

Organic Multiviologen Electrochromic Cells for a Color Electronic Display Application

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ABSTRACT: The electrochromic (EC) and optical properties of three new viologen compounds containing 1,1'-di-*n*-heptyl-4,4'-bipyridinium dibromide (DHBPDB; C₂₄H₃₈Br₂N₂), 1-heptyl-4-(4-pyridyl)pyridinium bromide (HPPB; C₁₇H₂₃BrN₂), and 1,1'-dis-(*p*-cyanophenyl)-4,4'-bipyridinium chloride (DCBPC; C₁₂H₈N₂OBr₂) for potential use in electrochromism applications were investigated. The repetitive stability of all of the EC cells could be improved through the addition of ferrocene as an electron donor (a counter redox material) to the electrolyte solution under several redox cycles. The experimental results demonstrate that the EC cell showed a reversible color change from clear (tintless) to three different colors with the application of electrochemical stimuli at specific potentials. The color of the EC cells turned red, green, or blue upon electrochemical reduction for DHBPDB, HPPB, and DCBPC in indium tin oxide sandwich-type cells. Because of the different viologen molecules competing to capture electrons and affecting the EC efficiency and life of the multiviologen cells, they could be improved by the optimization of the working voltage in the multiviologen cells from the modification of an operative potential based on the cyclic voltammetry measurements. In this article, we propose a prototype device of multicolor electrochromic display, which provides potential application for multicolor electronic displays or EC paper. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40485.

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INTRODUCTION

Viologen-type organic electrochromic (EC) compounds of interest have been widely investigated because of their various application fields, such as herbicides, photonic sensors, electron transfer devices, displays, and antiglare mirrors.^{1–10} EC materials show color changes from clear to three primary colors, red, green, and blue, which is required to realize full color in electronic paperlike imaging devices. Viologens naturally stay in a di-cation state without any applied potential, and this results in transparency. When an appropriate potential is applied to a viologen, it is reduced to a radical cation state and shows a specific color. Viologens have advantages for EC devices because of their low driving voltage for visual changes, high contrast, and simple cell construction.¹⁰ Hence, the stacking of three primary colored viologens in a single cell could result in differently colored cells. However, the EC mechanisms of multiviologen cells have not clearly been investigated in the past.

In this study, we studied the EC and optical properties of multiviologen cells under different applied potentials. Three different kinds of EC materials containing 1,1'-di-*n*-heptyl-4,4'-

bipyridinium dibromide (DHBPDB), 1-heptyl-4-(4-pyridyl)pyridinium bromide (HPPB), and 1,1'-dis-(*p*-cyanophenyl)-4,4'-bipyridinium chloride (DCBPC) showed color changes from clear (tintless) to three primary colors: blue, red, and green. The EC display exhibited a relatively high contrast, fast response, and low current consumption (<5 mA) when a low voltage (~3 V) was applied. These viologens were used as raw materials the multiviologen cells. To improve the repetitive properties between the coloring and bleaching of the cells with three different derivatives, ferrocene (Fc) was used as a counter redox species. Moreover, detailed information on the electrochromic characteristic in the prototype of multiviologen cells is provided.

EXPERIMENTAL

DHBPDB (Tokyo Kasei Kogyo Co., Ltd., Japan), HPPB (Sigma-Aldrich), and DCBPC (homemade) were used as EC materials. The fabrication process of DCBPC followed the method reported by Ryu et al.¹¹ Propylene carbonate (PC; 99.7%, Sigma-Aldrich) and Fc (Koch-Light Laboratories, Ltd., South Africa) were used as the solvent and counter redox species, respectively.

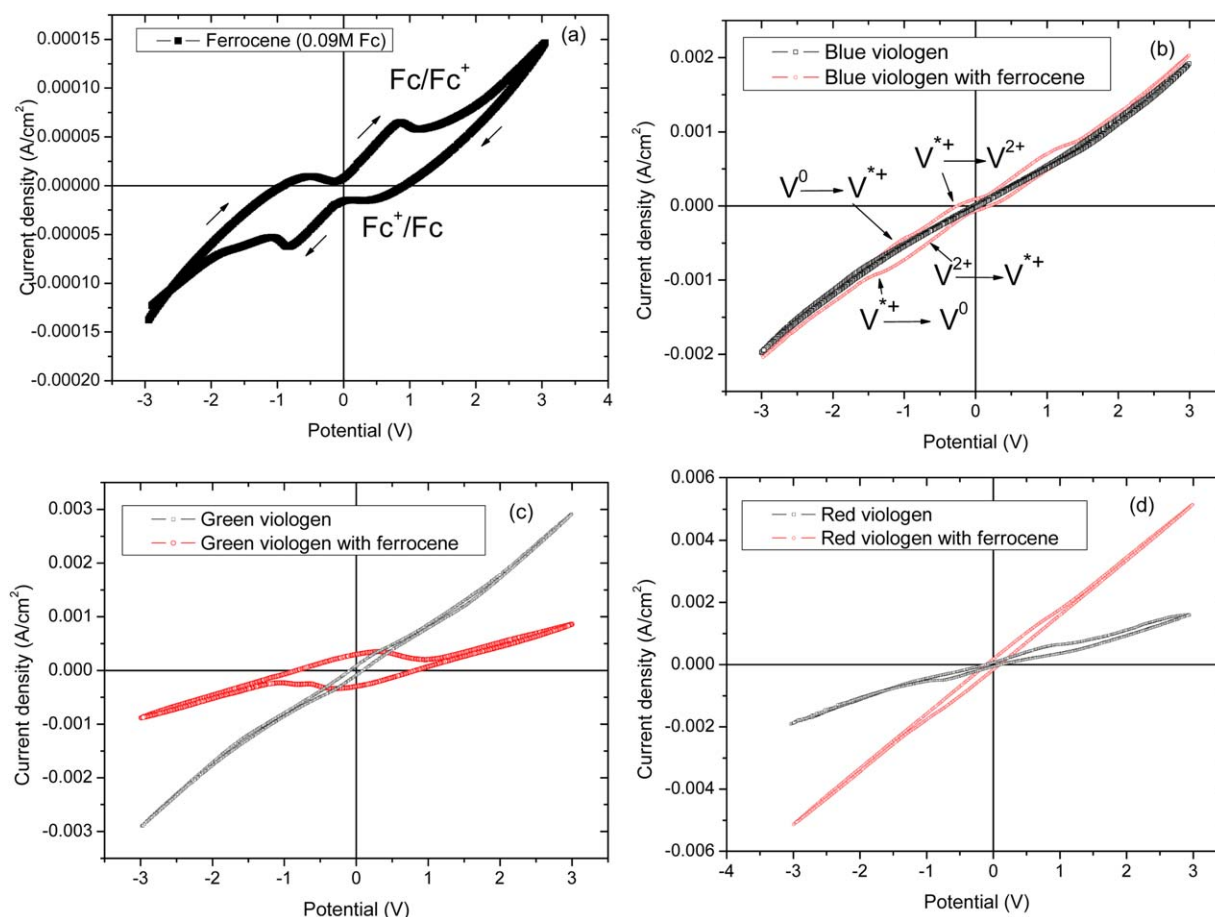


Figure 1. CVs of (a) a PC-based electrolyte solution including 0.09M Fc and (b–d) PC-based electrolyte solutions including 0.09M BF, GF, and RF, respectively, in the absence (black curves) and presence of 0.09M Fc (red curves). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The EC cells consisted of two indium tin oxide (ITO) glasses ($5\Omega/\text{square}$ resistivity; GemTech Optoelectronics Corp., Taiwan) on which the ITO layers faced each other. The cell gap was supported by a $75\ \mu\text{m}$ thick Teflon film spacer. The operational area of the cells was about $6 \times 8\ \text{cm}^2$. Three different kinds of viologens were mixed with Fc in PC to make the EC solutions. The mixtures were rubbed onto an ITO glass and sandwiched with another piece of ITO glass, and then, all edges of the cell were sealed with an insulating epoxy resin. The device fabrication process was carried out in a dry box filled with argon gas. Cyclic voltammetry (CV) and chronoamperometric measurement were recorded on an ALS model 660A potentiostat/galvanostat equipped with a computer. A two-electrode cell was constructed with two ITO glasses as the working electrode and counter electrode. The scan rate was $100\ \text{mV/s}$. Transmittance spectra data were recorded *in situ* during the potential sweep with an Ocean Optics USB2000 diode array detection system.

RESULTS AND DISCUSSION

In this study, we chose Fc as mediator because the EC cell with Fc as a counter redox species showed excellent cyclability compared to that without Fc. It was reported that the EC properties of a viologen in nonaqueous electrolyte were improved in the

presence of Fc.¹² Because of the concentration of 0.09M Fc with superior cyclability, we added 0.09M Fc to the PC solution. The CV of 0.09M Fc in the PC solution is shown in Figure 1(a). The change in transmittance was found to be limited to around -3.0 and $3.0\ \text{V}$. The oxidation peak was around $0\text{--}1.0\ \text{V}$; in relation to that, the oxidative current at $0.70\ \text{V}$ was used for the oxidation of Fe to Fe^+ .

First, CV of 0.09M DHBPDB was measured in a PC-based solution without Fc. The color of DHBPDB was labeled as blue viologen (BF). It is generally known that the viologen containing the heptyl substituent causes a blue color.¹³ On the other hand, HPPB and DCBPC were labeled as the green viologen (GF) and red viologen (RF), respectively, due to their different characteristic colors.

In general, there are three common viologen redox states. An initial viologen with dication (V^{2+}) is the most stable state and is colourless. As the V^{2+} occurs reduction reaction by obtaining one electron, i.e. the V^{2+} transforms to free-radical cation (V^{*+}), and the V^{*+} displays an apparent color. When the V^{*+} occurs further reduction to change into zero valence of V^0 , which exhibits a transparent color and is unfavorable for electrochromic operation. The reduction peak of BF was found around $-0.80\ \text{V}$ because of the reduction of V^{2+} to V^{*+} on the

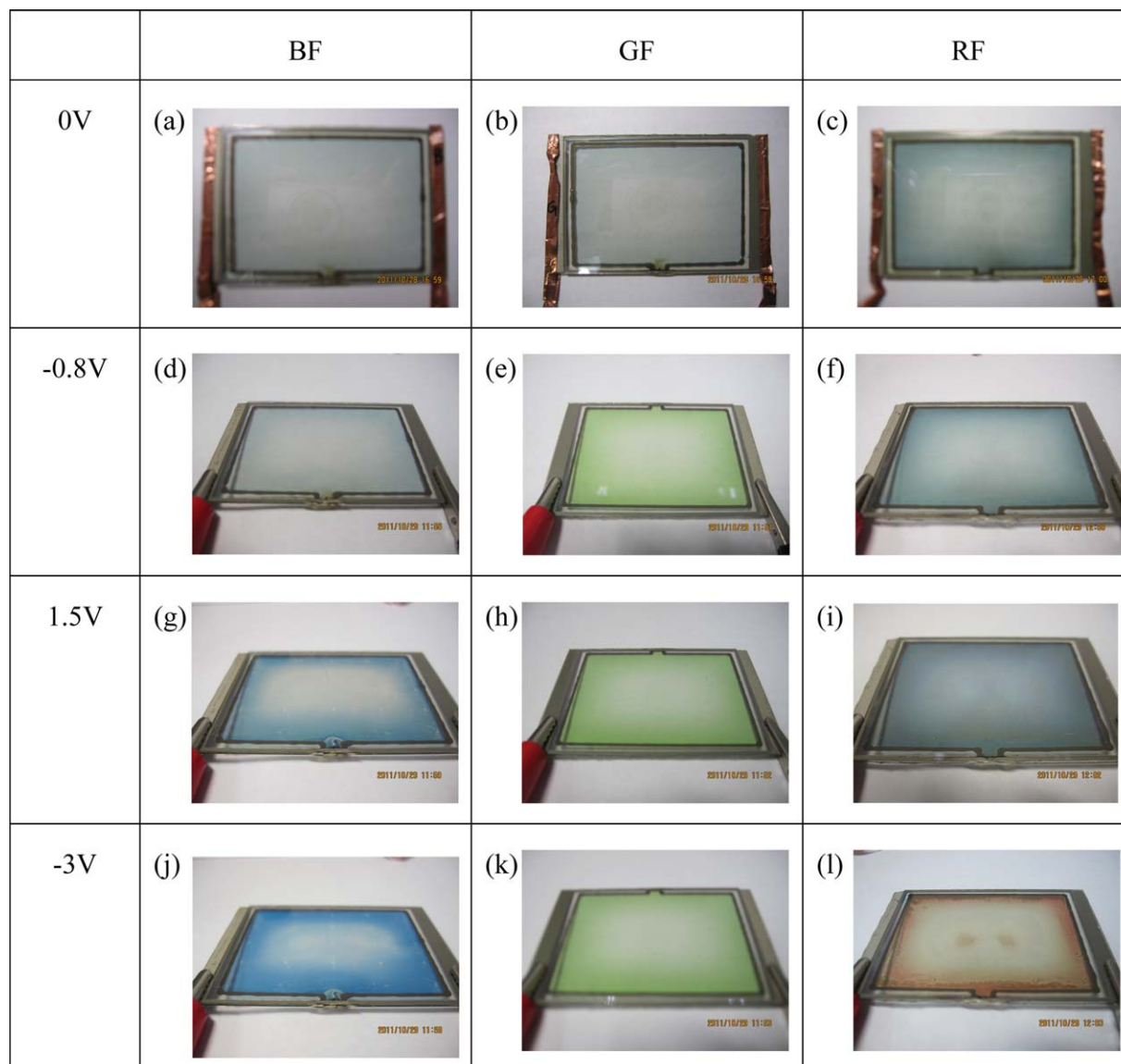


Figure 2. Digital camera images of a two-electrode EC cell containing PC-based electrolytes with different viologens (BF and DHBPDDB; GF and HPPB; and RF and DCBPC). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

surface of the ITO electrode, as shown in Figure 1(b). On the other hand, the oxidation peak was found around -0.20 V. When the applied potentials increased from 0.0 to 0.90 V, a color change from the original pale yellowish to blue was exhibited. When the applied voltage was released, the transmittance returned to its initial value by oxidation within a potential sweep cycle. However, the switching speed of the PC-based EC cell was found to be dependent on the diffusion of redox-active species, and a longer response time is not suitable for display applications. Similar CV curves were also found for the green and red EC solutions, as shown in Figure 1(c,d).

Second, similar experiments in the presence of Fc were carried out. The electrochemical properties of DHBPDDB in the PC-based solution in the presence of Fc were investigated. The reduction and oxidation peaks of a mixture of 0.090M Fc and 0.090M BF in the CV curve were also found, as shown in Figure 1(b).

No change in the potential of reduction of V^{*+} was found after the addition of Fc into the viologen-based solutions. However, the larger reduction current at -0.80 V and the short coloring/bleaching time supported this mediation mechanism. On the reflection of this mediation, the V^{*+} deposit was fully oxidized to V^{2+} ; this resulted in a color change of the electrode from blue to colorless clear. It was revealed that Fc worked well as a mediator to give better switching properties to the viologen-based EC cells. The significant increase in the EC efficiency was attributed to the addition of Fc to enhance the redox reaction. Similar experiments were carried out for the other two colored EC cells, which were the mixture of 0.090M GF with 0.090M Fc and that of 0.090M RF with 0.090M Fc. The results of CV for the GF and RF solutions are shown in Figure 1(c,d), respectively. We found that Fc worked well to mediate the reduction/oxidation of the viologen cations for the GF and RF solutions.

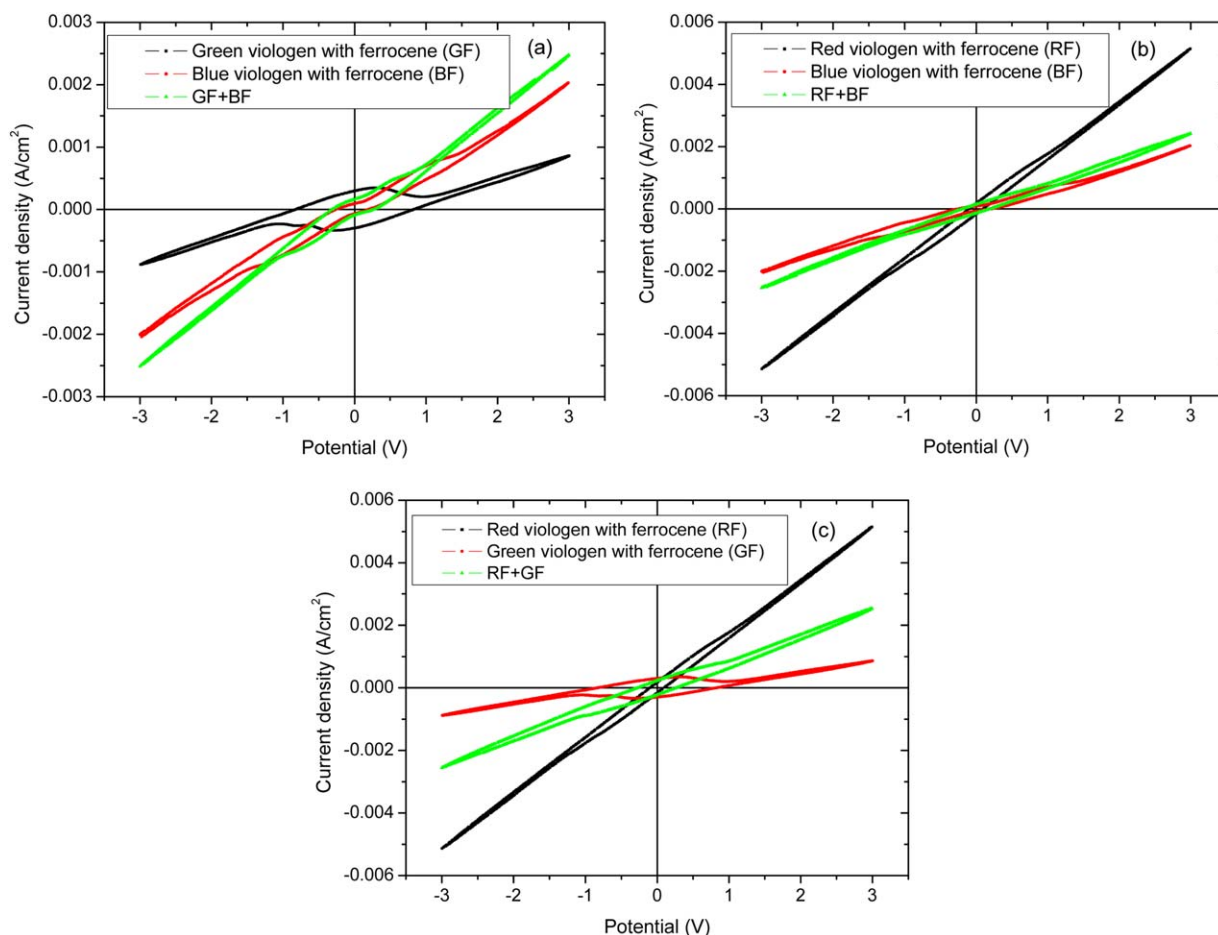


Figure 3. Comparison of CVs of the PC-based electrolytes from a single viologen with Fc and two mixed viologens with Fc. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2(a–l) shows digital camera images of the three colored EC cells. It shows three different colors, which were likely blue, red, and green. Transmittance differences with and without applied potential were used to investigate the optical properties of the different viologen molecule EC cells. In the off state of all of the viologen-based cells, the visible range transmittances were over 80%, and the display of all of the devices was colorless. There was a nonsignificant variation in the transmittance of the three viologens at -0.50 V; nevertheless, the occurrence of a transmittance decrease at an applied negative potential higher than -0.50 V was first found in the GF-based cell. This indicated that the GF owned the lowest reduction potential. HPPB in an electrolyte solution is colorless and clear but turned to blue at -0.80 V because of the formation of a redox reaction in the cell. Hence, with an increase in the operation voltage from -0.80 V to above 2.50 V, the electron-induced large amount of V^{*+} deposits on the electrode reduced the transmittance of the blue EC cell, and then, the color became deep blue, whereas the transmittance of the green EC cell increased with applied potentials of higher than -2.50 V. This was attributed to formation of irreversible V^0 in the cell. RF exhibited special EC characteristics with the application of potentials from 0.0 to -1.50 V, and over -3.0 V, there were color changes from colorless to blue and then to red, respectively. Accordingly, it seemed that

the transmittance of the RF EC decreased with increasing applied positive and negative potential because of an increase amount of V^{*+} . We already confirmed that it was possible to control a tone of color in each cell through the variation of the applied voltage, although the work is in an early stage. These facts clearly indicate that a viologen-based cell could be a potential candidate for multicolor or full-color electronic paper if multiviologen cells are available.

To confirm that the multicolor electrolyte worked well for the electrochemical reaction of EC devices, we mixed two different kinds of viologens with Fc and measured the CV. The CV curves of a mixed EC (GF + BF), including $0.090M$ GF and $0.090M$ BF, are shown in Figure 3(a). We found that the CV curve of a mixture of GF and BF was too close to that of BF, and the reduction peak at 0.0 to -0.80 V corresponded to the electroreduction of a fraction of V^{2+} of the mixed viologen. On the basis of the results, the electrochemical reaction of a mixed viologen of GF and BF seemed to be similar to that of the BF molecules, as shown in Figure 3(b), but also indicated that the electrochemical reaction of a mixture of RF and BF (RF + BF) was also influenced by the addition of BF. However, in the CV curve of the mixed RF and GF (RF + GF), EC was fairly identical to that of other two cells (the RF and GF cells) because of nonexistence of BF salt. The

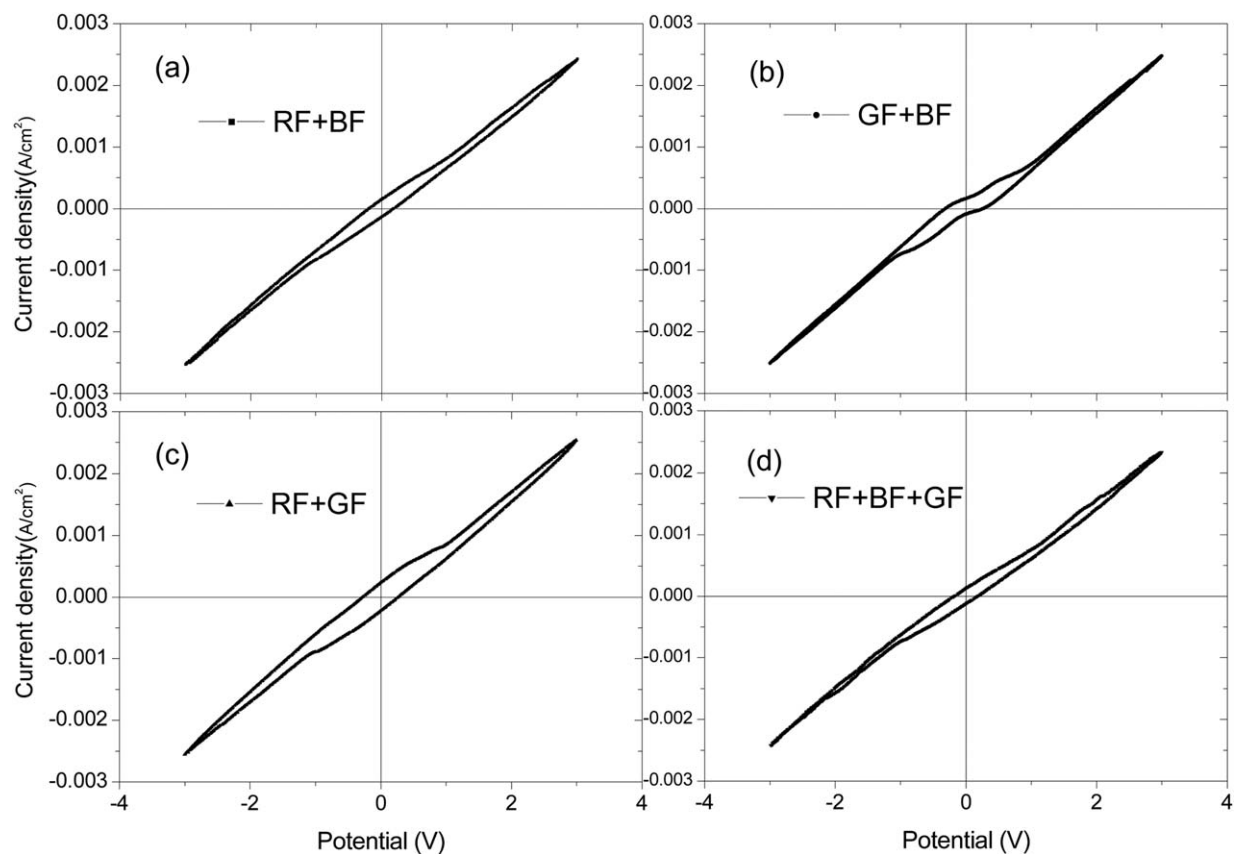


Figure 4. Comparison of the CV of PC-based electrolytes from two mixed viologens with Fc and three viologens with Fc.

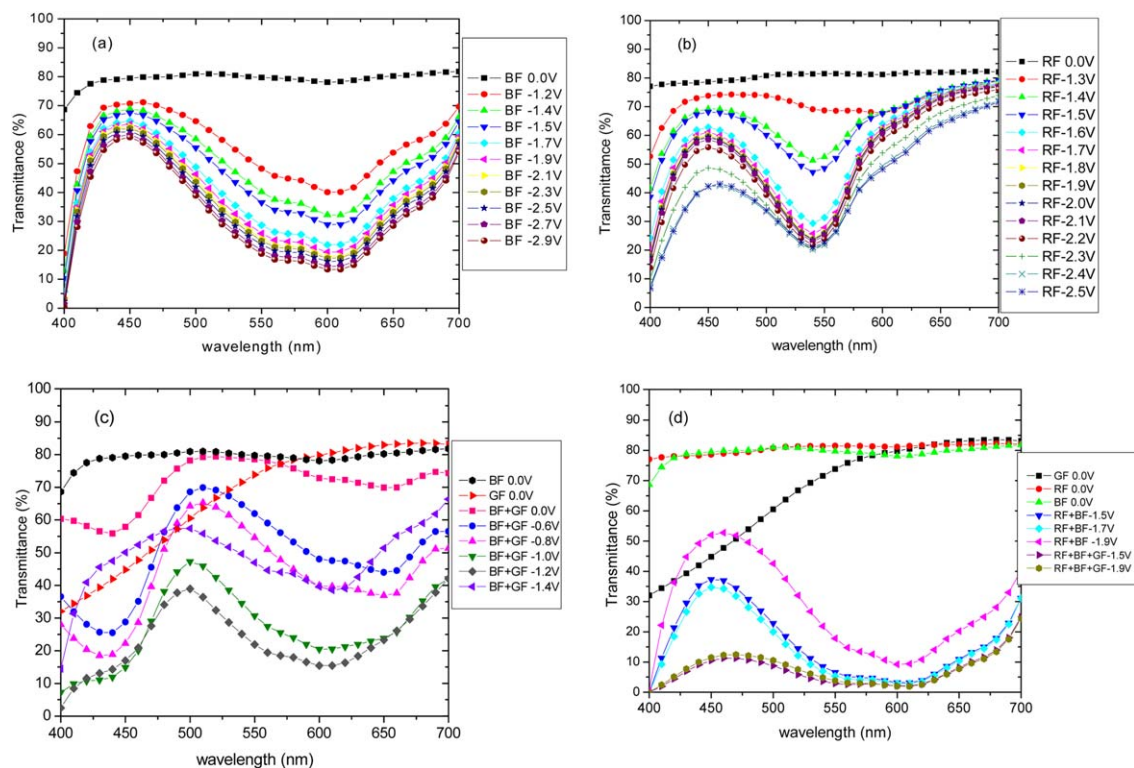


Figure 5. Spectrophotometric analysis of multiviologen cells depending on the potential: (a) BF, (b) RF, (c) GF + BF, and (d) RF + BF and RF + BF + GF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

result demonstrates that the CV of RF + GF was a combination of RF and GF, as shown in Figure 3(c).

Finally, we mixed two to three different viologens and then compared the CV curves of the mixtures: RF + BF [Figure 4(a)], GF + BF [Figure 4(b)], RF + GF [Figure 4(c)], and RF + GF + BF [Figure 4(d)]. The CV curve of the mixture with three viologens (RF + GF + BF) looked like a combination of the CV curves with RF + BF and GF + BF, as shown in Figure 4. The transmittance differences with and without applied potential were determined to investigate the optical properties of the multiviologen cells on the different viologen molecules, as shown in Figure 5. As shown in Figure 5(a), the BF cell appeared substantially transparent and exhibited a transmittance of up to about 80% over the 400–800-nm wavelength range. When a potential from -1.20 to -2.70 V was applied; wavelengths of 455 and 700 nm were intensely reflected, such that the BF–EC cell showed a blue color. The color of the RF–EC cell displayed a combination of red and blue colors, and the transmittance decreased when the applied positive potential was higher than 0.80 V because of the reduction of V^{2+} , as shown in Figure 5(b). It was significant that the decrease in the transmittance and color change in the single-viologen cells was dependent on the potential.

With regard to the previous results, with DHPDB as the viologen pendants, in which a wavelength of 530 nm was reflected, this indicated that the devices showed a green color under an applied negative potential of -3.0 V. However, the transmittance of the mixture of GF and BF was observed to decrease with an increase in the applied negative potential, but a sudden increase in the transmittance gave a negative potential higher than -1.40 V, as shown in Figure 5(c). It was interesting that the tendency of transmittance variation of the original BF and GF cells with an increase in the applied negative potential was found to be different from that of the mixture of GF and BF. As shown in Figure 5(d), a similar phenomenon was also found in the multiviologen cells with two viologen cells, including a mixture of RF and GF, and the three-viologen cell including a mixture of RF, GF, and BF at a higher applied negative potential of -1.90 V. This may have been due to the fact that the different viologen molecules shared electrons to restrict the chromic efficiency of the multiviologen cells. The failure potential was found to be dependent on the reduction/oxidation peaks of V^{2+} in single viologens. The failure potential could be determined on the basis of the analysis of CV measurement. It could be predicted with the appropriate potential to make the multiviologen cells work properly. Consequently, various colored EC cells could be prepared through the control of the viologen molecules with 0.090M Fc in multiviologen cells, and a multiviologen cell will work well before the failure potential is reached.

CONCLUSIONS

In this study, multiviologen cells were prepared by the mixture of different viologen molecules, and their optical and electrochemical properties were investigated. As a result, we found that

the Fc worked well as a mediator to give better switching properties to the viologen-based EC cells to mediate the reduction/oxidation of the viologen cations. The mixture of viologens to create a multiviologen cell was conducted. A multicolor change was found under the application of different potentials. However, the transmittance of a mixture of viologens was observed to decrease with increasing applied negative potential, but the sudden increase in the transmittance under a higher positive potential range was due to the fact that different viologen molecules may have shared electrons and restricted the chromic efficiency of the multiviologen cells. The failure potential value was found to be dependent on the reduction/oxidation peaks of V^{2+} of single viologens. Fortunately, the failure potential could be determined on the basis of the analysis of the CV measurement. Thus, we could predict the appropriate potentials needed to make the multiviologen cells work properly. Consequently, various colored EC cells could be prepared through the control of viologen molecules with 0.090M Fc in the multiviologen cells and were successfully achieved by the modification of the viologen molecules.

ACKNOWLEDGMENT

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