

The influences of operating voltage and cell gap on the performance of a solution-phase electrochromic device containing HV and TMPD

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Abstract

Electrochromic (EC) behaviors of 1,1'-diheptyl-4,4'-bipyridinium (heptyl viologen; HV) and *N,N,N,N*-tetramethyl-1,4-phenylenediamine (TMPD) were studied spectroelectrochemically. Suitable darkening potentials for HV and TMPD were determined to be -1.3 and -0.3 V (vs. Ag/AgClO₄), respectively, according to voltammetric and spectroelectrochemical measurements. A solution-phase electrochromic device (ECD) was fabricated by sandwiching both HV and TMPD in between two parallel indium tin oxide (ITO) electrodes with an intervening space. The influences of the applied voltage and the cell gap on the single-compartment ECD performance are discussed. The transmittance transients measured at 615 nm suggest that there is no need to darken the ECD beyond 1.0 V, while the ECD can be bleached at 0 V. Self-bleaching was possible with an open circuit. At 615 nm, a typical transmittance change of over 75% was observed. The reversible electrochromism was achieved only when the cell gap was maintained at 0.28 mm or less. Once reversible operating conditions were maintained, a coloration efficiency of 169 cm²/C at 615 nm for the ECD was obtained.

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1. Introduction

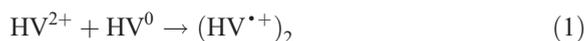
Complementary electrochromic devices (ECDs) [1–4] based on viologens were first studied in the 1970s and can provide high transmittance changes (of over 80%) and fast responses. The response times reported were on the orders of 10–50 ms for darkening and 10–100 ms for bleaching [1,4]. Viologen

is the common name for 1,1'-disubstituted-4,4'-bipyridinium salt since the radical cation of 1,1'-dimethyl-4,4'-bipyridinium (methyl viologen; MV) found by Michaelis and Hill [5] is of violet color. In addition to being used in ECDs [1–4,6], applications of viologens in herbicides [7], electron mediators [8], and catalysts [9] have also been demonstrated. Among viologens, 1,1'-diheptyl-4,4'-bipyridinium (heptyl viologen; HV) is usually used for electrochromic applications because its radical cation salt (denoted as HV^{•+}X⁻, in which X⁻ is the counterion) can form an insoluble violet film on an electrode surface when

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the dication HV^{2+} is reduced to $HV^{•+}$ in aqueous solutions [10]. The nature of the alkyl chain linked to the nitrogen atom of viologen does affect the solubility properties of the resulting reduced form [6,10]. Taking $[HV^{•+}Br^-]$ as an example, the structure of the film is amorphous when reduction begins. Then the phase gradually changes and becomes uneven in successive reactions, and the aging process occurs [11]. It was found that the aging effect is due to the crystallization of $[HV^{•+}Br^-]$ [12] and the dimerization of radical cations in solution to $(HV^{•+})_2$. This radical cation dimer is also formed following the reaction between the twice-reduced compound HV^0 (weakly colored) and the dication HV^{2+} . This phenomenon, called comproportionation [13], is usually observed in aqueous solutions and can be expressed by Eq. (1):



Once the $[HV^{•+}Br^-]$ film is crystallized or dimerization of the radical cation is complete, it is difficult to reoxidize the radical cation to a dication. As a result, yellow-brown stains appear on the electrode [14]. The method to prevent such an aging effect is to add an electron mediator, such as ferrocyanide, into the dication-containing solution [15,16]. The role of an electron mediator is to change the mechanism of the comproportionation (Eq. (1)) so as to prevent dimerization. This involves redox reactions among HV^0 , ferrocyanide, and HV^{2+} [16]. Other

methods use a proper organic solvent [17] and counterions [18] to overcome the aging problem. Also, the comproportionation in the viologen system does not lead to a significant amount of dimer in nonaqueous systems, unless the concentration of cation radicals is very high.

Although relevant studies began as early as the 1970s, patents and commercial products were not produced until the past 10–15 years [17–20] after overcoming the aging effect caused by the radical cation salt of viologen as mentioned. Efforts to improve the performances of viologen-based ECDs have recently been carried out. The memory effect (i.e., maintaining the darkened state) was improved by using a Prussian blue-coated polypyrrole film, which requires a lower level of charges than does a solution-type ECD [19]. A solid-state ECD based on poly-viologen (e.g., poly-(butyl viologen)) was also developed (i.e., used a polyelectrolyte) [21] to improve the sealing problem. Other studies used modified viologen compounds bound covalently or attached to the working electrode [22,23] as a modified electrode. A transmittance change of as high as 90% was achieved and was well displayed by using solution-phase matrix arrays [24]. Table 1 compares results obtained in this work to selected data taken from literature for the ECDs based on viologens. Generally, a transmittance change of 80% and a cycle life of greater than 10^4 can be reached. Possible counterelectrochromic materials are also listed in Table 1. In this study, N,N,N',N' -tetra-

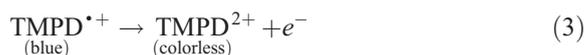
Table 1
Comparison of results obtained in this work with selected data taken from literature

Working material	Counter material	Solvent	Operating voltage (V)	Transmittance change (%)	Cell gap (mm)	Cycle life	Reference
HVBr ₂	–	Water	1	20:1 ^a	N/A	>10 ⁵	[1]
MV(ClO ₄) ₂	BT	DMF	1.5	90–10	0.2	>2 × 10 ⁴	[2]
BV(BF ₄) ₂	DMPZ	PC	1.1	81.5–6.0	0.13	>4 × 10 ⁴	[17]
pBPQ	PP-PB	Water	0.9	70.1–4.5	0.79	>5 × 10 ³	[25]
HV(ClO ₄) ₂	TMPD	CH ₃ CN	0.6	85–1	0.19	N/A	[24]
HV(BF ₄) ₂	TMPD	PC	1.0	75.7–0.2	0.14	>10 ²	This work

HVBr₂ = 1,1'-diheptyl-4,4'-bipyridinium dibromide; MV(ClO₄)₂ = 1,1'-dimethyl-4,4'-bipyridinium diperchlorate; BT = 3-ethyl-2-benzothiazolone; DMF = dimethylformamide; BV(BF₄)₂ = 1,1'-dibenzyl-4,4'-bipyridinium difluoroborate; DMPZ = 5,10-dihydro-5,10-dimethylphenazine; PC = propylene carbonate; pBPQ = poly- N,N' -bis[*p*-(trimethoxysilyl)benzyl]-4,4'-bipyridinium; PP-PB = polypyrrole-Prussian blue composite; HV(ClO₄)₂ = 1,1'-diheptyl-4,4'-bipyridinium diperchlorate; TMPD = N,N,N',N' -tetramethyl-1,4-phenylenediamine; HV(BF₄)₂ = 1,1'-diheptyl-4,4'-bipyridinium difluoroborate.

^a The contrast ratio.

methyl-1,4-phenylenediamine (TMPD) was chosen as the counter material for HV. The electrochemical oxidation of TMPD is formulated in Eqs. (2) and (3):



The radical cation, $\text{TMPD}^{\bullet+}$, has a stable resonance structure and exhibits a blue color. TMPD is an anodic electrochromic material, while HV^{2+} is a cathodic one, but the radical cation, $\text{TMPD}^{\bullet+}$, does not adhere tightly to the electrode surface whereas $\text{HV}^{\bullet+}$ does. For electrochromic applications, a thickener was added to the solution [18] to get a uniform darkening on the electrode. The main purpose of a thickener is to prevent the segregation of $\text{TMPD}^{\bullet+}$ from the electrode, and thus to minimize the possible bleaching recombination between $\text{TMPD}^{\bullet+}$ and $\text{HV}^{\bullet+}$.

Although HV-based ECDs have been widely investigated, only a few studies have addressed the effects of the operating voltage and the width of the cell gap on the performances of ECDs. Fig. 1 illustrates the working principle of a solution-phase ECD composed of HV and TMPD. When an appropriate voltage is applied to the device, the colored species $\text{HV}^{\bullet+}$ and $\text{TMPD}^{\bullet+}$ form and diffuse from the electrode surface to the bulk solution. In fact, both migration and diffusion are needed when describing the motion of each charged species [26,27].

However, a sufficient supporting electrolyte of 0.5 M tetrabutylammonium tetrafluoroborate (TBABF_4) was added so that the migration of active species, HV^{2+} , $\text{HV}^{\bullet+}$, and $\text{TMPD}^{\bullet+}$ can be minimized. Once $\text{HV}^{\bullet+}$ and $\text{TMPD}^{\bullet+}$ meet in the solution, they recombine to become HV^{2+} and TMPD, respectively. The wider the cell gap is, the larger the resistance to mass transfer becomes and the slower the recombination occurs. This not only influences the distribution of the potential between the two electrodes, but also affects the response time when the ECD is darkened or bleached. Increasing the viscosity of the electrolyte, and thus decreasing the diffusivity of each species, can reduce the recombination. When considering the applied cell voltage, undesired reactions have to be prevented. Once the potentials of two electrodes are out of control, undesired reactions, such as the double reduction of HV^{2+} to HV^0 , will occur and then the electrochromism becomes irreversible. Therefore, both the operating voltage and the cell gap are important factors for designing an HV-based ECD.

In this study, HV and TMPD were used as electrochromic materials, tetrabutylammonium tetrafluoroborate was added as supporting electrolyte, and propylene carbonate was chosen as solvent. The electrochromic behaviors of HV and TMPD were studied from voltammetric and spectroelectrochemical measurements. To eliminate the formation of HV^0 and TMPD^{2+} , a suitable potential window was selected from the cyclic voltammogram. According to the results, a solution-phase electrochromic device was

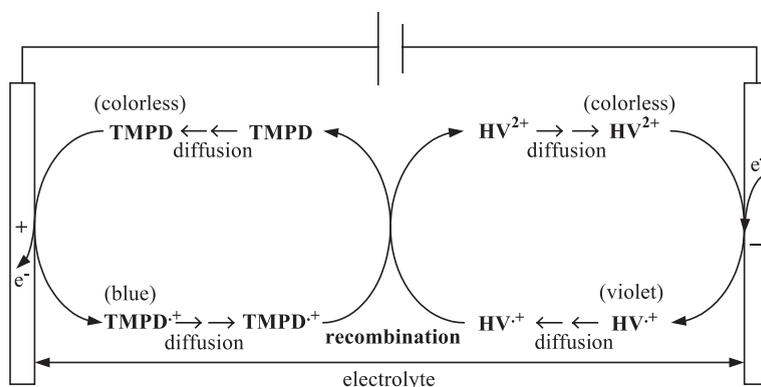


Fig. 1. Working principle of the solution-phase HV/TMPD ECD. Note that only the diffusion process is considered due to the presence of a sufficient supporting electrolyte.

fabricated by sandwiching both HV and TMPD between two parallel indium tin oxide (ITO) electrodes. The cell gap was controlled using a spacer of epoxy tape. Reversible electrochromism was achieved only when the cell gap was kept at 0.28 mm or smaller. Influences of the operating voltage on the cycle life were also evaluated. All of the above findings are thoroughly discussed in this paper.

2. Experimental

2.1. Materials

The main chemicals used in this work were 1,1'-diheptyl-4,4'-bipyridinium dibromide ($C_{24}H_{38}N_2Br_2$; $HVBr_2$), *N,N,N',N'*-tetramethyl-1,4-phenylenediamine ($C_{10}H_{16}N_2$; TMPD), sodium tetrafluoroborate ($NaBF_4$), tetrabutylammonium tetrafluoroborate ($C_{16}H_{36}NBF_4$; TBABF₄), polymethyl methacrylate (PMMA; $M_w = 350,000$), and propylene carbonate ($C_3H_6CO_3$; PC). All of them were ACS reagent grade and were not further purified before use. Here, the tetrafluoroborate ion served as a counterion to obviate the undesired electrodeposition and crystallization of $HV^{•+}$. Heptyl viologen with the BF_4^- counterion was prepared as follows: 1 ml of a saturated $HVBr_2$ aqueous solution was mixed with 1 ml of a saturated $NaBF_4$ aqueous solution. After mixing, the solid $HV(BF_4)_2$ was precipitated, and then the mixture was filtered. The filtered product was dissolved in ethanol and evaporated at 70 °C for recrystallization. The solvent used was PC, supplemented with 0.5 M TBABF₄ as an electrolyte, and $HV(BF_4)_2$ and TMPD as active materials. The ITO-conducting glass substrates, which served as optically transparent electrodes (OTEs), were obtained from a local supplier (Ritek, Hsinchu, Taiwan), and the sheet resistance was around 30 Ω /sq. The ITO substrates were cleaned ultrasonically in a 0.1 N HCl solution for 3 min and then in deionized water for 5 min. Finally, the substrates were dried in air.

2.2. Assembly of the HV/TMPD electrochromic device

An active area of 2×2 cm² was created on an ITO by attaching epoxy tape (3M, USA). The taped ITO was filled with a solution prepared through

dissolving 0.5 M TBABF₄, 2 wt.% PMMA, 0.05 M $HV(BF_4)_2$, and 0.05 M TMPD in the PC solvent. PMMA was also added to the solution to prevent the $TMPD^{•+}$ from peeling from the ITO when TMPD was oxidized on the ITO surface. Another ITO was tightly clipped to the taped ITO to form a sandwich-type device, and then the device was sealed with Torr Seal[®] cement (Varian, MA, USA). Various cell gaps on the ECD were attained by increasing the thickness of the epoxy tape from one layer (0.14 mm) to four layers (0.56 mm).

2.3. Spectroelectrochromic measurements

In the spectroelectrochemical studies of HV and TMPD, a three-electrode electrochemical system was used. The optical path length of the quartz cell was 1 cm. A homemade $Ag/AgClO_4$ [28] was used as the reference electrode, which provided a redox potential corresponding to 0.45 V vs. SCE. The auxiliary electrode was a Pt plate. The in situ spectroelectrochemical properties of $HV(BF_4)_2$ and the ECD were recorded with a potentiostat/galvanostat (model PGSTAT 30; Autolab) and a spectrophotometer (model UV-1601PC; Shimadzu).

3. Results and discussions

3.1. Electrochemical and optical properties of HV and TMPD

The typical cyclic voltammograms of $HV(BF_4)_2$ and TMPD in the PC solution are shown in Fig. 2. While performing cyclic voltammetry for HV, the potential window was constrained between 0 and -1.5 V (vs. $Ag/AgClO_4$) to avoid irreversible dimerization. From the average of the anodic and cathodic peak potentials in Fig. 2a, the approximate formal potential of $HV^{2+}/HV^{•+}$ was estimated to be -1.18 V (vs. $Ag/AgClO_4$). Fig. 2b shows the two-step redox reaction of TMPD. The formal potentials of $TMPD/TMPD^{•+}$ and $TMPD^{•+}/TMPD^{2+}$, judging from the cathodic (I_C , II_C) and anodic (I_A , II_A) peaks, were estimated to be -0.63 and 0.08 V (vs. $Ag/AgClO_4$), respectively. It is worthwhile to mention that no film was observed to form on the electrode and the variation of the transmittance was reversible when

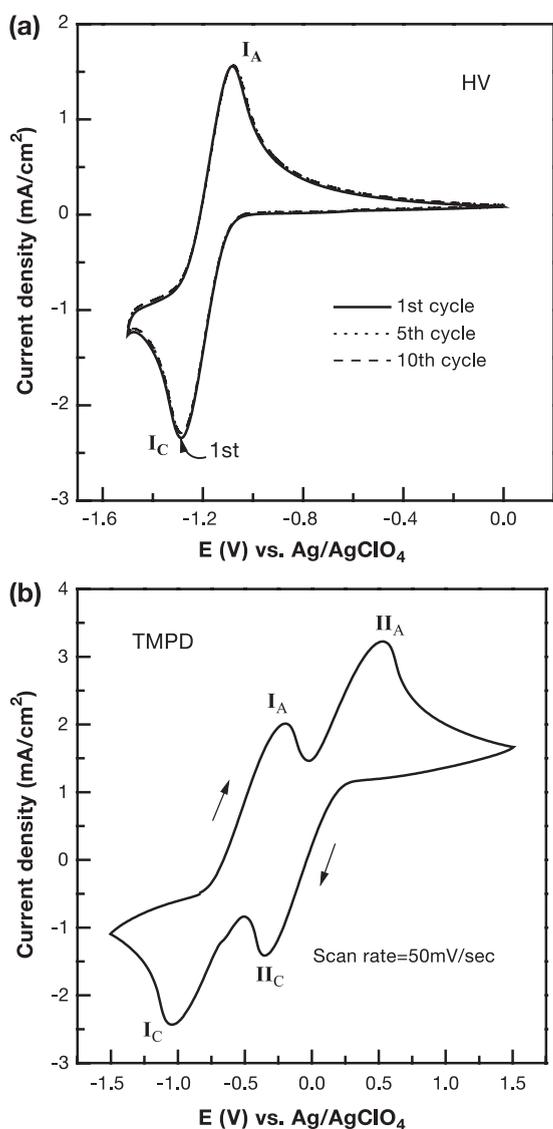


Fig. 2. (a) Cyclic voltammograms of 0.05 M $\text{HV}(\text{BF}_4)_2$ in PC supplemented with 0.5 M TBABF₄. (b) Cyclic voltammogram of 0.05 M TMPD in PC supplemented with 0.5 M TBABF₄. Scan rate = 50 mV/s.

applying double potential steps to a solution containing 0.05 M TMPD in PC supplemented with 0.5 M TBABF₄. This suggests that no film of oxidized polyTMPD is formed on the electrode. The in situ spectra of HVBF_4 on an ITO electrode, treated with different potential steps, are plotted in Fig. 3a. This was done in a solution containing 0.05 M $\text{HV}(\text{BF}_4)_2$

in PC supplemented with 0.5 M TBABF₄, as was used in obtaining Fig. 2a. It can be seen that HV^{2+} obviously darkened when the applied potential was more negative than -1.2 V, which is consistent with the cathodic peak potential in Fig. 2a. When the potential was more negative than -1.4 V, the absorbance reached a saturated value. Although the viol-

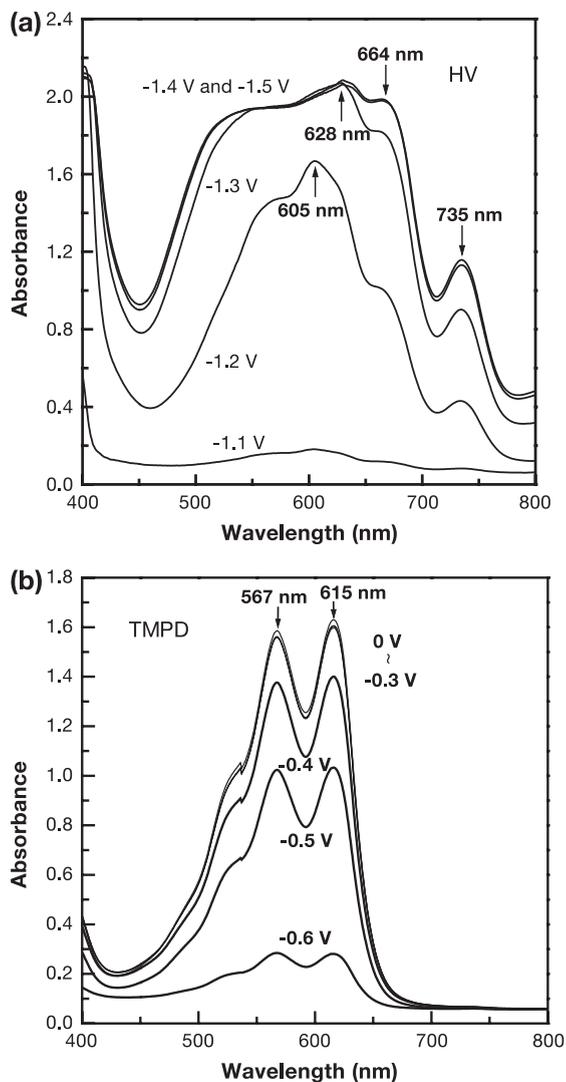


Fig. 3. (a) In situ spectra of HVBF_4 precipitated on an ITO electrode at different potentials (vs. Ag/AgClO_4) after steady-state currents have been established. (b) Spectra of TMPD^{++} in the PC solution taken 100 s after being treated at different potentials (vs. Ag/AgClO_4).

ogen radical cation salts are soluble in most nonaqueous systems, in our experiment, however, the heptyl viologen radical cation ($HV^{•+}$) precipitated onto the ITO surface in a PC solution containing tetrafluoroborate anions upon the application of a negative potential. This is because the solubility product of $[HV^{•+}BF_4^-]$ in PC was not large enough. Since a blue/violet “film” of $HVBF_4$ formed on the ITO surface during the operation, strong absorption from 550 to 650 nm was shown. The coloration efficiency of HV at 615 nm as evaluated by chronopotentiometry was about $100.5 \text{ cm}^2/\text{C}$. Because the colored species $TMPD^{•+}$ did not adhere to the ITO surface, its spectrum was obtained and carefully mixed in PC solution after some potentials were applied. Fig. 3b plots the spectra for $TMPD^{•+}$ in the PC solution taken 100 s after being treated at various potential steps. The solution used was the same as that in obtaining Fig. 2b. Because $TMPD^{2+}$ does not absorb in the visible region, the absorbance of $TMPD^{•+}$ was saturated when the potential was more positive than -0.3 V . The molar absorptivity of $TMPD^{•+}$ in the PC solution at 615 nm was about $9210 \text{ M}^{-1} \text{ cm}^{-1}$. By comparing Fig. 3a with Fig. 3b, $HVBF_4$ features a wide absorption band range from 550 to 650 nm and an absorption peak at 735 nm, whereas $TMPD^{•+}$ is characterized by two absorption peaks at 567 and 615 nm. These two colored species can be distinguished by their spectra based upon differences in their absorbances.

3.2. The effect of cell gap

From the above-mentioned spectroelectrochemical data, the proper potentials for darkening HV^{2+} and TMPD were determined to be -1.3 and -0.3 V (vs. $Ag/AgClO_4$), respectively. Therefore, the solution-phase ECD based on HV and TMPD theoretically prefers the darkening voltage of 1.0 V . When the ECD is darkened, HV^{2+} is reduced at the cathode and TMPD is oxidized at the anode, as illustrated in Fig. 1. Because of the diffusion effect, the cell gap of the ECD affects the recombination and thus switching performance. The ECD transmittance responses for darkening and bleaching under different cell gap conditions are shown in Fig. 4a and are compared in Table 2. All devices were darkened at 0.7 V for 20 s and bleached at 0 V until steady-state transmittance values were reached. All transmittance data reported

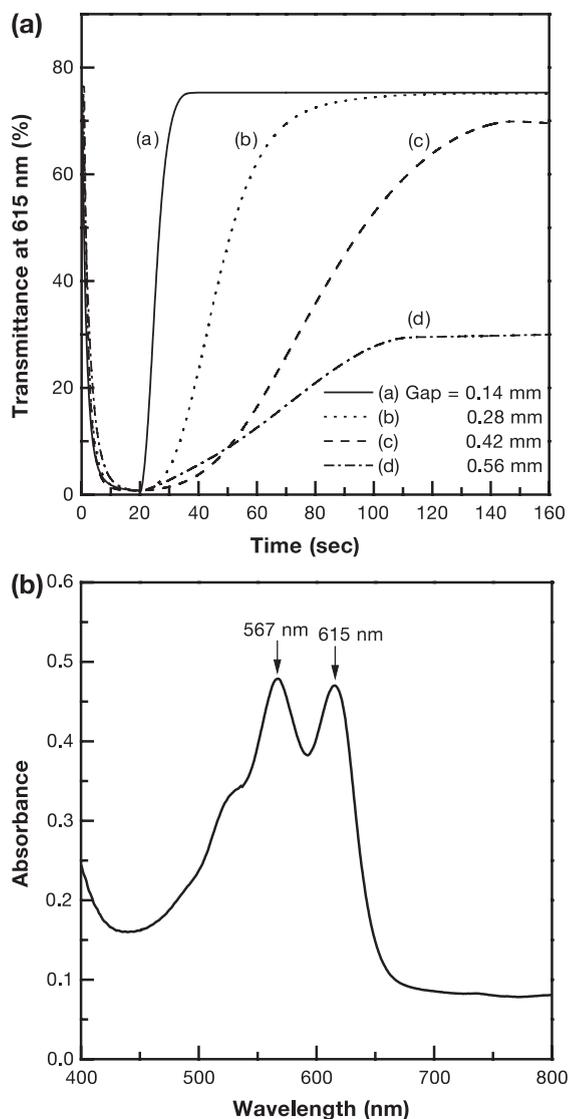


Fig. 4. (a) Transmittance time responses for HV/TMPD ECDs with different cell gaps, obtained by applying a darkening voltage of 0.7 V and a bleaching voltage of 0 V (at $t=20 \text{ s}$, the applied potential was switched from 0.7 to 0 V). (b) Spectroscopic characterization of the residual color in the HV/TMPD ECD with a cell gap of 0.56 mm .

included the optical contribution from both ITO glasses and the electrolyte. It can be seen that the responses of ECDs, both darkening and bleaching, were faster when the cell gap was narrower. It can be deduced that the IR drop in the solution increases as the cell gap increases and thus prolongs the switching

Table 2

Transmittance changes at 615 nm (ΔT_d , ΔT_b) and response times (τ_d , τ_b) for the darkening (0.7 V for 20 s) and bleaching (0 V) of ECDs with different cell gaps (δ)

Cell gap, δ (mm)	Transmittance change		Response time at 0.8 ΔT	
	ΔT_d (%)	ΔT_b (%)	τ_d (s)	τ_b (s)
0.14	75.5	75.5	2.5	8.0
0.28	76.7	75.3	2.9	37.8
0.42	76.5	69.5	3.0	83.9
0.56	74.6	30.0	4.1	70.7

response time. When the cell gaps were larger than 0.28 mm, the bleached state could not be completely recovered. This implies that either $HV^{\bullet+}$ or $TMPD^{\bullet+}$ did not entirely react. Fig. 4b shows the spectrum of the ECD with a cell gap of 0.56 mm. By observing maximum absorbances at 567 and 615 nm but no absorption at 735 nm in Fig. 4b, the incompletely reacted species was thought to be $TMPD^{\bullet+}$. Some portions of $HV^{\bullet+}$ may be oxidized to HV^{2+} by oxygen when $HV^{\bullet+}$ diffuses from the cathodic surface to the solution. Such an oxidation of $HV^{\bullet+}$ interferes with recombination with $TMPD^{\bullet+}$. Hence, a cell gap with 0.14 mm was chosen in the following experiments to obtain optimal electrochromism.

3.3. Effects of operating voltage

The two-electrode CVs of the HV/TMPD ECD (with a cell gap = 0.14 mm) are shown in Fig. 5. The first-step polarization of the redox species in the ECD (i.e., HV^{2+} and TMPD) began when the cell voltage was more positive than 0.4 V. Further polarization of the redox species of $HV^{\bullet+}$ and $TMPD^{\bullet+}$ occurred when the cell voltage exceeded 1.0 V. However, further polarization of $HV^{\bullet+}$ and $TMPD^{\bullet+}$ was not necessary because this does not contribute to the electrochromic effect. Consequently, it was better to maintain the darkening voltage of the ECD at below 1.0 V. Transmittances at 615 nm under different cell voltage conditions are plotted in Fig. 6a. When the darkening voltage was set to between 0.6 and 1.0 V and the bleaching voltage was set at 0 V, a reversible transmittance change of over 80% could be observed. The optical density changes (ΔOD) obtained at different voltages are plotted in Fig. 6b as a function of the injected charge density. The data shown in Fig. 6b were obtained from the same experiment that yielded

Fig. 6a during darkening at two sampling times. Two different sampling times of 10 and 20 s during darkening were selected for comparison. The regressive lines are plotted to fit from 0.4 to 1.0 V. Although it is possible that the capacitive current will reduce the coloration efficiency of the ECD, the value of the steady-state current measured during potential steps suggested that the recombination of $HV^{\bullet+}$ and $TMPD^{\bullet+}$ is the dominating factor responsible for the decrease of electrochromic efficiency at a longer sampling time.

The influences of operating voltage on the cycle life of the ECD were evaluated using the double potential step method. Potential step tests were carried out at three different darkening voltages but with the same bleaching voltage of 0 V. The step time was 5 s for darkening and 20 s for bleaching. Changes in transmittance and charge capacity are plotted in Fig. 7. Fig. 7a shows that the transmittance was most stable when $E_d = 1.0$ V and $E_b = 0$ V. But in the case of $E_d = 1.1$ V and $E_d = 1.2$ V, the transmittance of the bleached state decreased with the number of cycles. The decrease in the bleached state transmittance suggests that $TMPD^{\bullet+}$ did not totally react at $E_d = 1.1$ V and $E_d = 1.2$ V since HV^0 formed and became difficult to be reoxidized during the cycling test. This

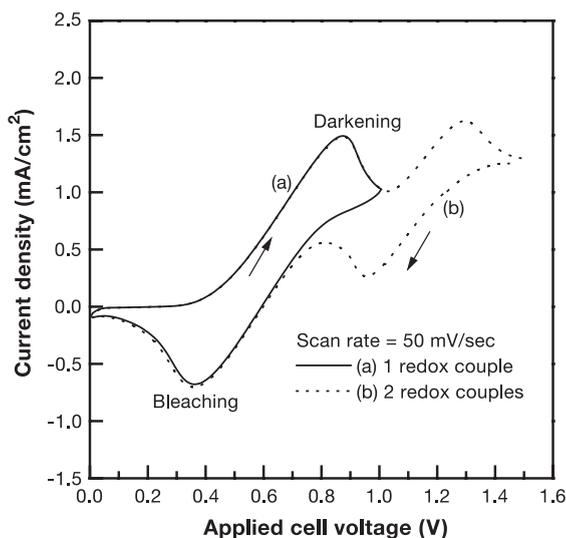


Fig. 5. Two-electrode cyclic voltammograms of a HV/TMPD ECD (cell gap = 0.14 mm) under two operating conditions: (a) 0–1.0 V and (b) 0–1.5 V. Scan rate = 50 mV/s.

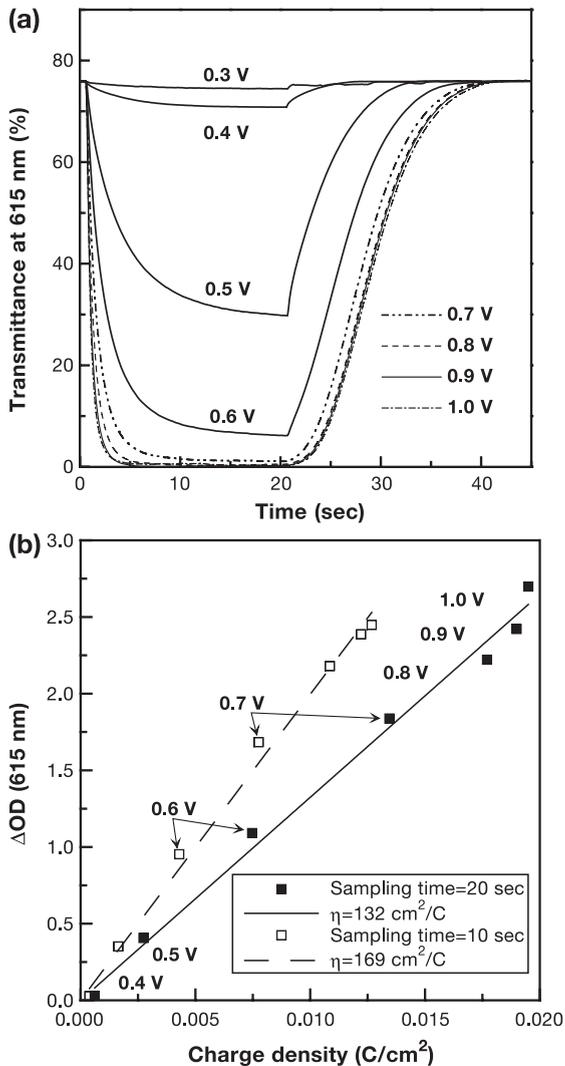


Fig. 6. (a) Transmittance variations at 615 nm by applying different darkening voltages but the same bleaching voltage of 0 V (at $t = 20$ s, the applied potential was switched between the darkening voltage E_d and 0 V). (b) Corresponding optical density changes at 615 nm during darkening as a function of the charge injected per unit area at two sampling times of a HV/TMPD ECD. Two slopes correspond to the coloration efficiency for two sampling time measurements with the applied cell voltage up to 1.0 V.

is judged by the similarity between the cell spectrum of the bleaching state at $E_d = 1.2$ V and the spectrum of TMPD^{*+} , both showing the absorbance peaks at 567 and 617 nm. Fig. 7b plots the darkening coloration efficiency ($\Delta OD_d/q_d$) as a function of the cycle number. ΔOD_d and q_d are the optical density change

and charge capacity recorded during darkening of the ECD, respectively. It is reasonable that the efficiency values in Fig. 7b are larger than those in Fig. 6b because the saturated transmittance was not attained by 5 s. It was found that the values of coloration efficiency for both $E_d = 1.1$ V and $E_d = 1.2$ V were smaller than that of $E_d = 1.0$ V and decreased during

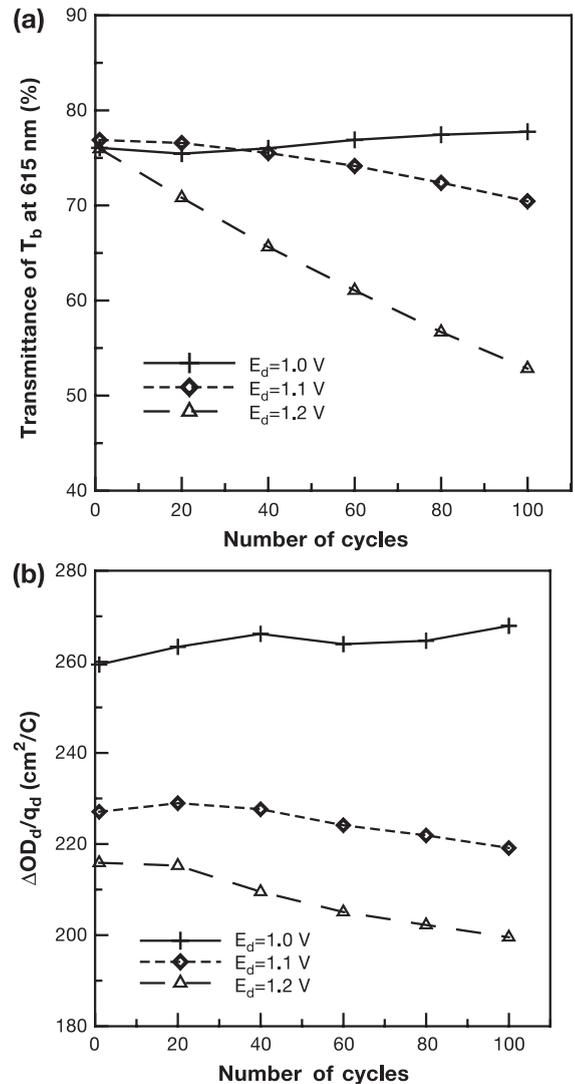


Fig. 7. (a) Variations in the bleached state transmittance (T_b) of HV/TMPD ECDs during 100 switching cycles. (b) Variations in the darkening coloration efficiency ($\Delta OD_d/q_d$) during 100 switching cycles. The switching test was carried out using the potential step method. The step time was 5 s for darkening and 20 s for bleaching.

cycling. At higher darkening voltages, the formation of two nonabsorbing species, HV^0 and $TMPD^{2+}$, resulted in the decrease of the coloration efficiency of the ECD measured during an experiment of darkening. According to the above preliminary data, the HV/TMPD ECD can be reversibly switched at least 100 times.

4. Conclusions

A complementary solution-phase electrochromic device based on HV and TMPD was fabricated, and the influences of cell gap and operating voltage on switching behavior were discussed. Based on spectroelectrochemical studies of HV^{2+} and TMPD, we found that the ECD does not need to be darkened above 1.0 V. By applying a darkening voltage more positive than 0.6 V, a reversible transmittance change of over 75% could be attained at 615 nm. The cell gap between the two electrodes was observed to be an important factor. The cell gap affects the diffusion and recombination nature of HV^{*+} and $TMPD^{*+}$. We found that reversible darkening and bleaching were achieved only when the cell gap was less than 0.28 mm. If the cell gap was larger than 0.28 mm, the $TMPD^{*+}$ was not completely reduced, thus contributing to residual color in the solution. Also, this increased the IR drop in the solution and retarded the electrochromic response. If the darkening voltage was above 1.0 V, HV^0 is formed, resulting in an irreversible decay in the transmittance of the ECD. Thus, it is important to apply an operating voltage of below 1.0 V. We also observed that the coloration efficiency of the solution-type ECD was time-dependent.

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