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A complementary electrochromic system based on Prussian blue and indium hexacyanoferrate

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Abstract A new complementary electrochromic device (ECD) based on Prussian blue (PB), indium hexacyanoferrate (InHCF), and KCl-saturated poly(2-acrylamido-2-methylpropanesulfonic acid) (K-PAMPS) was proposed and studied in this work. This novel PB-InHCF ECD (PIECD) exhibits blue-to-yellowish electrochromism with a high coloration efficiency of ca. $103 \text{ cm}^2/\text{C}$ at 690 nm. Although the operating voltages for the fully bleached and fully colored states were determined to be 1.2 V and 0 V (InHCF vs. PB), respectively, the major transmittance modulation occurs within a much narrower voltage window (0.9 V \leftrightarrow 0.5 V). That is, the PIECD is energetically favorable. Furthermore, it is unnecessary to precolor either electrochromic (EC) electrode during the cell assembly so that the charge balance between two electrochromic films becomes much easier. In addition to the above performance, the compatibility between the K-PAMPS electrolyte and EC electrodes was also demonstrated. In short, this work proposes another promising PB-based ECD and provides a new choice in the EC field.

Keywords Complementary electrochromic device · Indium hexacyanoferrate · Operating voltages · Poly(2-acrylamido-2-methylpropanesulfonic acid) · Prussian blue

Introduction

Electrochromic devices (ECDs) are electrochemical cells showing color changes upon a change in the cell voltage.

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To date, they have been investigated for applications in optical switching, such as seven-segment displays [1], anti-glare mirrors [2], and solar-attenuated windows [3]. To achieve higher coloration efficiency and better electrochemical reversibility, it has been suggested to assemble an ECD with two electrochromic (EC) electrodes, which exhibit “complementary” EC behavior and are compatible with the same electrolyte. Such an ECD is called a complementary ECD [4, 5, 6]. On the basis of the enhanced InHCF electrodeposition [7], a new complementary ECD based on Prussian blue (PB) and indium hexacyanoferrate (InHCF) is described here.

PB [iron(III) hexacyanoferrate] [8, 9] is a pivotal inorganic EC material. It shows polyelectrochromic features and has four redox states: the colorless Everitt's salt (ES), PB, Berlin green (BG), and Prussian yellow (PY), from the most reduced to the most oxidized state. With respect to InHCF [10, 11, 12], it is a PB analogue and exhibits a light, colorless-to-yellowish color change when being oxidized. It has been known that both of the EC reactions for PB and InHCF are accompanied by the insertion or extraction of monovalent cations. Among the monovalent cations, K^+ is the best candidate for both thin films [8, 9, 10, 11, 12, 13]. Moreover, it was reported that a PB electrode prefers an electrolyte with a moderate acidity, say pH 2–3, to attain the high reversibility of its EC reactions [14]. According to the similarity between PB and InHCF, presumably the acidity effect holds true for the EC reactions of InHCF. Therefore, by choosing the anodically colored PB electrode and the quasi-transparent InHCF electrode, a PB-InHCF ECD (PIECD) employing a K^+ -containing electrolyte is expected to possess a reversible, blue-to-yellowish electrochromism.

As for the cell assembly of the PIECD, precoloration is not required for both PB and InHCF. This is because InHCF exhibits light electrochromism and can be considered as a quasi-transparent counter-electrode [15]. In contrast, most of the WO_3 -based ECDs [4, 5, 6] need precoloration to achieve the complementary EC performance. Such a precoloration step increases the

complexity during scaling up and is difficult to control in the presence of air or moisture. As a consequence, InHCF is superior in precoloration to WO_3 from the viewpoint of eliminating the step when assembled with PB.

To assemble the PIECD, the KCl-saturated poly(2-acrylamido-2-methylpropanesulfonic acid) (K-PAMPS) electrolyte is employed. The K-PAMPS electrolyte is modified from poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS, a polyelectrolyte of H^+) [16, 17] to accommodate the conduction of K^+ and to provide a moderate acidity for the redox processes of PB and InHCF. Spectroelectrochemical studies on PIECD are here concerned mainly with the choice of the operating voltages and the dynamic and static in situ optoelectrochemical characteristics. The compatibility between hexacyanoferrate films and the K-PAMPS electrolyte will also be confirmed. In short, this work is to demonstrate the feasibility of the novel PIECD.

Experimental

All chemicals were reagent grade and were used as received. Deionized water (DIW) was used throughout this work. Optically transparent F-doped SnO_2 -coated (FTO) glass substrates ($R_{\text{sh}} = 20 \text{ } \Omega/\text{sq.}$, $T_{550\text{nm}} = 80\%$; Sinonar Corporation, Hsinchu, Taiwan) with an active area of $3.0 \times 1.5 \text{ cm}^2$ were used as the conducting substrates for the electrodeposition of EC thin films. Before using, the FTO substrates were cleaned and prepared according to a standard procedure described elsewhere [7].

When preparing a PB thin film, the deposition bath contained 10 mM FeCl_3 , 10 mM $\text{K}_3\text{Fe}(\text{CN})_6$, 0.1 M KCl, and 1 M HCl, and a constant cathodic current density of $20 \text{ } \mu\text{A}/\text{cm}^2$ was applied to the FTO substrate for 250 s. For the electrodeposition of an InHCF film, the plating solution was prepared according to an improved procedure [7] and was composed of 10 mM InCl_3 , 10 mM $\text{K}_3\text{Fe}(\text{CN})_6$, 1 M KCl, and 1 M HCl. While plating, a potential scanned back and forth between 0.2 and 1.3 V (vs. Ag/AgCl/sat. KCl) at a rate of 200 mV/s was exerted on the FTO substrate for six cycles.

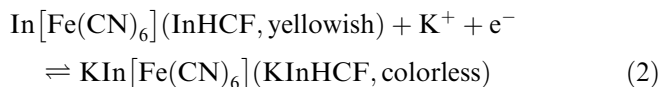
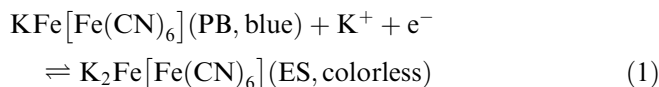
The PAMPS and K-PAMPS electrolytes were prepared by UV polymerization. The procedures were modified from those reported by Giglia [17]. An AMPS monomer solution for the formation of PAMPS was prepared as follows: 9.8 g of AMPS monomer was first dissolved into 10 mL water, and then 0.3 mL of tetra(ethylene glycol diacrylate) (TEGDA) was dropped into this solution as a cross-linking agent. The solution was stirred for 15 min at room temperature. Afterward, 0.01 g of benzoin methyl ether (BME), the initiator, was added and the resulted AMPS monomer solution was stirred for another 15 min before UV curing. Regarding the monomer solution for K-PAMPS, it was prepared in the same manner except the solution was saturated with KCl. When curing, both PAMPS and K-PAMPS were formed in a rectangular casting mold with inner dimensions of $3.0 \times 1.5 \times 0.2 \text{ cm}^3$ under an exposure of ca. $675 \text{ } \mu\text{W}/\text{cm}^2$ UV irradiation (Spectroline, SB-125) for 3 min.

When assembling a PIECD, a PB film and an InHCF film faced each other and sandwiched in between was the K-PAMPS or PAMPS electrolyte (with a thickness of 2 mm). Then the PIECD was clipped tightly and sealed with Torr Seal glue (Varian, USA) before testing. Afterward, three-electrode cyclic voltammetry (CV) was performed, using the same potentiostat/galvanostat (Autolab, model PGSTAT30), to characterize the PB and InHCF films individually in the K-PAMPS electrolyte and to provide necessary information for determining the operating voltages of a PIECD. To characterize the PIECD, two-electrode methods were employed,

including in situ spectroelectrochemical measurements for determining the EC performances and a 100-scan CV for evaluating the cycling stability.

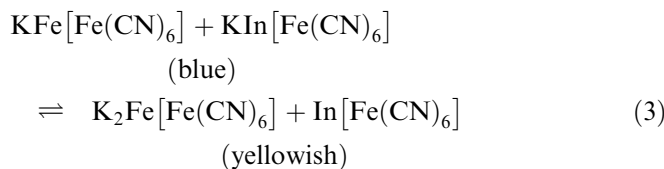
Results and discussions

The redox reactions for the PB and InHCF films in the presence of K^+ ions have been proposed as follows [8, 9, 10, 11, 12]:



To further illustrate the redox features for PB and InHCF, Fig. 1a and Fig. 1b give the CVs for PB and InHCF obtained in the K-PAMPS electrolyte at a scanning rate of 5 mV/s, respectively. It can be seen that the cathodic peak of PB is sharper and larger than the anodic peak (Fig. 1a), whereas the cathodic peak of InHCF is flatter and smaller than the anodic peak (Fig. 1b). This implies that the reduction at the PB electrode (PB \rightarrow ES), which shows blue-to-colorless electrochromism, is faster than the oxidation (coloration, ES \rightarrow PB); in contrast, InHCF shows rapid kinetics in oxidation, a colorless-to-yellowish EC reaction, rather than in reduction (bleaching). Of course, such kinetic features will affect the EC responses of a PIECD. Besides, it was observed experimentally that both PB and InHCF films show excellent cycling ability when using the K-PAMPS electrolyte, whereas much poorer cycle lives for both PB and InHCF were obtained when employing the PAMPS electrolyte. Presumably, the conduction of K^+ in the K-PAMPS electrolyte is responsible for the improvement of the cycle life. A detailed comparison between PAMPS and K-PAMPS on the cycling stability of the PIECD will be discussed later.

According to Eqs. 1 and 2, the overall EC reaction for a PIECD is given as follows:



The left-hand-side terms in Eq. 3 show redox species at the fully colored state, as well as the as-assembled state; the right-hand-side terms are for the fully bleached state. Accordingly, the PIECD exhibits blue-to-yellowish electrochromism. Concerning the operating voltages for a PIECD corresponding to the fully bleached

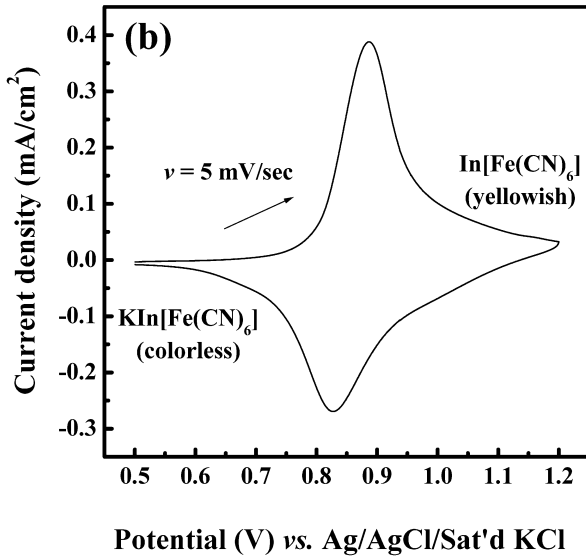
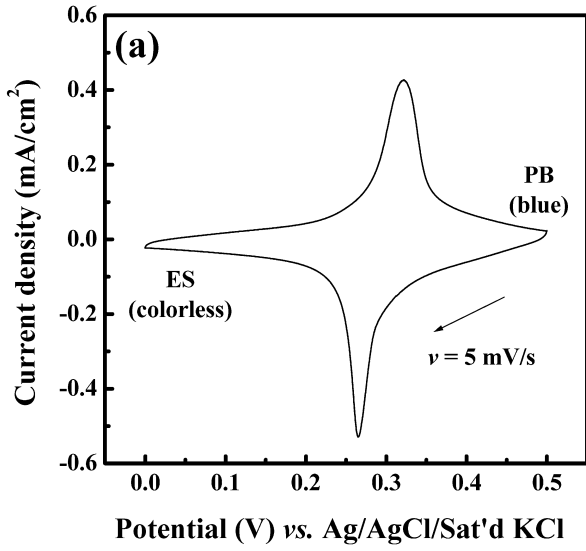


Fig. 1. Three-electrode CVs for (a) PB and (b) InHCF in the K-PAMPS electrolyte

(charged) and the fully colored (discharged) states, they were determined as follows:

$$V_{\text{PIECD}}^{\text{colored}} = E_{\text{KInHCF}} - E_{\text{PB}} = 0.5 - 0.5 = 0\text{V} \quad (4)$$

$$V_{\text{PIECD}}^{\text{bleached}} = E_{\text{InHCF}} - E_{\text{ES}} = 1.2 - 0 = 1.2\text{V} \quad (5)$$

where E_{PB} , E_{ES} , E_{InHCF} , and E_{KInHCF} were estimated from the scanning boundaries in PB's voltammogram (Fig. 1a) and InHCF's voltammogram (Fig. 1b). That is, to bleach the PIECD is to charge (polarize) the cell; on the contrary, to color the device is simply to short its two electrodes. The validity of these operating voltages is demonstrated in Fig. 2, which gives a definite, reversible two-electrode CV for a PIECD. In addition, the reversibility for the corresponding transmittance modulation was confirmed experimentally by an in situ

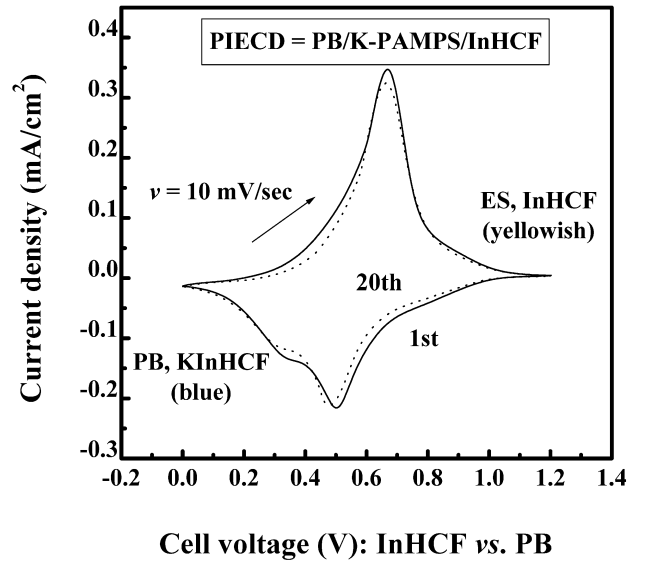


Fig. 2. Two-electrode CV of the PIECD (solid line: 1st scan; dashed line: 20th scan)

spectroelectrochemical measurement. Also, Fig. 2 shows that the voltammetric wave for the bleaching (the charging process) is sharper and larger than that for the coloration (the discharging process). This means that, for a PIECD, the response time required for bleaching is shorter than that for coloring, which can be predicted from the CV characteristics of PB and InHCF (Fig. 1).

Figure 3 gives the equilibrated transmittive spectra (from 400 nm to 800 nm) for a PIECD recorded at different applied voltages (V_{PIECD}). When increasing V_{PIECD} to bleach the device, there is no significant change of spectrum until $V_{\text{PIECD}} = 0.5$ V. By increasing the applied voltage, the blue-to-yellowish electrochromism takes place and leads to a decrease in the absorption band at ca. 690 nm but an increase at ca. 410 nm. After reaching $V_{\text{PIECD}} = 0.9$ V, i.e., when the bleached (yellowish) state is attained, the spectrum is almost identical to that obtained at $V_{\text{PIECD}} = 1.2$ V, the fully bleached state. According to the above observation, it is deduced that a PIECD can be operated in a very narrow voltage range as small as 0.4 V (from 0.5 V to 0.9 V) and still have an optical performance similar to that operated between 0 V and 1.2 V. This suggests that a PIECD is extremely favored for energy-saving considerations. Furthermore, Fig. 3 shows that the transmittance modulation at 690 nm gives the largest value, ca. 45%, although a transmittance window of 45% was obtained when the less transparent FTO glass substrates were used. Therefore, if a more transparent substrate is used, a PIECD has the potential to become a superior blue-color filter or EC display. Of course, it is equally applicable for solar-attenuated or anti-glare purposes.

In Fig. 4, the cycling reversibility of a PIECD using the PAMPS electrolyte (Fig. 4a) is compared with that of a PIECD using the K-PAMPS electrolyte (Fig. 4b). It is shown that a PIECD using the K-PAMPS electrolyte

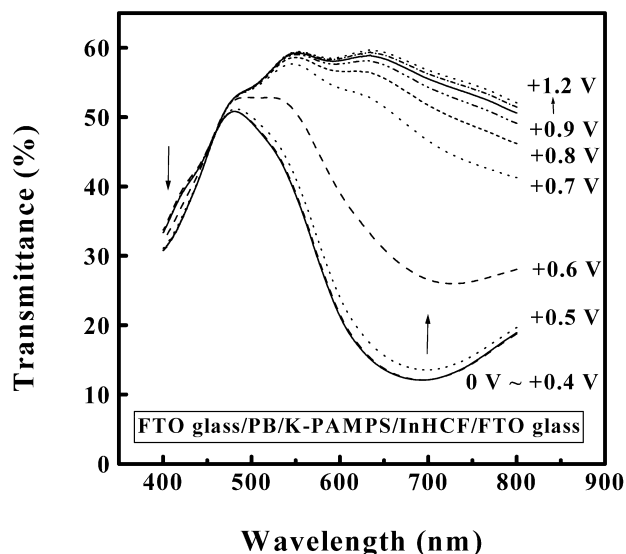


Fig. 3. Equilibrated transmittance spectra of the PIECD measured at different applied cell voltages. The optical influences of FTO glass substrates and K-PAMPS are not excluded

can be cycled reversibly 100 times without losing coulometric capacity, whereas the device employing PAMPS shows poor electrochemical stability, in which only ca. 20% capacity is retained after 40 cycles. Presumably, this is because both PB and InHCF films are compatible with a K^+ -containing electrolyte, especially for an electrolyte with a moderate acidity [14]. Therefore, the successful applicability of the K-PAMPS electrolyte to the PB-InHCF complementary system is demonstrated.

Conclusions

In this paper, we have demonstrated the feasibility of a new complementary system based on PB, InHCF, and the K-PAMPS electrolyte, namely PIECD. With promising electrochemical and spectral properties, the PIECD exhibits blue-to-yellowish electrochromism. According to the CVs for PB and InHCF, the operating voltages corresponding to the fully bleached and fully colored states are determined to be 1.2 V and 0 V, respectively. That is, to color the PIECD is simply to short the two electrodes of the device. Moreover, it is verified from equilibrated spectra that the PIECD can be operated between 0.9 V and 0.5 V without a significant decrease in transmittance modulation. Such a narrow voltage window of 0.4 V indicates that the PIECD is energetically favored. In addition, neither PB nor InHCF film needs precoloration during cell assembly, so a precise control on the charge balance between the two electrochromic electrodes can be attained easily. Moreover, the PIECD, the first complementary system composed of two transition metal hexacyanoferrate thin films, shows high electrochemical compatibility with the K-PAMPS electrolyte. Logically, the modification of PAMPS, a

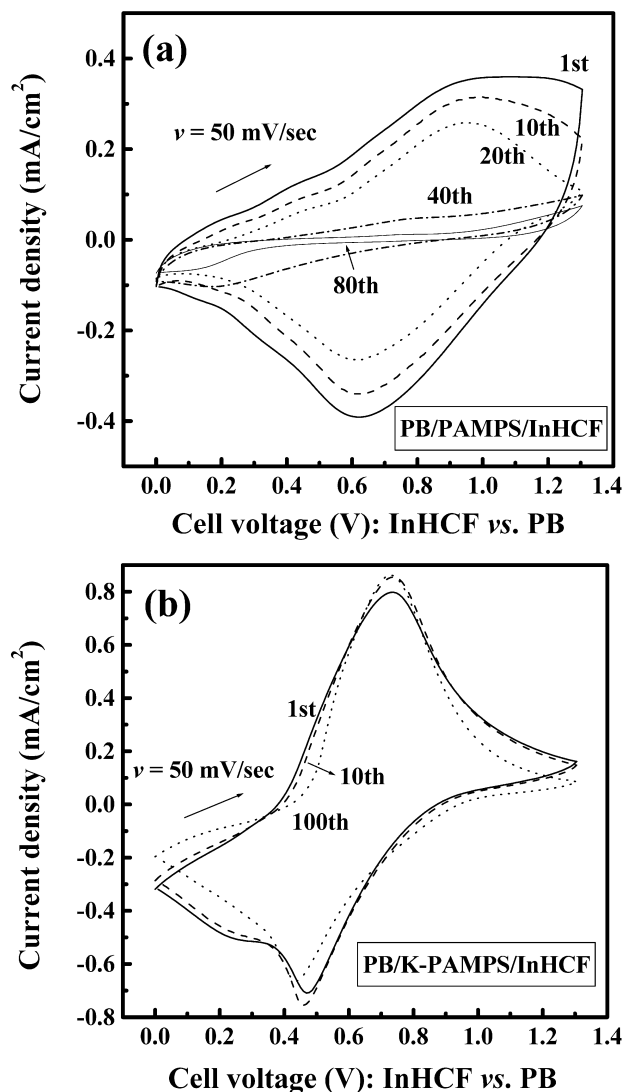


Fig. 4. Two-electrode CVs, showing the cycling reversibility and compatibility for (a) the PIECD using the PAMPS electrolyte and (b) the PIECD using the K-PAMPS electrolyte

polyelectrolyte of H^+ , by saturating with KCl can successfully accommodate the conduction of both K^+ and H^+ . To sum up, it is believed that the PIECD will become another promising PB-based complementary ECD following the well-developed PB- WO_3 ECD and will promote the successful introduction of other feasible InHCF-based complementary ECDs.

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