Multi-Layered Electrochromic Display

<u>Yoshihisa Naijoh</u>, Tohru Yashiro, Shigenobu Hirano, Yoshinori Okada, SukChan Kim, Kazuaki Tsuji, Hiroyuki Takahashi, Koh Fujimura, Hitoshi Kondoh

RICOH Company, Ltd., Research and Development Group, 16-1 Shinei-cho, Tsuzuki-ku, Yokohama-shi, Kanagawa, Japan

ABSTRACT

We had developed a full-color multi-layered electrochromic display (mECD) technology based on the subtractive color mixing theory. The mECD promises to improve brightness and color reproducibility of reflective display because of its unique structure.

We report the latest topic of applicability of mECD to flexible substrate in this paper.

INTRODUCTION [1]

Electronic papers are increasing in commercial mainly using black and white reflective display. [2] But bright full-color reflective displays are now still under development. Non-self-luminous display is difficult to achieve bright full-color image. Because, light efficiency of Red/Green/Blue color filter planarly separated into subpixels is too low such as in use by conventional liquid crystal displays, color reproducibility of reflective display with color filter becomes very narrow. Therefore, several technologies for full-color reflective display without color filter are being developed. [3,4]

Electrochromic technology is being developed as one of the technologies for full-color reflective display. Electrochromic compounds turn into a coloration state from transparence state reversibly by Redox reaction. Full-color performance was expected by stacked three display units* (*display unit; consisted by a pair of substrates with electrodes) using cyan, magenta and yellow colors. [5]

We had been developed a new full-color reflective display "multi-layered electrochromic display" consisting of one display unit*. [6] The reflectivity of white state was 70% at 550nm. This is a highest value of reflective color display all over the world. The color reproducibility had been estimated from chromaticity points on a*b* diagram compared with the standard color chart (JAPAN COLOR '97, Japan Printing Machinery Association). The mECD shows 27% color reproducibility compared with the standard color chart.

And then, we had also successfully demonstrated the Active Matrix panels using 3.5" QVGA LTPS-TFT. By optimizing the device constituents, especially electrolyte materials and counter electrodes, the mono-color panel achieved 113ppi resolution and displayed gray scale image well enough as shown in Fig. 1. And, the mECD panel could have expressed full-color image as shown in Fig. 2.

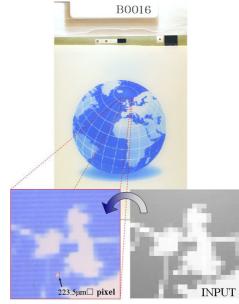


Figure 1. Demonstrated image of Active Matrix LTPS-TFT mono-color electrochromic display panel.



Figure 2. Demonstrated image of Active Matrix LTPS-TFT multi-layered electrochromic display panel.

To adopt many applications, for example mobile devices, display modules have to satisfy the requirement for high mechanical robustness, thinness, and lightness in weight. Using thin flexible plastic film as display substrate, instead of glass substrate, is one of the answers of these requests. In this paper, we report the latest topic of applicability of mECD to flexible substrate.

Electrochromic Compounds [6]

Electrochromic materials change in color by application of potential. (Fig. 3)

Figure 3. Example of electrochromic compound.

Electrochromic compounds can be injected charge carrier and reacted efficiently by adsorb in nano- TiO₂ porous electrode formed on a transparent electrode. [7]

New electrochromic compounds which color can be reversibly changed from transparent to each cyan, magenta and yellow, were successfully synthesized. All of the electrochromic compounds adsorbed on the surface of nanostructured ${\rm TiO_2}$ on transparent electrodes were colored by applied voltage of less than -2V (vs Ag/Ag+).

Device structure of mECD

The multi layered electrochromic display (mECD) technology is designed to mimic the appearance of ordinary ink on paper. In most color printing, the primary ink colors used are cyan, magenta, and yellow. Combinations of different amounts of the three inks can produce a wide range of colors. The structure of mECD is shown in Fig. 4. The frontplane includes three transparent electrodes with each electrochromic layer, and insulating layers formed between the electrodes. Detailed pattern is not necessary for each layer in a frontplane. The electrochromic layers are based on three kinds of organic electrochromic compounds; cyan, magenta and yellow dye. Furthermore a white reflective layer is formed on the frontplane. The frontplane is assembled to the backplane having counter electrode(s) together with electrolyte. The electrolyte is infiltrated into between the frontplane and the backplane.

The mECD technology has been developed aiming to simple and easy manufacturing. The mECD is consisted by single display unit* without any detailed patterning in a frontplane. This is the reason why the mECD can realize sufficient brightness and broad color reproducibility for the reflective display.

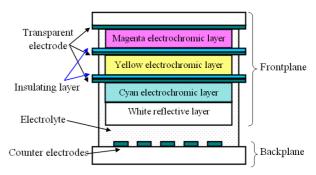


Figure 4. Schematic structure of the multi-layered electrochromic display (mECD).

Fabrication Procedure of Flexible mECD frontplane

One of fabrication method for flexible mECD is introduced as below. Thin flexible plastic film can be used as substrate, because the mECD is fabricated through annealing process at below 120 degrees Celsius.

At first, some elements of mECD, top and middle plastic films with electrochromic layer on working electrode are prepared previously (and bottom plastic film with counter electrode is also prepared.) The middle plastic films have to be porous, because the ions have to migrate enough between working and counter electrodes so that electrochromic compounds can react (Redox reaction). Each plastic film is set to rigid supporting substrate through the process by adhesion. Each plastic film has each electrode, and top and middle electrodes have to transparent. Electrochromic layer is formed onto top and middle plastic films with electrode. After the fabrication of elements of mECD, each element is peeled off from substrate. White reflective layer is formed behind electrochromic layers. Finally, every elements of mECD are assembled together with electrolyte.

- 1. Prepare the supporting substrates.
- 2. Form an adhesive layer onto the substrates.
- 3. Set each plastic film to the adhesive layer.
- 4. Form an electrode layer onto each plastic film by sputtering.
- 5. Form an electrochromic layer (form a porous TiO_2 electrode and adsorb each electrochromic material) onto the electrode by spin coating. And, form a white reflective layer onto appropriate layer.
- 6. Peel off the plastic films with electrode and electrochromic layer from the adhesive layer.
- 7. Assemble the plastic films with electrolyte.

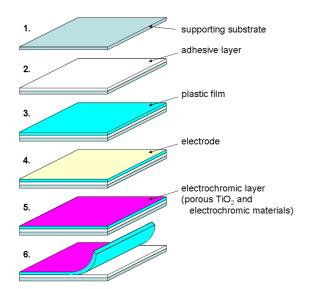


Figure 5. Schematic representation of fabrication method of flexible mECD element.

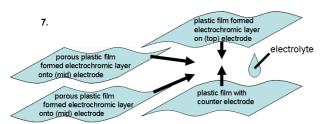


Figure 6. Schematic representation of flexible mECD assembly.

Herewith, flexible mECD can be fabricated very easily. We had fabricated flexible mECD simple device follow the procedure as described above, using 100um thick plastic films as top and bottom substrates and 25um thick porous plastic film as middle substrates. Fig. 7 and 8 show demonstrated image of Magenta/Yellow color mixing and Magenta/Yellow/Cyan color on flexible substrate. A simple device as shown in Fig. 7 and 8 has thickness of about 0.25mm and light weight of less than 50mg/cm², and the device was driven enough even if the device is bended at less than 1cm radius.

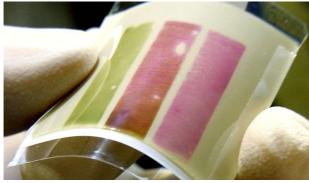


Figure 7. Demonstrated image of Magenta/Yellow color mixing on Flexible Substrate.

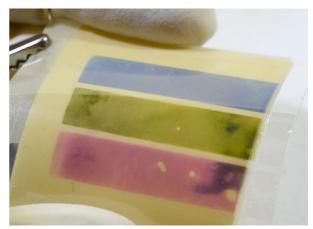


Figure 8. Demonstrated image of Magenta/Yellow /Cyan color on Flexible Substrate.

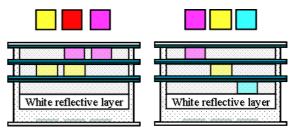


Figure 9. Schematic representation of coloration of mECD shown in fig. 7(left) and fig. 8(right).

Conclusion

We had developed a full-color reflective display "multi-layered electrochromic display (mECD)". With fewer elements, the mECD is thinner, less lightweight and less costly than existing devices and the reduced optical loss provides a brighter appearance. Light weight and flexible plastic substrates can be adopted for the mECD easily as described. The mECD is expected that can be the real full-color e-paper.

Acknowledgments

New electrochromic compounds were developed with Yamada Chemical Co., Ltd. (Kyoto / Japan).

This works was supported in part by the New Energy and Industrial Technology Development Organization (NEDO) based of funds provided by the Ministry of Economy, Trade and Industry, Japan (METI).

References

- [1] Tohru Yashiro, Shigenobu Hirano, Yoshihisa Naijoh, Yoshinori Okada, Kazuaki Tsuji, Mikiko Abe, Akishige Murakami, Hiroyuki Takahashi, Koh Fujimura, Hitoshi Kondoh, "Novel Design for Color Electrochromic Display", SID 11 Digest, 42-45, 1, (2011)
- 2] http://www.eink.com/display_products_pearl.htm
- http://www.frontech.fujitsu.com/services/products/ paper/flepia/

- [4] S. Hirano, T. Shibuya, T. Yashiro, Y. Manabe, S. Hayashi, T. Narizuka, S. Tanaka, N. Kobayashi, "Reflective Real-Full-Color Display Multi-layer Structure of Electrochromic Compounds -", Nippon Kagakukai Nenkai Yokosyu 89 2B1-15 (2009)
- [5] H. Urano, S. Sunohara, H. Ohtomo, N. Kobayashi, "Electrochemical and Spectroscopic Characteristics of Dimethylterephthalate", J. Mater. Chem., 14, 2366-2368, (2004)
- [6] K. Lenssen, P. Baesjou, F. Budzelaar, M. Delden, S. Roosendaal, L. Stofmeel, A. Verschueren, J. Glabbeek, J. Osenga, R. Schuurbiers, "Novel Design for FULL-Color Electronic Paper", SID Digest 08, 685–688, (2008)
- [7] D. Cummins, G. Boschloo, M. Ryan, D. Corr, S. Rao, D. Fitzmaurice, "Ultrafast Electrochromic Windows Based on Redox-Chromophore Modified Nanostructured Semiconducting and Conductiong Films", J.Phys. Chem. B 104, 11449-11459, (2000)