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SYNTHESIS, PHOTO- AND ELECTROCATALYTIC PROPERTIES OF NANOSTRUCTURED Ce-TiO₂ FILMS

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Electrocatalytic films based on nanodispersed titanium dioxide modified by Ce(III) were synthesized by sol-gel method and characterized by X-ray diffraction and ultravioletvisible photocurrent spectra. The average size of nanoparticles was no more than 11 nm. The XRD results indicated that TiO₂ and Ce–TiO₂ electrodes with Ce concentrations up to 5 % calcined at 500°C consisted of anatase as the unique phase. The photocurrent spectra of the Ce–TiO₂ electrodes ($0 \le \text{Ce concentration} \le 2\% \text{ mol.}$) showed a stronger current in the UV range and a shift in the flat-band potential (E_{fb}) towards more negative values than that of TiO₂ electrodes. Electrocatalytic properties of TiO₂ and Ce-TiO₂ electrodes were investigated in the process of oxygen electroreduction. It has been found by I–E curves measurements that the potential of oxygen reduction changes with the film composition. Modifying of TiO₂ films by Ce(III) improves catalytic activity of Ce-TiO₂ electrodes (Ce concentration up to 2% mol.) in the reaction of oxygen electroreduction, that appears in decreasing of oxygen reduction potential E_{O2} and increasing of dynamic range of O₂ electroreduction potentials. The high electrocatalytic activity of Ce–TiO₂ electrodes in the oxygen reduction process may be due to the formation of catalytically active centers which activity may decrease in the presence of an amorphous phase. The correlation between photo- and electrocatalytic properties and structural changes occurring in Ce–TiO₂ films on increasing the cerium content is observed. The electrodes investigated were distinguished by a high sensitivity to dissolved oxygen $((4-5)\cdot 10^{-6} \text{ g}\cdot 1^{-1})$ and high reproducibility of characteristics in long-time cycling. These electrodes promise much as reusable electrode materials in electrochemical sensors for the determination of oxygen in liquids.

K e y w o r d s: titanium dioxide, cerium, oxygen electroreduction, catalytic activity, photosensitivity.

INTRODUCTION. Titanium dioxide is a promising material for application in

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optical and protective coatings, electrochemical devices, as oxygen reduction catalyst environmental photocatalysis, for the generation of electricity in the solar cells, gas sensors, etc. The catalytic activity of titania increases greatly when rare earth dopednanoparticles are used [1]. In this paper we present study results of photo- and electrocatalytic properties of electrodes based on nanostructured titanium oxide films modified by Ce.

EXPERIMENT AND DISCUSSION OF THE RESULTS. Nanoscale titanium dioxide TiO₂ was synthesized by the sol-gel method from titanium(IV) tetraisopropoxide in the presence of the non-ionic surfactant Triton X-100 [1]. An appropriate amount of Triton X-100 was dissolved in ethanol (EtOH), after which acetic acid (AcOH) was added to the solution. Then a titanium dioxide precursor, titanium tetraisopropoxide (TTIP), was added to the solution with vigorous stirring. The molar ratio of the components was Triton X-100 : EtOH : AcOH : TTIP=0.5 : 69 : 6:1. To prepare TiO₂ modified with cerium ions, appropriate amounts of CeCl₃ were added into the precursor to reach the cerium content of 0.5, 1, 2, 3, 5, 8 and 10% mol. To fabricate TiO₂ and Ce-TiO₂ films, transparent sol was deposited on pre-prepared Ti substrates and annealed in air at 500 °C. Preliminary preparation of Ti substrate included degreasing with acetone or carbon tetrachloride, as well as chemical etching in a mixture of HF and HNO₃ acids for 3-5 minutes, which helps to remove the surface oxide layer from the titanium foil, and also provides better adhesion of TiO2 sol with substrate. Sol was deposited on a conducting substrate by the immersion method. To this

end, the first sol layer was deposited on a prepared substrate; after that, the electrode was dried in an SNOL 58/350 laboratory oven at 120 °C for 10 minutes. This procedure was repeated 10 times. The electrodes with deposited layers based on Ce–TiO₂ sol were annealed in air in an SNOL 7.2/900 muffle furnace at t=500°C for 30 min and cooled at room temperature.

The phase composition and crystal structure of the obtained samples were studied by means of a DRON-3M diffractometer (monochromatic CuK_{α} radiation with nickel filter, λ =1.5418Å) at 30 kV, 20 mA in an angle range of 20=10–90°. To identify the diffractograms, the JCPDS database was used. The diffractograms were processed using the computer programs X-Ray and Match. The size of crystallites (coherent-scattering regions) of the obtained samples was calculated from the Scherrer equation using the most intense (101) anatase diffraction peak.

The photosensitivity of the samples and photoelectrochemical characteristics (spectral dependence of the photocurrent quantum yield and flat-band potential) were estimated from photocurrent values in wave-250-600 length range of nm. The photoelectrochemical investigations were carried out in 1N KCl solution in a quartz electrochemical cell with separated cathode and anode spaces using an MDR-2 monochromator and a DKSSh 500 highpressure xenon lamp. An Ag/AgCl electrode was used as a reference electrode, and a platinum electrode was used as an auxiliary electrode.

The electrocatalytic activity of electrodes based on TiO₂ and Ce-TiO₂ films dur-

ing oxygen electroreduction and the possibility of using them in sensing system were studied under potentiodynamic conditions using a PC-based electrochemical setup, which had the following characteristics: measured currents $2 \cdot 10^{-9} \div 10^{-1}$ A, potential scan rate $0.01 \div 50$ mV·s⁻¹, working electrode potential range -4 \div +4 V. TiO₂- and Ce-TiO₂ – based films deposited on a titanium substrate were used as a working electrode. The measurements were made in a 0.9% NaCl solution.

Structure of powders. X-ray patterns of powders obtained from the precursors of TiO₂ and Ce–TiO₂ films with a cerium content of 0.5-10 % mol. are shown in fig 1. In the X-ray patterns of both the initial TiO₂ and cerium-doped TiO₂ there are reflections typical of the crystalline anatase phase (JCPDS, no 21-1272). The diffraction peaks at 25,3°, 37,8°, 48,0°, 53,9°, 55,0° and 62,7° are identified as the (101), (104), (200), (105), (211) and (204) reflections of the crystalline anatase phase. The diffraction peaks corresponding to the crystalline cerium phase in Ce–TiO₂ samples are not observed (fig 1).

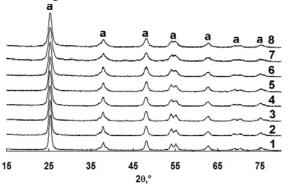


Fig 1. X-ray patterns of powders obtained at 500 °C from precursors of films with a cerium content of (% mol.) : I–0; 2–0,5; 3–1; 4–2; 5–3; 6–5; 7–8; 8–10.

As follows from Refs [2–8], cerium can be in the amorphous state [2], in the form of crystals of the cubic CeO_2 phase [3–5], but the incorporation of cerium ions into the anatase lattice is also possible [6]. It should be noted that the method used for making samples has a strong influence on the crystallization of mixed TiO_2 and $Ce-TiO_2$ oxides. When the sol-gel method is used, the cubic CeO_2 phase, besides anatase, crystallizes in the presence of surfactants at a higer molar Ce content (≥ 10 % mol.) [7, 8] and at a higher temperature than when using acids [2,4].

It can be seen that the anatase reflections become less intense with increasing Ce content $\pi p u \ 2\theta > 55^{\circ}$ (fig 1). According to the data of the authors of [2], who synthesized Ce–TiO₂ powders by the sol-gel method using Triton X-114 in cyclohexane without using an acid, this indicates that cerium in Ce–TiO₂ powders is probably present as an amorphous phase, and that the titanium dioxide crystallite size depends on the Ce content.

The broadening of diffraction peaks indicates that the obtained powders are nanocrystalline. The mean crystallite size was determined by the broadening of the most intense (101) peak from the Scherrer equation:

$$d = \frac{k\lambda}{\beta\cos\theta},$$

where d is the mean crystallite size, k is a constant (k = 0.9), β is peak half-width, λ and θ are X-ray wavelength and reflection agle respectively. The (101) diffraction peak half-width was determined as the half-width of the Lorentzian fitting function, which de

scribes the peak profile. The description of the profile of this diffraction peak by the Gaussian function was less satisfactory. The particle sizes calculated by the above procedure for TiO₂ and Ce-TiO₂ samples with a Ce content of 0.5, 1, 2, 3, 5 % mol. are listed in table 1. The effect of the Ce content on the crystallite size D of anatase TiO_2 is given in table 1.

As follows from table 1, when the

T a b 1e 1. Structural properties of investigated materials determined by using XRD

Composition	2θ,°	D, Á	Lattice parameters			
Composition			a(Å)	c(Å)	$V(Å^3)$	
TiO_2	25,35	108.1	3.7826	9.5057	136.01	
0.5%Ce/TiO ₂	25,33	97.8	3.7831	9.5175	136.21	
1%Ce/TiO ₂	25,31	97.2	3.7854	9.5236	136.46	
2%Ce/TiO ₂	25,30	82.6	3.7861	9.5230	136.50	
3%Ce/TiO ₂	25,33	84.7	3.7848	9.5271	136.47	
5%Ce/TiO ₂	25,34	72.6	3.7818	9.5372	136.40	

Ce content of modified samples is increased, the particle size decreases, which may be due to the presence of Ce–O–TiO₂ bonds, which impede the growth of crystalline grains [3,4].

The X-ray spectra of samples with a Ce content of 8 and 10 % mol. exhibit a weak broad peak at $2\theta = 70^{\circ}$ (fig 1, curves 7, 8), which corresponds to the presence of very small (~ 1 nm) CeO₂ crystallites, which agrees with the data of [2,5]. In spite of the fact that in the samples with high Ce content (8 and 10% mol.), cerium is in an amorphous phase, as was shown above, cubic CeO₂ crystallites can nucleate in the bulk of TiO₂ anatase [5]. However, they are difficult to detect by XRD because of very small size, which is below the limit of detection by XRD.

The X-ray patterns of $Ce-TiO_2$ samples with a Ce content of up to 2 %mol. , an

nealed at 500 °C (fig 1) exhibited a broadening of typical anatase peaks and their shift to smaller angles (table 1, fig 2).

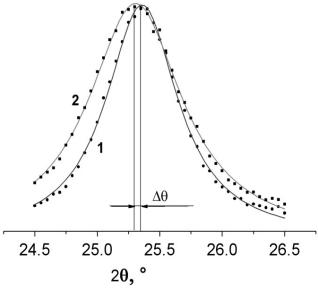


Fig 2. Decomposition of the (101) peak by means of the Lorentz function in X-ray patterns of films: $I - \text{TiO}_2$; $2 - 2\%\text{Ce-TiO}_2$.

This indicates that cerium ions are incorporated into the anatase lattice [6], though the difference in ionic radius between titanium ($Ti^{4+} = 0.68 \text{ Å}$) and cerium $(Ce^{4+} = 0.92 \text{ Å})$ is large. The values of the lattice parameters a and c as well as lattice volume V, calculated with the aid of the program X-Ray, increase with increasing the cerium content of samples to 2% (table 1), which also indicates the possibility of Ce⁴⁺ ion incorporation into the anatase lattice. The obtained data agree with the data of the authors of [6], who showed that in spite of the large difference in ionic radius, Ce ions can replace Ti⁴⁺ ions in the anatase lattice to form (≡ Ti-O-Ce-O-Ti≡) bonds. In this case, all TiO₂ can be saturated with a relatively small amount of Ce (because of the large difference between the radii of Ti⁴⁺ and Ce⁴⁺ ions); the rest of Ce is probably present on the surface as CeO₂. The authors of [6] also observed an expansion of the anatase unit cell for Ce-doped samples compared with pure TiO₂, which is an evidence of possible replacement of Ti⁴⁺ in the anatase lattice by Ce⁴⁺ ions.

In our case, increasing the Ce content (from 0,5 to 2 % mol.) in TiO₂ also led to an expansion of anatase lattice volume (table 1, fig 3). The increase in anatase lattice volume for the samples with a Ce content of up to 2 % mol. corresponds to the fact that Ce⁴⁺ ions are incorporated into the anatase lattice. At a Ce content of about 2% mol., the TiO₂ lattice is already saturated with Ce⁴⁺ ions, and CeO₂ is formed as an amorphous phase or very small nuclei, which agrees with the data of the authors of [4].

Photoelectrochemical properties of Ce- TiO_2 films. It has been found that the investi-

gated electrodes based on Ce-TiO₂ films (table 2, samples 1–6) were photosensitive in a wavelength range of 250–400 nm, and that the quantum yield η depended largely upon the Ce content (table 2, fig 3) and was a maximum for 1% Ce–TiO₂ films.

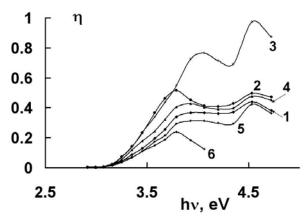


Fig.3. The spectral dependences of photocurrent quantum yield for TiO_2 and $Ce-TiO_2$ films with cerium content, % mol.: I-0; 2-0.5; 3-1; 4-2; 5-3; 6-5.

The flat-band potential E_{fb} and band gap energy E_g for indirect photo-transitions in the forbidden band of TiO2 have been determined from the photoelectrochemical current quantum yield spectra of electrodes based on obtained TiO₂ and Ce-TiO₂ films (table 2). The value of the flat-band potential E_{fb} was determined from plots of photocurrent I vs potential E by extrapolating the linear portions of these plots to intersection with the abscissa axis [9]. The value of E_{fb} allows one to estimate the change in the position of the conduction-band bottom of the obtained electrodes and the energy of electrons involved in reduction processes, including the oxygen electroreduction process [9]. To determine the band gap energy E_g , the photoelectrochemical current quantum yield spectra were reconstructed in the (hv

Table 2 Photoelectrochemical $(\eta, E_g \text{ and } E_{fb})$ and electrocatalytic $(E_{1/2} \text{ and } \Delta E)$ properties of Ce–TiO₂ electrodes depending on cerium content

№	Composition	Photocurrent quantum yield η, a.u.	Band gap E_g ,eV	Flat band potential E_{fb} , V	Oxygen half-wave potential $E_{1/2}$, V	Oxygen reduction range $\Delta E, V$
1	TiO_2	0.37	3.0	- 0.30	- 0.70	0,10
2	0.5%Ce/TiO ₂	0.52	3.0	-0.32	-0.62	0,18
3	1%Ce/TiO ₂	0.76	3.0	-0.35	-0.55	0,24
4	2%Ce/TiO ₂	0.43	3.0	-0.30	- 0.60	0,20
5	3%Ce/TiO ₂	0.31	3.0	-0.28	- 0.63	0,20
6	5%Ce/TiO ₂	0.24	3.0	- 0.25	- 0.65	0,16

 η)^{0.5}~hv coordinates for indirect allowed transitions in TiO₂, where η is quantum yield, and hv is quantum energy of light [9].

The value of quantum yield (η) for TiO₂ and Ce-TiO₂ samples was 0.24–0.76 (table 2). It should be noted that for the samples with Ce content of 0.5, 1 and 2% mol., a significant increase in their photosensitivity relative to unmodified TiO₂, which manifests itself by an increase in the quantum yield of photoelectrochemical current, η (table 2, samples 2–4), and a shift of the spectra to the long-wavelenth region (fig 3, curves 2-4) are observed. For the films with a Ce content of >2%, the values of the quantum yield of photocurrent were smaller compared with unmodified TiO₂ films (table2, fig 3, curves 5, 6). In this case, the band gap energy E_g of the investigated electrodes did not change greatly (table 2). Ta

king this into consideration, we can consider that modification with Ce ions leads to the formation of photoactive defects in the forbidden band of TiO_2 , whose activity may decrease with the formation of an amorphous phase (fig 3, curves 3, 5). The explanation of why the value of E_g does not change at different contents of Ce lies in its usually much lower sensitivity with respect to progressing structural changes [2].

Electrocatalytic properties of films. The electrocatalytic properties of the obtained films of cerium-modified titanium were studied during oxygen electroreduction. This process is the basis of the operation of electrochemical O₂ sensors, which are designed for the determination of oxygen concentration in liquid media [8].

The polarization curves for electrodes based on Ce–TiO₂ films in physiologic solu-

tion 0.9%NaCl (pH 6.8) exhibited one polarographic wave of current at potentials of -0.5 to -1.0 V (vs silver-chloride electrode) with limiting current corresponding to oxygen reduction current (fig 4). At potentials of E< - 1.0 V, a hydrogen evolution reaction proceeded at the electrodes.

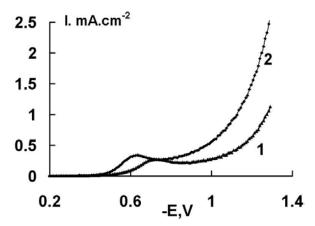


Fig 4. Polarization curves of oxygen electroreduction on Ce–TiO₂ electrodes: I – 5%Ce–TiO₂; 2 – 1%Ce–TiO₂. Potential scan rate 10 mV·s⁻¹. Potentials are given relative to Ag/AgCl reference electrode.

Important characteristics of electrodes for the analysis of dissolved oxygen concentration are oxygen reduction potential or oxygen reduction half-wave potential $E_{1/2}$ on the cathodic polarization curve and the width of "electrochemical window", ΔE (dynamic potential range in which the oxygen content of the solution can be analyzed). The value of $E_{1/2}$ should be minimal to eliminate possible electrochemical side reactions, and the value of ΔE should be maximal to achieve high electrode sensitivity and measurement accuracy. From fig 4 it follows that in physiologic NaCl solution (pH 6.8), the value of $E_{1/2}$ at the electrodes with cerium content of 1% is -0.55 V and is minimal among the

obtained Ce–TiO₂ electrodes. The dynamic potential range of O₂ reduction on these electrodes was 0.24 V. The values of $E_{1/2}$ and ΔE for other electrodes are listed in table 2.

From table 2 it follows that modification of TiO₂ films with cerium increases the catalytic activity of electrodes based on them in the oxygen electroreduction reaction compared with unmodified TiO₂, which manifests itself by a decrease in oxygen reduction half-wave potential and an increase in the dynamic range of O_2 electroreduction. The electrodes with cerium content of 1% ($E_{1/2}$ = -0.55V, $\Delta E = 0.24$ V) showed the maximum electrocatalytic activity. At higher cerium content of films (>2%), the electrocatalytic activity of electrodes decreased (table 2). For samples with 5% cerium content, the values of $E_{1/2} = -0.65 \text{ V}$, $\Delta E = 0.16 \text{ V}$ were obtained. The values of stationary potentials for samples with 1% and 5% cerium content are equal respectively to 0.17 V and 0.2 V. The decrease in catalytic activity with increasing cerium content may be due to, as in the case of photosensitivity, to the formation of catalytically active centers (crystalline defects), whose activity decreases during the formation of amorphous phase.

With repeated cycling of the potential, the polarization characteristics of the Ce – TiO₂ electrodes remained almost unchanged after the 3rd cycle, which indicates the high stability of the obtained electrodes and the possibility of using them to determine the concentration of dissolved oxygen.

Thus, electrodes based on Ce–TiO₂ films are distinguished by high electrocatalytic activity and stability in the process of oxygen reduction and are promising for use in electrochemical oxygen sensors.

The variation of the electrocatalytic $(E_{1/2})$ and photoelectrochemical (η and E_{fb}) properties of the Ce–TiO₂ films studied in this work as a function of cerium content is shown in fig 5.

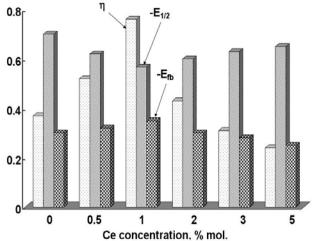


Fig 5. Dependence of the electrocatalytic $(E_{1/2})$ and photoelectrochemical (η and E_{fb}) properties of Ce–TiO₂ films on cerium content.

Thus, a correlation between photo- and electrocatalytic properties and structural changes occurring in Ce-TiO₂ films on increasing the cerium content is observed.

CONCLUSION. Powders and films of TiO₂ modified with Ce ions have been synthesized by sol-gel method. The Ce–TiO₂ powders with cerium content of 0.5–10% % mol. ($t_{\text{annealing}} = 500 \,^{\circ}\text{C}$) had an anatase crystal structure with a crystallite size of up to 11nm.

Electrodes based on Ce–TiO₂ films were photosensitive in a wavelength range of 250–400 nm. For samples with Ce content of 0.5, 1 and 2 % mol., an increase in the values of photocurrent quantum yield and a shift of spectra to the long-wavelength region compared with unmodified TiO₂ were observed. The subsequent increase of the ce-

rium content led to a decrease in the photoactivity of samples.

The Ce-TiO₂ films were distinguished by an increased catalytic activity in the process of oxygen electroreduction, which manifested itself by a decrease in oxygen reduction half-wave potential and an increase in the dynamic range of O₂ electroreduction compared with unmodified titanium dioxide films. An increase in electrocatalytic activity was observed for cerium ion concentrations of up to 1%; the subsequent increase of the dopant content led to decrease in the activity of samples probably because of the formation of an amorphous phase. Ce–TiO₂ showed high stability and reproducibility of characteristics in the process of O₂ Synthesized electroreduction. electrode materials are most promising for use in electrochemical sensors for the determination of O_2 in liquid media.

СИНТЕЗ, ФОТО- ТА ЕЛЕКТРОКАТАЛІТИЧНІ ВЛАСТИВОСТІ НАНОСТРУКТУ-РОВАНИХ ПЛІВОК $Ce-TiO_2$

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Електрокаталітичні плівки на основі нанодисперсного діоксиду титану, модифікованого Се(III), синтезовані золь-гель методом і охарактеризовані методами рентгенівської дифракції (XRD) та спектроскопії

фотоелектрохімічного струму. Середній розмір наночастинок не перевищу-вав 11 нм. Результати XRD показали, що TiO₂ i Ce-TiO₂ порошки з концентраціями Се до 5%, прожарені при 500 °C, мали кристалічну структуру анатазу. На спектрах фотоструму $Ce-TiO_2$ електродів (концентрація $0 \le Ce \le$ 2% мол.) спостерігався більш сильний струм в УФ-діапазоні і зсув потенціалу плоских зон (E_{fb}) до більш нега-тивних значень, у порівнянні з ТіО2 – електродами. Електрокаталітичні властивості електродів ТіО2 і Се-ТіО₂ досліджувалися в процесі електровідновлення кисню. За допомогою І-Евиявлено, кривих було ЩО потенціал електровідновлення кисню залежав від складу плівок. Модифікування плівок ТіО2 за допомогою Се (III) покращує каталітичну активність електродів Се-ТіО2 (концентрація Се до 2 %мол.) у реакції електровідновлення кисню, що проявляється у зменшенні потенціалу відновлення кисню Ео2 і збільшенні динамічного діапазону потенціалів електровідновлення О2. Висока електрокаталітична активність електродів Ce-TiO₂ у процесі відновлення кисню, ймовірно, може бути обумовлена утворенням каталітично активних центрів, активність яких може зменшуватися в присутності аморфної фази. Спостерігається взаємозв'язок між фото- та електрокаталітичними властивостями та структурними змінами, що відбуваються в плівках Се-ТіО2 при збільшенні вмісту церію. Досліджувані електроди відрізнялися високою чутливістю до розчиненого кисню $(4-5)\cdot 10-6 \, \text{г} \cdot \text{л}^{-1}$) і високою відтворюваністю характеристик при тривалому циклюванні. Синтезовані електродні матеріали можуть бути використані в електрохімічних сенсорах для визначення О2 у рідких середовищах.

Ключові слова: діоксид титану, церій, електровідновлення кисню, каталітична активність, фоточугливість.

СИНТЕЗ, ФОТО- И ЭЛЕКТРОКАТАЛИТИ-ЧЕСКИЕ СВОЙСТВА НАНОСТРУКТУРИ-РОВАННЫХ ПЛЕНОК $Ce-TiO_2$

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Электрокаталитические пленки на основе нанодисперсного диоксида титана, модифицированного Ce(III), синтезированы зольгель методом и охарактеризованы методами рентгеновской дифракции (XRD) и спектроскопии фотоэлектрохимического тока. Результаты XRD показали, что TiO₂ и Ce-TiO₂ порошки с концентрациями Се до 5%, отожженные при 500 °C, имели кристаллическую структуру анатаза. На спектрах фототока $Ce-TiO_2$ электродов (концентрация $0 \le Ce$ ≤ 2 % мол.) наблюдался более сильный ток в УФ-диапазоне и смещение потенциала плоских зон (E_{fb}) в сторону более отрицательных значений, по сравнению с ТіО2-электродами. Повышение электокаталитической активности Ce-TiO₂ электродов в процессе электровосстановления кислорода по сравнению с немодифицированным ТіО₂ наблюдается для пленок с концентрациями Се до 5%. Синтезированные пленки могут быть использованы в электрохимических сенсорах для определения O_2 в жидких средах.

Ключевые слова: диоксид титана, церий, электровосстановление кислорода, каталитическая активность, фоточувствительность.

REFERENCES

- Stengl V., Bakardjieva S., Murafa N. Preparation and photocatalytic activity of rare earth doped TiO₂ nanoparticles . *Mater. Chem. Phys.* 2009. 114: 217.
- 2. Stathatos E., Lianos P., Tsakiroglou C. Highly efficient nanocrystalline titania films made from organic/inorganic nanocomposite gels. *Micropor. Mesopor. Mat.* 2004. **75**: 255.
- 3. Matějová Lenka, Kočí Kamila, Reli Martin, Čapek Libor, Hospodková Alice, Peikertová Pavlína, Matěj Zdeněk, Obalová Lucie, Wach Anna, Kuśtrowski Piotr, Kotarba Andrzej. Preparation, characterization and photocatalytic properties of cerium doped TiO₂: On the effect of Ce loading on the photocatalytic reduction of carbon dioxide. *Appl. Catal., B.* 2014. **152–153**: 172.
- 4. Lin Jun, Yu Jimmy C. An investigation on photocatalytic activities of mixed TiO₂-rare earth oxides for the oxidation of acetone in air. *J.Photochem. Photobiology* A. 1998. **116(1)**: 63.
- 5. Fang J, Bi X, Si D, Jiang Z, Huang W. Spectroscopic studies of interfacial structures of CeO₂ –TiO₂ mixed oxides. *Appl Surf Sci.* 2007. **253**: 8952.

- Matejova L., Vales V., Fajgar R., Matej, Z., Holy V; Solcova O. Reverse micelles directed synthesis of TiO₂-CeO₂ mixed oxides and investigation of their crystal structure and morphology. *J. Solid State Chem.* 2013. 198: 485.
- López T., Rojas F., Alexander-Katz R., Galindo F., Balankin A. S., Buljan A. Porosity, structural and fractal study of sol-gel TiO₂-CeO₂ mixed oxides. *J. Solid State Chem.* 2004. 177: 1873.
- Pavasupree S., Suzuki Y., Pivsa-Art S., Yoshikawa S. Preparation and characterization of mesoporous TiO₂– CeO₂ nanopowders respond to visible wavelength. *J. Solid State Chem.* 2005. 178: 128.
- Kolbasov G. Ya., Vorobets V. S., Korduban A. M., Shpak A. P., Medvedskii M. M., Kolbasova I. G., Linyucheva O. V. Electrodes Based on Nanodispersed Titanium and Tungsten Oxides for a Sensor of Dissolved Oxygen. Russ. J. Appl. Chem. 2006. 79(4): 596.

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