THE CHOICE OF ANODE MATERIAL FOR THE ELECTROCHEMICAL SYNTHESIS OF PEROXYACETIC ACID

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A high-purity peroxyacetic acid may be produced electrochemically. The kinetics of anodic processes at electrolysis of acetic acid water solutions have been studied with application of different kinds of anodic materials. It has been shown that the formation of peroxyacetic acid is possible when the anodic potential is above 2,0 V. The choice of lead dioxide plated on titanium current-lead was justified. Application of lead dioxide in the electrochemical synthesis of peroxyacetic acid allows an increase in the current output up by 8-12 % compared to platinum.

Keywords: peroxyacetic acid, platinum anode, lead-dioxide anode, anodic process.

Peroxyacetic acid (PAA) is organic peroxide that belongs to strong oxidizers and may be used as a source of active oxygen. It is a strong disinfectant and it has a wide range of antimicrobial activities. Due to these properties peroxyacetic acid is mainly used in medicine and food industry. PAA is used as a pasteurizer at breweries and wineries, as a whitener in pulp and paper industry, for the synthesis of epoxy compounds etc.

However, the PAA cannot be widely used nowadays due to its high cost, limited production and short storage period. The PAA is obtained by chemical synthesis.

Application of electrochemical technologies for production the PAA in wide concentration range directly on the places of use excludes the storage and transport costs, and obtained acid may be used at once. The replacement of platinum with more affordable materials to increase the electrolysis efficiency is also a perspective way [1-3].

Research methodology
The electrolytes were obtained from pure concentrated acetic acid. The pH level of solution was determined using pH-150 M device.

The current-voltage curves were obtained by using a pulse potentiostat PP-50-1 and programmer PR-8. The potential scanning rate was 10 mV/s.

The polarization studies were performed in the electrochemical cell at 291 – 295 °K. The anode was made from platinum plate with a working surface of 1.32 cm^2 (version 1); from metal plate with lead-dioxide plating with a working area of 1 cm^2 (version 2). The platinum has been used as an auxiliary electrode. The reference silver chloride electrode has been connected to the anodic surface by glass key. All the potential values have been recalculated with reference to the hydrogen electrode.
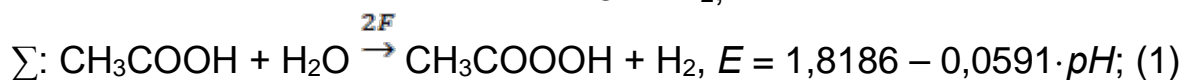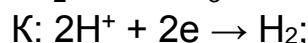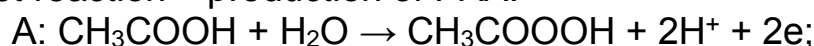
Results and Discussion

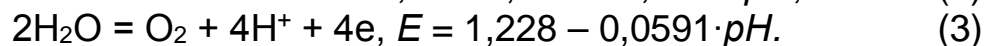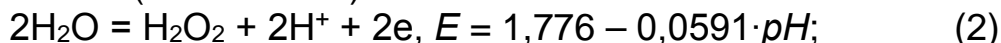The standard potential $E^0_{CH_3COOH/CH_3COOOH}$ is 1.82 V.

For realization of anodic processes the electrode materials should have a high oxygen overvoltage, that is why platinum and lead dioxide were chosen. These materials also have a high stability in the examined solutions.

The electrolysis processes are as follows:
1) target reaction – production of PAA:

A: $CH_3COOH + H_2O \rightarrow CH_3COOOH + 2H^+ + 2e$;

K: $2H^+ + 2e \rightarrow H_2$;

$\sum$: $CH_3COOH + H_2O \xrightarrow{2F} CH_3COOOH + H_2$, $E = 1,8186 - 0,0591 \cdot pH$; (1)

2) side reaction (or combined):

$2H_2O = H_2O_2 + 2H^+ + 2e$, $E = 1,776 - 0,0591 \cdot pH$;   (2)
$2H_2O = O_2 + 4H^+ + 4e$, $E = 1,228 - 0,0591 \cdot pH$.   (3)

In order to increase the current output of electrochemical synthesis of PAA we should apply the anode with polished surface and oxygen inhibitors. Thus, thiocyanates, chlorides, iodides and fluorides may be applied as inhibitors.

To determine the parameters of electrochemical synthesis we should establish the nature of substances involved into anodic process.

Figure 1 represents E-pH diagram for the system $CH_3COOH-H_2O$. Line 1 corresponds to the formation of PAA according to equation (1); line 2 corresponds to the formation of hydrogen peroxide according to equation (2); line b corresponds to the reaction of oxygen formation (equation 3). Having analyzed the diagram E-pH (pic. 1) for the range of acetic acid concentrations of 0,5–9,0 mol/dm^3 (pH = 1,4-2,7), we have made a conclusion that the target product (PAA) may be produced at potentials that are higher than hydrogen peroxide formation potential and, as a result, the formation of PAA may be performed through the following mechanism:

$CH_3COOH + H_2O_2 \leftrightarrow CH_3COOOH + H_2O$.   (4)

231

That is to say the target product may be produced as a result of two parallel reactions.
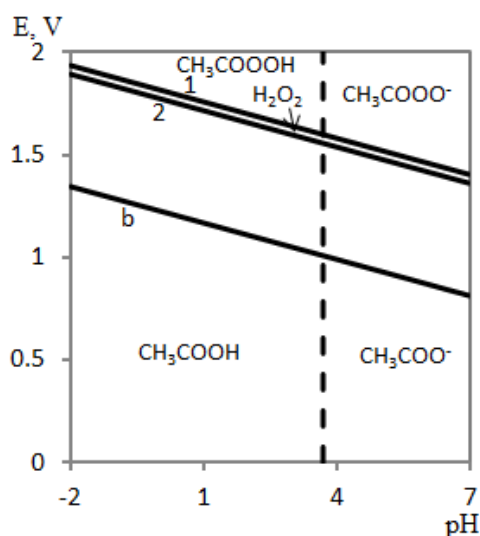

Figure 1. Diagram E-pH for the system CH₃COOH-H₂O

Table 1 represents the influence of anodic potential on $\dfrac{d\lg j}{d\lg C}$ (the kinetic parameters were defined from the current-voltage curves for platinum electrode).

Table 1. Influence of the anodic potential on $\dfrac{d\lg j}{d\lg C}$

E, V	1.8	1.9	2.0	2.2	2.6
$\dfrac{d\lg j}{d\lg C}$	1.25	0.86	0.81	0.77	0.68

Based on table 1 we can conclude that at potentials above 1.8 V the kinetic parameters of anodic process change rapidly. The oxygen reaction performs primarily at the potentials below 1.8 V. The combined processes perform at higher potentials, in particular the formation of hydrogen peroxide, PAA and ozone. The concentration of acetic acid also has a great influence on the current output of the combined processes.

Figure 2 represents the anodic potentiodynamical curves which were obtained on the platinum anode in the acetic acid without (a) and with potassium thiocyanate addition (b).

With the increase of the acetic acid concentration the current density decreases. On the one hand, this is due to the change of the acetate ions concentrations in CH₃COOH molecules, but on the other

hand this is due to the change of pH solutions. The paper [4] shows that the solutions of CH₃COOH with concentration of 2.1–4.5 mol/dm³ have the highest electrical conductivity. Considering this fact we suggest that the formation of peroxide in this concentration range performs with the presence of acetate ion in anodic reaction. At the higher concentrations of CH₃COOH the formation of peroxide performs through the chemical stage (4).
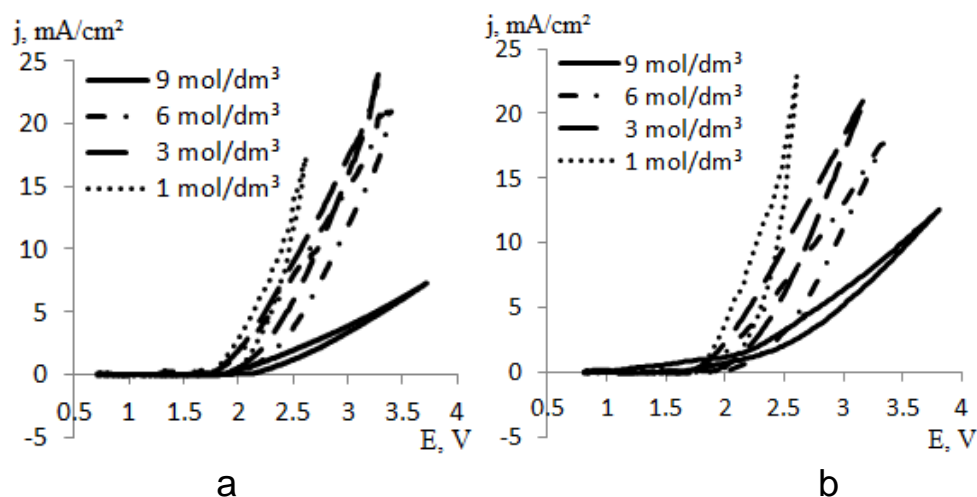

Figure 2. Anodic polarization curves on the platinum in the acetic acid without (a) and with potassium thiocyanate addition (b)

Figure 3 represents the anodic potentiodynamical curves obtained on the lead-dioxide electrode in the acetate acid solutions without (a) of with potassium thiocyanate addition (b).
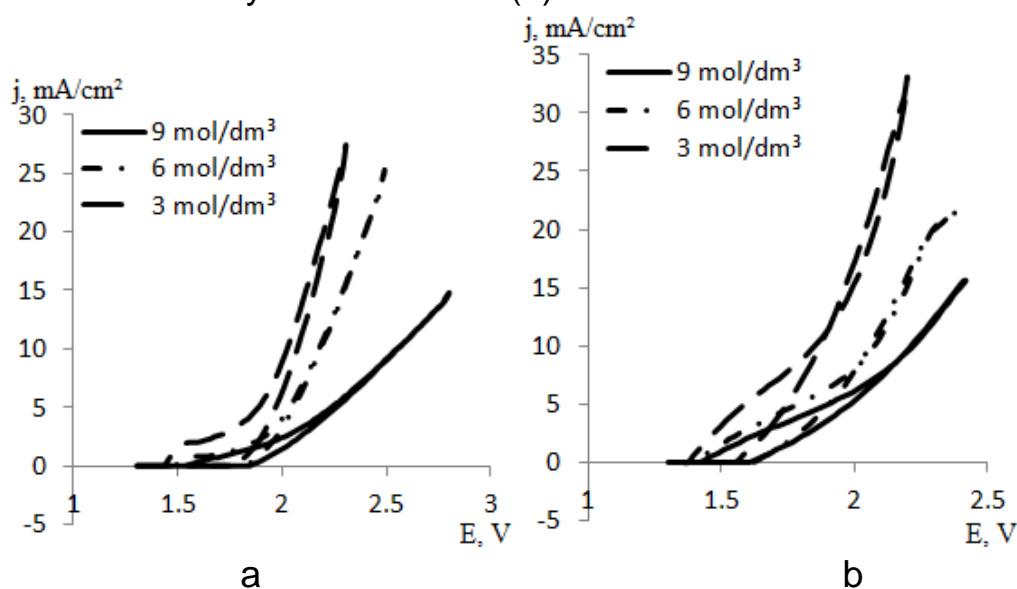

Figure 3. Anodic polarization curves on the lead-dioxide electrode in the acetate acid solutions without (a) and with potassium thiocyanate addition (b)

The kinetics of the anodic processes on platinum and lead-dioxide anodes is described in detail in [5-6]. According to these articles, we may

claim that the speed of the electrochemical processes on lead-dioxide anode is higher than on platinum and these processes occur at the lower anodic potentials. In this case, the application of lead-dioxide anode is very promising for acetic acid solutions electrolysis.

Having analyzed the diagram E-pH of the system CH_3COOH-H_2O (Fig. 1) and the current-voltage curves obtained on PbO_2 (Fig. 3), we can make the following conclusion: it is expedient to carry out the electrochemical synthesis of PAA in the range of anodic current densities about 90-180 A/m^2.

Conclusions

Electrochemical synthesis of PAA requires the application of anodic materials which have a high value of oxygen over-voltage and high adsorption properties in respect to acetate-ions. The investigation of kinetics of acetic acid electrolysis have shown that the application of PbO_2 as an anodic material allows higher current densities compared to platinum.

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