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Near-Electrode Plasma at Electrolyte Discharge on the Frequency Selective Surface

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Abstract**: *Near-cathode plasma of the discharge in electrolyte and its interaction with electrodes was researched in the work. Electrical parameters of the discharge for two electrolyte compositions were investigated. Temperature and concentration of the near-cathode plasma of this discharge were measured using spectral methods. Appearance of sphere-like formations and pores surface is observed on the surface of the titanium electrodes. Possible explanation of the formation of these superface structures is proposed. The effect of the discharge in the electrolyte on the electrode surface was studied in this work. We consider properties of electrical current near the titanium electrode due to the presence a pores structure on this electrode. We can suppose that the current near the surface of cathode consists from a number of separate current channels with the 0.1-2 μm thick at a current in the region 10-8-10-6 A in the separate channel.***

Keyword**: *near electrode plasma, electrolyte discharge, electrical parameters of the discharge, electrode surface.***

I. INTRODUCTION

Generation of a discharge in the electrolyte is followed by formation of an emission region near electrodes and convective streams connected with heating up of the fluid [1-3]. The electrodes can be located in the electrolyte itself or above its surface. Intense electric oscillations [2-6] can occur in the electrolytes at discharges. The spectra of these oscillations were studied and their possible origination mechanisms were considered in the works. These discharges are used in individual works for modification of the material surfaces, polishing of metal surfaces with a complex shape, more effective production of hydrogen [1, 2, 7-13].

II. METHODOLOGY

For the purpose of the experiments, the electrolyte vessels were made of organic glass (plexiglass) and had a capacity of 200-450 cm^3. Electrolytes based on sodium carbonate and sodium hydroxide were used. The experimental setup is presented in Fig. 1.

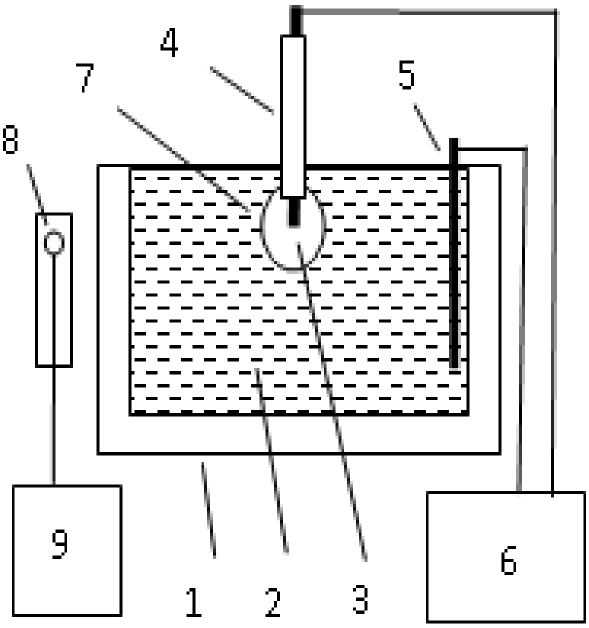

Fig. 1. Scheme of the experimental setup: 1-body, 2-electrolyte, 3-cathode, 4-ceramic tube, 5-anode, 6-power source, 7-discharge area, 8-magnetic probe, 9-spectrum analyzer

Spectral research of discharge emission was carried out with Ava Spec 2048 spectrometer (the operation range is λ=200-1000 nm, spectral distribution is 0.3 nm), MUM monochromator (the operation range is λ=200-800 nm, spectral resolution is 0.2 nm) and FEY-85 photoelectric multiplier (time resolution is Δt=5 ns).

Titanium and tungsten rods with a diameter of 1-2 mm were installed as the cathodes in the experiments for study of the electrode surfaces. The cathode was installed vertically at a distance of 0.5-1.0 cm from the surface of the fluid (Fig. 1). Electrolytes prepared with sodium carbonate and sodium hydroxide at concentration C=0.4-0.6 M were used. The area with 2-3-volt-ampere characteristics was chosen as the working area (Fig. 2). This interval is characterized by great stability in the chosen values of voltage and current. The level of high-voltage oscillations in the experiments was minimal. The duration of the experiments on the interaction was chosen within the range of 30-60 min.

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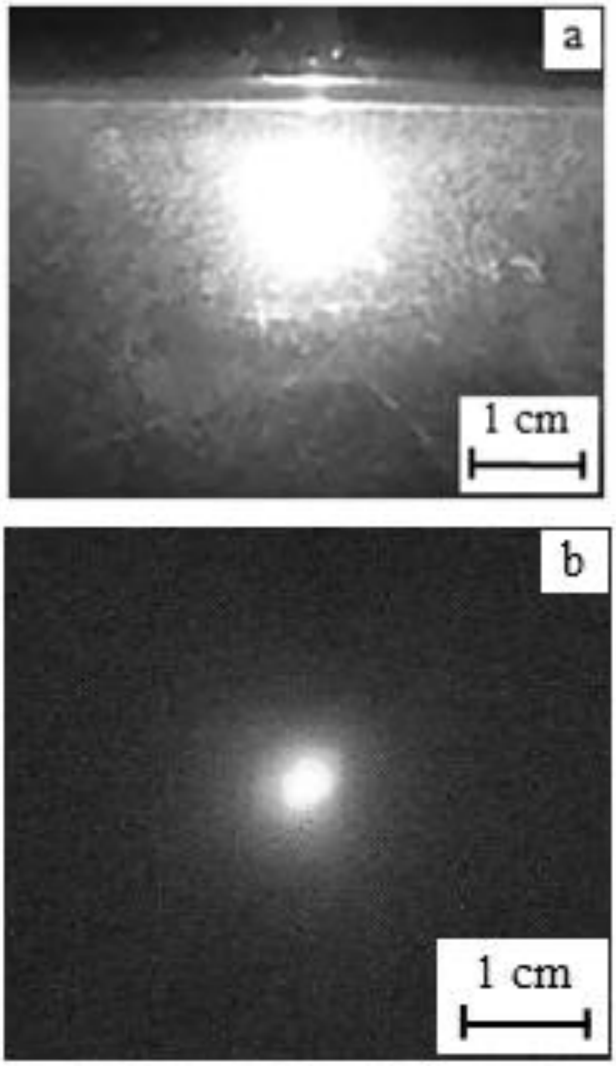


Fig. 2. Photo of the discharge in electrolyte: a) general view of the discharge; b) near-cathode region of the discharge

III. RESULTS AND DISCUSSION

A. Research of electrical discharge characteristics

Tungsten and titanium rods with diameter of 1-2 mm were used for cathodes, and stainless steel and molybdenum plates with thickness of 0.2-0.4 mm were used for anodes. The power source was a full wave rectifier with voltage of 0-240 V and frequency of 100 Hz. The cathode was positioned vertically in the electrolyte at different depths relative to the surfaces.

The discharge was ignited inside the electrolyte and accompanied by appearance of a glow. Panasonic Lumix DMC-FZ45 camera (time resolution is 1 ms) was used to record the discharge image. The image of the discharge of the cathode located close to the surface of the electrolyte is shown in Fig. 2a. The near-cathode area having the highest temperature is the most intensive (Fig. 2b). The most signature colors of the discharge, depending on the composition and concentration of the electrolyte, are yellow-red and dark blue.

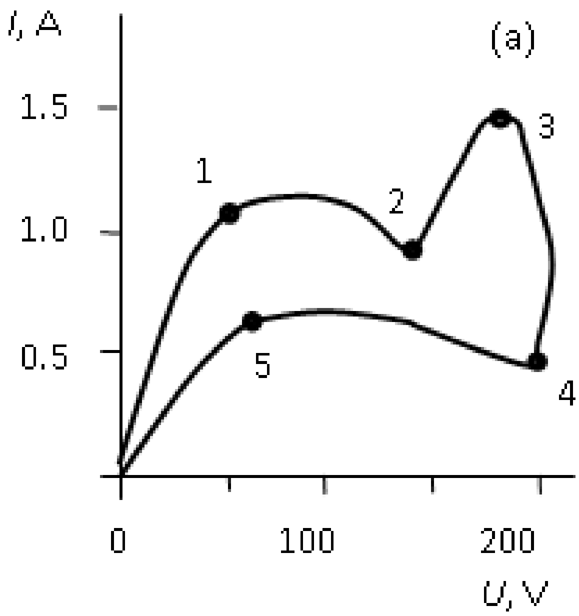
The processes in the near-electrode cathode area were of interest in this work. For this reason, the current-voltage characteristics were measured for two electrolyte compositions, with which experiments were carried out to study the effect on the electrodes.

The potential flow between the electrodes in the electrolyte was also measured. Typical current-voltage characteristics at a discharge in the electrolyte based on sodium carbonate Na_2CO_3 for concentration *C*=0.5 M (Fig. 3a) and sodium hydroxide NaOH for concentration *C*=0.5 M (Fig. 3b) (concentration of Na_2CO_3 *C*=1 M: 106 g per 1 L of distilled water) are presented in this work.

Breakdown and discharge ignition happen at point 1. Area 2-3 is the working range of the characteristics. Intensity of the discharge weakens in section 3-4 and dies out at point 4. Dependencies of the influence of the substance concentration on the form of the current-voltage characteristics of the discharge in the electrolyte were determined in the previous works [3-6].

The common pattern of the dependencies is a shape resembling a hysteresis. The discharge current density values are within the range of: $j = 15 - 80\ \text{A/cm}^2$. The main differences of the current-voltage characteristics are: various parameters for voltage and current at point 1 of the discharge ignition, different run of the working area (2-3) and the values for maximum voltage and current at point 3. The characteristic dependency of the potential between the electrodes in the electrolyte at discharge is shown in Fig. 3c.

The measurements were carried out using a tungsten probe located in the electrolyte environment. The starting point of the count on *x* axis was chosen on the cathode surface. According to this dependence, a considerable drop of the potential is observed in the near-cathode area of the discharge.



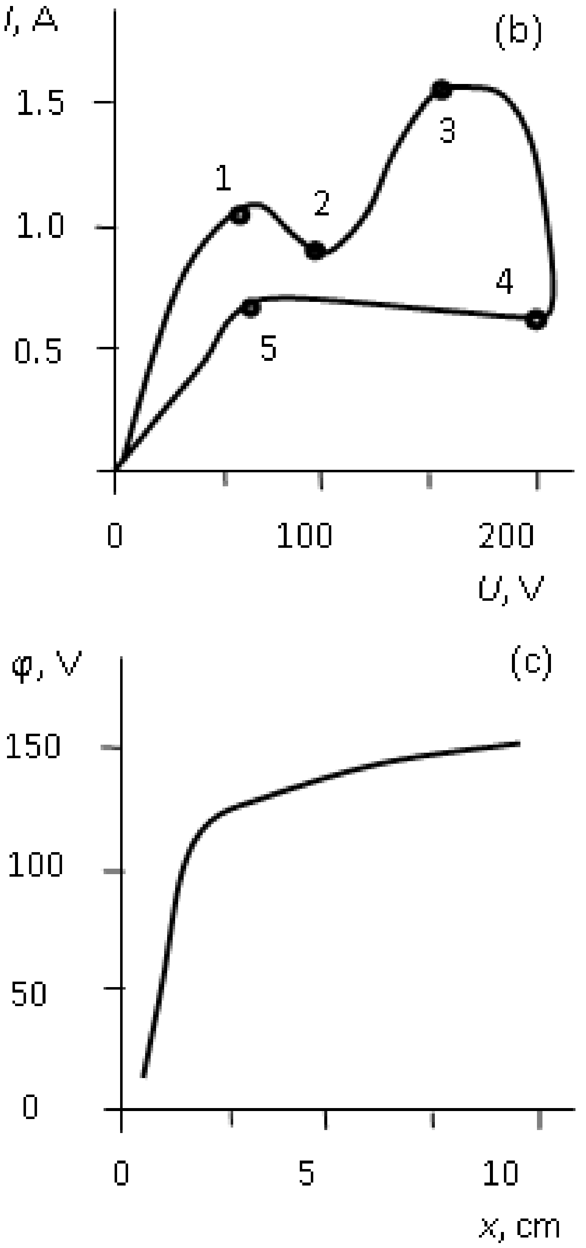


Fig. 3. Electro technical characteristics of the discharge in the electrolyte:
a) current-voltage characteristic of the discharge (sodium carbonate (C=0.5 M));
b) current-voltage characteristic of the discharge (sodium hydroxide (C=0.5 M));
c) potential dependence between electrodes (sodium carbonate C=0.5 M))

The breakdown effects at a discharge in the electrolyte are observed near point 1 of the volt-ampere characteristics (Fig. 3a). The breakdown occurs in the area with a size of about 1-2 mm surrounding the surface of the cathode. Generation of 0.1-0.5 mm hydrogen bubbles is observed on the cathode. A spark breakdown model is more preferable for puncture in the conductive liquid containing gas bubbles [14].

In earlier works, the frequency distributions of electrical oscillations at a discharge in the electrolyte were received by using sodium carbonate [3, 5].

The typical frequencies of oscillations for a discharge in the electrolyte on the basis of sodium carbonate are as follows: (110±6) kHz, (350±18) kHz, (610±31) kHz, (1.2±0.1) MHz, (2.2±0.1) MHz, (65±3) MHz, (102±5) MHz. Previously, presence of electric oscillation frequencies was attributed to formation of electronic cyclotron and ionic cyclotron plasma waves at a discharge in the electrolyte.

A frequency range was defined: 20 kHz-150 MHz for these plasma waves. Characteristic discharge parameters and also typical lengths of these waves were calculated: λ=1-50 mm.

B. Radiation characteristics of the discharge

The experiments were conducted with electrolytes prepared using sodium hydroxide and sodium carbonate. At photographic registration of the discharge, the 1-2 mm thick near-cathode area of the discharge has the greatest intensity. The lines of sodium atoms Na I 589 nm, 819 nm and sodium ion Na II 309 nm have the greatest intensity for a discharge on sodium hydroxide (Fig. 4). The least intensity of the emission is present for the following lines: atomic hydrogen H_α 656 nm, H_β 486 nm, sodium atoms Na I 439 nm, titan atoms Ti I 365 nm, 400 nm, 838 nm, magnesium atoms Mg I 518 nm.

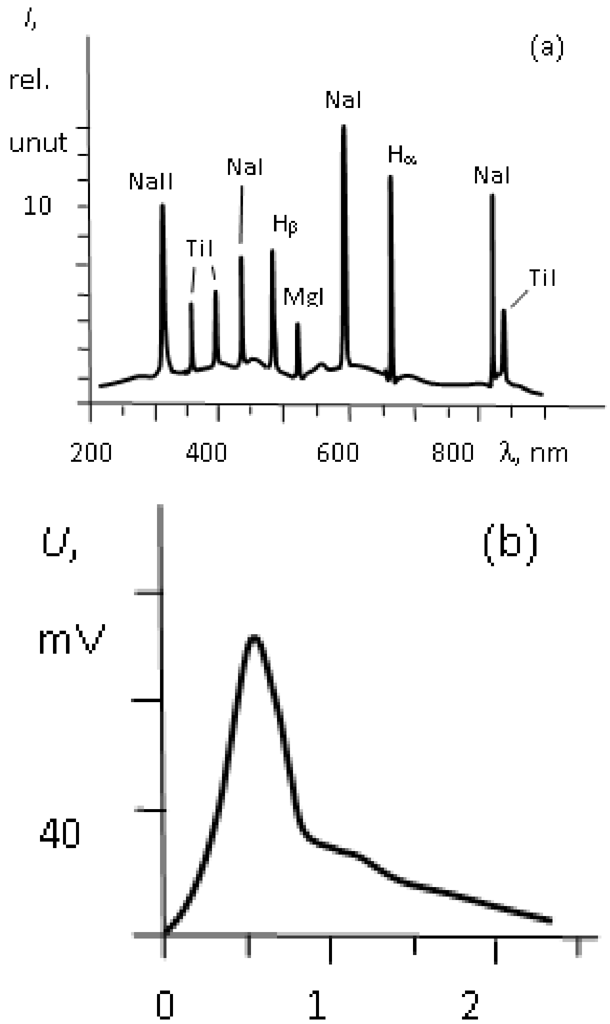


Fig. 4. Radiation of the discharge in the electrolyte on the basis of sodium hydroxide:
a) emission spectrum of discharge in the electrolyte;
b) emission oscillation of Na I 589 nm line

Temperature of plasma in the near-cathode area of plasma, which was T=2800±200 K for the electrolyte on sodium hydroxide in the operation mode of the discharge at current value I≈1.2 A (area 2-3) was calculated by the atomic hydrogen lines H_α and H_β by the relative intensities method [13-16]. At the discharge in the electrolyte on sodium carbonate, the temperature was T=2500±200 K in the operation mode of the discharge at current value I≈1.1 A (area 2-3). Plasma concentration n_e= (3.4±0.2)·10^{15} cm^{-3} in the discharge mode at current values of I≈1.2 A (area 2-3) was obtained by means of Stark broadening of hydrogen lines H_α and H_β for the electrolyte on sodium hydroxide.

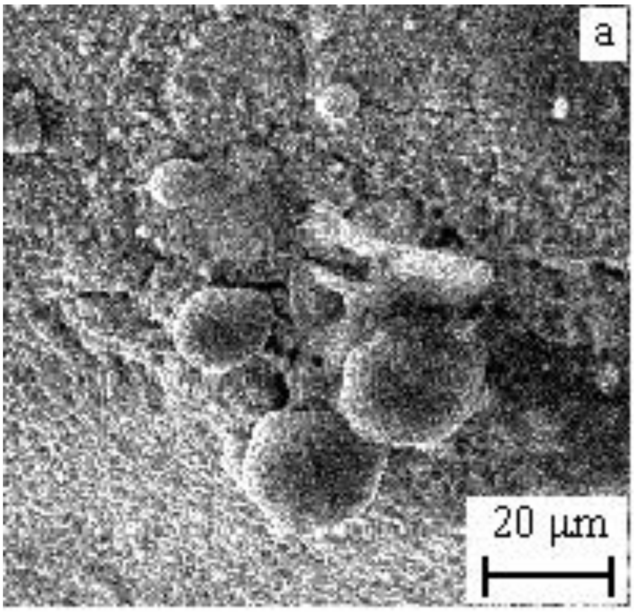
C. Research of the surface of electrodes

The surface of the cathode, through which the current passes during combustion of the discharge, was 0.25-0.5 mm^2. Density of the current in the experiments was in the range of 2-6 A/mm^2.

Plasma temperature in the near-cathode area according to the carried out spectral measurements acquired the values within the range of 2500-2800 K. These values exceed the titanium melting temperature of (t_{Ti}≈1725° C), but less than the tungsten melting temperature (t_W≈3416° C).

Tungsten and titanium cathodes and stainless steel and molybdenum anodes were used in these experiments. Change of the electrode surface structure after the effect of a discharge in the electrolyte was researched. Let us consider the surface of the titanium cathode at a discharge in the electrolyte on sodium carbonate. VEGA 3 SEM and Hitachi TM1000 microscopes were used for the exploration of the electrode surface. The surface of the titanium cathode near its tip is shown in Fig. 4a.

The following groups of objects and structures were noted on the surface. There are sphere-like formations with the size within the range of 5-40 µm. Alongside with them, irregular shape formations occurred near the spheres. There are small formations of spherical and irregular shapes with the size of 0.1-2 µm located with great density on the surface. Perhaps, these small formations are embryos for emergence of spherical structures. Also, 0.2-1 µm wide cracks can be seen on the surface.



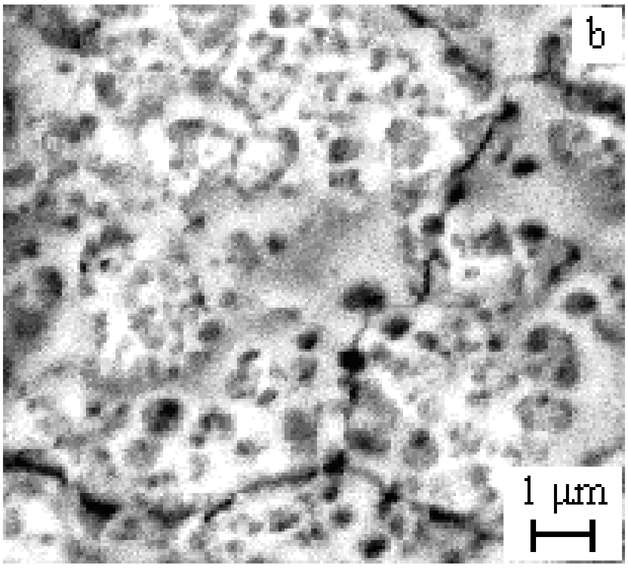


Fig. 5. The images of the titanium cathode after the effect of the discharge in the electrolyte: a) sphere-like formations; b) pores structure of the surface

The following distributions were received for the element composition of this surface:

- oxygen - about 71%,
- titanium - 18%,
- magnesium - 7%,
- sodium - 3%.

Magnesium as an element is included in the electrode material. The other material - sodium – is contained as ions in electrolyte. At the same time, the composition of spherical formations was interesting.

The average content of elements for them was as follows:

- oxygen - about 71%;
- titanium - 22%;
- magnesium - 6%.

Titanium hydroxide (IV) $TiO_2 \cdot nH_2O$ is the most stable compound of titanium and water. For quantitative assessments the formula $TiO_2 \cdot 2H_2O$ or $Ti(OH)_4$ is used. We suppose a possibility of the titanium hydroxide formation on the surface of titanium cathode. For this analysis at the mean percentage of titanium in 20% the oxygen quantity can be approximately in 4 times greater. The analyzers of the using microscopes don’t define the content of hydrogen. Therefore, the high oxygen content at an element analysis of surface layer of cathode can be fixed.

In the near cathode region of discharge the water electrolysis process and oxygen presence near the cathode surface arise. Therefore, on the surface of titanium cathode it is possible the formation of titanium dioxide TiO_2 and magnesium oxide MgO also.

A pores surface is another type of a surface structure on the titanium cathode (Fig. 5b). On the surface of electrode, it is observed the irregular placement of pores with dimensions in the region 0.1-1 µm. The typical form of pores is oval. Clusters of little pores with dimensions 0.1-0.3 µm are observed. Cracks with wrong form with width 0.2-0.5 µm are placed on the surface.

IV. CONCLUSION

For the discharges in electrolyte based on sodium hydroxide and sodium carbonate the temperature in the near-cathode region, which is equal *T*=2500-2800 K, was determined by spectral measurements. On the surface of titan electrodes, the two types of structures: sphere-like formations and a pores surface structure were registered.

Elemental analysis of the surface of the titanium electrode and the sphere-like formations showed that the surface composition, including the both types of the surface formations, corresponds to the presence of titan hydroxide (IV), as well as titanium dioxide and magnesium oxide.

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