Distinctive features of electric current passing through vapour gaseous envelope in anodic plasma electrolytic processes

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Abstract. This article focuses on the study of the effect of anodic composition of electrolyte on electric conductivity of a vapour gaseous envelope, formed in the mode of anode stationary heating. The investigation methods were based on measuring current-voltage characteristics in aqueous solutions of ammonium chloride, chlorohydric acid and hydrobromic acid at equal anion concentrations. It has been established that conductivity in vapour gas medium is primarily determined by electric field intensity which varies depending on its composition and thickness, ion mobility considered as factor of secondary importance. It has been assumed that emissive capacity of aqueous solutions can be limited by a critical concentration of their components.

1. Introduction

A specific feature which distinguishes plasma electrolytic technologies from conventional electrochemical processes is a vapour gaseous envelope surrounding a treated workpiece and allowing to carry out thermal or chemicothermal treatment, surface polishing or its cleansing, coating deposition etc. This envelope provides favourable conditions for fast heating and saturation of the surface layer of a treated workpiece with light elements such as boron, nitrogen or carbon.

Formation of a vapour-gas envelope, its stability, and conductivity features have been studied by a number of authors [1–3]. These works shed light on the role of some physical and electrochemical processes in the process of the envelope formation, the nature of its conductivity and the possibility of a steady-state condition necessary for stationary heating. Polarity of the active electrode significantly affects the conduction mechanism of the vapour-gas envelope. In the case of cathodic heating, it is generally accepted that current passage through the envelope is carried out by means of electrical discharges. During the anodic process, discharges appear at voltages above 400 V, and in the stationary heating mode (in the range of 100–300 V, depending on electrolyte composition) current passage through the envelope is explained by emission of ions from electrolyte solution under the action of an electric field [4]. This hypothesis explains the features of glow spectrum in the heated workpiece [5], the possibility diffusive saturation of the surface layer and the presence of critical voltages. By now, the dependence of critical voltage on the electrically conductive component concentration in electrolyte has been quantitively estimated [6], and calculation of the effect of space charge in the envelope [7] and its analysis [8] have been proposed. Conducting a quantitative estimate of envelope conductivity is challenging for various reasons. One of these reasons is the lack of extensive experimental data in the form of current-voltage characteristics of anodic heating in various aqueous electrolytes, which would to allow, specify the parameters of various conductivity models in a
vapour-gas envelope. The available results show a significant effect of electrolyte composition on current passage through the envelope and the temperature of an electrode with a minor surface; however the mechanism of this effect remains controversial and not substantiated. Well-known publications, as a rule, contain data about electrolytes, whose composition is selected for solving practical problems of diffusive saturation in metals and alloys, their polishing, oxidation, etc.

This work aims to search for dependencies of current passing through the system anode – vapour-gas envelope – electrolyte; including the effect of the composition of aqueous solutions on the current-voltage characteristics of the object under study. A comparative analysis of solutions with different anionic compositions is suggested to study the features of the current passing through the vapour-gas envelope.

2. Experimental

Current-voltage characteristics of the system were measured in an electrolyzer with an internal heat exchanger. The electrolyzer had the shape of a cylindrical plastic container 250 mm in diameter and 250 mm in height, at its bottom, an inner chamber 110 mm in diameter and 235 mm high was axisymmetrically adjusted. Electrolyte was circulated using a submersible pump located at the bottom of the working chamber. The solution was fed upward, overflowed over the edge of the chamber, and returned back through the holes in the lower part of its side wall.

A heat exchanger in the form of a coil made of corrugated stainless pipe 16 mm in diameter was located between the walls of the outer vessel and the inner chamber. The electrolyte was cooled by tap water flowing in the coil, its rate being controlled by a tap and measured using a rotameter RMF-0.4 ZhUZ (accuracy ±2.5 %). The solution temperature was maintained at 24 ± 1 °C.

Voltage was applied to the coil which functioned as a cathode and an anode-sample from a 15 kW power source (operating voltage 0–300 V, maximum current 40 A). The current in the circuit was determined by measuring voltage across a low-inductance resistor with a resistance of 0.22 Ohm (L = 20 μH). Voltage was measured with an LM–1 voltmeter (accuracy 0.5 %) and recorded with an AKIP 4109/2 digital oscilloscope, in self-recording mode, and an MS 8221 C multimeter (accuracy ±2 %).

Aqueous solutions of hydrochloric acid, ammonium chloride, and hydrobromic acid of various concentrations were used as one-component electrolytes. A two-component electrolyte was presented by an aqueous solution of ammonium chloride with a concentration of 1.32 mol/L and ammonia with a concentration of 2.74 mol/L. The measurements were carried out on cylindrical specimens of low carbon steel (0.2 % C), 15 mm long and 10 mm in diameter; in some experiments, one of the ends had a hemispherical shape with a radius of curvature of 10 mm. The anode heating temperature was measured with a chromel-alumel thermocouple placed in a blind hole on the sample axis. Measurements of current-voltage characteristics were performed as follows. A sample was exposed to the voltage of 180 V; thereafter it was immersed in the electrolyte to a depth equal to its height at a speed of 1.5 mm/s. As soon as the stationary heating mode was reached, the voltage was varied and the current in the system was measured.

3. Results and discussion

Electrical conductivity of the vapour-gas envelope is provided by ions interacting with neutral molecules. Ammonium chloride is a common component of solutions in many processes of plasma electrolyte treatment; therefore, let us assess the mobility of chlorine ion in water vapour using a single-component electrolyte as an example. Suppose that polarization forces prevail in collisions of anions with neutral molecules, therefore the transport cross section corresponds to the polarization cross section and the effective collision frequency does not depend on the relative velocity of ion and molecules motion. In this case, the mobility of the charge carrier does not depend on the electric field intensity and is equal to [9]:

...
\[ \mu_i = \frac{36\sqrt{1 + M/M_i}}{\sqrt{\left(\alpha/\alpha_0^3\right)}Ap}, \]  

(1)

where \( M \) – is the mass of a neutral molecule in a vapour-gas medium, \( M_i \) – is anion mass, \( \alpha \) – is polarizability of a medium molecule, \( a_0 = 0.529 \cdot 10^{-8} \text{ cm} \) – is the Bohr radius, \( A \) – is molecular mass of the gas, \( p \) – is reduced pressure determined using the ratio \( p \) (reduced) = \( p \) (true) \( 273/T \) [K].

Formula (1) is consistent with the experiment and accurately describes the effect the anion mass on their mobility in the same gas. In this case, value \( \mu_i \) is chosen for quantitative estimates, which makes it possible to ignore the effect of medium temperature. In this expression, the medium is characterized by the mass of molecules and their polarizability. In one-component electrolytes, the medium is mainly represented by neutral water molecules. In two-component solutions, molecules of saturating components and their decomposition products, for example, ammonia molecules involved in nitriding, are added to the envelope composition for the purpose of diffusive saturation. Table 1 shows the numerical values of polarizability of water and ammonia molecules in the ground state.

| Molecule | \( \alpha/(a_0)^3 \) | \( M \) (g/mol) |
|----------|----------------------|-----------------|
| H\textsubscript{2}O | 9.8                  | 18.01           |
| NH\textsubscript{3} | 15.4                 | 17.03           |

Substitution of numerical expressions in (1), results in the following estimates for the mobility of the chloride ion: in water vapour \( \mu_{i,p} [\text{Cl}^-] = 3.3 \text{ (cm}^2\text{-atm)}/(\text{V} \cdot \text{s}) \); in ammonia vapours \( \mu_{i,p} [\text{Cl}^-] = 2.7 \text{ (cm}^2\text{-atm)}/(\text{V} \cdot \text{s}) \). Compare the mobility of bromide and hydroxide ions in water vapour is 3 \( \text{ (cm}^2\text{-atm)}/(\text{V} \cdot \text{s}) \) and 3.9 \( \text{ (cm}^2\text{-atm)}/(\text{V} \cdot \text{s}) \), respectively. It is obvious that an increase in the mass of an ion leads to a decrease in its mobility.

Let us consider the effect of the electrically conductive component on the current in the electrolyte–vapour-gas envelope–anode system by means of current-voltage characteristics analysis.

Figures 1 and 2 show current-voltage characteristics of anodic plasma electrolyte heating in aqueous solutions of hydrochloric acid and ammonium chloride. Concentrations of the components were selected with the view to provide equal specific concentration of the chloride ion \( \text{Cl}^- \) of 1.3±0.02 mol/L in figure 1, and 1.9±0.02 mol/L in figure 2 in electrolyte solutions.

**Figure 1.** Current-voltage characteristics of anodic heating in aqueous solutions of hydrochloric acid (4.6%) and ammonium chloride (7%). The anode end is flat.

**Figure 2.** Current-voltage characteristics of anodic heating in aqueous solutions of hydrochloric acid (6.6%) and ammonium chloride (10%). The anode end is flat.

Smaller currents through the envelope in hydrochloric acid solution, as compared to those in ammonium chloride solution (figure 1) can be explained by different field intensity in the envelope or
its different composition. The temperature of the sample in a solution of hydrochloric acid at 140 V is 150 °C higher than in a solution of ammonium chloride. This difference decreases to 45 °C if voltage rises to 220 V. The increased temperature implies more intense vaporization, which entails a decrease in the proportion of chlorine ions in the envelope, an increase in its thickness, as well as a decrease in the current strength and field intensity in comparison with the heating characteristics in an ammonium chloride solution. The presence of ammonia in the envelope resulted from heating in a solution of ammonium chloride should promote reduction in average mobility of chlorine ions, however this did not lead to a decrease in the measured current as compared with a solution of hydrochloric acid.

The noted tendencies not only persist, but also intensify at higher concentrations of the components (figure 2). A voltage increase also reduces a gap between amperage and sample temperature observed in the two electrolytes. At a voltage of 220 V, the current in a solution of hydrochloric acid is higher than in a solution of ammonium chloride, where the sample temperature is 5 °C higher than that observed in a solution of hydrochloric acid. In addition, it is obvious that an increase in the concentration of the components reduced the current in the ammonium chloride solution and increased it in the hydrochloric acid solution. Presumably, it can be attributed to the emissive capacity of each electrolyte. Accumulation of excess charge on the electrolyte surface and its discharge into the envelope has been insufficiently studied. It can only be established that the findings show a limitation in the emissivity of an ammonium chloride solution at a concentration of 10 % and the absence of such limitations in a solution of hydrochloric acid with a concentration of 6.6 %.

The addition of ammonia to ammonium chloride solution significantly reduces current strength (figure 3). It seems obvious that the envelope composition is enriched with ammonia due to its high volatility. Consequently, the average mobility of chlorine ions will decrease, but in addition to this, an increase in the envelope thickness should be expected, which will also increase its resistance [10].

The effect of ion mobility on current in the system where the envelope consists only of water vapour and a monovalent ion was studies in solutions of anoxic acids of the same molar concentration. Figure 4 shows current-voltage characteristics corresponding to anodic heating in aqueous solutions of hydrochloric and hydrobromic acids with a concentration of 0.5 mol/L.

![Figure 3](image1.png) **Figure 3.** Current-voltage characteristics of anodic heating in an aqueous solution of ammonium chloride (7 %) and a two-component electrolyte with ammonium chloride and ammonia. The anode end is flat.

![Figure 4](image2.png) **Figure 4.** Current-voltage characteristics of anodic heating in an aqueous solution of hydrochloric and hydrobromic acids. The concentration of solutions is 0.5 mol/L. Rounded anode end.

Complete coincidence of current-voltage characteristics within the measurement accuracy is observed. It should be noted that for these solutions, not only volt-ampere but also volt-temperature characteristics coincided, i.e., in this case, it can be reasonably argued that the difference in the mobility of chlorine and bromine ions in water vapour did not play any role.
4. Conclusions
It has been established that electrical conductivity of the vapour-gas envelope in anodic stationary heating mode is determined by a combination of solution boiling processes and emission of electrolyte anions. On the example of ammonium chloride and hydrochloric acid solutions, it has been shown that equal proportion of chlorine ions in electrolytes is not the same in the vapour-gas envelope. The conclusion is confirmed by different values of the current and temperature in the heated sample and is explained by a change in the composition of the envelope, its thickness, and electric field intensity.

The role of ion mobility, providing charge transfer through the vapour-gas medium, can be considered secondary against the background of the influence of charge carriers concentration and the electric field in the envelope.

A hypothesis about a limiting electrolyte concentration that hinders its emissive capacity has been proposed.

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