A COMPLEMENTARY ELECTROCHROMIC SYSTEM BASED ON A PRUSSIAN BLUE THIN FILM AND A HEPTYL VIOLGEN SOLUTION

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1. Introduction

Many electrochromic (EC) materials have been investigated and found applications in displays, anti-glared mirrors, and solar-attenuated windows. A complementary electrochromic device (ECD) is the device in which both anodic and cathodic EC materials color or bleach in phase, thus a higher coloration efficiency can be achieved.

According to working principles of two EC materials within the complementary ECD, three types of devices could be categorized: (a) solution type, (b) precipitation type, and (c) thin-film type[1]. In this study, a new film/solution type complementary ECD based on a PB thin film and a heptyl viologen (HV) solution is described.

PB (iron (III) hexacyanoferrate (II))[2-3] is a pivotal inorganic EC material possesses four redox states: Everitt’s salt (ES), Prussian blue (PB), Berlin green (BG), and Prussian yellow (PY). With respect to viologen (1,1'-disubstituted-4,4-bipyridilium salt)[4], it has three redox states including dication (V^2+), radical cation (V^+), and di-reduced (V^0) states. By choosing the anodically colored ES/PB system and the cathodically colored V^2+/V^+ system, a complementary ECD possesses reversible, colorless-to-blue electrochromism can be realized.

2. Experimental

Indium-doped tin oxide (ITO) glasses (Ritek Display, Hsinchu Industrial Park) were used as the substrates (Rsh < 30 Ω/sq.) for the deposition of PB thin films. The PB films were electrodeposited from a solution containing 10 mM FeCl_3∙6H_2O, 10 mM K_3Fe(CN)_6, 0.1 M KCl and 0.1 M HCl. A constant cathodic current density of 20 µA/cm² was applied to the ITO substrate for 5 min.

In order to prepare the HV^2+ containing solution, the HV(BF_4)_2 powder was obtained first[4]. Afterward, the HV(BF_4)_2 powders were dissolved into an equal volume mixture of deionized water and iso-propanol with KCl in it. The solution was adjusted to pH = 2.5 by HCl. After the precipitant subsided, the HV(BF_4)_2 solution was obtained by collecting the upper layer of the solution. A PB film-coated and a bare ITO glasses were used to assemble the PHECD (ITO/PB/HV(BF_4)_2 in solution/ITO). The torr seal® (Varian) is used to seal around the ECD to prevent solution leakage.

3. Results and Discussions

Fig. 1 (a) and (b) show the double potential-step experiments with different anodic applying potentials for a PB thin film and the corresponding transmittance changes. The transmittances of the PB film reach different steady state values according to various oxidative applying potentials. The maximum transmittance window at 609 nm is 52%, which is obtained by applying the potentials between 0.5 V and 0 V. Fig. 2 (a) and (b) show the current responses and the corresponding transmittance changes of a HV(BF_4)_2 solution under double potential-step experiments with various reductive applying potentials. In comparing with the behavior of a PB film, as shown in Fig. 1, the current responses of a HV(BF_4)_2 solution approaching steady-state values other than zero, an extra current is required in supplying new HV^+ to maintain the equilibrium between the solution and the absorbed film.
As shown in Fig. 2 (b), the transmittance changes are difficult to restore to the initial value, this is because part of the HV$$^{++}$$ can’t be oxidized and diffuse back to the solution if the reductive applying potential is more negative than –0.55 V.

For a complementary ECD, its performance is greatly affected by the charge capacity ratio of the two electrodes. Theoretically, the transmittance window and the coloring efficiency of an ECD will reach a maximum value if the charge capacity ratio is equal to unity\textsuperscript{[5]}. Unlike thin-film ECDs, in which the charge capacities for both electrodes can be predetermined, the charge capacity of the PHECD, however, is time-dependent. Depending on the chosen operating potentials of the PHECD, different darkening times are required to darken the ECD safely.

Fig. 3 shows the current responses and the corresponding transmittance changes of a PHECD, which is switched between 0 V and 1.0 V for the first 100 cycles. A darkening potential of 1.0 V is applied for 8 seconds, which is predetermined by equalizing the charge capacities of the HV(BF\textsubscript{4})\textsubscript{2} solution (calculated from the integration of i-t curve in Fig. 2 (a)) to that of the PB film (calculated from area under the anodic peak in Fig. 1 (a)). Because it takes a longer time for the absorbed HV$$^{++}$$ to diffuse back into the solution, a potential of 0 V is applied for 100 seconds to bleach the PHECD. The transmittance window of the PHECD measured at 609 nm is 70% for operating potentials of 0 V (95%) and 1.0 V (25%).

For most of the complementary ECDs based on two solid films, one of the two films must be pre-darkened or pre-bleached before assembling. In this study, no pretreatment is needed, and thus making it superior as far as the cell assembling is concerned.

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References
Fig. 1 (a) Current – time response, and (b) transmittance spectra of a PB thin film measured at different oxidizing potentials.

Fig. 2 (a) Current – time response, and (b) transmittance spectra of a 0.05 M HV(BF₄)₂ solution measured at different reducing potentials.
Fig. 3 (a) Current – time response, and (b) transmittance spectra of the PHECD for the first 100 cycles. $E_d = 1.0\, \text{V for } 8\, \text{sec}; E_b = 0\, \text{V for } 100\, \text{sec}.$