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## GLOW DISCHARGE EMISSION SPECTRA IN AIR WITH LIQUID ELECTRODE BASED ON DISTILLED WATER

M. P. Chuchman,<sup>a\*</sup> L. V. Mesarosz,<sup>a</sup> A. K. Shuaibov,<sup>a</sup>  
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*The results of spectroscopic studies of a glow discharge plasma at atmospheric pressure in air with an electrode based on distilled water are presented. The parametric effects affecting the discharge emission are analyzed. The dependence of the emission intensity of the various discharge components and their spatial localization in the discharge gap on the current strength is explained by change in the discharge geometry and the conditions of oxidation with increase of the current. It is shown that the composition of the gas mixture in the electrode gap changes with increase of the discharge current from nitrogen-rich (12–19 mA) to rich in water vapor and its dissociation products (19–24 mA). At higher currents, the gas mixture is also rich in the products of plasma chemical reactions and nitric oxide in particular. The redistribution of the radiation intensity of the molecules of nitrogen and its oxide with increase of the current occurs mainly in the cathode region (at the plasma–fluid boundary), where the formation of oxides is improved as a result of increase in the amount of vaporized solution and in the effectiveness of oxidation reactions with increase of the water temperature and discharge current.*

**Keywords:** atmospheric pressure, glow discharge, liquid electrode, plasma liquid contact, plasma electrical discharge spectroscopy, redox reactions.

**Introduction.** Glow discharge between metallic and liquid electrodes in air at atmospheric pressure is marked by the simplicity of realization and control of the plasma characteristics, by the low cost of the starting materials, by a series of practical applications in plasma chemistry for the synthesis and conversion of chemical compounds in the discharge volume and on the surface of the liquid, in ecology for the purification of water and air, in medicine, agriculture, and the food industry for decontamination and sterilization on account of the manifestation of bactericidal and fungicidal characteristics, and in the treatment and surface modification of various materials, the synthesis of nanoparticles, and spectral analysis of solutions [1–3]. Experimental and theoretical investigations of a glow discharge with a liquid electrode [4, 5] are insufficient to explain the whole set of phenomena that occur in its positive column and also in the regions near the electrodes. Such discharges are unique as subjects for comprehensive study of physicochemical phenomena from the standpoint of plasma chemistry, electrochemistry, gas discharge physics, and emission electronics. Of course, the characteristics of such systems depend not only on the characteristics of the liquid and metallic electrodes but also on the characteristics of the gas phase. The amount of experimental data on plasma–liquid electrode systems is limited. The problem of the release of electrons from the surface of a liquid cathode has not been fully investigated, and the mechanisms of entry of the metal atoms of salts dissolved in the liquid into the region of the plasma above the surface of the solution etc. have not been established. The question of using such a plasma in sources of noncancerous UV radiation on the products from the degradation of water molecules and clusters has not been resolved.

Information on the properties of the gas discharge plasma and the transfer processes can be obtained on the basis of spectroscopic, electric, and spatial investigations of the glow discharge. These data also make it possible to forecast the occurrence of oxidation–reduction reactions and their effect on the synthesis of nanoparticles during the treatment of solutions by means of an electric discharge plasma. In the present work the emission characteristics of a glow discharge with

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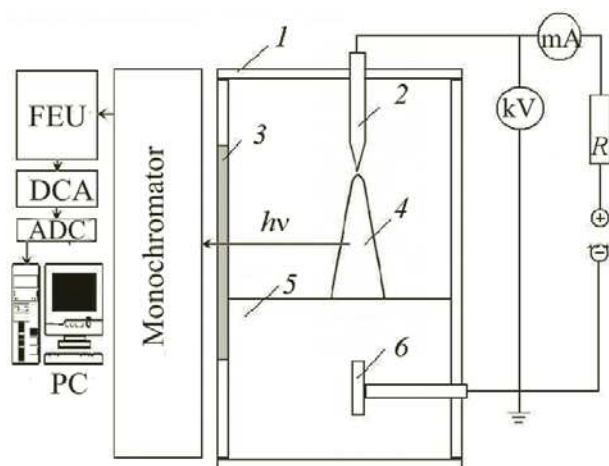


Fig. 1. Block diagram of the experimental setup: 1) Cell of acrylic polymer; 2) metallic electrode (needle); 3) quartz window; 4) plasma discharge; 5) surface of water; 6) cathode immersed in liquid.

a liquid electrode were investigated in relation to the discharge parameters and, in particular, the discharge current, the spatial distribution of the plasma between the electrodes, and the temperature of the liquid.

**Experimental.** The glow discharge was generated in a system with a copper needle and the surface of distilled water as electrodes. The copper electrode was in water, and thickness of the layer of water above it was 2 mm. The volume of the cell in the form of a cube was 1 dm<sup>3</sup>. The diameter of the window was 50 mm. The investigations were conducted with a distance of 8 mm between the metallic electrode and the surface of the water. The charge was powered by a high-voltage rectifier ( $U = 1\text{--}25$  kV,  $I = 1\text{--}100$  mA). In individual experiments a stainless steel capillary through which an inert gas (Ar) was passed was used in place of the copper needle.

The emission off the discharge plasma in air was analyzed in the spectral region of 200–700 nm by an MDR-2 monochromator with a diffraction lattice with 1200 lines/mm and a wavelength resolution of 0.2 nm. The emission was recorded by an FEU-106 photomultiplier, a U5-9 amplifier (DCA), and a system for automatic recording of the spectra based on an analog-digital converter (ADC) and a personal computer. A diagram of the experimental setup is presented in Fig. 1. In the experiments with the argon flow the emission spectra were recorded on a diffraction spectrometer (a 1200 lines/mm lattice) fitted with a line charge-coupled device (CCD). The spectra were interpreted with the aid of reference manuals [6, 7]. The spectral sensitivity of the photomultiplier and the CCD was taken into account during comparison of the intensities in the spectra.

**Results and Discussion.** A section of the glow discharge emission spectrum with the liquid electrode is shown in Fig. 2a. The strongest emission in this region of wavelengths corresponds to vibrational transitions between the electronic states  $A^2\Sigma^+ - X^2\Pi$ ; of the OH radical and  $C^3\Pi_u - B^3\Pi_g$  of the N<sub>2</sub> molecules. There are spectral lines of the copper atom with maximum intensity at wavelength Cu I 324.8 nm and also emission of the bands of the  $\gamma$  system of the NO molecule with maximum at 247.8 nm at the  $^2\Sigma \rightarrow ^2\Pi(0;2)$  transition and emission of the H $_{\alpha}$  hydrogen atom with maximum at 656.2 nm (Fig. 2b, c).

If air is substituted for the inert argon as working gas the bands of nitrogen are also observed in the discharge spectrum. In this case, however, the intensity of the bands depends strongly on the rate at which the argon is pumped through the capillary. Thus, if the flow rate of argon is increased from 15 to 60 cm<sup>3</sup>/min (under standard conditions) the nitrogen bands in the spectrum disappear, and the spectrum of the discharge plasma only contains the bands of OH and the spectral lines of the atoms of the electrode material submerged in water.

In the emission spectrum of molecular nitrogen the second positive system of N<sub>2</sub> with a maximum at 337.1 in the  $^3\Pi \rightarrow ^3\Pi(0;0)$  transition predominates. For the nitrogen molecule apart from the strongest band there are weaker bands with maxima at 357.7 (0;1), 375.5 (1;3), and 380.5 nm (0;2). In addition to the strong OH band in the region of 303–316 nm, hydroxyl emission with lower intensity also appears in the region of 275–290 nm.

The emission intensity of the various components of the plasma depends on the discharge current (Fig. 3) but in different ways. Thus, increase of the discharge current from 10 to 32 mA leads to increase in the intensity of the OH bands



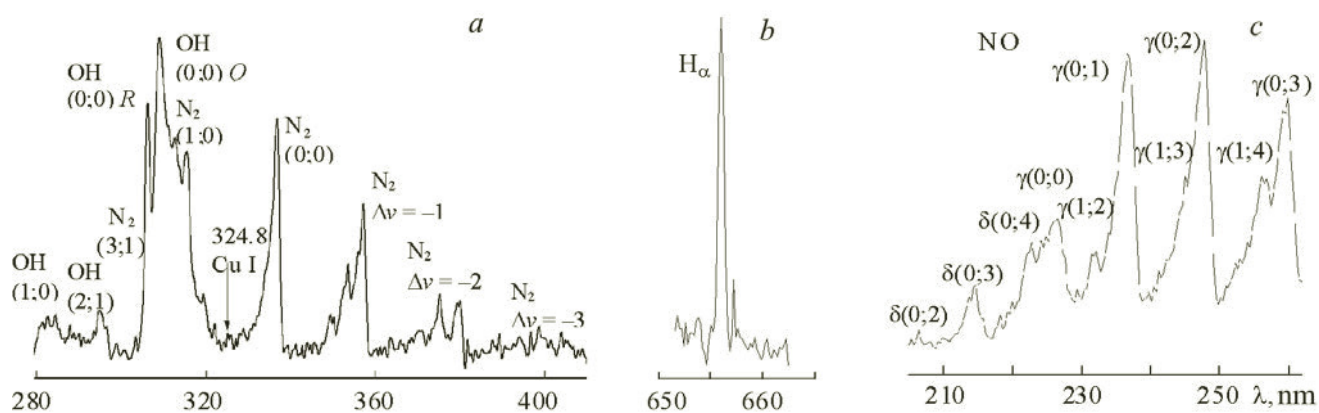


Fig. 2. The emission spectrum of the glow discharge with liquid electrode at current 17 mA (a) and sections of the spectra in the region of low-intensity glow at discharge current of 32 mA (b, c).

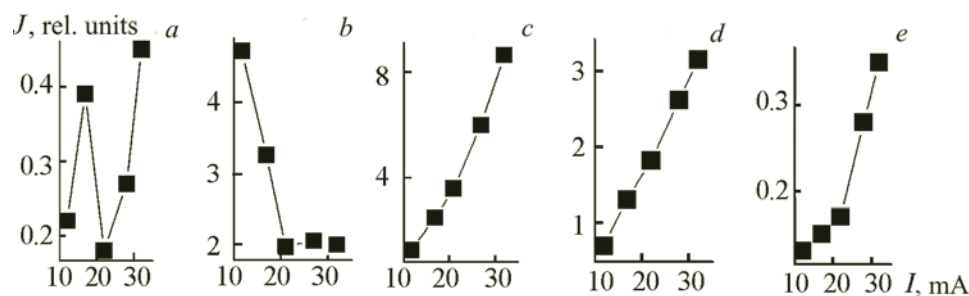


Fig. 3. The emission intensity of the discharge components in relation to the current: a) Cu I 324.8 nm; b) N<sub>2</sub> 337.1 nm  $^3\Pi \rightarrow ^3\Pi(0;0)$ ; c) OH 306.4 nm  $^2\Sigma \rightarrow ^2\Pi(0;0)$ ; d) NO 247.8 nm  $^2\Sigma \rightarrow ^2\Pi(0;2)$ ; e) H <sub>$\alpha$</sub>  656.2 nm.

and to a decrease in the intensity of the N<sub>2</sub> bands. By analyzing the change in the intensity of the OH bands with increase of current it can be seen that the intensity increases most quickly after a value of 24 mA. A similar type of behavior is observed for the emission of the hydrogen atoms. There is also a substantial increase in the intensity of the NO emission after 24 mA, while at lower currents the intensity is almost constant. Thus, the emission of N<sub>2</sub> dominates at small discharge currents. The intensity of the emission of N<sub>2</sub> molecules decreases with increase of the discharge current to 19 mA, after which it changes little. The dependence of the emission intensity of the copper ions on the discharge current is irregular in nature, and minima are observed at currents of 12 and 22 mA.

With increase of the discharge current together with change in the discharge geometry there are physicochemical processes that promote change in the composition of the gas mixture in the interelectrode space. As a result of the action of the charge on the liquid the amount of evaporated liquid is increased, and the plasma chemical processes involving the vapor are also intensified. It should be noted that the dependences of the charge emission intensity on the current indicate clearly that as the current increases from 12 to 24 mA the composition of the gas in which the discharge burns becomes rich in water vapor and in the products from dissociation of its molecules and, after 24 mA, even in the products from the plasma chemical reactions, among which nitric oxide appears most conspicuously in the emission products. The rate of change of intensity with increase of current in the ranges of 16–24 and 24–32 mA is increased by 1.9, 1.8, and 1.7 times respectively for the OH, H, and OH molecules.

In order to analyze possible influence of the parameters on the discharge processes the variation of the discharge emission in various spatial zones in relation to the current and the effect of the liquid temperature of on the emission intensity were also investigated. In order to analyze features of the emission spectra from the various spatial discharge zones emission from a region 2 mm wide at the electrodes and the center of discharge was selected by means of a slit. The emission from the lower, central, and upper parts of the discharge gap was recorded at currents of 12 and 32 mA (Fig. 4a). With increase

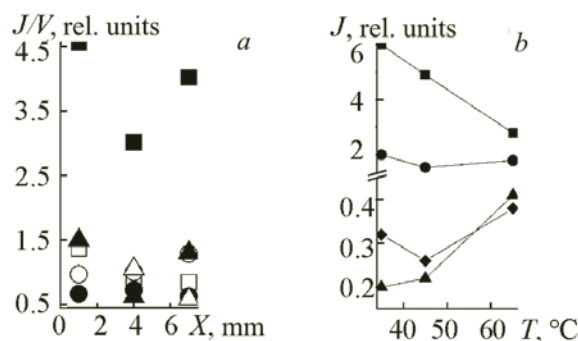


Fig. 4. Distribution of the intensity from unit volume of plasma (a) for the emission bands of OH ( $\square$ ,  $\blacksquare$ ),  $N_2$  ( $\circ$ ,  $\bullet$ ), and NO ( $\triangle$ ,  $\blacktriangle$ ) in the interelectrode gap at currents 12 ( $\square$ ,  $\circ$ ,  $\triangle$ ) and 32 mA ( $\blacksquare$ ,  $\bullet$ ,  $\blacktriangle$ ); the effect of the temperature of the water (b) on the emission intensities of the bands: OH 308.9 nm  $^2\Sigma \rightarrow ^2\Pi$  (0;0) ( $\blacksquare$ );  $N_2$  337.1 nm  $^3\Pi \rightarrow ^3\Pi$  (0;0) ( $\bullet$ ); NO 259.5 nm  $^2\Sigma \rightarrow ^2\Pi$  (0;3) ( $\blacktriangle$ ) and Cu I 324.8 nm ( $\blacklozenge$ ) at discharge current 32 mA.

of the current strength the intensity of the hydroxyl emission increases by three times over the whole discharge region. The intensity of nitric oxide emission above the surface of the distilled water is increased. The emission intensity of nitrogen, conversely, is reduced particularly above the surface of the water. It can therefore be supposed that the redistribution of the emission intensity of the various components in the space of the discharge channel arises from change of the conditions under which the chemical processes occur in the solution and in the gas with increase of the discharge current. In particular, the conditions for the formation of nitrogen oxide with the participation of atmospheric nitrogen and water vapor over its surface are improved if the current is increased. Variation of the electric field potential along the discharge also has a significant effect, and this is illustrated best by the emission of the hydroxyl at a current of 32 mA.

If the current is increased charged particles are formed as a result of ionization of the molecules with a lower ionization energy. As seen from Fig. 3, the intensity of the emission of the NO and OH molecules increases sharply with increase of current. The reason for this is the significant increase of the concentration of water molecules in the cathode region as a result of evaporation [8] and also the substantial increase in the effectiveness of electrodisassociative processes in the plasma at currents of  $>24$  mA.

The similar nature of the change in the OH and  $H_\alpha$  emission indicates that the hydrogen atoms are most likely formed as a result of interaction of the plasma with the surface of the water, the decomposition of which leads to the formation of hydrogen atoms and OH radical. Analogous behavior of the emission was observed in [9] in a glow discharge on an He– $H_2O$  mixture with increased water vapor density ( $\sim 2$  kPa) and also in [10] in a barrier discharge in a drop–air medium. At small discharge currents the intensity of the  $N_2$  band at 337.1 nm is higher than the intensity of the OH band at 308.9 nm, and its violet edge overlaps with the red edge of the OH [11]. If the current is increased the situation is reversed. The energetic action of the plasma on the liquid leads to an increase in the concentration of water molecules, the amount of which in the plasma–gas mixture becomes predominant [12]. As a result of their high concentration the water molecules, their decomposition products, and the nitrogen molecules will determine both the composition of the emitting components of the plasma and the initial stage of the chemical reactions. The accumulation of the products of such reactions with time and the secondary processes between them are interesting from the standpoint of the practical aspects of the discharge.

During analysis of the change of intensity at a discharge current of 32 mA it was found that the intensity of the OH band decreases by half when the temperature of the water in the cuvette is increased from 30 to 60°C. The dependence of the hydroxyl emission intensity on the temperature of the liquid cathode is shown in Fig. 4b. The change in the emission intensity of the other components of the plasma here was insignificant with the exception of NO, for which the intensity of the bands increases significantly with increase in the temperature of the liquid. The increased efficiency of the chemical reactions results from secondary reactions between the water vapor, the radicals formed during its decomposition, and components of the atmosphere. Here the amount of oxidizing components (radicals, oxygen atoms, and molecules capable of giving up oxygen) is increased. Nitrogen will be effectively oxidized under such conditions. We note that the rate of increases of the emission intensity of NO with increase of the current is higher than for hydrogen but lower than for OH. Under such conditions the synthesis will be more effective if the temperature of the water and, consequently, its vapor pressure are increased.

**Conclusions.** The dependence of the emission spectra of a glow discharge plasma with a liquid electrode on the discharge parameters was studied. It was shown that  $N_2$  emission at 337.1 nm  $^3\Pi \rightarrow ^3\Pi(0;0)$  and OH emission at 308.9 nm  $^2\Sigma \rightarrow ^2\Pi(0;0)$  predominate in the discharge spectra in air. Emission from NO at 247.8 nm  $^2\Sigma \rightarrow ^2\Pi(0;2)$  and from the hydrogen atom  $H_\alpha$  at 656.2 nm at lower intensity was observed. When the copper needle was replaced by a stainless steel capillary through which an inert gas (argon) was passed and the argon flow rate was increased from 15 to 60 cm<sup>3</sup>/min (under standard conditions) the nitrogen bands in the spectrum disappeared, and the plasma discharge spectrum only contained the bands of OH and the lines of the material of the electrode immersed in water. The dependence of the emission intensity of the various discharge components on the current strength and their spatial localization in the discharge gap were explained by change in the discharge geometry with increase of current and also by change in the conditions for the occurrence of the oxidation reaction. The redistribution of the intensity of the emission of the molecules of nitrogen and its oxide with increase of the current largely applies to the region saturated with water vapor near the cathode, where the formation of nitric oxide is improved. The increased effectiveness of the chemical oxidation reactions is a consequence of secondary reactions involving the products from decomposition of the surrounding gas and water vapor that take place at the plasma–liquid interface and become more effective with increase of the water temperature and the discharge current.

The obtained data are of interest for forecasting the effect of oxidation–reduction reactions when glow discharge with a liquid electrode is used in practical applications and, in particular, for the synthesis and modification of nanoparticles formed during discharge.

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