About the mechanism of electric discharge between the electrolyte flow and the metallic anode

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Abstract. An electrical discharge between a flowing electrolyte and a metal electrode was experimentally investigated in modes in which an intense transfer of a liquid electrolyte substance into the plasma column occurs. The cathode area of the discharge was investigated by the method of high-speed visualisation. A mathematical model for describing the processes of transfer of matter and charges from a liquid electrolyte cathode into a plasma was proposed.

1. Introduction

Electrical discharges with liquid electrodes are plasma sources with great potential for practical applications. They are forward-looking for use in the synthesis of various functional materials, plasma activation of liquid reagents, water purification, processing of metallic and non-metallic surfaces [1-5]. Such interest to electrical discharges primarily due to the fact that they allow to obtain a non-equilibrium plasma at atmospheric pressure. At the same time, they can be implemented with relatively simple technical means.

To date, significant progress has been made in the study of electrical discharges in the variant with a liquid electrolyte cathode at low currents [6]. However, despite the presence of a significant amount of experimental material, low-current electrical discharges remain little studied. Physical processes in electrical discharges become even more complicated with increasing current. The thermal effect on the electrolyte increases, the processes of evaporation and cathode sputtering intensify, a rapid gas evolution inside the electrolyte occurs. In this case, the electric discharge becomes extended and voluminous. It is possible to create a powerful plasma flow with characteristics that are acceptable for energy-intensive plasma technologies [7-8]. In this case, the aim of the work was to study the mechanisms that ensure the independence of high-current volumetric electric discharge between the electrolyte flow and the metal electrode.

2. Experiment

The scheme of the experimental setup is shown in Figure 1. The electric discharge I was ignited between the electrolyte flow 2, which flowed upward from the cylindrical channel 3, and the water-cooled metal electrode 4. Inside the cylindrical channel 3 a graphite plate 5 was mounted, and it was
connected to the negative pole of the power supply. The discharge burned at a constant current \( I = \text{const} \).

The electrolyte was a solution of sodium chloride in distilled water. Part of the aqueous solution was spent on plasma formation. The loss was compensated by the addition of distilled water 6 (solvent) to the working reservoir 7 of the hydraulic system. The volume of the aqueous solution in the hydraulic system of the experimental setup was maintained constant \( V_s = \text{const} \).

![Figure 1. Scheme of the experimental setup.](image)

Electric power was supplied from sources based on an inverter converter. Power supplies of this type have the advantage of being able to maintain current with high accuracy.

At the time of burning discharge, the electrolyte was heated. Its cooling was carried out by circulation through the heat exchanger 8 using by hydraulic pump 9.

The specific electrical conductivity \( \sigma \) of the electrolyte was determined by direct conductometry by using the device «АНИОН 4150». Measurement of hydrogen index of the aqueous solution pH was done by using potentiometric channel of instrument «АНИОН 4150». The adjustment was carried out in four buffer solutions with \( \text{pH} = 4.01, 6.86, 9.18 \) and 12.43, prepared from standard-titers.

High-speed video filming was done with a Photron FASTCAM SA4 camera. Its technical characteristics allow a detailed study of processes in systems with a liquid medium [9].

The voltage \( U \) and current \( I \) were recorded with AKHIP-15/1 digital storage oscilloscope with a bandwidth of 25 MHz. Spectrometric studies were carried out with an AvaSpec-3648 high-speed fiber optic spectrometer.

3. Mathematical model

The mathematical model of the process describes the situation when small portions of electrolyte removed from the hydraulic system are compensated in uninterrupted mode by adding a solvent-water, while the full volume of the aqueous solution \( V_s \) remains unchanged. Under these conditions, the relative concentration of electrolyte varies exponentially

\[
\frac{C}{C_0} = \exp\left(-\frac{k \cdot \Delta V}{V_s}\right). \quad (1)
\]

Here \( C_0 \) – is the initial molar concentration of the electrolyte; \( \Delta V \) – is the volume of distilled water added to the hydraulic system during the burning of the discharge.
The value of the option $k = 1$ corresponds to the situation when small portions of the electrolyte are removed without changing the concentration. Variants $k < 1$ and $k > 1$ means that the concentration of the solute (or any of its components) in the portion to be removed, respectively, is less or more than $k$ times that in an electrolyte with a volume of $V_s = \text{const}$.

4. Results of the experiment and their analysis

An aqueous solution of sodium chloride, serving as a cathode, is alkalized during the burning of the discharge, due to the occurrence of electrolysis processes. Chlorine ions Cl$^-$ in a 1:1 ratio are replaced by hydroxide ions OH$^-$. If hydrochloric acid is added to the solution, it is possible to neutralize its alkaline component. This procedure was carried out by titration of samples taken from the electrolyte-cathode. The titrant was added to the selected sample until the original pH value was completely restored.

From the material balance of the process of titration was obtained by the formula

$$
\frac{c}{c_0} = 1 - \frac{c_l}{c_0} \cdot \frac{\Delta V}{V},
$$

where $c_l$ and $\Delta V$ – is the molar concentration and volume of titrant; $V$ – is the volume of the sample.

The use of a mathematical model and titration results allowed us to determine the numerical values of the option $k$. All $k$ values were less than one when electrolytes with concentrations ranging from 0.02 to 0.3 mol/l were used. This means that in small portions that are removed from the electrolyte the concentration of sodium chloride is less than in the electrolyte itself. Moreover, with an increase in the initial concentration, the results shifted towards small values of the option $k$.

Conductometric measurements showed that despite the addition of a significant amount of distilled water to an aqueous solution during the discharge, the electrical conductivity $\sigma$ of the electrolyte did not decrease, but on the contrary, it increased slightly.

Assuming that all the Na$^+$ ions coming out from composition of electrolyte drops are returned, then in general, the total number of ions in the electrolyte should not change. At the same time, the Cl$^-$ anions that left the electrolyte will be replaced by the same number of OH$^-$ hydroxide ions. In such a situation, $\sigma$ should not decrease.

High-speed visualization clearly showed spraying of electrolyte in the form of small droplets (Figure 2).

![Explosions of electrolyte droplets in the discharge area. Discharge current: (a) – 1.5 A; (b) – 10 A.](image)

In video frames flashes were observed (highlighted in white circles). They arose due to the explosive evaporation of droplets exposed to the intense heat of plasma. The duration of the flashes was ~ 2 ms.
It can be seen at the bottom of the video frames (Figure 2), that the zone of the discharge binding to the cathode is inhomogeneous. Closer to the cathode, the glowing column splits into many channels. These channels rest on the surface of the electrolyte, forming small luminous spots. Single spots existed not long. The minimum lifetime was ~ 1 ms. The current density $j_k$ on them was within $(50-100)$ A/cm$^2$. The average value of $j_k$, defined as the ratio of current $I$ to the total area of the luminous zone on the electrolyte surface, was ~ 1 A/cm$^2$, i.e., it was within those values of $j_k$ that occur in low-current modes [10].

High-frequency pulsations in current oscillograms were recorded (Figure 3). It can be considered that such pulsations arise as a result of droplet explosions, since with each explosion new portions of carriers in the form of ions are injected into the plasma. Apparently, current and voltage pulsations that are observed in glow discharge [11-12] also arise due to fluctuations ion component of plasma.

Figure 3. Current and voltage oscillograms.

5. Conclusions
Thus, from the experiments, it follows that in high-current modes, there is an intense influx of the substance from the electrolyte into the plasma in the form of small droplets. Under these conditions, it can be considered that the current is mainly created by ions that are carried by droplets.

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