EXPERIMENTAL STUDY OF THE LIQUID CATHODE COMPONENTS TRANSFER TO THE DC DISCHARGE PLASMA AT ATMOSPHERIC PRESSURE

Sirotkin N. A. *, Titov V. A.

G.A. Krestov Institute of Solution Chemistry RAS, Ivanovo, Russia

* alexsad8@yandex.ru

Abstract. The transfer processes of solvent and dissolved substances in gas phase from aqueous solutions used as cathodes under the action of atmospheric pressure DC discharge were investigated.The electric field strength in plasma (E), cathode voltage drop (U_c) and rates of solution evaporation were measured. The transfer coefficients were calculated. The effect of transfer processes on plasma physical properties was experimentally studied. The threshold characteristics of cations transfer process were determined.

Keywords: DC electrical discharge, transfer processes, liquid cathode, cathode voltage drop, electric field strength.

1. Introduction

Atmospheric pressure discharges with liquid electrolyte electrodes are of interest as sources of active species for a variety of plasma-chemical applications [1–4] . The physical characteristics of liquid-cathode discharge were investigated in [5–8]. The properties of discharges with liquid cathode depend on the transfer of solvent and dissolved substances from the cathode to gas phase. There are two mechanisms of solvent transfer to gas phase: thermal evaporation and ion sputtering. Sputtering is induced by ion bombardment and it is considered to be similar to the cathode sputtering in low pressure glow discharge [9]. This process can be characterized by a transfer coefficient — number of particles transferred from liquid to gas phase per one ion bombarding solution surface [10, 11]. The transfer processes alters the composition of the gas phase and they lead to a change of discharge characteristics. The aim of this work is to study the transfer processes of solution components in the atmospheric pressure discharge with liquid cathodes and to investigate the influence of transfer products and physical characteristics of discharge.

2. Experimental details

Simplified scheme of experimental set-up is shown in Fig. 1. Direct current (DC) discharge ($i = 10$–70 mA) was excited by applying high voltage between the surface of aqueous cathode and copper anode which placed at the position 1–10 mm above the liquid surface. To excite the atmospheric pressure discharge the DC specially designed power supply with an 80 kΩ ballast resistor was used. Output voltage was 1.5–2 kV. Discharge was ignited in the air. Water solutions of calcium, barium, magnesium, strontium and sodium chlorides with concentrations of 0.1–0.5 mol l $^{-1}$ were used as cathodes. The volume of the solution was

230 ml. The discharge cell was equipped with a glass trap to collect the condensate formed by evaporation of solution-cathode. Total rate of evaporation was determined as the rate of condensate accumulation in the trap. The mass of condensate is measured accurate to 0.01 g.
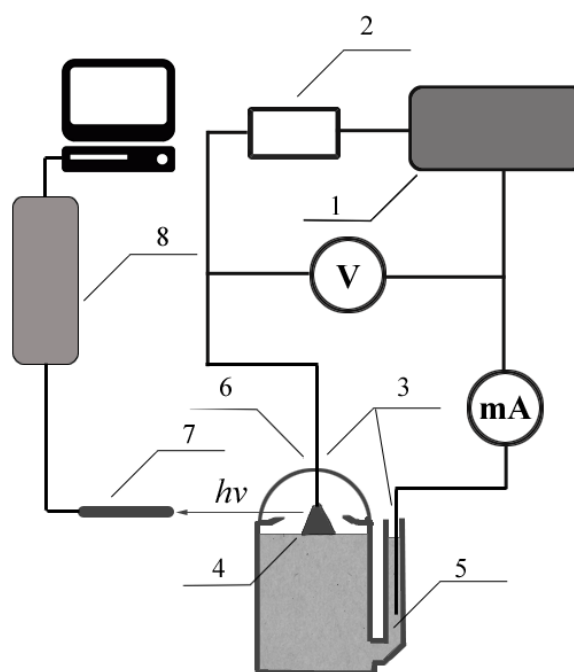

Figure 1. Experimental set-up.
1 — HV-source, 2 — ballast resistor, 3 — electrodes, 4 — discharge, 5 — solution, 6 — glass trap, 7 — optical fiber light guide, 8 — spectrometer.

The concentrations of cations in condensate were found by means of atomic absorption spectroscopy (spectrophotometer AAS-3, Carl Zeiss Jena, Germany). The concentrations of anions were found using gravimetric method by means of the precipitation of

chloride ions as AgCl and weighing of the precipitate. The electric field strength in plasma (E) and the cathode drop voltage (U_c) were calculated from dependences of the discharge voltage on the interelectrode distance as described in [6]. The emission spectra of the positive column ($\lambda = 200–950$ nm) were recorded by the AvaSpec-2048 spectrometer (grating 600 lines mm^{-1}). Gas temperature was found from the intensity distribution in the radiation band of $N_2(C^3\Pi_u \longrightarrow B^3\Pi_g, 0–2)$ transition as described in [12]. The typical dimensions of the discharge were determined from photographs taken by digital camera Canon 1100D (exposure 1/500) with a objective Canon EF 50 mm f/2.5 Compact Macro.

3. Results and discussions

Discharge images of an atmospheric pressure discharges are shown in Fig. 2. The optical emission spectroscopy measurements shows the resonance lines of metal atoms appeared in the spectra.
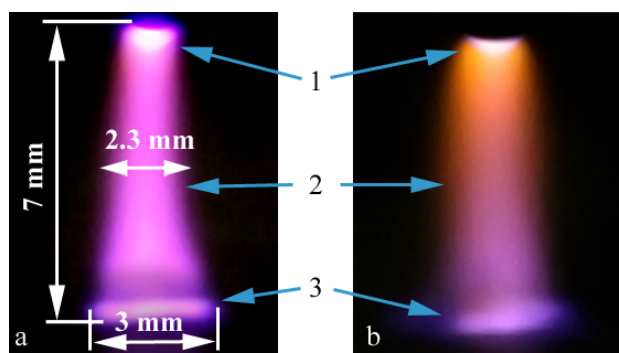

Figure 2.   Images of atmospheric pressure DC-discharge with liquid cathode (NaCl, $c = 0.5 \, mol \, l^{-1}$), $i = 10 \, mA$ (a) and 30 mA (b). 1 — anode glow, 2 — positive column of discharge, 3 — cathode glow.

Metal atoms resonance lines appears in the spectra at discharge current exceeding the threshold value. The threshold current values were obtained by extrapolation of experimental data of emission lines intensity of metal atoms (Fig. 3).

It can be supposed that there is a threshold power required for transfer of the solute into the gas phase. The maximum power input to solution by ion bombardment can be estimated as $p = iU_c$ and it increase with the discharge current. The threshold current (i_0) and $p_0 = i_0 U_0$ are shown in Fig. 4 as functions of the mass of hydrated cations in solution, since the cations of Na$^+$, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} are surrounded by six water molecules forming the first hydration shell [13]. The values of threshold current and threshold power increases with the mass of hydrated cations.

Experiments have shown that the composition of the liquid electrolyte cathode influences the values of cathode voltage drop (Fig.5) and the electric field strength in plasma (Fig.6). The maximum values of U_c and E are typical for discharge with water as a
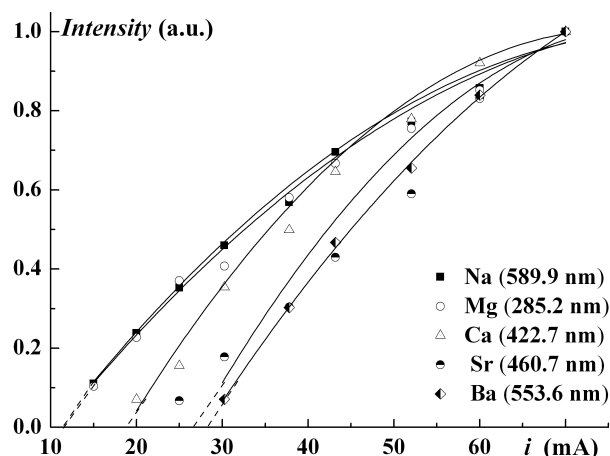

Figure 3.   The resonance lines intensities of metal atoms in the emission spectra of the positive column.
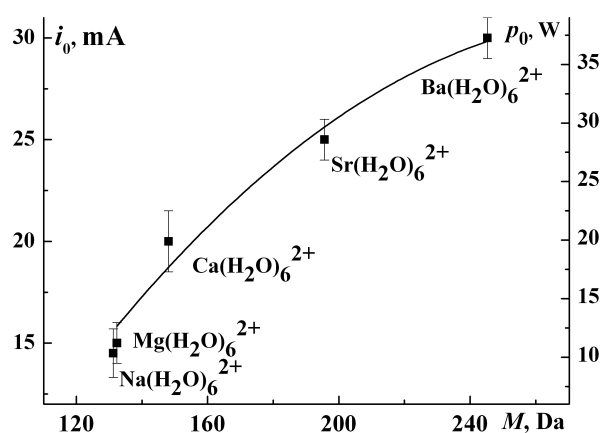

Figure 4. Threshold currents (i_0) and threshold powers (p_0) as functions of mass of hydrated cation.

cathode. Smaller U_c and E values were observed for the solutions of metal chlorides being used as cathodes. The cathode voltage drop in the discharge with water cathode is in a good agreement with the data from [5, 6]. The appearance of atoms with low ionization potentials in the gas-phase results in a decreases of the electric field strength and the cathode potential drop (Fig.7). Probably the product of transfer processes influences on the balance of the charged particles in the plasma.

Quantitative characteristic of the particles transfer from the cathode in the plasma is the transfer coefficient. Transfer coefficients (s) for components of liquid cathodes were found using the rate of condensate accumulation in the trap, and the concentrations of cations and anions in condensate. Experimental results showed that the transfer coefficients for water are 300–500 molecule ion^{-1} independently on composition of the liquid cathode, and it is in a good agreement with the literature data [11]. The transfer coefficients increase slightly with discharge current (Table 1). High values of transfer coefficients allow supposing that a significant part of molecules leave the solution in clusters or microdrops. The gas tempera-

Discharge current	s(H$_2$O) molecule ion^{-1}				
(mA)	NaCl	MgCl$_2$	CaCl$_2$	SrCl$_2$	BaCl$_2$
15	300 ± 30	340 ± 20	340 ± 20	320 ± 10	330 ± 10
20	350 ± 30	340 ± 20	360 ± 20	330 ± 15	330 ± 20
30	340 ± 50	390 ± 30	360 ± 30	350 ± 20	380 ± 30
40	400 ± 50	480 ± 30	470 ± 35	470 ± 20	460 ± 30
50	450 ± 50	500 ± 40	500 ± 40	520 ± 30	510 ± 40

Table 1. The transfer coefficients of water molecules for different liquid cathodes.

Power	s(Me) particle ion^{-1}				
(W)	NaCl	MgCl$_2$	CaCl$_2$	SrCl$_2$	BaCl$_2$
8	0.005 ± 0.001	0.002 ± 0.001	—	—	—
11	0.013 ± 0.004	0.062 ± 0.007	0.002 ± 0.001	—	—
14	0.034 ± 0.006	0.085 ± 0.007	0.012 ± 0.001	0.041 ± 0.005	—
17	0.019 ± 0.005	0.086 ± 0.006	0.022 ± 0.003	0.082 ± 0.006	0.005 ± 0.001
19	0.029 ± 0.006	0.072 ± 0.011	0.035 ± 0.006	0.096 ± 0.007	0.032 ± 0.006
27	0.038 ± 0.007	0.065 ± 0.007	0.057 ± 0.009	0.153 ± 0.012	0.182 ± 0.015
38	0.082 ± 0.006	0.098 ± 0.009	0.128 ± 0.012	0.132 ± 0.012	0.153 ± 0.012

Table 2. The dependences of the transfer coefficients of cations on the power input to solution by ion bombardment.
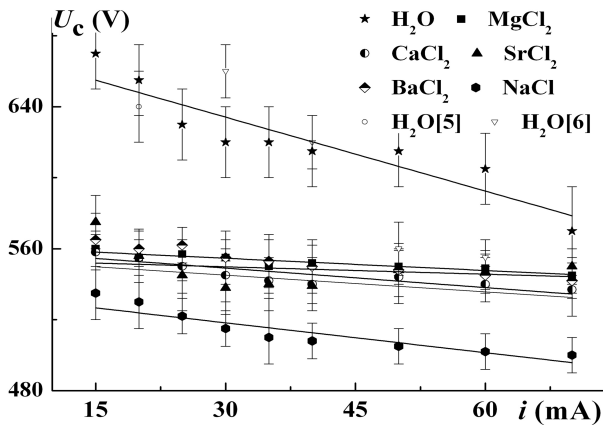
Figure 5. The cathode voltage drop of discharges with liquid cathodes in comparison with the literature data [5, 6]. Concentrations of solutions — $c = 0.5\,mol\,l^{-1}$.
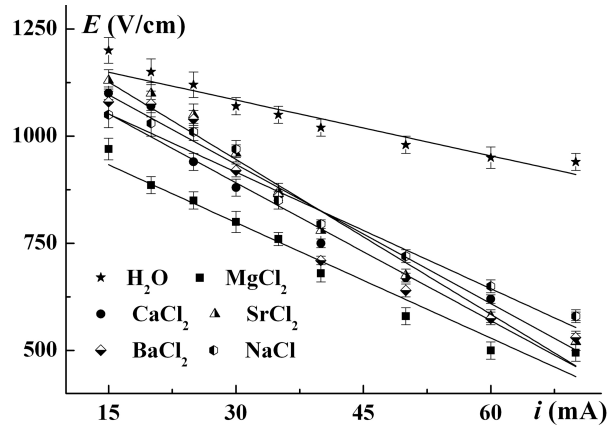
Figure 6. The electric field strength in plasma of discharges with liquid cathodes. Concentrations of solutions — $c = 0.5\,mol\,l^{-1}$.

ture in positive column is $(1\,600 \pm 100)\,$K and weakly depends on the discharge current and the composition of the electrolyte cathode. We assume that the gas temperature is in the positive column does not depend on the distance between the electrodes. Thus, there is a high temperature region above solution surface resulting in thermal evaporation of the solvent. The contribution of thermal evaporation in total transfer of water molecules to gas phase was estimated based on experiments with the change of the polarity of liquid electrode. The experiments showed that contribution of thermal evaporation was found to be 5–20 % for different discharge conditions. Consequently, ion sputtering is the main reason for transferring the solvent molecules to plasma. Transfer coefficients for

cations increase with the power input to solution by ion bombardment, they are directly proportional to the mole fraction of the solute, and decrease with increasing hydration energy of the cations (Table 2, Fig.8). The values of the transfer coefficients for anions are higher and depends on the mole fraction of the solute. The value of pH of solution decreases and conductivity of solution increases under the action of discharge. This can be explained by by nitrogen oxides dissolving in the solution. Nitrogen oxides are formed in the plasma as a result of reactions between molecules of the plasma gas. We did not observe a significant change in the appearance of the discharge in experiments. We consider that the change of the solution properties does not have a strong influence on the discharge properties and the characteristics of
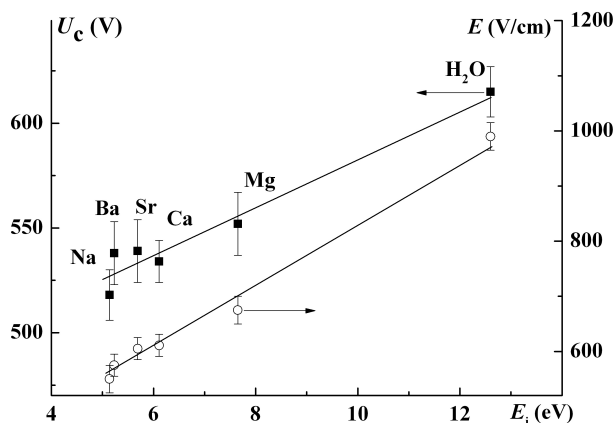
Figure 7. The dependences of the cathode voltage drop and the field strength in plasma on the ionization energy of metal atoms.

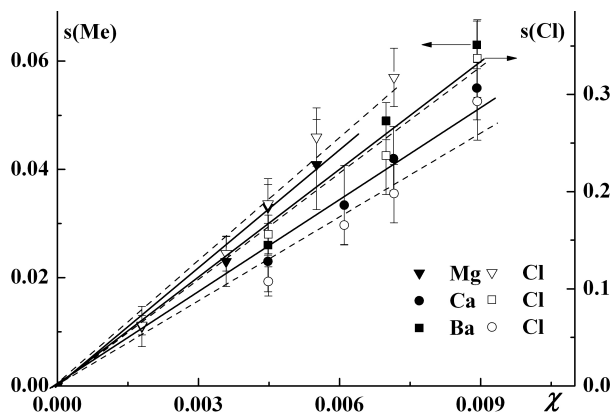discharge are determined by the intensity of solution components transfer to the plasma.

Figure 8. Transfer coefficients for cations and anions as functions of the mole fraction of the solute.

The concentration of water molecules N_{H_2O} in the plasma can be estimated using experimental data on the rate of condensate accumulation in the trap (w). If water molecules accumulation in the trap is a result of their random thermal motion, and accommodation coefficient is equal to 1, the rate of the mass condensate change in the trap can be calculated as:

$$w = \frac{dm}{dt} = \frac{1}{4} N_{H_2O} v_T S m_{H_2O}, \qquad (1)$$

where v_T is mean speed of molecules, S is square of input opening of trap, m_{H_2O} is mass of water molecule. The mole fraction of the water molecules in the plasma does not exceed ~ 0.02.

4. Conclusions

Ion bombardment of the liquid cathode results in the transfer of solvent and dissolved substances from liquid phase to plasma. The transfer processes alter the composition of the gas phase and they lead to a change of the values of cathode voltage drop and

the field strength in plasma. Moreover, the lowest values of cathode voltage drop and strength of electric field in plasma are observed for discharges with liquid cathodes where there are cations of the metals with low ionization potentials. Transfer coefficients for cations and anions depend on power input to solution by ion bombardment, solution concentration and hydration energy of cations in solution. The values of threshold current and threshold power increases with the mass of hydrated cations.

References

[1] A.G. Zakharov, A.I. Maksimov, and Yu.V. Titova. Physicochemical properties of plasma - solution systems and prospects for their use in technology. *Russ. Chem. Rev.*, 76(3):235–231, 2007.

[2] Y. Yang, Y.I. Cho, and A. Fridman. *Plasma Discharge in Liquid: Water Treatment and Applications*. New York: CRC Press, 2012.

[3] J. Ren, M. Yao, Wu Yang, Y. Li, and J. Gao. Recent progress in the application of glow-discharge electrolysis plasma. *Centr. Eur. J. Chem.*, 12(12):1213–1221, 2014.

[4] M. Moreau, N. Orange, and M. G. J. Feuilloley. Non-thermal plasma technologies: New tools for bio-decontamination. *Biotechnol. Adv.*, 26(6):610–617, 2008.

[5] P. Bruggeman and C. Leys. Non-thermal plasmas in and in contact with liquids. *J. Phys. D: Appl. Phys.*, 5(2):053001, 2009.

[6] V. A. Titov, V. V. Rybkin, A. I. Maximov, and H.-S. Choi. Characteristics of atmospheric pressure air glow discharge with aqueous electrolyte cathode. *Plasma Chem. Plasma P*, 25(2):503–518, 2005.

[7] M. R. Webb, F. J. Andrade, G. Gamez, R. McCrindle, and G. M. Hieftje. Spectroscopic and electrical studies of a solution-cathode glow discharge. *JAAS*, 20(1):1218–1225, 2005.

[8] P. Mezei and T. Cserfalvi. Critical review of published data on the gas temperature and the electron density in the electrolyte cathode atmospheric glow discharges. *Sens.*, 12(5):6576–6586, 2012.

[9] G. Ecker and K. G. Emeleus. Cathode sputtering in glow discharges. *Proc. P. Soc. Sec. B.*, 67(7):546–6586, 1954.

[10] A. V. Khlyustova, N.A. Sirotkin, and A.I. Maximov. Transfer coefficients of cations and anions upon glow discharge-induced nonequilibrium vaporization of solutions of alkaline earth metal salts. *High Energ. Chem.*, 44(1):75–77, 2010.

[11] A.M. Kutepov, A.G. Zakharov, A.I. Maksimov, and V.A. Titov. Physicochemical and engineering problems in studies on plasma-solution systems. *High Energ. Chem.*, 37(5):362–366, 2003.

[12] V. A. Titov, V. V. Rybkin, S. A. Smirnov, A. I. Kulentsan, and H.-S. Choi. Experimental and theoretical studies on the characteristics of atmospheric pressure glow discharge with liquid cathode. *Plasma Chem. Plasma Process.*, 26(6):543–555, 2006.

[13] J. Maehler and I. Persson. A study of the hydration of the alkali metal ions in aqueous solution. *Inorg. Chem.*, 51(1):425–438, 2011.