

A. Bayeshov¹, A.S. Kadirbayeva¹, A.K. Bayeshova^{2*}, A.A. Zharmenov¹

¹National Center on Complex Processing of Mineral Raw Materials of the Republic of Kazakhstan, Almaty, Kazakhstan;

²Al-Farabi Kazakh National University, Almaty, Kazakhstan

(*Corresponding author's e-mail: azhar_b@bk.ru)

Electrochemical Method for Producing a TiO₂ Film with Photocatalytic Properties

The purpose of this work is to study the production process of titanium dioxide during anode polarization in sulfuric acid and hydrochloric acid solutions. The studies were carried out by recording cyclic voltammogram and by measuring the titanium oxidation current with a change in the voltage between the electrodes. It has been established that with a change in the concentration of sulfuric acid in the range of 50–250 g/l and the voltage between the electrodes in the range of 0–25 V, the magnitude of the titanium oxidation current increases and reaches 29.4 mA. With an increase in the concentration of hydrochloric acid from 35 to 100 g/l and a change in the voltage between the electrodes, the titanium oxidation rate increases evenly, but in the voltage range of 10–12 V, a sharp increase in the current magnitude up to 360 mA is observed. A change in the oxidation current indicates an increase in the rate of titanium dissolution. With an increase in the duration of electrolysis, the magnitude of the anode current generally decreases. In all probability, at a voltage of 14 V and higher, a breakdown of the oxide semiconductor film of titanium dioxide is observed in the hydrochloric acid solution. In this regard, a noticeable dissolution of titanium occurs and, subsequently, an oxide film is not produced, but titanium ions are produced. Visual observations have shown that titanium passes into solution in the form of titanium (IV).

Keywords: titanium dioxide, coating, electrode, electrolyzer, polarization, voltage, sulfuric acid, hydrochloric acid.

Introduction

Titanium and its compounds have unique physical, chemical and technical characteristics, and therefore have many applications. Of particular interest is titanium dioxide in the form of powders, as well as in the form of a film produced on its surface. For example, nanocrystalline titanium dioxide (TiO₂) films have photocatalytic properties, and therefore are used in solar cells as an N-type conductivity material and a hole-blocking layer. The thickness of the TiO₂ film and its structure have a significant effect on the characteristics of the solar cell [1].

Titanium dioxide has semiconductor properties and is used in heterogeneous catalysis processes. The photocatalytic activity of titanium dioxide is determined by its physicochemical properties, which depend on the conditions of production [2–6]. Due to its photocatalytic activity, TiO₂ contributes to improving the efficiency of water and air purification processes from toxic organic impurities, to synthesize hydrogen as a result of water photocatalysis, to reduce CO₂ to CH₄ and its homologues [7–10].

Titanium dioxide is increasingly being used as a photocatalyst due to its high chemical resistance, lack of toxicity and low cost [11].

The authors [12] A.K. Abildina, K. Avchukir, R.Z. Dzhumanova, et al. present the results of a study of the morphological characteristics of an anode based on titanium dioxide powder using ellipsometry, scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD), as well as electrochemical properties by cyclic voltammetry. The main stages of anode production were: dispersing, mixing the initial reagents for obtaining homogenized paste and its coating to a substrate, drying and cutting the electrodes. The results of ellipsometry, SEM and EDS showed a uniformly distributed layer of about 200 μm thickness with porous structure, particle diameter in the range of 50–80 nm and titanium dioxide content (45.7 %). The XRD data confirm the formation of an active anode matrix with a monoclinic crystal lattice corresponding to the modification of titanium dioxide (B) with small inclusions of anatase. The electrochemical behavior of the resulting electrode was examined in an Mg(TFSI)₂ solution

based on acetonitrile. In [13], a self-organized nanotubular titanium dioxide (TiO₂) array was obtained by anodizing pure titanium in a mixture of glycerol, distilled water (8 % vol.), and ammonium fluoride using a system with two electrodes. The size and distribution of nanopores were controlled in the DC voltage range from 30 V to 60 V. It was shown that the diameter of TiO₂ nanopores depends on the anodizing voltage. There are research works [14], which show that electrodes for a supercapacitor were prepared by doping titanium dioxide with gold. It has been established that electrodes with a low gold concentration have the best electrochemical characteristics.

A one-step electrochemical method for the deposition of nanocrystalline titanium dioxide films on various carbon substrates is presented by authors [15]. By optimizing the synthesis conditions, the electrodeposition of layers of nanocrystalline and porous titanium dioxide was achieved in only a few minutes. The phase composition of TiO₂ was controlled by varying the composition of the solution. The photoelectrochemical performance of the electrodeposited titanium dioxide films was better or at least comparable to the benchmark P25 titanium dioxide films.

Ali, H.M. in the review [16] presented detailed information about the properties and applications of titanium dioxide. He emphasizes the distinctive characteristics of titanium dioxide, such as high refractive index, extremely high melting and boiling point, high toughness and hardness, photocatalytic nature, ability to absorb or reflect UV rays, DeNox catalyst, nontoxicity, inertness, etc., have led to massive use of TiO₂ in various traditional as well as advanced engineering applications.

The purpose of this work is to study the production process of titanium dioxide during anode polarization in sulfuric acid and hydrochloric acid solutions. The studies were carried out by recording cyclic voltammogram and by measuring the titanium oxidation current with a change in the voltage between the electrodes.

The novelty of the work is due to the fact that for the first time the investigation results of the TiO₂ oxide films formation process on the surface of a titanium electrode by measuring the value of the oxidation current depending on the voltage between the electrodes are presented.

Experimental

The mechanism of titanium dioxide production on the titanium surface was studied by recording anode-cathode cyclic voltammograms and by electrolysis under potentiostatic conditions. Voltammograms recorded with a Cortest CS120 single-channel potentiostat (potential range/resolution: ±10 V/10 mV, current measurement range ±2 A) (Corrtest Instruments Company, China). The voltammograms are recorded using the NOVA 1710 program installed on a personal computer. The main voltammograms were recorded at a potential scan rate of 100 mV/s. Polarograms were recorded in a three-electrode cell. The surface edge of a titanium wire with a diameter of 1.5 mm was used as the working electrode, and a platinum wire was used as the second additional electrode. A silver chloride electrode immersed in a saturated solution of KCl was used as a reference electrode ($E=+203$ mV).

Titanium was used for the experiments, the purity of which corresponds to the elemental analysis data given in Table 1 (all results in mass.%):

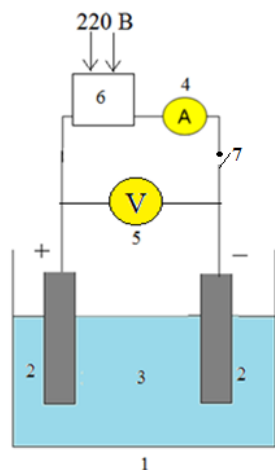
Table 1

Elemental composition of metallic titanium

Spectrum	Ti	Si	Al	O	Total
Spectrum 1	97.56	0.30	0.48	1.67	100
Spectrum 2	98.16	0.30	0.51	1.03	100
Spectrum 3	97.24	0.44	0.44	1.88	100
Average	97.65	0.34	0.48	1.52	100

Further, to clarify the mechanism of production of the titanium oxide film, electrolysis was carried out under potentiostatic conditions, i.e. at certain voltages between the electrodes. The schematic diagram of the installation for obtaining a titanium dioxide film on the titanium surface is shown in Figure 1.

The anodic behavior of the titanium electrode was studied in sulfuric acid (0–250 g/l) and hydrochloric acid (0–100 g/l) solutions. The experiments were carried out in an electrolyzer with a volume of 100 ml, a titanium plate was used as a cathode. The electrolysis was carried out under stationary conditions, i.e. in the absence of electrolyte mixing. The electrodes were polarized using a GPS-1830 D current rectifier.



1 — electrolyzer; 2 — titanium electrodes; 3 — electrolyte (different medium);
4 — ammeter; 5 — voltmeter; 6 — rectifier; 7 — key

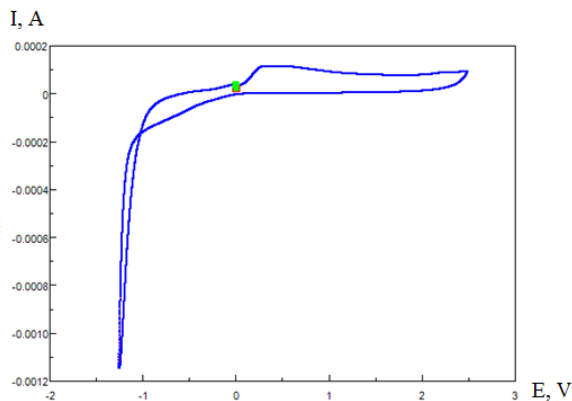
Figure 1. Schematic diagram of the installation for obtaining a TiO₂ film on the surface of a titanium electrode

We carried out preliminary studies, which showed that during the anode polarization of the titanium electrode, a very small current flows through the circuit. The electrode surface is instantly covered with an oxide film, and passivation occurs. In this regard, we studied the effect of the voltage between the electrodes on the current value to study the conditions for the production of titanium dioxide films on the surface of the titanium anode.

The structure of the titanium dioxide film obtained as a result of electrolysis was investigated by methods of physico-chemical analysis. Micrographs of the surface of the synthesized electrode and its elemental composition were obtained using a JSM-6610 LV Scanning Electron Microscope (JEOL company (Japan)). Images of the obtained films were taken using a Canon EOS 2000D EF-S 18-55 SLR camera (Canon company (Japan)).

Results and Discussion

On the anode-cathode voltammograms, obtained in a solution of sulfuric acid with a concentration of 100 g/l, a weakly noticeable maximum is observed at a potential of 0.01 V (Fig. 2). When the potential is shifted further, in the anode direction, the height of the current maximum does not increase. At the same time, it is visually seen that the titanium surface darkens, in all likelihood, titanium oxide films are produced. We believe that, at these potentials, titanium is oxidized through the stage of production of Ti_xO_y oxide films. With a further shift of the anode potential to “plus” 2.6 V, oxygen release on the surface of the titanium electrode is not observed. When the potential is shifted in the cathode direction, at potentials close to “minus” 1.2 V, the hydrogen ion reduction current is observed on the voltammogram.

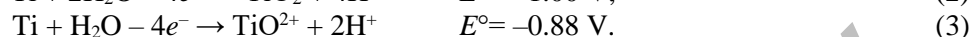
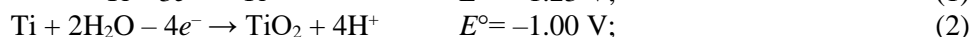
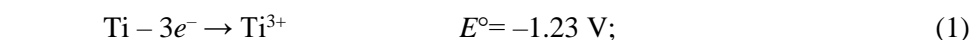


H₂SO₄ — 100 g/l; V = 100 mV/s; t = 25 °C

Figure 2. Cyclic anode-cathode voltammograms of titanium electrode in sulfuric acid solution

Then the anode-cathode cyclic voltammograms were recorded in hydrochloric acid solution. The voltammograms have a similar character, but the value of the anode trans-passivation current has a higher value. The voltammograms are analogous, but the value of the anode transpassivation current is higher. This indicates a more active anodic oxidation of titanium with the production of titanium oxide films.

Based on the analysis of the anode-cathode cyclic voltammograms, it can be assumed in acidic solutions during anode polarization, an oxide film is produced on the titanium surface and, possibly, the electrode is partially dissolved at a very low rate. In this case, the following reactions can occur on the titanium anode:



The main objective of this article is to obtain titanium dioxide on the surface of titanium metal in the form of a thin film. Preliminary studies have shown that during anode polarization of a titanium electrode in aqueous solutions, titanium dioxide (Ti_xO_y) is produced on its surface depending on the experimental conditions (i.e., on the voltage between the electrodes, current density, solution composition, electrolyte temperature, etc.). It is established that, depending on the polarization conditions, various colors of titanium dioxide is produced on the titanium surface.

With anodic polarization of the titanium electrode, apparently it is completely passivated immediately. However the detected currents on the voltammograms and the change in the color of the electrode surface show that titanium is not completely passivated, and its dissolution continues through a layer of oxide films. We have studied the processes occurring under various conditions of electrolysis. The results of the study showed that first a thin layer of titanium oxide with high electrical resistance is formed. Then there is a further increase in the thickness of the titanium oxide films at a very low rate. The oxidation of titanium and the formation of the next layer occur according to a very complex mechanism. The production of new TiO₂ oxide film layers can occur as a result of titanium ionization reactions through micropores of the obtained oxide films. These processes, depending on the conditions of electrolysis (the composition of the electrolyte, the voltage between the electrodes, etc.), the reaction rate of oxide films production proceed differently.

We have studied the rate of titanium oxidation and the production of TiO₂ on its surface depending on various parameters. The influence of the voltage between the electrodes on the current power of titanium oxide production at various concentrations of sulfuric acid is established. The results are presented in Table.2. It is shown that with the concentration growth of sulfuric acid and the voltage between the electrodes, the initial current value for obtaining titanium oxide films by reaction (2) increases (Table 2). For example, at a voltage between the electrodes of 15.0 V, the titanium oxidation current at concentrations of 50, 150, 250 g/l, respectively, is 11.7; 15.5; 18.9 mA. At a concentration of sulfuric acid of 150 g/l and at a voltage between the electrodes of 5.0 V, the oxidation current is 10.0 mpa, and at 25.0 V is 26.1 mA.

Table 2

Influence of voltage between the electrodes on the value of the anode current at various concentrations of sulfuric acid (the current value was measured 3 minutes after the voltage was applied)

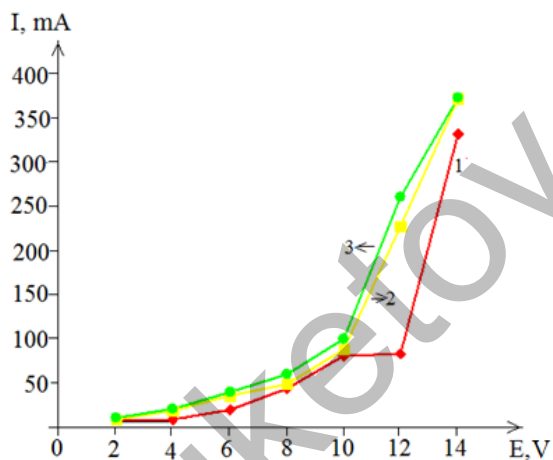
H ₂ SO ₄ , g/l	The value of the anode current, mA					
	E, V					
	0	5.0	10.0	15.0	20.0	25.0
50	0	1.1	5.0	11.7	16.0	23.4
150	0	10.0	12.4	15.5	19.3	26.1
250	0	12.2	13.3	18.9	20.8	29.4

The experimental results showed that, in all cases, the value of the anode oxidation current decreases over time (Table 3). At the beginning of the polarization process, the oxidation current has a large value, but after a while its decrease is observed. Within 60 minutes, the anode current decreases and its value reaches 0. This indicates that in a sulfuric acid solution, the anode current flowing through the titanium electrode is mainly consumed for the production of titanium dioxide on its surface.

Influence of the duration of electrolysis on the value of the anode current at different voltages between the electrodes in a solution of sulfuric acid: H_2SO_4 — 150 g/l, $t = 25\text{ }^\circ\text{C}$

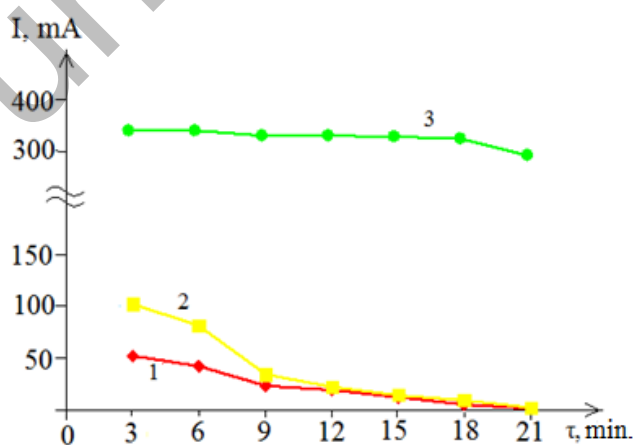
E, V	The value of the anode current, mA								
	τ , min								
	0	3	6	9	12	15	18	21	24
5.0	121.1	10.0	0.64	0.38	0.28	0.25	0.19	0.15	0.12
10.0	152.2	12.4	11.5	11.3	8.6	7.7	6.3	5.9	5.1
15.0	154.4	15.5	12.3	11.6	10.4	9.5	8.4	8.0	7.5

The process of production of an oxide film on titanium in hydrochloric acid solutions was studied. It was established that the oxidation of titanium in a hydrochloric acid solution proceeds more intensively compared to the process occurring in a sulfuric acid solution. There are dependences on the Figures 3 and 4 showing that with an increase in the concentration of hydrochloric acid and the voltage between the electrodes, the rate of titanium oxidation grows evenly. However, at a voltage of 10–12 V, a sharp increase in the dissolution rate of titanium is observed (judging by the magnitude of the oxidation current). At hydrochloric acid concentrations of 35, 70, 100 g/l, the anode current value is 325, 365, 366 mA, respectively (the current value was measured 3 minutes after the voltage was applied) (Fig. 3). With an increase in the duration of electrolysis, the value of the anode current decreases. However, at a voltage of 14 V, the anode current increases sharply within 30 minutes and slightly decreases from 360 to 320 mA (Fig. 4). We believe that a breakdown of the oxide film of titanium dioxide is observed in a hydrochloric acid solution at a voltage of 14 V and above. In this regard, titanium dissolves, further oxide production does not occur, but titanium ions are produced. It is visually observed the solution remains colorless, which indicates the production of tetravalent titanium ions. The production of trivalent ions is excluded, since they have a purple color.



Concentrations of hydrochloric acid, g/l:
1 — 35; 2 — 70; 3 — 100

Figure 3. Influence of the voltage between the electrodes on the value of the anode oxidation current on titanium at different concentrations of hydrochloric acid



HCl — 70 g/l, $t = 25\text{ }^\circ\text{C}$;
1 — 8.0 V; 2 — 10.0 V; 3 — 14.0 V

Figure 4. Influence of the duration of electrolysis on the value of the anode oxidation current of titanium at different voltages between the electrodes

Thus, we have established that in a hydrochloric acid solution with anode polarization, the production of titanium dioxide occurs only at low voltages between the electrodes, not exceeding 10 V, and in a sulfuric acid solution, inclusive, 25 V.

Identification of the TiO_2 film produced as a result of electrolysis of sulfuric acid solutions at a voltage not higher than 10 V was carried out using physical and chemical methods. As the results of the physical and chemical analysis showed, in all cases, titanium oxide of the composition TiO_2 is produced on the surface of titanium (Table 4).

Table 4

The composition of the oxide film produced on the surface of the electrode in a solution of sulfuric acid:
 H_2SO_4 — 50 g/l, $E=20$ V, $\tau=1$ hour, $t=25$ °C

Spectrum	O	Ti	Si	Al	Fe	Zn	Total
Spectrum 1	37.09	62.42	0.09	0.07	0.26	0.09	100
Spectrum 2	39.55	59.79	0.10	0.05	0.37	0.14	100
Spectrum 3	40.28	58.90	0.09	0.09	0.37	0.28	100
Average	38.97	60.37	0.09	0.07	0.33	0.17	100

Micrographs of films on a titanium electrode are shown in Figure 5. The micrograph in Figure 5a was obtained by a magnification of 3000 times, in Figure 5b — by a magnification of 1000 times. In both cases, the grain size of the particles is visible.

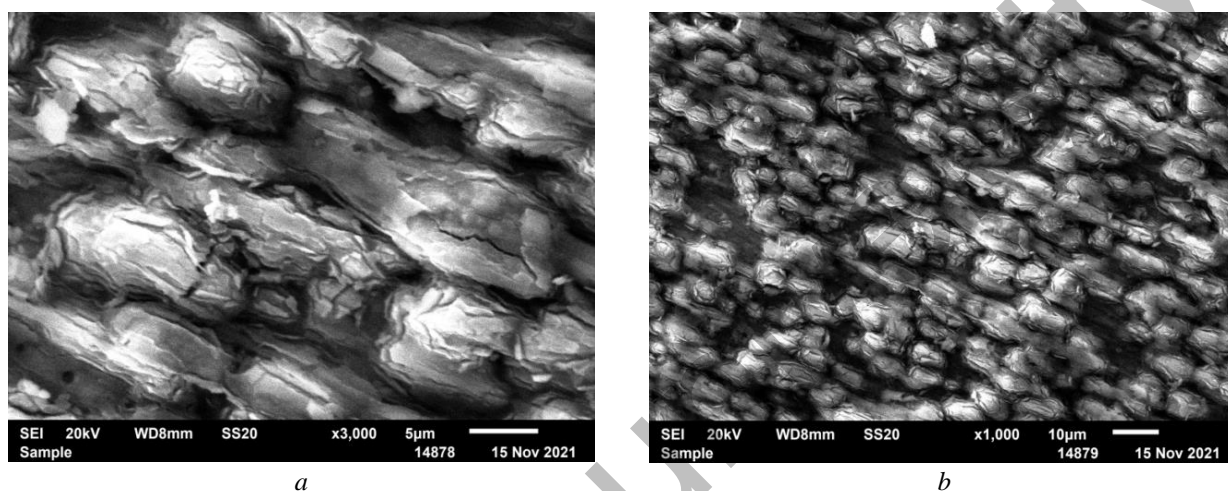
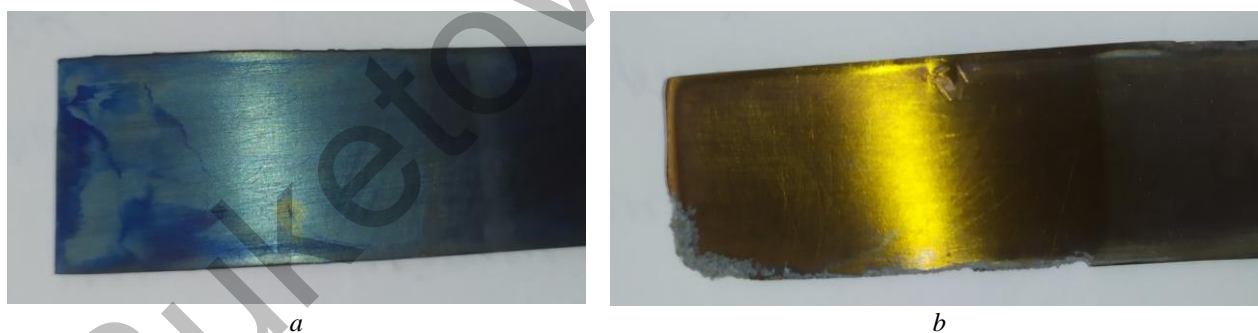


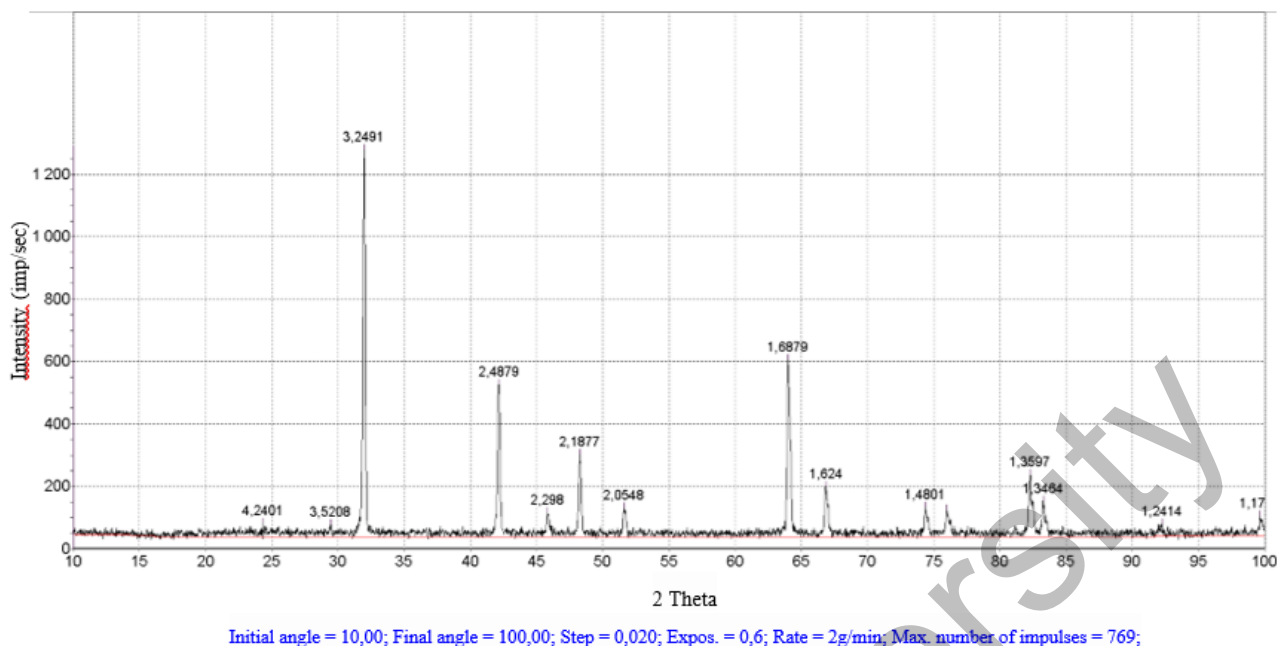
Figure 5. Micrographs of titanium dioxide films produced on the surface of a titanium anode in a sulfuric acid solution with an increase: a) 3000 times; b) 1000 times



a — H_2SO_4 — 150 g/l; $E = 10$ V; $\tau = 1$ hour; b — HCl — 70 g/l, $E = 10$ V; $\tau = 1$ hour

Figure 6. Photographs of the titanium surface after electrolysis of the coated oxide film

Researchers Kuz'mina M.Yu., Belik O.D. [17] argue that films often produced on the surface of metals have non-uniform thickness. Using X-ray diffraction analysis, they studied the composition of oxide layers on titanium during its anodization in aqueous solutions of acids and alkalis in galvanostatic and potentiostatic conditions. It is shown that the composition of the films obtained in aqueous electrolytes, along with the basic oxide TiO₂ (anatase), also includes a number of lower oxides (Ti₄O₇, Ti₃O₅, Ti₂O₃, TiO). It is known from the literature [18] that, during the electrochemical oxidation of titanium, oxide films with an interference color are formed. In our experiments, light blue films were obtained in a solution of sulfuric acid and golden yellow in a solution of hydrochloric acid (Fig. 6). The composition of the film was identified by X-ray phase analysis (Fig. 7) as titanium dioxide in the form of anatase (all reflections refer to TiO₂).



Reflexes: 3.24; 2.48; 2.29; 2.18; 2.05; 1.68; 1.62; 1.48; 1.35; 1.34; 1.24; 1.17 Å — TiO₂ (ASTM 73-2224)

Figure 7. X-ray of titanium dioxide

Conclusions

Titanium is an unusual metal with special properties. It does not dissolve under normal conditions in aqueous solutions of acids and during anodic polarization, i.e. it undergoes passivation, since an oxide film forms on its surface. It is believed that after the formation of an oxide film, the dissolution of titanium stops completely. However, the results of our studies have shown, titanium continues to oxidize even with further polarization. This can be judged by the increase current value of the titanium oxidation with a change in the voltage between the electrodes as a function of time. It has been established that transpassive dissolution occurs in the sulfuric acid medium, while the value of the oxidation current reaches 29.4 mA at a voltage of 25 V, and in the hydrochloric acid medium, the oxidation current reaches 360 mA at a voltage of 14 V. These data show that titanium continues transpassive oxidation in electrolyte solutions, and in a hydrochloric acid medium, the dissolution rate increases significantly.

Acknowledgments

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References

- 1 Малюков С.П. Исследование влияния толщины пленки TiO₂ на фотоэлектрические характеристики перовскитовых солнечных элементов / С.П. Малюков, А.В. Саенко, Д.А. Бондарчук // Инженер. вестн. Дона. — 2016. — № 4. — С. 63.
- 2 Shvets P.V. Suppression of the metal-insulator transition in magnetron sputtered Ti₂O₃ films / P.V. Shvets, D. Caffrey, K. Fleischer, I. Shvets, K. O'Neill, G.S. Duesberg, A.N. Vinichenko, Yu.K. Maksimova, & Yu.A. Goikhman // Thin Solid Films. — 2020. — 694, 137642. <https://doi.org/10.1016/j.tsf.2019.137642>
- 3 Бессель В.В. Изучение солнечных фотоэлектрических элементов: учеб.-метод. пос. / В.В. Бессель, В.Г. Кучеров, Р.Д. Мингалеева — М.: Изд. центр РГУ нефти и газа (НИУ) им. И.М. Губкина, 2016. — 90 с.
- 4 Wang X., Fang Y., He L., Wang Q., Wu T. Influence of compact TiO₂ layer on the photovoltaic characteristics of the organometal halide perovskite-based solar cells // Materials Science in Semiconductor Processing. — 2014. — Vol. 27. — P. 569–576. <https://doi.org/10.1016/j.mssp.2014.07.039>

- 5 Jung H.S., Park N.-G. Perovskite solar cells: From materials to devices // Small. — 2014. — Vol. 11, No. 1. — P. 10–25. <https://doi.org/10.1002/sml.201402767>
- 6 Minemoto T., Murata M. Device modeling of perovskite solar cells based on structural similarity with thin film inorganic semiconductor solar cells // Journal of Applied Physics. — 2014. — Vol. 116, No. 5. — P. 054505. <https://doi.org/10.1063/1.4891982>
- 7 Рыков А.Н. Фотокатализаторы на основе диоксида титана: получение и применение / А.Н. Рыков, В.А. Белоусова // Инженеры будущего: Открытая городская науч.-практ. конф. — 2020. — С. 367–370.
- 8 Сидак И.Л. Фотокаталитические устройства и способы очистки воды / И.Л. Сидак, В.Ф. Раков, В.М. Погибко // Инновационные перспективы Донбасса. — 2020. — С. 30–34.
- 9 Бубнов В.В. Разработка плазмодинамического метода синтеза ультрадисперсного диоксида титана TiO₂, обладающего фотокаталитическими свойствами получения водорода: магистер. дис. / В.В. Бубнов; Национальный исследовательский Томский политехнический университет; Инженерная школа энергетики; Отделение электроэнергетики и электротехники; науч. рук. А.А. Сивков. — Томск, 2019.
- 10 Деревщиков В.С. Способ получения метана из атмосферного диоксида углерода / В.С. Деревщиков, А.Г. Окунев, А.И. Лысиков, Ж.В. Веселовская. Патент № 2533710 С1 Российская Федерация, МПК C07C 9/04, C07C 1/12, B01J 23/60. № 2013143033/04: заявл. 23.09.2013; опубл. 20.11.2014; заявитель Федеральное государственное бюджетное учреждение науки Институт катализа им. Г.К. Борескова Сиб. отд. РАН.
- 11 Zhou Y., Gray-Weale A. A numerical model for charge transport and energy conversion of perovskite solar cells // Physical Chemistry Chemical Physics. — 2016. — Vol. 18, No. 6. — P. 4476–4486. <https://doi.org/10.1039/c5cp05371d>
- 12 Abildina A.K., Avchukir K., Dzhumanova, R.Z., Beiseyeva A.N., Rakhymbay G.S., Argimbayeva A.M. Preparation and electrochemical characterization of TiO₂ as an anode material for magnesium-ion batteries // Bulletin of the University of Karaganda Chemistry. — 2021. — Vol. 104(4). — P. 104–116. <https://doi.org/10.31489/2021ch4/104-116>
- 13 Zakir O., Idouhli R., Elyaagoubi M., Khadiri M., Aityoub A., Koumya Y., Rafqah S., Abouelfida A., Outzourhit A. Fabrication of TiO₂ nanotube by Electrochemical Anodization: Toward photocatalytic application // Journal of Nanomaterials. — 2020. — Vol. 1. — P. 11. <https://doi.org/10.1155/2020/4745726>
- 14 Shaalan N.M., Ahmed F., Rashad M., Kumar S., Saber O., Al-Naim A.F., Kotb H.M., Ezzeldien M., Mahmoud A.Z. Ceramic Ti/TiO₂/AuNP Film with 1-D Nanostructures for Selfstanding Supercapacitor Electrodes // Crystals. — 2022. — Vol. 12. — P. 791. <https://doi.org/10.3390/cryst12060791>
- 15 Endrődi B., Kecsenovity E., Rajeshwar K., Janáky C. One-step electrodeposition of nanocrystalline TiO₂ films with enhanced photoelectrochemical performance and Charge Storage // ACS Applied Energy Materials. — 2018. — Vol. 1, No. 2. — P. 851–858. <https://doi.org/10.1021/acsaem.7b00289>
- 16 Ali H.M. Titanium Dioxide-Advances and Applications. — London: IntechOpen, 2022. — 244 p. <https://doi.org/10.5772/intechopen.94670>
- 17 Кузьмина М.Ю. Изучение коррозионной стойкости оксидных плёнок на титане / М.Ю. Кузьмина, О.Д. Белик // Машины, агрегаты и процессы. Проектирование, создание и модернизация. — 2018. — С. 179–181.
- 18 Кузьмина М.Ю. Коэффициент контраста титанового электрохромного электрода / М.Ю. Кузьмина, М.П. Кузьмин // Вестн. ИрГТУ. — 2011. — № 8 (55). — С. 139–143.

А. Баешов, А.С. Кадирбаева, А.Қ. Баешова, А.А. Жарменов

Фотокаталитикалық қасиетке ие TiO₂ жабынын алудың электрохимиялық әдісі

Жұмыстың мақсаты күкіртқышқылды және тұз қышқылды ерітінділерде анодтық поляризация кезінде титан диоксидінің түзілу процесін зерттеу. Зерттеулер циклді потенциодинамикалық вольтамперлік қисықты түсіру және электродтар арасындағы кернеудің өзгеруіне байланысты титанның тотығу тогының шамасын өлшеу арқылы жүргізілді. Күкірт қышқылының концентрациясын 50–250 г/л аралығында және электродтар арасындағы кернеуді 0–25 В аралығында өзгерткенде, титанның тотығу тогының шамасы өсетіні және бұл шама 29,4 мА-ге жететіні анықталды. Тұз қышқылының концентрациясын 35-тен 100 г/л-ге дейін өзгерткенде және электродтар арасындағы кернеуді 0–14 В аралығында өзгерткенде, титанның еру жылдамдығы бір қалыпты өсетіні, бірақ кернеудің мәні 10–12 В арасында болғанда титанның тотығу тогы күрт өсіп, 360 мА-ге жететіні көрсетілді. Тотығу тогының өзгеруі титанның еру жылдамдығының артатынын дәлелдеді. Электролиз ұзақтығын арттыру кезінде анодтық токтың шамасы негізінен азаяды. Шамасы, кернеу 14 В және одан да жоғары болған кезде тұз қышқылды ерітіндіде жарғылай өткізгіштік қасиетке ие титан диоксидінің пленкасының тесілуі орын алады. Осыған байланысты титанның айтарлықтай мөлшерде еруі байқалады және одан ары қарай оксидтік пленка түзілмейді де, титан иондары түзіледі. Көрнекі бақылаулар титанның титан (IV) түріндегі ерітіндіге ауысатынын көрсетті.

Кілт сөздер: титан, титан диоксиді, пленка, электрод, тотығу тогы, поляризация, кернеу, күкірт қышқылы, тұз қышқылы.

А. Баешов, А.С. Кадирбаева, А.К. Башова, А.А. Жарменов

Электрохимический способ получения пленки TiO₂, обладающей фотокаталитическими свойствами

Целью работы является изучение процесса формирования диоксида титана при анодной поляризации в сернокислых и солянокислых растворах. Исследования проводили методом снятия потенциодинамической циклической вольтамперной кривой и методом измерения величины тока окисления титана при изменении напряжения между электродами. Установлено, что с изменением концентрации серной кислоты в интервале 50–250 г/л и напряжения между электродами в пределах 0–25 В величина тока окисления титана возрастает и достигает 29,4 мА. При увеличении концентрации соляной кислоты от 35 до 100 г/л и изменении напряжения между электродами величина скорости окисления титана растет равномерно, но в интервале значений напряжения 10–12 В наблюдается резкое повышение величины тока до 360 мА. Изменение тока окисления свидетельствует об увеличении скорости растворения титана. С увеличением продолжительности электролиза величина анодного тока в основном уменьшается. По всей вероятности при напряжении, равном 14 В и выше, в солянокислом растворе наблюдается пробой оксидной полупроводниковой пленки диоксида титана. В этой связи происходит заметное растворение титана и в дальнейшем оксидная пленка не образуется, а образуются ионы титана. Визуальные наблюдения показали, что титан переходит в раствор в виде титана (IV).

Ключевые слова: титан, диоксид титана, пленка, электрод, ток окисления, поляризация, напряжение, серная кислота, соляная кислота.

References

- 1 Maliukov, S.P., Saenko, A.V., & Bondarchuk, D.A. (2016). Issledovanie vliianiia tolshchiny plenki TiO₂ na fotoelektricheskie kharakteristiki perovskitovykh solnechnykh elementov [Investigation of the effect of TiO₂ film thickness on the photovoltaic characteristics of perovskite solar cells]. *Inzhenernyi vestnik Dona — Engineering Bulletin of the Don* [in Russian].
- 2 Shvets, P.V., Caffrey, D., Fleischer, K., Shvets, I., O'Neill, K., Duesberg, G.S., Vinichenko, A.N., Maksimova, Yu.K., & Goikhman, Yu.A. (2020). Suppression of the metal-insulator transition in magnetron sputtered Ti₂O₃ films. *Thin Solid Films*, 694, 137642. <https://doi.org/10.1016/j.tsf.2019.137642>
- 3 Bessel, V.V., Kucherov, V.G., & Mingaleeva, R.D. (2016). *Izuchenie solnechnykh fotoelektricheskikh elementov [Study of solar photovoltaic cells]*. Moscow: Izdatelskii tsentr RGU nefti i gaza (NIU) imeni I.M. Gubkina [in Russian].
- 4 Wang, X., Fang, Y., He, L., Wang, Q., & Wu, T. (2014). Influence of compact TiO₂ layer on the photovoltaic characteristics of the organometal halide perovskite-based solar cells. *Materials Science in Semiconductor Processing*, 27, 569–576. <https://doi.org/10.1016/j.mssp.2014.07.039>
- 5 Jung, H.S., & Park, N.-G. (2014). Perovskite solar cells: From materials to devices. *Small*, 11(1), 10–25. <https://doi.org/10.1002/sml.201402767>
- 6 Minemoto, T., & Murata, M. (2014). Device modeling of perovskite solar cells based on structural similarity with thin film inorganic semiconductor solar cells. *Journal of Applied Physics*, 116(5), 054505. <https://doi.org/10.1063/1.4891982>
- 7 Rykov, A.N., & Belousova, V.A. (2020). Fotokatalizatory na osnove dioksida titana: poluchenie i primeneniye [Photocatalysts based on titanium dioxide: production and application]. *Otkrytaia gorodskaiia nauchno-prakticheskaiia konferentsiia «Inzheneriy budushchego»*, 367–370 [in Russian].
- 8 Sidak, I.L., Rakov, V.F., & Pogibko, V.M. (2020). Fotokataliticheskie ustroistva i sposoby ochistki vody [Photocatalytic devices and water treatment methods]. *Innovatsionnye perspektivy Donbassa*, 30–34 [in Russian].
- 9 Bubnov, V.V. (2019). Razrabotka plazmodinamicheskogo metoda sinteza ultradispersnogo dioksida titana TiO₂, obladaushchego fotokataliticheskimi svoystvami polucheniia vodoroda [Development of a plasmodynamic method for the synthesis of ultrafine titanium dioxide TiO₂, which has photocatalytic properties for hydrogen production]. *Master's dissertation — masterskaia dissertatsiia*. Tomsk: Natsionalnyi issledovatel'skii Tomskii politekhnicheskii universitet [in Russian].
- 10 Derevshchikov, V.S., Okunev, A.G., Lysikov, A.I., & Veselovskaia, J.V. (2014). Sposob polucheniia metana iz atmosfernogo dioksida ugleroda [Method for producing methane from atmospheric carbon dioxide]. *Patent № 2533710 CI Rossiiskaia Federatsiia* [in Russian].
- 11 Zhou, Y., & Gray-Weale, A. (2016). A numerical model for charge transport and energy conversion of perovskite solar cells. *Physical Chemistry Chemical Physics*, 18(6), 4476–4486. <https://doi.org/10.1039/c5cp05371d>
- 12 Abildina, A.K., Avchukir, K., Dzhumanova, R.Z., Beiseyeva, A.N., Rakhymbay, G.S., & Argimbayeva, A.M. (2021). Preparation and electrochemical characterization of TiO₂ as an anode material for magnesium-ion batteries. *Bulletin of the Karaganda University. "Chemistry" Series*, 104(4), 104–116. <https://doi.org/10.31489/2021ch4/104-116>
- 13 Zakir, O., Idouhli, R., Elyaaoubi, M., Khadiri, M., Aityoub, A., Koumya, Y., Rafqah, S., Abouelfida, A., & Outzourhit, A. (2020). Fabrication of TiO₂ nanotube by Electrochemical Anodization: Toward photocatalytic application. *Journal of Nanomaterials*, 2020, 1–11. <https://doi.org/10.1155/2020/4745726>

- 14 Shaalan, N.M., Ahmed, F., Rashad, M., Kumar, S., Saber, O., Al-Naim, A.F., & Mahmoud, A.Z. (2022). Ceramic Ti/TiO₂/AuNP Film with 1-D Nanostructures for Selfstanding Supercapacitor Electrodes. *Crystals*, 12(6), 791. <https://doi.org/10.3390/cryst12060791>
- 15 Endrődi, B., Kecsenovity, E., Rajeshwar, K., & Janáky, C. (2018). One-step electrodeposition of nanocrystalline TiO₂ films with enhanced photoelectrochemical performance and Charge Storage. *ACS Applied Energy Materials*, 1(2), 851–858. <https://doi.org/10.1021/acsaem.7b00289>
- 16 Ali, H.M. (2022). Titanium Dioxide-Advances and Applications. <https://doi.org/10.5772/intechopen.94670>
- 17 Kuzmina, M.Yu., & Belik, O.D. (2018). Izuchenie korrozionnoi stoikosti oksidnykh plenok na titane. *Mashiny, agregaty i protsessy. Proektirovanie, sozdanie i modernizatsiia*, 179–181 [in Russian].
- 18 Kuzmina, M.Yu., & Kuzmin, M.P. (2011). Koeffitsient kontrasta titanovogo elektrokromnogo elektroda. *Vestnik IrGTU*, 8(55), 139–143 [in Russian].

Information about authors*

Bayeshov, Abduali — Doctor of Chemical Science, Professor, Academician of the National Academy of Sciences of the Republic of Kazakhstan, Republican State Enterprise “National Center on Complex Processing of Mineral Raw Materials of the Republic of Kazakhstan”, Karasay batyr street, 111–113, 050012, Almaty, Kazakhstan, e-mail: bayeshov@mail.ru; <https://orcid.org/0000-0003-0745-039X>

Kadirbayeva, Altnay — PhD, Senior researcher, Republican State Enterprise “National Center on Complex Processing of Mineral Raw Materials of the Republic of Kazakhstan”, MTF-2 street, 44/1, 040998, Almaty, Kazakhstan, e-mail: altnay_aidyn2789@mail.ru; <https://orcid.org/0000-0003-0702-1114>

Bayeshova, Azhar (*corresponding author*) — Doctor of Technical Sciences, Professor, Al-Farabi Kazakh National University, 050012, Almaty, Kazakhstan, e-mail: azhar_b@bk.ru; <https://orcid.org/0000-0002-9076-8130>

Zharmenov, Abdurassul — Doctor of Technical Sciences, Professor, Academician of the National Academy of Sciences of the Republic of Kazakhstan, Republican State Enterprise “National Center on Complex Processing of Mineral Raw Materials of the Republic of Kazakhstan”, Zhandosov street, 67, 050036, Almaty, Kazakhstan, e-mail: nc@cmrp.kz; <https://orcid.org/0000-0001-5651-5343>

*The author's name is presented in the order: *Last Name, First and Middle Names*