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Pilot Laboratory Electrolyzer for Electrosynthesis of Hydrogen Peroxide in Acid and Alkaline Solutions

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Abstract—Results of a preparative electrosynthesis of hydrogen peroxide by cathodic reduction of oxygen in a carbon black gas-diffusion electrode in acid and alkaline electrolyte solutions in a versatile pilot laboratory three-chamber electrolyzer are presented.

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Hydrogen peroxide as a high-potential redox agent possesses a number of unique properties. It is well soluble in water and nonpoisonous. No dangerous waste is formed upon its application because its decomposition yields water and oxygen. Hydrogen peroxide has a considerable oxidizing capacity and enables oxidation of various organic and inorganic compounds in both alkaline and acid media: $E°H_2O_2/H_2O = 1.776$ V in acid media and $E°H_2O_2/OH^- = 0.88$ V in alkaline media [1, 2]. The applicability field of hydrogen peroxide is unusually wide because of its being an ecologically clean oxidizing agent [1, 2].

In the last 20 years, a strong interest has been expressed in processes for indirect oxidation of organic and inorganic substances with hydrogen peroxide electrochemically generated from oxygen under in situ conditions [3–8]. This is due to the orientation of modern chemical industries to wide use of principles underlying conjugated processes [9] involving ecologically clean reagents, such as electric current and chemically bound active forms of oxygen (O_3, H_2O_2, HO., HO_2^-, HO_2., ROOH) [4, 7]. Based on a number of foreign reports, researchers come to a conclusion that hydrogen peroxide is a key reagent for development of high-efficiency advanced oxidation processes [3, 8, 10]. However, wider use of hydrogen peroxide in the national economy is limited by its comparatively high cost in manufacture by the conventional techniques [2].

It is known [3, 11, 12] that hydrogen peroxide s comparatively easily obtained by cathodic reduction of oxygen on carbon-graphite electrodes in alkaline solutions (Berl's process)

$$O_2 + 2e + H_2O \rightarrow HO_2^- + OH^- ,$$

and in acid solutions by the reaction

$$O_2 + 2H^+ + 2e = H_2O_2 .$$

This method is waste-free and makes it possible to obtain H_2O_2 at the consumption site in the form of aqueous solutions and use these solutions as a commercial product without preliminary isolation of H_2O_2, which substantially diminishes its cost [2, 3, 11, 12].

The solubility of oxygen in aqueous electrolyte solutions is low (approximately 10^{-3} M), and, therefore, the process of oxygen electroreduction on smooth electrodes is limited by the diffusion of the reagent to the electrode surface. The formation rate of hydrogen peroxide is comparable with the rate of the competing reactions and, therefore, the current efficiency by hydrogen peroxide is not high. Technologically admissible current densities can be reached by using high pressures; however, this approach is technically difficult to be implemented. Therefore, in electrosynthesis of hydrogen peroxide, precautions should be taken to eliminate diffusion limitations by oxygen by developing the contact area between the electrolyte, electrocatalyst, and reagent, as, e.g., this is done in bulk electrodes [13–15]. However, the most promising for this process are hydrophobized 3D gas-diffusion electrodes [3, 4, 12, 16, 17]. As is known, a highly developed electrocatalyst–electrolyte–reagent contact surface stable in the course time is created in electrodes of this kind automatically because of the capillary equilibrium and there are reliable channels for delivery of the reagent and electrolyte to this contact surface at a nearly zero pressure drop [4, 17].

In this communication, we present results of a preparative electrosynthesis of hydrogen peroxide in a pilot laboratory three-chamber electrolyzer by cathodic reduction of oxygen on a two-layer carbon black gas-diffusion electrode in acid and alkaline electrolyte solutions.

EXPERIMENTAL

A filter-press electrolyzer, fabricated from methyl methacrylate, comprised gas, anode, and cathode chambers. The gas-diffusion electrode (GDE) was situated between the gas and cathode chambers. The anode and cathode chambers were separated by an MK-40 cation-exchange membrane. As the cathode was used a double-layer hydrophobized electrode with a thickness of 2–2.2 mm, working surface area of 64 cm^2, and total porosity of 60–65 vol %. A437E acetylene black with 10–15 wt % fluoroplastic served as the working layer, and A437E black with 70 wt % fluoroplastic, as the blocking layer. The mass ratio of the working and blocking layers was 3 : 10. A stainless steel wire frame was in the middle of the blocking layer. The double-layer electrode was fabricated by the method described in detail in [18]. A ruthenium-titanium anode (ORTA) was used. The catholyte volume was 0.25 l. The cathode and anode chambers were cooled by water flowing through a glass cooling coil. The assembly was tightened using screw clamps and pins. The electrolyzer is shown schematically in Fig. 1.

We performed preparative electrosyntheses of hydrogen peroxide from oxygen in an acid electrolyte solution of composition (M): 0.2 H_2SO_4 + 0.5 K_2SO_4 + 0.01 TBABr (tetrabutylammonium bromide) with pH 1.4 and in an alkaline electrolyte of composition 0.5 M NaOH + 0.2% Na_2SiO_3, pH 14. Electrolysis conditions: total current 7 A; current densities 110 and 50 mA cm^{-2} for the acid and alkaline electrolytes, respectively; cathode chamber temperature 27°C. Oxygen (technical grade) was delivered from a cylinder into the electrode from its backside under atmospheric pressure.

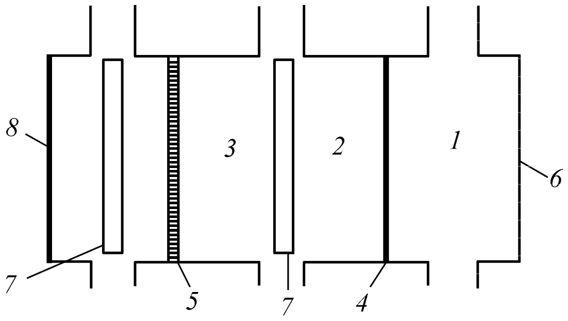

Fig. 1. Schematic of the pilot laboratory electrolyzer with a gas-diffusion electrode for electrosynthesis of hydrogen peroxide from oxygen. (*1*) Gas (oxygen) chamber, (*2*) cathode chamber, (*3*) anode chamber, (*4*) gas-diffusion electrode, (*5*) cation-exchange membrane, (*6*) methyl methacrylate case of the electrolyzer, (*7*) glass coils for cooling of the cathode and anode chambers, and (*8*) ORTA anode.

To determine the content of H_2O_2 in the electrolyte, we thoroughly agitated it with air every hour, took a sample, and titrated it with potassium permanganate. The results of electrosynthesis are presented in Figs. 2a and 2b, which shows the kinetic curve of H_2O_2 accumulation and the curve of the corresponding variation of the current efficiency. It can be seen in Fig. 2a that the experimental kinetic curve of H_2O_2 accumulation in the acid catholyte almost coincides with the run of the curve calculated by the equation [12, 19]:

$$c = \frac{AI\gamma}{kv}(1 - \mathrm{e})^{-k\tau} \quad \text{at} \quad V_\mathrm{d} = kc \quad \gamma = \text{const}, \tag{1}$$

Here, c is the concentration of H_2O_2 in the catholyte (M); I, electrolysis current (A); ν, catholyte volume (l); γ, fraction of current consumed for O_2 reduction to H_2O_2; τ, electrolysis duration (h); k, rate constant of H_2O_2 decomposition (h^{-1}); V_d, rate of H_2O_2 decomposition (M h^{-1}); and A, electrochemical equivalent of H_2O_2 (mol A^{-1} h^{-1}).

The experimental accumulation curves were used to calculate k and γ by the procedure described in [19]. The constant k is the overall rate constant of H_2O_2 decomposition in the electrolyte bulk and on the electrolyzer walls and membrane. The current

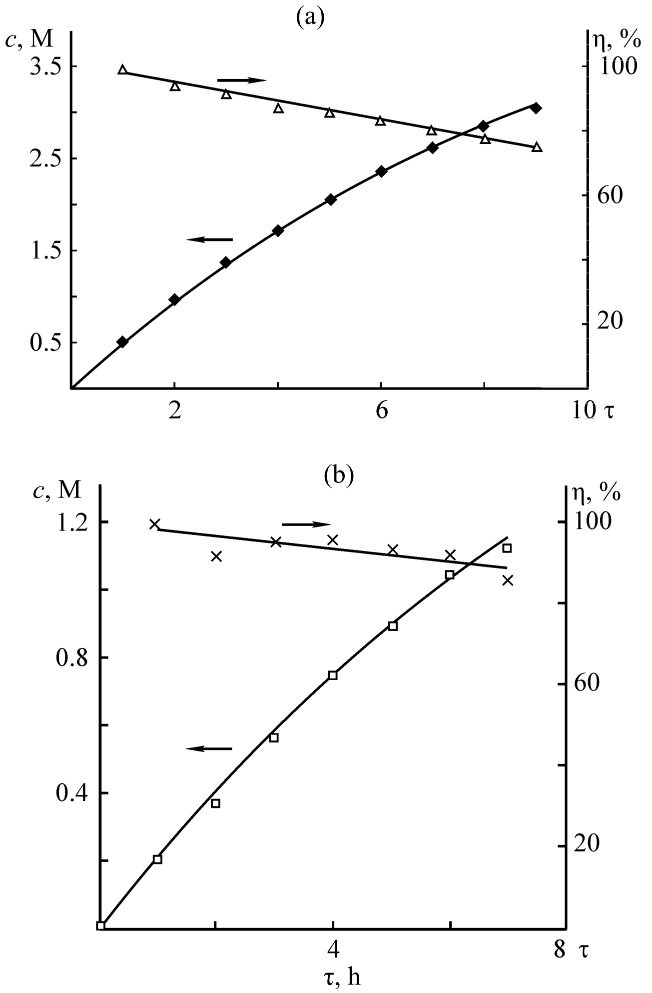

Fig. 2. Concentration c and current efficiency by H_2O_2 (η) in electrosynthesis from O_2 vs. the electrolysis duration τ. Solution composition (mol g^{-1}): (a) $0.2H_2SO_4 + 0.5K_2SO_4 + 0.05TBABr$ and (b) $0.5NaOH + 0.2\%\ Na_2SiO_3$. Points on the dependence of concentration, experimental values; line, calculation by Eq. (1) at (a) $k = 0.1\ h^{-1}$ and $\gamma = 0.99$ and (b) $k = 0.09\ h^{-1}$ and $\gamma = 0.93$.

efficiency (CE) by H_2O_2 was calculated from the H_2O_2 concentration in the catholyte, catholyte volume, and quantity of passed electricity. The value of γ depends both on the reaction of H_2O_2 reduction to water and on the decomposition rate of hydrogen peroxide within pores of the electrode to oxygen, which undergoes repeated reduction [12]. Thus, the value of γ reflects only process occurring in the electrode, and the current efficiency is related both to γ and to processes occurring in the catholyte chamber of the electrolyzer.

It is known that the process of hydrogen peroxide accumulation in acid electrolytes in electroreduction of oxygen depends on the relative rates of the following reactions of oxygen reduction and H_2O_2 decomposition [12, 19].

$$O_2 + 4H^+ + 4e = 2H_2O, \tag{I}$$

$$O_2 + 2H^+ + 2e = H_2O_2, \tag{II}$$

$$H_2O_2 + 2H^+ + 2e = 2H_2O, \tag{III}$$

$$2H_2O_2 = 2H_2O + O_2. \tag{IV}$$

It was found that, in the course of 9 h, the increase in the concentration of hydrogen peroxide in the catholyte and the decrease in the current efficiency result in that the rate of H_2O_2 accumulation decreases from 2 to 0.9 mmol cm^{-2} h^{-1} per unit geometric surface area of the electrode, or from 0.13 to 0.06 mol h^{-1} for the whole electrode. It can be seen in Fig. 2a that, after 9 h of electrolysis, the concentration of hydrogen peroxide in solution was 3.0 M and the current efficiency is about 80%.

It is known that decomposition of hydrogen peroxide is a rather complex process that depends on numerous factors [1, 2, 19–21]. The decomposition rate of hydrogen peroxide in an alkaline medium can be formally described by various equations:

$$V_d = kc\ [19], \tag{2}$$

$$V_d = kc_{und} + k_0\ [21], \tag{3}$$

$$V_d = kc_{und}c_p\ [22], \tag{4}$$

where c is the total concentration of H_2O_2; c_{und}, concentration of the undissociated part of H_2O_2; c_p, concentration of peroxide ions (HO_2^-); and k and k_0, constants.

However, it can be considered in the presence of Na_2SiO_3, a decomposition stabilizer for hydrogen peroxide, that the decomposition rate is described by Eq. (2) and the kinetics of H_2O_2 decomposition is also described by Eq. (2). This is indicated by the run of the experimental accumulation curve in Fig. 2b. It can be seen that electrolysis for 7 h in an alkaline electrolyte (0.5 M NaOH + 0.2% Na_2SiO_3) at a current density of 50 mA cm^{-2} yields a hydrogen peroxide solution with a density of 11 M and a current efficiency of 86%. In 7 h, the rate of H_2O_2 accumulation decreases from 0.06 to 0.019 mol h^{-1}. On replacing oxygen with air, the current efficiency decreases by 30% on average.

CONCLUSIONS

The preparative electrosyntheses of hydrogen peroxide by cathodic reduction of oxygen in a carbon black double-layer gas-diffusion electrode, performed in the study, demonstrated that a simple pilot laboratory three-chamber electrolyzer is highly efficient for obtaining acid solutions with a concentration of 3 M at a current efficiency of 75.0% and a current density of 110 mA cm^{-2} in the course of 9 h and alkaline solutions with a concentration of 1.1 M at a current efficiency of 86.0% and current density of 50 mA cm^{-2} in 7 h.

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