# OXYGEN EVOLUTION ON AN ELECTRODEPOSITED RUTHENIUM ELECTRODE IN ACID SOLUTION—THE EFFECT OF THERMAL TREATMENT

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Abstract—The ruthenium layer galvanostatically electrodeposited on a titanium substrate is unstable and dissolves during anodic polarization at the potentials of the oxygen evolution reaction in  $0.5 \text{ mol dm}^{-3}$  sulfuric acid. Thermal treatment of the electrodeposited layer at temperatures between  $450^{\circ}$ C and  $600^{\circ}$ C in air stabilizes the electrode surface. The decrease of oxygen evolution current is attributed to the decrease in electrode area and to the loss in the electrochemical activity. The latter conclusion is supported by the increase of the Tafel slope from 30 to 50 mV dec<sup>-1</sup> after thermal treatment.

# **INTRODUCTION**

The majority of research efforts in the electrochemistry of ruthenium has been devoted to the properties of  $RuO_2$  electrode formed by thermal decomposition of  $RuCl_3$  on a titanium substrate. Following the pioneering work of Beer and the invention of a dimensionally stable anodes (DSA) and their successful use in the chloro-alkali industry[1] much work has been done investigating  $RuO_2$  electrode, both from the fundamental and applied points of view[2-4].

The electrodeposited layer of ruthenium has also been investigated while studying the resolution of oxidation reduction processes in the oxide film 5–97, the oxygen[10-15] and chlorine evolution reactions[10, 13-15], anodic corrosion of ruthenium[16], the resolution of charging processes in the oxide film[17], the oxidation of benzyl and crotyl alcohols[18], the mechanism of ruthenium electrodeposition[19], the use of ruthenium as electrical contact material[20] and from the fundamental aspects of electron exchange reaction on metal electrodes[21]. Electrodeposition from Li–KCl melt[22] and anodic deposition of RuO<sub>2</sub>[23] have also been reported. As far as the electrocatalytic properties and the stability of the electrode material are concerned it is known that ruthenium exhibits the lowest overvoltage in the oxygen evolution reaction (OER). This reaction on ruthenium, as well as on other noble metals, occurs on the oxide covered electrode. In the case of ruthenium it is either hydrous  $RuO_2$  if electrolytically prepared, or anhydrous RuO<sub>2</sub> if prepared thermally. The OER on ruthenium proceeds via adsorption of hydroxyl radicals as intermediate step and with the formation of a hydrous oxide layer[24-29]. This layer is very efficient in the OER, the reaction does not take place only at the electrode surface, but also inside hydrous oxide pores. In connection with this, the concept of three dimensional electrocatalysis was proposed by Burke and O'Sullivan[30]. The hydrous oxide layer, however, suffers from corrosion during anodic polarization[10-13, 16, 25, 26] unlike RuO<sub>2</sub> which is much more stable[31]. Various attempts have been made to

stabilize the surface or to improve the service life of Ru or RuO<sub>2</sub> electrodes. Iwakura *et al.*[32] used thermal treatment to stabilize bulk hydrous ruthenium dioxide. Kötz and Stucki[33] have successfully stabilized ruthenium electrode by preparing the mixed Ru<sub>x</sub>Ir<sub>1-x</sub>O<sub>2</sub> where iridium played the role of the stabilizing substance. Addition of SnO<sub>2</sub>[34] and ZrO<sub>2</sub>[35] to the RuO<sub>2</sub> based DSA increased the service life of RuO<sub>2</sub> electrodes.

The present paper is the study of the properties of the ruthenium layer electrodeposited from acidic solutions on a titanium substrate in the OER and the effect of thermal treatment on the electrode performances. Titanium was chosen as a substrate material due to the fact that this metal serves as a substrate in preparation of DSA electrodes. Under anodic polarization it forms a TiO<sub>2</sub> layer on the surface which is isomorphous with RuO<sub>2</sub>[36], thus forming good compactness between two oxide layers.

# **EXPERIMENTAL**

A titanium wire (Goodfellow Metals; 99.9% purity; 0.25 cm<sup>2</sup> geometrical area) sealed in glass served as a substrate for electrodeposition. It was polished with emery paper and 1  $\mu$ m alumina powder, washed with quadruply distilled water and treated by a potentiodynamic sweeps from -0.2 V to +1.2 V vs sce at 2 Hz for 2 min in 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>. The electrodeposition of ruthenium was carried out galvanostatically from a stirred solution of 1 gdm<sup>-3</sup> (NH<sub>4</sub>)<sub>2</sub>RuCl<sub>6</sub>; 0.1 mol dm<sup>-3</sup> HCl (Fluka, puriss.) at a current density of 40 mA cm<sup>-2</sup> for 15 min at room temperature.

Thermal treatment was carried out in air for one hour. The history of the electrode before thermal treatment was the electrodeposition and recording of one cycling voltammogram from -0.2 to +1.15 V (without 100 mV increments as in Fig. 1) in order to characterize it potentiodynamically. The reverse scan was terminated at -0.2 V holding the potential at this value for 1 min.



Fig. 1. Cyclic voltammogram at a sweep rate of 50 mV s<sup>-1</sup> of a electrodeposited ruthenium electrode on a titanium substrate in 0.5 mol dm<sup>-3</sup>  $H_2SO_4$  (100 mV increments in anodic direction).

Electrochemical measurements were performed using a potentiostat/galvanostat (PAR 173), a function generator (either PAR 175 or Wavetek Mod. 164) and x-y recorder (Hewlett-Packard 7000B). Currents are expressed versus geometrical area of titanium substrate.

An H-type electrochemical cell with a platinum foil as counter and a *sce* as reference electrode were used. Solutions were prepared using sulfuric acid (Fluka puriss., p.a.) and quadruply distilled water. Purified nitrogen and oxygen were bubbled, when necessary, through the solution.

#### RESULTS

Figure 1 illustrates the resolution between oxidation and reduction processes of an electrodeposited and thermally untreated ruthenium electrode on a titanium substrate in 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> using potentiodynamic polarization. In the anodic direction after hydrogen ionization from -0.2 V to 0.0 V vs sce the family of curves up to +0.6 V represents reversible oxidation/reduction processes while the oxide formed at the more positive potentials is irreversibly reduced (curves 6–10). At +1.1 V the oxygen evolution commences and the reduction of oxide formed at this potential is overlapped with hydrogen deposition at 0.2 V. Before each polarization step was started the potential was held at -0.2 V for 1 min. Within this period the oxide was reduced and the recording of superimposable curves in anodic direction was thus possible. The kinetics of this irreversible reduction process was investigated in more details by Burke and Mulcahy[6] by recording current-time curves from various anodic values.

Figure 2 shows the potentiostatic polarization curves for the OER on an electrodeposited ruthenium electrode in 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> and on an electrodeposited electrode which was subjected to thermal treatment in air at 450°C for 1 h. The main characteristics of these curves are the Tafel slope of 30 mV dec  $^{-1}$  and a decrease of current at +1.2 V in the case of thermally untreated electrode. There is an increase in Tafel slope to 50 mV dec<sup>-1</sup> and absence of current decrease in the case of thermally treated electrode. It seems that the potentials about +1.2 V are the most interesting ones and the behaviour of the thermally untreated electrode was investigated in more details at +1.21 V by recording current-time curve. After a sharp decrease of current at the very beginning of the electrolysis there is an increase of current within five minutes followed by sharp decay afterwards, as shown in Fig. 3.

The potentiodynamic characteristics of the thermally treated electrodes are shown in Fig. 4. The electrode was transferred to the oven when the electrochemically grown oxide in the positive scan of the cyclic voltammogram was reduced in the cathodic scan at



Fig. 2. Potentiostatic polarization curves for OER on electrodeposited ruthenium on titanium substrate in  $0.5 \text{ mol dm}^{-3} \text{ H}_2 \text{SO}_4$  ( $\bigcirc$ ) and on electrodeposited ruthenium electrode followed by the heat treatment at  $450^{\circ}\text{C}$  ( $\times$ ). Data were taken after two minutes at each potential value.





Fig. 3. Current vs time curve of electrodeposited ruthenium electrode in 0.5 mol dm<sup>-3</sup>  $H_2SO_4$  at +1.21 V vs sce.

-0.2 V; the electrode was, therefore, in its reduced state. The difference between electrodeposited but thermally untreated electrode (Fig. 1) and the electrodes treated at elevated temperatures (450 and 600°C) is evident. The electrode treated at 200°C shows an unchanged potentiodynamic profile, while the electrodes treated at 450 and 600°C, respectively, show the absence of the main oxidation peak at +0.9 V. Also, the voltammetric charge is considerably smaller throughout entire potential range (note the difference in current axis between a and b, c).

The OER currents of two types of ruthenium elec-

Fig. 4. Cyclic voltammograms at a sweep rate of 50 mV s<sup>-1</sup> of electrodeposited ruthenium on Ti followed by the heat treatment at: (a) 200; (b) 450; (c) 600°C.

trodes polarized at +1.2 V are shown in Fig. 5. The current at the titanium substrate is also shown in order to compare it with the current at the ruthenium layers deposited on it. There is continuous decrease of current at the thermally untreated electrode contrary to the current at the thermally treated electrode. This current is lower at the beginning of the electrolysis, but increases during the first hour of polarization. There is a slight continuous decay of current after one hour, but the current, however, remains higher at the end of the experiment then it was at the beginning. This change in the activity of the electrode has been



Fig. 5. OER currents at +1.2 V vs sce in 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> of electrodeposited ruthenium electrode ( $\bigcirc$ ); electrodeposited electrode followed by the heat treatment at 450°C ( $\times$ ) and of pure titanium substrate ( $\nabla$ ).



Fig. 6. Cyclic voltammograms of thermally treated ( $450^{\circ}$ C) electrodeposited ruthenium electrode (dashed line) and the same electrode after 5 h of polarization at +1.2 V (full line).

examined by recording cyclic voltammograms at the beginning and at the end of polarization of thermally treated electrode. The results are shown in Fig. 6.

#### DISCUSSION

The potentiodynamic and potentiostatic characteristics of an electrodeposited thermally untreated ruthenium electrode on a titanium substrate in  $0.5 \text{ mol dm}^{-3} \text{ H}_2 \text{SO}_4$  (Figs 1 and 2) are the same as previously described when using platinum as substrate[5, 9]. This is not surprising because in both cases the metal loading was sufficient to eliminate any influence of the substrate, and in both cases, the electrodes behave as a ruthenium metal electrode. The decrease of current at +1.2 V of thermally untreated electrode (Fig. 2) is due to dissolution of ruthenium layer. Such a sharp decrease of current might lead to the conclusion that passivation of the electrode takes place. Indeed, there is a work by Llopis and Vazquez[37] about passivation of ruthenium sheet in HCl solution. Deposited layers of ruthenium, however, corrode under anodic polarization in HCl, as shown by Llopis et al.[16], as well as in  $H_2SO_4$ regardless of the method of preparation: electrodeposition[13], sputtering[26] or by melting ruthenpowder using vacuum electron beam ium technique[25]. During anodic polarization in the present work, as well as in those reported previously[11, 13, 25, 31], the color of the solution turns yellow from corrosion products which are known to be RuO<sub>4</sub> or H<sub>2</sub>RuO<sub>5</sub>[24–26]. It is evident from Fig. 3 that the potentiostatic polarization of electrodeposited ruthenium electrode is accompanied by several parallel processes. The current-time curve recorded at +1.21 V vs sce shows a sharp decay of current at the very beginning of the electrolysis. The initial bubble formation causes the decrease in the available surface area

until a steady-state condition is achieved. As far as the bubble formation and their release is concerned, it happens within a few seconds. After that there is an increase in current which reaches its maximum value after 5 min. The cyclic voltammogram recorded at this maximum showed the increase of the voltammetric charge. This suggests either oxide growth or the incorporation of active redox groups in the surface layer. Burke and O'Meara[11] have obtained similar results using ruthenized platinum. They have measured current-time behaviour at various anodic potentials. At +1.45 V vs rhe, for example, the peak was recorded after ten minutes. The sharp decay of current in Fig. 3 indicates that finally electrode dissolution predominates. Dissolution of this thermally untreated ruthenium layer caused the decay of current to less than 1% of its initial value after five hours of polarization at +1.2 V (Fig. 5). Thermal treatment in air, however, changed the performances of the electrode material in several ways. There were significant changes in the potentiodynamic profiles, electrocatalytic activity and stability in the OER. Cyclic voltammograms show the disappearance of the main oxidation peak at +0.9 V after heat treatment at 450 and 600°C. respectively (Fig. 4). Thermal treatment at 200°C. obviously, is not sufficient to change potentiodynamic response of the electrodeposited layer. Potentiostatic polarization experiments (Fig. 2) show the decrease in current after thermal treatment. There are probably two reasons responsible for this: firstly, the decrease of the electrode area which is often the case when hydrous oxide electrodes are subjected to thermal treatment and secondly, the loss in electrochemical activity. This is supported by the increase in the Tafel slope from 30 mV dec<sup>-1</sup> to 50 mV dec<sup>-1</sup> after thermal treatment. Both values fit in the range of  $30-60 \text{ mV dec}^{-1}$ observed with RuO<sub>2</sub> electrodes of various types of surface morphology[38]. It is clear from Fig. 5 that thermal treatment stabilizes the electrodeposited layer of Ru. This treatment oxidizes Ru to RuO<sub>2</sub>. There are numerous reports in the literature which support this conclusion. 450°C is the temperature of thermal decomposition of RuCl<sub>3</sub> to RuO<sub>2</sub> in preparation of DSA electrodes, as shown by TGA measurements[39]. Temperatures between 600 and 950 K are the conditions where ruthenium oxidizes to RuO<sub>2</sub> as shown by Cranstoun and Pyke[40] using field ion microscopy technique and by Klein et al.[41] using ESCA and thermal desorption spectroscopy. The fact that thermally treated electrodeposited ruthenium layers have much of the characteristics of the RuO<sub>2</sub> electrode is supported by their potentiodynamic profiles (Figs 4b and c), which are similar to those obtained by thermal decomposition of RuCl<sub>3</sub>[31]. Figure 5 shows the difference in stability between the hydrous type of ruthenium oxide and the thermally treated (anhydrous) one. The decay of current at thermally untreated electrodes is no doubt due to electrode dissolution. The slight decrease of current at the thermally treated electrode, however, can be attributed to a deactivation mechanism similar to that proposed for the nickel oxide electrode[42], rather than to dissolution. Difference in properties of hydrous and anhydrous metal oxides is a well known phenomenon. Hydrous types of oxide layer are more active electrochemically while thermally treated ones are more stable chemically and a compromise is often an optimal condition [43]. Hydrous  $RuO_2$  formed by anodic polarization in a potentiodynamic sweep can be reduced in the reverse scan polarizing the electrode in the hydrogen region at -0.2 V vs sce[7, 9, 31]. Thermally prepared  $RuO_2$  is stable when exposed to various electrochemical treatments and only treatment in flow of hydrogen at 200°C reduced it to metallic ruthenium [44]. Figure 6 shows that together with OER the oxide film itself undergoes some changes. The increase in voltammetric charge after polarizing the electrode for five hours at +1.2 V indicates oxide growth. The second possibility is that the oxide layer became hydrous with certain amount of active hydroxyl groups responsible for charge storage in the oxide film.

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