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ELECTROLYSIS OF NaCl SOLUTIONS IN FLOW SYSTEMS

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

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

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Abstract

The electrolysis of NaCl solutions in flow systems was investigated. It has been shown that in order to minimize the conversion of hypochlorite to chlorate at the anode and the reduction of hypochlorite ions at the cathode, one should perform electrolysis at a minimum stirring rate of the solution relative to the electrodes. Removal of the membrane from the cell leads to only a slight decrease in the current efficiency of sodium hypochlorite in the range of 1–3 % and a slight increase in the pH of the solution, which has a positive effect on its stability. Current efficiency of chlorates do not change. A positive effect is the reduction of cell voltage, which improves the energy efficiency of sodium hypochlorite synthesis. With a current load of 2 A and the use of two flow cells at a volumetric flow rate of 8.7 $L \cdot h^{-1}$, one can sinthesize a high-purity solution of sodium hypochlorite containing 500 $mg \cdot L^{-1}$ NaClO and 0.6 $mg \cdot L^{-1}$ $NaClO_3$. The current efficiency of hypochlorite and sodium chlorate is 78 and 0.2 %, respectively. Electrochemical reactor with three flow cells with a capacity of 9.2 $L \cdot h^{-1}$ at a current load of 3 A allows one to continuously produce a solution containing 1000 $mg \cdot L^{-1}$ NaClO and not more than 6 $mg \cdot L^{-1}$ $NaClO_3$. Created prototypes of electrolyzers have successfully passed the stages of laboratory and experimental tests.

Keywords: platinized titanium; flow cell; sodium hypochlorite; hydraulic circuit.

ЕЛЕКТРОЛІЗ РОЗЧИНІВ NaCl В ПРОТОЧНИХ СИСТЕМАХ

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

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

Анотація

Досліджено електроліз розчинів NaCl у проточних системах. Показано, що для мінімізації перетворення гіпохлориту в хлорат на аноді та відновлення іонів гіпохлориту на катоді слід проводити електроліз з мінімальною швидкістю перемішування розчину відносно електродів. Видалення мембрани з комірки приводить лише до незначного зниження виходу за струмом гіпохлориту натрію в межах 1–3 % і незначного підвищення pH розчину, що позитивно впливає стабільність розчину. Вихід за струмом хлоратів не змінюється. Позитивним ефектом є зменшення напруги на комірці, що покращує енергетичну ефективність синтезу натрію гіпохлориту. В разі сили струму 2 А і використання двох проточних комірок за об'ємної швидкості потоку 8.7 л/год можна синтезувати високочистий розчин натрію гіпохлориту, що містить 500 мг/л NaClO і 0.6 мг/л $NaClO_3$. Виходи за струмом натрію гіпохлориту та хлорату становлять 78 та 0.2 % відповідно. Електрохімічний реактор з трьома проточними елементами ємністю 9.2 л/год за струму 3 А дозволяє постійно отримувати розчин, що містить 1000 мг/л NaClO і не більше 6 мг/л $NaClO_3$. Розроблені прототипи електролізерів успішно пройшли етапи лабораторних та експериментальних випробувань.

Ключові слова: платинований титан; проточна комірка; натрію гіпохлорит; гідравлічна схема.

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

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ЭЛЕКТРОЛИЗ РАСТВОРОВ NaCl В ПРОТОЧНЫХ СИСТЕМАХ

Дмитрий В. Гиренко, Александр Б. Величенко, Олеся Б. Шмычкова*
ГВУЗ «Украинский государственный химико-технологический университет», просп. Гагарина 8, г. Днипро, 49005, Украина

Аннотация

Исследован электролиз растворов NaCl в проточных системах. Показано, что для минимизации преобразования гипохлорита в хлорат на аноде и восстановления ионов гипохлорита на катоде следует проводить электролиз с минимальной скоростью перемешивания раствора относительно электродов. Удаление мембраны из ячейки приводит лишь к незначительному снижению выхода по току гипохлорита натрия в пределах 1–3 % и незначительному повышению pH раствора, что положительно влияет на стабильность раствора. Выход по току хлоратов не меняется. Положительным эффектом является уменьшение напряжения на ячейке, что улучшает энергетическую эффективность синтеза гипохлорита натрия. В случае силы тока 2 А и использования двух проточных ячеек при объемной скорости потока 8.7 л/ч можно синтезировать высокочистый раствор гипохлорита натрия, содержащий 500 мг/л NaClO и 0,6 мг/л $NaClO_3$. Выходы по току гипохлорита натрия и хлората составляют 78 и 0.2 % соответственно. Электрохимический реактор с тремя проточными элементами емкостью 9.2 л/ч при силе тока 3 А позволяет постоянно получать раствор, содержащий 1000 мг/л NaClO и не более 6 мг/л $NaClO_3$. Разработанные прототипы электролизеров успешно прошли этапы лабораторных и экспериментальных испытаний.

Ключевые слова: платинированный титан; проточная ячейка; натрия гипохлорит; гидравлическая схема.

Introduction

Sodium hypochlorite solutions with low concentration of 0.2–1.0 $g \cdot L^{-1}$, additionally containing 5–20 $g \cdot L^{-1}$ of sodium chloride are widely recognized as antiseptics and disinfectants with a broad spectrum of action for the treatment of skin, mucous membranes, shells, burns, wounds and disinfection of the instruments, as well as infusions for direct detoxification of the body, treatment of hepatitis, HIV, the effects of other viral diseases [1–4].

The synthesis of high-purity low-concentrated solutions of sodium hypochlorite is a rather difficult task. On the one hand, in the process of electrolysis at the anode, a number of processes may occur simultaneously: reactions of oxygen, ozone, oxidation of Cl-ions with the formation of hypochlorites, chlorites, chlorates, and perchlorates [5; 6]. On the other hand, it is possible to implement a number of photochemical, dark and catalytic processes, which further reduces the purity of the resulting solutions [7]. The presence, at least as an impurity of chlorates, which are formed both in the process of sodium hypochlorite synthesis and can be accumulated during storage of solutions is a feature of NaOCl solutions. Often, even in freshly synthesized solutions, the chlorate content can be comparable to the concentration of sodium hypochlorite [8]. The presence of high concentrations of chlorates is due primarily to the use of anodes with low selectivity to the target product and suboptimal conditions of electrosynthesis. Contamination of NaOCl solutions with chlorates significantly limits their scope, especially in medicine and veterinary medicine [9].

The key and the most difficult problem is the creation of an anode with a predicted electrocatalytic activity and selectivity, which in turn is impossible without understanding the nature of the processes that are realized in low-concentration chloride solutions during anode polarization.

Electrolysis of sodium chloride solutions can be implemented in cells with separated and undivided electrode space. Both methods have their advantages and disadvantages. The absence of a membrane simplifies and reduces the cost of the electrolyzer, but there is a loss of sodium hypochlorite due to its reduction at the cathode [10–13]. The presence of the membrane allows one to obtain solutions with higher concentrations of active chlorine, but a significant decrease in pH in the anode space and, consequently, the formation of molecular chlorine requires the use of expensive ion-selective membranes or other measures to maintain pH of the anolyte at 7.5–9.0. Such measures include alkalizing the initial solution or dosing alkali into the anode space. In the synthesis of low-concentrated solutions of sodium hypochlorite (up to 1.0–1.5 $g \cdot L^{-1}$), maintaining the desired pH level can be achieved by mixing an acidic anolyte with an alkaline catholyte, and by sequentially directing the electrolyte through the anode space to the cathode or vice versa.

The presence in the design of the diaphragm cell creates additional difficulties in organizing the hydraulic circuit of the cell, consisting of one or more flow cells. In this case, both single-circuit and double-circuit circuit of the electrolyte flow is possible. The two-circuit scheme requires the presence of two pumps, tanks or bypass valves to organize mixing in certain proportions of the anolyte with the catholyte and obtain a solution with a given pH level [14].

Experimental and Methods

All chemicals were reagent grade. Platinized titanium electrodes were obtained by the original method, which includes the stages of preliminary preparation of the titanium substrate [15–17], followed by electroplating a platinum coating.

Next, a thin layer of platinum was electrodeposited (the platinum content in the active layer was 8 mg·cm^{-2}) from the alkaline electrolyte contained K_2PtCl_6; $NaNO_2$ and NH_3 solution [18; 19], with cathode current densities equal to 20 or 30 mA cm^{-2} and temperature of 343 K. The resulting electrodes were then chemically oxidized in a mixture (1 : 1) of concentrated H_2SO_4 and H_2O_2 and thermally treated in the air in a tube furnace at temperatures of 773 K for an hour. The choice of this temperature range was due to the allowance of a similar assessment of coatings properties, since the mechanisms of growth and migration of platinum on the surface at these temperatures are similar, at temperatures above 723 K the mechanism of interaction of platinum with TiO_2 changes, and at even higher temperatures, a new substance and a new phase may appear, which is titanium nitride, since the treatment of the electrodes was carried out in an air atmosphere. Also, in the selected temperature range, thermal diffusion of platinum over the surface occurs, while treatment at higher temperatures leads to the encapsulation of platinum with titanium oxide [20].

It should be noted that the technology for obtaining electrodes described in this work is more progressive, since it significantly reduces the time for obtaining electrodes, minimizes the filling of precious metals and allows one to obtain electrodes with fixed characteristics, in contrast to tin oxide-iridium electrodes obtained by the sol-gel technology [21]. In this case, replacing iridium with platinum leads to a significant reduction in the cost of the system.

Electrochemical processes were investigated on a Pt rotating disk electrode (Pt-RDE, 0.19 cm^2) by cyclic and steady-state voltammetry, voltammetry with linear potential sweep, inversion voltammetry (IVA) and electrode impedance. Before each experiment, the electrode surface was treated with a freshly prepared mixture (1 : 1) of concentrated H_2SO_4 and H_2O_2 [15–17]. This preliminary treatment technique permits to stabilize the electrode surface, which under the action of strong oxidizing medium is oxidized to a certain state (defined phase and chemical composition of the surface oxides), which determines the satisfactory reproducibility in taking of cyclic voltammograms in the background electrolyte. The measurements were carried out in a temperature controlled three-electrode cell with a Pt electrode as a counter electrode. Investigations were carried out on MTech PGP-550M potentiostat-galvanostat, which allows one to measure cyclic voltammograms in the range of potentials of the working electrode within ± 3 V with a scan velocity from 0.02 to 500 mV/s [22]. The permissible error given in measuring of the potential and current does not exceed 0.15 %. To communicate with a personal computer, the device is equipped with a high-speed USB interface and user-friendly software.

Cells with a tubular titanium anode with a diameter of 8 mm, which was coated with a SnO_2-Pt-Pd catalyst and an outer titanium cathode with an inner diameter of 14 mm, were fabricated. Diaphragm was made of zirconium dioxide.

Results and Discussion

As an initial model, a prototype of an electrochemical reactor for the synthesis of sodium hypochlorite solutions with an external pump module equipped with a system for monitoring and controlling technological parameters, described in [23], was used. The synthesis of sodium hypochlorite in undivided non-flowing cell is characterized by a number of features. The bulk concentration of NaOCl is determined by the ratio of the rates of its formation and subsequent conversion, both at the anode and cathode. The rate of NaClO formation depends on the electrolysis current and the current efficiency, which is determined by the process conditions and the catalytic activity of the anode material. The main contribution (75–95 %) to the loss of NaOCl is made by its reduction at the cathode and only 5–25 % – by its oxidation at the anode with the formation of chlorite and chlorate. In the accumulative electrolysis of low concentrated NaCl solutions, information on the dependence of the concentration of NaOCl in the solution on the bulk density of the electrolysis current (j_b) is of considerable interest. Usually, to increase the concentration and reduce the time to reach its set value, one should increase the current or reduce the electrolyte volume. Carrying out the process at high anode current densities often leads to a significant increase in the concentration of chlorates in solutions, which is not acceptable. However, an increase in j_b due to a decrease in electrolyte volume, under all other constant conditions of electrolysis, does not lead to a proportional increase in the concentration of NaOCl in the solution. For example, when ja = 40 mA·cm^{-2} and j_c = 20 mA·cm^{-2} decrease in the volume of electrolyte in the cell by 2 times (increase in the volumetric current density j_b from 0.6 to 1.2 A·L^{-1}) leads to an increase in the concentration of NaOCl only by 49 % from 450 to 670 mg·L^{-1}, and with increasing j_b from 1.2 to 2.4 A L^{-1} the concentration of NaOCl increases even less from 670 to 850 mg·L^{-1}, which is 27 % of theoretical value. It is possible to significantly reduce the loss of NaOCl at the cathode [24] by increasing the cathode current density. Indeed, reducing the area of the cathode by 4 times leads to a significant reduction in NaClO losses: at j_c = 80 mA·cm^{-2} an increase in the bulk current density j_b from 0.6 to 1.2 A·L^{-1} causes an 86 % increase the concentration of NaOCl from 462 to 855 mg·L^{-1}, and with increasing j_b from 1.2 to 2.4 A·L^{-1} the concentration of NaOCl increases by 53 % from 850 to 1300 mg·L^{-1} (Fig. 1, Table. 1).

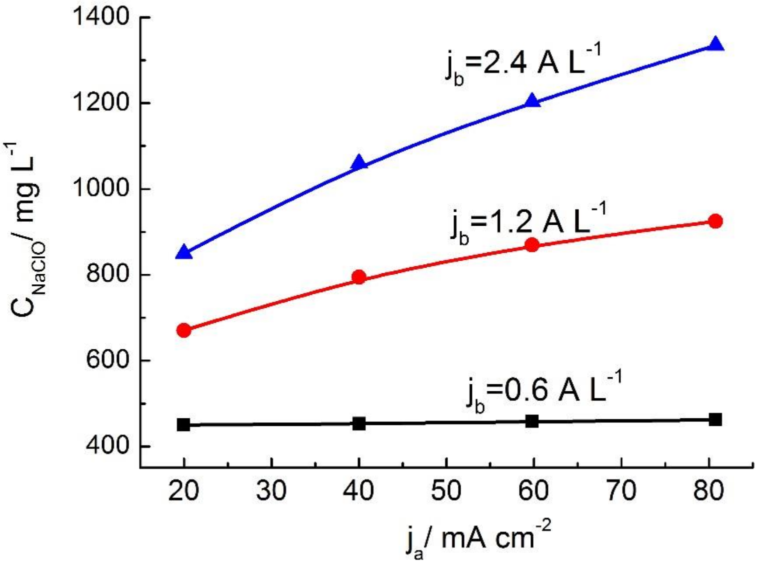

Fig. 1. NaOCl concentration versus cathode current density during 1 hour of accumulative electrolysis of 9 g·L^{-1} NaCl solution at Pt anode and polished titanium cathode under different bulk current density (j_b). Current I = 350 mA. Anode current density j_a = 40 mA·cm^{-2}

Table 1

Influence of bulk current density on the kinetics of accumulation of hypochlorite and sodium chlorate*

j_c, mA cm^{-2}	j_b = 2.4 A L^{-1}		j_b = 1.2 A L^{-1}		j_b = 0.6 A L^{-1}	
	C_{NaClO}/ mg L^{-1}	C_{NaClO3}/ mg L^{-1}	C_{NaClO}/ mg L^{-1}	C_{NaClO3}/ mg L^{-1}	C_{NaClO}/ mg L^{-1}	C_{NaClO3}/ mg L^{-1}
20	850	405	670	289	450	84
40	1060	414	794	185	453	72
80	1300	421	850	176	462	56

* Anode: Pt, cathode: Ti. j_a = 40 mA·cm^{-2}. Undivided cell. The duration of electrolysis is 60 minutes.

As is known [5; 25–27], the accumulation of chlorates during the electrolysis of NaCl solutions proceeds along several main routes: i) sequential oxidation on the surface of the anode or in the surface layer Cl^- to ClO_3^-; ii) oxidation at the anode of ClO^-, HClO or Cl_2 particles delivered from the bulk (main contribution); iii) bulk redox reactions. The contribution of a particular route of chlorate formation depends on the process conditions and the anode material. If the electrolysis is carried out without a diaphragm, there will be a contribution of the total concentration of chlorate to its reduction at the cathode. Under the conditions of obtaining solutions of sodium hypochlorite, the concentration of chlorates usually does not exceed 100 mg·L^{-1}. Analysis of kinetic data on the reduction of chlorate from 9 g·L^{-1} NaCl solution in a cell with a separated electrode space on the Ti cathode (current 360 mA; cathode area: 17.6; 8.8 and 4.4 cm^2; pH 8.4) showed that a noticeable reduction of chlorate begins at cathode current densities of more than 20 mA·cm^2. At j_c = 20 mA·cm^{-2} the decrease in the concentration of sodium chlorate for 60 min of electrolysis was

4 mg·L^{-1}; at 40 mA·cm^{-2} – 16 mg·L^{-1}, and at 80 mA·cm^{-2} – 25 mg·L^{-1}. The chlorates are reduced most rapidly at the platinum titanium cathode [28].

Platinum was used as an anode material with a high current efficiency of chlorate [29] in order to demonstrate the effect of bulk current density on $NaClO_3$ accumulation during electrolysis of a NaCl solution in a cell without a diaphragm. Variation in bulk current density leads to a significant change in the concentration of $NaClO_3$ in the solution. Thus, an increase in j_b from 0.6 to 2.4 A·L^{-1} (at j_a = 40 mA·cm^{-2}; j_c = 20 mA·cm^{-2}) leads to an increase in the concentration of chlorate in 5.75 times from 72 to 414 mg·L^{-1}. This is because the hypochlorite concentration increases as the electrolyte volume decreases. At low bulk current density (j_b = 0.6 A·L^{-1}), the increase in cathode current density (from 20 to 80 mA·cm^{-2}), on the one hand, has almost no effect on the concentration of NaClO in the bulk (see Fig. 1), and, on the other hand, leads to a decrease in the concentration of $NaClO_3$ by 1.5 times from 84 to 56 mg·L^{-1}, which agrees satisfactorily with the data above on the reduction of sodium chlorate in the cell with the diaphragm.

Thus, if the synthesis of sodium hypochlorite is realized by high bulk current densities (j_b > 1.0 A·L^{-1}), electrolysis must be performed at the maximum possible cathode current densities (j_c > 40 mA·cm^{-2}) in order to minimize NaOCl losses due to its reduction at the cathode and reduce the rate of chlorate accumulation.

The kinetics of accumulation of hypochlorite and chlorate during electrolysis in diaphragmless electrolyzers is also significantly influenced by the hydrodynamic mode of the process [24].

When electrolysis is peformed in a cell with a diaphragm in the absence of forced convection at the platinum anode, the current efficiency of hypochlorite is 42–47 %, and the current efficiency of chlorate is 8–12 % [29]. Carrying out electrolysis at the minimum intensity of electrolyte mixing leads to a step-like (1.4–1.5 times) increase in the concentration of hypochlorite and to an even more significant 2.5–3.0-fold decrease in chlorate content (Fig. 2). This behavior is due to several reasons. In the absence of mixing, there is a significant acidification of the anode space, along with diffusion restrictions on the delivery of Cl^- to the anode surface and the removal of ClO^-in the bulk.

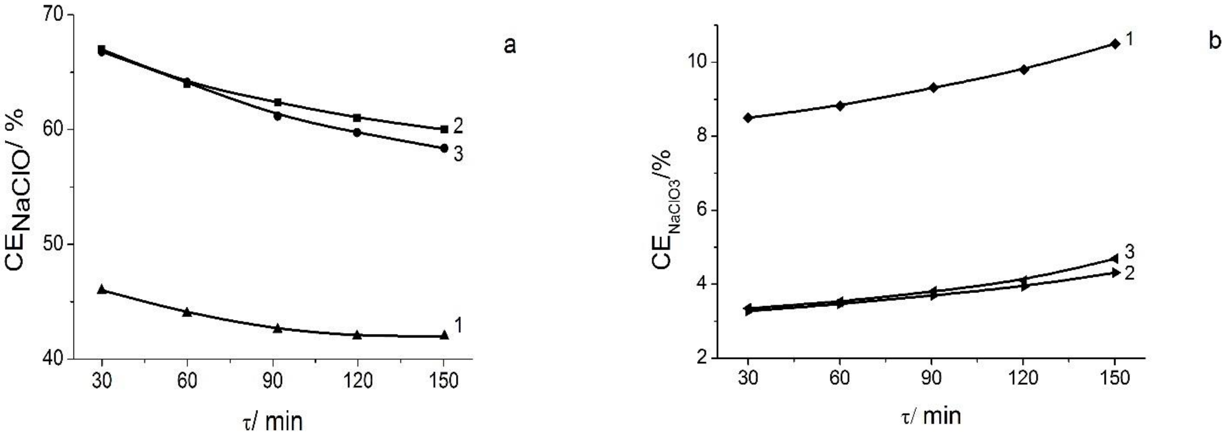

Fig. 2. The effect of mixing rate on the current efficiency of hypochlorite (a) and chlorate (b) by electrolysis of 0.15 NaCl solution (pH 8.4) on a platinum anode in divided cell at j_a = 40 mA cm^{-2}: 1 – natural convection; 2 – stirrer rate 500 rpm; 3 – 1100 rpm

As shown in Fig. 3, a decrease in the pH of the electrolyte leads to a decrease in the concentration of hypochlorite and an increase in the rate of chlorate accumulation. Depletion of the anode space by chloride ions also reduces CE (ClO^-). At the same time, the accumulation in the surface layer of ClO^- increases the rate of its further oxidation at the anode to chlorite and chlorate. Even a slight movement of the electrolyte along the surface of the anode leads to a decrease in the surface concentration of hypochlorite ions, which leads to a significant decrease in the rate of chlorate accumulation (see Fig. 2). At the same time, there is an increase in CE of ClO^- due to pH adjustment and increase in the surface concentration of Cl^-. A further increase in the mixing intensity leads to a slight decrease in the rate of NaClO accumulation and an increase in the $NaClO_3$ concentration in the solution bulk.

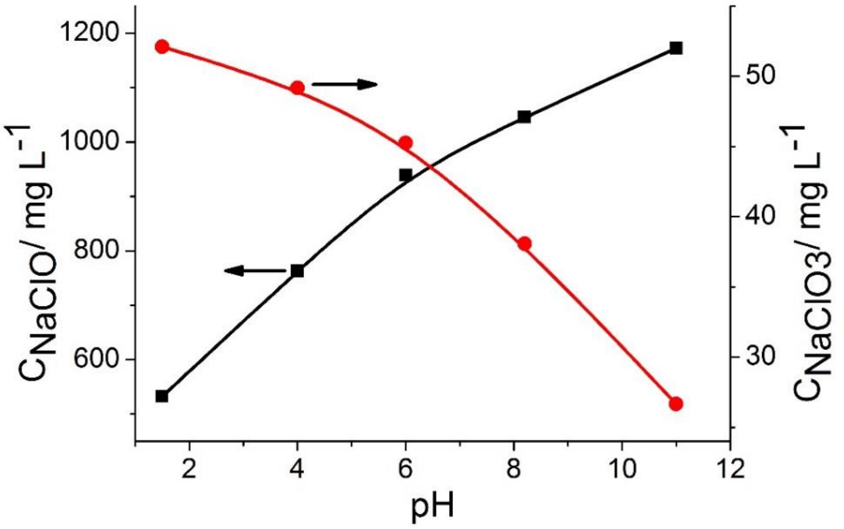

Fig. 3. Concentration of sodium hypochlorite and chlorate in the anolyte space after 120 minutes of electrolysis of 9 g L^{-1} NaCl under conditions of forced pH maintenance

The reduction of ClO^- at the cathode is controlled by the diffusion stage, which makes the kinetics of this process dependent on the intensity of electrolyte mixing. Carrying out electrolysis in a cell with a diaphragm showed that reducing the stirring intensity of the solution twice, leads to a decrease in the reaction of reduction of hypochlorite on titanium at 40 mA·cm^{-2} from 27 to 18 %, and at 20 mA·cm^{-2} from 50 to 31 %.

Thus, to minimize the conversion of hypochlorite to chlorate at the anode and the reduction of hypochlorite ions at the cathode, electrolysis must be performed at a minimum stirring rate of the solution relative to the electrodes.

The single-circuit scheme of inclusion of flow electrochemical cells with a diaphragm consists in consecutive movement of a solution through an anode electrode space in cathode or on the contrary. The hydraulic scheme is extremely simple and requires only one pump. To select the optimal hydraulic scheme, consider the operation of one flow cell with a diaphragm during the movement of the electrolyte in two directions: 1. from the cathode to the anode space (-C-A-); 2. from the anode to the cathode space (-A-C-).

If the initial NaCl solution is fed into the cathode space, then as it moves along the surface of the cathode it is alkalized to pH 12.3–12.5, due to the reaction of hydrogen evolution from the generated OH^-. Further, the alkaline gas-filled catholyte enters the anode space, where the synthesis of sodium hypochlorite and a simultaneous decrease in pH to 8.8–9.2 occurs (Table 2).

Table 2

Synthesis of sodium hypochlorite in a single-cell device with diaphragm*

I/ A	U/ V	catholyte pH	C_{NaClO}/ mg L^{-1}	CE_{NaClO}/ %	C_{NaClO3}/ mg L^{-1}	CE_{NaClO3}/ %	pH
2	4.34	12.28	296	90.5	6	3.85	9.16
3	4.94	12.37	440	89.7	11	4.71	9.26
4	5.50	12.50	580	88.7	16	5.13	9.34

* The flow of solution (8.5 L·h^{-1}) is directed from the cathode into the anode space (-C1-A1-).

The results of electrolysis when the hydraulic circuit consists of two flow coaxial cells with a diaphragm and flow direction -C1-A1-C2-A2- are summarized in Table 3. With such a connection scheme and a current of 2 A, there is a slight simultaneous increase in CE of NaClO and CE of $NaClO_3$. However, at a current of 3 and 4 A there is an increase of 2–3 % of the CE of NaClO and a decrease of the CE of $NaClO_3$. pH of the resulting solution is slightly lower at all currents. The increase in CE of NaClO when using two cells can be explained by a decrease in the rate of reduction of active chlorine at the cathode in the cathode chamber C2 due to increased gas filling and reduced loss of active chlorine at the cathode.

Table 3

Synthesis of sodium hypochlorite in a double-cell device with diaphragm*

I/ A	U/ V	catholyte pH	C_{NaClO}/ mg L^{-1}	CE_{NaClO}/ %	C_{NaClO3}/ mg L^{-1}	CE_{NaClO3}/ %	pH
2	8.85	604	92.3	15.2	4.9	8.9	2
3	10.20	908	92.5	17.4	3.7	9.2	3
4	11	1196	91.4	20.4	3.3	9.3	4

* The flow of solution (8.5 L h^{-1}) is directed from the cathode into the anode space (-C1-A1-C2-A2-).

An additional experiment was performed in order to understand the effect of gas filling of the interelectrode space on the kinetics of sodium hypochlorite and chlorate formation. Three cells without a diaphragm were connected in series and gas separators were installed between 1–2 and 2–3 cells. Two series of electrolyses were performed: one without and the other with a gas separator. As one can see from Table 4, gas evolution at all currents reduces the CE of NaClO by about 2.5–3.0 % and does not affect the CE of $NaClO_3$. A probable explanation for the observed effect is a decrease in the rate of reduction of active chlorine at the cathode in conditions of more intense gas filling of the interelectrode space due to additional blocking of the cathode surface and, consequently, an increase in true cathode current density.

Table 4

Synthesis of sodium hypochlorite in a triple-cell device without diaphragm*

Conditions	I/ A	C_{NaClO}/ mg L^{-1}	CE_{NaClO}/ %	C_{NaClO3}/ mg L^{-1}	CE_{NaClO3}/ %	pH
without gas separator	2	755	81.5	9.9	2.2	9.39
	3	1152	82.2	11.3	1.7	9.46
	4	1513	81.6	9.9	1.1	9.61
with gas separator	2	734	79.2	9.0	2.0	9.41
	3	1061	76.3	12.8	1.9	9.43
	4	1468	79.2	9.9	1.1	9.61

* The flow of solution (9.0 L•h^{-1}) is directed from the cathode into the anode space (-C1-A1-C2-A2-C3-A3-).

If hydraulic circuit consisting of one flow coaxial cell with a diaphragm and flow direction -A1-C1- and the initial NaCl solution is fed directly into the anode space of the cell, then at the outlet of the anode chamber we obtain an acidic gas-filled anolyte with a pH of 2.15–2.25, which is a solution of molecular chlorine (60–70 mol.%) and hydrochloric acid (30–40 mol%). From the anode space, the anolyte is sent to the cathode space of the cell, where it is alkalized to pH 8.9–9.3. Dissolved chlorine is converted into hypochlorite (95–98 at.%) and hypochlorous acid (3–5 at.%). There is a significant loss of active chlorine due to reduction at the cathode (Table 5). CE of NaClO drops from 88.7–90.5 % for –C-A- flow (see Table 2) to 83.6–87.1 % for such flow.

Table 5

Synthesis of sodium hypochlorite in a single-cell device with diaphragm*

I/ A	U/ V	catholyte pH	C_{NaClO}/ mg L^{-1}	CE_{NaClO}/ %	C_{NaClO3}/ mg L^{-1}	CE_{NaClO3}/ %	pH
2	4.31	2.25	285	87.1	12	7.70	8.9
3	4.95	2.20	415	84.6	15	6.42	9.1
4	5.50	2.15	547	83.6	18	5.78	9.3

* The flow of solution (8.5 L h^{-1}) is directed from the cathode into the anode space (-A1-C1-).

Thus, the scheme of supply of electrolyte from the cathode to the anode space is more rational in terms of preventing the partial loss of active chlorine at the cathode.

Removal of the membrane from the cell leads to only a slight decrease in the current efficiency of sodium hypochlorite within 1 % and a slight increase in the pH of the solution, which also increases its stability. Current efficiency of chlorates does not change. A positive effect is the reduction of cell voltage, which improves the energy efficiency of sodium hypochlorite synthesis (Tables 6, 7).

Table 6

Synthesis of sodium hypochlorite in a single-cell device without diaphragm*

I/ A	U/ V	C_{NaClO}/ mg L^{-1}	CE_{NaClO}/ %	C_{NaClO3}/ mg L^{-1}	CE_{NaClO3}/ %	pH
2	3.90	291	89.0	5	3.2	9.10
3	4.26	432	88.1	9	3.8	9.15
4	4.60	570	87.1	13	4.2	9.30

* The flow of solution (8.5 L•h^{-1}) is directed from the cathode into the anode space (-A1-C1-).

Table 7

Synthesis of sodium hypochlorite in a double-cell device without diaphragm*

I/ A	U/ V	C_{NaClO}/ mg L^{-1}	CE_{NaClO}/ %	C_{NaClO3}/ mg L^{-1}	CE_{NaClO3}/ %	pH
2	7.8	592	90.5	15	5.1	9.21
3	8.58	897	91.4	17	3.7	9.43
4	9.3	1193	91.2	20	3.3	9.44

* The flow of solution (8.5 L h^{-1}) is directed from the cathode into the anode space (-A1-C1-).

Thus, from the point of view of reducing energy consumption, simplifying the design of the cell, for the synthesis of low-concentrated solutions of sodium hypochlorite, the use of a cell with a separated electrode space is not appropriate.

In order to confirm this conclusion, an electrolyzer was assembled from two cells connected into the series with and without a diaphragm (Fig. 4). For maximum accuracy of the experiment, first the cell was composed of two cells with a separate electrode space, and then from these cells diaphragm was removed the and the fitting on the cathode was plugged. The solution was fed using a peristaltic pump at a volumetric rate of 9 L·h^{-1}. The anode current density was 60 mA·cm^{-2}.

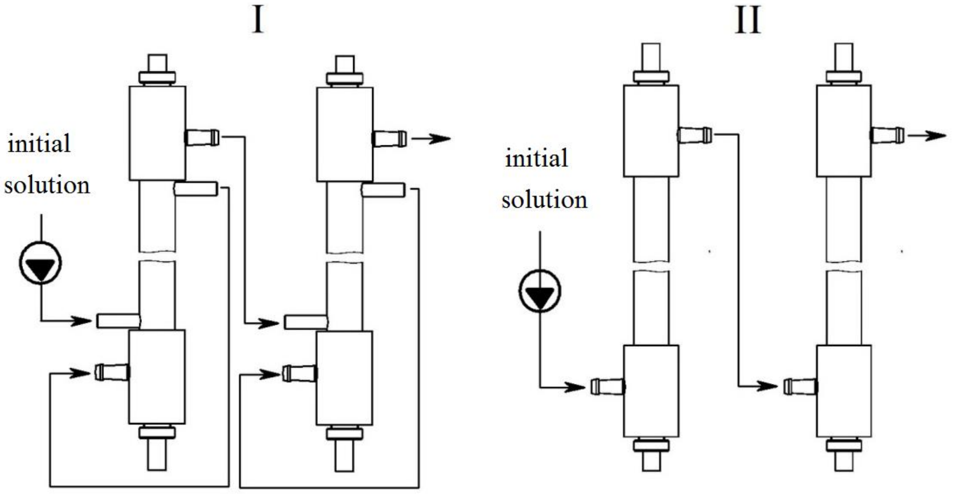

Fig. 4. Hydraulic circuit of cells -C-A-C-A- with diaphragm (I) and without diaphragm (II)

Both methods of carrying out the electrolysis process demonstrated close current efficiencies of sodium hypochlorite and the pH of the solutions obtained (Table 8). However, the total voltage on the cells and, as a consequence, the energy consumption for obtaining of 1 kg of NaClO in the presence of the diaphragm is almost 30 % higher than in the case of cells without a separate electrode space. In an electrolyzer without a diaphragm, the voltage on the second cell increases insignificantly (by 0.1 V) only due to an increase in the degree of gas filling of the interelectrode space.

In the case of cells with a divided space in the membrane there is an additional voltage drop. However, on the second of the series-connected cells there is an even more significant increase in voltage than on the first. This is due to the fact that there is a voltage drop in the diaphragm, in addition, the diaphragm reduces the effective interelectrode gap, which leads to an increase in the degree of gas filling of the electrode spaces and, consequently, to an additional increase in cell voltage. This is an additional heating of the electrolyte. An increase in temperature leads to some increase in the current efficiency of sodium chlorate. When using three series-connected cells with a diaphragm, the energy consumption for sodium hypochlorite increases even more significantly: 5.87 and 4.38 kilowatt-hours per kg for the cell, consisting of cells with a diaphragm and without a diaphragm, respectively.

Table 8

The main parameters of the device, which consists of two series-connected cells and the characteristics of the sodium hypochlorite solution*

Cell	I/ A	U_{cell1}/ V	U_{cell2}/ V	U_{Σ}/ V	C_{NaClO}/ mg L^{-1}	C_{NaClO3}/ mg L^{-1}	pH	Energy consumption / kW h kg^{-1}
with diaphragm	4	5.5	6.4	11.9	1096	20	9.0	4.83
without diaphragm	4	4.6	4.7	9.3	1090	12	9.2	3.79

* The flow of solution (9.0 L h^{-1}) is directed from the cathode into the anode space (-C1-A1-C2-A2-).

Another combination of one cell with a diaphragm and two flow cells without a diaphragm -C1-2-3-A1- were tested (Fig. 5). The initial NaCl solution is fed to the cathode space of cell 1 with a diaphragm (C1) where it is leached to pH 12.3. Next, the alkaline solution is electrolyzed in two series-connected cells without diaphragms, then to reduce the pH and simultaneously increase the concentration of hypochlorite is fed into the anode space of cell 1. In this scheme, the solution containing hypochlorite does not contact the cathode in one of the three cells. And should slightly increase the content of hypochlorite in the resulting solution. At a volumetric feed rate of the initial solution (9 g·L^{-1} NaCl) 9.5 L·h^{-1}, a current of 3.2 A in the solution is formed 1013 mg·L^{-1} NaClO, 10 mg·L^{-1} $NaClO_3$ at pH 9.30. The total voltage is 14.8 V. If you remove the membrane from the first cell, the same electrolysis parameters, the voltage is 13.4 V, and the composition of the solution is almost unchanged: pH 9.35 and 1010 mg·L^{-1} NaClO, 9 mg·L^{-1} $NaClO_3$.

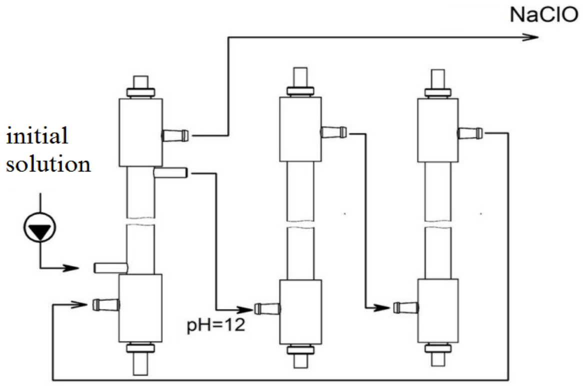

Fig. 5. Hydraulic circuit of cells –C1-2-3-A1-

Thus, to obtain low-concentrated solutions of sodium hypochlorite, the use of flow cells with a diaphragm in a single-circuit scheme of construction of the cell is not justified, both in terms of complexity and cost of the electrochemical modules, and in terms of increasing electricity consumption.

Removal of the membrane from the cell leads to only a slight decrease in the current efficiency of sodium hypochlorite in the range of 1-3% and a slight increase in the pH of the solution, which has a positive effect on its stability. Current efficiency of chlorates do not change. A positive effect is the reduction of cell voltage, which improves the energy efficiency of sodium hypochlorite synthesis.

The inexpediency of installation in the hydraulic line between the flow cells of the device for separation of electrolysis gases is shown. The decrease in the rate of reduction of active chlorine at the cathode in the conditions of more intensive gas filling of the interelectrode space due to additional blocking of the cathode surface is demonstrated.

Conclusions

Compact flow electrochemical cells with a titanium cathode and a titanium tubular anode with electrocatalytic coating based on the oxides of platinum and palladium allowed to create an original design of the highly efficient electrochemical devices for the synthesis of high-purity solutions of sodium hypochlorite have been developed.

The investigation of the influence of different parameters of electrolysis on the indicators of the obtained solutions allowed one to propose two optimal configurations of the device from two and three series-connected flow cells.

With a current load of 2 A and the use of two flow cells at a volumetric flow rate of 8.7 L•h^{-1}, one can sinthesize a high-purity solution of sodium hypochlorite containing 500 mg•L^{-1} NaClO and 0.6 mg•L^{-1} $NaClO_3$. The current efficiency of hypochlorite and sodium chlorate is 78 and 0.2 %, respectively. Electrochemical reactor with three flow cells with a capacity of 9.2 L•h^{-1} at a current load of 3 A allows one to produce a solution, containing 1000 mg•L^{-1} NaClO and not more than 6 mg•L^{-1} $NaClO_3$ continuously.

Created prototypes of electrolyzers have successfully passed the stages of laboratory and experimental tests. The results of long-term work in the conditions of obtaining experimental batches of solutions showed the correctness of the concept, which was the basis for the design of these devices. The supply of high-purity NaCl source solutions with a given constant velocity to the developed original flow cells with the highly efficient electrocatalytic coating of the anode, power supply of the power circuit with a reliable galvanostatic DC source and control of all electrolysis parameters allowed one to synthesize the high-purity solutions.

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