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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

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ABSTRACT

Ti/TiO_2 and $Ti/TiO_2/Pt$ 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 $Ti/TiO_2/Pt$ electrodes platinum is present in an atomic state in the form of nanoparticles. $Ti/TiO_2/Pt$ 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 $Ti/TiO_2/Pt$ electrode showed several advantages including low cost and high stability.

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 semiconductor and characterized by high dielectric constant, refraction coefficient, and chemical stability in aggressive media. Thin TiO_2 films can be used as sensors for different ions [5–9]. TiO_2 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

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* 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).

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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 TiO_2 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 hydrofluorine and nitric acids (ratio $HF:HNO_3 = 1:3$) at a temperature of 60–80 °C for 2–3 s.

Oxide films on titanium Ti/TiO_2 were formed using the PEO method in 0.1 M aqueous solution of $Na_2B_4O_7$ under galvanostatic conditions ($i = 0.2\ A\ cm^{-2}$) 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/TiO_2^*).

To modify with platinum, titanium plates with oxide layers deposited using the PEO method (PEO-method) were immersed in aqueous solutions of H_2PtCl_6 of concentrations 3×10^{-1} M ($Ti/TiO_2/Pt^1$), 1×10^{-4} M ($Ti/TiO_2/Pt^2$) 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, $AgNO_3$, $Ce(SO_4)_2$, $K_2Cr_2O_7$, and EDTA-Na of different concentrations were used as titrants in potentiometric titration measurements. Solutions of NaOH, $AgNO_3$ 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 our 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 $1 \times 1\ \mu m^2$ 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 $1 \times 1\ mm^2$ 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/TiO_2) and platinum-modified PEO-electrodes are linear over the whole pH range under study, Fig. 1. The $E = a–b$pH 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/TiO_2 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 H_2PtCl_6 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