PHYSICAL PROPERTIES OF A SECONDARY DISCHARGE IN LOW-PRESSURE PLASMA—LIQUID SYSTEMS

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We investigate physical properties of a secondary discharge in two-phase plasma—liquid systems. The discharge is maintained by means of an additional source of a plasma flow based on a low-pressure discharge in liquid vapors. It is shown that the volt-ampere characteristics of the secondary discharge in such systems have a form typical of secondary gas discharges: in the case where the potential of liquid with respect to plasma is positive, the current of the secondary discharge is two orders higher than that in the case where the potential is negative. The conditions for the development of a thermal instability in the plasma column essentially depend on the distance from the liquid surface. The population temperatures for the electronic levels of atoms and the vibrational levels of molecules are practically equal. Physico-chemical processes running in the liquid are significantly influenced by gases dissolved in it under the plasma treatment.

Introduction

In plasmochemical technologies, the high chemical activity of a plasma medium was attributed for a long time to either a high temperature or high concentrations of highly active particles: ions, electrons, radicals, excited particles, and photons. However, it has become clear to date that the unique chemical activity of plasma is the payment for a very low selectivity of plasmochemical transformations, that is, their multichanneling and, respectively, very weak controllability of plasmochemical processes [1]. Moreover, it was traditionally supposed that the principal way of increasing the selectivity lies in the transition to nonequilibrium plasmochemical systems. However, the possibilities of the existing sources of nonequilibrium plasma (especially at high pressures equal to the atmosphere one and higher) can provide at best only the nonisothermality of plasma (with the electron temperature being different from that of heavy particles) at an average energy of electrons lower than energies where the cross sections for inelastic processes of the first kind, such as the dissociation of molecules, are maximal.

It is clear that the latter remark concerns the volume of plasma, rather than the transition region where plasma contacts a solid-phase or liquid-phase substance. It is just the first-priority reason for plasma chemists to show intense interest in studying the physico-chemical properties of plasmochemical systems and trying to use them in technological processes [1]. Typical plasma generators in plasma—liquid systems are self-maintained discharges in a liquid having two electrodes immersed in it as well as discharges having one electrode immersed in a liquid and another located in the gas phase. Such kinds of discharges are often called liquid-electrode discharges [2—3]. The discharges that can be attributed to the first class are as follows: a contact glow discharge of electrolytes [4], an electrolyte-plasma discharge [5], a diaphragm discharge [6], microdischarges with a valve metal electrode [7], corona, barrier, and spark discharges with electrodes immersed in a liquid electrolyte [4]. Electric self-maintained discharges having one liquid electrode [2] were used as far back as one hundred years ago for the electrolysis of aqueous solutions, where one electrode was taken out of the electrolyte to the gas phase in order to avoid reactions running on the surface of this electrode. Since the mid-forties of the past century, one has started to use these discharges for heating metals and alloys in electrolytes.

Unfortunately, despite a wide field for using plasma—liquid systems, their physics and chemistry are practically unstudied. Moreover, the mentioned kinds of discharges have no theoretical description allowing one to explain all the totality of phenomena taking place in the positive column, near-electrode layers, and especially in the intermediate plasma-liquid layer, and even a generally accepted terminology is absent.

The principal peculiarity of plasma—liquid systems is the presence of a free liquid surface which always represents an intense source of liquid molecules brought into the discharge volume at the expense of both evaporation of the solution and formation of gas phase products of plasmochemical processes. That's why such systems are characterized by a generation of plasma at pressures of the order of the saturated vapor pressure of the liquid and higher. For aqueous solutions, the lower
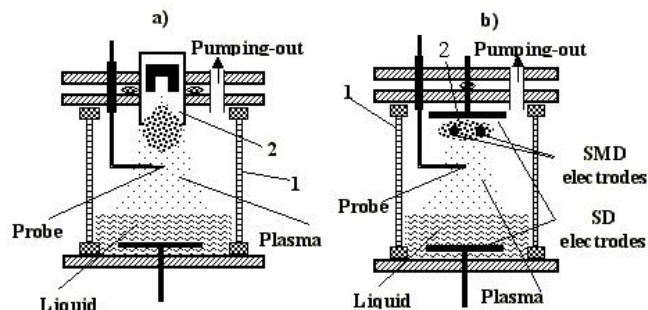
Fig. 1. Plasmochemical reactors used for the study of low-pressure plasma—liquid systems: a — for $P < 30$ Torr, b — for $P = 10 \div 300$ Torr

boundary of the pressure in plasma of the order of 10 Torr can be maintained only in the dynamic mode when the volume is continuously pumped. However, as plasma generators in such systems are electric gas discharges, one should take into account that, under such conditions, the discharge burning is described by the right (ascending) branch of the Paschen curve, which corresponds to the conditions favorable for the development of the thermal instability [8]. One of the additional factors contributing to the development of instabilities in plasma-liquid systems with gas discharges lies in the presence of negative ions in plasma. It is clear that the development of instabilities in a plasmochemical system can in no case promote solving the principal problem of increasing the selectivity of carrying out the processes of conversion of substances.

It is obvious that the number of the channels of plasmochemical conversions of a substance in plasma—liquid systems can be decreased due to [9]:
— transition to stationary plasma systems characterized by a high level of ionization nonequilibrium;
— realization of the high uniformity of parameters at the plasma-liquid boundary;
— an essential increase (as compared to traditional electric discharges) of the number of the external parameters which influence the parameters of the plasma-liquid interaction and can be controlled in a real plasmochemical process.

On the ground of these considerations, a special attention should be paid to the secondary discharges maintained by means of a plasma flow in plasma—liquid systems with one liquid electrode [10]. In these discharges, one metal electrode is immersed into liquid while another one is the electrode of an auxiliary self-maintained discharge in the gas-vapor medium. In the present work, we consider the fundamental physical processes in such low-pressure (0.1—300 Torr) systems. The lower boundary of the interval of pressure variations

in the system was of the order of the saturated vapor pressure of the liquid.

Experimental Methods of Investigating Plasma-liquid Systems

The diagrams of the experimental setups used for investigating the plasma—liquid systems at a low pressure P are depicted in Fig. 1. They consisted of a glass vacuum chamber 1 and a source of a plasma flow 2. The latter could be a coaxial-end discharger (Fig. 1,a) or a bare source (Fig. 1,b). The electric field of the secondary discharge was created by means of a system of electrodes of either a similar form (for example, disk-shaped) or different ones, or the voltage of the secondary discharge was applied between the electrode immersed into liquid and one of those of the auxiliary self-maintained discharge. When using a coaxial-end source of the plasma flow, its anode was an electrode of the secondary discharge at the same time. The distance between the source of the plasma flow and the surface of the solution didn't exceed 70 mm, while the height of the solution column was usually equal to 30 mm.

In order to investigate the axial distributions of the potential of the electric field in plasma—liquid systems, we used a probe technique. The population temperatures for the electronically excited levels of atoms and the vibrationally excited levels of molecules in plasma were determined from emission spectra [2].

The investigations of the physical properties of the solutions treated in plasma—liquid systems were carried out by means of spectrophotometric and ionometric techniques. We used a SDL-2 setup for the spectrophotometric measurements and a general-purpose ionometer EV-74 for the ionometric ones.

Investigation Results

The working solutions used for investigating the peculiarities of the burning of secondary discharges in plasma—liquid systems were as follows: liquid-phase substances having a low saturated vapor pressure (glycerin), those having a high saturated vapor pressure (distilled water), and the aqueous solutions of inorganic compounds: an alkali (NaOH) and a salt (Na_2SO_4).

The investigations of the volt-ampere characteristics (VAC) of secondary discharges in low-pressure plasma—liquid systems have demonstrated that, in the range of low currents I_d, they are similar to customary VAC of a probe, while, in the range of high currents, one can
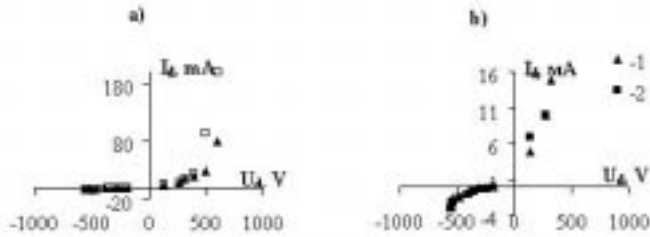
Fig. 2. Volt-ampere characteristics of the "plasma — glycerin" system at high (*a*) and low (*b*) discharge currents I_d at a pressure of 0.1 Torr. The current of an auxiliary discharge in the coaxial-end source $I_s = 60$ mA (*1*) and 200 (*2*)

Fig. 3. Axial distributions of the potential in the "plasma — distilled water" system

observe a rapid increase of the current, which is characteristic of secondary gas discharges in strong electric fields [7]. Typical dependences of the current of the secondary discharge on the potential of the "liquid" electrode U_d are represented in Fig. 2.

If we use liquids having a low electroconductivity (glycerin $(CHOH(CH_2OH)_2)$, distilled water), the plasma column of the secondary discharge in plasma—liquid systems (Fig. 1) at a pressure of the order of 1 Torr looks like a cut cone with its larger basis leant on the liquid surface. Moreover, the additional expansion is observed on the surface of the distillate. With increase in the discharge current from 30 to 100 mA, the apparent size of the cross section of the plasma column, which amounts to $D_3 \approx 20$ mm near the exit of the source, rises from 10 to 30 mm at a distance of 50 mm and from 20 to 80 mm near the liquid surface.

With increase in the pressure of the gas-vapor mixture up to 30 Torr, the cross section of the plasma column decreases almost half as much again. A further increase in the pressure of the gas-vapor mixture results in the disruption of the discharge that breaks into an unstable mode. The discharge contracts into a filament 7—5 mm in diameter which ramifies near the liquid surface by forming several branches approximately 1 mm in diameter. During the discharge burning, the branches move chaotically on the liquid surface. This fact testifies that with increase in the distance from the liquid surface, the conditions for the development of the thermal instability in the plasma column of the gas discharge essentially change.

If we use the aqueous solutions of an alkali (NaOH) and a salt (Na_2SO_4), the conditions for the burning of the discharge are practically the same as those for the distillate except the fact that, at equal discharge currents, the burning voltage of the discharge onto the aqueous solution decreases with increase in the
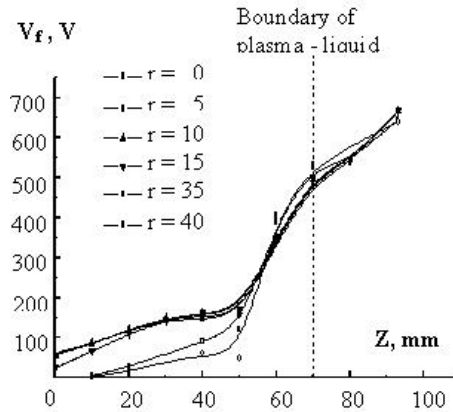
concentration of the solution. The concentration of the solution also influences the form of the plasma column: there are no regions of its abrupt extension near the liquid surface, and the form of the plasma column is cylindrical or even spindle-shaped, i.e. it narrows near the liquid surface with increase in the solution concentration.

In Fig. 3, we represent the typical axial distributions of the floating potential in a plasma—liquid system with a liquid anode (Fig. 1,*(a)*) for the "plasma — distilled water" system at

$P = 1$ Torr, $I_d = 100$ mA, and $I_s = 150$ mA at various distances r from the axis of the system. The given dependences indicate the existence of a region near the liquid surface where the axial gradient of the plasma potential abruptly increases. Such an increase of the voltage drop in the region, where plasma contacts liquid, can be interpreted as a decrease of the electroconductivity of plasma in it at the expense of the processes of dissociative attachment of electrons to water molecules, $e + H_2O \rightarrow OH^- + H$. The presence of negative ions in plasma also explains the fact that the conditions for the development of the thermal instability in the discharge become milder [8], which is observed when approaching the liquid in systems with one positive liquid electrode.

Earlier [10], just a great part of the ion component among negative charges of plasma was considered to be the reason explaining the existence of the axial minima on the radial distributions of the potential of the electric field in the "plasma — distilled water" system near the liquid surface. As the measured radial distributions of the concentration of charges are of monotonic character and the radial profile of the potential in the plasma

column of the discharge is formed at the expense of the ambipolar diffusion of charges, it was assumed that, for the case of pure water and the positive polarity of a liquid electrode, the mobility of negative charge carriers OH^- in the near-surface region of plasma at the axis of the discharge is lower than the mobility of positive ions H^+.

However, the existence of the near-surface jump of the potential in a plasma—liquid system with a secondary discharge cannot be accounted for solely by peculiarities of the kinetics of elementary processes, because the axial jump of the potential is also observed in plasma—liquid systems, where the radial distributions of the potential monotonically decrease near the liquid surface, namely in a "plasma — distilled water" system with a negative liquid electrode and the "plasma — aqueous solution of an alkali (NaOH) or a salt (Na_2SO_4)" system in the range of concentrations $2 \times 10^{-5} - 3$ mole/l regardless of the polarity of the liquid electrode.

The existence of the potential jump at the plasma-liquid interface in the considered plasma—liquid systems with a secondary discharge can be also associated with a fundamental peculiarity of the discharge itself maintained due to a plasma flow that is created by means of an auxiliary discharge.

For example, a secondary gas discharge which is maintained due to the plasma flow coming from an auxiliary source is also characterized with a potential jump near the electrode of the secondary discharge at both low pressures [11] and pressures of the order of the atmospheric one [12]. The three-electrode system of such a gas discharge can be considered from another position [11]: two electrodes of such a system are the electrodes of a plasma generator, while the third one is immersed into the plasma of the flow coming from the plasma generator, that is can be regarded as an analog of a Langmuir probe in plasma. However, unlike the probe, it has a large area, and the current of the secondary discharge flowing onto it is comparable to the discharge current of the plasma generator. That's why, the third electrode can essentially perturb the surrounding plasma. But, as is well known, an electrode having a potential different from that of the medium is shielded with a layer of space charge, when being immersed in plasma. In other words, there exists a potential jump between the electrode and plasma, and its width is determined by the width of the space charge region.

Investigations of the secondary gas discharge [11] indicate the possibility of controlling the magnitude of the voltage jump near its electrode in the range 0—100 V

by means of the variation of the discharge voltage U_d if the width of the potential jump is less than the free path of electrons. It is worth noting that it is just the energies lower than 100 eV that correspond to the maxima of the excitation functions for many inelastic processes of the first kind with participation of electrons, which are interesting for plasmochemistry [8].

A more detailed investigation of the plasma composition in the considered secondary discharge in a heterophase medium was carried out by using emission spectroscopy. For a low-pressure plasma-liquid system with a coaxial-end source of the plasma flow (Fig. 1,a), we investigated the radiation spectra of the plasma layer which contacts distilled water in the wavelength range from 200 to 1000 nm. The discharge current I_d was varied in the range 60—200 mA while the pressure in the vacuum chamber was changed in the interval 4—35 Torr. It was observed that the spectral composition of the radiation in the visible region was also influenced by the time moment of switching on the discharge, namely, whether it was switched on: 1) before the water stopped to boil or 2) after that.

In the first case, the measured spectra have a rather complicated composition including both single atomic lines and molecular bands. In turn, molecular bands have both red and violet tones, which testifies to their belonging to the spectra of different molecules. The most intense components are atomic lines of hydrogen H_α, H_β, H_γ, and H_δ and the bands corresponding to the spectra of OH and N_2 molecules.

In the second case, the water was preliminary evacuated up to a pressure corresponding to the evaporation of dissolved gases. In other words, vigorous boiling of water took place. In this case, the pressure P in the investigated volume was equal to $10 - 35$ Torr. Vigorous boiling of water lasting for 10 min was accompanied by the almost complete evaporation of dissolved gases, and then boiling practically stopped. After that, we switched on the secondary discharge and carried out the spectral analysis of the radiation of the discharge in the wavelength range from 200 to 1000 nm. The discharge currents were varied in the ranges: $I_d = 100 \div 150$ mA, $I_s = 200 \div 250$ mA. The distance d between the water surface and the end-plate source was changed from 20 to 65 mm. The most intense bands in the obtained spectra were those corresponding to the $A — X$ transition of OH radical and separate spectral lines of atomic hydrogen.

From the measured radiation spectra, we obtained the population temperatures for the electronic levels of hydrogen atoms and for vibrational levels as functions
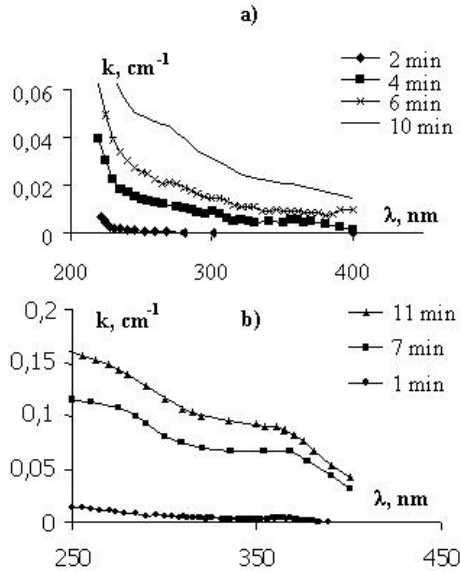
Fig. 4. Absorption spectra of precipitated (a) and non-precipitated (b) water after plasma treatment

Fig. 5. pH of distilled water after a plasma treatment. The current of an auxiliary discharge $I_s =$ 200 mA and that of a secondary discharge I_d=100 mA. Dashed curves ($1'$, $2'$, $3'$) correspond to the treatment by the plasma of a "liquid"-electrode secondary discharge, solid curves (1, 2, 3) — to the case of the "liquid" anode. 1, $1'$ — water degassed up to pH = 5.8, 2, $2'$ — 6.5, 3, $3'$ — 6.8

of the layer width. It was observed that the population temperatures for the electronic levels of hydrogen atoms is constant, whereas the population temperature of vibrational levels slightly increases with the width of the water layer, and its value (T_v = 0.33 ÷ 0.41 eV) is practically equal to the population temperature of electronic levels (T^*=0.35 eV).

The absorption spectra of the solutions treated by plasma were investigated on a SDL-2 setup using a 10-cm quartz cell. We have observed that the absorption spectra of distillate after a plasma treatment depend on the duration of the time interval, during which the distillate is settled before its treatment in a plasmochemical reactor. Therefore, we carried out experiments both with settled distilled water and unsettled one. In the first case, we used the water settled for at least 6 days after distillation. In the second case, water was not settled more than 5 h. Before starting a plasma treatment, the volume containing water was evacuated for 10 min. The distance between the water and the end-plate source d was equal to 55 mm, and the width of the water layer l amounted to 15 mm. The parameters of the secondary discharge having an end-plate source as one electrode and distilled water as another were as follows: I_d = 150 mA, U_d = 450 ÷ 1250 V, I_s = 250 mA, U_s = 320 ÷ 340 V, and P = 27 ÷ 30 Torr. The duration of the existence of a discharge was varied in the interval from 1 to 12 min. The absorption coefficient for water was measured in the spectral region 200—400 nm. The typical absorption spectra for settled
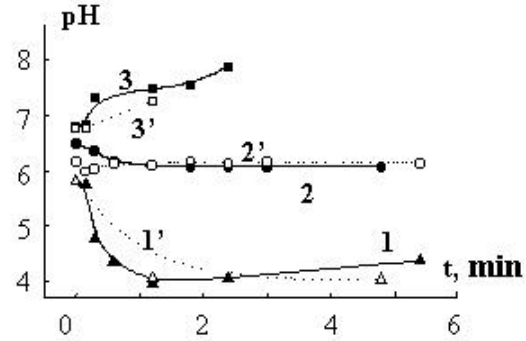
and non-settled water after the plasma treatment are depicted in Fig. 4.

The absorption spectra given in Fig. 4,a are typical of the water solution of hydrogen peroxide H_2O_2. The presence of ozone in the spectrum (the band near 260 nm) [13] becomes evident only after a 10-min treatment. The absorption spectra given in Fig. 4,b testify to both a significant increase of the absorption and the presence of NO_2^- ions in water after its treatment (the band near 360 nm) [13].

Since the differences noticed in absorption can be related to the gases dissolved in water, we have investigated their influence on the acidity of water after a plasma treatment. For this purpose, the initial distillate having pH=5.5 was preliminarily degassed by means of keeping it for some time at a pressure of 8 Torr. A variation of the exposition duration in the range 0—10 min resulted in an increase of pH of distilled water from 3.5 to 6.8. After reaching a certain level of pH, we initiated a discharge and started the treatment. The experimental dependences of pH of water after a treatment on the exposition duration are given in Fig. 5.

The presented dependences testify to that the variation of the pH of water resulting from the plasma treatment is greatly influenced by the dissolved gas. In addition, as seen in Fig. 5, the acid effect can turn into the alkaline one if the plasma treatment is carried out at a low pressure (curves 3, $3'$) and if the initial level of pH is higher than a certain value $pH_{кр}$. The polarity of the liquid electrode influences only the form of the initial region of the considered dependences of pH on t.

Conclusions

Taking into account the results of experimental investigations of the secondary discharges in low-pressure plasma—liquid systems, we can draw the following conclusions:

The volt-ampere characteristics of a secondary discharge in a plasma—liquid system maintained due to a plasma flow are similar to those of classical secondary gas discharges, for which the current in the low-voltage region is determined only by an external ionizer and ionization processes in the discharge gap gain in importance with increase in the voltage. Moreover, the polarity of liquid with respect to plasma practically doesn't influence the beginning of the ionization processes, but the discharge currents are significantly different: in the case where the potential of liquid with respect to plasma is positive, the current of the secondary discharge is almost two orders of magnitude higher than that in the case of the negative potential.

The conditions for the development of the thermal instability in a plasma column of the gas discharge in a plasma—liquid system essentially depend on the distance from the liquid surface. In this case, an increase of the electroconductivity of the solution arising from the dissolution of an alkali or a salt of alkali metals in the investigated range of concentrations practically doesn't change the stable burning of a secondary discharge in a plasma—liquid system, but results in both a decrease of the voltage drop and a variation of the form of the plasma column.

In the plasma of a liquid-electrode secondary discharge maintained due to a plasma flow, there exists a jump of the potential on the liquid surface.

In the plasma of a secondary discharge, the population temperatures for the vibrational levels of molecules are practically equal to those for the electronic levels of atoms.

Physico-chemical processes in a solution treated by plasma are greatly influenced by the gas dissolved in it.

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ФІЗИЧНІ ВЛАСТИВОСТІ НЕСАМОСТІЙНОГО РОЗРЯДУ В ПЛАЗМОВО-РІДИННИХ СИСТЕМАХ НИЗЬКОГО ТИСКУ

В.Я. Черняк, С. В. Ольшевський

Р е з ю м е

Досліджено фізичні властивості несамостійного розряду в двофазних системах плазма—рідина. Розряд підтримується додатковим джерелом плазмового потоку на основі розряду низького тиску в парах рідини. Показано, що вольт-амперні характеристики (ВАХ) несамостійного розряду в таких системах мають вигляд, типовий для несамостійних газових розрядів; струм несамостійного розряду в разі позитивного потенціалу рідини відносно плазми на два порядки більший за такий струм в разі негативного потенціалу. Умови розвитку іонізаційно-перегрівної нестійкості в плазмовому стовпі суттєво залежать від відстані до поверхні рідини. Температури заселення електронних рівнів атомів і коливальних рівнів молекул практично однакові. На фізико-хімічні процеси в рідині при плазмовій обробці суттєво впливають розчинені в ній гази.