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# Investigation of electro-optical properties for electrochemical luminescence device with a new electrode structure

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ABSTRACT

In this paper, we investigate electrochemical luminescent (ECL) device with a new structure and the ECL cell device with proposed electrode configuration works reliably at AC voltage. In particular, the conventional ECL cell has counter electrodes in which a cathode and an anode are opposed to each other, whereas the proposed structure has parallel electrodes in which a cathode and an anode are arranged on a single substrate. The proposed electrode configuration has a structural feature that electric short-circuiting is less likely to occur during bending than the conventional electrode configuration. The electro-optical characteristics of the new electrode configuration such as the current density, the light emission intensity, and the time evolution of the emission are investigated. The proposed ECL device exhibited higher light emitting efficiency than the conventional structure. Especially, at AC operation mode, the new structure showed the distinctive luminescence characteristic which is combined the first luminescence near the surface of electrode with the delayed second luminescence near the center of between electrodes. It was closely related to the behavior of luminescent particles. The proposed the ECL cell structure is expected to be utilized as a flexible display device by taking advantage of its characteristics and practicality.



## 1. Introduction

Generally, a fluorescent and a phosphorescent material are used to generate a light which is a core of a light emitting device [1–10]. Because fluorescence uses only a singlet of a luminescent material, it has a low luminous efficiency, but a high luminous efficiency can be expected in the case of a phosphorescent material which can utilize both singlet and triplet. From this point of view, research using a light emitting material having a metal coordination structure has attracted much attention [11–13]. For example, when ruthenium (Ru) is used as the metal center of the coordination bond, a complex transition state (metal-to-ligand charge transfer, MLCT) including the d orbit of the metal center (Ru) ion and the π electronic configuration of the ligand is formed, thus, the transition can be made smooth and the phosphorescence of high quantum efficiency can be obtained by using triplet. Among such technologies, using electrochemical luminescence (ECL) is a promising way for light emitting device [14–17]. The ECL cell is composed of two transparent conductive oxide (TCO) electrodes and a light emitting material injected between electrodes. It is simple in structure, easy to manufacture, and has merits such as transparency and variety of colors. Therefore, it is expected to be an alternative for wide range of practical applications. However, issues of technology barriers remain to be met to reach the commercialization level such as efficiency, long-term stability, and development of high-purity RGB luminescent materials [18–21]. To solve this problem, more systematic and continuous research is required.

In this work, we propose a novel electrode structure of ECL cell operating in alternating current (AC) operation mode, and study how to utilize it as a flexible display device by taking advantage of the operating principle and structural characteristics. First, a conventional ECL cell structure having a counter electrode where the cathode and the anode faces each other and a proposed structure having a parallel electrode configuration in which cathode and anode are alternately arranged on one substrate were fabricated. Then, electro-optical properties of the ECL cells were investigated. The light emission and the current of the manufactured device operating in the AC mode were also observed to compare with the conventional structure and to examine the enhanced performance of proposed structure.

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## 2. Basic principle and of ECL device

In general, an ECL device has a simple structure in the order of a TCO electrode, Ru-based light emitting material, and TCO electrode. Indium Tin Oxide (ITO) or F-doped $SnO_2$ (FTO) is typically used as the TCO layer. The luminescence principle of the Ru-based ECL device is illustrated in Fig. 1. The Ru-based light emitting material has a structure in which an organic material (ligand) is bonded around Ru metal atoms, and is usually stabilized in the form of $Ru(bpy)_3^{2+}$ [Ru(II)]. The entire process from applying voltage to this material to luminescence in Fig. 1 can be summarized as follows [22,23]. When a voltage (about 3 V) is applied on the electrodes, Ru(II) ions in the Ru-based luminescent electrolyte are reduced to $Ru(bpy)_3^{+}$ [Ru(I)] from the cathode and oxidized to $Ru(bpy)_3^{3+}$ [Ru(III)]. These Ru(I) and Ru(III) ions are accelerated by the applied electric field and diffused toward the counter electrode. In the process, recombination occurs and Ru (I) and Ru (III) are excited to the excited state of $Ru(bpy)_3^{2+*}$ [$Ru(II)^*$] by the exchange of electrons. $Ru(II)^*$ is again transformed to Ru(II), which is in a ground state. At this time, light emission occurs and the entire process is completed. The efficiency of the light emitting device is greatly influenced by the oxidation-reduction action of Ru(II) in the vicinity of the electrode and the recombination process between Ru(I) and Ru(III). The reaction formulas of the Ru-based metal coordination complex in the light emitting device are summarized in the following equations (1)–(4).

$$Ru(bpy)_3{}^{2+} - e^- \rightarrow Ru(bpy)_3{}^{3+} E^{\circ}_{Ru}{}^{2+/3+} = +1.2\ \text{V vs. Saturated Calomel Electrode(SCE)} \quad (1)$$

$$Ru(bpy)_3{}^{2+} + e^- \rightarrow Ru(bpy)_3{}^{+} E^{\circ}_{Ru}{}^{2+/1+} = -1.4\ \text{V vs. SCE} \quad (2)$$

$$Ru(bpy)_3{}^{3+} + Ru(bpy)_3{}^{+} \rightarrow Ru(bpy)_3{}^{2+*} + Ru(bpy)_3{}^{2+} \quad (3)$$

$$Ru(bpy)_3{}^{2+*} \rightarrow Ru(bpy)_3{}^{2+} + h\nu(\sim 2.1\ \text{eV}, 610\ \text{nm}) \quad (4)$$

Here, $Ru(bpy)_3{}^{2+*}$ represent the excited molecule that light-emitting, and $h$ is a photon of light.

The cross sectional structure of the investigated ECL cell structure in this study are shown in Fig. 2; (a) the conventional ECL device with counter electrode configuration, (b) the proposed ECL device with parallel electrode configuration. As shown in the figure, the difference between the two structures is the electrode configuration. The conventional structure is a counter electrode in Fig. 2(a) which a cathode surface and an anode surface face each other, while a new structure is a parallel electrode in Fig. 2(b) which a cathode and an anode are alternately arranged on one substrate. However, the principle of light emission and materials in both structures are the same. In this work, ITO was used as a TCO electrode in both structures and the gap between electrodes was maintained at 60 μm.

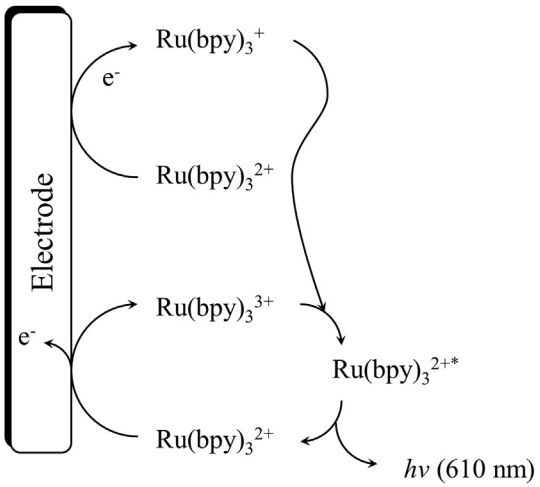
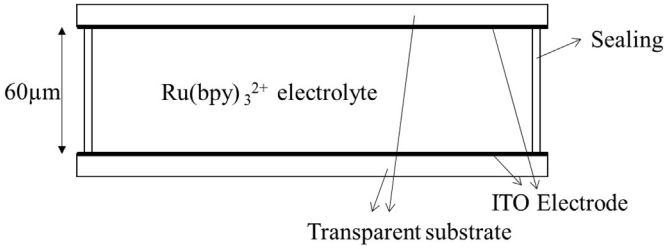



**Fig. 1.** The luminescence mechanism for $Ru(bpy)_3^{3+}/Ru(bpy)_3^{+}$ in ECL device.

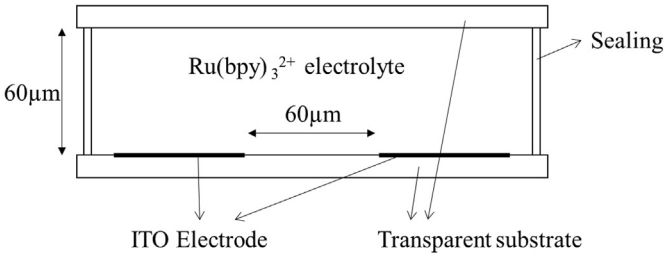
## 3. Experimental setup

### 3.1. Synthesis of luminescent material

As luminescent material, $Ru(bpy)_3^{2+}$ has properties of a strong redox potential and a strong absorption due to charge transfer between metal and ligand in visible light region, and an unnecessary photochemical reaction. In particular, it emits phosphorescence of about 610 nm from triplet excitation. The synthetic procedure of the luminescent material in this work is shown in Fig. 3 [24–26]. $Ru(bpy)_3(PF_6)_2$, in which $PF_6^-$ is used as a counter ion, is synthesized in order to obtain chemically stable $Ru(bpy)_3^{2+}$. Also, as initial materials, commercially available 1 g of Tris(bipyridine) ruthenium(II) chloride ($Ru(bpy)_3Cl_2$; Sigma-Aldrich) and 0.5 g of ammonium hexafluorophosphate ($NH_4PF_6$; Sigma-Aldrich) are dissolved in high purity distilled water. After a mixture of the two aqueous solutions was stirred for 1 h, a precipitate of $Ru(bpy)_3(PF_6)_2$ can be observed while the reaction between the solutions occurs due to the ion exchange process. After drying precipitate is collected from purification by filtering out the solutions and by recrystallizing them, purer $Ru(bpy)_3(PF_6)_2$ is obtained. After filtering the solutions again in the vacuum state, removing moisture in them, then mixing them with propylene carbonate (PC; Sigma-Aldrich), one can accumulate $Ru(bpy)_3^{2+}$.




(a) The conventional ECL cell structure with the counter electrode




(b) The proposed ECL cell structure with the parallel electrodes

**Fig. 2.** The investigated ECL cell structures.