Study of the discharge with a liquid cathode with organic impurities

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Abstract. Dynamics of the discharge with a liquid cathode was studied using the method of high-speed visualization. The video data was compared with the emission spectra of the discharge plasma. Electrical parameters of the discharge were measured. The effect of organic impurities in the solution on the discharge parameters was investigated.

The direct current discharge between the electrode and the surface of the liquid is a promising object of study, both in terms of the applicability of such discharges in plasma-chemical technologies [1, 2] and in terms of the relatively poor knowledge of the processes occurring in such a discharge [3, 4]. In this paper, we investigated the dc discharge between a metal electrode rod and the surface of a conducting fluid that was the cathode. Sodium hydroxide solution in deionized water with a concentration of 60 mg/l was used as the liquid cathode (electrical conductivity 330 $\mu$S/cm). A tungsten rod 2 mm in diameter was used as the anode. The discharge occurred at atmospheric pressure in air. The study was conducted in the range of currents 25–100 mA. The effect of organic impurities in the solution (alcohols, phenols) on the discharge parameters was investigated.

High-speed video recording showed the presence of discharge heterogeneity, which manifests itself most strongly near the surface of the liquid. Near the surface, the discharge channel is divided into separate filaments [figure 1(a)], which randomly move along the surface at speeds in the order of several meters per second. It is assumed that this movement is due to the process of non-equilibrium evaporation of liquid in cathode spots, which leads to the displacement of plasma from these zones and, as a result, to the movement of individual filaments and the separation of large filaments into smaller ones.

Steam jets emanating from cathode spots sometimes lead to the dropping of micro-droplets of liquid into the discharge zone. Since the solution contains sodium ions, evaporation of the micro-droplets leads to the appearance of characteristic yellow flashes in different discharge zones [figure 1(b)].

High-speed recording shows that the duration of these flashes is less than 100 $\mu$s in most cases. Adding of up to 1% of organic impurities (isopropyl alcohol, phenol) to the solution did not have a noticeable effect on the appearance of the discharge, the dynamics of the movement of the filaments and their number.
Figure 1. Images of high-speed video recording of the discharge with a liquid cathode (a) normal burning, (b) yellow colored flash. The exposure time is 250 µs, the discharge current is 100 mA, the distance between the electrode and the surface of the liquid is 2 mm.

Figure 2. Dependence of the voltage drop across the discharge element upon the size of the discharge gap for a discharge with a liquid cathode at different currents.

The study of the electrical parameters of the discharge was carried out in the range of currents 25–100 mA. At different currents, the dependence of the voltage drop across the discharge cell on the distance between the electrode and the surface of the solution was measured. For all currents in this range of values, the dependence of the voltage on the discharge cell on the distance between the electrode and the surface of the solution turned out to be close to linear in figure 2.
Figure 3. Distribution of luminescence intensity of OH radical bands and N$_2$ ($2^+$) molecules depending on the concentration of isopropyl alcohol in solution: (a) deciphering of the spectrum in the central part of the discharge without isopropyl alcohol; (b) intensity distribution in the absence of isopropyl alcohol in the solution; (c) intensity distribution at a concentration of 1% isopropyl alcohol in the solution. The distance between the electrode and the surface of the liquid is 2 mm, the discharge current is 100 mA, the electrode is above the solution.
The linearity of this dependence allows extrapolating the voltage drop across the discharge cell to zero distance between the electrode and the surface of the liquid. The cathode voltage drop can be estimated as the difference between the extrapolated value of the voltage drop at the zero value of the discharge gap and the value of the voltage drop on the discharge cell when the electrode actually touches the solution. In the range of currents of 25–100 mA, the cathode potential drop turned out to be 610±50 V, with an accuracy of measurement error, independent of the discharge current value.

The investigation of a solution with organic impurities (a solution of isopropyl alcohol with a concentration of 0 to 1%) showed that the voltage drop across the discharge cell is independent of the concentration of isopropyl alcohol in this concentration range with an error measurement accuracy.

During the investigation of the discharge with a liquid cathode by the methods of emission spectroscopy, the image of the discharge was projected by a short-focus quartz lens onto the plane in which the entrance slit of the spectrometer was placed. The use of the Andor matrix at the output of the spectrometer made it possible to study the spatial distribution of the spectra.

Deciphering the emission spectra of the discharge with a liquid cathode showed the presence of OH—radicals and molecular nitrogen N₂, as well as atomic hydrogen H and oxygen O lines. The emission intensity distribution of individual lines and bands was investigated depending on the distance to the liquid surface. It has been established that the distributions of the luminescence intensity of the molecular nitrogen bands N₂, (2⁺) and N₂, (1⁺), as well as the lines of atomic hydrogen H and oxygen O, are almost independent of the discharge current and organic impurities in the solution. The distribution of the luminescence intensity of the OH—radical band, on the contrary, significantly depends on the size of the discharge current and on the impurities of organic compounds in the solution in figure 3.

In the studied range of currents (25–100 mA), the dependence of the luminescence intensity distribution of the OH—radical band on organic impurities is most pronounced at a current of 100 mA. At a current of 100 mA, in the absence of an organic impurity, the brightness of the OH—radical band monotonically increases as it moves from the surface of the liquid to the electrode. In the case of, for example, a 1% solution of isopropyl alcohol, with the same current and the same conductivity of the solution, the intensity of the luminescence of the OH-radical band remains almost constant throughout the discharge gap in figure 3.

Thus, we can conclude that the addition of 1% organic volatile impurities of isopropyl alcohol in aqueous solution has no significant impact neither on the structure and dynamics of the discharge nor on its volt-ampere characteristics, nor on the distribution of intensity of bands of molecular nitrogen N₂, atomic lines of hydrogen H and oxygen O. However, the addition of 1% isopropyl alcohol radically changes the intensity distribution of OH—radical bands at the studied discharge current of 100 mA, shifting the maximum intensity of these bands from the electrode to the surface of the solution.

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References
[1] Kutepov A M, Zakharov A G and Maksimov A I 2004 Vacuum-Plasma and Plasma-Solution Modification of Polymeric Materials (Moscow: Nauka)
[2] Locke B R, Sato M, Sunka P, Hoffmann M R and Chang J S 2006 Ind. Eng. Chem. Res. 45 882–905
[3] Bruggeman P and Leys C 2009 J. Phys. D: Appl. Phys. 42 1–28
[4] Bruggeman P, Kushner M and Locke B 2016 Plasma Sources Sci. Technol. 25 053002