlösung: 0,5 % Toluol Lösung

12.11.2009: Lambda9: Magenta Polymer (Dip coated substrate - 11.11.2009)

**Fig. 6.18. Transmission spectra of the “Dip coated substrate (11.11.2009)” measured with the “Lambda9”. Polymer layer on both sides of the substrate: dc11nov1; polymer layer only on the ITO coated side of the glass substrate: dc11nov2**

It was important to determine the thickness of the magenta polymer layer, since the colour intensity is related to the layer thickness.

Law of attenuation:

$$\boldsymbol{\frac{I}{I_0} = e^{-a \cdot d}}$$

$\boldsymbol{I}$...measured spectrum: light intensity
$\boldsymbol{I_0}$...reference spectrum: light intensity
$\boldsymbol{a}$...attenuation coefficient, absorption coefficient (material property)
$\boldsymbol{d}$...thickness of the polymer layer

$$\boldsymbol{ln\left(\frac{I}{I_0}\right) = -a \cdot d}$$

$$\boldsymbol{-ln\left(\frac{I}{I_0}\right) = -ln(T) = a \cdot d}$$

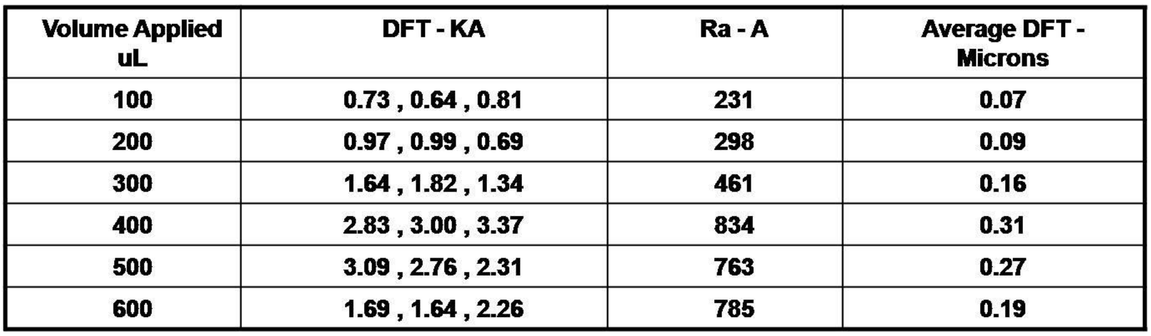
$$\boldsymbol{d = \frac{-ln(T)}{a}}$$

$\boldsymbol{T}$...transmission
$\boldsymbol{-ln(T)}$...optical density

So with the knowledge of the absorption coefficient of the magenta polymer the thickness of the polymer layer can be calculated from the transmission spectrum.

David Yale from Ciba sent absorption spectra of magenta polymer layers of different thicknesses. A table, including different average layer thicknesses with the corresponding applied polymer-toluene solution volume values (Ciba produced the polymer layers by spray-coating), was sent too.
With these data it was possible to calculate the absorption coefficient.

**Table 6.1. Table gratefully provided by Ciba (now part of BASF) – David Yale: Magenta Polymer – Batch 280 – Airbrush Applied 0.5 % Toluene Solution (Small ITO – 7 x 50 mm). DFT…dry film thickness, Ra…(surface) roughness average**



| Volume Applied uL | DFT - KA | Ra - A | Average DFT - Microns |
|---|---|---|---|
| 100 | 0.73 , 0.64 , 0.81 | 231 | 0.07 |
| 200 | 0.97 , 0.99 , 0.69 | 298 | 0.09 |
| 300 | 1.64 , 1.82 , 1.34 | 461 | 0.16 |
| 400 | 2.83 , 3.00 , 3.37 | 834 | 0.31 |
| 500 | 3.09 , 2.76 , 2.31 | 763 | 0.27 |
| 600 | 1.69 , 1.64 , 2.26 | 785 | 0.19 |

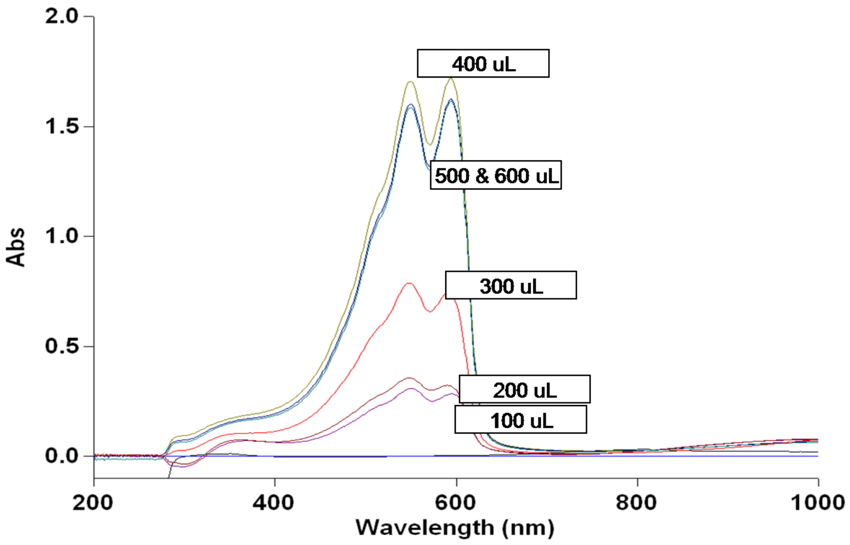


**Fig. 6.19. Absorption spectra of magenta polymer layers (gratefully provided by Ciba (now part of BASF) – David Yale)**

The absorption values at 550 nm were read out (figure 6.19) and after that the optical density was calculated for every dry film thickness (see table 6.2).

**Table 6.2. Average DFT (dry film thickness) of the magenta polymer layers in dependence on the absorption and the optical density at 550 nm**

| Absorption A<br>$\Delta A = \pm 0{,}08$ | Transmission T<br>$T = 10^{-A}$ | Optical density<br>$-ln(T)$ | Volume applied<br>µl | Average DFT<br>µm |
|---|---|---|---|---|
| 0,3080 | 0,4920 ± 0,100 | 0,7093 ± 0,23 | 100 | 0,07 |
| 0,3587 | 0,4378 ± 0,089 | 0,8260 ± 0,23 | 200 | 0,09 |
| 0,7856 | 0,1623 ± 0,035 | 1,8091 ± 0,25 | 300 | 0,16 |
| *1,5770 | 0,0264 | 3,6344 | 600 | 0,19 |
| 1,6043 | 0,0249 ± 0,005 | 3,6929 ± 0,22 | 500 | 0,27 |
| 1,6969 | 0,0201 ± 0,004 | 3,9070 ± 0,22 | 400 | 0,31 |

*outlier

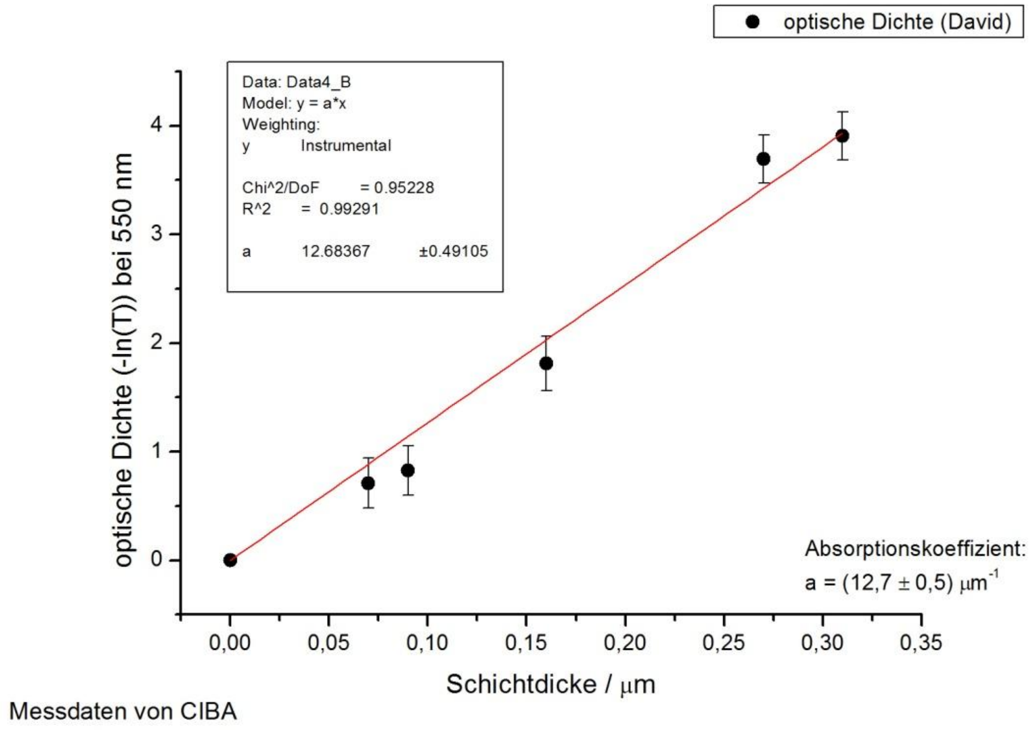


**Fig. 6.20. Optical density in dependence on the layer thickness at 550 nm of the magenta polymer**

Figure 6.20 shows the optical density in dependence on the layer thickness of the magenta polymer. Over a linear fit the absorption coefficient for magenta polymer ($a_m$) at 550 nm was determined:

$$a_m = (12{,}7 \pm 0{,}5)\ \mu m^{-1}$$

Figure 6.15 and 6.18 shows the transmission spectra of the ITO coated glass substrates with the polymer layer. For the calculation of the thickness of the magenta polymer layer the transmission of just the polymer layer is needed. So it was necessary to correct the measured transmission spectra and this could be done with the transmission spectra of the single ITO coated glass substrate without polymer layer:

$$\boldsymbol{T_{cor}} = \frac{\boldsymbol{T}}{\boldsymbol{T_0}}$$

$\boldsymbol{T}$...measured transmission (transmission of the ITO coated glass substrate with polymer layer)
$\boldsymbol{T_0}$...reference transmission (transmission of the ITO coated glass substrate)
$\boldsymbol{T_{cor}}$...corrected transmission (transmission of the polymer layer)

The transmission of the polymer free part of the “Dip coated substrate (11.11.2009)” was measured with the “Lambda9” (see figure 6.21 and 6.22).

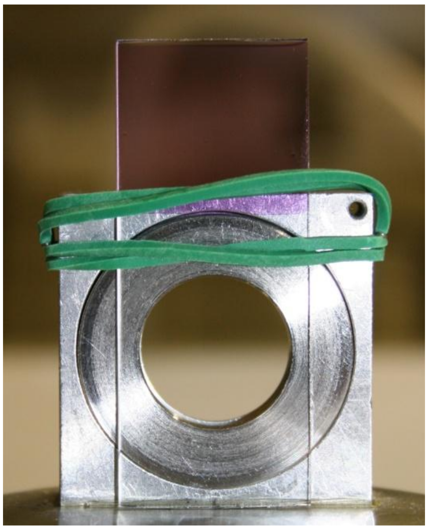
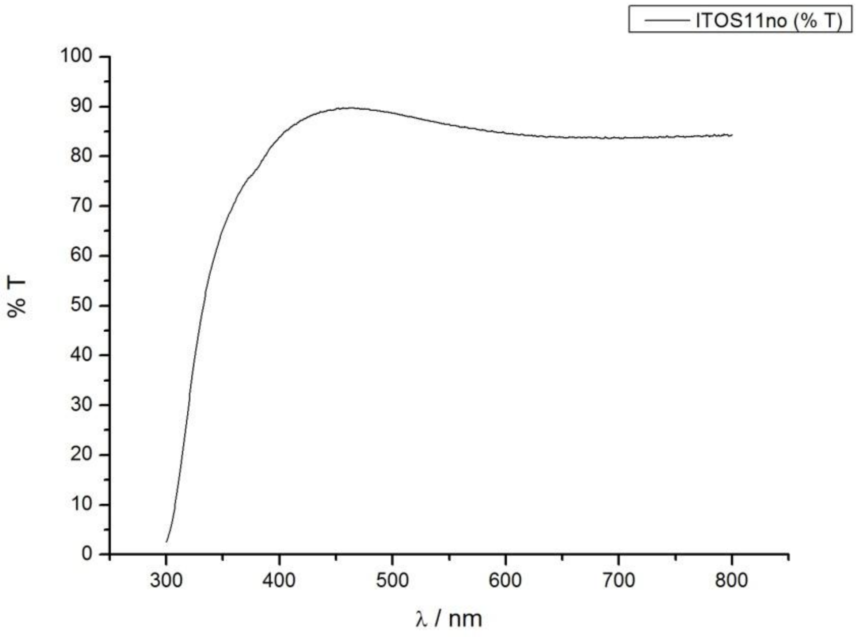


**Fig. 6.21. "Dip coated substrate (11.11.2009)" fixed on the sample-holder for the transmission measurement of the ITO-CG 1 in the "Lambda9".**



13.11.2009: Lambda9: (Dip coated substrate - 11.11.2009) - eine Stelle des Substrats vermessen, wo keine Polymerschicht drauf ist

**Fig. 6.22. Transmission spectrum of the ITO-CG 1 (polymer free part of the "Dip coated substrate (11.11.2009)") measured with the "Lambda9".**

From this reference spectrum the corrected transmission spectra (transmission spectra of the magenta polymer layers) of the "Dip coated substrate (9.11.2009)" and the "Dip coated substrate (11.11.2009)" were calculated (see figure 6.23 and 6.24).

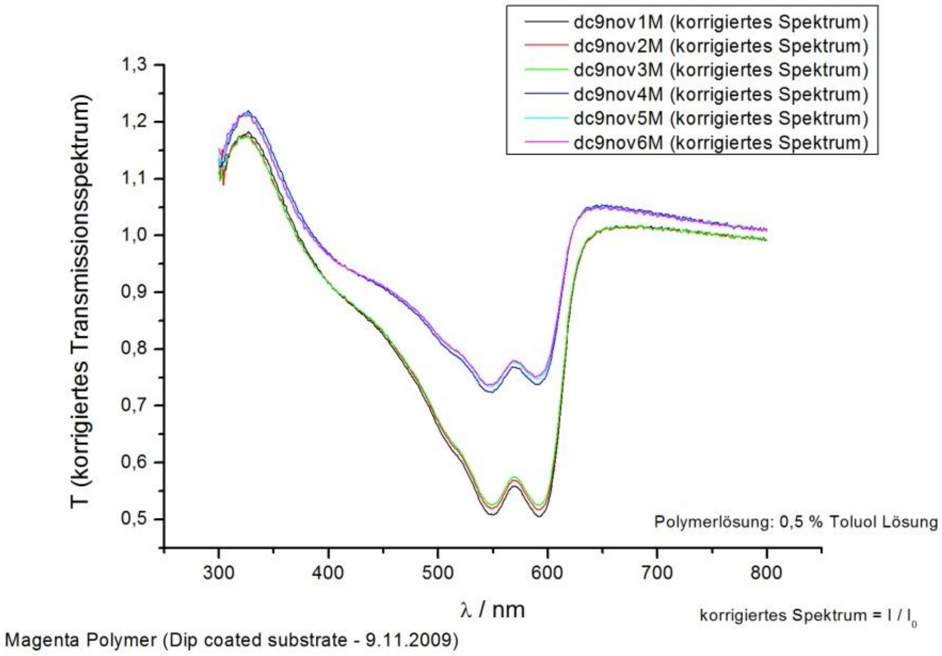


**Fig. 6.23. Transmission spectra of the double and the single polymer layer of the "Dip coated substrate (9.11.2009)" for three different measuring positions, in each case corrected with the transmission spectrum of the ITO-CG 1 (see figure 6.22)**
**dc9nov1M to dc9nov3M…as prepared – polymer layer on both sides of the substrate (two polymer layers)**
**dc9nov4M to dc9nov6M…polymer layer only on the ITO coated side of the glass substrate, after removing the polymer layer on the backside**

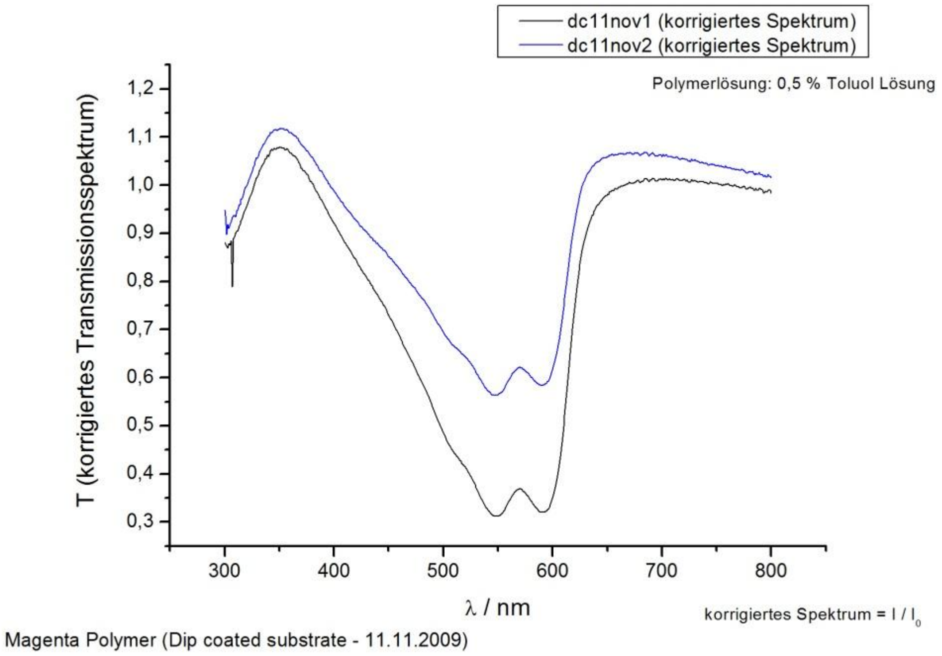


**Fig. 6.24. Transmission spectra of the double and the single polymer layer of the "Dip coated substrate (11.11.2009)" corrected with the transmission spectrum of the ITO-CG 1 (see figure 6.22)**
**dc11nov1…as prepared – polymer layer on both sides of the substrate (two polymer layers)**
**dc11nov2…polymer layer only on the ITO coated side of the glass substrate, after removing the polymer layer on the backside**

Next step was to calculate the optical density ($-ln(T)$) from the transmission of the magenta polymer layer.

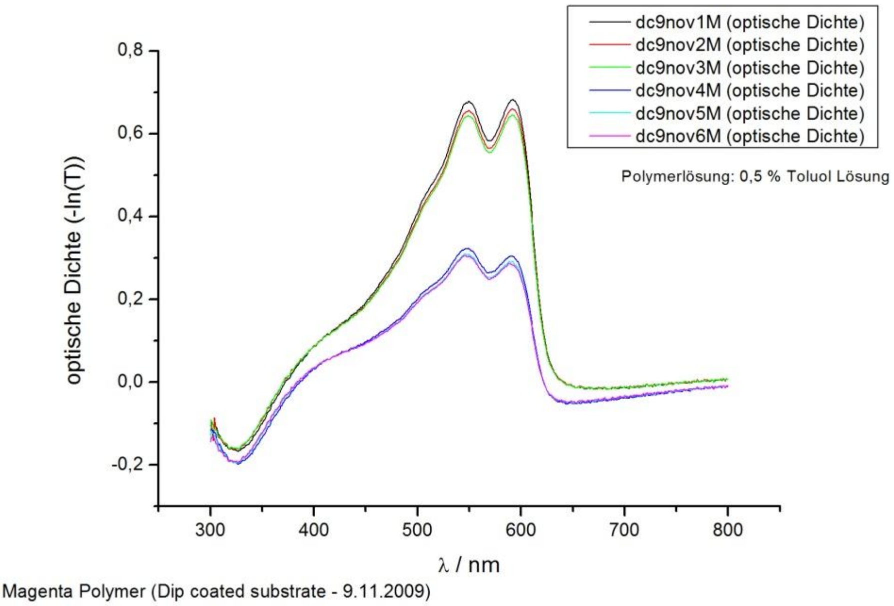


**Fig. 6.25. Optical density of the double and the single polymer layer of the "Dip coated substrate (9.11.2009)" for three different measuring positions, in each cases calculated from the transmission of the double and single magenta polymer layer respectively (see figure 6.23): ($-ln(T)$)**
**dc9nov1M to dc9nov3M…as prepared – polymer layer on both sides of the substrate (two polymer layers)**
**dc9nov4M to dc9nov6M…polymer layer only on the ITO coated side of the glass substrate, after removing the polymer layer on the backside**

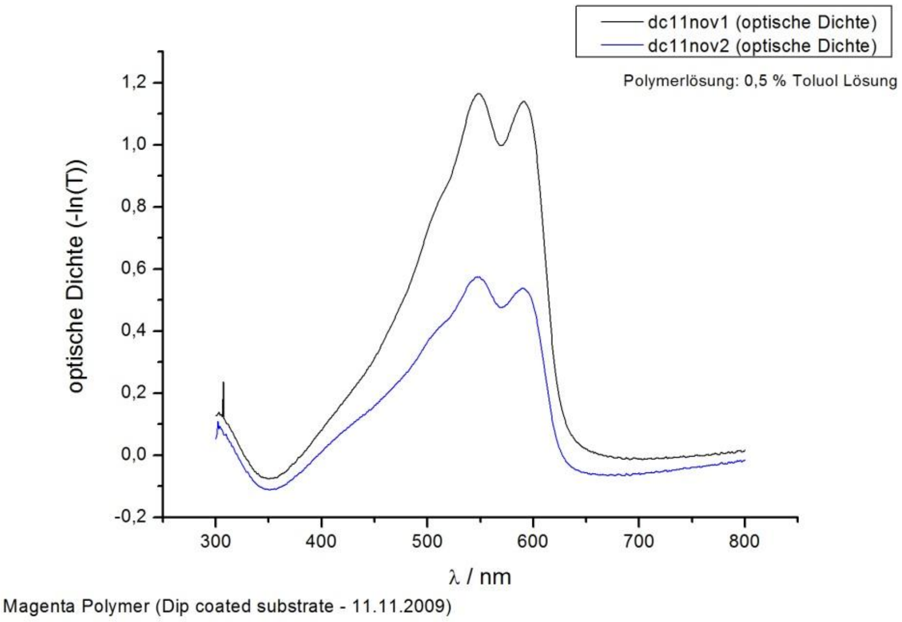


**Fig. 6.26. Optical density of the double and the single polymer layer of the "Dip coated substrate (11.11.2009)" calculated from the transmission of the double and single magenta polymer layer respectively (see figure 6.24): ($-ln(T)$)**
**dc11nov1…as prepared – polymer layer on both sides of the substrate (two polymer layers)**
**dc11nov2…polymer layer only on the ITO coated side of the glass substrate, after removing the polymer layer on the backside**

The optical density values at 550 nm were read out (figure 6.25 and 6.26) and with the absorption coefficient for magenta polymer at 550 nm ($a_m = (12{,}7 \pm 0{,}5)\ \mu m^{-1}$) the thicknesses of the magenta polymer layers were calculated (see table 6.3).

**Table 6.3. Thickness of the magenta polymer layers calculated from the optical density and the absorption coefficient for magenta polymer $a_m$ at 550 nm for the "Dip coated substrate (9.11.2009)" and the "Dip coated substrate (11.11.2009)". $\boldsymbol{a_m = (12,7 \pm 0,5)\ \mu m^{-1}}$**

| | | Optical density $-ln(T)$ $\Delta(-ln(T)) = \pm 0{,}005$ | Thickness / µm $d = \frac{-ln\ (T)}{a_m}$ |
|---|---|---|---|
| "Dip coated substrate (9.11.2009)" | dc9nov1M | 0,6762 | 0,0532 ± 0,002 |
| | dc9nov2M | 0,6542 | 0,0515 ± 0,002 |
| | dc9nov3M | 0,6420 | 0,0506 ± 0,002 |
| | dc9nov4M | 0,3211 | 0,0253 ± 0,001 |
| | dc9nov5M | 0,3085 | 0,0243 ± 0,001 |
| | dc9nov6M | 0,3035 | 0,0239 ± 0,001 |
| "Dip coated substrate (11.11.2009)" | dc11nov1 | 1,1635 | 0,0918 ± 0,004 |
| | dc11nov2 | 0,5705 | 0,0449 ± 0,002 |

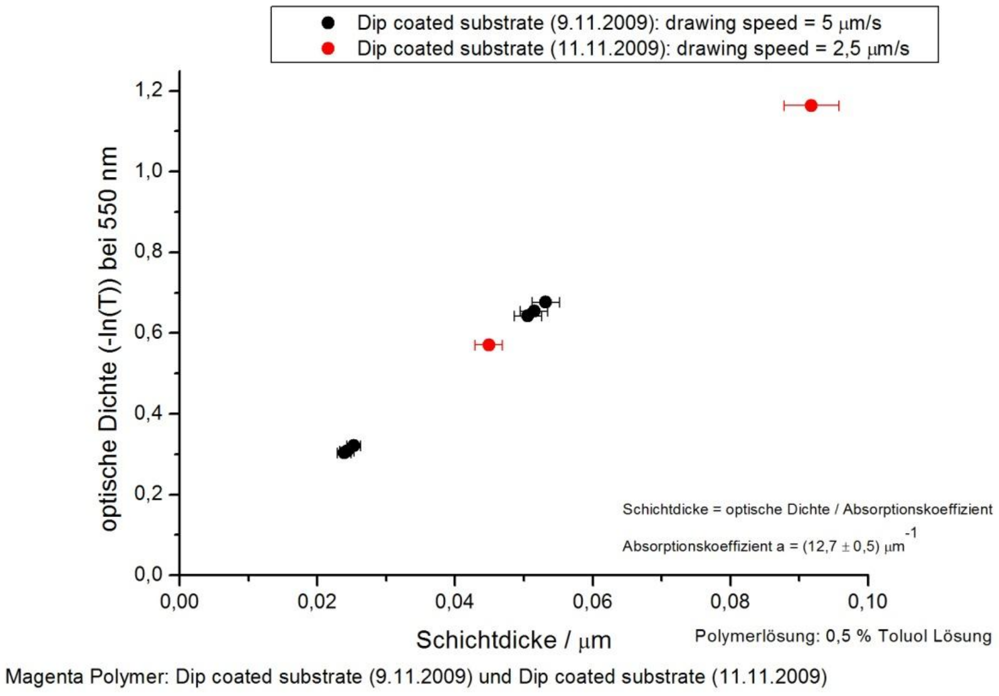


**Fig. 6.27. Optical density at 550 nm in dependence on the thickness of the magenta polymer layer of the "Dip coated substrate (9.11.2009)" and "Dip coated substrate (11.11.2009)"**

As shown in table 6.3 and figure 6.27 the thickness of the magenta polymer layer almost doubles when the drawing speed is halved. And it demonstrates that the polymer layers on both sides of the ITO coated glass substrate have almost the same thickness.

With the next dip coating experiment (17.11.2009) the concentration of the used magenta polymer – toluene solution was increased to about 1 % (see chapter 6.1.1). The dip coating process itself was carried out in the same way as on the 11.11.2009 (drawing speed: 2,5 μm/s; drawing path length: 20000 μm). Used ITO coated glass: ITO-CG 1. The results of the investigations with the optical microscope (Olympus BX51) and the “Lambda9”, the calculated corrected transmission spectra (transmission spectra of the magenta polymer layer), the optical density are shown in figure 6.28 to figure 6.32.

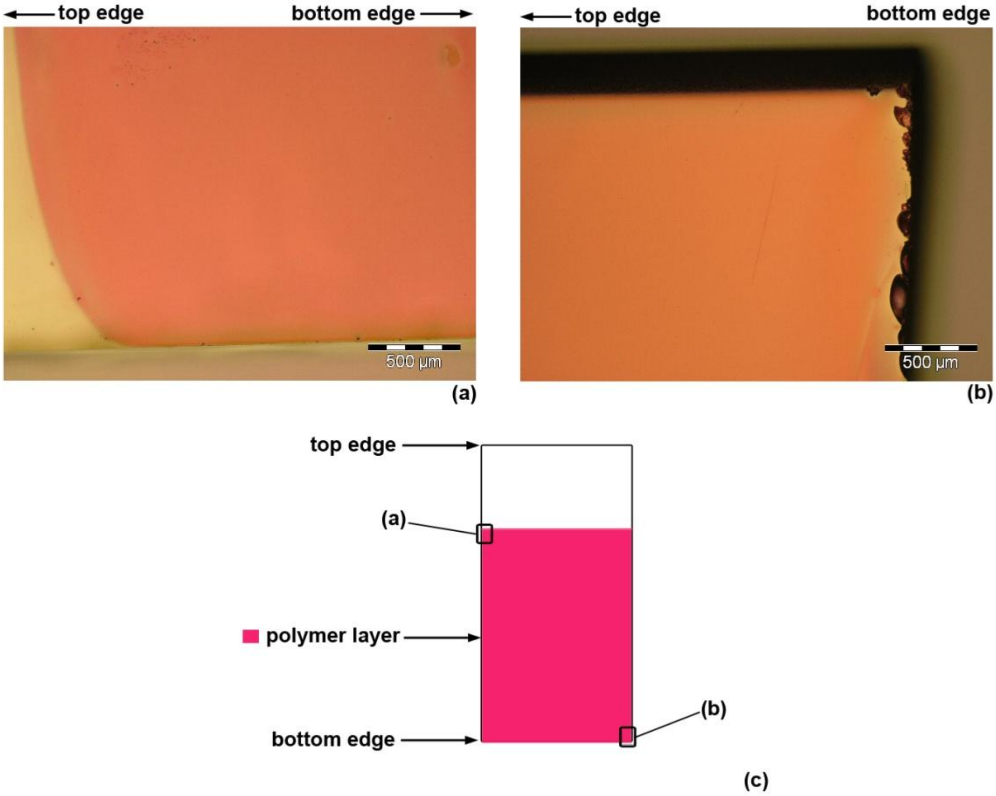


**Fig. 6.28. Magenta polymer layer on the ITO coated side of the “Dip coated substrate (17.11.2009)” investigated with an optical microscope (Olympus BX51): (a), (b) photos; (c) scheme**

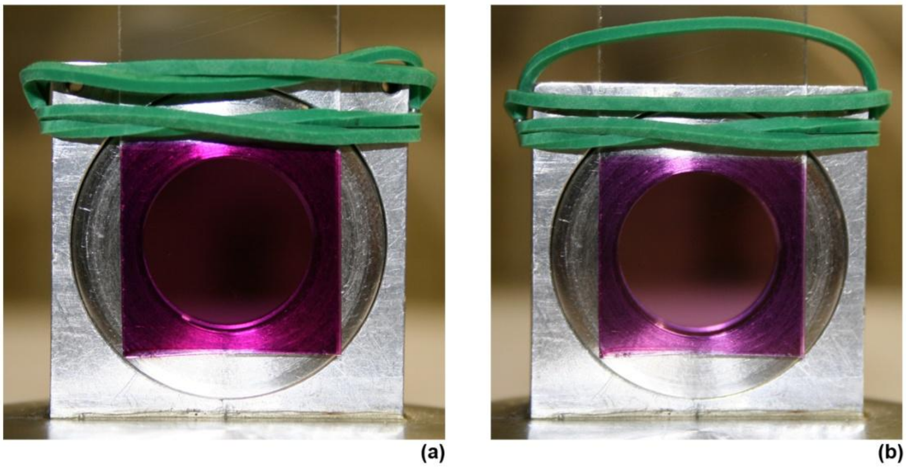


**Fig. 6.29. “Dip coated substrate (17.11.2009)” fixed on the sample-holder for the transmission measurements in the “Lambda9”. (a)…polymer layer on both sides of the substrate; (b)…polymer layer only on the ITO coated side of the glass substrate**

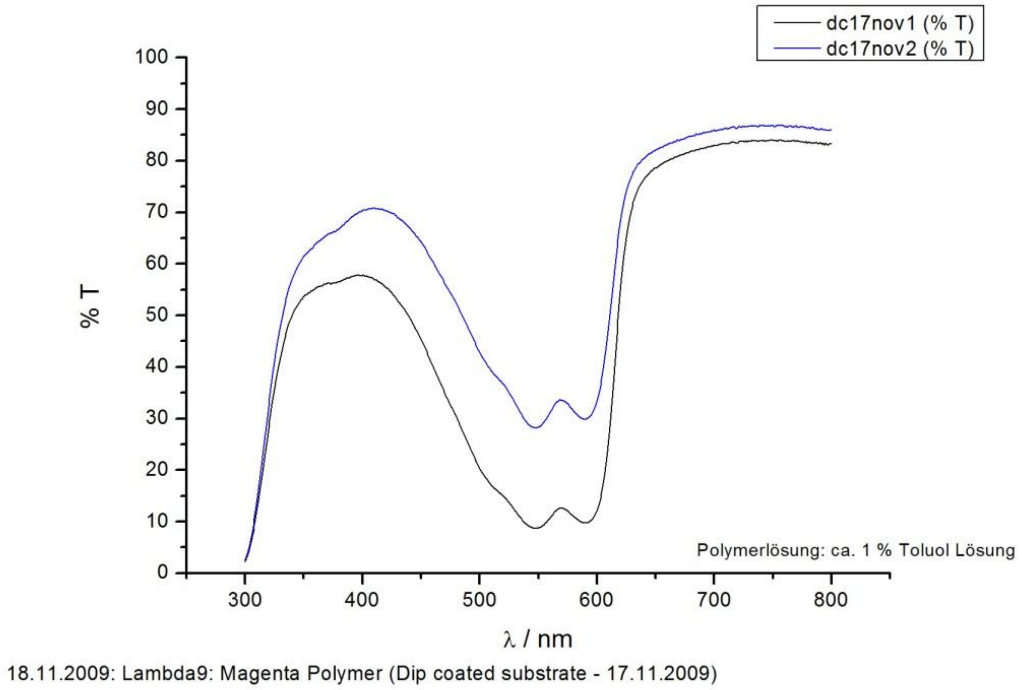


**Fig. 6.30. Transmission spectra of the “Dip coated substrate (17.11.2009)” measured with the “Lambda9”. Polymer layer on both sides of the substrate: dc17nov1; polymer layer only on the ITO coated side of the glass substrate: dc17nov2**

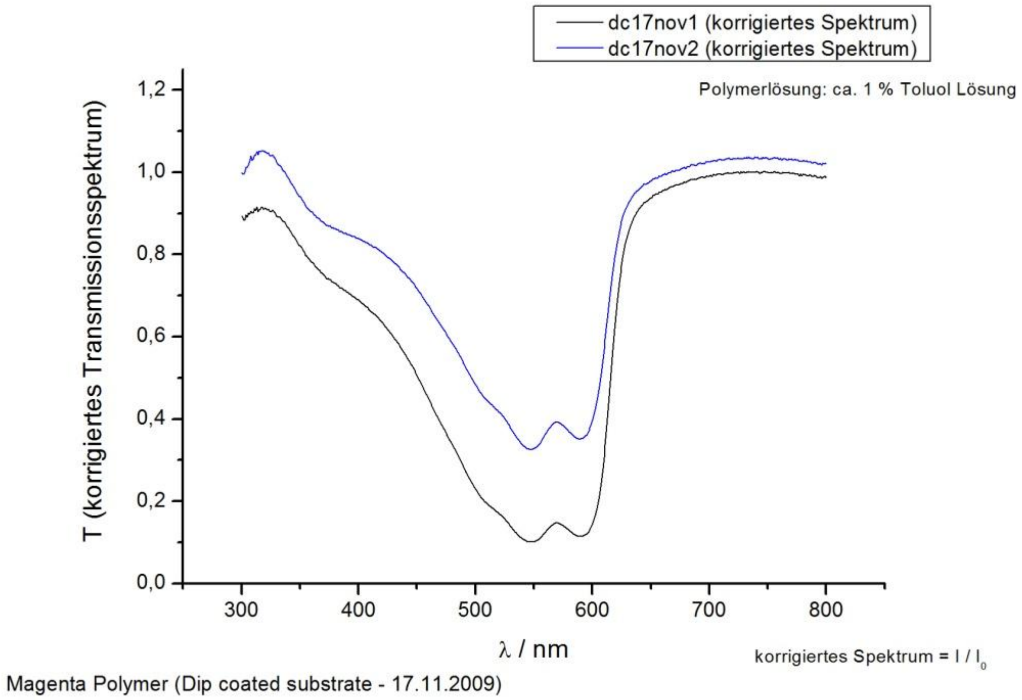


**Fig. 6.31. Transmission spectra of the double and the single polymer layer of the “Dip coated substrate (17.11.2009)” corrected with the transmission spectrum of the ITO-CG 1 (see figure 6.22)**
**dc17nov1…as prepared – polymer layer on both sides of the substrate (two polymer layers)**
**dc17nov2…polymer layer only on the ITO coated side of the glass substrate, after removing the polymer layer on the backside**

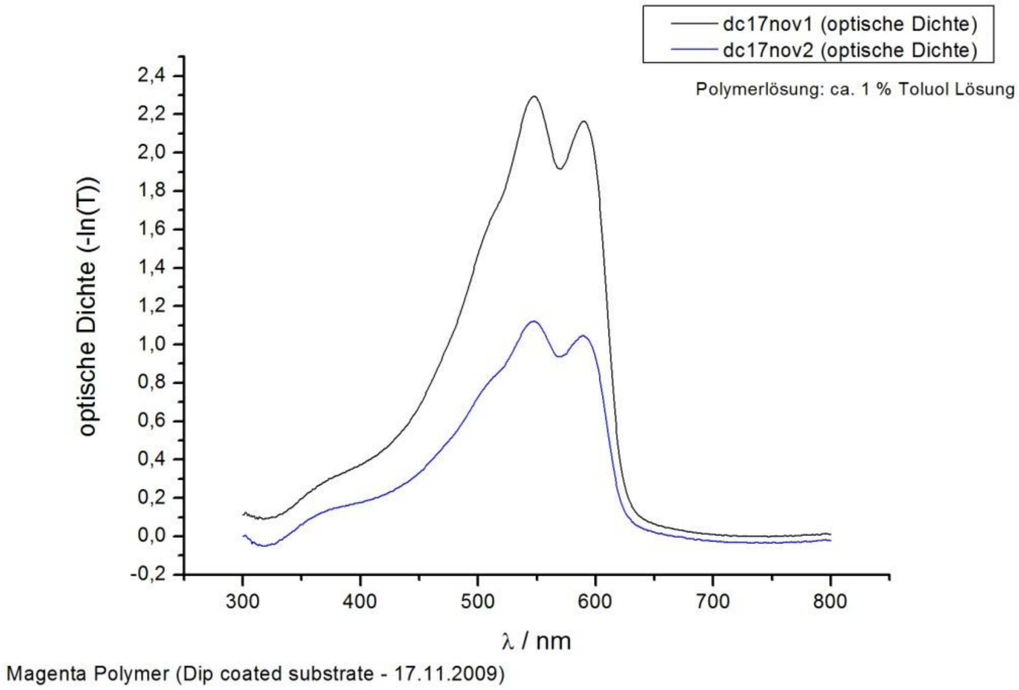


**Fig. 6.32. Optical density of the double and the single polymer layer of the "Dip coated substrate (17.11.2009)" calculated from the transmission of the double and single magenta polymer layer respectively (see figure 6.31): $(-ln(T))$**
**dc17nov1…as prepared – polymer layer on both sides of the substrate (two polymer layers)**
**dc17nov2…polymer layer only on the ITO coated side of the glass substrate, after removing the polymer layer on the backside**

Again the optical density values at 550 nm were read out (figure 6.32) to calculate the thickness of the magenta polymer layer.

**Table 6.4. Thickness of the magenta polymer layers calculated from the optical density and the absorption coefficient for magenta polymer $a_m$ at 550 nm for the "Dip coated substrate (17.11.2009)". $a_m = (12,7 \pm 0,5)\ \mu m^{-1}$**

| | | Optical density $-ln(T)$ $\Delta(-ln(T)) = \pm 0,005$ | Thickness / µm $d = \frac{-ln\ (T)}{a_m}$ |
|---|---|---|---|
| "Dip coated substrate (17.11.2009)" | dc17nov1 | 2,2848 | 0,1799 ± 0,007 |
| | dc17nov2 | 1,1148 | 0,0878 ± 0,004 |

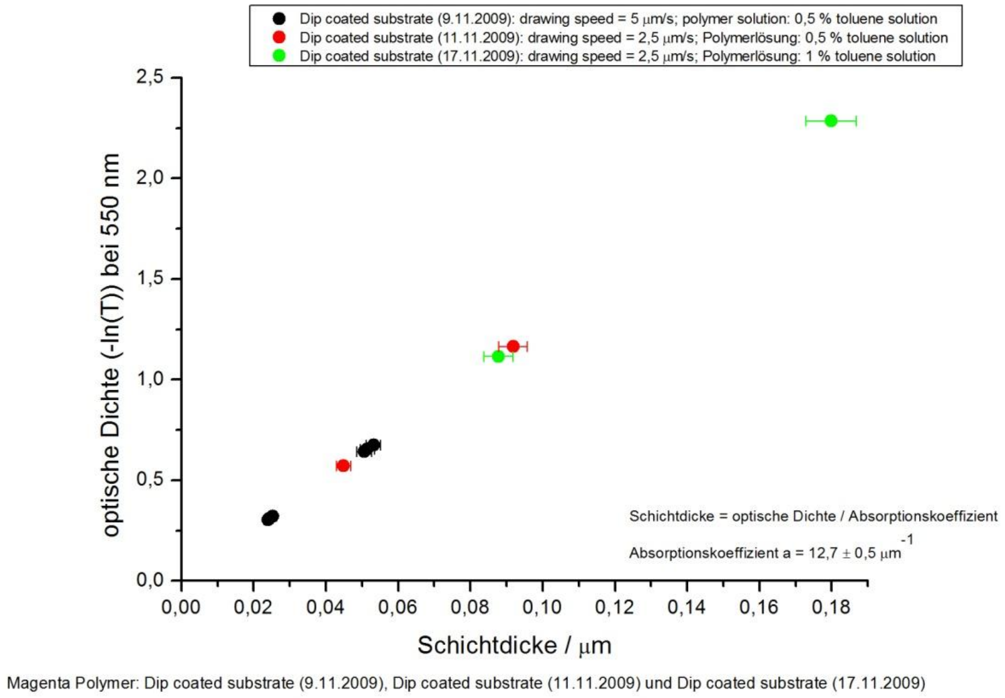


**Fig. 6.33. Optical density at 550 nm in dependence on the thickness of the magenta polymer layer of the "Dip coated substrate (9.11.2009)", "Dip coated substrate (11.11.2009)" and "Dip coated substrate (17.11.2009)"**

With increasing concentration of the magenta polymer – toluene solution the thickness of the magenta polymer layer increased too.

Based on the subjective colour impression a polymer thickness of ~0,1 µm was chosen for the demonstrator. So the dip coating process for the ITO coated glass substrates for the demonstrator had to be run with the same parameters as on the 17.11.2009.

The ITO coated glass substrates for the demonstrator were larger (length: 60 to 65 mm; width: 45 mm) than the ITO coated glass substrates for the previous dip coating experiments. Because of that the cuvette with inner dimensions of 52,5 mm height, 50 mm width, 10 mm depth was used (see figure 6.8). For the dip coating process with this cuvette more magenta polymer solution than for the previous dip coating experiments was needed. The remaining amount of magenta polymer solution (about 1 % toluene solution) was not sufficient for the dip coating. So 5 ml toluene was added, but no magenta polymer, since at that time magenta polymer was not available (see chapter 6.1.1), and the concentration of the solution was lowered.

As mentioned before in this chapter the concentration of the polymer – toluene solution changes slightly during the dip coating experiments, since toluene is a volatile solvent and for that evaporates during the pull out process. It is not proved that the concentration of the magenta polymer – toluene solution was still 1 % after the last dip coating experiment.

The dip coating process with the magenta polymer solution for the ITO coated glass substrate (ITO-CG 2; length: 65 mm; width: 45 mm) for the demonstrator was done on the 2.2.2010. It was carried out in the same way as on the 17.11.2009 except for following items:

→ the cuvette with inner dimensions of 52,5 mm height, 50 mm width, 10 mm depth was used;
→ the drawing path length was set to 50000 µm;
→ instead of the plastic bucket an acrylic plastic cuboid (see figure 6.34) was put over the drawing device to prevent disturbances caused by air circulations.

**Fig. 6.34. Acrylic plastic cuboid: During the dip coating process the acrylic plastic cuboid was put over the mechanical drawing device to prevent disturbances caused by air circulations**

The results of the investigations of the “Dip coated substrate (2.2.2010)” with the “Lambda9”, the calculated corrected transmission spectrum (transmission spectrum of the magenta polymer layer), optical density are shown in figure 6.36, 6.37, 6.40, 6.41.

Since the “Dip coated substrate (2.2.2010)” was larger than the previous ones, a different sample-holder (“second sample holder”) for the measurements in the “Lambda9” was used (see figure 6.35).

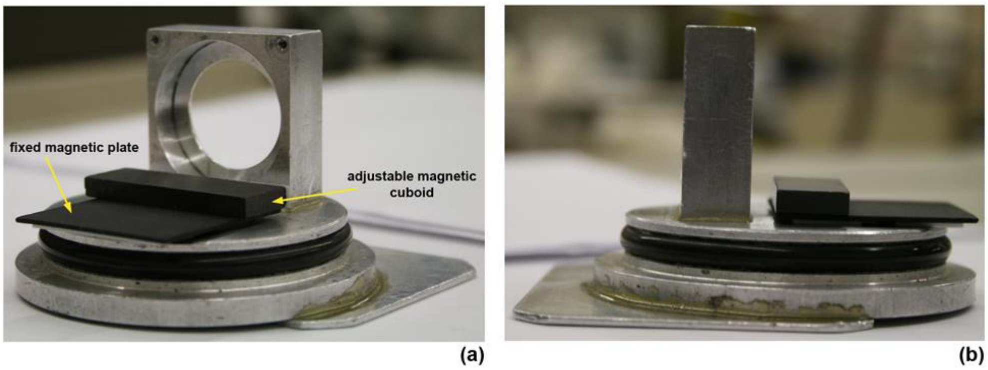


**Fig. 6.35. Second sample-holder of the “Lambda9”: The adjustable magnetic cuboid clamps the substrate. (a)…front view; (b)…side view**

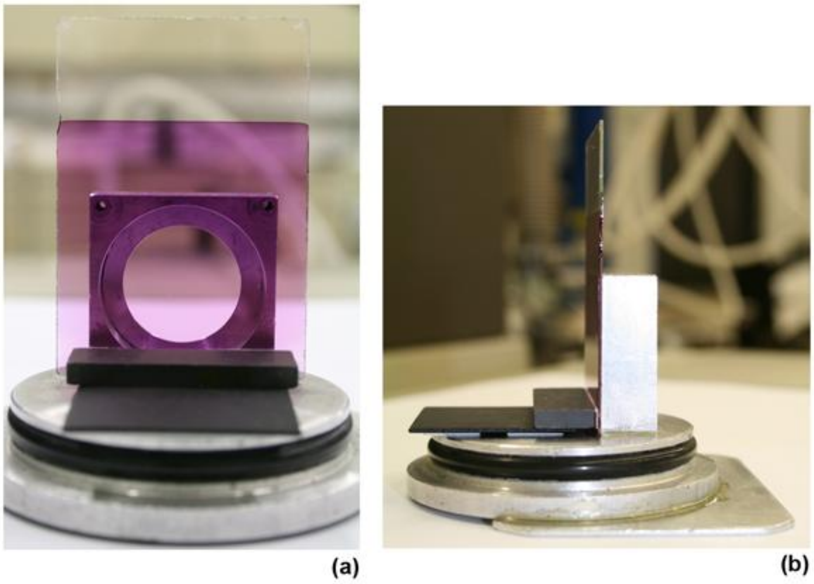


**Fig. 6.36. "Dip coated substrate (2.2.2010)" clamped on the second sample-holder for the transmission measurement in the "Lambda9". Magenta polymer layer only on the ITO coated side of the glass substrate (after removing the polymer layer on the backside). (a)…front view; (b)…side view**

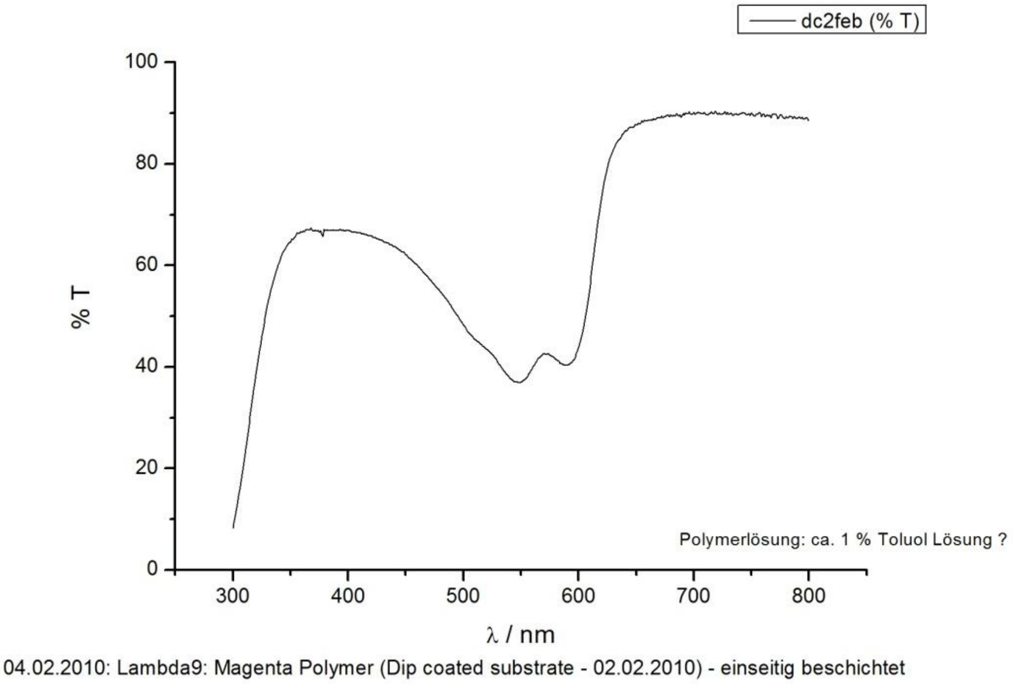


**Fig. 6.37. Transmission spectra of the "Dip coated substrate (2.2.2010)" measured with the "Lambda9". Polymer layer only on the ITO coated side of the glass substrate, after removing the polymer layer on the backside**

The transmission of the ITO-CG 2, which was used for the "Dip coated substrate (2.2.2010)", was measured with the "Lambda9" (see figure 6.38 and 6.39).

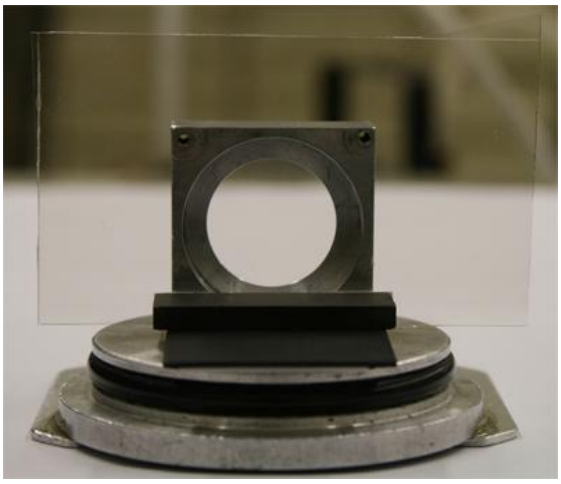


**Fig. 6.38. A piece of ITO-CG 2 clamped on the sample-holder for the transmission measurement in the "Lambda9"**

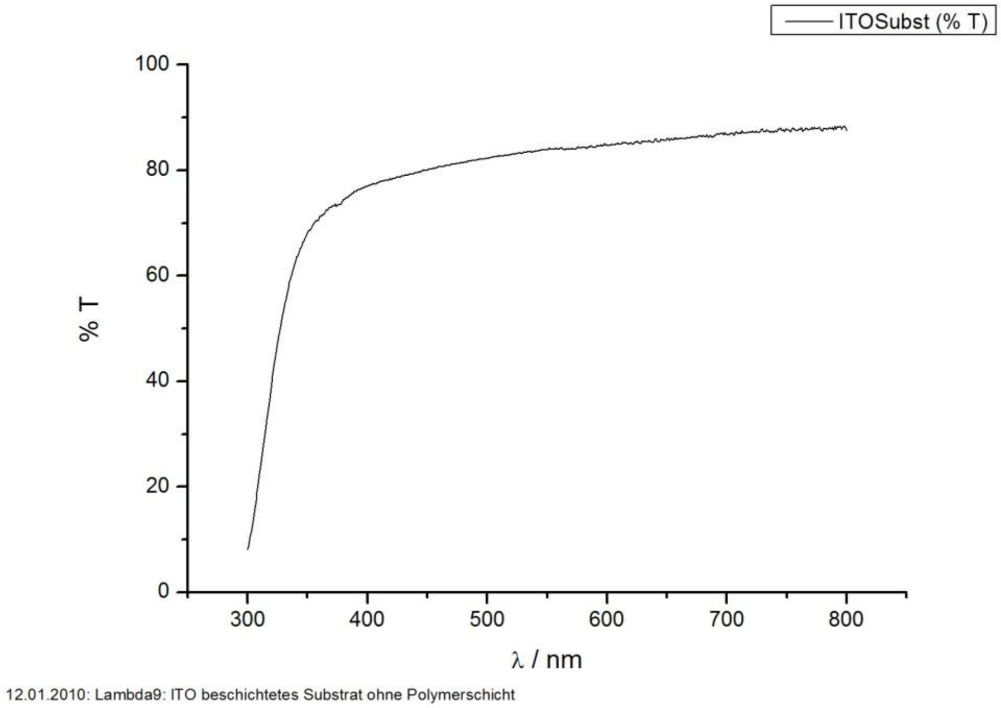
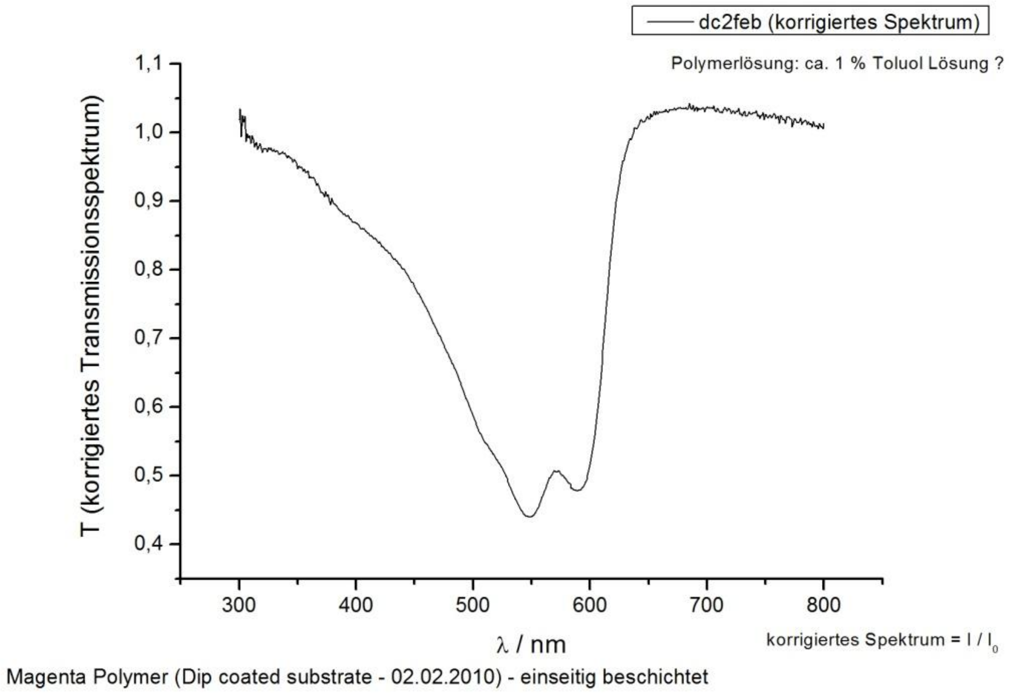


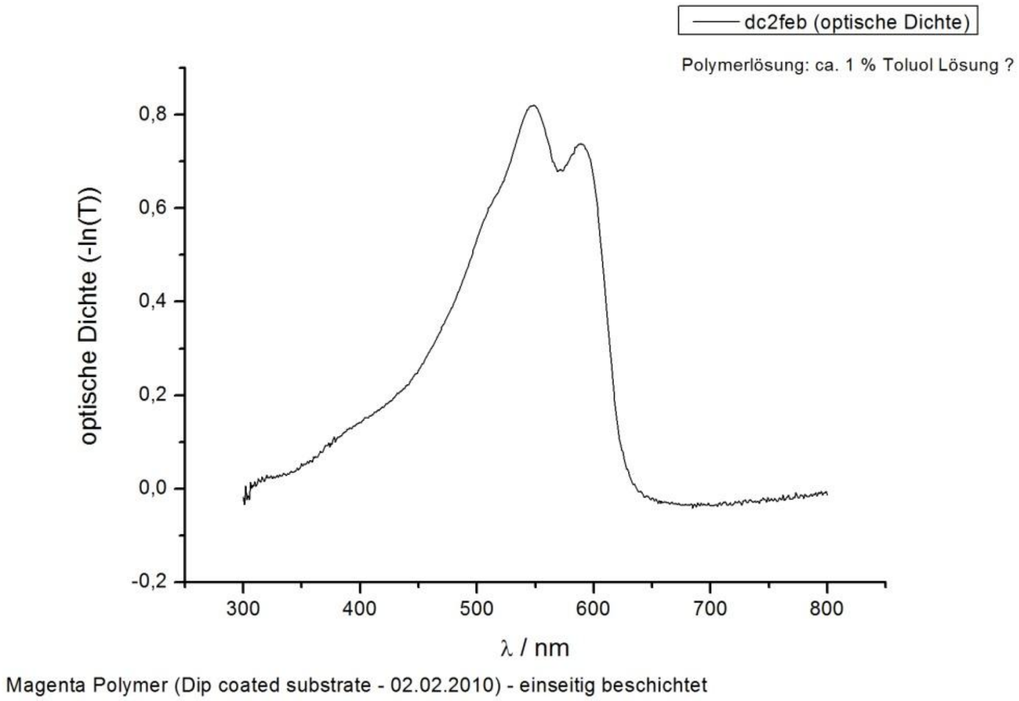
**Fig. 6.39. Transmission spectrum of the ITO-CG 2 measured with the "Lambda9"**

From this reference spectrum the corrected transmission spectrum (transmission spectrum of the magenta polymer layer) of the "Dip coated substrate (2.2.2010)" was calculated (see figure 6.40).



Magenta Polymer (Dip coated substrate - 02.02.2010) - einseitig beschichtet

**Fig. 6.40. Transmission spectra of the single polymer layer of the "Dip coated substrate (2.2.2010)" corrected with the transmission spectrum of the ITO-CG 2 (see figure 6.39). Polymer layer only on the ITO coated side of the glass substrate, after removing the polymer layer on the backside**



Magenta Polymer (Dip coated substrate - 02.02.2010) - einseitig beschichtet

**Fig. 6.41. Optical density of the single polymer layer of the "Dip coated substrate (2.2.2010)" calculated from the transmission of the single magenta polymer layer (see figure 6.40): $(-\boldsymbol{ln}(\boldsymbol{T}))$**
**Polymer layer only on the ITO coated side of the glass substrate, after removing the polymer layer on the backside**

The optical density value at 550 nm was read out (figure 6.41) to calculate the thickness of the magenta polymer layer.

**Table 6.5. Thickness of the magenta polymer layer calculated from the optical density and the absorption coefficient for magenta polymer $a_m$ at 550 nm for the "Dip coated substrate (2.2.2010)". $a_m = (12,7 \pm 0,5)\ \mu m^{-1}$**

| | | Optical density<br>$-ln(T)$<br>$\Delta(-ln(T)) = \pm 0{,}005$ | Thickness / µm<br>$d = \frac{-ln\ (T)}{a_m}$ |
|---|---|---|---|
| "Dip coated substrate (2.2.2010)" | dc2feb | 0,8190 | 0,0645 ± 0,003 |

The thickness of the single magenta polymer layer of the "Dip coated substrate (2.2.2010)" is lower than the thickness of the single magenta polymer layer of the "Dip coated substrate (17.11.2009)". It was decided that the colouring at 0,065 µm thickness is sufficient for the demonstrator.

Dip coating experiments with regioregular P3HT – toluene solution (see chapter 6.1.3) are described in the following:
For these dip coating experiments the dimensions of the ITO coated glass substrates were approximately 55 mm in length and 20 mm in width. So the cuvette with inner dimensions of 43,7 mm height, 30 mm width, 10 mm depth was used (see figure 6.8).

On the 19.1.2010 the first dip coating experiment with regioregular P3HT – toluene solution was carried out. Drawing speed was set to 10 µm/s and the drawing path length to 33000 µm. Used ITO coated glass: ITO-CG 1.
Already, the plastic bucket was replaced by the acrylic plastic cuboid, mentioned before and shown in figure 6.34. This acrylic plastic cuboid was used in all following dip coating experiments.

A photo of the "Dip coated substrate (19.1.2010)" is shown in figure 6.42.

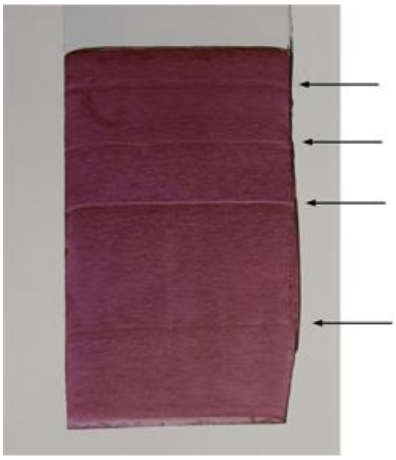


**Fig. 6.42. Photo of the "Dip coated substrate (19.1.2010)"; length: 56 mm, width: ~20 mm (regioregular P3HT polymer layer on both sides of the substrate)**
**Four horizontal lines, marked with arrows, are visible in the polymer layer.**

The used quantity of regioregular P3HT didn´t dissolve completely in the used quantity of toluene (details see chapter 3.1.3). Therefore the solution contained small dark grains of unsolved polymer. During the pull out process of the dip coating process these dark grains deposited on the surface of the substrate too. This had an effect on the appearance of the regioregular P3HT polymer layer shown in figure 6.42.

On the photo in figure 6.42 also four horizontal lines in the polymer layer are visible.

To control the immersion process the ITO coated glass substrate was immersed stepwise in the regioregular P3HT – toluene solution, and this caused the horizontal lines in the polymer layer. The substrate was immersed automatically under the control of the control unit but not continuously over the whole path length of 33000 µm. It was done in five steps: 10000 µm; 10000 µm; 5000 µm; 5000 µm; 3000 µm. In each step the immersing was carried out continuously, the breaks between the steps took few seconds. During these breaks the level of the regioregular P3HT – toluene solution in the cuvette was checked to avoid an overflow.

At the next dip coating experiment with regioregular P3HT – toluene solution less polymer solution was put into the cuvette, so it was not necessary to check the level of the regioregular P3HT – toluene solution in the cuvette during the immersion of the substrate. The immersion was carried out continuously over the whole path length of 33000 µm (under the control of the control unit).

The results of the investigations of the “Dip coated substrate (19.1.2010)” with the optical microscope (Olympus BX51) and the“Lambda9”, and the calculated corrected transmission spectra (transmission spectra of the regioregular P3HT polymer layer) are shown in figure 6.43, 6.44, 6.45, 6.46.

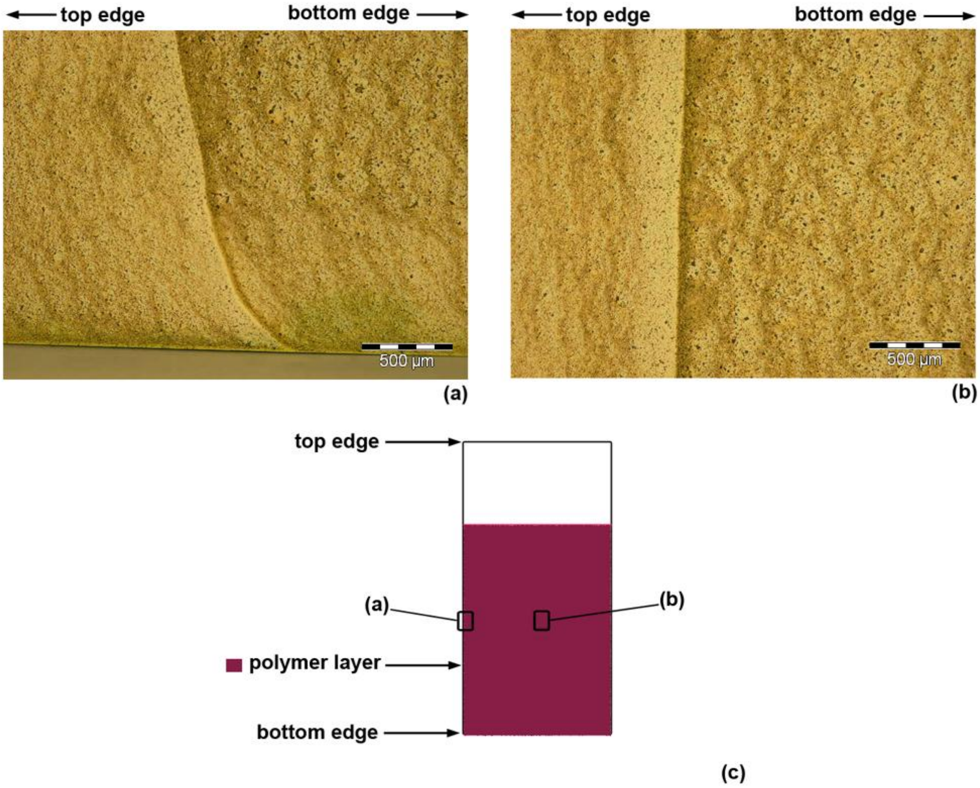


**Fig. 6.43. Regioregular P3HT polymer layer on the ITO coated side of the “Dip coated substrate (19.1.2010)” investigated with an optical microscope (Olympus BX51): (a), (b) photos; (c) scheme**

On the photos in figure 6.43 the dark regioregular P3HT polymer grains were clearly visible in the polymer layer.

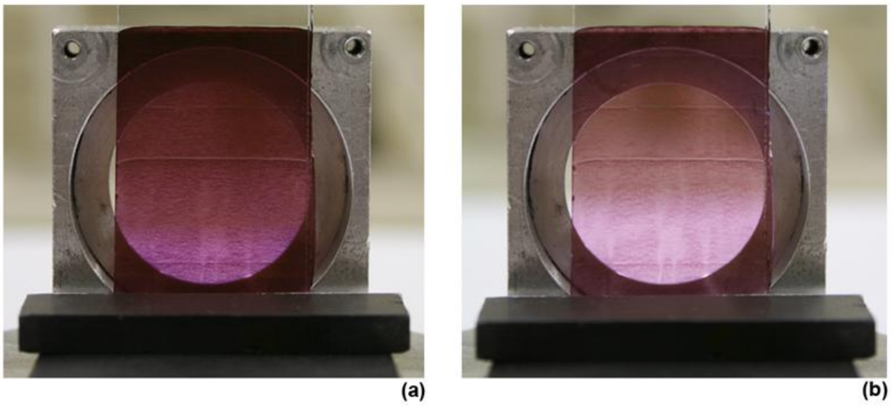
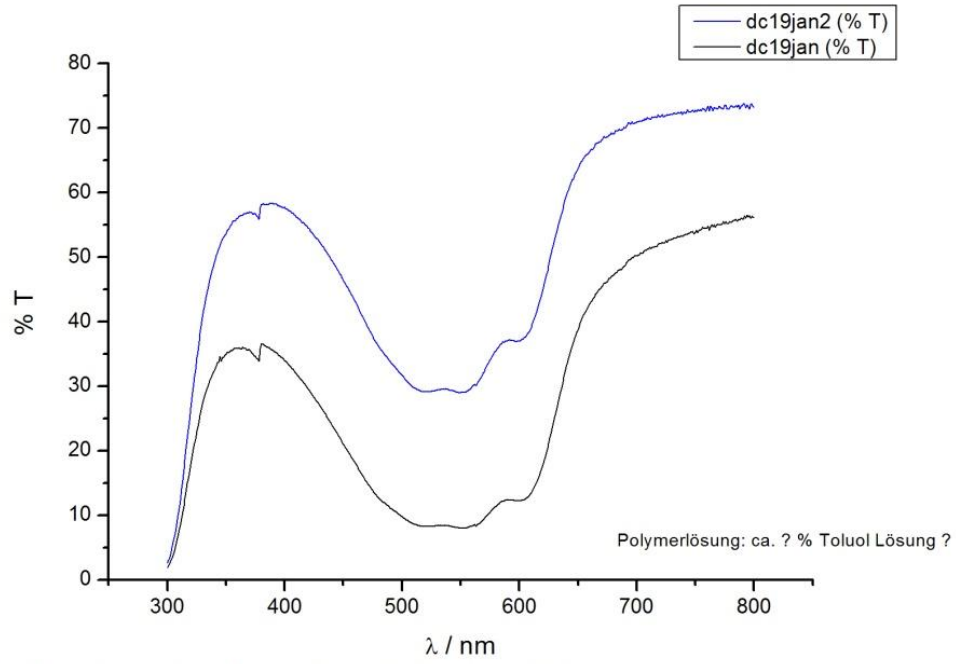


**Fig. 6.44. "Dip coated substrate (19.1.2010)" clamped on the second sample-holder for the transmission measurements in the "Lambda9". (a)…polymer layer on both sides of the substrate; (b)…polymer layer only on the ITO coated side of the glass substrate**



Polymerlösung: ca. ? % Toluol Lösung ?

04.02.2010: Lambda9: r.r. P3HT (Dip coated substrate - 19.01.2010)

**Fig. 6.45. Transmission spectra of the "Dip coated substrate (19.1.2010)" measured with the "Lambda9". Polymer layer on both sides of the substrate: dc19jan; polymer layer only on the ITO coated side of the glass substrate: dc19jan2**

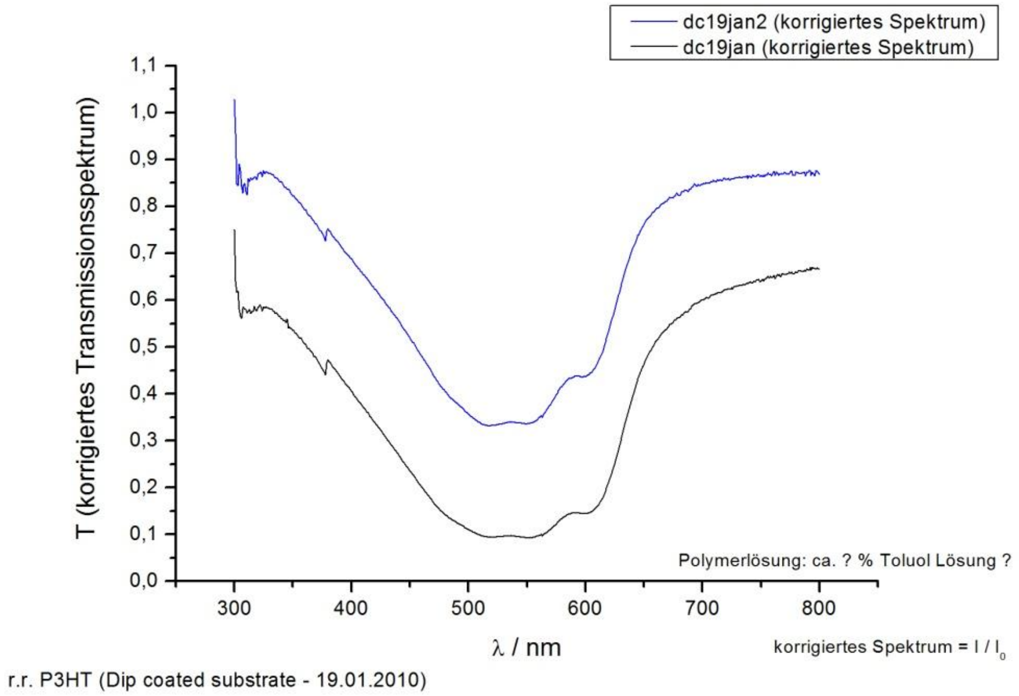


**Fig. 6.46. Transmission spectra of the double and the single polymer layer of the "Dip coated substrate (19.1.2010)" corrected with the transmission spectrum of the ITO-CG 1 (see figure 6.22)**
**dc19jan…as prepared – polymer layer on both sides of the substrate (two polymer layers)**
**dc19jan2…polymer layer only on the ITO coated side of the glass substrate, after removing the polymer layer on the backside**

On the 20.1.2010 the second dip coating experiment with regioregular P3HT – toluene solution was carried out in the same way as on the 19.1.2010 (drawing speed: 10 µm/s; drawing path length: 33000 µm) except the immersion of the ITO coated glass substrate (ITO-CG 1): the ITO coated glass substrate was again immersed automatically under the control of the control unit but this time continuously over the whole path length of 33000 µm.
A photo of the "Dip coated substrate (20.1.2010)" is shown in figure 6.47.

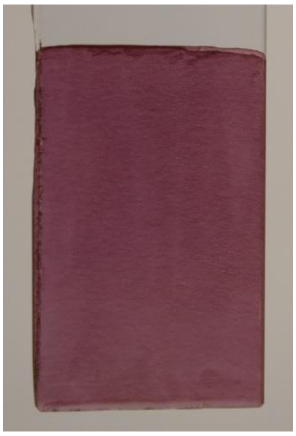


**Fig. 6.47. Photo of the "Dip coated substrate (20.1.2010)"; length: 55 mm, width: 20-21 mm (regioregular P3HT polymer layer on both sides of the substrate)**

The homogenous regioregular P3HT polymer layer of the “Dip coated substrate (20.1.2010)” is comparable to the polymer layer of the “Dip coated substrate (19.1.2010)”.

The results of the investigations of the “Dip coated substrate (20.1.2010)” with the optical microscope (Olympus BX51) and the“Lambda9”, and the calculated corrected transmission spectra (transmission spectrum of the regioregular P3HT polymer layer) are shown in figure 6.48, 6.49, 6.50, 6.51.

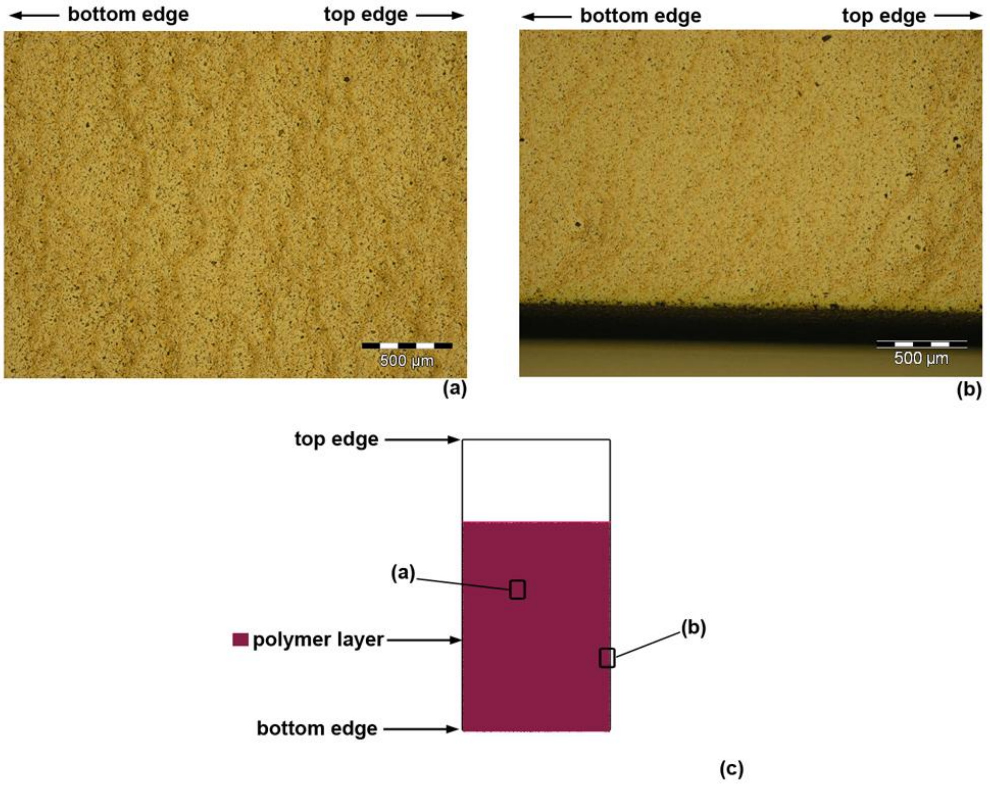


**Fig. 6.48. Regioregular P3HT polymer layer on the ITO coated side of the “Dip coated substrate (20.1.2010)” investigated with an optical microscope (Olympus BX51): (a), (b) photos; (c) scheme**

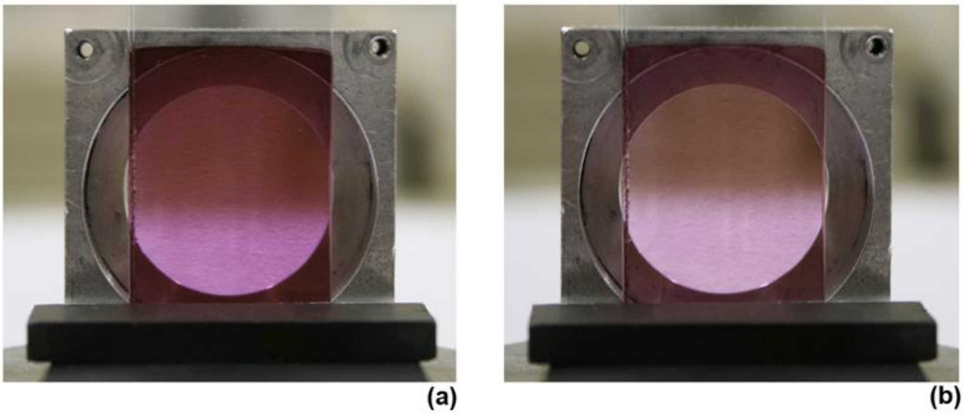


**Fig. 6.49. “Dip coated substrate (20.1.2010)” clamped on the second sample-holder for the transmission measurements in the “Lambda9”. (a)…polymer layer on both sides of the substrate; (b)…polymer layer only on the ITO coated side of the glass substrate**

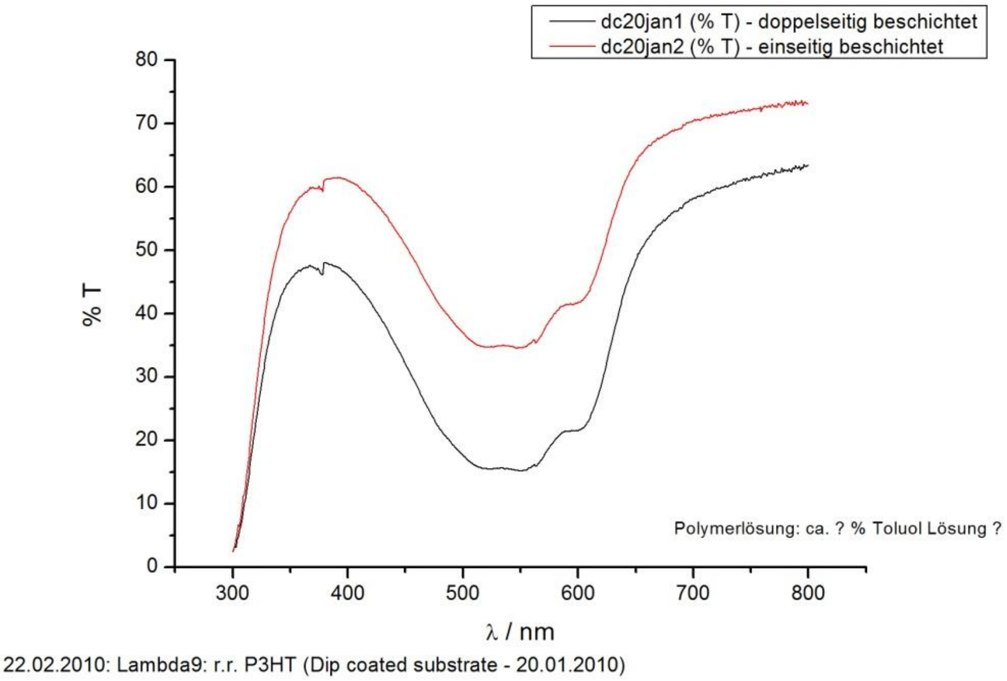


**Fig. 6.50. Transmission spectra of the “Dip coated substrate (20.1.2010)” measured with the “Lambda9”. Polymer layer on both sides of the substrate: dc20jan1; polymer layer only on the ITO coated side of the glass substrate: dc20jan2**

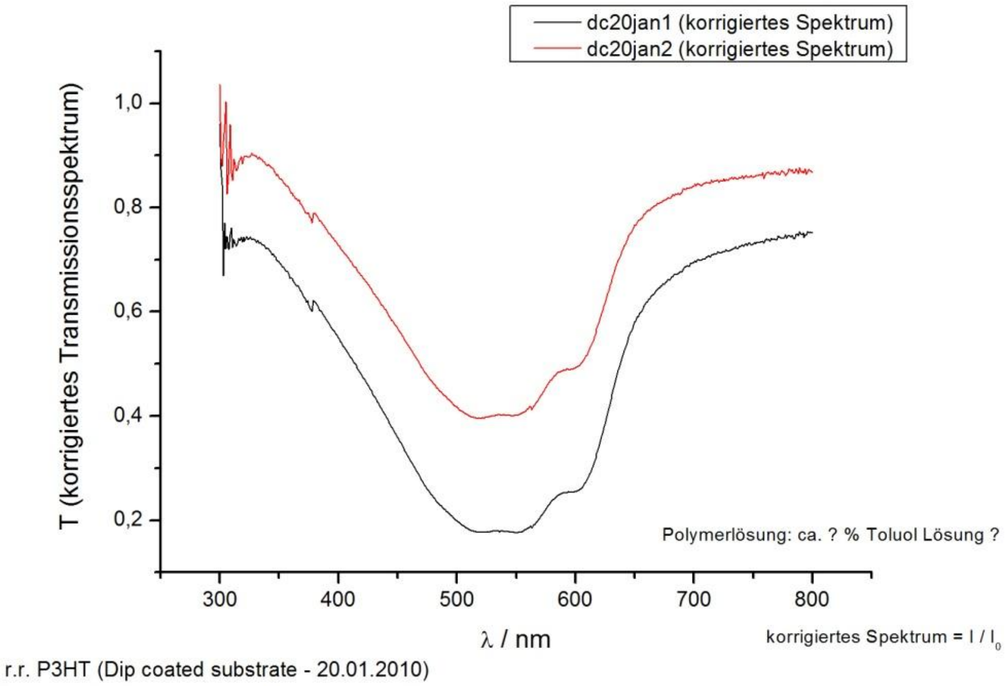


**Fig. 6.51. Transmission spectra of the double and the single polymer layer of the “Dip coated substrate (20.1.2010)” corrected with the transmission spectrum of the ITO-CG 1 (see figure 6.22)**
**dc20jan1…as prepared – polymer layer on both sides of the substrate (two polymer layers)**
**dc20jan2…polymer layer only on the ITO coated side of the glass substrate, after removing the polymer layer on the backside**

It was decided to build electrochromic devices with these regioregular P3HT polymer coated substrates (“Dip coated substrate (19.1.2010)”, “Dip coated substrate (20.1.2010)”).

For the fabrication of the two regioregular P3HT polymer electrochromic devices and the magenta polymer demonstrator ITO coated glass substrates with clear polymer (non colouring polymer) layer were required, too.

The ITO coated glass, which was used for the dip coating processes with clear polymer – toluene solution, was the ITO-CG 2.

On the 3.2.2010 the first dip coating experiment with clear polymer solution (0,9 % toluene solution) was carried out. The dimensions of the ITO coated glass substrate were 55 mm in length and 18-20 mm in width. So the cuvette with inner dimensions of 43,7 mm height, 30 mm width, 10 mm depth was used (see figure 6.8). Drawing speed was set to 2,5 µm/s and the drawing path length to 33000 µm.

The results of the investigations of the “Dip coated substrate (3.2.2010)” with the optical microscope (Olympus BX51) and the “Lambda9”, and the calculated corrected transmission spectra (transmission spectra of the clear polymer layer) are shown in figure 6.52, 6.53, 6.54, 6.55.

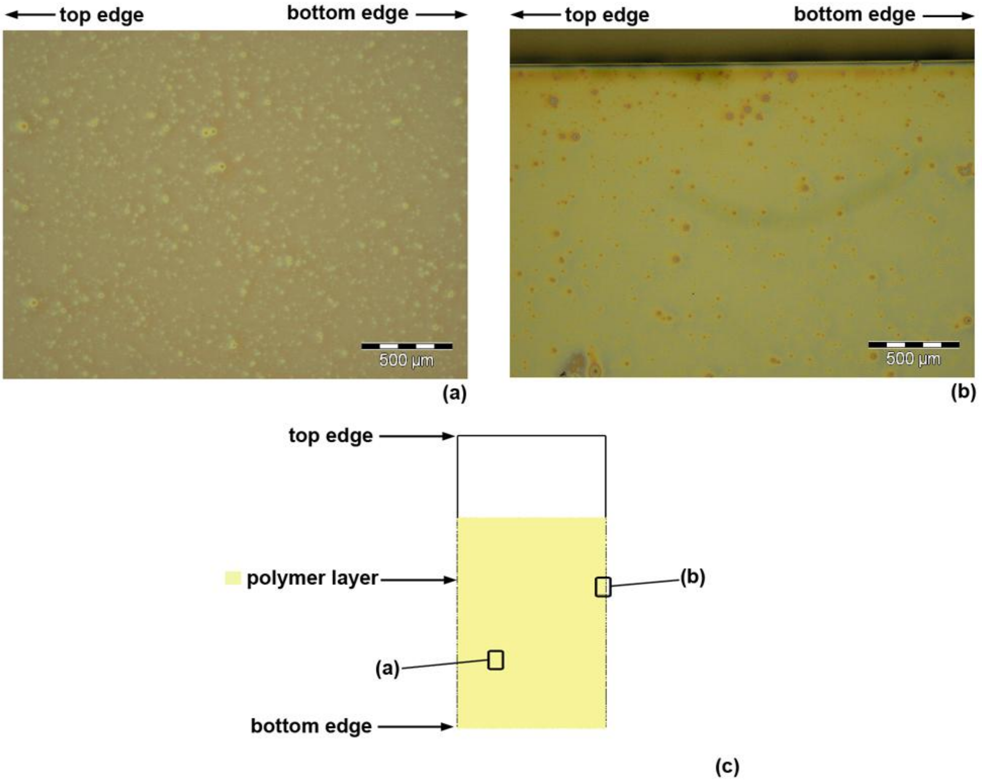


**Fig. 6.52. Clear polymer layer on the ITO coated side of the “Dip coated substrate (3.2.2010)” investigated with an optical microscope (Olympus BX51): (a), (b) photos; (c) scheme**

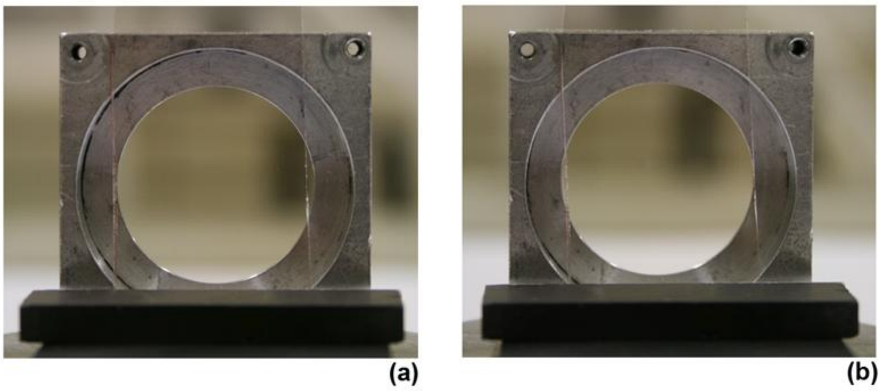
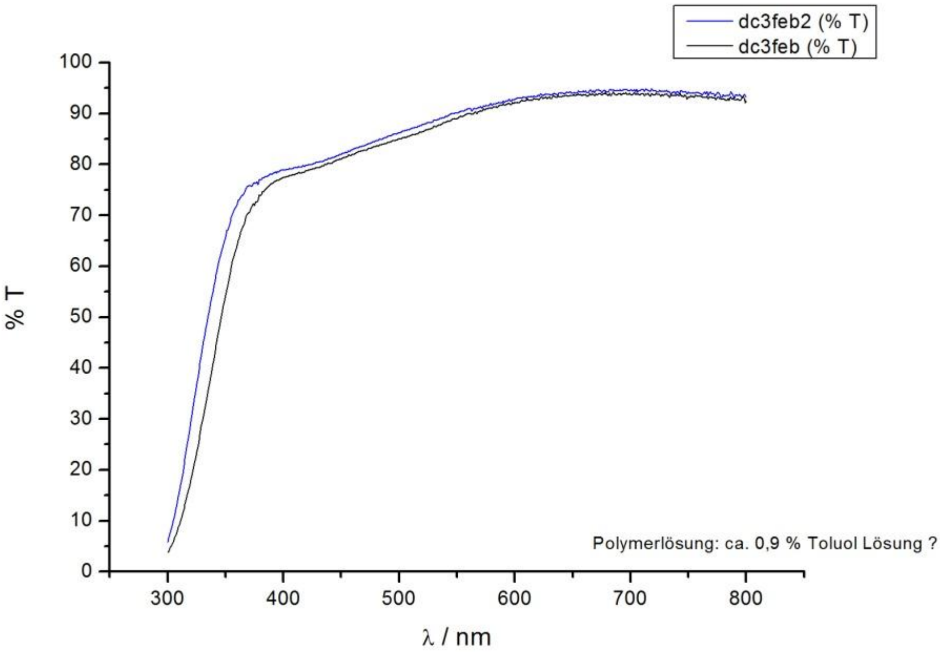


**Fig. 6.53. "Dip coated substrate (3.2.2010)" clamped on the second sample-holder for the transmission measurements in the "Lambda9". (a)…polymer layer on both sides of the substrate; (b)…polymer layer only on the ITO coated side of the glass substrate**



04.02.2010: Lambda9: Non Coloring Counter Polymer (Dip coated substrate - 03.02.2010)

**Fig. 6.54. Transmission spectra of the "Dip coated substrate (3.2.2010)" measured with the "Lambda9". Polymer layer on both sides of the substrate: dc3feb; polymer layer only on the ITO coated side of the glass substrate: dc3feb2**

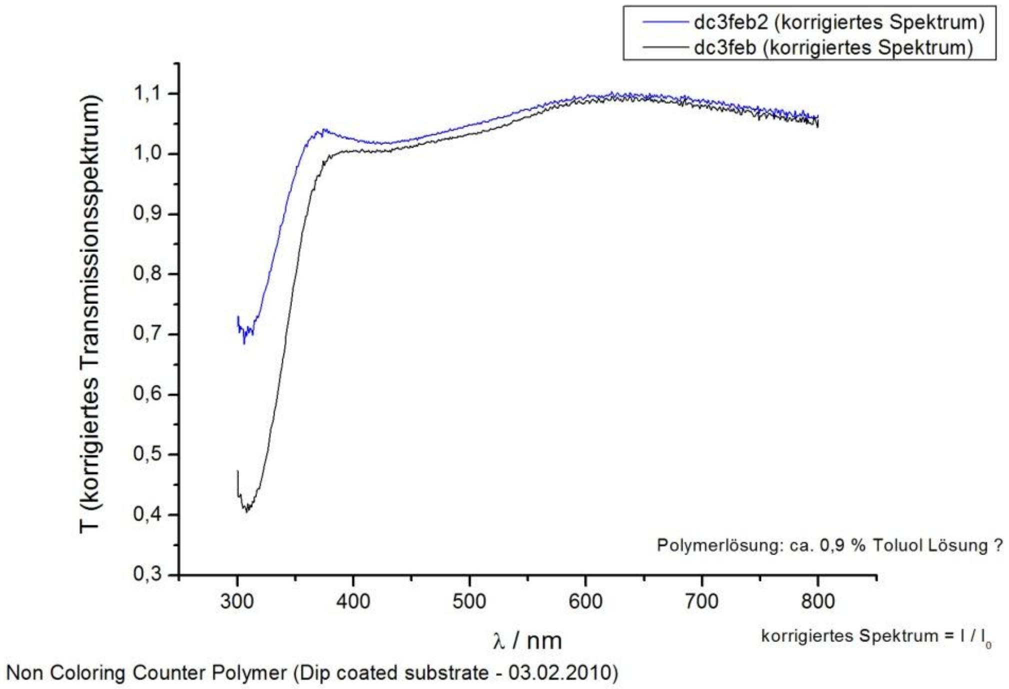


**Fig. 6.55. Transmission spectra of the double and the single polymer layer of the "Dip coated substrate (3.2.2010)" corrected with the transmission spectrum of the ITO-CG 2 (see figure 6.39)**
**dc3feb…as prepared – polymer layer on both sides of the substrate (two polymer layers)**
**dc3feb2…polymer layer only on the ITO coated side of the glass substrate, after removing the polymer layer on the backside**

For the next dip coating process (4.2.2010) an ITO coated glass substrate with dimensions of 60,5-61 mm length, 45-46 mm width and the cuvette with inner dimensions of 52,5 mm height, 50 mm width, 10 mm depth were used.

The same clear polymer solution was taken and the same drawing speed (2,5 µm/s) was chosen as on the 3.2.2010. The drawing path length was set to 50000 µm.

The results of the investigations of the "Dip coated substrate (4.2.2010)" with the optical microscope (Olympus BX51) and the "Lambda9" and the calculated corrected transmission spectra (transmission spectra of the clear polymer layer) are shown in figure 6.56, 6.57, 6.58, 6.59.

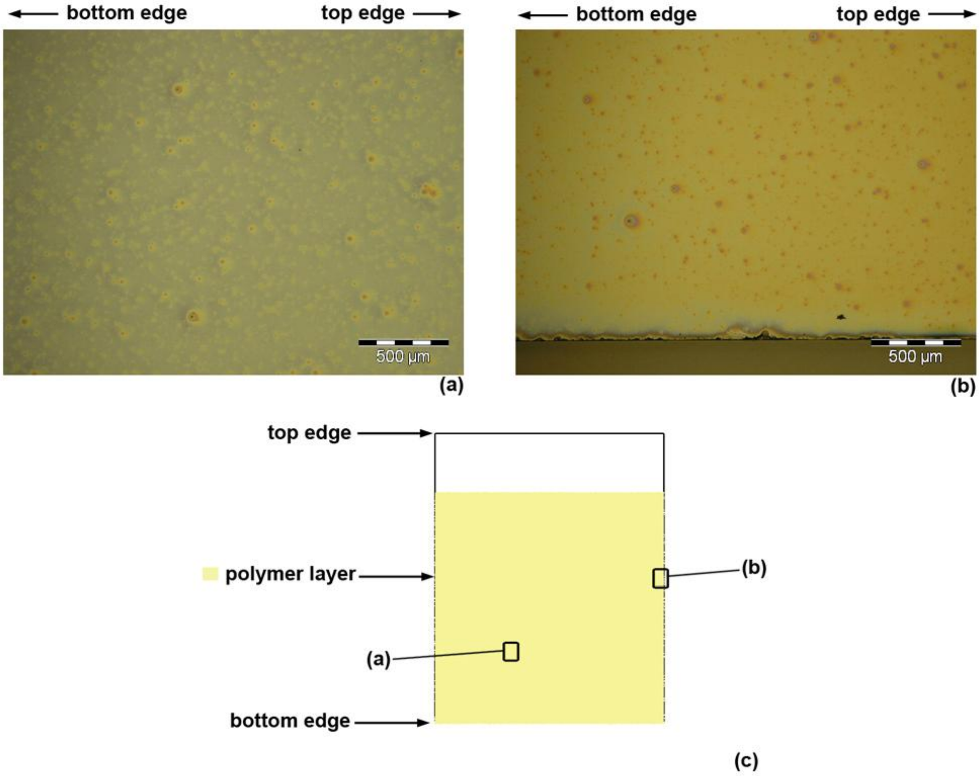


**Fig. 6.56. Clear polymer layer on the ITO coated side of the "Dip coated substrate (4.2.2010)" investigated with an optical microscope (Olympus BX51): (a), (b) photos; (c) scheme**

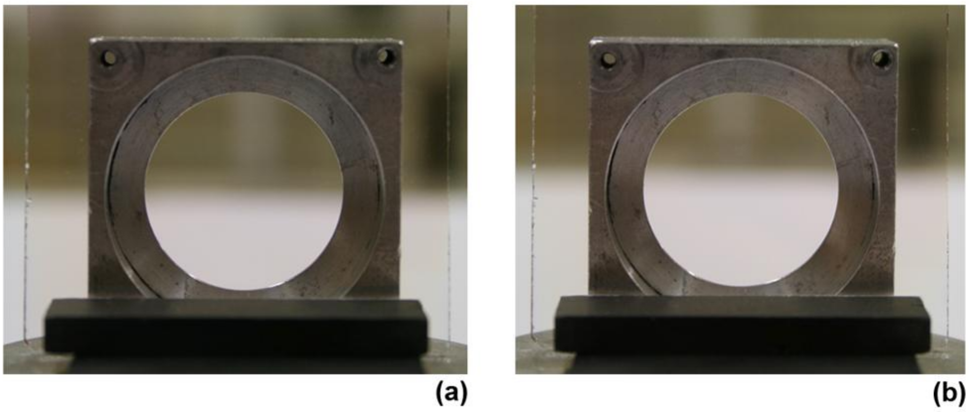
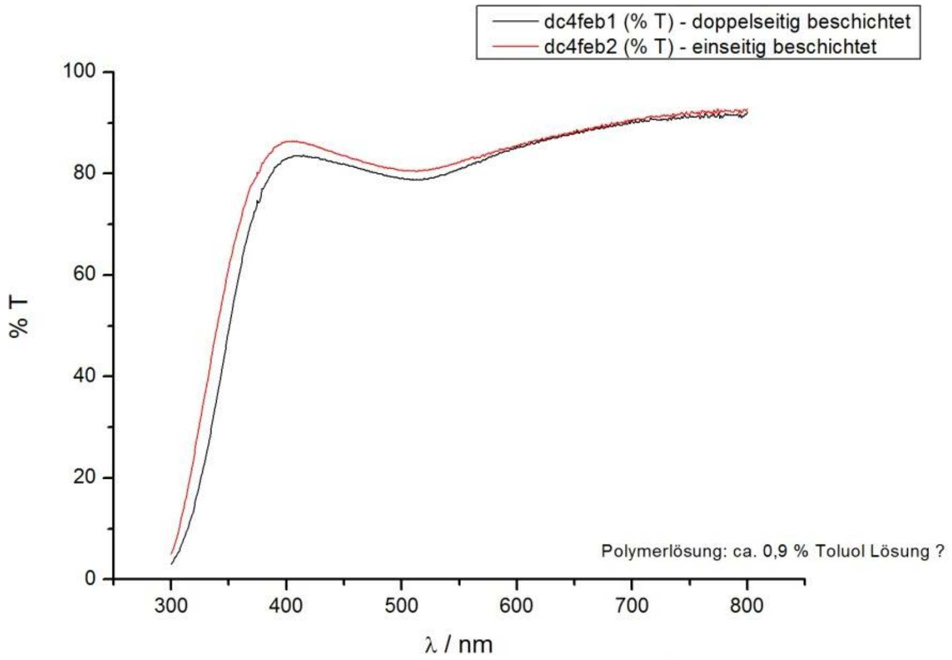
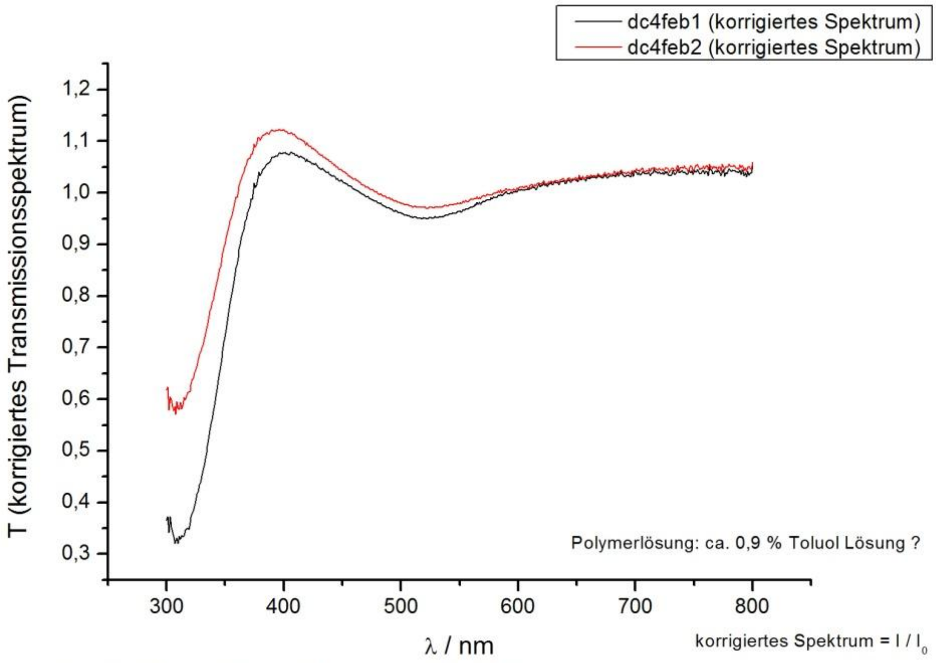


**Fig. 6.57. "Dip coated substrate (4.2.2010)" clamped on the second sample-holder for the transmission measurements in the "Lambda9". (a)…polymer layer on both sides of the substrate; (b)…polymer layer only on the ITO coated side of the glass substrate**



22.02.2010: Lambda9: Non Coloring Counter Polymer (Dip coated substrate - 04.02.2010)

**Fig. 6.58. Transmission spectra of the “Dip coated substrate (4.2.2010)” measured with the “Lambda9”. Polymer layer on both sides of the substrate: dc4feb1; polymer layer only on the ITO coated side of the glass substrate: dc4feb2**



Non Coloring Counter Polymer (Dip coated substrate - 04.02.2010)

**Fig. 6.59. Transmission spectra of the double and the single polymer layer of the “Dip coated substrate (4.2.2010)” corrected with the transmission spectrum of the ITO-CG 2 (see figure 6.39)**
**dc4feb1…as prepared – polymer layer on both sides of the substrate (two polymer layers)**
**dc4feb2…polymer layer only on the ITO coated side of the glass substrate, after removing the polymer layer on the backside**

For the next dip coating process (22.2.2010) the same clear polymer – toluene solution was taken as on the 4.2.2010.

The dimensions of the ITO coated glass substrate were 58-59 mm in length and 20-21 mm in width. So the cuvette with inner dimensions of 43,7 mm height, 30 mm width, 10 mm depth was used (see figure 6.8). Drawing speed was set to 2,5 µm/s and the drawing path length to 33000 µm.

The results of the investigations of the “Dip coated substrate (22.2.2010)” with the “Lambda9” and the calculated corrected transmission spectra (transmission spectra of the clear polymer layer) are shown in figure 6.60, 6.61, 6.62.

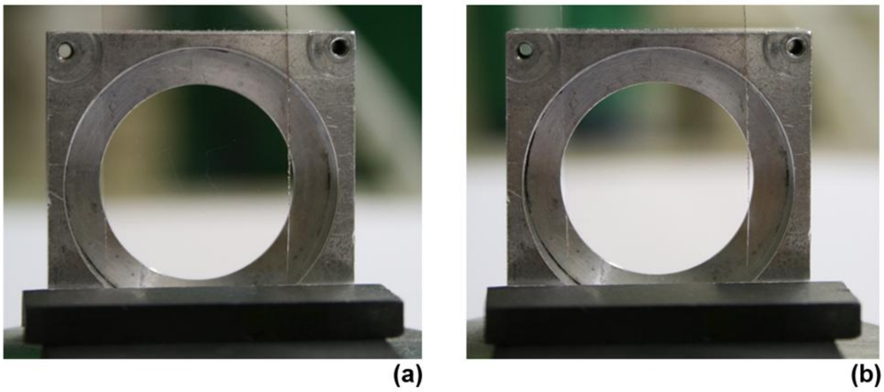
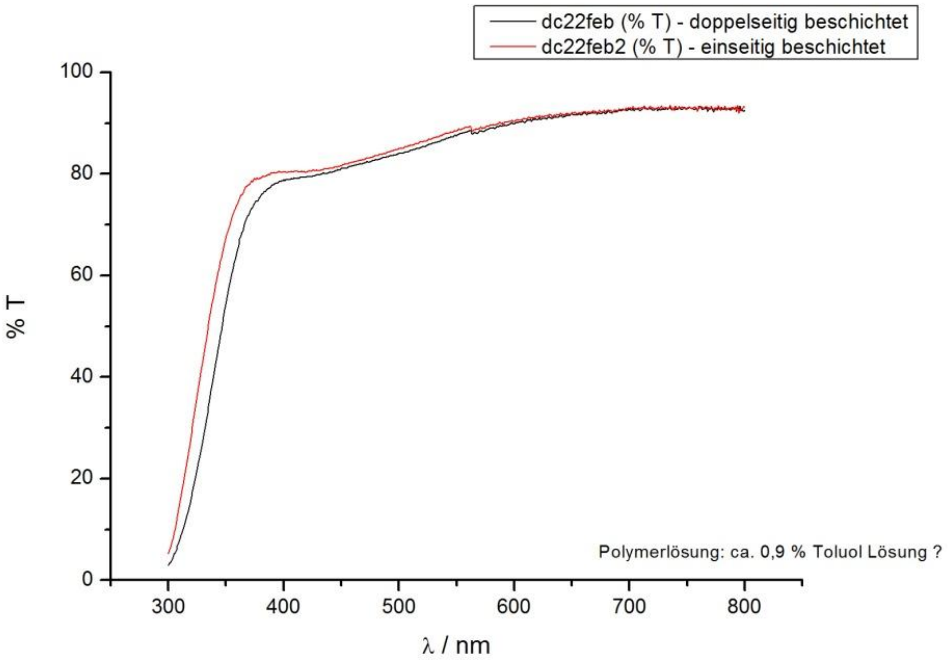


**Fig. 6.60. “Dip coated substrate (22.2.2010)” clamped on the second sample-holder for the transmission measurements in the “Lambda9”. (a)…polymer layer on both sides of the substrate; (b)…polymer layer only on the ITO coated side of the glass substrate**



22.02.2010: Lambda9: Non Coloring Counter Polymer (Dip coated substrate - 22.02.2010)

**Fig. 6.61. Transmission spectra of the “Dip coated substrate (22.2.2010)” measured with the “Lambda9”. Polymer layer on both sides of the substrate: dc22feb; polymer layer only on the ITO coated side of the glass substrate: dc22feb2**

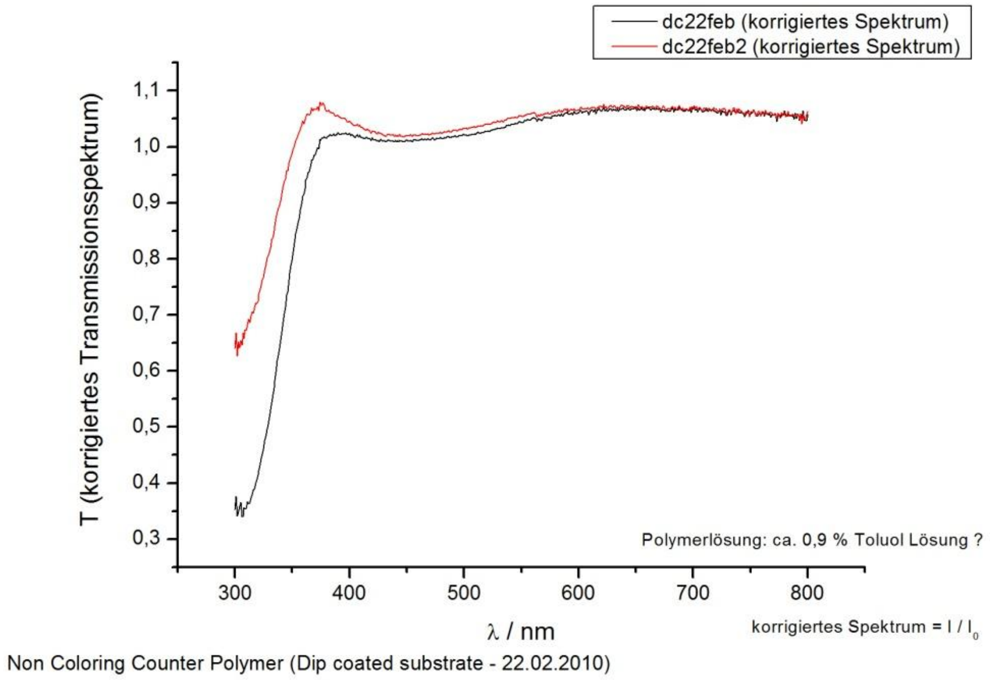


**Fig. 6.62. Transmission spectra of the double and the single polymer layer of the "Dip coated substrate (22.2.2010)" corrected with the transmission spectrum of the ITO-CG 2 (see figure 6.39).**
**dc22feb…as prepared – polymer layer on both sides of the substrate (two polymer layers)**
**dc22feb2…polymer layer only on the ITO coated side of the glass substrate, after removing the polymer layer on the backside**

## 6.5. Customization of the polyester spacer

The polyester panels provided by Ciba (thickness: 166 µm ± 5 µm, see figure 4.8) were used for the fabrication of the polyester spacers.
Spacers are shown in figure 6.63.

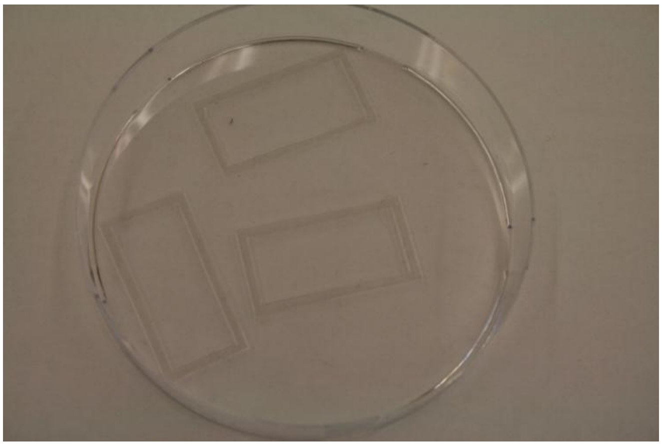


**Fig. 6.63. Three polyester spacers lying in a petri dish**

For the first fabricated device "Device I" an ITO coated glass substrate (length: 56 mm; width: ~20 mm) with regioregular P3HT layer and an ITO coated glass substrate (length: ~55 mm; width:

18-22 mm) with clear polymer layer were used. Both polymer-layers had a length of 33 mm. A polyester spacer with outer dimensions: 36 mm length and 18,5 to 17,5 mm width; and inner dimensions: 32 mm length and 13,5 to 14,5 mm width was taken. So the width of the spacer-edge was 2 mm.

The polyester spacer was cut out of the polyester panels with a scalpel (Surgical Blades 10A; RS Components: Made in England; BS 2982; ISO 7740) using a set square. A glass slab served as cutting pad. To avoid the polyester panel to slip during the cutting process it was fixed on the glass slab with double faced adhesive tape. The double faced adhesive tape was put in the centre of the polyester panel in such a way that there was no double faced adhesive tape on the finished cut out spacer.

For the second fabricated device “Device II” again an ITO coated glass substrate (length: 55 mm; width: 20-21 mm) with regioregular P3HT layer (length: ~31,5 mm) and an ITO coated glass substrate (length: 58-59 mm; width: 20-21 mm) with clear polymer layer (length: ~33 mm) were used. A spacer with outer dimensions of 34 mm length and 19 mm width and inner dimensions of 31 mm length and 16 mm width was cut out (see figure 6.64). So the spacer-edge width was now 1,5 mm.

**Fig. 6.64. Polyester spacer for the Device II (dimensions: outer: length: 34 mm, width: 19 mm; inner: length: 31 mm, width: 16 mm; spacer-edge width: 1,5 mm)**

It was decided that all following spacers would have a spacer-edge width of 1,5 mm.

For the demonstrator the dimensions of the ITO coated glass substrate with magenta polymer layer were 65 mm in length and 45 mm in width, and the dimensions of the ITO coated glass substrate with clear polymer layer were 60,5 to 61 mm in length and 45 to 46 mm in width. The length of the magenta polymer layer and the clear polymer layer was ~46,5 mm and ~46 mm respectively. So the demonstrator required a spacer with outer dimensions of 48 mm length and 44 mm width and inner dimensions of 45 mm length and 41 mm width (see figure 6.65).

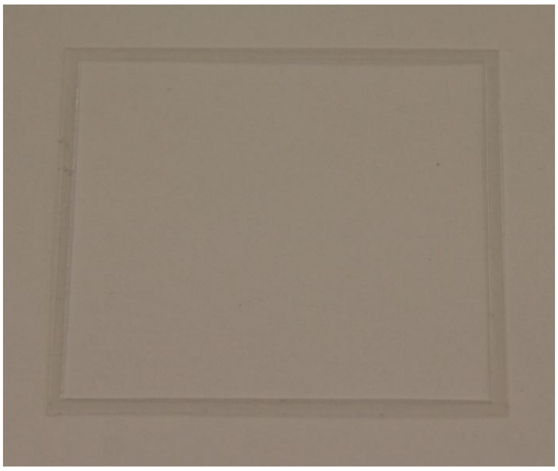


**Fig. 6.65. Polyester spacer for the demonstrator (dimensions: outer: length: 48 mm, width: 44 mm; inner: length: 45 mm, width: 41 mm; spacer-edge width: 1,5 mm)**

## 6.6. Assembly of the single components

Now the single components were put together.

Single components:

- ITO coated glass substrate with regioregular P3HT polymer layer and magenta polymer layer respectively (on the ITO coated side of the glass substrate)
- Polyester spacer
- Gel electrolyte
- ITO coated glass substrate with clear polymer layer (on the ITO coated side of the glass substrate)

The assembly of the single components in chronological order:

- The polyester spacer was fixed on the ITO coated glass substrate with regioregular P3HT polymer layer and magenta polymer layer respectively with super glue (UHU Sekundenkleber mini):

  First the spacer was placed on the polymer layer in such a way that there was about half a millimeter space between the spacer edge (on three sides of the spacer) and the edge of the ITO coated glass substrate with polymer layer (see figure 6.66). Then a tiny drop of super glue was applied next to two opposite corners of the spacer so that the super glue spread between the spacer and the substrate. This process was carried out with a microscope. To enable the drop to be tiny enough a fine wire (it had to be stiff enough) was used to apply the super glue.
  A piece of metal was put on the substrate and the positioned spacer to avoid the spacer to slip during the adhesion. The piece of metal was kept on the substrate and the spacer until the super glue was dry.

If the spacer didn´t lie flat on the substrate yet, further drops of super glue were applied on one or more side edges of the spacer.

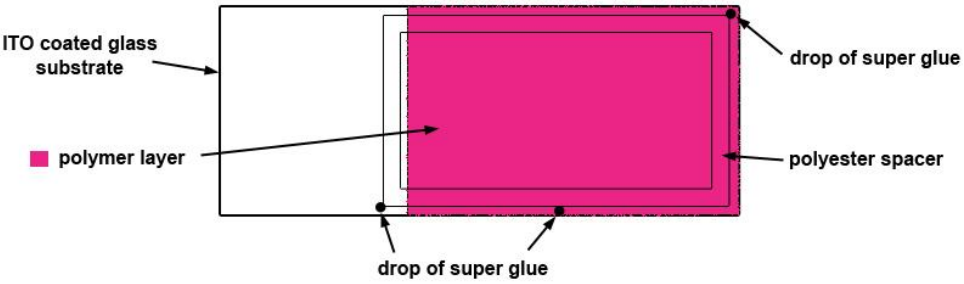


**Fig. 6.66. Scheme of the polyester spacer placed and fixed on the ITO coated glass substrate with regioregular P3HT polymer layer and magenta polymer layer respectively**

- Applying the gel electrolyte:

The gel electrolyte was applied to the ITO coated glass substrate with regioregular P3HT polymer layer and magenta polymer layer respectively, inside the fixed polyester spacer.
A petri dish cap (diameter: 92 mm) was put upside down on a scale (ACCULAB Sartorius group). In the centre of the petri dish cap a smaller petri dish cap (diameter: 39 mm) was placed upside down, and on this one the ITO coated glass substrate with polymer layer and fixed polyester spacer was lying. A spatula was used to drop gel electrolyte onto the polymer layer inside the polyester spacer.
After some experiments an approximation for the needed amount of gel electrolyte was found: The volume of the cuboid inside the polyester spacer was calculated.

$$\boldsymbol{V = l \cdot w \cdot h}$$

$\boldsymbol{l}$...inner length of the polyester spacer
$\boldsymbol{w}$...inner width of the polyester spacer
$\boldsymbol{h}$...height or thickness of the polyester spacer

From the density of propylene carbonate ($\rho = 1{,}205\ g/ml = 1{,}205\ g/cm^3$) a mass value was obtained.

$$\boldsymbol{m = V \cdot \rho}$$

$\boldsymbol{V}$...volume of the cuboid inside the polyester spacer
$\boldsymbol{\rho}$...density of propylene carbonate: $\rho = 1{,}205\ g/ml = 1{,}205\ g/cm^3$

This mass value was to multiply with 2,25.

Once the gel electrolyte was applied the substrate was taken out of the scale.

- The ITO coated glass substrate with clear polymer layer was added:

  A generation of bubbles inside Device I was observed (see figure 6.71).
  Therefore experiments with glass slides, polyester spacers and gel electrolyte were done to find the optimum amount of gel electrolyte, the optimum position for the gel electrolyte, an optimum method to put the second substrate on the first one (with the spacer and the gel electrolyte) to avoid air bubbles. (An approximation for the needed amount of gel electrolyte is given above.)
  A convenient way of putting the second substrate on the first was to put the edge of the second one on the edge of the first one, which was in a flat position, and then to let the second substrate slowly lay down on the first one until the opposite edge reached the opposite edge of the first one.
  If the two substrates were kept lop-sided, the gel electrolyte spread in this hanging down direction and fine corrections were possible. The two substrates were hold together, without pressing, for about 5 minutes. Seeping out of gel electrolyte was no matter.

  Concerning Device I, Device II and the demonstrator it was necessary for the polymer layers to lie exactly one over another. At the same time the ITO coated glass substrates had to be staggered in such a way that it was possible to contact each ITO coated glass substrate (see figure 6.67).

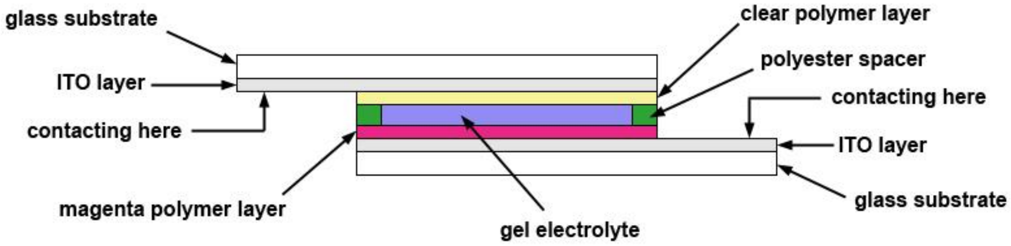


**Fig. 6.67. Scheme of Device I, Device II and the demonstrator (longitudinal section)**

The gel electrolyte was applied mostly on this half of the polymer layer, where the both substrates were put together first. Close to the polyester spacer less of the gel electrolyte was applied than in the centre.

To optimize the application and spreading of the gel electrolyte experiments with same glass slides (length: 76 mm, width: 26 mm) and different spacers were carried out.

- Polyester spacer of the “first specimen”
  - outer dimensions: length: 35 mm, width: 18,5 mm
  - inner dimensions: length: 31 mm, width: 14,5 mm
- Polyester spacer of the “second specimen”
  - outer dimensions: length: 25 mm, width: 21 mm
  - inner dimensions: length: 22 mm, width: 18 mm

The final suitable results are shown in figure 6.68.

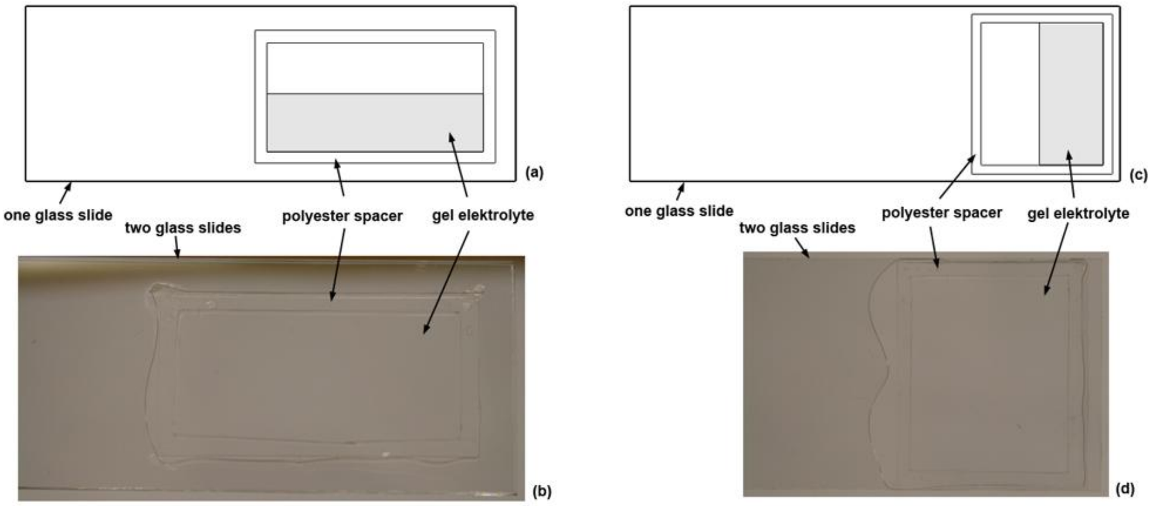


**Fig. 6.68. Schemes of the first glass slide with fixed polyester spacer and applied gel electrolyte for the first specimen (a) and the second specimen (c). Photos of the first specimen (b) and the second specimen (d) after adding the second glass slide**
**First specimen: glass slides (length: 76 mm, width: 26 mm); spacer (outer dimensions: length: 35 mm, width: 18,5 mm; inner dimensions: length: 31 mm, width: 14,5 mm); gel electrolyte (scale: 0,1992 g)**
**Second specimen: glass slides (length: 76 mm, width: 26 mm); spacer (outer dimensions: length: 25 mm, width: 21 mm; inner dimensions: length: 22 mm, width: 18 mm); gel electrolyte (scale: 0,1796 g)**

Concerning the first specimen the application of the second glass slide started on the long edge of the first glass slide. In case of the second specimen the application started on the short edge close to the spacer. No air bubbles appeared inside the polyester spacer.

Before the single components of the demonstrator were assembled, experiments with a polyester spacer of the same dimensions as used for the demonstrator were carried out too.

- The polymer and ITO coated glass substrates with the polyester spacer and gel electrolyte in between were fixed together with glue:

To finish the assembly of the Device I two-component adhesive (UHU plus schnellfest) was used. Five days later the glue was partly swollen and the Device I wasn´t closed any more (see figure 6.72).
As next attempt the margins of the two specimens (see figure 6.68) were glued with a hot glue gun (STEINEL® gluematic 3002).
The first specimen was placed flat on a piece of metal (see figure 6.69 (a)) to put hot glue on the edges. To close every gap the specimen was turned upside down and the procedure was carried out a second time.
In case of the second specimen the short edges of the glass slides were a little bit staggered. This situation made it easier to seal the short side edges with glue (it was done in a flat position of the specimen). To apply the glue to the long side edges the specimen was clamped between two pieces of metal (see figure 6.69 (c)). As soon as possible the specimen was put in a flat position to keep the gel electrolyte from seeping out.

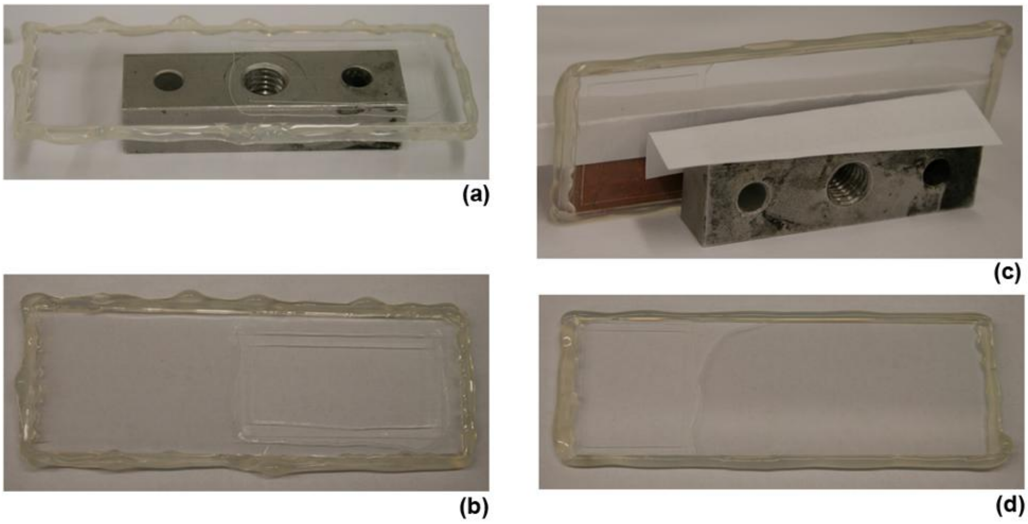


**Fig. 6.69. Specimens closed with glue:**
**The open edges of the two specimens shown in figure 6.68 were closed with a hot glue gun.**
**First specimen: placed on a piece of metal for the applying of the hot glue (a); first specimen closed with hot glue (b)**
**Second specimen: clamped between two pieces of metal for the applying of the hot glue on the long side edges (c); second specimen closed with hot glue (d)**

With the method used for the second specimen it was possible to apply the glue well-proportioned.

About five days later the glue on the first and the second finished specimen looked almost the same and was as firm as on the first day after the drying. So it was decided to close and fix the Device II and the demonstrator with the hot glue gun in the same way as the second specimen.

*Device I:*

Single components for the Device I:

- “Dip coated substrate (19.1.2010)” – regioregular P3HT polymer layer
  dimensions: length: 56 mm, width: ~20 mm
  dimensions of the polymer layer: length: 33 mm, width : ~20 mm
- “Dip coated substrate (3.2.2010)” – clear polymer layer
  dimensions: length: ~55 mm, width: 18-22 mm
  dimensions of the polymer layer: length: 33 mm, width: 20-22 mm
- Polyester spacer
  outer dimensions: length: 36 mm, width: 17,5 to 18,5 mm
  inner dimensions: length: 32 mm, width: 13,5 to 14,5 mm
  spacer-edge: 2 mm
- Gel electrolyte: ~0,1733 g

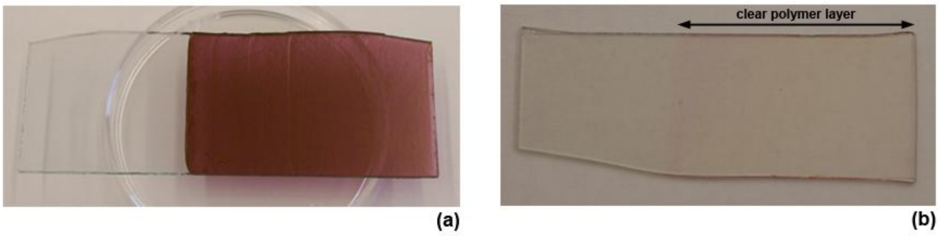


**Fig. 6.70. (a)…"Dip coated substrate (19.1.2010)" lying on an upside down petri dish cap (diameter: 39 mm): after dip coating – regioregular P3HT polymer layer on both sides (the polymer layer on the backside was removed afterwards for the assembly of the Device I)**
**(b)..."Dip coated substrate (3.2.2010)": clear polymer layer only on the ITO coated side of the glass substrate, after removing the polymer layer on the backside**

First the polyester spacer was fixed on the regioregular P3HT polymer layer with super glue (UHU Sekundenkleber mini) as described above.

The gel electrolyte was put inside the fixed polyester spacer: 0,0876 g gel electrolyte was applied on the centre of the polymer layer. (Later on it turned out that this was a too small amount.)

Next, the ITO coated glass substrate with clear polymer layer was put on the ITO coated glass substrate with regioregular P3HT polymer layer and the fixed polyester spacer and the gel electrolyte.
The polymer layers had to be positioned exactly one over the other. At the same time the ITO coated glass substrates had to be staggered so that it was possible to contact each ITO coated glass substrate (see figure 6.67).

Problems occurred with the amount of gel electrolyte and air bubbles inside the gel electrolyte, so several times the single components were separated and assembled again.

The open edges of the assembled polymer and ITO coated glass substrates with the polyester spacer and gel electrolyte in between were closed with two-component adhesive (UHU plus schnellfest).

A photo of the finished Device I is shown in figure 6.71.

**Fig. 6.71. Device I (the photo was made about 22 hours after the assembly)**

Five days later the glue was swollen and the Device I wasn´t closed any more (see figure 6.72).

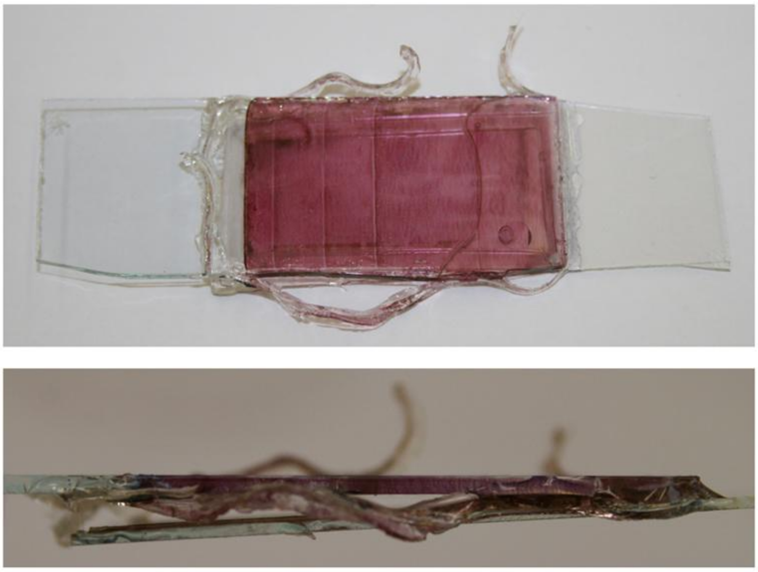


**Fig. 6.72. Device I (the photo was made about five days after the assembly)**

This first try out was followed by the experiments with glass slides, polyester spacers and gel electrolyte to determine the optimum amount of gel electrolyte, the optimum position for the gel electrolyte, the optimum method to put the second substrate on the first one (with the spacer and the gel electrolyte), the optimum method to close the open edges of the device.

*Device II:*

Single components for the Device II:

- “Dip coated substrate (20.1.2010)” – regioregular P3HT polymer layer
  dimensions: length: 55 mm, width: 20-21 mm
  dimensions of the polymer layer: length: ~31,5 mm, width : 20-21 mm
- “Dip coated substrate (22.2.2010)” – clear polymer layer
  dimensions: length: 58-59 mm, width: 20-21 mm
  dimensions of the polymer layer: length: ~33 mm, width: 20-21 mm
- Polyester spacer (see figure 6.64)
  outer dimensions: length: 34 mm, width: 19 mm
  inner dimensions: length: 31 mm, width: 16 mm
  spacer-edge: 1,5 mm
- Gel electrolyte: 0,2229 g

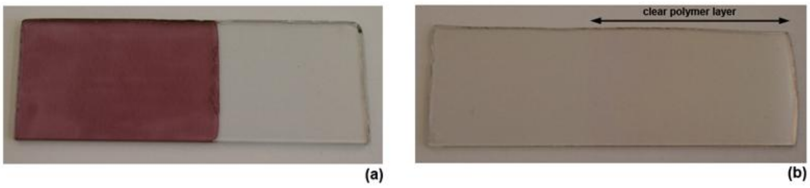


**Fig. 6.73. (a)…"Dip coated substrate (20.1.2010)": regioregular P3HT polymer layer only on the ITO coated side of the glass substrate, after removing the polymer layer on the backside**
**(b)..."Dip coated substrate (22.2.2010)": clear polymer layer only on the ITO coated side of the glass substrate, after removing the polymer layer on the backside**

The polyester spacer was fixed on the regioregular P3HT polymer layer with super glue (UHU Sekundenkleber mini) as described above.

Gel electrolyte (scale: 0,2229 g) was applied on the ITO coated glass substrate with regioregular P3HT polymer layer, inside the fixed polyester spacer (see figure 6.74).

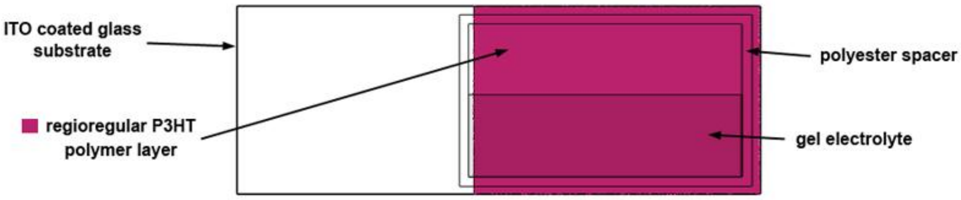


**Fig. 6.74. Scheme of the "Dip coated substrate (20.1.2010)" with fixed polyester spacer and applied gel electrolyte**

Close to the polyester spacer less gel electrolyte was applied than in the centre.

Next, the ITO coated glass substrate with clear polymer layer was put on the ITO coated glass substrate with regioregular P3HT polymer layer and the fixed polyester spacer and the gel electrolyte in the same way as with the first and the second specimen. The laying down started on the long edge of the "Dip coated substrate (20.1.2010)", where the mostly part of the gel electrolyte had been applied.

The open edge of the assembled polymer and ITO coated glass substrates with the polyester spacer and gel electrolyte in between were closed with glue. This time a hot glue gun was used. The Device II was closed and stuck in the same way as the second specimen (described above, see figure 6.69 (c)).

Photos of the finished Device II are shown in figure 6.75.

**Fig. 6.75. Device II**

*Demonstrator:*

Single components for the demonstrator:

- “Dip coated substrate (2.2.2010)” – magenta polymer layer
  dimensions: length: 65 mm, width: 45 mm
  dimensions of the polymer layer: length: ~46,5 mm, width : 45 mm
- “Dip coated substrate (4.2.2010)” – clear polymer layer
  dimensions: length: 60,5-61 mm, width: 45-46 mm
  dimensions of the polymer layer: length: ~46 mm, width: 45-46 mm
- Polyester spacer (see figure 6.65)
  outer dimensions: length: 48 mm, width: 44 mm
  inner dimensions: length: 45 mm, width: 41 mm
  spacer-edge: 1,5 mm
- Gel electrolyte: 0,8009 g

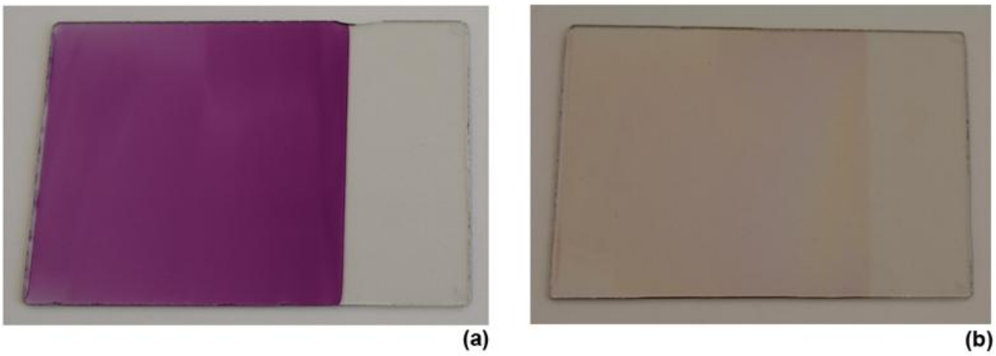


**Fig. 6.76. (a)…“Dip coated substrate (2.2.2010)”: magenta polymer layer only on the ITO coated side of the glass substrate, after removing the polymer layer on the backside**
**(b)...“Dip coated substrate (4.2.2010)”: clear polymer layer only on the ITO coated side of the glass substrate, after removing the polymer layer on the backside**

The polyester spacer was fixed on the magenta polymer layer with super glue (UHU Sekundenkleber mini).

0,8009 g of gel electrolyte was applied on the ITO coated glass substrate with magenta polymer layer, inside the fixed polyester spacer (see figure 6.77).

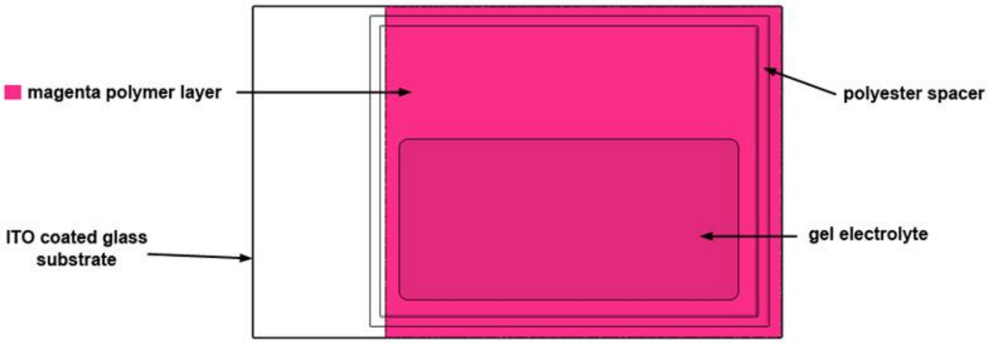


**Fig. 6.77. Scheme of the “Dip coated substrate (2.2.2010)” with fixed polyester spacer and applied gel electrolyte**

The ITO coated glass substrate with clear polymer layer was put on the ITO coated glass substrate with magenta polymer layer and the fixed polyester spacer and the gel electrolyte in the same way as for the first and the second specimen. The laying down started again on the long edge of the “Dip coated substrate (2.2.2010)”, where the mostly part of the gel electrolyte had been applied.

The demonstrator was closed and stuck the same way as the second specimen with hot glue.

Photos of the finished demonstrator are shown in figure 6.78.

**Fig. 6.78. Demonstrator**

## 6.7. Testing and characterization of the completed devices

*Device I:*

To investigate the Device I cyclovoltammograms (see chapter 5.1) were made on the 10.2.2010. The electrical assembly was the same as described in chapter 5.1.1.1. Figure 5.1 shows a schematic circuit diagram for cyclovoltammetry. The Device I was connected to the source measure unit (Keithley 236 source measure unit): The ITO coated glass substrate with regioregular P3HT polymer layer was connected to the plus output of the source measure unit.

While the first 6 cyclovoltammograms were run no colour change was visible. After manually voltage cycling until a bleaching was visible, cyclovoltammograms were made again.
During the 15th cyclovoltammogram (1STD_100210_15M) photos of the Device I were taken at different voltage values. The optical setup for investigation with a camera was the same as described in chapter 5.1.1.2.2 except one item: the Device I was placed on a sheet of paper on a desk.
The settings for the 15th cyclovoltammogram (1STD_100210_15M):
“high level”: +3,0 V
“low level”: -2,5 V
step size: 0,02 V
delay time: 2000 ms
one cycle was run, it took about 18 minutes and 30 s

Photos are shown in figure 6.80. The positions, where the photos have been taken, are marked in figure 6.79.

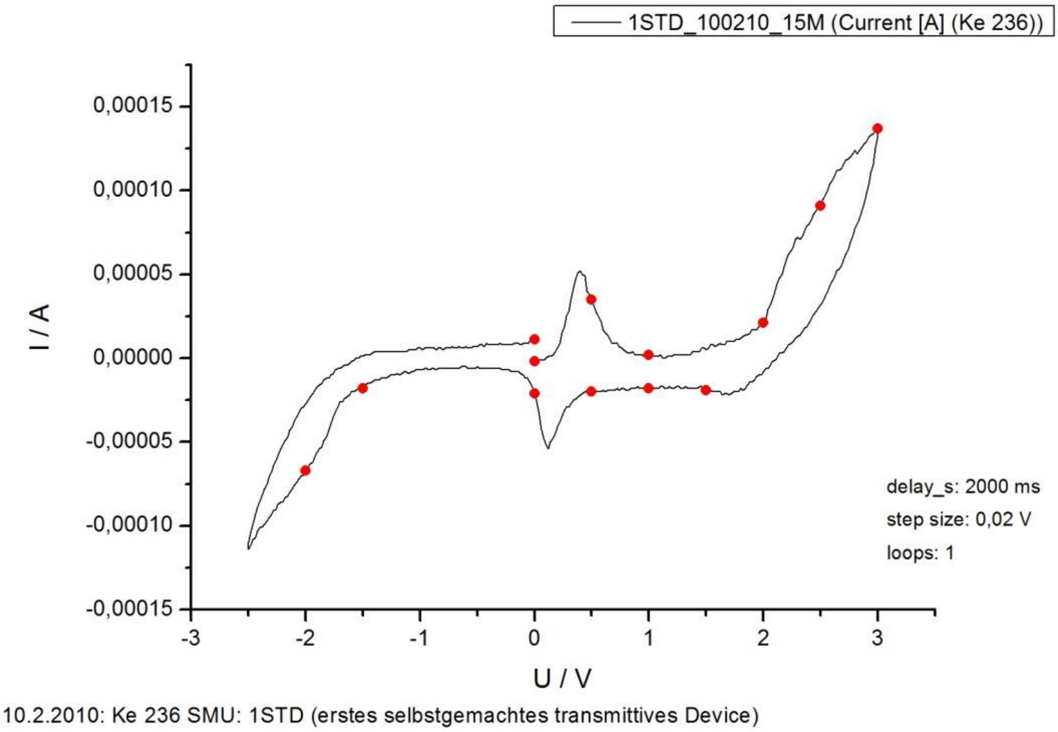


**Fig. 6.79. Cyclovoltammogram “1STD_100210_15M” of the Device I measured on the 10.2.2010; voltage positions are marked, where the photos shown in figure 6.80 have been taken**

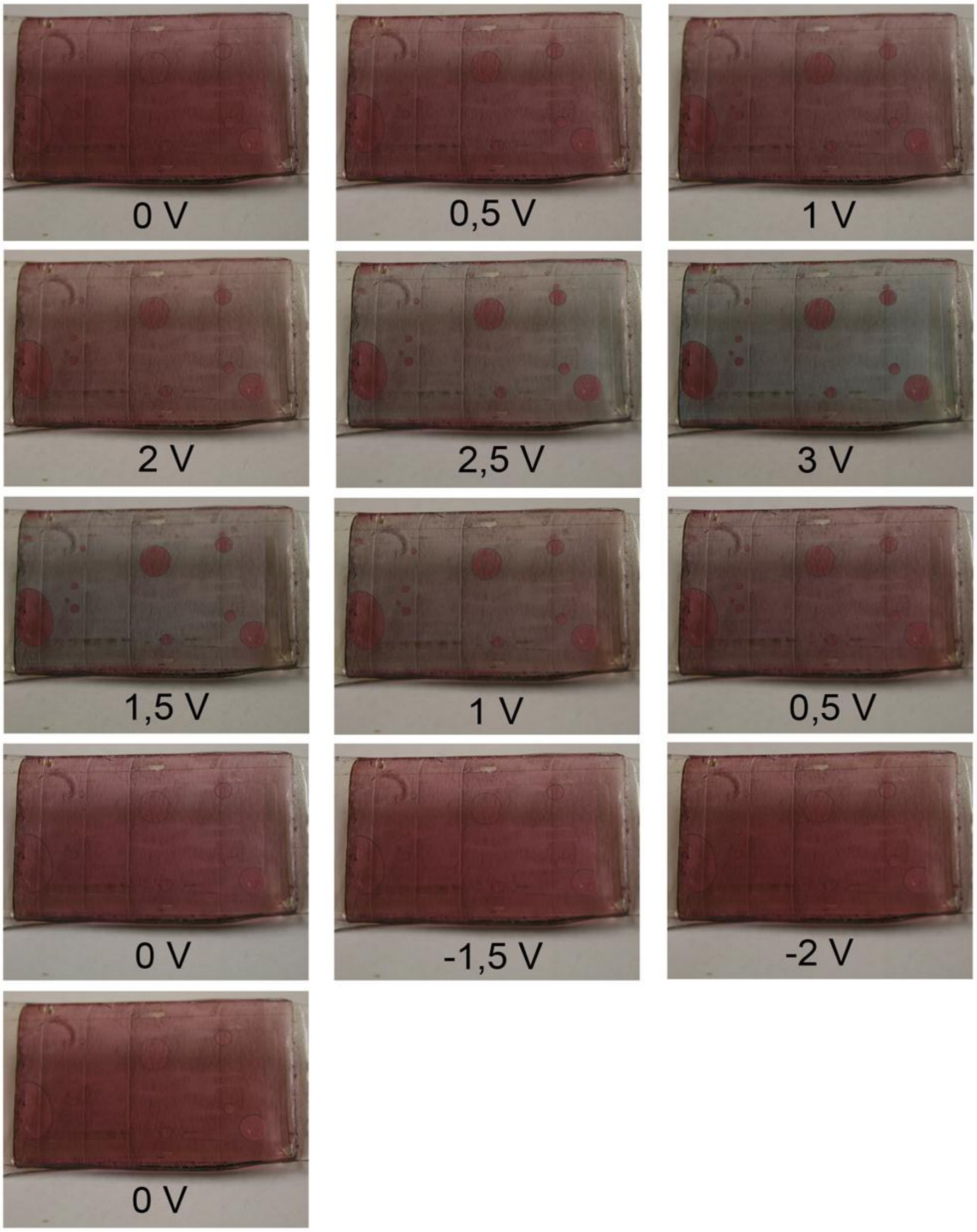


**Fig. 6.80. Photo series of the Device I taken at different voltage values during the cyclovoltammogram "1STD_100210_15M" on the 10.2.2010**

After the cyclovoltammetry the Device I was investigated with the spectrophotometer "Lambda9" (PERKIN-ELMER – Lambda9 – UV/VIS/NIR Spectrophotometer). The transmission was measured at three different voltage values: +3 V, 0 V, -2 V.

Figure 6.81 shows the Device I fixed on a sample-holder, used for the measurements in the "Lambda9".

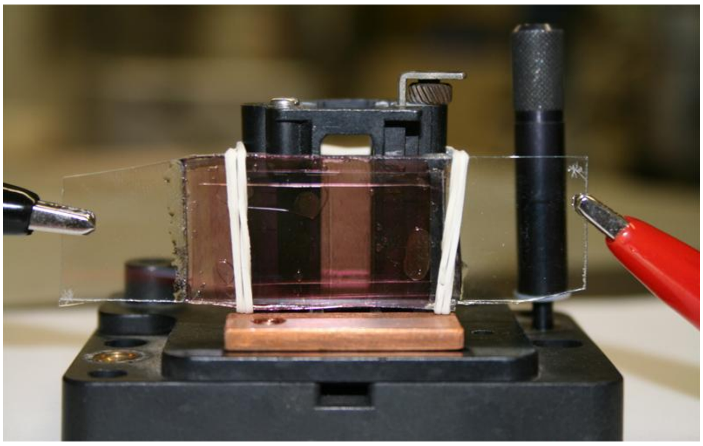


**Fig. 6.81. Device I fixed on a sample-holder for the transmission measurements in the “Lambda9”**

The Device I was connected to a programmable voltage source (Keithley 230 programmable voltage source): The ITO coated glass substrate with regioregular P3HT polymer layer was connected to the plus output of the programmable voltage source. Figure 6.82 shows a schematic circuit diagram and a photo of the voltage source.

**Fig. 6.82. (a)…schematic circuit diagram; (b)…KEITHLEY 230 programmable voltage source**

The transmission spectra of the Device I are shown in figure 6.83.

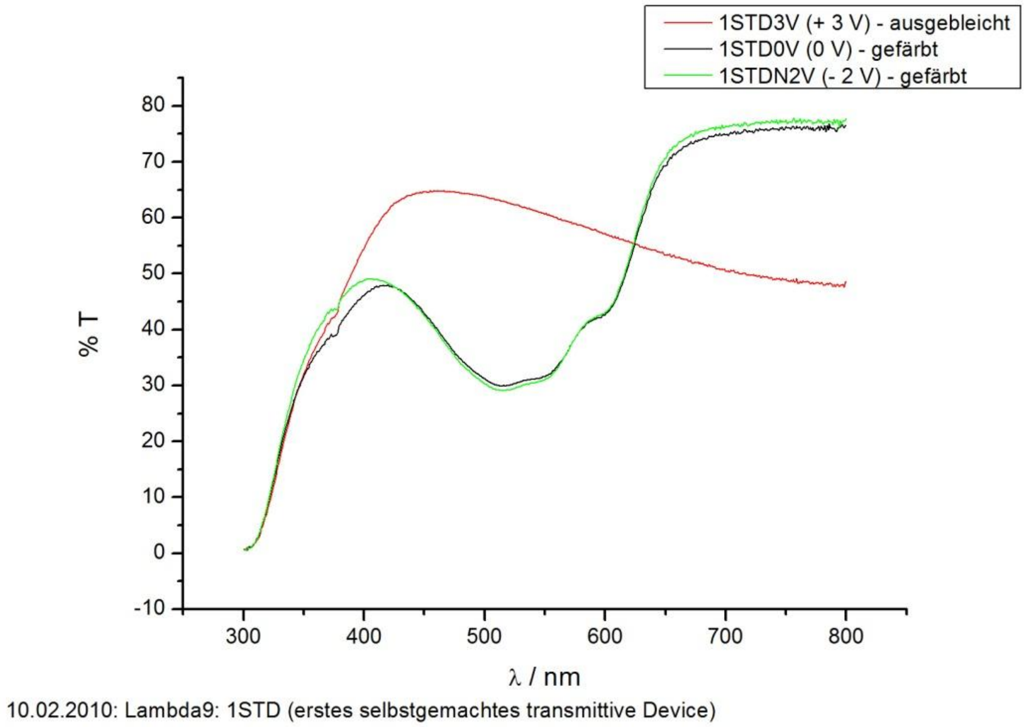


**Fig. 6.83. Transmission spectra of the Device I at three different voltage values measured with the "Lambda9" on the 10.2.2010**
**1STD3V…voltage: +3 V**
**1STD0V…voltage: 0 V**
**1STDN2V…voltage: -2 V**

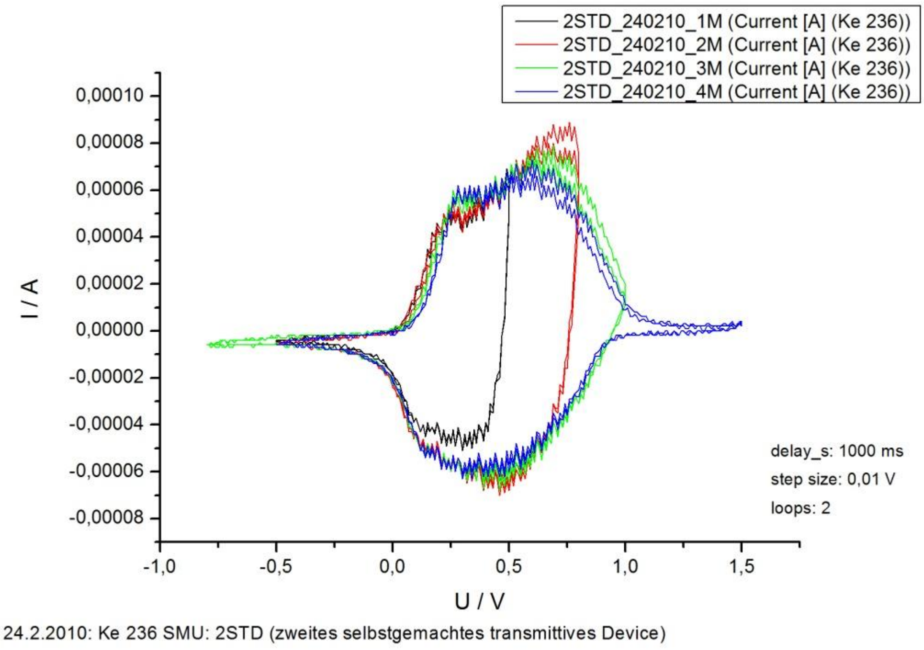
The transmission spectra at 0 V and -2 V differ only a little bit. According to it the Device I is nearly completely coloured at 0 V.

Regioregular P3HT polymer is a cathodically colouring substance since it forms colour when it is reduced at a cathode (see chapter 2.2.2).

*Device II:*

With the Device II cyclovoltammograms (see chapter 5.1) were made on the 24.2.2010. Again the electrical assembly was the same as described in chapter 5.1.1.1. The ITO coated glass substrate with regioregular P3HT polymer layer was connected to the plus output of the source measure unit (Keithley 236 source measure unit).

Already during the first cyclovoltammogramm a noticeable colour change was visible.
The 1st, 2nd, 3rd, 4th cyclovoltammograms are shown in figure 6.84. The four cyclovoltammograms had different "high level"- and "low level" values but the same step size (0,01 V) and the same delay time (1000 ms). With each cyclovoltammogram two cycles were run.

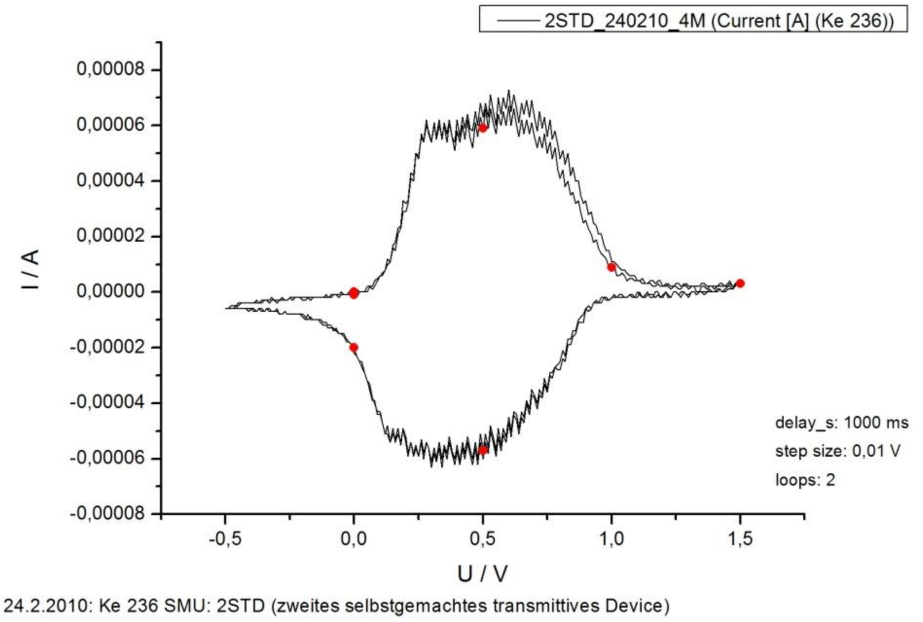


24.2.2010: Ke 236 SMU: 2STD (zweites selbstgemachtes transmittives Device)

**Fig. 6.84. Cyclovoltammograms of the Device II measured on the 24.2.2010**

During the 4th cyclovoltammogram (2STD_240210_4M) photos of the Device II were taken at different voltage values. The optical setup for investigation with a camera was the same as described in chapter 5.1.1.2.2 except one item: the Device II was placed on a sheet of paper on a desk, and a gold mirror was below the device.

A photo series, taken from the second cycle of the 4th cyclovoltammogram, is presented in figure 6.86. The corresponding voltage positions in the cyclovoltammogram are marked in figure 6.85.



24.2.2010: Ke 236 SMU: 2STD (zweites selbstgemachtes transmittives Device)

**Fig. 6.85. Cyclovoltammogram "2STD_240210_4M" of the Device II measured on the 24.2.2010; voltage positions are marked, where the photos shown in figure 6.86 have been taken during the second cycle**

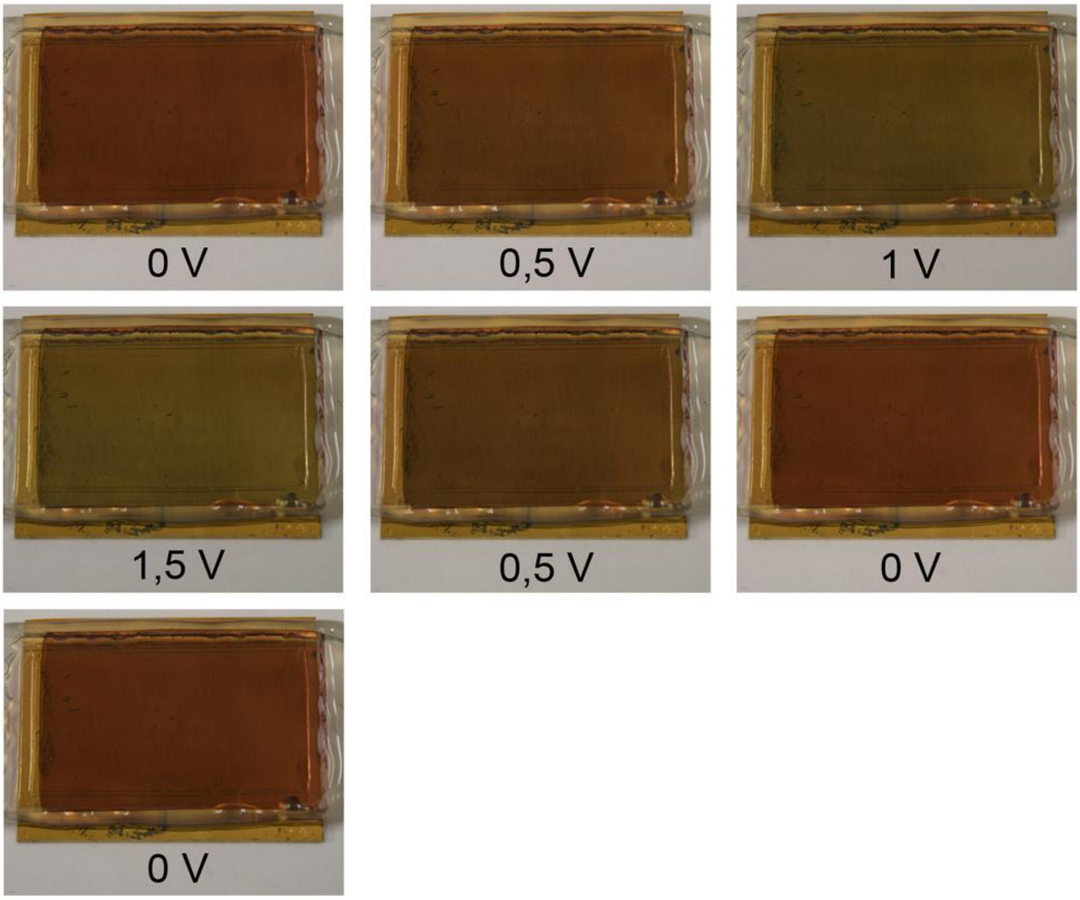


**Fig. 6.86. Photo series of the Device II taken at different voltage values during the second cycle of the cyclovoltammogram "2STD_240210_4M" on the 24.2.2010**

*Demonstrator:*

On the 10.3.2010 cyclovoltammograms (see chapter 5.1) with the demonstrator were made (see figure 6.87).

The ITO coated glass substrate with magenta polymer layer was connected to the minus output of the source measure unit (Keithley 236 source measure unit).

Already during the first cyclovoltammogramm an intensive colour change was visible.

The cyclovoltammograms in figure 6.87 had different "high level"- and "low level" values, whilst the step size of 0,01 V and the delay time of 1000 ms were the same. With each cyclovoltammogram two cycles were run.

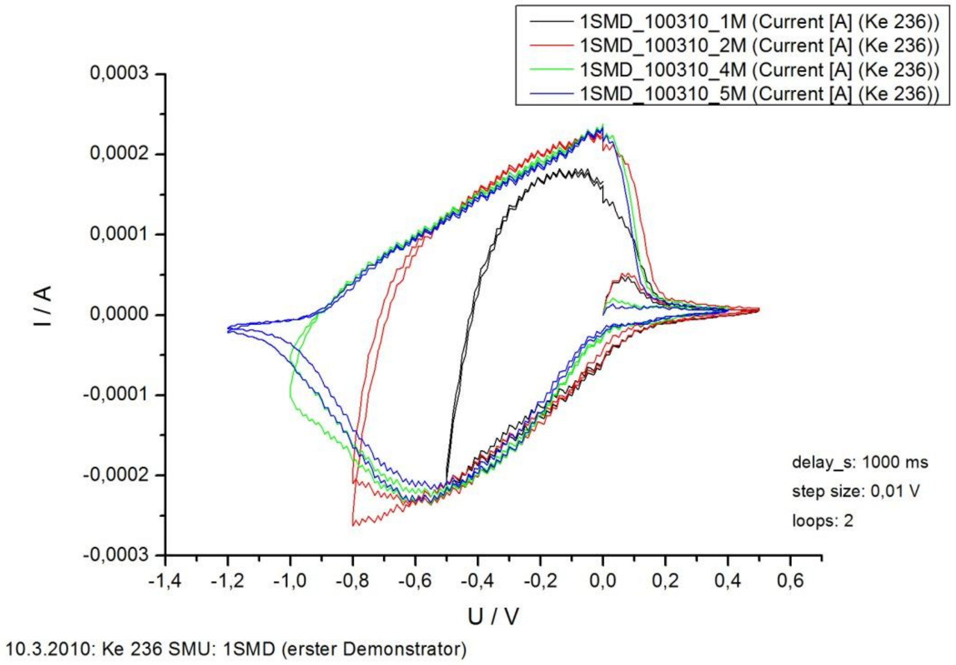


**Fig. 6.87. Cyclovoltammograms of the demonstrator measured on the 10.3.2010**

A photo series taken during the second cycle of the cyclovoltammogram “1SMD_100310_5M” is presented in figure 6.89. The optical setup for investigation with a camera was the same as described in chapter 5.1.1.2.2 except one item: the demonstrator was placed on a sheet of paper on a desk and a gold mirror was put underneath.

Figure 6.88 shows the voltage positions in the cyclovoltammogram, where the photos were taken.

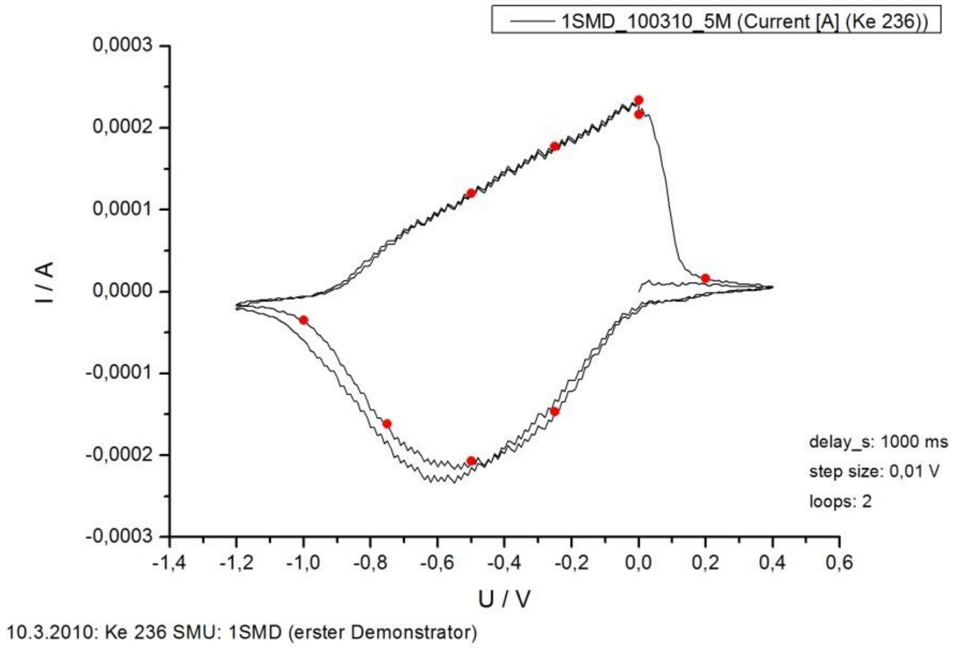
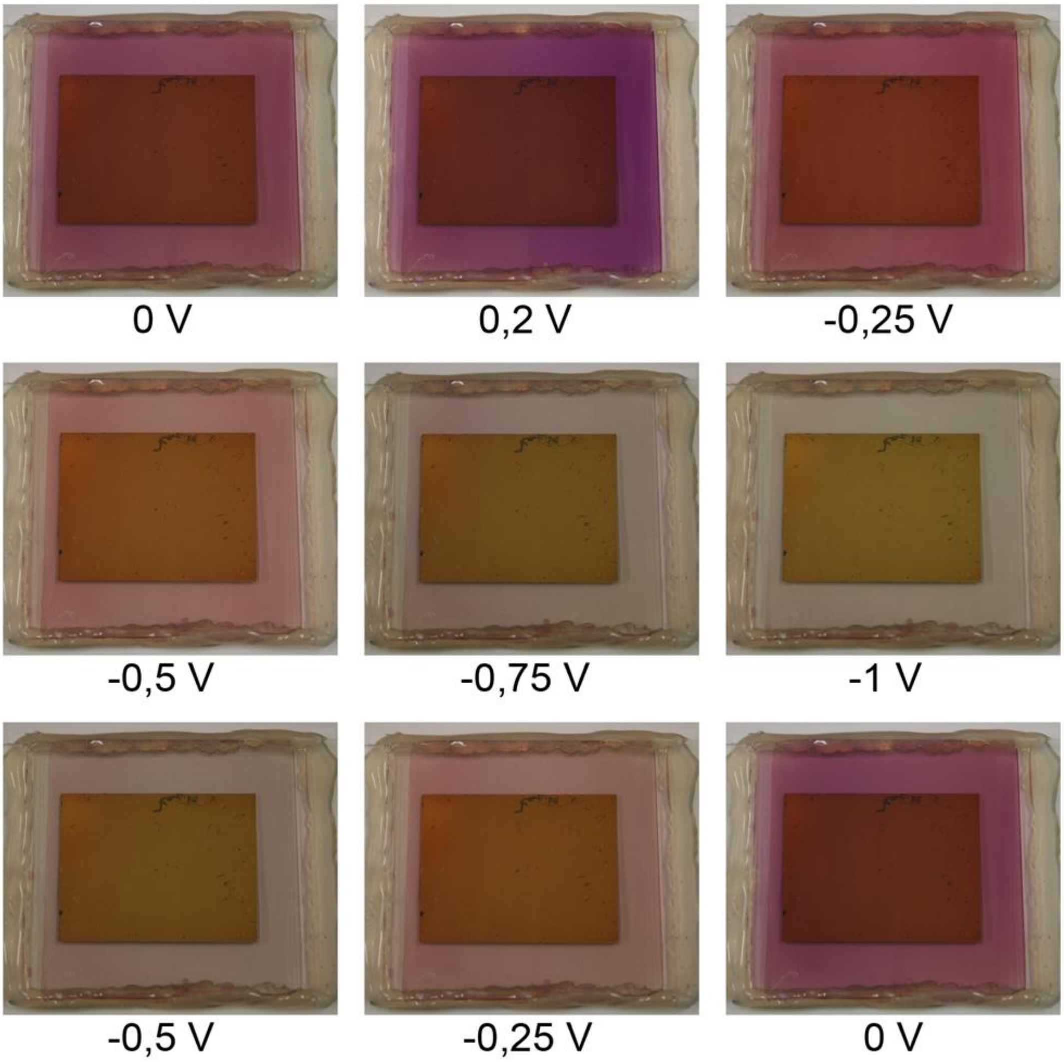


**Fig. 6.88. Cyclovoltammogram “1SMD_100310_5M” of the demonstrator measured on the 10.3.2010; voltage positions are marked, where the photos shown in figure 6.89 have been taken during the second cycle**



0 V
0,2 V
-0,25 V
-0,5 V
-0,75 V
-1 V
-0,5 V
-0,25 V
0 V

**Fig. 6.89. Photo series of the demonstrator taken at different voltage values during the second cycle of the cyclo-voltammogram "1SMD_100310_5M" on the 10.3.2010**

The colour impression of the demonstrator with coloured aluminium foils as background was investigated. For this the demonstrator was connected to the source measure unit (Keithley 236): The ITO coated glass substrate with magenta polymer layer was connected to the minus output of the source measure unit.

Figure 6.90 shows the results for blue and gold coloured aluminium foils.

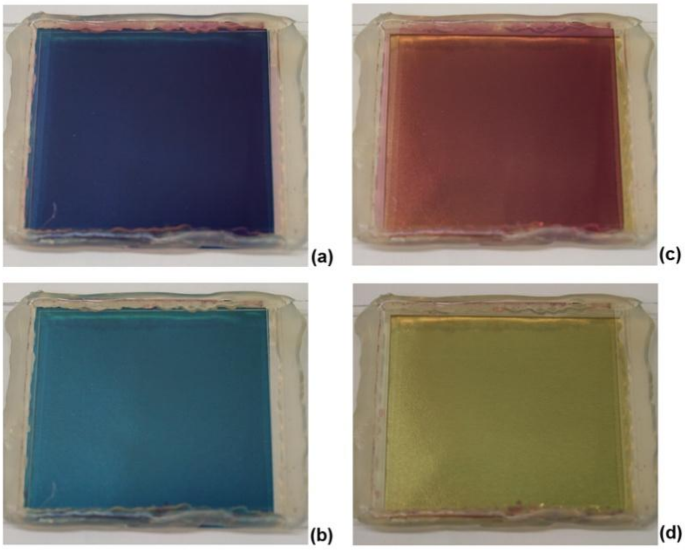


**Fig. 6.90. Demonstrator with coloured aluminium foil as background**
**with blue coloured aluminium foil: (a)...at 0,4 V, (b)...at -1 V**
**with gold coloured aluminium foil: (c)...at 0,4 V, (b)...at -1 V**

The demonstrator and the aluminium foil were placed inside a plastic casing with an acrylic plastic window.

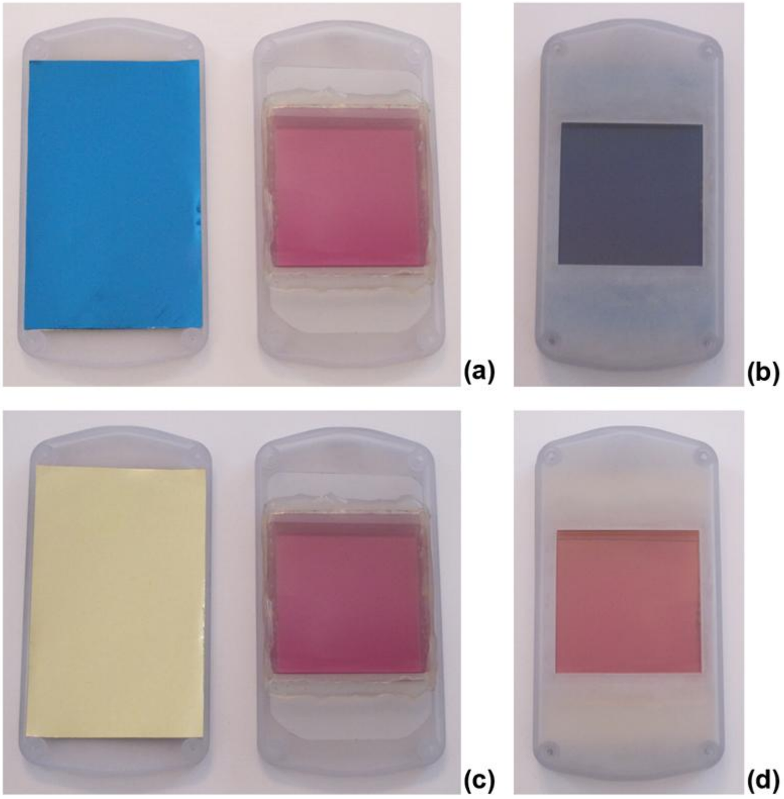


**Fig. 6.91. Demonstrator with coloured aluminium foil inside a plastic casing with an acrylic plastic window**
**with blue coloured aluminium foil: (a)...lower part (with foil) and upper part (with the demonstrator) of the open plastic casing, (b)...closed plastic casing**
**with gold coloured aluminium foil: (c)...lower part (with foil) and upper part (with the demonstrator) of the open plastic casing, (d)...closed plastic casing**

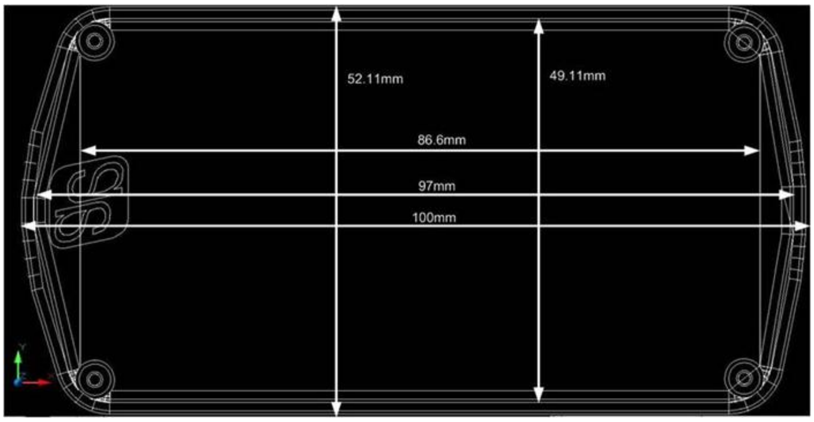


Fig. 6.92. Dimensions of the lower part of the plastic casing (top view)

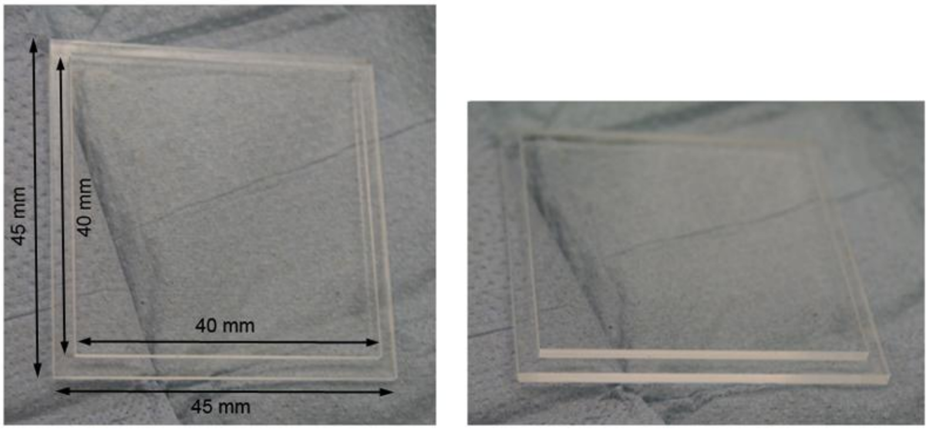


Fig. 6.93. Acrylic plastic window (absolute thickness: 3 mm)

# 7. Error analysis

Each reflective and transmittive electrochromic device was placed on the base plate of the reflectometer in such a way that an investigation of the same point for all measurements with the S1000 CCD spectrometer and the Si-photodiode was assured. Small deviations of this position are probably.

Moving and touching the optical fiber during investigations with the S1000 CCD spectrometer results in fluctuations of the measured reflection spectra, so it was important to avoid contact with the optical fiber during measurements.

The measured photodiode signal is influenced by the temperature of the Si-photodiode. Since the experiments were carried out at constant room temperature and the intensity of the incoming light beam was too weak to warm up the Si-photodiode, it was assumed that the temperature of the Si-photodiode stayed constant during the measurements.

Error equation for the calculated transmission T in table 6.2:

$$\Delta T = \left|10^{-(A-\Delta A)} - T\right|$$

Error equation for the calculated optical density $\left(-ln(T)\right)$ in table 6.2:

$$\Delta\left(-ln(T)\right) = \left|-ln(T-\Delta T) - \left(-ln(T)\right)\right|$$

Error equation for the calculated thickness d of the magenta polymer layer in table 6.3, 6.4, 6.5:

$$\Delta d = \left(\frac{\Delta\left(-ln(T)\right)}{-ln(T)} + \frac{\Delta a_m}{a_m}\right) \cdot d$$

# 8. Summary

Reflective and transmittive organic electrochromic devices were fabricated and investigated concerning their optical and optoelectronical properties.

The electrochromic devices change between coloured state and bleached state in a voltage range from about -1 V to +1 V.

If the coloured state and bleached state respectively is reached only a small current (~0,5 mA) is needed to maintain this redox state (memory effect).

Cyclovoltammetry was used to locate the oxidation and reduction potential positions of the electrochromic devices.

Switching times for colour change of about 1 s were derived from experiments with DC voltage-pulse-packets.

The electrochromic devices contain a conjugated polymer, which forms colour when it is reduced at a cathode (cathodically colouring polymer).

Organic electrochromic devices were fabricated: Two ITO coated glass substrates with electrochromic polymer layers (one colouring polymer, the other one non colouring polymer) and gel electrolyte enclosed in between were mounted with a spacer, fixed and sealed with glue. Different conjugated polymers were used, one of them was “regioregular P3HT” (regioregular poly(3-hexylthiophene-2,5-diyl)).

For generating polymer layers on ITO coated glass substrates the dip coating technique was used. For a polymer concentration of 1 % (solvent: toluene) a drawing speed of 2,5 µm/s caused a layer thickness of 0,09 µm. On ITO coated glass substrates up to 65 x 45 mm size homogeneous polymer layers were produced, with active polymer layer areas up to 46 x 45 mm. Transmission spectra together with colour intensity impression were decisive for the choice of layer thickness.

With cyclovoltammetry possible colour-stability-points were found and checked. The reflective organic electrochromic devices possess colour-stability-points at three different voltage values (-1,07 to -1,12 V; +0,64 to +0,66 V; +1,00 V).

# 9. Literature

[1] “Verfärbung und Lumineszenz. Beiträge zur Mineralphysik.” by K. Przibram, Springer, Vienna, 1953; “Irradiation Colours and Luminescence” by K. Przibram, Translated and revised by J. E. Faffyn, Pergamon Press, London, 1956
[2] J. F. Dreyer, U.S. Patent No. 3,196,743, Patented July 27, 1965
[3] J. R. Platt, J. Chem. Phys. 34 (1961) 862
[4] P. Chandrasekhar, U.S. Patent No. 5,995,273, Patented November 30, 1999
[5] P. R. Somani, Mat. Chem. Phys. 77 (2002) 117
[6] A. A. Argun, Chem. Mat. 16 (2004) 4401
[7] R. J. Mortimer, Displays 27 (2006) 2
[8] A. L. Holt, J. Chem. Phys. 123 (2005) 044704
[9] “Grundlagen der Festkörperphysik (4.Auflage)” by Ch. Weißmantel; C. Hamann, Johann Ambrosius Barth Verlag, Heidelberg · Leipzig, 1995
[10] C. L. Gaupp, Macromol. Rapid Commun. 23 (2002) 885
[11] “Chemie – Das Basiswissen der Chemie in Schwerpunkten” by C. E. Mortimer, Georg Thieme Verlag, Stuttgart, 1973
[12] “Electrochromism – Fundamentals and Applications” by P. M. S. Monk; R. J. Mortimer; D. R. Rosseinsky, VCH, Weinheim, 1995