

Mineralization of Formic Acid by the OH[·] and HO₂[·] Intermediates Generated *in situ* from H₂O and H₂O₂ in a Membrane-Free Electrolyzer in Electrolytes with Different pH

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Abstract

The conditions of indirect destructive oxidation of formic acid to CO₂ and H₂O by OH[·] and HO₂[·] intermediates generated from water and hydrogen peroxide in an electrolyzer without a membrane in the electrolytes with different pH are described. The effect of cathode current density and pH of the medium on the conversion of formic acid is investigated. It is shown that the conversion of formic acid in acidic electrolytes is higher than in alkaline ones and accounts for 99 % at pH 3.2.

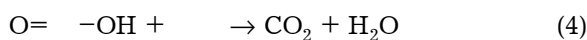
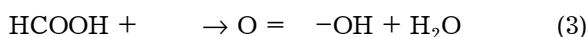
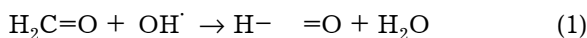
INTRODUCTION

Electrochemical purification of waste water relates to ecologically safe technologies allowing one to generate the media with required composition and properties with a minimal amount of reagents [1]. At present, the problem involving purification of waste waters of different origin from formic acid does not decrease its urgency because formic acid is the strongest toxic agent and intermediate product of the oxidation of formaldehyde and methanol.

A large number of works dedicated to the oxidation of formic acid and its salts [2–4] show that the main reaction products are CO₂ and H₂O. However, in those investigations the major attention is paid to the direct oxidation of formic acid on the electrodes made of platinum group metals at low current density (10⁻³–10 mA/cm²) which is of no interest for the industrial application. In addition, the direct anode oxidation turns out to be successful not in all the cases because the oxidation of

formic acid is preceded by its adsorption, and then chemisorption on the electrode surface, which causes non-reproducibility of the results with respect to oxidation and destruction degrees.

In [5] we have made an attempt to mineralize formaldehyde by hydrogen peroxide generated from oxygen in carbon-black gas diffusion electrode in the presence of Fe(II) salts in acidic electrolytes where the formation of hydroxyl radicals occurs (Fenton's reagent). It was established that the hydroxyl radicals efficiently oxidize formaldehyde to CO₂ and H₂O with an intermediate formation of formic acid *via* the reactions:

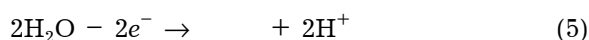


However, introduction of a salt of heavy metal (FeSO₄ · 7H₂O) into the reaction system

decreases ecological attraction of this process for practical implementation.

An analog of the above-presented system can be the process in a membrane-free electrolyzer combining generation of radicals from water at the anode with the generation of H_2O_2 from O_2 in the carbon-black gas diffusion cathode.

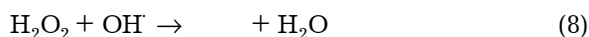
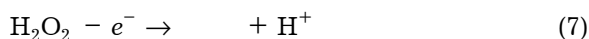
It is known that under the conditions existing in electrochemical cell the radicals can be generated by means of anode oxidation of water in acidic medium according to reaction [6]



and in alkaline media according to reaction



In addition, the generation of HO_2 radicals is possible *via* reactions [6]



So, destructive oxidation of formic acid is possible without introducing Fe(II) salt in an electrochemical cell without a membrane, equipped with gas diffusion carbon-black electrode, with anodic generation of highly reactive intermediates and .

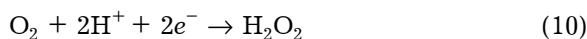
The goal of the present work is the investigation of destructive oxidation of formic acid by and intermediates generated *in situ* from H_2O and H_2O_2 in a membrane-free cell with electrolytes characterized by different pH values.

EXPERIMENTAL

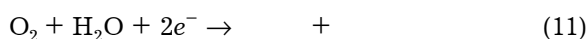
A two-chamber glass electrolyzer cell with non-separated cathode and anode space consisting of the gas and electrolyte chambers was used to carry out electrolysis and to obtain H_2O_2 . The cathode was a carbon-black gas diffusion hydrophobized electrode, and the anode was a platinum plate. The procedure of manufacturing gas diffusion electrodes was described in [7, 8]. Before the start of experiments, the electrodes were impregnated with

electrolyte under carrying current. Oxygen was admitted into the electrode continuously through a gas chamber under atmospheric pressure with a small excess which was evolved into the atmosphere. In all the experiments, the electrolyte was permanently mixed by bubbling argon through the electrolyte chamber. Electrolytes (with a volume of 30 ml) were aqueous solutions: 0.45 M K_2SO_4 + 0.05 M H_2SO_4 (pH 2.2), 0.495 M K_2SO_4 + 0.005 M H_2SO_4 (pH 3.2), 0.4975 M K_2SO_4 + 0.0025 M H_2SO_4 (pH 4.2), 0.0005 M NaOH + 0.4995 M Na_2SO_4 (pH 10.6), 0.05 NaOH + 0.495 M Na_2SO_4 (pH 12.1), 0.05 M NaOH + 0.45 M Na_2SO_4 (pH 13.0), 0.25 M NaOH (pH 14.0). The cathode potential was measured with respect to the saturated silver chloride reference electrode. Current density was calculated per unit visible front surface of the electrode; its area was 5 cm².

Potentiodynamic polarization curves were recorded with the potential scanning rate of 4 mV/s. Preparative electrolysis was carried out in the galvanostatic mode at 20 °C for 1 h. Cathode potential was -0.4...-0.6 V in all the cases. At the beginning of each experiment, the fraction of current γ [9] consumed for the reaction was determined using gasometric procedure, in the acidic medium [10]:



and in alkaline medium [10]:



Model solutions with the initial concentration of formic acid in electrolyte 0.5 g/l were used for oxidation. The concentration of formic acid was determined by back titration with potassium permanganate [11]; the concentration of hydrogen peroxide was determined by titration with potassium permanganate according to a standard procedure [12]. Before analyzing formic acid, we decomposed the hydrogen peroxide remaining in the electrolyzer after electrolysis in order to avoid errors in precise quantitative determination of formic acid. The following method was used for hydrogen peroxide decomposition. An excess of 1 M NaOH solution was added into each sample of the solution and heated with a boiling water bath for 10 min. This allowed decreasing H_2O_2 concentration in electrolyte down to zero. Carbon

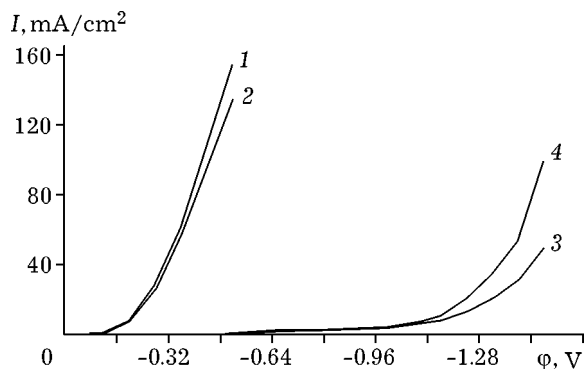


Fig. 1. Polarization curves of the gas diffusion carbon-black electrode with oxygen feeding into the cathode (1, 2) and without oxygen feeding in (3, 4) in the electrolyte of the composition 0.45 M K_2SO_4 + 0.005 M H_2SO_4 and with formic acid added ($[HCOOH] = 0.5$ g/l) (2, 4).

dioxide evolved during electrolysis was detected with lime water turbidity during passing the gases leaving the electrolyte chamber of the electrolyzer [13].

RESULTS AND DISCUSSION

First of all, we investigated the stability of the cathode generation of H_2O_2 from O_2 in the carbon-black gas diffusion electrode in acidic medium in the presence of formic acid in a membrane-free cell. Figure 1 shows the polarization curves obtained on the cathode, with feeding oxygen into the electrode (curves 1, 2) and without feeding it in (curves 3, 4) in the electrolyte of the composition: 0.45 M K_2SO_4 + 0.05 M H_2SO_4 with formic acid added into it ($[HCOOH] = 0.5$ g/l) (curves 2, 4). One can see that the reduction of oxygen in gas diffusion cathode occurs with insignificant polarization, and the presence of formic acid in the electrolyte has almost no effect on the electrode performance.

It follows from the analysis of curves 3 and 4 (see Fig. 1) that in the case when oxygen is not fed into the gas diffusion cathode formic acid decreases its polarization substantially. It may be assumed that formic acid is reduced to form formaldehyde [3].

The current efficiency for H_2O_2 in the electrolyte without formic acid at the current density of 100 mA/cm² within the first hour of electrolysis was 46–48 %, and its concentration was 4.9–5.1 g/l within pH range 2.2–4.2. Under

similar conditions in the electrolyzer with a membrane, the current efficiency for H_2O_2 was 96–99 %, and its concentration was 14.51–15.13 g/l. We believe that such a substantial decrease in the current efficiency for H_2O_2 and lower concentration in membrane-free electrolyzer are connected with the oxidation of hydrogen peroxide at the anode (eqn. (7)) and interaction with OH⁻ radicals (eqn. (8)). It is necessary to note that in the presence of formic acid, the fraction of current which was consumed for the reduction of oxygen to H_2O_2 , as determined by means of gasometry [9] at the beginning of all the experiments, was 96–98 %. Similar results were obtained also for the processes in alkaline media.

Figure 2 shows the effect of the cathode current density on the conversion of formic acid in the experiments with oxygen supplied into the cathode, with the electrolyte containing 0.495 M K_2SO_4 + 0.005 M H_2SO_4 with formic acid added ($[HCOOH] = 0.5$ g/l). One can see that the conversion of formic acid increases with an increase in current density up to 100 mA/cm², then it reaches its maximum and remains unchanged further on. That is why all the further experiments were carried out in galvanostatic mode with current density 100 mA/cm². We suppose that an increase in the rate of formic acid destruction with an increase in current density is connected with an increase in the concentrations of and radicals in the anode layer.

The results of experiments in acidic and alkaline media under oxygen feeding into the carbon-black gas diffusion cathode (GDC) and without oxygen fed are shown in Table 1.

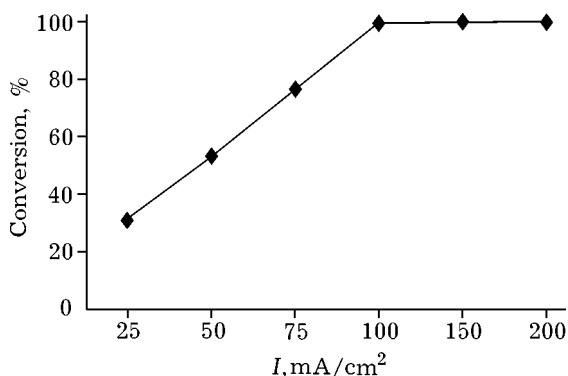


Fig. 2. Effect of current density on the conversion of formic acid.

TABLE 1

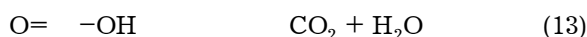
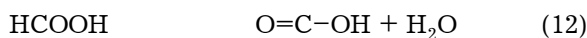
The results of experiments on the oxidation of formic acid with oxygen feeding into the GDC and without feeding it ($[\text{HCOOH}] = 0.5 \text{ g/l}$)

Electrolyte	pH	$[\text{H}_2\text{O}_2]$, g/l, residual	HCOOH conversion, %	Oxygen feed
<i>Acidic medium</i>				
0.45 M K_2SO_4 + 0.05 M H_2SO_4	2.2	0.564	85	Yes
		–	70	No
0.495 M K_2SO_4 + 0.005 M H_2SO_4	3.2	0.500	99	Yes
		–	90	No
0.4975 M K_2SO_4 + 0.0025 M H_2SO_4	4.2	0.554	88	Yes
		–	75	No
<i>Alkaline medium</i>				
0.0005 M NaOH + 0.4995 M Na_2SO_4	10.6	0.850	81	Yes
		–	63	No
0.005 M NaOH + 0.495 M Na_2SO_4	12.1	1.55	75	Yes
		–	63	No
0.05 M NaOH + 0.45 M Na_2SO_4	13.0	1.87	74	Yes
		–	58	No
0.25 M NaOH	14.0	3.40	74	Yes
		–	62	No

It should be noted that in all the experiments performed with oxygen feeding in, the presence of residual H_2O_2 and evolution of carbon dioxide (turbidity of lime water observed within 20 min after the start of experiment) were detected in the electrolyte after electrolysis. These results are the evidence of destructive oxidation of formic acid to CO_2 and H_2O . The presence of H_2O_2 in the electrolyte after electrolysis proves that not the whole amount of H_2O_2 is consumed for the reaction with formic acid. Attention should be paid to the fact that the amount of non-consumed H_2O_2 increases in alkaline media with an increase in pH. It is probable that additional investigations aimed at an increase in the efficiency of the consumption of electrolytically generated hydrogen peroxide are necessary.

One can see in Table 1 that both in acidic and in alkaline media the conversion of formic acid is higher with oxygen feed in the electrode, which is likely to be due to the formation of an additional oxidizing intermediate in the system. The conversion of formic acid in acidic media is higher than in alkaline ones. It is possible that in alkaline medium preferably OH^\cdot radicals are generated at the

anode according to reaction (9), while reaction (6) giving raise to OH^\cdot radicals is suppressed. It is known that the reactivity of OH^\cdot radicals is 5–6 orders of magnitude lower than that of H_2O_2 radicals [14]. In addition, for different organic substances, an increase in the rate of electrolytic oxidation is observed at pH close to the pK of dissociation for this substance. For formic acid, pK of dissociation is equal to 3.75 [4]. We suggest that one of the possible schemes of the oxidation of formic acid with H_2O_2 and OH^\cdot radicals can be represented as follows:



CONCLUSIONS

1. The possibility of destructive indirect oxidation of formic acid with H_2O_2 and OH^\cdot intermediates generated *in situ* from H_2O_2 and H_2O in an electrolyzer without a membrane in electrolytes with different pH was established.

2. The conversion of formic acid is higher in acidic electrolytes than in alkaline ones and makes up 99 % at pH 3.2.

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