



The influence of charge capacity ratio on the performance of a complementary electrochromic system

Kuo-Chuan Ho*

Department of Chemical Engineering, National Taiwan University, Taipei, 10617, Taiwan

Abstract

One of the problems encountered with complementary, solid-state electrochromic devices is the development of discoloration as a result of storage or cycling. The cause of discoloration in the bleached state is the charge imbalance on one of the electrodes. This paper deals with balancing the electrode capacities in a complementary, solid-state electrochromic device so as to optimize its optical attenuation range. Complementary electrochromic system, comprising a tungsten oxide and Prussian blue (PB) thin film couple in combination with a proton-conducting, copolymer electrolyte, is studied. It has been shown experimentally that, for two complementary electrochromic layers each with an individual thickness, the charge capacities of the two electrochromic layers have to be matched in order to achieve the maximum optical attenuation range. The effect of cell size on the switching response of the complementary system is also studied. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Charge balance; Charge capacity; Electrochromic; Prussian blue; Transparent electrode; Tungsten oxide

1. Introduction

The complementary tungsten oxide-Prussian blue electrochromic devices (ECDs), in combination with Li^+ , K^+ or H^+ -based electrolytes, has been proposed by many

*E-mail: kcho@ms.cc.ntu.edu.tw

Table 1
A partial list of ECDs containing the WO_3 –PB couple

Configurations	References
$\text{K}_x\text{WO}_3/\text{KCF}_3\text{SO}_3$ in PEO-based PU/PB	[1]
$\text{K}_x\text{WO}_3/\text{H}_3\text{PO}_4$ – KH_2PO_4 in PVA/PB	[2]
$\text{Li}_x\text{WO}_3/\text{Li}^+$ –OMPE/PB	[3]
$\text{Li}_x\text{WO}_3/\text{LiCF}_3\text{SO}_3$ in PAA–PEO/PB	[4]
$\text{Li}_x\text{WO}_3/\text{LiClO}_4$ in PC/PB	[5–8]
$\text{H}_x\text{WO}_3/\text{Poly-AMPS}^a/\text{PB}$	[9]
$\text{H}_x\text{WO}_3/\text{P(VSA-V P)}/\text{PB}$	This work

^aAMPS is a registered trademark of Lubrizol Corporation. OMPE = oxymethylene poly(oxyethylene), PAA = poly(acrylic acid), PC = propylene carbonate, PEO = poly(ethylene oxide), Poly-AMPS = poly(2-acrylamido-2-methylpropane sulfonic acid), P(VSA-VP) = copolymer of vinylsulfonic acid (VSA) and 1-vinyl-2-pyrrolidinone (VP).

researchers [1–9] for solar attenuation and glare reduction applications. A partial list of complementary, electrochromic configurations using the WO_3 –PB couple is summarized in Table 1.

Tada et al. [1] reported an electrochromic device based on the WO_3 –PB couple using a polyethylene oxide-based polyurethane (PU) network containing KCF_3SO_3 electrolyte. The solar transmittance of the device varied between 56% and 14%. Habib et al. [2] constructed a device based on the WO_3 –PB couple with the polymer electrolyte prepared from polyvinyl alcohol (PVA) doped with H_3PO_4 and KH_2PO_4 . The electrolyte accommodates both H^+ and K^+ ions; H^+ for WO_3 and K^+ for PB insertion/extraction. The transmittance of the device varied from 52% to 12% at 690 nm. With a Li^+ -doped oxymethylene polyoxyethylene (OMPE) electrolyte, Habib et al. [3] fabricated a device also based on the WO_3 –PB couple. The transmittance of the device varied from 63% to 32% at 790 nm. Oyama et al. [4] reported a device based on the WO_3/PB couple while dispersing LiCF_3SO_3 in the intermolecular complex of poly(acrylic acid)–poly(ethylene oxide) electrolyte (PAA–PEO). No switching data were reported. Miyamoto et al. [5] described a device based on the WO_3 –PB couple using 1 M LiClO_4 in propylene carbonate (PC) as the electrolyte. Transmittances were varied from 60% to 10%, although the wavelength was not specified. Inaba et al. [6] disclosed an electrochromic device having the WO_3 –PB couple and an auxiliary electrode disposed in a marginal region of the space between the two complementary electrodes; an electrolyte occupies the remaining space. The electrolyte was 1 M LiClO_4 in PC. The auxiliary electrode serves two purposes: (1) to provide a means for the initial darkening of the WO_3 electrode or for the initial bleaching of the PB electrode, and (2) to recover the device's performance arising from the loss of the redox balance between the two electrochromic layers, either by repeated darkening/bleaching or by the influence of an impurity in the electrolyte. Kawai et al. [7] disclosed a device with an auxiliary electrode similar to the one mentioned by Inaba et al. [6] mentioned earlier. However, conjugated polymers were used as the

electrochemically oxidizable and reducible materials for the auxiliary electrode because of higher charge-carrying capabilities. This modification was needed for the proper function of the auxiliary electrode, especially for a large-area electrochromic device. Kase et al. [8] reported a device based on the WO_3/PB couple by using a 1 M LiClO_4 in PC with 1–2% H_2O as the electrolyte. Typical luminous transmittances in the darkened state were 5–10%, while those of the bleached state were 50–70%. Ho et al. [9] reported a new solid-state electrochromic system comprised of a tungsten oxide and Prussian blue couple in combination with a proton-conducting polymer electrolyte, Poly-AMPS. By controlling the amount of water in the Poly-AMPS, the transmittance of the device at 550 nm went from 3% to 55% and vice versa. Electrochemical stability for at least 20 000 cycles at room temperature has been established. Cycle times were 30 s for darkening and 60 s for bleaching.

Despite the well-known principle of electrochromic switching reactions involving WO_3 and Prussian blue electrodes, as shown in Fig. 1, one of difficulties in addressing the stability of the electrochromic system is the lack of reproducibility; that is, electrochromic performance varies from one sample to the other, even for two samples supposedly made under the same conditions. This is due to the early oxidation of the precharged WO_3 in air; the rate and degree of oxidation varies from plate to plate. A procedure has been established in this study for precharging the WO_3 plate in the copolymer electrolyte solution, rather than HCl, so as to minimize oxidation in air. This seems to work very well for half cells consisting of copolymer/ H_xWO_3 /conducting glass. The primary motivation for the present investigation is to examine the connection between the optical attenuation range, or the transmittance switching window and the charge capacity ratio of H_xWO_3 relative to PB. The ultimate goal is to attain better balance of charge between two electrochromic thin film electrodes, and hence the more reproducible performance, over periods of testing.

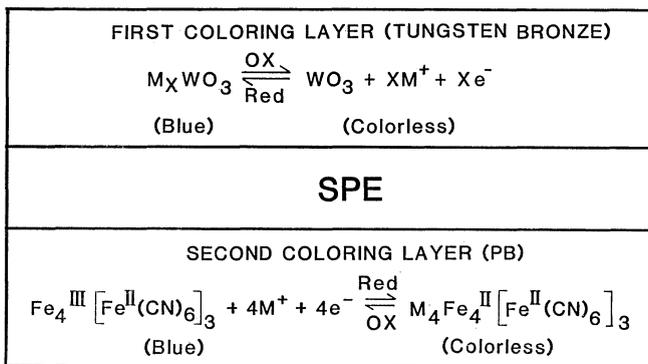


Fig. 1. Principle of electrochromic switching for $\text{M}_x\text{WO}_3/\text{SPE}/\text{PB}$ ($\text{M} = \text{H}$).

2. Experimental

2.1. WO_3 working electrode

WO_3 was vacuum-deposited on fluorine-doped tin oxide (FTO) coated glass substrates. The sheet resistance of FTO-coated glass substrates was measured by the four-point probe method and was $10 \Omega/\text{square}$. Conductive copper bus bars were applied on all four sides of the FTO-coated substrate. FTO-coated glass substrates (A: $6.0 \times 7.0 \times 0.23 \text{ cm}^3$, B: $13.0 \times 17.5 \times 0.23 \text{ cm}^3$, C: $17.5 \times 43.0 \times 0.23 \text{ cm}^3$, and D: $43.0 \times 43.0 \times 0.23 \text{ cm}^3$) were precleaned ultrasonically in an aqueous cleaner solution reported previously [10,11]. The experimental procedures for preparation of WO_3 were described elsewhere [10]. Tungsten oxide films were prepared by resistive evaporation beginning at 6×10^{-6} torr. The source material was WO_3 powder (purity $> 99.9\%$, Li Tungsten Corporation) contained in an Al_2O_3 -coated tungsten boat. In advance the substrate was cleaned further by argon ion sputtering. No substrate preheating was provided. Tungsten oxide films prepared in this way had a thickness of $3700 \pm 500 \text{ \AA}$. X-ray diffraction analysis, with a Rigaku diffractometer (Model D-2655) using monochromatized Cu K_α incident radiation, showed all the films to be lacking crystallinity.

2.2. Prussian blue counter electrode

The sacrificial anode (SA) method, which is based on the cathodic electrodeposition (ED) mentioned by Ellis et al. [12] for PB deposition, was modified and used in this work. The modified sacrificial method for PB deposition is described elsewhere [13]. The solution contained 5 mM of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 5 mM of $\text{K}_3\text{Fe}(\text{CN})_6$. It takes about 30 min to deposit the desired amount of PB on FTO-coated glass. The thickness of the PB film was controlled at $4750 \pm 250 \text{ \AA}$ by counting the passed charge, which is proportional to the amount of PB deposited. In all cases, the charge capacity for the deposition was controlled at 13.2 mC/cm^2 . X-ray diffraction analysis, with a Rigaku diffractometer (Model D-2655), using monochromatized Cu K_α incident radiation, showed all the films to be crystalline.

2.3. Solid polymer electrolyte

The transparent, H^+ -conducting polymer electrolyte is the copolymer based on the copolymerization of sodium vinylsulfonic acid (Na^+ -vsa) and 1-vinyl-2-pyrrolidinone (vp) [14]. The sodium form of this copolymer is exchanged to the acid form for use as the electrolyte in electrochromic devices. Na^+ -vsa/vp copolymerization is intentionally done with a slightly enriched vp than desired. 1.6 : 1 Na^+ -vsa/vp to obtain $\sim 2 : 1$ poly(Na^+ -vsa/vp) copolymer for example. Preparation of a vinylsulfonic acid (vsa) and vp copolymer having a 2 : 1 vsa to vp molar ratio is carried out as follows. A 25% aqueous solution of sodium vinylsulfonic acid (Aldrich Chemical) was triple filtered through fresh activated charcoal impregnated filter (Schleicher & Schuell) and 1.5 μm retention glass fiber filter (Whatman) stacks. The 25% filtered solution, weighted

2782.4 g, was concentrated on a rotovac at 35–40°C to 2295.6 g or 30.3%. The 30.3% Na⁺-vsa solution was combined with 371.2 g of 1-vinyl-2-pyrrolidinone (purity > 99%, Polysciences, Inc.) into a 5 l jacketed reaction kettle equipped with condenser, overhead stirrer, thermometer, and sparge tube. The monomer solution was mixed and sparged with nitrogen for 30 min, during which time 5.33 g of 2,2-azobisisobutyronitrile catalyst, AIBN, (Polysciences, Inc.) was added. After sparging, the sparge tube was removed, and nitrogen gas was introduced into the system after the condenser. The batch was then heated to 60°C from an external water bath while stirring under nitrogen blanket. The copolymerization reaction continued for 21 h. The poly(Na⁺-vsa/vp) copolymer was precipitated out of solution with 7.6 l of methanol. The methanol was decanted from the taffy-like solid, and replaced with 1.9 l of 100% ethanol (Quantum) to harden the copolymer. Subsequent ethanol treatments may be necessary to harden the copolymer to a filterable solid. The copolymer was vacuum filtered through a 100–160 µm retention glass frit filter, washed with 100% ethanol, and vacuum dried at 60°C for three days. By comparison of %S and %N from elemental analysis, one can calculate the molar ratio of Na⁺-vsa to vp for the copolymer. To convert the sodium form of the copolymer to the acid form, two equivalents of freshly washed Amberlite IR-120 (plus) ion-exchange resin (Aldrich) were added to one equivalent of dried copolymer dissolved in distilled water as a 10% solution. The copolymer/resin slurry was stirred for 30 min at room temperature, then vacuum filtered through a 1.5 µm retention glass fiber filter (Robu) to recover the acidic copolymer solution. The solution was dried in glass trays at low relative humidity to yield the ~ 2 : 1 vsa-vp copolymer solid.

2.4. Cell assembly

Before assembling the cells, the WO₃ electrode was precharged with protons. The precharging of the tungsten oxide electrode was carried out in copolymer solution at a constant current density of 0.11 mA/cm². It takes about 4 min to get the proper amount of protons into the tungsten oxide thin film. The tungsten bronze, H_xWO₃, was then rinsed with the distilled water and dried under N₂. The polymer electrolyte was flow coated on both electrodes. Cells were intimately laminated together with H_xWO₃ as the working electrode and PB as the counter electrode. The lamination process was carried out in an autoclave at a pressure of 1.03 × 10⁶ N/m² and a temperature of 93°C for 1 h. This procedure resulted in an averaged thickness of 100 µm for the copolymer electrolyte, as measured by a micrometer across samples. The electroactive areas of the ECDs were A: 4.8 × 5.4 cm², B: 10.2 × 15.2 cm², C: 16.0 × 41.5 cm², and D: 41.7 × 41.7 cm².

2.5. Electrochemical runs

The coloration and bleaching of cells were carried out by applying a constant DC voltage (Keithley voltage/current source, Model 228A). The transmittance, current and the drift of the cell voltage were recorded. The change in optical transmittance during coloration and bleaching was measured at 550 nm with a Cary-14

spectrophotometer. Transmittance data were taken at the center of the cell in all cases.

3. Results and discussion

3.1. Charge capacity ratio

WO_3 electrodes of $5'' \times 7''$ size (active area = $10.2 \times 15.2 \text{ cm}^2$), were precharged in copolymer solution in order to optimize precharging conditions, to match the charge capacity of the PB electrode with the same size (size B). The WO_3 electrodes were precharged at different proton levels just before cells were put together. Fig. 2 plots the initial transmittance window measured at 550 nm, $\Delta T_{550, t=0} \equiv T_{b, t=0} - T_{d, t=0}$, against the ratio of charge capacity, q , of the H_xWO_3 to that of the PB, $r \equiv q_{\text{H}_x\text{WO}_3}/q_{\text{PB} \rightarrow \text{PW}}$. The charge capacity of the H_xWO_3 , denoted by $q_{\text{H}_x\text{WO}_3}$, is the amount of charge injected per unit area of electrode. The charge capacity of the PB, denoted by $q_{\text{PB} \rightarrow \text{PW}}$, is the charge consumption per unit electrode area in reducing PB to Prussian white (PW). The value of $q_{\text{PB} \rightarrow \text{PW}}$ was determined experimentally by switching the PB electrode in the copolymer solution cathodically at -0.6 V against a Pt electrode. The value of $q_{\text{PB} \rightarrow \text{PW}}$ is 21.61 mC/cm^2 for a PB of $5'' \times 7''$, with an active area of 155.0 cm^2 . The precharging capacities on the tungsten oxide electrode were varied from 14.22, 17.78, 21.33, 24.89, 28.44, and 32.00 mC/cm^2 , corresponding to the

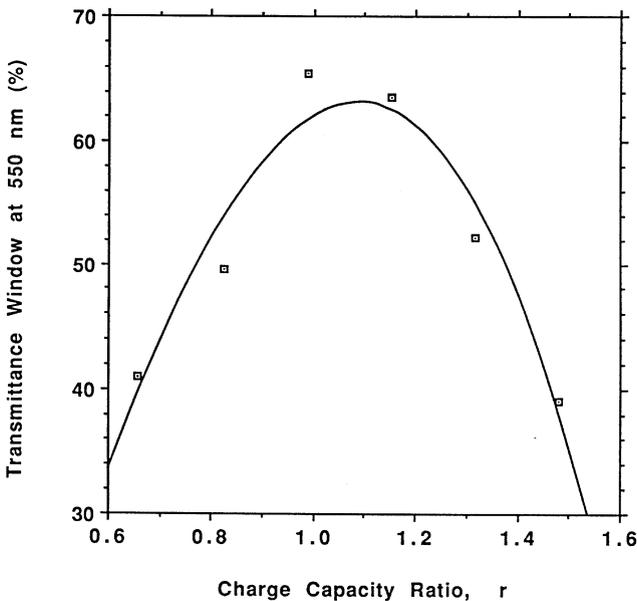


Fig. 2. Transmittance window at 550 nm vs. charge capacity ratio for $A = 155.0 \text{ cm}^2$.

acharge capacities ratio of 0.66, 0.82, 0.99, 1.15, 1.32, and 1.48, respectively. For the first time, we were able to confirm experimentally that the closer the ratio of two charge capacities to unity ($r \rightarrow 1.0$), the wider the transmittance window. In fact, this experimental result is expected by considering the general charge limitation model in a complementary electrochromic system as proposed by Rauh and Cogan [15].

Furthermore, Fig. 2 can be used to explain the closing of the transmittance window, as a result of irreversible oxidations in the H_xWO_3 electrode, for cells left at rest in the darkened state. It is therefore inferred that the key to approaching at-rest stability lies in the ability to first generate and then to maintain balanced charge capacity between the working and the counter electrodes over extended periods of time. Similar trend of $\Delta T_{550,t=0}$ vs. r for electrode size of $2'' \times 3''$ size, with an active area of $4.8 \times 5.4 \text{ cm}^2$, was observed. Again, the value of $q_{PB \rightarrow PW}$ is determined experimentally and found to be 28.47 mC/cm^2 for PB of $2'' \times 3''$.

3.2. Electrochromic performance

The transmittance (at 550 nm) at geometric center and current during cyclic potentiostatic switching, for sample B, is presented in Fig. 3 for the first three cycles. The sample was darkened or bleached by the application of $+1.2$ or -0.6 V , respectively. The voltage is the potential difference between the PB electrode and the tungsten oxide electrode (PB vs. WO_3). These voltages are within the electrochemically safe voltage limits, which were predetermined from cyclic voltammetry of the cell with the same electrochromic configuration. Fig. 4 is a plot of the optical density change at 550 nm, ΔOD , as a function of the charge injected/extracted per unit area, q . This is shown for a fresh sample B. Darkening was done at room temperature. The coloration efficiency of the device, η , is determined from the slope and is $73.5 \text{ cm}^2/\text{C}$ at 550 nm. This value is very close to $75.1 \text{ cm}^2/\text{C}$, a value reported earlier [11] for

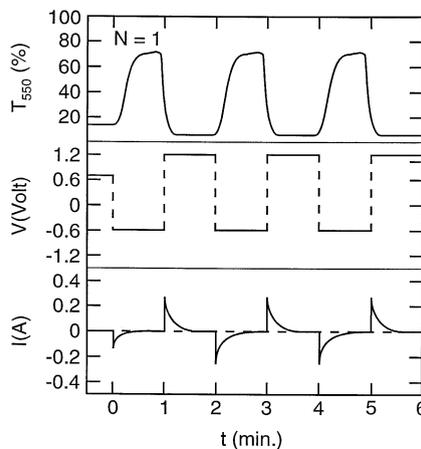


Fig. 3. The transmittance (at 550 nm) and current density during cyclic potentiostatic switching for H_xWO_3 /vsa-vp copolymer/PB.

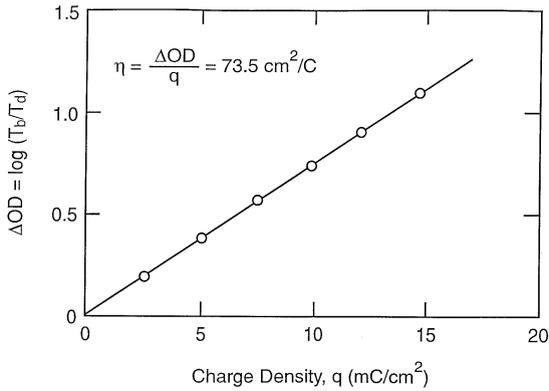


Fig. 4. Change of optical density at 550 nm as a function of charge injection/ejection per unit area.

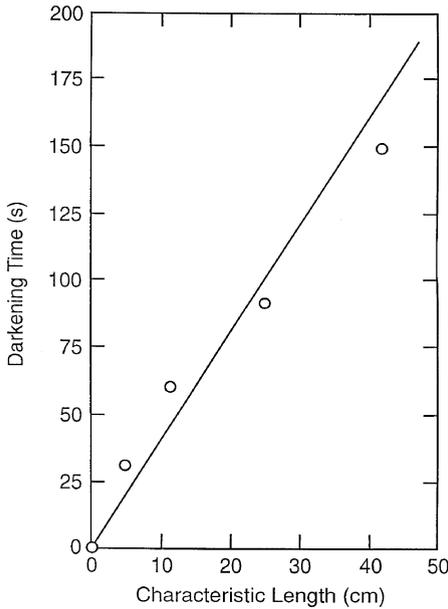


Fig. 5. Darkening times vs. square root of the active area for four samples with the H_xWO₃/vsa-vp copolymer/PB configuration.

a sample of the same size with the configuration WO₃/Poly-AMPS/PB. This implies that the present configuration exhibits a successful insertion/extraction of protons into and out of both tungsten oxide and PB films.

3.3. Size effect

It has been shown by Viennet et al. [16], both theoretically and experimentally, that the switching time of an ECD increases with increasing active area. We found in this

Table 2
Electrochromic samples of various sizes switched at + 1.2 V and – 0.6 V

Samples	Size(cm ²)	$T_{550}(\%)$	ΔOD	$Q(C)$	$\eta(\text{cm}^2/C)$	$t_d(s)/t_b(s)$
A	4.8 × 5.4	3.0 ⇌ 64.5	0.89	0.467	73.9	30/45
B	10.2 × 15.2	6.0 ⇌ 71.5	1.08	2.270	73.5	60/75
C	16.0 × 41.5	4.3 ⇌ 64.5	1.18	11.110	70.3	90/150
D	41.7 × 41.7	5.0 ⇌ 62.0	1.09	24.990	76.1	150/240

work, at constant temperature and switching potentials, that the switching times of an ECD are mainly determined by the size of the sample. Switching times were recorded for four electrochromic samples with different sizes. Fig. 5 plots the darkening times as a function of the square root of the active area for four samples with the $H_xWO_3/2:1$ vsa-*vp* copolymer/PB configuration. It follows from Fig. 5 that the darkening time is proportional to the square root of the active area, regardless of the difference in the aspect ratio among samples. For all four samples switched at room temperature, the bleaching time took approximately 1.5 times as long as the darkening time. Table 2 summarizes the switching results when samples were freshly darkened at + 1.2 V and bleached at – 0.6 V.

4. Conclusions

The main conclusions from this study are:

1. Good compatibility of copolymer of vinylsulfonic acid (VSA) and 1-vinyl-2-pyrrolidinone (VP) with both Prussian blue and WO_3 is verified by the additive coloration efficiency of the complementary $H_xWO_3/2:1$ vsa-*vp* copolymer/PB system, denoted by $H_xWO_3/P(VSA-VP)/PB$.
2. The charge capacities of two electrochromic layers in a complementary ECD have to be matched in order to achieve the maximum optical attenuation range. This was confirmed experimentally by showing that the closer the ratio of two charge capacities to unity ($r \rightarrow 1.0$), the wider the transmittance window.
3. The prevention of the oxidation of H_xWO_3 electrode before assembling is critical for the optimal performance of the complementary electrochromic system.
4. Electrochromic switching time of the complementary $H_xWO_3/P(VSA-VP)/PB$ system is proportional to the square root of the active area, regardless of the difference in shape (aspect ratio) among samples.

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