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ELECTROOXIDATION OF CHLORIDE-IONS ON Ti/Pt ANODES

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The main features of the processes occurring during the oxidation of chloride ions on the platinum surface were investigated as well as the catalytic activity and selectivity of platinum in the anodic synthesis of hypochlorite were determined. It was assumed that the oxidation of chloride ions on the platinum surface occurs with the participation of particles like OH_{ads} or O_{ads} , which are active centers on the surface, according to the mechanisms of chlorine evolution described in literature. In addition, it was taken into consideration that polarization at high anodic potentials decreases the degree of surface filling with labile and simultaneously increases the degree of surface filling with inert particles. The obtained results showed that the formation of chlorine and hypochlorite proceeds with the participation of labile oxygen-containing particles. It was shown that the main three parallel processes are observed during the electrolysis of NaCl as follows: (i) the oxidation of Cl⁻ to hypochlorite, (ii) the formation of chlorate, and (iii) the oxygen evolution reaction. On a pre-reduced surface, the current efficiency of hypochlorite reaches 90% and the process proceeds at polarizations lower by 400-450 mV in comparison to process occurred on an oxidized surface. Under these conditions, chlorates are practically not formed. However, the reduced surface is gradually oxidized in the course of electrolysis process. Therefore, the ratio of active sites at which Cl⁻ oxidation occurs is declined. It was established that weakly bounded (labile) particles take part in the formation of hypochlorite. On the passive surface, the oxidation of Cl^- even in 1-2 M NaCl solutions occurs at the limiting current, the value of which is determined by the fraction of active surface centers. Comparison of the values of the limiting currents on the active and passive surfaces allows us to conclude that the ratio of the active centers of the latter does not exceed 5-10%. It was established that the surface of platinum is easily activated during short-term cathodic polarization in the region of hydrogen evolution.

Keywords: platinum, platinized titanium, anode, sodium hypochlorite, electrolysis.

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Introduction

Electrochemical synthesis of high-purity lowconcentrated solutions (0.01-0.10%) of sodium hypochlorite is known to be a challenge with regard to the electrolyzer design, electrode materials and conditions of process [1,2].

Synthesis of sodium hypochlorite solutions can be carried out in electrolyzers with divided and nonseparated interelectrode space. Both methods have their advantages and limitations. The absence of a diaphragm simplifies and reduces the cost of the electrolyzer, however, there is a partial loss of sodium hypochlorite due to its reduction at the cathode, and therefore the maximum possible concentration of the resulting solutions does not exceed 8 g L^{-1} NaClO. The presence of a diaphragm allows

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obtaining solutions with a higher concentration of active chlorine, however, a significant decrease in pH in the anode space and, as a result, the formation of molecular chlorine requires the use of expensive ion-selective membranes or the keeping of pH level of anolyte within 8.0-9.5. General characteristics of the synthesis of high-purity sodium hypochlorite solutions in a diaphragmless electrolyzer were considered in detail in our recent publication [3]. Anode is the main element of any electrolyzer used for the synthesis of sodium hypochlorite solutions. As it is known, anode with an electrocatalytic coating based on mixed ruthenium oxides and titanium oxides has proven itself in the best way for the electrolysis of concentrated solutions of NaCl [4,5]. Anodes with a coating of mixed oxides of titanium, tin and iridium

have proven themselves for the electrolysis of low concentrated solutions of NaCl (less than 30 g L^{-1}) [6,7]. However, these anodes are expensive and labor intensive. The basic way for obtaining such multilayer coatings is the sol-gel method, followed by pyrolysis.

One of the most available dimensionally stable anodes (DSA) is platinized titanium, which can be converted into a composite anode Ti-TiO_v-Pt by thermal treatment. This material has a number of unique electrocatalytic properties [8]. Platinum coating can work at high anodic and cathodic polarizations and has a corrosion resistance in the presence of strong oxidizing agents. However, the current efficiency (CE) of hypochlorite on platinum and platinized titanium usually does not exceed 40-60% during the electrolysis of low-concentrated NaCl solutions. In addition, platinum exhibits a high catalytic activity in the oxidation of hypochlorite to chlorate and perchlorate [9,10], with CE of chlorates more than 10% [3]. One of the ways to increase CE of NaClO is to obtain platinized titanium with a highly developed surface. However, the variation in current density does not have a significant effect on the CE of NaClO [9,11]. At the same time, the data on the CE of hypochlorite on platinum and platinized titanium differ significantly from one paper to another. Most likely, an important role is played not by the specific surface of the catalyst, but also by the surface state of platinum.

In this paper, we consider the main features of the processes occurring during the oxidation of Cl^{-} ions on the platinum surface; we suggest the reasons of shift in the catalytic activity and selectivity of platinum in the anodic synthesis of hypochlorite.

Material and methods

All chemicals were reagent grade. Electrochemical measurements were carried out in 1 M HClO₄ with PGP-550 M potentiostat in a standard temperature-controlled three-electrode cell. All potentials were recorded and reported vs. Ag/AgCl/KCl (sat.). The temperature was $25\pm1^{\circ}$ C.

Platinized Ti was used as an anode. The content of Pt was 2.5 mg per cm², the surface area of anode was 4 cm². The catalytic activity of the obtained anodes in the reaction of sodium hypochlorite synthesis was determined by the electrolysis of 1.0 M NaCl solution in undivided cell with a Ti cathode (its surface area was 1 cm²). The volume of electrolyte was 300 cm³. Mixing was carried out with a magnetic stirrer, the rotation velocity of which was proportional to the supplied voltage.

The concentration of NaClO and NaClO₃ in the resulting solutions was determined by iodometric titration [12]. The standard deviation in determination

of the concentration does not exceed $\pm 3 \text{ mg } \text{L}^{-1}$ and $\pm 2 \text{ mg } \text{L}^{-1}$ for sodium hypochlorite and sodium chlorate, respectively. The standard deviations for CE are ± 1.0 and $\pm 0.5\%$ for hypochlorite and chlorate, respectively.

Results and discussion

On the anodic branch of cyclic voltammogram (CV) recorded for a Ti/Pt sample in 1 M HClO₄, a characteristic current wave is observed for Pt (Fig. 1) due to the formation of phase surface oxides, and there is a reduction peak of these oxides on the cathodic branch. Moreover, the position and shape of this peak depends on the conditions under which the oxides involved were formed (Fig. 1). The curve in the first cycle was recorded on the pre-oxidized surface of platinized titanium; the subsequent curves (2) and (3) were obtained after reducing the surface on the cathodic branch of the curve. It can be seen that the reduction peak of phase oxides of the oxidized surface is shifted to higher electrode potentials. The shift of the peak indicates the formation of thermodynamically more stable surface phase oxides of platinum during the polarization at high anodic potentials.



Fig. 1. CV recorded on Ti/Pt electrode in 1 M HClO₄. υ =50 mV s⁻¹. First cycle was obtained on a pre-oxidized surface. The numbering of curves is explained in text

A current wave appears at potentials higher than 1.2 V when sodium chloride is added to 1 M HClO₄ solution, beginning with 0.2 mM concentration (Fig. 2). Already at 0.01 M NaCl, the wave turns into a wave with a current plateau. The dependence of the wave current (I_p) vs. the concentration is linear. In this case, a current peak appears on the cathodic branch. The potentials of the anodic and cathodic half-waves coincide, which indicates the reversible nature of the intensity of solution stirring, the

current of the anode wave increases, and the height of the cathode peak somewhat decreases. However, even with vigorous stirring of the solution, the cathode peak does not disappear. It should be noted that the electrode surface is covered with a layer of small gas bubbles at low sweep rates without stirring, in the range of anodic wave potentials. There is a characteristic smell of chlorine or hypochlorous acid if the electrode is placed in close proximity to the surface. The presence of a cathode peak and the described dependence of its height on the hydrodynamic conditions of the process indicate the formation of Cl⁻ oxidation products, including chlorine, which are weakly bounded to the surface.



Fig. 2. CV recorded on Ti/Pt in 1 M HClO₄+X mM NaCl, where X is 0 (1); 0.2 (2); 1.0 (3); 2.0 (4); 5.0 (5); 10.0 (6). υ =50 mV s⁻¹. Inset: wave current (I_p) vs. the concentration of NaCl

CV recorded on metallic platinum electrode (Fig. 3) almost completely reproduces that obtained on platinized titanium (see Fig. 2). The main difference is that the cathodic peak corresponded to the reduction of phase oxides is sharper and more symmetrical on the Pt electrode than on Ti/Pt. This peak disappears in the presence of even a minimal concentration of NaCl (0.2 mM) in the electrolyte. As one can see from Fig. 3, the displacement of the potential reverse to the anode region by 100 mV leads to the appearance of an exponential current increase due to the oxygen evolution reaction (OER), however, does not change the area of the cathodic peak. This may indicate, on the one hand, the achievement of a limiting surface filling with chlorinecontaining products before OER, and, on the other hand, the simultaneous OER and Cl- oxidation at various active surface centers. Otherwise, the surface concentration of the bounded chlorine should decrease substantially when oxygen is released and, as a result, the area of the cathodic peak should decrease. One can observe such a decrease, but it is not significant.



Fig. 3. CV recorded on Pt electrode in 1 M $HClO_4+X$ mM NaCl, where X is 0 (1); 0.2 (2); 10.0 (3) (scan range is from -0.2 to 1.4 V); 10.0 (4) (scan range is from -0.2 to 1.5 V). $v=50 \text{ mV s}^{-1}$

We think it is important to note that the surface state has a significant effect on the kinetics of oxidation of chloride ions. As is shown above, the surface of platinum can be both in an oxidized and a reduced state (Fig. 1). Platinum becomes oxidized with anodic polarization, which is accompanied by the oxygen evolution, and it becomes reduced in the process of hydrogen evolution.

In order to get further insight into the anodic processes, steady-state polarization curves were obtained on Ti/Pt electrode in 2 M NaCl in galvanostatic mode (Fig. 4). Curves 1 and 2 are consistently obtained on a strongly oxidized surface after 40 minutes of the electrolysis in 1 M NaCl at $j_a=60 \text{ mA cm}^{-2}$. Further, the electrode was polarized with a $j_c = -10$ mA cm⁻² until reaching a potential of -0.25 V. Curves 3 and 4 were recorded after cathode polarization. As one can see, the electrode polarization decreased by 420 mV. Next, the sample was briefly (during 20 s) polarized with $j_a=30$ mA cm⁻². Curves 5, 6 were obtained after polarization. One can see that a wave appeared in the region of 1.2...1.55 V in these curves. In this potential range, gas release is observed as the growth of small bubbles over the entire electrode surface. There is a characteristic smell of chlorine from the cell. Larger gas bubbles, separately sitting on the surface, appear

at potentials higher than 1.55 V. It should be noted that a similar wave is also observed on curves 1 and 2, however, its current is significantly less. When curves 3 and 4 in the region of the exponential growth of the current are corrected for the wave current, then they should coincide with curves 1 and 2. Similar phenomenon for the Ti/Pt sample was also detected in 1 M NaCl solution. Therefore, one can distinguish three states of the platinum surface: reduced, oxidized, and intermediate. On the reduced surface, Cl⁻ oxidation proceeds with minimal polarization. In this case, potentials are realized, at which neither phase oxides are formed on the surface of metallic platinum nor oxides with weak oxygen-metal bond energy are formed. The exponential current growth observed at potentials higher than 1.55 V on an oxidized surface with formed phase oxides resulted from OER. Here, one can observe a weakly pronounced current wave (Fig. 4, curves 1, 2, 5, and 6).



Fig. 4. Steady-state polarization curves on Ti/Pt in 2 M NaCl. The numbering of curves is explained in text

In order to promote deeper understanding of the nature of current wave in 1.20–1.55 V potential range and the exponential growth of current on the reduced surface of platinized titanium (Fig. 4), a series of potentiodynamic measurements have been carried out. Figure 5 shows the behavior of a Ti/Pt sample in solutions free of NaClO (such processes are characteristic of the initial electrolysis moments). Initially, the sample was polarized at $j_c = -10 \text{ mA cm}^{-2}$ until reaching a potential of -0.25 V. Two reproducible curves 1 and 2 (Fig. 5) were consistently obtained in 1 M NaCl solution, which are characterized by an exponential increase in current in the 1.15-1.25 V potential range. Further, the sample was briefly polarized at $j_a=50$ mA cm⁻² to a potential of 1.5 V and then curve 3 was recorded.

There is a slight shift of the curve in the range of anodic potentials after anodic polarization. The nature of the curve has not changed. Then, the sample was again polarized at $j_a = 50 \text{ mA cm}^{-2}$ to a potential of 1.85 V. A characteristic current wave with a maximum appeared on curve 4 recorded after this. As is shown above, this wave, which always precedes the exponential growth of current if oxygen is released with relatively high overvoltage, is associated with the presence of chloride ions in the solution, even in minimal concentrations (0.2 mM in acidic media). In the following curves 5-7, the maximum current decreases and the subsequent curves reproduce curve 7. Thus, as the curves 4-7are sequentially recorded at a potential sweep rate of 5 mV s^{-1} , the electrode surface is oxidized to the state when the subsequent curves begin to reproduce.



Fig. 5. Potentiodynamic polarization curves recorded on Ti/Pt in 1 M NaCl. The numbering of curves is explained in text. ν =5 mV s⁻¹

On a highly oxidized (passive) surface, potentiodynamic curves were recorded for various speed rate of an electric stirrer (Fig. 6). It should be noted that the curves are well reproduced, for example, when sequentially recording in the direction of increasing, and then reducing the intensity of stirring of the solution. One can see from Fig. 6 that the current of the wave increases with an increase in the intensity of the solution stirring, which indicates its diffusion nature. Taking into account the data cited earlier, it can be confidently stated that this wave is a limiting current wave due to the oxidation of Cl⁻ ions. The reduced surface of platinum during the recording of potentiodynamic curves with a low potential scan rate gradually oxidizes.





in 1 M NaCl at different intensities of stirring. The stirrer rotation speed, rpm: 0 (1); 360 (2); 810 (3); 1700 (4); 2600 (5). ν =5 mV s⁻¹

This phenomenon is showed below on platinized titanium with a low surface content of platinum (0.7 mg cm⁻²). Eleven consistently recorded curves are showed in Fig. 7. On the 4th curve, a wave with a maximum already appears, and by the 10–11th the surface is completely oxidized. Further polarization of the electrode at j_c =-25 mA cm⁻² within 2 minutes reduces the surface to its original state (curve 12).



Fig. 7. Potentiodynamic polarization curves recorded on Ti/Pt with 0.7 mg Pt per cm² in 1 M NaCl solution. The numbering of the curves corresponds to the sequence of their recording. $v=5 \text{ mV s}^{-1}$

To briefly sum up, we observed on the reduced

surface an exponential increase in current at 1.2 V, which is caused by Cl⁻ oxidation processes; the Tafel slope is 64 mV dec $^{-1}$. Further, the curve passes the region of mixed kinetics and falls into the region of diffusion control with a limiting current. At the same time, a gradual oxidation of the surface occurs. In this case, a decrease in the limiting current most likely indicates that the ratio of the active surface suitable for the oxidation reaction of Cl⁻ decreases. Only for the recorded curves 4-11 (Fig. 7), the wave current decreases by a factor of 10, i.e. the active surface is also reduced by an order of magnitude and the surface becomes passivated. At the same time, the nature of the wave remains diffusive. Thus, obtaining coatings with a highly developed surface allows one to increase the concentration of active centers on the passive surface.

We considered several mechanisms for the chlorine evolution with oxygen-containing particles participation described in literature [4,13]:

(i) L.K. Burke and J.F. O'Neill, 1979: O_{ads}+Cl⁻=OCl_{ads}+ē; OCl_{ads}+Cl⁻=Cl₂+O_{ads}+ē;
(ii) R.G. Erenburg, 1984: S-OH₂+⇔S-OH+H⁺; S-OH⇔S-O+H⁺+ē; S-O+Cl⁻→S-OCl+ē; S-OCl+Cl⁻⇔S-O+Cl₂+ē; S-OCl+Cl⁻+H⁺⇔S-OH+Cl₂;
(iii) L.I. Krishtalik and R.G. Erenburg, 1981: H₂O⇔SOH_{ads}+H⁺+ē; SOH_{ads}+Cl⁻→S(HO)Cl+ē;

HOCl+HCl⇔Cl₂+H₂O,

where S means the active center on the surface.

Based on the above mechanisms, we assume that the oxidation of chloride ions on the platinum surface occurs with the participation of particles like OH_{ads} or O_{ads} , which is an active center on the surface, and that polarization at high anodic potentials decreases the degree of surface filling with labile and simultaneously increases the degree of surface filling with inert particles. In this case, the formation of chlorine and hypochlorite should proceed with the participation of labile oxygen-containing particles. The obtained results have confirmed our assumptions.

In order to prove the influence of oxidation state of the platinum surface, a cumulative electrolysis was performed on a Ti/Pt sample as an anode in 1 M NaCl at low anode current densities of 5, 10, and 20 mA cm⁻². Two series of electrolysis were made: the first on the anode with a pre-reduced surface (j_c =-10 mA cm⁻² during 5 min), and the second on

the previously oxidized surface (j_a =+70 mA cm⁻² during 5 min). A higher CE of NaClO and a lower CE of NaClO₃ is observed during accumulative electrolysis at the reduced anode, at all current densities, compared to the similar electrolysis on the previously oxidized anode surface. After electrolysis at 20 mA cm⁻², polarization curves were obtained in 1.0 M NaCl (Fig. 8).



Fig. 8. Potentiodynamic polarization curves recorded on Ti/Pt in 1 M NaCl solution after 60 min of the accumulative electrolysis at $j_a=50$ mA cm⁻² on the pre-reduced (curve 1) and

the pre-oxidized surface (curve 2). $\upsilon=5 \text{ mV s}^{-1}$

The nature of the curves indicates that the initially reduced anode was oxidized during electrolysis, but did not reach the state of the preoxidized surface. In the process of electrolysis, the surface of the anode probably undergoes changes from the initial state depending on the current density, the duration of the electrolysis, the pH and the concentration of the produced hypochlorite. As one can see from the data obtained (Table), the total CE of hypochlorite and chlorate on the reduced surface is almost 95%, and on the oxidized surface it is 85% at $j_a=5$ mA cm⁻².

The current efficiency of NaClO and NaClO₃ after 60 min of the electrolysis in 1.0 M NaCl on Ti/Pt anode

$mA cm^{-2}$	CE on pre-reduced surface, %		CE on pre-oxidizied surface, %	
	NaClO	NaClO ₃	NaClO	NaClO ₃
5	83.40	6.7	71.40	11.6
10	83.75	7.1	77.10	12.8
20	84.70	5.1	74.41	9.2

It is noteworthy that a sufficiently high hypochlorite current efficiency is observed (75-85%)during accumulating electrolysis on platinized titanium in 1 M NaCl in a wide range of current densities (10-80 mA cm⁻²). However, CE of NaClO does not exceed 35-40% in 0.15 M NaCl solution. The process of Cl⁻ oxidation occurs on the extremely oxidized inert surface of platinum in dilute solutions. To stabilize the active centers, palladium in an amount of 0.1 mg cm⁻² was deposited on the surface of Ti/Pt. Palladium and its oxides have a high catalytic activity and selectivity in the hypochlorite synthesis reaction [14]. The accumulative electrolysis on the surface of platinized titanium micromodified with palladium showed that the value of NaClO CE in 0.15 M NaCl was 90% and 81% at $j_a=80$ mA cm⁻² and $j_a=90$ mA cm⁻², respectively; the current efficiency of NaClO₃ was 3 and 5%, respectively. This significant effect makes it possible to apply platinized titanium coatings micromodified with palladium in the electrolysis of low-concentrated

Conclusions

NaCl solutions.

The platinum surface can be in an oxidized (passive) and reduced (active) state. The electrolysis of NaCl solutions over the entire concentration range usually takes place on an oxidized surface. On the reduced surface, the current efficiency of hypochlorite reaches 90% and the process proceeds at polarizations lower by 400–450 mV in comparison to the process occurred on a oxidized surface. Under these conditions, chlorates are practically not formed. However, the reduced surface is gradually oxidized in the course of electrolysis process. In this case, the ratio of active sites at which Cl- oxidation occurs is declined. It has been established that weakly bounded (labile) particles take part in the formation of hypochlorite. On the passive surface, the oxidation of Cl⁻ even in 1-2 M NaCl solutions occurs at the limiting current, the value of which is determined by the fraction of active surface centers. Comparison of the values of the limiting currents on the active and passive surfaces allows us to conclude that the ratio of the active centers of the latter does not exceed 5-10%. However, the surface of platinum is easily activated during short-term cathodic polarization in the region of hydrogen evolution. This feature of platinum and platinized titanium can be used by implementing electrolysis in a pulsed mode or by periodically reversing the polarity of two identical platinized electrodes. It is also possible to preserve active centers by micromodifying the surface, for example, by palladium or iridium.

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ЕЛЕКТРООКИСНЕННЯ ХЛОРИД-ІОНІВ НА Ті/Рt АНОДАХ

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Встановлено основні закономірності процесів, що відбуваються під час окиснення хлорид-іонів на поверхні платини, а також визначені каталітична активність і селективність платини в анодному синтезі натрій гіпохлориту. Передбачалося, що окислення хлорид-іонів на поверхні платини відбувається за участю таких частинок, як OH_{adc} або O_{adc}, які є активними центрами на поверхні, відповідно до механізмів виділення хлору, описаних у літературі; і що поляризація за високих анодних потенціалів зменшує ступінь заповнення поверхні лабільними і одночасно збільшиє стипінь заповнення поверхні інертними частинками. Отримані результати показали, що утворення хлору і натрій гіпохлориту відбувається за участю лабільних оксигеновмісних частинок. Було показано, що в процесі електролізу NaCl реалізуються три основних паралельні процеси: 1) окислення Ĉl - до гіпохлориту, 2) хлорату, 3) реакція виділення кисню. На попередньо відновленій поверхні вихід за струмом гіпохлориту досягає 90%, і процес відбувається за поляризацій нижчих на 400-450 мВ порівняно з процесом, що відбувається на окисленій поверхні. У цих умовах хлорати практично не утворюються. Однак в процесі електролізу відновлена поверхня платини поступово окислюється. У цьому випадку співвідношення активних центрів, на яких відбувається окислення СІ-, зменшується. Встановлено, що в утворенні гіпохлориту беруть участь слабко зв'язані із поверхнею (лабільні) частинки. На пасивній поверхні окислення Cl- навіть в 1-2 М NaCl відбувається за граничного струму, величина якого визначається часткою активних поверхневих центрів. Зіставлення значень граничних струмів на активній і пасивній поверхнях дозволяє зробити висновок, що співвідношення активних центрів останніх не перевищує 5—10%. Встановлено, що поверхня платини легко активується за короткочасної катодної поляризації в області виділення водню.

Ключові слова: платина, платинований титан, анод, натрію гіпохлорит, електроліз.

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The main features of the processes occurring during the oxidation of chloride ions on the platinum surface were investigated as well as the catalytic activity and selectivity of platinum in the anodic synthesis of hypochlorite were determined. It was assumed that the oxidation of chloride ions on the platinum surface occurs with the participation of particles like OH_{ads} or O_{ads} , which are active centers on the surface, according to the mechanisms of chlorine evolution described in literature. In addition, it was taken into consideration that polarization at high anodic potentials decreases the degree of surface filling with labile and simultaneously increases the degree of surface filling with inert particles. The obtained results showed that the formation of chlorine and hypochlorite proceeds with the participation of labile oxygen-containing particles. It was shown that the main three parallel processes are observed during the electrolysis of NaCl as follows: (i) the oxidation of Cl⁻ to hypochlorite. (ii) the formation of chlorate, and (iii) the oxygen evolution reaction. On a pre-reduced surface, the current efficiency of hypochlorite reaches 90% and the process proceeds at polarizations lower by 400-450 mV in comparison to process occurred on an oxidized

surface. Under these conditions, chlorates are practically not formed. However, the reduced surface is gradually oxidized in the course of electrolysis process. Therefore, the ratio of active sites at which $Cl^$ oxidation occurs is declined. It was established that weakly bounded (labile) particles take part in the formation of hypochlorite. On the passive surface, the oxidation of Cl^- even in 1-2 M NaCl solutions occurs at the limiting current, the value of which is determined by the fraction of active surface centers. Comparison of the values of the limiting currents on the active and passive surfaces allows us to conclude that the ratio of the active centers of the latter does not exceed 5-10%. It was established that the surface of platinum is easily activated during short-term cathodic polarization in the region of hydrogen evolution.

Keywords: platinum; platinized titanium; anode; sodium hypochlorite; electrolysis.

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