INFLUENCE OF ELECTROLYTE COMPOSITION ON THE ELECTROCHEMICAL SYNTHESIS OF PEROXYLACTIC ACID

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Peroxy lactic acid (PLA) is a strong disinfectant with a wide scale of antimicrobial activity. It is widely used as a disinfectant and antimicrobial agent in medicine and food industry; as a pasteurizer in breweries and wineries, as a bleaching agent in pulp, paper and textile industries; in chemical industry for the epoxy compounds synthesis etc. Hence, using of PLA is limited by its high price and short lifetime. Nowadays PLA can be produced by the chemical synthesis which includes the interaction between lactic acid (LA) and concentrated hydrogen in the area of acid catalyst (sulfuric acid) [1, 2].

Chemical formation of PLA is accompanied by losses of hydrogen peroxide, as soon as the final product requires using stabilizers and special storing conditions. Electrochemical technologies of producing of PLA directly at the point where it is supposed to be used eliminates the costs associated with chemical synthesis, transportation and storage [3-5]. Electrochemical synthesis will make it possible to produce PLA in the amount required for consumption.
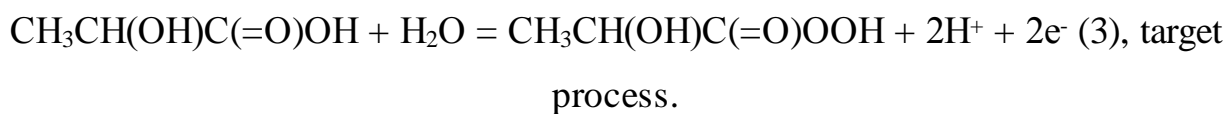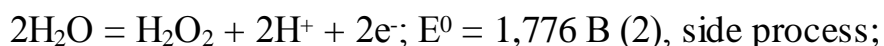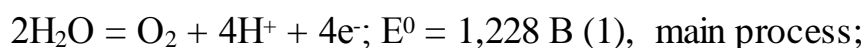
The goal of the current research is to establish the origin of substances involved in combined processes at the platinum anode in a wide range of lactic acid concentrations at high anodic potentials.

1. Methodology

Electrolytes are based on chemically pure concentrated lactic and sulfuric acids. Polarization measurements have been carried out at the potentiostat P-45X in an electrochemical cell at a temperature about 291 ... 295 K. Pure polished platinum anode has the reaction area of 1.13 cm2. The back and the end sides of the platinum anode have been insulated with a polymer coating. The auxiliary electrode is

platinum. The reference electrode is silver chloride, brought to the surface of the main anode with a glass key. All potential values are presented relatively to the hydrogen electrode. The concentration of the produced PLA and hydrogen peroxide was determined by iodometric titration [6].

Experimental results and their discussion. Electrolysis of aqueous solutions of lactic acid on a low-wear anode includes the following processes:

$$2H_2O = O_2 + 4H^+ + 4e^-; E^0 = 1,228 \text{ B (1), main process;}$$

$$2H_2O = H_2O_2 + 2H^+ + 2e^-; E^0 = 1,776 \text{ B (2), side process;}$$

$$CH_3CH(OH)C(=O)OH + H_2O = CH_3CH(OH)C(=O)OOH + 2H^+ + 2e^- \text{ (3), target process.}$$

Information about the standard reaction potential (3) is absent, both in reference literature and in professional scientific publications. A significant amount of research is devoted to the electrochemical synthesis of peroxyacetic acid (PAA). The research of the standard potential for the $CH_3C(=O)OH$ « $CH_3C(=O)OOH$ system was summarized by Zhang, Brownb and Hu in [7]. The proposed range covers 1.06 ... 1.96 V [1, 8-10]. The calculation of the redox potential for this reaction is not completely understandable. It is known that oxidation-reduction potentials depend significantly on the pH value. At the same pH values such potentials should have comparable values. The lack of information on the redox potentials of PAA, PLA and other peroxycarboxylic acids makes it impossible to analyze the course of the current-voltage lines for the electrochemical synthesis of such compounds.

Considering the fact that peroxycarboxylic acid is produced by the action of a concentrated solution of hydrogen peroxide (35 ... 50%) on concentrated solutions of the corresponding carboxylic acids in the area of catalyst (10 $g \cdot dm^{-3}$ H_2SO_4), redox compounds the potentials of peroxycarboxylic acids cannot exceed the redox potential of a concentrated hydrogen peroxide solution at pH »1.2.

In [11], the values of the enthalpy of dissociation of the O–O bond for $HC(=O)OOH$ i $CH_3C(=O)OOH$, are 48 $kcal \cdot mol^{-1}$ at 298 K. For H_2O_2 the enthalpy of dissociation of the O – O bond was 50 $kcal \cdot mol^{-1}$. The given data indicates the

similarity of the thermodynamic characteristics of the O – O bond, both in hydrogen peroxide and in peroxycarboxylic acids. However, this similarity of thermodynamic characteristics still excludes the traditional approach to the mechanism of peroxic compounds in the study of PLA formation mechanism

The given standard potentials of processes (2) and (3) are close and significantly exceed the standard potential of the oxygen reaction (1). Therefore, the electrochemical synthesis of PLA will be combined with the processes of oxygen release and the formation of hydrogen peroxide. It is known that part of hydrogen peroxide, due to low stability, will decompose on contact with platinum to form oxygen.

2. Results and discussion

To determine the parameters of the electrochemical synthesis of the target product, it was necessary to establish the conditions for controlling the combined anodic processes and to propose possible mechanisms of these processes at high anode potentials. In the current study we usedthe aqueous solutions of lactic acid (LA) with the concentration range of $0.5 ... 9$ mol dm^{3}, which corresponds to the range of pH = 1,4...2,7.

To achieve high anode potentials for the implementation of the process (1), an anode material with a high overvoltage of oxygen evolution, platinum, was chosen. In addition, the kinetics of the anodic process on platinum in acidic aqueous solutions has been well studied in a wide range of pH and potentials [3, 4, 12]. During the research, the anodic potentials were limited to $2.2 ... 2.5$ V to prevent the occurrence of the Kolbe, Gopher-Mesta reactions and the processes of substitution and addition [13, 14].

Figure 1 shows anodic current-voltage lines obtained on a platinum electrode in aqueous solutions of $0.5 ... 8.0$ mol dm^{-3} (LA) (Fig. 1, a) and with the addition of 0.5 mol dm^{-3} H$_2$SO$_4$ (Fig. . 1, b). The platinum anode already has a formed oxide layer and, therefore, the current is not consumed for the formation of a platinum oxide surface layer. The rise of the current density for the entire range of the studied

concentrations of lactic acid (Fig. 2, a) starts in the potential range of 1.40 ... 1.50 V (Fig. 1, a). That is, the appearance of the current, upon reaching this potential range, corresponds to the release of oxygen. To potentials of 1.6 ... 1.7 V, oxygen evolution proceeds with a significant overvoltage, which makes it possible to achieve the potentials of the formation of peroxide compounds.
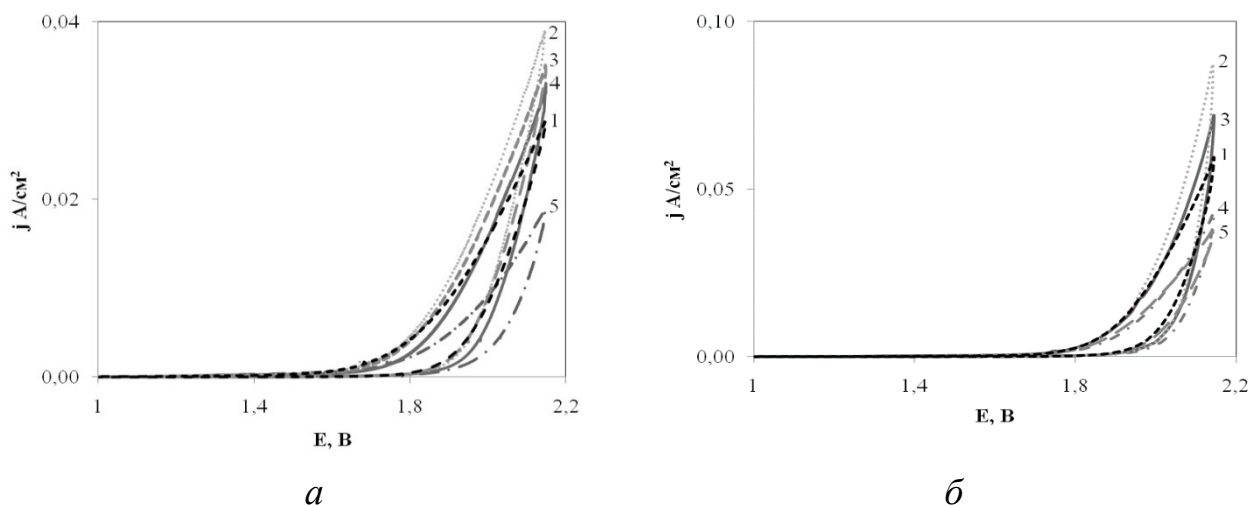

Fig. 1. Anodic polarization dependences on platinum in LA solutions (a) and in (LA) solutions with the addition of 0.5 mol·dm– 3 H_2SO_4 (b). Concentration of lactic acid mol·dm– 3: 1 - 0.5; 2 - 1; 3 - 2; 4 - 3; 5-4

The inflection of the current-voltage line at potentials above 1.70 ... 1.75 V (Fig. 1, a), indicates the course of the combined processes of the formation of peroxide compounds, proceeding with a significant inhibition of the oxygen reaction at the Pt/PtO_2 anode surface. The part of the current that is consumed for each of these processes can be determined from the results of the analysis of the amount of oxygen that was released, and H_2O_2 and PLA are produced The potential gap between the forward and reverse reactions of the current-voltage lines indicates a significant effect of LA on the adsorption processes on the anode surface. The results confirmed the validity of the choice of the Pt/PtO_2 anode for the electrochemical synthesis of PLA.

However, low current density values indicate the inexpediency of electrochemical oxidation of aqueous LA solutions without catalysts. Analysis of current-voltage lines 1, 4, 5 (Fig. 1, a) indicates a significant contribution of the

ohmic component to the potential leap at the electrode-electrolyte interface in LA solutions with low (0.5 mol dm^{-3}) and high (6, 0… 8.0 mol·dm^{-3}) concentrations. Raise of the LA concentration is followed by the displacement of water molecules from the anode water gets involved less in the anodic process. At low values of the anodic current density (0.01 A cm^{-2}), the potentials of the electrochemical synthesis of peroxide compounds are not achieved.

To increase the conductivity of aqueous solutions of lactic acid and inhibit the combined reaction of oxygen evolution there has been used an admixture of 0.5 mol dm^{-3} sulfuric acid. Sulfuric acid has been used for the chemical synthesis of peroxycarboxylic acids[15, 16]. The impurity concentration of 0.5 mol·dm^{-3} of sulfuric acid was substantiated in [17, 18].

The addition of 0.5 mol·dm^{-3} sulfuric acid to lactic acid solutions changes the course of the current-voltage lines of the anodic process (Fig. 2, b). The onset of the current rise is shifted by more than 300 mV to the positive side, which can be explained by the suppressing adsorption of sulfate ions on the Pt/PtO$_2$ anode surface. The adsorption of sulfate ions leads to the displacement of a certain proportion of water molecules beyond the boundaries between the phase boundaries. An almost twofold increase in the anodic current density was also noted at the potentials of the electrochemical synthesis of peroxide compounds.

To substantiate the working concentrations of LA in the electrolyte, the dependence of the current density at an anode potential of 2.0 V on the MC concentration was plotted (Fig. 2).
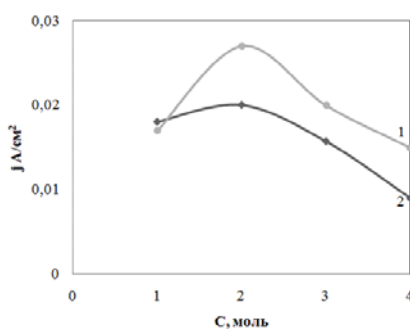

Fig. 2. Influence of the anode current density on the concentration of LA at an anode potential of 2.0 V. 1 – added 0.5 mol·dm $^{-3}$ H$_2$SO$_4$, 2 – without added H$_2$SO$_4$

This character of the lines, and the presence of a maximum value indicate the competitive effect of adsorption of LA molecules with solvent molecules on the Pt/PtO$_2$ anode surface. Considering the fact that at high anodic potentials (more than 2.2 ... 2.3 V), the beginning of the processes which are described by Kolbe reactions and the Gofer-Mest reaction, it is inappropriate to perform the electrolysis at such potentials, and choose. We consider as an appropriate the concentration of lactic acid 2 mol·dm^{-3}. To substantiate the mechanism of the anodic process, during the oxidation of aqueous solutions of LA, it is necessary to determine in what form LA takes part in the anodic process. But the process of oxidation of LA proceeds directly, due to the oxidation of the intermediate - with hydrogen peroxide, formed as a result of the anodic process.

The table shows the pH values for the studied LA solutions and the corresponding equilibrium potentials of the oxygen and peroxy-oxygen reactions for such pH values. Equilibrium potentials are given for PLA and H$_2$O$_2$ concentrations in 1 mol·dm^{-3}.

Table. pH value and equilibrium potentials of the studied system

Electrolyte content, mol·dm^{-3}		pH of the electrolyte	E_{H_2O/O_2}, V	E_{H_2O/H_2O_2}, V
MK	H$_2$SO$_4$			
0,5		2,08	1,105	1,653
1,0		1,93	1,114	1,662
2,0	–	1,78	1,123	1,671
3,0		1,69	1,128	1,676
4,0		1,63	1,132	1,680
0,5				
1,0				
2,0	0,5	0,30	1,210	1,758
3,0				
4,0				

The calculated values of the equilibrium potentials of oxygen and peroxy-oxygen reactions for the solutions under study make it possible to analyze the possibility of the course of combined reactions during the electrolysis of aqueous solutions of MC. Thus, for (Fig. 1, a), a significant inhibition of the oxygen reaction is observed. The displacement of the potentials of the appearance of the current, which corresponds to the release of oxygen, is 350 ... 400 mV through the inhibitory effect of the PtO_2 layer of the platinum anode and the high adsorption of LA. In LA solutions (researched concentrations), the potentials of the formation of hydrogen peroxide and PLA are achieved, but it is not possible to establish the current efficiency of these reactions. The addition of sulfuric acid to aqueous solutions of LA inhibits the oxygen release by the oxidation of water. An increase in the current (Fig. 2b) is observed at the potentials of the hydrogen peroxide reaction. Therefore oxygen in such electrolytes is produced from the hydrogen peroxide:

$$2H_2O = H_2O_2 + 2H^+ + 2e^-;$$
$$2H_2O_2 = O_2 + H_2O.$$
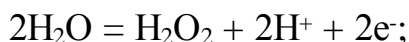
An important issue is to define the mechanism of LAoxidation. The distribution of acid-base forms of LA was calculated depending on pH (Fig. 3). The given distribution of forms as a function of pH indicates a large role of LA molecules in the anodic process.
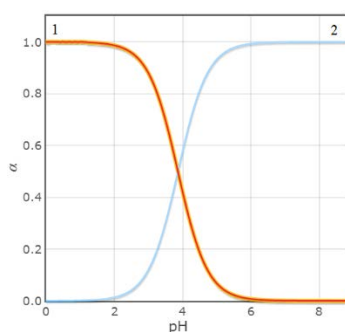

Fig. 3. - Distribution of acid-base forms of LA as a function of pH.
1 – $CH_3CH(OH)C(=O)OOH$, 2 – $CH_3CH(OH)C(=O)OOH^-$

For the further studies there has been chosen the following electrolyte composition: 2 mol·dm^{-3} LA, 0.5 mol·dm^{-3} H_2SO_4, the ionic form of LA does not

exist. The LA molecule has a dipole structure through the negative charge of the carboxyl group. Due to this, the LA molecule is incorporated into the structure of the near-electrode layer with a carboxyl group directed to the anode surface. Further research will be aimed at establishing the stages of oxidation of the carboxyl group in the LA molecule.

3. Conclusions

Due to the adsorption of LA on the surface of the PtO_2 layer of the platinum anode, the shift of potentials is 350 ... 400 mV and corresponds to the oxygen release. That allows to achieve the potential of peroxide formation. The addition of sulfuric acid to LA solutions shifts the potential of the current appearance to the positive area. The addition of 0.5 mol·dm^{-3} sulfuric acid to LA makes is possible to release oxygen through the formation of H_2O_2. It has been shown that the LA molecule gets incorporated into the structure of the near-electrode layer with a carboxylic group directed to the anode surface.

The composition of the electrolyte for the electrochemical synthesis of PLA has been substantiated as 2 mol·dm^{-3} LA, 0.5 mol dm^{-3} sulfuric acid. The anodic potential of the electrochemical synthesis of PLA is limited by the value of the Kolbe reaction potential for the chosen electrolyte.

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