

Anodic stability of electrodeposited ruthenium: galvanostatic, thermogravimetric and X-ray photoelectron spectroscopy studies

D. MARIJAN, D. ČUKMAN, M. VUKOVIĆ
Ruder Bošković Institute, P.O.Box 1016, 41001 Zagreb, Croatia

M. MILUN
Institute of Physics, P.O.Box 304, 41001 Zagreb, Croatia

The anodic stability of an electrodeposited ruthenium electrode was measured by anodic galvanostatic polarization in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution. The role of water and adsorbed hydroxyl groups in electrode stability was determined by means of thermogravimetric analysis. A continuous weight loss due to water removal and condensation of hydroxyl groups was detected between 120 and 430°C . The loss of a hydrous component of the oxide layer was in direct correlation with the increase of the anodic stability. Between 430 and 480°C a weight gain was detected on the thermogravimetric curve. It was attributed to the formation of the ruthenium oxide layer in a higher oxidative state. This finding was confirmed by X-ray photoelectron spectroscopy measurements.

1. Introduction

Gas-evolving reactions, such as chlorine and hydrogen evolution, play an important role in industrial electrochemical processes. Various electrode materials have been used in meeting optimal working conditions [1,2]. Ruthenium-based electrodes deserve special attention in this field. Dimensionally stable anodes (DSA), a trade name for RuO_2 coatings, prepared by thermal decomposition of RuCl_3 on titanium, have been used since 1965 in a chlor-alkali technology [3], replacing electrocatalytically less-active and chemically less-stable carbon anodes. In the water electrolysis, the oxygen evolution reaction is the slowest step in the overall process, and from the electrocatalytic point of view, ruthenium and RuO_2 , particularly in their hydrous forms, exhibit the lowest overvoltage [4]. A serious limitation for their use is corrosion of the electrode layer. Several successful attempts, such as thermal treatment [5,6] and addition of iridium [7–9], have been achieved in improving their service life.

Speaking generally, about the role of anhydrous and hydrous oxide films in electrochemistry, it is known that thermally prepared anhydrous oxide films exhibit better stability, while hydrous oxide films, prepared either by anodic polarization or by precipitation, exhibit better electrocatalytic properties [10]. It was the aim of the present work to determine firstly, whether some optimal conditions between stability and activity in the oxygen evolution reaction on electrodeposited ruthenium exist and secondly, what was the role of water and surface hydroxyl groups in the electrode stability. In this connection, the thermo-

gravimetric analysis (TGA) of an electrodeposited ruthenium layer was carried out. The idea was to examine whether some inflection points on the TGA curve exist. In other words, whether some fixed temperatures exist at which a loss of water and/or a condensation of hydroxyl groups occur, and, if these phenomena happen, to what extent they determine the anodic stability of electrodeposited ruthenium.

Four different materials, namely nickel, titanium, stainless steel and platinum, have been used in probing the quality of electrodeposited ruthenium coatings in connection with the anodic stability in the oxygen evolution reaction. From the applied points of view, in any industrial application, relatively cheap materials such as stainless steel, nickel or titanium would be the materials of choice. From the fundamental point of view, however, platinum has some advantages. Its surface, when free of adsorbed organics, is defined electrochemically by a well-known potentiodynamic profile [11].

This was the reason why, in the majority of experiments in this work, platinum was used as a substrate.

2. Experimental procedure

The ruthenium electrode was prepared by a galvanostatic electrodeposition on a platinum foil (Goodfellow, $0.4 \text{ cm} \times 0.4 \text{ cm}$ in size, 0.01 cm thick) from a stirred solution of $1 \text{ g dm}^{-3} (\text{NH}_4)_2\text{RuCl}_6$ in $0.1 \text{ mol dm}^{-3} \text{ HCl}$ (Fluka puriss. p. a.) for 15 min at 25°C . The electrochemical measurements were carried out in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ (Fluka puriss. p. a.) using an EG&G Model 273/97 potentiostat/galvanostat.

Before thermogravimetric measurements, the ruthenium electrode was potentiodynamically polarized between -0.2 and $+0.9$ V versus SCE in order to preserve the surface in its oxidative state. An H-type electrochemical cell with a platinum foil as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode were used. The solution was prepared with quadruply distilled water.

The TGA was carried out using a Harrop Model TG 722 thermal analyser which consisted of a Cahn Model C 2000 electrobalance (sensitivity ± 0.1 μg), a West Model 2050 programmable temperature controller and an Allen Datagraf Model 700 x - y recorder. The thermogravimetric curve was recorded at a heating rate of $0.7^\circ \text{C min}^{-1}$ in air at reduced pressure (70 Pa) where optimal conditions between thermomolecular noise and apparent weight loss have been found. At typical points on the TGA curve, the specimen was removed from the oven, attached to an electrode holder and transferred to the electrochemical cell where cyclic voltammetric and anodic stability experiments were carried out. The stability test was carried out galvanostatically at 40 mA cm^{-2} . The criterion for the life-time was a complete dissolution of the electrode layer, indicated by a sharp increase of the potential, which occurred when the surface of a substrate was exposed to the solution. The anodic stability test was next to platinum, carried out also on ruthenium electrodes deposited on titanium, stainless steel and nickel (Goodfellow, wires of 0.25 cm^2 geometrical area).

The specimen of electrodeposited ruthenium for the X-ray photoelectron spectroscopy (XPS) measurements were prepared on a platinum foil 0.3 cm^2 in area and elliptical in shape. They were dried and immediately inserted into an ultrahigh vacuum (UHV) apparatus equipped for XPS measurements. The X-ray excitation source was a magnesium anode (MgK_α line). The out-going electrons were analysed using a vacuum science workshop (VSW) 180° hemispherical analyser in FAT 50 mode. Data acquisition and manipulation were performed using the VSW E-C 7.02 program package.

3. Results

3.1. The effect of substrate

The anodic stability was monitored by measuring the electrode potential during anodic galvanostatic polarization of the electrodeposited ruthenium layers. Fig. 1 shows the anodic stability test for an electrodeposited ruthenium electrode on different substrates at 40 mA cm^{-2} in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. The lifetime of ruthenium coatings on platinum and titanium is about three times longer than the lifetime of coatings electrodeposited on nickel and stainless steel.

3.2. Thermogravimetric analysis

The thermogravimetric curve of the electrodeposited ruthenium on platinum is shown in Fig. 2. An almost continuous weight loss is evident without any significant inflection points. The electrode lost 50% of its

total weight when reaching 430°C . The weight gain of about 7% was detected between 430 and 480°C .

3.3. Anodic stability

Fig. 3 shows the dissolution process of the electrodeposited ruthenium on platinum in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. The small inflection is detected after 60 s before the sharp increase of potential which, after 100 s, overlaps with the potential values obtained with the pure platinum electrode.

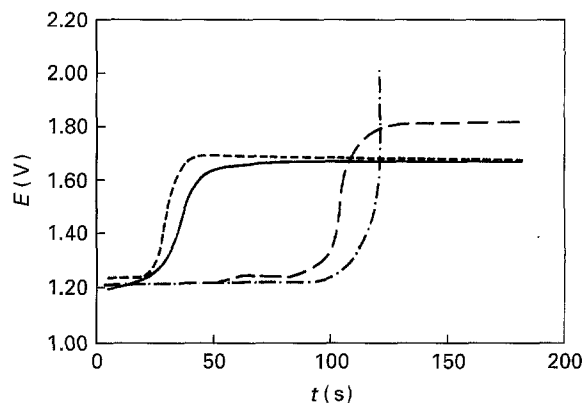


Figure 1 Anodic stability test at 40 mA cm^{-2} in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ of an electrodeposited ruthenium electrode on different substrates: (· · ·) titanium, (---) platinum, (—) nickel, (- · - ·) stainless steel.

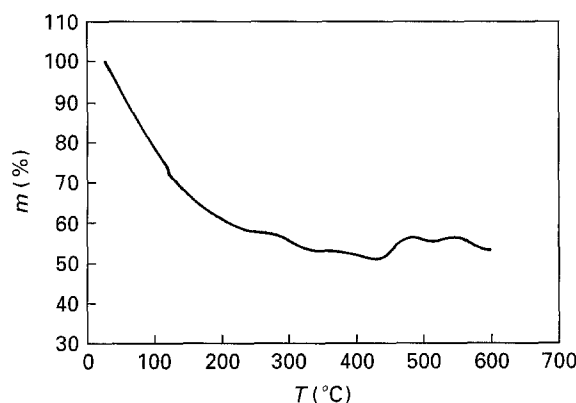


Figure 2 Thermogravimetric analysis of electrodeposited ruthenium on platinum.

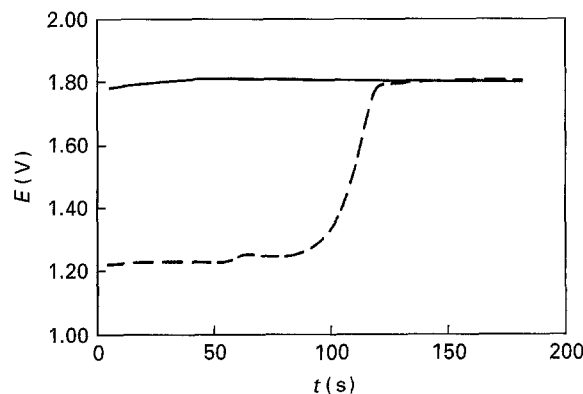


Figure 3 Anodic stability test at 40 mA cm^{-2} in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ of an electrodeposited ruthenium electrode on platinum: (—) pure platinum, (---) ruthenium on platinum.

In the absence of pronounced inflection points on the TGA curve, the specimens were removed from the oven at preselected temperature values and the stability test was carried out in the electrochemical cell. These temperatures were: (i) 25° C, the room temperature before the thermal treatment; (ii) 120° C, when the bulk water (moisture) was removed; (iii) 250° C, when the sharp decrease of the TGA curve recorded in previous experiment was detected; (iv) 320° C, when smaller decay of the TGA curve was detected; (v) 450 and 550° C, just before and after weight gain; and finally (vi) at 600° C, when the weight loss was again detected. After the thermal treatment at the above-mentioned temperatures, the cyclic voltammograms were recorded and the corresponding voltammetric charges were integrated (Fig. 4) in order to measure the electrochemical activity of the electrode. The lifetime test (Fig. 5) shows the sharp increase of the anodic stability between 200 and 300° C followed by a slower increase afterwards. The corresponding voltammetric charges (Fig. 4) exhibit an almost linear decrease with thermal treatment.

3.4. X-ray photoelectron spectroscopy

The XPS oxygen 1s spectra of the electrode heated at 400° C, exhibit a peak at 531.7 eV binding energy, with a shoulder at 529.9 eV (Fig. 6). When the electrode was

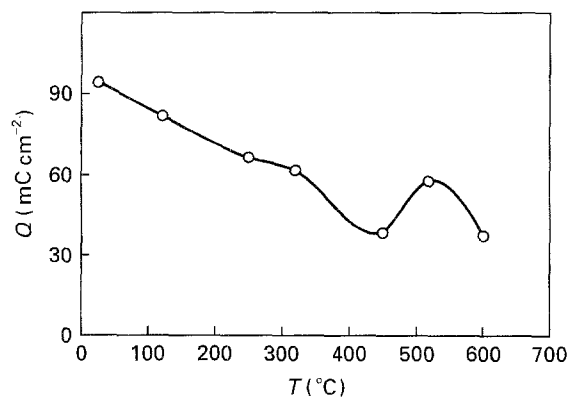


Figure 4 Anodic voltammetric charge from 0.1–1.1V versus SCE of an electrodeposited ruthenium on platinum as a function of thermal treatment.

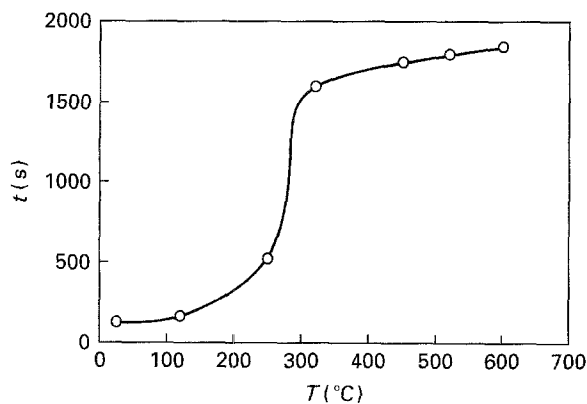


Figure 5 Anodic stability test at 40 mA cm⁻² in 0.5 mol dm⁻³ H₂SO₄ of an electrodeposited ruthenium on platinum as a function of thermal treatment.

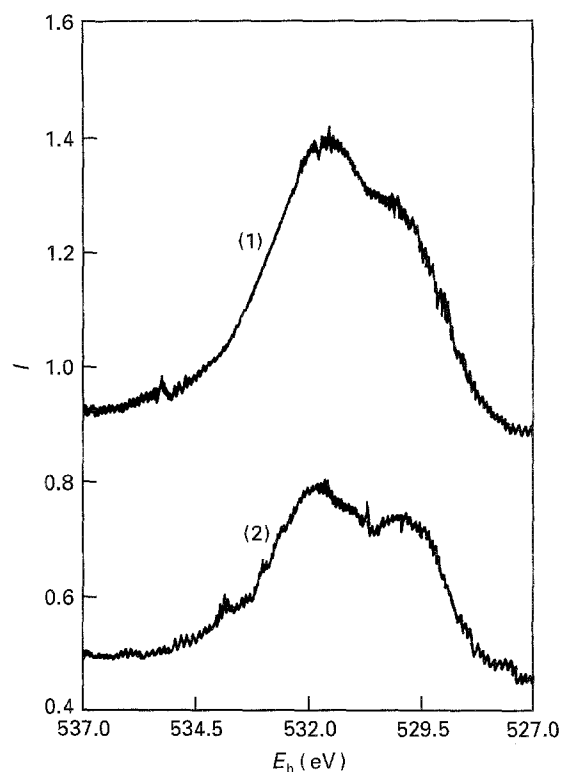


Figure 6 Oxygen 1s XPS spectra of an electrodeposited ruthenium on platinum: (1) electrode heated at 450° C; (2) electrode heated at 550° C.

heated at 500° C, the shoulder developed into a peak. The full-width-at-half-maximum (FWHM) values in both cases are about 4 eV.

4. Discussion

The ruthenium oxide layers on platinum and titanium exhibit about three times better stability than those deposited on nickel and stainless steel, as shown in Fig. 1. It is somewhat surprising that titanium behaved as well as did platinum, bearing in mind that it is difficult to remove oxide layer from a titanium surface. This was obviously not a barrier for a good coating in the present case. It is known that TiO₂ and RuO₂ are of the same rutile structure [12] and, moreover, titanium is used in DSA electrodes in the chlor-alkali industry.

An interesting phenomenon was observed on the *E*-*t* curve of anodic dissolution of ruthenium (Fig. 3) namely, the appearance of a small inflection after 60 s. Two effects are possible. First, after almost complete dissolution of ruthenium, a mixed Ru-Pt layer could be formed contributing to the increase of the overvoltage, and second, it is possible that after 60 s a hydrous oxide film was dissolved and a monolayer of a compact anhydrous oxide exposed to the solution. More precisely, the oxygen evolution starts on the hydrous oxide exhibiting an overvoltage of 1.22 V. Physically and chemically bonded water molecules, together with hydroxyl groups, are adsorbed on the electrode surface. Until the hydrous oxide was present, the overvoltage remained the same regardless of the oxide thickness. When the compact oxide was finally exposed to the solution, the electrocatalytic activity

decreased resulting in the increase of the overvoltage for about 20 mV.

The relationship between TGA data, anodic stability and electrochemical activity can be deduced on the basis of the results presented in Figs 2–5. The sharp decrease of weight between 25 and 120°C as shown in the TGA curve (Fig. 2) is due to moisture removal. This part of the TGA curve is followed by a continuous decrease without any significant inflection points. This is not surprising in the case of hydrous oxides. In fact, the majority of hydrous oxides exhibit a continuous loss of adsorbed water and hydroxyl groups [13]. It follows also from the TGA curve that water and hydroxyl groups were removed before 430°C when the weight gain was detected between 430 and 480°C. The uptake of oxygen is a reasonable assumption for this phenomenon. On the basis of XPS measurements in our previous paper [14], evidence was provided for the presence of oxide, hydroxide and water in a hydrous oxide film formed anodically on electrodeposited ruthenium. A nonstoichiometric formula of the type $\text{RuO}_x(\text{H}_2\text{O})_y(\text{OH})_z$ was suggested. In the present case, after 430°C, water and hydroxyl components are removed, and only oxide components exist. Two reactions are possible, namely $\text{Ru}_2\text{O}_3/\text{RuO}_2$ and/or $\text{RuO}_2/\text{RuO}_3$ transition. Before TGA measurements, the electrodes were removed from the electrochemical cell at 0.85 V; they were, therefore, in at least the Ru(III) state [15]. With the uptake of one oxygen atom per one ruthenium, RuO_2 would be formed. This reaction probably took place at 450°C. This is also the temperature at which RuCl_3 thermally decomposes to RuO_2 in DSA production. Another possibility is the formation of volatile RuO_3 . It was reported that $\text{RuO}_2/\text{RuO}_3$ transition takes place at temperatures above 500°C [16]. This could be also the case here, because the TGA curve exhibits a weight loss after 550°C. The oxygen uptake and formation of a higher oxide is confirmed by XPS measurements (Fig. 6). The major change in XPS spectra of two electrodes thermally treated at 450 and 550°C, respectively, are at 530 eV binding energy when a shoulder developed into a much better pronounced peak. It is known from literature data [17] that binding energies of oxygen 1s spectra are around 530, 532 and 534 eV for oxides, hydroxides and water, respectively. It follows, therefore, that this change can be attributed to the oxide component. From the XPS spectra in Fig. 6, it follows from a relatively broad FWHM of 4 eV, that all three components of a hydrous oxide, namely oxide, hydroxide and water, are present. This is in contradiction to thermogravimetric data in Fig. 2 which show an absence of both hydroxide and water after 430°C. However, we must bear in mind that during the transfer of a specimen from the oven to the UHV chamber, some water was adsorbed. Our previous experiments support this assumption [18]. By heating the electrodeposited ruthenium directly in the UHV chamber, in the absence of oxygen, a much narrower (2.5 eV) FWHM was obtained without any change of the spectrum, which would indicate the formation of a higher oxide. Only decomposition of an electrodeposited layer was observed at temperatures above 600°C.

The following calculations support the assumption that an uptake of oxygen was detected thermogravimetrically in Fig. 2. From the weight of the coating at 450°C, 47 µg (52% of 90 µg, 0.32 cm² electrode area) corresponds to 6.6×10^{17} RuO_2 molecules/cm². Taking into account that 1 cm² RuO_2 contains 1.5×10^{15} molecules [19], the number of deposited ruthenium layers is 439. The weight gain at 450°C is about 7% (6.3 µg). By assuming an uptake of one oxygen per one ruthenium atom, the calculated number of oxygens is 7.6×10^{17} sol/cm². This is in a fair agreement with the above calculated number of RuO_2 molecules.

The voltammetric data, expressed through anodic charge, also provide some pieces of information on the electrochemical activity of the electrode (Fig. 4). By comparing these data with those in the TGA curve it is evident that the decrease in activity follows the loss of water and hydroxyl groups from the electrode surface. The calculations show, taking into account the number of RuO_2 molecules calculated above and four exchanged electrons, that the voltammetric charge would be 422 mC cm⁻², if all of the ruthenium atoms were involved in electrochemical reaction. It follows from the Fig. 4 that 23% and 10% of ruthenium atoms were involved in electrochemical reaction at 25 and 440°C, respectively.

By combining all of the above data, the conclusion can be drawn, that the increase of the anodic stability of electrodeposited ruthenium in the oxygen evolution reaction is directly correlated with the loss of both water and hydroxide components from the electrode layer. In other words, the optimum of this reaction shifts towards an anhydrous oxide film.

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