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INFLUENCE OF CATHODE MATERIAL ON THE ELECTROCHEMICAL SYNTHESIS OF SODIUM HYPOCHLORITE IN COAXIAL FLOW CELLS

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The features of synthesis of sodium hypochlorite solutions in membraneless flow electrolyzers are mainly determined by the electrolyzer design, electrolysis parameters, and electrode material. In most models, titanium is traditionally used for the cathode, while other materials have not been sufficiently studied in this role. This article discusses alternative cathode materials, such as titanium Grade 2 pre-treated in different ways, various types of platinized titanium, palladium-plated titanium, and stainless steel. A comparative analysis of their effect on the efficiency of the electrolysis process and the quality of the resulting solutions is performed. It is shown that smooth titanium Grade 2 is the optimal cathode material for preparing low-concentration (up to 1500 mg/L) sodium hypochlorite solutions in many respects. An increase in the specific surface area of this material reduces the current efficiency of hypochlorite. However, when using titanium, the electrolysis process is the most energy-intensive. To reduce electricity consumption by 20–25%, it is advisable to use cathodes made of platinized titanium. Heat treatment of platinized titanium under air atmosphere additionally leads to an increase in the integral current efficiency of sodium hypochlorite from 65 to 70% and a slight increase in the energy efficiency of synthesis. The cathode material has practically no effect on the sodium chlorate impurity content, and all obtained solutions have sufficiently high purity for medical applications.

Keywords: sodium hypochlorite, electrolysis, cathode materials, flow electrolyzer, coaxial electrochemical cell.

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Introduction

Flow membraneless electrolyzers are widely used to synthesize low-concentration (up to 0.8%) sodium hypochlorite (NaClO) solutions. Titanium anodes with a catalytic coating based on ruthenium and iridium dioxides are the most common in such devices. The cathode material in almost all industrially produced models is titanium. Such electrolyzers are relatively cheap and simple in design, and they are actively used at water treatment stations, in swimming pools, as well as for medical and veterinary purposes.

Sodium chlorate ($NaClO_3$) is always present in NaClO solutions as an undesirable impurity. Its formation is caused by both anodic processes during synthesis [1,2] and the presence of impurities in the initial reagents, which can act as catalysts for the decomposition of hypochlorite ion (OCl^-) by the chlorate mechanism [3]. By changing the electrolyzer design, the anode material and the electrolysis conditions (NaCl concentration, reagent purity, electrolyte feed rate, electrode and volume current densities, temperature, etc.), it is possible to obtain

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NaClO solutions with specified parameters, including high-purity solutions suitable for medical and veterinary use, in which the $NaClO_3$ content does not exceed 10 mg/L [4].

The main disadvantage of NaClO synthesis in membraneless electrolyzers is the partial loss of active chlorine due to its reduction at the cathode (parasitic cathodic reactions) [5]. In practice, first of all, electrolysis is carried out in specific electrolyzer in various modes (the NaCl concentration, the current strength, the volumetric feed rate of the initial solution are being varied), and the composition of the resulting solutions is determined. Then the dependence of the current efficiency (CE) of sodium hypochlorite and sodium chlorate is calculated and analyzed, and the optimal electrolysis parameters are found at which the CE(NaClO) is maximum and the CE($NaClO_3$) is minimum. It should be noted that the CEs obtained in this case are integral and, basically, are the difference between the CE of the formation of the oxygen-containing form of chlorine at the anode and the CE of its reduction at the cathode. However, insufficient attention has been paid to the effect of the cathode material and its surface condition on the rate of reduction of NaClO and $NaClO_3$. The cathode material should have high corrosion resistance in Cl^-- and OCl^--containing solutions, be non-toxic for humans and animals, and, if possible, be inexpensive. There are a fairly limited number of materials that meet these requirements. The most suitable are titanium, platinized or palladium-plated titanium, and stainless steel, such as AISI 321 or AISI 304. Other classic cathode materials cannot be used for these purposes. For example, metallic nickel has low corrosion resistance, and in the absence of cathodic polarization is quickly oxidized by OCl^- to form products close to NiOOH [6].

This article examines the influence of the cathode material and its preliminary treatment on the regularities of the synthesis of high-purity low-concentration isotonic NaClO solutions in coaxial flow cells.

Materials and methods

All chemicals were purchased from Sigma-Aldrich (ALSI, Kyiv, Ukraine). Bidistilled water with an electrolytic conductivity of 1.5 μS/cm was used for the preparation of solutions. The acidity of the solutions was 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 25^0C. All electrode potentials were measured using a Luggin capillary and are given in the work versus the saturated silver chloride reference electrode.

To study the influence of the cathode material on the regularities of NaClO synthesis, coaxial flow cells with a rod central anode with the outer diameter of 8 mm (area of 50 cm^2) and an outer tubular cathode with the inner diameter of 14 mm (area of 80 cm^2) were manufactured. The electrodes were mounted in two fluoroplastic heads equipped with inlet and outlet fittings for the electrolyte flow [7]. The anode was made of a titanium Grade 2 rod coated with the electrocatalytic coating based on mixed oxides of tin and ruthenium (Ti/SnO_2-RuO_2) applied by the pyrolytic method [8]. For the experiment, four types of materials for tubular cathodes ∅16×1.0 mm were used: stainless steel AISI 321 (SSt), titanium Grade 2, platinized titanium (Ti/Pt) and palladium-plated titanium (Ti/Pd). The process of platinizing the inner surface of a tubular titanium cathode was described in our work [7]. The palladium plating of the cathode was carried out in a similar manner from an electrolyte of the following composition: 5 g/L $PdCl_2 \cdot 2H_2O$, 100 g/L Na_2HPO_4, 20 g/L $(NH_4)_2HPO_4$, 3.0 g/L benzoic acid at overall pH 9.0–9.5. The cathode current density during the plating was 4 mA/cm^2 at 60–70^0C.

To fabricate cathodes with increased specific surface area for individual experiments, the titanium tube (Ti(smooth)) was treated in a boiling 6 M HCl solution for 10 minutes (further is designated as Ti (etched)). The Ti/Pt surface in some cases was modified by heat treatment in air environment at 500–530^0C for 2 hours in a muffle furnace (further is designated as Ti/Pt(heat-treated)).

During the electrolysis, the initial electrolyte was fed into the flow cells using the BT 100-2J peristaltic pump (Baoding Longer Precision Pump Co., Ltd). The electrodes were polarized using the Matrix MPS-3605LP DC source.

The study of the electrode surface morphology was carried out using the Tescan Vega 3 LMU scanning electron microscope (SEM).

The concentrations of NaClO and $NaClO_3$ in working solutions was determined by iodometric titration [9]. The integral CEs (%) were calculated using equations (1) and (2):

$$CE(NaClO) = \frac{2 \cdot F \cdot w \cdot C(NaClO)}{74.5 \cdot n \cdot I} 100\% , \quad (1)$$

$$CE(NaClO_3) = \frac{6 \cdot F \cdot w \cdot C(NaClO_3)}{106.5 \cdot n \cdot I} 100\% , \quad (2)$$

where $C(NaClO)$, $C(NaClO_3)$ are the concentration of sodium hypochlorite and sodium chlorate in the resulting solutions, g/L; w is the volumetric flow rate of the initial NaCl solution to the cell, L/h; *n* is the number of series-connected electrochemical cells; *F*=26.8 A·h is the Faraday constant; and *I* is the electrolysis current, A.

Results and discussion

To establish the influence of the cathode material on the patterns of OCl^- reduction, voltammetric measurements were carried out. The voltammograms obtained on electrode materials that can potentially be used as cathodes in the synthesis of NaClO solutions are shown in Fig. 1. An electrolyte with a composition and pH close to that used in medicine (8.0 g/L NaCl and 1.0 g/L NaClO) was chosen as the working solution.

As seen, the cathode material has a significant effect on the overvoltage of hypochlorite ion reduction. Thus, , a noticeable increase in current corresponding to ClO^- reduction is observed at +0.4 V, −0.4 V, and −0.9 V on platinum, steel, and titanium, respectively. With a further shift of polarization to the cathode region, a plateau of the limiting current of hypochlorite ion reduction, which has a diffusion nature, is observed on the voltammograms for all electrodes [1]. For four electrodes Ti/Pt, Ti/Pd, SSt, Ti(etched), the value of the limiting current is practically the same and is, under the given hydrodynamic conditions of the experiment, −10 mA/cm^2, which indicates their similar active specific surface. On the Ti(smooth) electrode the limiting current is lower than on the surface of Ti(etched) (Fig. 1, curves 1 and 2). This is due to the difference in the morphology and, consequently, in the specific surface of these electrodes, as evidenced by the SEM data (Fig. 2). The surface of etched titanium is more developed, which causes a higher value of the limiting current. For Ti/Pt and Ti/Pt(heat-treated), the limiting currents of hypochlorite reduction also differ (Fig. 1, curves 4 and 5). The SEM images of the surface of the initial and heat-treated platinized titanium with a surface platinum content of 2.2 mg/cm^2 are shown in Fig. 3. Four Ti/Pt electrodes were cut from one platinized titanium plate for voltammetric measurements and SEM. Two of them were heat-treated. This approach to obtaining samples eliminates the error in the analysis of SEM images and interpretation of the effect of heat treatment on the I vs. E curves. As follows from the SEM images, there are no visual differences in the surface morphology of Ti/Pt and Ti/Pt(heat-treated) (Fig. 3). Thus, the decrease in the limiting current for Ti/Pt(heat-treated) is associated with a decrease in the active surface of the platinum coating, that is, its partial passivation during heat treatment. Similar behavior of heat-treated platinized titanium with respect to cathodic processes has been described previously [10].

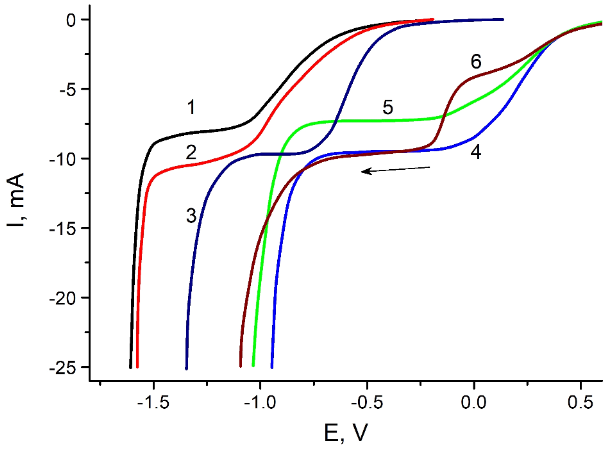


Fig. 1. Voltammograms on stationary electrodes (1 cm^2) in a solution of 8.0 g/L NaCl and 1.0 g/L NaClO (pH 9.4) under stirring (scan rate 5 mV/s): 1 – Ti(smooth); 2 – Ti(etched); 3 – SSt; 4 – Ti/Pt; 5 – Ti/Pt(heat-treated); 6 – Ti/Pd

Based on the analysis of partial curves of hydrogen evolution and hypochlorite ion reduction on platinum under galvanostatic conditions of NaClO synthesis, it was previously shown [1] that an increase in the cathode current density is realized due to an increase in the rate of hydrogen evolution at a practically constant rate of OCl^- reduction, which occurs in the region of diffusion kinetics at the limiting current. An increase in the cathode current density leads to a decrease in the current efficiency of OCl^- reduction, and, consequently, to a decrease in the losses of NaClO on the cathode. Along with the hydrodynamic conditions of the electrolysis process, which affect the value of the limiting current, the real surface area of the electrode should play a significant role. Consequently, on a cathode with a developed surface, the loss of NaClO will be more significant than on an electrode with a smooth surface.

Thus, the cathode material should not have a significant effect on the undesirable NaClO loss, however, the surface condition will have an effect, which determines the true partial current density of OCl^- reduction. The cathode material should have a significant effect on the energy efficiency of sodium hypochlorite synthesis.

For preparing high-purity NaClO solutions, flow electrolyzers based on electrochemical cell modules with coaxial electrode arrangement are promising. The advantages of the coaxial cell design are uniform distribution of the electrolyte flow along the electrode surfaces, equal flow rate in any section of the electrode chamber, the absence of stagnant zones, and compactness.

In practice, NaClO synthesis is most often carried out on titanium anodes with pyrolytically applied electrocatalysts based on ruthenium and iridium oxides [11,12]. Note that it is technologically more convenient to apply the electrocatalytic coating to the outer surface of a tube or rod, especially when using pyrolytic method. Applying a uniform and compact pyrolytic coating to the inner surface of a tubular electrode is a rather complex technological task. In this regard, the central electrode usually acts as an anode, and the outer cylindrical electrode of the cell is a cathode with an internal working surface. With such a mutual arrangement of the electrodes, the cathode can be made of a titanium or steel pipe. The inner surface of titanium tubular cathodes can be coated with Pt or Pd via electroplating.

To study the effect of the cathode material and its surface condition on the synthesis patterns of low-concentration NaClO solutions, an electrolyzer was assembled consisting of three series-connected coaxial flow cells. The cells used a central Ti/SnO_2-RuO_2 anode, and six types of cathodes: Ti(smooth) (Fig. 2a), Ti(etched) (Fig. 2b), Ti/Pt and Ti/Pt(heat-

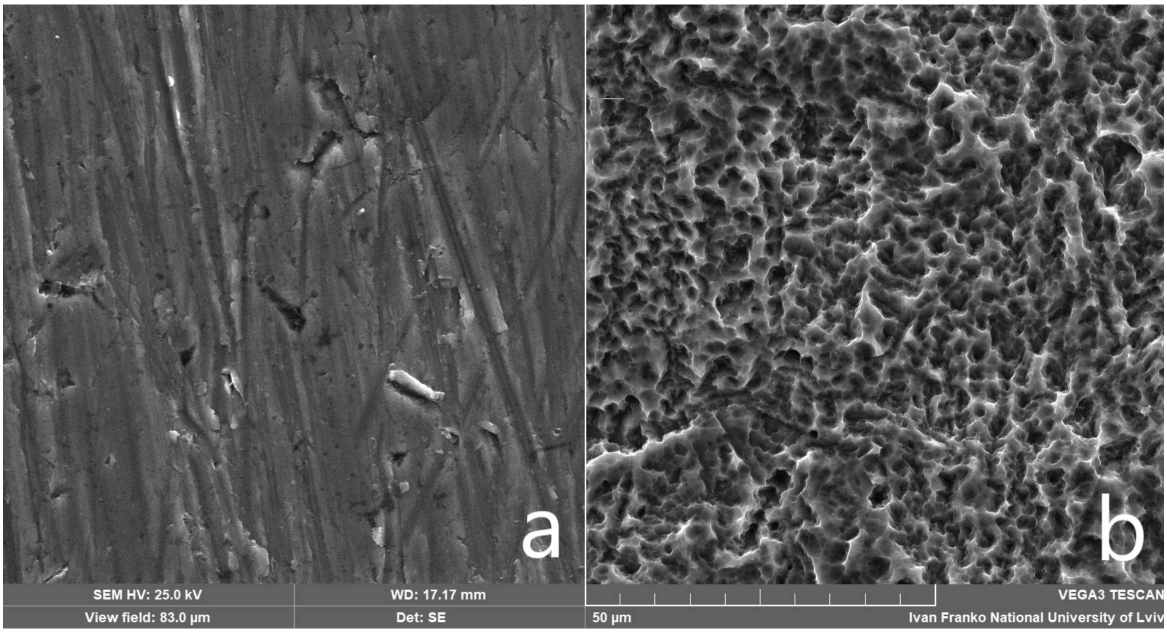


Fig. 2. SEM images of titanium surface: (a) smooth; (b) etched in 6 M HCl

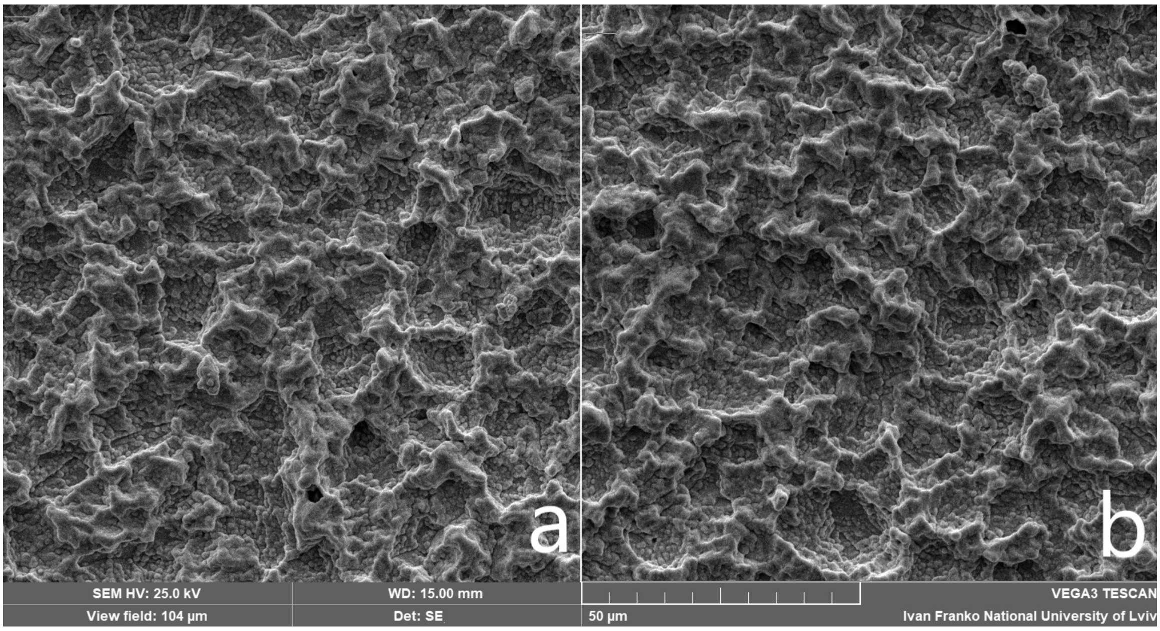


Fig. 3. SEM images of Ti/Pt surface: (a) initial; (b) heat-treated

treated) (Fig. 3), Ti/Pd, and SST. The electrolyte 9 g/L NaCl was fed into the cell using a peristaltic pump at a volumetric flow rate of 6 L/h. Samples of solutions for analysis were taken after the 1st, 2nd and 3rd cells after electrolysis of 3 liters of the initial solution, when the electrolyzer was guaranteed to reach a steady-state electrolysis mode.

The main characteristics of electrolysis processes carried out using different cathode materials in electrolyzers composed of 1, 2 and 3 series-connected coaxial flow-type cells with an electrolysis current of 2.5 A are given in Table 1.

As follows from Table 1, when using Ti(etched), Ti/Pt, Ti/Pd and SSt cathodes, no significant difference in the integral current efficiencies of NaClO and $NaClO_3$ in the resulting solutions was found. In the case of cathodes made of smooth titanium and heat-treated platinized titanium, higher current efficiencies of NaClO were obtained. These data are in agreement with the voltammetry (Fig. 1). In the case of Ti(smooth), a higher true cathode current density is realized compared to the etched surface. Heat-treated platinized titanium, compared to non-heat-treated one, has a smaller proportion of the active surface on which the OCl^- reduction is realized. Thus, from the point of view of reducing NaClO losses on the cathode, it is advisable to make the cathode from a titanium tube with, preferably, a polished inner surface, or from heat-treated platinized titanium.

At comparable CE(NaClO), the main influence of the electrode material is the energy efficiency of sodium hypochlorite synthesis due to the polarization of the cathode at a given electrolysis current. At a current of 2.5 A (in each flow cell, the anode current density is 50 mA/cm^2, and the cathode is 30 mA/cm^2), the maximum voltage (4.07–4.08 V) on one cell is observed when using a smooth titanium anode, and the minimum voltage (3.22–3.23 V) is observed in the case of using non-heat-treated platinized titanium. It should be noted that as the current increases, this difference in voltages on cells with different cathodes decreases due to the growing contribution of ohmic losses in the gas-filled electrolyte. At a current of 2.5 A and when using a Ti/Pt(heat-treated) cathode, the maximum energy efficiency of NaClO synthesis was observed, which is no more than 3.4·kW·h/kg, and when using a Ti cathode, this value is higher than 4.5 kWh/kg.

It is obvious that from the point of view of material cost the most advantageous is a cathode made of stainless steel tube. However, the use of a steel cathode is advisable for continuous electrolysis. If the electrolyzer operates in a periodic mode, there is a high probability of developing pitting corrosion of the reduced surface in chloride-hypochlorite solutions after removing the cathode polarization [13,14]. In this case, the corrosion products, which are catalysts for the NaClO decomposition, enter the final solutions, which significantly reduces their purity and shortens their shelf life.

The data in Table 1 also show that the cathode material does not significantly affect the chlorate

Table 1

Effect of cathode material on the parameters of NaClO synthesis in a flow membraneless electrolyzer

Cathode material	Number of cells	CE(NaClO), %	CE($NaClO_3$), %	Voltage on one cell, V	Energy efficiency, W·h/kg
Ti(smooth)	1	73.4	1.56	4.080	4048
	2	68.4	1.57	4.068	4297
	3	65.0	1.58	4.071	4506
Ti(etched)	1	70.5	1.56	4.055	4136
	2	65.9	1.56	4.045	4423
	3	62.4	1.56	4.047	4667
Ti/Pt	1	69.5	1.56	3.225	3338
	2	66.7	1.56	3.220	3478
	3	64.5	1.56	3.215	3592
Ti/Pt(heat-treated)	1	73.7	1.57	3.290	3213
	2	71.3	1.57	3.301	3324
	3	69.7	1.58	3.281	3398
Ti/Pd	1	70.5	2.07	3.284	3349
	2	67.4	2.59	3.280	3502
	3	64.1	2.85	3.275	3678
SSt	1	69.0	1.56	3.391	3536
	2	67.4	1.56	3.406	3626
	3	64.3	1.56	3.402	3803

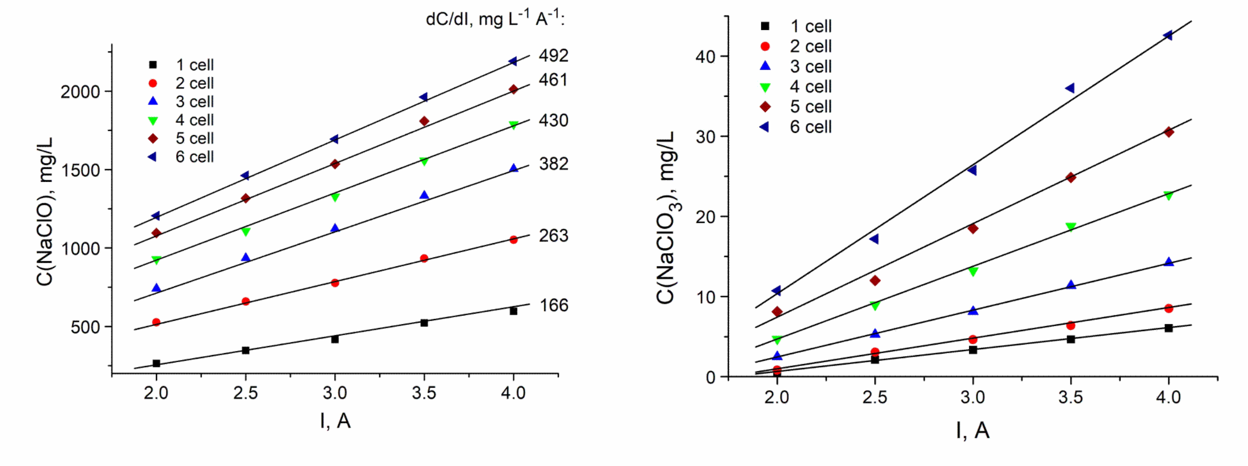
content in the resulting NaClO solutions. Thus, the optimal cathode material for the manufacture of flow electrochemical reactors, especially with a coaxial arrangement of electrodes, is titanium Grade 2 with a smooth working surface. However, if it is necessary to carry out large-scale synthesis of solutions with the highest possible NaClO concentration and minimal electricity costs, it becomes advisable to use heat-treated platinized titanium as a cathode.

To demonstrate the negative effect of cathodic processes on the NaClO synthesis in flow modular systems, electrolysis of the initial 9.0 g/L NaCl solution was carried out in an electrolyzer with a different number of series-connected electrochemical cells (modules) with Ti(smooth) cathodes at a current load of 2.0–4.0 A. The obtained dependences of the compositions of the resulting solutions on the current strength for a different number of series-connected cells are shown in Fig. 4.

As follows from Fig. 4a, adding each additional cell to the electrolyzer at a given current strength does not lead to a directly proportional increase in the NaClO concentration in the resulting solution. Only in the case of two series-connected cells is there a close to 2-fold increase in the NaClO concentration compared to one cell. Adding two more cells leads to an increase in the concentration of NaClO by only 1.4 times. This is due to an increase in the time that the conventional volume of the initial solution remains in the flow system. At the input of each subsequent cell, the NaClO concentration increases, therefore, in each subsequent cell, the current efficiency of OCl^- reduction at the cathode increases with a virtually constant CE of NaClO formation at the anode. In this case, the angular coefficient dC/dI increases with an increase in the number of cells. An increase in the cathode current density decreases the CE of ClO^- reduction, and this effect is more noticeable, the higher the NaClO concentration in the cell, which is consistent with the data of the study [1]. The chlorate concentration increases linearly with increasing current and disproportionately with increasing number of cells. This is due to the anodic oxidation of OCl^- to ClO_3^-: the rate of this transformation increases both with increasing anodic current density and with increasing ClO^- concentration. At the same time, chlorate is not reduced on the cathode at the cathode current densities realized in the electrolyzer. If we plot the dependence of the ClO^-/ClO_3^- current efficiency ratio on the electrolysis current and the number of cells, we can determine the optimal configuration of the electrolyzer and the electrolysis parameters for obtaining NaClO solutions minimally contaminated with $NaClO_3$ impurities (Fig. 5).

From the analysis of the dependences in Figs. 4 and 5, it can be concluded that a series connection of two cells at a current load of 2.0 A is optimal. In this case, it is possible to obtain 9 L/h of a highly pure isotonic solution containing 550 mg/L NaClO with an admixture of no more than 1 mg/L $NaClO_3$. To obtain a solution containing 1.1 g/L NaClO, it is advisable to use three series-connected cells at a current load of 3.0 A. The chlorate concentration in this case will be approximately 8 mg/L, which also makes such a solution suitable for use in veterinary and medicine.

The effect of preliminary treatment of a titanium cathode in boiling HCl using an electrolyzer composed



a b

Fig. 4. Effect of electrolysis current on the concentration of NaClO and $NaClO_3$ for different number of series-connected cells with a smooth titanium cathode

of a different number of series-connected cells under electrolysis current strength of 3.0 A is demonstrated in Fig. 6.

As seen from Fig. 6, the use of a cathode with a developed surface leads to a regular decrease in the NaClO concentration in the resulting solution, and this regularity is more pronounced with an increase in the number of cells. Thus, for three consecutive cells, the NaClO concentration decreases from 1100 to 1000 mg/L. For six cells, the loss of NaClO is even more noticeable: from 1700 to 1500 mg/L (Fig. 6). Increasing the cathode surface leads to a decrease in the CE(NaClO). The use of heat-treated platinized titanium as a cathode allows for a maximum increase in the integral CE(NaClO) in the entire range of currents.

Conclusions

In the process of preparing low-concentration NaClO solutions by electrolysis of 9 g/L NaCl solution in an electrolyzer without a separated electrode space, the reduction of ClO^- ions on the cathode occurs in the region of diffusion kinetics. In this case, NaClO losses are practically independent of the cathode material and can be minimized if the process is carried out at high cathode current densities. In this case, the rate of hydrogen evolution increases with an almost unchanged rate of hypochlorite ion reduction at the limiting current, which leads to a decrease in the CE of the ClO^- reduction reaction. If it is not possible to significantly increase the cathode current density by reducing the cathode area, it is necessary to reduce the cathode specific surface area by polishing its surface or applying a platinum coating. To obtain low-concentration (up to 1500 mg/L NaClO) solutions in membraneless flow electrolyzers, the most optimal cathode material is smooth titanium Grade 2. However, in this case, the energy consumption will be approximately 4.5 kW·h/kg. To reduce electricity consumption by 20–25%, it is advisable to use cathodes made of platinized titanium. Heat treatment of platinized titanium at 500^{0}C in an air environment leads to an increase in the integral CE(NaClO) from 65 to 70% and a slight increase in the energy efficiency of synthesis from 3.6 to 3.4 kW·h/kg.

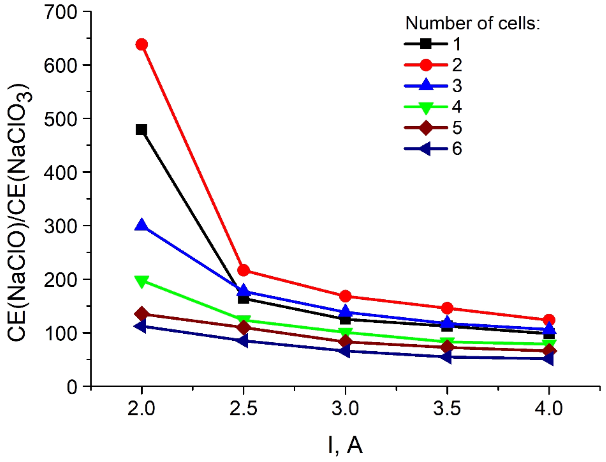


Fig. 5. Effect of electrolysis current on CE(NaClO)/CE($NaClO_3$)

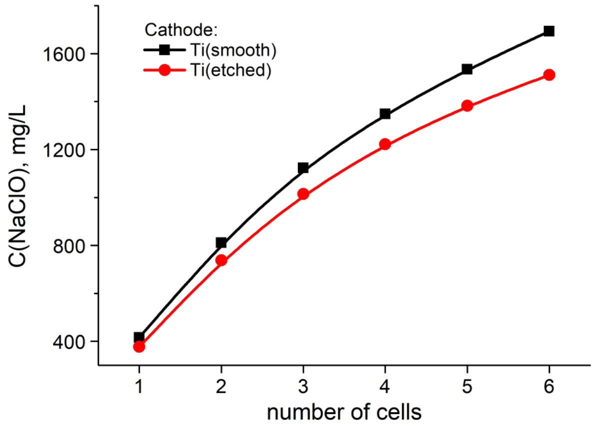


Fig. 6. The effect of the titanium cathode surface condition on the NaClO concentration depending on the number of series-connected cells

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ВПЛИВ МАТЕРІАЛУ КАТОДА НА ЕЛЕКТРОХІМІЧНИЙ СИНТЕЗ ГІПОХЛОРИТУ НАТРІЮ В КОАКСІАЛЬНИХ ПРОТОЧНИХ КОМІРКАХ

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Закономірності синтезу розчинів гіпохлориту натрію в проточних безмембранних електролізерах в основному визначаються конструкцією електролізера, параметрами електролізу та матеріалом електродів. У більшості моделей для виготовлення катода традиційно використовується титан, а інші матеріали в цій ролі вивчені недостатньо. У даній статті розглянуто альтернативні катодні матеріали, а саме титан Grade 2, попередньо оброблений різними способами, різні види платинованого титану, титан з паладієвим покриттям та нержавіюча сталь, а також виконано порівняльний аналіз їх впливу на ефективність процесу електролізу та якість одержуваних розчинів. Показано, що гладкий титан Grade 2 за багатьма параметрами є оптимальним катодним матеріалом для отримання низькоконцентрованих (до 1500 мг/л) розчинів гіпохлориту натрію. Збільшення питомої поверхні цього матеріалу знижує вихід за струмом гіпохлориту. Однак при використанні титану процес електролізу є найбільш енергоємним. Для зниження витрат електроенергії на 20–25% доцільно використовувати катоди з платинованого титану. Термічна обробка платинованого титану в повітряному середовищі додатково призводить до підвищення інтегрального виходу за струмом гіпохлориту натрію з 65 до 70% і незначного підвищення енергоефективності синтезу. Матеріал катода практично не впливає на вміст домішки хлорату натрію, а всі отримані розчини мають високу чистоту, достатню для їх медичного застосування.

Ключові слова: гіпохлорит натрію, електроліз, катодні матеріали, проточний електролізер, коаксіальна електрохімічна комірка.

INFLUENCE OF CATHODE MATERIAL ON THE ELECTROCHEMICAL SYNTHESIS OF SODIUM HYPOCHLORITE IN COAXIAL FLOW CELLS

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The features of synthesis of sodium hypochlorite solutions in membraneless flow electrolyzers are mainly determined by the electrolyzer design, electrolysis parameters, and electrode material. In most models, titanium is traditionally used for the cathode, while other materials have not been sufficiently studied in this role. This article discusses alternative cathode materials, such as titanium Grade 2 pre-treated in different ways, various types of platinized titanium, palladium-plated titanium, and stainless steel. A comparative analysis of their effect on the efficiency of the electrolysis process and the quality of the resulting solutions is performed. It is shown that smooth titanium Grade 2 is the optimal cathode material for preparing low-concentration (up to 1500 mg/L) sodium hypochlorite solutions in many respects. An increase in the specific surface area of this material reduces the current efficiency of hypochlorite. However, when using titanium, the electrolysis process is the most energy-intensive. To reduce electricity consumption by 20–25%, it is advisable to use cathodes made of platinized titanium. Heat treatment of platinized titanium under air atmosphere additionally leads to an increase in the integral current efficiency of sodium hypochlorite from 65 to 70% and a slight increase in the energy efficiency of synthesis. The cathode material has practically no effect on the sodium chlorate impurity content, and all obtained solutions have sufficiently high purity for medical applications.

Keywords: sodium hypochlorite; electrolysis; cathode materials; flow electrolyzer; coaxial electrochemical cell.

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