

## New electrolyte for electrochromic devices

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*The paper presents the results of the research on a new polymer-gel electrolyte for electrochromic devices. In the performed studies, various electrolytes were used. They all contained an ionic conductor, a matrix of polymer gel and organic solvent or mixture of polar organic solvents. The electrolyte which had the best properties contained 8% LiCF<sub>3</sub>SO<sub>3</sub> as an ionic conductor, a matrix consisting of two polymers: 10% PMMA, 6% PEO, and a mixture of the following two polar organic solvents: 38% propylene carbonate and 38% ethylene carbonate. The high conductivity ( $\sigma = 4.8$  mS/cm), which provides easy deposition in layers, gives stability (resistance) in time and high transmittance value of radiation in the visible region makes the electrolyte very useful for electrochromic devices. A seven-layer electrochromic device with this new gel electrolyte was assembled according to the following formula: glass<sub>1</sub>/ITO/WO<sub>3</sub>/electrolyte/BP/ITO/glass<sub>2</sub>, where ITO was an indium-tin film oxide, WO<sub>3</sub> was an electrochemically deposited tungsten oxide film and BP an electrochemically deposited film of prussian blue. The density of the current flowing through the unit and the transmittance at the wavelength  $\lambda = 550$  nm are given in the paper as a function of sinusoidal voltage. The transmittance varies from 70–50% (coloured) to 25–10% (for fully bleached) in the range of visible radiation and the colouration efficiency is high (above 100 cm<sup>2</sup>/C). These results are considerably better than those reported in the other similar studies.*

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**Keywords:** gel-electrolyte, conductivity, lithium salt, based polymer, polar organic solvent, electrochromic devices, colouration efficiency.

### 1. Introduction

One of the most important elements of a multilayer electrochromic device is a layer of an electrolyte having sufficiently high value of the specific electric conductivity (much higher than  $10^{-4}$  S/cm). This layer performs a function of an insulator when the device does not work.

Moreover, the electrolyte must be durable and easily spread on the electrochromic layers, as well as it should be temperature-resistant and must keep its properties within a wide range of temperature (from  $-20^{\circ}\text{C}$  to  $60^{\circ}\text{C}$ ). Many research centres were engaged in this problem solution [1–12].

In general, the solid (gel) electrolyte described in the literature contains, as a basic compound, an ionic conductor (most frequently it is a lithium salt), organic matrix being a purposely designed plastic and organic solvents (anhydrous ones). These solvents must cause ionic dissociation and provide required ionic mobility, in other words they should provide a suitable conductivity.

Recently, the research has been carried out to obtain the highest possible values of conductivity and durability pro-

viding long life of the electrochromic device. At the same time, the basic characteristics must be kept after several thousand of the device's cycles of performance. Su *et al.* [1] applied an ionic conductor composed of lithium perchlorate (LiClO<sub>4</sub>) and a poly(ethylene oxide) (PEO) matrix as solid electrolytes. Propylene carbonate (PC) was applied as a basic solvent. Conductivity vs. temperature dependence for the electrolyte is an Arrhenius type.

The energy of activation  $E_a$  has been determined from the slope of  $\sigma$  vs.  $1/T$  curve dependence. The dependence  $\sigma = \sigma_0 \exp(-E_a/kT)$ , where  $k$  is the Boltzmann constant and  $T$  is the temperature, has been used. The value of the pseudoactivation for the gel electrolyte was 31.7 kJ/mol, whereas the activation energy value for LiClO<sub>4</sub> solution in PC was 13.1 kJ/mol. Conductivity of such an electrolyte reached initially  $4.6 \times 10^{-4}$  S/cm, whereas in 3-days period it was  $3.2 \times 10^{-4}$  S/cm and changed slightly after several days. In another publication by Su *et al.* [2], the results were presented of research on a solid electrolyte with poly(vinyl chloride) (PVC) matrix. This electrolyte contained PVC, PC, EC (ethylene carbonate), and LiClO<sub>4</sub>. The obtained high value of conductivity (approximately 2.0 mS/cm) of the PVC matrix electrolyte testifies to the fact that the matrix choice does not influence considerably the resistance value. Application of the EC-PC mixture as a solvent

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causes high degree of lithium salts dissociation as well as a low viscosity value which supplies high ion mobility.

Application of tetrahydrofuran (THF) as a solvent and change of PVC content resulted in getting of an electrolyte with conductivity of 2.3 mS/cm [3].

Employment of PEO matrix and determination of optimum concentration of LiClO<sub>4</sub> in a solvent mixture (propylene carbonate to ethylene carbonate weight ratio 1:3) resulted in a gel electrolyte composition having specific conductivity of 2.3 mS/cm [9]. Using voltamperometric method with a three-electrode system, the diffusion coefficient has been determined. The obtained value of  $D = 3 \times 10^{-10}$  cm<sup>2</sup>s was comparable with the values obtained using other method characteristics of these types of electrolytes [5].

Another step oriented towards meeting all demands for an electrochromic device consists in applying poly(methyl methacrylate) (PMMA) as a matrix and THF as a solvent supporting the process of its formation.

It is remarkable that conductivity of this electrolyte dropped only 0.14 mS/cm during 3 days, whereas conductivity of a simple LiClO<sub>4</sub> solution (1 mol/dm<sup>3</sup>) in propylene carbonate dropped up to 0.8 mS/cm within the same period of time.

Sekhon *et al.* [7,8] undertook research and discussion on the problem of solvents' role in preparation and further properties of the obtained solid electrolytes. Reference 8 presents the results of research on the electrolyte composed of:

- poly(methyl methacrylate) matrix,
- monocomponent or two-component solvent basing on PC, EC,  $\gamma$ -butyrolactone ( $\gamma$ -BL),
- ionic conductor: lithium trifluoromethanesulfonate (LiCF<sub>3</sub>SO<sub>3</sub>).

The early investigations [9] proved that PMMA does not influence considerably the conductivity of the electrolyte. The polymer presents high transmittance within ultraviolet (UV) wavelength, so there exists a possibility of its application in electrochromic devices. Agnihotry *et al.* [10,11] have obtained a new electrolyte designed for "smart windows" having the conductivity of 3.0 mS/cm composed of LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> (lithium trifluoromethanesulfonimide) or LiCF<sub>3</sub>SO<sub>3</sub> and a solvent mixture containing: PC, EC,  $\gamma$ -BL (unicomponent solvent), PC +  $\gamma$ BL, PC + EC, EC +  $\gamma$ -BL (bicomponent solvent). There has been shown that the lowest conductivity under conditions of the fixed salt concentration has occurred for PC. The sequence of conductivity values was as follows: PC < PC + EC < PC +  $\gamma$ -BL < EC +  $\gamma$ -BL <  $\gamma$ -BL < EC.

The other publications by Sekhon *et al.* [12] presented the results of research on an electrolyte containing polyacrylonitrile (PAN) matrix, electrolyte LiCF<sub>3</sub>SO<sub>3</sub> and the solvents: EC and PC. Different ratios of solvent-lithium salt and application of different kind of matrices were tested. The final choice of electrolyte was as follows: LiCF<sub>3</sub>SO<sub>3</sub> concentration amounted to 1 mole/dm<sup>3</sup>, 20%

mass fraction of PAN, PC + EC = 1 + 3. Conductivity of the electrolyte was approximately 2.0 mS/cm.

The conclusion to be drawn from the literature review [1–12] is that the solid (gel) electrolyte should contain the following components:

- ionic conductor in the form of a lithium salt, e.g. LiClO<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub> or LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>,
- polymer matrix, e.g. PMMA, PVC, PEO, or PAN,
- a suitable solvent or solvent mixture containing PC, EC or  $\gamma$ -BL,
- solvent for preparation of matrix solvent, e.g. acetonitrile (CH<sub>3</sub>CN) or tetrahydrofuran (THF).

The lowest possible conductivity should not be less than 10<sup>-4</sup> S/cm (advisable value of the conductivity is higher than 10<sup>-3</sup> S/cm. A suitable durability, high transmittance within a visible range as well as high adhesiveness are also very important.

## 2. Solid electrolyte preparation

The following chemical compounds have been applied:

- PVC [–CH<sub>2</sub>CH(Cl)–]<sub>n</sub> poly(vinyl chloride) produced by Aldrich,
- PEO [–CH<sub>2</sub>CH<sub>2</sub>O]<sub>n</sub> Mca 600.000 poly(ethylene oxide) produced by Aldrich,
- PC – propylene carbonate produced by Aldrich,
- EC – ethylene carbonate produced by Fluka,
- LiClO<sub>4</sub> – lithium perchlorate produced by POCH in Gliwice,
- CH<sub>3</sub>CN- acetonitrile of chromatographic purity (applied in HPLC) produced by Merck,
- LiCF<sub>3</sub>SO<sub>3</sub> – lithium trifluoromethanesulfonate produced by Merck,
- $\gamma$ -BL –  $\gamma$ -butyrolacton produced by Merck,
- PMMA – poly(methyl methacrylate) produced by Aldrich,
- THF – tetrahydrofuran of chromatographic purity (applied in HPLC) produced by Merck.

Basing on the literature data and general descriptions presented in the attainable publications, there has been prepared a variety of electrolytes composed of different constituents. Specific conductivity, easiness of electrochromic layers' deposition, effectiveness and ratio of gelation, transmittance in visible wavelengths and temperature performance have been estimated.

### 2.1. Preparation of solid electrolyte with PVC matrix

Basing on the literature data, there has been worked out the electrolyte containing: 15% of PVC, 40% of PC, 40% of EC, and 5% of LiClO<sub>4</sub>. THF has been applied as an extra-solvent that allows for forming a homogeneous solvent. PVC was initially dissolved in THF and then the remaining components were introduced into the solution. Application of the above electrolyte was not successful due to difficulties to obtain a homogeneous gel.

Moreover, the plates were not stuck together properly and there appeared matrix separation and inhomogeneity of the electrolyte layer in form of white spots. These destructive phenomena decreased transmittance of the electrochromic device within the visual range and the results were not repeatable.

## 2.2. Electrolyte containing PEO as a gel matrix

Initially, the following electrolyte composition has been prepared: 15% of PEO, 40% of PC, 40% of EC, and 5% of  $\text{LiClO}_4$ . Powdered PEO has been dissolved in acetonitrile whereas  $\text{LiClO}_4$  has been dissolved in PC + EC mixture. When stirred intensively, using a magnetic mixer, the electrolyte showed a low value of specific conductivity (lower than  $10^{-4}$  S/cm) which indicated too small concentration of ionic conductor. Thus, the concentration of lithium salt has been increased up to 10% of  $\text{LiClO}_4$ .

To verify this electrolyte's usability, typical electrochromic structures have been prepared according to the scheme: glass/ITO/ $\text{WO}_x$ /gel electrolyte/BP/ITO/glass, where ITO is the thin layer of conductive indium-tin oxide,  $\text{WO}_x$  is the tungsten oxide layer deposited electrochemically, and BP is the electrochemically deposited layer of Prussian blue. Quality of the gelation process has been estimated in 3–5 days. It turned out that in spite of a high value of conductivity of the electrolyte (approximately 6.4 mS/cm) it could not be applied due to bad gelation of the layer, not reproducible results and low durability of the manufactured device. Specific conductivity measurements have been carried out using CC-551 Elmetron conductometer.

It appeared that increase in ionic conductor concentration brought about increase in conductivity, however, other properties, such as quality of gelation and durability worsened substantially. Application of the solvents: PC and EC was well-grounded with regard to the high values of dielectric constant of these compounds (64.4 for PC at a temperature of 25°C and 89.0 for EC at 40°C). This factor influenced directly dissociation ratio of the ionic conductor, i.e., the conductivity. Nevertheless, it appeared that also the anion produced by the lithium salt influences considerably both conductivity and the final stability of the electrolyte. From this fact it results further investigation and application of compounds different from lithium perchlorate [10–12].

## 2.3. Binary matrix electrolyte (PMMA + PEO)

Basing on the cited articles [10–12],  $\text{LiCF}_3\text{SO}_3$ , PMMA as a matrix and  $\gamma$ -BL as a solvent a new electrolyte has been worked out. The manufacturing procedure was as follows: an appropriate amount of the salt has been dissolved in the mixture of organic solvents: EC, PC,  $\gamma$ -BL, then mixed with the bulk of polymer matrix PMMA and PEO which has been earlier dissolved in THF. After intensive and precise mixing with a magnetic mixer and next heating it up to

40–50°C, simultaneous polymerisation and evaporation of THF occurred. This solvent has been applied only to get a proper colloidal system of the electrolyte. Slow transformation of the solution into the gel took about 3–4 hours.

Application of PMMA as a matrix made it possible to obtain an electrolyte having good gelation and being easy in handling. Measurements of conductivity by CC-551-Eltron conductometer shown that application of PMMA as a matrix considerably reduced the conductivity. This operation has been carried out in the range of 0–30% (by weight) concentration of PMMA in the obtained electrolyte (Fig. 1). Then, it has been noticed that the influence of PMMA on a conductivity value was stronger than it was in the PEO case.

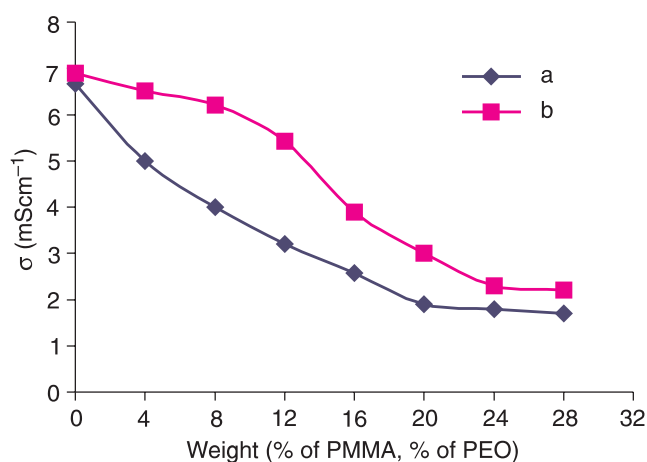


Fig. 1. Conductivity at 25°C as a function of PMMA (a) or PEO (b) added to 8%  $\text{LiCF}_3\text{SO}_3$  electrolytes in EC +  $\gamma$ -BL (1:1).

It was only when a mixture of polymers as an electrolyte matrix was introduced that advantages of matrixes components were fully made of (e.g. lower influence of PEO on the final electrolyte's conductivity and easiness of gelating process, than it was in the PMMA case). It is essential to maintain a proper concentration of ionic conductor, because maximum value of conductivity is obtained for some percentage of the conductor. For  $\text{LiCF}_3\text{SO}_3$  case it amounted to 8% by weight.

Taking into account the above data there has been manufactured and applied electrolytes of the following contents: EI-4 (35% PC, 35% EC, 5%  $\text{LiClO}_4$ , 25% PMMA, 5 cm<sup>3</sup> THF per 10 g of electrolyte,  $\sigma = 1.9$  mS/cm), EI-5 (40% EC, 40% PC, 5%  $\text{LiClO}_4$ , 15% PMMA, THF (3 cm<sup>3</sup> per 10 g of electrolyte,  $\sigma = 2.6$  mS/cm), EI-6 (40% EC, 40% PC, 5%  $\text{LiClO}_4$ , 10% PMMA, 5% PEO, THF (3 cm<sup>3</sup> per 10 g of electrolyte,  $\sigma = 2.9$  mS/cm), EI-7 (38% EC, 38%  $\gamma$ -BL, 8%  $\text{LiCF}_3\text{SO}_3$ , 16% PMMA, THF (3 cm<sup>3</sup> per 10 g of electrolyte),  $\sigma = 3.3$  mS/cm), EI-8 (38% EC, 38% PC, 8%  $\text{LiCF}_3\text{SO}_3$ , 10% PMMA, 6% PEO, THF (3 cm<sup>3</sup> per 10 g of electrolyte),  $\sigma = 4.8$  mS/cm), EI-9 (38% EC, 38%  $\gamma$ -BL, 8%  $\text{LiCF}_3\text{SO}_3$ , 13% PMMA, 3% PEO, THF (3 cm<sup>3</sup> per 10 g of electrolyte,  $\sigma = 4.2$  mS/cm).

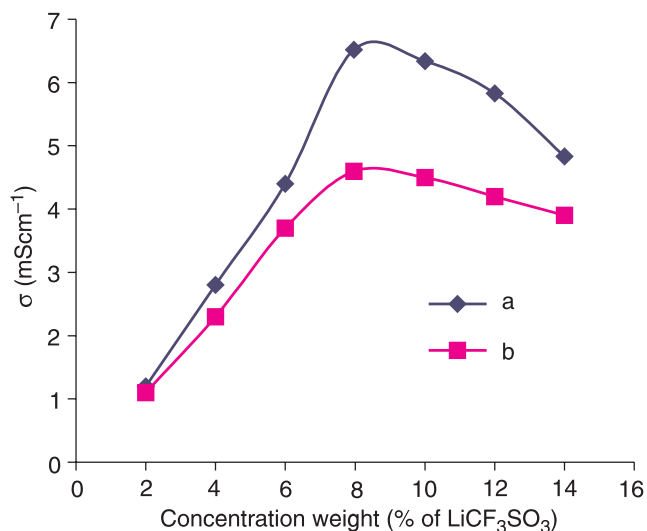


Fig. 2. Conductivity at 25°C as a function of LiCF<sub>3</sub>SO<sub>3</sub> concentration in EC + γ-BL(1:1) (a) and PC + EC (1:1) (b).

### 3. Characteristics of electrochromic device using EI-8 electrolyte

Usefulness of the electrolytes has been estimated applying the results of electrooptical measurements of the worked out electrochromic cell made up of seven layers (Fig. 3), glass<sub>1</sub>/ITO/WO<sub>x</sub>/electrolyte/BP/ITO/glass<sub>2</sub>. A layer of tungsten oxide (WO<sub>x</sub>) has been deposited on a conductive layer of ITO. Another basic element has been a thin conductive layer of Prussian blue (BP) deposited using the electrochemical process. An electrolyte has been placed at the layer of WO<sub>x</sub> using a proper device made of glass. Then, the plate with a BP layer has been pressed to the whole system.

Characteristics of the electrochromic device have been determined making use of the measurements carried out in the system presented in Fig. 4. The measurement stand consists of:

- PM5192, 0.1 Hz – 20 MHz Philips generator,
- UV-Vis-NIR CARY 5E Varian spectrophotometer,

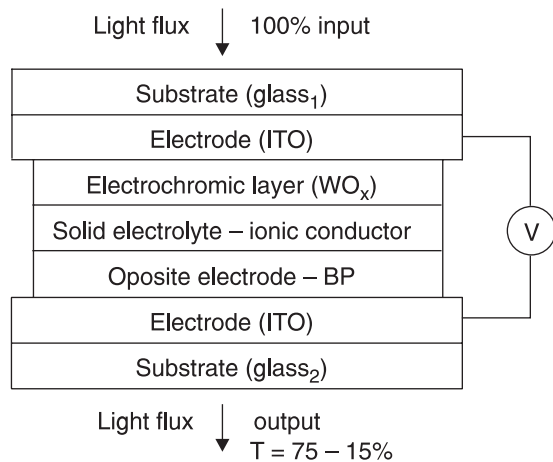


Fig. 3. Scheme of electrochromic device.

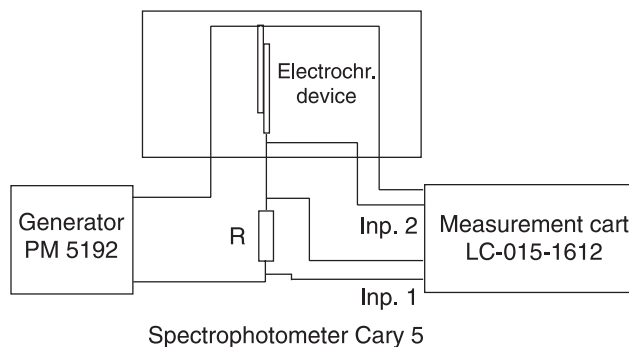


Fig. 4. Scheme of measuring stand used for determining electrochromic device characteristics.

- LC-015-1612 measuring and controlling Ambex modulus equipped with AD678 KN AC transducer and PGA202KP amplifier installed in the form of an extension card in a PC unit with the Windows software,
- measuring resistor  $R = 56 \Omega$ .

Electrochromic device and the measuring resistor connecting in series have been supplied with a programmed alternating voltage. Typical parameters of the input sinusoidal voltage are 1.5–5.0 V for amplitude and 0.01 Hz for frequency.

This voltage is equal to the voltage drops occurring in the electrochromic cell, measuring device and on the output resistance of the generator. The electric current flowing in the closed circuit produced a voltage drop on the resistor  $R$  which in turn was recorded by the measuring card. At the same time, in the second channel of the card there was registered a voltage drop between the two electrodes of the electrochromic cell. Transmittance changes of the device occurring when the charge was flowing were recorded by the spectrophotometer for the wavelength  $\lambda = 550 \text{ nm}$ . The reference transmittance  $T = 100\%$  was fixed for the system of two clean glass base plates put in the reference beam of the spectrophotometer. The current density  $I$  was determined from  $I = U_R/RS$  dependence, where  $U_R(V)$  is the voltage drop on the measuring resistor,  $R = 56 \Omega$ ,  $S = 20 \text{ cm}^2$  (active surface of the electrochromic device). Basing on the measurements, the  $I = f(V)$  and  $T = f(V)$  characteristics were determined, where  $U(V)$  is the voltage drop between the electrodes of the electrochromic cell,  $T$  is the transmittance of the cell for the wavelength  $\lambda = 550 \text{ nm}$ .

Characteristics of increase in the absorbance value  $\Delta A = f(q)$ , where  $q = Q/S$  is the density of the charge  $Q$  flowing between the electrodes of electrochromic cell having the active surface  $S$ , has been determined basing on the previously performed measurements. The value  $Q$  has been calculated by numerical integration of time dependence of the current in the circuit.

The characteristics  $T = f(\lambda)$  has been found basing on the measurements performed with a spectrophotometer operating in the wavelength range 300–1500 nm. The measurements have been made applying the basic line of the



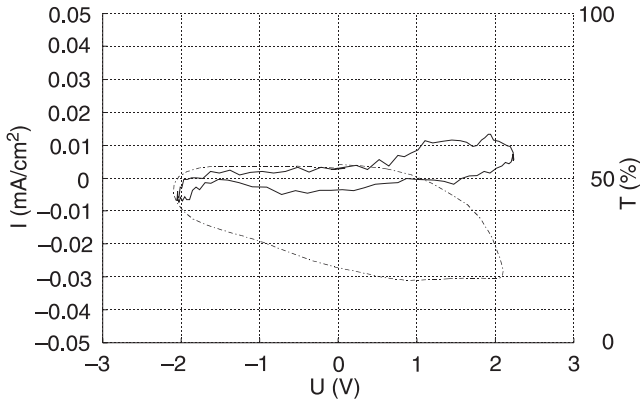


Fig. 5. Current density-potential graphs (broken line) and transmittance-potential ( $\lambda = 550$  nm) graphs (solid line) of the system: glass<sub>1</sub>/ITO/WO<sub>3</sub>/gel electrolyte/BP/ITO/glass<sub>2</sub>. Scan rate  $f = 0.01$  Hz with sinusoidal voltage.

spectrophotometer for the air range of 300–1500 nm. Scanning speed was 2000 nm/min. Light or blackened plates working under the employed constant voltage supplied by a generator were measured (in the absence of the measuring resistor  $R$ ). Time of recording of transmittance change averaged 30–60 s.

The properties of such a device have been presented in Figs. 5, 6, and 7. Considerable changes of transmittance for the dark and illuminated regimes (the difference reaches 60%, Fig. 7) and high optimal efficiency defined as an area of the electrochromic element changing its absorbance (optimal density) when it is supplied an unitary charge of 1 C, lead to the conclusion that the new electrolyte (38% EC, 38%  $\gamma$ -BL, 8%LiCF<sub>3</sub>SO<sub>3</sub>, 10% PMMA, 6% PEO shows very good properties: high conductivity ( $\sigma = 4.8$  mS/cm), high transmittance value of radiation in visible region, easy gelation, durability, good thickness, easiness with depositing and joining the layers. The electrochromic device with this new gel electrolyte possesses very advantageous parameters. The transmit-

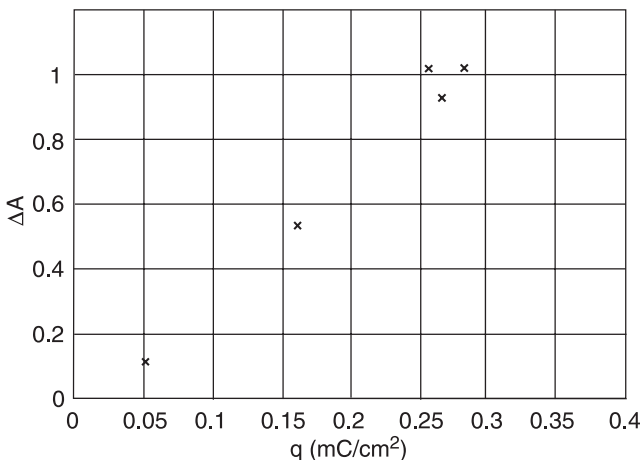


Fig. 6. The optical density ( $\Delta A$ ) change of the electrochromic device (system: glass<sub>1</sub>/ITO/WO<sub>3</sub>/gel electrolyte/BP/ITO/glass<sub>2</sub>) at 550 nm vs. the amount of charge injected ( $\text{mC}/\text{cm}^2$ ).

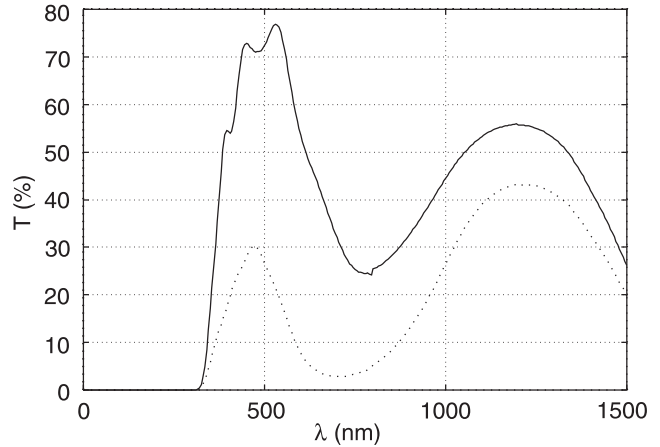


Fig. 7. Transmittance spectrum of electrochromic device (system: glass<sub>1</sub>/ITO/WO<sub>x</sub>/gel electrolyte/BP/ITO/glass<sub>2</sub>). Solid line-bleached, broken line-coloured, reference transmittance 100% for glass plates only.

tance varies from 70–50% (coloured) to 25–10% (for fully bleached) in the range of visible radiation and the colouration efficiency is high (above 100  $\text{cm}^2/\text{C}$ ). These results are considerably better than those reported in the other similar studies.

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