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About the nature of electrical conductivity a gas discharge plasma with a water-solution cathode

G K Tazmeev¹, B A Timerkaev¹ and K K Tazmeev²

¹Kazan National Research Technical University named after A.N. Tupolev, 10 K. Marx str., Kazan, 420111, Russian Federation
²Kazan Federal University, Naberezhnye Chelny Institute, 68/19 Mira Street, Naberezhnye Chelny, 423810, Russian Federation

E-mail: tazmeevg@mail.ru

Abstract. A gas discharge between an aqueous solution of sodium chloride and a copper electrode – anode in air at atmospheric pressure was studied. It was been shown that the electrical conductivity of a gas discharge plasma with a water-solution cathode is predominantly ionic.

1. Introduction
In recent decades, studies of physicochemical processes in gas discharges of atmospheric pressure in contact with a liquid have been actively conducted [1]. The range of possibilities for practical applications of plasma of such discharges is continuously expanding. Plasma sources, in the use of liquid as electrodes, are promising for water purification, initiation of chemical reactions in solutions, and many other practical applications [2-7]. However, understanding the nature of the complex phenomena that form processes in a discharge with an intensely evaporating liquid electrode, including a water-solution cathode, at present remains extremely limited. In particular, the nature of the electrical conductivity of the plasma is not fully disclosed. As is known, a heated metallic cathode emits electrons. Thermionic emission occurs. There are no free electrons in the water. Therefore, in the case of the water-solution cathode, electron emission is practically absent. The main current carriers in aqueous solutions are cations and anions. The electrical conductivity of the aqueous solution is ionic. What is the electrical conductivity of the plasma above the water-solution cathode? What are the mechanisms of the formation of current carriers in it? This work is aimed at studying these issues.

2. Experiment
In figure 1 schematically shows a cathode assembly of a gas discharge device. It consists of a small container 1, in which a metal rod 2 is mounted.
After ignition of the gas discharge, an aqueous solution was supplied to container 1. The liquid level was rose and the metal rod is immersed in an aqueous solution. Thus, a smooth transition from a metallic cathode (thermionic emission) to a water-solution cathode (without electron emission) was carried out.

The characteristics of a gas discharge with a water-solution cathode were investigated in an experimental setup, a detailed description of which is given in [8].

High-speed video shooting was made by the Photron FASTCAM SA4 camera. Its technical characteristics make it possible to study in detail the processes in systems with a liquid medium [9].

3. The experimental results and their analysis
In figure 2 shows instant photographs of two types of gas discharge. To the left is a gas discharge with thermonic cathode. It burns between two copper electrodes in the air. On the right is a gas discharge with a water-solution cathode.

Figure 2. Transition from a thermionic cathode to a water-solution cathode. Cathode: (a) – copper rod with a diameter of 10 mm; (b) – an aqueous solution of sodium chloride with a concentration of 0.5% by mass. The interelectrode distance is 5 cm. The exposure of photos is 0.2 ms. (c) and (d) are oscillograms of voltage and current.
The transition from one type of gas discharge to another was carried out without changes in the electric power supply system. However, as can be seen from the photos, the cathode spot has disappeared. The binding of the discharge to the cathode expanded and covered a relatively large area on the surface of the aqueous solution. The plasma column above the cathode also expanded. Anode binding of the discharge remained unchanged. In both cases it pointwise.

As can be seen from the presented oscillograms, changes in the voltage and current of the discharge was abruptly occurred. The voltage increased by more than an order of magnitude: from 100 to 1200 V. It should be noted that the increase in voltage is largely due to an increase in the cathode voltage drop. The latter depends on the concentration of the aqueous solution. In this embodiment, it is about 600 V. There is a voltage drop inside the aqueous solution (approximately 100 V). When these parameters are taken into account, approximately a 5-fold increase in voltage is obtained. The discharge current decreased by approximately 3 times: from 11 to 3 A.

The most likely cause of these transformations in a gas discharge is the change in the electrical conductivity of the plasma. In the variant with a metal cathode, electronic conduction predominates. Electrons move easily under the influence of a weak electric field. Therefore, the voltage in the discharge is small. Compared to electrons, ions are less mobile. To create an ion current, a stronger electric field is necessary, and an increase in voltage is required, respectively. Consequently, ionic conductivity predominates in the variant with water-solution cathode.

In the plasma column above the water-solution cathode, many small flashes are observed. In the video frame, they are visible in the form of light circles (Figure 3a). Flashes are formed as a result of the explosion of small droplets of solution, which fall into the discharge region. They can be called secondary explosions. Primary explosions occur on the surface of a water-soluble cathode. As a result of primary explosions, cathode sputtering occurs and droplets are formed. Each droplet is a bunch of cations and anions taken out of the aqueous solution. After a secondary explosion, they fly off and become carriers of current. With each explosion, a certain number of current carriers are added. Because of this, current ripples occur. They are recorded on oscillograms (Figure 3b). The current ripple frequency is quite large. It is in the megahertz range.

![Figure 3. Secondary explosions and high-frequency current pulsations. (a) – video frame, shooting frequency 10,000 frames per second. (b) – oscillograms of current and voltage.](image)

In the electric field of the discharge, cations and anions drift in opposite directions. The chlorine ions Cl\(^{-}\) are drifting towards the anode and thus they are removed, forming molecular chlorine. The amount of chlorine in the aqueous solution decreases. Sodium ions Na\(^{+}\) are drifting towards the cathode and are returned in an aqueous solution. On the surface of the graphite plate with a negative potential, they are restored. Metallic sodium immediately reacts with water, forming the hydroxide NaOH, which in turn dissociates into ions Na\(^{+}\) and OH\(^{-}\). Thus, chlorine ions Cl\(^{-}\) that have departed the
aqueous solution are replaced by the same amount of hydroxyl OH⁻ ions. The solution is alkanalized. Hydroxyl OH⁻ ions also participating in the creation of ion current in the discharge. In the end at the anode, in addition to chlorine, oxygen and water vapor are released. And molecular hydrogen is released on the cathode. In the discharge gap, water vapor is formed from the droplets.

Sodium ions Na⁺ released from the aqueous solution in the composition of droplets, practically they all return back. The amount of sodium ions Na⁺ is not changed in a solution and the amount of solvent (water) is reduced. The loss can be compensated by adding distilled water, i.e. during the burning of the discharge, the volume of the aqueous solution can be maintained unchanged. Such experiments were carried out at a fixed value of the current. Aqueous solutions with different initial concentrations \( C_0 \) were used.

\[
\sigma/\sigma_0 = \frac{\text{specific electrical conductivity of the solution}}{\text{initial specific electrical conductivity}}
\]

\[
\Delta V/V_s = \frac{\text{volume of distilled water added to the solution}}{\text{total working volume of the solution}}
\]

**Figure 4.** Change of the specific electrical conductivity of the aqueous solution. \( \Delta V \) – is the volume of distilled water added to the solution. \( V_s \) – is the total working volume of the solution. \( I - C_0 = 0.02 \text{ mol/l; } 2 - 0.1 \). The discharge current is 8 A.

Measurements performed before and after experiments showed that, the specific electrical conductivity of the solution varies insignificantly. Such results confirm the circulation of sodium ions Na⁺. As a part of the drops, they leave the solution, and then return back. Their concentration practically does not change. As can be seen from the presented graphs (Figure 4), there is a tendency to increase the specific electrical conductivity with increasing duration of the discharge burning. To some extent, this is explained by the fact that chlorine ions Cl⁻ are replaced in the solution by more mobile hydroxyl ions OH⁻.

**4. Conclusions**

Experimental facts are obtained, which are explained by the fact that the electrical conductivity of a gas discharge plasma with a water-solution cathode is predominantly ionic.

1. The exchange of metal cathode an aqueous solution causes increase burning voltage of a gas discharge under otherwise identical conditions.
2. In compliance with measures that compensate the loss of water (solvent), electrical conductivity of the aqueous solution changes slightly.
3. In gas discharge plasma the explosion of droplets of the solution are transpired, which cause the ripple current in the megahertz range.

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