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VOLTAMETRIC BEHAVIOR OF PLATINIZED TITANIUM ELECTRODES

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Abstract

The method for the combined synthesis of dimensionally stable anodes with an active Ti_xO_y/Pt layer on the metallic titanium substrates is proposed it is based on electrolytical deposition of the thin layer of platinum on the substrate and the further thermal treatment in air, which allows one to control the composition and the properties of the obtained materials. The content of the platinum decreases from the surface to the substrate with an increase in the ratio of metallic titanium and TiO_2. It has been determined that coatings with the content of the platinum of up to 8 mg per cm^{-2} are represented by the titanium which is almost completely coated with the platinum with cracks and cavities. Thermal treatment leads to significant changes in the surface morphology, because the Pt is distributed over the surface and in the bulk due to diffusion and sintering, as well it leads to the increasing of the degree of crystallinity. It has been shown that the semiconductor properties of the composite Ti_xO_y/Pt electrodes on a titanium substrate are caused by the formation of titanium dioxide, which is an n-type semiconductor. It has been established that with the increasing of platinum coating thickness and the temperature of treatment, the potential of flat zones and the number of carriers also increases. Anomalously high values of the slopes of the polarization curves are explained by the presence of a space charge zone in the semiconductor. The data obtained indicate the possibility of using the reduction peak of oxygen-containing platinum compounds on the inversion voltammogram as a correlation parameter for predicting the electrocatalytic activity of the thermally treated Ti/Pt electrodes in the oxygen transfer reactions.

Keywords: platinized titanium; composites; inversion voltammetry; Mott–Schottky approach.

ВОЛЬТАМПЕРОМЕТРИЧНА ПОВЕДІНКА ПЛАТИНОВАНИХ ТИТАНОВИХ ЕЛЕКТРОДІВ

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Анотація

Запропоновано метод комбінованого синтезу малозношуваних анодів із активним шаром Ti_xO_y/Pt на металічних титанових колекторах струму, який полягає в електролітичному осадженні тонкого шару платини на колектор із наступною термічною обробкою на повітрі, що дозволяє контролювати склад і властивості одержуваних матеріалів. Вміст платини зменшується від поверхні до колектора струму зі збільшенням співвідношення металічного титану та TiO_2. Було встановлено, що покриття зі вмістом платини до 8 мг/см^2 являє собою титан, майже повністю вкритий платиною, зі розломами та западинами. Термічна обробка приводить до значних змін морфології поверхні через розподіл Pt на поверхні та в об'ємі внаслідок дифузії та спікання, а також до збільшення ступеня кристалічності. Було показано, що напівпровідникові властивості композитних електродів Ti_xO_y/Pt на титановому колекторі струму обумовлені утворенням діоксиду титану, який являється напівпровідником n-типу. Встановлено, що зі збільшенням товщини платинового покриття та температури обробки потенціал пласких зон і кількість носіїв також збільшуються. Аномально високі значення нахилів поляризаційних кривих пояснюються наявністю зони просторового заряду в напівпровіднику. Отримані дані вказують на можливість використання піку відновлення оксигеновмісних сполук платини на інверсійній вольтамперограмі в якості кореляційного параметра для прогнозування електрокаталітичної активності термічно оброблених електродів Ti/Pt в реакціях із перенесенням оксигену.

Ключові слова: платинований титан; композиційні матеріали; інверсійна вольтамперометрія; графік Мотта-Шоттки.

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ВОЛЬТАМПЕРОМЕТРИЧЕСКОЕ ПОВЕДЕНИЕ ПЛАТИНИРОВАННЫХ ТИТАНОВЫХ ЭЛЕКТРОДОВ

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Аннотация

Предложен метод комбинированного синтеза малоизнашиваемых анодов с активным слоем Ti_xO_y/Pt на металлических титановых подложках, который заключается в электролитическом осаждении тонкого слоя платины на подложку с последующей термической обработкой на воздухе, что позволяет контролировать состав и свойства получаемых материалов. Содержание платины уменьшается от поверхности к подложке с увеличением соотношения металлического титана и TiO_2. Было установлено, что покрытия с содержанием платины до 8 мг/см^2 представляют собой титан, почти полностью покрытый платиной, с разломами и впадинами. Термическая обработка приводит к значительным изменениям морфологии поверхности из-за распределения Pt по поверхности и в объеме вследствие диффузии и спекания, а также к увеличению степени кристалличности. Было показано, что полупроводниковые свойства композитных электродов Ti_xO_y/Pt на титановой подложке обусловлены образованием диоксида титана, который является полупроводником n-типа. Установлено, что с увеличением толщины платинового покрытия и температуры обработки потенциал плоских зон и количество носителей также увеличиваются. Аномально высокие значения наклонов поляризационных кривых объясняются наличием зоны пространственного заряда в полупроводнике. Полученные данные указывают на возможность использования пика восстановления кислородсодержащих соединений платины на инверсионной вольтамперограмме в качестве корреляционного параметра для прогнозирования электрокаталитической активности термически обработанных электродов Ti/Pt в реакциях с переносом кислорода.

Ключевые слова: платинированный титан; композиционные материалы; инверсионная вольамперометрия; график Мотта-Шоттки.

Introduction

Composite materials based on titanium oxides and the metals of the platinum group are widely used as catalysts [1; 2], photo [3; 4] and electrocatalysts [5; 6], as well as in electrochemical processes for the synthesis of strong oxidizing agents [7], in the destruction of organic and inorganic substances in wastewater [8–10], as the active layer of dimensionally stable anodes for electroplating and in hydrometallurgy [11]. There are various methods of the obtaining of the materials of this type, for example, the sol-gel technology, plasma-chemical precipitation, chemical precipitation from the solutions in the presence of reducing agents, etc. [12–14]. Materials that include titanium oxides may be of considerable interest to this area. As it is known, the main difficulty arising during the operation of anodes of this type is their high tendency to passivation [15]. This problem can be solved by modifying the surface of the electrodes with a small amount of platinum [16]. Despite the variety of methods for producing such materials, combined electrochemical methods should be distinguished as the most promising ones, which, thanks to the ease of implementation and the possibilities for smoothly changing of the technological parameters of the processes, make it possible to control the composition and the properties of composites over a wide range.

In this regard, there is a need to develop the new anode materials for such processes. The most promising are the materials containing as an active layer TiO_2-Pt composite with a low content of the latter. However, the issue of the directional synthesis of materials of this type remains unclear, because the effect of the preparation conditions on the composition, physicochemical and electrochemical properties and the selectivity of the target process is not sufficiently studied for the resulting composites.

Experiment and Methods

All chemicals were reagent grade. Platinized titanium electrodes were obtained by the original method, which includes the stages of preliminary preparation of the titanium substrate [17; 18] and the further electroplating of the platinum coating.

Next, a thin layer of platinum was electrodeposited (the content of the platinum in the active layer was 8 mg per cm^{-2}) from the alkaline electrolyte, wich contained K_2PtCl_6; $NaNO_2$ and NH_3 solution [16], with cathode current densities equal to 20 or 30 mA cm^{-2} and temperature 343 K. Then the resulting electrodes were being chemically oxidized in a mixture (1:1) of concentrated H_2SO_4 and H_2O_2 and thermally treated in the air in a tube furnace at temperatures of 503, 583 or 683 K for an hour. The choice of this temperature range was caused by the allowance to accurately compare the properties of the coatings. The mechanisms of growth and migration of platinum on the surface at these temperatures are similar, but at temperatures above 723 K the mechanism of interaction of platinum with TiO_2 changes. As the treatment of the electrodes is carried out in the air atmosphere, a new substance and a new phase may appear (which is titanium nitride) even at higher temperatures. Also, in the selected temperature range, thermal diffusion of the platinum over the surface occurs, while the treatment at higher temperatures (683 K) leads to the encapsulation of platinum with titanium oxide.

Electrochemical processes were investigated on a Pt rotating disk electrode (Pt-RDE, 0.19 cm^2) by the cyclic and the steady-state voltammetry, voltammetry with the linear potential sweep, the inversion voltammetry (IVA) and the electrode impedance. Before each experiment, the electrode surface was treated with a freshly prepared mixture (1:1) of concentrated H_2SO_4 and H_2O_2 [17; 18]. This preliminary treatment technique allows to stabilize the electrode surface, which is oxidized to a certain state (defined phase and chemical composition of the surface oxides), under the action of strong oxidizing medium. It determines the favourable reproducibility of taking of the 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 three different potentiostats in order to validate devices. They are

i) PI-50-1.1 pulse potentiostat, a PR-8 programmer, and an H-307/1 two-coordinate potentiometer;

ii) GAMRY Potentiostat / Galvanostat / ZRA Reference 3000 potentiometer; and

iii) MTech PGP-550M potentiostat-galvanostat, which allows one to measure cyclic voltammograms in the range of potentials of the working electrode within ± 3 V with a scan velocity from 0.02 to 500 mV/s [19]. 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 the user-friendly software. It should be noted that all obtained data were identical. Temperature was maintained of 298 ± 1 K. All potentials were recorded and reported vs. Ag / AgCl / KCl $_{(sat.)}$.

Platinum oxides, which are formed in the region of the potentials of oxygen evolution, were investigated by the IVA method. At the first stage, the electrode was polarized at $j_a = 100$ mA cm^{-2} for 120 s, and then a cathode voltammogram was obtained at a potential scan rate of 100 mV s^{-1}.

The semiconductor properties of the electrodes were investigated by the electrode impedance method at 20 Hz frequency.

The surface morphology of Ti/Pt based coatings was investigated by the scanning electron microscopy (SEM) using a SEM-106I scanning electron microscope. Images were taken in the mode of the operation in secondary electrons with a gun current of 120 mA. The limiting residual pressure in the microscope column did not exceed 6.7×10^{-4} Pa.

Results and Discussion

The electrodes based on Ti/Pt can be obtained both by the electrodeposition of the metal and by the pyrolytic reduction of platinum from its salts. In the latter case, due to the interaction with the oxygen of the air, the surface of platinum is oxidized and forms the composites containing platinum and titanium oxides in the surface layer [20]. In this paper, a combined method for synthesizing of platinized titanium was used, according to which at the first stage a thin discontinuous coating of platinum (8 mg per cm^{-2}) was galvanically deposited onto the titanium surface and then the electrode was thermally treated at various temperatures. This method allows one to expand the possibilities of obtaining composite materials, which differ significantly from traditional Ti/Pt anodes both in the composition of the surface layer and in the electrocatalytic activity. We investigated the electrochemical and physico-chemical properties of such electrodes.

Fig. 1 shows the CVA of the platinum electrode in 1 M $HClO_4$. On the anode branch of CVA, a weakly marked peak of the desorption of the hydrogen is observed. The current plateau (1.0–1.3 V) corresponds to the formation of the platinum phase oxides and the exponential increase in the current is caused by the evolution of the oxygen at E ≥ 1.3 V. Cathodic branch of the curve is characterized by the presence of a reduction peak of oxygen-containing platinum compounds of different nature. With a gradual increase in the range of cycling potentials, platinum is increasingly oxidized, forming both phase oxides and strongly bounded chemisorbed oxygen; as a result the peak current increases and the peak potential shifts to the lower values (Fig. 2). As the cycling potential increases to 1.8 V, a second reduction peak appears on the cathodic branch of CV, indicating the presence of another form of chemisorbed oxygen or phase oxide, which differs in energy characteristics [21].

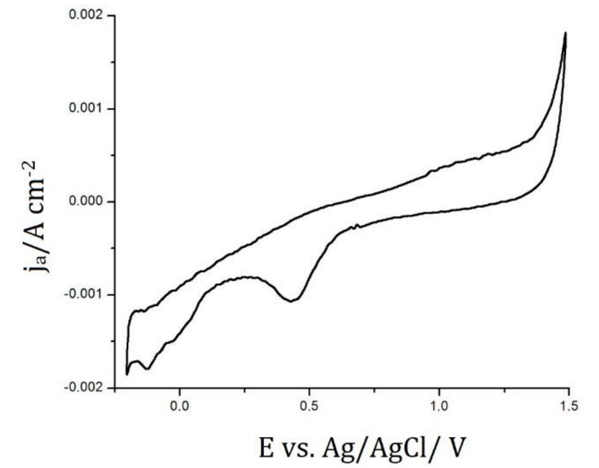


Fig. 1. Cyclic voltammogram of Pt in 1MHClO$_4$ v=100 mV/s

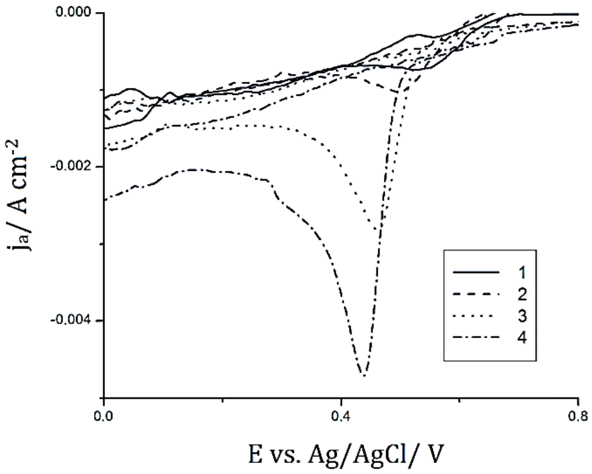
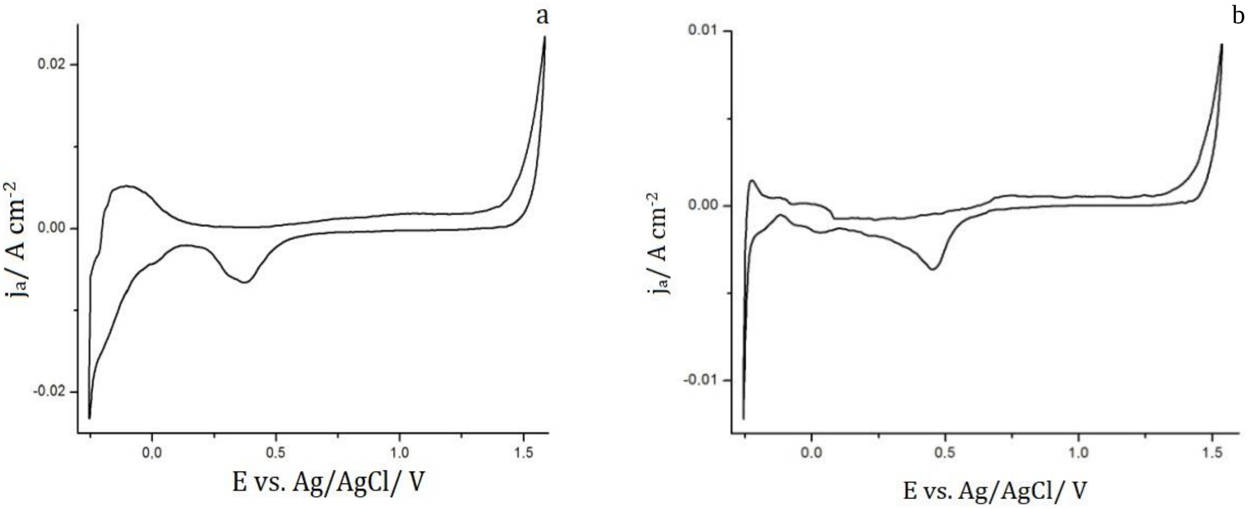


Fig. 2. Cyclic voltammograms of Pt in 1MHClO$_4$ with a different range of potentials sweep: 1 – -0.2 – 1.2; 2 – -0.2 – 1.4; 3 – -0.2 – 1.6; 4 – -0.2 – 1.8 V. v=100 mV/s

CV obtained for platinized titanium electrodes with the content of the platinum of 8 mg per cm^{-2} (which is about 1 micron) resembles the curve obtained for the platinum and is characterized by the presence of the same characteristic regions (Fig. 3a-d). One can note higher currents that are implemented on platinized titanium compared to the platinum (Fig. 3a), which is most likely due to the developed surface of the Ti/Pt electrode. At the same time, the overvoltage of the oxygen evolution reaction remains unchanged, although the current has increased by almost an order of magnitude, which confirms our assumption about the nature of the observed changes. Most likely, matching of the currents to the values of true surfaces of the electrodes will lead to the coincidence of the polarization curves.



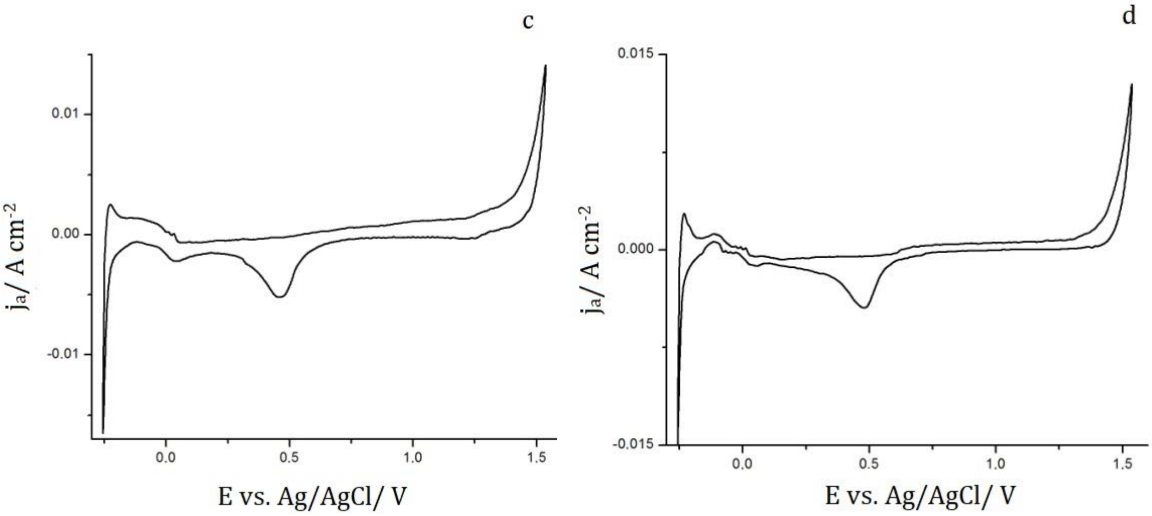
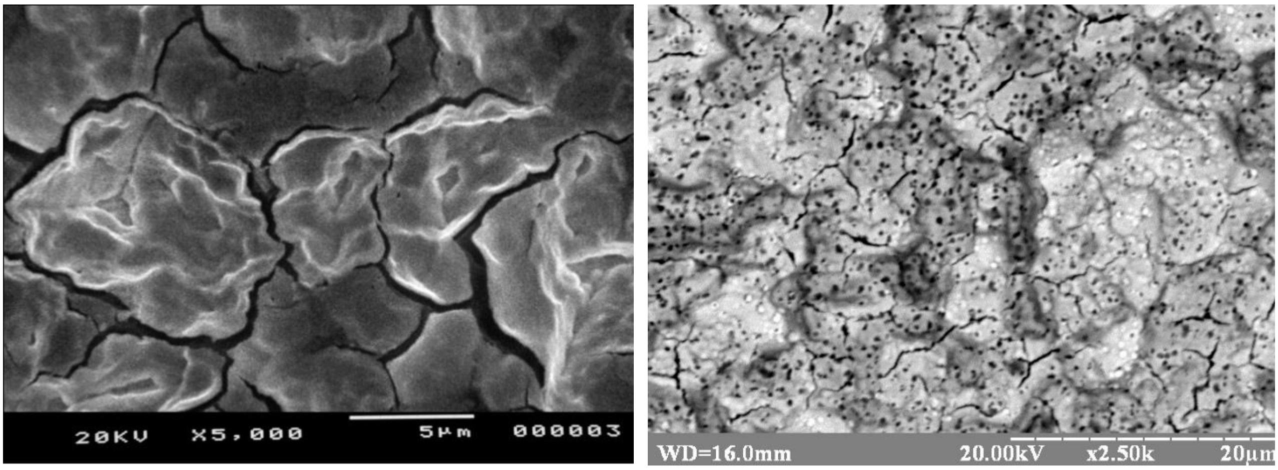


Fig. 3. Cyclic voltammogram in 1MHClO$_4$ of Ti/Pt (8 mg cm^{-2}) termally treated at 298 (a), 503 (b), 583 (c) and 683 K (d). v=100 mV/s

Such a distinction in the electrochemical activity of Ti/Pt electrodes treated at various temperatures is possible because of the differences in the surface morphology and its chemical composition. Unfortunately, generally when it comes to electrocatalytic processes, these two groups of factors are almost impossible to separate, because changing the conditions for obtaining a material has a complex effect on its composition and physicochemical properties. However, by changing its properties and the composition to varying degrees, the most significant factors can be identified. In this regard, we investigated the surface morphology of various samples of platinized titanium. As one can see from the SEM-image (Fig. 4a), titanium is almost completely coated with platinum with cracks and cavities on the Ti/Pt coatings with the content of the platinum of 8 mg per cm^{-2}.

As follows from Fig. 4b, thermal treatment of Ti/Pt at 683 K leads to the significant changes in the surface morphology. First, the coating becomes more uniform, which is probably caused by the distribution of Pt over the surface because of thermal diffusion and sintering [22]. In addition, during the heat treatment, the degree of crystallinity of the platinum coating increases.



a b

Fig. 4. SEM images of non treated Ti/Pt (a) and termally treated at 683 K

In order to determine the distinction in the nature and the number of platinum oxides, formed in the region of the potentials of OER on the Pt and Ti/Pt-electrodes, the method of inversion voltammetry with a linear potential sweep was used.

IVA curves for Pt electrode are presented on the Fig. 5. With an increase in the sweep rate, a significant shift of the potential peak to smaller values is observed, which indicates an irreversible electron transfer. The dependence of the peak current on the square root of the potential sweep rate is linear (Fig. 5b) and follow the Delahay equation [23], as described in the literature for analogous conditions [24].

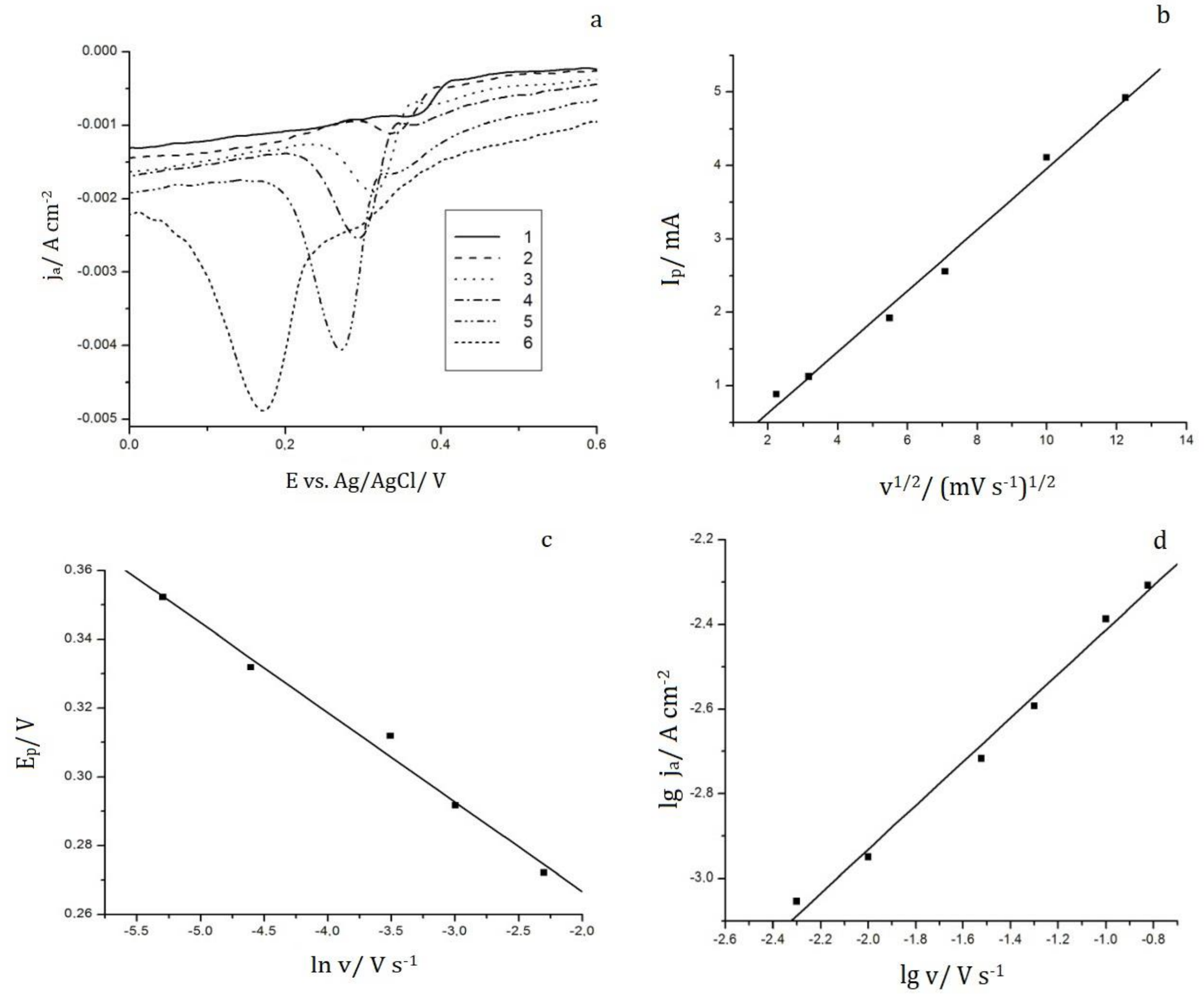


Fig. 5. (a) Hydrogen reduction peak of Pt in1 M $HClO_4$ at various potential sweep rate: 5 (1); 10 (2); 30 (3); 50 (4); 100 (5); 150 mV/s (6). (b) Peak current vs. square root of potential sweep rate. (c) Peak potential vs. potential sweep rate in semi-logarithmic coordinates. (d) Peak current vs. potential sweep rate in logarithmic coordinate

The dependence of the peak potential on the natural logarithm of the potential sweep rate is also linear (Fig. 5c), which indicates that the limiting stage is the irreversible transfer of an electron. This conclusion is also confirmed by the value of the Semerano criterion for the Pt electrode obtained from the slope of the dependence log j – log V (Fig. 5d) which is 0.5 [22].

Platinized titanium electrodes with a platinum content of 8 mg per cm^{-2} are characterized by the large values of the peak potentials of the cathode reduction of the platinum oxides (Fig. 6).

Since the thickness of the active layer of such materials is substantially greater than of the other ones, such coatings are uniform and the potentials of the peaks for the electrodes thermally treated at 503 and 583 K coincide. Probably, the processes of mutual penetration of the active layer and the substrate are less pronounced for the thick platinum coatings because of thermal diffusion.

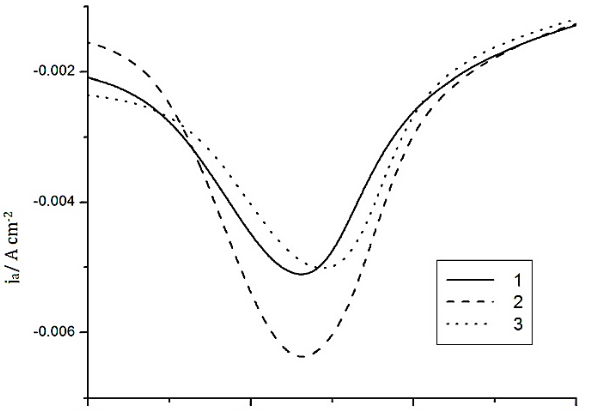


Fig. 6. Reduction peak of platinum oxides in 1 M $HClO_4$ for Ti/Pt electrodes (8 mg Pt per cm^2) thermally treated at 503 (1), 583 (2) and 683 K (3). v=100 mV/s

The peak current for Ti/Pt thermally treated at 583 K is somewhat higher, which is caused by the growth of the true surface of the active layer because of the more uniform distribution of the platinum. Thermal treatment at 683 K leads to thermal diffusion of platinum into titanium and to its oxidation, as a result the peak current decreases.

An increase in the peak potential indicates the formation of mixed oxides of titanium and platinum. An indirect proof of this is the change in the morphology of the electrode surface (see Fig. 4b).

According to the data obtained (Fig. 7a), the overpotential of the oxygen evolution depends on the conditions for obtaining the electrode material. It should also be noted that for all the cases considered there are high slopes of the polarization curves (Table 1), built in semi-logarithmic coordinates (Fig. 7b). The values of the slopes which significantly exceed the theoretical value and the linear form of the dependences clearly indicate the presence of a semiconductor component of the capacitance of the electrode.

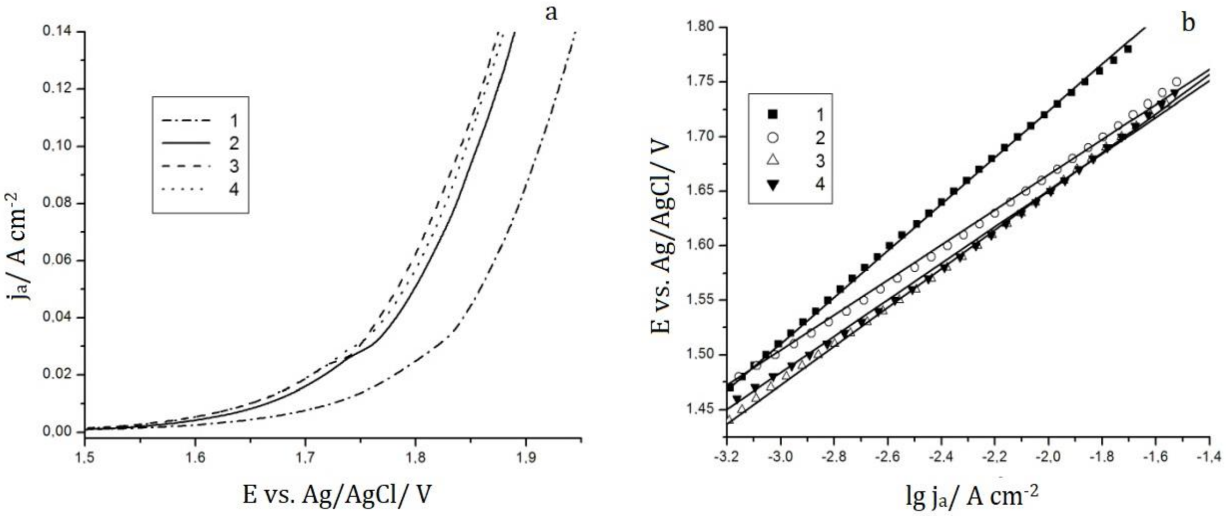


Fig. 7. Polarization curves (a)and E vs. log j_a plots (b) for Ti/Pt electrodes thermally treated at 298 (1), 503 (2), 583 (3) и 683 К (4). Supporting electrolyte 1M $HClO_4$, v=5 mV/s

Table 1

Semiconductor properties of composite Ti/Pt electrodes with 8 mg/cm^{-2} Pt content

Temperature of treatment	The intersept (a) and the slope(b)		Semiconductor characteristics	
	a, V	b, mV	E_{FB}, V	N×10^{-23}, cm^{-3}
298	2.14	212	0.650	2.8
503	1.99	161	0.214	1.3
583	2.00	178	0.530	3.7
683	1.99	167	0.51	2.0

The semiconductor properties of platinized titanium electrodes are caused by the formation of titanium dioxide, which, as it is known [25], is an n-type semiconductor. Devilliers et al. [26] noted that the presence of titanium dioxide in the coating, in the transition layer or substrate affects the electrochemical behavior of other materials, for example, the lead dioxide, which itself has metallic conductivity [27]. The characteristics of titanium dioxide as a semiconductor largely depend on the method of preparation and are determined by the thickness of the oxide film, the stoichiometry of the oxide and its allotropic form [28].

In this regard, we investigated the semiconductor properties of an oxide film obtained on titanium during its thermal treatment in a tube furnace in air at 683 K for an hour (Fig. 8a). Such a material is an n-type semiconductor with a potential of flat zones equal to –0.589 V and a carrier concentration of 6×10^{20} cm^{-3}. Such a high carrier concentration is obviously caused by the small thickness of the oxide film and its nonstoichiometricness, as a result of which the surface is not very depleted of electrons, since metallic titanium acts as their donor. Ti/Pt electrodes are high-alloyed semiconductors, because in this case, along with the metallic titanium, platinum also acts as an electron donor.

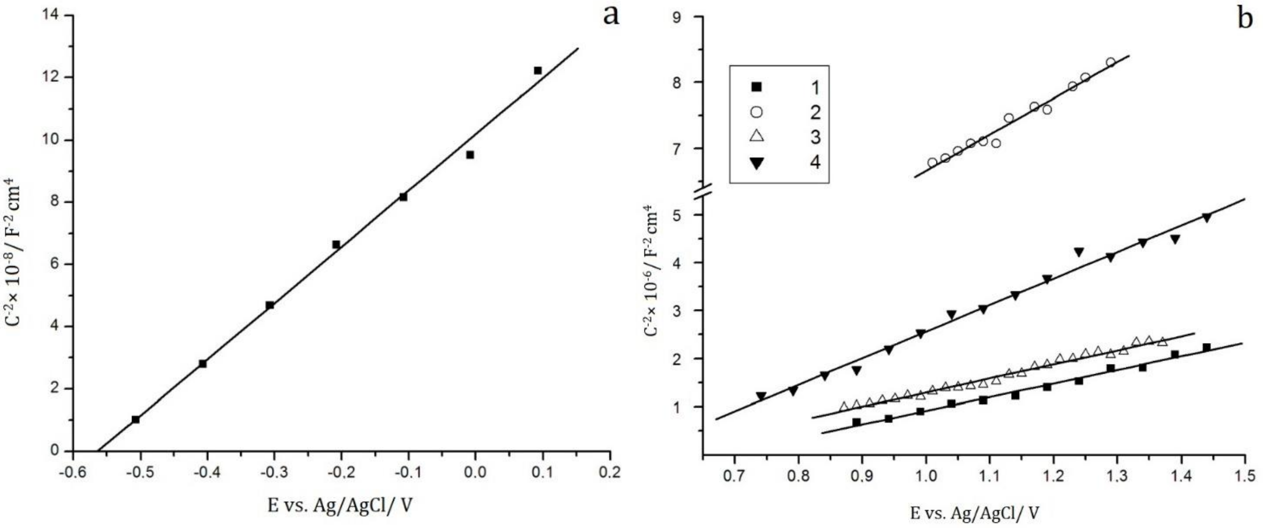


Fig. 8. Mott-Schottky plots of (a)TiO_2, obtained by thermal treatment of titanium at 683 K for one hour and (b) Ti/Pt electrodes thermally treated at 298 (1), 503 (2), 583 (3) and 683 K (4). Alternating current frequency 20 Hz

The number of carriers does not almost depend on the treating temperature for the Ti/Pt electrodes (Fig. 8b). Such phenomenon is observed since the amount of platinum on the surface does not change and such coatings are less defective. The anode, which was not thermally treated, is characterized by a high value of the potential of flat zones (see Table 1), which is caused by a significant amount of platinum (electron donors) on its surface.

As a result, carrier depletion of semiconductor occurs at higher potential. The thermal treatment of such a material leads to the oxidation of platinum with the atmospheric oxygen, as well as to its diffusion to the titanium substrate and the formation of a larger amount of titanium dioxide. At the same time, the potential of flat zones decreases. An increase in the treatment temperature to 583 K leads to an increase in the potential of the flat zones, which may be caused by the thermal diffusion of the Pt into the substrate and its distribution over the volume of titanium dioxide. A further increase in temperature does not lead to a noticeable change in the semiconductor properties, since in the case of thick platinum coatings, the processes of thermal diffusion proceed with great difficulty.The data presented in the Table 1 are agreed upon with the experiment and explain the nature of the change in the slope of the polarization curves given in semi-logarithmic coordinates. Thus, an increase in the number of carriers leads to a decrease in the contribution of the semiconductor component, as a result of which the slope of the polarization curves decreases [27].

Since the peak of the oxygen reduction on the IVA characterizes the number of electrochemically active Pt compounds on the surface of the Ti/Pt electrodes, the amount of electricity used for the reduction of the platinum oxides can be used to predict the electrocatalytic activity of thermally treated materials with the same Pt content. As follows from the data obtained, the electrocatalytic activity of thermally treated Ti/Pt electrodes increases with the increasing of the peak area, i.e. of the amount of electricity (Table 2).

The amount of electricity used for the reduction of Pt oxides for electrodes, thermally treated at 583 K, has a maximum value, because in this case there is the thermal diffusion of platinum over the surface. However, the treatment at higher temperatures leads to the encapsulation of platinum with the titanium oxides.

Table 2

Comparison of the amount of electricity used for the reduction of Pt oxides formed in the OER potential region (E=1.8 V) with the electrocatalytic activity thermally treated Ti/Pt electrodes with 8 mg/cm^{-2} Pt content

Temperature of treatment, K	Q, mC	I, mA
503	0.55	50.0
583	0.65	62.4
683	0.57	51.0

A method for the combined synthesis of dimensionally stable anodes with an active Ti_xO_y/Pt layer on the metallic titanium substrates is proposed, it is based on the electrolytical deposition of the thin layer of platinum on the substrate and the further heat treatment in air, which allows one to control the composition and the properties of the electrodes.

Conclusions

During the platinum deposition on a titanium substrate, a composite coating is formed. It consist of oxides of titanium, metallic titanium, platinum, and the intermetallic compound Ti_xPt_y. The content of the platinum decreases from the surface to the substrate with an increase in the ratio of metallic titanium and TiO_2. Coatings with the content of the platinum of up to 8 mg per cm^{-2} are represented by the titanium, almost completely coated with the platinum with cracks and cavities. Thermal treatment leads to the significant changes in the surface morphology, because the Pt is distributed over the surface and in the bulk due to diffusion and sintering, as well as it leads to an increase in the degree of crystallinity.

The semiconductor properties of composite Ti_xO_y/Pt electrodes on a titanium substrate are caused by the formation of titanium dioxide, which is an n-type semiconductor. It has been established that with the increasing of platinum coating thickness and the temperature of the treatment, the potential of the flat zones and the number of carriers increases. Anomalously high values of the slopes of the polarization curves are caused by the presence of a space charge zone in the semiconductor.

The data obtained indicate the possibility of using the reduction peak of oxygen-containing platinum compounds on the inversion voltammogram as a correlation parameter for predicting the electrocatalytic activity of thermally treated Ti/Pt electrodes in oxygen transfer reactions.

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