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ELECTROCHEMILUMINESCENCE: FROM SUBMICRON CELLS TO MATRIX DISPLAYS

P. V. JAGUIRO

*Belarusian State University of Informatics and Radioelectronics, 6 Brovka Str.,
Minsk, 220013, Belarus*

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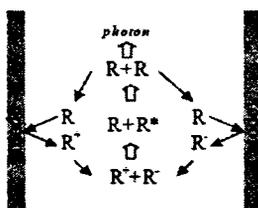
Construction and basic principals of organic direct current electrolyteless electrochemiluminescent (E rational layer at electrode - liquid dielectric interface, charge injection into solution and charge carrying by electrohydrodynamic flows. Practical applications, including matrix displays are discussed.

Keywords: electrochemiluminescence, electrolyteless, molecular crystal excitons, matrix display

Introduction

Carrying out analogy with light emission diodes and gas discharge lamps leads us to classify electrochemiluminescence (ECL) as a liquid-phase recombination electroluminescence. Liquid environment creates specific conditions for electroluminescence process - high concentration of active particles with opportunity of their redistribution in space by hydrodynamic carrying. Investigation of liquid phase organic electrolum人之生 (traditionally named "electrochemiluminescence" or "electro-generated chemiluminescence") is being 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 ECL. Another material, which is actively used in OLEDs, AluminumQuinolate (Alq3) came to ECL and demonstrates high electrochemiluminescence quantum yield (~0.5%) [1].

ECL process is represented in fig 1 - on electrodes from neutral molecules anion and cation radicals are produced, these radicals recombine in bulk of the solution and form the excited molecules, which let out a photon and begin new ECL cycle. From the electrochemical point of view, ECL is a self-regenerating process providing high brightness light radiation due to recombination of oppositely charged dye radicals. Triplet mechanism of radiation is more complicated, but as a whole corresponds to the cycle in fig 1.



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Fig.1. E发

Construction, operation and parameters of thin film direct current electrolyteless ECL devices

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 construction was proposed by Phillips corporation in 1982 [2]. 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.

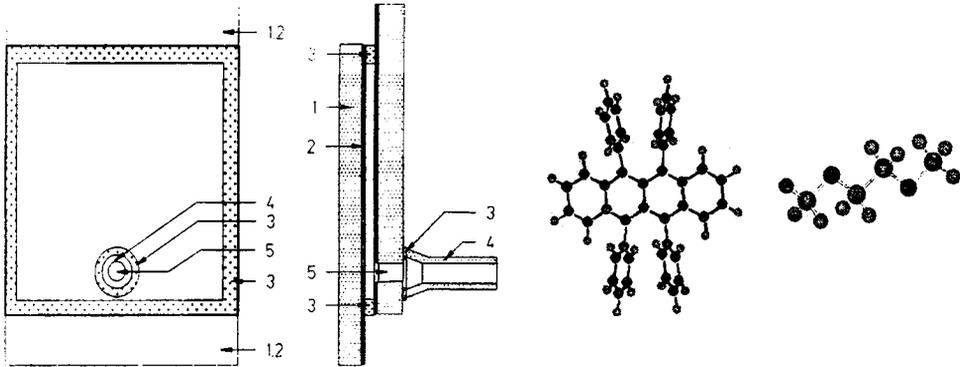


Fig. 2. Direct current thin film ECL-cell

Assemble (left): 1. Glass plate 2. ITO-layer 3. Ceramic glue 4. Capillary 5. Hole
 Luminofor (center): Rubrene - (5,6,11,12- tetraphenylanthracene) $C_{26}H_{18}$ $\lambda_{ECL}=0.56\mu$
 Solvent (right): Dimethoxyethane (glim) - $CH_3-O-CH_2-CH_2-O-CH_3$ $\epsilon=7$

ECL displays have a competitive suit of parameters:

- light efficiency 6 ...8 lm/Wt
- power consumption (at 50 Cd/m²) 5 mWt/cm²
- driving voltages 3 ...5 V DC
- response time 5 ...30 μs
- spatial resolution 10... 50 μm
- optical transmission 80 %
- operating temperature -55... + 50°C

Samples of ECL displays, including matrix microdisplay and microECL cell, which are designed at Belarusian State University of Informatics and Radioelectronics, are presented in fig. 3, 4.

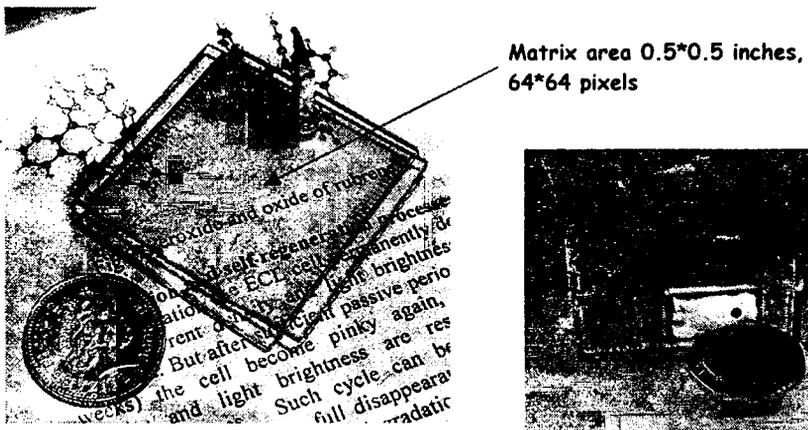


Fig. 3. ECL displays

The microelectrochemical cells with submicron inter-electrode gap, which is easy for filling and interchange of reagents with macro-volume of solution is shown in fig. 4. These cells were fabricated by microelectronics technology and consist of Indium-Tin Oxide cornice hanging over the silicon substrate and distanced from it by dielectric foot. This cornice is formed in self-alignment etching process of dielectric layer throughout the hole in covered transparent electrode. Silicon substrate and thermal oxidation for dielectric layer formation are chosen for better compatibility with standard microelectronics technology. Special solution for etching silicon oxide dielectric layer selectively to Indium-Tin Oxide is designed [3]. Accuracy of inter-electrode gap is very high and is determined by thickness of dielectric layer. The hole in covered electrode is used for filling and interchanging of reagents.

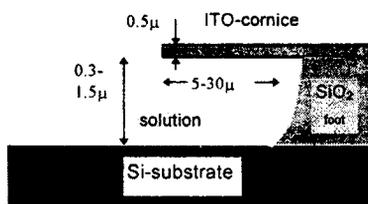


Fig. 4. Micro electrochemical cell

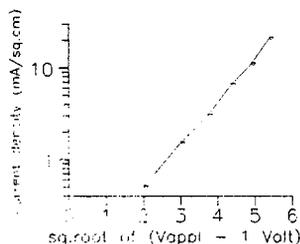


Fig. 5. I-V characteristic of the microcell

It's easy to make array of such electrochemical cells with total area reaching some square centimeters. In such cells it is possible to carry out reactions, usual for ultra micro-electrode systems, for example - electrochemical reactions in electrolyte-less solutions. By using an array of the cells it is possible to have macro amount of output reagents. Optical measurements are possible throughout transparent cover electrode.

Such cells have been used in investigations of DC electrolyte-less electrochemiluminescence. The array of the cells was fabricated on 3-inch silicon substrate with 5mm*20mm chip size and 1mm*1mm array's area.. Light emission was registered throughout Indium-Tin Oxide electrode. Thin inter-electrode gap (from 0.3 to 1.08 micrometer) removes current limitation by space charge and gives opportunity for investigation of charge injection mechanism [4]. I-V characteristic of ultra thin cell with 0.8 μm gap filled by glim is presented in fig. 5 in Frenkel-Pool coordinates. Straight line indicates Shottky emission. Note that the energy barrier consists of two parts. The first part with potential difference about 1 Volt is tunneling thin and corresponds to space of double electric layer. This part of energy barrier does not limit the electric current. Another part is outside of double layer, is changed under applied electric field and limits the current by Shottky rule.

Electrolyteless Paradox

In DC ECL-cells with supporting electrolyte the solution is electrically neutral and so current and brightness are limited by diffuse kinetics (see fig. 6, line - electrolyte).

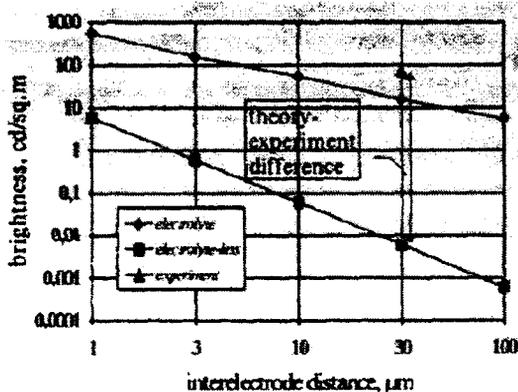


Fig. 6. Difference between experimental and theoretical data is the electrolyteless paradox

Experimental and theoretical investigation of E D streams

Charge transport in electrolyteless ECL cells is very specific. Solution really is dielectric media, but under electrostatic forces electro hydrodynamic instability appears and streams with speed to some meters per second come into existence. Carry of ion-radicals by so high speed streams in 10-50 micron gaps produces current of some mA/cm² at 5 V applied bias. ECL convection shapes at different applied voltages in 25-μm cell [5] and diagram of thin film EHD convection are shown in fig. 7.

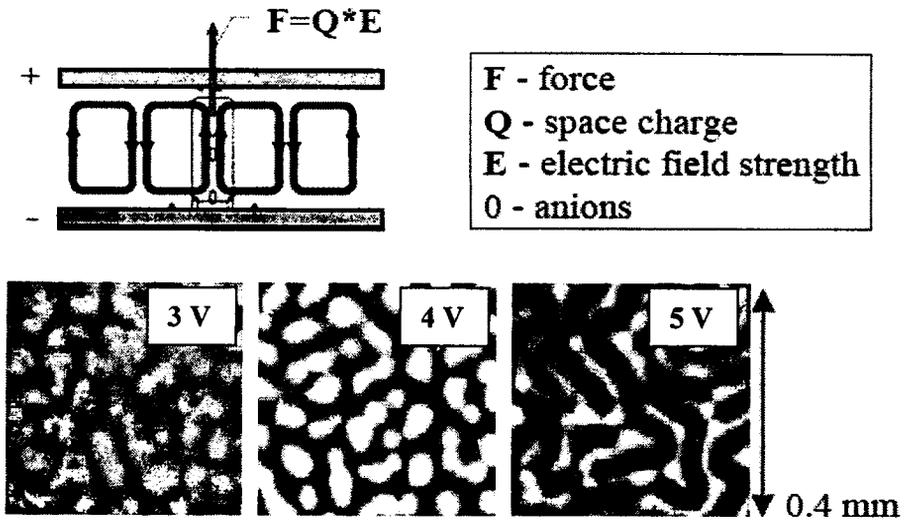


Fig. 7. EHD convection diagram and ECL shapes at different applied voltages

The main idea of the experiment is fast interruption of current in working ECL cell. In this case the formation of new ion-radicals at interfaces is fast broken, but due to existence of double layer capacitance, the conditions for recombination process in anode region are conserved. The ECL brightness does not change while the stream covers interelectrode distance because some amount of anion-radicals exists in the cell volume. After this moment the brightness must decrease. Decay of brightness is determined by diffusion of the anion-radicals from inner stream regions to more active outer regions. Graphs of the brightness decay at different applied voltages are presented on the left part of fig. 8, and the right part of the figure illustrates the graph stream velocity vs. brightness, which are derived from the previous data [6]. Theoretical curves will be described below.

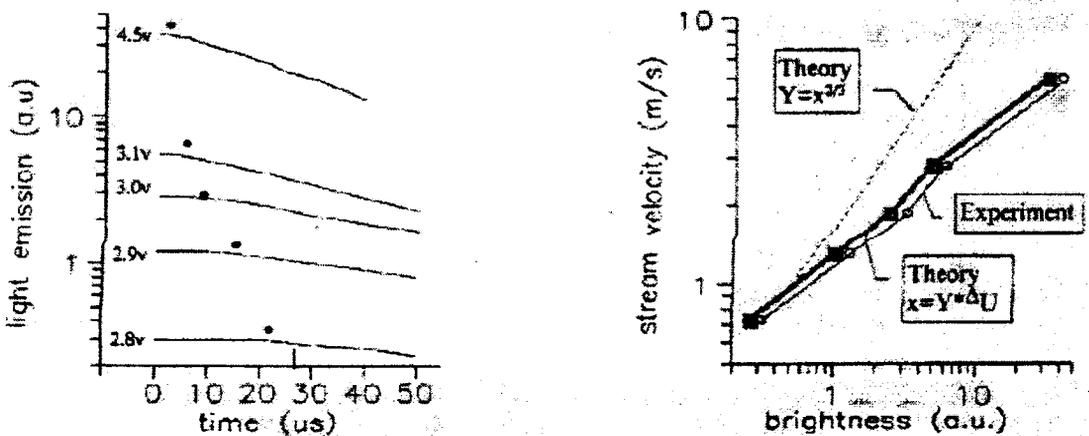


Fig.8. Decay curves at different applied voltages (raphic (left) and stream's velocity vs. brightness (right)

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Similar experimental technique‡ technique was used to determine the influence of initial stream's velocities on⁶ start-up of ECL ECL [6]. 5-V pulse was applied to ECL cell operated at lower voltages. These start-up curves are presented in fig.10. The curvesнде curves have sharp inflection: fast start up is provided by saturaw

tion of existing stream with new portions of anion-radicals and slower parts are determined by stream acceleration and saturation the volume ion-radicals.

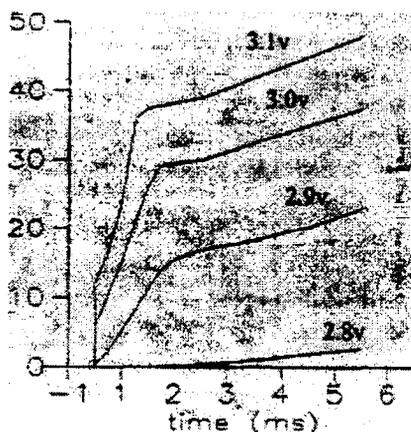
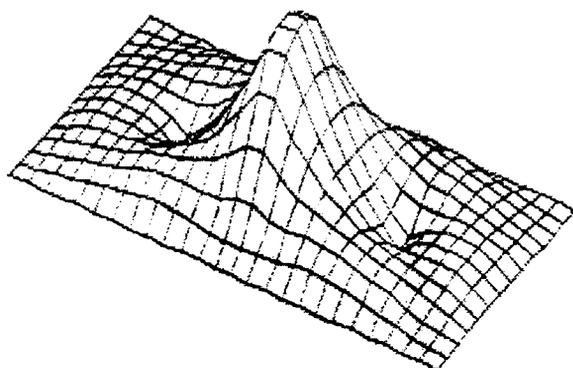


Fig.9. Start-up curves of brightness at different initial voltage

Ruffle theoretical simulation is carrying out for the ECL-cell [6]. Simulation was carrying out for "honeycomb" ordered structure in cylindrical region (see fig. 7). In the base of the physical model are experimental observations:

- monopolar injection from cathode
- existence of local regions with the highest velocities of streams
- concentration of charged particles in this regions.

The theoretical results are presented in fig. 10 and in following formulas:



$$J = \frac{Q}{\delta} V_{\max} \frac{1}{\pi \delta^2} = 16.8 \epsilon^2 \epsilon_0^2 \frac{U^3}{\eta \delta^3}$$

$$V_{\max} = 4.4 \epsilon \epsilon_0 \frac{U^2}{\delta \eta}$$

Fig. 10. Velocity's field in the cell

where: δ - cell gap, η - dynamic viscosity (0.0035 Poise for glim), V_{\max} - velocity in middle of the cell. Q - limited charge, U - applied voltage, ϵ - dielectric constant (7.2 for glim).

The equations are used as theory forecast in fig. 8.

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Electrode Processes and Molecular Crystal Excitons

The liquid in thin film ECL cells is a carefully purified low polar dielectric media. It is seemed unlikely, that amount of ionic impurities in the cell microvolume is enough to form electrical double layers at electrodes. Probably, the electrical double layers are formed from luminophor's molecules or ion-radicals. Measurements of ECL cell discharge kinetics shows that the double layers has anomaly high specific capacity [7]. Note, that conducting polymer PPV also demonstrates high specific capacitance in similar measurements [8]. Results of analyses the data from [7] are presented on fig 11. If double layer is formed from singly charged ions, their specific weight must be $(22/\epsilon)$ g/cm³. In double layer ϵ decreases to optical corresponding values and goes to unrealistic calculated specific weights.

So, questions as “is double layer formed from multicharged rubrene ions, or exist another mechanism for its anomaly high capacity?” and “are low polar solvent or rubrene molecules directly contacted with electrode in double layer?” are open.

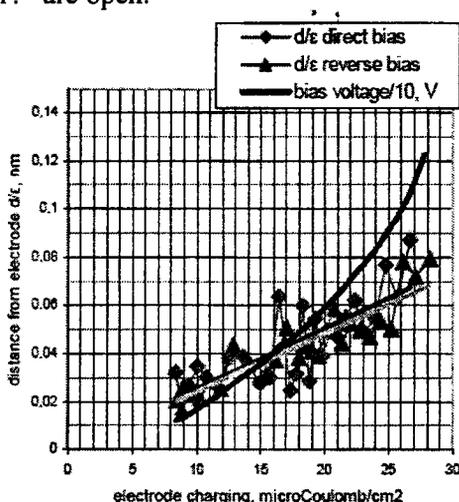
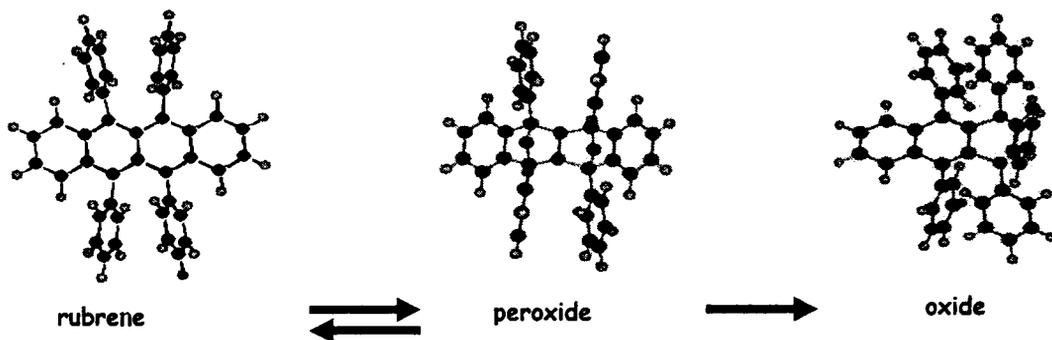


Fig 11. Space charge distribution in the double layer

Electrochemiluminescence of rubrene is realized in T-way and neutral molecule with triplet excited electron is formed as a result of ion-radical recombination. If electrode area is some form of charged rubrene crystal, then lot of specific features must be appeared due to high concentration of triplet excited molecules (molecular crystal excitons). Efficiency of triplet energy transfer between aromatic molecules is extremely high, for example triplet electron changes $10^{11} \dots 10^{12}$ molecules and singlet electron – only $10^1 \dots 10^2$ [9, p.147]. Usually dye crystals don't demonstrated new continuous absorbance bands, which correspond to formation a conductive/valence bands. It means that electrons at normal or singlet levels are not jointed. But the same crystals demonstrate photoconductivity, which can be explained by jointing of triplet levels [10]. Such band is really anomalous the gap is not indirect, it is “forbidden”. Maybe this is a key for another ECL paradox – luminescence appears directly at the anode, but not quenched by the metal electrode.

Degradation and Regeneration Processes

Light exposition excites dye molecules into triplets, which easier reacts with triplet oxygen molecules and produces the peroxide (see fig. 12, the center).. In ECL process, when dye triplets are generated electrochemically, system reactive to oxygen must be extremely high. But peroxide can be effectively regenerated, for example by heating at 145°C. On some catalyzes the peroxide can irreversible and exothermically transformed into stable oxide [11] (see fig. 12, the right).



During operation the ECL cell permanently decolorized, current density and light brightness are decreased. But after sufficient passive period (few weeks) the cell become pinky again, current density and light brightness are restored to previous values. Such cycle can be repeated many times, even for full disappearance of light emission, without visible degradation time after 100 warta. It seems to be a rubrene peroxide formation/decomposition, but there not enough amount of oxygen in the solution. Possible source of oxygen, which is in direct contact with rubrene, is transparent electrode $\text{In}_2所未$. 0,25 μ film of In_2O_3 contains 100 times more amount of oxygen, then it is necessary for complete rubrene oxidation, so possible stoichiometric changes is rather small. Note that this surmise is not experimentally checked yet.

Conclusion

Electrolyteless direct current thin film electrochemiluminescence is very complicated physical phenomena with attractive prospectus to practical applications.

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