

FTi/TiO₂,Au Electrodes Prepared by Plasma Electrolytic Oxidation and Electron Beam Evaporation

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Abstract. Ti/TiO₂,Au electrodes were prepared via plasma electrolytic oxidation (PEO) of Ti plate, followed by deposition of a thin (10 nm) Au layer by electron beam evaporation (EBE). The electrodes obtained were used for potentiometric indication of different types of chemical reactions. Ti/TiO₂,Au electrodes showed an excellent performance for end point indication in the oxidation-reduction and complexometric titrations similar to the traditional Pt and in the acid-base titration similar to glass electrode.

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]. 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. One of the ways that allows in a short time to form oxide coatings on metals is plasma electrolytic oxidation (PEO) - the electrochemical oxidation of the surface of a metal or alloy under electric spark and arc discharges [4, 5].

Additional modification of PEO layers with metals or oxides allows obtaining composite materials with catalytic, photocatalytic and sensor properties [6-10]. It has been demonstrated [6] that modification of oxide layers on titanium by platinum nanoquantities increases potential jump value during oxidation-reduction and complexometric potentiometric titrations. On the other hand, it is known [11] that thin film gold electrode modified with lead dioxide nanoparticles have a high pH sensitivity. Therefore, it was suggested that the plasma electrolytic titania layers modified by gold nanoquantities could have polyfunctionality and act as multisensors in various types of potentiometric analysis.

The purpose of this work is investigating the electroanalytical properties of PEO electrodes modified with gold by electron beam evaporation (EBE) in potentiometric indication of different types of chemical reactions.

Experiment

The samples of VT1-0 technical titanium (99.9% in purity) of a size of 2.0×2.0 cm were stripped with emery buff and polished chemically in a mixture of concentrated acids (HF:HNO₃ = 1:3) at 60–80°C for 2–3 s, and then rinsed in distilled water and dried in air.

PEO treatment of titanium samples was carried out in a thermal glass of 1000 mL in volume using TER4-63/460H thyristor unit (Russia) with unipolar pulse current as power source. The Ti/TiO₂ composites were formed at effective anodic current density 0.1 A/cm² for 10 min in an aqueous electrolyte containing 0.1 mol/L Na₂SO₄.

The thin gold layers (10 nm in thickness) were deposited on the PEO coating using a VACLEADER system for electron beam evaporation (ADVAVAC Surface Technologies). During Au evaporation, the pressure, maximal temperature and averaged rate of Au deposition in vacuum camera were equal $\sim 4.5 \times 10^{-6}$ mbar, 54 °C and 1.5 A/s, respectively.

To obtain the information on the coatings morphology and composition, the methods of X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), energy-dispersive X-ray spectral analysis (EDX) and X-ray photoelectron spectroscopy (XPS) were used.

XRD patterns of the samples with coatings were recorded on a D8 ADVANCE diffractometer (Germany) in CuK_α radiation. Identification of the compounds contained in the samples under study was performed in the EVA automatic search mode using the PDF-2 database. Additionally to standard recording at a rate of 2°/min, the recording with signal accumulation was used at increment scanning every 0.02° and time of signal accumulation in the point 15 s.

The surface morphology and elemental composition were studied using a Hitachi S-3400 high-resolution scanning electron microscope (SEM) with an Ultra Dry energy-dispersive spectrometer (Thermo Scientific, USA).

The XPS spectra were recorded on a Specs high-vacuum device (Germany) using a 150-mm electrostatic hemispheric analyzer. MgK_α radiation was used for ionization. The spectra calibration was performed on C1s-lines for hydrocarbons, whose energy was taken to be equal to 285.0 eV. Bombardment with argon ions having the energy of 5000 eV was applied for surface layers etching. The etching rate was about 0.1 Å/s; the etching times were 5 and 15 min.

The electrode studies were performed in the absence of external polarization under the conditions of potentiometric titration with one indicator electrode.

The behavior of the formed electrodes in the potentiometric acid-based titration was studied on the example of titration of 0.1 M solution HCl by 0.1 M solution NaOH; in a the oxidation–reduction titration – 0.05 M Fe(II) by 0.05 M Ce(SO₄)₂ solution; in a the complexometric titration – 0.1 M Fe (III) solution by 0.1 M EDTA solution.

The titration end point was found from the potential jump corresponding to the point of chemical reaction completion. The silver chloride electrode EVL-1-M-1As was used as reference electrode. The PEO-electrodes were used as indicator electrodes.

3. Results and Discussions

As was established by the XRD analysis, the oxide coatings before and after deposition of Au layer contain crystalline TiO₂ in rutile and anatase modifications. XRD patterns obtained in the mode with signal accumulation additionally showed the presence of metallic gold in the modified coatings (Fig. 1).

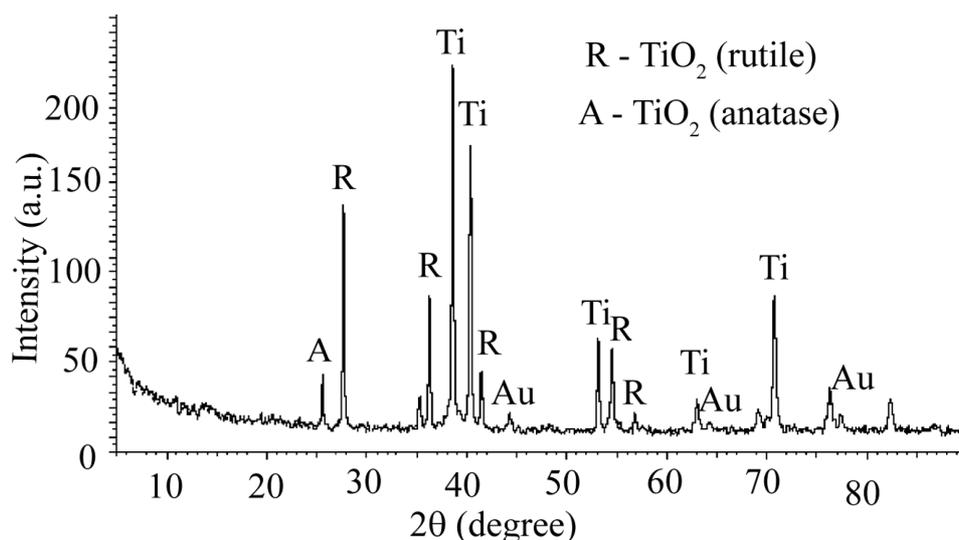


Fig. 1. X-ray diffraction patterns for Ti/TiO₂,Au electrode.

As to SEM, the deposition of thin film of Au does not change the morphology of the PEO coatings formed. SEM image of the surface of the Ti/TiO₂,Au electrode is presented in Fig. 2. On the surface of the Ti/TiO₂,Au electrode, alternating elevations and depressions are observed. There are pore throats, which, apparently, are the channels of the spark electric discharges. Pores are distributed rather evenly over the surface.

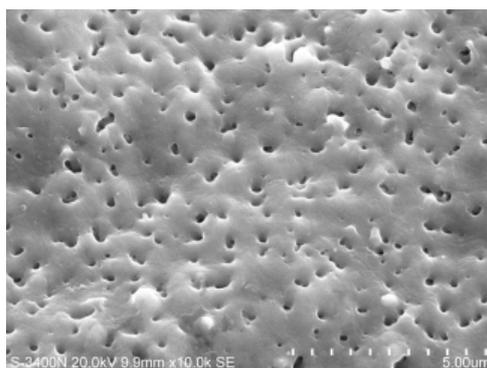


Fig. 2. SEM images of the surface of Ti/TiO₂,Au electrode.

According to EDX (scanning surface area is 100×100 μm), the average elemental composition of the Ti/TiO₂,Au sample surface is (at. %): 8.9 C; 2.6 N; 53.1 O; 33.7 Ti; 1.6 Au. One should also mention a high carbon content on the surface of all electrodes under study. From these data, we can conclude that gold is deposited as a uniform thin film. The dispersed gold particles and their agglomerates are not found on the surface of Ti/TiO₂,Au 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. With respect to the modified electrode, in addition to the above factors, one should know the type of modifying agent (in this case gold) present on the surface. To determine the chemical composition of the sample surface (layer of a depth of ~3 nm), the method of XPS was used.

Figure 3 shows X-ray photoelectron spectra of the surface layers of Ti/TiO₂,Au electrode before and after the surface etching. As to XPS, the initial surface layer (~3 nm) includes Au (30.6 at. %), O (17.8 at. %), and C (51.5 at. %) (Table 1). The gold in the surface layer is in an unoxidized state (Au⁰). Most of the carbon (2/3) is present in the organic form (CC, CH), while the remaining carbon (1/3) is in the oxidized state (CO, COO) (Table 1). The oxygen quantitatively and qualitatively correlates with these oxidized forms of carbon.

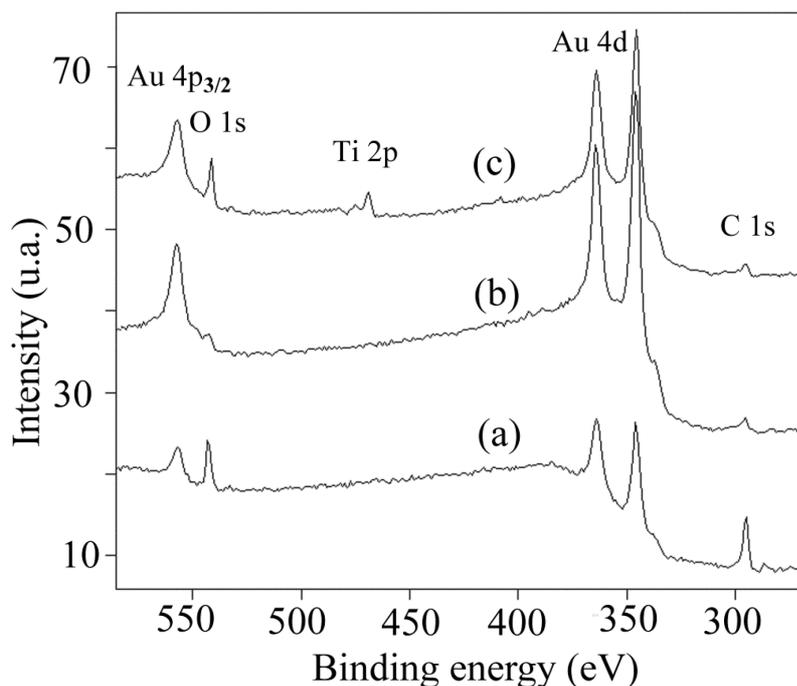


Fig. 3. XPS spectra of the surface layers of Ti/TiO₂,Au electrode prior etching (a); after etching for 5 min (b) and after etching for 10 min (c).

Table 1. Binding energies (eV) and elemental content (at. %) in the surface of Ti/TiO₂,Au electrode from XPS data.

Element	Before etching		After etching 1		After etching 2		Chemical groups or compounds
	E _b (eV)	C (at. %)	E _b (eV)	C (at. %)	E _b (eV)	C (at. %)	
O (1s)	532.1	17.8	531.8	4.5	530.8	21.8	CO _x , TiO ₂
Ti (2p _{3/2})	-	-	458.2	1.0	458.7	5.8	TiO ₂
C (1s)	285.0 (CC)	51.6	285.0	19.3	285.0	14.3	COO, CO, CC, CH,
Au (4f _{7/2})	84.5	30.6	84.2	75.2	84.2	58.1	Au ⁰

After the first etching, the upper layer (~ 3 nm in thickness) contaminated with impurities is removed and the underlying layer consisting predominantly of Au⁰ is exposed (Fig. 3b). As to the data of Table 1, titanium concentration in this layer is low (~1 at. %). This indicates that the gold layer is continuous and its thickness is more than 3 nm. The subsequent etching of the 3-nm underlying layer results in the Au starts to be removed exposing the lower titania layer (Fig. 3c, Table 1).

The behavior of the Ti/TiO₂,Au electrodes in the potentiometric oxidation-reduction and complexometric titrations was studied in parallel with Pt electrode, in the acid-base titration - in parallel with glass electrode (GE).

Fig. 3a shows integral curve of the oxidation-reduction titration. This curve is characterized by pronounced potential jumps near the final titration point. For locating end points, better results are obtained by constructing a plot of $\Delta E/\Delta V$ against V of titrant. Fig. 3b represents $\Delta E/\Delta V$ against V for the potentiometric titrations. The titration curves for other types of reactions have the same form.

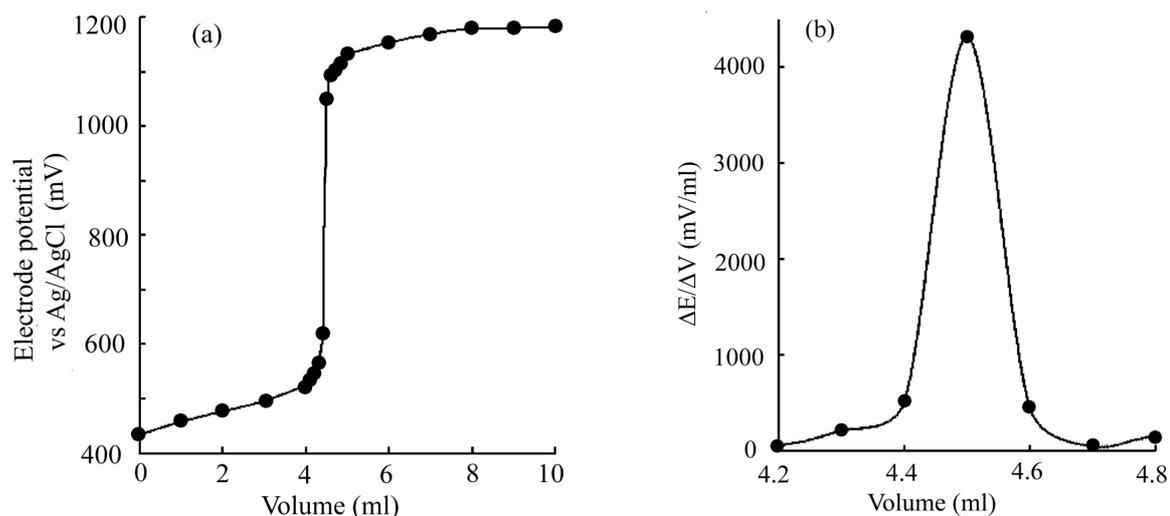


Fig. 4. Integral (a) and differential (b) curves of potentiometric oxidation–reduction titration with of Ti/TiO₂,Au electrode.

The values of potential jumps $\Delta E/\Delta V$ at the end points of the titration corresponding to the maximum in the titration curves are listed in Table 2.

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

Electrode	Titration type		
	Oxidation-reduction	Complexometric	Acid-base
Pt	4630	1120	-
Glass electrode	-	-	1560
Ti/TiO ₂	no signal	no signal	156
Ti/TiO ₂ ,Au	4400	570	1460

According to these data, the magnitudes of analytical signals for Ti/TiO₂,Au electrode are comparable with ones of conventionally used glass electrode (in the acid-base titration) and Pt electrode (in the oxidation-reduction and complexometric titrations). For the unmodified Ti/TiO₂ electrode, the absence of a signal in the oxidation-reduction and complexometric titrations was demonstrated. The absence of indicator properties in these electrodes must be caused by their low electronic conductivity.

4. Conclusions

Thus, Ti/TiO₂,Au electrodes manifesting electroanalytical properties typical for metal-oxide electrodes were obtained using combination of plasma electrolytic oxidation and electron beam evaporation. The polyfunctionality of Ti/TiO₂,Au and the possibility of their application in potentiometric indication of different types of chemical reactions have been revealed. Ti/TiO₂,Au electrodes showed an excellent performance for indication of potentiometric titration end points similar to the traditional Pt and glass electrodes. Compared with the monolith Pt electrode, the Ti/TiO₂,Au electrodes are less expensive. In comparison with the glass electrode, they have high mechanical stability. Moreover, these sensors have high sensitivity and good reproducibility.

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