Indirect Oxidation of Organic Substances by Hydrogen Peroxide Electrochemically Generated *in situ* from Oxygen (the Review)

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Abstract

The most urgent and promising lines of investigations in the field of indirect oxidation of organic substances by hydrogen peroxide electrochemically generated *in situ* from oxygen in aqueous solutions of electrolytes with varied pH are considered: 1) application of gas-diffusion electrodes for intensification of electroreduction of oxygen; 2) the potentialities of a simultaneous production of electric power and valuable products electrosynthesis, hybrid systems a fuel element − electrolyzer; 3) production of the same product at the anode and cathode; 4) electrolysis in cells with a cation-exchange membrane and without a membrane; 5) increasing the selectivity of indirect electrosynthesis; 6) destruction of pollutants.

INTRODUCTION

The processes of indirect electrochemical oxidation of organic substances for obtaining new chemical products (electrosynthesis) and cleansing of sewage from organic toxicants attract a significant attention during the last 20 years [1−4]. Their essence consists in electrochemical generation of an oxidizing agent at the cathode or anode and the subsequent chemical reactions of it with organic substrates in the electrolyte solution. Thus, the process consists of two consecutive stages: electrochemical (heterogeneous) and chemical (homogeneous). As opposed to the direct electrochemical oxidation of organic substances proceeding usually in the field of high anode potentials, where the problems of corrosion stability of anode materials and thermodynamic stability of aqueous electrolytes are almost universally present, in indirect oxidation these problems do not arise, as the processes of the anode and cathode generation of oxidizers proceed under rather low electrode potentials [4, 5].

The literature contains evidence of several industrial processes with metals of variable valency applied as mediators-oxidizers, for example, Cr(VI) [6, 7], Mn(III) [8], Ce(IV) [9−12] for indirect electrosynthesis, and Ag(II) for neutralization of sewage [13−15].

Hydrogen peroxide, as redox reagent, has a number of unique properties in indirect electrochemical oxidation, which put it on the first place among the similar reagents. Among these there are the ecological cleanness (with the use of H_2O_2 only H_2O and O_2 are produced), high solubility in aqueous solutions, *i. e.* the absence of restrictions as to mass transfer, high standard reduction-oxidation potential (E^0 H_2O_2/H_2O is equal +1.776 V in acid medium and E^0 H_2O_2/OH^- is equal +0.88 V in alkaline medium [16]) and the ease of obtaining. Hydrogen peroxide is generated at the graphitized carbon electrodes under soft conditions in the process of electrochemical reducing of oxygen in the alkaline medium (the Berl process) by the reaction [17]:

$$O_2 + 2e^- + H_2O = HO_2^- + OH^- \qquad (1)$$
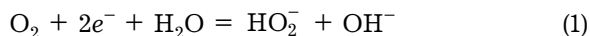
In addition, the cheap source reagents (oxygen, air) and electric power predetermine the rather low cost price of the electrosynthesized product. The electric power is known to be generally cheaper than equivalent amount of various widely used oxidizers, its cost is close to the cost of such the widespread oxidizer, as nitric acid [18].

The possibility of production of H_2O_2 from O_2 with a high current effeciency in neutral and acid media in laboratory conditions has been evidenced recently by the reaction [19, 20]:

$$O_2 + 2H^+ + 2e^- = H_2O_2 \qquad (2)$$
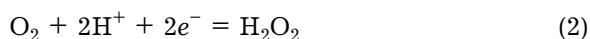
Generation of the diluted solutions of hydrogen peroxide from oxygen (air) at the site of its consumption as a finished product (with no need of cleaning or separating) or its application under *in situ* conditions make it possible to consider this way as showing the considerable promise and economically favourable. It is worth noting that the electrochemical technology enables the rather simple rise in manufacture by increase of the quantity of electrolysis cells.

Many works and reviews are devoted to electroreduction of oxygen to hydrogen peroxide in alkaline medium, the last and the most complete of them being the work [21]. The most significant achievements in application of hydrogen peroxide electrosynthesized from oxygen are presented in the work [3].

In this review the author, being the specialist in electrosynthesis of chemical substances in porous gas-diffusion electrodes [21, 22] and indirect electrochemical oxidation [4], considers the most urgent and promising lines of investigations in the field of indirect electrochemical oxidation of organic substances by hydrogen peroxide generated *in situ* by cathode reduction of oxygen in aqueous solutions.

APPLICATION OF GAS-DIFFUSION ELECTRODES

The efficiency of oxidation is known to depend on the ratio of H_2O_2 and substrate concentrations and the more this ratio, the more efficient is the process [3]. The solubility of oxygen in aqueous solutions is low, so current density does not reach 1 mA/cm^2 at smooth electrodes. It is natural that such low rate of hydrogen peroxide generation is unacceptable for practical purposes. The three-dimensional electrodes of three types are used to increase the rate of oxygen electroreduction: bulk, mesh glass-carbon [3, 23–27] and gas-diffusion ones made from the homogenized mixture of black carbon (electrocatalyst) and PTEE (hydrophobic binding) [28–32]. The gas-diffusion electrodes are known to allow the creation of the high-developed surface of three phases contact: the electrocatalyst – aqueous electrolyte – gaseous reagent with zero pressure drop and to provide the reliable channels for reagent and electrolyte delivery to this contact boundary [33]. The application of gas-diffusion electrodes has enabled the considerable intensifying of oxygen electroreduction, the increase of current density up to 200 mA/cm^2 and the rate of hydrogen peroxide generation by more than 200 times with a rather high yield in respect to current [4, 34].

Further intensifying of the electrochemical stage of the process of indirect electrochemical oxidation is related to the selection of still more active electrocatalysts and enhanced structural characteristics, allowing one to develop the gas-diffusion electrodes of the durable operation life time, that is extremely important to offer them to industry [3].

The application of gas-diffusion electrode has made the researchers to be confronted with a question of the possible location of the chemical reaction, namely: whether the reaction occurs in the porous body of the electrode or outside of it, in the electrolyte. The point is that until recently the porous gas-diffusion electrodes were considered only as the high effective devices for hydrogen peroxide generation from oxygen. However, the homogeneous chemical reaction between electrosynthesized H_2O_2 and substrate was not assumed to be possible in the body of their pores. Theoretical consideration of this question and experimental check of the possible variants have been made by us in [35]. It has been found that distribution of chemical reaction in the course

of indirect electrosynthesis between the body of the electrolyte chamber and the body of the electrode pores varies for the different reaction orders, and at a rather high rate constant of the chemical reaction the share of the process proceeding inside the pores body of the electrode can be equal to one. The result obtained by us opens the new prospects of gas-diffusion electrode application in indirect oxidation of organic substances. For example, the processes may be performed, for which the higher concentration of an oxidizer is necessary, than the one attainable during accumulation in the body of electrolyte outside of the pore body of the electrode. In H_2O_2 electrosynthesis from O_2, the hydrogen peroxide concentration in the pore body of gas-diffusion electrode is known to be several times greater, than in the body of catholyte [36, 37].

HYBRID SYSTEMS FUEL ELEMENT — ELECTROLYZER

Progress in intensification of an electrochemical stage of the indirect oxidation process by means of the porous gas-diffusion PTEE electrode has allowed the researchers to concentrate their efforts in the realization of an idea of creation of fuel elements (FE) of a hybrid type. The hybrid system FE-electrolyzer allows the simultaneous production of electric energy and valuable chemical products, for example, alkaline and acid solutions of hydrogen peroxide during the functioning of the H_2/O_2 fuel element. These solutions can be used in oxidation of organic substances both under *in situ* conditions, and outside of electrolyzer [38–41]. In the work [41] benzene and oxygen were brought to the cathode through its rear side in the gas phase at the temperature of 353 K. In so doing, the increase of the rate of phenol formation was observed, if Pd and Fe oxide (III) added in the composition of the cathode. However, the electrochemical cell has been noted to be short-lived, and its weak point is the oxygen electrode, which operating life time is comparatively short.

In [42] the H_2/O_2 fuel element with improved cathode electrocatalysts producing H_2O_2 with acceptable efficiency is developed. In [43] the H_2/O_2 fuel element with the gas-diffusion

anode and cathode capable of working both in alkaline (2 M NaOH), and in acid (HCl, H_2SO_4, H_3PO_4) and neutral (K_2SO_4, Na_2SO_4) media at normal temperature and atmospheric pressure is described. In the short-circuited mode FE is capable of producing the 1.11 % H_2O_2 solution with the current yield of 46 % for 2 h of operation.

The further progress in this line of investigations is connected, first of all, with the life time increase of an oxygen electrode. On the successful solution of the problem the commercial appeal of the hybrid type of FE will considerably increase.

PRODUCTION OF THE SAME PRODUCT AT THE ANODE AND CATHODE

In connection with the fact that the same quantity of electricity flows through the electrodes (anode and cathode) of electrochemical cell, it seems showing considerable promise to select the conditions for the processes for generation of the same product simultaneously at the anode and cathode. This would double the productivity of an electrochemical cell and the rate of chemical conversion [3]. In [44, 45] the oxidation of toluene to benzaldehyde in the divided cell is described. The oxidation of Mn(II) to Mn(III) in sulfuric acid occured at the anode, and at the graphite cathode, reduction of O_2 to H_2O_2. Oxidation of toluene was carried out under *in situ* conditions in the body of catholyte, with V(IV) used as a mediator, and a solution with Mn(III) used for toluene oxidation outside of the cell. The formal value of the total yield in respect to current (referred to as total below) was 171 % (84 % at the anode and 87 % at the cathode). In [46] anthracene was oxidized to anthraquinone in undivided cell in concentrated acid as an electrolyte. The oxidation of V(IV) to V(V) occured at the anode. V(IV) acted as the catalyst for activation of hydrogen peroxide formed at the graphite plate-cathode. The total yield in respect to current comprised 151 % for anthraquinone, and selectivity, 98 %. In [47] the oxidation of *n*-butanol into *n*-butane acid in the alkaline solution in the undivided cell has been carried out: anode process is the direct oxida-

tion at the nickel anode, cathode process is the electroreduction of oxygen to hydrogen peroxide and oxidation of alcohol by it without the catalyst. The total yield in respect to current comprised more than 170 %. To disinfect the sewage, in [48], the destruction of phenol by hypochlorite generated at the anode, and by hydrogen peroxide generated at the cathode, has been carried out. In [49] the mediator system tungstate/pertungstate was created in the cathode area of the undivided cell with participation of hydrogen peroxide generated at the cathode by the reaction
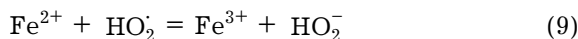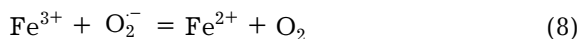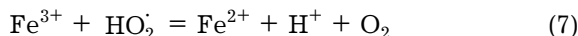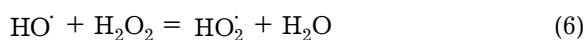
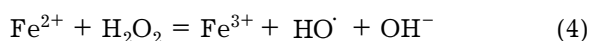$$HWO_4^- + H_2O_2 = HWO_5^- + H_2O \qquad (3)$$
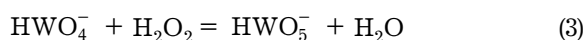
Bromine was generated at the anode. It was involved in the oxidation of the N−OH group of dibutylamine into N-butylidenebutylamine-N-oxide with the total yield in respect to current of more than 180 %.

It should be noted that in all the works considered above, hydrogen peroxide was generated from oxygen at the graphite plates, where the current density, naturally, was low. Therefore the application of gas-diffusion electrodes for the cathode would allow to intensify considerably the hydrogen peroxide generation and to improve the operation parameters of the cells as a whole for industrial use.

ELECTROLYSIS IN CELLS
WITH CATION-EXCHANGE MEMBRANE AND WITHOUT IT

Hydrogen peroxide is known to act frequently in chemical reactions in the form of intermediates (HO_2^-, $HO_2^\cdot$, $HO^\cdot$) of various activity, which structure depends on the conditions of their production [50]. Hydroxyl radicals, $HO^\cdot$ are the most reactive; the least reactive ones are perhydroxyl radicals. Their activity differs by 5−6 orders. For deep oxidation of organic substances the well-known Fenton's reagent (H_2O_2 + Fe(II)) is frequently used. It enables $HO^\cdot$ generation with high efficiency. The following set of consecutive stages in H_2O_2 + Fe_2^+ system is now commonly accepted [51]:

$$Fe^{2+} + H_2O_2 = Fe^{3+} + HO^\cdot + OH^- \qquad (4)$$

$$Fe^{2+} + HO^\cdot = Fe^{3+} + OH^- \qquad (5)$$

$$HO^\cdot + H_2O_2 = HO_2^\cdot + H_2O \qquad (6)$$

$$Fe^{3+} + HO_2^\cdot = Fe^{2+} + H^+ + O_2 \qquad (7)$$

$$Fe^{3+} + O_2^- = Fe^{2+} + O_2 \qquad (8)$$

$$Fe^{2+} + HO_2^\cdot = Fe^{3+} + HO_2^- \qquad (9)$$

Under electrochemical cell conditions $HO^\cdot$ can be generated in anode oxidation of water by the reaction

$$2H_2O - 2e^- = 2HO^\cdot + 2H^+ \qquad (10)$$
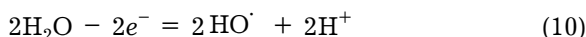
and $HO_2^\cdot$, in the anode oxidation by the reaction

$$HO_2^- - e^- = HO_2^\cdot \qquad (11)$$

Thus, the electrochemistry presents a unique opportunity to perform oxidizing processes of different depth with electrosynthesized hydrogen peroxide by means of cells with cation-exchange membrane and without it. This makes possible to generate various intermediates using the anode itself and the anode area. Smooth platinum, lead dioxide *etc.* can be used as anode materials. Highly effective version of Fenton's reagent, so-called electro-Fenton's, and Raff's system (H_2O_2 + Fe(III)), can be very simply realized in the electrochemical cell, if the iron is used as the anode, and hydrogen peroxide is generated in the gas-diffusion cathode [52, 53]. In the majority of works, Fe_2^+ is introduced into the electrolyte solution in the form of various salts [3].

In [4] formaldehyde has been quantitatively oxidized to formic acid by electrosynthesized hydrogen peroxide (HO_2^-) in an electrolyzer with cation-exchange membrane in alkaline medium. Mineralization of formic acid was not observed in these conditions. The realization of this process in electrolyzer with cation-exchange membrane in the presence of Fe_2^+ in acid medium made possible practically complete mineralization of the formic acid [54]. In [55] the indirect oxidation of phenol by hydrogen peroxide (HO_2^-) electrochemically generated *in situ* from oxygen in the gas-diffusion carbon-black cathode in the electrolyzer with cation-exchange membrane in alkaline medium has been studied. The products were found to be the organic acids and ketones. The realization of this process in the electrolyzer without a membrane with the platinum anode has allowed the destructive oxidation of phenol

with the conversion degree of more than 90 % depending on current density [56].

Thus, through changing the medium pH, the anode material, current density, by using of the divided and undivided electrochemical cells, different intermediates of various reactivity can be obtained, and organic substrates oxidation of variable depth can be performed.

INCREASING OF ELECTROSYNTHESIS SELECTIVITY

It has been known that, owing to the high content of active oxygen, hydrogen peroxide can be used as oxidizing, hydroxylating and epoxidating agent in chemical industry [57]. The large number of works [51] is devoted to catalytic hydroxylation of an aromatic ring by Fenton's reagent. Here, hydroxylation of benzene, phenol and their derivatives in water medium is performed through generation of radicals, which interact with the appropriate substrates through the stage of various intermediate substrate radicals formation. For example, benzene hydroxylation produces oxycyclohexadienyl radical, which is turned to phenol or diphenyl in subsequent disproportionation or dimerization respectively [51]. The selectivity of hydroxylation of benzene and phenol derivatives by Fenton's reagent is rather low, and the reaction proceeds by a radical mechanism. The efficiency of benzene hydroxylation by Fenton's reagent depends much on the ratio between reagents, medium pH and other factors [51]. More selective oxidation can be achieved by use of the suitable mediator for the reaction H_2O_2/organic substrate. For example, the tungstate/pertungstate mediator system has been suggested to use in [49]. In [58] the comparison of the catalytic properties of Fe(II), Cu(II), V(IV) has been made for the reactions of toluene oxidation by hydrogen peroxide. It was found that the highest yield of benzaldehyde, nearly the quantitative one, was achieved in the system with V(IV).

In [59] an incomplete ethane oxidation into acetaldehyde (80 %) and ethanol (20 %) in rather soft conditions has been made, the quantity of electrogenerated hydrogen peroxide being 24 mmol. The suggestion has been made that the Nafion membrane, probably, has a catalytic impact on the C_2H_6 molecule activity.

Other catalysts of mediator type, for example, molybdate [60], polyoxymetals, containing transition metals, such as Ru, Mn, Cr [61], RuO_2 [62], CH_3ReO_3 [63] are also suggested in the literature.

In [64] the 5 times increase of cyclohexanol yield has been observed in cyclohexane oxidation in the presence of Cl^-. The suggestion that $Cl^.$ is involved in the oxidation has been made. Among the catalysts of indirect oxidation processes with the participation of hydrogen peroxide electrogenerated from oxygen, particular attention has been paid to the ferments-biocatalysts [3]. There are works on horse-radish peroxidase application as the catalyst in indirect oxidation of organic substrates [65−67]. The application of enzymes opens up the wide opportunities for increasing the selectivity in the processes of indirect oxidation of organic substances. The oxidation of 2,4,6-trimethylphenol by electrogenerated H_2O_2 catalyzed by horse-radish peroxidase in the phosphate buffer at pH 7 is described in [65]. The correlation between the nature of products and current density, together with the quantity of electricity flown is established. In addition, the yield of products was considerably higher, than in the classic chemical oxidation in homogeneous reactors. The yield of the product of condensation was more than 50 %, and chemical oxidation did not result in its formation. This implies that the electrochemistry makes available the new routes of the reactions in biotransformations. The choice of ferment is not restricted by only horse-radish peroxidase, though the peroxidases are known to enable the selective and often chiral transformations in the presence of H_2O_2, for example, the conversion of sulphides into sulphoxides, anilines into hydroxylamine or nitrobenzene, olefines into olefine oxides, alkylbenzenes into alcohols or aldehydes, indoles into oxyindoles [66, 67].

The biocatalysts can be used in the form of solutions under homogeneous conditions, and under heterogeneous conditions, in the form of immobilized ferments on the surface of graphitized carbon electrocatalysts of gas-diffusion electrodes. The oxidizing processes may then proceed by variable routes depending on electrocatalysis. From the preceding it follows that the potentialities to increase the selectivi-

ty of the processes of indirect electrosynthesis of organic compounds are far from being exhausted and, probably, only the first steps are made in this direction. In addition it should be noted that not the most efficient electrodes are used for hydrogen peroxide generation in the overwhelming majority of works, therefore concentration of H_2O_2 was low, that could have a very significant effect on the selectivity of processes [3]. Use of gas-diffusion electrodes for hydrogen peroxide generation and use of selective catalysts opens up new avenues and represents a fruitful line for the further investigation.

DESTRUCTION OF POLLUTANTS

The electric power consumption for destruction of organic toxicants in the sewage is known to be proportional to their concentration and the number of electrons necessary for organic toxicants conversion into CO_2. The deep oxidation of organic molecules can usually include from 20 to 150 e^- [3]. The electric power consumption for electrosynthesis of hydrogen peroxide from oxygen is more than 4.4 kW h recalculated to 1 kg of 100 % H_2O_2 [68]. This implies that application of the method of indirect oxidation of organic substrates in sewage by electrogenerated hydrogen peroxide is economically expedient at low concentrations of organic substrates, so-called tails (before a delivery to biological cleansing), so that the ratio H_2O_2/organics is high. Hydrogen peroxide is able to oxidize destructively many organic substrates into CO_2 and H_2O in the presence of Fe(II) [69]. Such processes are accompanied by change in chemical consumption of oxygen (CCO), by CO_2 releasing and/or by organic intermediates formation. The works [31, 52–54, 56, 70-73] report the complete oxidation of organic toxicants up to CO_2. In [74, 75] the dependence of phenol and formaldehyde destruction on medium pH has been studied.

Hydrogen peroxide was generated at the graphite plate with current density of 0.4 mA/cm^2. It has been found that phenol (CCO of 260–2600 ppm) can be efficiently oxidized to CO_2 in the presence of Fe(II) at pH 1–4 with final CCO being less than 40 ppm [74]. Formalde-

hyde can be efficiently oxidized to formic acid at pH 13, and its complete mineralization has been observed only in acid medium in the presence of Fe(II).

The similar results are obtained in [4, 54] with the use of carbon-black gas-diffusion electrodes at the cathode current density from 25 to 200 mA/cm^2. The removal of phenol, cresol, catechin, quinone, hydroquinone, aniline, oxalic acid and amaranthus azo dye from subacid solutions in the presence of Fe(II) is studied in [73]. Hydrogen peroxide was generated at the mesh glass-carbon cathode at current density of 20 mA/cm^2. It is shown that the chemical consumption of oxygen could be reduced for each of the compounds from 50–500 ppm to 10 ppm and less with the yield in respect to current being more than 50 %. The bulk of carbon in solutions is identified as CO_2.

The authors [31] examined an indirect oxidation of aniline and 4-chloraniline in aqueous solutions at pH 10.1–12.7. Hydrogen peroxide was generated in the gas-diffusion electrode at current density up to 200 mA/cm^2. They succeeded in decreasing the CCO from 100 to 5 ppm. In [52] they investigated sulphate solutions with pH 3. They also observed the complete oxidation of aniline in the presence of Fe(II) and have established the acceleration of oxidation process with the UV irradiation. However, the current density of hydrogen peroxide generation was appreciably lower, than in alkaline medium, and comprised 30 mA/cm^2. In [53, 70, 71] the undivided electrochemical cell and electro-Fenton have been used, i. e. H_2O_2 was generated in situ in the gas-diffusion cathode and Fe(II) was generated from the iron anode in acid medium. Rather fast decomposition of aniline with initial concentration of 100 and 1000 ppm has been shown to occur in these conditions. The same approach was shown in [72] as application of an acid Fe/O_2 accumulator for preliminary processing of sewage containing 0.5 M Na_2SO_4 and aniline in amount from 129 up to 1000 ppm. It was found that aniline is most effectively decomposed in solutions with pH more than three, where intermediate products coagulate together with $Fe(OH)_3$ being deposited. At the concentration of aniline of 129 ppm, pH 4.0 and 35 °C 95 % of aniline was removed for 1 h. In addition,

the relatively high electric power was produced by the battery.

The considered examples demonstrate that electrosynthesized hydrogen peroxide can be used with high efficiency for purification of sewage from organic toxicants in the wide range of pH with various variants of high-reactive HO_2^-, $HO_2^{\cdot}$, $HO^{\cdot}$ intermediates generation, and different process design. The application of the oxygen gas-diffusion carbon electrodes made possible an increasing of rate of hydrogen peroxide generation by more than one order, which already is of material interest for practical purposes. Mineralization of organic substrates in electrochemical cells without a membrane also offers promise, that is the possibility of high-reactive intermediates generation from HO_2^- and H_2O at the anode. In this case, the voltage across the cell may be lowered, the cations of heavy metals used as the catalysts may be prevented from being additionally brought into the cleansed solution. The yield of oxidizers in respect to current may be essentially increased.

CONCLUSIONS

On the basis of the research general results we may state with confidence that the indirect electrochemical oxidation of organic substances by hydrogen peroxide generated *in situ* from oxygen in gas-diffusion electrodes can be considered as a new highly effective way of generation of organic products (electrosynthesis) and disinfection of organic toxicants in the sewage at low concentrations before their delivery to biological cleansing. The considered lines of investigation in this area are envisioned as the most urgent and perspective ones. But a key problem for all of them is the creation of the highly active oxygen gas-diffusion electrode, and in the long term, the air electrode having the life time of stable work acceptable for industrial use. This complicated problem must be the one on which the efforts of the researchers would be concentrated first of all [21].

In the near future, one should expect the wide use of local compact units-cells of vari-

ous productivity for production of the diluted acid, neutral and alkaline solutions of hydrogen peroxide from oxygen at the consumption site. These units are also expected to be used in the most diversified areas of industrial manufacture, household chemicals and agriculture. The author places special emphasis on the creation of H_2/O_2 fuel elements of a hybrid type, which will make possible the successful and complete solving of the problem of independent power supply and manufacturing the solutions of ecologically pure reagent of extraordinary wide application area.

The ecological and commercial appeal of the considered scientific, engineering and technological field is beyond question.

Acknowledgements

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