An optically efficient full-color reflective display with an electrochromic device and color production units

Ik Jang Ko, Jin Hwan Park, Gyeong Woo Kim, Raju Lampande and Jang Hyuk Kwon

Department of Information Display, Kyung Hee University, Seoul, Republic of Korea

ABSTRACT

In this paper, we report a full-color reflective display device by combining reflective electrochromic device (ECD) and different color production units (conventional color filter (CF) and transmittance controllable electrochromic color filter (TCECF)). A full-color reflective device with TCECF showed an excellent diffuse reflectance of 47.2% in the white state owing to the high transmittance of TCECF in the bleached state than that of CF (19.5%). This device structure can easily provide various colors with high brightness and saturation with a broad grayscale. Particularly, in the colored state, TCECF and CF-based full-color reflective device displayed color coordinates of (0.59, 0.34), (0.31, 0.66), (0.24, 0.30) and (0.65, 0.33), (0.27, 0.61), (0.15, 0.06), for red, green and blue, respectively, and alongside also exhibited color gamut of 36.8% (for TCECF) and 73.1% (for CF) for full color reflective devices.

1. Introduction

The full-color reflective display has received remarkable attention of late in various fields [1–8] owing to its low power consumption for a clear image under strong daylight conditions. Although the reflective display has good electro-optical properties, including high outdoor visibility and low power consumption compared with the emissive display [9,10], its device performance is deteriorated by its weak ambient-light intensity. To overcome this inevitable drawback, a high reflectance and contrast ratio in ambient light is crucial for the high performance of the full-color reflective display.

Normally, the ambient light is simply converted to three primary colors (red, green, and blue) from the color filters (CFs) to produce a full-color image [11]. The reflectance and contrast ratio, however, has been reduced by the considerable optical loss in the filtered light. By considering the above hurdle in achieving high device performances, the electrochromic device (ECD) can be made the most ideal technology for reflective-display applications in terms of performances compared with CF. Typically, ECDs are categorized according to their materials, such as metal oxide [12–14], organic materials [15,16], viologen [17,18], and polymers [19–22]. Among the reported electrochromic materials, lactone-ring-based leuco dye can be an inevitable choice due to its excellent electro-optical properties, such as high transparency, fast switching time, and low power consumption [23,24].

Demonstrated herein is a full-color reflective display consisting of a reflective ECD and different color production units (CF and TCECF) as a reflectivity control unit and a color display unit, respectively. As the transmittance of ECD can be reversibly changed according to the redox states of the electrochromic materials, the full-color reflective display can shows a full-color image according to the different driving conditions. A reflective device displays excellent diffuse reflectance in the white state compared with CF, owing to the high transmittance of TCECF in the transparent state. Furthermore, good color coordinates are observed for red, green, and blue in each colored state.

2. Experiment

All the materials that were used in this research work were purchased from Sigma-Aldrich and Yamada Chemical Co., Ltd.

2.1. Fabrication of reflective ECD

To fabricate the reflective ECD, ITO glasses were sequentially cleaned in acetone and isopropyl alcohol for 10 min using an ultrasonic washer, and then rinsed using deion-
ized water followed by drying using nitrogen gas. Initially, a white reflector was deposited on the bottom electrode of the reflective ECD using the previous method [25]. Then a 70-μm-thick spacer film (ROLLPACK, vacuum sealer rolls) was attached to the cleaned ITO glass with an active area of $3 \times 3 \text{cm}^2$. The active area was filled with electrochromic gel. Finally, the ITO glass containing electrochromic gel was covered by another ITO glass, and then the two ITO glass substrates were tightly held together using clamps.

### 2.2. Fabrication of TCECF

The spacer film was used to form a $3 \times 3 \text{cm}^2$ active area on the pre-cleaned ITO substrate without a white reflector. Then the active area was filled with electrochromic solution including each red, green, and blue electrochromic leuco dye, and was covered with the other cleaned ITO substrate.

### 2.3. Electrochromic solution preparation

To produce the red, green, blue, and black colors, an electrochromic solution of leuco dyes – (6′-(ethyl (p-tolyl) amino)-2′-methyl-3H-spiro[isobenzofuran-1,9′-xanthene]-3-one) (red dye), (1-ethyl-8-(ethyl (p-tolyl) amino)-2,4-trimethyl-1,2-dihydro-3′H-spiro[chromeno[2,3-g]quinoline]-11,1′-isobenzofuran]-3′-one) (green dye), 3,3-bis-4-dimethylaminophenyl-7,6-dimethoxyanilino-3H-spiro[isobenzofuran-1,9′-xanthene]-3-one (DATMF; black dye) – were utilized. In addition, 2,3-dimethylhydroquinone (DMHQ), tetra-n-butylammonium tetrafluoroborate (TBTF), 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (BMPBT), and polyvinyl butyral (PVB) were employed as a proton donor, supporting electrolyte, ionic liquid, and supporting polymer, respectively, to improve the performances of the device. Electrochromic solutions were prepared for each color at room temperature, with the following compositions:

- **Red TCECF:** red dye (3.2 wt%), PVB (7.7 wt%), DMHQ (5.2 wt%), TBTF (1.3 wt%), and BMPBT (12.9 wt%); and 2-ethoxyethanol (69.7 wt%).
- **Green TCECF:** green dye (3.2 wt%), PVB (7.7 wt%), DMHQ (5.2 wt%), TBTF (1.3 wt%), BMPBT (12.9 wt%), and 2-ethoxyethanol:THF (69.7 wt%).
- **Blue TCECF:** blue dye (3.2 wt%), PVB (7.7 wt%), DMHQ (5.2 wt%), TBTF (1.3 wt%), BMPBT (12.9 wt%), and 2-ethoxyethanol:THF (69.7 wt%).
- **Black ECD:** black dye (3.2 wt%), PVB (7.7 wt%), DMHQ (5.2 wt%), TBTF (1.3 wt%), BMPBT (12.9 wt%), and 2-ethoxyethanol (69.7 wt%).

### 2.4. Fabrication of a full-color reflective display with the conventional CF

An about 0.50 ml CF solution was spin-coated on the glass side of the pre-cleaned ITO substrates at 1000 rpm, followed by an annealing process at 150°C for 30 min in the ambient atmosphere. Then an ITO substrate with a 2-μm-thick CF layer was used as the top substrate of the reflective ECD.

### 2.5. Fabrication of a full-color reflective display with TCECF

The reflective ECD and TCECF were combined using an adhesive film, as shown in Figure 1(b). The adhesive film was prepared by mixing 2-ethoxyethanol and PVB.

### 2.6. Measurement

Diffuse reflectance measurements were performed using an ultraviolet–visible spectrophotometer (Perkin Elmer, Lambda 650S). A chromameter (Konica Minolta, CS-100A) was used to measure the color coordinates. All the driving photographs were captured using a digital camera (Panasonic, DMC-LX100).

### 3. Results and discussion

The schematic of full-color reflective displays consisting of a reflective ECD and color display units (CF and TCECF) is shown in Figure 1. Recently, we reported a reflective ECD [25] with a titanium-dioxide-(TiO2)-based white reflector and simultaneously utilized a high-performance black ECD to display the basic optical information (black and white) using reflected ambient light. This reflective ECD showed high reflectance (58.5%) in the white state owing to the excellent reflectivity property of the TiO2 white reflector, which reflects most of the ambient light (95.5%) in the visible wavelength range (400–700 nm) with negligible optical loss (4.5%). Besides, the transmittance and optical density of the black ECD in the bleached (0.0 V) and colored (1.7 V) states were around 83.2% and 1.5, respectively. Particularly, in the colored state, two very broad and high-optical-density peaks with increasing applied voltage appeared at 435 and 585 nm. Those two peaks were almost included in the visible light spectrum due to the different chemical state of leuco dye. As shown in Figure 2, leuco dye can reversibly exhibit both the bleached and colored states...
Figure 1. Schematic of full-color reflective displays fabricated by integrating a reflective ECD and different color production units (CF and TCECF). (a) full-color reflective display with CF. (b) full-color reflective display with TCECF.

Figure 2. Coloring and bleaching mechanism of electrochromic leuco dye.

According to the chemical status of the lactone ring, which can be determined from the reaction of leuco dye with the acid species, such as a proton donor compound. In addition, the reflective ECD displayed 3.5 and 43.4 s coloring and bleaching response times, respectively at the driving voltages of 1.7 and 0 V. Likewise, the diffuse reflectance of the reflective ECD in the white and black states was stable (about 10% optical change) after 10,000 driving cycles, and it showed a total power consumption of only 10 mW.

For displaying the full-color information without the conventional CF, the performances of each TCECF based on red/green/blue leuco dye were evaluated prior to the fabrication of a full-color reflective ECD. Our TCECFs showed excellent average transmittance (about 80.2%; red: 82.3%, green: 76.3%, and blue: 81.8%) in the bleached state, thus, it is expected to have a highly improved optical efficiency compared with the CF. In addition, the optical densities of the red, green, and blue TCECFs dramatically increased at 500–550 nm, 400–500 nm (as well as 600–700 nm), and 600 nm, respectively, with increasing applied voltages. Thus, each TCECF revealed very good color characteristics of (0.62, 0.34) for red, (0.33, 0.65) for green, and (0.18, 0.09) for blue in the colored state, with a low driving voltage (1.7 V) and an about 10 mW power consumption. In particular, each TCECF displayed 1.9 s (R), 1.3 s (G), and 0.9 s (B) coloring response times and 16.0 s (R), 11.5 s (G), and 11.9 s (B) bleaching response times at the 1.7 and 0 V driving voltages, respectively, with only a small optical change (10%) under continuous driving (1000 cycles). This result revealed the excellent color-tunable properties of TCECF for full-color reflective-display application.
Considering the excellent transmittance as well as the optical densities of the red-, green-, and blue-colored TCECFs in the bleached and colored states, it is expected that their use will realize excellent optical performances for full-color reflective devices. To evaluate the optical performances of the full-color reflective displays with TCECF, diffuse reflectance and color coordinate measurements were performed. A full-color reflective display was fabricated by combining the reflective ECD and TCECF with an adhesion film consisting of polyvinyl butyral, widely used as an adhesive resin for automotive and architectural applications, as a protective interlayer on the glasses [26]. Particularly, the optical loss from the interface of the two glasses almost disappeared because its reflective index \( n = 1.5 \) was similar to that of glass. Additionally, a full-color reflective display with the conventional CF was prepared as a reference device for a valid comparison of the performances.

As shown in Figure 3(a and c), the full-color reflective display with CF clearly expressed the red, green, and blue colors due to the excellent color filtering characteristic of CF. This device, however, exhibited a very poor white color state with considerably decreased diffuse reflectance (about 19.5%; red: 26.6%, green: 20.2%, and blue: 11.6%). On the other hand, the full-color reflective display with TCECF indicated a remarkably clear white color with very high diffuse reflectance (47.2%; red: 46.9%, green: 44.1%, and blue: 50.6%) due to the reversible color change properties of TCECF, as shown in Figure 3(b and d). Particularly, this device can display various colors owing to the independent driving state of the reflective ECD and TCECF. In the colored mode, only TCECF was in operating condition, whereas the full-color reflective display simply provided all three primary colors with good color coordinates of \((0.59, 0.34), (0.31, 0.66), \) and \((0.24, 0.30)\) for red, green, and blue, respectively. Similarly, in the black mode (the reflective ECD
was in operating condition), the device showed very low diffuse reflectance (about 9.8%; red: 9.7%, green: 6.5%, and blue: 13.4%) due to the high optical density of the reflective ECD in the colored state; this diffuse reflectance value was similar to that of CF (9.0%). In addition, the full-color reflective display with TCECF demonstrated a relatively low color gamut (36.8%) compared with CF (73.1%) owing to the weak color performance of the blue TCECF (Figure 4 and Table 1). The difference between the color coordinates of the green- and blue-colored TCECFs and CFs was very small, however, and the optical characteristic of the blue TCECF was still lower than that of the blue CF despite its excellent transmittance in the bleached state. Indeed, it is expected to have an improved color gamut in the TCECF-based full-color reflective display by enhancing the optical properties of the blue TCECF with a suitable solvent and stabilizer for enhanced ionic-state stability [27,28]. In addition, the full-color reflective display with TCECF is more suitable for providing various colors with high brightness and saturation with a broad grayscale because of its clear white color in the off-state of both the reflective ECD and TCECF compared to that of CF.

### 4. Conclusion

In summary, we developed a full-color reflective display by combining a reflectivity control unit (reflective ECD) and a color display unit (conventional CF and TCECF). The full-color reflective display with TCECF (CF) showed average diffuse reflectance (47.2% [19.5%] and 9.7% [9.0%]) in the white and black color states, respectively. The full-color reflective device with CF and TCECF displayed (0.65, 0.33) and (0.59, 0.34), (0.27, 0.61) and (0.31, 0.66), and (0.15, 0.06) and (0.24, 0.30) color coordinates for red, green, and blue, respectively, in the colored state. Additionally, both full-color reflective devices demonstrated a color gamut of 36.8% (for TCECF) and 73.1% (for CF) owing to the weak color performance of the blue TCECF. Indeed, it is expected that the color gamut in the full-color reflective display with TCECF can be improved by enhancing the optical properties of the blue TCECF with an efficient blue material, a suitable solvent, and a stabilizer. Therefore, further research work is needed to improve the performances of this attractive technology. It is anticipated that the studied approach will be very useful for the future reflective display applications.

### Disclosure statement

No potential conflict of interest was reported by the authors.

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### Notes on contributors

**Ik Jang Ko** received his BS degree in Electronic Physics from Hallym University, South Korea in 2016, and his MS degree in Information Display from Kyung Hee University, South Korea in 2017. He is currently pursuing his Ph.D. degree under the supervision of Prof. Jang Hyuk Kwon at the Department of Information Display, Kyung Hee University. His research focuses on the design and fabrication of efficient OLED and ECD devices.

**Jin Hwan Park** received his BS and MS degrees in Information Display from Kyung Hee University, South Korea in 2016 and 2018, respectively. He is now working as a Research Engineer at LG Display, South Korea.
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Gyeong Woo Kim received his BS degree in Display Engineering from Hoseo University, South Korea in 2011, and his MS and Ph.D. degrees in Information Display from Kyung Hee University in 2013 and 2018, respectively. He is currently working as a Senior Research Engineer, at LG Display, South Korea.

Raju Lampande received his BSc and MSc degrees in Electronics from Nagpur University, India in 2004 and 2006, respectively, and his Ph.D. degree in Information Display from Kyung Hee University, South Korea in 2016. He is presently working as a Research Professor at the Department of Information Display, Kyung Hee University. His research interests include the development of efficient organic/inorganic optoelectronic devices including OLEDs, QD-LEDs, and next-generation smart window devices.

Jang Hyuk Kwon is a Professor in the Department of Information Display at Kyung Hee University, South Korea. He received his Ph.D. degree in Chemistry from Korea Advanced Institute of Science and Technology (KAIST), South Korea in 1993. Before joining the Kyung Hee University, he was a Chief Researcher at Samsung SDI (South Korea) in 1993-2005. His research interests include the development of new organic materials for optoelectronic devices including OLEDs, QD-LEDs, OPV, and electrochromic devices. He has authored/co-authored over 145 SCI-indexed papers and also has about 98 registered patents (national and international).

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