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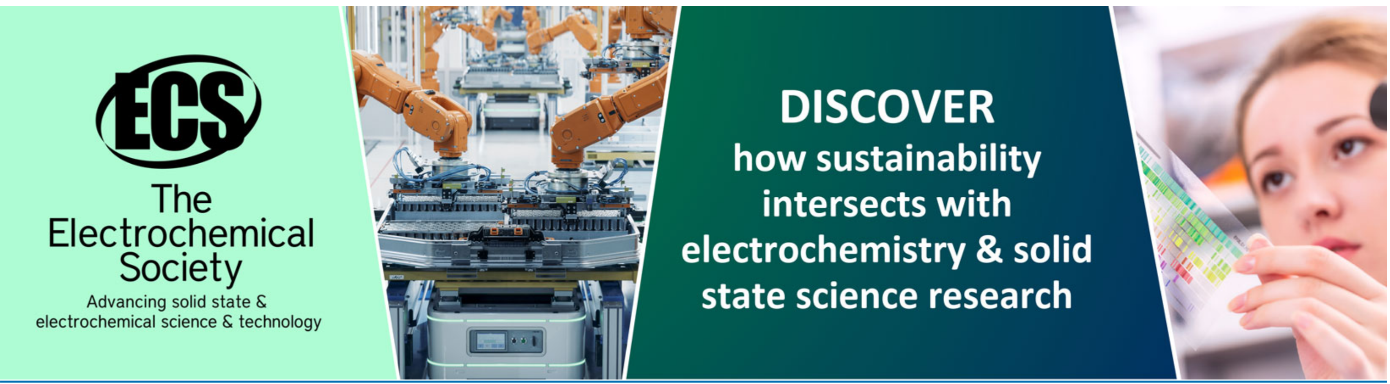

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Investigation of plasma properties of discharge in electrolyte surface layer

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Abstract. The parameters of discharge close to electrolyte surface have been investigated in the work. The current-voltage discharge characteristics have been measured for the main discharge modes. The electric discharge oscillations have been studied and spectra determined in the range of 10 kHz–300 MHz for two electrolyte compositions. The study of discharge radiation in the visible and ultraviolet ranges of electromagnetic range has been carried out and plasma temperature determined. The influence of discharge on microstructure of electrodes surface has been investigated.

1. Introduction

The discharge formation in electrolyte is related to current flow through electrolyte environment and occurrence of luminosity near electrodes. In this case one of the electrodes can be placed over electrolyte surface [1, 2]. The emergence of discharge in electrolyte is accompanied by the appearance of radiating area and convective flows related to liquid heating. Various electric oscillations can take place in case of discharges in electrolytes [3–5]. These discharges are used for modifying surfaces of materials, polishing metal surfaces of intricate shape, more efficient hydrogen production.

2. The investigation of discharge electrical characteristics

The vessels featuring capacity of 150–350 cm^3 and electrolytes based on sodium carbonate and potassium hydroxide have been used for experiments in this work. The experimental setup is shown in figure 1. The rods of tungsten and titanium with diameter of 1–3 mm have been used for cathodes, and the plates of stainless steel and molybdenum with thickness of 0.1–0.5 mm have been used for anodes. The power source has corresponded to double half-period rectifier with voltage of 0–250 V and frequency of 100 Hz. The cathode has been placed in electrolyte surface layer. The discharge has been ignited from inside of electrolyte or at the boundary between electrolyte and air.

The dependences of influence of substance concentration on the shape of current-voltage characteristic (CVC) of discharge in electrolyte [4, 5] have been determined in the previous works. This work has been studying comparative characteristics in case of discharge in electrolyte based on sodium carbonate Na_2CO_3 and potassium hydroxide KOH. The investigations have been carried out in the range `of concentrations $C = 0.1$–1 M (concentration of Na_2CO_3 $C = 1$ M: 106 g per 1 l of distilled water). CVC for these two electrolytes for one and the same concentration $C = 0.4$ are presented in figure 2. A breakdown and ignition of discharge takes place in point 1. Section 2–3 is the working range of characteristic. The intensity of discharge grows weak at sector 3–4 and the discharge dies out in point 4. A shape resembling hysteresis is a common regularity of dependences. The values of current discharge density are in the range: $j = I/S$ = 10–50 A/cm^2. The basic differences of these CVC are as follows: different parameters for voltage and current in point 1 of discharge ignition, different run of working section (2–3) and different values for maximum voltage and current in point 3.

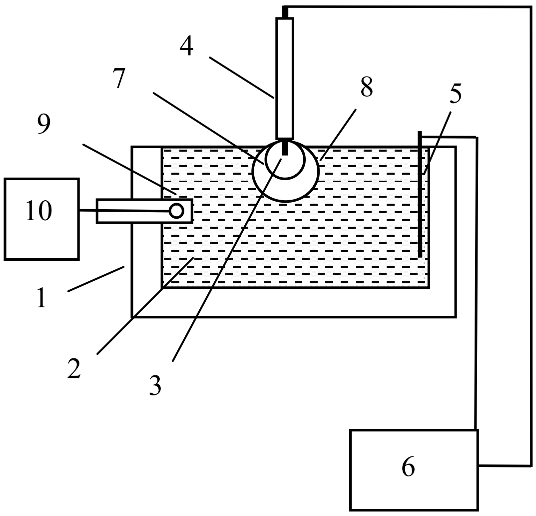

Figure 1. Experimental setup: 1 – chamber, 2 – electrolyte, 3 – cathode, 4 – ceramic tube, 5 – anode, 6 – power source, 7 – near cathode discharge region, 8 – middle region, 9 – magnetic probe, 10 – frequency analyzer.

A stage of discharge breakdown is related to phenomena in near cathode area of discharge with dimensions of 1–2 mm surrounding surface of cathode [4, 5]. Hydrogen bubbles measuring 0.1–0.5 mm are observed at cathode. It is supposed that hydrogen pressure in a separate bubble is close to atmospheric pressure. The evaluation of electric field intensity in near cathode area with thickness $d \sim 1$ mm equals $E \sim 1.1 \cdot 10^3$ V/cm. The formula for coefficient of ionization with electrons features the following view [6]: $\alpha = Ap\,\exp(-Bp/E)$. The evaluation of coefficient of ionization for characteristic discharge parameters gives the following value: $\alpha \approx 14$ cm^{-1}. A model of spark discharge is more preferable for breakdown in the conductive liquid comprising gas bubbles [7]. The values of drift velocity of electrons calculated with the use of expression for mobility are available in the range: $v = 10^5$–10^6 cm/s. The assessment of time of cathode layer passage by electron avalanche gives the following values: $\Delta t = d/v = 10^{-7}$–10^{-6} s.

3. The investigation of electric oscillations

The frequency distributions of electric oscillations in case of discharge in electrolyte have been obtained in the course of earlier works in case of using sodium carbonate [4, 5]. The sodium carbonate and potassium hydroxide have been used in this work as substances. The registration of electric fluctuations has been carried out by means of magnetic and electric probes and Tektronix TDS 2024B oscilloscope in the mode of spectrum analyzer. The individual pulses of discharge current had a shape of attenuating sine wave with a period of ~1.2 ms with periods number of 3–4. The high-frequency fluctuations have been registered at the beginning of every first current pulse period. The magnetic probes have been fabricated in the form of coils (diameter – 2–3 mm, quantity of turns – 80–150). The probes have been introduced into electrolyte in protective housing (figure 1), or have been arranged outside of a chamber. The electric oscillations have been investigated in the range of frequencies of 10 kHz–300 MHz.

The typical frequencies of oscillations are as follows for a discharge in electrolyte on the basis of sodium carbonate: (110±6) kHz, (350±18) kHz, (610±31) kHz, (820±41) kHz, (65±3) MHz, (102±5) MHz. The characteristic frequencies of oscillations are as follows in case of using potassium hydroxide for discharge in electrolyte: (350±18) kHz, (610±31) kHz, (41±2) MHz, (65±3) MHz, (102±5) MHz, (130±7) MHz. Figure 3a shows frequencies for potassium hydroxide in kilohertz range and figure 3b shows frequencies in Megahertz spectrum range. It should be noted that there exist frequency oscillations characteristic to particular electrolyte only. For sodium carbonate these are the following frequencies: (110±6) kHz, (820±41) kHz, and for potassium hydroxide: (41±2) MHz, (130±7) MHz. In case of sodium carbonate the following number of frequencies in Megahertz range has been registered too: (1.2±0.1) MHz, (1.5±0.1) MHz, (1.8±0.1) MHz, (2.0±0.1) MHz, (2.2±0.1) MHz.

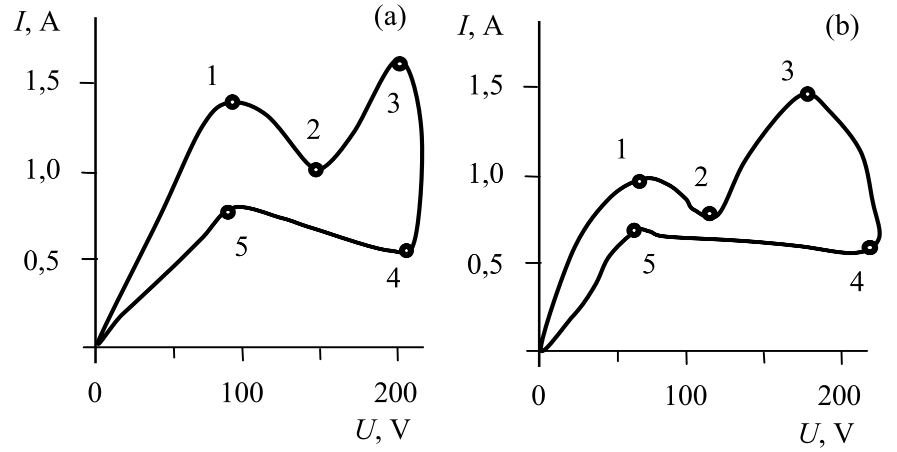

Figure 2. The current-voltage characteristic at the electrolyte discharge: (a) sodium carbonate Na_2CO_3 (C=0,4 M), (b) potassium hydroxide KOH (C = 0,4 M).

The presence of frequencies of electric fluctuations has been interlinked earlier with shaping electronic-cyclotron and ionic-cyclotron plasma waves in the course of discharge in electrolyte [4, 5]. The frequency range has been determined: 20 kHz–600 MHz for characteristic discharge parameters as well as typical wave lengths have been calculated: λ = 1–50 mm. Besides, the interrelation of frequencies oscillations with breakdown in the discharge cathode area is possible. The time of passing the near cathode area by electron avalanche obtained earlier equals $\Delta t = 10^{-7}$–10^{-6} s. Using this method it is possible to generate electric fluctuations with characteristic frequencies: ν = 1–10 MHz. This frequency range is present in the registered sodium carbonate fluctuations. In view of this fact the emergence of electrical oscillations at the stage of breakdown of near cathode layer in electrolyte can be also assumed in line with the emergence of plasma waves.

In case of using a substance comprising sodium or potassium for the discharge in electrolyte the electric oscillations will be registered at the same frequencies, as well as there are frequencies characteristic for every electrolyte only. It shows a dependence of oscillations from the type of substance comprised by electrolyte and from the particular metal ions contained in electrolyte.

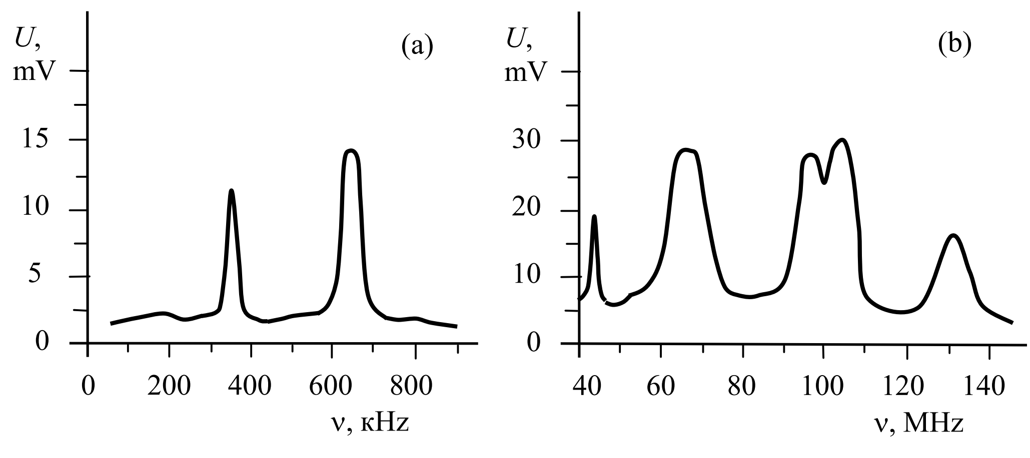

Figure 3. The electric oscillations spectra of the discharge at the potassium hydroxide using (concentration C = 0,5 M): (a) region 50–900 kHz, (b) region 40–140 MHz.

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4. The investigation of radiation characteristics of discharge

The radiation characteristics have been obtained in electromagnetic range of 200–1000 nm for the discharges in case of presence of sodium carbonate and potassium hydroxide in electrolyte. The lines of elements comprised by radiation have been determined in each of the above cases. In case of discharge based on sodium carbonate the lines of sodium atoms Na I 589 nm, 819 nm, and sodium ion Na II 309 nm, as well as tungsten atoms W I 384 nm feature the maximum intensity. The least intensity of radiation is observed for the following lines: tungsten atoms W I 360 nm, 420 nm, and hydrogen atoms H_α 656 nm, H_β 486 nm.

In case of discharge based on potassium hydroxide the following lines feature the maximum intensity: potassium atom K I 769.9 nm, potassium ion K II 394.2 nm, sodium atom Na I 589.5 nm, Na I 588.9 nm. The least intensity is present with the following lines: potassium atom K I 404.4 nm, and hydrogen atoms H_α 656 nm, H_β 486 nm.

Due to presence of lines of atomic hydrogen H_α and H_β in radiation the plasma temperature has been calculated using a method of relative intensities. With respect to discharge based on sodium carbonate the temperature of plasma in the near cathode area of plasma has amounted to $T = 2100 \pm 200$ K in the working mode of discharge at current value: $I = (1.20 \pm 0.05)$ A. In case of discharge based on potassium hydroxide the temperature of plasma in the near cathode area of plasma has amounted to $T = 2300 \pm 200$ K in the working mode of discharge at current value $I = (1.10 \pm 0.05)$ A.

5. The investigation of surface of electrodes

The cathodes of tungsten and titanium and anodes of stainless steel and molybdenum have been used in experiments. A study of changes in structure of electrodes' surface has been carried out after effect of discharge in electrolyte. The surface of titanium cathode after affect of discharge in electrolyte based on sodium carbonate is shown in figure 4. The surface images have been obtained by means of VEGA 3 SEM and Hitachi TM1000 microscopes. The surface of cathode shows a formation of objects of irregular shape featuring size of 0.1–2 μm and bigger featuring length of 2–30 μm. At the same time the sections with micro porous structure featuring size of 0.2–1 μm are present at the surface (figure 4).

The analysis of element composition of this surface has been performed. In this case the following average elements distribution has been observed: oxygen (72%), titanium (16%), magnesium (7%), sodium (3%). High content of oxygen is, presumably, related to the presence of atomic oxygen close to cathode surface and possibility of oxidation processes. The sodium registration is caused by its deposition from electrolyte solution. Magnesium is included into original cathode alloy. Therefore, it may be supposed that electrolysis appeared close to cathode surface and atomic oxygen is present. Owing to the fact that temperature of plasma at cathode surface is higher than the temperature of titanium melting, a presence of titanium melt becomes possible in the form of seeds featuring size of 0.1–0.2 μm. At the same time a process of titanium oxidation at cathode surface is also possible.

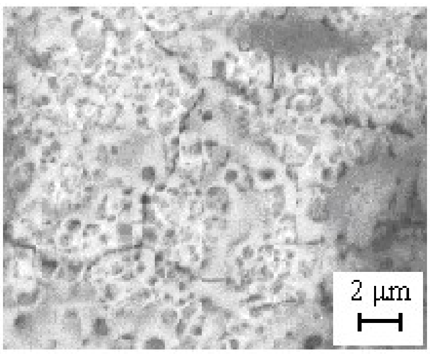

Figure 4. The image of micro porous structure on the cathode surface after the electrolyte discharge influence.

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6. Conclusion

The current-voltage characteristics of discharge in electrolyte have been obtained in the course of this investigation in case of using sodium carbonate and potassium hydroxide as the working substance. The measured CVC possess definite characteristic features. A study of oscillation discharge processes has been carried out and a number of basic frequencies of electric fluctuations in the range of $\nu = 80$ kHz–200 MHz have been determined. The discriminative moments of spectra of sodium carbonate and potassium hydroxide are present. The emergence of electric oscillations at the stage of spark breakdown in case of shaping electronic avalanches is also possible alongside with the emergence of plasma waves. The temperature in near cathode area being in the range of $T = 2100$–2300 K is measured by means of spectral methods. The appearance of micro porous structure and presence of oxidation processes of titanium is observed at cathode surface.

Acknowledgements
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