Organic Electrochromic Materials and Device toward Color Electronic Paper

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Abstract

We prepared solid-state electrochromic (EC) cells based on phthalate derivatives and containing a gel electrolyte. The cells showed vivid color changes via electrochemical reactions, i.e., from being water transparent to assuming one of the three primary colors (cyan, magenta, and yellow). Moreover, we obtained continuous-tone images by using the three primary-color EC cells. The formation of continuous-tone images by using the EC cells was realized by applying a rectangular-wave voltage with various duty ratios. In addition, according to a subtractive color-mixture process, we obtained multiple color representations, including intermediate red, green, and blue colors, by stacking two of the three primary-color EC cells.

Introduction

An electrochromic display (ECD) has attracted considerable attention as a strong candidate for application in novel paper-like displays. Flexibility is an essential requirement for realizing paper-like features and texture that are required in an electronic paper-like display. With regard to flexibility, an ECD has the advantage of utilizing a flexible plastic substrate, a flexible gel electrolyte, and organic materials[1-5]. Furthermore, an ECD has a high reflective contrast ratio and satisfies high visibility requirements.

In the early 2000s, many researchers focused extensively on viologen[6-10] or conductive polymers, such as poly(3,4-ethylenedioxythiophene) (PEDOT)[11-14], as typical organic EC materials that can be used for fabricating color ECDs. Recently, many of their derivatives were studied for realizing a flexible and color ECD[15-18]. Currently, some of them showed good properties such as memory effect, coloration efficiency and long lifetime. However, these derivatives have still not achieved the color change from the perfectly clear transparent state (at visible region) to three primary colors state. EC materials that show color changes from being colorless and clear to assuming one of the three primary colors (such as red, green, and blue, or cyan, magenta, and yellow) are required for realizing full-color electronic paper-like imaging devices. On this basis, we studied the electrochemical properties of phthalate derivatives[19]. In previous studies, the three primary colors cyan, magenta, and yellow were electrochemically obtained using diacetyl benzene (DAB), dimethyl terephthalate (DMT), and biphenyl dicarboxylic acid diethyl ester (PCE), respectively, in an ITO sandwich cell. Each color obtained was confirmed as one of the three primary colors by colorimetric measurements based on CIE 1931 standard colorimetric observer. The Y*xy* values for the colored state of DAB, DMT and PCE were (0.21, 0.24), (0.38, 0.25) and (0.41, 0.48), respectively[20]. It was revealed that the anion radical of dimethyl terephthalate generated at the cathode was magenta in color and that the coloration was affected by a supporting electrolyte and solvent. In addition, we have demonstrated that red, green, and blue colors could be obtained by stacking two of the three primary-color EC cells[20]. Flexible EC cells with a gel electrolyte containing N-methyl-2-pyrrolidinone (NMP) as the solvent have been demonstrated[21]. The coloring and bleaching properties of flexible EC cells are comparable to those of liquid-electrolyte-based cells. However, the use of NMP as the solvent did not improve the memory properties considerably, even in the case of gel-electrolyte-based cells. After further discussion, it was established that the coloring and memory properties of phthalate-derivative-based EC cells were clearly improved by employing dimethyl sulfoxide (DMSO) as the solvent[22].

It is necessary to control the tone of the color in display devices. Until now, the formation of continuous-tone images by using phthalate-derivative-based EC cells was not sufficiently examined. In this study, in order to realize the formation of continuous-tone images by using phthalate derivatives, we investigated EC cells with gel matrices containing DMSO as the solvent, and successfully obtained continuous-tone images using EC cells by applying various voltages[23].

Experimental

Materials and reagents

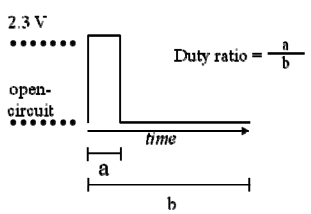
We used dimethyl terephthalate (DMT; Tokyo Chemical Industry Co., Ltd.), 4,4′-biphenyl dicarboxylic acid diethyl ester (PCE; Tokyo Chemical Industry Co., Ltd.), and 1,4-diacetyl benzene (DAB; Tokyo Chemical Industry Co., Ltd.) as EC materials. In addition, tetra-n-butylammonium perchlorate (TBAP; Kanto Chemical Co. Inc.) and ferrocene (Fc; Tokyo Chemical Industry Co., Ltd.) were used as a supporting electrolyte and a counter material, respectively. EC materials, TBAP and Fc were used as received. DMSO (Sigma-Aldrich Co.) was used as the solvent after removing the water using molecular sieves. Poly(vinyl butyral) (PVB; BX-1; Sekisui Chemical Co., Ltd.) was used as the host polymer for the gel electrolyte used in this study.

Preparation of gel electrolyte

A PVB-based gel electrolyte for use in the EC cell fabricated in this study was prepared according to the following procedure. An EC solution was prepared by dissolving 50 mM of a phthalate derivative, 50 mM of TBAP, and 25 mM of Fc in DMSO. One gram of this EC solution was mixed with an appropriate amount of PVB, and the resulting mixture was allowed to stand for a week for obtaining a uniform PVB-based gel electrolyte.

Cell fabrication and EC measurements

A gel-electrolyte-based EC cell was fabricated by sandwiching the obtained gel electrolyte containing the EC solution between a pair of ITO electrodes, maintaining an inter-electrode distance of 300 μm with a spacer. Absorption spectra were recorded in situ by using a diode-array detection system (USB2000; Ocean Optics, Inc.). The continuous-tone images generated by the EC cells were examined by employing a multifunction synthesizer (WF1944A; NF Corporation) and a handmade analog switch. The analog switch was placed between the synthesizer and EC cells. The analog switch contains a relay circuit and converts a 0 V output voltage to an open-circuit output voltage. The applied voltage was rectangular-wave voltage whose values alternatively switched between −2.3 V and 0 V. In this driving system, a voltage of −2.3 V was directly applied to the EC cells through the analog switch when the function synthesizer generated an output of −2.3 V. On the other hand, the EC cells were maintained in an open-circuit state when the function synthesizer generated an output of 0 V. This is because of the fact that the bleaching rate in the open-circuit state is slower than that in the short-circuit (0 V) state. The use of the analog switch is effective in reducing the duty ratio of the applied bias wave, leading to reduction in energy consumption. Duty ratio is defined as the ratio of the period for which a voltage of −2.3 V was applied, to one cycle period of a rectangular wave. The waveform of applied rectangular wave voltage is shown in Scheme 1. All experiments were conducted at the ambient laboratory temperature (20–25 °C).



***Scheme 1**. Waveform of applied rectangular wave voltage.*

Results and discussion

Continuous-tone images were obtained by applying rectangular-wave voltages of −2.3 V/open-circuit with various duty ratios. The change in the absorption spectra and tone of continuous-tone digital camera images are shown in Fig. 1 and Fig. 2, respectively. The absorbance of the DMT cell at a duty ratio of 5% increased and then reached a constant value after 300 s. This constant value of the absorbance depended on the duty ratio. However, the time required for reaching the constant absorbance at different duty ratios was nearly the same. This result clearly indicated that a continuous-tone image could be obtained using the gel-electrolyte-based DMT cell by applying a rectangular-wave voltage with various duty ratios. Similar results were obtained for the DAB and PCE cells. The detailed mechanism of continuous-tone image formation by using the gel-electrolyte-based DMT cell can be explained as follows. When we applied a rectangular-wave voltage with a 5% duty ratio at 5.0 Hz to the DMT cell, −2.3 V was applied during the first 10 ms and DMT was reduced to a colored state on the surface of the cathode. After this process, the drive circuit became open and colored DMT diffused into the gel electrolyte from the cathode, depending on the concentration gradient. No bleaching due to an electrode reaction was observed. The coloration reaction and diffusion were repeated at cycles of 5 Hz. When the rectangular-wave voltage was applied, the absorbance of the DMT cell continued to increase because the coloration rate was faster than the bleaching rate. The amount of colored species, therefore, gradually increased with each cycle. However, as time progressed, the bleaching reaction of the colored species occurred because of the instability of the anion radicals of phthalate derivatives and/or collision between the anion radicals and diffused ferrocenium ions generated at the counter electrode. Finally, the absorbance reached a constant value because of an appropriate balance between the generated and quenched amount of the colored species.

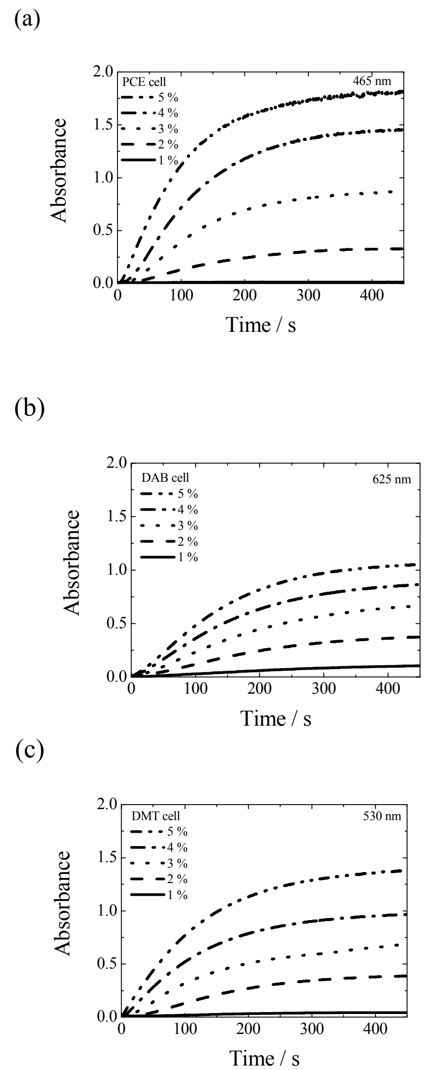


***Figure 1**. Change in the absorbance of (a) PCE, (b) DAB, and (c) DMT cells containing a gel electrolyte under the application of –2.3 V/open-circuit rectangular-wave voltages with various duty ratios.*

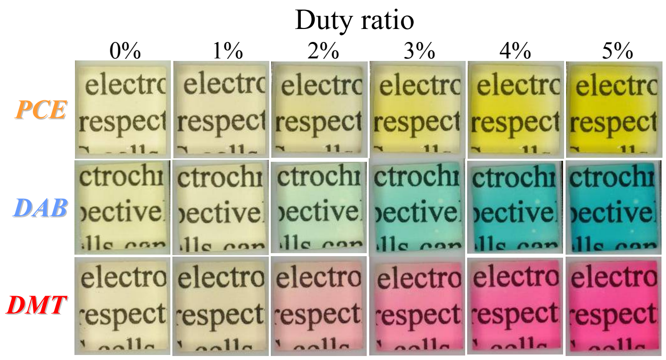


***Figure 2**. Photographs of each phthalate-derivative-based EC cell with a gel electrolyte after the application of –2.3 V/open-circuit rectangular-wave voltages with various duty ratios for more than 400 s. The coloration area of the EC cells was 1.0 × 1.0 cm^2.*

The constant value of the absorbance of each gel-electrolyte-based EC cell was plotted against the duty ratios applied to each EC cell, as shown in Fig. 3. Interestingly, the constant value of the absorbance followed a linear relationship with the duty ratio for each cell. This indicates that we can easily control the tone of the three primary-color EC cells containing a gel electrolyte by changing the duty ratio. This characteristic is very useful for using EC cells in display devices. Thus, continuous-tone representation was realized using the three phthalate-derivative-based, primary-color EC cells containing a gel electrolyte. This clearly indicates that this system can be used in the fabrication of full-color display devices. In addition, high absorbance can be obtained in all EC cells by applying a duty ratio less than 5%; thus, the driving procedure described in this paper helps in realizing constant coloration with low energy consumption. A low duty ratio would reduce any damage to the EC cell and would increase its lifetime. At least, we could not observe any degradation of gel-electrolyte-based EC cells during experiment. And in the case of NiO counter material system, we achieved 10 times higher switching stability than in the Fc counter material system[24].

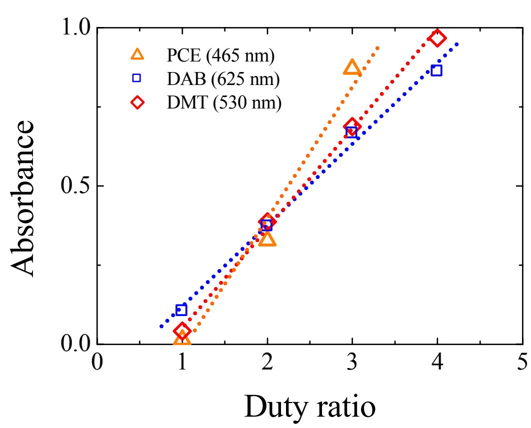


***Figure 3**. Maximum absorbance of each phthalate-derivative-based EC cell as a function of duty ratio. –2.3 V/(open-circuit rectangular-wave voltages with various duty ratios were applied for more than 400 s.*

Parameters such as frequency, duty ratio, and voltage can be improved by material modification, choice of counter material, and stabilization of the colored species.

We also obtained an intermediate color image by stacking two gel-electrolyte-based EC cells for fabricating a full-color display. Fig. 4 shows the photographs of several stacked EC cells. For example, we stacked the "cyan" (DAB) and "yellow" (PCE) cells, and then varied the intensity of the cyan and yellow colors. As a result, we could obtain multiple colors between cyan and yellow, including intermediate green color. We successfully controlled multiple colors, including intermediate red, green, and blue colors, according to a subtractive color-mixture process. On the basis of these results, we expect that the fabrication of a full-color display is feasible by using phthalate derivatives showing three primary colors and continuous-tone images.

Conclusion

***Figure 4**. Photographs of stacked phthalate-derivative-based EC cells, two of which are stacked together for examining multiple color representation according to a subtractive color-mixture process. The coloration area of the EC cells was 1.0 × 1.0 cm^2.*

We successfully obtained continuous-tone images and multiple color representation by using phthalate-derivative-based EC cells containing a gel electrolyte. Each EC cell enabled continuous-tone representation when a rectangular-wave voltage with various duty ratios was applied to each cell. According to a subtractive color-mixture process, we achieved multiple colors, including intermediate red, green, and blue colors, by stacking two of the three primary-color EC cells. It is expected that the phthalate-derivative-based EC cells can be used for realizing full-color electronic paper, EC displays, and other EC applications.

Acknowledgments

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