

# Numerical Simulation of Kinetic Processes in Thin-layer Electrochemiluminescent Light Emitting Cells

Danylo Martynov<sup>1,2</sup>, Yuriy Zholudov<sup>1</sup>, Mykola Slipchenko<sup>2,3</sup>, Olena Slipchenko<sup>4</sup> and Kyryl Korobchynskiy<sup>5</sup>

<sup>1</sup> Kharkiv National University of RadioElectronics, Nauky Ave. 14, Kharkiv, 61166, Ukraine

<sup>2</sup> Institute for Scintillation Materials of the National Academy of Sciences of Ukraine, Nauky Ave. 60, Kharkiv, 61072, Ukraine

<sup>3</sup> Institute of Quantum Optics, Leibniz University Hannover, Welfengarten 1, Hannover, 30167, Germany

<sup>4</sup> European Educational Scientific Technological Center, National Technical University "Kharkiv Polytechnic Institute", Kyrpychova Str. 2, Kharkiv, 61002, Ukraine

<sup>5</sup> Mathematical Modeling and Artificial Intelligence Department, National Aerospace University "Kharkiv Aviation Institute", Vadyrna Manka Str. 17, Kharkiv, 61070, Ukraine

## Abstract

This study presents a comprehensive mathematical modeling and numerical simulation of electrochemiluminescent (ECL) cells, which are the main elements of ECL sensors and light emitters. The ECL cell is designed to generate optical signal, and its efficiency is crucial for the overall performance of ECL sensors and light emitting devices. The mathematical model is based on the physical principles of electrochemiluminescence, which involve electron transfer reactions between electrochemiluminophores and electrodes. The model takes into account the diffusion of particles, recombination rates, and emission processes, resulting in a system of nonlinear partial differential equations. Two types of ECL cell designs are considered: a cell with counter diffusion of anions and cations, and a cell with a thin film of electrochemiluminophore on the anode. The numerical solutions of the model equations are presented, and the results show that the cell with a thin film of electrochemiluminophore exhibits superior efficiency and a more favorable distribution of emitters. The study also estimates the photon yield in both types of cells and compares their light emission efficiency. The results indicate that the cell with a thin film of electrochemiluminophore would have significantly higher ECL efficiency than the cell with counter diffusion of anions and cations. Overall, this study provides a fundamental understanding of the processes involved in thin-layer ECL cells and offers valuable insights into the design and optimization of thin-layer ECL sensors and light emitters.

## Keywords

Diffusion, electrochemiluminescence, mathematical modeling, modified electrode, recombination, thin-layer electrochemical cell

## 1. Introduction

Recently, there has been a surge in global interest in the advancement of electrochemiluminescence (ECL) light-emitting devices. This heightened attention stems from the extensive availability of electrochemiluminophores, which possess radiative properties capable of encompassing nearly the entire spectrum of the visible frequency range. Consequently, ECL devices exhibit remarkable versatility, enabling a diverse array of potential applications, including (bio)chemical sensors, light-emitting devices and even lasers [1-3].

The majority of the developed ECL light-emitting devices are non-coherent devices, such as indicators and transducers (sensors) [4-7]. However, the development of coherent devices, specifically organic lasers with electrochemical pumping, is also known from literature and attracts certain research interest [8].

In the mid-1970s, research into the development of an ECL quantum generator (laser) emerged [8-9]. However, due to the limited computational capabilities of that era, precise mathematical

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✉ martynov.d.yu@gmail.com (D. Martynov); yurets.zh@gmail.com (Yu. Zholudov); naukovets.big@gmail.com (M. Slipchenko); Olena.Slipchenko@khpi.edu.ua (O. Slipchenko); k.korobchinskiy@khai.edu (K. Korobchynskiy)

ORCID 0000-0002-3143-5280 (Yu. Zholudov); 0000-0002-4242-4800 (M. Slipchenko); 0000-0002-3676-6070 (K. Korobchynskiy)



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modeling proved challenging, hindering the device's creation [8]. By the end of the millennium, Japanese scientists have successfully developed the ECL laser and identified potential applications for this technology [3]. It is not inferior to semiconductor lasers, but its power characteristics make it much more favorable in application. Since these are only the initial steps in this direction, there are still many unresolved issues (durability, efficiency of such devices, low power, thermal instability, etc.).

In the present work, we set the task of computer modeling of the main element of light-emitting ECL devices, the thin-layer ECL cell, in which all processes up to radiation take place. This paper explores the fundamental principles underlying the electrochemiluminescence phenomenon and present three viable approaches for designing an ECL cell capable of efficient generation of light.

## 2. Physical principles of ECL

Electrochemiluminescence is a phenomenon where light is emitted due to electrochemical reactions occurring in an optoelectronic device upon the application of voltage. This process involves electron transfer within the electrochemiluminophore solution and at the interface between the electrode and the electrochemiluminophore [10, 11].

Upon the application of voltage, with positive polarity at the anode and negative polarity at the cathode, reduction (anode) and oxidation (cathode) reactions transpire in the vicinity of the electrodes, leading to the formation of cation- and anion- radicals (CR, AR)  $A^{\bullet+}$  and  $A^{\bullet-}$  respectively. These processes take place at the appropriate reduction  $\varphi_{red}^A$  and oxidation  $\varphi_{ox}^A$  potentials for a given substance.



As AR and CR diffuse deep into the solution, they may undergo collisions with each other if the lifetime of these particles allows them to approach. Upon collision, the radicals recombine to possibly form the following particles:

1. An excited singlet state  $^1A^*$  and a ground singlet state:



2. A triplet state  $^3A$  and a ground singlet state:



3. An excimeric singlet state  $^1A_2^*$ :



ECL quanta  $\gamma_{ECL}$  are typically emitted by radiative deactivation of the excited singlet state  $^1A^*$ :



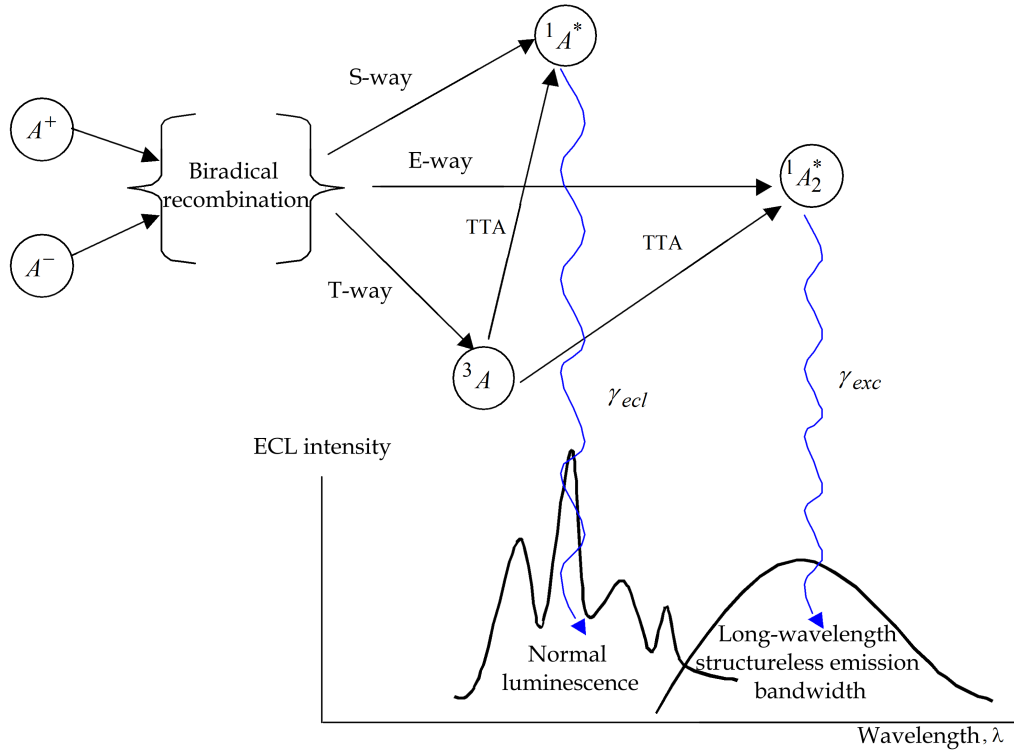
There is also emission in the longer wavelength region produced by the deactivation of the excimeric state  $^1A_2^*$ :



Emitters (excited singlet states and excimers) are sometimes formed through a triplet-triplet annihilation (TTA) stage:



Equations (3)-(8) are schematically represented in Figure 1.



**Figure 1:** Main pathways of electrochemiluminescence

### 3. ECL cells design and models

One variant of ECL cell design is the cell proposed by Measures [8]. In this cell (“Measures cell”), the auxiliary and counter electrodes are obtained by modulating the voltage applied to the electrode, i.e., one electrode serves as both the cathode and anode. Modulation is performed by rectangular pulses of varying duration and amplitude.

For a cell of this type, the mathematical model is written by the following system of equations:

$$\frac{\partial c_1}{\partial t} - D_1 \frac{\partial^2 c_1}{\partial x^2} = k_s \cdot c_3 + k_t \cdot c_2 + c_4 \cdot c_5, \quad (9)$$

$$\frac{\partial c_2}{\partial t} - D_2 \frac{\partial^2 c_2}{\partial x^2} = (1 - k_s) \cdot c_4 \cdot c_5 + \beta \cdot c_3 - k_t \cdot c_2, \quad (10)$$

$$\frac{\partial c_3}{\partial t} - D_3 \frac{\partial^2 c_3}{\partial x^2} = k_s \cdot c_4 \cdot c_5 - (k_s + \beta) \cdot c_3, \quad (11)$$

$$\frac{\partial c_4}{\partial t} - D_4 \frac{\partial^2 c_4}{\partial x^2} = -c_4 \cdot c_5, \quad (12)$$

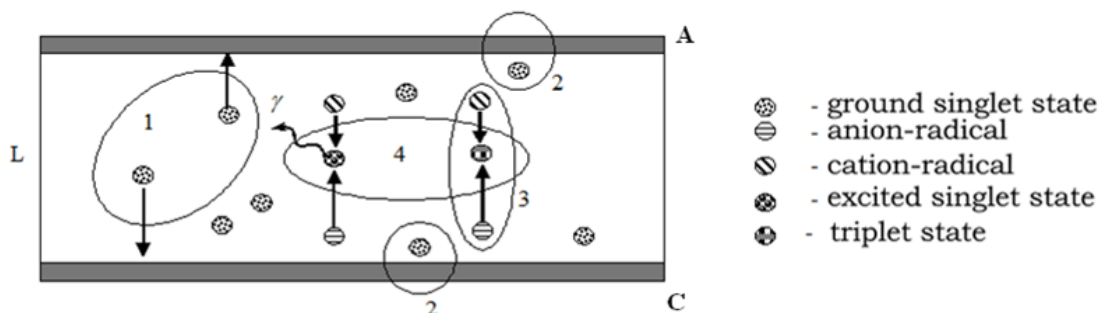
$$\frac{\partial c_5}{\partial t} - D_5 \frac{\partial^2 c_5}{\partial x^2} = -c_4 \cdot c_5. \quad (13)$$

Where,  $C_1$  - concentration of phosphor molecules in the ground state;  $C_2$  - concentration of triplet states;  $C_3$  - concentration of excited singlet states;  $C_4$  - CR concentration;  $C_5$  - AR concentration;  $D_1$  - corresponding diffusion coefficients for each of the particles participating in the electrochemiluminescence process;  $k_t$ ,  $k_s$  - rate constants, i.e., values inverse to the lifetimes of triplets and singletons;  $\beta$  - the rate of transitions from singlet to triplet states;  $\varphi_s$  - the probability of singlet state release at recombination.

This model is based on a system of parabolic partial differential equations that describe diffusion process and represent Fick’s laws of diffusion [12]. The right hand side of equations represents reactions taking place with the involved species, as was first introduced for thin layer ECL cells by R.M Measures [13].

In this system, the reduced unit concentration  $c_i = c_i^*/c_x$  of phosphor molecules in various states is employed, significantly simplifying the system and calculations. Furthermore, instead of coordinates and time, their reduced analogs, which are related to typical process velocities and distances within the ECL cell, are utilized.

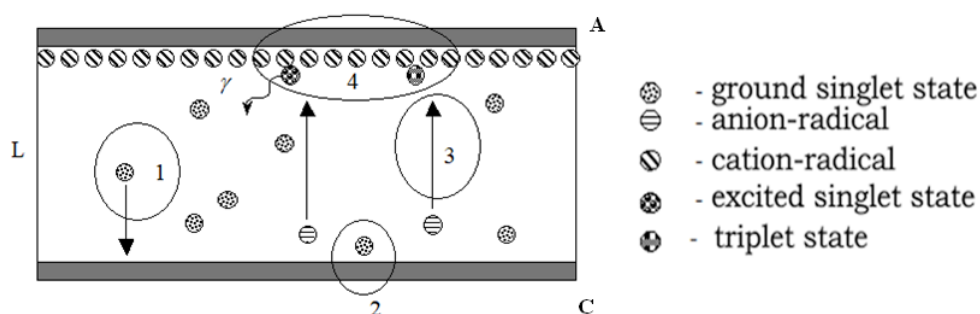
The two other cell types of interest are as follows. The first is a closed, rectangular parallelepiped-shaped volume filled with an electrochemiluminophore solution (“Symmetric cell”). Electrodes (cathode and anode) are applied to one pair of parallel walls. Its schematic is presented in Figure 2.



**Figure 2:** Schematic diagram of “Symmetric” ECL cell with rectangular plane-parallel electrodes (1 - diffusion of ground states to the electrodes along the concentration gradient; 2 - oxidation-reduction reactions at the electrodes; 3 - diffusion of radicals deep into the solution; 4 - biradical recombination with creation of triplet and singlet states)

In the case of such a cell, the mathematical model described above remains valid. However, it is necessary to modify the boundary conditions in order to solve the system of equations. The initial conditions for both types of cells are identical: at the moment of time  $t = 0$ , when there is no voltage at the electrode(s), only particles in the ground state are present in the solution, and the concentrations of AR, CR, triplets, and excited singlet are all zero.

An alternative cell design involves depositing a thin organic film of electrochemiluminophore on the anode using various technologies (“Asymmetric cell”) [6, 9, 14-17]. This approach enhances the likelihood of interaction between the analyte and the electrochemiluminophore, as it enables the orientation of the electrochemiluminophore molecules with their reaction surfaces facing the solution and, consequently, the analyte. The schematic representation of this design is provided in Figure 3.



**Figure 3:** Schematic diagram of an “Asymmetric” ECL cell with a thin film of electrochemiluminophore deposited on the anode (1 - diffusion of ground states to the cathode along the concentration gradient; 2 - oxidation reactions at the cathode; 3 - diffusion of anion-radicals to the anode; 4 - biradical annihilation with creation of triplet and singlet states)

For this kind of cell, the mathematical model can be written by analogy to models introduced by R.M Measures [13]:

$$\frac{\partial c_1}{\partial t} - D_1 \frac{\partial^2 c_1}{\partial x^2} = k_s \cdot c_3 + k_t \cdot c_2, \quad (14)$$

$$\frac{\partial c_2}{\partial t} - D_2 \frac{\partial^2 c_2}{\partial x^2} = \beta \cdot c_3 - k_t \cdot c_2, \quad (15)$$

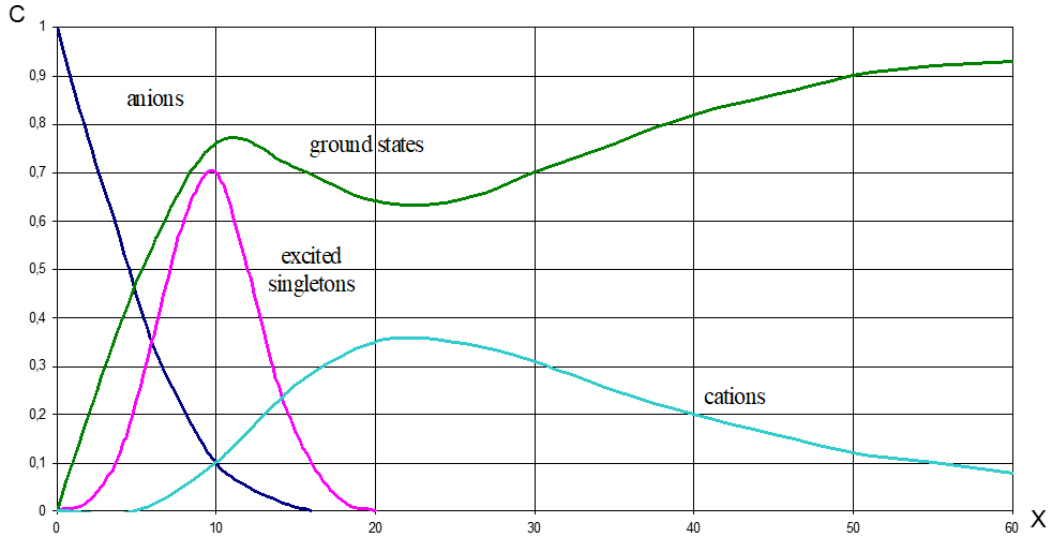
$$\frac{\partial c_3}{\partial t} - D_3 \frac{\partial^2 c_3}{\partial x^2} = -(k_s + \beta) \cdot c_3, \quad (16)$$

$$\frac{\partial c_4}{\partial t} - D_4 \frac{\partial^2 c_4}{\partial x^2} = 0 \quad (17)$$

The system operates due to the high concentration of CRs within the plane. Their number remains relatively constant because the AR is significantly smaller than the CRs. The boundary conditions indicate that the electrode with a deposited thin film of electrochemiluminophore serves as a direct source of excited-state molecules. The number of these molecules is equivalent to the number of ARs reaching the electrode through diffusion. The recombination rate of AR and CRs far exceeds the AR diffusion rate to the anode. Consequently, RCs are always present, ensuring a 100% probability of recombination for ARs arriving at the electrode.

#### 4. Results of numerical simulation

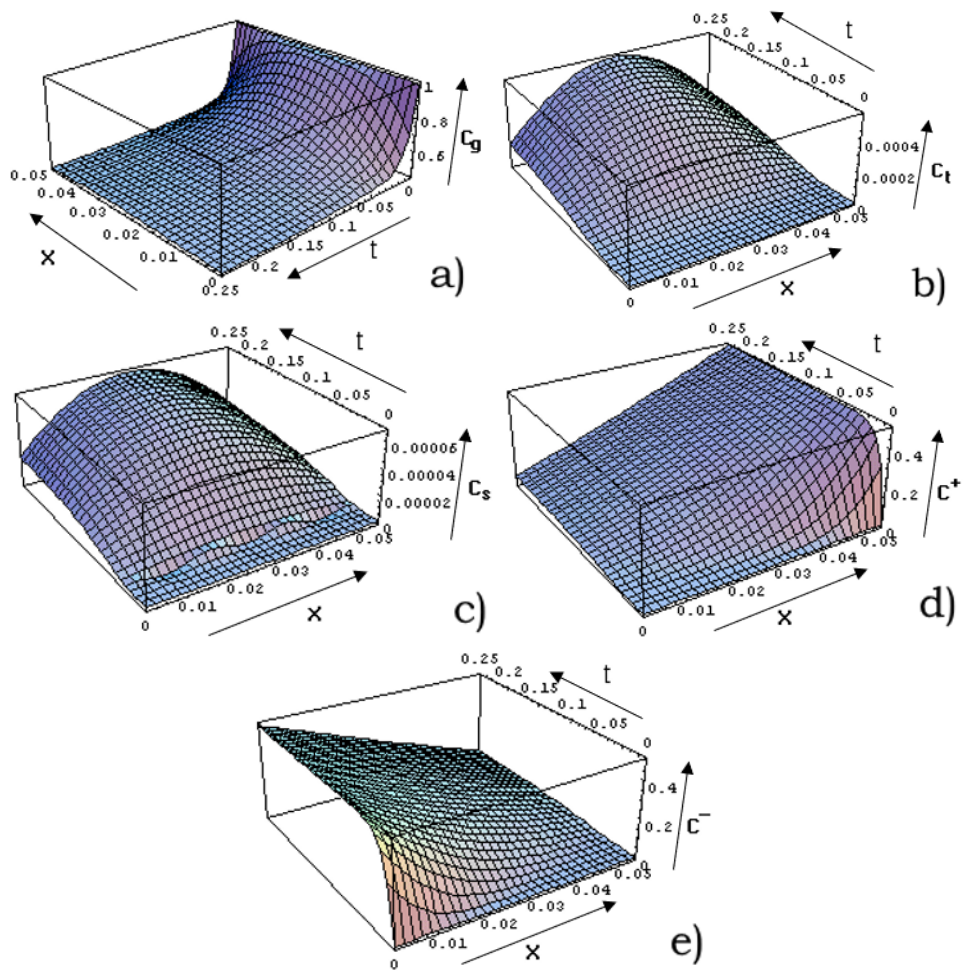
The resolution of the system of equations for the “Measures cell” yields the distribution of particles in space and time, as depicted in Figure 4. These results were computed for the time interval of 10  $\mu$ s after the electrode’s polarity change, which corresponds to essentially “equilibrated” situation [8]. Since “Measures cell” is mostly discussed here for comparison reasons and to verify proper operation of the developed models and simulation algorithms, no deeper discussion of that cell type will be made.



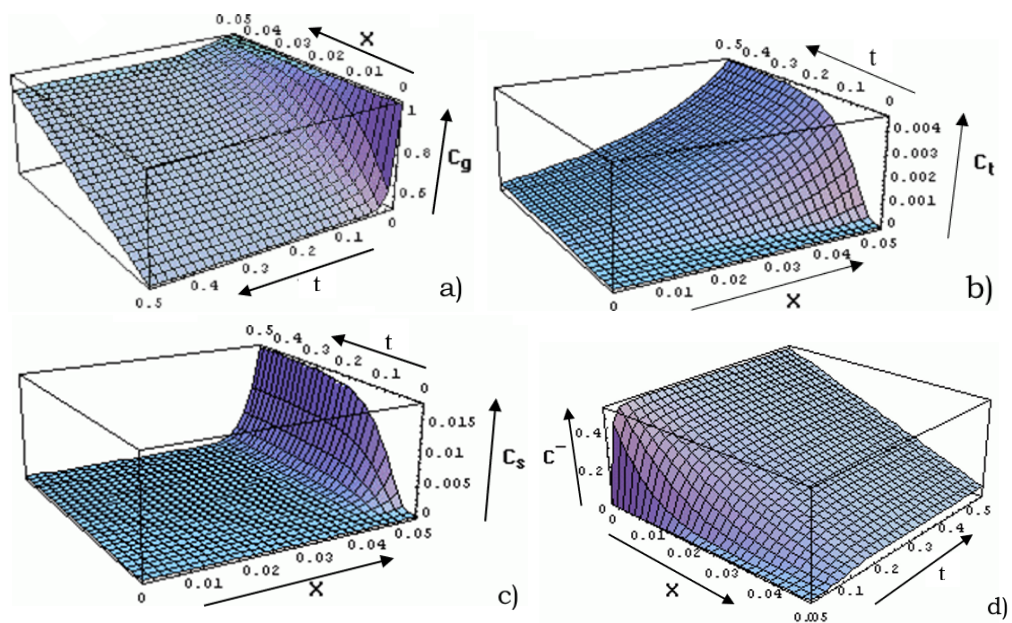
**Figure 4:** Distribution of particles along the x-coordinate from the electrode 10  $\mu$ s after polarity change

The solution of the equations system for the “Symmetric cell” is represented as a distribution of particles in time and interelectrode space, as illustrated in Figure 5. Here “x” coordinate corresponds to the direction of the inter electrode spacing L, while “t” coordinate allows tracing the diffusion profiles of concentrations of corresponding species in time.

Accordingly, Figure 6 shows the solution of the equations system in a form of distribution of particles in time and space for the “Asymmetric cell”.



**Figure 5:** Concentration distributions of electrochemiluminophore particles in a cell with rectangular plane-parallel electrodes: a) ground states, b) triplets, c) excited singletons, d) cations, e) anions

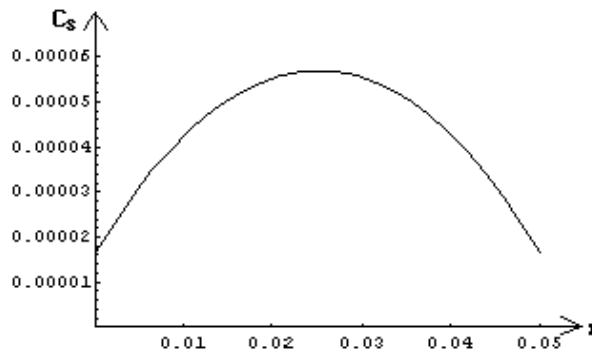


**Figure 6:** Distribution of particle concentrations in an "Asymmetric" ECL cell with a thin film of electrochemiluminophore: a) ground states, b) triplets, c) singletons, d) anions

## 5. Comparative analysis of the obtained results

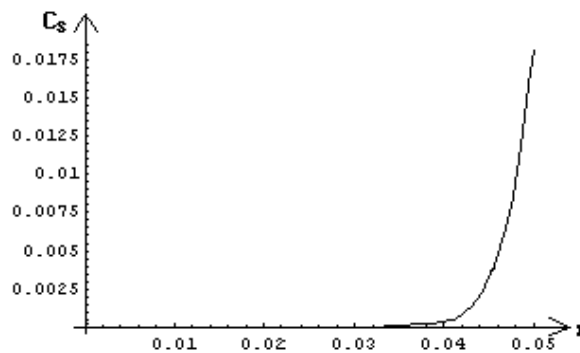
To comprehensively assess the performance and practicality of the two types of ECL cells under consideration, numerous simulations were conducted. The outcomes were meticulously compared with the fundamental model proposed by Measures [8]. Furthermore, an in-depth analysis was undertaken to elucidate the impact of varying cell and phosphor parameters on the generation of ECL emitters, specifically singlet states. Notably, the primary findings obtained for both models, characterized by identical cell dimensions and consistent phosphor parameters, are as follows.

1. The distribution of ECL emitters in the first type of cell (cell with counter diffusion of anions and cations) is relatively uniform along the length, and the concentration at the maximum is significantly lower compared to the second type of cell (cell with diffusion of one of the ions and a phosphor film on the electrode) (Figures 7 and 8).



**Figure 7:** Stationary distribution of emitters in the cell of the first “Symmetric” type

2. During the analysis, a substantial concentration of emitters was observed near the electrodes in the first type of cell (Figure 7). This phenomenon may result in re-ionization of the emitters without emission, leading to a reduction in the process efficiency. Notably, under the same parameters, this issue was not observed in the second type of cell. However, it is crucial to acknowledge that this phenomenon is highly dependent on the specific parameters of the cell and phosphor, particularly the lifetime of singlet states. In the context of creating a laser under stimulated emission conditions, the singlet lifetime can be significantly reduced, effectively eliminating this undesirable phenomenon.

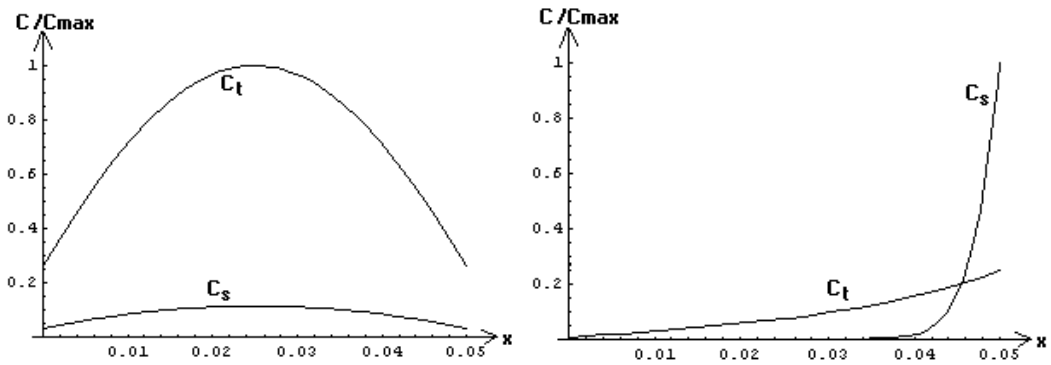


**Figure 8:** Stationary distribution of emitters in the cell of the second “Asymmetric” type

3. In the second-type cell, the emitter concentration exhibits a markedly non-uniform distribution, peaking at the interface between the film electrode and the phosphor solution. Notably, the concentration at this peak significantly surpasses the corresponding value observed in the first-type cell (refer to Figure 8). This concentrated distribution of emitters is more favorable for laser creation as it enhances the likelihood of achieving an inverted population of laser levels and a positive optical gain value. Additionally, it improves the spatial confinement of optical radiation, a crucial factor for

realizing single-mode operation. Furthermore, it enables the establishment of a four-level energy scheme, which is advantageous for laser design and analysis. However, the pronounced inhomogeneity in the distribution of excited molecules may result in substantial optical inhomogeneity within the generation region. This necessitates further investigation and potentially the implementation of additional measures to mitigate this inhomogeneity, such as employing mixing techniques or active medium pumping.

4. It is important to note that in the singlet mechanism of ECL emitter formation (in our model  $\varphi_s = 0.8$ ) in a cell of the first type, the concentration of triplet states along the entire length of the cell exceeds the concentration of singlet states (Figure 9a), which is associated with a much longer triplet lifetime. At the same time, in a cell with a film electrode in the near-electrode region, the concentration of emitters exceeds the concentration of triplet states (Figure 9b). This fact is of great importance in the case when the phosphor in the triplet state can absorb light quanta emitted by ECL emitters with a transition to a higher energy level.



**Figure 9:** Stationary distribution of concentrations of singlet and triplet states of phosphor a) in a cell of the first type b) in a cell with a film electrode ( $\varphi_s = 0.8$ )

## 6. Estimation of photon yield in the cells of the considered designs

A comprehensive analysis of diffusion processes involving phosphor molecules within two distinct cell configurations has been conducted, supported by numerical calculations. The development of an ECL laser model necessitates an accurate description of both spontaneous and stimulated emission processes associated with the phosphor. Additionally, the propagation direction of optical radiation must be carefully selected. The Measures model assumes that the radiation direction lies within the electrode plane, perpendicular to the phosphor diffusion direction ( $x$ ). However, this choice significantly complicates the mathematical model of the cell due to the introduction of an additional coordinate ( $z$ ). To address this challenge, certain simplifications may be necessary to reduce the system's dimensionality to two dimensions. This approach is feasible, for instance, when considering solely stationary processes without accounting for transient effects at the onset of stimulated emission.

In the event that the radiation direction is selected perpendicular to the electrode plane, there are no complications in the three-dimensional problem. Simultaneously, a challenge arises with the emission of radiation from the cell. To address this issue, it is feasible to utilize electrodes composed of materials that exhibit optical transparency at the wavelength of phosphor radiation, or to employ non-continuous electrodes that possess optically transparent radiation output.

During the analysis of the solutions obtained for both types of ECL cells, an attempt was made to qualitatively and quantitatively assess the nature of spontaneous emission of the active medium, namely luminescence. In this case, the emission in the medium is determined by the spontaneous deactivation of singlet states of the phosphor and is characterized by the intrinsic singlet lifetime  $\tau_s$  (the model uses the inverse of the lifetime  $\eta \sim 1/\tau_{ss}$ ). In the model equations, this is described by the term  $\eta_5 c_3(x,t)$ . To estimate the spontaneous emission, we can introduce into the system of model

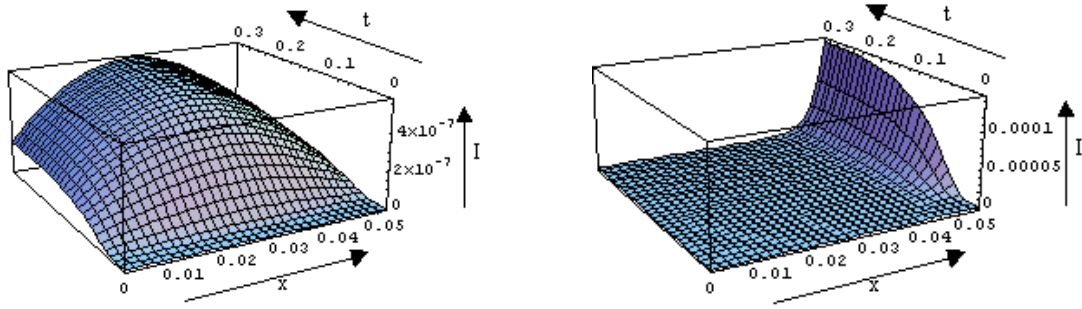


equations a quantity proportional to the photon density  $c_f$ . It is also necessary to introduce a quantity characterizing the lifetime of photons in the cell volume  $\tau_f \sim 1/s$  (by analogy with the lifetime of photons in the optical resonator of a laser), where  $c = 3 \cdot 10^8$  m/s is the speed of light. In contrast to the laser optical resonator,  $\tau_f \sim 1/s$  indicates that photons immediately leave the cell volume at a velocity of  $c$ . The resulting equation has the form:

$$\frac{\partial c_f}{\partial t} = \eta_5 c_3 - \frac{c_f}{\tau_f}, \quad (18)$$

with initial condition:  $c_f = 0$  at  $t = 0$ .

The obtained estimated radiation distributions for both types of cells are shown in Figure 10.



**Figure 20:** Comparative distribution of photon density in a cell of type a) one and b) two

To calculate the total number of photons emitted by the cell at time  $T$ , we can integrate the photon density distribution function from  $c_f$  along the  $x$  coordinate. By denoting  $c_{f1}$  as the photon density distribution in a cell of the first type, and  $c_{f2}$  as the photon density distribution in a cell of the second type, we can compare the luminescence efficiency of both cells under equal conditions and parameters. For the distributions shown in Figure 6, when the steady-state regime is established, the ratio is obtained:

$$\frac{\int_0^L c_{f2}(x, T) dx}{\int_0^L c_{f1}(x, T) dx} \approx 19,088 \quad (19)$$

This estimation is approximate as it excludes factors such as uniform radiation distribution, absorption in the medium, and optical properties of electrodes. However, it provides valuable insights into the advantages and potential of the selected ECL cell model.

## 7. Conclusions

In this report, we analyze the distributions of particles involved in electrochemiluminescence light quanta emission for three distinct ECL cell designs. Our findings indicate that the cell with a thin film of electrochemiluminophore deposited on the anode should have superior efficiency. Conversely, the cell employing reversed voltage polarity of a working electrode exhibits significantly lower efficiency compared to cells with two electrodes. Further verification of the developed models and obtained results requires design and experimental study of the proposed ECL cell types under identical conditions.

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