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Chemiluminescent display

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Abstract. Investigation of organic liquid phase electroluminescence (traditionally, the so-called "electro-chemiluminescence" or "electrogenerated chemiluminescence") is of special interest as a competitor for "liquid" and "solid" organic light emitted diodes (OLEDs). From the electrochemical point of view, chemiluminescence is a self-regenerating process providing high brightness light radiation due to recombination of oppositely charged dye radicals. Chemiluminescent displays have a competitive set of parameters: high light efficiency, low power consumption, low driving voltages, fast response time, high spatial resolution, very high optical transmission and wide operation temperature range. No polarizers or alignment layers are required. Samples of chemiluminescent displays, including matrix microdisplays and micromechanically made cells are available; its design and parameters are discussed in details. Theoretical and experimental investigations of thin film DC chemiluminescence phenomena are carried out. On the basis of obtained experimental results, the most important physical processes have been investigated: charge injection into solution and charge transfer by electrohydrodynamic flows. Further prospects of chemiluminescent display devices are discussed.

Keywords: nanostructure, chemiluminescence display.

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1. Introduction

Ambient liquid medium creates specific conditions for electroluminescence process – high concentration of active particles with opportunity of their redistribution in space by hydrodynamic transport. Investigation of liquid-phase organic electroluminescence is of special interest as a way to compare "liquid" and "solid" organic light emitted diodes (OLEDs), because both systems use the same luminophores. For example, luminophore rubrene, which effectively emits light by triplet-triplet annihilation, comes to OLEDs from electrochemiluminescence (ECL). ECL process is represented in Fig. 1. On electrodes from neutral molecules anion and cation radicals are produced, these radicals recombine in the solution bulk and form the excited molecules that emit photon and begin new ECL cycle. From the electro-chemical viewpoint, ECL is a self-regenerating process providing high brightness light radiation due to recombination of oppositely charged dye radicals. The triplet mechanism of radiation is more complicated, but as a whole corresponds to the cycle in Fig. 1.

2. ECL displays

There are different types of ECL devices, but only thin film direct current electrolyteless ECL devices will be considered in this paper, because their operation is the most similar to OLED's one. At first, such a construction was proposed by Phillips corporation in 1982 [1]. ECL-cells are similar to liquid-crystal cells and consist of two glass substrates with transparent electrodes assembled with a cell gap of 10-50 μm and filled with a mixture of organic dyes in aprotic solvent (see Fig. 2). No polarizers or alignment layers are required.

ECL displays have a competitive set of parameters:
- light efficiency 6-8 lm/W;
- power consumption (at 50 $\mathrm{Cd/m^2}$) 5 $\mathrm{mW/cm^2}$;
- driving voltages 3-5 V DC;
- response time 5-30 ms;
- spatial resolution 10-50 μm;
- optical transmission 80 %;
- operating temperature from –55 to +50 °C.

Samples of ECL displays that include matrix microdisplay and micro-ECL cell [2] are depicted in Figs 3 and 4.

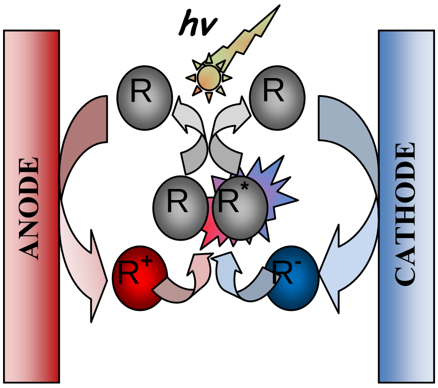

Fig. 1. ECL cycle.

3. ECL phenomena

Charge transport in electrolyteless ECL cells is very specific. In reality, solution is dielectric medium, but under electrostatic forces electrohydrodynamic instability appears, and fluxes with the speed to some meters per second come into existence. Transfer of ion-radicals by these fast fluxes in 10-50 µm gaps produces the current density of several mA/cm^2 at the 5-V applied bias. ECL convection shapes at different applied voltages in 25-µm cell [3] and diagram of thin film EHD convection are shown in Fig. 5. Fig. 6 shows results of the ECL cell (with 25 µm gap) luminance measurements by LumiCam 1300 equipment at Pforzheim University. The bias was 5 V DC, correspondent current density was ~50 µA/cm^2, luminance ~2.5 Cd/m^2.

Theoretical simulation is carried out for the ECL cell [4, 5]. Simulation was carried out for "honeycomb" ordered structure in a cylindrical region (see Fig. 5). In the base of the physical model there are experimental observations:

– monopolar injection from cathode;

– existence of local regions with the highest velocities of fluxes;

– concentration of charged particles in this regions.

The theoretical results are presented by the following formulae:

$$J=\frac{Q}{\delta}V_{\max}\frac{1}{\pi\delta^2}=16.8\,\varepsilon^2\varepsilon_0^2\,\frac{U^3}{\eta\delta^3},$$

where δ is the cell gap, η – dynamic viscosity;

$$V_{\max}=4\,\varepsilon\,\varepsilon_0\,\frac{U^2}{\delta\eta}$$

(0.0035 Poise for glim), $V_{\max}$ is the velocity in the middle of the cell, Q – limited charge, U – applied voltage, ε – dielectric constant (7.2 for glim).

It is possible to verify the theory by recent measurements of ECL luminescent cells with a wide range of gaps [6, 7]. Corresponding results are summarized in Fig. 7.

Special experimental technique was used to determine the influence of initial flow velocities on start-up of ECL [5]. 5-V pulse was applied to ECL cell operating at lower voltages. These start-up curves are

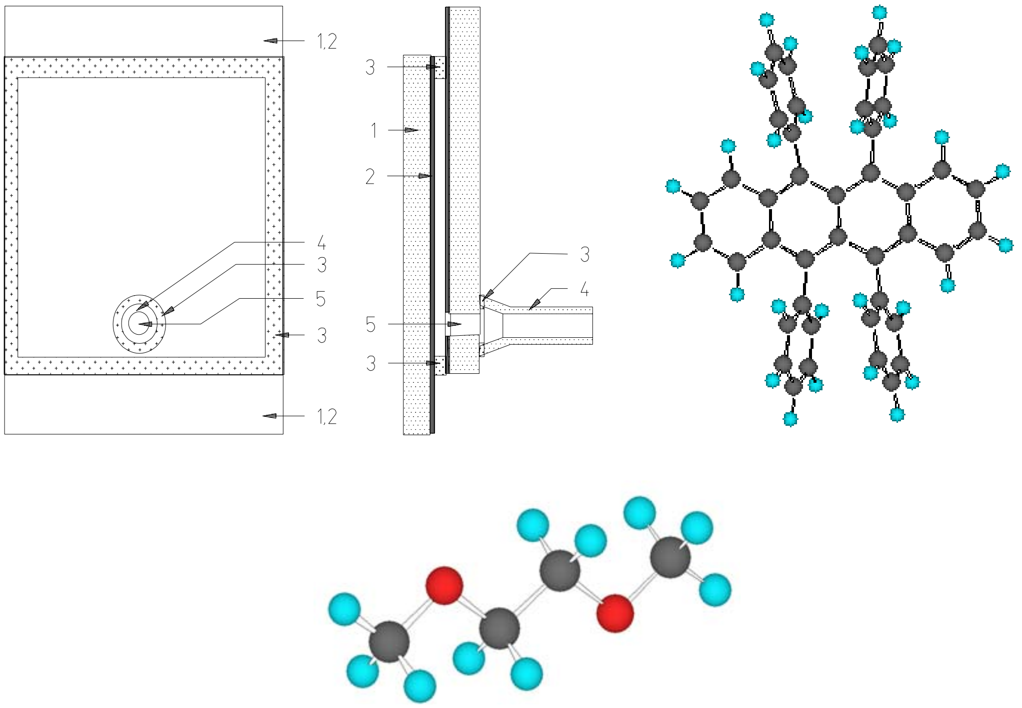

Fig. 2. Direct current thin film ECL cell assemble: glass plate (1), ITO (2), ceramic glue (3), capillary (4), hole luminophor – rubrene (5,6,11,12-tetraphenylnaphthacene), solvent – dimethoxyethane (glim) CH_3-O-CH_2-CH_2-O-CH_3 (5).

Fig. 3. ECL displays.

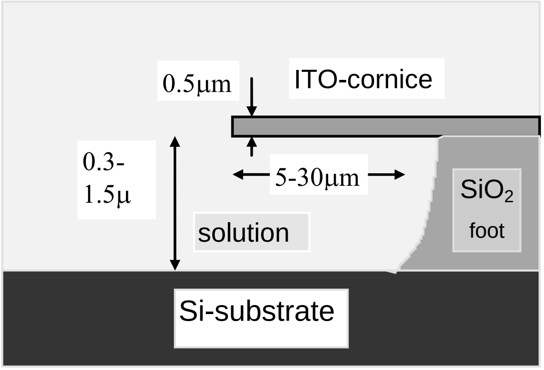

Fig. 4. Microelectrochemical cell.

presented in Fig. 8. These curves have sharp inflection: fast start-up is provided by saturation of the existing flux with new portions of anion-radicals, and slower parts are determined by flow acceleration and saturation by bulk ion-radicals.

It is possible to achieve rather fast response time (several ms), if the sell permanently works at practically negligible level of luminance (see the curve “from 2.9 to 5 V” in Fig. 8).

4. Passive matrix applications

Light emissive passive matrix displays require very high performance electroluminescent elements. Particularly, the elements should have a very high peak luminance, fast response time and sharp control characteristics.

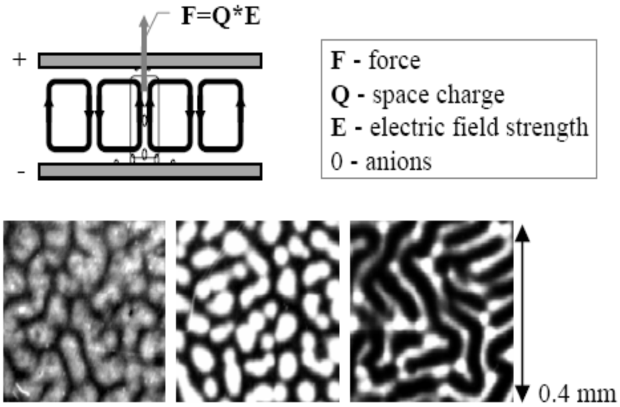

Fig. 5. EHD convection diagram and ECL shapes at different applied voltages.

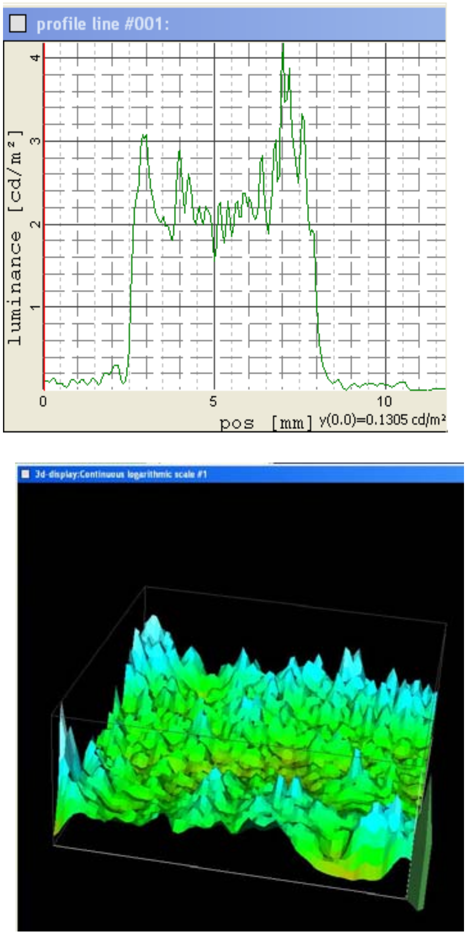

Fig. 6. Luminance spatial distribution for ECL cell.

ECL cells have a sharp current-voltage characteristics with the threshold at about 2.7 V. It means that the maximum applied voltage should be about 5 V or less to depress parasitic luminescence. All alternative current ways, which include two serial cells, do not show any luminance, because at least one of the serial cell voltage will be biased lower than the threshold.

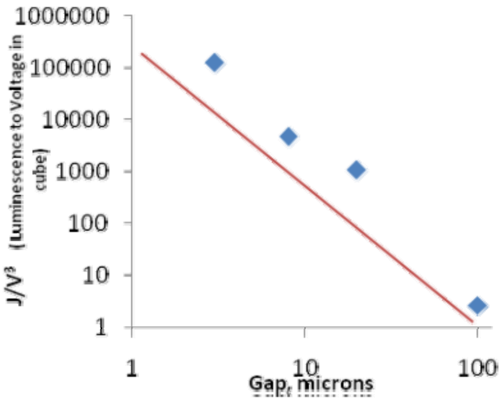

Fig. 7. Theoretical and experimental data comparison.

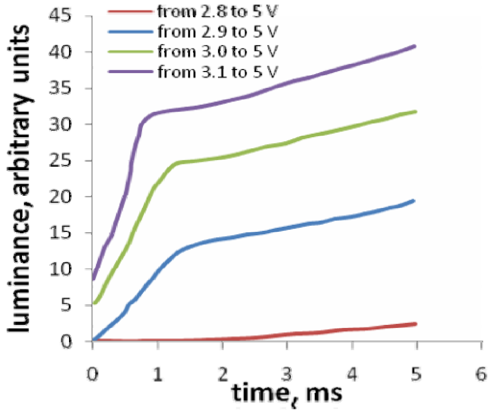

Fig. 8. Start-up curves of brightness at different voltages.

If we going to achieve average luminance 50 Cd/m^2 in 64 rows passive matrix display, the peak luminance should be about 64×50≅3000 Cd/m^2. The luminance can be achieved in 2.5-µm gap ECL cell.

Background bias should be adjusted carefully. On the one hand, it should be enough to provide background electrohydrodynamics flows and corresponding fast response time. On the other hand, for 1:100 dynamic range the background luminance should be 0.5 Cd/m^2. It is 6000 times smaller than the peak luminance.

Additional limitation is a distance between rows. Nearby cell can lighting at low level – as the cell with a gap like a row's pitch. To have enough dynamic range, this kind of lighting should be lower than 0.5 Cd/m^2 and corresponding pitch will be about 50 µm for 2.5-µm gap ECL cell. It is significant limitation for microdisplay design.

5. Conclusion

It is possible to realize ECL passive matrix displays with a performance compatible to solid OLED. However, it only complicated, top ECL cells are suitable for this design. Note that special passive matrix display applications like moving point or cross can be realized easily in traditional large gap ECL cells.

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