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THE NON-LINEAR EFFECTS IN THE SOLUTION COMPONENTS TRANSFER PROCESSES IN THE SYSTEM OF GLOW DISCHARGE WITH LIQUID CATHODE

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A combination of gas discharge plasma with electrolyte solutions gives many interesting options to the solution of environmental and engineering technological problems [1]. Further development of such methods of material treatment requires a better understanding of solution activation processes that are associated with properties of plasma zone and plasma-solution interface. Basic characteristics of plasma-solution systems are associated with the properties of dynamic plasma-solution boundaries, existing within the near-to-electrode potential fall. There are many similarities between the classic low-pressure glow discharge with a metallic cathode and a glow discharge with an electrolytic cathode. Firstly, γ-electron emission occurs from the cathode due to the ion bombardment. Secondly, there is a cathode sputtering effect, which in the case of electrolyte causes a transfer of the solution components into the plasma. The latter process makes plasma composition dependent on electrolyte solution. Such feedback has to be taken into account when investigating the fundamentals of such plasma-solution systems. This work presents experimental results studies of transfer processes in the glow discharge with electrolyte cathode system. We consider the non-equilibrium evaporation under glow discharge action and emission features of such discharge as transfer processes in the plasma-solution system.

Experimental setup

1. Setup for spectral studies.

The intensities of spectral lines of alkali metal atoms are measured by spectral method by monochromator UM 2 with prism as dispersive element. The principal scheme is presented in fig. 1.
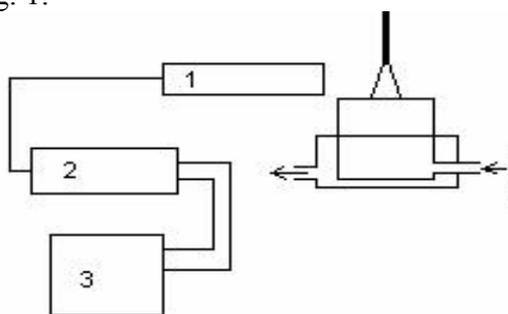

Fig. 1. The principal scheme of setup for spectral studies. 1 – monochromator UM 2; 2 – photodetector of signal (photosensor F-23) with amplifier of signal; 3 – recorder. The experimental cell is circulated type. The movement of solution in the cell shown by pointers. The glow discharge is shown by triangle.
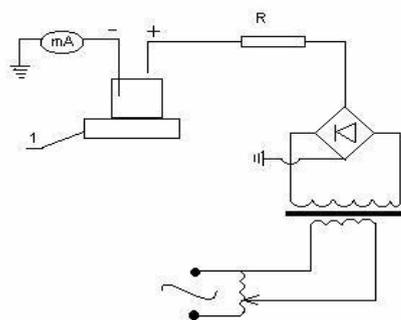
Fig. 2. The principal setup for transfer processes studies by gravimetric method. 1 – electronic balance eK-300.

The circulation type of cell allows to maintain the constant electrode gap. The potential electrode (anode) is situated above solution surface. The grounded electrode (cathode) immersed in the solution. The metallic electrodes were made from Cu wire.

Solution of LiCl, NaCl and $CaCl_2$ were used as electrolyte cathodes. The concentrations of dissolved salts were 0.01-0.1 mol/l. The discharge currents are varied in the range of 15-75 mA.

The intensity of spectral lines of Li (670 nm), Na (588-589 nm) and Ca (657.2 nm) are measured in the dependence from discharge current, dissolved salt concentration and initial acidity of solution (pH).

2. The gravimetric studies of transfer processes.

The transfer processes are investigated by gravimetric method with using setup shown in fig. 2. The method of investigation is consisted in continuous weighing of cell with solution before discharge ignition during discharge action and after off. The surface of solution is blowed off by compressor. It needs for evaporating solution is gone from surface. The contribution of natural evaporation is determined by measuring mass changes before and after discharge action.

The electrodes were made from Cu wire with diameter of 2 mm. The solutions of NaCl, LiCl with concentration of 0.01-0.1 mol/l are used as liquid cathode. The work currents were 5-70 mA.

Experimental results and their discussion

The dependence of spectral line intensity from discharge current is shown in fig. 3. It can see that the threshold value of discharge current is exists. It is discharge current value of dissolved atom radiation appearance. This value depends from nature and concentration of the dissolved salts and varied in range of 8-12 mA. It should be noted that the values of intensities are concerned to 5 minutes after ignition discharge. Our preliminary experiments showed that the intensities of spectral line are changed during burning discharge.
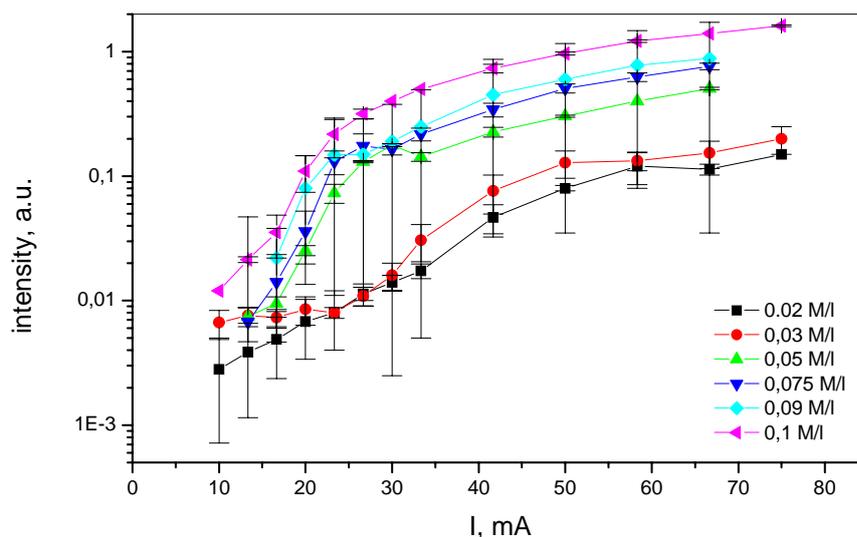

Fig. 3. The dependence of Na atom spectral line intensity from discharge current at various concentrations.

The typical curve of mass change during burning discharge is presented in fig. 4. The whole graph consists of three parts: part 1 is mass transfer before igniting discharge, part 2 is mass change during burning discharge and part 3 is mass transfer after off discharge. Experiments of mass transfer are carried out at various discharge currents: at low discharge current is about 5 mA (until threshold value) and high current (50 mA).
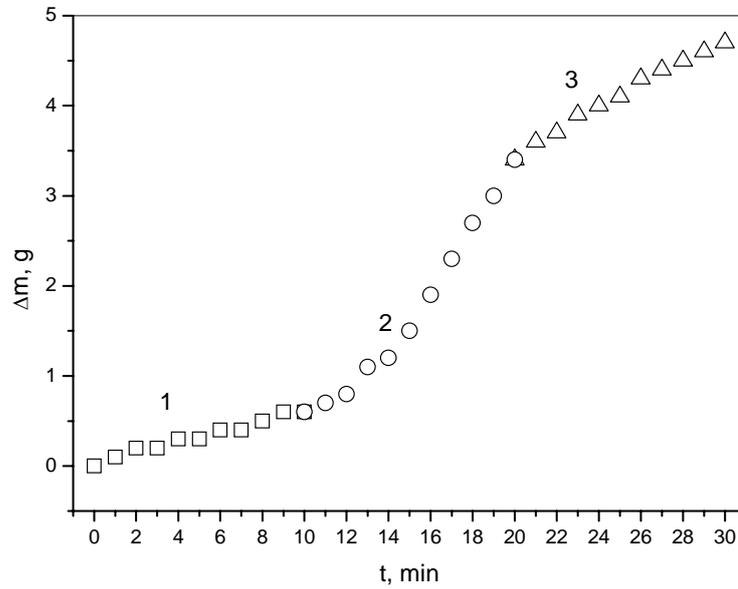

Fig. 4. The typical curve of mass change during transfer process studies. □ – before igniting discharge, ○ – discharge action, Δ - after discharge off. Discharge current is 35 mA, NaCl 0.09 mol/l as a liquid cathode.

We calculated the velocity of non-equilibrium flow from solution into gas phase under discharge action. We described of the curve 2 by polynomial of the second order and then derived of it. Thus we obtained data for velocity of non-equilibrium flow at various discharge current. In the fig. 5 the dependences of intensity and velocity flow from current are presented. It can see that the correlation between both dependences exists.
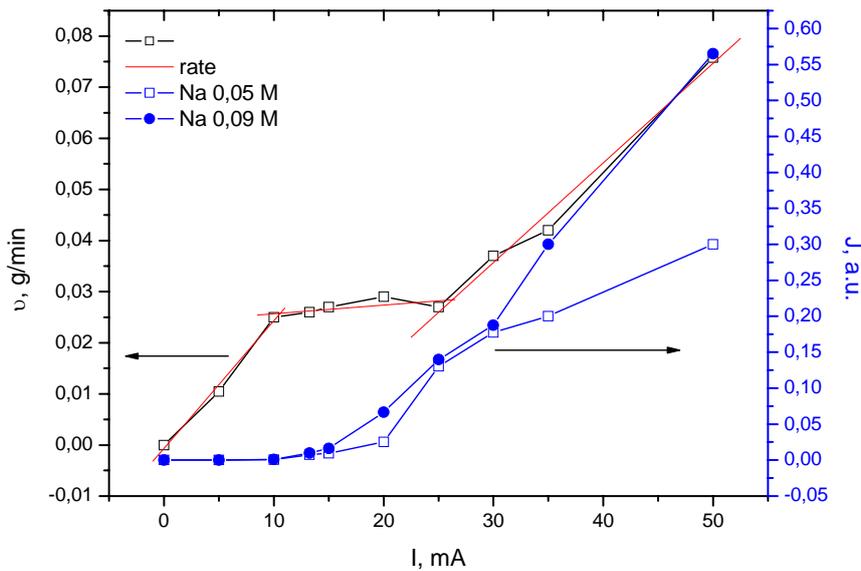

Fig. 5. The dependence of spectral line intensity and velocity of mass transfer from discharge current.

Data at fig. 5 are show that three regions are appeared. The region of low discharge current is characterized very low intensities of spectral lines. The intensity is absent almost and flow velocity increases. The region of middle currents from 15 to 25-30 mA is characterized the appearance of the dissolved metal atom radiation. The flow velocity is constant in the whole region of current. And finally, the large current region is characterized increasing spectral line intensity and velocity of mass transfer – the non-equilibrium flow.

Experimental data allow assume hypothesis about mechanism of non-equilibrium transfer of solution components into plasma zone. It should be noted that energy of exciting alkali metal atoms is units of electron Volt. It means that the appearance of metal atom radiation is confirmation of transfer process beginning. The transfer of alkali metal atoms from solution into plasma zone has a threshold character.
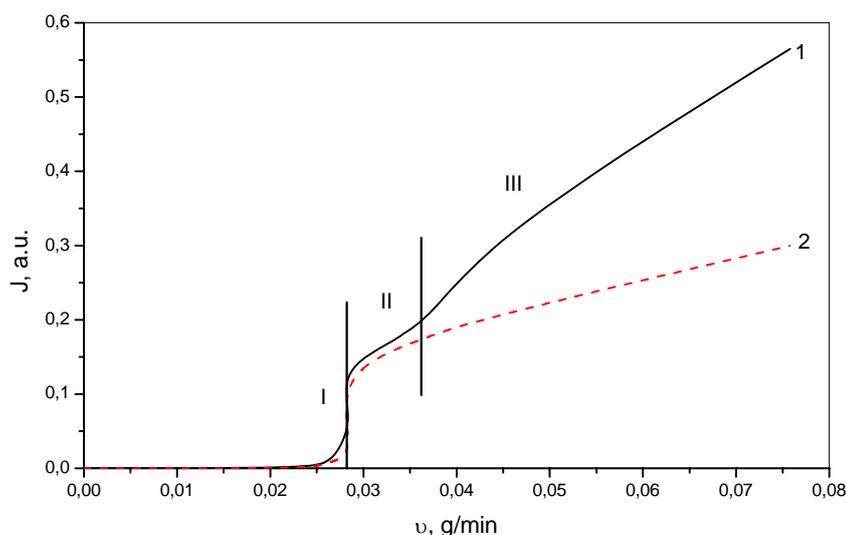

Fig. 6. The connection between intensity of Na atom and non-equilibrium evaporation flux. Solution NaCl, 1 - 0.09 M/l, 2 - 0.05 M/l; I=5-50 mA.

We suppose that the dissolved substance is transferred from solution into plasma zone at condition of discharge current exceeding of the some critical value. The dissolved substance is appeared as salt molecules and neutral products of their dissociation. The alkali metal chlorides exist as ions: anions, cations and ion pairs. Hence, we assume the dissolved substance transfer is possible as ion pair inside water clusters only. According to mention above we formulated the question: What mechanism of non-equilibrium evaporation? Is it cluster or molecular?

We assume the existing analogue between non-equilibrium evaporation and MALDI process that initiated by laser radiation [2]. The laser radiation action on the organic matrix with distributed large biomolecules in their leads to molecular evaporation at low density of laser radiation. However, at energy exceeding a threshold value the evaporation as cluster containing biomolecules occurs.

In the case of non-equilibrium evaporation of solution the solvent can describe as matrix. In that matrix the ion pairs of dissolved substance are distributed. At low energy flow the evaporation occurs in the molecular form (the low discharge currents). At these conditions the non-volatile dissolved substances is not transferred into gas phase (region 1 in fig. 6). That evaporation is like ordinary quasi-equilibrium evaporation. The transfer of molecules of the solvent into gas phase takes place as separate molecules form and as small clusters – dimmers and trimers, probably. At high energetic density the basic mechanism of the evaporation is cluster mechanism (region 3 at fig. 6). The decreasing energetic expenditures on the transfer

of one water molecule during burning discharge can explain the break hydrogen bonds. We assumed that in separate regions of solution volume the pred-clusters are formed. These regions have high degree of breaking H-bonds. The H-bond net exists inside each region and it absent between these regions. Thus the transfer of such regions into gas phase is became more favorable then the transfer of separate molecules. These separate regions – clusters contains ion pairs that recombines into molecule during moving cluster into gas phase. A possible explanation of that is in high vibration excitation of the molecules of dissolved substances contained in the water cluster. In the case of the molecule with ionic bonding, potential curves of ionic and covalent states intersect in the region of the high vibration numbers. The transition between these states becomes therefore possible. The transition to the covalent state results in dissociation of the molecule and formation of neutral atoms (Fig. 7) [3]. The accumulation of both metal and halogen atoms in the non-excited state can thus be observed in the plasma volume. If the molecule in a water cluster develops not only vibration but also electron excitation then its dissociation leads to the formation of an excited metal atom. As a result, the resonance radiation occurs in the thin layer near the solution surface [4].
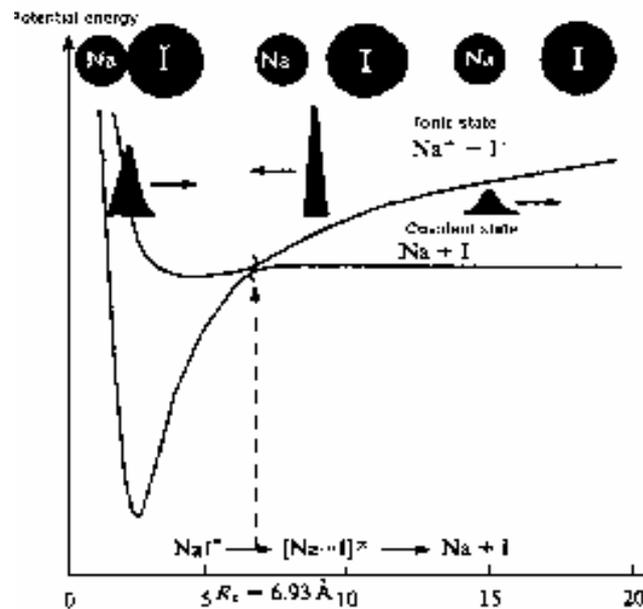

Fig. 7. The potential energy curves for the NaI molecule.

Our experimental data say about non-linear nature of glow discharge with electrolyte cathode. In the first the feature of non-equilibrium is existence of threshold current of alkali metal atom radiation appearance. In the second during our experiments we observed "spread of discharge" effect on the cathode surface. It should be remind that the cathode is electrolyte solution (fig. 8). The luminous parts of discharge moved on the external wall of the inner cell from fig. 2.

The "discharge spread" accompanied by extinction of discharge and fluctuation of discharge current. This process of fluctuation we presents in graphic view (fig. 9). It is oscillatory and non-periodic process. The view of "spread" is like a bright garland that "droops" from border of inner glass of experimental cell.

Fig. 8. The view of "effect of discharge spread" on the solution surface. NaCl solution as cathode 0.09 mole/l. The discharge current is 40 mA.
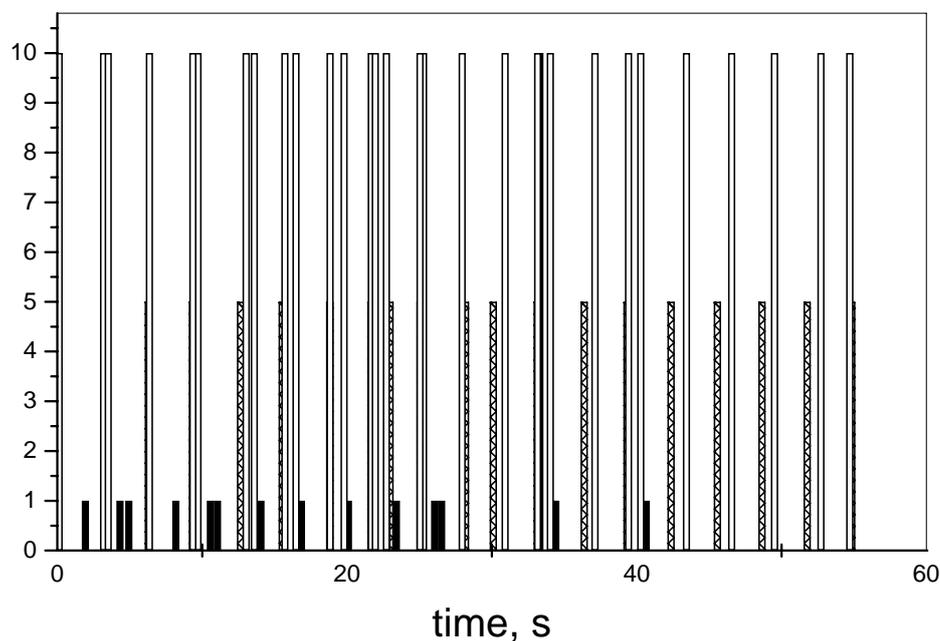

Fig. 9. The bar graph of "spread of discharge" effect. The high column referred to sparking discharge by solution surface. The middle column is normal regime of discharge burn. The black small column is discharge off.

One can see that the discharge off was very often phenomena at first time of the "spread of discharge" effect. It should be note that this effect is not observed at LiCl solution at the same conditions.

Conclusion

Experimental data showed that the plasma solution system is non-equilibrium. It has a threshold character of transfer processes of solution components. It is appeared at the threshold characteristics of discharge current, emission radiation and dissolved substances transfer into gas phase. The correlation between alkali metal line intensities and non-equilibrium evaporation flow rate had shown three regions with different transfer process mechanism. In the region of small current we suppose that the molecular mechanism occurs. At the large current region there is cluster mechanism of solution components transfer.

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