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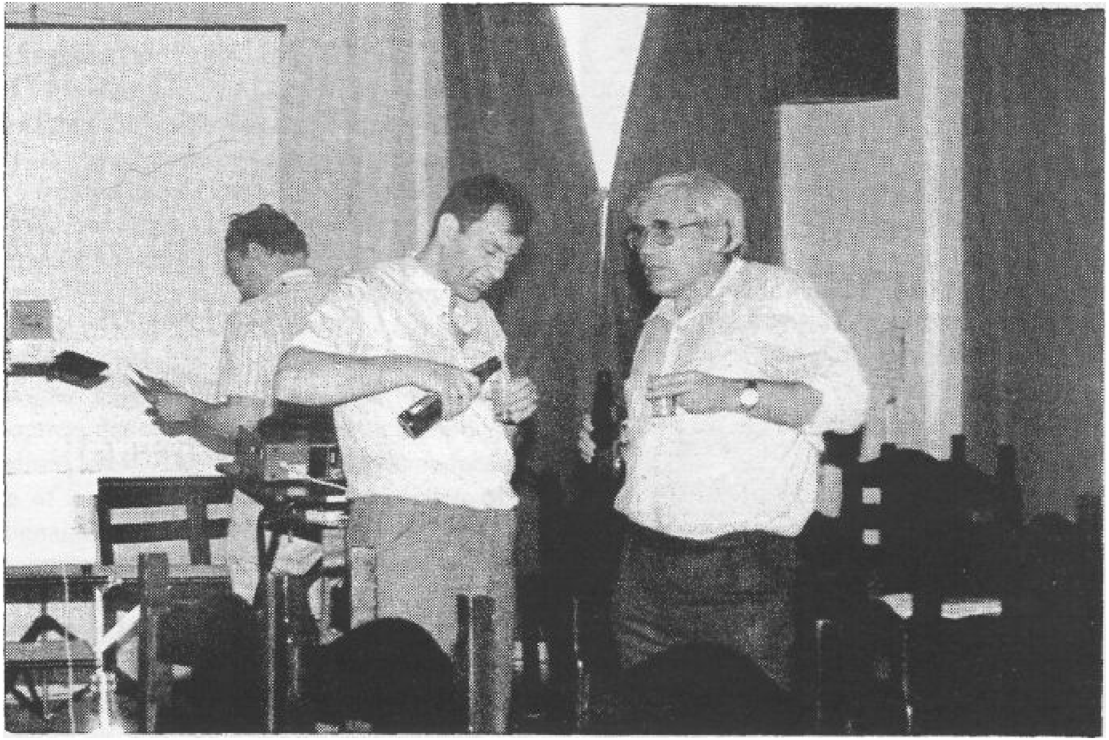
Pavel V. Jaguiro (left) was graduated in 1979 from the Belorussian State University, Radiophysics and Electronics Department (Minsk). From 1979 to 1984 he worked as an engineer in a hydroacoustic measurement laboratory of this university and then has been working as a researcher in a laboratory of electrochemical technologies (Microelectronics Department) at the Belorussian State University of Information and Radioelectronics. In 1991 he got the title of senior researcher and became the head of a research group. He authored more than 40 publications and 9 patents. His current interests are in electroluminescence.



Before his invited lecture, Yuri N. Dubnistchev (right) has become hot and mineral water *Mazowszanka* makes him feel cool and quieter. He refreshes himself in Pavel V. Jaguiro's company. Henryk Fiedorowicz, in contrast to them, seems to be absorbed by reading the conference program or the abstracts of papers.

Invited Paper

Electrochemiluminescence observation and measurements of electrohydrodynamic streams

Pavel Jaguiro

Belorussian State University of Informatics and Radioelectronics, Minsk, Belarus

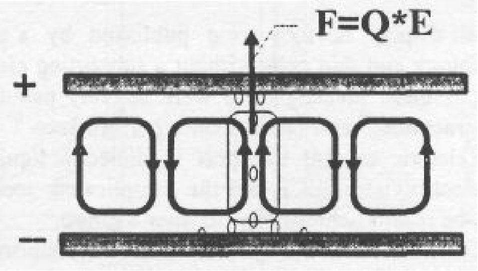
ABSTRACT

Electrohydrodynamic (EHD) convection in thin cells filled by dielectric liquids is considered. First, it is presented a brief review of practical applications of the cells, which includes liquid pumps, dynamic light scattering and electrochemiluminescence (ECL) displays. In the ECL devices EHD streams play the main role in ion transport, increasing current density in more than 1000 times. ECL permits to observe the shapes of EHD streams while correlation between electrical and optical kinetic characteristics gives information to the conclusion about the structure and velocities of the streams. Physical model is proposed to explain obtained dependencies and experimental results are compared with theoretical ones.

Keywords: electrohydrodynamic convection, DC electrochemiluminescence, thin cell, stream velocities

1. INTRODUCTION

Even Faraday observed electrohydrodynamic (EHD). convection in dielectric liquid (experiment N 1595). This phenomena has many aspects and manifestations, but only EHD convection in thin cells filled by dielectric liquids is described in this article. The simple diagram of thin film EHD convection is shown in fig.l.



F- force
Q - space charge
E - electric field strength
0 - anions

Fig.l. Diagram of thin film EHD convection

The injection of anions from cathode is represented in the diagram. This is a typical case, because the injection of cathions from anode requires the introduction of special chemical additives. The figure shows, that anions are formed at cathode and discharge at anode. The electrical force acts on part of the flow, which transports the anions. This force overcomes losses of viscous friction and supports EHD convection.

This phenomenon is frequently harmful, because it increases conductivity and leads to breakdown of liquid dielectrics. However the useful applications of this effect are more interesting:

A). *Dynamic light scattering in liquid crystals (LC).* This effect was discovered in the 60's and opened expansion of LC displays. Note, that dynamic light scattering is observed at occurrence of EHD flows, but is not practically connected with their velocities, because it is caused only by rotation- of LC molecules.

B). *DC electrochemiluminescent displays.* In these devices the streams intense ion transport. Stream's velocity determines • light brightness and efficiency of energy conversion. Intensification of charge transport significantly improves display's parameters. For example.the list with parameters of DC ECL-displays, achieved at experimental samples, is shown below:

-light efficiency	6...8Lm/W;
-power consumption	5 mW/cm^2 at 50 Cd/m^2 brightness;
-driving voltages	4...6 V DC;
-response time	10...30ms;
-spatial resolution	25... 50 mm;
-optical transmission	75...80%;
-operating temperature range	-55...+50°C.

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C). *EHD pumps.* These devices execute the direct transformation of electrical energy to rectilinear motion of liquid. These pumps have not driving parts, are chemically stable and demonstrate high efficiency (15 ...20 %). They can work with specific liquids (for example with liquid nitrogen) and in the most diverse conditions. It is possible to make micropumps by using microelectronics technology[1], The size of such pump is 3 mm * 3 mm * 0.7 mm, it can pump 14 cm^3/min of ethanol and develops the static pressure 2.5 kPa at applied voltage 700 V.

Below EHD convection in electrochemiluminescent (ECL) cells is considered in details. The reason of such attention to it is in distinctions of ECL devices. Chemiluminescence investigates high energy reactions and so level of purification is the best in all organic chemistry. Many efforts were applied to improve ECL by choosing solvents and luminofors, purification methods and design of the cell. But brightness and efficiency are related with stream velocities and as a result - ECL cell with ultra high stream's velocities (10 m/s) has been made. This experience is useful for all EHD investigations.

2. HISTORY AND PRINCIPALS OF DC ECL

ECL, as an independent scientific direction, has been developed in the 60's, when a few groups discovered high brightness luminescence during electrolysis in organic dye solution [2]. This ECL was excited by alternating current and so had some significant disadvantages.

In the 70's, practically all groups working in the ECL field made efforts to design DC thin cells. In March 1970, the DC ECL laser is patented [3]; in November 1972 - the planar cell with possibility of DC operation [4]; in November 1973 - the DC thin cell, filled by organic dye and supporting electrolyte solution [5]. In October 1974 investigations were carried out on DC thin cells with (as in previous experiments) a supporting electrolyte and also without. The lifetimes of the former were only 3 minutes, of the latter-10 minutes [6].By 1977 the lifetimes of DC thin cells with a supporting electrolyte had increased to 30 minutes with a current efficiency of 1.5% [7,8]. In 1979 detailed investigations of DC thin cells with a supporting electrolyte were made, even with thorough purification the lifetime grew to only 1 hour, and it was concluded, that thin ECL cells would not prove useful as display devices [9].

During the early 1980's almost all works in the field of DC thin cell display devices were published by a group of H.Schaper (Germany, "Philips"). By using industrial hermetic technology and thin cells without a supporting electrolyte they achieved rather long lifetimes (200...400 hours)[10]. Results of these investigations were actively patented and published [11,12,13]. They were the first to observe light emitting ordered structures [14] and fast-response performance [10] of these cells. Some attempts to explain the processes of charge injection and electric current transport in dielectric liquids were not convincing [13,15]. Probably that a deficient understanding of DC electrolyteless ECL and the complicated technology were the reasons why no further attempts have been made to reproduce the results achieved by Schaper's group.

For better illustration of difficulties in understanding of DC ECL it is needed to discuss basic mechanisms of it performance and compare predictions of simplest theories with experiment. Figure 2 shows main ECL reactions while in figure 3 theory and experiment data are compared.

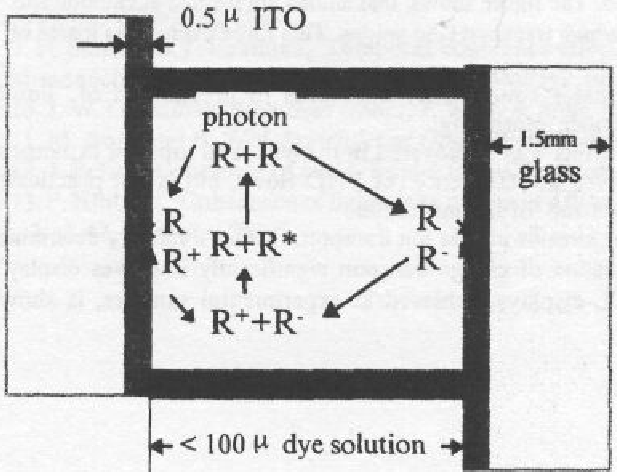

Fig.2. DC thin cell construction and main ECL processes.

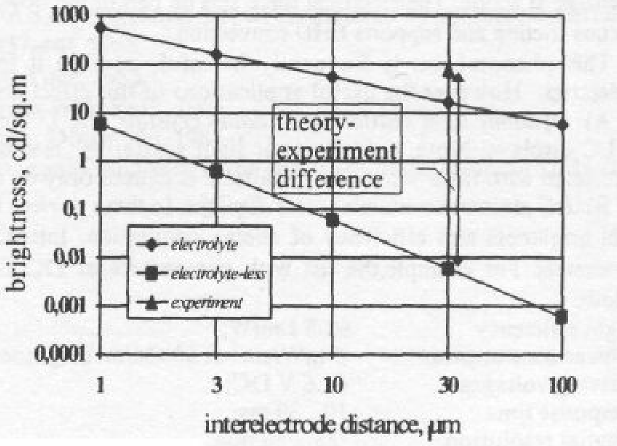

Fig.3. Brightness vs. cell gap.

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 aprotonic solvent. No polaroids or alignment layers are required. 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.

; In DC ECL-cells with supporting electrolyte the solution is electrically neutral and so current through the cell is limited by diffuse kinetics. The corresponding brightness is present in figure 3 (line - electrolyte). In electrolyte less ECL-cells situation is significantly different. The solution is not electrically neutral because space charge of anions exists in volume of the cell. In absence of liquid motion current is limited by space charge field. The corresponding brightness is present in I figure 3 (line - electrolyteless). Predicted brightness is low and so these cells are not investigated for a long time.

The great difference between experimental and theoretic data for electrolyteless DC ECL-cells could not be explained by existing EHD theories because usually the theories suppose low stream velocities. For example Schaper calculated[12] that stream's velocity is only 2...3 mm/s.

Now new physical model, based on high velocity of EHD streams, is proposed and several characteristics of DC ECL are explained by it.

3. PREPARATION OF THE EXPERIMENTAL CELL

Design of ECL-cell and used materials are presented in figure 4, filling system - in figure 5. Main principals of purification and filling are the same as in previous work[12].

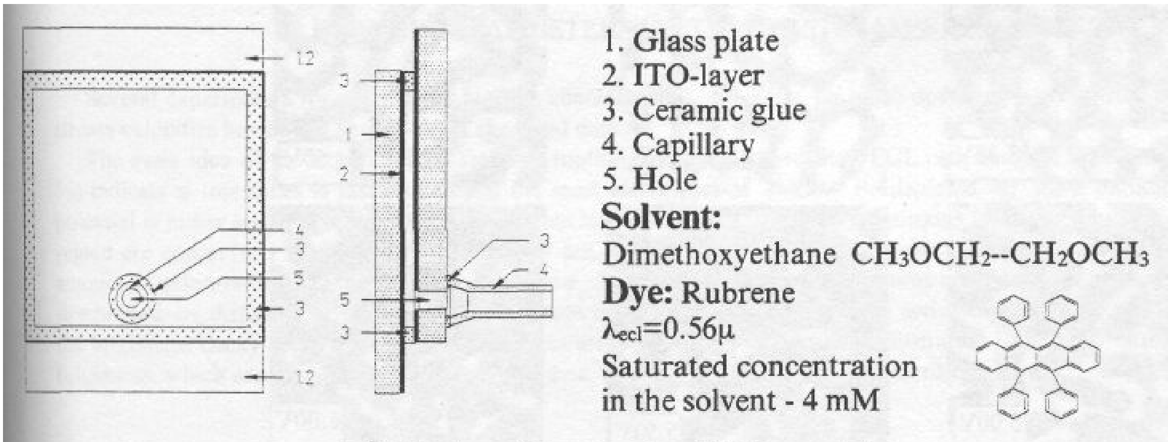

Fig.4. Design of the cell and used ECL-materials

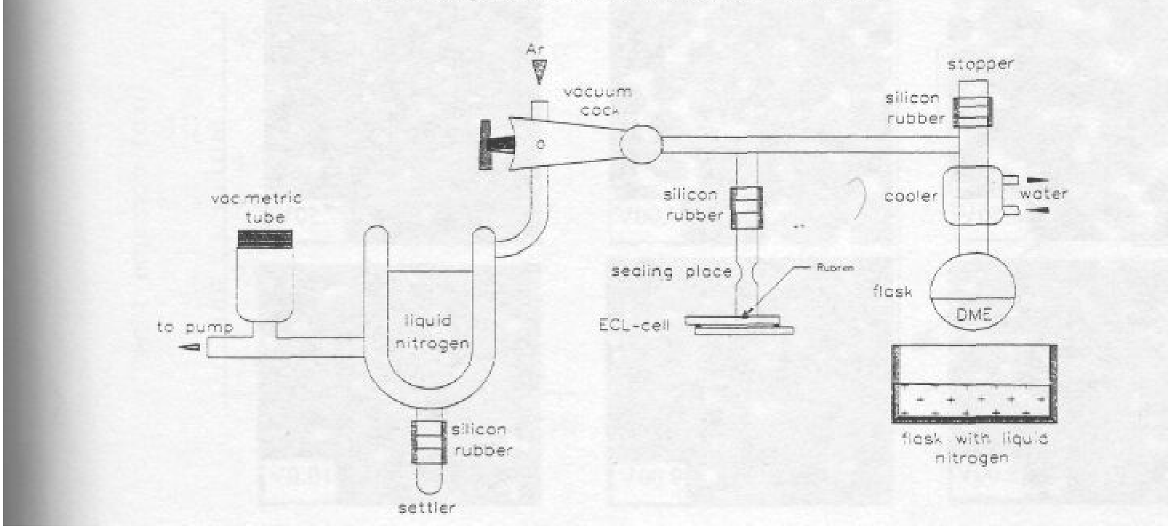

Fig.5. Filling system

3. ELECTROHYDRODYNAMIC CONVECTION: ORDERED STRUCTURES IN ECL

As was said before, light emission in DC electrolyteless cells is not uniform, but localised in ordered structures.) structures. Pictures of ECL convection at an applied voltage 5 V in cells with 12, 26, 50, 100 μm gaps have also been presented [14]. We have investigated ECL convection shapes at applied voltages from 2.8 V to 10 V in 25-μm gap cell[16]. We did not observe unstructured light, ordered structures appeared after delays of 10...20 s even at 2.8 V. It can be seen from figure 6, which shows ECL at different applied voltages, that size step of the structures remained constant and it is equal to 48±5 μm. Figure 7 represents relative area of dark space vs. applied voltage and illustrates method of it calculation.

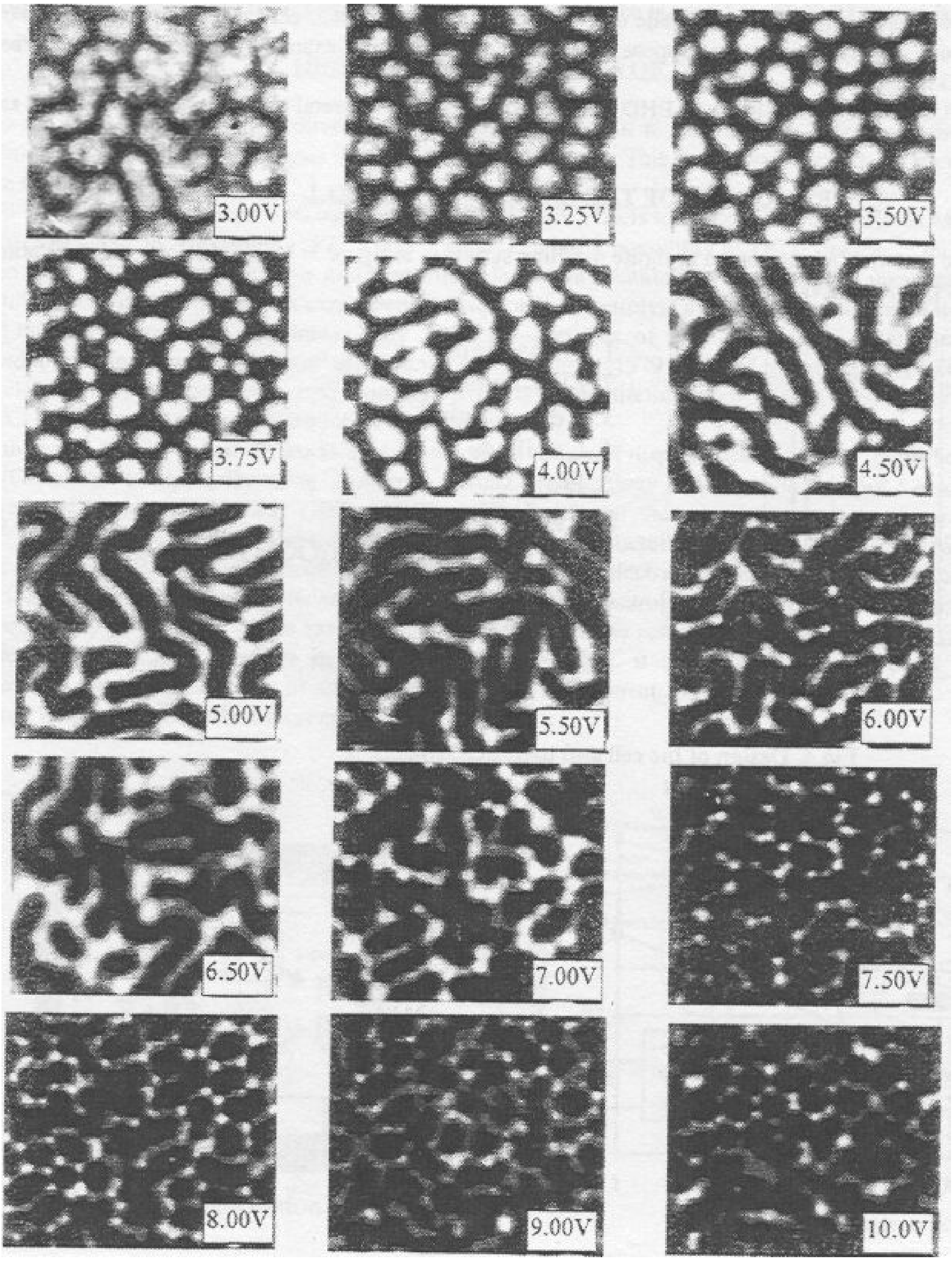

Fig.6. Photos of electrochemiluminescent streams (size 300p,*300(i)

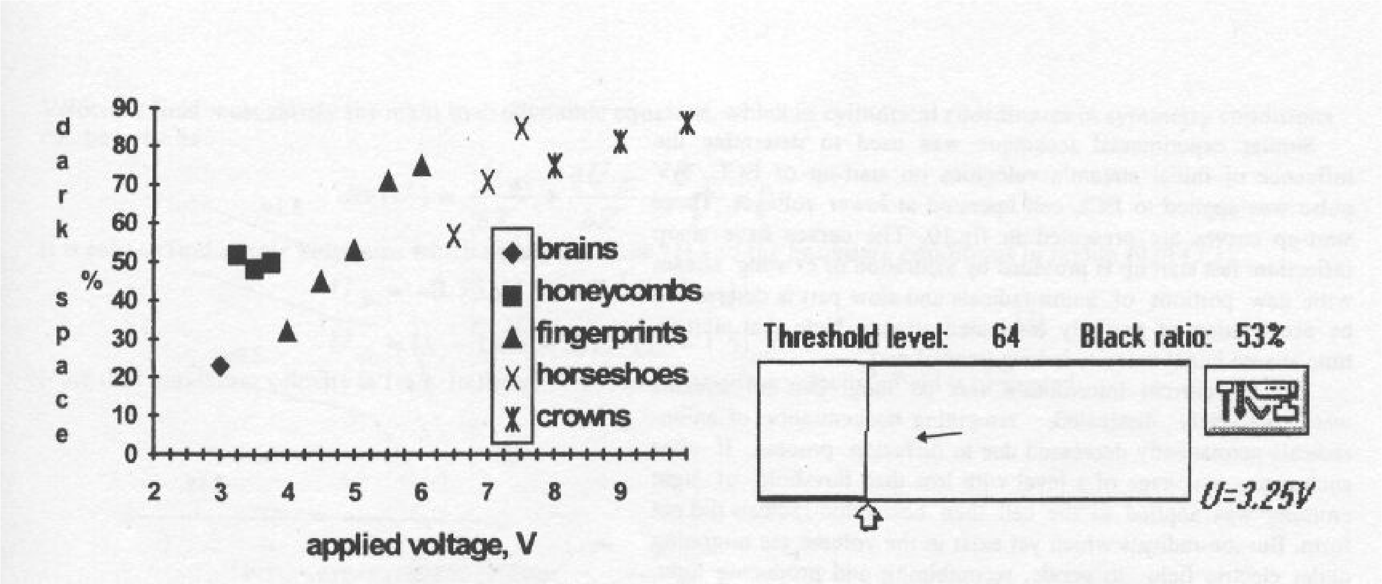

Fig.7. Dark space area vs. voltage, brightness statistics and determination of dark space by Photostyler program

4. EXPERIMENTAL DETERMINATION OF STREAM'S VELOCITIES

Several experiments for measuring kinetic characteristics of ECL by pulse operating were carried out and values of stream velocities have been derived from observed data.

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 and the most active part of stream is depleted of these particles. The interface potential is rather stable due to existence of double layer capacitance and 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. In figure 8 graphs of the brightness decay at different applied voltages are presented and figure 9 illustrates the graph stream velocities vs. brightness, which are derived from the previous data. Theoretical curves will be described below.

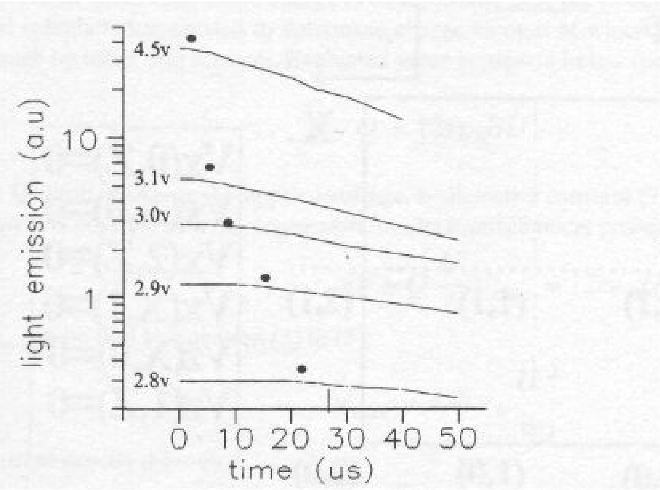

Fig.8. Decay curves at different applied voltage

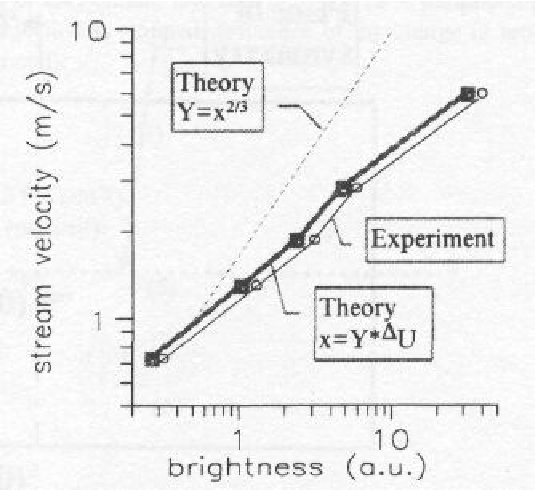

Fig.9. Stream's velocity vs. brightness

Similar experimental technique was used to determine the influence of initial stream's velocities on start-up of ECL. 5-V pulse was applied to ECL cell operated at lower voltages. These start-up curves are presented in fig.10. The curves have sharp inflection: fast start up is provided by saturation of existing stream with new portions of anion-radicals and slow part is determined by acceleration of partially dissipated stream. Note that start-up time at zero initial velocity is long (tens of ms).

If the current interruption was so long, that all streams were completely dissipated, remaining concentration of anion-radicals permanently decreased due to diffusion process. If after such pause, a voltage of a level with less than threshold of light emitting was applied to the cell then new anion-radicals did not form. But ion-radicals which yet exist in the volume are migrating under electric field to anode, recombining and producing light. Varying pause duration one can estimate ion-radical lifetime. In our experiments we have registered by photomultiplier the light emission when we applied 2 V after one minute pause. This experiment is a convincing example of high protection from impurities in electrolyteless sealed off cells.

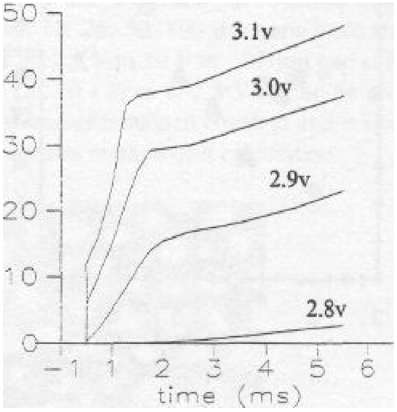

Fig.10. Start-up curves of brightness at different initial voltage

5.MATHEMATIC SIMULATION OF EHD-CONVECTION

In the base of the physical model are experimental results:

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

Ruffle simulation is carry out as a first step. Such modeling allows to evaluate only order of stream's velocities and to qualitatively compare theoretical and experimental parameters of ECL-cells.

Simulation was carry out for 'honeycomb" ordered structure in cylindrical region. This region with boundary conditions and plane of symmetry is presented in figure 11.

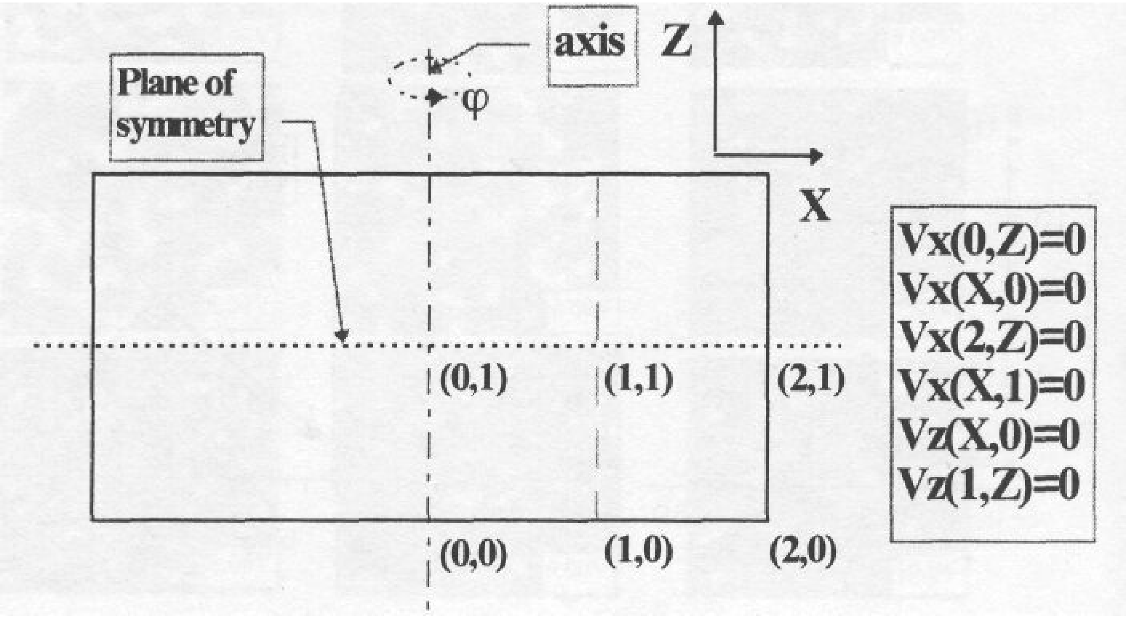

Fig. 11. Cylindric cell and boundary conditions

Velocity's field must satisfy the main hydrodynamic equation, which in cylindrical coordinates in symmetry conditions can be write as

$$div(U) = \frac{\partial U_X}{\partial X} + \frac{\partial U_Z}{\partial Z} + \frac{U_X}{X} = 0 \qquad (1)$$

It is easy to find simple polynoms which satisfy equation (1) and the boundary conditions in region (0,0)-(2,1):

$$\begin{aligned} U_X &= -0.75X(X-2)^2 Z(Z-1) \\ U_Z &= (x-1)(x-2)Z^2(Z-1.5) \end{aligned} \qquad (2)$$

Note that maximum velocity is 1m/s. In figure 12 the corresponding velocity's field is presented.

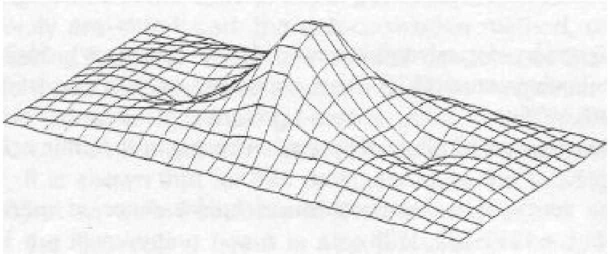

Fig. 12. Velocity's field in the cell

The figure shows that average velocity is not high, but in middle part of the cell streams significantly accelerates. This is cross-section of the field, at all the streams form torus.
By using well known formulas friction losses can be calculated for considered velocity's field (per cell):

$$F = \frac{153}{175}\pi\delta\eta V_{max}^2 \qquad (3)$$

where δ- cell gap, η- dynamic viscosity (0.0035 Poise for DME), V_{max}- velocity in middle of the cell.

For situation when total space charge is concentrated near the middle of the cell and injection is observed in peripheral part special calculation is needed to determine charge amount at which injection is stopped. Influence of the charge in around cells must be taken into account. Evaluated value is present below (per cell):

$$Q = 12\varepsilon\varepsilon_0\delta U \qquad (4)$$

where **Q**- limit of charge, **U**- applied voltage, $\boldsymbol{\varepsilon}$- dielectric constant (7.2 for DME).

Now it is possible to write expression for electromechanical power (per cell):

$$H = Q\frac{U}{\delta}V_{max} = 12\varepsilon\varepsilon_0 U^2 V_{max} \qquad (5)$$

$\mathbf{V_{max}}$ can be find by equation (3) to (5):

$$V_{max} = 4.4\varepsilon\varepsilon_0\frac{U^2}{\delta\eta} \qquad (6)$$

and current density J too:

$$J = \frac{Q}{\delta}V_{max}\frac{1}{\pi\delta^2} = 16.8\varepsilon^2\varepsilon_0^2\frac{U^3}{\eta\delta^3} \qquad (7)$$

Note, that it is more correctly use internal cell voltage, which is corrected on potential step in electrochemical double layer (for described system it is equal to 2.7 Volts). In first approximation brightens is proportional to current density and so it is possible to derive their relationship from (6) and (7). If first variant of (7) - with direct including V_{max} - is used and if voltage for **Q** calculation is corrected, then good agreement between theory and experiment is achieved.

6.REFERENCES

1. A.Richter, H.Sandmaier, "An electrohydrodynamic micropump", - IEE Micro.Electro.Mech.Syst. 3rd Workshop, Napa Valley, Calif, Febr. 1990, Proc.- New York, p.99-100,1990
2. D.M.Hercules, " Chemiluminescence resulting from electrochemically generated species," - Science, Vol.145, pp.808-809, 1964.
3. P.P. Schafer, "Method of and device for exciting liquid lasers," patent 2010929 (Germany), 1273929 (GB).
4 .A.Pighin, R.A.Creswell, D.P.Malanka, "Electrochemiluminescent device having a mixed solvent," patent N 3868534 (USA).
5. J.Dunnet, M.Voinov, "Device for light emission by electrolyse," patent 2356940 (Germany), 55-48641 (Japan).
6. AJ.Bard, D.Laser, "Electrogenerated Chemiluminescence XXIII. On the operating and lifetime of ECL devices," J. Electrochem. Soc., Vol.122, N 5, pp.632-640, 1975.
7. J.S.Dunnet, M.Voinov, "Electrochemical luminescent of rubren dissolved in benzonitrile in thin cells," J. Chem. Soc., Faraday Trans. I, Vol. 73, pp.853-857, 1977.
8. J.S.Dunnet, M.Voinov, "Reasons for the decay of the electrochemical luminescence of rubrene dissolved in benzonitrile," J. Electroanal. Chem., Vol. 89, N 1, pp.181-189,1978.
9. AJ.Bard, G.H.Brilmyer, "Electrogenerated Chemiluminescence XXXVI. The production of steady direct current ECL in thin layer and flow cells," J. Electrochem. Soc., Vol.127, N 1, pp.104-110,1980.
10. H.Schaper, H.Kostlin, patent 2949967 (Germany).
11.H.Schaperand others, patents NN 2928725, 3029469, 3110879, 3201048 (Germany), 2502292 (France).
12. H.Schaper, H.Kostlin, E.Schnnedler, "New Aspects of DC Electrochemiluminescence," J. Electrochem. Soc., Vol.129, N 6, pp.1289-1294,1982.
13. H.Schaper, H.Kostlin, E.Schnnedler, "Elektrochemolumineszenz in elektrolytfreien Losungen," GIT Fachz. Lab., Vol. 26, pp.745-748, 858-862, 943-946,1982.
14. H.Schaper, H.Kostlin, "Electrochemiluminescence by DC of rubrene displaying highly organised electrohydrodynamic convection," Physics Letters, Vol. 76A, N 5-6, pp.455-458, 1980.
15. H.Schaper, E.Schnnedler, "On the Charge Distribution in Thin-layer Cells under Electrostatic Conditions", J. Electroanal. Chem., Vol. 137, pp. 39-49,1982.
16. P. Zhagiro (Jaguiro), V.Zhivnov, V.Solodkov, "Using of electrochemiluminescence for investigation of liquid dielectrics," Elektronnaya obrabotka materialov (Rus.), Vol.152, N 2, pp.34-36, 1990. (journal is published in the USA under the name "Soviet Surface Engineering and Applied Electrochemistry").