About changes in the physicochemical properties of aqueous solutions used as a liquid electrolyte cathode

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Abstract. The gas discharge between liquid electrolyte cathode and metal anode was experimentally investigated. Aqueous solutions of sodium chloride, potassium chloride, sodium sulfate, sodium hydroxide, and potassium hydroxide were used as the electrolyte cathode. Decrease aqueous solution was compensated by adding distilled water (solvent) in a continuous mode in the discharge burning process. It was found that, despite the significant dilution with a solvent, the specific electrical conductivity of aqueous solutions of alkali metal salts and alkalis varies slightly.

1. Introduction
Gas discharges that are in contact with liquids are promising for various applications [1–6]. However, at present they remain poorly understood. The mechanisms of transfer of electric charges through the liquid-plasma boundary zone are not fully disclosed. The processes of interaction between liquid electrolyte and plasma have been little studied. In particular, there are no clear ideas about the mechanisms by which the components of the liquid electrolyte enter the plasma and the formation of a reverse flow of particles.

In work [7], the droplet mechanism for the transfer of a substance from an electrolyte into a plasma was considered. Developed a mathematical model of the process. Formula was proposed, which can determine the change in the concentration of electrolyte. The applicability of the model was justified experimentally. A solution of sodium chloride in distilled water was used as the liquid cathode. The purpose of this work was to conduct research with the use of aqueous solutions with a different chemical composition.

2. Experiment
In a simplified form, the scheme of 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 \( I = \text{const} \).

In the burning process of gas discharge is loss of electrolyte. Part of electrolyte is spent on plasma formation. With long-term burning of discharge requires the completion of loss. In experiments,
electrolyte loss was compensated by the addition of distilled water. At the same time, the total volume $V_s$ of the electrolyte remained unchanged, i.e. the condition $V_s = \text{const}$ was satisfied.

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

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

3. Results of the experiment and their analysis

According to the mathematical model of [7], the molar concentration of the electrolyte should be changed according to the law

$$\frac{c}{c_0} = \exp\left(-\frac{k \cdot \Delta V}{V_s}\right).$$

(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 $V_s = \text{const}$.

In the experiments, alkalization of aqueous solutions of alkali metal salts (sodium chloride, potassium chloride and sodium sulfate) was observed. Recovery of pH was carried out by titration with hydrochloric acid. Formula obtained from the material balance of titration process

$$\frac{c}{c_0} = 1 - \frac{c_t}{c_0} \cdot \frac{\Delta \nu}{\nu},$$

(2)

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

In figure 2 shows results of calculations using formula (1), as well as results of experiments processed using formula (2). It also shows the results of experiments that were carried out without igniting the gas discharge. In these experiments, the concentration of an aqueous solution of sodium chloride was measured using the device ANION 4150.

As can be seen, the results obtained in experiments with gas discharge differ significantly from experiments without discharge. All experimental points are in the zone where the parameter $k$ is less than one ($k < 1$). This means that in droplets that are removed from aqueous solution, concentration of sodium chloride is less than in the solution itself. Moreover, with an increase in the molar concentration of solution, the difference increases (the experimental points shift towards small values...
of the parameter $k$). The experimental results obtained using an aqueous solution with concentration of $c_0 = 0.02 \text{ mol·l}^{-1}$ are in good agreement with the calculations for $k = 0.3$. And results obtained for $c_0 = 0.3 \text{ mol·l}^{-1}$, correspond to calculations performed for values of $k$, that are in the range (0.1–0.05 mol·l$^{-1}$).

**Figure 2.** The change of relative concentration of an aqueous solution of sodium chloride. 1 – experiments without gas discharge ($c_0 = 0.1 \text{ mol·l}^{-1}$). 2, 3, 4, 5 and 6 – experiments with gas discharge. Discharge current 8 A. 2 – $c_0 = 0.02 \text{ mol·l}^{-1}$; 3, 4 – 0.05 mol·l$^{-1}$; 5 – 0.1 mol·l$^{-1}$; 6 – 0.3 mol·l$^{-1}$.

Similar results were obtained when using aqueous solutions of potassium chloride and sodium sulfate. Such results are explained by the fact that the Cl$^-$ and SO$_4^{2-}$, anions, which emerge from aqueous solution in composition of droplets, are removed from cathode irrevocably.

In figure 3 shows results of measurements of the specific electrical conductivity of aqueous solutions.

**Figure 3.** The change in the electrical conductivity of aqueous solutions used as a liquid electrolyte cathode. 1 – 0.1M Na$_2$SO$_4$; 2 – 0.1M KCl; 3 – 0.1M NaCl; 4 – 0.1M NaOH; 5 – 0.1M KOH. Discharge current 7.5 A.

As can be seen, despite the dilution of an aqueous solution with a solvent (distilled water), the specific electrical conductivity of aqueous solutions of alkali metal salts (sodium chloride, potassium chloride, sodium sulfate) increases. This effect is explained as follows. In the composition of the droplets, Na$^+$ and K$^+$ cations are removed from the aqueous solution. They are attracted to the cathode, and some of them are returned to aqueous solution. Ion neutralization occurs on the surface of a graphite plate and metallic sodium (or metallic potassium) is formed. Alkali metals react instantly with water to form hydroxides, which dissociate into positive ions Na$^+$, K$^+$ and negative ions OH$^-$. As a result, the replacement of less mobile ions Cl$^-$ and SO$_4^{2-}$ by the more mobile hydroxyl ion OH$^-$ is
made. The solution is enriched with more mobile ions and therefore its specific electrical conductivity increases.

In variants of gas discharges with alkaline cathodes (with aqueous solutions of sodium hydroxide and potassium hydroxide), the enrichment mechanism with more mobile ions is absent. Therefore, in these embodiments, there is a decrease in the electrical conductivity of aqueous solutions used as the cathode.

4. Conclusion
Thus, it has been established experimentally that, despite significant solvent dilution, the specific electrical conductivity of aqueous solutions of alkali metal salts and alkalis varies slightly. In this work was studied the mechanism of this phenomenon. The main elements of the mechanism were revealed: 1) drip removal of ions from the electrolyte due to cathode sputtering; 2) drift of positive alkali metal ions to the cathode and their return to the electrolyte; 3) alkalization of aqueous solutions of alkali metal salts.

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