



Electroanalytical properties of metal–oxide electrodes formed by plasma electrolytic oxidation

Galina I. Marinina^a, Marina S. Vasilyeva^{a,b,*}, Antonina S. Lapina^a, Alexander Yu. Ustinov^{a,b}, Vladimir S. Rudnev^{a,b}

^a Far Eastern Federal University, ul. Sukhanova 8, Vladivostok 690950, Russia

^b Institute of Chemistry, Far Eastern Branch of Russian Academy of Sciences, Prosp. 100-letiya Vladivostoka 159, Vladivostok 690022, Russia

ARTICLE INFO

Article history:

Received 21 June 2012

Received in revised form 10 October 2012

Accepted 23 October 2012

Available online 29 November 2012

Keywords:

Metal oxide electrode

Plasma electrolytic oxidation

Potentiometric titration

ABSTRACT

Ti/TiO₂ and Ti/TiO₂/Pt electrodes were prepared using the method of plasma electrolytic oxidation (PEO) and applied for potentiometric indication of different types of chemical reactions. The structural features of surface electrodes have been investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and energy-dispersive spectroscopy (EDS) techniques. On the surface of modified Ti/TiO₂/Pt electrodes platinum is present in an atomic state in the form of nanoparticles. Ti/TiO₂/Pt electrodes showed an excellent performance for end-point indication potentiometric titrations similarly to the traditional Pt electrodes. In addition, this sensor has some good analytical characteristics such as sensitivity, good reproducibility, and simple preparation procedure. As compared with the monolith Pt electrode, the Ti/TiO₂/Pt electrode showed several advantages including low cost and high stability.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Development and studies of novel highly sensitive and selective, reliable, and durable sensors enables one to expand the possibilities of application of electrochemical methods of analysis in solving analytical problems focused on ecological issues. Semiconductor electrodes, including metal–oxide ones modified in some cases by noble metals, appear to be promising as sensors for different types of potentiometric titration [1–3]. Although the development of novel sensors based on semiconductor materials for liquid media analysis does not attract sufficient interest, their good combination of properties, namely, high hardness, chemical stability in aggressive media, and surface structural features provides broad prospects for application in creating electrochemical sensors. The metal–oxide electrode behavior is determined by properties of its oxide film: chemical composition, electro- or ionic conductivity, surface structure, and other factors [3]. The authors [4] demonstrated polyfunctional features of electrodes of this type and the possibilities of their application as indicator electrodes in different variants of potentiometric titration. In view of the above, a special interest is concerned with studies of electroanalytical properties of metal–oxide electrodes produced by deposition of oxides of specific properties on different substrates. In particular, one should mention here films of titanium dioxide which is an *n*-type

* Corresponding author. Present Address: Far Eastern Federal University, ul. Sukhanova 8, Vladivostok 690950, Russia. Tel.: +79245252136.

E-mail address: vasilyeva_ms@sns.dvfu.ru (M.S. Vasilyeva).

semiconductor and characterized by high dielectric constant, refraction coefficient, and chemical stability in aggressive media. Thin TiO₂ films can be used as sensors for different ions [5–9]. TiO₂ films can be produced by means of the magnetron scattering method [10], sol–gel processes [11], metal–organic chemical vapor (gas) deposition (MOCVD) [12], or chemical vapor deposition (CVD) [13].

Oxide layers having versatile chemical compositions and high adhesion to a substrate can be obtained on the surface of valve metals, including titanium, using a simple single-stage method of plasma electrolytic oxidation (PEO) [14–18]. PEO is accompanied by the inclusion of electrolyte components into coatings and formation, under certain conditions, of developed (porous, defect) surface that in a number of cases could be characterized by high sorption and ion exchange properties.

Depending on the electrolyte composition and the oxidation conditions, on the titanium surface one can obtain, using the PEO method, titanium oxide in anatase or rutile modifications [14–17]. The authors of [19] demonstrated the possibility of using oxide layers on titanium formed by PEO in phosphate electrolyte as indicator electrodes in the process of precipitation potentiometric titration of phosphate solutions by silver ions. The presence of the pH-function and strengthening of the “phosphate” function with the phosphorus content increase in a coating were established. The authors also revealed indicator properties of PEO–titanium samples at potentiometric acid–base titration and established the dependencies of stationary potentials on the redox-system nature and their independence of the system components concentration

ratio as well as the absence of a signal at potentiometric oxidation–reduction titration indicating to the coatings low electronic conductivity.

As was demonstrated in [15], in borate electrolyte on titanium the PEO method yielded the formation of films containing TiO₂ in the rutile modification – a thermodynamically stable phase characterized by high stability in chemically aggressive media. Such oxide layers have low electrical conductivity as in air as in 3% NaCl solution. According to [20], the increase of the electronic conductivity and improvement of electrocatalytical and operational properties of PEO-layers on titanium can be attained by deposition of ruthenium hydroxochloride or its mixture with titanium chloride on these structures. At the same time, titanium–oxide film electrodes doped with microquantities of platinum group metals are known as efficient catalysts of many electrochemical processes [21,22]. The advantages of these electrode systems consist in relatively inexpensive cost due to low noble metal content and high electrocatalytical activity that is in some cases higher than that of platinum electrode due to high dispersion of platinum particles in the titanium–oxide substrate. According to [22], the effect of increasing activity of the dispersed particle on a substrate, as compared to electrocatalyst of the same chemical composition, can be attained through electronic interaction of microparticles with the substrate. Such systems are promising in view of their application as indicator electrodes because of the simplicity of fabrication, operation, and storage as well as low cost and high stability in aggressive media. One of the most promising directions in creation of such electrode systems consists in thermal decomposition of noble metal salts on the surface of an electrode substrate: it is evident that PEO-layers can be used in the role such a substrate. The most important advantages of this method include its affordability and simplicity of implementation as well as the possibility of using platinum-containing waste processing products as promoting agents. Thus, the combination of the PEO method and deposition of noble metal salts on the formed layers followed by salts thermal decomposition enables one to form electrode systems that are promising for application as indicator electrodes.

The objective of the present work was to study electroanalytical properties of metal–oxide electrodes formed using the PEO method in tetraborate electrolyte, including those additionally modified by platinum.

2. Experimental

2.1. Preparation of electrodes

Electrodes were produced from sheet titanium of VT1-0 grade as plates of a size of 2.5 × 1.0 × 0.1 cm. For metal surface layer removal and surface standardization, the samples were chemically polished in a mixture of concentrated hydrofluoric and nitric acids (ratio HF:HNO₃ = 1:3) at a temperature of 60–80 °C for 2–3 s.

Oxide films on titanium Ti/TiO₂ were formed using the PEO method in 0.1 M aqueous solution of Na₂B₄O₇ under galvanostatic conditions ($i = 0.2 \text{ A cm}^{-2}$) for 10 min in accordance with the technique described in [15]. A part of the samples was annealed at 500 °C for 4 h (Ti/TiO₂).

To modify with platinum, titanium plates with oxide layers deposited using the PEO method (PEO-method) were immersed in aqueous solutions of H₂PtCl₆ of concentrations 3 × 10⁻¹ M (Ti/TiO₂/Pt¹), 1 × 10⁻⁴ M (Ti/TiO₂/Pt²) at stirring for 1 h, dried and annealed at 500 °C for 4 h.

2.2. Chemicals

During studies of pH-sensitivity of PEO-layers on titanium, universal buffer solutions in a broad pH range were used. Solutions of

NaOH, AgNO₃, Ce(SO₄)₂, K₂Cr₂O₇, and EDTA-Na of different concentrations were used as titrants in potentiometric titration measurements. Solutions of NaOH, AgNO₃ were pre-standardized. Other solutions were prepared by dissolution of accurately weighed samples. The chemicals were of analytical pure grades.

2.3. Potentiometric measurements

The electrode studies were performed in the absence of external polarization under the conditions of potentiometric titration with one indicator electrode. The titration end point was found from the potential jump corresponding to the point of chemical reaction completion.

Potentiometric measurements were carried out using a Radelkis OP-265/1 ion- and pH-meter. An Ag/AgCl reference electrode was used.

The titration was carried out using an OP-930/1 automatic burette in a 50 mL chemical glass. The solution was stirred by a magnetic stirrer. The electrodes (working and reference) were placed into the solution to be titrated. Titrant was added by 1 mL portions. The potential value was measured upon reaching a stationary value.

To determine the rate of establishment of a stationary potential value, the method of building kinetic curves in the process of titration was used. Upon addition of the next in turn titrant portion in the process of potentiometric titration, the values were recorded within specified periods of time until a constant value is attained.

2.4. Surface element analysis and coatings morphological characteristics

X-ray spectral analysis (XSA) and X-ray photoelectron spectroscopy (XPS) methods were applied to determine the film surface element composition. In the former case, a JEOL SUPERPROBE JXA 8100 microprobe spectral analyzer was used. The obtained data were averaged over 1 × 1 μm² surface area. The depth of the analyzed layer was about 2–5 μm. Simultaneously, the surface electron microscopy images were obtained. The XPS spectra were measured on a SPECS ultrahigh vacuum system unit using a 150-mm electrostatic hemispheric analyzer. The Mg Kα radiation was applied for ionization. The spectra calibration was made on C1s-lines of hydrocarbons whose energy was assumed to be equal to 285.0 eV. The obtained data were averaged over 1 × 1 mm² surface area.

3. Results and discussion

3.1. Application of PEO-electrodes as indicator electrodes in potentiometric acid-base titration in aqueous solutions

3.1.1. E-pH dependence for PEO-electrodes

E-pH electrode functions of both unmodified (Ti/TiO₂) and platinum-modified PEO-electrodes are linear over the whole pH range under study, Fig. 1. The $E = a - bpH$ equation and correlation coefficients (r^2) of these dependencies are shown in Table 1. The correlation coefficients of all PEO-electrodes approximated 1 that indicates to the E-pH function linearity. Since upon annealing the Ti/TiO₂ electrode function did not virtually change, PEO-electrodes annealing does not affect their pH-sensitivity (Table 1). PEO-coatings impregnation in 10⁻³ M solution of H₂PtCl₆ results in some increase of the E-pH curve slope. However, upon impregnation in more concentrated solution, the curve slope of the of PEO-coatings electrode function decreases down to the initial value. One can assume that titanium oxide present in the coating composition has the main role in the potential formation. The reaction

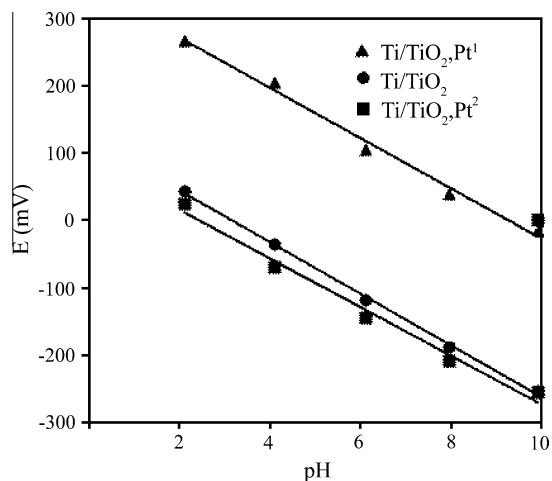


Fig. 1. E-pH function for PEO-electrodes.

Table 1

Parameters of linear regression $E = a - bpH$ ($n = 3$; $P = 0.95$).

Electrode	E (mV)		
	a	b	r^2
Ti/TiO ₂	155.9	-30.9	0.91
Ti/TiO ₂ ²	71.5	-30.4	0.97
Ti/TiO ₂ /Pt ¹	227.4	-29.1	0.98
Ti/TiO ₂ /Pt ²	122.7	-38.5	0.98

TiO₂ + 4H⁺ + 4e = Ti + 2H₂O (E^0 (NHE) = -0.86 V), whose potential corresponds to the equation $E = a - bpH$, occurs on the metal-oxide titanium electrode Ti/TiO₂. In this case the slope coefficients in the equation are lower than the Nernst ones, which is characteristic for a metal-oxide system and can be related to the differences in stoichiometric compositions of oxides of the metals under study, their semiconductor properties, method of synthesis, surface conditions, and the presence of borate groups incorporated into the PEO-film during the oxidation process. The value of the coefficient a depends on the electrode surface conditions, oxide nature etc. In this case its value approximates that of the unmodified PEO-electrode indicating to the effect of titanium dioxide PEO-layers on pH-functions. Impregnation of PEO-layers in more concentrated H₂PtCl₆ solution shifts the pH-function to more positive potential range which must be caused by the effect of a noble metal on the potential value. Taking into account the fact that the correlation coefficients of the dependence E-pH are close to 1, such electrodes can be applied in acid-base titration as indicator ones.

3.1.2. Potentiometric acid-base titration

Fig. 2 shows integral curves of the acid-base titration for modified and unmodified PEO-electrodes. For all the electrodes under study, a potential jump of a value about 500 mV/mL takes place in the equivalence point. The value of the analytical signal is comparable for platinum-modified and unmodified electrodes (Table 2). Thus, PEO-layers on titanium manifest the pH-function the most characteristic for metal-oxide electrodes as in direct potentiometry as in acid-base titration.

3.1.3. Kinetic curves of electrodes under study in acid-base titration

Kinetic titration curves were obtained on the example of potentiometric acid-base titration. As seen from Fig. 3, a constant potential value is established quite rapidly – within 30–60 s. In the equivalence point of the modified electrode Ti/TiO₂/Pt¹ (Fig. 3b), one observes some potential drift that is characteristic

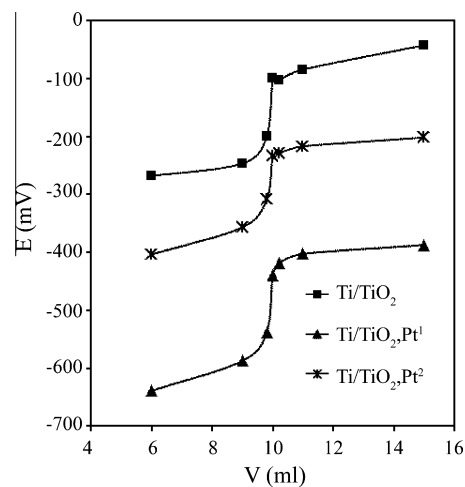


Fig. 2. Integral curves of acid-base titration of 0.1 M HCl by 0.1 M NaOH.

for a majority of indicator electrodes used in potentiometric titration.

3.2. Potentiometric oxidation–reduction titration

The behavior of the electrodes under study in potentiometric oxidation–reduction titration was examined on the example of titrations of the component of a reversible system by that of an irreversible one (Fe (II)–Cr(VI)) and two reversible systems (Fe (II)–Ce(IV)). The oxidation–reduction systems were selected to reveal common regularities in the electrodes behavior. According to the notion put forward by Michaelis, any material with the electronic conductivity in some specific potential and pH range can be an oxidation potential indicator [23].

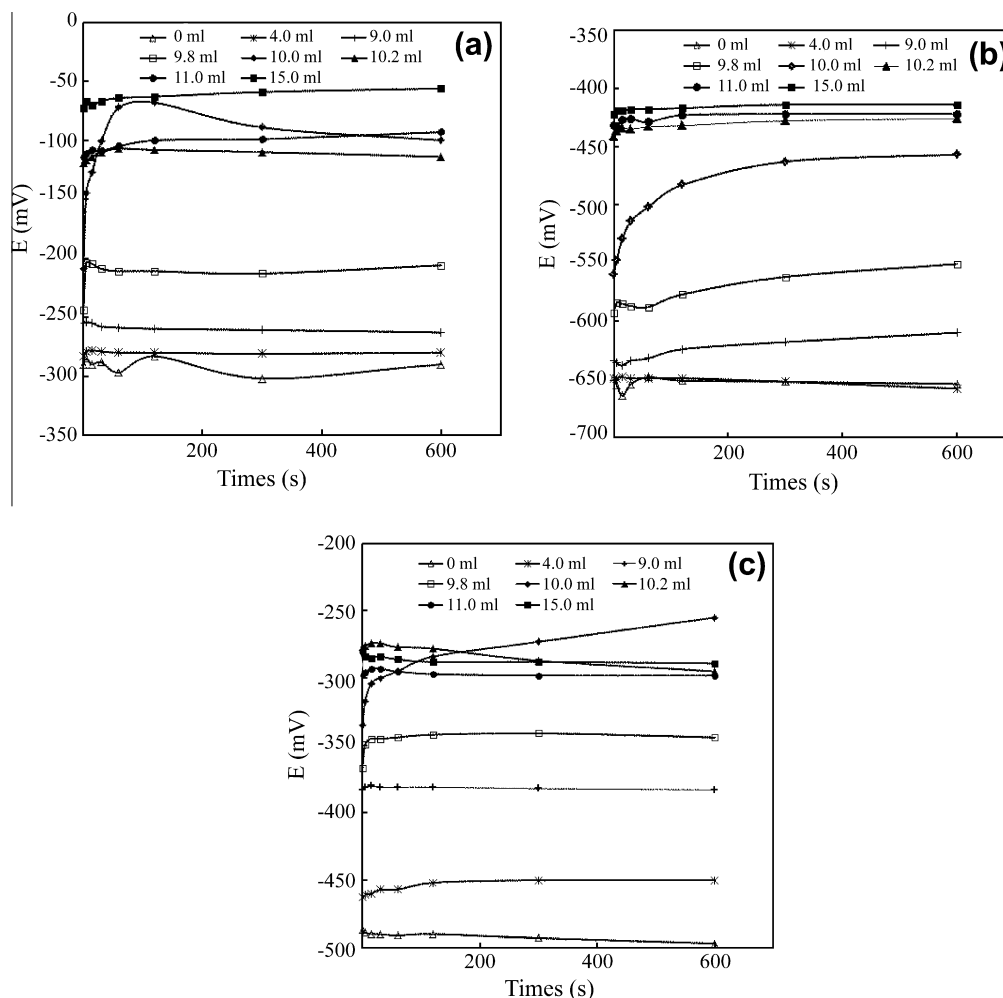
As seen from Fig. 4a, the curves of potentiometric titration of 0.05 M Fe (II) by 0.017 M Cr(VI) with Pt-electrode and Ti/TiO₂/Pt¹ have, upon differentiation, maxima in the equivalence point. The potential jump is the highest one during titration with Pt-electrode. For the unmodified Ti/TiO₂ PEO-electrode and Ti/TiO₂/Pt² electrode (impregnated in solution with the lowest H₂PtCl₆ concentration), the absence of a signal upon titration of a reversible system by an irreversible one was demonstrated. The absence of indicator properties in these electrodes must be caused by low electronic conductivity characteristic for PEO oxide layers and samples modified by small amounts of platinum, especially in the presence of an irreversible system.

Differential titration curves of 0.05 M solution of Fe (II) by 0.1 M solution of Ce (IV) are presented in Fig. 4b. The potential jump during the titration with participation of two reversible systems is substantially larger for all the electrodes under study than in the case of one irreversible system. Probably, this is caused by the fact that for irreversible systems the constant of the rate of the oxidation–reduction process and the exchange current are lower than for reversible ones. Therefore, to make $\Delta E/\Delta V$ a noticeable value, one should apply potentiometric titration with polarized electrodes. Upon the samples annealing, the potential jump value decreases that indicates to deterioration of their analytical properties. Possibly, this is related to the increase of the PEO-electrode film electrical resistance. Along with the increase of the platinum concentration in the impregnation solution, the value of the analytical signal increases: it is evident that the PEO-layers modification by platinum improves their electroanalytical properties by increasing the film electronic conductivity.

In case of participation of two reversible systems in titration, the value of the potential jump on the titanium electrode is comparable

Table 2Values of potential jumps $\Delta E/\Delta V$ (mV/mL) at titration with different electrodes in accordance with different reaction types ($n = 10$; $P = 0.95$).

No.	C (H ₂ PtCl ₆) (M)	Titration type			
		Oxidation–reduction (titration of 0.05 N Fe (II) by 0.1 N Ce (IV))	Precipitation (titration of 0.05 M NaCl by 0.05 M AgNO ₃)	Complexometric (titration of 0.05 M Fe(III) by 0.05 M EDTA-Na)	Acid-base (titration of 0.1 M HCl by 0.1 M NaOH)
1	–	314 ± 2.48	118 ± 9.93	10 ± 7.85	503 ± 16.34
2	3 × 10 ⁻¹	440 ± 5.36	197 ± 14.55	177 ± 10.73	438 ± 4.53
3	1 × 10 ⁻⁴	392 ± 13.02	172 ± 4.3	99 ± 7.17	493 ± 13.21
4	Pt	413 ± 5.91	126 ± 11.34	142 ± 7.17	–
5	Ag	–	205 ± 13.14	–	–
6	GE ^a	–	–	–	1087 ± 10.63

^a Glass electrode.**Fig. 3.** Kinetic curves of acid-base titration of HCl by 0.1 N NaOH. Electrodes: (a) Ti/TiO₂; (b) Ti/TiO₂/Pt¹; (c) Ti/TiO₂/Pt².

to that of the Pt electrode. This fact should be considered practically important in view of increasing the number of indicator electrodes to be applied in potentiometric oxidation–reduction titration.

3.3. Potentiometric complexometric titration

Potentiometric titration of Fe(III) was carried out by EDTA-Na with PEO-layers on titanium under study as indicator electrodes. Titration with a Pt electrode was carried out in parallel.

According to the data of Fig. 5, during the complexometric titration of iron (III) all the electrodes under study generate a signal in the titration end point. However, the unmodified Ti/TiO₂ electrode produces a weak signal, as compared to Ti/TiO₂/Pt¹ and Ti/TiO₂/Pt²

electrodes. One should mention that the value of the potential jump for the Ti/TiO₂/Pt¹ electrode is somewhat higher than that for the Pt electrode. Thus, the modification of PEO-layers by platinum results in increase of the analytical signal during the complexometric titration as well. The mechanism of Ti/TiO₂/Pt¹ functioning in the presence of the reversible electrochemical system Fe(III)/Fe(II) is, probably, similar to that of the classic Pt electrode, as in the case of oxidation–reduction titration [24].

3.4. Potentiometric precipitation titration

The indicator properties of the PEO-layers on titanium under study were examined in precipitation potentiometric titration of

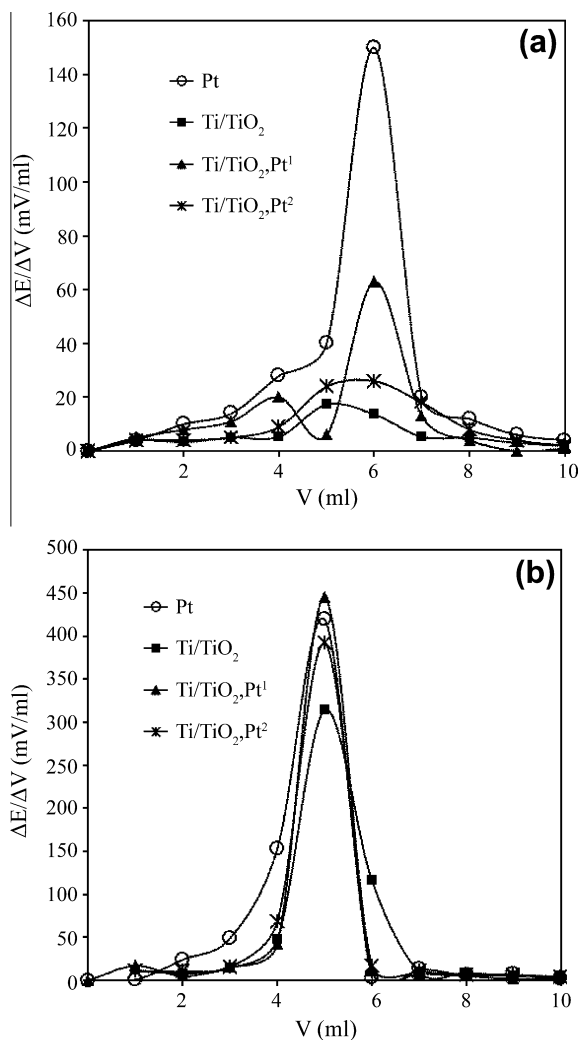


Fig. 4. Differential curves of oxidation-reduction titration: (a) Fe(II) – Cr(VI); (b) Fe(II) – Ce(VI).

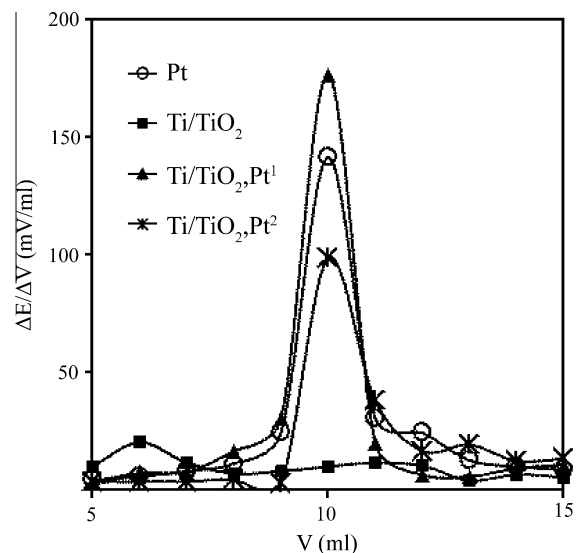


Fig. 5. Differential curves of complexometric titration of 0.05 M Fe(III) by 0.05 M EDTA-Na.

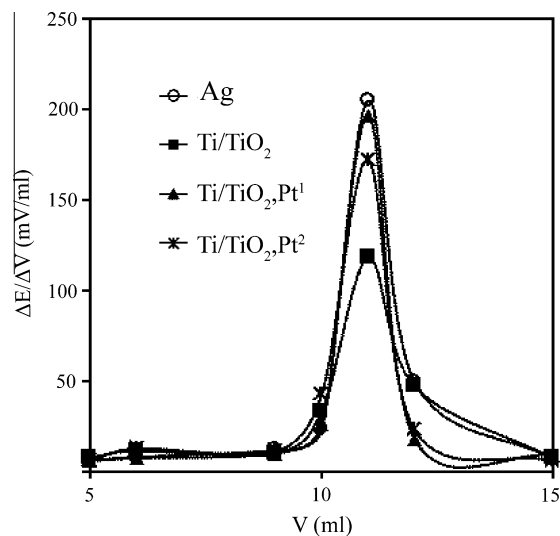


Fig. 6. Differential curves of precipitation titration of 0.05 M NaCl by 0.05 M AgNO₃.

0.05 M of sodium chloride solution by 0.05 M silver nitrate solution (Fig. 6). Titration with Pt and Ag electrodes was carried out in parallel. An analytical signal of a sufficient value was obtained for all the electrodes under examination. The functioning mechanism of metal-oxide electrodes in this type of reactions is caused by the electrode surface modification with adatoms of an electropositive metal (silver), which was demonstrated for classic metal-oxide and semiconductor [1,2,25] electrodes.

The results of mathematical processing of the value of the potential jump for all the reaction types are shown in Table 2. The results analysis enables one to conclude on polyfunctional character of the electrodes under study and their applicability in potentiometric indication of chemical reactions. The potential jump values are comparable to the known Pt-, Ag-electrodes.

3.5. Composition and morphology of PEO-layers on titanium

The surface conditions of solid electrodes belong to the factors affecting the characteristics of electrode processes and, therefore, the parameters of analytical signals during electrochemical analysis.

As seen on SEM-images (Fig. 7), the modification of Ti/TiO₂ electrodes by platinum substantially affects the surface morphology. Nanosized spherical particles (Fig. 7d, point 1) and agglomerates of such particles (Fig. 7d, point 2) located in surface cavities are observed in insignificant amounts on the Ti/TiO₂/Pt¹ electrode surface. According to the element analysis data, up to (at.%) 17.2 C, 72.1 O, 8.8 Ti, 1.9 Pt was found in the agglomerate composition. Up to (at.%) 10.6 C, 64.9 O, 24.5 Ti, 0.03 Pt was found in the composition of individual particles. Thus, it is evident that platinum is present on the surface of modified samples in the form of nanoparticles and their agglomerates located in surface cavities.

According to the averaged element analysis data (scanning surface area 10 × 10 μm), carbon, oxygen, and titanium were found on the Ti/TiO₂ samples surfaces (Table 3). The averaged qualitative and quantitative element compositions of the oxide layers surface do not virtually change as upon thermal treatment of PEO-layers as upon their modification by platinum. Platinum is not fixed that could be related to its low and heterogeneous content and specific location on a surface (in pores and cavities). One should also mention high carbon content on the surface of all the studied electrodes.

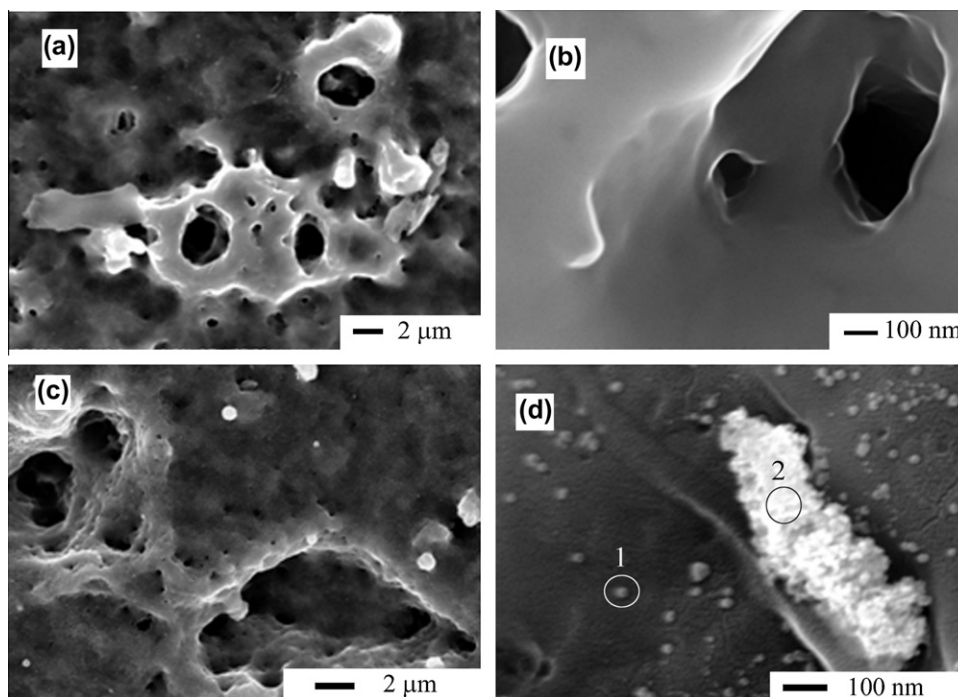


Fig. 7. SEM images of the electrode surfaces: (a and b) – Ti/TiO₂; (c and d) – Ti/TiO₂/Pt¹.

Table 3
Element composition of PEO-layers surface on titanium.

Electrode	Element composition (at.%)		
	C	O	Ti
Ti/TiO ₂	17.9	67.4	14.7
Ti/TiO ₂ ²	16.8	69.4	13.8
Ti/TiO ₂ ,Pt ¹	13.0	74.3	12.8
Ti/TiO ₂ ,Pt ²	12.9	73.7	13.4

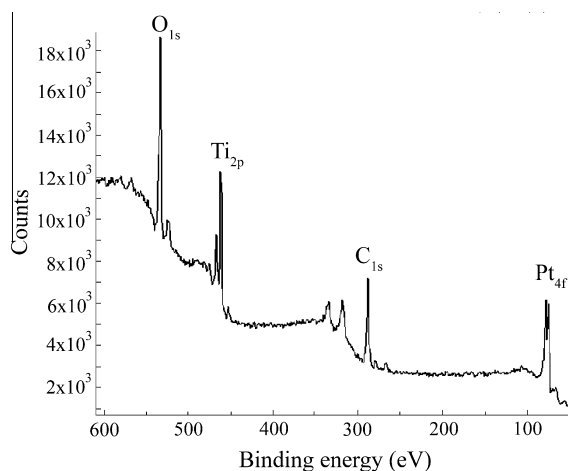


Fig. 8. XPS spectrum of the surface of Ti/TiO₂/Pt¹ electrode.

At the same time, one should emphasize that indicator properties of metal–oxide electrodes are substantially affected by the composition, structure, and properties of the surface in immediate contact with solution. As regards the modified electrode, one should know, aside from the above factors, the form of the modifying additive (in this case platinum) presence on the surface. To

determine the sample surface chemical composition (layer of a depth of ~ 3 nm), the method of X-ray photoelectron spectroscopy was applied. The XPS spectrum of the modified electrode Ti/TiO₂/Pt¹ shown in Fig. 8 indicates that the composition of the initial surface layer (~ 3 nm) includes platinum (4.6 at.%), titanium (10.3 at.%), oxygen (40.9 at.%), and carbon (44.7 at.%). The data obtained using the XPS methods are somewhat different from those of the X-ray spectral analysis (XSA). Such a difference could be caused by the fact that the films formed on titanium by the PEO method are sufficiently dense, and the surface modification at the preparation stage and possible interaction with environment occur exclusively in uppermost coating layers.

Fig. 9a presents XPS spectra of Pt 4f_{7/2} and Pt 4f_{5/2} films on the Ti/TiO₂ electrode prior to the surface etching. On the basis of the presented spectra, one can conclude that on the surface of the modified electrode platinum is present predominantly in the metal form Pt⁰ (71.4 and 75.0 eV for Pt 4f_{7/2} and Pt 4f_{5/2}, respectively) and, to a lower degree, in states close to Pt²⁺ (73.1 and 76.5 eV for Pt 4f_{7/2} and Pt 4f_{5/2}, respectively) and Pt⁴⁺ (74.4 and 78.2 eV for Pt 4f_{7/2} and Pt 4f_{5/2}, respectively) [26–28]. The formation of metal platinum occurs upon thermolysis of H₂PtCl₆ in accordance with the reaction: H₂PtCl₆ = Pt + 2Cl₂ + 2HCl. One could assume that platinum is present in the nanosized metal Pt⁰ form prior to and upon the surface etching. The fact that the oxidized platinum was also found must be caused by the sample surface interaction with air in the process of annealing. This assumption is corroborated by the fact that in the subsurface layer (upon etching of the uppermost layer of a thickness of ~ 30 Å) the amount of strongly oxidized platinum noticeably decreases, whereas the amount of platinum in the metal form increases accordingly (Fig. 9b).

To sum up, on the basis of the data of XPS and electron microscopy one can conclude that on the surface of modified electrodes platinum is present in an atomic state in the form of nanoparticles whose presence, in some cases, results in improvement of the electrodes electroanalytical properties manifested in the increase of the potential jump during potentiometric titration in accordance with different reaction types.

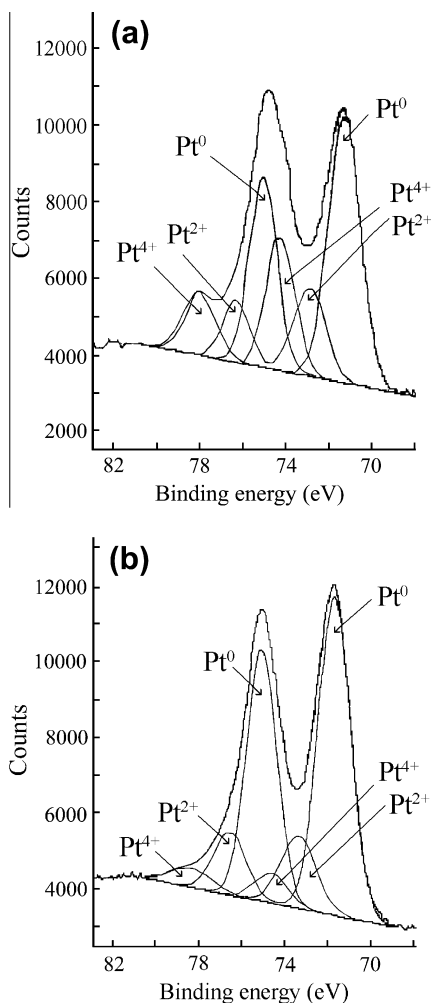


Fig. 9. XPS spectrum of Pt 4f surface of modified PEO-electrode Ti/TiO₂/Pt¹: (a) –before etching; (b) – after etching.

4. Conclusions

Oxide layers, including those modified by platinum, manifesting electroanalytical properties characteristic for metal–oxide electrodes were obtained on titanium using the PEO method. It has

been demonstrated that modification of oxide layers on titanium by platinum nanoquantities affects insignificantly the slope (angle coefficient) of the pH-function, but has an effect on the potential jump value during oxidation–reduction, complexometric, and precipitation titration. The polyfunctionality of metal–oxide electrodes with modified PEO-layers and the possibility of their application in potentiometric indication of different types of chemical reactions have been revealed.

References

- [1] V.A. Burakhta, S.S. Sataeva, *J. Anal. Chem.* 66 (2011) 1201.
- [2] I.A. Pašti, T. Lazarević-Pašti, S.V. Mentus, *J. Electroanal. Chem.* 665 (2012) 83.
- [3] N.A. Ghalwa, M. Hamada, H.M. Abu-Shawish, A.A. Swareh, M.A. Askalany, *T. Siam, J. Electroanal. Chem.* 664 (2012) 7.
- [4] G.I. Marinina, B.I. Tyrin, *Russ. J. Anal. Chem.* 37 (1982) 1948 (In Russian).
- [5] P.K. Shin, *Appl. Surf. Sci.* 214 (2003) 214.
- [6] C. Ludwig, P.W. Schindler, *J. Colloid Interface Sci.* 169 (1995) 284.
- [7] Z.H. Liu, S.Y. Huan, J.H. Jiang, G.L. Shen, R.Q. Yu, *Talanta* 68 (2006) 1120.
- [8] A. Fog, R.P. Buck, *Sens. Actuators* 5 (1984) 137.
- [9] Yu.G. Vlasov, Yu.G. Ermolenko, A.V. Legin, A.M. Rudnitskaya, V.V. Kolodnikov, *Russ. J. Anal. Chem.* 65 (2010) 880.
- [10] D.R. Acosta, A. Martinez, C.R. Magana, J.M. Ortega, *Thin Solid Films* 490 (2005) 112.
- [11] N. Kaliwot, J.Y. Zhang, I.W. Boyd, *Surf. Coat. Technol.* 125 (2000) 424.
- [12] T. Leistner, K. Lehmbacher, P. Arter, C. Schmidt, A.J. Bauer, L. Frey, H. Rysse, *J. Non-Crystalline Solids* 303 (2002) 64.
- [13] V.G. Bessergenev, R.J.F. Pereira, M.C. Mateus, I.V. Khmelinskii, D.A. Vasconcelos, R. Nicula, E. Burkel, A.M. Botelho do Rego, A.I. Saprykin, *Thin Solid Films* 503 (2006) 29.
- [14] P.S. Gordienko, S.B. Bulanova, O.A. Khrisanfova, N.G. Vostrikova, *Russ. J. Electronic Mater. Treat.* 3 (1991) 35 (In Russian).
- [15] M.S. Vasil'eva, V.S. Rudnev, L.M. Tyrina, I.V. Lukiyanchuk, N.B. Kondrikov, P.S. Gordienko, *Russ. J. Appl. Chem.* 75 (2002) 569.
- [16] J.F. McAller, L.M. Peter, *J. Electrochem. Soc.* 129 (1982) 125.
- [17] F. Jahalov, J. Zahavi, *Electrochim. Acta* 15 (1970) 1429.
- [18] A.L. Yerokhin, X. Nie, A. Leyland, A. Matthews, S.J. Dowey, *Surf. Coat. Technol.* 122 (1999) 73.
- [19] G.I. Marinina, M.F. Reznik, V.I. Tyrin, P.S. Gordienko, *Russ. J. Anal. Chem.* 51 (1996) 896.
- [20] M.S. Vasil'eva, V.S. Rudnev, L.M. Tyrina, N.B. Kondrikov, V.G. Kuryavyi, E.V. Shchitovskaya, *Russ. J. Appl. Chem.* 77 (2004) 1945.
- [21] N.V. Korovin, E.V. Kasatkin, *Russ. J. Electrochem.* 29 (1993) 448 (In Russian).
- [22] D.V. Malevich, A.F. Mazetz, V.B. Drozdovich, I.M. Zharskii, *Russ. J. Appl. Chem.* 70 (1997) 1264.
- [23] I.M. Schultz, A.M. Pisarevsky, I.P. Polozova, *Oxidation Potential*, Leningrad, Khimia, 1984 (In Russian).
- [24] G. Schwarzenbach, H. Flaschka, *Die Komplexometrische Titration*, Enke, Stuttgart, 1965.
- [25] V.A. Burakhta, L.I. Khasainova, *J. Anal. Chem.* 56 (2001) 560.
- [26] T.L. Barr, *J. Phys. Chem.* 82 (1978) 1801.
- [27] G.K. Wertheim, J.H. Wernick, S. Hufner, *XPS Core Line Asymmetries in Metals*, Bell Laboratories, Murray Hill, NJ, 1975.
- [28] D. Briggs, M.P. Seah (Eds.), *Practical Surface Analysis – Auger and X-ray Photoelectron Spectroscopy*, Wiley Interscience, 1990.