Simulation of anodic heating in low-temperature plasma between liquid and solid electrodes

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Abstract. A model of anodic heating in an electric discharge between an electrolyte and a solid electrode is presented. The mathematical model of the vapor-gas shell of an electric discharge is built on the example of a vertical cylindrical electrolytic cell. Experimental current-voltage characteristics of the cell, depending on the concentration of the electrolyte, were obtained by applying a voltage that increases linearly at a constant speed. The current-voltage characteristics depend on the electrolyte concentration, and at high concentrations, they are a direct relationship. The emission mechanism of the conductivity of the vapor-gas near-anode shell makes it possible to explain the experimentally observed deposition of solution components on the anode surface.

1. Introduction
The study of processes occurring in a low-temperature plasma between liquid and solid electrodes is of particular interest from the point of view of their practical application [1 – 6]. Mathematical description and modeling of these processes are of great importance for the development of industrial technology [7 – 11]. At the same time, the theoretical basis for achieving practical use of the results of scientific research in this area is still insufficient.

2. Materials and methods
The peculiarity of the investigated electric discharge is that the current passes through the electrolytic cell, in which the anode surface is much smaller than that of the cathode. At low voltages, the passage of current in the volume of the solution is described by Ohm’s law, and the processes on the electrodes are described by Faraday’s laws. An increase in voltage leads to the heating of the electrolyte mainly in the near-anode zone, since almost all the resistance of the electrolytic cell is concentrated in it.

Transitions from one current passing mode to another occur when the critical voltage values are reached. For the formation of a continuous vapor-gas shell (Figure 1), albeit an unstable one, it is necessary to ensure the release of energy in the near-anode zone that is sufficient to boil the electrolyte in a certain volume.

To form a vapor-gas shell, it is necessary to heat the anode layer of the solution to the boiling point. Consider boiling the solution on the example of a vertical cylindrical cell (Figure 2).

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In order for the surfaces of the electrodes to be equally accessible, the anode is extended through a sealed hole in the dielectric base of the cell. This design provides a uniform distribution of current density on the surfaces of the electrodes.

**Figure 1.** The formation of vapor-gas shell in the electric discharge between the electrolyte and the workpiece.

**Figure 2.** Vertical electrolytic cell: \( \delta \) – the anode layer thickness; \( R_A \) – the anode radius; \( R_K \) – the cathode radius.

Volt-ampere characteristics (VAC) of the cell were recorded using the two-coordinate recorder PDP-4-002 when the voltage was applied, increasing linearly at a constant speed in the interval from 1 to 30 V/s and are presented in Figure 3.

### 3. Results and discussion

The dependencies obtained were, as a rule, linear. In solutions of high concentrations, the resistance of the cell is almost constant throughout the entire voltage range (curves 1 and 2 in Figure 3).

![Volt-ampere characteristics of a cylindrical cell. Concentration NH\(_4\)NO\(_3\): curves 1 and 2 – 25 %; curves 3 and 4 – 5%. Voltage growth rate: curve 1 – 1.3 V/s; curve 2 – 10.9 V/s; curve 3 4.0 V/s; curve 4 – 25.0 V/s.](image)

In order to evaluate the effect of the system parameters on the boiling rate and the first critical voltage, consider the heat balance in the cylindrical cell shown in Picture 2. The potential distribution in the medium between two coaxial cylinders is found by solving the Poisson’s equation if the anode potential is taken to be \( U \) and the one of the cathode is zero:

\[
\ln(\frac{R_K}{r}) = U \ln(\frac{R_K}{R_A})
\]

where \( r \) - radial coordinate. Then, according to Ohm’s law, the current density in the solution is found by the following

\[
j = \sigma \frac{d\varphi}{dr} = \frac{\sigma U}{r \ln(\frac{R_K}{R_A})}
\]
where $\sigma$ – electrical conductivity of the solution. The current through a cylindrical surface with height $h$, radius $r$ and area $S$ is equal to

$$I = jS = j2\pi rh = \frac{2\pi h\sigma U}{\ln(R_k/R_A^2)}$$

and, of course, doesn't depend on $r$. In the anode layer of the thickness $\delta = r - R_A$ the electric power will be allocated

$$P = I[U - \varphi(r)] = \frac{2\pi h\sigma U^2}{\ln(2)(r/R_A)}$$

The mass of the thin anode layer of the thickness $\delta$ for $\delta \ll R_A$

$$m = \gamma V = \pi \gamma (r^2 - R_A^2)h = \pi \gamma h(\delta^2 - R_A^2) \approx 2\pi h\delta R_A$$

where $V$ - layer volume, $\gamma$ - electrolyte density.

Suppose that all the power released in the layer will be spent on its heating to boiling and evaporation. Neglecting the heat removal from the layer into the anode and into the solution, we get:

$$m\tilde{c}(T_s - T_0) + m\lambda = P\Delta t$$

where $\tilde{c}$ - specific heat of the solution, $T_s$ - the solution boiling point, $T_0$ - the initial temperature, $\lambda$ - specific heat of vaporization, $\Delta t$ - the duration of heating before boiling.

Substituting (4) and (5) into (6) taking into account the fact that $\ln(1 + \delta/R_A) \approx \delta/R_A$, allows to find the time of occurrence of interruptions:

$$\Delta t = \frac{\gamma R_A^2(c\Delta T + \lambda)\ln^2(R_k/R_A)}{\sigma U^2}$$

where $\Delta T = T_s - T_0$, therefore: the higher the voltage is, the faster the boiling up will occur, the more equitable is the neglecting of the heat removal from the cell and the formula (7) itself.

In case of $U = f\cdot t$, where $f$ - constant growth rate of voltage, it is possible to compare the measured time before the start of interruptions and the first critical voltage $U_c$ to the calculated data.

As $U_c = f\Delta t$,

$$\Delta t = \sqrt{\frac{\gamma R_A^2(c\Delta T + \lambda)\ln^2(R_k/R_A)}{f^2\sigma}}$$

So, the first critical voltage will be:

$$U_c = \frac{\sqrt{\gamma R_A^2(c\Delta T + \lambda)\ln^2(R_k/R_A)}}{\sigma}$$

At more significant voltages, the surface of the solution acquires a noticeable negative charge, due to increased concentrations of anions. Let’s note that the double layer that exists at the interface in the absence of an external electric field is not considered here. To estimate the magnitude of the surface charge, we assume that the change in the concentration of ions depending on the potential is described by the Boltzmann law [2] (Figure 4).
Figure 4. The surface layer of the solution and the electric field in the shell.

The volt-ampere characteristic of a constant-thickness gas-vapor shell can be calculated using the standard system of equations, which take into account the possible role of space charge, and the dependence of the current density $j$ on the field strength $E$ is considered to be linear:

$$\varepsilon_0 \varepsilon \text{div } \vec{E} = -\rho_e$$
$$\vec{j} = \mu \rho_e \vec{E}$$
$$\phi(r) = (2\pi)^{2/3} \exp(i k \cdot r)$$

(10)

where $\rho_e$ - bulk charge density, $\mu$ - ion mobility.

For a one-dimensional problem in accordance with Figure 4, we get

$$\frac{dj}{dx} = \mu E \frac{dp}{dx} + \mu \rho_e \frac{dE}{dx} = 0$$

(11)

Therefore,

$$E \frac{d^2E}{dx^2} + \left(\frac{dE}{dx}\right)^2 = 0$$

(12)

Suppose that the potential of the surface of the solution $\phi_s$ is negligible compared with the potential of the anode, equal to the voltage $U$. On the surface $x = \delta$ the field $E_0$ must be maintained, providing the emission of the excess charge. By integrating (12) and solving the equation under the conditions $\phi(\delta) = 0$ and $\phi(0) = U$ we obtain the volt-ampere characteristic as follows:

$$j = \frac{9\mu \varepsilon U^2}{8 \delta}$$

(13)

The higher the voltage is, the faster the boiling up will occur, the more equitable is the neglecting of the heat removal from the cell and the formula itself (7).

In case of $U = f \cdot t$, where $f$ - constant growth rate of voltage, it is possible to compare the measured time before the start of interruptions and the first critical voltage $U_c$ to the calculated data.

4. Conclusion

The emission mechanism of the conductivity of the vapor-gas near-anode shell makes it possible to explain the experimental data and patterns. The experimentally observed deposition of the solution components on the anode surface is associated with the emission of ions of both signs into the vapor –
gas shell, with a predominance of negative ones. Outside the solution, the interaction of ions of opposite signs will no longer be weakened by hydration, which will lead to crystallization of the nonvolatile components of the solution. The crystallized compounds will go into the atmosphere together with the vapor, accumulate on the walls of the working chamber, or deposit on the anode in a continuous layer. In some cases, the deposition on the anode can lead to a gradual decrease of current, and as a result, a decrease in the temperature of the anode, up to condensation of the shell and to the termination of the process.

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