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ELECTROCHEMICAL SYNTHESIS AND PROPERTIES OF TITANIUM DIOXIDE– TITANIUM SUBOXIDES COMPOSITE FOR CATHODIC PROTECTION

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This study reports a combined electrochemical method for preparation of a titanium dioxide–suboxide composite with an electrochemically deposited non-continuous platinum layer on the surface, which can be used for cathodic protection of metal structures. Platinum significantly modifies the properties of TiO_2, stabilizes the surface, and prevents the formation of a passive non-conductive layer. The coating has significant advantages compared to Ti/Pt, traditionally used for electrochemical protection, as the platinum content in the composite is significantly reduced. Unlike a continuous precious metal layer, this method of composite formation, particularly thermal treatment in an air atmosphere at 500⁰C, allows protecting the platinum, which is encapsulated in titanium oxides, and avoiding the creeping passivation typical of traditionally used materials. The surface of the coatings was investigated using X-ray photoelectron spectroscopy, X-ray diffraction, scanning electron microscopy, and X-ray microanalysis. Studies of the electrocatalytic properties, especially concerning the oxygen evolution reaction, revealed deviations of the Tafel slope from the theoretical value, which is explained by structural heterogeneity and the presence of a semiconductor component. The stability and corrosion resistance of the composites were studied. It was found that the properties remain unchanged even after prolonged exposure to a corrosive environment.

Keywords: cathodic protection, titanium dioxide, corrosion protection, conductivity, oxygen deficiency.

Introduction

Cathodic protection against corrosion is one of the primary methods for safeguarding structures made of various metals from the adverse effects of corrosion [1]. When the metal of the protected item is not prone to passivation, electrochemical cathodic protection against corrosion is primarily used.

Cathodic protection can be practically applied to protect steel, copper, lead, and aluminum in various soils and waters when the metal has a more negative potential than the protected metal. In externally powered protective current systems, protective anodes are usually made of iron, graphite, or titanium alloyed with platinum metals (Pt, Ru, Rh) [2]. The negative pole of the direct current source should be connected to the component being protected. If zinc or magnesium, which are less noble in the electromotive series than the protected iron, are used as anode materials, it is possible to do without an external current source, and the protective anode becomes an active or sacrificial anode. When the protected metal is cathodically polarized by external current, it becomes passivized.

The advantages of using zinc anodes, for example, include good performance, availability, and moderate cost. However, such materials have a limited-service life, especially in aggressive environments. Another significant problem is that the use of a sacrificial anode requires the system to be reassembled after the electrode's service life has ended. Magnesium anodes are characterized by their effectiveness in highly aggressive environments and long service life, but come at a higher cost compared to zinc anodes. These materials dissolve, although their installation does not

require an external current source. Zinc and aluminum are usually used in salty water, where the specific resistance is typically lower. Typical applications include ship and boat hulls, marine pipelines, and production platforms, marine engines with saltwater cooling, small boat propellers and rudders, as well as the interior surfaces of storage tanks [3]. As for aluminum anodes, they offer good performance, a long service life, and suitability for various conditions. However, they come at a higher cost. The use of titanium coated with a thin layer of magnesium is unsatisfactory since such coating becomes passive over time due to gradual oxygen uptake, and when used in aqueous environments, manganese can react chemically, leading to system reversal [4].

Titanium dioxide (TiO_2) is generally not used directly in the cathodic protection of metallic structures. It is primarily utilized as a material with a significantly enhanced photoelectrochemical cathodic protection effect [5]. Considerable research attention has been devoted to the use of TiO_2 photoanodes in photoelectrochemical cathodic protection, specifically photocathodic protection, for protecting metals from corrosion. The synthesis of TiO_2-based composite materials, as photoanodes, to enhance their photoelectrochemical performance has become a challenge among the investigators. The field has attracted considerable interest because TiO_2 coating functions such as a non-sacrificial anode when used for the cathodic protection of steel [6].

TiO_2 itself is a valve metal oxide, chemically stable in aggressive environments and electrochemically inert, giving it an advantage for use as a template. In terms of corrosion resistance, it is comparable to platinum and iridium oxides. Titanium oxide has a high affinity for oxygen evolution, which, in the presence of certain components in solution, promotes water oxidation while the remaining components oxidize more slowly.

Platinized titanium is widely used for cathodic protection of structures [6]. However, in such systems, the precious metal layer must have a thickness of at least 10 micrometers. Platinum is susceptible to degradation, and the rate of its degradation is proportional to the rate of oxygen evolution. Authors propose significantly reducing the platinum content and creating a composite with a small amount of platinum, which will prevent the passivation of the composite over time and give it another advantage for use as a prospective material for cathodic protection.

The method of depositing a composite and its subsequent heat treatment allows creating a porous developed surface of the matrix for the electro-deposition of platinum catalytic layers, and further heat treatment under different partial oxygen pressure allows forming composites of different compositions. The high number of cationic vacancies in the matrix and oxygen ion deficit will significantly increase the mobility of platinum group metal atoms during heat treatment, and the formed composite will have virtually metallic conductivity, high catalytic activity, selectivity for chosen processes, and extended service life due to the introduction of metals into the oxide matrix. In fact, platinum will be encapsulated in the coating and protected from degradation. This method is fast and inexpensive to implement, does not require expensive equipment, allows one to control the composition and properties of materials of this type, and forms catalyst layers directly on the current collector, including complex-profiled ones.

In this case, platinum will act as an electron donor, and the resulting composite will represent an Ebonex®-type coating, but it will be protected from passivation and can be used as a material for the cathodic protection of structures. In practice, an insoluble anode will be used, essentially DSA®, and if it fails, the active coating can be mechanically removed from the substrate and reapplied.

One should believe that the use of modified titanium dioxide as an anode for cathodic protection is quite promising. Such a coating can be used for an extended period, as it does not dissolve and becomes passivated over a long time without active oxygen evolution. A significant advantage of such an electrode is that it does not degrade during reduction and is not affected by current reversal. Moreover, the cost of applied platinum is comparable to the cost of the substrate, which is undeniable evidence of the advantages of using such a system.

Having in mind the above-mentioned, this work considers the possibility of using materials based on titanium with an electrolytically applied layer of platinum as anodes for cathodic protection.

Materials and methods

All chemicals were analytical reagent grade. NaOH, HCl, $NaClO_4$, and $HClO_4$ were purchased from Honeywell Research Chemicals / Fluka (Germany), Ti foil and noble metals precursors were purchased from Merck (ALSI, Ukraine).

Composites were fabricated by the original method, which included the stages of preliminary preparation of the titanium substrate [7], such as degreasing in NaOH and etching in 6 M HCl. The original TiO_2 nanotubes were prepared by anodizing Ti foil in ethylene glycol with 0.3 wt.% ammonium fluoride and 2 vol.% water at a constant potential for 4 h (anodization). The reduction was conducted in 1 M $NaClO_4$ for several hours (electrochemical reduction). Some samples were thermally treated in the air using a tube furnace at 500⁰C for 3 hrs (thermal

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treatment). A few pieces of anodes were loaded with platinum. It should be noted that platinum is not deposited on the surface of unreduced nanotubes. This phenomenon can be explained both by the blocking of the surface by hydroxides or by the low electrical conductivity of titanium dioxide as a semiconductor [7]. If the synthesized composite is reduced, then a layer of metal can be applied electrochemically to the pretreated surface. The samples were loaded with Pt in aqueous solution of nitrite electrolyte. The amount of deposited platinum was 0.3 ± 0.0001 or 0.5 ± 0.0001 mg/cm^2, which was determined gravimetrically.

Surface morphology was studied by scanning electron microscopy (SEM) with Tescan Vega 3 LMU with energy-dispersive X-ray microanalyzer Oxford Instruments Aztec ONE with X-Max^{N}20 detector. X-Ray powder diffraction (XRPD) data were collected in the transmission mode on a STOE STADI P diffractometer with Cu$K\alpha_1$-radiation, curved Ge (1 1 1) monochromator on primary beam, $2\theta/\omega$-scan, angular range for data collection of $20.000-110.225^0$ 2θ with an increment of 0.015, linear position sensitive detector with step of recording of 0.480^0 2θ and times per step of $75-300$ s, U=40 kV, I=35 mA, T=298 K. A calibration procedure was performed utilizing SRM 640b (Si) and SRM 676 (Al$_2$O$_3$) NIST standards. Preliminary data processing and X-ray qualitative phase analysis were performed using STOE WinXPOW and PowderCell program packages. The crystal structures of the phases were refined by the Rietveld method with the program FullProf.2k, applying a pseudo-Voigt profile function and isotropic approximation for the atomic displacement parameters, together with quantitative phase analysis.

XPS studies were carried out on a PHI 5000 spectrometer using monochromatic Al$K\alpha$ radiation for excitation. The BE value of C(1s), due to adventitious carbon and residual solvent, is 284.8 ($\pm$0.3) eV. The charge correction was performed by setting the Ti $2p_{3/2}$ peak at 459.0 eV, corresponding to titanium in TiO$_2$. For detailed analysis, the spectra were fitted onto several peaks. The line shapes were approximated by the product of Gaussian and Lorentz functions.

Oxygen evolution reaction was investigated by the potential sweep method. It should be noted that obtained quasi steady-state polarization curves at chosen potential rate (5 mV·s^{-1}) are practically indistinguishable from steady-state ones.

Impedance measurements were carried out in order to investigate the semiconducting properties of the samples involved. Computer controlled GAMRY Potentiostat/Galvanostat/ZRA Reference 3000 was used for these purposes (at frequency of 1000 Hz). Solution of 1 M HClO$_4$ was used for impedance measurements to eliminate effects of adsorption.

If the near-surface region of the semiconductor electrode is depleted in charge carriers within the investigated potential range, the experimental data obtained from measuring the electrode capacitance should exhibit linearity in the C^{-2} vs. E coordinates and follow the Mott-Schottky equation.

Preliminary studies have indicated that the materials under investigation are highly doped semiconductors (N>10^{18} cm^{-3}). Therefore, it is necessary to consider the capacitance of the Helmholtz layer C_H in the Mott-Schottky equation.

The slopes in the equations are the same, but the value of E_{fb} would consider the capacitance of the Helmholtz layer:

$$E_{fb} = E_{C^{-2}=0} + \frac{e\varepsilon\varepsilon_0 N}{2C_H^2} - \frac{kT}{e}. \tag{1}$$

Carrier concentrations were found from the slopes of the lines, and flat-band potentials were determined from the segments cut off from the curves using equation (1).

Results and discussion

The morphology of the obtained composites revealed the formation of a porous coating with a highly developed surface area. The coating has a multi-wall structure with an inner diameter ranging from 70 to 100 nm and a wall thickness of approximately 15 to 20 nm, as shown in Fig. 1. The pores appear to be weakly ordered, forming a nanocombed pattern. The resulting coating possesses a mesoporous structure. It is likely that there is incomplete dissolution of dense layers of titanium oxide on the coating's surface, leading to the external surface becoming ribbed.
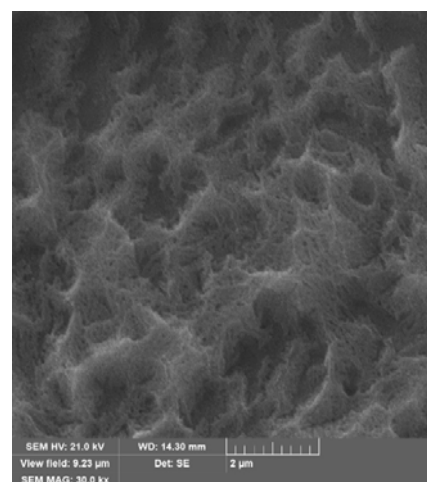

Fig. 1. SEM image of native TiO$_2$ composite

According to the EDX diagrams, there was an even distribution of elements within the TiO_2 lattice (53.9% O and 37.5% Ti). The presence of fluorine atoms in the structure is associated with the use of fluoride electrolytes, the anions of which are incorporated into the film during growth. In addition, as was shown earlier [8], F^- ions have a higher migration rate through the titanium oxide film as compared to oxygen ions O^{2-}. This difference in rate results in the formation of a fluorine-rich layer at the interface between the oxide and the titanium substrate.

Electron microscopic studies have shown that after heat treatment in air there is a transition from a tubular mesostructure of the surface to a microcrystalline one, consisting of a set of randomly located particles with linear sizes up to 1 μm (Fig. 2). However, in contrast to the work where annealing is carried out at 620^0C, rutile reflections [9] do not appear in the coatings under study. It should also be noted that heat treatment at higher temperatures (up to 700^0C) will lead to the formation of titanium nitrides, which is undesirable.

For further structural analysis of the obtained composites, X-ray diffraction was used (Fig. 3). The results indicated that after calcination at 500^0C for 3 hours, the coating is transformed into highly crystalline anatase phases. The diffraction peaks at 2θ values of 25.3^0, 37.8^0, 48.0^0, and 55.1^0 corresponded to the (101), (004), (200), and (215) anatase planes of TiO_2, respectively [10]. The phase composition of these films was as follows: anatase TiO_2 15.3(5) percent; and Ti 38.5(7) percent. However, an unidentified phase was determined too: broad reflections appeared at $2θ\sim35.97^0$, 40.96^0, and 59.26^0. If considering SEM/EDX data, it may be a titanium hydride (e.g., TiH_2 or TiH_{2-x} with a structure similar to CaF_2)
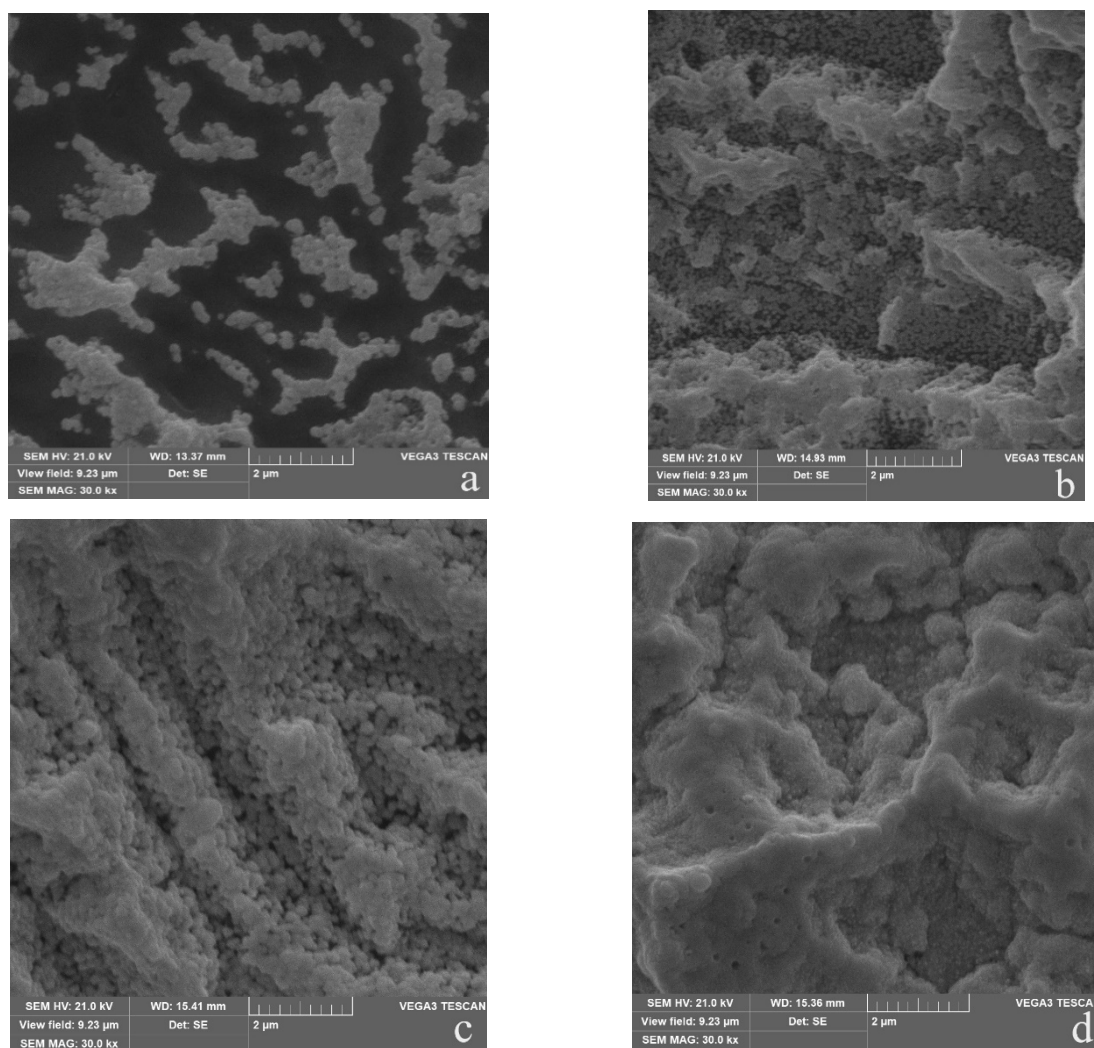

Fig. 2. SEM images: a − coatings with 0.3 mg cm^{-2} Pt; b − thermally treated composites with 0.3 mg cm^{-2} Pt; c − composites with 0.5 mg cm^{-2} Pt; and d − thermally treated coatings with 0.5 mg cm^{-2} Pt

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[7]. Before annealing, the coatings were X-ray amorphous; after annealing, they crystallized from the amorphous phase into anatase, which is confirmed by the appearance of reflections characteristic of anatase in the diffraction pattern (Fig. 3).

Phase composition and microstructural parameters are summarized in Table 1. As one can see, thermal treatment at 500⁰C in an air atmosphere for 3 hours leads to an increase in the proportion of the crystalline phase.

To get further insight into the effects of doping, we investigated the surface layers by X-ray photoelectron spectroscopy (Fig. 4). The XPS spectra of native TiO_2 reveal that the Ti 2p and O 1s signals are the main components. The Ti 2p signal, showing the reported Ti $2p_{3/2}$ and Ti $2p_{1/2}$ binding energies and peak separation of ~4 eV, can be assigned to Ti(IV) [11], in accordance with the literature [12]. The energy values belonging to TiO_2 in the metal-loaded TiO_2 samples are very close to those of the native TiO_2 (Fig. 4a).

The peak O 1s (531 eV) is split into two maxima at 529.4 and 532.3 eV. Since the second peak is blurred, oxygen reflexes in Ti oxides also could be layered on this peak and one can fit it into two peaks (Fig. 4b). The binding energy of this peak is too high for oxide-hydroxide compounds of metals and instead is characteristic of the O atom in adsorbed H_2O molecules [11,13]. Most likely, the first peak corresponded to the O of TiO_2 and the second peak is associated with OH^- ions, which compensated for the excess charge of cationic vacancies, and outer layers of water [11]. The proportionality of the O 1s peaks indicates the dominant contribution to the oxygen peak at 529.4 eV corresponds to being strongly bonded to the surface oxygen in the crystal lattice of TiO_2. These peaks were also observed in the metal loaded TiO_2 samples. The peak intensity of inert oxygen-containing particles with respect to that of weakly bonded is slightly lower for the metal loaded samples. The maximum at 70.0 eV for Pt $4f_{7/2}$ (Fig. 4c) with $\Delta=3.4$ eV peak separation shows that the loaded metal on the nanotube structured TiO_2 surface is in the metallic form [14].

Studying the electrocatalytic properties of materials in relation to the oxygen evolution reaction (OER) is of great importance in the field of electrochemistry, especially for applications like water
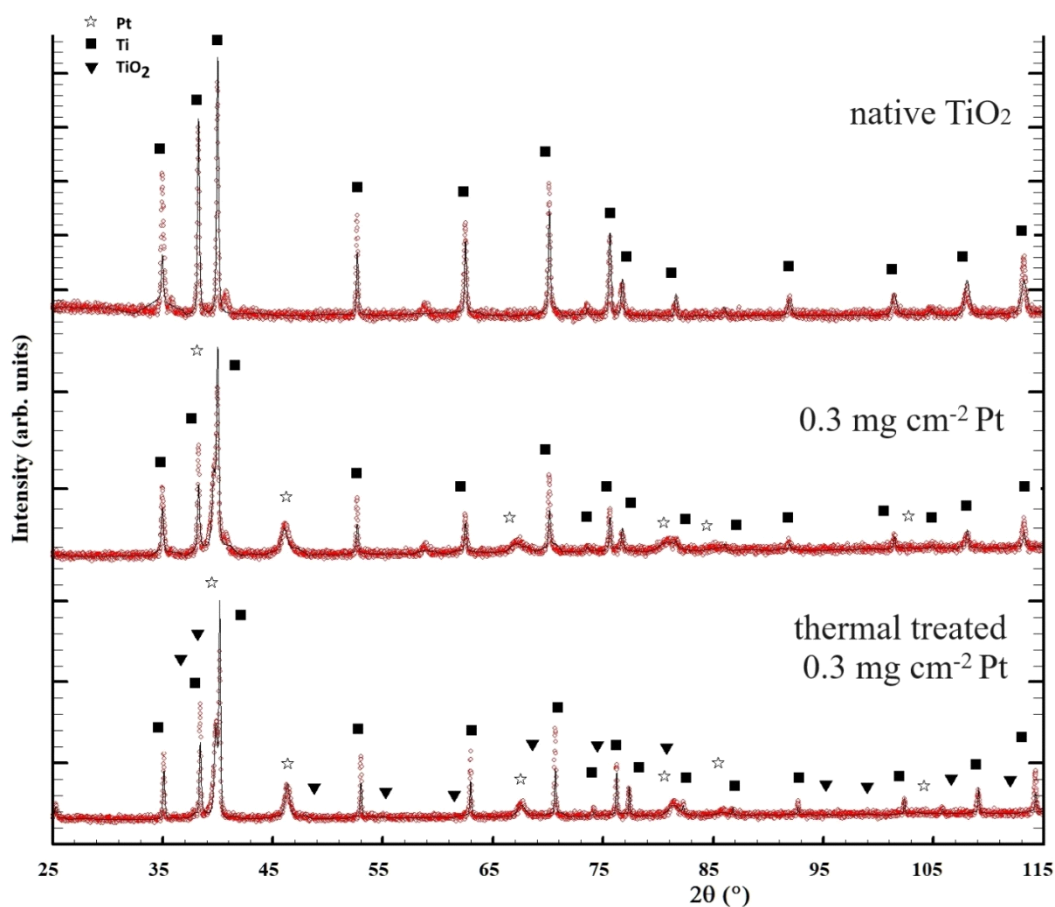

Fig. 3. Observed and calculated X-ray powder profiles for samples containing with 0.3 mg Pt

Table 1

Phase composition of the investigated samples, crystallographic data and microstructural parameters for the phases with fcc structure

Sample description	Phases [1]	Lattice parameter, a, Å	Unit cell volume, V, Å^3	D, Å/ε
Composites with 0.3 mg cm^{-2} Pt	Pt 12.1(4) wt.%	3.9198(4)	60.226(11)	99/0.0098
	Ti [2] 87.9(1.5) wt.%			
	UP [3]			
Thermal treated composites with 0.3 mg cm^{-2} Pt	Pt 15.3(3) wt.%	3.9174(3)	60.115(7)	115/0.0085
	Ti 75.6(1.1) wt.%			
	TiO$_2$ ana [4] 9.1(6) wt.%			
Composites with 0.5 mg cm^{-2} Pt	Pt 27.3(4) wt.%	3.9165(2)	60.077(6)	101/0.0097
	Ti 72.7(1.1) wt.%			
	UP [3]			
Thermally treated composites with 0.5 mg cm^{-2} Pt	Pt 36±1 wt.%	3.91608(17)	60.056(4)	155/0.0063
	Ti 53±2 wt.%			
	TiO$_2$ ana 11±3 wt.%			

Notes: [1] − the quantitative phase ratio refers to the sample's surface; [2] − Ti has a structure type similar to Mg, with a space group of $P6_3/mmc$; [3] − unidentified phase (UP); [4] − TiO$_2$ anatase has a space group of $I4_1/amd$.
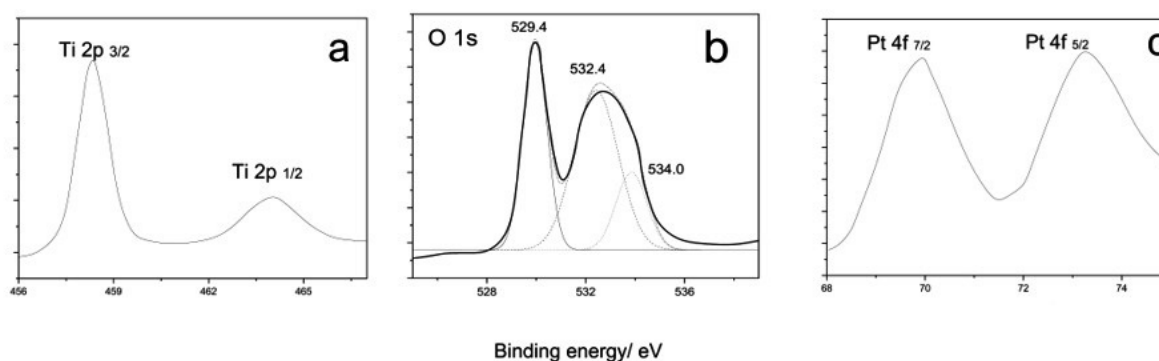

Fig. 4. Ti 2p, O 1s and Pt 4f core level structures in the TiO$_2$ composites with 0.3 mg cm^{-2} Pt

splitting, fuel cells, and electrolysis and electrochemical protection of metals in particular. The OER is a key step in these processes, and improving the efficiency of this reaction is crucial for the development of clean and sustainable energy technologies.

Polarization curves, presented in semilogarithmic coordinates, are shown in Fig. 5. The measurements were conducted in a 1 M HClO$_4$ solution to exclude undesirable effects that could be caused by the specific adsorption of electrolyte components.
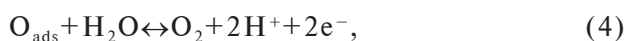
The complexity of the four-electron oxygen evolution reaction is due to its multistep nature and the involvement of adsorbed oxygen on the electrode. There is an opinion, initially proposed by Ferster [15], that oxygen has evolved as a result of the breakdown of intermediate unstable higher oxides. The transition of these intermediates into stable oxides (or into the original state of the metal with the simultaneous release of oxygen in gaseous form)

determines the kinetics of the entire electrode reaction.

Subsequently, numerous of kinetic schemes for this reaction have been proposed [15]. In almost all of them, it is assumed that the first stage involves the formation of adsorbed oxygen-containing particles, such as OH$_{ads}$ or O$_{ads}$, on the electrode surface through the discharge of water molecules or OH$^-$ ions:

$$H_2O \leftrightarrow OH_{ads} \leftrightarrow O_{ads} \tag{2}$$

Further, various steps of their transformation are possible, both purely chemical and proceeding according to the type of electrochemical desorption (3)−(5) and many others, including similar reactions involving OH$_{ads}$.
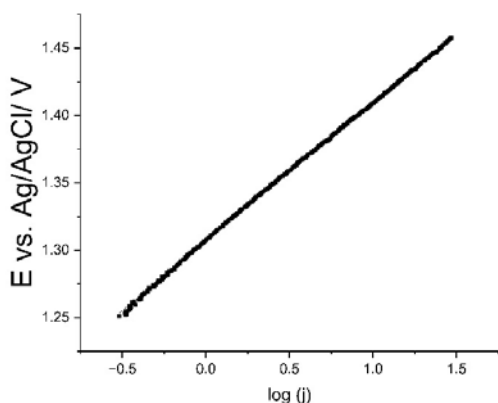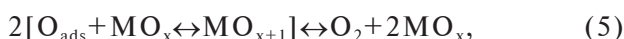
$$2O_{ads} \leftrightarrow O_2, \tag{3}$$

$$O_{ads} + H_2O \leftrightarrow O_2 + 2H^+ + 2e^-, \tag{4}$$

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Fig. 5. Polarization curves of oxygen evolution reaction represented in semilogarithmic scale. Curves were recorded in 1 M $HClO_4$. Potential scan rate was 5 mV·s^{-1}. Electrode: thermally treated coatings with 0.5 mg cm^{-2} Pt

$$2[O_{ads}+MO_x \leftrightarrow MO_{x+1}] \leftrightarrow O_2+2MO_x, \qquad (5)$$

where M is the electrode material.

The occurrence of oxygen overpotential is typically associated with the sluggish progress of one of the following steps: the discharge of hydroxide ions or water molecules (2), oxygen atom recombination (3), electrochemical desorption of O_{ads} radicals (4), or the formation and decomposition of unstable intermediate oxides (5). It is highly likely that at moderate current densities, the reaction rate is determined by the kinetic characteristics of the oxygen-containing particle formation stage. This can readily explain the observed experimental values of the coefficient b≈0.12 V/dec. Under different conditions, one of the subsequent stages of transforming these particles may become a rate-determining step, or several consecutive stages may proceed with similar kinetic parameters [15].

Sometimes, Tafel plots exhibit a kink when transitioning from low to high overpotentials. This can be explained by three different reasons: (i) a change in the reaction mechanism, (ii) a change in the rate-determining step while the mechanism remains constant, and (iii) a change in surface coverage [15].

In all investigated cases, the E vs. log(j) curves are linear and characterized by a slope of 221 mV/dec and 103 mV/dec for TiO_2 and for platinum loaded surfaces, respectively. For TiO_2, an atypical Tafel slope is observed, almost twice the theoretical value. Since there are no ions in the solution that could specifically adsorb onto the electrode surface and block it, this effect clearly points to the presence of a semiconductor component in the electrode's capacitance [7].

In the this case, some deviations from the theoretical value can be explained by either structural inhomogeneity of the material (presence of oxygen-evolution centers of different nature on the coating, leading to different rate-determining steps) or the extended surface of the coating.

As prepared, the electrode is an unstable system, which over time can acquire oxygen or undergo some structural changes. However, after 6 hours of cathode pretreatment, the unstable coating surface comes to a stationary state with a stable chemical composition and is not subject to passivation during the process of oxygen evolution (Fig. 6).
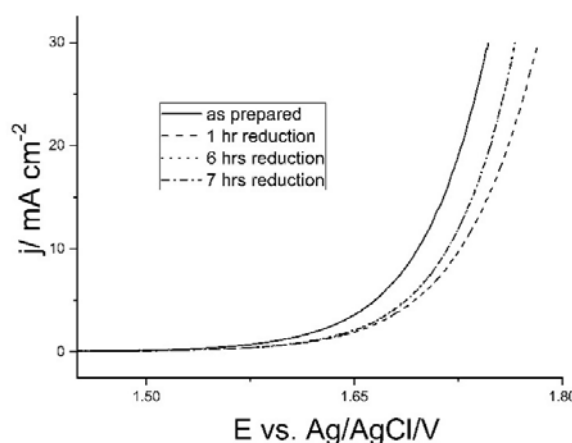

Fig. 6. Polarization curves of oxygen evolution on TiO_2 after various time of cathodic reduction in 1 M $NaClO_4$ at 5 mA/cm^2, 20^{0}C

It has been revealed that the materials involved have a flat-band potential of −0.6 V and a carrier concentration of 6·10^{20} cm^{-3}. It must be close to the equilibrium Fermi level and that confirms the TiO_2 n-type semiconductor behavior after the potential zone depletion. Such value is in the same range as those reported in the literature regardless of the preparation method, whether it is spectroscopic or electrochemical techniques.

The high concentration of carriers is likely attributed to the thinness of the oxide film and its non-stoichiometry, which prevents significant electron depletion at the surface due to the donor behavior of titanium metal.

During thermal treatment, the flat-band potential and carrier concentration increase, possibly due to the more crystalline structure of the material (Table 2). This structural change is accompanied by an increase in the proportion of metallic titanium, which acts as an electron donor. A similar phenomenon is observed when a discontinuous platinum coating is applied to the reduced composites.

Table 2

Semiconductor properties of TiO$_2$-composites

Material	Carriers' concentration $N \cdot 10^{-20}$, cm^{-3}	Flat band potential E_{fb}, V
native coating	6	−0.6
thermal treated	80	0.1
reduced	100	0.3
reduced and thermal treated	300	0.4
reduced platinized	600	0.5
reduced and thermal treated platinized	900	0.8

In this case, heat treatment causes platinum migration into the bulk of the composite, which, when dispersed within the oxide, further increases the number of carriers.

The obtained data confirm the significant influence of the semiconductor component and the flat band potential on the oxygen evolution reaction.

Investigation into the corrosion resistance of the materials involved was also carried out. It has been established that the properties of the coating remain unchanged even after 61 hours of operation in 1 M HClO$_4$ at 0.5 A.

Conclusions

A combined electrochemical method is proposed for preparation of a composite active layer on an electrically conductive transition metal substrate, which can be used for the cathodic protection of metallic structures. The resulting coating is not titanium dioxide but a titanium dioxide−titanium suboxides composite, exhibiting high electrical conductivity. Cathodic reduction of the formed material allows for the electrolytic deposition of a discontinuous layer of platinum on the surface. Platinum serves as an electron donor, significantly modifying the properties of TiO$_2$. Essentially, platinum reduces the coating, which stabilizes the surface and prevents the formation of a barrier layer.

A mesoporous structure, attributed to incomplete dissolution of dense layers of titanium oxide, is formed during electrosynthesis of TiO$_2$ suboxides.

The EDX analysis revealed a balanced distribution of elements within the TiO$_2$ lattice, including oxygen (53.9%) and titanium (37.5%). Additionally, the presence of fluorine is associated with the use of fluoride electrolytes, leading to a fluorine-rich layer at the interface. After heat treatment, a transition from porous mesostructured to a microcrystalline one is observed, with the emergence of crystalline anatase phases, which is confirmed by X-ray diffraction analysis. XPS analysis of the coating surface revealed that Ti 2p signal can be assigned to Ti(IV). The peak O 1s (531 eV) is split into two maxima at 529.4 and 532.3 eV. Most likely, the first peak corresponded to the O of TiO$_2$ and the second

to merged OH$^-$ ions, which compensated for the excess charge of cationic vacancies and outer layers H$_2$O. The loaded Pt on the nanotube structured TiO$_2$ surface is in the metallic form. The investigation of electrocatalytic properties, particularly for the oxygen evolution reaction, reveals linear E vs. log(j) curves and Tafel slope deviations, which can be attributed to structural inhomogeneity and the presence of a semiconductor component in the electrode's capacitance. It has been revealed that the materials involved are n-type semiconductors with a flat-band potential of −0.6 V and a carrier concentration of 6·10^{20} cm^{-3}. That is likely attributed to the thinness of the oxide film and its non-stoichiometry, which prevents significant electron depletion at the surface due to the donor behavior of titanium metal.

The prepared electrode reaches a stable state after cathode pretreatment, and the coating's properties remain unchanged even after 61 hours of operation in a corrosive environment.

The coating has significant advantages compared to Ti/Pt, traditionally used for electrochemical protection, as the platinum content in the composite is significantly reduced. Unlike a continuous precious metal coating, this method of composite formation, thermal treatment in air at 500^{0}C in particular, allows protecting the platinum, which is encapsulated in titanium oxides, and avoids the creeping passivation typical of traditionally used materials.

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ЕЛЕКТРОХІМІЧНИЙ СИНТЕЗ ТА ВЛАСТИВОСТІ КОМПОЗИТУ ДІОКСИД ТИТАНУ−СУБОКСИДИ ТИТАНУ ДЛЯ КАТОДНОГО ЗАХИСТУ

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Запропоновано комбінований електрохімічний метод одержання композиту діоксид титану−субоксиди титану з електролітично нанесеним несуцільним шаром платини на поверхні, який може бути використаний для катодного захисту металевих конструкцій. Платина істотно модифікує властивості TiO_2, стабілізує поверхню і запобігає утворенню пасивного неелектропровідного шару. Покриття має значні переваги порівняно з Ti/Pt, традиційно використовуваним для електрохімічного захисту, оскільки вміст платини в композиті значно знижений. На відміну від суцільного шару дорогоцінного металу, цей метод формування композиту, зокрема термічне оброблення у повітряній атмосфері за температури 500^0C, дозволяє захищати платину, яка інкапсульована в оксидах титану, і уникати повзучої пасивації, характерної для матеріалів, що традиційно використовуються для цієї мети. Поверхня покриттів була досліджена методом рентгенівської фотоелектронної спектроскопії, рентгенівської дифракції, сканувальної електронної мікроскопії та рентгенівського мікроаналізу. Дослідження електрокаталітичних властивостей, особливо щодо реакції виділення кисню, виявило відхилення тафелевського нахилу від теоретичного значення, що пояснюється структурною неоднорідністю та наявністю напівпровідникової складової. Було досліджено стабільність і корозійну стійкість композитів. Виявлено, що властивості композиту залишаються незмінними навіть після тривалого впливу корозійного середовища.

Ключові слова: катодний захист, діоксид титану, захист від корозії, електропровідність, вакансії кисню.

ELECTROCHEMICAL SYNTHESIS AND PROPERTIES OF TITANIUM DIOXIDE−TITANIUM SUBOXIDES COMPOSITE FOR CATHODIC PROTECTION

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This study reports a combined electrochemical method for preparation of a titanium dioxide−suboxide composite with an electrochemically deposited non-continuous platinum layer on the surface, which can be used for cathodic protection of metal structures. Platinum significantly modifies the properties of TiO_2, stabilizes the surface, and prevents the formation of a passive non-conductive layer. The coating has significant advantages compared to Ti/Pt, traditionally used for electrochemical protection, as the platinum content in the composite is significantly reduced. Unlike a continuous precious metal layer, this method of composite formation, particularly thermal treatment in an air atmosphere at 500^0C, allows protecting the platinum, which is encapsulated in titanium oxides, and avoiding the creeping passivation typical of traditionally used materials. The surface of the coatings was investigated using X-ray photoelectron spectroscopy, X-ray diffraction, scanning electron microscopy, and X-ray microanalysis. Studies of the electrocatalytic properties, especially concerning the oxygen evolution reaction, revealed deviations of the Tafel slope from the theoretical value, which is explained by structural heterogeneity and the presence of a semiconductor component. The stability and corrosion resistance of the composites were studied. It was found that the properties remain unchanged even after prolonged exposure to a corrosive environment.

Keywords: cathodic protection; titanium dioxide; corrosion protection; conductivity; oxygen deficiency.

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