# Reflective and Emissive Dual Mode Display Cell with Electrochromism and Electrochemiluminescence

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## Abstract

*We are studying novel dual-mode display (DMD) driven by electrochemical reaction. Our DMD cell shows electrochromic (EC) properties as reflective mode and electrochemiluminescent (ECL) properties as emissive mode. In this paper, we reported the effect of structure and materials on characteristics of reflective-emissive dual-mode display cell.*

## Introduction

Present display devices are classified into two categories: reflective mode and emissive mode. The reflective-mode displays, such as printed material and electronic paper (EP), have a high visibility under daylight conditions but are useless in dark places. Conversely, the images on emissive-mode displays, such as plasma display panels (PDPs) and organic light-emitting diodes (OLEDs), can be seen clearly in a darkened room but are difficult to see under conditions of direct sunlight. In addition, reflective displays can be driven at lower rates of energy consumption than emissive displays. Therefore, a dual-mode display (DMD) is desirable in order to exploit both advantages. Since the DMD has both reflective and emissive display mechanisms, we can choose either as the situation demands. However, a DMD is difficult to realize because it must implement two display mechanisms in a single device. In the past, there have been only a few reports about DMDs using different display mechanisms.[1] Moreover, these previously reported DMDs involved complex structures and driving systems.

Electrochromism (EC) is defined as reversible color change that occurs with an electrochemical redox reaction. An electrochromic display (ECD) is thus a reflective display that has many advantages such as high visibility, a memory effect, and color variation.[2-25] Therefore, the ECD has been attracting significant interest as a strong candidate for a paper-like reflective display. Electrochemiluminescence (ECL) is a well-known light emission phenomenon based on electrochemical reactions. Its emission occurs from an excited state formed in collisions of cation and anion radicals generated by a cathode and anode, respectively.[26] ECL devices can be driven by the direct-current (DC) or alternating-current (AC) method. The response time for emission in the common DC method was very slow (approximately one second),[27] because the emission occurred after diffusion of the cation and anion radicals generated by the anode and cathode, respectively. On the other hand, in the case of AC-driven ECL (AC-ECL), both cation and anion radicals were generated at the same electrode due to consecutive changes in electrode polarity. Improvement of the turn-on response (to millisecond time scale) and luminescence intensity has been reported by using the AC driving method.[28-31]

In order to achieve the dual-mode operation with a simple single cell, we focused on the electrochemical reactions that can lead to EC for reflective display and ECL for emissive display. We successfully invented a novel DMD cell with reflective and emissive modes by combining both EC and ECL mechanisms in a simple cell as schematically represented in Fig.1. That is, EC material was affixed on one electrode as the reflective layer and ECL material was affixed on the other electrode as the emissive layer. This DMD cell was fabricated by sandwiching an electrolyte layer between these modified electrodes. The reflective mode is driven by DC voltage (Fig.1a). Under the application of DC voltage, the color change of the EC material occurs by the oxidative or reductive reaction in the reflective layer. In contrast, emission by the ECL material does not occur because only cation radicals or anion radicals, not both, are generated in the emissive layer. Therefore, the reflective mode must be operated by applying DC voltage. Conversely, the emissive mode can be achieved by applying AC voltage (Fig.1b). When AC voltage is applied, the emission by the ECL material occurs by generation of both cation radicals and anion radicals in the emissive layer. Meanwhile, no detectable color change should occur in the reflective layer because reactions of oxidation and reduction occur in rapid succession. As a result, by application of AC voltage we can produce emission alone. Accordingly, we can realize both the reflective mode of EC and the emissive mode of ECL by selecting the operation method as the situation demands.[32, 33]

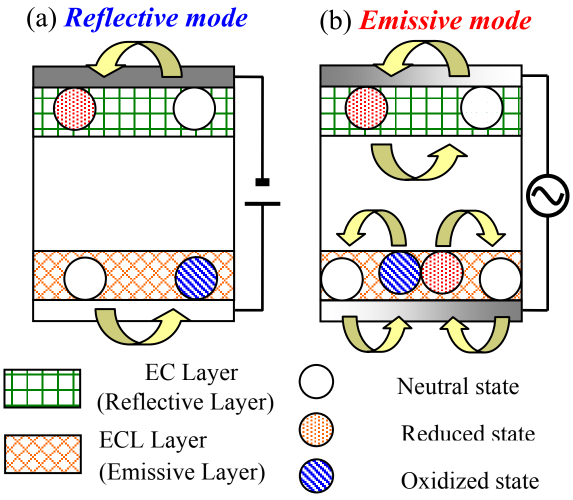

*Fig.1 Driving mechanisms of the DMD cell at (a) the reflective mode and (b) the emissive mode.*

In this paper, we reported the effect of structure and materials on characteristics of reflective-emissive dual-mode display cell.

## Experimental

### Materials and reagents

Solvent-soluble polyethylene terephthalate (PET) derivative (VYLON200, TOYOBO CO. Ltd.) and Ru(bpy)32+ complex (Ru(bpy)3Cl2, Tokyo Chemical Industry Co. Ltd.) were used as EC and ECL material, respectively. Dimethyl sulfoxide, DMSO (Sigma-Aldrich Co.) and tetrahydrofuran, THF (Kanto Chemical Co. Ltd.) were used as solvent after removing water by molecular sieves. Tetra-butyl ammonium perchlorate (TBAP) (Kanto Chemical Co. Ltd.) as supporting electrolyte, poly(vinyl butyral) (PVB) (BX-1, Sekisui Chemical Co. Ltd.) as a host polymer for the gel electrolyte, hexamethylene diisocyanate-based polyisocyanate (DURANATE P-301-75E, Asahi Kasei Chemicals Corporation) as cross-linking agent and ion-exchange membrane (Flemion, Asahi Glass Co. Ltd.) were used as received

### .Preparation of modified electrode and cell fabrication

PET and polyisocyanate were dissolved in THF with mixture ratio of OH:NCO = 1:2. PET film as EC layer was spin-coated with 10 wt.% PET solution on the ITO glass electrode, and then heated at 100 °C for 1 h as cross-linking treatment. Flemion-coated ITO glass electrode was soaked in 10 mM Ru(bpy)$_3$Cl$_2$ aqueous solution for 12 h to prepare the ECL-material modified electrode. One gram of the 50 mM TBAP/DMSO solution was mixed with the appropriate amount of PVB and the resulting mixture was allowed to stand for a week to obtain the PVB-based gel-like electrolyte. DMD cell was fabricated by sandwiching gel electrolyte with 300 μm spacer between EC- and ECL- material modified electrodes.

### Electrochemical easurements

AC and DC voltages were applied to DMD cell with a function generator (IWATAU SG-4105). The ECL optical spectra were measured with a photonic multichannel analyzer (Hamamatsu PMA C10027). Absorption spectra were recorded in situ during the DC voltage applying using Ocean Optics USB2000 diode array detection system. All experiments were conducted at room temperature (20-25 $^{o}$C) under ambient pressure.

## Results and discussion

We confirmed behaviors of the invented DMD cell (Figure 2a). Figure 3 showed differential absorption spectrum of the DMD cell under application of DC -4 V to EC electrode. When the DC -4 V was applied, PET film as the EC layer changed its color from colorless to magenta color (absorption peak : 530 nm) by reductive reaction. This color change of the cell was in agreement with the electrochromism of PET electrode without ECL electrode. Photograph of this reflective mode DMD cell was shown in Figure 2b. We could confirm clear color change of PET film modified electrode on the near side of DMD cell. On the other hand, ECL was not observed because oxidative reaction of Ru complex occurred in the ECL layer. In this way, we were able to obtain only reflective mode by applying DC voltage.

(a) Initial state

(b) ***Reflective mode***

(c) ***Emissive mode***

*Fig. 2 Photographs of DMD cell at (a) initial state, (b) reflective mode under the application of DC voltage and (c) emissive mode by applying AC voltage.*

Next, we tried to demonstrate emissive mode by applying AC voltage. Figure 3 shows emission spectrum of DMD cell under application of AC voltage of 4 V at 50 Hz. The emission spectrum and photograph of the cell (Figure 2c) clearly indicated the generation of AC-ECL from Ru complex. This is because both oxidative and reductive reactions of Ru complex occur alternately by applying AC voltage. Also in the EC layer, both reductive reaction from neutral to anion radical state and oxidative reaction from anion radical to neutral state occur as with ECL layer. In

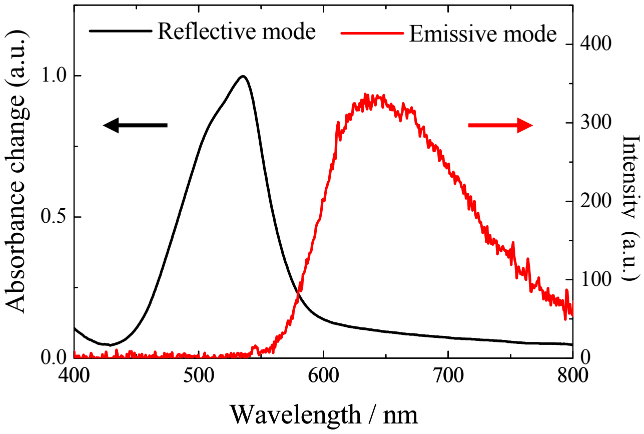

*Fig. 3 Difference absorption spectrum and emission spectrum of DMD cell at (black line) reflective mode and (red line) emissive mode.*

other words, PET film repeated color change between colorless and magenta color quickly. The time of half cycle at 50 Hz is only 0.01 sec. Enough reductive reaction for detectable color change did not occur during mere 0.01 sec because of the slow response time of EC reaction. Therefore, we could not recognize color change of DMD cell by naked eye before and after applying AC voltage. Thus we could obtain only emission of ECL by applying AC voltage. As seen from the above results, we demonstrated that invented DMD cell was effective for dual-mode driving.

We also fabricated DMD with poly(3,4-ethylene-dioxythiophene) (PEDOT, kind of conducting polymer) as EC layer. The PEDOT-DMD cell was fabricated by sandwiching gel electrolyte containing Ru(bpy)$_3$(PF$_6$)$_2$ between a bare ITO electrode and one modified with PEDOT film, keeping the inter-electrode distance at 300 μm by using a Teflon spacer. Fig.4 shows a cyclic voltammogram (current vs. voltage) and the corresponding in situ spectroscopic response for the PEDOT-DMD cell (voltage vs. ECL electrode). Oxidative reaction of Ru(bpy)$_3^{2+}$ complex, reductive reaction and color change (600 nm) of PEDOT film were observed by applying DC voltages higher than –1.0 V. The $V_{\mathrm{onset}}$ of DC-reflective mode of the PEDOT-DMD cell became lower than that of the solution-based DMD cell and PET-DMD cell because the reductive potential of the PEDOT film was lower than that of the PET and Ru(bpy)$_3^{2+}$ complex.

AC-ECL of the cell was observed by applying AC voltage higher than 1.8 V at 50 Hz. The $V_{\mathrm{onset}}$ of AC-ECL was different from CV measurement. Although we are still analyzing details, the PEDOT-DMD cell achieved AC-ECL at lower voltage than Ru(bpy)$_3^{2+}$ complex-based ECL cell (>2.4 V). The $V_{\mathrm{onset}}$ of the PEDOT-DMD cell was drastically decreased by utilizing PEDOT. Fig.4 also shows photographs of the PEDOT-DMD cell in the off state (open-circuit), reflective mode (DC 2 V), and emissive mode (AC 2 V, 50 Hz). As shown in photographs, we achieved DC-reflective mode and AC-emissive mode in the PEDOT-DMD cell at low voltage. From these results, modified electrode-based DMD has a great potential to achieve the improvement of DMD cell characteristics by selecting appropriate combination of materials.

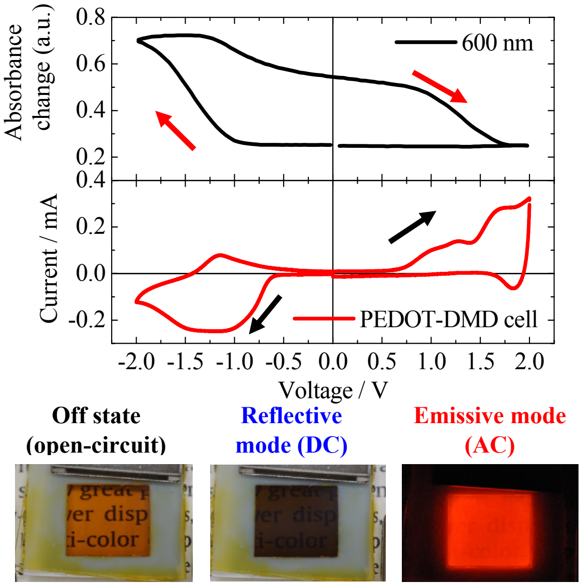

*Fig.4 Change in absorbance (top) and cyclic voltammogram (middle) of the PEDOT-DMD cell. Photographs (bottom) of PEDOT-DMD cell at off state (open-circuit), reflective mode (DC) and emissive mode (AC).*

## Conclusion

In conclusion, we successfully demonstrated the novel DMD cell based on EC and ECL. The DMD cell achieved dual-mode behaviors by the application of DC and AC voltage. Furthermore, this model can be applicable to fabricate advanced DMD using combination of other EC and ECL materials. Those DMD cells would develop DMD application such as color variations of reflective and emissive mode, low power consumption and simplify of cell configuration.

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