Study of a discharge with a liquid cathode by the methods of high-speed visualization and emission spectroscopy

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Abstract. In this work the detailed structure of a direct current discharge with a liquid cathode was studied by high-speed imaging and emission spectroscopy. The movement of filaments into which the discharge channel is divided is studied. The processes of formation and destruction of filaments are investigated. Spectra were recorded at different distances from the liquid surface on the discharge axis. The dependences of the luminescence intensity of the main spectral lines and bands on the distance to the liquid surface at different discharge currents are found.

Introduction
Systems in which plasma interacts with the surface of a liquid are interesting objects in terms of both applied and fundamental research.

Among the areas of application of systems in which plasma interacts with the surface of a liquid, we can distinguish: destruction of organic pollutants in water, modification of the surface of polymeric materials, spectral analysis of the content of metal ions in water and aqueous solutions, obtaining ultrafine powders in aqueous solutions, biomedical applications.

The simplest way to organize a system in which plasma interacts with the surface of a liquid is a discharge cell with a liquid electrode [1]. The most intense plasma-chemical processes in a liquid occur when the liquid electrode is a cathode. It is assumed that the bombardment of high-energy ions in this case leads to non-equilibrium dissociation, first of all, of solvent molecules, which triggers the subsequent chain of physicochemical processes in the liquid [2, 3].

Another feature of a DC discharge with a liquid cathode is that in this type of discharge there is a non-equilibrium transfer of solvents and solutes molecules into the gas phase under the action of ionic bombardment of a liquid cathode, similar to the process of cathode sputtering in a classical glow discharge [4]. The analysis of the processes taking place is hampered by the fact that the composition of the gas phase is substantially determined by the processes of transfer of the solution components to the gas phase [2, 3]. These complex processes that occur near the surface of a liquid in a DC discharge with a liquid cathode make it difficult to build a detailed mathematical model of such a discharge. In addition, the detailed structure of such a discharge with a high temporal and spatial resolution remains poorly studied experimentally.

The aim of this work was to study the detailed structure of a DC discharge with a liquid cathode. In particular, the study of the movement of filaments and cathode spots, the study of the formation and
death of filaments and cathode spots. As well as the study of plasma composition in different discharge zones at different discharge currents by emission spectroscopy.

**Experimental setup and measurement methods**

In this work, we investigated a direct current discharge, in which an aqueous solution was used as the cathode. The discharge occurred at atmospheric pressure in the air. A tungsten electrode with a diameter of 2 mm was used as the anode; the tip radius was 1 mm. Sodium hydroxide solution in deionized water with a concentration of 60 mg/l and an electrical conductivity of 330 μS/cm was used as a liquid cathode. The discharge was performed in a flow discharge cell.

The high-speed video recording of the discharge was made with a colored video camera Phantom VEO 410S and a black and white video camera Phantom MIRO M110, with a recording speed of up to 10,000 frames per second. AvaSpec 2048 three-channel fiber optic spectrometer with a spectral resolution of 0.15 nm and a MS-5204i high-resolution spectrograph with a spectral resolution of 0.03 nm with an Andor CCD matrix at its outlet were used to study the discharge plasma by the methods of emission spectroscopy. The image of the discharge was formed by a quartz lens in the plane in which the entrance slit of the spectrometer or the inlet of the optical fiber was placed, which made it possible to study the spatial distribution of the spectra.

**Results**

According to the data of high-speed video filming, near the surface of the liquid, the discharge channel is divided into separate filaments (figure 1).

![Figure 1](image)

**Figure 1.** Frames of high-speed video recording of the discharge with a liquid cathode. Exposure 250 μs, discharge current 100 mA, the distance between the electrode and the surface of the liquid: a) 1 mm, b) 2 mm, c) 4 mm

High-speed video shows that the filaments and cathode spots randomly move along the surface of the liquid. Characteristic speeds are on the order of several meters per second. At the same time, the number of filaments and the area occupied by cathode spots on the surface of the solution do not remain constant, but fluctuate in time around some average values.

As shown by high-speed video, the main mechanism for the formation of new filaments and cathode spots is the separation of filaments and cathode spots. The main mechanism of the destruction of filaments and cathode spots is their displacement to the periphery zone and extinction over the course of hundreds of microseconds.

The study of high-speed video frames also showed that each cathode spot bends the surface of the liquid and forms a small deepening (recess) on it. When the cathode spots move along the surface of the liquid, the recesses follow them. As a result, capillary waves are formed on the surface of the liquid, which diverge concentrically from the discharge zone (figure 1).

The average number of filaments and the average area occupied by cathode spots on the surface of the solution increase with increasing discharge current [5]. Also, with an increase in the discharge
current, the distance between the solution surface and the branch point (point where discharge channel is broken down into the filaments) increases. At a certain critical current, the position of the branch point coincides with the electrode. When the current is equal to or greater than the critical filamentation of the discharge begins directly from the electrode (figure 1a).

Interpretation of the emission spectra of the discharge plasma showed the presence of emission bands of OH - radicals, molecular nitrogen $\text{N}_2 (2^\text{+})$ and $\text{N}_2 (1^\text{+})$, molecular ion $\text{N}_2^+$, the bands of which are very weak against the background of molecular nitrogen bands and visible only near the surface of the liquid figure 2, as well as atomic hydrogen lines $\text{H}_\alpha$ and $\text{H}_\beta$ and oxygen $\text{OI}$. The sodium line 589 nm is completely absent in the spectrum. This suggests that sodium ions are not transferred to the gas phase under these conditions.

![Figure 2 (a)](image-a)

**Figure 2.** Fragment of the discharge spectrum: a) near the electrode, b) near the surface of the liquid. The distance between the electrode and the surface of the liquid is 2 mm, the current is 100 mA.

Cathode spots are the brightest points on high-speed images figure 1. As shown by spectral measurements, a sharp increase in the intensity of the emission of atomic hydrogen lines $\text{H}_\beta$ and $\text{H}_\alpha$ is observed near the surface of the liquid (figures 2 and 3), and only these lines; therefore, we associate the bright luminescence of the cathode spots with the luminescence of atomic hydrogen.
Figure 3. Emission of the atomic hydrogen H$_\alpha$ line in different discharge zones. The distance between the electrode and the surface of the liquid is 2 mm, the current is 100 mA.

Figure 4. The intensity distribution of the glow bands of OH radicals and N$_2$ molecules in a discharge with a liquid cathode, a discharge gap of 2 mm, an electrode is on the top: a) spectrum interpretation, b) discharge current 100 mA, c) discharge current 50 mA.
According to spectral measurements, the emission maximum of the second positive system of molecular nitrogen $N_2(2')$ is always located near the electrode, regardless of the discharge current, in the range of studied currents from 10 to 100 mA. The position of the maximum radiation of OH - radicals significantly depends on the discharge current. At a current of 100 mA, the OH - radical emission maximum is located near the electrode. When the discharge current decreases, the radiation maximum shifts to the surface of the liquid (figure 4).

![Figure 5. Comparison of a fragment of the experimental spectrum of the second positive molecular nitrogen system $N_2(2')$ with the model one built in the Specair program. Black is an experiment, red is the model.](image)

At a current $I = 100$ mA and an interelectrode distance of 2 mm, near the surface of the liquid, the vibrational and rotational temperatures of the plasma were determined from the emission spectrum of the second positive molecular nitrogen system $N_2(2')$. The determination of the vibrational and rotational temperatures was carried out by comparing the recorded spectrum with the model spectrum built in the Specair program (figure 5).

For the axial part of the discharge, near the surface of the liquid, at a current $I = 100$ mA and an interelectrode distance of 2 mm, rotational and vibrational temperatures were obtained, respectively: $T_r = 2800\,\text{K} \pm 10\%$, $T_v = 3800\,\text{K} \pm 20\%$. Which agrees well with the data [6] obtained under similar conditions.

**Discussion**

It is known that in the DC discharges with a liquid cathode there is a non-equilibrium transfer of the solvent and solute substances into the gas phase under the action of ion bombardment of a liquid cathode [2, 3]. In this case, one incident ion, according to direct measurements carried out in [4], has from 300 to 500 molecules of sprayed water associated with it. Such a large number of sprayed water molecules per incident ion indicates a high energy of ions bombarding the surface of the liquid. That, in turn, is associated with a large amount of cathode potential voltage drop, which, according to [4], ranges from 500 to 700 V.

Simple estimates show that the rate of outflow of non-equilibrium steam from cathode spots is several meters per second. At the same time, a reactive force acts on the surface of the liquid from the jet of a nonequilibrium vapor, which is balanced by the forces of the surface tension of the liquid. This leads to the formation of characteristic deepenings under the cathode spots.
The steam jet flowing from the cathode spot along the filament axis reduces the temperature on its axis, thus making its position unstable. This is supposed to cause the filament and the associated cathode spot to move along the surface of the liquid.

Conclusion
Near the surface of the solution in a discharge with a liquid cathode, the discharge channel is divided into separate filaments that are in constant chaotic motion. Each filament on the surface of the solution ends with a separate cathode spot. In this case, near the anode, the discharge channel may not have a filamentous structure. The point where discharge channel breaks apart into filaments (branching point) is determined by the discharge current. With increasing discharge current, the distance between the surface of the solution and the branching point on the discharge channel increases.

The number of filaments and cathode spots do not remain constant, but fluctuate over time around some average values. The main mechanism of formation of new filaments and cathode spots is the division of filaments and cathode spots. The main mechanism of death of filaments and cathode spots is their movement to the periphery and extinction.

Interpretation of emission spectra of discharge plasma shows the presence of radiation bands of OH radical, molecular nitrogen \( N_2(2+) \) and \( N_2(1+) \), molecular ion \( N_2^+ \), as well as lines of atomic hydrogen \( H_\alpha \) (and \( H_\beta \)) and oxygen \( OI \). The emission of most molecular bands and atomic lines on the discharge axis is highly inhomogeneous in height. In the entire range of the studied currents from 10 to 100 mA, the atomic hydrogen lines have a sharp maximum near the liquid surface, and the intensity of the molecular nitrogen bands \( N_2(2+) \) reaches a maximum near the metal anode. The position of the OH – radical emission maximum significantly depends on the discharge current. At a current equal to 100 mA, the maximum emission of OH-radicals is near the metal electrode. When the discharge current decreases to 50 mA and below, the emission maximum is shifted to the liquid surface.

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References
[1] Kutepov A.M., Zakharov A.G., Maximov A.I. Vacuum-plasma and plasma-solution modification of polymeric materials. // Moscow. Nauka, 2004. 497 p.
[2] Bruggeman P., Leys C. Non-thermal plasmas in and in contact with liquids // J. Phys. D: Appl. Phys. 2009. V. 42. № 5. P. 1-28.
[3] Bruggeman P., Kushner M., Locke B. et al. Plasma–liquid interactions: a review and roadmap // Plasma Sources Sci. Technol., 2016, 25, 053002.
[4] Sirotkin N.A., Gurina D.L. The influence of the transfer processes of the components of a liquid cathode on the properties of a dc discharge at atmospheric pressure // International Journal of Applied and Fundamental Research. 2016, №11, pp.94-99.
[5] Khlyusto A. V., Maksimov A. I. Double Electrical Layer at the Plasma-Solution Interface. // Contrib. Plasma Phys. 2013. V. 53. №6. P. 481-489.
[6] Bruggeman P., Liu J.J., Degroote J., Kong M.G., Vierendeels J., Leys C. Dc excited glow discharges in atmospheric pressure air in pin-to-water electrode systems // J. Phys. D: Appl. Phys. 2008. V. 41.215201.