Some features of anodic plasma electrolytic processes in aqueous solution

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Abstract. Effect of the electrolyte temperature on the current-voltage and temperature-voltage characteristics of the anode plasma electrolytic treatment of a steel sample, as well as the features of the formation of a stable vapour-gaseous envelope were considered. Spectral analysis revealed the glow of the heated anode zone without lines of elements of electrolyte and electrode. The result of the influence of the plasma electrolytic treatment mode on the surface condition was shown.

1. Introduction

Historically, the term "plasma electrolytic processes" refers to a variety of ones, a common element of which is the appearance of a glow around one of the electrodes, called active. As a rule, this is an electrode with a smaller surface compared to another electrode. The active electrode is known to be surrounded by a vapour-gaseous envelope (VGE), the state of which and, above all, the mechanism of passage of electric current through it depend on many quantitative and qualitative factors. These include the polarity of the active electrode, its material, composition and temperature of the electrolyte, hydrodynamic conditions in the electrolyser, etc. A change in the VGE state is clearly observed on the current–voltage characteristics (CVC). The first study of the cathode CVC characteristics in a solution of sodium carbonate has pointed out the modes of electrolysis, current interruptions, and stable discharges, such as glow, and arc at higher voltages [1]. Anodic CVC for thin wires under conditions of natural convection has contained modes of electrolysis, unstable current, stable one with a decreased dependence, and a discharge mode of a glow type [2]. Measurement of the temperature of the steel anode in solutions of ammonium chloride showed that the section of the incident CVC contains two modes: heating and polishing [3]. The high-temperature heating used for the diffusion saturation of metals and alloys with interstitial elements occurs at voltage from 100 V to 300 V [4]. Contrary, the temperature of the workpiece does not exceed 110–120 °C during polishing mode [5]. There is a different sequence of modes for the transition metals due to the formation of a dielectric layer on their surface [6]. Electric discharges of the glow type appear in the anodic VGE at voltages above 400 V [7]. The sequence of current flow modes turned out to depend on the temperature of the electrolyte. The high-temperature heating mode was not detected in a 5 wt. % solution of ammonium sulphate at the temperatures of plasma electrolytic polishing (PEP) [5]. It was shown in the same article that the VGE glow is electrochemical luminescence rather than electric discharges.
The aim of this work is to elucidate the effect of the electrolyte temperature on the modes of current passage and the nature of the glow in the anodic VGE. Spectral analysis of the glow will make it possible to evaluate its nature under the conditions of force hydrodynamics in a cooled electrolyser with stabilization of the electrolyte temperature.

2. Experimental
Cylindrical samples (a diameter of 10 mm, a length of 15 mm) of medium carbon steel (0.45 wt.% C) were subjected to plasma electrolytic treatment in a cylindrical electrolyser with an axially symmetric electrolyte flow supplied through a nozzle located at the bottom of the electrolyzer. In the upper part of the electrolyzer, the electrolyte was overflowing into the sump and was further pumped through a heat exchanger at a rate of 1 l/min, which was measured with an RMF-0.16 GUZ flowmeter (accuracy of ±2.5 %). This scheme provides the stabilization of processing conditions. The samples were connected as the positive output, and the electrolyser was connected as the negative output of the 15 kW DC power supply. An aqueous solution of ammonium sulphate (NH₄)₂SO₄ (5 wt.%) and ammonium chloride NH₄Cl (10 wt.%) were used as the working electrolyte.

The CVC and temperature–voltage characteristic were determined at the electrolyte temperature from 30 °C to 90 °C. The sample temperature was measured with a MY K-type thermocouple and multimeter APPA109N. The thermocouple was fixed in a hole made in the samples at a distance of 2 mm from the sample’s bottom. The voltage and current were measured using DP6-DV voltmeter and DP6-DA amperemeter.

A spectral analysis of the glow of the VGE during anodic heating was performed at the electrolyte temperature of 25±2 °C using an optical emission spectrometer AvaSpec-3648 (Avantes) with a specific remote fiber-optic sensor and software AvaSoft 8.00.

The morphology of the steel surface was studied using a metallographic microscope.

3. Results and discussion
It was found that a maximum current corresponding to the lowest resistance of the system without vapour areas on the anode surface is observed, when voltage increases in the range of 10–350 V (figure 1).

![Figure 1. Current–voltage characteristic of system in solution of ammonium sulphate (5 wt.%).](image-url)
It corresponds to the transition from electrolysis to current interruptions. Such areas are formed with a further increase in voltage, which leads to a decrease in the contact area of the electrolyte with the electrode, an increase in resistance, and a reduction of the effective current value. The current maximum shifts to the region of lower voltages as the electrolyte temperature growth, since local boiling of the heated electrolyte requires less power. After increasing the voltage to 180 V, the current decreases to a constant minimum value, which indicates the formation of a continuous VGE around the anode.

This fact is confirmed by heating the anode sample in an electrolyte whose temperature is not higher than 50 °C (figure 2). In other cases, the temperature of the sample does not exceed the boiling point of the electrolyte.

![Figure 2](image)

**Figure 2.** Temperature–voltage characteristic of system in 5 wt.% solution of ammonium sulphate.

Thus, two ranges of electrolyte temperatures are identified which provide anodic heating (up to 50 °C) and anodic PEP (60–90 °C). In the first case, a continuous VGE is formed around the anode, and its glow corresponds to the emission spectrum of two heated bodies (figure 3). A higher temperature is typical for VGE with a maximum at a wavelength of 700 nm, lower temperature refers to the surface of the anode with a maximum at 900 nm, since the heat flux into the anode comes from the VGE. This fact confirms that the analogy of the formation of a VGE with a boiling crisis [1] is unlawful, since in the system under consideration there are no conditions for the occurrence of bubble boiling, requiring a heat-transfer surface. Heat generation near the anode leads to local boiling of the electrolyte due to the high current density, the observed bubbles relate to gas liberation due to electrolysis. A continuous VGE becomes stable owing to the passage of a stationary current through it, which provides the necessary energy release. The absence of symptoms of ionization and excitation in the vapour-gaseous phase is confirmed by spectral analysis of the radiation of the anodic VGE in a 5% solution of ammonium sulphate at voltages up to 300 V [2]. Under these conditions, lines of elements related to the surface of the anode made of 20X13 steel appear only at 350 V, which points out the electrochemical luminescence rather than plasma in the VGE formed at a voltage above 400 V [3].
Figure 3. Glow spectrum of an anodic envelope in ammonium chloride solution (10 wt.%) at 25 °C its temperature and 190 V.

When a continuous VGE is formed in the process of anodic heating, three processes simultaneously take place on the surface of the anode: electrochemical dissolution of the metal, its oxidation to oxides, and diffusion saturation of the surface layer with interstitial elements include possible phase transitions. Oxidation, diffusion saturation, and phase transitions occur due to the heating of the anode sample to high temperatures with the formation of an oxide layer and a modified structure of substrate (figure 4).

Figure 4. Microstructure cross-section of the steel surface after heating in ammonium chloride solution (10 wt.%) at 850 °C with quenching: 1 – oxide layer, 2 – martensitic layer and 3 – initial structure.

Contrary, the formation of oxide films is comparable to the rate of their removal under PEP conditions. As a result of PEP, the surface morphology becomes more uniform than after heating (figure 5).
Figure 5. Morphology of the steel surface after PEP in ammonium sulphate solution (5 wt. %) at 30 °C (a) and 80 °C (b) its temperature.

4. Conclusions
The current-voltage characteristic of the passage of current through a 6 % aqueous solution of ammonium sulphate with a steel anode is determined. It was found that the critical values of voltage and current corresponding to a cease of electrolysis decrease with increasing temperature of the electrolyte. An increase in voltage is shown to result in a transition from electrolysis to current interruptions, then to stationary heating of the anode, then to a polishing mode and, ultimately, to a glow discharge mode, when the temperature of the ammonium sulphate solution is below 50 °C. Vice versa, no stationary heating mode occurs at solution temperatures above 50 °C; the current interruption mode goes directly to the polishing mode. It was established that the radiation of the anode zone in the stationary heating mode corresponds to the glow of two heated bodies, namely, a vapour-gaseous envelope and a metal anode. The radiation dynamics shows that heating of the low-inertia envelope precedes an increase in the temperature of the electrode, which confirms the transfer of heat from the envelope to the anode.

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