Evaluating the Effect of WO$_3$ on Electrochemical and Corrosion Properties of TiO$_2$-RuO$_2$-Coated Titanium Anodes with Low Content of RuO$_2$

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Abstract
The electrochemical and corrosion characterization of Ti$_{0.97}$Ru$_{0.03}$O$_2$/Ti electrodes modified with WO$_3$ was reported. Modification of Ti$_{0.97}$Ru$_{0.03}$O$_2$/Ti electrodes with WO$_3$ was previously described as improving the effectiveness of an azo dye degradation in a photoelectrochemical treatment. Thus, the effect of WO$_3$ introduction to oxide film on electrode surface on electrochemical behaviour and stability of the modified electrodes was investigated. Moreover, corrosion behaviour of Ti$_{0.97}$Ru$_{0.03}$O$_2$/Ti electrodes modified with WO$_3$ was evaluated with the application of potentiodynamic polarization sweep method and open circuit potential measurement. Electrodes modified with WO$_3$ revealed higher anodic and cathodic peak currents in K$_4$[Fe(CN)$_6$] solution (by 35% for 6%WO$_3$ content) indicating higher electroactive surface area and faster electron transfer reaction. An increase in WO$_3$ amount in the oxide layer caused an increase in the number of active sites determined in Na$_2$SO$_4$ and most of them (more than 80%) were located in the outer and more accessible surface. The investigation of the tested electrodes at high potentials at which oxygen evolution is observed, allowed their classification in the following order showing an increase in their activity towards oxygen evolution reaction: Ti$_{0.97}$Ru$_{0.03}$O$_2$/Ti < Ti$_{0.94}$Ru$_{0.03}$O$_2$-W$_{0.03}$O$_3$/Ti < Ti$_{0.91}$Ru$_{0.03}$O$_2$-W$_{0.06}$O$_3$/Ti. Although the electrode modification with WO$_3$ resulted in lower resistance to corrosion in Na$_2$SO$_4$ solution regarding corrosion potential, corrosion current densities were clearly lower in comparison with the non-modified electrode, especially after longer immersion in the solution. ASTs showed that even a small addition of WO$_3$ increased the lifetime of the electrodes. The Ti$_{0.97}$Ru$_{0.03}$O$_2$/Ti electrode modification with WO$_3$ seemed to be advantageous for their application in electrochemical and photoelectrochemical degradation of organic pollutants.

Keywords Anode material · Electrochemistry · Active surface · Corrosion · Stability

Introduction
In recent years, the investigation of electrocatalytic and corrosion properties of oxide electrodes has received considerable attention [1–9]. Metal oxide–coated titanium electrodes are called DSAs (dimensionally stable anodes) and are the most important electrodes in electrochemical engineering due to their electrocatalytic properties and stability [10, 11]. DSA-type electrodes are widely used in many fields of electrochemistry such as chlorine production, electroplating and metal electrowinning, cathodic protection, water electrolysis and wastewater treatment [10, 12–18]. TiO$_2$-RuO$_2$/Ti electrodes are typical DSAs which are commonly applied in the oxidation of organic compounds which occurs with simultaneous evolution of oxygen. However, the oxide electrodes applied in electrochemical industry have some limitations including a limited service lifetime [10, 19]. RuO$_2$ is a metallic oxide and exhibits good activity in oxygen evolution reaction (OER) and chlorine evolution reaction (CIER). This metal oxide ensures proper electric conductivity but is unstable under oxygen evolution reaction due to concurrent reaction of its dissolution [20]. TiO$_2$ is a semiconductor generally regarded as the most effective photoinduced catalyst and commonly applied in oxidation of organic and inorganic pollutants in air and water [21, 22]. Moreover, the electrodes containing TiO$_2$ in the oxide layer can be also applied in photoelectrochemical treatment of organic pollutants [23].
The application of mixed oxides containing more than two components can improve not only electrocatalytic properties of an electrode material but also its stability. Introduction of the third metal oxide which is a semiconductor with a bandgap which enables its photoexcitation with irradiation from VIS region can improve the efficiency of a photoelectrochemical degradation of organic pollutants and enable application of an irradiation with lower wavelengths. Thus, in the previous paper [24], we suggested modification of TiO2-RuO2/Ti electrodes by introduction of WO3 to the oxide layer.

WO3 is characterized by a bandgap of 2.6 eV, which is about 0.6 eV narrower than TiO2 bandgap, and makes it capable of being excited by visible light [25]. Moreover, its high stability in acidic solutions, resistance to photocorrosion and high conductivity is also important when it is applied in the treatment of wastewater contaminated by organic pollutants, especially acids [26, 27]. Thus, it seems to be purposeful to couple WO3 with other semiconductors, i.e. TiO2, ZnO, BiVO4 [28–30]. WO3 can be also applied in photocatalytic water splitting to produce hydrogen gas simultaneously with organic pollutant degradation using visible solar light [28, 31, 32]. The addition of WO3 to TiO2 results in an increase in photoelectrocatalytic activity of the electrodes applied in the degradation of organic pollutants present in industrial wastewater [28, 32–34]. The contribution of WO3 in enhanced photoelectrocatalytic activity can be explained by increased surface adsorption affinity and improved charge carrier separation. However, an excessive amount of WO3 sometimes does not enhance the activity of the electrodes due to the transition of W6+/W5+[27].

These electrodes are exposed to corrosive media, i.e. industrial wastewater. As the result of corrosion or dissolution, some properties of the oxide film on electrode surface can change [35]. Thus, it is important to determine an effect of WO3 incorporation to the oxide film on corrosion characterization and stability of the modified electrodes. The effect of the electrode modification by WO3 addition on OER should also be investigated. The OER accounts for a large part of overpotential in the case of semiconductors [36], and its investigation is important in searching for efficient photoanodes.

The composition and properties of active compounds in the oxide film at the electrode surface strongly affect the properties of the electrode material taking into consideration not only its electrochemical and corrosion characterization but also its stability. The electrode stability can be evaluated by accelerated stability tests (ASTs). The electrochemical activity of electrodes is related to the development of their surface and an increase in the number of active centres [37]. Changes in the electroactive surface area (EAS) caused by electrode modification can be determined based on voltammetric determination [38–41] which enables monitoring of the surface of the oxide electrodes. However, the surface charging of oxide electrodes, particularly semiconductor metallic oxides, is complex. This depends on the supporting electrolyte and the acid/base surface properties of the oxides related to proton injection/ejection process including the solid-state surface re- dox transitions (SSSRTs) [42, 43].

In the recent paper [44], the results of electrochemical and corrosion investigations of the electrodes with higher content of RuO2 and modified with WO3, i.e. Ti0.7xRu0.3O2-WxO3/Ti electrodes, were presented. In this paper, the results of detailed electrochemical and corrosion properties of the electrodes with lower content of RuO2 and modified with WO3, i.e. Ti0.97xRu0.03O2-WxO3/Ti electrodes, are reported. The results of the experiments are compared with the non-modified electrode in order to determine an effect of WO3.

### Experimental

#### Chemicals and Materials

Electrochemical measurements were carried out in solutions of K4[Fe(CN)6] (5 mM) prepared by dissolving hexacyanoferrate(II) trihydrate (K4[Fe(CN)6]·3H2O, Merck) in 0.1 M KCl, and in the solution of Na2SO4 at the concentration of 0.1 M. Double distilled water was used in preparation of all solutions and throughout all experiments. All the chemicals applied in experiments were of analytical grade.

\[ \text{TiO}_{2-x} \text{RuO}_{2-x} \text{WO}_x/Ti \]

The nominal compositions of the coatings were achieved by properly adjusted concentrations of chloride precursor mixtures in n-butanol. The content of TiO2 was changed according to the amount of WO3 introduced to the oxide layer while RuO2 content was constant in order to ensure the electrical conductivity and catalytic activity of the tested anodes. The geometric surface area of the tested electrodes exposed to solutions was the same and totalled 2 cm². The non-modified electrode, i.e. TiO2-RuO2-WO3/Ti was applied in electrochemical measurements in order to compare results obtained for the modified electrodes.

#### Characterization of Electrodes

Electrochemical and corrosion measurements were carried out in the three-electrode cell connected to the electrochemical workstation—μAutolab III (Metrohm Autolab B.V., The Netherlands). The cyclic voltammetry method was applied in recording curves presenting a dependence of current vs. potential. Voltammetric curves were analysed with the application of Nova software vs. 2.1. Platinum electrode was used as a counter electrode. The potential of the working electrode was measured vs. saturated calomel electrode (SCE) in all measurements.
Cyclic voltammograms were recorded in solutions with a volume of 20 mL at different scan rates in the range from 2 to 500 mV s\(^{-1}\). Before measurements, dissolved oxygen was removed from solutions by purging with argon for at least 20 min. Argon blanket was kept over solution surface during measurements in order to prevent oxygen diffusion to the bulk solution. Voltammetric measurements were performed at least thrice.

Corrosion properties of the tested electrodes were determined in Na\(_2\)SO\(_4\) solution and were evaluated using electrochemical techniques such as open circuit potential (OCP) measurement followed by potentiodynamic polarization sweep. The potential of a tested electrode was measured as a function of time in order to determine the OCP value after its immersion in a solution. The OCP measurement was performed by 1 h or was stopped earlier when its value was established (\(dE/dt \leq 1 \mu V s^{-1}\)). Next, the tested electrodes were polarized in the potential range of OCP ± 200 mV. Linear polarization curves were recorded with the scan rate \(v\) of 5 mV s\(^{-1}\).

Additionally, an electrode stability was assessed in accelerated stability tests (ASTs) carried out in Na\(_2\)SO\(_4\) solution and in a three-electrode cell at room temperature. Measurements were performed at a constant current density of 0.2 A cm\(^{-2}\) supplied by a potentiostat/galvanostat Autolab PGSTAT 302N (Metrohm Autolab B.V.). The lifetime of the tested electrodes was evaluated as the electrolysis time at which the anodic potential exceeded the value of at least 2 V higher than its initial value recorded at time zero.

The morphological characteristics of all tested electrodes were investigated using S-4700 Hitachi (Japan) scanning electron microscope. SEM micrographs were obtained at a magnification of \(\times10,000\), scale bar 5.00 \(\mu m\).

**Results and Discussion**

**Cyclic Voltammetry Study in Ferrocyanide Solution**

Cyclic voltammetry (CV) in K\(_4\)[Fe(CN)\(_6\)] solution was applied in the investigation of the electrochemical properties of Ti\(_{0.97-x}\)Ru\(_{0.03}\)O\(_2\)-W\(_x\)O\(_3\)/Ti electrodes. The exemplary cyclic voltammograms recorded at the scan rate \(v\) of 5 mV s\(^{-1}\) for the tested electrodes are presented in Fig. 1. Electrochemical parameters characterizing [Fe(CN)\(_6\)]\(^3^-/[Fe(CN)\(_6\)]\(^4^-\) redox system are listed in Table 1.

The modification of Ti\(_{0.97-x}\)Ru\(_{0.03}\)O\(_2\)/Ti electrodes by introduction of WO\(_3\) to the oxide layer in their surface results in an increase of the anodic and cathodic peak currents (by about 35% for the electrode with 6%WO\(_3\)). The anodic and cathodic current ratio is almost the same for all tested electrodes and very close to 1, which indicates the reversible character of the redox couple. WO\(_3\) does not influence the half-wave potential \(E_{1/2}\) determined from the anodic \((E_{pa})\) and cathodic \((E_{pc})\) peak potentials by using the expression \((E_{pa} + E_{pc})/2\). However, the peak-to-peak separation \((\Delta E_p)\) is lower by 56 mV while the content of WO\(_3\) in the oxide layer is 3 and 6%. \(\Delta E_p\) is directly correlated to the electron transfer kinetics and indicates that the electrode modification with WO\(_3\) results in more reversible electron transfer in the electrochemical reaction. Moreover, electrochemical parameters presented in Table 1 \((I_{pa} and I_{pc})\) also indicate the faster electron transfer reaction at the modified electrodes.

In order to determine and compare electroactive surface area (EAS) of the tested electrodes, cyclic voltammograms were recorded at the tested electrodes at various scan rates. The Randles-Sevcik equation [38, 45] often applied for the determination of EAS can be used in the case of all electrochemical processes which are controlled by diffusion. Thus, dependences of peak current \((I_p)\) on the square root of the scan rate \(v\) were determined and are presented in Fig. 2.

These dependences are linear in the case of all tested electrodes and prove a diffusion-controlled process. The dependency for the non-modified electrode (Ti\(_{0.97}\)Ru\(_{0.03}\)O\(_2\)/Ti) is presented only in the scan rate range from 2 to 100 mV s\(^{-1}\) since anodic and cathodic peaks were poorly shaped in curves recorded at higher scan rates. Moreover, the diffusion control of the process was confirmed by dependences of \(\log I_p\) vs. \(\log v\) determined for anodic and cathodic peaks. The equations describing these dependences are presented in Table 2.

The linear dependences of \(\log I_p\) vs. \(\log v\) are characterized by an experimental slope of 0.38–0.40 for the anodic peaks and 0.37–0.42 for the cathodic peaks. These values are lower than 0.5 which is expected theoretically for the \(\log I_p\) vs. \(\log v\) plots under diffusion control. This is probably due to the existence of a kinetic contribution to the reaction control [46, 47]. Moreover, an increase in the scan rate results in significant increase in the value of \(\Delta E_p\) (0.560 V at 0.5 V s\(^{-1}\)), indicating more irreversible electron transfer electrochemical reaction. Taking these into consideration, determination of...
EAS calculated using the above mentioned Randles-Sevcik equation was not performed because it could result in incorrect EAS values. However, it can be predicted that the EAS values for the modified electrodes should be higher than the EAS value for the non-modified electrode, and the higher content of WO₃ should also result in higher EAS. Thus, EAS was also evaluated by determination of number of electroactive sites on the surface of the tested electrodes and is presented in the next section.

The results of the electrochemical characterization of Ti₀.97₋ₓRu₀.03O₂₋ₓWOₓO₃/Ti electrodes were also compared with the results obtained for Ti₀.7₋ₓRu₀.3O₂₋ₓWOₓO₃/Ti electrodes which were described in the paper [44]. The electrochemical reaction observed in K₄[Fe(CN)₆] solution is more irreversible in the case of Ti₀.97₋ₓRu₀.03O₂₋ₓWOₓO₃/Ti. The electrode modification with WO₃ causes an increase in reversibility of the process in comparison with the non-modified electrode in contrary to Ti₀.7₋ₓRu₀.3O₂₋ₓWOₓO₃/Ti electrodes. Moreover, the higher content of WO₃ in Ti₀.97₋ₓRu₀.03O₂₋ₓWOₓO₃/Ti results in higher values of Iₚa and Iₚc also in contrary to Ti₀.7₋ₓRu₀.3O₂₋ₓWOₓO₃/Ti electrodes. It can be concluded that the introduction of WO₃ to Ti₀.97Ru₀.03O₂/Ti modified with WO₃.

The tested electrodes were also applied in electrochemical degradation of an azo dye (Acid Orange 7) described in the paper [24]. The highest value of the dye oxidation current determined at the specified potential in the CV curves was observed at Ti₀.9₁Ru₀.0₃O₂₋ₓWOₓO₃/Ti electrode and was only slightly lower than in the case of electrodes with higher content of RuO₂. Moreover, the degradation of the dye observed in the electrochemical process was also the highest at Ti₀.9₁Ru₀.0₃O₂₋ₓWOₓO₃/Ti electrode, taking into consideration the dye conversion calculated as a change in chemical oxygen demand (COD) and total organic carbon (TOC). This proves purposefulness of Ti₀.9₇Ru₀.0₃O₂/Ti electrode modification with WO₃.

**Cyclic Voltammetry Study in Na₂SO₄ Solution**

The electrochemical properties of Ti₀.9₇₋ₓRu₀.0₃O₂₋ₓWOₓO₃/Ti electrodes were also investigated in Na₂SO₄ solution which can be applied as the supporting electrolyte in electrochemical and photoelectrochemical degradation of organic compounds, especially dyes [23]. CV curves were recorded at the tested electrodes with various scan rates. The voltammetric charge determined from a cyclic voltammetry curve recorded in the potential range between hydrogen and oxygen evolution has been found to be proportional to EAS and has been attributed to the number of electrochemically active sites on the electrode surface [40, 41]. The voltammograms recorded at the tested electrodes reveal the rectangular shape with the

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**Table 1** CV parameters determined for Ti₀.9₇₋ₓRu₀.0₃O₂₋ₓWOₓO₃/Ti electrodes (Iₚ—a peak current, Eₚ—a peak potential, ΔEₚ—difference between anodic and cathodic peak potential, E₁/₂—half-wave potential) from CV curves presented in Fig. 1

| Electrode                  | Eₚa (V) | Iₚa (mA) | Eₚc (V) | Iₚc (mA) | Iₚa/Iₚc | ΔEₚ (V) | E₁/₂ (V) |
|----------------------------|---------|----------|---------|----------|---------|---------|---------|
| Ti₀.9₇Ru₀.0₃O₂/Ti          | 0.268   | 0.516    | 0.103   | −0.498   | 1.04    | 0.165   | 0.186   |
| Ti₀.9₄Ru₀.0₃O₂₋ₓWOₓO₃/Ti    | 0.236   | 0.644    | 0.127   | −0.600   | 1.07    | 0.109   | 0.182   |
| Ti₀.9₁Ru₀.0₃O₂₋ₓWOₓO₃/Ti    | 0.240   | 0.709    | 0.131   | −0.666   | 1.06    | 0.109   | 0.186   |

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**Fig. 2** Dependence of Iₚa and Iₚc vs. v¹/₂ for Ti₀.9₇₋ₓRu₀.0₃O₂₋ₓWOₓO₃/Ti electrodes, determined in K₄[Fe(CN)₆] solution (5 mM in 0.1 M KCl) at various scan rates between 2 and 500 mV s⁻¹. Inset: CV curves recorded at Ti₀.9₁Ru₀.0₃O₂₋ₓWOₓO₃/Ti electrode at various scan rates
increasing scan rate, indicating a pseudo-capacitive behaviour. However, some differences between Ti_{0.97}Ru_{0.03}O_2/Ti electrode and the electrodes modified with WO_3 are observed. In the case of the non-modified electrode, the cyclic voltammogram is similar to the voltammogram recorded for Ti_{0.7}Ru_{0.3}O_2/Ti electrode in the same solution [44]. Scarcely visible one pair of anodic and cathodic peak probably corresponds to the redox transition between Ru(III) and Ru(IV). The pseudo-capacitive character of this electrode can result from the solid-state surface redox transitions (SSSRT) of rhenium species related to proton exchange reaction [42]. However, these peaks are not observed at CV curves recorded at the modified electrodes. In the case of Ti_{0.7}Ru_{0.3}O_2-W_xO_3/Ti electrodes, a pair of anodic and cathodic peaks appears at lower potentials (about 0.2 V). As these peaks were not observed at the non-modified electrode, it can be predicted that they are attributed to the change of transition state between W(VI) and W(V) [48–50] according to the following reaction [51, 52]:

\[
\text{WO}_3 + x\text{H}^+ + xe^- \rightarrow x\text{H}_2\text{WO}_3
\]

and resulting in the formation of hydrogen tungsten bronzes.

In contrary to Ti_{0.7}Ru_{0.3}O_2-W_xO_3/Ti electrodes [44], not only change in the CV curves was observed but also the current values observed for Ti_{0.97}Ru_{0.03}O_2-W_xO_3/Ti electrodes were clearly higher than those observed for the non-modified electrode. The higher content of WO_3 in the oxide film resulted in higher current in the CV curves. This can be attributed to an increase in the number of active sites contributing to SSSRT. In order to prove the increase in active site number, the cyclic voltammograms were recorded in Na_2SO_4 electrolyte, with various scan rates in the range from 5 to 500 mV s^{-1}. If voltammetry charge is determined in a potential range where hydrogen and oxygen is not evolved, then it can be applied in estimation of EAS according to the procedure described in the paper [44]. The reversibility of the pseudo-capacitance process, and dependences of \(1/q^* = f(v^{-1/2})\) and \(q^*\) = \(f(v^{-1/2})\) obtained for the tested electrodes are presented in Figs. 3 and 4. The results of total, inner and outer charge calculations are shown in Table 3.

The ratio of anodic to cathodic charge (\(q^*_a/q^*_c\)) indicating the reversibility of the redox process, slightly exceeds 1 in the case of the tested electrodes and indicates almost reversible behaviour of the solid-state surface redox transitions. The lowest value of \(q^*_a/q^*_c\) was observed in the case of the electrode modified with 6% WO_3. This can be explained by higher electro-negativity of W than Ru, and by the fact that WO_3 is more acidic than RuO_2, assuming that the rise in capacitive performance results from proton exchange between the catalyst surface and the electrolyte. If the electrode is modified by 6% WO_3 which is more acidic than RuO_2, then the SSSRT become more reversible.

Figure 4 and Table 3 prove that modification of Ti_{0.97}Ru_{0.03}O_2/Ti electrodes with WO_3 increases the number of active surface sites by 19% (3%WO_3) and 46% (6%WO_3) in comparison with the non-modified electrode. Moreover, Ti_{0.94}Ru_{0.03}O_2-W_0.03O_3/Ti and Ti_{0.91}Ru_{0.03}O_2-W_0.06O_3/Ti electrodes exhibit slightly lower values of \(q^*_\text{out}/q^*_\text{tot}\) ratio than the non-modified one, which indicate that most of the active sites are more accessible. In the case of Ti_{0.91}Ru_{0.03}O_2-W_0.06O_3/Ti electrode, 88% of the voltammetric charge is associated with outer and more accessible active sites, while 12% of the voltammetric charge is due to the inner and less accessible active sites located in pores. That electrode should be the most active in the electrochemical degradation of organic compounds taking into consideration its highest number of outer active sites on the electrode surface in comparison with the non-modified electrode and the electrode modified with 3% WO_3. Similar values of \(q^*_\text{out}/q^*_\text{tot}\) and \(q^*_\text{in}/q^*_\text{tot}\) calculated for the electrodes with 3 and 6% WO_3 in their oxide layers indicate the similarity of their surface morphology.

Figure 5 shows some representative SEM micrograph of Ti_{0.97}Ru_{0.03}O_2-W_xO_3/Ti electrodes. The non-modified
electrode (Ti$_{0.97}$Ru$_{0.03}$O$_2$/Ti) reveals “mud” structure with some micrometre cracks. The cracks can result from the solvent evaporation during electrode preparation. Much less cracks, which are narrower, are observed in the case of the electrode modified with 3% WO$_3$. Probably, WO$_3$ covers some cracks. In the case of the electrode modified with twice higher amount of WO$_3$ (6%), cracks are scarcely visible and some excessive amounts of WO$_3$ exist as micrometre random deposits overlaying the electrode surface with cracks.

The value of \( q^*_{\text{in}}/q^*_{\text{tot}} \) ratio can be used in estimation of electrode porosity [53]. The tested electrodes reveal relatively low and comparable porosity (Table 3). But this factor is slightly higher for Ti$_{0.94}$Ru$_{0.03}$O$_2$-W$_{0.03}$O$_3$/Ti in comparison with Ti$_{0.67}$Ru$_{0.3}$O$_2$-W$_{0.03}$O$_3$/Ti electrode [44]. The results of the investigation prove that the modification of Ti$_{0.97}$Ru$_{0.03}$O$_2$/Ti electrodes with WO$_3$ has a significant impact on the electroactive surface area. The number of active sites increases with an increase of WO$_3$ amount in the oxide film on the electrode surface. They are mainly (more than 80%) located at the outer and more accessible surface of the electrodes. Taking into consideration the previous results described in the paper [24], the electrooxidation currents of the azo dye observed at the voltammograms recorded at the tested electrodes and determined at the specified potential (0.8 V vs. SCE) were also higher than at the non-modified electrode. This is in accordance with higher number of active sites at the surface of the modified electrodes. Moreover, the electrochemical degradation of the azo dye was more efficient at the modified electrodes taking into consideration not only discoloration but also mineralisation expressed as a decrease in chemical oxygen demand (COD) and total organic carbon (TOC).

### Anodic Polarization Curves—Oxygen Evolution

The behaviour of electrode materials at high potentials is interesting in studies on the treatment of recalcitrant organic pollutants by electrochemical methods. Oxygen evolution reaction (OER) is one of the most important electrochemical processes occurring simultaneously with the electrochemical oxidation of organic compounds. Thus, OER was investigated on the tested electrodes. Figure 6 presents representative anodic polarization curves recorded in 0.1 M Na$_2$SO$_4$ solution in the potential range to 1.4 V and with the scan rate of 5 mV s$^{-1}$. Taking into consideration that voltammetric charge is related to EAS and changes for modified and non-modified electrodes, the measured currents in the polarization curves were normalized with the respect to outer charge (Table 3) in order to describe true electrocatalytic effects.

The comparison of the electrocatalytic properties of electrode materials can be based on exchange current density determined at specified potential and Tafel slope which is related to reaction mechanism. High current densities and low Tafel slopes indicate an electrocatalyst characterized by high activity [9, 43]. Differences in exchange current densities related to OER observed at Ti$_{0.7-x}$Ru$_{0.3}$O$_2$-W$_x$O$_3$/Ti electrodes are presented in Fig. 6. The activity of these electrodes can be compared based on potential values determined at the specified current density. The potential values at 0.068 mA mC$^{-1}$ show a decrease in the activity of the electrodes in the following order: Ti$_{0.91}$Ru$_{0.03}$O$_2$-W$_{0.06}$O$_3$/Ti (1.339 V) > Ti$_{0.94}$Ru$_{0.03}$O$_2$-W$_{0.03}$O$_3$/Ti (1.357 V) > Ti$_{0.97}$Ru$_{0.03}$O$_2$/Ti (1.400 V). This is quite an opposite order in comparison with the activity order presented for the Ti$_{0.7-x}$Ru$_{0.3}$O$_2$-W$_x$O$_3$/Ti

### Table 3

| Electrode                        | \( q^*_{\text{tot}} \) (mC) | \( q^*_{\text{out}} \) (mC) | \( q^*_{\text{out}}/q^*_{\text{tot}} \) | \( q^*_{\text{in}}/q^*_{\text{tot}} \) |
|----------------------------------|-----------------------------|----------------------------|----------------------------------------|----------------------------------------|
| Ti$_{0.97}$Ru$_{0.03}$O$_2$/Ti   | 18.36                       | 16.63                     | 0.91                                   | 0.09                                   |
| Ti$_{0.94}$Ru$_{0.03}$O$_2$-W$_{0.03}$O$_3$/Ti | 21.93                   | 18.92                     | 0.86                                   | 0.14                                   |
| Ti$_{0.91}$Ru$_{0.03}$O$_2$-W$_{0.06}$O$_3$/Ti | 26.76                   | 23.50                     | 0.88                                   | 0.12                                   |

![Dependences of 1/q* vs. v^1/2 \( (a) \) and q* vs. v^-1/2 \( (b) \) determined for Ti$_{0.97-x}$Ru$_{0.03}$O$_2$-W$_x$O$_3$/Ti electrodes in 0.1 M Na$_2$SO$_4\)](image-url)
electrodes. If RuO₂ content in the oxide layer was higher (30%), then the highest activity of the electrode material was observed in the case of the non-modified one [44]. This can be related to different acid-base properties of the electrodes with higher (30%) and lower (3%) contents of RuO₂ in the oxide layer of the electrode surface and an effect of the modification with WO₃.

Tafel plots determined for OER observed at Ti₀.₉₇ₓRu₀.₀₃₋ₓO₂-WₓO₃/Ti electrodes (Fig. 6) are similar and indicate the same reaction mechanism. However, especially in the case of Ti₀.₉₁ₓRu₀.₀₃₋ₓO₂-WₓO₃/Ti electrode, slight deviation from Tafel line can be noticed at higher current densities. This deviation can result from a change in a Tafel slope (change in reaction mechanism) or from uncompensated ohmic drop. Thus, Tafel plots were corrected in the case of all tested electrodes, according to the procedure described in the paper [54] and applied in the previous investigation [44]. After IR-compensation, the Tafel plots revealed only one slope in the case of Ti₀.₉₇ₓRu₀.₀₃₋ₓO₂-WₓO₃/Ti electrodes. OER generally proceeds in three steps in acidic and alkaline media [44, 54, 55]. The rate determining step (rds) for an electrode corresponds to its Tafel slope of OER and depends on strength of the adsorption of intermediates, which in turn depends on the composition of the oxide layer [55]. In the case of the supporting electrolyte (0.1 M Na₂SO₄) applied in the investigation described in this paper, IR-compensated Tafel plots are characterized by the following slope values: 220.2 mV dec⁻¹ (Ti₀.₉₇Ru₀.₀₃O₂/Ti), 223.3 mV dec⁻¹ (Ti₀.₉₄Ru₀.₀₃₋ₓO₂-WₓO₃/Ti) and 194.1 mV dec⁻¹ (Ti₀.₉₁Ru₀.₀₃₋ₓO₂-WₓO₃/Ti).

Ti₀.₉₇₋ₓRu₀.₀₃₋ₓO₂-WₓO₃/Ti electrodes reveal relatively high Tafel slopes, higher than 120 mV dec⁻¹ which can result from the non-stoichiometry of the oxides at electrode surface and the number of sites to absorb the hydroxyl ions from water [56]. These values are also higher than Tafel slopes determined for Ti₀.₇ₓRu₀.₀₃₋ₓO₂-WₓO₃/Ti by 30–60 mV and prove their lower activity. Moreover, the values of Tafel slope b indicate that the first step of OER including the formation and adsorption of the first intermediate S–OHads is the rds. Before oxygen evolution occurs at a catalytic oxide electrode, the hydroxyl radicals are first adsorbed at the active sites of the electrode. If the number of active sites to absorb the hydroxyl ions from water increases, oxygen evolution occurs more easily and the Tafel slope lowers. The highest current intensity and the lowest Tafel slope are observed in the case of Ti₀.₉₁Ru₀.₀₃₋ₓO₂-WₓO₃/Ti electrode, indicating good electrocatalytic properties of the oxide film at the electrode surface.

The obtained results show that the electrodes modified with WO₃ reveal higher activity towards OER. The electrode with 6% WO₃ seems to be more active than the electrode with 3% WO₃. Moreover, the application of Ti₀.₉₁Ru₀.₀₃₋ₓO₂-WₓO₃/Ti electrode in electrochemical and photoelectrochemical degradation of the azo dye described in the paper [24] resulted in the highest efficiency of the dye degradation calculated as a change in TOC and COD, in comparison with the electrode modified with 3% WO₃ and the non-modified one.
Mineralisation of the dye solution observed as a decrease in TOC value can be observed at higher potentials at which other reactive oxygen species can be formed.

**Corrosion Properties**

The stability of the oxide electrodes, applied in processes of electrochemical oxidation of organic pollutants present in industrial wastewater, is very important. RuO$_2$ plays a significant role in stability of Ti$_x$Ru$_{1-x}$O$_2$/Ti electrodes because it undergoes serious corrosion in the oxygen evolution reaction. The stability of Ti$_x$Ru$_{1-x}$O$_2$/Ti electrodes can be attributed to reactions of RuO$_2$ dissolution [20, 44]. The rate determining step includes the following reaction:

$$\text{RuO}_2 + H_2O \rightarrow \text{RuO}_2\cdot\text{OH} + H^+ + e^- \quad (2)$$

The tested electrodes are characterized by relatively low amount of RuO$_2$ (3%) in the oxide layer on the electrode surface. Thus, it can be predicted that their corrosion can result from the formation of an interlayer of passivation on the substrate much more than from RuO$_2$ dissolution. Taking into consideration that products of the metal oxide degradation are soluble, the oxide film layer can be gradually enriched by insulating TiO$_2$ [57]. The electrode passivation results from application of TiO$_2$ as a stabilizing component of the oxide layer and TiO$_2$ comes from the titanium substrate.

Taking into consideration the lower content of RuO$_2$ (3%) and the higher content of TiO$_2$ (91–97%), it was necessary to determine the corrosion resistance of the tested electrodes and effect of WO$_3$ used in their modification. In order to assess an electrode stability, first of all, determination of the open circuit potential (OCP) was performed in the solution of 0.1 M Na$_2$SO$_4$. The obtained OCP values were 0.216 V (Ti$_{0.97}$Ru$_{0.03}$O$_2$/Ti), 0.226 V (Ti$_{0.94}$Ru$_{0.03}$O$_2$–WO$_{0.03}$O$_3$/Ti) and 0.210 V (Ti$_{0.91}$Ru$_{0.03}$O$_2$–WO$_{0.06}$O$_3$/Ti). Introduction of WO$_3$ into the oxide film on the electrode surface results in lower resistance to corrosion than in the case of the non-modified electrode. On the other hand, j$_{\text{corr}}$ determined from polarization curves recorded during the first measurement (Table 4) was observed for Ti$_{0.91}$Ru$_{0.03}$O$_2$–WO$_{0.06}$O$_3$/Ti electrode in comparison with Ti$_{0.94}$Ru$_{0.03}$O$_2$–WO$_{0.03}$O$_3$/Ti and Ti$_{0.97}$Ru$_{0.03}$O$_2$/Ti electrodes. Introduction of 3% WO$_3$ did not change E$_{\text{corr}}$ value, but in the case of 6% WO$_3$ addition, E$_{\text{corr}}$ was lower by almost 30 mV. Taking into consideration that the corrosion potential is a thermodynamic parameter and determines corrosion tendency, it can be concluded that modification of the electrodes with higher amount of WO$_3$ (6%) results in lower resistance to corrosion than in the case of the non-modified electrode. On the other hand, j$_{\text{corr}}$ is a kinetic parameter which determines the corrosion rate. The lowest j$_{\text{corr}}$ value determined from polarization curves recorded during the first measurement (Table 4) was observed in the case of the modified electrode with 6% WO$_3$—lower by 35% in comparison with the non-modified electrode. However, introduction of 3% WO$_3$ into the oxide film on the electrode surface resulted in slight increase (by 12%) in j$_{\text{corr}}$. Similar measurements were performed at different immersion times in Na$_2$SO$_4$ solution, and their results were compared with the corrosion parameters determined in the first measurement. The cathodic and anodic slopes determined for the tested electrodes immersed in Na$_2$SO$_4$ solution were almost independent on the immersion time and comparable for all tested electrodes (Table 5).

This means that the corrosion mechanism did not vary for Ti$_{0.97-x}$Ru$_{0.03}$O$_2$–WO$_{3}$/Ti electrodes even after 4-h...
immersion. However, changes in \( E_{corr} \) values were clear (Table 4). In the case of all tested electrodes, \( E_{corr} \) shifted towards more negative potentials with increasing immersion time which proves less resistance to corrosion phenomena. The non-modified electrode revealed \( E_{corr} \) value lower by 98 mV, while the modified electrodes were characterized by \( E_{corr} \) value lower by 188 mV (3% WO\(_3\)) and 233 mV (6% WO\(_3\)) after 4-h immersion. The differences between \( E_{corr} \) determined for the tested electrodes immersed in Na\(_2\)SO\(_4\) solution for 4 h prove that the electrodes modified with WO\(_3\) became less resistant to corrosion in comparison with the non-modified one. On the other hand, the comparison of the corrosion current density determined for different immersion times (Table 4) was interesting. In the case of Ti\(_{0.97}\)Ru\(_{0.03}\)O\(_2\)/Ti electrode, the increase in immersion time resulted in an increase in \( j_{corr} \) by 67% (4 h). The electrode modified with 3% WO\(_3\) revealed a decrease in \( j_{corr} \) by 20% after the 4-h immersion while \( j_{corr} \) values determined for the electrode modified with 6% WO\(_3\) were independent on the immersion time. Comparison of \( j_{corr} \) values determined after the 4-h immersion resulted in the conclusion that the introduction of WO\(_3\) into the oxide film at the electrode surface resulted in a decrease of \( j_{corr} \) by 47% (3% WO\(_3\)) and 61% (6% WO\(_3\)) in comparison with the non-modified electrode. This proves that the electrode modification with WO\(_3\) results in lower corrosion rate which does not increase while the electrode is immersed in Na\(_2\)SO\(_4\) solution. The higher amount of WO\(_3\) in the oxide layer on electrode surface seems to be more advantageous.

### Accelerated Stability Tests

Stability of electrode material is very important in the process of organics degradation in wastewater. Thus, accelerated stability tests (ASTs) were performed under similar conditions as it was described in the case of Ti\(_{0.97}\)Ru\(_{0.03}\)O\(_2\)/Ti electrodes modified with 3 and 6% WO\(_3\) [44]. The results of AST for Ti\(_{0.97}\)Ru\(_{0.03}\)O\(_2\)/Ti electrodes modified with 3 and 6% WO\(_3\) are presented in Fig. 8.

In the beginning of the AST, the potential recorded for all tested electrodes decreased by 0.13 V during first 300 s. The decrease can be attributed to wetting of inner and less accessible surface of the tested electrodes [10]. This step was almost 5 times shorter than it was observed in the case of the Ti\(_{0.7}\)Ru\(_{0.3}\)O\(_2\)/Ti electrodes modified with 3 and 6% WO\(_3\) [44], and can be explained by lower porosity of the tested electrodes. Afterward, clear increase in the potential was observed except for Ti\(_{0.91}\)Ru\(_{0.03}\)O\(_2\)-W\(_{0.06}\)O\(_3\)/Ti electrode which potential increased much slower. However, the final significant increase in the potential, indicating quick deactivation, was observed at clearly lower times than in the case of Ti\(_{0.7}\)Ru\(_{0.3}\)O\(_2\)/Ti electrodes modified with 3 and 6% WO\(_3\) [44]. The lifetimes determined for the anodic potential of

### Table 4

Comparison of corrosion parameters determined from the polarization curves recorded during measurements after 2- and 4-h immersion in Na\(_2\)SO\(_4\) solution

| Electrode                          | Immersion time (h) | \( E_{corr} \) (V) vs. SCE | \( j_{corr} \) (mA mC\(^{-1}\)) |
|------------------------------------|--------------------|-----------------------------|-------------------------------|
| Ti\(_{0.97}\)Ru\(_{0.03}\)O\(_2\)/Ti | 0                  | -0.018                      | 6.90 \times 10\(^{-5}\)       |
|                                    | 2                  | -0.116                      | 9.44 \times 10\(^{-5}\)       |
|                                    | 4                  | -0.126                      | 11.55 \times 10\(^{-5}\)      |
| Ti\(_{0.92}\)Ru\(_{0.05}\)O\(_2\)-W\(_{0.05}\)O\(_3\)/Ti | 0                  | -0.018                      | 7.72 \times 10\(^{-5}\)       |
|                                    | 2                  | -0.132                      | 7.10 \times 10\(^{-5}\)       |
|                                    | 4                  | -0.206                      | 6.17 \times 10\(^{-5}\)       |
| Ti\(_{0.91}\)Ru\(_{0.03}\)O\(_2\)-W\(_{0.06}\)O\(_3\)/Ti | 0                  | -0.046                      | 4.49 \times 10\(^{-5}\)       |
|                                    | 2                  | -0.170                      | 4.48 \times 10\(^{-5}\)       |
|                                    | 4                  | -0.251                      | 4.49 \times 10\(^{-5}\)       |

### Table 5

The mean values of Tafel slopes (anodic—\( b_a \) and cathodic—\( b_c \)) determined for Ti\(_{0.97-x}\)Ru\(_{0.03}\)O\(_2\)-W\(_x\)O\(_3\)/Ti electrodes immersed in Na\(_2\)SO\(_4\) solution

| Electrode                          | \( b_a \) (V dec\(^{-1}\)) | \( b_c \) (V dec\(^{-1}\)) |
|------------------------------------|-----------------------------|-----------------------------|
| Ti\(_{0.97}\)Ru\(_{0.03}\)O\(_2\)/Ti | 0.048                        | 0.034                        |
| Ti\(_{0.92}\)Ru\(_{0.05}\)O\(_2\)-W\(_{0.05}\)O\(_3\)/Ti | 0.045                        | 0.033                        |
| Ti\(_{0.91}\)Ru\(_{0.03}\)O\(_2\)-W\(_{0.06}\)O\(_3\)/Ti | 0.050                        | 0.030                        |

![Fig. 8](image-url) Potential variation vs. time in ASTs for Ti\(_{0.97}\)Ru\(_{0.03}\)O\(_2\)-W\(_x\)O\(_3\)/Ti electrodes, recorded at 0.2 A cm\(^{-2}\) in 0.1 M Na\(_2\)SO\(_4\)
2 V higher than the potential at the time zero, were 1.27 h (Ti0.97Ru0.03O2/Ti), 1.55 h (Ti0.94Ru0.03O2-W0.03O3/Ti) and 1.76 h (Ti0.91Ru0.03O2-W0.06O3/Ti). The modification of the electrodes with WO3 results in their higher lifetime. However, lower content of RuO2 (3%) in comparison with the electrodes containing 30% RuO2 in the oxide film has significant effect on the electrode lifetime which is about 6 times lower.

The introduction of WO3 into the oxide layer of Ti0.97Ru0.03O2/Ti electrodes seems to be advantageous taking into consideration their stability. One of possible reasons of electrode deactivation can be attributed to formation of insulating TiOx interlayer [10, 58]. In comparison with Ti0.97Ru0.03O2/Ti electrode, the electrodes modified with WO3 reveal less cracked structure (Fig. 5) which might result in retardancy of the electrolyte penetration into the substrate resulting and in a delay in the formation of insulating TiO2 interlayer. The results prove that introduction of WO3 into the oxide layer can improve the stability of Ti0.97Ru0.03O2/Ti electrode. Moreover, the higher content of WO3 results in higher electrode lifetime. This also evidences the higher corrosion resistance of the modified electrodes, in Na2SO4 solution.

Conclusions

The Ti0.97Ru0.03O2/Ti electrodes modified with WO3 are characterized by relatively low content of RuO2 which is an electrocatalyst and has influence on electrode stability. The introduction of WO3 to the oxide layer resulted in higher values of \( I_{pa} \) and \( I_{pc} \) determined for the electrode reaction in K4[Fe(CN)6] solution, which also became more reversible in comparison with the non-modified electrode. A kinetic contribution to the reaction control was proved beside diffusion control. Thus, EAS of the tested electrodes was not determined with the application of the Randles-Sevcik equation, although the higher EAS for the modified electrodes could be predicted taking into consideration the obtained results. EAS determination in Na2SO4 solution proved an increase in the number of active sites in the oxide film for the modified electrodes. These sites were located mainly (more than 80%) at the outer and more accessible surface.

The investigation of the tested electrodes at potentials at which oxygen evolution is observed allowed their classification in the following order showing an increase in their activity towards OER: Ti0.97Ru0.03O2/Ti < Ti0.94Ru0.03O2-W0.03O3/Ti < Ti0.91Ru0.03O2-W0.06O3/Ti. The latter electrode was also characterized by clear enhancement in the efficiency of electrochemical and photoelectrochemical degradation of an azo dye calculated as a decrease in COD and TOC corresponding to the dye solution mineralisation, which was described in [24]. Significant mineralisation was achieved at the potentials at which other reactive oxygen species could be formed.

Although the electrode modification with WO3 resulted in lower resistance to corrosion taking into consideration \( E_{cor} \) (thermodynamic parameter) values after the 4-h immersion, \( f_{cor} \) values were lower by 47% (3% WO3) and 61% (6% WO3) in comparison with the non-modified electrode, what indicates a lower corrosion rate. Accelerated stability tests confirmed purposefulness of the electrode modification with WO3. A small addition of WO3 increased the lifetime of Ti0.97Ru0.03O2/Ti electrode. However, the lifetimes of the tested electrodes were about 6 times lower in comparison with the lifetimes determined for Ti0.97Ru0.03O2/Ti electrodes modified with the same amount of WO3. That can be attributed to the lower content of RuO2 (only 3%) and easier formation of insulating TiO2 interlayer.

Summing up, the modification of Ti0.97Ru0.03O2/Ti electrodes with WO3 seems to be advantageous taking into consideration their application in electrochemical and photoelectrochemical degradation of organic compounds, e.g. azo dyes. Even though these electrodes are characterized by lower stability and corrosion resistance than Ti0.7-Ru0.3O2-W0.03O3/Ti electrodes, Ti0.91Ru0.03O2-W0.06O3/Ti electrode enables higher efficiency of electrochemical and photoelectrochemical treatment of wastewater containing organic pollutants.

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