Variation of Temperatures of Discharge with a Liquid Electrode on the Basis of Distilled Water near the Ignition Threshold Mode

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Abstract. Emission spectra of glow discharge with copper and a liquid electrode on the basis of distilled water in the range of wavelengths of 200-700 nm are investigated. For discharge currents from 12 mA to 32 mA the values of the electron, vibrational and rotational temperatures are obtained.

Keywords: Electron, vibrational and rotational temperatures, glow discharge, ignition threshold mode, distilled water.

1 Introduction

The glowing discharge of atmospheric pressure in the air between the metal anode and the liquid cathode is simply to realize and control the parameters of the plasma. For glow discharge, where not expensive initial materials are used, therefore, there is a considerable amount of practical applications in plasma chemistry for the synthesis and conversion of chemical compounds in the volume of discharge and on the surface of the liquid. It also used in ecology for water and air purification and for the synthesis of nanoparticles, in plasma physics, for spectroscopic analysis of solutions [1-4]. Such discharge is unique as object for a comprehensive study of physical and chemical phenomena [5, 6].

The results of the averaged plasma parameters study near the ignition threshold are fewness, although the effect on the chemical composition of liquid is small. A significant improvement in the plasmachemical reactions has a current threshold. The plasma composition and temperature are various in different spatial regions. So the temperature averaged by volume and calculated using the emission of different particles differs [7, 8]. In addition, the plasma parameters are sensitive to the spatial and electrical characteristics of the discharge and to the properties of the liquid electrode. The ratios of vibrational and rotational temperatures are as follows: T_r (OH) > T_r (N_2), and $T_r < T_v$ [9].

We investigated of electron temperature and the rotational and vibrational temperatures of discharge plasma above the distilled water in ignition threshold mode, when electrochemical processes just begin to manifest themselves in plasma and it is possible to control the effect on the liquid.

2 Experimental Setup and Calculation Method

A glow discharge in free air was ignited over the surface of the distilled water in a Plexiglas cuvette. The test bench diagram is presented in [10]. The metal anode placed over the surface of distilled water in air was made in the form of a copper needle 2 mm in diameter. The copper anode was attached in a special mobile device to vary the spacing between the needle tip and the distilled water surface from 1 to 12 mm. The second copper electrode in the form of a plate was situated in the distilled water. The distance between the upper plate metal surface and the distilled water surface could be varied from 1 to 10 mm. The container volume was about 10^3 cm^3. The main experiments were carried out at an anode tip-distilled water surface spacing of 7 mm and a water thickness of 5 mm over the metal cathode surface. A high-voltage rectifier with the peak output characteristics (voltage U = 1−25 kV; current I = 1−100 mA) was used to ignite a glow discharge. A ballast resistance of R = 434 kΩ was used to stabilize the glow discharge [11].

Plasma emission was analyzed in the spectral area of 200–700 nm. Emission intensities were corrected for the detector + monochromator spectral response. The measurement system consists of an MDR-2 monochromator (1200 grooves/mm), FEU-106 photomultiplier and a KSP-4 recorder. The intensity was measured with an accuracy of no less than 10 %. The spectra were interpreted using the data [12]. Knowing the spectral sensitivity of the photomultiplier can compare the relative intensities of the spectral lines. From the relative emission intensities and spectroscopic constants of these transition [11], one can calculate the populations of the excited states [13]:

$$\mathrm{N}_m = \lambda_{mi}\, I_{mi} \;/\; A_{mi}. \tag{1}$$

where N_m is the concentration of particles in the m th excited state, I_{mi} is the intensity of the emission corresponding to the transition from the m th to the i th energy level, A_{mi} is the transition probability, and λ_{mi} is the wavelength of the spectral line (band). The radiation of the hydrogen atoms, hydroxyl and nitrogen molecules were used to constructions of Boltzman distribution and determination of temperatures:

$$T = \Delta E \;/\; \Delta \ln(\mathrm{N}/g). \tag{2}$$

where g is the statistical weight, ΔE – energy difference of excited states. Constants for calculation are given in [14-16].

3 Results

The interpretation of most intensive part of plasma emission is presented in fig. 1. Most intensive is a radiation of molecules of nitrogen and hydroxyl. The radiation of spectral lines of copper atom on the wavelength of 324.8 nm Cu I, the radiation of γ-bands of NO molecule on the transition of 247.8 nm $^2\Sigma\rightarrow{}^2\Pi$ (0;2) and the radiation of hydrogen at 656.2 nm H_α are with maximal intensity [17].

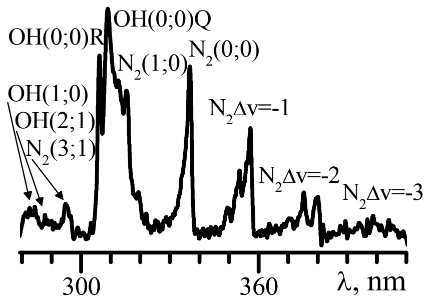

Figure 1. Spectrum of radiation of glow-discharge with a liquid electrode on the basis of the distilled water at the current of 17 mA. The bands show the vibration transitions between electron states $A^2\Sigma$+-$X^2\Pi_i$ for OH and $C^3\Pi_u$-$B^3\Pi_g$ for N_2.

Fig. 2 presents the dependences of electron temperature variation on discharge current. From the analysis of fig. 2 evidently, the higher electron temperature of discharge plasma for the cathode on the basis of distilled water was observed at the discharge current 12 mA, immediately after the ignition of discharge, and with current rise to 32 mA gradually fell [18]. The value of T_e was in the range (0.31-0.22) eV.

Fig. 3 presents the dependences of change vibrational temperature from discharge current determined using radiation of nitrogen and hydroxyl molecules. The vibrational temperature of the discharge plasma is determined for N_2 increases (0.15-0.33) eV with increasing of discharge current. The vibrational temperature of the discharge plasma is determined by OH radiation has a specific behaviour, after a sharp decrease (0.4-0.37) eV there is a repeated growth to 0.4 eV and a decrease to 0.35 eV.

Fig. 4 presents the dependence of rotational temperature is determined using radiation of nitrogen and hydroxyl molecules on discharge current. The rotational temperature determined by the radiation of OH decreases from 0.32 to 0.26 eV. The rotation temperature of nitrogen molecules increases from 0.034 to 0.043 eV.

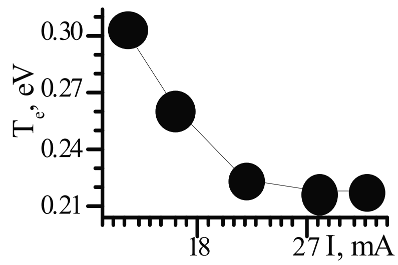

Figure 2. Dependence of electron temperature on discharge current.

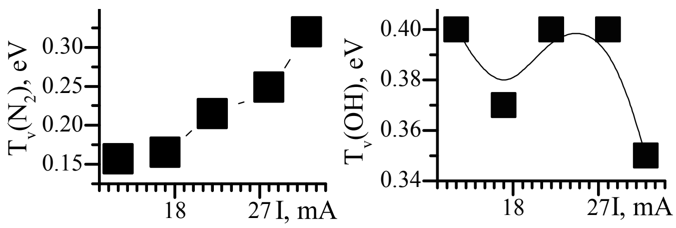

Figure 3. The dependence of vibrational temperature of nitrogen molecules and hydroxyl radicals on discharge current.

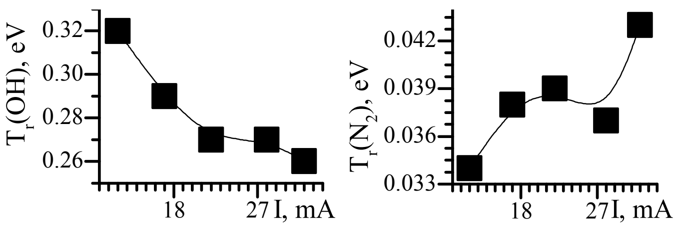

Figure 4. The dependence of the rotational temperature of OH and N_2 molecules on the current of a glow discharge with a liquid electrode on the basis of distilled water.

4 Discussion

The most intensive is emission of N_2 molecules and OH radicals. The hydroxyl emission becomes dominant when current grows. Plasma radiation contains small intensity of Cu, H and NO emission. The discharge is ignited in the air and is localized over the water. If current increases then plasma occupies the interelectrode distance at first, and then increases in volume. The form of plasma formation varies from cone to cylinder, and then to oval. The action of the plasma on water causes it to evaporate in a discharge gap and decomposes it into H and OH. Growth of concentration of OH leads to its domination in radiation. The destruction of the anode due to the action of electrons and electronegative molecules leads to the appearance of copper radiation. The plasmochemical processes in the mixture of nitrogen molecules, water and the products of their decomposition lead to the appearance of molecules NO. The burning of the discharge requires the constant formation of charged particles in the most high-energetic cathode layer, and the growth of the current leads to an increase in their amount, increasing the effect on the surface of water. Thus, molecules with small ionization energies that appear in plasma at current growth will supplant nitrogen molecules from high-energy layers of the plasma [19]. Near the electrode, the brightness of the plasma of the discharge correlates with the electrical characteristics [20]. In the distance from the surface of the liquid, a prolonged afterglow appears in the peripheral layers of the discharge, where the temperature is lower. The study of discharge characteristics above the surface of the water under atmospheric air pressure in [21] makes it possible to develop lamps on nitrogen molecules and water vapour decomposition products [22], and also indicates the optimization of processes that initiate decomposition of pollution.

The temperature is determined by the radiation of various components of the plasma will also reflect the described specificity. That is, the temperature will depend on the mechanism of the appearance of particles and their spatial localization in plasma, ionization energy. With the growth of the current, the gas mixture is enriched with water, products of its decomposition and chemical reactions. Along with the increase in volume and the change in the shape of the plasma, the electronic temperature drops. This correlates with the decrease of the cathode voltage drop and the growth of the plasma volume [19]. Vibrational temperature shows that up to current of 25 mA the hydroxyl is situated in the most energetic plasma layer and the distribution of intensity indicates the gradual dominance of its radiation in the whole plasma [23]. With increasing current, the vibrational temperature of nitrogen approaches to the vibrational temperature of hydroxyl [23], which is evenly distributed over the entire plasma volume. The rotational temperature of nitrogen at low currents shows the gas temperature (384-488 K or 111-215 C), it is insignificantly higher then boiling point of water. When the discharge becomes the elliptical form, the rotational temperature begins to grow. The behaviour and the value of vibrational temperature of hydroxyl are like the behaviour and the value of the electron temperature determined on the basis the radiation of hydrogen. In the similar case of dependence of intensity on the current it can show the same conditions at which they are formed due to the disintegration of water molecules.

The average value of T_e according to different authors [7-9, 24-26] is in limits of 0.2 - 0.5 eV. As the discharge gap increases, the average temperature increases. The highest temperature (up to 0.7 eV) is in the cathode region. The average values of rotational and vibrational temperatures are in the range of 0.15-0.45 eV.

5 Conclusions

The plasma radiation shows molecules of N_2, OH, NO, and atoms of H, Cu. Using the N_2, OH and H emissions the electron, vibrational and rotational temperatures of plasma are obtained. The temperature depending on the formation process, the concentration, the position and the ionization energy of plasma components is discussed. The values of the electron, vibrational and rotational temperatures in the 12-32 mA range of discharge currents vary within limits: $T_e(H)=(0.31\text{-}0.22)$ eV, $T_v(N_2)=(0.15\text{-}0.33)$ eV, $T_v(OH)=(0.4\text{-}0.35)$ eV, $T_r(N_2)=(0.034\text{-}0.043)$ eV, $T_r(OH)=(0.32\text{-}0.26)$ eV.

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