Transmission properties for individual electrochromic layers in solid state devices based on polyaniline, Prussian Blue and tungsten oxide

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In order to investigate the transmission properties in the whole solar spectrum for individual electrochromic layers in solid state devices incorporating polyaniline (PANI), Prussian Blue (PB) and tungsten oxide (WO_3), the devices were fabricated with and without holes in the electrochromic coatings in several combinations. Both PANI and WO_3 were deposited electrochemically on indium–tin oxide (ITO) glass substrates, while PB was deposited on top of the PANI coatings or directly on the ITO glass plates. Solid state devices were made by gluing the glass plates together with the solid polymer electrolyte poly(2-acrylamido-2-methyl-propane-sulphonic acid) (PAMPS), and thus, with and without holes in the three electrochromic coatings in different combinations, enabling us to study the optical properties of PANI, PB and WO_3 separately, that is, the 'hole' method. This method gives good qualitative, and to a certain degree quantitative, information, which may be of valuable help in designing electrochromic devices with specific tailor-made optical properties.

Keywords: transmission properties, individual electrochromic layers, solid state devices, polyaniline, Prussian Blue, tungsten oxide

1. Introduction

Dynamic sun radiation control in windows may be achieved by use of electrochromic windows, so-called '*smart windows*' [1–3], which change colour with applied voltage. In addition to the colour change, which can be observed with the eye (400–700 nm), electrochromic windows may also have regulable transmission properties in other parts of the electromagnetic spectrum, for example, in the near infrared region (700–3000 nm), where almost half of the solar energy lies [2–7]. Extensive overviews of electrochromic materials may be found in Granqvist [8] and Monk *et al*. [9]. As the development of electrochromic materials proceeds, commercial applications may start with car mirrors, thereafter sun roofs in cars, and finally, windows in buildings. In other words, there would be a continual increase in the available active electrochromic area. In addition to the energy regulation, visible colour changes may be exploited architecturally, i.e. so called '*fancy windows*' [10].

The objective of this work is to present a method for studying the optical properties in the whole solar spectrum for each individual electrochromic layer in complete solid state devices, hereafter referred to as the 'hole' method. This method was first applied on devices based on PANI and WO_3 [11], and later PB was introduced as a third electrochromic coating [10, 12], making it of vital interest to obtain information about the contribution of solar radiation

modulation from each of the three different electrochromic layers in the solid state device. Such information may be of value in designing electrochromic devices with specific tailor-made optical properties. Furthermore, the hole method is believed to be applicable for several different electrochromic materials and devices, that is, not only restricted to those presented here.

The transmission properties of each of these electrochromic materials cannot be studied in aqueous electrolytes for the whole solar spectrum due to water absorbing heavily in the near infrared region. The transmission spectra for the electrochromic materials immersed in a liquid electrolyte may also be different from the spectra obtained in a solid state device.

2. Experimental details

For all device configurations polyaniline films were deposited electrochemically at a constant current of 0.015 mA cm^{-2} for 2000 s on ITO glass plates ($90 \ \Omega \ \square^{-1}$) from aqueous solutions of aniline in sulphuric acid (0.02 M aniline and 0.5 M H_2SO_4).

All the Prussian Blue films were thereafter deposited onto the PANI coatings by applying a constant current of $-0.0031 \text{ mA cm}^{-2}$ for 1500 s in an electrolyte consisting of 0.5 M $KHSO_4$, 0.001 M $K_3[Fe(CN)_6]$ and 0.001 M $Fe_2(SO_4)_3$. In addition, one PB film was deposited directly onto the ITO glass for comparison reasons ($-0.0031 \text{ mA cm}^{-2}$ for 1500 s).

The electrolyte for the tungsten oxide formation was prepared by dissolving 4.52 g of tungsten in 60 ml 30% hydrogen peroxide, and diluting with distilled water to a total volume of 500 ml, thus giving a tungsten concentration of 0.049 M. All the WO_3 films were formed on ITO glass plates by applying a constant potential of -700 mV vs Ag/AgCl (3.0 M KCl) for 300 s. Before further use, the WO_3 films were heated at 140 °C for 1 h.

Platinum was used as a counter electrode for the electrodepositions of PANI, PB and WO_3 layers, while Ag/AgCl (3.0 M KCl) was applied as a reference electrode.

The electrochromic electrodes (PANI and WO_3, PANI|PB and WO_3) for all device configurations were glued together with the solid polymer electrolyte poly(2-acrylamido-2-methyl-propane-sulphonic acid) (PAMPS) after a procedure described earlier [13], and sealed with epoxy resin. The electrochromic device area was 1.0 cm × 3.1 cm = 3.1 cm^2. The PANI, PB and WO_3 films were each less than 1 μm thick, while the PAMPS layer was about 0.1 mm. A schematic drawing of the device configurations with and without PB is shown in Fig. 1 (holes are not depicted), with electrode reactions as described elsewhere [10].

Ten different electrochromic devices were fabricated, with and without holes, abbreviated D1 to D10, and one reference device consisting of two ITO glass plates glued together with PAMPS, as listed in Table 1. Holes in the electrochromic coatings were made using an adhesive mask with diameter 0.8 cm during the film deposition. The joining of two ITO glass plates, with a hole through one of the electrochromic coatings, also depicting the electrical connections, is shown in Fig. 2. In referring to the different devices, all the materials listed under sandwich configuration were incorporated in the actual device. However, the bracketed materials were not present at the hole location (Fig. 2) of the device, for example, Glass|ITO|PANI|PB|PAMPS|(WO$_3$)|ITO| Glass has a hole in the WO_3 coating, where the transmission spectra are measured.

All transmission spectra were measured at the same position in the middle of the window. Due to nonuniform current distribution during film deposition, the electrochromic layer thickness varies somewhat from top to bottom of the ITO glass plate. This inhomogenity problem, especially seen for the WO_3 coatings where interference patterns (Newton rings) are observed, becomes more pronounced for large film surfaces. The variation in electrochromic layer thickness over the film surface makes it difficult to study holes in the PANI, PB and WO_3 layers on the same device sample. Consequently, several individual devices (Table 1) had to be studied.

An AutoLab PGSTAT20 potentiostat/galvanostat was used in the electrochemical deposition of PANI, PB and WO_3 films. The transmission experiments were carried out with a Cary 5 UV–VIS–NIR spectrophotometer in the 290–3300 nm wavelength region. Before recording the transmission spectra a constant potential was applied for several minutes (sometimes hours) with a Gerhard Bank Elektronik Göttingen potentiostat MP81 in order to stabilize the colour changing films. Long stabilization times were especially necessary for the devices with no electrochromic coating on the counter electrode in the hole area, i.e. PANI|PB||(WO$_3$), PANI|(PB)||(WO$_3$), (PANI)|PB||(WO$_3$), (PANI)|(PB)||WO$_3$, PANI|| (WO$_3$) and (PANI)||WO$_3$. The potential was also applied during the wavelength scan. Applying a positive potential to the PANI or the PANI|PB electrode, both PANI, PB and WO_3 turned to a blue colour, while the window was bleached (made almost transparent) by reversing the polarity of the electrodes.

3. Results and discussion

Cyclic voltammograms (5 mV s^{-1}) in the potential region -1800 to $+1200$ mV of electrochromic windows of the same type as the devices treated here have shown that only a low voltage (<2 V) and small current densities (<40 μA cm^{-2}) are needed to drive the electrochemical processes resulting in a sufficient colour change [10]. Integrating the positive and the negative current for one scan in the voltammograms, the charge passed through the windows (both with and without PB) is calculated to about 3 mC cm^{-2} for both the colouring and the bleaching process, respectively. This corresponds to an energy consumption of about 0.01 Wh m^{-2} for one whole cycle [10].
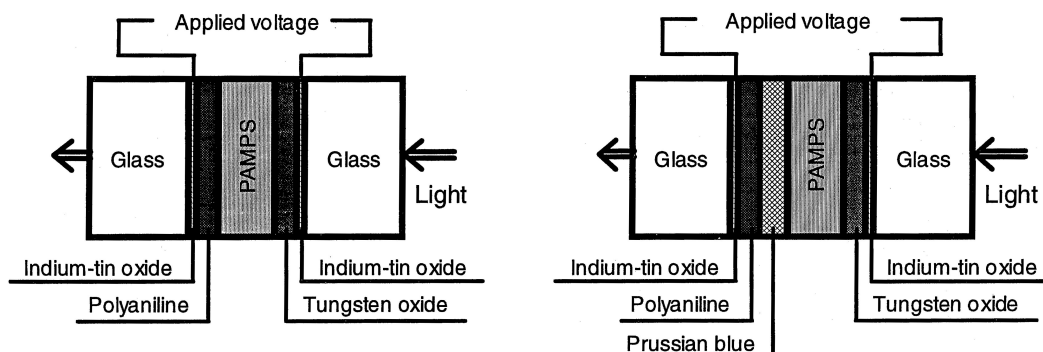

Fig. 1. Schematic drawing of the device configurations with and without PB, indicating the different materials and layers used (holes are not depicted).

Table 1. Different electrochromic device configurations fabricated and the reference device

All materials listed on sandwich form are incorporated in the actual device. However, only materials without brackets around are present at the hole location (Fig. 2) of the device, where the transmission spectra are measured, e.g. Glass|ITO|PANI|PB|PAMPS|(WO₃)|ITO|Glass has a hole in the WO_3 coating

Device	Sandwich configuration	Abbreviation
D1	Glass|ITO|PANI|PAMPS|WO₃|ITO|Glass	PANI||WO₃
D2	Glass|ITO|PANI|PB|PAMPS|WO₃|ITO|Glass	PANI|PB||WO₃
D3	Glass|ITO|PANI|PB|PAMPS|(WO₃)|ITO|Glass	PANI|PB||(WO₃)
D4	Glass|ITO|PANI|(PB)|PAMPS|WO₃|ITO|Glass	PANI|(PB)||WO₃
D5	Glass|ITO|(PANI)|PB|PAMPS|WO₃|ITO|Glass	(PANI)|PB||WO₃
D6	Glass|ITO|PANI|(PB)|PAMPS|(WO₃)|ITO|Glass	PANI|(PB)||(WO₃)
D7	Glass|ITO|(PANI)|PB|PAMPS|(WO₃)|ITO|Glass	(PANI)|PB||(WO₃)
D8	Glass|ITO|(PANI)|(PB)|PAMPS|WO₃|ITO|Glass	(PANI)|(PB)||WO₃
D9	Glass|ITO|PANI|PAMPS|(WO₃)|ITO|Glass	PANI||(WO₃)
D10	Glass|ITO|(PANI)|PAMPS|WO₃|ITO|Glass	(PANI)||WO₃
REF	Glass|ITO|PAMPS|ITO|Glass	||

Combining the spectral distribution of the sunlight, that is, the solar spectral irradiance [14], with observed transmission spectra for the electrochromic windows, the solar transmission, T_{sol}, may be calculated as

$$T_{sol}(V) = \int \Phi(\lambda) T(\lambda, V) d\lambda \bigg/ \int \Phi(\lambda) d\lambda \qquad (1)$$

where Φ denotes the solar spectral irradiance and T the transmission in the window dependent upon both the wavelength, λ, and the applied potential, V. Earlier we found that electrochromic windows based on PANI and WO_3 are typically able to regulate 39% of the total solar energy, while windows with the additional incorporation of PB manage to regulate as much as 50% of the solar radiation [10]. Both the colouring and the bleaching process take about half a minute for complete colouring and bleaching, except the colouring process for the windows including PB, which takes a somewhat longer time (∼2 min.).

The measured transmission spectra in the 290–3300 nm wavelength region for all the electrochromic devices (D1–D10) are given in Fig. 3. The applied potentials are listed from top to bottom in the figures, corresponding to a decreasing order of the transmission spectra, if not otherwise indicated.

(D1) PANI||WO₃ and (D2) PANI|PB||WO₃

D1 in Fig. 3 shows the transmission spectra for Glass|ITO|PANI|PAMPS|WO₃|ITO|Glass, abbreviated PANI||WO₃, that is, through a complete electrochromic device based on PANI and WO_3 without any hole, while D2 gives the transmission in PANI|PB||WO₃ (i.e. including a PB layer). It is observed that it is particularly in the visible and at the beginning of the near infrared region that PANI|PB||WO₃ blocks off considerably more light than PANI||WO₃ at high positive potentials, while still regaining approximately the same transparency during bleaching of the device. That is, in otherwise identical electrochromic devices based on PANI and WO_3, the incorporation of PB enhances the transmission modulation.
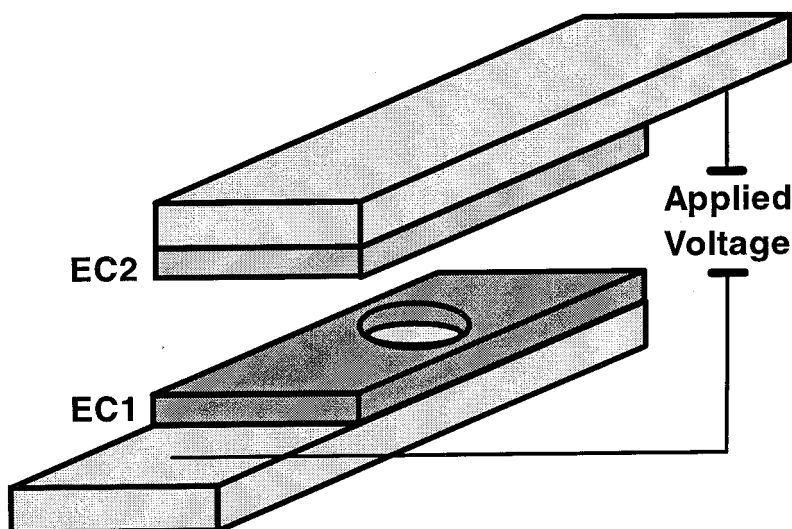

Fig. 2. Schematic drawing of the joining of two ITO glass plates, with a hole through one of the electrochromic coatings (in the middle of the device), also depicting the electrical connections. The PAMPS layer between the two electrochromic coatings is not shown for simplicity reasons. (EC1 = electrochromic coating 1, EC2 = electrochromic coating 2.)
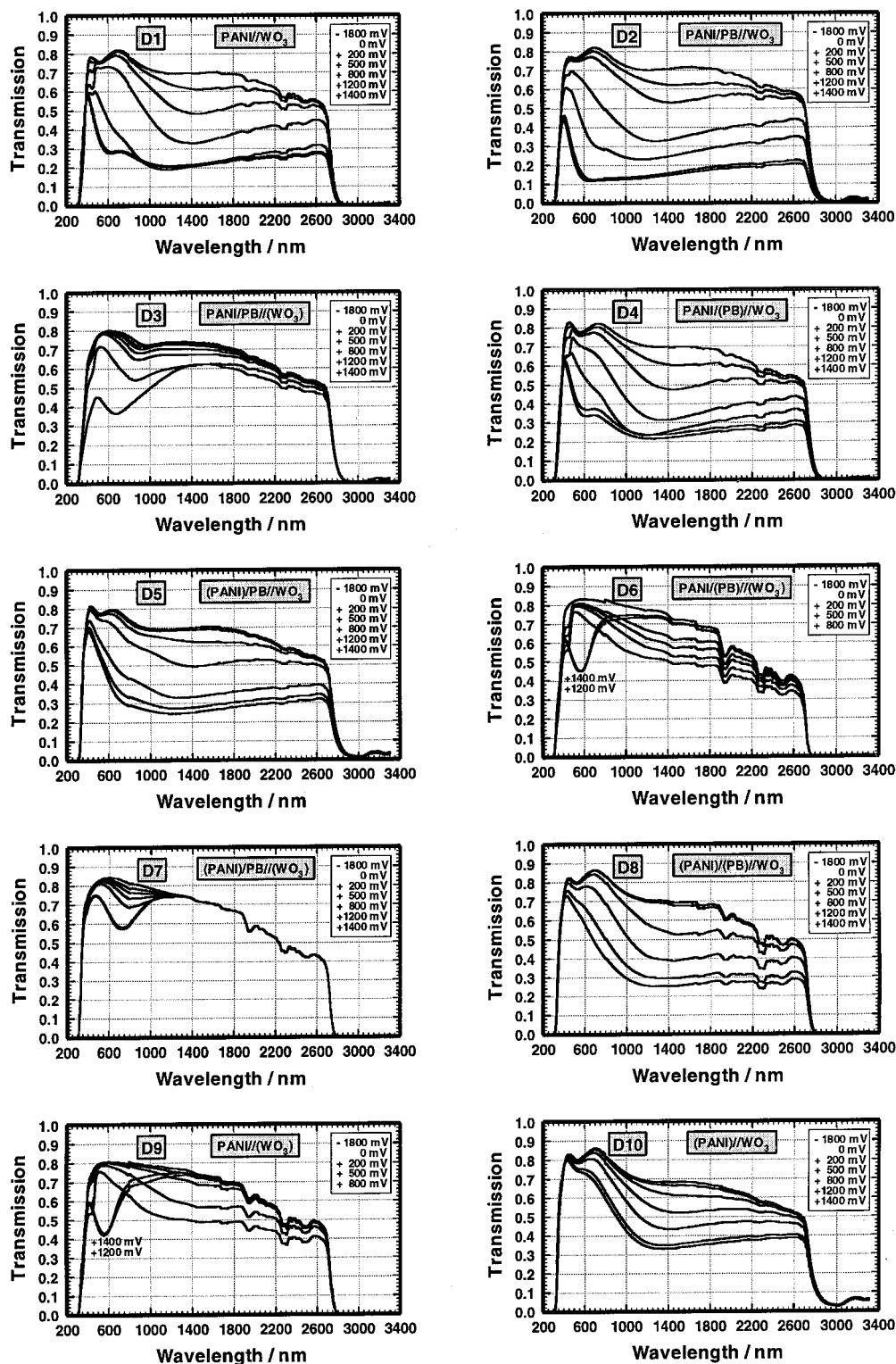
Fig. 3. Transmission against wavelength for ten electrochromic devices (D1–D10), with and without holes, at different applied potentials. Applied potentials are listed from top to bottom (insets) corresponding to a decreasing order of the transmission spectra, if not otherwise indicated.

(D3) PANI|PB||(WO₃)

D3 gives the transmission through PANI|PB||(WO₃), that is, for an electrochromic device based on PANI, PB and WO₃ with a hole in the WO₃ coating where the transmission spectra are measured. As seen from D3, PANI|PB mainly regulates the transmission in the end of the ultraviolet (UV), entire visible (VIS) and start of the near infrared (NIR) region with a

growing absorption peak shifting from about 1000 nm to 670 nm with increasing positive potentials. In the far NIR region there is only a minor transmission regulation.

(D4) PANI|(PB)||WO₃

D4 shows the transmission through PANI|(PB)||WO₃, that is, through PANI and WO₃ (plus

glass and PAMPS) and with a hole in the PB coating where the transmission spectra are measured. As can be seen from Fig. 3, D1 and D4 have similar transmission spectra at all applied potentials, which is natural, since they both depict the transmission through PANI and WO_3.

(D5) $(PANI)|PB||WO_3$
The transmission through $(PANI)|PB||WO_3$ is shown in D5, depicting a broad transmission regulation in the whole NIR region, in addition to a growing regulation for higher wavelengths in the VIS region.

(D6) $PANI|(PB)||(WO_3)$
D6 depicts the transmission through $PANI|(PB)||(WO_3)$, where the largest transmission modulation is found in the middle of the NIR, with smaller regulations in the VIS and far NIR region, for potentials up to $+800$ mV. For higher potentials (e.g. $+1400$ mV) the transmission spectrum for PANI regain the -1800 mV level in the NIR region, while an absorption peak is growing up in the middle of the VIS region, located around 560 nm. The characteristic shoulder at 420 nm for PANI is also seen [15].

(D7) $(PANI)|PB||(WO_3)$
D7 gives the transmission through $(PANI)|PB||(WO_3)$, where it is seen that PB has no transmission regulation at all in the NIR region from about 1300 nm and above. The only transmission modulation for PB lies in the VIS and the start of the NIR region, with an absorption peak located around 720 nm at $+1400$ mV. It is also important to note that the *PB film deposited directly on the ITO glass* (hole in PANI coating) in this *solid state device* has been changed reversibly back and forth several times between transparent and light blue. In a liquid device the PB coating falls off the electrode after only one cycle; see our earlier results [10, 12] for the symbiotic relationship between PANI and PB.

(D8) $(PANI)|(PB)||WO_3$
The transmission through D8, that is, $(PANI)|(PB)||WO_3$, shows that WO_3 regulates fairly well in the whole NIR region. In the VIS region the transmission regulation for WO_3 is largest at the longest wavelengths.

(D9) $PANI||(WO_3)$
D9 shows the transmission through $PANI||(WO_3)$, which is fairly identical to the transmission modulation in D6, as both D6 and D9 depict the transmission in identical PANI coatings.

(D10) $(PANI)||WO_3$
D10 gives the transmission through $(PANI)||WO_3$, and shows mainly the same characteristics as D8, as both D8 and D10 depict the transmission in identical WO_3 coatings. However, D8 attains lower transmission values than D10 at high positive potentials,

which represents the largest discrepancy in all measurements presented here.

It may be noted that for all the devices except D3, the difference between spectra at $+1200$ mV and $+1400$ mV for each device is not so large, indicating that the lower voltage may be used, thereby diminishing the risk of degradation of the devices (e.g. [12]). The larger difference in D3 may be explained by the fact that in this device the charge transport is more obstructed as *two* electrochromic layers on one electrode (PANI and PB) have *no* electrochromic coating on the opposite electrode (WO_3 hole).

The total solar energy regulation is 41% for the device based on PANI and WO_3 (D1), while the inclusion of PB (D2) yields a total solar energy modulation of 53% (applying Equation 1). For D1 the light modulation in the 290–700 nm wavelength region is 34% of what is theoretically possible in this region, whereas 48% of the light in the NIR region can be modulated. Corresponding values for D2 are 47% (290–700 nm) and 58% (NIR) regulation of what is theoretically possible, respectively.

As seen from Fig. 3, PANI regulates the transmission in the whole visible (VIS) and near infrared (NIR) region, with a characteristic shift in modulation from the NIR to the VIS region by applying high positive potentials. PB regulates the transmission only in the VIS and the start of the NIR region (400–1300 nm). WO_3 is able to modulate the transmission in the whole VIS and NIR region, where the regulation in the VIS region is largest at the highest wavelengths. This information may now be utilized in designing electrochromic devices based on PANI, PB and WO_3 with specific tailor-made transmission properties.

The transmission spectra of Glass|ITO and Glass|ITO|PAMPS|ITO|Glass are given in Fig. 4(a), showing quite good transparency properties for the polymer electrolyte PAMPS. The sharp transmission cutoffs located around 400 and 2700 nm are due to the large absorption in the Glass|ITO|PAMPS|ITO|Glass system, into the ultraviolet and infrared region, respectively.

Figure 4(b) shows the transmission spectrum of PB deposited on the whole surface of the ITO glass plate (PB1) and PB deposited on the ITO glass in a PANI hole (PB2). The two spectra are almost identical, with a minor deviation between 650–800 nm. As the two spectra are nearly identical, it can be concluded that the hole method is feasible in this respect.

By combining the transmission spectra of electrochromic devices with holes in Fig. 3 and the transmission spectra of Glass|ITO|PAMPS|ITO|Glass in Fig. 4(a), the spectra of the complete devices D1 and D2 (without holes) can be *calculated*, which ideally should correspond to the measured spectra of D1 and D2 given in Fig. 3.

A few examples of these calculated combination spectra are presented in Fig. 5 (for example, D6D7D8 should correspond to D2 $(PANI|PB||WO_3)$
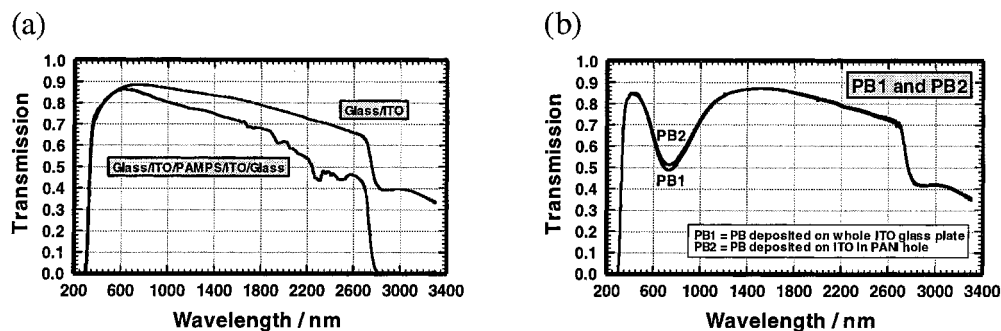
(a)

(b)

Fig. 4. Transmission against wavelength in (a) Glass|ITO and Glass|ITO|PAMPS|ITO|Glass and (b) PB deposited on the whole surface of the ITO glass plate (PB1) and PB deposited on the ITO glass in a PANI hole (PB2).

as this represent the summation of D6 (PANI), D7 (PB) and D8 (WO$_3$)) and show generally qualitative good agreement with the observed spectra (Fig. 3). This also demonstrates that the spectral characteristics from the different electrochromic materials in a device can be studied individually as a function of applied potential by the hole method. Generally, it is noticed that the calculated spectra (e.g. Fig. 5) give a lower transmission modulation (i.e. the difference between the highest and lowest transmission) than the observed spectra. The calculated transmission spectra at −1800 mV and +1400 mV lies lower and higher, respectively, than the observed spectra. This is probably due to a more obstructed charge transport and higher voltage drop in the hole area. In addition, the electrochromic coating properties will be influenced by the other electrochromic layers, for example, PANI and PB will affect each other.

Conditions not directly related to the hole method itself, such as uneven film depositions and difficulties in determining stabilization times, may cause variations in the results presented. It should be noted that the typical small difference between transmission spectra at +1200 mV and +1400 mV as observed

here, may indicate that the stabilization times are satisfactory.

In addition, before more refined experiments are undertaken, conditions directly related to the hole method, such as obstructed charge transport and higher voltage drop in the hole area, should be studied in order to obtain quantitatively more exact results. Moreover, the different electrochromic materials in a complete device are affecting each other, and hence, the transmission properties of for example PANI and PB as single electrodes added together may differ from the properties of the PANI|PB combination electrode. However, the good agreement between the results obtained here, demonstrates that the relatively simple hole method enable us to study the optical properties of PANI, PB and WO$_3$ separately, which may be of valuable help in designing electrochromic devices with specific optical properties.

4. Conclusions

The hole method, described in this text, has enabled us to study the optical properties of polyaniline (PANI), Prussian Blue (PB) and tungsten oxide
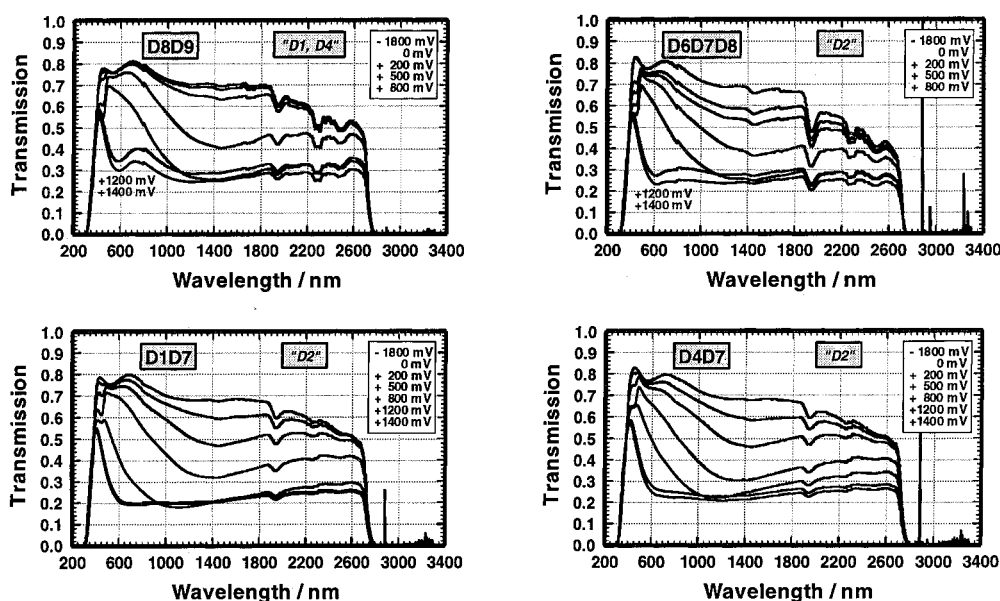

Fig. 5. Transmission against wavelength in calculated electrochromic devices at different applied potentials (from Fig. 3 and Fig. 4). The spectra of D1 (or D4) may, for example, be calculated from D8 and D9 (D8D9), while the spectra of D2 may, for example, be calculated by D6D7D8, D1D7 or D4D7.

(WO_3) individually, and gives good qualitative, and to a certain degree quantitative, information. It has been shown that PANI regulates the transmission in the whole visible (VIS) and near infrared (NIR) region, with a characteristic shift in modulation from the NIR to the VIS region by applying high positive potentials. PB regulates the transmission only in the VIS and the start of the NIR region (400–1300 nm). WO_3 is able to modulate the transmission in the whole VIS and NIR region, where the regulation in the VIS region is largest at the longest wavelengths. Furthermore, the hole method is also believed to be applicable for other electrochromic materials and devices, and may be valuable in designing electrochromic devices with specific optical properties.

Acknowledgements

References

[1] J. S. E. M. Svensson and C. G. Granqvist, *Appl. Phys. Lett.* **45** (1984) 828.

[2] J. S. E. M. Svensson and C. G. Granqvist, in 'Optical materials technology for energy efficiency and solar energy conversion III' (edited by C. M. Lampert), The Society of Photo-Optical Instrumentation Engineers, Bellingham, Washington *Proc. SPIE – Int. Soc. Opt. Eng.* **502** (1984) 30–7.

[3] J. S. E. M. Svensson and C. G. Granqvist, *Sol. Energy Mater.* **12** (1985) 391.

[4] C. G. Granqvist, *The Physics Teacher*, **22** (Sept. 1984) pp. 372–83.

[5] C. G. Granqvist, in 'Window Industries' (edited by P. de Lacey), Turret-Wheatland (Aug. 1987) pp. 22–4.

[6] C. G. Granqvist, in 'Electricity. Efficient End-use and New Generation Technologies, and their Planning Implications' (edited by T. B. Johansson, B. Bodlund and R. H. Williams), Lund University Press (1989), pp. 89–123.

[7] C. G. Granqvist, in 'Material Science for Solar Energy Conversion Systems', (edited by C. G. Granqvist), Pergamon Press (1991), pp. 106–67.

[8] C. G. Granqvist, 'Handbook of Inorganic Electrochromic Materials', Elsevier (1995).

[9] P. M. S. Monk, R. J. Mortimer and D. R. Rosseinsky, 'Electrochromism: Fundamentals and Applications', VCH (1995).

[10] B. P. Jelle and G. Hagen, *J. Electrochem. Soc.* **140** (1993) 3560.

[11] B. P. Jelle, G. Hagen, S. Sunde and R. Ødegård, *Synth. Met.* **54** (1993) 315.

[12] B. P. Jelle, G. Hagen and S. Nødland, *Electrochim. Acta* **38** (1993) 1497.

[13] B. P. Jelle, G. Hagen and R. Ødegård, *ibid.* **37** (1992) 1377.

[14] 'CRC Handbook of Chemistry and Physics' (edited by R. C. Weast, D. R. Lide, M. J. Astle and W. H. Beyer) 70th edn, CRC Press, Boca Raton, FL (1989–1990), p. F-167.

[15] Y. H. Kim, C. Foster, J. Chiang and A. J. Heeger, *Synth. Met.* **29** (1989) E285.