SYNCHRONOUS ELECTROSYNTHESIS OF HYDROGEN PEROXIDE AND OZONE

1. Topological model

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The regularities of the influence of the modification of the surface layer of tissue carbon and graphite fibrous materia on the composition, the amount of superficial functional oxygen-containing groups by different methods have been studied. The relationship between the electrocatalytic and corrosion characteristics of cathodes from tissue carbon and graphite fibrous materia has been established during electrosynthesis of \( \text{H}_2\text{O}_2 \). They were tested during electrosynthesis of \( \text{H}_2\text{O}_2 \) in a diaphragm cell with a current load of up to 100 A. A topological model of synchronous electrosynthesis hydrogen peroxide and ozone was developed.

Keywords: electrosynthesis, hydrogen peroxide, ozone, topological model.

Introduction

Hydrogen peroxide (\( \text{H}_2\text{O}_2 \)) today is one of the most perspective products among other chemicals. Interest to it is due to successful combination of physical and chemical properties and high ecological safety of decomposition products – water and oxygen.

In the world market of industrial \( \text{H}_2\text{O}_2 \) production three main technologies prevail [1]: by anthraquinone, by isopropyl and electrochemical one. In Russia 94% of the market of production of \( \text{H}_2\text{O}_2 \) is carried out by an isopropyl methode (KHIMPROM) and only 3% of the market – by electrochemical method. On this technology \( \text{H}_2\text{O}_2 \) is produced through oxidation on Pt anodes solutions of sulfuric acid or its salts to persulphates which then hydrolyzed and distilled with sharp steam, receiving \( \text{H}_2\text{O}_2 \).

Power and operational expenses at the same time are high. By data [1] they make up to 40% of prime cost of \( \text{H}_2\text{O}_2 \). Besides, the traditional electrochemical technology ecologically is also dangerous because of formation of considerable volumes of molecular hydrogen and application of Pb as the cathodic material. However the electrochemical technology allows to receive the cleanest \( \text{H}_2\text{O}_2 \), with a wide range of concentration from 30% to 98%. Sales market of the electrochemical \( \text{H}_2\text{O}_2 \) – pharmaceutics, medicine, electronics and radio engineering, the space equipment etc. In this regard the problem of improvement of electrochemical production of \( \text{H}_2\text{O}_2 \) is very relevant.

Experiment part

Experiments were carried out in the laboratory electrochemical cell with cathode made from the carbon – graphite fibrous material of tissue structure reinforced in the Ni grid (UGVMt-Ni) (Figure 1). In the experiments processes of modifying surface of UGVMt and also electrosynthesis of \( \text{H}_2\text{O}_2 \) were investigated. The cathodic and anodic spaces are divided by a cation-exchange membrane MF-SK.

Composition of the surface layer of UGVMt was investigated by method of the reverse titration by the bases of NaHCO₃, Na₂CO₃, NaOH [2]. Several functional groups with various acidity are distinguished as results of sodium–hydrogen exchange.

In Figure 2 the module – electrolyzer for current loading up to 100 A is shown in which we carried out synchronous receiving \( \text{O}_3 \) and \( \text{H}_2\text{O}_2 \).
Catalytic covering of the anode was Pt, and the cathode material – UGVMt-Ni. The anode and cathodic spaces are divided by cation-exchange membrane. As anolyte 5 m NaClO₄ and as catholyte – 1% NaOH solutions were used. All applied solutions were prepared from reactants of the brand "chemically pure".

**Results and discussion**

Earlier in [3, 4] we considered the possibility of intensification of technology of electrochemical production of H₂O₂. Main attention was concentrated on creation of highly effective, cheap electrode materials. The following industrially released carbon materials were investigated: for anode – glassy carbon, and for cathode – carbon-graphite fibrous material of fabric structure. The surface of the specified electrode materials was exposed to chemical and electrochemical modifying that allows to change purposefully composition of the surface layer, its electrocatalytic and corrosion characteristics during the process of electrosynthesis of H₂O₂.

For example, in electrosynthesis of H₂O₂ on UGVMt-Ni cathode in solutions: 1% of NaOH + 0.1 g/l of MgSO₄ + 10⁻³ M C₆H₄(OH)₂ under the impact of generated on anode ozone – oxygen mix abnormally high current efficiency was reached for H₂O₂ (696.9–911%). It was suggested that the mixed way of electrosynthesis of H₂O₂ was realized, including the direct electro-reduction of oxygen-containing gas catalyzed by redox processes in superficial oxygen-containing groups of UGVMt, glassy carbon and chemical processes of oxidation.

In the paper [5] without hydroquinone C₆H₄(OH)₂ the synchronous electrosynthesis of O₃ and H₂O₂ on glassy carbon (SU-20) anodes and cathodes from UGVMt-Ni with total current efficiency of oxidizers production more than 130% was established.

The influence of content and feed rate of oxygen-containing mixture on electrosynthesis of hydrogen peroxide was studied. It is established that injecting ozone – oxygen mix instead of pure oxygen or air accelerates electrosynthesis of hydrogen peroxide and creates almost non-corroded cathode. Such technical solution provides increase in content of oxygen in a catholyte without use of additional pressure and equipment.

In development of our researches [3–5] there was investigated the influence of conditions of modification of UGVMt surface on its chemistry, governing electrocatalytic (current efficiency, %) and corrosion (g/A·h) characteristics during electrosynthesis of H₂O₂ in standard conditions (when injecting pure air in catholyte). Content of the formed surface functional oxygen-containing groups (SFOG) is presented in the Table 1.
As we see, the correlation between current efficiency (\% \text{H}_2\text{O}_2) and the number of phenolic and hydroxyl groups on the surface of UGVM_{\text{r}}-\text{Ni} is observed.

Electrocatalytic properties of UGVM_{\text{r}}-\text{Ni} are highest after modifying by anode oxidation, and corrosion – the worst, than at electrochemical fluorination. It is possible to assume that complex modification by anode oxidation and fluorination the surface of UGVM creates hydrophobic and hydrophilic conditions under which the speed of diffusion of \text{H}_2\text{O}_2 into main solution volume is higher, than in fiber pores with reduction \text{H}_2\text{O}_2 into \text{H}_2\text{O}.

We also performed tests of the diaphragm electrolyzer for current loading up to 100 A in the course of synchronous synthesis of \text{O}_3 and \text{H}_2\text{O}_2. Results of tests are presented in the Table 2.

From the data of Table 2 it follows that fabric UGVM_{\text{r}}-\text{Ni} cathodes are perspective for producing diluted alkaline \text{H}_2\text{O}_2 solutions. We will note that replacement of usual Pb cathodes by the combined cathodes from UGVM_{\text{r}}-\text{Ni} allows us to receive instead of \text{H}_2 alkaline \text{H}_2\text{O}_2 solutions as a commodity product and to avoid Pb pollution of environment.

It is necessary to pay attention to the experimental fact that the rate of formation of \text{H}_2\text{O}_2 in the presence of additive 0.001 m \text{C}_6\text{H}_4(\text{OH})_2 becomes seven times higher, that confirms suggestion about complex mechanism of hydrogen peroxide electro-synthesis by combined electrochemical and anthraquinone ways.

Functioning of electrochemical productions is impossible without their optimization, creation of mathematical model of the electrolyzer, separate technological processes of electrolysis [6]. High-quality and optimum control of technology requires use of the mathematical model of process of electrolysis which is adequately describing warm and a mass exchange in the electrolyzer, changes of material balance, electrobalance, to the hydrodynamics engineer of solutions. Creation of mathematical model of electrolysis – a way of modification of the existing production of hydrogen peroxide, introduction new technical the solution of process, improvement of quality of management of technology.

Work [7] in which aluminum electrolysis process is investigated is known, key parameters of process are determined, their interrelations are revealed, the most essential communications are chosen. The topological model of process of electrolysis of aluminum is developed. On the basis of the developed topological model the method of the structural and parametrical analysis of systems of automatic control of production is considered. In other work [8] by means of a topological method on the basis of the structural count the mathematical model of

| Table 1. Content of the formed surface functional oxygen-containing groups (SFOG). Electrocatalytic and corrosion characteristics of UGVM_{\text{r}}-\text{Ni} in direct electrosynthesis of \text{H}_2\text{O}_2 in 10% NaOH, the speed of injecting air 120–160 m\text{l}/h, \text{I} = – 10 \text{mA} |
|---|---|---|
| Content of SFOG, \text{g}\text{-equiv/g} | Anodic oxidation in 1% NaOH | Electrochemical fluorination in 40% NH_3HF_2 | Chemical processing in 1% of NaOH + O_3, time – 30 min |
| Carboxyl | 155 | 86.9 | 156 |
| Carboxyl lactone | 466 | 318.6 | 219 |
| Phenolic | 1980 | 1560 | 1380 |
| Hydroxyl | 248 | 348 | 4800 |
| Current efficiency, % | H_2O_2 | 84.4 | 15 | 9.3 |
| Corrosion rate, g/A·h | | 7.8 | 1.68 | 5.1 |

| Table 2. Production of hydrogen peroxide. The stream of O_3–O_2 mix generated on anode is injected in cathodic space with a rate 4 l/h. Concentration of O_3 is 5–6 vol. %. The cathode material is UGVM_{\text{r}}-\text{Ni} |
|---|---|---|---|
| Composition of catholyte | Current, A | Time, minutes | Concentration of H_2O_2, N |
| 1% NaOH | 20 | 30 | 0.0012 |
| 1% NaOH + 0.1 g/l MgSO_4 | 20 | 20 | 0.001 |
| % NaOH + 0.1 g/l MgSO_4 + 0.001 M \text{C}_6\text{H}_4(\text{OH})_2 | 20 | 20 | 0.007 |
process of anode effect in aluminum production is created.

In work [8] the topological model of process of electrosynthesis of nadserny acid is created. Cathodic process is in which release of molecular hydrogen.

The growing need of the market for peroxide of hydrogen demands an intensification, modernization of productions. The technology of obtaining hydrogen peroxide combining electrochemical and anthraquinone methods is relevant Therefore a perspective priority is development of topological model of process of synchronous electrosynthesis of hydrogen peroxide and ozone that will allow to create mathematical model. On the basis of the received topological model the main quantitative characteristics of synchronous electrosynthesis of peroxide of hydrogen and ozone will be calculated.

In Figure 3 the simplified topological scheme of synchronous electrochemical production of O₃ and H₂O₂ is submitted. The topological model of system shown in Figure 3 contains information on structure of physical streams.

For drawing up topological model of technological process of simultaneous generation several inorganic oxidizing components the structure of streams 1–5 (which can be received by analysis of local processes in nodes) is required.

In anode node – anode reactions:
2 H₂O → 4 e⁻ → O₂ + 4 H⁺ (+)
3 H₂O → 6 e⁻ → O₃ + 6 H⁺

In cathode node (blue color) – cathodic reactions, including
2 H₂O + O₂ + 2 e⁻ → 2 H₂O₂ (−)

For example, ozone–oxygen mix is formed on anode in node (+) and will be present only in stream 2. Hydrogen peroxide is formed in node (−), i.e. in cathodic space, and will be present only in stream 4. Ions of H⁺ are formed in anode space and will be present in stream 5. The combination of block diagrams of streams of substances shown in Fig. 4 gives the general block diagram provided on Figure 3.

From the analysis of the processes proceeding in nodes (diffusion, filtration and evaporation of streams in the first approximation can be neglected) it is possible to construct topological schemes for separate components (Figure 4).

The general scheme already contains information on what substances are contained in group streams 1–5. For example, the stream 4 contains substances: H₂O, HO₂⁻±.

The structure of streams of substances in reactions in each node and system in general can be represented graphically. Such problem is solved on the basis of the data of stoichiometric equations of the reactions proceeding in separate nodes. The equations specify the directions of streams in education reactions (products of reactions) or consumption (initial substances).

The example of the scheme of transformation of substances is shown in Figure 5.

At combination of block diagrams of processes of transfer and transformation we receive the full technological scheme (Figure 6).

This scheme unambiguously and fully reflects the nature of material processes in system: appearance and disappearances of substances in separate nodes as a result of processes of different physical nature.

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**Fig. 3.** Topological scheme of simultaneous producing O₃ and H₂O₂: 1 – H₂O input, 2 – O₂ + O₃, 3 – NaOH, 4 – H₂O₂ + NaOH, 5 – migration of protons through a cation-exchange membrane. Dotted line – gaseous stream; continuous lines – liquid.
Fig. 4. Structure of substances streams (transfers) in the technological system of producing O₃ and H₂O₂.

Fig. 5. Structure of streams of substances in reactions in the technological system of producing O₃ and H₂O₂.

Fig. 6. Full technological scheme of process of electrosynthesis of O₃ and H₂O₂. P_a, P_c – correspond to anode and cathodic reactions. Numbers – to transfer streams according to Figures 3,4; continuous – in solution; dotted – in the gas phase.
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These elements characterizing dynamics of material processes in technological system are the basis for drawing up mathematical model of the technology (which describes material transformations) having the form of the equations of balance of substances.

By drawing up the balance equations the use of block diagrams considerably facilitates work and guarantees an exception of mistakes.

Equation of balance O₁ + O₂ in node (+) according to graph of Figure 6 is:

\[ +g \text{pA} - g₂ = 0, \]

where \( g \text{pA} \) and \( g₂ \) mass streams of \( O₁ \) and \( O₂ \), kg/s, i.e. production rate in anode reaction of generation of ozone – oxygen mix and removal from the node in stream 2.

The considered block diagrams reflect technological topology of concrete processes and they are called process graphs. Graphs contain the same information, as the balance equations in general view, so actually they are a graphic form of algebraic equations of balance of substances:

\[
\begin{align*}
O₁ & \quad g₂ = g₁ + g \text{pA}, \\
O₂ & \quad g₂' = g₁ + g \text{pA}, \\
H₂O₂ & \quad g₄ = g₃ + g \text{pK} + g₂ + g₅, \\
H₂O (−) & \quad g₃ = -g \text{pK} + g₅.
\end{align*}
\]

Except material, in the technological scheme power processes proceed. As the partial problem of the analysis of power balance of the electrochemical device usually the balance of thermal streams is considered which determine solution of temperature in working area. Structure of thermal streams of anode and cathodic reactions (q), radiation and convection (m) are represented graphically in Figure 7.

![Diagram](image)

**Fig. 7.** Structure of thermal (qₐ, mₐ – anode and qₜ, mₜ – cathodic) technological system of producing \( O₃ \) and \( H₂O₂ \); numbers – as in Figure 3.

Conclusions

1. The regularities of the effect of modification of the surface layer of UGVM₁ on the amount of surface functional oxygen-containing groups (SFOG) are studied.

2. The interrelation between electrocatalytic, corrosion characteristics of fabric UGVM₁–Ni in the course of electrosynthesis of \( H₂O₂ \) and quantity of SFOG is established.

3. Tests of cathodes made from the fabric UGVM₁–Ni reinforced by Ni in the course of electrosynthesis of \( H₂O₂ \) in the diaphragm electrolyzer for current loading up to 100 A are carried out.

4. The topological structural model of synchronous electrochemical synthesis of \( O₃ \) and \( H₂O₂ \) is created.

References


HİDROGEN PEROKSİDİN VƏ OZONUN SİNXRON ELEKTROSİNTEZİ
1. Topoloji model
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Müxtəlif üsullarla modifikasiya edilmiş toxuma karbon qrafit lifli materialın sıth təbəqəsinin sıthda oksigentərkibli qrupların tərkibində və miqdarda təsirinə qanunauyğunluqları öyrənilmişdir. H₂O₂-ning elektrosintez prosesində toxuma KQLM₄-dan (KQLM₄-Ni) olan katodların elektrokatalitik və korroziya xarakteristikaları arasında qarşılıqlı əlaqənin olması müəyyən edilmişdir. Bu katodlar H₂O₂-ning elektrosintez prosesində 100 A qədər cərəyan yükündə diafraqmalı elektrolizərə sınağдан çıxarılmışdır. Hidrogen peroksidin və ozonun sinxron elektrosintezinin topoloji modeli tərtib edilmişdir.

Açar sözlər: elektrosintez, hidrogen peroksid, ozon, topoloji model.

СИНХРОННЫЙ ЭЛЕКТРОСИНТЕЗ ПЕРЬКОСИДА ВОДОРОДА И ОЗОНА
1. Топологическая модель
Г.Ф.Потапова, Э.В.Касаткин, М.Р.Манафов, В.Л.Ключихин, П.С.Воронцов
Различными способами изучены закономерности влияния модификации поверхностного слоя тканевых углеродфитовых волокнистых материалов на состав, количество поверхностных функциональных кислородсодержащих групп. Установлена взаимосвязь между поверхностными функциональными кислородсодержащими группами и электрокатализитическими, коррозионными характеристиками катодов из тканевых углеродфитовых волокнистых материалов, армированных в Ni сетку в процессе электросинтеза H₂O₂. Проведены испытания этих катодов в процессе электросинтеза H₂O₂ в диафрагменном электролизере с токовой нагрузкой до 100 A. Построена топологическая модель синхронного электросинтеза пероксида водорода и озона.

Ключевые слова: электросинтез, пероксид водорода, озон, топологическая модель.