

UDC 544.65+661.43

*D. Girenko*<sup>a</sup>, *B. Murashevych*<sup>b</sup>, *A. Velichenko*<sup>a</sup>**SYNTHESIS OF SODIUM HYPOCHLORITE SOLUTIONS IN COAXIAL FLOW CELLS IN CURRENT REVERSE MODE**<sup>a</sup> Ukrainian State University of Chemical Technology, Dnipro, Ukraine<sup>b</sup> Dnipro State Medical University, Dnipro, Ukraine

Electrodes made of platinized titanium with a surface platinum content of 2–3 mg/cm<sup>2</sup> can be used in non-diaphragm flow- and accumulative-type electrolyzers for the electrolysis of low-concentrated NaCl solutions in order to obtain pure NaClO solutions. If electrolysis of 0.15 M NaCl solution is carried out on platinized titanium electrodes in the usual mode at current densities of 20–40 mA/cm<sup>2</sup>, then the anode surface passes into an oxidized passive state. In this case, the current efficiency of hypochlorite does not exceed 40%, and the current efficiency of chlorate is more than 20%. During a short electrolysis on a preliminarily reduced surface of platinized titanium, the current efficiency of hypochlorite reaches 90% with almost no accumulation of chlorate. Carrying out the long-term electrolysis of low-concentrated NaCl solutions in the regime of periodic polarity reverse makes it possible to significantly (up to 10 times) reduce the content of chlorate in the resulting sodium hypochlorite solutions. The most promising is the synthesis of sodium hypochlorite solutions in flow-type electrochemical reactors consisting of several series-connected electrochemical modules with an undivided electrode space in the mode of periodic current reverse. The electrolyzer of two series-connected cells in the mode without current reverse allows obtaining a solution that contains 500 mg/L of sodium hypochlorite and 130 mg/L of sodium chlorate. Carrying out the electrolysis in the reverse current mode every 30 s reduces the content of sodium chlorate to 25 mg/L, which makes it possible to produce high-purity NaClO solutions.

**Keywords:** platinized titanium, flow cell, sodium hypochlorite, reverse polarity electrolysis, electrocatalysis.

**DOI:** 10.32434/0321-4095-2023-151-6-59-67

**Introduction**

The electrochemical synthesis of sodium hypochlorite NaClO via electrolysis of sodium chloride NaCl solutions is most often implemented on dimensionally stable anodes (DSA) with composite coatings based on titanium and tin oxides modified with oxides of platinum group metals [1]. For the electrolysis of concentrated (higher than 0.5 M) NaCl solutions, titanium anodes with a catalyst based on mixed oxides of ruthenium and titanium [2] proved to be the best, and for dilute (0.05–0.5 M) NaCl solutions coatings of mixed oxides of iridium, titanium or tin are the most effective [3,4]. Anodes similar to Ti/TiO<sub>2</sub>-IrO<sub>2</sub> DSAs, along with high performance, have the significant

disadvantages, which are expressed in their high price, low availability, and laboriousness of their manufacture.

One of the most accessible DSAs is platinized titanium (Ti/Pt) [5]. The platinum coating is relatively cheap, can be easily formed by the electrochemical methods, can operate in the region of high anodic and cathodic polarizations, has high corrosion resistance in the presence of strong oxidizing agents and chlorides, etc. However, during the electrolysis of low-concentrated (less than 0.3 M) NaCl solutions on such electrodes, the current efficiency (CE) of hypochlorite does not exceed 50% [6]. In addition, platinum is characterized by high selectivity with respect to the oxidation of

© D. Girenko, B. Murashevych, A. Velichenko, 2023



This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

*Synthesis of sodium hypochlorite solutions in coaxial flow cells in current reverse mode*

hypochlorite to chlorite  $\text{NaClO}_2$  and chlorate  $\text{NaClO}_3$  [7].

One of the ways to increase the purity (mainly to reduce the amount of chlorate impurity) of the resulting  $\text{NaClO}$  solutions on Ti/Pt electrodes is to implement the electrolysis in the mode of periodic reverse of the electrolyzer power supply polarity [8]. Thus, accumulative electrolysis of 0.15 M  $\text{NaCl}$  solution in the current reverse mode makes it possible to increase the  $\text{CE}(\text{NaClO})$  from 25 to 40% on average, with a significant decrease in  $\text{CE}(\text{NaClO}_3)$  from 20% to 5%. During the electrolysis of a more concentrated 0.3 M  $\text{NaCl}$  solution, the  $\text{CE}(\text{NaClO})$  increases from 55% to 75%, and the  $\text{CE}(\text{NaClO}_3)$  decreases almost 10 times from 11.0% to 1.5%. However, the implementation of electrolysis in the accumulative mode, despite the simplicity of the electrolyzer design, has a number of disadvantages, the main of which is the impossibility of continuously obtaining solutions of a given composition. This problem can be solved by synthesizing  $\text{NaClO}$  solutions in flow type electrolyzers [9].

The most promising is the synthesis of sodium hypochlorite from low-concentrated (lower than 0.5 M) sodium chloride solutions in flow type electrolyzers consisting of one or several series-connected electrochemical modules with an undivided electrode space. The flow system makes it possible to continuously obtain a solution with a given concentration, and the absence of a membrane simplifies and reduces the cost of the design, reduces

energy costs, and makes it possible to obtain sodium hypochlorite solutions that do not require additional pH adjustment. However, the absence of a membrane leads to some loss of active chlorine due to the possibility of its reduction on the cathode. The optimal organization of the electrolysis process can make it possible not only to minimize the loss of active chlorine, but also to increase the efficiency of the synthesis of  $\text{NaClO}$  and to reduce the content of undesirable toxic chlorates. Such high-purity solutions can be used for medical purposes, in particular, as antiseptics, raw materials for obtaining multifunctional solutions of N-chlorotaurines, for aerosol air disinfection [10], for obtaining chlorine-active polymeric materials [11], etc.

#### Materials and methods

All chemicals were purchased from Sigma-Aldrich (ALSI, Kyiv, Ukraine). Bidistilled water with an electrolytic conductivity of  $1.5 \mu\text{S}/\text{cm}$  was used for the preparation of solutions. The acidity level of the solutions was being determined using ADWA AD1030 pH meter.

Polarization measurements were carried out using an MTEch PGP-550M potentiostat-galvanostat in a three-electrode thermostated cell at  $25^\circ\text{C}$ .

All electrode potentials were measured using a Luggin capillary and are given in the work versus the saturated silver chloride reference electrode.

Platinized titanium flat electrodes were obtained according to the following procedure. First the surface of Ti plate (VT 1-0, 0.8 mm thick) was prepared

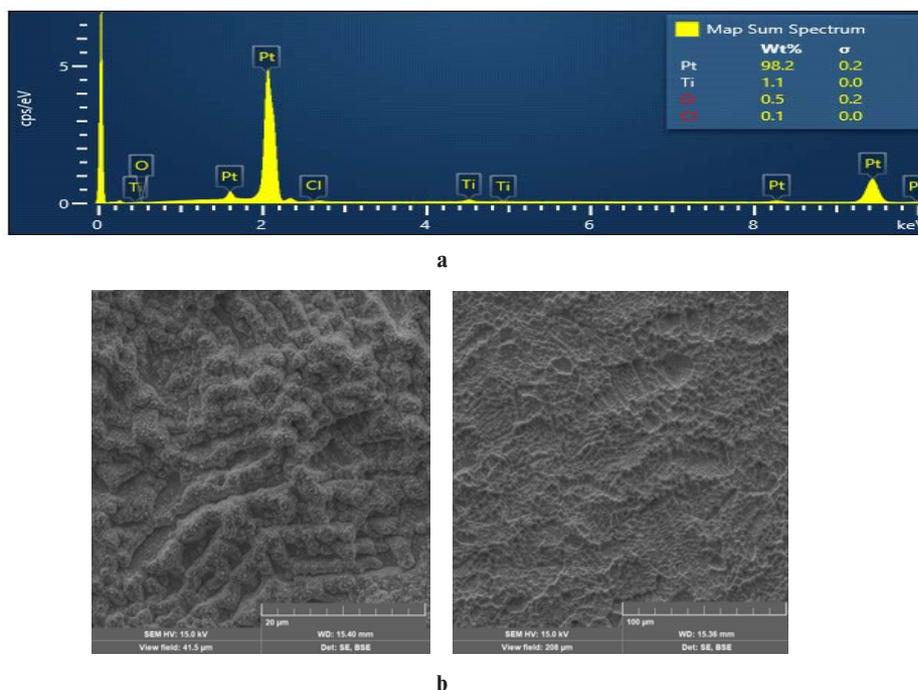


Fig. 1. EDX spectrum (a) and SEM images (b) of the Ti/Pt electrode surface

mechanically by an abrasive paper; after rinsing it was degreasing with 4 M KOH at room temperature; after removal of degreasing solution it was chemically etched in 6 M HCl at 90°C for 30 min; then the surface was rinsed and thin layer of platinum was electrodeposited from the following electrolyte: 20 g/L  $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ ; 10 g/L  $\text{NaNO}_2$ ; 100 g/L  $\text{NH}_4\text{NO}_3$ ; and 50 g/L solution of  $\text{NH}_4\text{OH}$  ( $\rho=0.915$  g/mL). Electrodeposition was carried out at a cathodic current density of 10 mA/cm<sup>2</sup> at a temperature of 85–95°C. The content of platinum in the coating, according to energy-dispersive X-ray spectroscopy (EDX) (Fig. 1,a), was 98–99%. The resulting coating is fine-crystalline, homogeneous, non-porous, with high adhesion to the titanium surface (Fig. 1,b). The average platinum surface content determined gravimetrically was 2–3 mg/cm<sup>2</sup>.

To carry out the synthesis of sodium hypochlorite solution in a flow, we constructed the non-diaphragm cells, which consist of two coaxially arranged tubular electrodes made of titanium Grade 2 (Fig. 2). The internal tubular electrode (outer diameter 10 mm) has the working area of 60 cm<sup>2</sup>, the external tubular electrode (inner diameter 14 mm)

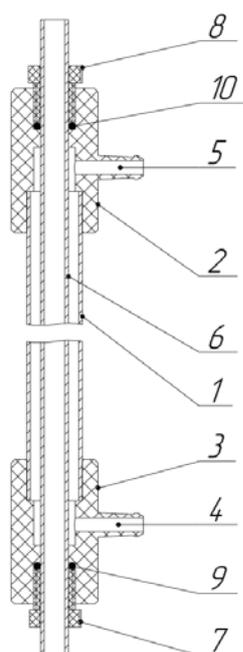


Fig. 2. The section of the constructed electrochemical non-diaphragm cell for NaOCl synthesis in a flow: 1 – external tubular electrode from the inside with inner working surface; 2 – upper collector head made of PTFE; 3 – lower collector head made of PTFE; 4 – solution supply fitting; 5 – fitting for removing the solution; 6 – internal tubular electrode outside with outer working surface; 7 and 8 – bushings with external thread; 9 and 10 – sealing rings

has the working area of 80 cm<sup>2</sup>.

The platinum coating on electrodes 1 and 6 (Fig. 2) was formed as follows. The surface of titanium electrodes 1 and 6 was prepared in the same way as flat electrodes, but the platinization process was carried out using a specially developed technique. A cell, whose design corresponds to Fig. 2, was placed vertically in a MicroMed VB-4 thermostat with bidistilled water heated to 95°C. A container with platinization electrolyte was placed in the same thermostat. Outside the thermostat there was a peristaltic pump connected in suction mode to fitting 5. During the pump operating, the platinum electrolyte at a volumetric rate of 100 mL/min was sucked from the container, directed into fitting 4, passed through the cell from the bottom up and was discharged through the pump back into the container. This cyclic method of supplying electrolyte during the electroplating process ensured platinization at an optimal temperature about 95°C, effective removal of electrolysis gases, and made it possible to get by with a minimum volume of electrolyte. First, the internal electrode 6 acted as the cathode, on which, accordingly, a platinum coating was applied. Upon completion of deposition, electrode 6 was removed, rinsed, dried, weighed and analyzed. The inner surface of the outer electrode 1 was platinized in a similar way, with the central platinated titanium electrode acting as an anode. Platinization directly in the flow cell allows forming the coating only on the working surface of both electrodes, which increases the service life of the expensive platinization electrolyte. Gravimetric measurements of the coated tubular electrodes showed that the surface platinum content in all cases was 2–3 mg/cm<sup>2</sup>. The surface characteristics did not differ from those of flat electrodes (Fig. 1).

The current reverse was carried out using a relay module controlled by a cyclic timer. The device was connected between the current source Matrix MPS-3605LP and the cell.

The concentration of NaClO and NaClO<sub>3</sub> in solutions was determined by iodometric titration [12].

The integral current efficiency (%) of hypochlorite and chlorate during the electrolysis of NaCl solutions in a flow electrolyzer was calculated using the next equations:

$$\text{CE}(\text{NaClO}) = \frac{2 \cdot F \cdot w \cdot C(\text{NaClO})}{74.5 \cdot n \cdot I} \cdot 100\%,$$

$$\text{CE}(\text{NaClO}_3) = \frac{6 \cdot F \cdot w \cdot C(\text{NaClO}_3)}{106.5 \cdot n \cdot I} \cdot 100\%,$$

where  $C(\text{NaClO})$ ,  $C(\text{NaClO}_3)$  are the concentrations of sodium hypochlorite and chlorate in the solution, respectively (g/L);  $w$  is the volumetric flow rate of the initial solution to the flow electrolyzer (L/h);  $n$  is the number of series-connected electrochemical cells;  $F=26.8 \text{ A}\cdot\text{h}$  is the Faraday constant; and  $I$  is the electrolysis current (A).

### Results and discussion

As shown earlier [8], three states of the platinum surface can be conventionally distinguished with respect to the  $\text{Cl}^-$  oxidation reaction: reduced-active, oxidized-passive, and transition. The electrolysis of NaCl solutions in the entire range of concentrations usually proceeds on an oxidized surface of the anode. In this case, three main parallel processes with comparable current efficiencies are realized:  $\text{Cl}^-$  oxidation to hypochlorite, hypochlorite oxidation to chlorate, and oxygen evolution reaction. On the reduced surface, when the electrode is polarized in the galvanostatic mode, the oxidation of  $\text{Cl}^-$  in concentrated 1.0–2.0 M NaCl solutions occurs at electrode polarizations lower by 400–450 mV compared with the oxidized surface. However, during electrolysis, the reduced surface gradually oxidizes. In this case, the fraction of active sites on which  $\text{Cl}^-$  oxidation occurs, decreases.

According to modern theories about the course of reactions with oxygen transfer, potentials are realized on the reduced surface, at which labile oxygen-containing particles of the  $\text{OH}_{\text{ads}}$  type with a low oxygen-metal binding energy are formed. On an oxidized surface with formed phase oxides stoichiometrically closed to  $\text{PtO}_2$ , the formation of oxygen-containing inert particles with significantly higher energies  $\text{O}_{\text{ads}}$  becomes possible. The chloride ion acts as a depolarizer. During discharge, it interacts with surface oxygen-containing particles, thereby slowing down the formation of surface phase oxides. On the reduced surface of platinum,  $\text{Cl}^-$  oxidation is possible both in a direct electrochemical reaction and in a secondary chemical reaction upon interaction with labile oxygen-containing particles of the  $\text{OH}_{\text{ads}}$  type, as indicated by the recorded Tafel slopes of 30–40 mV/dec. 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. The main process in this case is the oxygen evolution reaction with a characteristic Tafel slope close to 120 mV/dec.

It should be noted that the activation of even a deeply oxidized surface of Ti/Pt (previously the electrode was polarized in 0.15 M NaCl with an anodic current of 40 mA/cm<sup>2</sup> for 600 seconds)

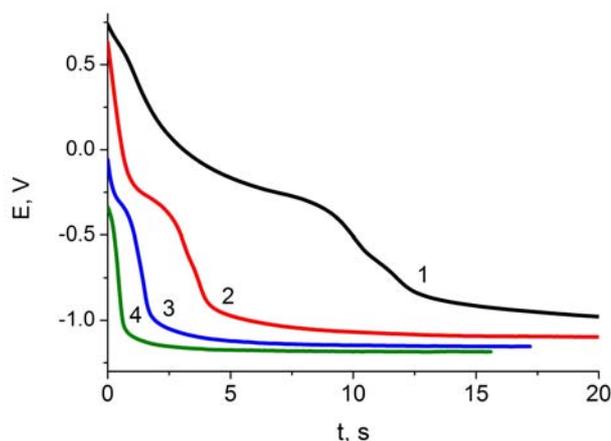


Fig. 3. Chronopotentiograms in 0.15 M NaCl solution on the oxidized Ti/Pt surface at cathodic current densities, mA/cm<sup>2</sup>: 1 – 5; 2 – 10; 3 – 15; and 4 – 20

proceeds quite quickly when the electrode is polarized by the cathodic current. The higher the cathodic current density, the faster the surface reduction occurs. At a cathodic current density of  $-5 \text{ mA/cm}^2$ , the surface is completely reduced within 15 s; at  $-10 \text{ mA/cm}^2$ , reduction takes 5 s (Fig. 3).

If the surface of the Ti/Pt electrode is previously activated in 0.15 M NaCl with the cathodic current of 20 mA/cm<sup>2</sup> for 100 seconds and further is polarized by the anodic current, then the chronopotentiogram will have an S-shaped character with an initial period during which the potential in 0.1–2.0 M NaCl solutions does not exceed +1.4 V, which corresponds to the active state of the surface (Fig. 4). If the electrolysis of sodium chloride solutions is carried out on the active surface, then chlorates in the solution are not detected or are at a minimum level, and the CE of sodium hypochlorite is close to 90%.

Further, there is an increase in the potential to values more positive than +1.7 V, which corresponds to the transition of the surface into a passive state. During anodic polarization of the Ti/Pt electrode in 0.15 M NaCl with a current of 10 mA/cm<sup>2</sup>, 20 mA/cm<sup>2</sup> and 40 mA/cm<sup>2</sup>, the surface is in an active state for 1000 s, 100 s, and 10 s, respectively (Fig. 4). At a given electrolyte concentration, a 2-fold increase in current density leads to a 10-fold decrease in the time the surface is in the active state. With an increase in the concentration of chloride ions in the solution, the rate of passivation of the Pt surface decreases significantly, for example, in 0.3 M NaCl at a current density of 20 mA/cm<sup>2</sup>, the active state lasts 1200 s.

In low-concentrated NaCl solutions, the duration of the induction period is significantly affected by the hydrodynamic conditions of the

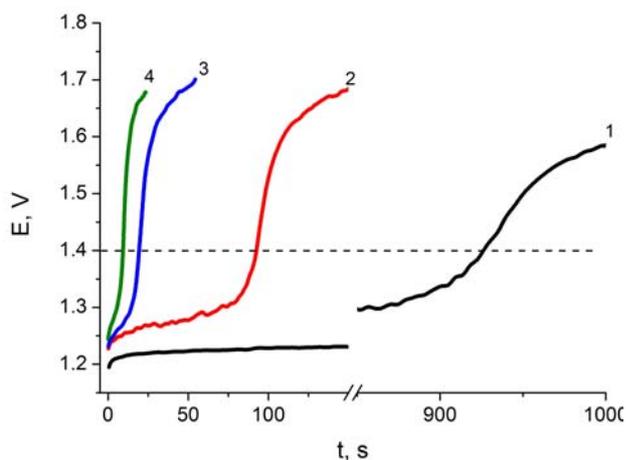


Fig. 4. Chronopotentiograms in 0.15 M NaCl solution on the reduced Ti/Pt surface at anodic current densities, mA/cm<sup>2</sup>: 1 – 10; 2 – 20; 3 – 30; and 4 – 40

process. For example, in 0.15 M NaCl at a polarization current of 20 mA/cm<sup>2</sup>, an increase in the stirrer speed from 660 to 2100 rpm leads to an increase in the duration of the active state of the electrode surface from 100 to 300 s. This is due to the fact that the oxidation of chloride ions proceeds at a high rate on the active surface of platinum, and diffusion control of the process takes place in low-concentrated NaCl solutions. An increase in the intensity of mixing of the solution leads to an increase in the surface concentration of the depolarizer (Cl<sup>-</sup>), which leads to a significant decrease in the rate of platinum surface passivation (Fig. 5)

The demonstrated property of chloride ions to slow down the rate of reduced platinum surface passivation can be used to improve the quality of sodium hypochlorite solutions obtained on Ti/Pt

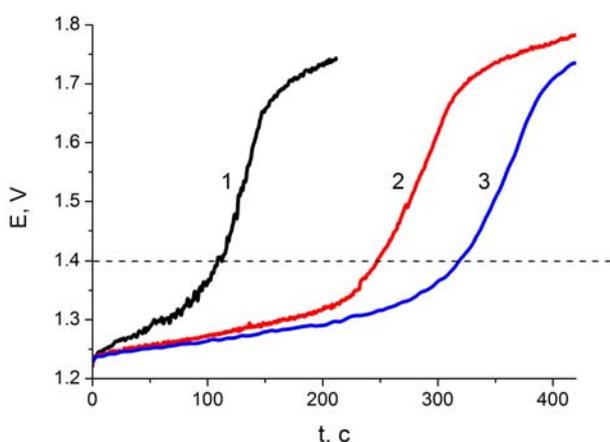


Fig. 5. Chronopotentiograms in 0.15 M NaCl on a reduced Ti/Pt surface at an anodic current density of 20 mA/cm<sup>2</sup> and various stirrer speeds, rpm: 1 – 660; 2 – 1400; and 3 – 2100

electrodes. As was shown earlier [8], if the electrolysis of concentrated sodium chloride solutions begins with the reduction of the anode, then in 1.0–2.0 M NaCl solutions in non-diaphragm electrolyzers, sodium hypochlorite can be synthesized with the CE of more than 80% when the CE of the accompanying chlorate is less than 5%.

It is possible to lower the working concentrations of NaCl solutions while maintaining the high purity of the obtained NaClO solutions by carrying out electrolysis in the current reverse mode [9]. If accumulative electrolysis of 0.15 M NaCl is carried out in the usual mode at anodic current densities of 20–40 mA/cm<sup>2</sup>, then the CE(NaClO) usually does not exceed 25%, and the CE(NaClO<sub>3</sub>) is more than 20%. Conducting electrolysis in the reverse mode allows increasing the CE(NaClO) to 40% with a simultaneous decrease in the CE(NaClO<sub>3</sub>) to 5%. Increasing the NaCl concentration to 0.3 M improves the performance of reverse electrolysis even more. Under these conditions, CE(NaClO) increases to 78%, and CE(NaClO<sub>3</sub>) decreases to 1–3%.

Thus, carrying out the synthesis of hypochlorite under conditions of reverse current in an accumulative mode can significantly increase the purity of the resulting solutions. However, it is more promising to carry out electrolysis in a flow, when a NaClO solution with the necessary parameters and a given productivity is directly synthesized. To implement this kind of synthesis, coaxial-type flow cells were used, described above (Fig. 2). During the experiment, the initial NaCl solution was fed into the flow cell at a volume flow rate of 6 L/h using a peristaltic pump. Samples for the analysis of the solution during the electrolysis were taken after the steady state parameters of the electrolysis were reached. Unfortunately, such a design of the flow cell does not allow electrolysis to be carried out with the same cathodic and anodic current densities. The area of the external electrode is 1.3 times larger than the area of the internal electrode, as a result, to implement the same anodic current density of 40 mA/cm<sup>2</sup> on the inner and outer surfaces of the flow cell, the current in one case should be 2.4 A, and in the other 3.2 A. At a constant current, the current densities on the internal and external electrodes will differ by 1.3 times. If electrolysis is carried out using one cell in the normal mode without current reverse at the anodic current density of 40 mA/cm<sup>2</sup>, then the CEs of NaClO and NaClO<sub>3</sub> practically do not depend on which electrode (internal or external) acts as the anode, and are 35–36% and 20–21%, respectively (Table 1).

In the case of electrolysis under current reverse

conditions, a significant decrease in chlorate CE and a slight decrease in hypochlorite CE are observed. If the polarity is changed every 30 seconds (polarity reverse time  $t_{rev}=30$  s), then  $CE(NaClO)$  changes from 37% to 32%, while  $CE(NaClO_3)$  decreases 4 times, from 21% to 5.5%. If decreasing  $t_{rev}$  to 10 s, then  $CE(NaClO)$  changes more significantly from 37% to 25%, however,  $CE(NaClO_3)$  decreases 10 times from 21% to 2% (Table 1). If the polarity reverse time is increased to 60 s, then  $CE(NaClO)$  becomes comparable to electrolysis without current reverse, while  $CE(NaClO_3)$  decreases only 2.5 times from 22% to 8%. In any case, when conducting electrolysis in the current reverse mode, a significant increase in the purity of solutions is achieved. The pH of the resulting solutions indicates that the main form of active chlorine in them is sodium hypochlorite (>99%). Such solutions have the highest stability under storage.

As follows from the obtained data, a comparison of the sodium hypochlorite synthesis in the normal and reverse modes shows that during accumulative electrolysis, the integral CE of hypochlorite increases, and in the case of synthesis in a flow, it decreases. This is caused by the conditions that are responsible for the reduction rate of the hypochlorite ion at the cathode. Previously, we showed [13] that during anodic polarization,  $Cl^-$  oxidation products ( $Cl_2$ ,  $HClO$ ) are adsorbed on the platinum surface, and the anode is not freed from them even after washing in bidistilled water. When the potential in 1 M  $HClO_4$  solution is swept into the cathodic region, even on an electrode washed in water, a characteristic peak of the reduction of the products of  $Cl^-$  anodic oxidation is observed. Thus, during electrolysis in a flow cell, at the moment when the electrode polarization changes from anode to cathode, an additional reduction of active chlorine occurs, compared with non-reverse electrolysis, which leads to a decrease in the integral  $CE(NaClO)$ .

The performance of the device and the chemical composition of sodium hypochlorite solutions obtained during the operation of the designed flow-

type electrochemical module depend on several factors: the design of the electrochemical cell, electrode material, electrolyte volume flow rate and its concentration, and current. The volume flow rate of the electrolyte (NaCl solution) supply and the geometrical parameters of the electrochemical cell determine the linear rate of the solution with respect to the electrodes and the duration of the front movement through the electrolyzer (the duration of electrolysis of the conditional volume of the solution). The following parameters can be used as criteria chosen for optimizing the operation parameters of the cell: the concentration of hypochlorite and chlorate in the solution, as well as the ratio of their current efficiencies  $CE(NaClO):CE(NaClO_3)$ . In this case, the resulting solutions should contain maximum of hypochlorite with a minimum concentration of chlorate. It should be noted that no chlorite ions were found in the obtained solutions. This is consistent with the data for electrolysis in non-flowing electrolyzers and is explained by the ability of  $ClO_2^-$  to be easily oxidized at the anode to chlorate, reduced at the cathode, and enter into a rapid reaction with an excess of hypochlorite [14].

For the creation of an autonomous device with a given performance for the continuous production of solutions with given parameters it is advisable to consider the possibility of building an electrochemical circuit made of several series-connected flow electrochemical universal cells. The length and diameter of the internal electrode and inner diameter of the external electrode determine the ratio of the electrode current densities and the volumetric current density (without taking into account the gas filling of the interelectrode space), and the number of cells determines the conditional length of the electrolyzer, hence the electrolysis time per unit volume of the initial solution. In addition, there is an induction period after the change of polarization from cathode to anode, during which hypochlorite synthesis does not occur. Depending on the current density, it ranges from 0.5 to 5 s. The contribution of this factor to the decrease in  $CE(NaClO)$  is the higher, the lower

Table 1  
Parameters of solutions obtained via electrolysis in one flow cell with the supply of the initial 0.15 M NaCl solution at the volume flow rate of 6 L/h

Current, A	$t_{rev}$ , s	$C(NaClO)$ , mg/L	$CE(NaClO)$ , %	$C(NaClO_3)$ , mg/L	$CE(NaClO_3)$ , %	pH
2.4	without reverse	207	37	55	22.2	9.05
3.2	without reverse	266	36	71	21.4	9.03
2.4	10	156	28	5	1.9	8.85
2.4	30	179	33	15	5.5	8.90
2.4	60	205	36	22	8.3	9.01

Table 2

**Parameters of solutions obtained via electrolysis in several series-connected flow cell with the supply of the initial solution of 0.15 M NaCl at the volume flow rate of 6 L/h and the electrolysis current of 2.4 A**

Number of cells	$t_{Rev}$ , s	C(NaClO), mg/L	CE(NaClO), %	C(NaClO <sub>3</sub> ), mg/L	CE(NaClO <sub>3</sub> ), %	CE(NaClO):CE(NaClO <sub>3</sub> )	pH
1	without reverse	253	45.5	56	21.1	2.2	9.05
2	without reverse	495	44.5	128	24.2	1.8	9.31
3	without reverse	711	42.6	194	24.4	1.7	9.39
1	30	180	32.4	14	5.3	6.1	8.88
2	30	350	31.5	25	4.7	6.7	9.17
3	30	503	30.2	46	5.8	5.2	9.20
1	60	206	37.1	23	8.7	4.3	9.01
2	60	397	35.7	47	8.8	4.1	9.20
3	60	573	34.4	73	9.18	3.7	9.27

$t_{Rev}$ : with an increase in  $t_{Rev}$  from 10 to 60 s, CE(NaClO) increases from 28% to 36% (Table 1).

As follows from Table 2, an increase in the number of series-connected cells leads to a regular decrease in the integral CE(NaClO) and an increase in CE(NaClO<sub>3</sub>). This is due to an increase in the electrolysis time of each unit volume of electrolyte, in which, as it moves inside the cells, the concentration of the hypochlorite ion increases, therefore, the rate of its reduction at the cathode and oxidation at the anode increases. It should be noted that if, under conditions of long-term accumulative electrolysis of a 0.15 M NaCl solution without current reverse, the CEs of hypochlorite and chlorate are often comparable with each other and are at the level of 20–30%. At the same time, in a flow system without current reverse, CE(NaClO) almost twice as high as CE(NaClO<sub>3</sub>) (Table 2).

The electrolyzer of two series-connected cells, operating in the mode without current reverse, generates a solution with a sodium hypochlorite concentration of 495 mg/L. A solution with a similar content of NaClO (503 mg/L) can be obtained in the reverse current mode at  $t_{Rev}=30$  s in three flow cells. However, the current efficiency of chlorate in the latter case will be 4 times less.

The use of the reverse electrolysis mode leads to the expected decrease in the chlorate current efficiency depending on the number of cells and the reverse time from 2 to 4 times (Table 2). Analyzing the CE(NaClO):CE(NaClO<sub>3</sub>) criterion for this design of flow cells, we can conclude that a sodium hypochlorite solution with a minimum chlorate content (350 mg/L NaClO and 25 mg/L NaClO<sub>3</sub>) can be obtained using two series-connected cells in the current reverse mode with a polarity reverse period of 30 s.

It should be noted that when obtaining disinfectant NaClO solutions by electrolysis of sodium chloride solutions prepared from unprepared water and low purity raw material, or from sea water, there is a problem of deposition of poorly soluble compounds on the electrodes [15]. Carrying out electrolysis in the current reverse mode solves this problem, reducing the frequency of the necessary washing of the electrolyzer.

#### Conclusions

Thus, platinized titanium electrodes can be used in non-diaphragm flow type electrolyzers for the electrolysis of low-concentrated NaCl solutions in order to obtain high-purity NaClO solutions. The electrolysis must be carried out in the current reverse mode, while the period of polarity reverse is determined in accordance with the specified electrolysis parameters (current density, NaCl concentration, hydrodynamic conditions, etc.). Carrying out the electrolysis of such solutions under the indicated conditions makes it possible to significantly (up to 10 times) reduce the chlorate content in the target solutions of sodium hypochlorite, that is, it makes it possible to obtain more pure NaClO solutions.

#### Acknowledgements

This work was supported by National Research Foundation of Ukraine [grant number 0123U102758] and by the Max Planck Society represented by the Max Planck Institute for Chemistry under the programme «The EIRENE Max Planck-Ukraine Cooperation & Mobility Grant» (Research Project «Complex disinfection systems based on high-purity active chlorine/oxygen compounds for the prevention and treatment of infectious diseases»).

## REFERENCES

1. *A review of chlorine evolution mechanism on dimensionally stable anode (DSA)* / Kim J., Kim C., Kim S., Yoon J. // *Korean Chem. Eng. Res.* – 2015. – Vol.53. – No. 5. – P.531-539.
2. *Cornell A., Hakansson B., Lindbergh G.* Ruthenium based DSA in chlorate electrolysis - critical anode potential and reaction kinetics // *Electrochim. Acta.* – 2003. – Vol.48. – P.473-481.
3. *Adams B., Tian M., Chen A.* Design and electrochemical study of SnO<sub>2</sub>-based mixed oxide electrodes // *Electrochim. Acta.* – 2009. – Vol.54. – P.1491-1498.
4. *Active Ti/SnO<sub>2</sub> anodes for pollutants oxidation prepared using chemical vapor deposition* / Yao P., Chen X., Wu H., Wang D. // *Surf. Coat. Technol.* – 2008. – Vol.202. – No. 16. – P.3850-3855.
5. *Pavlovic M.G., Dekanski A.* On the use of platinized and activated titanium anodes in some electrodeposition processes // *J. Solid State Electrochem.* – 1997. – Vol.1. – P.208-214.
6. *Girenko D., Shmychkova O., Velichenko A.* Electrooxidation of chloride ions on Ti/Pt anodes // *Voprosy Khimii i Khimicheskoi Tekhnologii.* – 2019. – No. 6. – P.39-46.
7. *On the electrolysis of dilute chloride solutions: Influence of the electrode material on Faradaic efficiency for active chlorine, chlorate and perchlorate* / Neodo S., Rosestolato D., Ferro S., De Battisti A. // *Electrochim. Acta.* – 2012. – Vol.80. – P.282-291.
8. *Girenko D., Shmychkova O., Velichenko A.* Electrolysis of sodium chloride solutions on Ti/Pt anodes under current reversal conditions // *Voprosy Khimii i Khimicheskoi Tekhnologii.* – 2020. – No. 2. – P.36-43.
9. *Girenko D., Velichenko A., Shmychkova O.* Electrolysis of NaCl solutions in flow systems // *J. Chem. Technol.* – 2021. – Vol.29. – No. 1. – P.31-41.
10. *Acute inhalation toxicity of aerosolized electrochemically generated solution of sodium hypochlorite* / Murashevych B., Girenko D., Maslak H., et al. // *Inhal. Toxicol.* – 2022. – Vol.34. – No. 1-2. – P.1-13.
11. *Virucidal properties of new multifunctional fibrous N-halamine-immobilized styrene-divinylbenzene copolymers* / Murashevych B., Stepanyki D., Toropin V., et al. // *J. Bioact. Compat. Polym.* – 2022. – Vol.37. – No. 6. – P.453-468.
12. *Girenko D.V., Gyrenko A.A., Nikolenko N.V.* Potentiometric determination of chlorate impurities in hypochlorite solutions // *Int. J. Anal. Chem.* – 2019. – Vol.2019. – Art. No. 2360420.
13. *Girenko D., Shmychkova O., Velichenko A.* Influence of Ti/Pt electrodes history on its electrochemical properties during electrolysis of NaCl // *Voprosy Khimii i Khimicheskoi Tekhnologii.* – 2020. – No. 1. – P.18-24.
14. *Occurrence of bromate, chlorite and chlorate in drinking waters disinfected with hypochlorite reagents. Tracing their origins* / Garcia Villanova R.J., Dantas Leite M.V.O., Hierro J.M.H., et. al. // *Sci. Total Environ.* – 2010. – Vol.408. – No. 12. – P.2616-2620.
15. *Electrochemical calcareous deposition in seawater. A review* / Carre C., Zanibellato A., Jeannin M., et. al. // *Environ. Chem. Lett.* – 2020. – Vol.18. – No. 4. – P.1193-1208.

Received 24.07.2023

**СИНТЕЗ РОЗЧИНІВ ГІПОХЛОРИТУ НАТРІЮ В ПРОТОЧНИХ КОМІРКАХ КОАКСІАЛЬНОГО ТИПУ В РЕЖИМІ РЕВЕРСУ СТРУМУ***Д. Гиренко, Б. Мурашевич, О. Веліченко*

Електроди з платинованого титану з поверхневим вмістом платини на рівні 2–3 мг/см<sup>2</sup> можуть бути використані в бездіафрагмових електролізерах проточного та накопичувального типу для електролізу низькоконцентрованих розчинів NaCl з метою одержання чистих розчинів NaClO. Якщо виконувати електроліз 0,15 М розчину NaCl на електродах з платинованого титану в звичайному режимі при густині струму 20–40 мА/см<sup>2</sup>, то поверхня анода переходить в окислений пасивний стан. В цьому випадку вихід за струмом гіпохлориту не перевищує 40%, а вихід за струмом хлорату становить понад 20%. При виконанні нетривалого електролізу на попередньо відновленій поверхні платинованого титану вихід за струмом гіпохлориту досягає 90% при практично повній відсутності накопичення хлорату. Виконання тривалого електролізу низькоконцентрованих розчинів NaCl в режимі періодичної зміни полярності дозволяє суттєво (до 10 разів) знизити вміст хлорату в одержуваних розчинах натрій гіпохлориту. Найбільш перспективним є синтез розчинів натрій гіпохлориту в електрохімічних реакторах проточного типу, що складаються з декількох послідовно з'єднаних електрохімічних модулів з нерозділеним електродним простором в режимі періодичного реверсу струму. Електролізер із двох послідовно з'єднаних модулів у режимі без реверсу струму дозволяє одержувати розчин, що містить 500 мг/л натрій гіпохлориту та 130 мг/л натрій хлорату. Виконання електролізу в режимі реверсу струму кожні 30 с знижує вміст натрій хлорату до 25 мг/л, що дозволяє одержувати високоякісні розчини NaClO.

**Ключові слова:** платинований титан, проточна комірка, натрій гіпохлорит, реверсивний електроліз, електрокаталіз.

## SYNTHESIS OF SODIUM HYPOCHLORITE SOLUTIONS IN COAXIAL FLOW CELLS IN CURRENT REVERSE MODE

D. Girenko <sup>a,\*</sup>, B. Murashevych <sup>b</sup>, A. Velichenko <sup>a</sup>

<sup>a</sup> Ukrainian State University of Chemical Technology, Dnipro, Ukraine

<sup>b</sup> Dnipro State Medical University, Dnipro, Ukraine

\* e-mail: [dvgir1970@gmail.com](mailto:dvgir1970@gmail.com)

Electrodes made of platinized titanium with a surface platinum content of 2–3 mg/cm<sup>2</sup> can be used in non-diaphragm flow- and accumulative-type electrolyzers for the electrolysis of low-concentrated NaCl solutions in order to obtain pure NaClO solutions. If electrolysis of 0.15 M NaCl solution is carried out on platinized titanium electrodes in the usual mode at current densities of 20–40 mA/cm<sup>2</sup>, then the anode surface passes into an oxidized passive state. In this case, the current efficiency of hypochlorite does not exceed 40%, and the current efficiency of chlorate is more than 20%. During a short electrolysis on a preliminarily reduced surface of platinized titanium, the current efficiency of hypochlorite reaches 90% with almost no accumulation of chlorate. Carrying out the long-term electrolysis of low-concentrated NaCl solutions in the regime of periodic polarity reverse makes it possible to significantly (up to 10 times) reduce the content of chlorate in the resulting sodium hypochlorite solutions. The most promising is the synthesis of sodium hypochlorite solutions in flow-type electrochemical reactors consisting of several series-connected electrochemical modules with an undivided electrode space in the mode of periodic current reverse. The electrolyzer of two series-connected cells in the mode without current reverse allows obtaining a solution that contains 500 mg/L of sodium hypochlorite and 130 mg/L of sodium chlorate. Carrying out the electrolysis in the reverse current mode every 30 s reduces the content of sodium chlorate to 25 mg/L, which makes it possible to produce high-purity NaClO solutions.

**Keywords:** platinized titanium; flow cell; sodium hypochlorite; reverse polarity electrolysis; electrocatalysis.

### REFERENCES

- Kim J, Kim C, Kim S, Yoon J. A review of chlorine evolution mechanism on dimensionally stable anode (DSAR). *Korean Chem Eng Res.* 2015; 53(5): 531-539. doi: 10.9713/kcer.2015.53.5.531.
- Cornell A, Hakansson B, Lindbergh G. Ruthenium based DSAR in chlorate electrolysis—critical anode potential and reaction kinetics. *Electrochim Acta.* 2003; 48: 473-481. doi: 10.1016/s0013-4686(02)00679-5.
- Adams B, Tian M, Chen A. Design and electrochemical study of SnO<sub>2</sub>-based mixed oxide electrodes. *Electrochim Acta.* 2009; 54: 1491-1498. doi: 10.1016/j.electacta.2008.09.034.
- Yao P, Chen X, Wu H, Wang D. Active Ti/SnO<sub>2</sub> anodes for pollutants oxidation prepared using chemical vapor deposition. *Surf Coat Technol.* 2008; 202: 3850-3855. doi: 10.1016/j.surfcoat.2008.01.026.
- Pavlovic MG, Dekanski A. On the use of platinized and activated titanium anodes in some electrodeposition processes. *J Solid State Electrochem.* 1997; 1: 208-214. doi: 10.1007/s100080050050.
- Girenko D, Shmychkova O, Velichenko A. Electrooxidation of chloride-ions on Ti/Pt anodes. *Voprosy Khimii i Khimicheskoi Tekhnologii.* 2019; (6): 39-46. doi: 10.32434/0321-4095-2019-127-6-39-46.
- Neodo S, Rosestolato D, Ferro S, De Battisti A. On the electrolysis of dilute chloride solutions: influence of the electrode material on Faradaic efficiency for active chlorine, chlorate and perchlorate. *Electrochim Acta.* 2012; 80: 282-291. doi: 10.1016/j.electacta.2012.07.017.
- Girenko D, Shmychkova O, Velichenko A. Electrolysis of sodium chloride solutions on Ti/Pt anodes under current reversal conditions. *Voprosy Khimii i Khimicheskoi Tekhnologii.* 2020; (2): 36-43. doi: 10.32434/0321-4095-2020-129-2-36-43.
- Girenko D, Velichenko A, Shmychkova O. Electrolysis of NaCl solutions in flow systems. *J Chem Technol.* 2021; 29(1): 31-41. doi: 10.15421/082111.
- Murashevych B, Girenko D, Maslak H, Stepanskyi D, Abramova O, Netronina O, et al. Acute inhalation toxicity of aerosolized electrochemically generated solution of sodium hypochlorite. *Inhal Toxicol.* 2022; 34(1-2): 1-13. doi: 10.1080/08958378.2021.2013348.
- Murashevych B, Stepanskyi D, Toropin V, Mironenko A, Maslak H, Burmistrov K, et al. Virucidal properties of new multifunctional fibrous N-halamine-immobilized styrene-divinylbenzene copolymers. *J Bioact Compat Polym.* 2022; 37(6): 453-468. doi: 10.1177/08839115221121852.
- Girenko DV, Gyrenko AA, Nikolenko NV. Potentiometric determination of chlorate impurities in hypochlorite solutions. *Int J Anal Chem.* 2019; 2019: 2360420. doi: 10.1155/2019/2360420.
- Girenko D, Shmychkova O, Velichenko A. Influence of Ti/Pt electrodes history on its electrochemical properties during electrolysis of NaCl. *Voprosy Khimii i Khimicheskoi Tekhnologii.* 2020; (1): 18-24. doi: 10.32434/0321-4095-2019-128-1-18-24.
- Garcia-Villanova RJ, Oliveira Dantas Leite MV, Hernandez Hierro JM, de Castro Alfageme S, Garcia Hernandez C. Occurrence of bromate, chlorite and chlorate in drinking waters disinfected with hypochlorite reagents. Tracing their origins. *Sci Total Environ.* 2010; 408: 2616-2620. doi: 10.1016/j.scitotenv.2010.03.011.
- Carre C, Zanibellato A, Jeannin M, Sabot R, Gunkel-Grillon P, Serres A. Electrochemical calcareous deposition in seawater. A review. *Environ Chem Lett.* 2020; 18: 1193-1208. doi: 10.1007/s10311-020-01002-z.