Study of the dependence of the structure and luminescence of the discharge channel in a discharge with a liquid cathode from the electrochemical properties of a liquid cathode

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Abstract. In the present work, the structure of the discharge channels glow of a discharge with a liquid cathode at different pH values of the solution at a given concentration of alkali metal (Na) ions in the solution is investigated by the methods of emission spectroscopy and high-speed photography. The dependence of the atomic sodium line intensity in the emission spectrum of the discharge plasma from the pH value of the solution is investigated. The dependence of the discharge channels filaments shape on the presence of sodium impurities in them is found. The spatial and temporal inhomogeneity of sodium luminescence in the emission spectrum of the discharge channel of a discharge with a liquid cathode at different pH values of the solution is studied. Its connection to the mechanism of sodium transfer into the gas phase is discussed.

Introduction

In the last two decades, there has been a great increase in interest to the studies of the interaction of plasma with a liquid surface. One of the promising areas of practical use of systems in which plasma interacts with a liquid surface is spectral analysis of the content of metal ions in water and aqueous solutions [1]. The most frequently used method of organizing the interaction of plasma with the surface of a liquid for spectral analysis of metal ions in aqueous solutions is using a direct current discharge and making a liquid cathode out of a solution that is being analyzed [1].

In a direct current discharge with a liquid cathode, a nonequilibrium transfer of the liquid cathode substance to the gas phase occurs under the action of ion bombardment of the liquid cathode, as a result of which metal atoms transfer from the solution into the gas-discharge plasma region, where they are excited [2, 3]. Determination of the concentration of metal atoms in plasma is carried out by the methods of emission spectroscopy.

One of the important stages of this process is the transfer of the analyzed substance from the liquid phase to the plasma zone. It is known that the transfer of metals from solution to the gas phase in a discharge with a liquid cathode effectively occurs only for solutions with a high acidity level (pH≤2) [1]. However, the reasons for this, and the transfer mechanism itself, remain unknown.

In this work, we investigated a DC discharge with a liquid cathode, which was an aqueous electrolyte solution. The aim of this work was to study the dependence of the structure of the discharge channel of a DC discharge with a liquid cathode and its emission spectra near the surface of the liquid cathode from the acidity level (pH) of the solution.

Earlier, we showed that near the surface of the solution in a discharge with a liquid cathode, the discharge channel is divided into separate filaments, which are in constant chaotic motion [4]. Each filament on the surface of the solution ends with a separate cathode spot. At the same time, the discharge channel near the anode may not have a filamentary structure [4].

Deciphering the emission spectra of the plasma of a discharge with a liquid cathode, which occurs at atmospheric pressure in air, shows the presence of emission bands of OH - radicals, molecular nitrogen N₂ (2') and N₂ (1'), molecular ion N₂⁺ (very weak against the background of N₂ (2'))), as well as lines of atomic hydrogen H I (Hα and Hβ) and oxygen O I [4]. In addition, in the case of using solutions with a low pH level, the presence of atomic metal lines in the electrolyte solution is noted in the emission spectra [1,5].
Experimental setup and measurement methods

In this work, a solution of sodium nitrate in deionized water with a concentration of \(2.5 \times 10^{-3}\) mol/l was used as an electrolyte, to which nitric acid was added to change the pH of the solution. Thus, in all experiments, the concentration of sodium ions in the solution was the same value equal to \(2.5 \times 10^{-3}\) mol/l.

The discharge was created between a tungsten rod electrode 2 mm in diameter, which plays the role of an anode, and a liquid cathode in a flow-through discharge cell at atmospheric pressure in air. The distance between the rod anode and the electrolyte surface was 2 mm. To study the discharge plasma by emission spectroscopy, an AvaSpec 2048 three-channel fiber-optic spectrometer with a spectral resolution of 0.15 nm was used. The discharge image was formed by a quartz lens on the plane in which the optical fiber guide was placed, which made it possible to study the spectra in the selected region of the discharge channel. In this work, all spectral measurements were carried out in the axial part of the discharge channel near the surface of the solution. High-speed photography of the discharge was carried out with a Nikon D500 camera. The exposure time of one frame was 125 \(\mu\)s.

Results and discussion

Fragments of emission spectra of the discharge in the region of the NaI 589 nm line, taken near the surface of the liquid electrolyte at different pH values, are shown in Figure 1.

From the spectra shown in Figure 1, it can be seen that at a given concentration of sodium ions in the solution in the investigated range of pH values, the highest luminescence intensity of the Na line is achieved at pH = 2.0, that is, at the highest level of solution acidity. With an increase in the pH of the solution, the brightness of the sodium line decreases and at pH ≥ 2.6, the sodium line practically disappears from the emission spectrum of the discharge plasma.

In the images from high-speed photography at pH ≥ 2.6, the discharge looks like white-violet (Figure 2 D). At pH < 2.6, a characteristic yellow glow of NaI appears near the surface of the liquid (Figure 2 A-C). Moreover, the brightness of this yellow glow increases on average as the pH decreases.

It is important to emphasize that the decrease in the brightness of the NaI luminescence with a decrease in pH occurs when recorded images are averaged. On the whole, the NaI luminescence at the same pH value for different high-speed recorded images with an exposure time of 125 \(\mu\)s has both a strong scatter in intensity and in the position of the NaI luminous region inside the discharge channel. So, for example, in Figure 2 C, a yellow glow is observed at the base of only one of the two filaments.
The irregularity of the NaI luminescence both in space and in time indicates an uneven emission of sodium from the solution into the region of the gas-discharge plasma.

![Typical images from high-speed photography of a discharge with a liquid cathode at a constant Na ion concentration in a solution of 2.5\times10^{-3} \text{ mol/l} and the following pH values: A) 2.0, B) 2.25, C) 2.4, D) 2.6. Discharge gap 2 mm, discharge current 60 mA, flow-through discharge cell. Exposure time 125 \mu s. For the correct comparison, images with a similar filament structure were selected.](image1)

**Figure 2.** Typical images from high-speed photography of a discharge with a liquid cathode at a constant Na ion concentration in a solution of 2.5\times10^{-3} \text{ mol/l} and the following pH values: A) 2.0, B) 2.25, C) 2.4, D) 2.6. Discharge gap 2 mm, discharge current 60 mA, flow-through discharge cell. Exposure time 125 \mu s. For the correct comparison, images with a similar filament structure were selected.

It is also noteworthy that the appearance of sodium in a certain filament of the discharge channel changes its shape near the liquid cathode, where the NaI glow is the brightest (Figure 2 A-D). In the immediate vicinity of the surface of the liquid cathode, the diameter of the filaments in which Na I glow is observed decreases. As a result, such filaments acquire a characteristic barrel-shaped surface, which is not typical for filaments in which there is no NaI luminescence (Figure 2 A-D). It would be logical to associate the change in the shape of the filaments with a change in the plasma parameters due to the penetration of easily ionized sodium atoms into it.

However, a comparison of the nitrogen N\(_2\) (2\(^+\)) bands in the emission spectrum of the discharge plasma with a liquid cathode near the solution surface at different pH values at a given Na concentration in the solution did not reveal any noticeable differences (Figure 3). This means that the appearance of NaI in the discharge plasma at these concentrations, even if it has an effect on the vibrational and rotational temperatures of molecular nitrogen N\(_2\), it is very insignificant.

![N\(_2\) nitrogen bands in the wavelength range of 280-360 nm in the emission spectrum of the plasma of a discharge with a liquid cathode at a constant concentration of Na ions in a solution of 2.5\times10^{-3} \text{ mol/l} at pH values of 2.0 and 2.6. Discharge gap 2 mm, discharge current 60 mA, flow-through discharge cell. The spectra were taken on the discharge axis near the solution surface.](image2)

**Figure 3.** N\(_2\) nitrogen bands in the wavelength range of 280-360 nm in the emission spectrum of the plasma of a discharge with a liquid cathode at a constant concentration of Na ions in a solution of 2.5\times10^{-3} \text{ mol/l} at pH values of 2.0 and 2.6. Discharge gap 2 mm, discharge current 60 mA, flow-through discharge cell. The spectra were taken on the discharge axis near the solution surface.
Considering that sodium ejections into plasma are uneven, images taken with large amount of sodium ejections are of particular interest.

It is characteristic that such ejections have a highly inhomogeneous spatial structure and often have inclusions observed in the form of brightly glowing microspheres, which are clearly visible in high-speed images (Figure 4 A-D). Such a distribution of the NaI impurity in the plasma zone can be explained only by the ejection of microdroplets from the solution into the plasma zone. It is assumed that their evaporation in the plasma zone leads to the corresponding spatial inhomogeneities.

**Figure 4.** Frames of high-speed photography of a discharge with a liquid cathode at a constant concentration of Na ions in a solution of $2.5 \times 10^{-3} \text{ mol/l}$ and pH = 2.0 on which glowing yellow spheres are present. Discharge gap 2 mm, discharge current 60 mA, flow-through discharge cell, exposure time 125 μs.

Thus, Figure 4 A-D is a direct confirmation of the ejection of micro drops from the liquid surface in a discharge with a liquid cathode. But, if from the surface of a liquid in a discharge with a liquid cathode, the ejection of micro droplets visible to the naked eye is possible, then it is quite possible that in such a discharge there is a constant ejection of smaller nano droplets capable of creating a diffuse glow in the images from the high-speed photography (Figure 2 A-C). An indirect confirmation of this mechanism of sodium ejection from the solution into the discharge plasma is the high temporal and spatial inhomogeneity of the NaI glow in the discharge channel of the discharge with a liquid cathode on a time scale of about 125 μs.

Since the pH of the solution has a significant effect on the intensity of the NaI line luminescence, a change in the pH of the solution should in this case affect the probability of the ejection of micro and nano drops from the surface of the solution in a discharge with a liquid cathode. In order to test this hypothesis, we calculated the percentage of frames of high-speed photography of a discharge with a liquid cathode, in which the characteristic yellow glow of NaI is absent at different pH values of the solution.

For this, 50 frames were taken of the discharge glow with a liquid cathode with an exposure time of 125 μs at four different pH values of the solution of 2.0, 2.25, 2.4, 2.6. And for each pH value, the number of frames was counted in which the yellow glow characteristic to NaI was completely absent, as was the case in Figure 2 D.

The results, expressed as a percentage, are presented in the histogram Figure 5.

As seen from Figure 5 at pH = 2.0, high-speed frames without traces of NaI are generally absent in the sample, but with an increase in the pH of the solution, the percentage of such frames increases rapidly, and at pH = 2.6, almost all frames do not contain traces of NaI. This is convincing evidence in favor of the hypothesis according to which the transfer of sodium ions from solution to the gas phase in a discharge with a liquid cathode at a discharge current of 60 mA in the pH range of 2.0-2.6 is carried out mainly due to the emission of micro and nano drops from the surface of the solution. However, we have no reason to assert that this mechanism of the transfer of sodium ions from solution to the gas phase in a discharge with a liquid cathode remains dominant under the same conditions at pH <2.0.
Figure 5. Dependence of the percentage of high-speed photographs of a discharge with a liquid cathode in which there is no characteristic yellow glow of NaI on the pH of the solution. The concentration of Na ions in the solution is $2.5\cdot10^{-3}$ mol/l, the discharge gap is 2 mm, the discharge current is 60 mA. The exposure time of high-speed photographs is 125 μs.

Conclusion

It has been shown experimentally that the pH of the solution has a significant effect on the transfer of metal ions from the electrolyte solution to the gas phase in a discharge with a liquid cathode. At a sodium ion concentration in the solution of $2.5\cdot10^{-3}$ mol/l, a discharge current of 60 mA and pH = 2.6, the luminescence of sodium 589 nm line in a discharge with a liquid cathode is practically absent. Whereas under the same conditions, but at pH = 2.0, the luminescence of the sodium 589 nm line in the emission spectrum of the discharge plasma is very significant. This indicates that the mechanism of the transfer of nonvolatile compounds from solution to the gas phase, whatever it may be, should significantly depend on the pH level of the solution.

It is shown that the filaments of the discharge channel, in the emission spectrum of which the sodium line is present, have a characteristic barrel-like shape near the surface of the solution. For filaments without a sodium line in the emission spectrum, this shape is not typical. At the same time, no noticeable effect of sodium at a given concentration in plasma on the intensity of the bands of molecular nitrogen $N_2$ ($2^+$), as well as on the vibrational and rotational temperatures calculated from $N_2$ ($2^+$), is observed.

It is shown that the NaI luminescence on a time scale of 125 μs at a discharge current of 60 mA and a solution pH of 2.0–2.6 has both a strong spread in intensity and in the position of the NaI luminous region inside the discharge channel. The nature of this spatial and temporal inhomogeneity indicates that the main mechanism for the transfer of nonvolatile compounds from solution to the gas phase in a discharge with a liquid cathode at these parameters is the emission of micro and/or nano sized droplets from the surface of the solution.

Acknowledgments

This work was partially supported by the Russian Foundation for Basic Research grant No. 20-08-00866 in the part of spectroscopic studies and partially supported by the Russian Foundation for Basic Research grant No. 20-08-00898 in the part of high-speed photography.

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