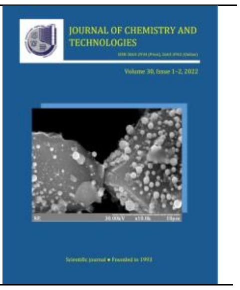
Journal of Chemistry and Technologies

pISSN 2663-2934 (Print), ISSN 2663-2942 (Online).

journal homepage: http://chemistry.dnu.dp.ua



UDC 544. 653.2

REVIEW ON INFLUENCE OF ELECTRODE MATERIAL NATURE ON ANODIC PROCESSES IN CHLORIDE SOLUTIONS

Olesia B. Shmychkova*, Dmitry V. Girenko, Alexander B. Velichenko

Ukrainian State University of Chemical Technology, 8, Gagarina Ave., 49005 Dnipro, Ukraine

Received 3 April 2022; accepted 5 June 2022, Available online 25 July 2022

Abstract

In the review article, a critical analysis of the literature was carried out, which showed the almost complete absence of systematic studies of electrochemical processes implemented at anodes in low-concentrat~~ion~~ed sodium chloride solutions. The vast majority of works are devoted to the study of the regularities of chlorine evolution reaction in highly concentrated NaCl solutions on the surface of oxide catalysts, which often contain oxides of ruthenium and iridium. Taking into account the variety of works, today there is no universal mechanism that describes the reaction of chlorine evolution under various conditions and on the surfaces of electrocatalysts of various nature. Comprehensive data on the peculiarities of such processes in low concentrated chloride solutions are presented. It is shown that the regularities of such processes are due to the participation of oxygen-containing particles with different bond strengths in individual steps. It was found that the electrocatalytic activity of electrodes in anodic processes in low concentrat~~ion~~ed chloride solutions was due to the strength of the bond of chemisorbed oxygen-containing particles of different nature with the anode surface. Participation in the oxidation of Cl^- labile oxygen-containing particles of a certain energy increases the rate of formation of hypochlorous acid and leads to inhibition of undesirable reactions of oxygen evolution and synthesis of chlorates and chlorites. It is shown that the modification of the anode surface with palladium makes it possible to significantly increase their selectivity for the synthesis of hypochlorous acid from low concentration chloride solutions.

Keywords: hypochlorous acid; electrolysis; chlorine evolution reaction; oxygen evolution reaction.

ОГЛЯД: ВПЛИВ ПРИРОДИ МАТЕРІАЛУ ЕЛЕКТРОДА НА АНОДНІ ПРОЦЕСИ У ХЛОРИДНИХ РОЗЧИНАХ

Олеся Б. Шмичкова,*Дмитро В. Гиренко, Олександр Б. Веліченко

ДВНЗ «Український державний хіміко-технологічний університет», просп. Гагаріна 8, м. Дніпро, 49005 Україна

Анотація

В оглядовій статті проведено критичний аналіз літератури, що показав практично повну відсутність систематичних досліджень електрохімічних процесів, які реалізуються на анодах в низькоконцентрованих розчинах натрію хлориду. Переважна більшість робіт присвячена вивченню закономірностей проходження реакціїї виділення хлору в висококонцентрованих розчинах NaCl на поверхні оксидних каталізаторів, які містять , найчастіше, оксиди рутенію та іридію. Зважаючи на різноманіття робіт, на сьогодняшній день не вснує універсального механізму, який описує реакцію виділення хлору в різних умовах і на поверхнях електрокаталізаторів різної природи. Наведено комплексні дані про закономірності проходження електродних процесів у низькоконцентрованих хлоридних розчинах. Показано, що особливості перебігу таких процесів обумовлені участю в окремих стадіях кисеньвмісних частинок з різною міцністю зв'язку. Виявлено, що електрокаталітична активність електродів у анодних процесах у низьконцентрованих хлоридних розчинах зумовлена міцністю зв'язку хемосорбованих кисеньвмісних частинок різної природи з поверхнею анода. Участь в окисненні Cl^- лабільних оксигеновмісних частинок певної енергії збільшує швидкість утворення гіпохлоритної кислоти та веде до гальмування небажаних реакцій виділення кисню та синтезу хлоратів та хлоритів. Показано, що модифікування поверхні анодів паладієм дозволяє істотно підвищити їх селективність до синтезу гіпохлоритної кислоти з низькоконцентрованих хлоридних розчинів.

Ключові слова: гіпохлоритна кислота; електроліз; реакція виділення хлору; реакція виділення кисню.

---

*Corresponding author: Tel.: +380562473627; fax: +380562473627; e-mail address: o_shmychkova@ukr.net

doi: 10.15421/jchemtech.v30i2.254438

Introduction

Significant interest shown by researchers in the electrolysis of chloride solutions is associated with the production of chlorine-containing products, such as molecular chlorine and oxygen-containing chlorine compounds, among which sodium hypochlorite or hypochlorous acid is of the greatest practical application. These compounds are traditionally used as disinfectants and in medical practice as preparations.

Sodium hypochlorite solutions have been actively used in medicine and veterinary medicine during the last 15 years [1]. Huge positive experience of their use is accumulated, the areas of application are expanded, all new methods of treatment are developed. According to the pharmacological action, NaClO-based solutions have disinfectant, antiseptic, antimicrobial, detoxifying effect [2]. In addition, the immunostimulatory and regenerative properties of medicines of this type are noted. The solutions are virtually non-toxic, do not cause allergic reactions, and their components do not accumulate in humans and animals. In this regard, the development of medical and veterinary pharmaceuticals based on sodium hypochlorite is of considerable interest. The basic requirements for such medicines are following:

i) high purity (absence of impurities of organic and inorganic substances that are toxic to animals and humans);

ii) high stability of solutions in time (not less than a year at temperatures close to room temperature);

iii) high biological activity of solutions;

iv) the possibility of creating a unified production of the required volume of solution.

The vast majority of veterinary and medical solutions have the following composition:

i) active substance: sodium hypochlorite (up to 1 g L^{-1}).

ii) excipient: sodium chloride (5-20 g L^{-1}).

iii) solvent: water.

iv) possible impurities: chlorites, chlorates, organic substances, transition metal ions.

In addition, attention is paid to the elimination of food contamination by residual amounts of veterinary drugs that may be dangerous to humans, such as antibiotics, sulfonamides, etc. It is also important to enable the safe and effective use of drugs in veterinary practice by maintaining their effectiveness. The most promising way to prevent the accumulation of residual drugs is the withdrawal of antibiotics and sulfonamides by developing new drugs that can be an alternative to them and will not accumulate in food and the environment. These requirements will be met by drugs based on hypochlorous acid, which is an endogenous substance, because in the process of life it is formed inside the cell by the enzyme myeloperoxidase [3]. The interest in hypochlorous acid (HOCl) grew over last year given its verified power as a disinfectant against COVID-19 [4; 5]. Decomposition products of hypochlorous acid are Cl^- ions and water, which are environmentally friendly.

In general, depending on the purpose (which final product is necessary to obtain and the field of application), various chloride solutions are used. These can be highly concentrated NaCl solutions, there can be solutions with a low and medium content of NaCl (technical sea water) and low-concentrated solutions that are used in medical practice.

Solutions of technical sodium hypochlorite, which is obtained on an industrial scale by a two-stage scheme [6], can not be used as veterinary drugs, because they contain large amounts of alkalis, as well as impurities of oxygen-containing chlorine compounds of high oxidation, which is dangerous. The most attractive method for the synthesis of new drugs based on hypochlorous acid from an economic and technological point of view is electrochemical, where the source is an isotonic or dilute sodium chloride solution. The synthesis of high-purity and stable solutions based on hypochlorous acid is quite a difficult task. On the one hand, in the process of electrolysis at the anode it is possible to simultaneously undergo a number of processes: oxygen evolution, oxidation of chloride ions with the formation of hypochlorites, chlorites, chlorates, perchlorates. On the other hand, it is possible to implement chemical, photochemical and catalytic processes, which further affects the purity of the resulting solutions [7]. A feature of medicines based on hypochlorous acid, in contrast to antibiotics and sulfonamides, is the absence of residual amounts of the drug in livestock products (meat and dairy products, honey and others). However, chlorate impurities may form during synthesis and accumulate during storage of solutions [8]. Often, even in freshly synthesized solutions, the chlorate content may be commensurate with the concentration of hypochlorous acid. Despite the presence of some drugs based on sodium hypochlorite used in veterinary medicine, full-scale production of pharmaceuticals of this type is constrained by the lack of technology for the production of stable solutions (with a shelf life of at least 6 months). The presence of a large number of impurities also prevents the use of such solutions in veterinary medicine, and even more so in medicine. The main problem now is the lack of materials and devices on which it is possible to implement the synthesis of solutions of high-purity and stable solutions of hypochlorous acid.

In general, the purity of the resulting product is affected by both the composition of the initial solution and the nature of the electrode material. At the moment, these data are not systematized in the literature. There was a lot of data on the production of molecular chlorine and interest in the study of anodic chlorine evolution faded as all problems were solved.

Recently, there has been interest in the scientific community in the electrolysis of chloride solutions in small compact devices that can be used at points of consumption to produce disinfectants.

In any case, the primary intermediate formed during electrolysis is molecular or atomic chlorine, which, as a result of further transformations, turns into oxygen-containing chlorine compounds, the properties ofwhich should be considered.

Oxygen-containing chlorine (+1) compounds. Since the electronegativity of oxygen is greater than the electronegativity of chlorine, the degree of oxidation of chlorine in its oxygen-containing compounds is always positive [9]. All compounds of this type are recognized as strong oxidants. Chlorine oxides and their oxygen-containing acids usually have low stability, which increases with increasing of oxidation number of chlorine [9; 10]. In this case, in pure concentrated form, there is only perchloric acid ($HClO_4$) and its anhydride (Cl_2O_7). Analysis of the chemical properties of substances of this type showed that compounds in which chlorine is in a low oxidation state have the maximum oxidative activity. Chlorine compounds in which it is in low and intermediate oxidation states are prone to disproportionation. Typically, ionic forms of oxygen-containing chlorine compounds are weaker oxidants than the corresponding acids. However, they are more stable and can exist not only in solutions but also in pure form in the crystalline state [11]. Below we consider in detail the main physicochemical properties of oxygen-containing chlorine compounds in the oxidation state +1.

Hipochlorous acid. Hypochlorous acid is characterized by high chemical activity and relatively low stability [11–15]. The HClO molecule may exist in the gas phase and in solution. From the surface of the aqueous solution hypochlorous acid evaporates easily, goes into the gas phase. HClO is one of the strongest and most stable hypohalous acids in the solution, with high oxidative activity compared to other oxygen-containing chlorine compounds. Despite its low commercial use, HClO is an important intermediate in the production of various organic and inorganic compounds, and is widely used as a disinfectant and oxidant in water treatment. Some of corporations produces a line of preparations for wound care and skin care based on an aqueous 0.01 % solution of hypochlorous acid [16; 17].

Hypochlorous acid and chlorine monoxide (Cl_2O) remain in equilibrium in both liquid and gaseous phases. Diluted acid solution is colorless. As the HClO concentration increases, the color of the solution changes from yellow to yellow-orange due to a corresponding increase in the equilibrium Cl_2O content. In the liquid phase at 0 °C 5 % acid solution contains approximately 0.03 % chlorine monoxide, at 25 % the concentration of Cl_2O will increase to 1 %. In the gas phase at acid concentrations up to 5 %, HClO is the predominant form and in equilibrium with the vapor solution. A further increase in the concentration in the HClO gas phase leads to a predominance of Cl_2O. Equilibria between liquid and gas can be described by the following reactions (equilibrium constants are given for a temperature of 20 °C) [18; 19]:

$$2\,HClO_{(l)} \leftrightarrows Cl_2O_{(l)} + H_2O, \quad K = 8.7\cdot10^{-3} \qquad (1)$$

$$HClO_{(l)} \leftrightarrows HClO_{(g)}, \quad K = 65.3 \qquad (2)$$

$$2\,HClO_{(l)} \leftrightarrows Cl_2O_{(g)} + H_2O, \quad K = 196.0 \qquad (3)$$

$$2\,HClO_{(g)} \leftrightarrows Cl_2O_{(g)} + H_2O_{(g)}, \quad K = 1.45 \qquad (4).$$

Hypochlorous acid is very soluble in water: at 20 °C the Henry constant H_{HClO} is 0.06 atm, and the dimensionless Henry constant (where y is the equilibrium concentration of HClO in the gas, C is in the liquid phase in mole m^{-3}) is $m = 4.52\times10^{-5}$ [20].

According to the chemical properties hypochlorous acid should be attributed to strong oxidants, which interact with a large number of inorganic and organic compounds, free radicals [13–15; 21].

Hypochlorous acid can decompose both under the influence of light and temperature. In the presence of sodium chloride, the rate of decomposition increases significantly. The mechanism of decomposition, its rate and the reaction products formed depend on the concentration, temperature, pH of the solution, the presence of impurities and light. There is a slow decomposition of the reaction in an acidic environment ($pH < 3$) at room temperature [22; 23]:

$4\,HClO \rightarrow 2\,Cl_2 + O_2 + 2H_2O$ (6)

If hydrochloric acid is used for acidification, a rapid reaction takes place, the equilibrium of which is shifted to the right. Increasing the concentration of Cl^- further shifts the equilibrium towards the formation of molecular chlorine:

$HClO + HCl \leftrightarrows Cl_2 + H_2O$ (7)

The autocatalytic process occurs in the range of pH 3.0–7.5:

$2\,HClO \rightarrow O_2 + 2HCl$ (8)

Lighting accelerates this reaction, and visible light has a stronger effect than ultraviolet. The introduction of transition metal ions into the solution, for example, Co^{2+}, Ni^{2+}, Cu^{2+}, accelerates the reaction (8). It should be noted that increasing the pH of the solution weakens the catalytic action of ions. This can be due to both a decrease in the concentration of hypochlorous acid due to its dissociation with the formation of the ClO^- ion, and hydration of transition metal ions, which reduce the concentration of the catalyst.

In aqueous solutions at $pH < 4$ equilibrium is established according to equation (7), in the pH range 5–8, when the solution simultaneously contains hypochlorous acid and hypochlorite ion, a disproportionation reaction may occur [24; 25]:

$2HClO + ClO^- \rightarrow ClO_3^- + 2H^+ + 2Cl^-$ (9)

$3HClO \rightarrow 2HCl + HClO_3$ (10)

The parallel route can be realized with the participation of hypochlorous acid instead of hypochlorite ion (10), however, the rate of the process in this case is about three orders of magnitude lower. It should also be noted that at room temperature the reaction rate is relatively low, and the "chlorate" decomposition mechanism is not predominant. The maximum rate of decomposition of hypochlorous acid is observed at pH 6.89 [24].

Hydrochloric acid solutions containing chloride ions are usually prepared by reacting chlorine gas with water or alkalis. There is a rapid hydrolysis in the first case with the formation at the maximum saturation of chlorine (standard temperature and pressure) of approximately 6 % solution of hypochlorous acid. Neutralization of hydrochloric acid formed allows one to shift the balance to the right and increase the concentration of HClO. Despite the fact that chloride ions increase the rate of decomposition of hypochlorous acid, such solutions are of interest for use. Diluted solutions for use can be stored for a relatively long time in a dark place at low temperatures.

Hypochlorites, both in the form of solutions and in the crystalline state, are more stable compared to hypochlorous acid [22–25]. Highly concentrated solutions of sodium hypochlorite are one of the main commercial products of this class, which are widely used as bleaching agents and disinfectants. In the anhydrous state, metal hypochlorites are unstable and decompose with an explosion. Hydrates are more stable, but still under normal conditions spontaneously decompose. Hypochlorites of alkali and alkaline earth metals are well soluble in water (g/100 g H_2O at 20 °C): LiOCl – 72; NaOCl – 54.3; $Ca\,(OCl)_2$ – 33.3 [22].

In the ultraviolet spectrum in aqueous solution in ClO^-, the absorption maximum is observed at 292 nm (368 $mol^{-1}\,cm^{-1}$) [12; 24–26].

Hypochlorites can decompose both under the influence of light and temperature. In the process of photolysis of alkaline solutions of sodium hypochlorite under the action of ultraviolet radiation, chlorites, chlorates, chlorides and molecular oxygen are usually formed. The primary (light) reactions are following [12; 27; 28]:

$ClO^- + h\nu \rightarrow Cl^- + O(^3P)$ (11)

$ClO^- + h\nu \rightarrow Cl^- + O(^1D)$ (12)

$ClO^- + h\nu \rightarrow Cl + O^-$ (13)

The resulting radicals are involved in subsequent chemical reactions (dark stages), which lead to the formation of more stable end products. Despite the fact that hypochlorite solutions are more stable compared to hypochlorous acid, they are also prone to spontaneous decomposition over time. The main effect is the concentration, ionic strength and pH of the solution, temperature and impurities. The following reactions can occur during the decomposition of sodium hypochlorite [22; 23; 29; 30]:

$2\,ClO^- \rightarrow 2\,Cl^- + O_2 \quad k = 8.95\cdot10^{-10}\,M^{-1}s^{-1}$ (14)

$2\,ClO^- \rightarrow Cl^- + ClO_2^- \quad k = 7.7\cdot10^{-9}\,M^{-1}s^{-1}$ (15)

$ClO^- + ClO_2^- \rightarrow Cl^- + ClO_3^- \quad k = 1.54\cdot10^{-6}\,M^{-1}s^{-1}$ (16)

Reactions (15) and (16) can be formally described by second-order kinetic equations. The limiting stage of the process of decomposition of hypochlorite with the formation of chlorate is the reaction of bimolecular formation of chlorite (15), which in the rapid step (16) forms the final product [23; 29]. The process described by total equation (14) is a bimolecular reaction with an activation energy of 111.3 kJ mol^{-1}. It can be accelerated by impurities of transition metal ions (e.g., cobalt, nickel, copper, and iron and manganese to a lesser extent), while these impurities do not affect the rate of reactions (15) and (16). However, the latter can significantly increase its rate in the presence of iridium salts.

Solutions of sodium hypochlorite, both on a laboratory and industrial scale, are obtained in two basic ways: chemical (by the interaction of sodium hydroxide with molecular chlorine) and electrochemical (electrolysis of sodium chloride solutions). The chemical process can be described by the following summary equation:

$$2NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O \qquad (17)$$

The initial concentration of alkali depends on the purpose of the final product. 14 % NaOH is used in the case when one wants to get a standard solution of sodium hypochlorite with a concentration of about 12.5 %. If one wants to get a more concentrated solution containing a smaller proportion of sodium chloride, then one should use a 50 % solution of alkali. The product was concentrated by crystallization of NaCl, resulting in a solution containing 32 % NaOCl and 6 % NaCl. It should be noted that the chemical technology of obtaining solutions of sodium hypochlorite due to the chemical interaction between chlorine and alkali is now basic and is actively used in industry to obtain commercial products based on sodium hypochlorite. Detailed technological information is given in a huge number of publications, including books and reviews [31–33].

Solutions of sodium hypochlorite can also be obtained by direct electrolysis of electrolytes based on sodium chloride with a concentration of 20–40 g L^{-1} in cells without membrane or diaphragm [32; 33]. This method usually produces solutions in which the concentration of sodium hypochlorite does not exceed 0.4–0.8 %. Carrying out electrolysis in electrolyzers with a diaphragm allows one to obtain solutions with a concentration of sodium hypochlorite up to 15–20 %. In recent years, increased attention to the electrochemical synthesis of sodium hypochlorite, which was reflected in the emergence of a number of new works on the theory, technology and new designs of electrolyzers to obtain this product. The main research in the field of electrosynthesis of sodium hypochlorite is aimed at creating perfect, usually small in size and performance electrolyzers, which are designed mainly for electrolysis of dilute solutions of chloride (up to 50 g L^{-1}), sea water, mineralized groundwater or produced water [33; 34]. In some cases, chloride-containing wastewater can be directly electrolyzed to form hypochlorite, which oxidizes organic matter impurities [35–40].

Acid-base equilibria in hypochlorite solutions. The dissociation constants at different temperatures and ionic strengths of the solutions are determined in order to balance the dissociation of HClO in aqueous solutions [41]:

$$HClO \leftrightarrows H^+ + ClO^- \qquad (18)$$

or:

$$HClO + nH_2O \leftrightarrows [H_3O^+(n-1)H_2O] + ClO^- \qquad (19).$$

Hypochlorous acid was found to be the weakest (pKa = 7.53) among the oxygen-containing chlorine acids, due to the relatively high bond between hydrogen and oxygen atoms. The thermodynamic characteristics of the HCl dissociation process were determined: $\Delta H^o = +23.5$ kJ mol^{-1}, $\Delta S^o = -60.7$ J mol^{-1} K^{-1}, $\Delta G^o = +41.6$ kJ mol^{-1} [42]. Since the number of particles in the system increases with the dissociation of HClO molecules, an increase in entropy should be expected, but its value, on the contrary, decreases quite sharply. Obviously, the main reason (driving force) for the dissociation of HClO should be considered as the hydration processes of the formed ions. Therefore, when considering the acid-base equilibria of HClO for reactions (18) and (19), it is necessary to take into account both the polarizing effect of water molecules and the processes of rearrangement of hydrate shells of reacting molecules and ions.

It is assumed that together with the dissociation process in hypochlorous acid solutions, an equilibrium is established between HClO and hydrated chlorine monoxide [26; 43]:

$$2HClO \leftrightarrows H_2O{\cdot}Cl_2O, \qquad (20)$$

The equilibrium constant of this reaction at 50 °C is 3×10^{-2}. From the comparison of isobaric-isothermal potentials of HClO formation (–79.9 kJ mol^{-1}) and Cl_2O (+97.9 kJ mol^{-1}) it follows that spontaneous HClO dehydration process is practically impossible and requires quite high energy costs. It should also be noted that the content of Cl_2O oxide in solutions also strongly depends on their acidity. When acidifying solutions containing chloride ions, the concentration of Cl_2O oxide also decreases rapidly, due to the intermolecular oxidation-reduction reaction [11; 42; 43]:

$$HClO + H^+ + Cl^- \leftrightarrows Cl_2 + H_2O \qquad (21)$$

The ability of HClO to intermolecular oxidation-reduction sharply distinguishes hypochlorous acid from all other oxygen-containing chlorine acids. In contrast, the concentration of HClO in the acidification of solutions containing even relatively small amounts of chlorine ions decreases rapidly. The equilibrium constant of the reaction (21) is relatively large and at room temperature is K = 2.103. The reasons for this abnormal instability of hypochlorous acid in acidic solutions can be understood on the basis of comparing the acid-base properties of the molecules HOCl and H_2O. The fact is that hydrogen oxochlorate (I) can theoretically be considered as a compound derived from a water molecule in which a hydrogen atom is replaced by a monovalent chlorine atom. During the transition from H–O–H to H–O–Cl, the effective negative charge of the oxygen atom is markedly reduced due to the presence of a Cl atom with high electronegativity. This explains the sharp difference between the molecules of water and hydrogen oxochlorate(I) in the ability to attach an additional hydrogen ion, for example, by the reactions $H_2O + H^+ \rightarrow H_3O$ + and $HClO + H^+ \rightarrow H_2OCl^+$. As noted above, the possibility of dissociation of HClO or H_2OCl^+ by the main type ($HClO \rightarrow OH^- + Cl^+$ and $H_2OCl^+ \rightarrow H_2O + Cl^+$) has not been found experimentally. However, in acidic solutions and especially in the presence of excess chloride ions, the formation of protonated H_2OCl^+ particles can be considered as an intermediate in the intermolecular oxidation-reduction reaction:

$$HClO + H^+ + Cl^- \rightarrow [H_2OCl^{+\cdots}Cl^-] \rightarrow H_2O + Cl_2 \quad (22)$$

According to this scheme, the reaction of combined oxidation and reduction of chlorine atoms is essentially the result of the movement of the chlorine atom in the activated complex from hypochlorite to chlorine anion. Therefore, the addition of a hydrogen ion can be considered as a process that initiates the processes of breaking the O–Cl bond and the simultaneous formation of the Cl–Cl bond. This conclusion is well confirmed by known experimental facts: at a pH close to 5, when the concentration of hydrogen ions in comparison with the concentration of reacting particles decreases by several orders of magnitude, the process of intermolecular oxidation-reduction is almost non-existent.

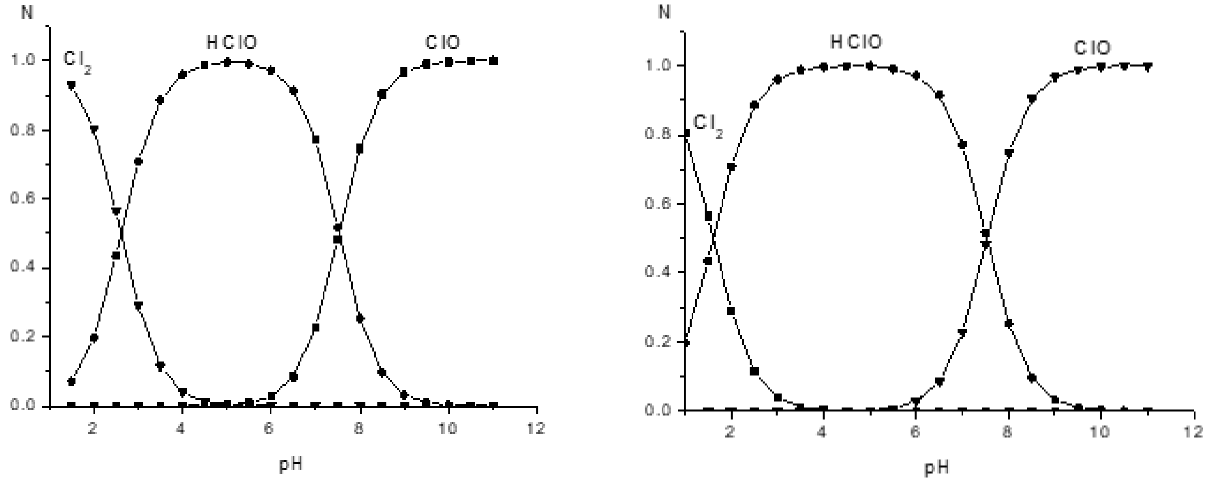
It should also be noted that the considered scheme of the process of intermolecular oxidation-reduction of HClO well explains the experimental data on the absence of Cl^+ cations in solutions. The fact is that the formation of Cl^+ cations in aqueous solution must simultaneously form their solvate shells, consisting of water molecules, which are mainly oriented to the cation with their oxygen atoms, as they are concentrated relatively large effective negative charge. As is known from thermodynamic data, the interaction between chlorine and oxygen atoms is characterized by a positive value of the isobaric formation potential [11; 42]. There is no reason to believe that this pattern is not observed for intermolecular bonds (H_2O) n… Cl^+ formed in such solvate complexes. Quantum chemical modeling by MNDO and AM1 methods of a model compound of the composition $[H_2O\ldots Cl]^+$ showed that the maximum gain in the energy of its formation is observed not in the state of its dissociation into chlorine cation and water molecule, but in the formation of chemical bonds between oxygen atoms and chlorine and the dispersion of excess positive charge on all atoms of the particle.

Thus, the analysis of possible chemical transformations in hypochlorite solutions occurring with explicit or indirect participation of hydrogen ions shows that the dependence of their compositions on the acidity of the solution is described mainly by the equilibria of processes (18) and (21). Equilibrium (20) can be neglected in practical calculations, as the error allowed will not exceed the error associated with the variation of the values of the equilibrium constants used in the calculations due to changes in, for example, temperature or ionic strength of solutions.

The results of calculations of the compositions of hypochlorous acid solutions depending on the pH and concentration of Cl^- ions, which are calculated taking into account the pK_a reactions (18) and (23), are shown in Figs. 1 and 2.

$$Cl_{2(aq)} + H_2O \leftrightarrows HClO_{(aq)} + H^+ + Cl^- \ (pK_a=2.98) \quad (23)$$

According to these data, with a decrease in the content of Cl^- ions in solutions with fixed pH values, a regular decrease in the content of chlorine molecules and a simultaneous proportional increase in the content of hypochlorous acid molecules is observed. This pattern is due to the establishment in the dynamic equilibrium solutions of intermolecular oxidation-reduction reactions of HClO and Cl_2 disproportionation. The decrease in the concentration of chloride ions causes a natural shift in the equilibrium of the reaction (21) to the left and the content of free chlorine in the solution decreases relatively sharply.



a **b**

Fig. 1. Diagram of the distribution of molar particles of chlorine, molecules and ions of hypochlorous acid at C(NaCl) = 0.9 % (a) and 0.09 % (b)

One should consider the mechanisms of chlorine evolution, since this will help to evaluate the influence of the electrode material nature on the resulting intermediate species.

Mechanisms of chlorine evolution. Active study of the kinetics of electrochemical synthesis of chlorine from aqueous NaCl solutions began in 1965 after the patented the first high-performance dimensional-stable anode (DSA®) with composite electrocatalytic coating TiO_2-RuO_2 by Henri Beer together with the Italian company De Nora. Due to the fact that the main attention was paid to the optimization of industrial chlorine synthesis, almost all works were devoted to the study of the kinetics of anodic processes in concentrated chloride solutions.

Titanium electrodes with active coating based on IrO_2 and RuO_2 are an example of classic dimensionally stable DSA® anodes for the synthesis of oxygen and chlorine, respectively. These are the most effective materials in terms of their electrochemical activity and selectivity. Ruthenium and titanium oxide electrodes are still the best type of anode for electrolysis of concentrated (20–25 %) NaCl solutions. IrO_2 was introduced into the composite coating in order to prevent corrosion destruction of RuO_2 [44] during the electrolysis of less concentrated NaCl solutions.

There is an increase in the oxidation state of the metal in the oxide coating of the anode during the electrolysis of aqueous electrolytes. There is a so-called conversion of lower oxides into higher ones. Since the chlorine evolution reaction (CER) usually takes place simultaneously or through common initial stages with the oxygen evolution reaction (OER), a correlation was found between the overvoltage of oxygen evolution and the enthalpy of oxide transition from lower to higher [45–47]. The dependence of the electrocatalytic activity of the catalyst on the reaction of oxygen evolution from the nature of the catalyst is volcanic in nature and corresponds to the Sabotier principle. Most of the considered oxides are located on the ascending branch of the curve. In this region, the OER overvoltage increases with increasing enthalpy of transition of the oxide metal from the lower to the highest oxidiation state ($\Delta H°_f$). A further increase in $\Delta H°_f$, in the case of Co_3O_4 and Fe_3O_4, leads to a decrease in OER overvoltage. The authors explain this dependence from the standpoint of changes in the energy of interaction of the oxide surface with intermediate oxygen-containing particles. Inert oxides (PbO_2 and NiO_x) do not show high catalytic activity due to the fact that intermediate oxygen-containing products have low adsorption energy. In this case, the discharge of the water molecule is the limiting stage. Oxides that oxidize too easily (Co_3O_4 and Fe_3O_4) also have low catalytic activity due to the fact that the intermediate particles have a high affinity for the surface. For these electrocatalysts, oxygen desorption is the limiting stage. In the case of RuO_2 and IrO_2, for which the optimal binding energy between the oxide surface and oxygen-containing particles is observed, the maximum catalytic activity both in OER and CER is observed. However, in later work it was shown by the XPS method that oxygen-containing intermediate particles, for example, on the surface of PbO_2, on the contrary, are characterized by high bond strength to the surface [48]. The author shows that there is an increase in OER overvoltage and vice versa when modifying lead dioxide with ionic additives that increase the binding energy of intermediate particles with the surface. This circumstance indicates the incomplete correctness of the comparison of the enthalpy of transition of the metal in the oxide $Me^{Z}\rightarrow Me^{Z+1}$ and the energy of interaction of intermediate oxygen-containing particles with the electrode surface.

When constructing similar correlations of η-ΔH°_{f} for different electrocatalysts, some factors are not taken into account, for example, differences in Tafel slopes are not taken into account, which reflect different OER mechanism or different contribution of semiconductor properties of the coating in the form of bulk charge, etc. [49; 50]. However, this approach works satisfactorily and has a satisfactory prognostic character. Conceptually, the Sabotier correlation does not contradict other ideas, according to which catalytic activity is expressed in terms of the correspondence between the potential for oxygen evolution and the potential for the transition of the catalyst oxide to the oxidized state [51].

It is believed that the evolution of chlorine and oxygen are related processes that occur through the common initial stages [45; 46]. The method of a rotating disk electrode with a ring has shown that the evolution of oxygen and chlorine on the IrO_x catalyst, which is deposited on carbon glass, occurs independently of each other [52]. The results of these studies show that the evolution of oxygen on IrO_x is not inhibited by Cl^- ions and does not depend on the route of the chlorine evolution reaction. These processes occur simultaneously and in parallel on the electrode surface.

Consider another experimentally obtained correlation that connects the OER overvoltage with the Raman shift. The combinational shift and overvoltage of the chlorine evolution reaction depending on the electrode material, show that the vibrational energy of the Cl-O bond has the closest value to the vibrational energy of Ru-O or Ir-O in oxides RuO_2 and IrO_2 [53]. At the same time the evolution of chlorine occurs with minimal overvoltage on these oxides.

The first kinetic schemes for the chlorine evolution at Ti/RuO_2 anodes were almost complete analogues of the mechanisms of hydrogen evolution reaction (HER). In 1972, Erinburg, Krishtalik, Faita, Fiori, and later Janssen proposed mechanisms that included the stages of Folmer's discharge, Tafel recombination, electrochemical descent of Geirowski, and subsequent desorption of molecular chlorine [54]:

$$Cl^- \leftrightarrows Cl_{ads} + e \qquad (24a)$$

$$Cl_{ads} + Cl_{ads} \rightarrow Cl_{2(ads)} \qquad (24b)$$

$$Cl_{2(ads)} \rightarrow Cl_{2(aq)} \qquad (24c)$$

$$Cl_{ads} + Cl^- \leftrightarrows Cl_2 + e \qquad (24d)$$

In 1975, Krishtalik suggested the possibility of an irreversible stage of formation of the adsorbed cation Cl^+_{ads} [55]:

$$Cl^- \leftrightarrows Cl_{ads} + e \qquad (25a)$$

$$Cl_{ads} \rightarrow Cl^+_{ads} + e \qquad (25b)$$

$$Cl^+_{ads} + Cl^- \leftrightarrows Cl_2 \qquad (25c)$$

Jansen calculated the Tafel slope for each stage for this Erinburg-Krishtalik mechanism in 1983. If the limiting stage is the stage of electrochemical adsorption of Folmer (25a) with the transfer of the first electron, the Tafel slope should be 118.4 mV. For the limiting stage of oxidation of adsorbed chlorine with the transfer of the second electron (25b), the Tafel slope should be 39.5 mV. If the rate is determined by the last chemical stage (25c), the slope will be 29.6 mV. Quite often the experimental Tafel slope is about 30 mV, which indicates a delayed stage of desorption of chlorine from the anode surface [56; 57]. At the Pt electrode, the Tafel slope is between 30–40 mV, which indicates the effect of the electrode surface on the kinetics of desorption of chlorine from the surface [58].

However, the above mechanisms did not take into account the features of the surface of oxides and metals during anodic polarization. Further development of ideas about the mechanisms of chlorine evolution was made by Ehrenburg, Krishtalik, Jansen, Burke, and others. Based on the analysis of the results of complex kinetic studies of particular orders, limiting stages and the nature of intermediates, it is shown that most often chlorine synthesis is limited by the stage of electrochemical desorption (25c). At the same time, the possibility of the formation of adsorbed particles on the anode surface, such as $(Cl_{ads})^+$ and $(ClO_{ads})^-$. A mechanism for CER on ruthenium dioxide was proposed in 1978, which provided the possibility of the formation of adsorbed hypochlorite ion on the surface [59]:

$$RuO_2 + H_2O \rightarrow RuO_3 + 2H^+ + 2e^- \qquad (26a)$$

$$RuO_3 + Cl^- \rightarrow RuO_2(ClO_{ads})^- \qquad (26b)$$

$$RuO_2(ClO_{ads})^- + Cl^-_{ads}(\text{or } Cl^-) + 2H^+ \rightarrow Cl_2 + H_2O \qquad (26c)$$

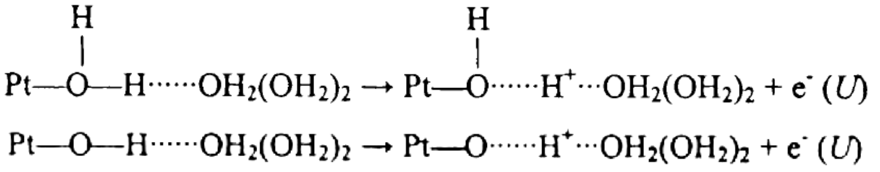
As noted in the J. Augustynski works, according to XPS spectroscopy, the process of oxidation of the surface of Ru(IV) to Ru(VI) by oxygen occurs before the adsorption of chlorine ions [59]. On the other hand, with the development of surface analysis technology by the XPS method, the change in the oxidation state of the metal in the oxides of the surface layer of the electrode during the evolution of chlorine was experimentally confirmed. The question of the nature of adsorbed oxygen, which is involved in the oxidation of Cl^-, is debatable. This oxygen is adsorbed as a result of the discharge of the water molecule (the conventional adsorption evolution mechanism, AEM) or it is the oxygen of the crystal lattice of oxide (the lattice oxygen mechanism, LOM) [60; 61]. The discussion concerned the possibility of the existence of $M\text{-}OH_{ads}$-type particles adsorbed on the surface and the reaction of Cl^- ions with them. As a result, several mechanisms of chlorine evolution were proposed, which took into account the possibility of formation of oxygen-containing adsorbed particles, which, depending on the pH of the electrode layer, may be in equilibrium with $OH_2{}^+{}_{ads}$ and $O^-{}_{ads}$:

$H_2O_{ads} \rightarrow OH_{ads} + H^+ + e^-$ (27a)
$OH_{ads} \rightarrow O_{ads} + H^+ + e^-$ (27b)
$OH_{ads} + H^+ \leftrightarrows OH_2{}^+{}_{ads}$ (27c)
$OH_{ads} \leftrightarrows O^-{}_{ads} + H^+$ (27d)

Anderson [75; 77] showed that the discharge of the water molecule on platinum, through the mechanism of electrochemical deprotonation with the formation of OH_{ads} (28a, b), is possible starting from potentials of 0.57 V (SCE) and the activation energy of deprotonation adsorbed water molecules at 0.57 V (SCE) is insignificant and is 0.0–0.14 eV. Deprotonation of OH_{ads} with the formation of O_{ads} (28c) at 1.32 V (SCE) becomes thermodynamically possible with an activation energy of 0.25–0.5 eV.

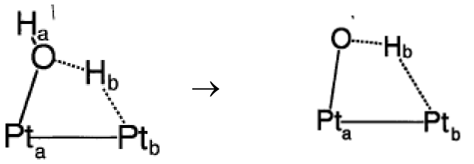
$H_2O_{ads} \rightarrow OH_{ads} + H_{ads}$ (28a)
$H_{ads} \rightarrow H^+{}_{aq} + e^-$ (28b)
$OH_{ads} \rightarrow O_{ads} + H^+ + e^-$ (28c)

The binding energies of Pt and H_2O_{ads}, H_{ads}, OH_{ads} and O_{ads} are estimated as 0.65; 2.8; 2.9 and 5.1 eV. The most strongly bounded particle is O_{ads}. The binding energies of H_{ads} and OH_{ads} are comparable, and proton desorption occurs after H_{ads} discharge. Based on the conducted quantum chemical calculations, the water molecule is adsorbed on one Pt site and the precursor $OH_2(OH_2)_2$ participates in its successive deprotonation [62]:



$$\mathrm{Pt{-}\overset{H}{\overset{|}{O}}{-}H\cdots OH_2(OH_2)_2 \rightarrow Pt{-}\overset{H}{\overset{|}{O}}\cdots H^+\cdots OH_2(OH_2)_2 + e^-}\ (U) \quad (29a)$$

$$\mathrm{Pt{-}O{-}H\cdots OH_2(OH_2)_2 \rightarrow Pt{-}O\cdots H^+\cdots OH_2(OH_2)_2 + e^-}\ (U) \quad (29b)$$



$+ H^+ + e^-$ (29b)

Optimization of the surface structure of the adsorbed water molecule and OH_{ads} (29b) suggests that after further deprotonation with Pt_a-O formation, the adjacent Pt_b platinum atom becomes free, for example, for the Cl^- discharge by the Folmer mechanism.

Due to the fact that in low concentrated NaCl solutions the oxidation of Cl^- occurs simultaneously with OER, it is appropriate to give a modern view of the mechanism of oxygen formation at oxide anodes. According to Rossmeisl and Norskov [39], the oxygen evolution occurs in four stages with the formation of the intermediate $HOO^\bullet$:

$H_2O + M \rightarrow M\text{-}OH + H^+ + e^-$ (30a)
$M\text{-}OH \rightarrow M\text{-}O + H^+ + e^-$ (30b)
$M\text{-}O + H_2O + \rightarrow M\text{-}OOH + H^+ + e^-$ (30c)
$M\text{-}OOH \rightarrow O_2 + H^+ + e^-$ (30d)

Consider several mechanisms of chlorine evolution involving oxygen-containing adsorbed particles:

i) Denton and Harrison (1979) suggest the possibility of electrochemical adsorption of chlorine at the active site in the vicinity of the adsorbed particle OH_{ads} and their subsequent recombination with the formation of hypochlorous acid [63]:

$Cl^- + \leftrightarrows Cl_{ads} + e^-$ (31a)
$H_2O + \leftrightarrows OH_{ads} + H^+ + e^-$ (31b)
$Cl_{ads} + OH_{ads} \rightarrow HOCl_{ads}$ (31c)

However, at high occupancy rate of the surface with oxygen-containing particles, the probability of direct discharge of Cl^- (31a) is unlikely, which is also indicated by the results of studying the surface of RuO_2 by Raman spectroscopy [53].

(ii) Burke and O'Neill (1979) tried to describe the rout of the chlorine evolution reaction on the surface of oxides in the region of potentials where the surface is filled with O_{ads} particles that act as active centers and regenerate during electrochemical desorption of chlorine molecules to form O_{ads} [64]:

$O_{ads} + Cl^- = OCl_{ads} + e^-$ (32a)
$OCl_{ads} + Cl^- = Cl_2 + O_{ads} + e^-$ (32b)

(iii) Krishtalik and Erenburg (1981) suggested two successive main steps: discharge of the water molecule adsorbed on the active center with the formation of OH_{ads} particles and subsequent discharge of the Cl^- ion with the formation of the adsorbed hypochlorous acid molecule, which in acidic environment is converted into chlorine molecule [65; 66]:

$H_2O \leftrightarrows OH_{ads} + H^+ + e^-$ (33a)
$OH_{ads} + Cl^- \rightarrow M(HO)Cl + e^-$ (33b)
$HOCl + HCl \leftrightarrows Cl_2 + H_2O$ (33c)

(iv) Erenburg (1984) extended the Burke and O'Neill mechanism taking into account the possibility of Cl^- ion discharge at the active centers of two types of M–OH and M–O with their subsequent regeneration without the adsorption-desorption stage of oxygen-containing particles, which is energetically advantageous for surfaces with high oxygen affinity [67]:

$M{-}OH_2^+ \leftrightarrows M{-}OH + H^+$ (34a)
$M{-}OH \leftrightarrows M{-}O + H^+ + e^-$ (34b)
$M{-}O + Cl^- \rightarrow M{-}OCl + e^-$ (34c)
$M{-}OCl + Cl^- + H^+ \leftrightarrows M{-}OH + Cl_2$ (34d)
$M{-}OCl + Cl^- \leftrightarrows M{-}O + Cl_2 + e^-$ (34f)

Currently, the nature of chlorine particles adsorbed on the anode surface is still under discussion: electrochemical adsorption occurs directly on the active center of the metal oxide M^{z+}(35a) or on the active center with adsorbed oxygen-containing particle M-OH or M-O (35b).

$(M^{z+1}) + Cl^- \rightarrow (M^{z+1})Cl + e^-$ (35a)
$M{-}OH + Cl^- \rightarrow M(OH)Cl + e^-$ (35b)

Krishtalik and Ehrenburg showed that hydroxyl radicals, which are formed during the electrolysis of water on the electrode surface, have a significant effect on the kinetics of chlorine formation [65]. Due to the development of technologies, single-crystal RuO_2 electrodes were fabricated and surface reactions for different crystallographic orientations were studied. It is known that the anodic formation of oxygen-containing particles proceeds with the generation of a proton (27) and is a pH-dependent step and, as a consequence, the kinetics of chlorine evolution must also depend on pH. However, in practice such dependence is not always fulfilled. The effect of pH on the course of CER was studied by Krystalik and, taking into account the effect of pH, a mechanism (33) was proposed. However, later works [68–70] showed that the correlation between the kinetics of chlorine formation and pH depends on the morphology of the electrode surface. While the order of the chlorine formation reaction on the RuO_2 (230) surface is inversely proportional to the H^+ concentration, on the RuO_2 (110) surface the chlorine evolution kinetics is independent of pH. Thus, the mechanism of chlorine evolution on the faces (110) and (230) of RuO_2 is different. The surface (230) usually has a high density of defects and is more hydrophilic compared to the surface (110), which is more hydrophobic. It is assumed that on the surface (230) the oxidation of the water molecule precedes the oxidation of chloride ion. Due to above mentioned, the evolution of chlorine on (230) is a pH-dependent process. Since the surface (110) is relatively hydrophobic, the oxidation of chlorine ions precedes the discharge of the water molecule and, thus, the kinetics of CER is practically independent of pH. Since RuO_2-based electrodes used in practice for chlorine synthesis (ruthenium and titanium oxide electrodes) are polycrystalline but have a predominant surface orientation (110), the kinetics of the chlorine evolution reaction at such anodes is weakly dependent on pH.

Based on the measurement of polarization resistance by Fernandez and coworkers, a kinetic analysis of Cl^- oxidation was performed, the results of which allowed one to propose another mechanism of chlorine evolution reaction on Ti/RuO_2 anodes [71]:

$M^z \leftrightarrows M^{z+1} + e^-$ (36a)
$M^{z+1} + Cl^- \leftrightarrows MCl^{z+1} + e^-$ (36b)
$MCl^{z+1} + Cl^- \leftrightarrows M^z + Cl_2$ (36c)
$2MCl^{z+1} \leftrightarrows 2M^{z+1} + Cl_2$ (36d)

The first step of the mechanism is the oxidation of active centers of the surface, which then undergo electrochemical adsorption of chloride ions with the formation of an intermediate product - atomic chlorine by the Folmer mechanism. The evolution of chlorine, according to this mechanism, can occur either by Tafel recombination, or due to the reaction of adsorbed chlorine and chloride ion with the reduction of the active center of the surface.

H.A. Hansen and colleagues, based on the density functional theory (DFT) established linear relationships between the adsorption energies of Cl, ClO and O on the surface of rutile oxides MO_2 (M – Ir, Ru, Pt, Ti) [69]. These linear energy dependences allowed the authors to construct a generalized surface phase diagram, where OER overvoltage and oxygen binding energy are descriptors that determine the surface composition. Thus, the lower limit of the overvoltage required for the reaction is defined as a function of the oxygen adsorption energy. Combining the surface phase diagram and Sabatier correlation, the authors made assumptions about the state of the surface under the conditions of the chlorine evolution reaction and showed that the reaction mechanism differs depending on the catalyst material. The flexibility of the reaction path explains the high activity of different materials with a wide range of oxygen-oxide bond energies in relation to the chlorine evolution reaction. The authors proposed a kinetic scheme that takes into account the interaction of chloride ion with surface oxygen atoms O^c in the coordinatively unsaturated sites (CUS) [72] on the surface [69]:

$O^c\text{-}O^c + Cl^- \rightarrow (O^c)_2\text{-}Cl + e^-$ (37a)

$(O^c)_2\text{-}Cl + Cl^- \rightarrow O^c\text{-}O^c + Cl_2 + e^-$ (37b)

It is concluded that ClO^c or $Cl(O^c)_2$ will be spontaneously formed in the coordination unfilled places of the IrO_2 and RuO_2 surface with the potential required for chlorine evolution. The authors believe that this indicates that the evolution of Cl_2 occurs through these intermediates, although the potentials required for the evolution of Cl_2 for most oxides are always less than the potentials for the evolution of oxygen.

Analysis of the literature showed almost complete lack of comprehensive studies of the kinetics of oxidation of chloride ions in relatively low concentrated (0.05–0.5 M) NaCl solutions at pH close to neutral, with the formation of hypochlorite and hypochlorous acid. The vast majority of studies are devoted to the study of the reaction of chlorine evolution in highly concentrated (1–4 M) NaCl solutions on the surface of electrocatalysts based on ruthenium oxides, iridium and other oxides. In those works where the kinetics of the formation of active chlorine and chlorate are studied, authors often rely on already existing mechanisms of chlorine evolution [73–76]. This approach is largely justified, because the formation of chlorine, on the one hand, in some mechanisms is considered through the formation of intermediate oxygen-containing chlorine(+1), and on the other hand, the formation of hypochlorite is considered as a result of interaction of molecular chlorine with water in neutral (23) and hydroxide ions in alkaline (18) media.

The issue of how the ClO^- ion is formed remains quite controversial. Whether it is formed on the surface of the anode, taking into account the acidification of the anode layer, in the form of hypochlorous acid or in the form of molecular chlorine. The absence of gas formation on Ti/Pt-Pd-500 °C anode, which accompanies the electrolysis of 0.15 M NaCl, also can not answer this question with certainty. The literature review considers several mechanisms that correspond to modern ideas about the path of the chlorine evolution reaction in concentrated chloride solutions within the concept of oxygen transfer reactions. These are the mechanisms, proposed by Denton & Harrison (31); Burke & O'Neill (32); Krishtalik & Erenburg (33); Erenburg (34); H.A. Hansen (37). In the framework of all these mechanisms, it is possible to describe with some success the processes that accompany the synthesis of sodium hypochlorite in low-concentrated NaCl solutions. But, in our opinion, the regularities of processes described above can best be described from the standpoint of the Krishtalik & Erenburg mechanism (33).

If one omits the chemical stage of conversion of hypochlorous acid HOCl to Cl_2 (33c) and add the stage of adsorption of the water molecule to the catalytic center S, the Krishtalik-Erenburg mechanism can be written as follows:

$H_2O_{aq} + S \leftrightarrows S\text{-}OH_2$ (38a)

$S\text{-}OH_2 \leftrightarrows S\text{-}OH + H^+ + e^-$ (38b)

$S\text{-}OH + Cl^- \rightarrow S(HO)Cl + e^-$ (38c)

$S(HO)Cl + H_2O_{aq} \leftrightarrows S\text{-}OH_2 + HOCl_{aq}$ (38d)

For example, the catalytic active site of the surface S in the case of Pd-containing catalysts may be PdO sites that have a high affinity for hydroxylation [7]. According to this mechanism, the oxidation of Cl^- leads to the formation of hypochlorous acid on the surface, which, taking into account the pH, is partially or completely converted into hypochlorite in the bulk. The slowness of step (38c) can be explained by the 40 mV Tafel slopes observed in 0.15 M NaCl on most of the metal and oxide composite anodes [7; 77].

Based on the initial stages (38a, b), one can compile the mechanisms of formation of chlorite and chlorate, which are realized at higher polarizations with the participation of OH_{ads} particles with higher energies:

$HOCl + S\text{-}OH = S + ClO_2{}^-{}_{aq} + 2H^+ + e^-$ (38e)

$ClO^- + S\text{-}OH = S + ClO_2{}^-{}_{aq} + H^+ + e^-$ (38f)

$ClO_2{}^- + S\text{-}OH = S + ClO_3{}^-{}_{aq} + H^+ + e^-$ (38g)

Obtaining a disinfectant involves the use of either synthetically obtained solutions or sea water, and the flow of several parallel processes reduces the purity of the resulting product. The nature of the electrode also plays an important role. Basically, as practice shows, electrodes containing metals or metal oxides of the platinum group are used for electrolysis. They have proven themselves in the production of molecular chlorine. But there are also a number of problems. Their use is quite expensive, a number of materials become unstable with an increase in the oxygen current efficiency, they are quickly destroyed. Alternatively, metal platinum can be used.

Platinum surface can be in the oxidized-passive and reduced-active state [78]. Electrolysis of NaCl solutions in the entire concentration range usually takes place on the oxidized surface [79]. At the same time, the main three parallel processes with comparable current efficiencies are realized: oxidation of Cl^- to hypochlorite and chlorate and oxygen evolution reaction. The current efficiency of hypochlorite reaches 90 % and the process proceeds at lower (400–450 mV) polarizations on the reduced surface. Chlorates are practically not formed under these conditions. However, during anodic polarization, the pre-reduced Ti/Pt surface undergoes a number of transformations. Layers of labile and then inert chemisorbed oxygen-containing particles begin to form on the Pt surface in the region of low polarizations. With increasing polarization, the formation of atomic oxygen becomes possible, the formation of phase oxide layers occurs. The formation of phase surface oxides occurs rapidly in background solutions, and the reaction of oxygen evolution takes place on a completely oxidized surface. The presence of Cl^- in solution significantly decelerates this process. Chloride ion acts as a depolarizer, discharging, interacting with surface oxygen-containing particles, thereby slowing down the oxidation of the surface. Thus, both direct oxidation of Cl^- and its oxidation by labile oxygen-containing particles (OH_{ads}) are possible on the reduced platinum surface. On the oxidized surface, the formation of hypochlorite occurs directly on the surface of the layer of phase oxides of platinum with the participation of more strongly bound (inert) chemisorbed oxygen-containing particles and atomic oxygen. The desorption of Cl^- primary oxidation products is decelerated, and an increase in the degree of filling of the surface with active oxygen-containing particles O_{ads} leads to a significant increase in the rate of chlorate formation.

On the passive surface, before the beginning of active oxygen evolution, the oxidation of Cl^- even in 1 M NaCl takes place at the limiting current, the magnitude of which is determined by the proportion of active centers of the surface, i.e., has a surface nature. Comparison of the limiting currents values on the active and passive surface Ti/Pt allows one to conclude that the ratio of active centers of the latter does not exceed 5–10 % of the initial. However, the platinum surface is easily activated by short-term cathodic polarization in the region of hydrogen evolution.

Short-term electrolysis on the reduced-active surface of platinum, even in low-concentrated 0.15 M NaCl solution, is realized with anomalous for platinum and platinized titanium integrated current efficiency of NaClO close to 90 %. On the oxidized-passive surface, under the same process conditions, CE (NaClO) does not exceed 40 %.

Analysis of cyclic voltammograms obtained in 1 M $HClO_4$ shows that the application of platinum on a porous titanium substrate leads to a 5–10-fold increase in the electrochemically active surface of the electrode. Voltammetric measurements showed that at porous Ti/Pt anodes in 1 M $HClO_4$ polarization by 140 mV, and in 1.0–2.0 M NaCl by 400–500 mV smaller compared to non-porous samples of Ti/Pt and metallic Pt. This behavior gave reason to expect a significant increase in hypochlorite and a decrease in chlorate current efficiency when using porous anodes during the electrolysis of NaCl solutions. However, the results of cumulative electrolysis showed that in low-concentrated NaCl solutions (0.15–0.5 M) the current efficiencies of hypochlorite on porous anodes are lower than at nonporous ones. This is due to several reasons – low electrical conductivity of solutions and a fairly high current efficiency of oxygen, which leads to blockage of pores and parts of the surface with oxygen. However, the low polarization of the electrode does not create conditions for the accumulation of chlorates with high rate. The only conditions where porous Ti/Pt has shown greater efficiency compared to non-porous anode is the electrolysis of concentrated solutions (1.0–2.0 M) at an overall current density of 20–60 mA cm^{-2} with hypochlorite current efficiency close to 85–90 % and current efficiency of chlorate was less than 7 %.

Heat treatment at 250 °C of non-porous sample leads to a slight increase in the current efficiency in the entire range of current densities. Heat treatment at 400 °C leads to a significant drop in the CE of NaClO in the low anode current densities (20–40 mA cm^{-2}) range. There is an increase in CE of NaClO with increasing current density. Current efficiencies on non-heat-treated and heat-treated samples become equal at

80 mA cm^{-2}. The current efficiency of chlorate on heat-treated samples is slightly lower than on non-heat-treated in the whole range of investigated current densities. Thus, when using Ti/Pt as anodes for the synthesis of sodium hypochlorite in low-concentrated NaCl solutions, it is possible to recommend short-term (during 1 hour) heat treatment of Ti/Pt at 250 °C. Increasing the heat treatment temperature to 400–500 °C, due to the reduction of the current efficiency of NaClO and the transition time of the anode from active to passive state, is impractical, both for normal and for reverse mode electrolysis.

Treatment of porous Ti/Pt at 250 °C does not change the catalytic activity. However, heat treatment at 400 °C leads to a significant increase in CE of NaClO during the electrolysis of 0.15 M NaCl at the low current density of 20–40 mA cm^{-2} from 32 to 54 %. There is a decrease of 20–25 % CE of $NaClO_3$ in the whole range of current densities. This feature, along with high current efficiency of NaClO in the low current density region, justifies the use of heat-treated at 400 °C porous Ti/Pt with a platinum surface content of 2.5 mg cm^{-2} for the synthesis of sodium hypochlorite in low-concentrated NaCl solutions at 20–40 mA cm^{-2}.

It is possible to reduce working concentrations of solutions at preservation of high current efficiencies of hypochlorite and low current efficiencies of chlorates at the expense of carrying out electrolysis in the reverse current mode. If electrolysis of 0.15 M NaCl is carried out in the usual mode at anode current densities of 20–40 mA cm^{-2}, the current efficiency of hypochlorite does not exceed 26 % and the current efficiency of chlorate is not less than 21 %. Carrying out electrolysis in the reverse mode allows one to increase the current efficiency of hypochlorite up to 40 % while reducing the current efficiency of chlorate to 5 %. Increasing the NaCl concentration to 0.3 M further significantly improves characteristics of reverse electrolysis. At the same time CE of NaClO increases to 78 %, and CE of $NaClO_3$ decreases to 2 %.

It is shown that heat treatment of Ti/Pt at 400 and 500 °C reduces the residence time of the anode in the active state by 3–5 times, which makes the use of heat-treated Ti/Pt electrodes for reverse electrolysis unjustified.

It was shown [80] that Ti/Pt electrodes with 2 mg cm^{-2} of platinum can be used in non-diaphragm flow and cumulative cells for electrolysis of low-concentrated NaCl solutions in order to obtain pure NaClO solutions. Electrolysis must be carried out in the reverse mode, the duration of which is determined in accordance with the specified parameters of electrolysis (current density, concentration of NaCl and NaClO, hydrodynamic conditions).

Palladium in the Ti/SnO_2-Pt-Pd coating exists in the form of PdO phase, as has been shown in [7] by X-ray diffraction analysis. In the same work X-ray photoelectron spectroscopy has shown that adsorbed OH groups and water are present only on the surface of palladium-doped SnO_2-based coatings. Moreover, their number is proportional to the palladium content in the coating. The surface oxygen concentration in H_2O_{ads} and OH_{ads} is comparable to the oxygen content of the phase oxides of tin and palladium, indicating a high surface content of adsorbed water in the anode containing 19.5 at. % Pd. Thus, palladium oxides are the main centers of water adsorption, and their presence on the surface of the anodes contributes to the hydroxylation of the surface. Most likely, this property of palladium compounds provides its high electrocatalytic activity in the reaction of formation of hypochlorite, which involves labile oxygen-containing particles with low bond strength to the surface.

It is known [81–86] that lead dioxide and other catalytic coatings based on it are also characterized by high overvoltage of oxygen, and as a consequence, high electrocatalytic activity in reactions occurring at high anode potentials involving adsorbed oxygen-containing particles.

According to [45; 81], the reaction of oxygen evolution on PbO_2 is limited by transfer of the second electron (electrochemical desorption). Increasing the bond strength of chemisorbed oxygen will increase the overvoltage of oxygen and, accordingly, increase the energy of oxygen-containing particles. According to researchers [45; 81; 87], one of the factors influencing the electrocatalytic activity of the anode material is the nature of these oxygen-containing particles, which can be inert or labile depending on the strength of the bond with the electrode surface. The change in the properties of the modified coatings with respect to the oxygen evolution reaction mainly depends on the change in the chemical properties of the oxide surface, which in turn leads to a change in the bond strength of oxygen-containing particles chemisorbed on the electrode surface. Lead dioxide electrodes modified with various additives are of great interest [88], because while maintaining the basic properties of PbO_2, their catalytic activity can vary widely [89–91]. The oxygen evolution overvoltage can vary depending on the nature and amount of modifying additives [92].

In general, materials containing platinum group metals or their oxides have a low oxygen evolution overvoltage, but it is of interest to use oxide materials containing a small amount of platinum group metals. Such electrodes usually characterized by high overvoltage of oxygen evolution. Here it is of interest to see the influence of the composition of the base material.

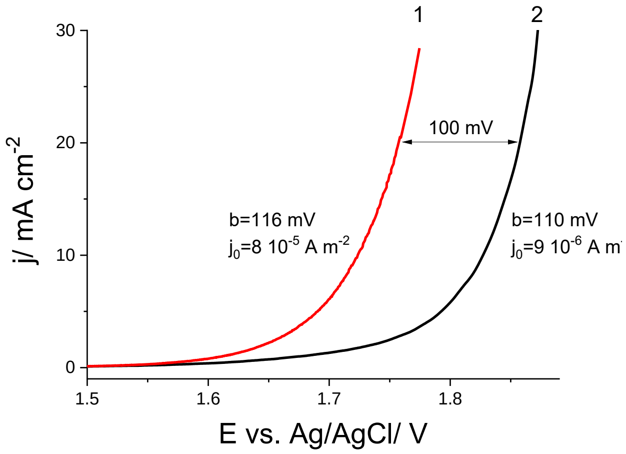


Fig. 2. Quasi steady-state j-E curves (5 mV s^{-1}) obtained on Ti/Pt (1) and Ti/Pt/PbO$_2$ in 1 M HClO$_4$

Potentiodymamic curves were recorded on 1 cm^2 electrode in 1 M HClO$_4$, 1 M NaCl (pH 9.2), 0.15 M NaCl (pH 9.2), 1 M NaClO$_4$ (pH 9.2), and accumulative electrolysis of NaCl was performed on 5 cm^2 anode.

As expected, the OER polarization curve obtained on Ti/Pt-PbO$_2$ anode is shifted by 100 mV to the region of more positive potentials compared to Ti/Pt in 1 M HClO$_4$ (Fig. 2).

The addition to 1 M NaClO$_4$ (pH 9.2) chloride ions in the form of NaCl leads to a shift of the polarization curves by approximately 80 mV towards lower potentials (Fig. 3).

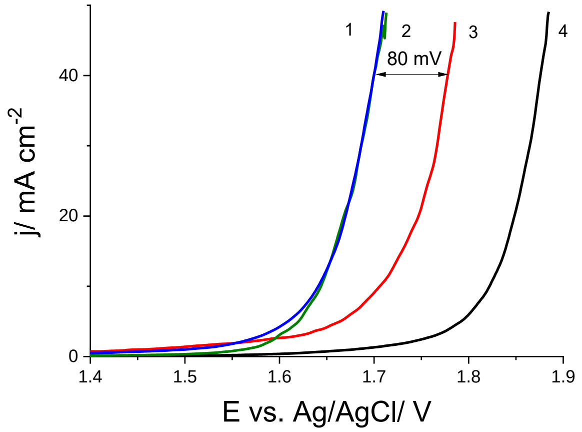


Fig. 3. Quasi steady-state j-E curves (5 mV s^{-1}) obtained on Ti/Pt-PbO$_2$ in the next solutions: 1 – 0.15 M NaCl; 2 – 1.0 M NaCl; 3 – 1.0 M NaClO$_4$; 4 – 1.0 M HClO$_4$

The catalytic coating was applied to the surface of Ti/Pt from nitrate electrolyte 0.1 M HNO$_3$ + 0.1 M Pb(NO$_3$)$_2$ at anode density current 4 mA cm^{-2} during 60 minutes The average thickness of the coatings is 50 μm. The dried electrodes have a uniform dark gray color characteristic for PbO$_2$ coatings synthesized from nitrate bath.

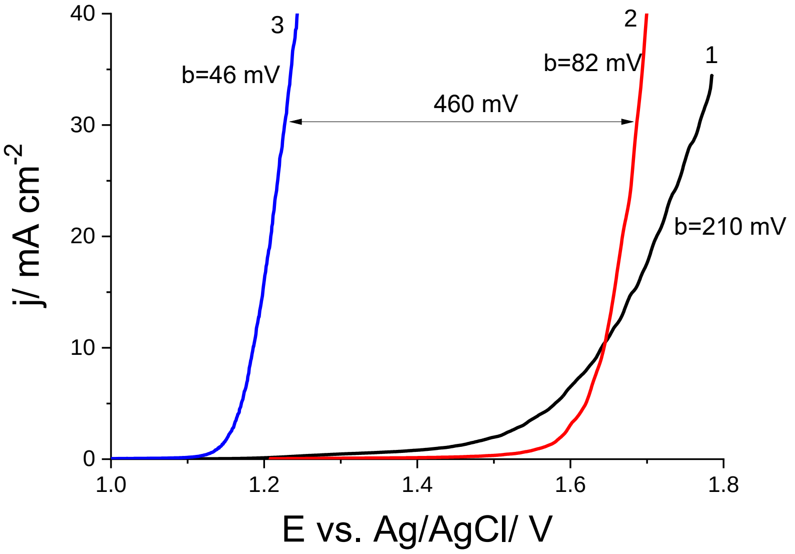


Fig. 4. Quasi steady-state j-E curves (5 mV s^{-1}) obtained on next electrodes: 1 – Ti/Pt; 2 – Ti/Pt-PbO$_2$; 3 – heat treated at 500 °C Ti/Pt-Pd in 0.15 M NaCl (pH 9.2)

Moreover, in the presence of NaCl in a concentration of 0.15 and 1.0 M polarization curves are almost the same, their potentials under current are in the range of 1.6–1.7 V, which is 460 mV more positive compared to the heat-treated at 500 °C reference Ti/Pt-Pd anode [93]

(Fig. 4). If the above correlation criterion is met for anodes with an active coating based on lead dioxide in the oxidation of Cl^-, it is possible to predict relatively low current efficiencies of NaClO (30–50 %) as well as high current efficiencies of $NaClO_3$.

The results of cumulative electrolysis confirmed the suitability of the correlation criterion for this anode. The current efficiency of NaClO was 44 % and the current efficiency of $NaClO_3$ was 34 % on the Ti/Pt-PbO_2 anode in 0.15 M NaCl. Increasing the concentration of NaCl to 30 g L^{-1} did not significantly change the results of electrolysis: CE of NaClO increased to 55%, and CE of $NaClO_3$ decreased to 28 % (Table 1).

Table 1

Data on cumulative electrolysis of NaCl on Ti/Pt-PbO_2 electrode

C(NaCl)/ g L^{-1}	j_a/ mA cm^{-2}	CE(NaClO)/ %	CE($NaClO_3$)/ %
9	40	44	34
30	40	55	28

As mentioned above, lead dioxide anodes cannot be used for the synthesis of high-purity sodium hypochlorite solutions for medicine, veterinary medicine and the food industry. However, during the preparation of sodium hypochlorite solutions, for example, for chemical synthesis, disinfection of ballast water of marine vessels, anodes based on lead dioxide can be successfully used [94; 95]. Especially when their operation will take place under conditions of low anode current densities (up to 50 mA cm^{-2}), when the possible rate of destruction of the anodes is minimal.

Several more anodes based on lead dioxide doped with Co, Bi and F were prepared. Part of the PbO_2 coatings of this series were deposited on a Ti/Pt substrate from nitrate and part from methanesulfonate electrolytes [81]. Anode deposition current densities of PbO_2 ranged from 4 to 50 mA cm^{-2} and a temperature from 20 to 60 °C. Additives were introduced into the electrolyte in the form of the corresponding salts of methanesulfonic and nitric acid. Fluoride was introduced in the form of NaF.

As is known [96–98], doping with iron [96], fluorine [97] and bismuth [81] changes the ratio of labile and inert oxygen-containing particles on the PbO_2 surface, which leads to changes in the anodic polarization of OER. Fig. 5 shows the polarization curves obtained on modified PbO_2 anodes. Modification with fluorine and bismuth ions leads to an additional increase in the polarization of Ti/Pt-PbO_2 electrode and a decrease in the OER exchange current, and modification with cobalt has the opposite effect (Table 2).

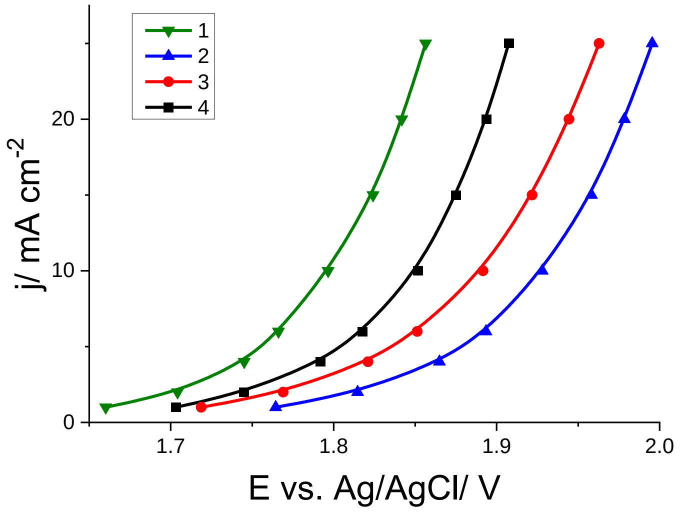


Fig. 5. Quasi steady-state j-E curves obtained in 1 M $HClO_4$ on next electrodes: 1 – Ti/Pt-PbO_2-Co; 2 – Ti/Pt-PbO_2-F; 3 – Ti/Pt-PbO_2-Bi; 4 – Ti/Pt-PbO_2

Table 2

Kinetic characteristic for doped lead dioxide anodes

Anode	a	b/ V dec^{-1}	α·n	j_o(α·n)/ A m^{-2}	j_o(α=0.5)/ A m^{-2}
Ti/Pt-PbO_2-Co	0.5115	0.1389	0.425	2.08×10^{-4}	4.70×10^{-5}
Ti/Pt-PbO_2-Bi	0.5323	0.1747	0.338	8.97×10^{-4}	3.14×10^{-5}
Ti/Pt-PbO_2	0.5457	0.1470	0.402	1.94×10^{-4}	2.42×10^{-5}
Ti/Pt-PbO_2-F	0.5906	0.1644	0.360	2.55×10^{-4}	1.01×10^{-5}

The catalytic activity of the electrodes involved was evaluated in relation to the processes of of hypochlorite and chlorate synthesis. Electrolysis was performed during 60 min at 40 mA cm^{-2} in a cell with a separated electrode space under conditions of forced maintenance of the pH of the anolyte at 8.2–8.5. Two solutions were used as base electrolytes for the tests: a solution of 27 g L^{-1} NaCl + 4.5 g L^{-1} Na_2SO_4, which is artificial sea water, and reduced sea water from evaporated sea salt of the Yellow Sea.

If one compares the current efficiencies of hypochlorite and chlorate during the electrolysis of a above mentioned solution on pure and doped PbO_2 coatings, one should register a slight increase in CE of NaClO and a decrease in CE of $NaClO_3$. When lead dioxide doped with bismuth and fluorine (additives that increase the polarization of OER, see Fig. 5) there is a decrease in CE of NaClO and an increase in CE of $NaClO_3$ (Table 3).

Ruthenium titanium oxides electrode and that same coated with PbO_2 demonstrated maximum activity and selectivity. CE of NaClO at these anodes is close, but CE of $NaClO_3$ is much higher on Ti/TiO_2-RuO_2-PbO_2, due to higher OER overvoltage in the presence of PbO_2.

Table 3

Electrolysis of 27 g L^{-1} NaCl + 4.5 g L^{-1} Na_2SO_4 solution at 40 mA cm^{-2}

Anode, deposition conditions	CE (NaClO)/ %	CE ($NaClO_3$)/ %	E_a/V
Ti/Pt	19.4	8.3	1.99
Ti/TiO_2-RuO_2	79.0	1.5	1.23
Ti/Pt-PbO_2 1M $Pb(MS)_2$+0.11M MSA; j=4 mA cm^{-2}; t=25 °C	53.8	15	1.77
Ti/Pt-PbO_2 1M $Pb(MS)_2$+0.11M MSA; j=10 mA cm^{-2}; t=65 °C	51.4	17	1.72
Ti/Pt-PbO_2 1M $Pb(MS)_2$+0.11M MSA; j=10 mA cm^{-2}; t=25 °C	41.7	19	1.80
Ti/Pt-PbO_2-F 0.1M $Pb(MS)_2$+1M MSA+0.01M NaF; j=10 mA cm^{-2}; t=25 °C	36.4	25	1.96
Ti/Pt-PbO_2-Bi 0.1M $Pb(MS)_2$+1M MSA+0.01M Bi^{3+}; j=10 mA cm^{-2}; t=25 °C	34.2	28	1.83
Ti/Pt-PbO_2-Co 0.1M $Pb(MS)_2$+1M MSA+0.01M Co^{2+}; j=10 mA cm^{-2}; t=25 °C	43.8	15	1.75
Ti/TiO_2-RuO_2-PbO_2 1M $Pb(MS)_2$+0.11 M MSA; j=10 mA cm^{-2}; t=65 ºC	77.8	9.3	1.25

Electrolysis of reduced seawater with a total salt concentration of 33 g L^{-1}, as in the previous case, showed better results for Ti/TiO_2-RuO_2 and Ti/TiO_2-RuO_2-PbO_2 (Table 4). The current efficiency of hypochlorite was 84–87 %. High CE of hypochlorite was obtained on lead dioxide, which was deposited from the nitrate electrolyte 1 M $Pb(NO_3)_2$ + 0.1 M HNO_3 at 65 °C.

As the experiment showed, the state and nature of the transition layer have a significant effect on the properties of the coatings. One of the most catalytically active among PbO_2-based coatings is a composite coating of lead dioxide, which is applied to a thin sublayer of TiO_2-RuO_2. Most likely, this is due to the modification of lead dioxide by ruthenium compounds, which partially pass into PbO_2 deposit in the process of its formation due to the achievement of critical potential.

Table 4

Electrolysis of restored sea water 33 g L^{-1}

Anode, deposition condition	CE(NaClO)/ %	CE($NaClO_3$)/ %	E_a/V
Pt	39.6	16.1	1.98
Ti/TiO_2-RuO_2	87.0	4.2	1.33
Ti/Pt-PbO_2 1 M $Pb(MS)_2$+0.11 M MSA j=10 mA cm^{-2}; t=65 °C	70.6	8.3	1.84
Ti/Pt-PbO_2 1M $Pb(NO_3)_2$+ 0.1 M HNO_3 j=5 mA cm^{-2}; t=65 °C	81.0	6.0	1.82
Ti/Pt-PbO_2 1M $Pb(NO_3)_2$+ 0.1 M HNO_3 j=5 mA cm^{-2}; t=25 °C	70.0	7.8	1.83
Ti/TiO_2-RuO_2-PbO_2 1 M $Pb(MS)_2$+0.11 M MSA j=10 mA cm^{-2}; t=65 °C	84.0	6.4	1.72

Lead dioxide electrodes show high catalytic activity in relation to oxygen transfer reactions. Modification by ionic additives while maintaining the basic properties of PbO_2 changes its catalytic activity in a wide range. On these anodes OER is realized with rather high overvoltage. This fact makes the PbO_2 electrode another successful object to confirm the relationship between oxygen overvoltage and catalytic activity in reaction of sodium hypochlorite synthesis.

The introduction of chloride ions into the background electrolyte leads to a slight shift in the polarization of the PbO_2 anode by 80 mV in the region of lower potentials. The potentials under current are in the range of 1.6–1.7 V, which is 450-500 mV more positive than the equilibrium reaction potential of chlorine. For such an anode, it is possible to predict rather low NaClO current efficiencies at high current efficiencies of $NaClO_3$. The results of cumulative electrolysis confirmed the compliance of anodes based on PbO_2 with the proposed correlation dependence. Current efficiency of NaClO was 44 % and a fairly high current efficiency of $NaClO_3$ 34 % was recorded on the anode with a lead dioxide coating in 0.15 M NaCl.

Lead dioxide and coatings based on it are characterized by a high degree of filling of the surface with inert, strongly bounded particles [81; 96; 97]. Doping with iron group metals, fluorine, bismuth and other additives slightly changes the energy of particle distribution, but in any case, on these coatings, the reaction of oxygen evolution is realized with fairly high polarizations. The introduction of Cl^- depolarizer into the solution, especially at low concentrations, does not lead to a significant reduction in the average energy of surface particles. All related reactions proceed at comparable rates: oxygen evolution, oxidation of chloride with the formation of hypochlorite, chlorite and chlorate at the working potentials. Changing the state of the surface by modifying or changing the conditions for obtaining PbO_2 coatings only slightly changes the ratio of current efficiencies of the reactions involved.

Conclusions

It has been shown that the product current efficiencies and their nature strongly depend on the composition of the solution and the electrode material. Considering the platinum group metals, platinum has the lowest current efficiency of sodium hypochlorite, despite the high overvoltage of oxygen evolution. As shown in the mechanisms of chlorine evolution, the formation of oxygen-containing chlorine compounds occurs through the formation of oxygen-containing particles adsorbed on the electrode surface. Based on this, an increase in the overvoltage of oxygen evolution will not lead to an increase in the current efficiency of chlorine-containing products. At the same time, materials based on lead dioxide as a cheap alternative to platinum group metals may be of interest for the technical electrolysis of sea water.

Acknowledgement

The authors express their gratitude to the Ministry of Education and Science of Ukraine and the National Research Foundation of Ukraine who financed this work.

References

[1] Kim, H. J., Lee, J. G., Kang, J. W., Cho, H. J. (2008). Effects of a low concentration hypochlorous acid nasal irrigation solution on bacteria, fungi, and virus, *Laryngoscope*, *118*(10), 1862–1867. https://doi.org/10.1097/MLG.0b013e31817f4d34

[2] Sakarya, S., Gunay, N., Karakulak, M. (2014). Hypochlorous acid: an ideal wound care agent with powerful microbicidal, antibiofilm, and wound healing potency, *Wounds*, *26*(12), 342–350.

[3] Strzepa, A, Pritchard, K. A., Dittel, B. N. (2017). Myeloperoxidase: A new player in autoimmunity, *Cell Immunol.*, 317, 1–8. https://doi.org/10.1016/j.cellimm.2017.05.002

[4] Block, M. S., Rowan, B. G. (2020). Hypochlorous acid: A review, *J. Oral Maxillofac. Surg.*, *78*(9), 1461–1466. https://doi.org/10.1016/j.joms.2020.06.029

[5] Kampf, G., Todt, D., Pfaender, S., Steinmann, E. (2020). Persistence of coronaviruses on inanimate surfaces and their inactivation with biocidal agents, *J. Hosp. Infect.*, 104, 246–251. https://doi.org/10.1016/j.jhin.2020.01.022

[6] Wilhelm, N., Kaufmann, A., Blanton, E., Lantagne, D. (2018). Sodium hypochlorite dosage for household and emergency water treatment: updated recommendations, *J. Water Health*, *16*(1), 112–125. https://doi.org/10.2166/wh.2017.012

[7] Shmychkova, O., Girenko, D., Velichenko, A. (2022). Noble metals doped tin dioxide for sodium hypochlorite synthesis from low concentrated NaCl solutions, J. Chem. Technol. Biotechnol., *97*(4), 903–913. https://doi.org/10.1002/jctb.6973

[8] Shmychkova, O., Borovik, I., Girenko, D., Davydenko, P., Velichenko, A. (2021). The effect of impurities on the stability of low concentrated eco-friendly solutions of NaOCl, *Voprosy Khimii i Khimicheskoi Tekhnologii*, 2021(4), 142–150. https://doi.org/10.32434/0321-4095-2021-137-4-142-150

[9] *Chemical compounds* (2006). Ed. N. Schlager, J. Weisblatt, D. E. Newton., Detroit: Thomson Gale.

[10] Myers, R. L. (2007). *The 100 Most Important Chemical Compounds: A Reference Guide*. –Westport: Greenwood Press.

[11] House, J. E.; House, K. A. (2016). *Halogens. In Descriptive Inorganic Chemistry*, Amsterdam: Academic Press.

[12] Nicoson, J. S., Perrone, T. F., Huff Hartz, K .E., Wang, L., Margerum, D. W. (2003). Kinetics and mechanisms of the reactions of hypochlorous acid, chlorine, and chlorine monoxide with bromite ion, *Inorg. Chem.*, *42*(19), 5818–5824. https://doi.org/10.1021/ic0301223

[13] Johnson, D. W., Margerum, D. W. (1991). Non metal redox kinetics: a reexamination of the mechanism of the reaction between hypochlorite and nitrite ions, *Inorg. Chem.*, 30(25), 4845–4851. https://doi.org/ 10.1021/ic00025a031

[14] Gerritsen, C. M., Margerum, D. W. Non metal redox kinetics: hypochlorite and hypochlorous acid reactions with cyanide, *Inorg. Chem.*, *29*(15), 2757–2762. https://doi.org/10.1021/ic00340a010

[15] Castagna, R., Eiserich, J. P. Budamagunta, M. S., Stipa, P., Cross, C. E., Proietti, E., Voss, J. C., Greci, L. (2008). Hydroxyl radical from the reaction between hypochlorite and hydrogen peroxide, *Atmos. Environ.*, 42, 6551–6554. https://doi.org/10.1016/j.atmosenv.2008.04.029

[16] Wang, L., Bassiri, M., Najafi, R., Najafi, K., Yang, J., Khosrovi, B., Hwong, W., Barati, E., Belisle, B., Celeri, C., Robson, M. C. (2007). Hypochlorous acid as a potential wound care agent: part I. Stabilized hypochlorous acid: a component of the inorganic armamentarium of innate immunity, *J. Burns Wounds*, 6, 65–79.

[17] Ennis, C. A., Birks, J. W. (1985). Applications of a new laboratory source of gaseous hypochlorous acid (HOCl): product distribution in the atomic Cl + HOCl reaction and equilibrium constant for the reaction $Cl_2O + H_2O = 2HOCl$, *J. Phys. Chem.*, 89(1), 186–191. https://doi.org/10.1021/j100247a039

[18] Ennis, C. A., Birks, J. W. (1988). Rate constants for the reactions $OH + HOCl \rightarrow H_2O + ClO$ and $H + HOCl \rightarrow$ products, *J. Phys. Chem.*, 92(5), 1119–1126. https://doi.org/10.1021/j100316a024

[19] Blatchley, E. R., Johnson, R. W., Alleman, J. E., McCoy, W. F. (1992). Effective henry's law constants for free chlorine and free bromine, *Water Res.*, 26(1), 99–106. https://doi.org/10.1016/0043-1354(92)90117-M

[20] Feng, Y., Smith, D. W., Bolton J. R. (2007). Photolysis of aqueous free chlorine species (HOCl and OCl^-) with 254 nm ultraviolet light, *J. Environ. Eng. Sci.*, 6, 277–284. https://doi.org/10.1139/s06-052\

[21] Robson, M. C., Payne, W. G., Ko, F., Mentis, M., Donati, G., Shafii, S. M., Culverhouse, S., Wang, L., Khosrovi B., Najafi, R., Cooper, D. M., Bassiri, M. (2007). Hypochlorous acid as a potential wound care agent, Part II. Stabilized hypochlorous acid: its role in decreasing tissue bacterial bioburden and overcoming the inhibition of infection on wound healing, *J. Burns Wounds*, 6, 80–90.

[22] Sizeneva, I. P., Kondrashova, N. B., Val'tsifer, V. A. (2005). Spontaneous decomposition of industrially manufactured sodium hypochlorite solutions, *Russ. J. Appl. Chem.*, *78*(4), 541–545. https://doi.org/10.1007/s11167-005-0336-6

[23] Adam, L. C., Gordon, G. (1999). Hypochlorite ion decomposition: effects of temperature, ionic strength, and chloride ion, *Inorg. Chem.*, 38(6), 1299–1304. https://doi.org/10.1021/ic980020q

[24] Remucal, C. K., Manley, D. (2016). Emerging investigators series: the efficacy of chlorine photolysis as an advanced oxidation process for drinking water treatment, Environ. Sci. Water Res. Technol., 2(4), 565–579. https://doi.org/10.1039/c6ew00029k

[25] Chen, T. (1967). Spectrophotometric determination of microquantities of chlorate, chlorite, hypochlorite, and chloride in perchlorate, Anal. Chem., 39(7), 804–813. https://doi.org/10.1021/ac60251a023

[26] Adam, L. C., Fabian, I., Suzuki, K., Gordon, G. (1992). Hypochlorous acid decomposition in the pH 5-8 region, *Inorg. Chem.*, *31*(17), 3534–3541. https://doi.org/10.1021/ic00043a011

[27] Buxton, G. V., Subhani, M. S. (1972). Radiation chemistry and photochemistry of oxychlorine ions. Part 1. – Radiolysis of aqueous solutions of hypochlorite and chlorite ions, *J. Chem. Soc., Faraday Trans. 1*, 68, 947–957. https://doi.org/10.1039/F19726800947

[28] Buxton, G. V., Subhani, M. S. Radiation chemistry and photochemistry of oxychlorine ions. Part 2. – Photodecomposition of aqueous solutions of hypochlorite ions, *J. Chem. Soc., Faraday Trans. 1*, 68, 958–969. https://doi.org/10.1039/F19726800958

[29] Garcia Villanova, R. J., Dantas Leite, M. V. O., Hierro, J. M. H., Alfageme, S. C., Hernandez, C. G. (2010). Occurrence of bromate, chlorite and chlorate in drinking waters disinfected with hypochlorite reagents. Tracing their origins, *Sci. Total Environ.*, *408*(12), 2616–2620. https://doi.org/10.1016/j.scitotenv.2010.03.011

[30] Siddiqui, M. S. (1996). Chlorine-ozone interactions: formation of chlorate, *Water Res.*, *30*(9), 2160-2170. https://doi.org/10.1016/0043-1354(96)00071-1

[31] Crook, J., Mousavi, A. (2016). The chlor alkali process: a review of history and pollution, *Environ. Forens.*, 17(3), 211-217. https://doi.org/10.1080/15275922.2016.1177755

[32] Karlsson, R. K. B., Cornell, A. (2016). Selectivity between oxygen and chlorine evolution in the chlor alkali and chlorate processes, *Chem. Rev.*, 116(5), 2982–3028. https://doi.org/10.1021/acs.chemrev.5b00389

[33] Trasatti, S. (2000). Electrocatalysis: understanding the success of DSA®, *Electrochim. Acta,* 45(15-16), 2377-2385. https://doi.org/10.1016/S0013-4686(00)00338-8

[34] Simon, F. X., Berdalet, E., Gracia, F. A., (2014). Seawater disinfection by chlorine dioxide and sodium hypochlorite. A comparison of biofilm formation, *Water Air Soil Pollut.*, 225, 1921-1932. https://doi.org/10.1007/s11270-014-1921-1

[35] Polcaro, M., Vacca, A., Mascia, M., Ferrara, F. (2008). Product and and by product formation in electrolysis of dilute chloride solutions, *J. Appl. Electrochem.*, 38, 979–984. https://doi.org/10.1007/s10800-008-9509-3

[36] Yao, P., Chen, X., Wu, H., Wang D. (2008). Active Ti/SnO_2 anodes for pollutants oxidation prepared using chemical vapor deposition, *Surf. Coat. Technol.*, 202, 3850–3855. https://doi.org/ 10.1016/j.surfcoat.2008.01.026

[37] Chen, G. (2004). Electrochemical technologies in wastewater treatment, *Sep. Purif. Technol.*, *38*(1), 11–41. https://doi.org/10.1016/j.seppur.2003.10.006

[38] Cano, A., Canizares, P., Barrera Diaza, C., Saez, C. A., Rodrigo, M. (2012). Use of conductive diamond electrochemical oxidation for the disinfection of several actual treated wastewaters, Chem. Eng. J., 211-212, 463–469. https://doi.org/10.1016/j.cej.2012.09.071

[39] Rossmeisl, J., Qu, Z-W., Zhu, H., Kroes, G-J., Norskov, J. K. (2007). Electrolysis of water on oxide surfaces, *J.*

Electroanal. Chem., *607*(1-2), 83–89. https://doi.org/10.1016/j.jelechem.2006.11.008

[40] Grimm, J., Bessarabov, D., Sanderson, R. (1998). Review of electro-assisted methods for water purification, *Desalination*, 115(3), 285-294. https://doi.org/10.1016/S0011-9164(98)00047-2

[41] Morris, J. C. (1966). The acid ionization constant of HOCl from 5 to 35°, *J Phys. Chem.*, *70*(12), 3798–3805. https://doi.org/10.1021/j100884a007

[42] Wojtowicz, J. A. (2004). Dichlorine monoxide, hypochlorous acid, and hypochlorites. In *Kirk Othmer Encyclopedia of Chemical Technology*, Wiley: New York, 1074 p.

[43] Hui, F., Zhengyu, Z., Xinming, Z. (2003). Hydrogen bonding between chlorine oxide and water ($H_2O·ClO$) radical complex, *Chem. Phys. Lett.*, *382*(3), pp 466–474. https://doi.org/10.1016/j.cplett.2003.10.022

[44] Cornell, A., Haakansson, B., Lindbergh, G. (2003). Ruthenium based DSA in chlorate electrolysis critical anode potential and reaction kinetics, *Electrochim. Acta*, 48(5), 473-481. https://doi.org/10.1016/S0013-4686(02)00679-5

[45] Trasatti, S. (1984). Electrocatalysis in the anodic evolution of oxygen and chlorine, *Electrochim. Acta*, *29*(11), 1503–1512. https://doi.org/10.1016/0013-4686(84)85004-5

[46] Trasatti, S. (1987). Progress in the understanding of the mechanism of chlorine evolution at oxide electrodes, *Electrochim. Acta*, *32*(3), 369–382. https://doi.org/10.1016/0013-4686(87)85001-6

[47] Trasatti, S. (1980). Electrocatalysis by oxides – Attempt at a unifying approach, *J. Electroanal. Chem. Interf. Electrochem.*, *111*(1), 125–131. https://doi.org/10.1016/S0022-0728(80)80084-2

[48] Shmychkova, O., Zahorulko, S., Girenko, D., Luk'yanenko T., Dmitrikova, L., Velichenko, A. (2021). Material selection and optimization of conditions for electrooxidation of nitrofurazone: A comparative study of tin and lead dioxides, *J. Electrochem. Soc.*, 168(8), 086507. https://doi.org/10.1149/1945-7111/ac1e58

[49] Cahan, B. D., Chen, C. T. (1982). Questions on the kinetics of O_2 evolution on oxide-covered metals, *J. Electrochem. Soc.*, *129*(4), 700–705. https://doi.org/10.1149/1.2123954

[50] Schultze, J. W., Elfenthal, L. (1986). Electron-transfer reactions on pure and modified oxide films, *J. Electroanal. Chem. Interf. Electrochem.*, *204*(1–2), 153-171. https://doi.org/10.1016/0022-0728(86)80515-0

[51] Exner, K. S., Over, H. (2019). Beyond the rate-determining step in the oxygen evolution reaction over a single-crystalline IrO_2(110) model electrode: kinetic scaling relations, *ACS Catalysis, 9*(8), 6755–6765. https://doi.org/10.1021/acscatal.9b01564

[52] Vos, J. G., Koper, M. T. M. (2018). Measurement of competition between oxygen evolution and chlorine evolution using rotating ring-disk electrode voltammetry, *J. Electroanal. Chem.*, 819, 260–268. https://doi.org/10.1016/j.jelechem.2017.10.058

[53] Schuhmann, W. (2012). Role of water in the chlorine evolution reaction at RuO_2-based electrodes – understanding electrocatalysis asa resonance phenomenon, *ChemSusChem.*, 5, 1897–1904. https://doi.org/10.1002/cssc.201200193

[54] Erenburg, R., Krishtalik, L., Yaroshevskaya, I. (1975). Mechanism of chlorine evolution at a ruthenium-titanium oxide electrode, *Sov. Electrochem.*, 11, 989.

[55] Erenburg, R., Krishtalik, L., Bystrov, V. (1972). Chlorine evolution mechanism at a ruthenium dioxide titanium dioxide electrode, *Sov. Electrochem.*, 8, 1240.

[56] Janssen, L., Visser, G., Barendrecht, E. (1983). Effect of molecular chlorine diffusion on theoretical potential-current density relations for chlorine evolving electrode, *Electrochim. Acta*, 28, 155–163. https://doi.org/10.1016/0013-4686(83)85102-0

[57] Janssen, L., Starmans, L., Visser, J., Barendrecht, E. (1977). Mechanism of the chlorine evolution on a ruthenium oxide/titanium oxide electrode and on a ruthenium electrode, *Electrochim. Acta*, 22(10), 1093–1100. https://doi.org/10.1016/0013-4686(77)80045-5

[58] Faita, G., Fiori, G. (1972). Anodic discharge of chloride ions on oxide electrodes, *J. Appl.Electrochem.*, *2*(1), 31–35. https://doi.org/10.1007/BF00615189

[59] Augustynski, J., Balsenc, L., Hinden, J. (1978). X-ray Photoelectron spectroscopic studies of RuO_2-based film electrodes, *J. Electrochem. Soc.*, *125*(7), 1093 https://doi.org/10.1149/1.2131626

[60] Song, J., Wei, Ch., Huang, Zh. F., Liu, Ch., Zeng, L., Wang, X., Xu, Zh. J. (2020). A review on fundamentals for designing oxygen evolution electrocatalysts, *Chem. Soc. Rev.*, 49, 2196–2214. https://doi.org/10.1039/C9CS00607A

[61] Zagalskaya, A. Alexandrov, V. (2020). Role of defects in the interplay between adsorbate evolving and lattice oxygen mechanisms of the oxygen evolution reaction in RuO_2 and IrO_2, *ACS Catal.*, *10*(6), 3650–3657. https://doi.org/10.1021/acscatal.9b05544

[62] Anderson, A. B., Neshev, N. M., Sidik, R. A., Shiller, P. (2002). Mechanism for the electrooxidation of water to OH and O bonded to platinum: quantum chemical theory, *Electrochim. Acta*, *47*(18), 2999–3008. https://doi.org/10.1016/S0013-4686(02)00203-7

[63] Denton, D., Harrison, J., Knowles, R. (1979). Chlorine evolution and reduction on RuO_2/TiO_2 electrodes, *Electrochim. Acta*, 24, 521–527. https://doi.org/10.1016/0013-4686(79)85027-6

[64] Burke, L. D., O'Neill, J. F. (1979). Some Aspects of the chlorine evolution reaction at ruthenium dioxide anodes, *J. Electroanal. Chem. Interf. Electrochem.*, 101, 341–349. https://doi.org/10.1016/S0022-0728(79)80045-5

[65] Krishtalik, L. I. (1981). Kinetics and mechanism of anodic chlorine and oxygen evolution reactions on transition metal oxide electrodes, *Electrochim. Acta*, *26*(3), 329–337. https://doi.org/10.1016/0013-4686(81)85019-0

[66] Krishtalik, L., Erenburg, R. (1981). *Kinetika slozhnykh elektrokhimicheskikh reaktsii* (The kinetics of complex electrochemical reactions), Moscow: Nauka. (In Russian).

[67] Erenburg, R. (1984). Mechanism of the chlorine reaction of ruthenium titanium oxide anodes, *Sov. Electrochem.*, 20, 1481–1486.

[68] Cai, Y., Anderson, A. B. (2005). Calculating reversible potentials for Pt-H and Pt-OH bond formation in basic solutions, *J. Phys. Chem. B*, 109, 7557–7563. https://doi.org/10.1021/jp0458102

[69] Hansen, H. A., Man, I. C., Study, F., Abild-Pedersen, F., Bligaard, Th., Rossmeisl, J. (2010). Electrochemical chlorine evolution at rutile oxide (110) surfaces. *Phys. Chem. Chem. Phys.*, 12, 283–290. https://doi.org/10.1039/B917459A

[70] Consonni, V., Trasatti, S., Pollak, F., O'Grady, W. E. (1987). Mechanism of chlorine evolution on oxide

anodes study of pH effects, *J. Electroanal. Chem. Interf. Electrochem.*, *228*(1-2), 393–406. https://doi.org/10.1016/0022-0728(87)80119-5

[71] Fernandez, J. L., Gennero de Chialvo, M. R., Chialvo, A. C. (2002). Kinetic study of the chlorine electrode reaction on Ti/RuO_2 through the polarisation resistance: part III: proposal of a reaction mechanism, *Electrochim. Acta*, *47*(7), 1145–1152. https://doi.org/10.1016/S0013-4686(01)00839-8

[72] Kokcam-Demir, U., Goldman, A., Esrafili, L., Gharib, M., Morsali, A., Weingart, O., Janiak, Ch. (2020). Coordinatively unsaturated metal sites (open metal sites) in metal–organic frameworks: design and applications, *Chem. Soc. Rev.*, 49, 2751–2798. https://doi.org/10.1039/C9CS00609E

[73] Neodo, S., Rosestolato, D., Ferro, S., De Battisti, A. (2012). On the electrolysis of dilute chloride solutions: Influence of the electrode material on Faradaic efficiency for active chlorine, chlorate and perchlorate, *Electrochim. Acta*, 80, 282–291. https://doi.org/10.1016/j.electacta.2012.07.017

[74] Tomcsanyi, L., De Battisti, A. (1996). Identification of the adsorbed intermediate of the electrooxidation of chloride by the CV technique, *Electrochim. Acta*, 41(18), 2917–2919. https://doi.org/10.1016/0013-4686(96)00109-0

[75] Tomcsanyi, L., De Battisti, A., Hirschberg, G., Varga, K., Liszi, J. (1999). The study of the electrooxidation of chloride at $RuO_2 \cdot TiO_2$ electrode using CV and radiotracer techniques and evaluating by electrochemical kinetic simulation methods, *Electrochim. Acta*, 44, 2463–2472. https://doi.org/10.1016/S0013-4686(98)00381-8

[76] Landolt, D., Ibl, N. (1972). Anodic chlorate formation on platinized titanium, *J. Appl. Electrochem.*, 2, 201–210. https://doi.org/10.1007/BF02354977

[77] Shmychkova, O., Girenko, D., Velichenko, A. (2021). Cl^-/ClO^- process on SnO_2 based electrodes in low concentrated NaCl solutions, *Electrochem. Sci. Adv.*, e2100086. https://doi.org/10.1002/elsa.202100086

[78] Girenko, D., Shmychkova, O., Velichenko, A. (2019). Electrooxidation of chloride-ions on Ti/Pt anodes, *Voprosy Khimii i Khimicheskoi Tekhnologii*, 2019(6), 39–46. https://doi.org/10.32434/0321-4095-2019-127-6-39-46

[79] Girenko, D., Shmychkova, O., Velichenko, A. (2020). Influence of Ti/Pt electrodes history on its electrochemical properties during electrolysis of NaCl, *Voprosy Khimii i Khimicheskoi Tekhnologii*, 2020(1), 18–24. https://doi.org/10.32434/0321-4095-2020-128-1-18-24

[80] Girenko, D. V., Velichenko, A. B., Shmychkova, O. B. (2021). Electrolysis of NaCl solutions in flow systems, *J. Chem. Technol.*, 29(1), 31–41. https://doi.org/10.15421/082111

[81] Shmychkova, O., Luk'yanenko, T., Velichenko, A., Meda, L., Amadelli, R. (2013). Bi-doped PbO_2 anodes: electrodeposition and physico-chemical properties, *Electrochim Acta*, 111, 332–338. https://doi.org/10.1016/j.electacta.2013.08.082

[82] Payne, D. J., Egdell, R. G., Hao, W., Foord, J. S., Walsh, A., Watson, G. W. (2005). Why is lead dioxide metallic? *Chem. Phys. Lett.*, 411, 181–185. https://doi.org/10.1016/j.cplett.2005.06.023

[83] Munichandraiah, N., Sathyanarayana, S. (1987). Kinetics and mechanism of anodic oxidation of chlorate ion to perchlorate ion on lead dioxide electrodes, J. *Appl. Electrochem.*, 17, 33–48. https://doi.org/10.1007/BF01009129

[84] Amadelli, R., Armelao, L., Velichenko, A. B., Nikolenko, N. V., Girenko, D. V., Kovalyov, S. V., Danilov, F. I. (1999). Oxygen and ozone evolution at fluoride modified lead dioxide electrodes, *Electrochim. Acta*, *45*(4-5), 713–720. https://doi.org/10.1016/S0013-4686(99)00250-9

[85] Velichenko, A. B., Girenko, D. V., Nikolenko, N. V., Amadelli, R., Baranova, E. A., Danilov F. I. (2000). Oxygen evolution on lead dioxide modified with fluorine and iron, Russ. J. Electrochem., 2000, 36(11), 1216-1220. https://doi.org/10.1007/BF02757697

[86] Amadelli, R., De Battisti, A., Girenko, D. V., Kovalyov, S. V., Vekichenko, A. B. (2000). Electrochemical oxidation of trans-3,4 dihydroxycinnamic acid at PbO_2 electrodes: Direct electrolysis and ozone mediated reactions compared, Electrochim. Acta, 46(2-3), 341-347. https://doi.org/10.1016/S0013-4686(00)00590-9

[87] Trassatti, S., Lodi, G. (1981). Oxygen and chlorine evolution at conductive metallic oxide anodes, *Electrodes of conductive metal oxides*, 2, 521–626.

[88] Velichenko, A. B., Luk'yanenko, T. V., Shmychkova, O. B., Knysh, V. O. (2021). New approaches to the creation of nanocomposite anode materials based on PbO_2: a review, *Theor. Experim. Chem.*, *57*(5), 331–342 https://doi.org/10.1007/s11237-022-09709-6

[89] Velichenko, A., Luk'yanenko, T., Shmychkova, O., Dmitrikova, L. (2020). Electrosynthesis and catalytic activity of PbO_2-fluorinated surfactant composites, *J. Chem. Technol. Biotechnol.*, 95(12), 3085-3092. https://doi.org/10.1002/jctb.6483

[90] Velichenko, A., Luk'yanenko, T., Shmychkova, O. (2020). Lead dioxide-SDS composites: design and properties, *J. Electroanal. Chem.*, 873 114412. https://doi.org/10.1016/j.jelechem.2020.114412

[91] Luk'yanenko, T., Shmychkova, O., Velichenko, A. (2020). PbO_2-surfactant composites: electrosynthesis and catalytic activity, *J. Solid State Electrochem.*, *24*(4), 245-256. https://doi.org/10.1007/s10008-020-04572-8

[92] Velichenko, A., Luk'yanenko, T., Nikolenko, N., Shmychkova, O., Demchenko, P., Gladyshevskii, R. (2020). Composite electrodes PbO_2-Nafion®, *J. Electrochem. Soc.*, *167*(6), 063501. https://doi.org/10.1149/1945-7111/ab805f

[93] Shmychkova, O. B., Girenko, D. V., Knysh, V. A., Velichenko, A. B. (2021). Electrochemical characterictic of Ti/Pt and Ti/Pt-Pd electrodes, *J. Chem. Technol.*, *29*(3), 370–379. https://doi.org/10.15421/JCHEMTECH.V29I3.239282

[94] Chen, S., Hu, W., Hong, J. (2016). Electrochemical disinfection of simulated ballast water on PbO_2/graphite felt electrode, *Marine Pollut. Bull.*, 105(1), 319–323. https://doi.org/10.1016/j.marpolbul.2016.02.003

[95] Nanayakkara, K. G., Zheng, Y.-M., Khorshed Alam, A. K. M., Zou, Sh., Chen, J. P. (2011). Electrochemical disinfection for ballast water management: technology development and risk assessment, *Marine Pollut. Bull.*, *63*(5–12), 119–123. https://doi.org/10.1016/j.marpolbul.2011.03.003

[96] Velichenko, A. B., Kovalyov, S. V., Gnatenko, A. N., Amadelli, R., Danilov, F. I. (1998). Lead dioxide electrodeposition and its application: influence of fluoride and iron ions, *J. Electroanal. Chem.*, 454, 203–208. https://doi.org/10.1016/S0022-0728(98)00256-3

[97] Velichenko, A. B., Devilliers, D. (2007). Electrodeposition of fluorine doped PbO_2, *J. Fluorine Chem.*, 128, 269–276. https://doi.org/10.1016/j.jfluchem.2006.11.010

[98] LaCourse, W. R., Hsiao, Y. L., Johnson, D. C. (1989). Electrocatalytic oxidations at electrodeposited bismuth(III) doped beta lead dioxide film electrodes, *J. Electrochem. Soc.*, 136, 3714–3719. https://doi.org/10.1149/1.2096536