JOURNAL OF APPLIED ELECTROCHEMISTRY 21 (1991) 203-207

A tungsten-trioxide/prussian blue complementary electrochromic cell with a polymer electrolyte

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Received 27 March 1990; revised 5 June 1990

Optically variable windows (smart windows), which control the transmission of light into buildings and vehicles, are of interest both for the control of solar heat load and for privacy applications. Such windows are likely to utilize electrochromic technology to achieve optical control. An electrochromic device consisting of a cathodically colouring tungsten trioxide (WO_3) film, an anodically colouring Prussian blue (PB) film, and a polymer electrolyte was made. The polymer electrolyte was prepared from polyvinyl alcohol doped with H_3PO_4 and KH_2PO_4 to accommodate the conduction of both H^+ and K^+ ions. The electrochromic WO_3 and PB films functioned in a complementary way such that the device was coloured or bleached by the application of -0.5 V or $+0.5$ V (WO_3 films vs PB film), respectively. The spectral characteristics of the coloured device confirmed the complementary colouration of WO_3 and PB in the device.

1. Introduction

The individual electrochromic characteristics of tungsten trioxide (WO_3) and Prussian blue (PB) are well known [1-5]. 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 electrochromic 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 sufficient 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, returning the electrochromic device to a transparent state.

The advantage of such complementary electrochromic cells over more conventional cells which utilize a single electrochromic film, is that less electrical charge is required to achieve comparable colouration.

Kase *et al.* [6] reported a complementary electrochromic device with WO_3 and PB. 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 co-workers [7]. 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 [8]. Such deficiency would result in the eventual degradation of the electrochromic performance of these devices.

More recently, all solid state complementary electrochromic cells with WO_3 and PB have been reported [9, 10] which also show a reasonable electrochromic response. In both systems a solid polymer electrolyte is used which conducts one alkali cation species, K^+ or Li^+, between the WO_3 and PB films. However, for the optimal electrochromic response from each of these films individually, it has been shown that for kinetic reasons H^+ ions are preferred for the electrochromic reaction of WO_3 films [11] and K^+ ions for the reaction of PB films [12]. Therefore, we examine here the use of a solid polymer electrolyte which can conduct both H^+ and K^+ ions in an electrochromic cell.

Solid films of polyvinyl alcohol (PVA) doped with H_3PO_4 have been shown to be good H^+ conductors [13] and should be compatible with the electrochromic reaction of WO_3 which involves the transport of protons [2]. To provide the mobile K^+ ions required for the electrochromic reaction of PB, KH_2PO_4 was added to the polymer electrolyte. This work introduces PVA/H_3PO_4-KH_2PO_4 as a new electrolyte for electrochromic devices.

2. Experimental details

2.1. *Film preparation*

Thin films of WO_3 and PB were deposited on fluorine-doped tin oxide-coated (FTO) glass surfaces. The conducting glass substrates were cut into $0.9 \times 5\,cm^2$ pieces. FTO-coated glass substrates were supplied by the Watkins-Johnson Co. (California). The resistance of the FTO layers was in the range of 10-15 Ω per square. Prior to the deposition of the electrochromic films, the glass slides were cleaned in a solution of Alconox followed by an ultrasonic cleaning in tri-distilled water. In some cases, the glass slides were

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further cleaned with dilute HNO_3 solution (aqueous) and rinsed with isopropyl alcohol. The cleaned substrates were stored in tri-distilled water.

The WO_3 films were prepared on the FTO-coated glass substrates by a non-electrochemical method discussed previously [14]. WCl_6 was dissolved in a solvent (isopropyl alcohol) and the resulting solution was used to spin coat the substrates. PB films were cathodically deposited from an acidic ferric ferricyanide solution (pH 4) on to the FTO-coated glass substrates using the mothod of Itaya and coworkers [15]. A current density of $10\,\mu A\,cm^{-2}$ was used for 500 s.

2.2. *Electrolyte preparation*

Polyvinyl alcohol (PVA) (hydrolysed) was obtained from J.T. Baker Chemical Co. (New Jersey). Free standing films of PVA doped with H_3PO_4 and KH_2PO_4 were made by dissolving 4 g of PVA in 100 ml of tri-distilled water at 70° C. This yielded a viscous solution of PVA to which H_3PO_4 (85%) and KH_2PO_4 were added to make the solution 1% in both H_3PO_4 and KH_2PO_4 (ignoring acid equilibria). The clear, viscous solution was then cooled to room temperature and used as a stock solution for the synthesis of free-standing films of PVA/H_3PO_4-KH_2PO_4 electrolyte. The stock solution was poured onto the smooth, clean surface of a polysulphone plate, and was left to dry overnight. The resulting film could be easily peeled off of the polysulphone surface.

2.3. *Cell configuration*

The configuration of the assembled electrochromic device is depicted in Fig. 1. A PVA/H_3PO_4-KH_2PO_4 film was sandwiched between a WO_3 film and a PB film each previously made on FTO-glass substrates. For better contact, both sides of the PVA film were wetted with the PVA stock solution containing H_3PO_4 and KH_2PO_4 before cell assembly. Contact of the PVA film with the WO_3 and PB films was maintained with the use of metal clips across the FTO-glass substrates.

For the measurements of colouration efficiencies of individual WO_3 and PB electrodes, a cuvette cell [16] containing the stock solution as the electrolyte and a platinum counter electrode were used.

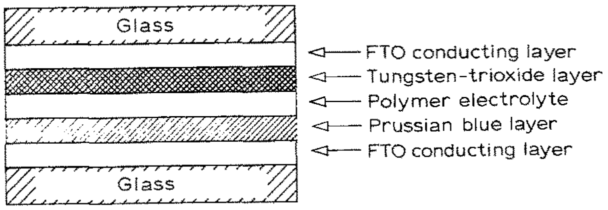

Fig. 1. Schematic diagram of a complementary WO_3-Prussian blue electrochromic cell with the polyvinyl-alcohol-based solid polymer electrolyte.

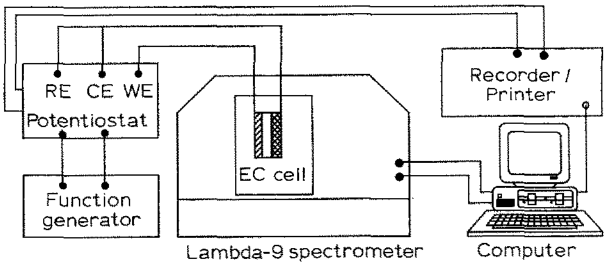

Fig. 2. Schematic representation of the experimental set-up for the spectro-electrochemical measurements. WE, CE, and RE on the potentiostat represent the connections for the working electrode, counter electrode, and the reference electrode, respectively. EC Cell represents the electrochromic cell in the sample chamber of the spectrophotometer.

2.4. *Electrochemical and spectroscopic measurements*

Electrochemical instrumentation included a PAR Model 173 Potentiostat/Galvanostat, a PAR Model 175 Function Generator, and a Hewlett-Packard 7090A recorder for recording both the current versus potential and the current versus time curves. A Perkin-Elmer Lambda-9 spectrophotometer was used for the UV-Vis-NIR 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* set-up 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.

3. Results and discussion

3.1. *Cyclic voltammetry*

The colouration-bleaching phenomena in the WO_3 films occur as a result of the insertion of protons or alkali metal ions and electrons into the film [2],

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

where M^+ represents H^+, Li^+, K^+, Na^+, etc.

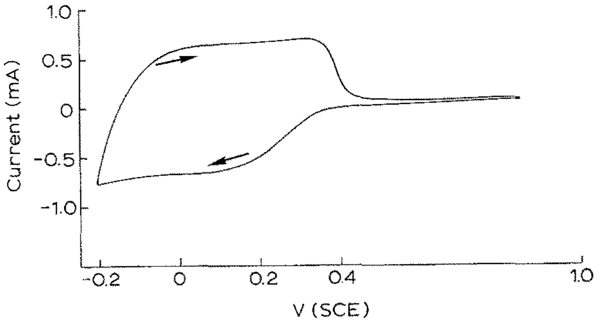

Fig. 3. Cyclic voltammogram of a WO_3 film on the FTO-coated glass in 0.5 M H_2SO_4 solution (aqueous). (Scan rate = $20\,mV\,s^{-1}$).

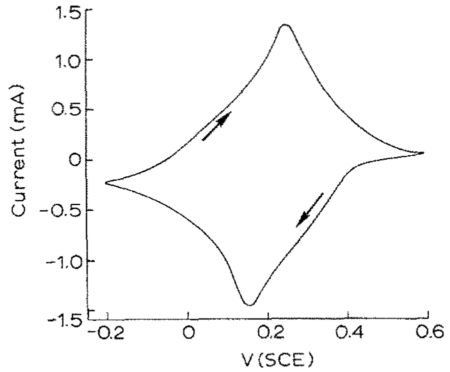

Fig. 4. Cyclic voltammogram of a PB film on the FTO-coated glass in an acidic aqueous solution of KCl (pH 4). (Scan rate = 10 mV s^{-1}).

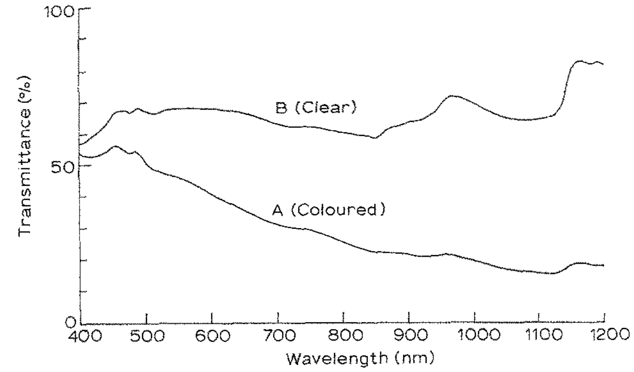

Fig. 6. UV-Vis.-NIR spectra of a WO_3 film. A = Coloured state at -0.4 V/SCE, and B = Clear state at $+0.4$ V/SCE. Electrolyte = 0.5 M H_2SO_4 solution (aqueous).

A cyclic voltammogram of a WO_3 film in H_2SO_4 solution (aqueous) is shown in Fig. 3. The onset of reduction current at $+0.3$ V corresponds to the reduction of WO_3, according to Reaction 1, while hydrogen gas evolution is responsible for the steadily increasing currents at more negative potentials. Re-oxidation of H_xWO_3 is accomplished on the return sweep, as shown by the anodic current obtained. These results are similar to those reported previously for WO_3 [17, 18].

Films of Prussian blue are an intense blue colour and can be reversibly bleached to the transparent Everitt's salt by electrochemical reduction as follows [15]:

$$\underset{\text{(Prussian blue)}}{KFeFe(CN)_6} + K^+ + e^- \Longleftrightarrow \underset{\text{(Everitt's salt)}}{K_2FeFe(CN)_6} \quad (2)$$

A cyclic voltammogram of PB electrode in a slightly acidic solution containing K^+ ions is shown in Fig. 4. The voltammetric peaks for the reduction to Everitt's salt and re-oxidation to Prussian blue are separated by about 100 mV. Since the peak separation is nearly zero for Prussian blue films on platinum substrates [12], the peak separation of 100 mV in Fig. 4 may be attributed to the resistivity of the FTO substrate layer.

The cyclic voltammogram of the assembled WO_3–PB complementary cell with WO_3 as the working electrode is shown in Fig. 5. The potentials were recorded versus the PB electrode. The cell voltammetry strongly resembles the voltammetric features of the WO_3 electrode in Fig. 3. Visual observation reveals that the cell is fully coloured by the application of -0.5 V. While reduction of the WO_3 can occur by either K^+ or H^+ ion insertion according to Reaction 1, insertion of H^+ ion is more likely [11]. The steadily increasing reduction current seen for the negative portion of the scan near the cathodic limit (-1.0 V) (Fig. 5) suggests that hydrogen evolution still occurs in the assembled cell, presumably from the reduction of water entrained in the electrolyte. This reaction can be minimized in a device by keeping the cathodic limit positive of -0.5 V, since colouration of the device is driven to completion with the application of -0.5 V.

3.2. *Optical response*

Transmittance spectra of single films of WO_3 and PB on FTO-coated glass, comparable in thickness to those used in the WO_3–PB complementary device, are shown in Figs 6 and 7, respectively. The WO_3 film in the reduced state has a broad band which extends from 500 nm in the visible region to wavelengths greater than 1200 nm in the near infrared (NIR) region (Fig. 6). In the oxidized state, the film has minimal absorption from 400 to 1200 nm. For the oxidized PB film (Fig. 7), a strong, broad band centered at 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+} [12]. The absorption of this film in the reduced state is minimal.

The optical response of the combined WO_3–PB

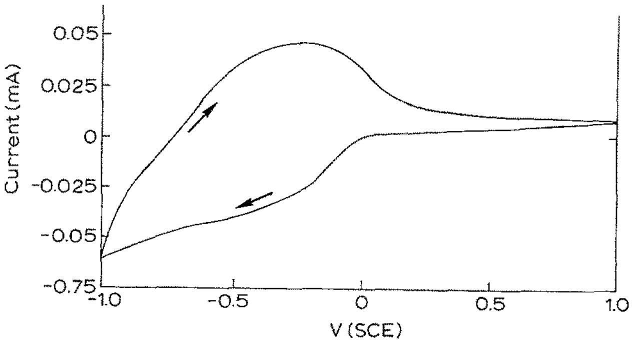

Fig. 5. Cyclic voltammogram of the complementary WO_3–PB cell with solid polymer electrolyte based on polyvinyl alcohol doped with H_3PO_4 and KH_2PO_4. Cell voltage is the potential applied to the WO_3 electrode versus the PB electrode. (Scan rate = 20 mV s^{-1}).

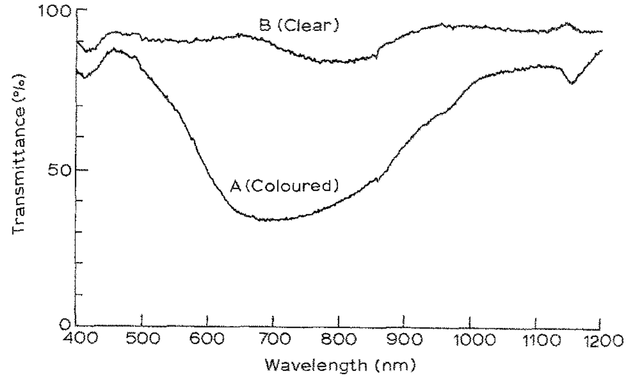

Fig. 7. UV-Vis.-NIR spectra of a PB film in an aqueous acidic solution of 1 M KCl (pH 4). A = Coloured state at $+0.6$ V/SCE, B = Clear state at -0.2 V/SCE.

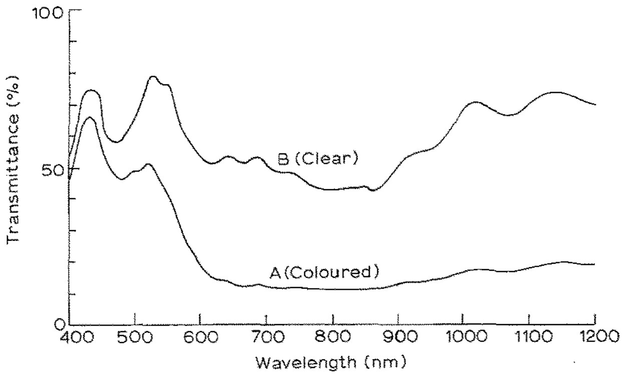

Fig. 8. UV-Vis.-NIR spectra of the complementary WO_3–Prussian blue electrochromic cell with PVA/H_3PO_4–KH_2PO4 electrolyte. A = Coloured state at −0.5 V and B = Clear state at +0.5 V against the PB electrode.

cell can be seen in Fig. 8, which shows the absorbance spectra of the cell in both the coloured and clear states. A change of more than 30% transmittance occurred over a large spectral region, about 600–1200 nm, upon electrochromic switching between the two states. The residual absorption in the clear state (0.5 V applied potential) centered about 800 nm is probably due to incomplete bleaching of both the WO_3 and PB films. The spectrum taken at −0.5 V applied potential shows the coloured state of the cell. The transmittance decreases with increasing wavelength, from 500 nm to a broad plateau which extends from about 650 to 850 nm. At wavelengths greater than 850 nm, in the NIR region, the transmittance is somewhat increased. From a comparison of the coloured spectra in Figs 6, 7, and 8, it can be seen that the spectrum of Fig. 8 is due to absorption by both the WO_3 and PB films. This inference is also evidenced by the measured colouration efficiency of the complementary cell as discussed below.

3.3. *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. Colouration efficiences have been measured individually for both the WO_3 and the PB electrodes in PVA solution containing KH_2PO_4 and H_3PO_4 electrolytes, and for a combined WO_3–PB cell with the same electrolyte. The efficiency of the latter cell was found to be similar to that of the solid state PB/PVA/WO_3 cell.

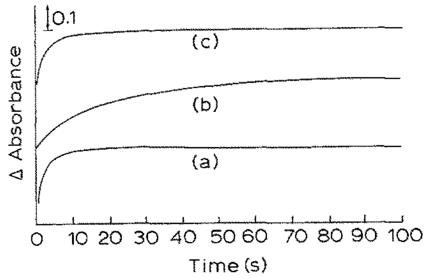

Fig. 9. Variation of absorbance with time at λ = 690 nm. (a) WO_3, Potential pulsed from +0.6 V to −0.3 V/SCE, Charge injected, ΔQ = 4.44 mC cm^{-2}; (b) PB, −0.3 V to +0.6 V, ΔQ = 3.59 mC cm^{-2}; (c) WO_3–PB, +0.5 V to −0.5 V, ΔQ = 1.88 mC cm^{-2}. The amounts of charge injected, ΔQ, were simultaneously recorded. Electrolyte solution = PVA containing 1% H_3PO_4 and 1% KH_2PO_4.

Table 1. Colouration efficiencies of the complementary cell and the individual electrodes

Electrodes	*Wavelengths (nm)*	*Colouration efficiencies ($cm^2\,C^{-1}$)*
WO_3	690	58.5
PB	690	61.3
WO_3–PB	690	127.7
WO_3	850	81.8
PB	850	63.3
WO_3–PB	850	138.0

In Fig. 9, the changes in absorbance as a function of time after defined amounts of charge have been injected are shown for WO_3 and PB films along with that for the combined electrodes. Absorbance gradually increased with time, and after about 30 s became nearly constant. From the data of Fig. 9, colouration efficiences of the WO_3 and the PB electrode in PVA solution containing KH_2PO_4 and H_3PO_4 electrolytes were found to be 58.5 and 61.3 cm^2 C^{-1}, respectively, at λ = 690 nm (Table 1). At 850 nm, the colouration efficiences were found to be 81.8 and 63.3 cm^2 C^{-1} for WO_3 and PB electrodes, respectively. When these two electrochromic electrodes were combined in a cell containing the same polymeric electrolyte, the colouration efficiencies were found to be 127.7 and 138 cm^2 C^{-1} at λ = 690 and λ = 850 nm, respectively. Thus, the colouration efficiency of the complementary WO_3–PB electrochromic cell is the summation of the individual colouration efficiencies of the WO_3 and the PB electrode as expected.

3.4. *Stability*

The optical response of the electrochromic cell was seen to degrade after switching only several times between the coloured and bleached states. The optical contrast between the two states decreased significantly, with the films not colouring as much as before. Since both WO_3 and PB films have demonstrated good stability toward repeated electrochromic switching in other systems [2, 5], we believe that the degradation in the complementary cell is associated with the electrolyte. Since water is undoubtedly entrained in the PVA/H_3PO_4–KH_2PO_4 electrolyte, the degradation in performance may well be associated with a loss of water in the electrolyte and a concomitant reduction in the mobility of K^+ and/or H^+ ions. Modification of the electrolyte structure to increase the hydration energy of the polymer backbone and/or proper sealing of the device may contribute to its increased stability.

Acknowledgements

Thanks are due to Drs Donald MacArthur and Dennis Corrigan for critical reading of the manuscript and for several useful discussions, and to the Watkins-

Johnson Company for their donation of FTO-coated glass.

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