



UDC 544. 653.2

## ELECTROCHEMICAL CHARACTERISTIC OF Ti/Pt AND Ti/Pt-Pd ELECTRODES

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Received 27 August 2021; accepted 14 October 2021, available online 27 October 2021

### Abstract

The electrochemical characteristics of Ti/Pt and Ti/Pt-Pd electrodes in oxygen evolution reaction and synthesis of sodium hypochlorite from low concentrated NaCl solutions were investigated in this work. It has been shown that the surface content of palladium has almost no effect on the value of the polarization of the electrode. The calculated effective activation energies of oxygen evolution reaction at  $E = 1.6$  V are 38.11 for Ti/Pt(2.0); 35.27 for Ti/Pt(2.0)-Pd(0.2) and 34.88 kJ mol<sup>-1</sup> for heat-treated Ti/Pt(2.0)-Pd(0.2). That is, the palladation of titanium with its subsequent heat treatment reduces the activation energy of oxygen evolution reaction compared to Ti/Pt by 3.33 kJ mol<sup>-1</sup>. Heat treatment leads to a significant reduction of the Tafel slope in the area of oxygen evolution potentials from 232 for Ti/Pt to 86 mV on Ti/Pt-Pd. CE (NaClO) = 84-93% with CE (NaClO<sub>3</sub>) less than 0.5 % were obtained on heat-treated Ti/Pt-Pd anodes in 0.15 M NaCl. Service life of the electrodes involved was 1000 hours without change of activity.

**Keywords:** platinized titanium; palladium; polarization curve; sodium hypochlorite.

## ЕЛЕКТРОХІМІЧНА ХАРАКТЕРИСТИКА Ti/Pt ТА Ti/Pt-Pd ЕЛЕКТРОДІВ

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### Анотація

У цій роботі досліджено електрохімічні характеристики Ti/Pt та Ti/Pt-Pd електродів в реакції виділення кисню та синтезі гіпохлориту натрію з низькоконцентрованих розчинів NaCl. Було показано, що вміст паладію на поверхні практично не впливає на величину поляризації електрода. Розраховані ефективні енергії активації реакції виділення кисню при  $E = 1.6$  В становлять 38,11 для Ti/Pt(2,0); 35,27 для Ti/Pt (2,0)-Pd(0,2) та 34,88 кДж моль<sup>-1</sup> для термообробленого Ti/Pt(2,0)-Pd(0,2). Тобто паладіювання титану з подальшою його термічною обробкою зменшує енергію активації реакції виділення кисню порівняно з Ti/Pt на 3,33 кДж моль<sup>-1</sup>. Термічна обробка приводить до значного зменшення тафелівського нахилу в області потенціалів виділення кисню з 232 для Ti/Pt до 86 мВ на Ti/Pt-Pd. Вихід за струмом натрію гіпохлориту 84-93 % та вихід за струмом натрію хлорату менше 0.5 % було отримано на термооброблених анодах Ti/Pt-Pd в 0.15 М NaCl. Термін служби досліджуваних електродів становив 1000 годин без зміни активності.

**Ключові слова:** платинований титан; паладій; поляризаційна крива; натрію гіпохлорит.

## ЕЛЕКТРОХИМИЧЕСКАЯ ХАРАКТЕРИСТИКА Ti/Pt И Ti/Pt-Pd ЭЛЕКТРОДОВ

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### Аннотация

В этой работе исследованы электрохимические характеристики Ti/Pt и Ti/Pt-Pd электродов в реакции выделения кислорода и синтезе гипохлорита натрия из низкоконцентрированных растворов NaCl. Было показано, что содержание палладия на поверхности практически не влияет на величину поляризации электрода. Рассчитанные эффективные энергии активации реакции выделения кислорода при  $E = 1.6$  В составляют 38.11 для Ti/Pt(2.0) 35.27 для Ti / Pt (2.0) - Pd (0.2) и 34.88 кДж моль<sup>-1</sup> для термообработанного Ti/Pt(2.0)-Pd(0.2). То есть палладирование титана с последующей его термической обработкой уменьшает энергию активации реакции выделения кислорода по сравнению с Ti/Pt на 3.33 кДж моль<sup>-1</sup>. Термическая обработка приводит к значительному уменьшению тафелевского наклона в области потенциалов выделения кислорода с 232 для Ti/Pt до 86 мВ на Ti/Pt-Pd. Выход по току гипохлорита натрия 84-93 % и выход по току натрия хлората менее 0.5 % был получен на термообработанных анодах Ti/Pt-Pd в 0,15 М NaCl. Срок службы исследуемых электродов составлял 1000 часов без изменения активности.

**Ключевые слова:** платинированный титан; палладий; поляризационная кривая; натрия гипохлорит.

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doi: 10.15421/jchemtech.v29i3.239282

## Introduction

The creation of electrode materials with the required physical and mechanical properties has recognized as an important task in theoretical and applied electrochemistry [1]. Electrode materials traditionally used in electrolysis processes and chemical sources of electrical energy, as well as for supercapacitors, must be chemically and electrochemically stable in corrosive media, have good electrical conductivity, a developed reaction surface and selectivity [2]. Composite materials based on titanium oxides and platinum group metals are widely used as catalysts [3; 4], photo- and electrocatalysts [5-7], as well as in the electrochemical processes of the synthesis of strong oxidants [8], the destruction of organic and inorganic substances [9], wastewater treatment [10; 11], the active layer of dimensionally stable anodes for electroplating and hydrometallurgy [12]. There are various methods of obtaining materials of this type, for example, sol-gel technology, plasma-chemical, chemical deposition from solutions in the presence of reductants, etc. [13]. In this case, direct or combined electrochemical methods are recognized as one of the most promising, which, due to the ease of implementation and the possibility of smoothly changing the technological parameters of the processes, allow one to control the composition and properties of composites over a wide range [14].

It should be noted that there are no universal anode materials suitable for use in any type of system. This is due to significant differences both in the composition of the solutions and in the requirements for dimensionally stable anodes [15]. So, for example, if high selectivity and electrocatalytic activity to the target process is required in electrosynthesis processes, then in electroplating the oxidation rates of electrolyte components should be minimized, and it is preferable to have oxygen evolution from water as the main reaction. Unfortunately, at the moment there is no general strategy for the creation and selection of anode materials, therefore, for each specific process, such a problem is solved using an individual approach.

Palladium is one of the most affordable and demanded platinum group metals. Being a universal catalyst and possessing high anticorrosive properties, palladium is widely used, and it is used in the form of a compact metal, blacks, nanopowders, alloying additives, and galvanic deposition [16]. The unique properties of galvanic palladium deposits predetermined the

high interest in electrochemical studies of this metal.

For the development of the technology of low-temperature fuel cells, for example, it is necessary both to search for new convenient methods for the synthesis of catalysts and to comprehensively study the kinetics and mechanism of electrochemical reactions occurring on them. Materials exhibiting catalytic activity to the oxidation of the simplest carbon-containing compounds are of particular interest for such technologies [17]. In this respect, composites containing platinum and/or palladium and oxides of d-elements such as ruthenium, tungsten, molybdenum, and titanium are promising. Having in mind the above mentioned we investigated the electrochemical characteristics of Ti/Pt and Ti/Pt-Pd electrodes in this work.

## Experimental and Methods

All chemicals were analytical reagent grade. Platinized titanium electrodes were obtained by the original method, which includes the stages of preliminary preparation of the titanium substrate [18], followed by electroplating a platinum coating.

Next, a thin layer of platinum was electrodeposited (the platinum content in the active layer was  $8 \text{ mg cm}^{-2}$ ) from the alkaline electrolyte containing  $\text{K}_2\text{PtCl}_6$ ;  $\text{NaNO}_2$  and  $\text{NH}_3$  solution [18], with cathode current densities equal to  $12 \text{ mA cm}^{-2}$  and temperature  $70 \text{ }^\circ\text{C}$ . The resulting electrodes were then chemically oxidized in a mixture (1 : 1) of concentrated  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  and thermally treated in air in a tube furnace at temperatures of  $500 \text{ }^\circ\text{C}$  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  $450 \text{ }^\circ\text{C}$  the mechanism of interaction of platinum with  $\text{TiO}_2$  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 [19]. Herein all the values in parentheses near the element indicate its content on the surface.

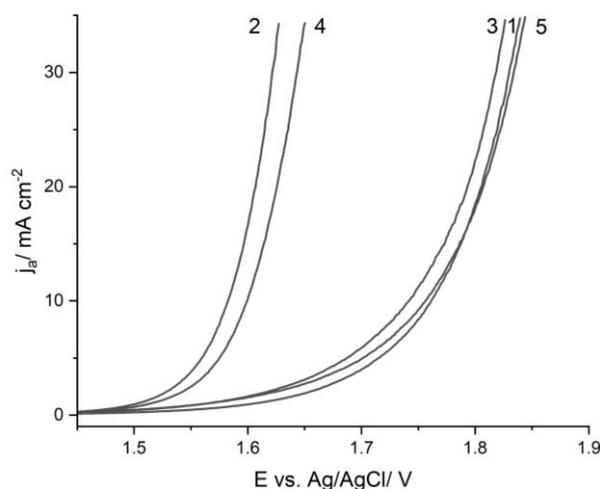
Electrochemical processes were investigated on a Pt rotating disk electrode (Pt-RDE,  $0.19 \text{ cm}^2$ ) by steady-state voltammetry, chronoampero-

metry. Before each experiment, the electrode surface was treated with a freshly prepared mixture (1 : 1) of concentrated  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  [14; 18]. 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  $\pm 3$  V with a scan velocity from 0.02 to 500  $\text{mV/s}$  [20]. The permissible error given in measuring 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.

## Results and Discussion

**Voltammetric measurement.** Quasi steady-state  $j$ - $E$  curves in 1 M  $\text{HClO}_4$  were obtained at the heat-treated Ti/Pt and Ti/Pt-Pd electrodes (Fig. 1). For comparison, a voltammogram was recorded on heat-treated Ti/Pt electrode with 2  $\text{mg cm}^{-2}$  Pt on the surface. The minimum polarization of 1.606 V at 20  $\text{mA cm}^{-2}$  was observed on Ti/Pt-Pd(0.5). 20 mV higher polarization was recorded at the anode Ti/Pt-Pd(0.2) (1.626 V). However, heat treatment of initial electrodes at 700–740 °C led to a significant increase in polarization: 200 mV for Ti/Pt-Pd (0.5) and 167 mV for Ti/Pt-Pd(0.2), respectively. These curves practically coincide with the curve on Ti/Pt(2.0), which indicates the

absence of Pd or its oxides on these electrodes, i.e. there is a sublimation of palladium when Ti/Pt-Pd electrodes are heat treated at 700 °C.



**Fig. 1. Quasi steady-state  $j$ - $E$  curves obtained at various electrodes in 1M  $\text{HClO}_4$ , where 1 - Ti/Pt(2.0); 2 - Ti/Pt(2.0)-Pd(0.5); 4 - Ti/Pt(2.0)-Pd(0.2) heat treated at 500°C; 3 - Ti/Pt(2.0)-Pd(0.5); 5 - Ti/Pt(2.0)-Pd(0.2) heat treated at 700 °C.  $v = 5 \text{ mV s}^{-1}$**

A series of cumulative electrolyses in 0.15 M NaCl was performed at an anode current density of 40  $\text{mA cm}^{-2}$  for the presented anodes. As follows from the experimental data (Table 1), heat-treated at 500–530 °C palladium-modified anodes revealed close to 90 % current efficiency (CE) of hypochlorite and less than 2 % current efficiency of chlorate. On Ti/Pt, as expected,  $\text{CE}(\text{NaClO}) = 40 \%$  with  $\text{CE}(\text{NaClO}_3) = 18 \%$ . On heat-treated at 700 °C anodes Ti/Pt(2.0)-Pd(0.2) and Ti/Pt(2.0)-Pd(0.5) current efficiencies of NaClO and NaClO<sub>3</sub> are close to those on Ti/Pt. This also confirms the assumption of sublimation of the palladium coating under conditions of prolonged heat treatment at 700 °C.

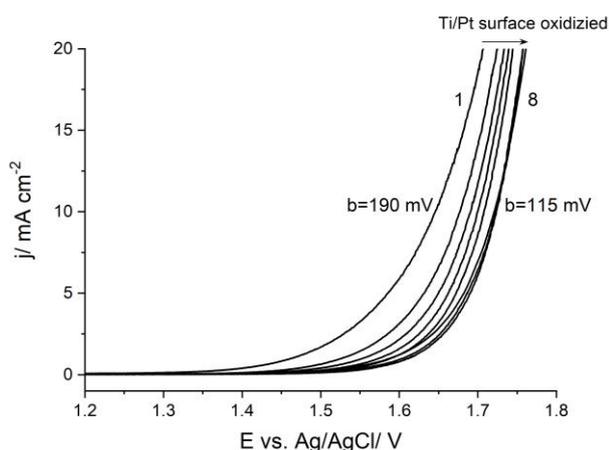
**Table 1**  
**Current efficiencies of NaClO and NaClO<sub>3</sub> at various anodes under conditions of cumulative electrolysis of 0.15 M NaCl solution\***

Material	CE(NaClO)/ %	CE(NaClO <sub>3</sub> )/%
Ti/Pt(2.0) heat treated at 500 °C	41	18
Ti/Pt(2.0)-Pd(0.5) heat treated at 500 °C	91	0.5
Ti/Pt(2.0)-Pd(0.2) heat treated at 500 °C	89	1.0
Ti/Pt(2.0)-Pd(0.5) heat treated at 700 °C	45	11
Ti/Pt(2.0)-Pd(0.2) heat treated at 700 °C	41	15
Ti/Pd(2.0) heat treated at 500 °C	91	0.7
Ti/Pd(2.0) heat treated at 700 °C	86	1.1

\*Cathode: Ti.  $j_a = 40 \text{ mA cm}^{-2}$ . Undivided cell. The duration of electrolysis is 60 minutes.

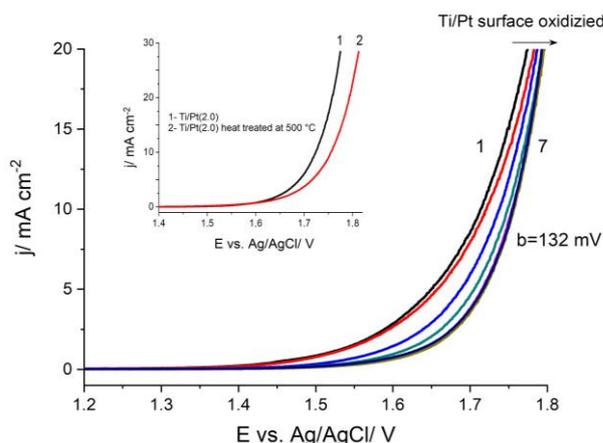
A series of anodes was made on a standardized Ti/Pt substrate (2.0) in order to understand the reasons for the catalytic action of the palladium-based coating. Palladium was applied from the phosphate palladium electrolyte on substrates of 2×1 and 1×1 cm, which were cut from a solid plate of platinum titanium with a surface platinum content of 2.0 mg cm<sup>-2</sup>. The electrochemical properties of the obtained Ti/Pt-Pd anodes were compared with each other, as well as with the anode without heat treatment Ti/Pt (2.0) and heat treated at 530 °C.

When registering several successive quasi steady-state potentiodynamic j-E curves at the Ti/Pt(2.0) anode, a shift of each subsequent curve to the region of higher potentials is observed, which is probably due to the oxidation of the surface phase oxide PtO<sub>x</sub> to stoichiometric oxide PtO<sub>2</sub> [21]. At the same time there is a slight decrease in the Tafel slope. Reproducibility is observed after registration of the 6<sup>th</sup> curve. The surface turns into a completely oxidized state (Fig. 2).



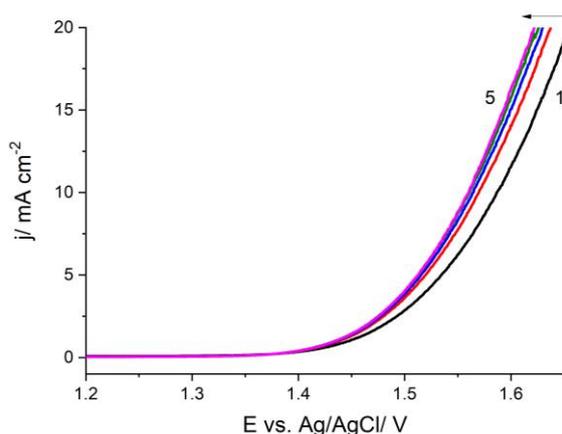
**Fig. 2.** Quasi steady-state j-E curves obtained at Ti/Pt(2.0) without heat treatment in 1M HClO<sub>4</sub>.  $\nu = 5 \text{ mV s}^{-1}$ . The numbering of the curves corresponds to the sequence of their registration

The surface of Ti/Pt (2.0) heat treated at 500 °C is also gradually oxidized in the process of sequential recording of quasi steady-state j-E curves. At the same time, higher polarization values are observed on the oxidized surface of the heat-treated anode in comparison with the non-heat-treated one (Fig. 3): the potential increases by 35 mV at 20 mA cm<sup>-2</sup>.



**Fig. 3.** Quasi steady-state j-E curves obtained at Ti/Pt(2.0) heat treated at 500 °C in 1M HClO<sub>4</sub>.  $\nu = 5 \text{ mV s}^{-1}$ . The numbering of the curves corresponds to the sequence of their registration. Inset: Quasi steady-state j-E curves obtained at Ti/Pt(2.0) without and heat treated at 500 °C in 1M HClO<sub>4</sub>.  $\nu = 5 \text{ mV s}^{-1}$ .

On all palladated samples in the process of anodic polarization the opposite regularity is observed - at consecutive registration of quasi steady-state j-E curves polarization of electrodes slightly decreases as it is shown in Fig. 4 for Ti/Pt(2.0)-Pd(0.2) and in Fig. 5 for heat treated Ti/Pt(2.0)Pd(0.2). At the same time on heat-treated electrodes already after registration of the second curve good reproducibility is observed. The remaining heat-treated anodes Ti/Pt(2.0)-Pd(0.5) are also characterized by high reproducibility of current-voltage curves, and, consequently, and rapid achievement of a quasi steady state of the surface.



**Fig. 4.** Quasi steady-state j-E curves obtained at Ti/Pt(2.0)-Pd(0.2) without heat treatment in 1M HClO<sub>4</sub>.  $\nu = 5 \text{ mV s}^{-1}$ . The numbering of the curves corresponds to the sequence of their registration

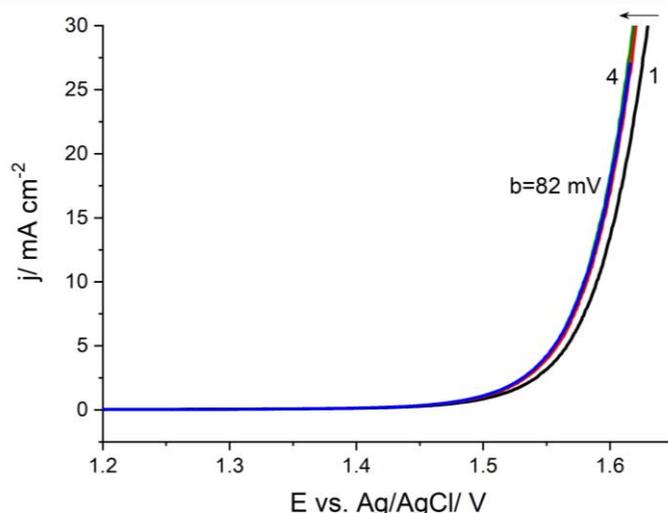


Fig. 5. Quasi steady-state  $j$ - $E$  curves obtained at Ti/Pt(2.0)-Pd(0.2) heat treated at 500 °C in 1M HClO<sub>4</sub>.  $\nu = 5 \text{ mV s}^{-1}$ . The numbering of the curves corresponds to the sequence of their registration

Fig. 6 shows reproducible polarization curves on Ti/Pt(2.0)-Pd and heat-treated Ti/Pt(2.0)-Pd anodes in 1 M HClO<sub>4</sub>. For comparison, in Fig. 6 additionally presented curves for Ti/Pt(2.0) and heat treated Ti/Pt(2.0). In comparison with heat-treated Ti/Pt(2.0) on heat-treated Ti/Pt(2.0)-Pd

anodes at 20 mA cm<sup>-2</sup> the decrease in polarization is about 190 mV. On all heat-treated electrodes Ti/Pt(2.0)-Pd with different palladium content, a decrease in the Tafel slope on the polarization curves is observed.

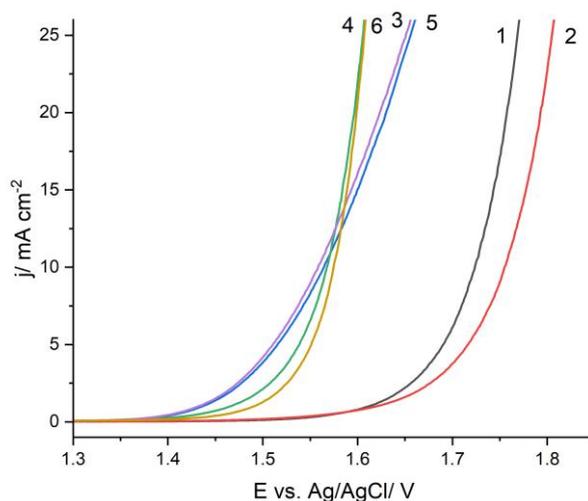


Fig. 6. Quasi steady-state  $j$ - $E$  curves obtained at various electrodes in 1M HClO<sub>4</sub>, where 1 - Ti/Pt(2.0); 3 - Ti/Pt(2.0)-Pd(0.2); 5 - Ti/Pt(2.0)-Pd(0.5) without heat treatment; 2 - Ti/Pt(2.0); 4 - Ti/Pt(2.0)-Pd(0.2); 6 - Ti/Pt(2.0)-Pd(0.5) heat treated at 500 °C;  $\nu = 5 \text{ mV s}^{-1}$

The surface content of palladium has almost no effect on the value of the polarization of the electrode: an increase in the surface content of Pd (0.2 and 0.5 mg cm<sup>-2</sup>) at a current density above 15 mA cm<sup>-2</sup> leads to a decrease in polarization by 3–5 mV. Thus on voltammograms in the semi-logarithmic coordinates received on not heat-treated Ti/Pt(2.0)-Pd electrodes one can allocate two linear sites with slopes of 105 mV in the low polarizations area and 232 mV in the high one. Such a significant increase in the slope of the

curve at potentials above 1.55 V is most likely caused by blocking the surface with oxygen, due to its slow desorption from the surface. Heat treatment leads to a significant reduction of the Tafel slope in the area of oxygen evolution potentials from 232 to 86 mV (Fig. 7). Probably the heat-treated surface becomes more homogeneous, it is easier to desorb oxygen or the mechanism changes – the rate of transfer of the first electron increases [22].

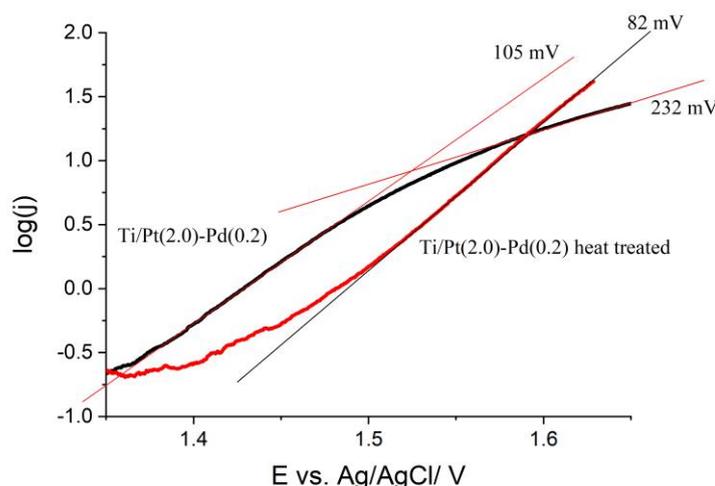


Fig. 7. Quasi steady-state  $j$ - $E$  curves obtained at Ti/Pt(2.0)-Pd(0.2) in 1M HClO<sub>4</sub> built in semi-logarithmic scale.  $\nu = 5 \text{ mV s}^{-1}$ .

Value of the Tafel slope in 1 M HClO<sub>4</sub> does not depend on temperature for heat-treated Ti/Pt-Pd anodes. Fig. 8 shows a series of polarization curves on the anodes involved at different temperatures. As one can see from Fig. 8, heat-treated Ti/Pt(2.0)-Pd(0.2) at currents of 10, 20 and 40 mA cm<sup>-2</sup> is characterized by a constant temperature polarization coefficient of 18 mV K<sup>-1</sup>. For the anode without heat treatment with increasing current density, the temperature polarization coefficient increases from 35 to 58 mV K<sup>-1</sup>. As shown above, the magnitude of the polarization and the Tafel slope of the oxygen evolution reaction (OER) affect the current efficiency of NaClO and its dependence on the anode current density. Thus, one should expect that the composition of the obtained solutions of sodium hypochlorite on the heat-treated anodes Ti/Pt-Pd will be less dependent on the temperature of the electrolysis and the anode current density.

The calculated effective activation energies of OER at  $E = 1.6 \text{ V}$  are 38.11 for Ti/Pt(2.0); 35.27 for Ti/Pt(2.0)-Pd(0.2) and 34.88 kJ mol<sup>-1</sup> for heat-treated Ti/Pt(2.0)-Pd(0.2). That is, the palladation of titanium with its subsequent heat treatment reduces the activation energy of OER compared to Ti/Pt by 3.33 kJ mol<sup>-1</sup>.

The kinetics of the oxygen evolution reaction at the metal anodes Ti/Pt, Ti/Pt-Pd in background indifferent solutions is rather weakly dependent on pH. Thus, the polarization of OER in 1 M HClO<sub>4</sub> (pH 0.2) and in 1 M NaClO<sub>4</sub> (pH 9.0) differs at  $j = 20 \text{ mA cm}^{-2}$  by 45–55 mV.

A series of voltammetric measurements was performed in a low-concentrated 0.15 M NaCl solution in order to explain the nature of the high catalytic activity and selectivity of palladium for ClO<sup>-</sup> synthesis. In previous works [23–25], the property of Ti/Pt anodes to be passivated in NaCl solutions during anodic polarization was demonstrated. In chloride-containing solutions, in contrast to Ti/Pt, the palladium surface is not passivated, and the polarization curves are well reproduced. The surface content of Pd and the state of the surface (heat treatment) has no significant effect on the course of polarization curves. The Tafel slope for these polarization dependences is 40–44 mV. In comparison with the oxidized heat-treated Ti/Pt (2.0), the reduction of polarization on heat-treated anodes containing Pd is 550 mV. The Ti/Pd(2.0) anode has a minimum polarization of 0.15 M NaCl.

*Chronopotentiometric measurements.* In 1 M HClO<sub>4</sub>, the current-free potential on the reduced Ti/Pt surface has almost the same value of 0.65–0.70 V (vs. Ag/AgCl). There is a monotonic increase in potential, when polarizing the current meander +5 mA cm<sup>-2</sup> for 40 s on Ti/Pt(2.0); and after disabling the polarization, the potential drops rapidly to 1.2–1.3 V, then slowly drifts to the value of 1.1–1.2 V, and then to the initial potential of 0.65–0.70 V. The potential of 1.2–1.3 V after anodic polarization in 1 M HClO<sub>4</sub> is due to the presence on the surface of adsorbed oxygen [21]. The shift of the currentless potential after anodic polarization to 0.65–0.70 V is due to the slow desorption of oxygen from the anode surface.

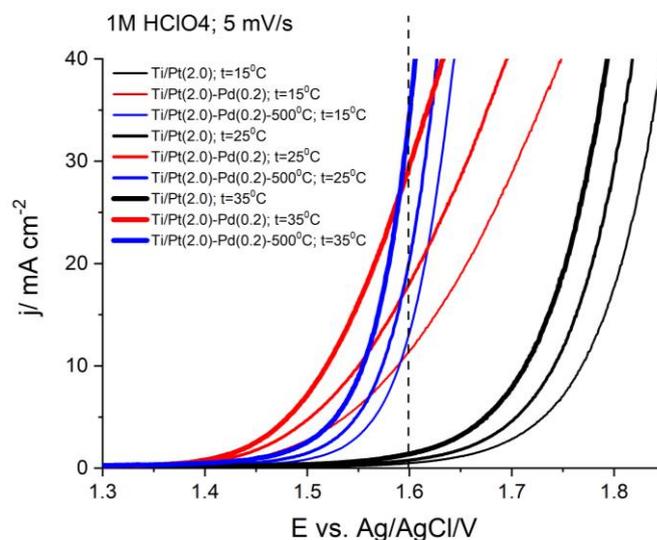


Fig. 8. Quasi steady-state  $j$ - $E$  curves obtained at various electrodes in 1M  $\text{HClO}_4$  at 15, 25 and 35 °C.  $\nu = 5 \text{ mV s}^{-1}$

If the surface of Ti/Pt(2.0) is reduced, and during the cycle of anodic polarization it does not have time to go into a completely oxidized state (passivation), then after turning off the current potential for 200–400 s relaxes to its original currentless value. If the surface is almost completely oxidized (the potential during polarization current becomes greater than +1.4 V), then after turning off the current current-free potential is set at 1.1–1.2 V and then very slowly in 10–15 minutes shifts to 0.65–0.70 V (Fig. 9). Thus, on the oxidized surface of platinum, the desorption of oxygen is much slower than on the reduced.

At the palladated electrode Ti/Pt(2.0)-Pd(0.5) at polarization the quasi stationary potential is established almost instantly. After disabling the polarization, the potential drifts fairly quickly for 100–200 s to its original currentless value. Thus, the desorption of oxygen proceeds approximately twice as fast as for platinum, from the palladated surface of the anode. If the anode Ti/Pt(2.0)-Pd(0.5) is heat treated, the rate of relaxation and, consequently, the desorption of oxygen from the surface decreases. In any case, the desorption of oxygen from the surface of Ti/Pt-Pd occurs several times (almost 10 times) faster than from the surface of Ti/Pt.

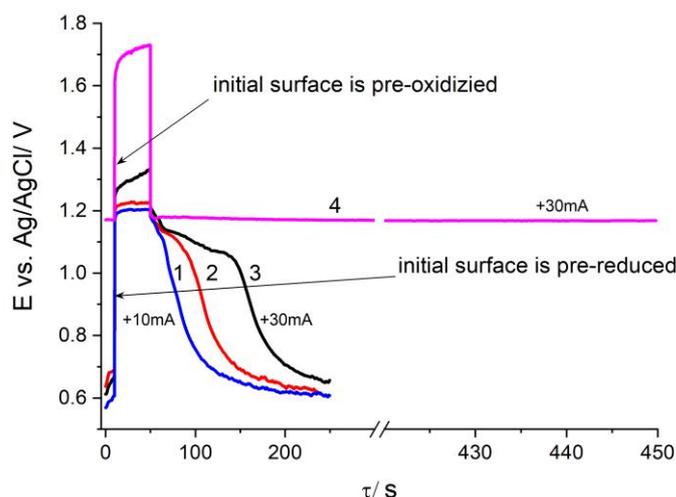


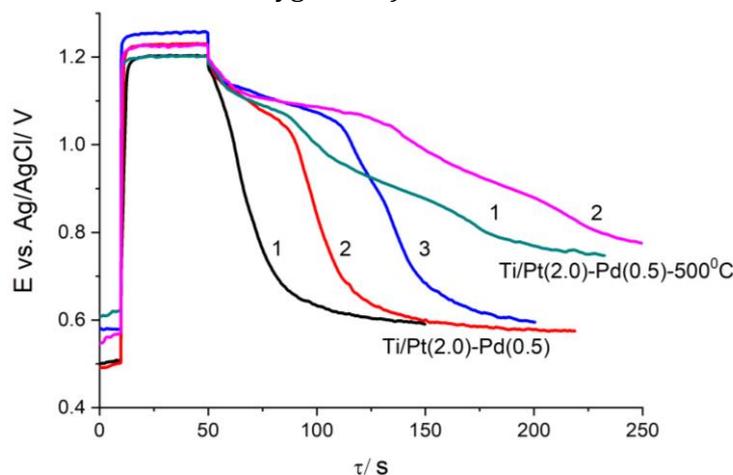
Fig. 9. Chronopotentiogram in 0.15 M NaCl on Ti/Pt(2.0) electrode during polarization by the anode current meander during 40 s. The electrode surface is pre-reduced;  $j_a$ ,  $\text{mA cm}^{-2}$ : 10 (curve 1), 20 (curve 2) and 30 (curve 3). The surface is pre-oxidized,  $j_a = 30 \text{ mA cm}^{-2}$  - curve 4

As shown earlier [23–25], unusually high current efficiencies of sodium hypochlorite at the level of 85 % were recorded on the reduced Ti/Pt surface during short-term electrolysis of 0.15 M

NaCl. On palladated Ti/Pt-Pd, the NaClO current efficiencies are close to 90 %. One can find the correlation between the rate of desorption of oxygen from the surface of the anode and the

current efficiency of NaClO. On the reduced surface Ti/Pt (2.0), Ti/Pt(2.0)-Pd and heat treated Ti/Pt(2.0)-Pd after short-term anodic polarization there is a comparable rate of relaxation of the potential to the original current-free value, i.e. there is a close rate of oxygen

desorption. Moreover, on the heat-treated surface the rate of oxygen desorption is slightly lower than on the non-heat-treated anode (Fig. 10). On the oxidized (passive) Ti/Pt surface the rate of oxygen desorption is very low (see Fig. 9, curve 4).



**Fig.10. Chronopotentiograms in 0.15 M NaCl on Ti/Pt(2.0)-Pd (0.5) without and heat treated at 500 °C electrodes with polarization of the anode current meander during 40 s.  $j_a$ , mA cm<sup>-2</sup>: 10 (curve 1), 20 (curve 2) and 30 (curve 3)**

It should be noted that Ti/Pt-Pd anodes without heat treatment in chloride solutions have no practical interest. Under conditions of anodic polarization in the presence of Cl<sup>-</sup> palladium dissolves from the electrode surface, the electrolyte gradually takes on a characteristic yellowish color. Heat treatment of Ti/Pt-Pd allows one to obtain a dimensionally stable anode for the synthesis of sodium hypochlorite.

To minimize the consumption of precious metals while maintaining satisfactory parameters of catalytic activity, selectivity and service life, a series of electrodes Ti/Pd and Ti/Pt-Pd with different content of Pt and Pd was prepared. To

determine the current efficiencies of hypochlorite and chlorate on the obtained anodes, a series of accumulative electrolyses were performed in 0.15 M NaCl in a cell without a diaphragm. The data obtained are given in Table 2, which also compares the test results of Ti/Pt, OIRTA and OITA anodes. Excluding the proportion of hypochlorite that is reduced at the cathode and the desorption of hydrochloric acid from the surface of the solution, the current efficiency of NaClO at all anodes containing palladium at a current density of 40 mA cm<sup>-2</sup> is approximately 91 % at CE (NaClO<sub>3</sub>) less than 1% .

Table 2

**Current efficiencies of NaClO and NaClO<sub>3</sub> at various anodes under conditions of cumulative electrolysis of 0.15 M NaCl solution**

Anode	$j_a$ / mA cm <sup>-2</sup>	CE(NaClO) / %	CE(NaClO <sub>3</sub> ) / %
Ti/Pt(2.0)	40	37	20
Ti/Pt(2.0)-500 °C	40	41	18
Ti/IrO <sub>x</sub> (OITA)	40	78	<0.1
Ti/RuO <sub>x</sub> -IrO <sub>x</sub> (OIPTA)	40	70	<0.1
Ti/Pd(2.0)-500 °C	20	92	0.5
Ti/Pd(2.0)-500 °C	40	91	0.7
Ti/Pd(2.0)-500 °C	80	82	2.9
Ti/Pd(2.0)-700 °C	80	86	1.1
Ti/Pt(2.0)-Pd(0.2)-500 °C	20	89	0.5
Ti/Pt(2.0)-Pd(0.2)-500 °C	40	89	1.0
Ti/Pt(2.0)-Pd(0.2)-500 °C	40	92	0.3
Ti/Pt(2.0)-Pd(0.2)-500 °C	80	84	1.3
Ti/Pt(2.0)-Pd(0.5)-500 °C	20	93	0.5
Ti/Pt(2.0)-Pd(0.5)-500 °C	40	91	0.5
Ti/Pt(2.0)-Pd(0.5)-500 °C	80	91	1.0
Ti/Pt(2.0)-Pd(0.2)-700 °C	40	41	15
Ti/Pt(2.0)-Pd(0.5)-700 °C	40	45	11

Heat-treated Ti/Pd anodes with a Pd surface content of 2.0 mg cm<sup>-2</sup> showed high catalytic activity and selectivity for the hypochlorite synthesis reaction. Despite the high catalytic properties of the anodes Ti/Pd(2.0), the service life of all such anodes in 0.15 M NaCl was not more than 40 hours. The coating begins to dissolve. Thus, heat-treated Ti/Pd has no practical application for the synthesis of sodium hypochlorite.

As concerns the Ti/Pt-Pd anodes, the most optimal is the heat treatment temperature of 500-530 °C. At 700 °C palladium is sublimated from the electrode surface, as shown above. In this case, coating is actually converted into an anode made of heat-treated Ti/Pt. In confirmation of the absence of palladium on the surface, at this anode were recorded current efficiencies of hypochlorite and chlorate close to the anodes Ti/Pt (see Table 2).

CE (NaClO) = 84–93 % with CE (NaClO<sub>3</sub>) less than 0.5% were obtained on heat-treated Ti/Pt-Pd anodes in 0.15 M NaCl. Changing the platinum content in the sublayer up to 3.0 mg cm<sup>-2</sup> does not affect the catalytic activity and selectivity of the electrode. Changing the surface content of palladium from 0.2 to 2.0 mg cm<sup>-2</sup> also does not lead to a significant change in the catalytic properties of the anode. Control samples of anodes in 0.15 M NaCl at a current density of 40 mA cm<sup>-2</sup> for 1000 hours of operation did not change their activity.

## Conclusions

It has been revealed, that the surface content of palladium has almost no effect on the value of the polarization of the electrode: an increase in the surface content of Pd (0.2 and 0.5 mg cm<sup>-2</sup>) at a current density above 15 mA cm<sup>-2</sup> leads to a decrease in polarization by 3-5 mV. One can allocate two linear sites with slopes of 105 mV in the low polarizations area and 232 mV in the high one on voltammograms in the semi-logarithmic coordinates received on not heat-treated Ti/Pt(2.0)-Pd electrodes. Such a significant increase in the slope of the curve at potentials above 1.55 V caused by blocking the surface with oxygen, due to its slow desorption from the surface. Heat treatment leads to a significant reduction of the Tafel slope in the area of oxygen evolution potentials from 232 to 86 mV. This phenomenon can be described either by the heat-treated surface homogeneity, or by facilitating of oxygen desorption because of increasing of the first electron transfer rate in OER. Heat-treated Ti/Pd anodes with a Pd surface content of 2.0 mg

cm<sup>-2</sup> are characterized by high catalytic activity and selectivity for the hypochlorite synthesis reaction. Despite the high catalytic properties of the anodes Ti/Pd(2.0), the service life of all such anodes in 0.15 M NaCl was not more than 40 hours. CE (NaClO) = 84–93% with CE (NaClO<sub>3</sub>) less than 0.5% were obtained on heat-treated Ti/Pt-Pd anodes in 0.15 M NaCl. Changing the platinum content in the sublayer up to 3.0 mg cm<sup>-2</sup> does not affect the catalytic activity and selectivity of the electrode. Changing the surface content of palladium from 0.2 to 2.0 mg cm<sup>-2</sup> also does not lead to a significant change in the catalytic properties of the anode. Control samples of these anodes in 0.15 M NaCl at a current density of 40 mA cm<sup>-2</sup> for 1000 hours of operation did not change their activity.

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