Flexible Electrochromic Display

Tohru Yashiro, Yoshinori Okada, Yoshihisa Naijoh, Shigenobu Hirano, Toshiya Sagisaka, Daisuke Gotoh, Mamiko Inoue, SukChan Kim, Kazuaki Tsuji, Hiroyuki Takahashi, and Koh Fujimura

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

Keywords: electronic paper, electrochromic, reflective display

ABSTRACT

We have developed Electrochromic materials that show various colors based on bi-pyridine compounds. These are adsorbed on the surface of nanostructured Ttitanium dioxide layer as a Grätzel cell structure by low-temperature solution-process. By utilizing flexible TFT, we have demonstrated full-color flexible electronic papers.

1. INTRODUCTION

Electric papers have been commercialized utilizing the feature of reflective displays. The main advantages of reflective display are low power consumption and a high contrast display image under the sunlight. Current electric papers are almost all B/W displays, because it is difficult for conventional reflective displays based on the additive color mixing model with Red, Green and Blue, to achieve colorful images. Full-color electric papers are expected for future applications such as digital signage, bulletin board, textbook etc.

We have developed a full-color reflective multi-layered electrochromic display (mECD) based on the subtractive color mixing model with Cyan, Magenta and Yellow. The color performance is highly improved by mECD technologies. [1,2,3,4].

The mECD have a simple structure, consisting of a front-plane substrate which has three kinds of electrochromic layers and an active-matrix (AM) TFT array as a backplane substrate (Fig.1). Each electrochromic layer can reversibly change their color from transparent to cyan, magenta, and yellow respectively by electrochemical reduction. Color images appear on each selected electrochromic layer by injecting electric charge between electrochromic layer (cathode) and selected pixel electrode (anode) of AM-TFT array. The mECD has a memory property. The image can kept for a certain period of time even after the power is turned off. As a result, a sequential selection of electrochromic layers gives a full-color image on the mECD front-plane.

Flexibility is expected as one of characteristics of next generation display. It will realize thinness and bendability of display panel. AM-OLED is mainly studied for flexible display because of it has simple structure, which is consisted of a monolithic stack of organic layers and electrodes on an AM-TFT substrate. [5] The mECD is also a candidate of flexible display. We have reported applicability of mECD to flexible substrate. The intermediate electrochromic layers are formed on porous plastic films in the fabrication process of flexible mECD [3]. In this report, we refer to improved electrochromic compounds, optimized intermediate electrode for mECD, and demonstrated full-color flexible AM-mECDs by utilizing flexible TFT.

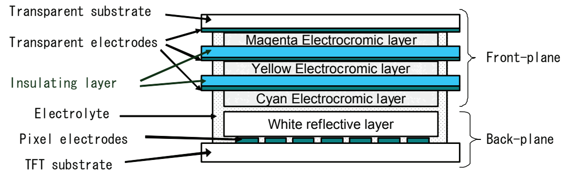

Fig.1 The Schematic image of mECD

2. EXPERIMETAL

2.1 Electrochromic materials.

The electrochromic materials are changed own color by electrochemical reaction. The electrochromic devices are developed for electric papers, smart window, auto dimming mirrors etc.

New electrochromic materials based on bi-pyridine compounds were synthesized. Changing the unit between pyridines, absorption spectra of the materials can be shifted by tuning the pi conjugation length of the chromophore. The absorption spectra of compound A in the colored state (reduction state) shows two or more absorption peaks (Fig.2). We improved electrochromic compounds of cyan, magenta, and yellow for full-color display. Additionally electrochromic compounds of black which has some absorption peak in visible range were newly developed. Absorption spectra of black colored compound are shown in Fig.3.

Electrochromic compounds were chemically bound to the surface of nanostructured Titanium dioxide by a phosphate group substituted at the both ends of the molecules as a Grätzel cell structure.

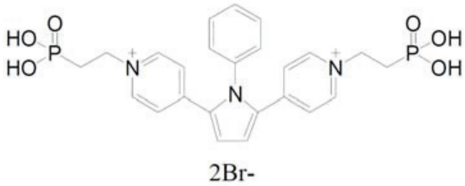

Fig.2(a) The molecular structure of the electrochromic compound A

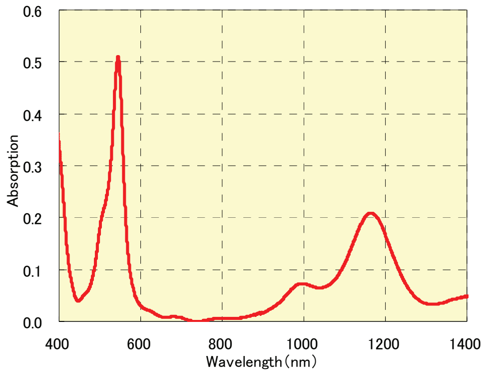

Fig.2(b) Absorption spectra of A (colored state)

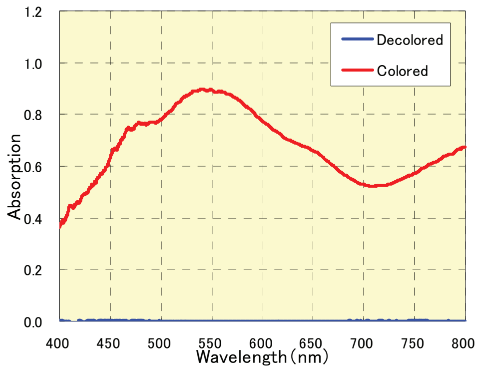

Fig.3 Absorption spectra of a new electrochromic compound of black

Electrochromic layers were easily fabricated by two steps of spin coating. The nanostructured Titanium dioxide layer is formed on the surface of the transparent electrode using TiO2/water dispersion as 1st step. Then electrochromic compound is adsorbed on the nanostructured Titanium dioxide using electrochromic /organic solvent solution as 2nd step.

To check the color shift at the various contrasts by amount of injecting electric charge, we prepared test devices with Yellow, Magenta and Cyan electrochromic compounds respectively. The electrochromic layer was formed on a sputtered the Indium Tin Oxide (ITO) substrate as a front-plane. And the white reflective layer was formed on a patterned Titanium electrode as a counter substrate. Then the front-plane and the counter substrate were assembled together with electrolyte.

2.2 Fabrication of Flexible mECD

Flexible mECD was fabricated using top (100μm) and intermediate (25μm) polyethylene terephthalate (PET) films. At first, the ITO electrodes were formed on both PET films by vacuum sputtering deposition. Then, Titanium dioxide aqueous dispersion (approximately 20nm in diameter) was spincoated on ITO electrodes and annealed on a hotplate at 120°C. Then each electrochromic compound solution of Cyan, Yellow and Magenta was spincoated on the nanostructured Titanium dioxide layer respectively, and each electrochromic layer on the PET film was obtained.

The intermediate PET films and ITO electrodes on it have to be porous, because the ions have to migrate enough between top electrode and bottom pixel electrodes of AM-TFT so that electrochromic compounds can react (Redox reaction).

Next, flexible TFT on plastic film (about 100μm) for ECD was prepared. Then an insulating white reflective layer was formed on the surface of pixel electrode of flexible AM-TFT by spincoating Titanium dioxide dispersion (approximately 250nm in diameter).

Finally, every elements of mECD were assembled together with electrolyte. Nematic liquid crystalline electrolyte was used in order to improve the resolution of the display image [4]. (Fig.4).

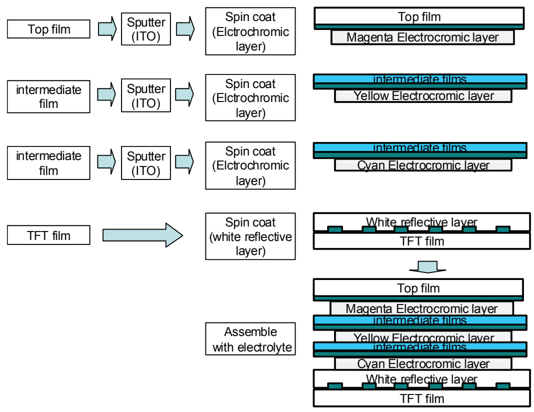

Fig.4 Fabrication process of Flexible mECD

3 RESULTS AND DISCUSSIONS

3.1 Color reproducibility of the single layer ECD

Fig.5 shows the Chromaticity points of Yellow (B), Magenta (C), and Cyan (D and E) test devices at the various contrasts plotted on a*b* diagram. Electrochromic compounds B, C, D show less color shift, although electrochromic compounds E shows issue of color shift by amount of injecting electric charge.

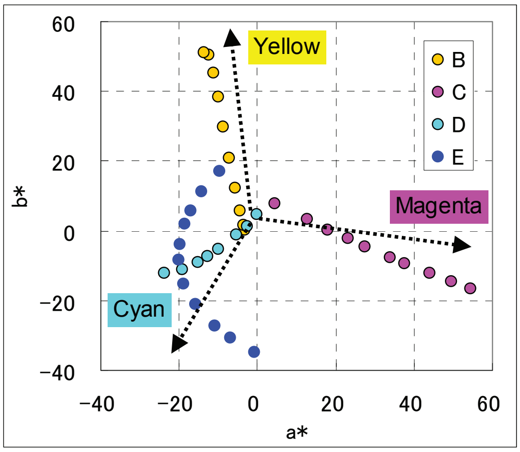

Fig.5 Chromaticity points on a*b* diagram

Measured by MCPD7700(OTSYKA ELECTRONICS CO,LTD)

3.2 Flexible ECD driving by AM-TFT

Fig.6 shows the demonstrator panel of flexible B/W AM-ECD. This panel consists of only one electrochromic layer that have been fabricated same as mECD without intermediate films and electrochromic layers. Panel specification in demo is below. Test image was obtained by applying 5V for driving.

*Size : 3.5inch (53.6mm*71.5mm)
*Resolution : 113.6ppi
*Gray level : 64/color
*Thickness : 0.25mm
*Weight : 4g

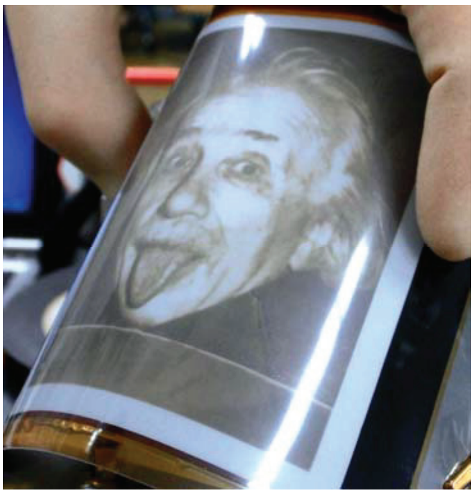

Fig.6 Photograph of B/W flexible AM-ECD using an electrochromic compound of black.

Intermediate PET films and ITO electrodes on it must be porous as described above. These constituents are act as disincentives of ionic conduction. In other words, clogged or airtight structures of them make ionic conduction poor, leads insufficient electrochromic reaction of top electrochromic layer. On the other hand, higher porosity of ITO electrode makes the surface conductivity degraded. It is known as the percolation theory, over 40% of porosity makes the surface conductivity seriously undermined.

Fig.7 shows the result of response speed of top electrochromic layer with one intermediate PET films and ITO electrode on it by varying the porosity of ITO electrode. A DC current (0.32mA/cm2) was applied to the top electrochromic layer, and the time and voltage until 4mC was injected were summarized. It was clearly showed that over 20% of porosity of intermediate ITO electrode was sufficient for fluent mECD drive with lower voltage.

Fig.8 shows the demonstrator panel of full-color AM-ECD. Panel specification in demo is same as B/W panel. We succeeded in displaying full-color image by flexible AM-mECD panel.

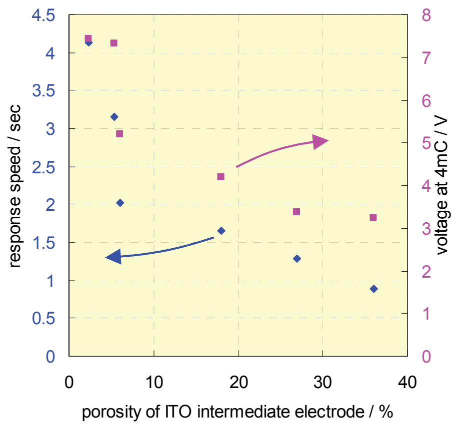

Fig.7 Response speeds of mECD with an intermediate PET film with porous ITO by changing the various porosity of ITO intermediate electrode.

Fig.8 Photograph of full-color flexible AM-mECD

4. CONCLUSION

We have improved electrochromic compounds. Color in the colored state was adjusted by the structure of unit between pyridines, Additionally electrochromic compounds of black were newly developed. Also the color shift at the various contrasts by amount of injecting electric charge was evaluated

To optimize the porosity of intermediate electrode for mECD, we have demonstrated full-color flexible AM-mECDs by utilizing flexible TFT successfully.

5. ACKNOWLEDGEMENT

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] 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-“, National Meeting of the Chemical Society of Japan, 89, 2B1-15 (2009)

[2] T. Yashiro, S. Hirano, Y. Naijoh, Y. Okada, K. Tsuji, M. Abe, A. Murakami, H. Takahashi, K. Fujimura, H. Kondoh, “Novel Design for Color Electrochromic Display”, SID 11 Digest, 42-45, 1, (2011)

[3] Y. Naijoh, T. Yashiro, S. Hirano, Y. Okada, S. C. Kim, K. Tsuji, H. Takahashi, K. Fujimura, H. Kondoh, “Multi-Layered Electrochromic Display”, Proc. of IDW ‘11, EP1-1, 375-378 (2011)

[4] Y. Okada, T. Yashiro, Y. Naijoh, S. Hirano, S. C. Kim, K. Tsuji, H. Takahashi, K. Fujimura, H. Kondoh, “High Resolution Technology for Multi-Layered Electrochromic Display”, Proc. of IDW’12, EP3-2, 641-644, (2012)

[5] K. Teramoto, E. Fukumoto, T. Fukuda, K. Shimokawa, T. Saito, T. Tanikawa, M. Suzuki, G. Izumi, M. Noda, S. Kumon, T. Arai, T. Kamei, M. Kodate, S. No, T. Sasaoka, K. Nomoto “A 9.9-in. qHD Top-Emission Flexible OLED Display Driven by Oxide TFTs”, Proc. of IDW’12, AMD8/FLX7-2, 855-858, (2012)