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Electrochromic characteristics of a complementary tungsten trioxide/Prussian blue cell

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Optically switchable electrochromic materials are of importance in the automobile industry for the control of solar heat load, glare reduction, and privacy applications. A complementary electrochromic cell consisting of a cathodically colouring tungsten trioxide (WO_3) film, an anodically colouring Prussian blue (PB) film, and a Li^+ conducting polymer electrolyte was made. Cycling characteristics and colouration efficiency of the cell at various stages of cycling were evaluated. It was shown that the complementary cell requires less energy for operation compared to cells with a single film. The WO_3/PB was cycled up to 1300 times. A gradual decrease in the contrast between the coloured and the bleached states upon cycling was observed during the first 400 cycles. The colouration efficiency of $102\,cm^2\,C^{-1}$ at the first cycle decreased to $67\,cm^2\,C^{-1}$ after 387 cycles. The cause of degradation is attributed to the lack of K^+ ions available to PB film.

1. Introduction

Electrochromic materials have significant potential for architectural, automotive, and many other applications. Modern trends in automobile styling and aerodynamic requirements lead to increased glass areas for vehicles. The increased solar loading from increased glazing raises interior temperature and increases the load on the air conditioning system. Thus, the need for the control of solar transmission through glass is greatly enhanced. Recent advances in optical switching technology have stimulated research and development of electrochromic materials for 'smart windows', the name usually adopted for multilayer window glazings that act as variable transmittance or reflectance device [1, 2]. The colour change of electrochromic materials can be best demonstrated by making thin films of these materials on transparent conductive surfaces. An electrochromic electrode would be capable of variable light transmission by electrochemical oxidation or reduction. When the polarity of the applied potential is reversed, the direction of the change in optical density is also reversed. Thus, an electrochromic panel may function as a shutter with variable transmission that can be electrically controlled.

Tungsten trioxide, WO_3, is the most widely studied electrochromic material [1–3]. It is essentially colourless, but when hydrogen or alkali metal ions are inserted into the interstitial sites of this oxide, this material absorbs light and turns blue. Research work in the late 1960s and early 1970s showed that the reduction of WO_3 involves the formation of a tungsten bronze as a result of ion insertion [3],

$$WO_3 + xM^+ + xe^- \rightleftharpoons M_xWO_3 \qquad (1)$$

where $M^+ = H^+$, Li^+, K^+, or Na^+. This mechanism, Equation 1, is well established today.

Another well-studied electrochromic material is Prussian Blue (PB) which becomes blue upon oxidation. The electrochromic transition of PB, from blue in the oxidized state to transparent in the reduced state, occurs reversibly [4]. Two types of PB have been identified: 'soluble' PB, $KFeFe(CN)_6$ and 'insoluble' PB $Fe_4[Fe(CN)_6]_3$, both of which generally contain an indeterminate amount of water in the interstices of their nominally cubic lattice structures. (The terms 'soluble' and 'insoluble' reflect the relative ease of peptization rather than the actual solubility). Both forms of PB can be reversibly reduced by an injection of electrons accompanied by the intercalation of alkali metal ions, M^+, to yield the transparent Everitt's salt (ES). This electrochromic reaction for the soluble form of PB is given by,

$$\underset{\text{(Prussian Blue)}}{MFeFe(CN)_6} + M^+ + e^- \rightleftharpoons \underset{\text{(Everitt's salt)}}{M_2FeFe(CN)_6} \qquad (2)$$

When M^+ is a potassium ion, PB can be repeatedly reduced to Everitt's salt and reoxidized to PB. PB can also be oxidized forming Prussian Yellow (PY),

$$KFeFe(CN)_6 \rightleftharpoons \underset{\text{(Prussian Yellow)}}{FeFe(CN)_6} + K^+ + e^- \qquad (3)$$

The electrochemical potential of Reaction 3 is close to the decomposition potential of PY and to the potential required for oxygen evolution [4] in aqueous media. It is to be noted that Reaction 2 is more reversible than Reaction 3.

Since WO_3 is a cathodically colouring material and PB is an anodically colouring one, these materials can be used together in a single device so that their elec-

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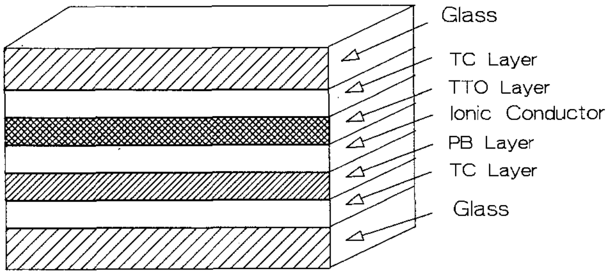

Fig. 1. Schematic representation of a complenentary WO_3/polymer electrolyte/PB electrochromic cell. TC: transparent conductor; PB = Prussian Blue; TTO: tungsten trioxide.

trochromic reactions are complementary to one another. The construction of such a device is shown in Fig. 1; thin films of these materials deposited on transparent electronic conductors are separated by a layer of a transparent ionic conductor. The films can be coloured simultaneously when a small voltage is applied between them such that the WO_3 electrode is the cathode and the PB electrode is the anode. Conversely, the coloured films can be bleached to transparency when the polarity is reversed. The advantage of such complementary electrochromic cells over more conventional single film cells is that less electrical charge is required to achieve comparable colouration.

Kase *et al.* [5] reported a complementary electrochromic device with WO_3 and PB. This device was used in an optically switchable sunroof of a prototype Nissan car (CUE-X) shown at the 26th International Auto Show in Tokyo in 1986. The electrolyte used was a liquid consisting of $LiClO_4$ in propylene carbonate with 1–2% H_2O. A similar electrochromic device has also been reported by Kawai and coworkers [6]. However, from a thermodynamic point of view, the electrolyte used in these devices is susceptible to becoming Li^+ deficient due to the formation of Li_2O or LiCl or Li_2CO_3 [7]. Such deficiency results in the eventual degradation of electrochromic performance of these devices.

More recently, solid-state complementary electrochromic cells with WO_3 and PB have been reported [8, 9] which also show a reasonable electrochromic response. Long cycle life of these cells was not reported. We report here the results on the cycle life and optical performance of a WO_3–PB complementary electrochromic cell with a Li^+ doped polymer electrolyte, oxymethylene polyoxyethylene.

2. Experimental details

2.1. *Electrolyte preparation*

Oxymethylene polyoxyethylene polymer was prepared from dichloromethane, CH_2Cl_2 (99.9%, Aldrich Chemicals, Milwaukee, Wisconsin), and polyethylene glycol (99%, PEG 400) (J. T. Baker, Phillipsberg, NJ). Under a nitrogen atmosphere, 50 ml of PEG 400 was gradually added to a mixture of 50 g of finely ground KOH (87.4%, J. T. Baker) in a 200 ml of CH_2Cl_2 in a flask with constant stirring. The reaction vessel was wrapped with aluminium foil to exclude light and the reaction was continued for 20 h with stirring at room temperature. The resulting solution was filtered through CELITE on a glass frit. The excess CH_2Cl_2 was evaporated using a rotary-evaporation apparatus at 40–50 °C. In order to dope the polymer with Li^+ ions, it was dissolved in acetonitrile (99.9%, E.M. Science, Gibbstown, NJ) and $LiClO_4$ (99.9%, J.T. Baker) was added to the solution so that the ratio of the weights of $LiClO_4$ and the polymer was 1 : 6. Acetonitrile was evaporated using a rotary evaporator at 80–85 °C. The polymer was dried under vacuum at 90 °C overnight to remove trace amounts of acetonitrile.

2.2. *Cell configuration*

The configuration of the assembled electrochromic device is depicted in Fig. 1. The OMPE (Li^+) polymer electrolyte was sandwiched with a teflon spacer (0.15 mm thickness) between a WO_3 film and a PB film (each about 400 nm thick), previously made on flourine doped tin oxide (FTO) coated glass substrates. The area of each film exposed to the polymer electrolyte was 9.2 cm^2. The components of the cell were held together by a set of metal clips across the FTO-glass substrates.

2.3. *Electrochemical and spectroscopic measurements*

Electrochemical instrumentation included a PAR Model 173 potentiostat/galvanostat, a PAR Model 175 function generator, a PAR Model 379 coulometer

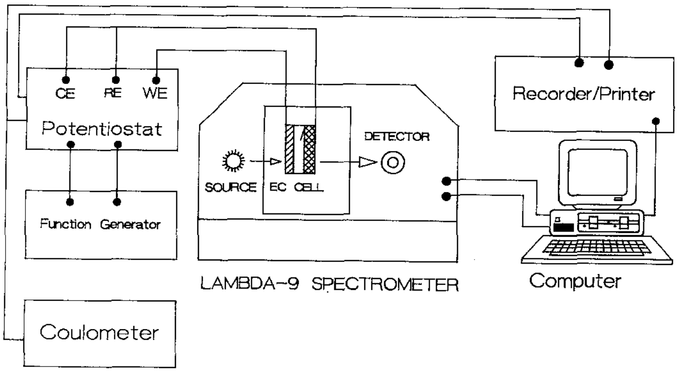

Fig. 2. Experimental apparatus for spectroelectrochemical measurements.

and a Hewlett-Packard 7090A recorder for measuring both the current or charge against potential and the current or charge against time curves. A Perkin-Elmer Lambda-9 spectrophotometer was used for the u.v.-vis-n.i.r. spectral measurements. The assembled WO_3-PB cell was placed in the spectrophotometer sample chamber and the electrodes were connected to the electrochemical equipment outside the chamber. The schematic representation of this *in situ* apparatus is shown in Fig. 2. For electrochemical measurements involving a single film (WO_3-only or PB-only), a saturated calomel reference electrode (SCE) and a coiled platinum counter electrode were used. For the assembled WO_3-PB cell, no reference electrode was used and potential was applied between the WO_3 and PB electrodes. Voltages of the cell are reported as applied to the WO_3 electrode against the PB electrode.

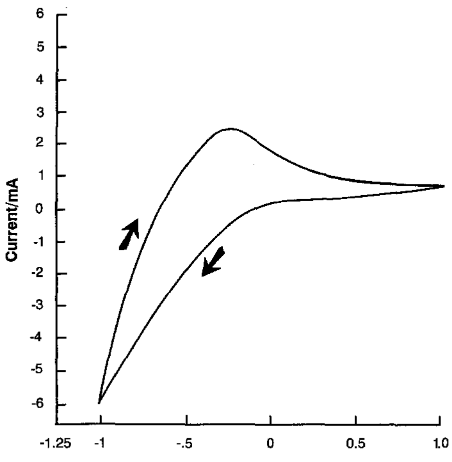

Fig. 3. Cyclic voltammogram of a WO_3 film in 1 M $LiClO_4$ solution in propylene carbonate (scan rate: 100 mV s^{-1}).

3. Results and discussion

3.1. *Electrochemical and electrochromic characteristics*

A cyclic voltammogram of a WO_3 film in a solution of propylene carbonate containing Li^+ ions is shown in Fig. 3. The main features of this voltammogram are the large anodic peaks at potentials negative to 0.0 V (relative to SCE) and the cathodic currents which continue to increase up to -1 V. In aqueous acidic solution hydrogen evolution reaction sets in [10] at a potential close to that of Reaction 1. Both amorphous and polycrystalline WO_3 films undergo electrochromic phenomena with performance improving with a decrease in crystal size in polycrystalline films [11]. The value of x in M_xWO_3 usually varies between 0 and 0.5 and depends on the variation in density and crystallinity of the films which result from different methods of preparation [12]. The WO_3 films used in this work were amorphous and the value of x in Li_xWO_3 in the fully coloured state was 0.4. Deb [13, 14] was the first to apply this concept to the construction of an optically switchable layered device in the late 1960s. A typical optical density variation upon electrochemical reduction of WO_3 is shown in Fig. 4 [3]. The optical absorbance of the film in the entire visible region of the spectrum (400–850 nm) increases with the increase of cathodic polarization. Since the dynamics of colouration are limited by the diffusion of protons and alkali metal ions, the colouration process starts at the WO_3–electrolyte interface and advances towards the substrate from the electrolyte side [15]. From *in situ* infrared spectroscopic measurements, Habib *et al.* [16] have reported that during the colouration process, H_2O molecules also are incorporated into the H_xWO_3 structure. Using potentio-

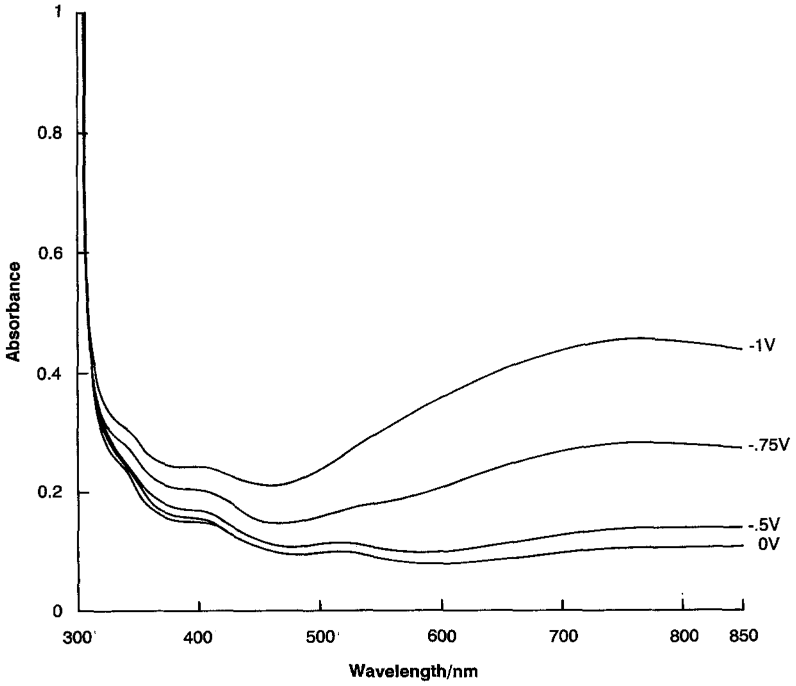

Fig. 4. Absorbance spectra of a WO_3 film at various cathodic polarization (electrolyte solution = 1 M $LiClO_4$ in propylene carbonate).

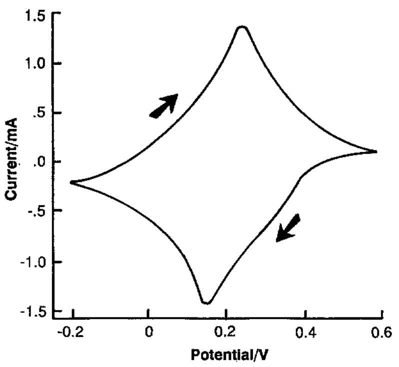

Fig. 5. Cyclic voltammogram of a PB-film in an aqueous solution of 1 M KCl (pH 4); scan rate: 10 mV s^{-1}.

dynamic techniques, Habib *et al.* [3] have measured the diffusion coefficient of Li$^+$ ions in WO$_3$ films, in contact with propylene carbonate solution containing LiClO$_4$, to be 3 × 10^{-11} cm^2 s^{-1}. This value may be compared with 2.8 × 10^{-11} cm^2 s^{-1} found by Huggins *et al.* [17] by an a.c. impedance technique, and 2 × 10^{-11} and 5 × 10^{-9} cm^2 s^{-1} reported by Green [18] and Mahapatra [19], respectively, by potentiostatic measurements.

A cyclic voltammogram of a PB electrode in a slightly acidic solution containing K$^+$ ions is shown in Fig. 5. The voltammetric peaks for the reduction to Everrit's salt and reoxidation to Prussian Blue are separated by about 100 mV. Since the peak separation is nearly zero for PB films on platinum substrates [20], the peak separation of 100 mV in Fig. 5 may be attributed to the resistivity of the FTO substrate layer. When the anodic potential exceeds 0.6 V, the Everitt's salt is further oxidized to Prussian Yellow (Equation 3).

The absorbance spectra of PB in the bleached and in the coloured states are shown in Fig. 6. For the oxidized PB film, a strong, broad absorption band centred around 690 nm gives rise to the blue colour. This band corresponds to the intervalence charge transfer between low spin Fe^{2+} and high spin Fe^{3+} [20]. The absorption of this film in the reduced state is minimal (Fig. 6).

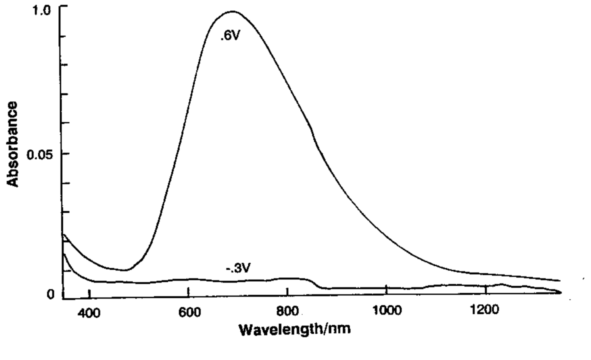

Fig. 6. Absorbance spectra of a PB film in the clear (−0.3 V) and coloured (+0.6 V) states in 1 M KCl solution of pH 4 (aqueous).

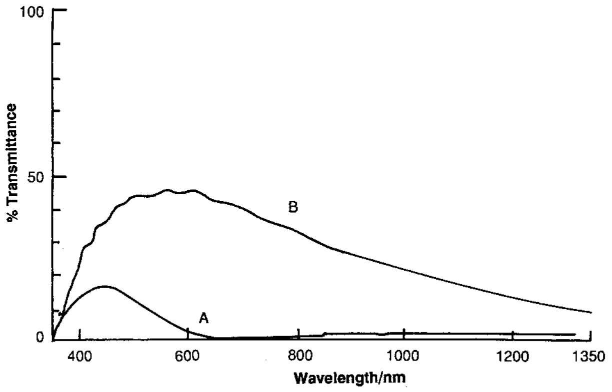

Fig. 7. Transmittance spectra of the complementary WO$_3$–PB cell with Li$^+$ doped OMPE polymer electrolyte. B = clear at 1.0 V; A = coloured at −1.0 V.

The optical response of the combined WO$_3$–PB cell can be seen in Fig. 7, which shows the transmittance spectra of the cell in both the coloured and clear states. A change of 45% transmission occurred over a broad spectral region, around 600 nm, upon electrochromic switching between the two states. In the coloured state (−1.0 V applied potential), there is a minimum transmission (~15%) in the region between 350 and 600 nm. At λ > 600 nm, there is practically no transmission of light through the cell. The spectrum taken at 1.0 V applied potential shows the clear state of the cell. From a comparison of the 'coloured' spectra in Figs 4, 6, and 7, it can be seen that the spectrum of Fig. 7 is due to the complementary absorbance of the WO$_3$ and PB films. This conclusion is further supported by measured colouration efficiency of the complementary cell (discussed below).

3.2. *Cycling durability*

3.2.1. Transmittance spectra. When a potential is applied between the WO$_3$ and the PB electrode so that the WO$_3$ is cathode and the PB is anode, then both the electrodes get coloured. By reversing the polarization, the electrodes get bleached. One colouration and one subsequent bleaching phenomenon constitute a cycle. Figure 8 shows u.v.–vis. spectra of the cell in the coloured state after various number of cycles at room temperature. Any changes in the cell temperature during cycling was not monitored. With an increase in the number of cycles up to 385, the colouration intensity decreases slightly giving rise to an increase in

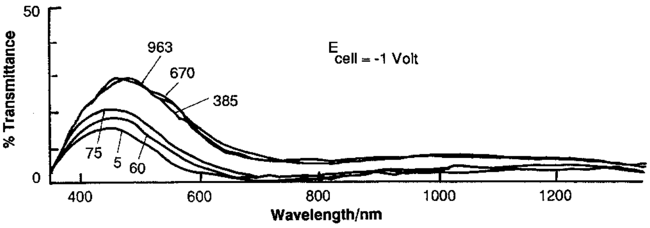

Fig. 8. Transmittance spectra of the complementary WO$_3$–PB cell in the coloured state after indicated number of cycles.

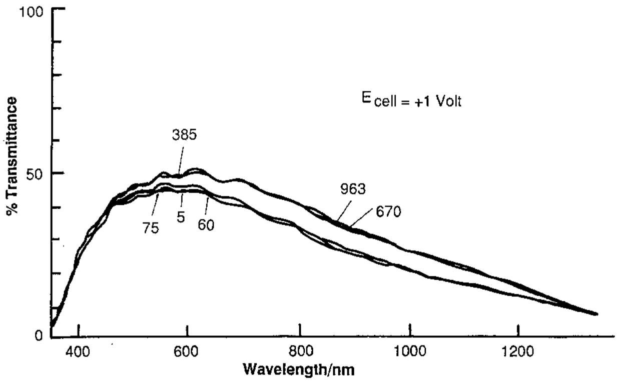

Fig. 9. Transmittance spectra of the complementary WO_3-PB cell in the bleached state after indicated number of cycles.

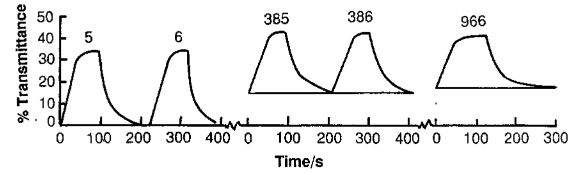

Fig. 11. Variation of transmittance with time upon switching (λ = 550 nm) during indicated number of cycles.

transmittance of about 15% around 500 nm (Fig. 8). After the 385th cycle, the transmittance spectrum remains essentially constant upon additional cycling (up to 963 cycles). In the bleached state (Fig. 9), the cell transmittance increases by about 5% around 600 nm up to 385 cycles and remains constant thereafter. The cycling of the cell has been continued up to 1200 cycles with no further degradation.

Figure 10 shows variation of transmittance with time upon switching during the first few cycles. Bleaching occurs at a faster rate than the colouring process. This is caused by the difference in diffusivity of the M^+ ions in the films in the coloured and in the bleached states.

The change in transmittance at λ = 550 nm upon switching during more extensive cycling is shown in Fig. 11. At the 5th cycle the change in transmittance upon switching was found to be 34% which was reduced to 27% at the 386th cycle, and to 23% at the 967th cycle (Fig. 11). As the number of cycles increased the residual colour of the films also increased as shown by the rising base line in Fig. 11.

3.2.2. Charge variation.. Starting with a fresh cell, 9.1 mC cm^{-2} of charge (Fig. 12) was needed to colour the cell. As the cycling proceeded, the amount of charge consumed during colouration decreased from 9.1 mC cm^{-2} on the first cycle to 6.4 mC cm^{-2} at the 67th cycle, 4 mC cm^{-2} at cycles > 400, and less than 4 mC cm^{-2} at cycles > 1000 (Fig. 12). Since the change in optical density is directly proportional to the amount of charge consumed, i.e.,

$$\Delta OD = -\alpha Q \qquad (4)$$

the decrease in the saturation value of the charge with the increase of cycle number (Fig. 12) corresponds to the decrease in the change of optical density, as found in Fig. 8.

3.2.3. Colouration efficiencies.. The colouration efficiency of an electrochromic film or device is defined as the change in absorbance per unit charge injected per unit area of the active electrode. From the changes in absorbance as a function of time after the cell had been switched from the coloured to bleached state and the corresponding change in the amount of charge upon switching, the colouration efficiency of the cell was found to be 102 cm^2 C^{-1} at λ = 550 nm at the start of cycling (Fig. 13). In Fig. 14, the changes in absorbance with the change of the amount of charge injected for coloration are shown after 385 and 963 cycles. The colouration efficiency decreased to 67 cm^2 C^{-1} and 58 cm^2 C^{-1} after 385 and 963 cycles, respectively.

3.3. *Cause of degradation in optical performance*

When cycled individually, the WO_3 film in a Li^+-containing electrolyte and the PB film in a K^+-containing electrolyte have shown excellent durability [2, 4]. We believe that the degradation of the optical activity of the complementary cell is associated with

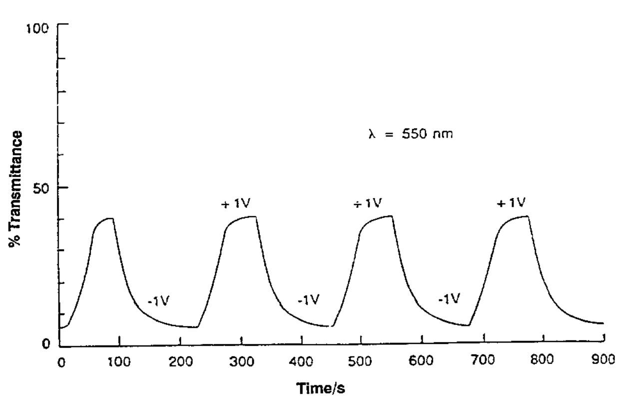

Fig. 10. Variation of transmittance with time upon switching (λ = 550 nm).

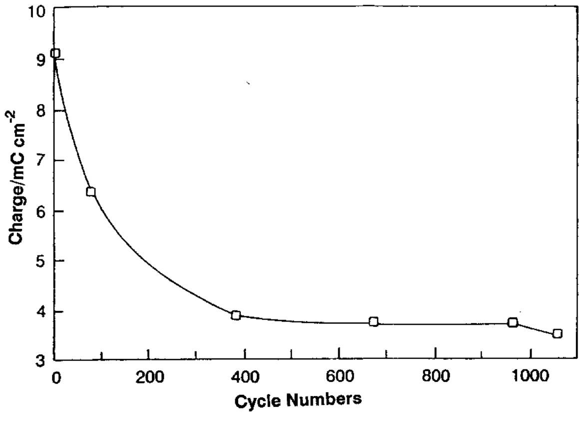

Fig. 12. Variation of the amount of injected charge during colouration as a function of cycle number.

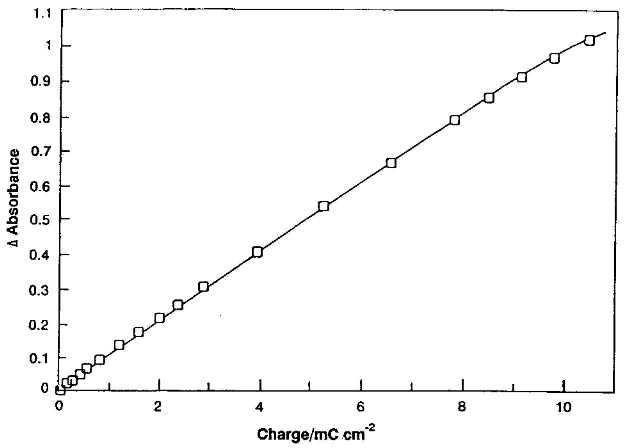

Fig. 13. The change in absorbance as a function of charge density at the beginning of cycling.

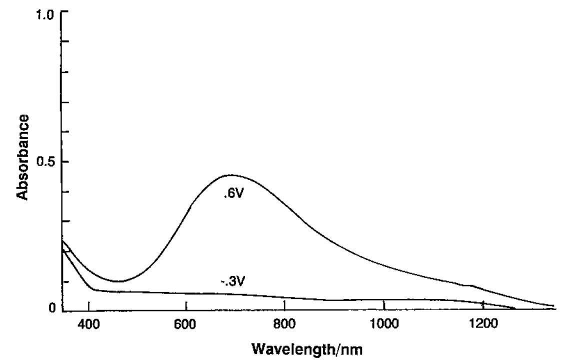

Fig. 15. Absorbance spectra of a PB film in the coloured (+0.6 V) and clear (−0.3 V) states in $LiClO_4$ solution (aqueous).

the ionic transport characteristics of the electrolyte. The OMPE (Li^+) polymer electrolyte used in this cell contained only Li^+ cations, and PB films have been found to be less reversible with Li^+ ions than with K^+ ions [20] in aqueous solutions. Thus, as the PB film was cycled, the original concentration of K^+ ions in the film decreased as the number of ions going into the film during bleaching was progressively less than the number of ions coming out of the film during colouration (Equation 2). With repeated cycling in K^+ deficient electrolyte, the PB film finally became deficient in K^+ ions resulting in a decrease in optical performance.

The above explanation for the degradation in optical performance was verified by the following experiments with the PB film only. In Fig. 15, the absorbance spectra of a PB film in $LiClO_4$ solution (aqueous) are shown in the coloured and bleached states. The spectral difference at $\lambda = 690\,\text{nm}$ was about 0.45 absorbance unit between the coloured and the bleached states. This difference progressively decreased with cycling (Fig. 16). After 12 cycles this difference became negligible (Fig. 17), signifying K^+ deficiency in the film. These results are consistent with the earlier reports that PB films are less reversible with Li^+ ions than with K^+ ions [20, 21]. In a $KClO_4$ solution (aqueous), the spectral difference at the beginning of cycling was found to be about 0.8 absorbance unit which slowly decreased to about 0.6 after the 10th cycle. This decrease may be attributed to the solubility effect of $KClO_4$ which is sparingly soluble in water; prior to the start of cycling the solution was heated in order to increase the solubility of $KClO_4$. During the cycling test, the solution cooled resulting in the precipitation of $KClO_4$ at room temperature. Consequently, the spectral difference also decreased. The electrode was then taken out of the $KClO_4$ solution and was immersed in a KCl solution (aqueous). No further degradation in optical performance was observed upon cycling.

In Fig. 6, the spectral characteristics of a PB film in KCl solution was shown. In the KCl electrolyte solution, the difference between the coloured and bleached states did not decrease with cycling (Figs 18 and 19). This supports our conclusion that the decrease in optical performance of the complementary WO_3–PB cell is due to the lack of available K^+ ions in the electrolyte for the PB film.

4. Conclusions

(i) A Li^+ doped polymer electrolyte, oxymethylene polyoxyethylene (OMPE) was found effective for the functioning of a complementary WO_3/PB electrochromic cell.

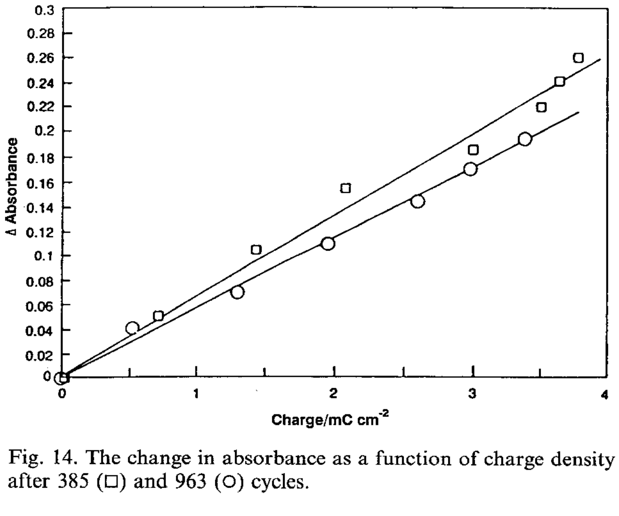

Fig. 14. The change in absorbance as a function of charge density after 385 (□) and 963 (○) cycles.

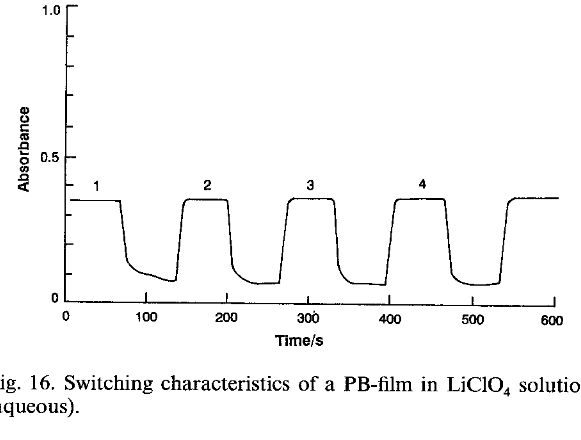

Fig. 16. Switching characteristics of a PB-film in $LiClO_4$ solution (aqueous).

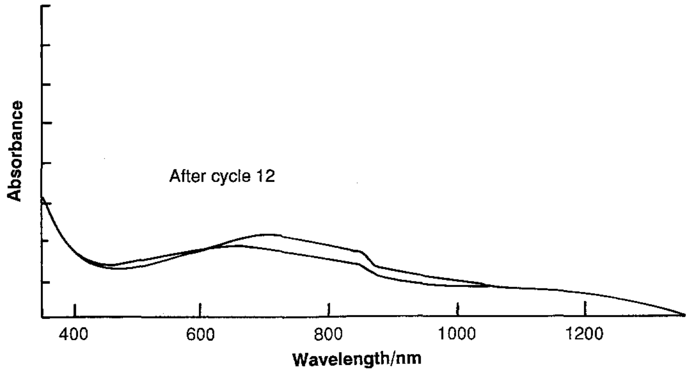

Fig. 17. Absorbance spectra of the PB-film in $LiClO_4$ solution (aqueous) after 12 cycles. The absorbance curve with lower absorbance around 800 nm is the spectrum at the bleached state (−0.3 V), and the upper curve is that at the coloured state (0.6 V).

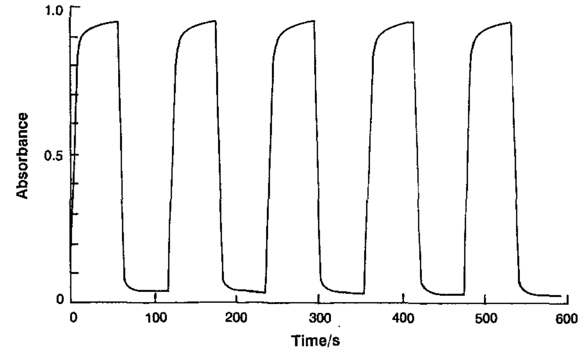

Fig. 18. Switching characteristics of a PB-film in KCl solution (aqueous) during the first 5 cycles.

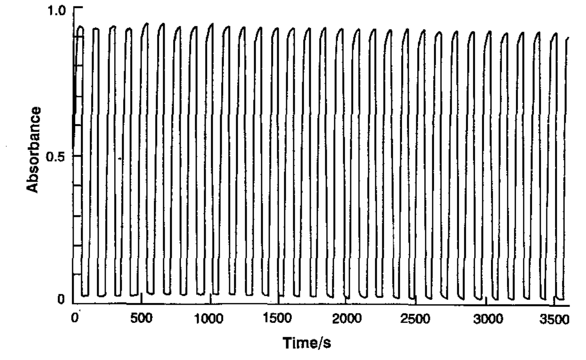

Fig. 19. Switching characteristics of a PB-film in KCl solution (aqueous) during 5 to 34 cycles.

(ii) The colouration efficiency of 102 $cm^2 C^{-1}$ at the first cycle decreased to 67 $cm^2 C^{-1}$ after 387 cycles.

(iii) The cause of degradation in optical performance was attributed to the lack of K^+ ions available to the PB film.

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