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OXYGEN EVOLUTION ON REDUCED MESOPOROUS TITANIUM OXIDE

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The possibility of using materials based on electrochemically reduced mesoporous titanium dioxide, including those micro-modified with platinum, as anodes in processes where oxygen evolution is the primary reaction was studied. The materials were obtained by anodizing metallic titanium for 3–4 hours. The resulting material was an n-type semiconductor. Then mesoporous TiO_2 was electrochemically reduced under cathodic polarization at a current density of 5 mA/cm^2. According to the data obtained, an increase in the reduction time of titanium dioxide leads to an increase in the number of charge carriers in the semiconductor and in the flat-band potential. It was shown that the Tafel slope decreases as the reduction time increases up to 60 minutes, from 221 to 121 mV/dec. The higher experimental values observed initially indicate the influence of the semiconductor component and polarization curve distortion. Micro-modification of the reduced oxide with metallic platinum leads to the stabilization of properties over time during prolonged anodic polarization.

Keywords: mesoporous TiO_2, electrochemical reduction, semiconductor properties, oxygen evolution, anodic polarization.

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Introduction

Materials based on titanium oxides are widely used in the manufacture of anodes for applied electrochemistry [1–4]. For instance, Dimensionally Stable Anodes (DSA) contain up to 70% TiO_2. Due to the high content of platinum group metals or their oxides (up to 30%), such materials exhibit high electrocatalytic activity and selectivity toward oxygen and chlorine evolution reactions, high electrical conductivity, and a significant operational lifetime.

However, these electrodes possess several serious drawbacks. Specifically, the sol-gel technology used for their fabrication is complex, labor-intensive, and fails to produce materials with standardized properties; furthermore, the cost remains high due to the precious metal content [5]. Additionally, these electrodes are unsuitable for use in complex electrolytes where oxidation of solution components is undesirable, such as in electroplating.

As previously shown, anodes based on titanium suboxides, characterized by low oxidation rates of electrolyte components, could serve as an alternative [6]. However, such anodes exhibit poor mechanical properties and are prone to passivation during long-term operation. To prevent this, it has been proposed to apply a thin, non-continuous layer of platinum followed by heat treatment to disperse the metal both on the surface and within the titanium oxide bulk.

While this resolves the passivation issue and reduces platinum content to 2 mg/cm^2, it does not address the mechanical strength or shape limitations of these electrodes [6].

Consequently, reduced titanium oxides obtained by electrochemical methods represent a viable alternative [7,8]. This method offers numerous advantages over chemical or sol-gel technologies, allowing flexible control over the synthesis process using inexpensive equipment and low energy consumption.

This study investigates the feasibility of using reduced and platinum micro doped titanium oxides as anodes in processes where oxygen evolution is the primary reaction. Such materials can function as independent anodes or as substrates for DSAs, eliminating the need for a transition layer to prevent titanium passivation in case of active layer cracking or pore formation. For example, using platinized porous titanium as a substrate for modified lead dioxide anodes enables high current yields of ozone [9]. The main differences from already known systems are one-step anodization process, optimized electrochemical reduction procedure and low content of platinum.

Experimental

The method for obtaining the materials includes several stages of preliminary preparation of the titanium substrate (grade VT1-0 titanium). The first stage is the anodization of Ti foil in ethylene glycol with the addition of 0.3 wt.% ammonium fluoride and 2 vol.% water for a certain period of time at a voltage of 40 V. Electrochemical reduction was carried out in 1 M $HClO_4$ at a current density of 5 mA/cm^2 for various durations. After this, if necessary, a platinum layer was deposited from a nitrite-based plating electrolyte [7]. The amount of platinum was controlled gravimetrically. The electrode area was 1 cm^2. Reagents of «chemically pure» (c.p.) and «pure for analysis» (p.a.) grades, as well as bidistilled water, were used for the work.

Quasi steady-state voltammetry and cyclic voltammetry were applied to study the electrochemical properties of the obtained materials using a VERSASTAT 3A-500 potentiostat/galvanostat. All potentials are reported vs to the silver/silver chloride (Ag/AgCl) reference electrode.

Results and discussion

The starting point for developing new anodic materials was the standard procedure for obtaining TiO_2 nanotubes on a titanium substrate [10]. The advantage of this method is the presence of the titanium substrate itself, which serves as a current collector in DSA systems. Typically, TiO_2 nanotubes are produced in two stages: anodization in a fluoride electrolyte followed by a phosphate solution. To simplify the method, we omitted the second stage, as it leads to the formation of more stoichiometric titanium dioxide, which is inconsistent with the objectives of this work. Anodizing the titanium plate for 3–4 hours results in a mesoporous TiO_2 layer.

Most titanium oxides are n-type semiconductors. It should be noted that requirements for titanium oxide-based photocatalysts and electrocatalysts differ significantly. For the former, more stoichiometric TiO_2 in the anatase form with a low carrier concentration and flat band potential is required [11,12]. Such materials cannot be successfully applied as electrocatalysts for anodic oxygen transfer reactions (for instance, oxygen evolution) due to significant electron depletion in the space charge region during anodic polarization.

Therefore, the semiconductor properties of the obtained titanium oxides were studied using impedance spectroscopy. If the surface region of a semiconductor electrode is depleted of majority charge carriers within the studied potential range, the experimental capacitance data should be linear in C^{-2} vs. E coordinates according to the Mott–Schottky equation:

$$C^{-2} = \frac{2}{e\varepsilon\varepsilon_0 N}\left(E - E_{fb} - \frac{kT}{e}\right), \quad (1)$$

where C is the capacitance of the electrode; e is the charge of the electron; N is the concentration of charge carriers; $E-E_{fb}$ is the potential of the flat zone; k is the Boltzmann constant; T is the absolute temperature; ε is the dielectric constant; and ε_0 is the electrical constant.

Since in most cases titanium oxides are highly doped semiconductors ($N>10^{18}$ cm^{-3}), therefore, in the Mott–Schottky equation, it is necessary to take into account the capacitance of the Helmholtz layer C_H [6]:

$$C^{-2} = C_H^{-2} + \frac{2}{e\varepsilon\varepsilon_0 N}\left(E - E_{fb} - \frac{kT}{e}\right). \quad (2)$$

The coefficients in Equations (1) and (2) are the same, but in contrast to the value of the flat bond potential E_{fb} obtained from equation (1):

$$E_{fb} = E_{C^{-2}=0} - \frac{kT}{e}, \quad (3)$$

in the second case, we have:

$$E_{fb} = E_{C^{-2}=0} + \frac{e\varepsilon\varepsilon_0 N}{2C_H^2} - \frac{kT}{e}. \quad (4)$$

For the calculations, a 1 M $HClO_4$ solution was

used to eliminate adsorption effects. At a frequency of 1000 Hz, the C^{-2} vs. E dependence for the material anodized in fluoride electrolyte for 3 hours is linear over a wide potential range (Fig. 1). Carrier concentrations were determined from the slope, and flat band potentials were derived using Equation (4).

The results (Table 1) indicate that a 3-hour anodization forms an oxide layer that behaves as a heavily doped n-type semiconductor. The high carrier concentration is likely due to the small thickness and non-stoichiometry of the oxide film. Consequently, the surface does not undergo significant electron depletion, and the metallic titanium acts as an electron donor. Increasing the anodization time to 4 hours leads to a slight increase in both carrier density and flat band potential. Beyond 4 hours, the surface morphology and semiconductor properties stabilize, making further increases in duration unnecessary.

However, the carrier density and flat band potential of these materials remain relatively low for creating an effective anode. Electrochemical reduction of anodically formed TiO_2 was performed in 1 M $HClO_4$ at a current density of 5 mA/cm^2 for varying durations. As shown in Table 1, the carrier density and flat band potential increase significantly during the first hour of reduction and then remain nearly constant.

The materials obtained after one hour of reduction are slightly inferior to titanium suboxides of the General Formula Ti_nO_{2n-1} (n=4−10) in terms of semiconductor characteristics but significantly exceed the purely anodic materials. For example, for Ebonex, the flat band potential and carrier density are 0.42 V and $8\cdot10^{24}$, respectively [6]. Thus, under the condition of electrochemical reduction, it is hardly possible to completely transform the anode titanium dioxide into Ebonex, the main phase of which is suboxides of the total composition of Ti_6O_{11}. However, due to electrochemical reduction, oxides with a sufficiently large non-stichometry for oxygen are formed.

The electrocatalytic activity was studied in the oxygen evolution reaction (OER). The quasi steady-state polarization curves presented in semi-logarithmic coordinates for electrodes in 1 M $HClO_4$ (at a potential scan rate of 5 mV/s) are shown in Fig. 2.

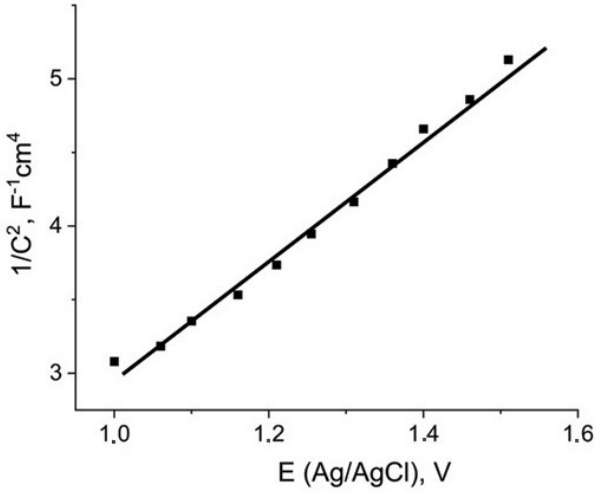

Fig. 1. Mott−Schottky dependence for a titanium plate anodized in a fluoride electrolyte for 3 hours at 40 V. Frequency 1000 Hz. 1 M $HClO_4$ solution

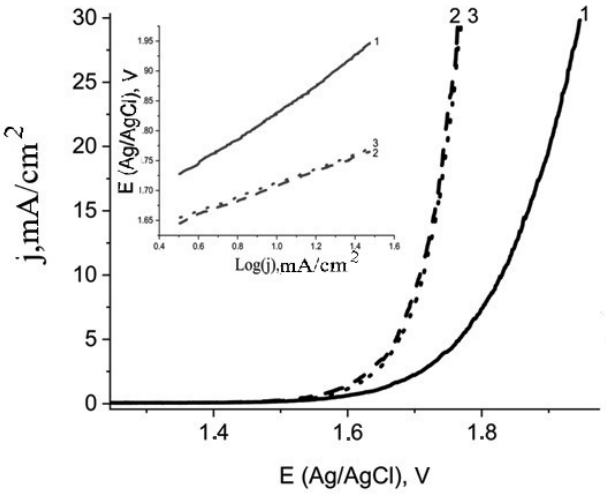

Fig. 2. Quasi steady-state polarization curves in 1 M $HClO_4$ electrodes obtained under different conditions: 1) anodization (4 h); 2) anodization (4 h) − electrochemical reduction (60 min); 3) anodization (4 h) − electrochemical reduction (60 min) + 0.25 mg/cm^2 Pt

Table 1

Semiconductor properties

No.	Synthesis conditions	N, cm^{-3}	E_{FB}, V
1	Anodizing (3 h)	$8.49\cdot10^{20}$	0.12
2	Anodizing (4 h)	$9.50\cdot10^{20}$	0.14
3	Anodizing (4 h), electrochemical recovery (10 min)	$3.40\cdot10^{22}$	0.30
4	Anodizing (4 h), electrochemical recovery (30 min)	$1.20\cdot10^{23}$	0.37
5	Anodizing (4 h), electrochemical recovery (60 min)	$2.10\cdot10^{23}$	0.38
6	Anodizing (4 h), electrochemical recovery (120 min)	$2.80\cdot10^{23}$	0.38

As it can be seen from the polarization curves (Fig. 2), the overpotential decreases with an increase in reduction time and does not change after 1 hour.

The overpotential of OER depends on the conditions for the electrochemical synthesis of oxide materials. In all cases, the dependences of E on log j are linear, which made it possible to calculate the Tafel parameters for the OER on titanium oxides (Table 2).

According to Table 2, the Tafel slope decreases with an increase in reduction time to 60 minutes, and then almost does not change. As is known [6], on titanium oxide electrodes in acidic solutions, the rate-determining step is the transfer of the first electron (electrochemical adsorption) with the theoretical Tafel slope of 118 mV/dec. However, in most cases (Table 1), higher values are observed, which indicates the contribution of the semiconductor component and the distortion of polarization curves. Increasing electrochemical reduction times gradually offset this effect by increasing the number of carriers and the flat bond potential.

It should be noted that long-term anodic polarization of titanium oxide electrodes leads to their gradual passivation. In this case, there is an increase in the overpotential of OER and an increase in the Tafel slope to values close to electrodes without reduction. To avoid the negative effects of prolonged anodic polarization, titanium oxide electrodes were modified with low content of platinum (0.25 mg/cm^2 Pt).

It was shown that platinum cannot be electrodeposited on TiO_2 surface after anodization which due to its low electrical conductivity. However, platinum can be electrodeposited onto the reduced oxide surface with a current efficiency of 28%. Platinum coating (0.25 mg/cm^2 Pt) is not continuous and has a small island character. In fact, a small amount of platinum on the surface of titanium oxides acts as an electron donor.

Cyclic voltammograms recorded for the electrode obtained under the mode: anodization (4 hours) – electrochemical reduction (1 hour) – electrodeposition of 0.25 mg/cm^2 of Pt. It is important to note that its electrochemical behavior does not differ in appearance from the curve for metallic platinum. An increase in the range of cycling potentials in the anodic direction leads to the formation of phase platinum oxides (mainly PtO for the given anode potentials). As a result, an increase in the reduction peak current is observed, and the peak potential is shifted to lower potential values (Fig. 3).

As can be seen from the polarization curves (Fig. 2, Table 2), the Tafel slope completely coincides with the theoretical value. According to the electrode impedance data, such an electrode completely loses its semiconductor properties. The main advantage of this system is the stability of electrochemical properties over time. Such an anode is not passivated during long-term anodic polarization. Thus, in order to preserve the properties of the reduced titanium oxide electrodes, it is recommended of its micro modification with platinum, which acts as an electron donor.

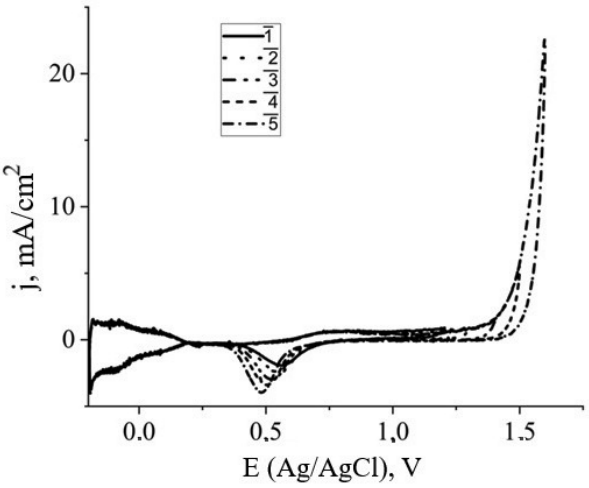

Fig. 3. Cyclic voltammograms obtained on an electrode (4 hours of anodizing and 60 minutes of recovery) containing 0.25 mg/cm^2 of platinum, with different cycling ranges: 1) −0.2...+1.2 V; 2) −0.2...+1.3 V; 3) −0.2...+1.4 V; 4) −0.2...+1.5; 5) −0.2...+1.6 V. Solution – 1 M $HClO_4$. The potential sweep rate is 50 mV/s

Table 2

Tafel slope (b) for the oxygen release reaction in 1 M $HClO_4$

No.	Anode Synthesis Conditions	b, mV/dec
1	Anodizing (4 h)	221
2	Anodizing (4 h), electrochemical recovery (10 min)	185
3	Anodizing (4 h), electrochemical recovery (30 min)	124
4	Anodizing (4 h), electrochemical recovery (60 min)	121
5	Anodizing (4 h), electrochemical recovery (120 min)	120
6	Anodizing (4 h), electrochemical recovery (60 min), 0.25 mg/cm^2 Pt	118

Conclusions

The method of electrochemical synthesis of an electrocatalyst based on titanium oxides is based on a combination of anodization and electrochemical reduction. The test material is an n-type semiconductor. An increase in the time of anodization and oxide electrochemical reduction for 1 hour leads to the formation of a material characterized by a high number of charge carriers and the value of the flat bond potential. The value of the Tafel slope for the oxygen evolution reaction is determined by the semiconductor characteristics, which in turn depend on the stoichiometry of the synthesized oxide. The combination of anodization and electrochemical reduction makes it possible to create a material with high electrical conductivity, which provides electrolytic deposition of platinum and significantly increases the stability of anodes over time under anodic polarization conditions. The main differences from already known systems are one-step anodization process, optimized electrochemical reduction procedure and low content of platinum.

Conflict of interest

A. Velichenko is an Editorial Board Member of the journal but was not involved in the peer-review process or the decision-making regarding this manuscript. All other authors declare no conflict of interest.

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ВИДІЛЕННЯ КИСНЮ НА ВІДНОВЛЕННОМУ МЕЗОПОРУВАТОМУ ОКСИДІ ТИТАНУ

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Було оцінено можливість використання матеріалів на основі електрохімічно відновленого мезопоруватого діоксиду титану, включаючи ті, що мікромодифіковані платиною, як анодів у процесах, де основною реакцією є виділення кисню. Матеріали були одержані шляхом анодування металевого титану протягом 3–4 годин. У результаті був отриманий напівпровідник n-типу. Потім мезопоруватий TiO_2 електрохімічно відновлювався під катодною поляризацією при густині струму 5 мА/см^2. Згідно з отриманими даними, збільшення часу відновлення діоксиду титану призводить до збільшення кількості носіїв заряду в напівпровіднику та потенціалу пласких зон. Було показано, що нахил Тафеля зменшується при збільшенні часу відновлення до 60 хвилин з 221 до 121 мВ/дек. Експериментальні значення, спостережені спочатку, свідчать про вплив напівпровідникової компоненти та спотворення кривої поляризації. Мікромодифікація відновленого оксиду металевою платиною призводить до стабілізації властивостей з часом під час тривалої анодної поляризації.

Ключові слова: мезопоруватий TiO_2, електрохімічне відновлення, властивості напівпровідників, виділення кисню, анодна поляризація.

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