Comparative Study of Anodic Behaviour of Electrodeposited Ruthenium, Iridium and Rhodium Coatings on Titanium in Acid Solution*

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The electrocatalytic activity and anodic stability of electrodeposited ruthenium, iridium and rhodium coatings on titanium in oxygen evolution reaction from 0.5 mol dm^{-3} sulphuric acid have been investigated. The voltammetric charge of oxide formation was taken as a measure for electrochemically active surface area. The currents in the Tafel polarization plots were normalized according to these data. Ruthenium exhibited the highest electrocatalytic activity evidenced by the lowest Tafel slope of 30 m V/decade and the highest normalized current density. Anodic galvanostatic polarization, carried out at 0.016 A cm^{-2} and 1 A cm^{-2}, respectively, proved rhodium to be the most stable coating.

INTRODUCTION

The oxygen evolution reaction (OER) on both noble and transition metal oxides proceeds on the surface covered with their oxides. In fact, the entire electrochemistry of these metals in the anodic region is the electrochemistry of their oxides.[1] Among them, platinum was most thoroughly investigated. However, the invention of DSA (an acronym for dimensionally stable anode based on RuO_2 prepared by calcination of $RuCl_3$ on titanium) by Beer[2] in 1965, and its world-wide use in chlorine production, turned attention to other noble metals. Indeed, it was found that ruthenium and iridium exhibit the lowest overvoltage in oxygen evolution reaction in acid solution. Only a few complex transition metal oxides,[3] like $NiCo_2O_4$ and $NiLa_2O_4$, have been claimed to match their electrocatalytic properties in alkaline solution.

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Oxygen evolution on noble metals is accompanied by dissolution of the oxide film and every metal exhibits a different rate of corrosion.[4] Ruthenium, for example, dissolves at a rate five orders of magnitude faster than platinum.[5] It should be pointed out that these metals dissolve also during potentiodynamic cycling, *i.e.* during continuous oxide formation and reduction. Michell *et al.* reported[6] dissolution rates varying from 2 ng cm^{-2} per cycle in the case of gold electrode to 3080 ng cm^{-2} in the case of ruthenium electrode. Another problem that prevents the use of noble metals on a large scale is their high cost. This is usually solved, like in the case of DSA electrodes, by preparing relatively thin films deposited on some conductive metallic substrate. In our work, we have used electrodeposition as a convenient way of preparing noble metal coatings.

Literature data presenting the electrochemical properties of rhodium, iridium and particularly ruthenium are abundant, and several review articles have been published.[7-9] The electrochemistry of electrodeposited ruthenium, iridium and rhodium has also been investigated with respect to their voltammetric and electrocatalytic behaviour in a number of papers from our laboratory.[10-15] The coatings exhibited different electrocatalytic as well as different stability performances. Due to the different electroplating efficiencies in the first place, it was not possible to make a direct comparison of these properties. It is the purpose of the present paper to make a more accurate comparative analysis of the data first, by their normalization to the same electrochemically active surface area and, second, by normalization of the coatings to the amount of deposited metals.

EXPERIMENTAL

The substrate for electrodeposition was a titanium wire (Goodfellow Metals, 99.6% purity, 0.25 cm^2 geometrical area) fixed in a glass tube with epoxy resin. The wire was polished by emery paper and 1 μm alumina powder, washed with quadruply distilled water and treated potentiodynamically from –0.2 V to 1.2 V *vs.* saturated calomel electrode (SCE) for 2 minutes at 1 Vs^{-1} in 0.5 mol dm^{-3} H$_2$SO$_4$ (Fluka *p.a.*). This procedure was undertaken in order to clean the surface of surface active substances in a similar way as it is usually done with platinum.[16] In comparison with platinum, some differences arise, while subjecting titanium to this procedure. Anodic polarization of titanium forms an oxide layer which might influence the process of electrodeposition. However, we have shown that ruthenium coating on titanium[11] exhibited the same potentiodynamic profile while using platinum as substrate. In other words, titanium did not prevent electrodeposition of noble metals.

Electrodeposition was carried out galvanostatically at 40 mA cm^{-2} current density from 1 g dm^{-3} solution of diammonium hexachloro salts of Ru(IV), Ir(IV) and Rh(IV) (Fluka *puriss. p.a.*), respectively for 15 minutes. Ruthenium and rhodium were deposited at 25 °C, efficient electrodeposition of iridium required higher temperature.[15] It was deposited at 70 °C.

The electrochemical set–up consisted of an EG&G 273/97 potentiostat/galvanostat and a Helwett-Packard Mod. 7004B x-y recorder. A three compartment electrochemical cell with a platinum electrode as counter electrode and a SCE as reference electrode were used. All experiments were carried out at 25 ± 0.1 °C. The corrections for IR-drop and a charge integration were done by using Model 273/97 built-in current interrupter and charge integrator, respectively.

Scanning electron microscopy (SEM) was carried out using a Cambridge Stereo Scan 600 microscope. The photographs were taken before any electrochemical examination, as they emerged from plating baths.

RESULTS AND DISCUSSION

Cyclic Voltammetric Characterization of Coatings

The most convenient way of characterizing metal coatings in electrochemistry is by recording their potentiodynamic current-voltage curves called by Trasatti[17] »electrochemical spectra«. There are many similarities as well as differences in the shapes of cyclic voltammograms of electrodeposited ruthenium, iridium and rhodium coatings on titanium, as seen in Figure 1. The general shapes of cyclic voltammograms of these metals are in agreement with the literature data when different plating baths and/or different substrates are used.[18-22] The voltammograms (Figure 1) show the first
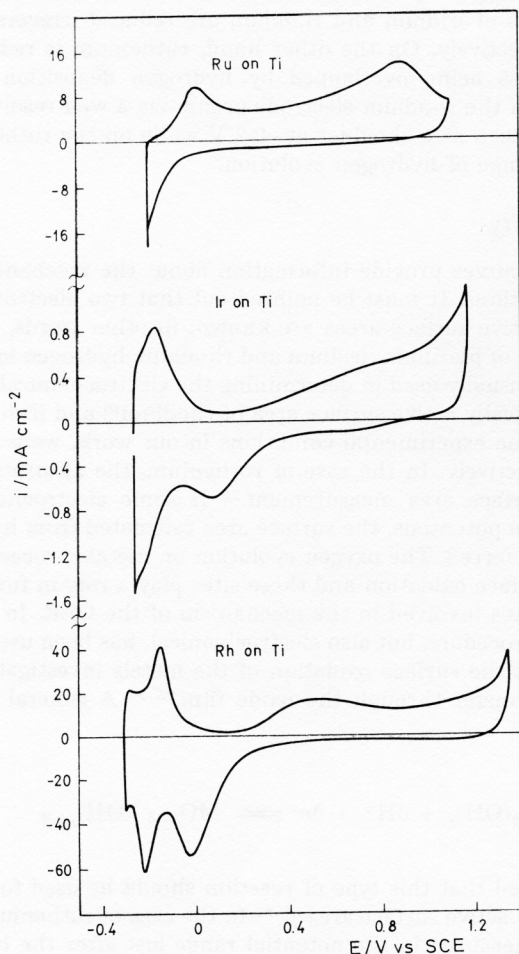

Figure 1. Cyclic voltammograms at a 50 mV s^{-1} sweep rate in 0.5 mol dm^{-3} H$_2$SO$_4$ of ruthenium, iridium and rhodium galvanostatically electrodeposited on titanium.

potentiodynamic scan of the electrode, as prepared. We have shown previously that, repetitive potential scans of ruthenium and rhodium are almost reproducible when increasing the positive limits for 100 mV (c.f. Figure 1 in Ref. 11 and Figure 3 in Ref. 10). The slight decrease of currents in the hydrogen ionization region and at the potential of the surface oxidation was probably due to the electrode dissolution (this phenomenon will be discussed later). In the case of ruthenium electrode, it could be achieved only if the potential at the negative side was held up for 40 s before the subsequent scan was recorded. This was necessary in order to reduce the oxide, namely the oxide reduction exhibited an induction period depending on the positive limit of potential excursion.[23,24] In the case of all three metals, the potentiodynamic scan starts with the hydrogen ionization process which is, in the case of ruthenium, followed by an immediate oxidation of the surface. Iridium and rhodium exhibit a short, about 100 mV wide, double layer region before the commencement of surface oxidation. In the reverse scan, the oxides of iridium and rhodium are reduced irreversibly with peaks at 0.1 V and 0 V, respectively. On the other hand, ruthenium is reduced even more irreversibly, the process being overlapped by hydrogen deposition and evolution. Hydrogen deposition on the rhodium electrode occurs via a well resolved peak at –0.2 V, on the iridium it is seen as a shoulder at –0.2 V while on the ruthenium it is completely placed in the range of hydrogen evolution.

Electrocatalytic Activity

Tafel polarization curves provide information about the mechanism and activity of electrochemical reactions. It must be pointed out that two electrodes can be compared if their electroactive surface areas are known; in other words, they have to be determined. In the case of platinum, iridium and rhodium, hydrogen ionization and/or deposition charges are usually used in determining the electrochemically active surface area.[8] The electrochemically active surface area of rhodium[10] and iridium[15] electrodes, prepared under the same experimental conditions in our work, were found to be 198 cm² and 7.6 cm², respectively. In the case of ruthenium, the absorption of hydrogen complicates precise surface area measurement.[25] If some electrochemical reactions were studied at negative potentials, the surface area calculated from hydrogen charges would, of course, be preferred. The oxygen evolution on metals proceeds on the active sites created by the surface oxidation and these sites play a role in further adsorption of hydroxyl intermediates involved in the mechanism of the OER. In this connection a somewhat different procedure, but also electrochemical, has been used in the present paper. It is known that the surface oxidation of the metals investigated in this work proceeds via proton transfer through the oxide film.[26-30] A general formula can be written as:[17]

$$MO_x(OH)_y + \delta H^+ + \delta e^- \rightleftharpoons MO_{x-\delta}(OH)_{y+\delta} \qquad (1)$$

and it has been proposed that this type of reaction should be used for determination of the electrochemically active surface area.[31-33] In the case of ruthenium the oxide formation charges were measured in the potential range just after the hydrogen ionization peak, (see Figure 1) and in the case of iridium and rhodium after the double layer region. In all three cases, the positive limit was the potential before the commencement of OER. These charges are 38 mC, 2mC and 75.5 mC in the case of ruthenium, iridium

and rhodium coatings, respectively. The question which arises is to which extent these charges are influenced by the electrode dissolution. Michell *et al.* [6] reported that ruthenium dissolved at a rate of 3080 μg per cycle; rhodium with 126 μg per cycle and iridium with rate of 38.5 μg per cycle. Expressed in coulombs, it was 0.363 mQ per cycle in the case of rhodium. There is a charge of 75.5 mQ in the electroplated rhodium in the present work, *i.e.* 0.5% of rhodium was dissolved during one potentiodynamic scan. The data obtained by Michell *et al.* for ruthenium dissolution, namely 3080 μg per cycle, was obtained, however, by potential excursion to 1.54 V *vs.* reversible hydrogen electrode (RHE), (1.3 V *vs.* SCE), which is relatively far into the oxygen evolution region where ruthenium dissolves significantly. These authors reported that ruthenium dissolution commenced between 1.2 and 1.3 V *vs.* RHE, At 1.0 V the cathodic charge was almost equal to the anodic charge of the oxide formation. Since the oxidation of ruthenium commences at 0 V *vs.* SCE, most of the charge is not influenced by surface dissolution. The potentiodynamic scan of ruthenium in Figure 1 was terminated at 1.15 V. Our recent results, using a rotating ring-disc measurement at electrodeposited ruthenium electrode,[13] support the finding that significant dissolution of electrodeposited ruthenium started at 1.2 V *vs.* SCE. In our opinion, the current of metal dissolution is negligible in comparison with the current of metal oxidation. The voltammetric charge data obtained by integrating oxide formation currents in Figure 1 were used in normalizing the currents obtained by potentiostatic polarization measurements in which the currents were divided by these values. Although the conditions of electrode preparation were the same, except for the plating temperature, the differences in voltammetric charges arose from different current efficiencies in electroplating. These values were determined to be 0.38%, 0.05% and 2.3% in the case of ruthenium,[12] iridium[15] and rhodium[14] electrodes, respectively. As seen from Figure 2, the electrodeposited ruthenium exhibits the lowest Tafel slope (30 mV/decade) and, measured for example at 1.2 V, the highest current density. Therefore, this electrode
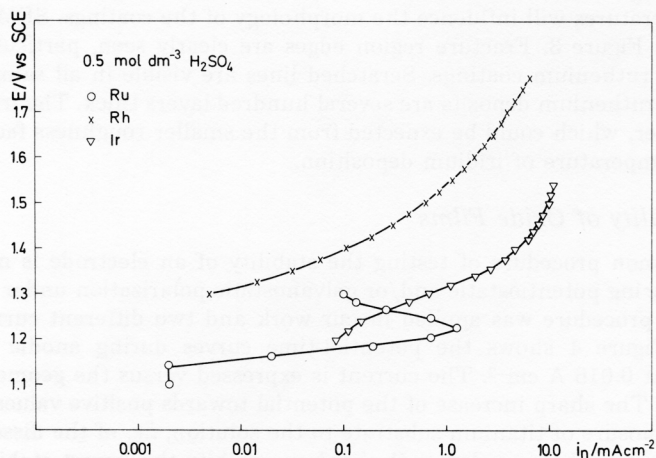

Figure 2. Potentiostatic polarization curves of the OER in 0.5 mol dm^{-3} H$_2$SO$_4$ for electrodeposited ruthenium, iridium and rhodium electrodes normalized to the electrochemically active surface area.

exhibits the highest electrocatalytic activity. The Tafel slope of iridium electrode in its linear part is 90 mV/decade with a break at 1.38 V, indicating a change in the mechanism of OER. There is no linear part in the polarization curve of the rhodium electrode. This electrode, as evident from the current efficiency in electroplating and seen from the anodic voltammetric charge, has the greatest surface roughness and will exhibit the greatest unnormalized current under potentiostatic polarization. Such conditions, accompanied by a comparatively large amount of oxygen bubbles in the pores, cause extra ohmic loss, influence the measured potential and distort the linear shape of the current-potential curve. Nonuniform current distribution, due to the decrease of the effective surface area, leads to hyperpolarization and concentration polarization effects,[34] which can be as high as 100 mV and cannot be corrected by current interruption. Despite these anomalies, it is evident that, at lower current densities, the slope drawn through these points will be similar to the slope of iridium polarization curve at lower current densities. Inspection of the ruthenium polarization curve shows that this electrode exhibits a sharp decrease in the current after 1.2 V. This is known to be due to ruthenium dissolution.[11] Its stability will be discussed later in the text. Iwakura et al.[35] have also obtained 30 mV/decade as a Tafel slope for ruthenium electrode in acid solution and suggested that the mechanism of the OER on ruthenium proceeds as follows:

$$S + H_2O = SOH + H^+ + e^- \tag{2}$$

$$2SOH = SO + S + H_2O \tag{3}$$

$$2SO = 2S + O_2 \tag{4}$$
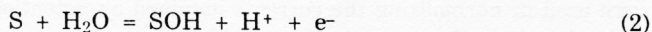
where S is an active metal site.

Morphology of the Coatings

The question which arises is whether different current efficiencies and different plating temperatures will influence the morphology of the coatings. SEM micrographs are shown in Figure 3. Fracture region edges are clearly seen, particularly those of rhodium and ruthenium coatings. Scratched lines are visible in all samples although rhodium and ruthenium deposits are several hundred layers thick. The iridium coating looks smoother, which could be expected from the smaller roughness factor and from the higher temperature of iridium deposition.

Anodic Stability of Oxide Films

The common procedure of testing the stability of an electrode is measuring the service life during potentiostatic and/or galvanostatic polarization under working conditions. This procedure was applied in our work and two different current densities were used. Figure 4 shows the potential-time curves during anodic galvanostatic polarization at 0.016 A cm^{-2}. The current is expressed versus the geometrical area of the electrode. The sharp increase of the potential towards positive values is an indication of the exposure of titanium substrate to the solution, i.e. of the dissolution of the noble metal below the monolayer. Ruthenium exhibits the lowest stability. There is an S shaped curve at the beginning of iridium dissolution, for which we have shown previously[15] that the oxide consists of a compact inner oxide and a hydrous oxide exposed to the solution. It does not necessarily mean that the ruthenium electrode does not consist of two different types of oxide. The dissolution is probably too fast to allow
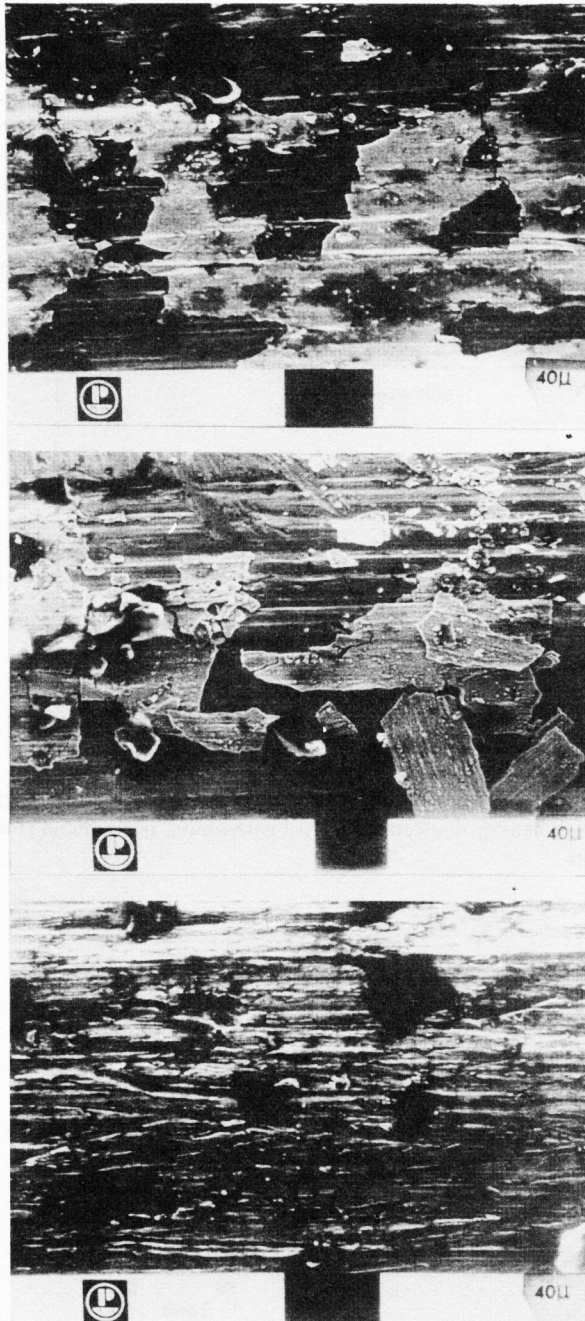
Figure 3. Scanning electron micrographs (from top to bottom) of electrodeposited ruthenium, rhodium and iridium electrodes on titanium.

their resolution. Rhodium electrode is the most stable electrode. It must be pointed out, however, that different current efficiencies in electroplating resulted in different amounts of metal loading. We have previously determined these amounts as 55 μg; 9 μg and 2.3 μg in the case of electrodeposited rhodium,[14] ruthenium,[12] and iridium[15] electrodes, respectively. In order to make a more accurate comparison of the service-life of the electrode, the time values of the service-life in Figure 5 were obtained by normalizing them to the amounts of rhodium deposit. More precisely, the service life of ruthenium electrode was multiplied by 6.1, and for iridium by 23.9. An accelerated corrosion test, using higher current density (1 A cm^{-2}), presented in Figure 5, shows that iridium coating is more stable than ruthenium coating, while rhodium exhibited the most stable coating.
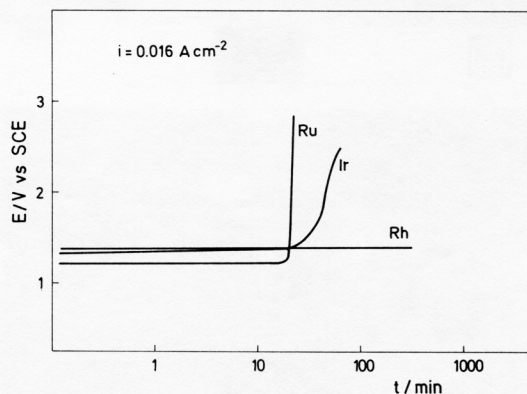

Figure 4. Potential-time curves during anodic galvanostatic polarization at 0.016 A cm^{-2} (geometrical area) current density of electrodeposited ruthenium, iridium and rhodium electrodes in 0.5 mol dm^{-3} H$_2$SO$_4$.
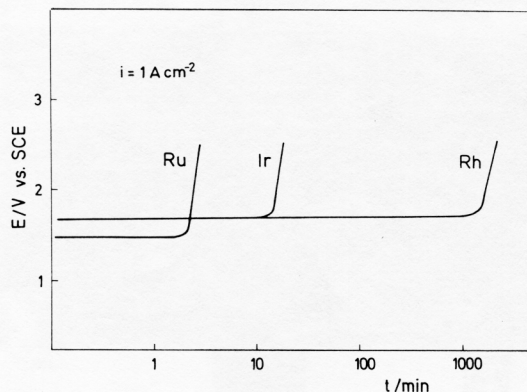

Figure 5. Same as Figure 4, but with 1 A cm^{-2} current density normalized to the amount of electrodeposited rhodium.

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SAŽETAK

Poredbena istraživanja anodnog ponašanja elektrodeponiranih slojeva rutenija, iridija i rodija na titanu u kiselim otopinama

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Istraživana je elektrokatalitička aktivnost i anodna stabilnost pri elektrokemijskom razvijanju kisika iz otopina koja je sadržavala sumpornu kiselinu na elektrodeponiranim slojevima rutenija, iridija i rodija na titanu. Voltametrijski naboj stvaranja oksida uzet je kao mjera elektroaktivne površine te su struje u Tafelovim polarizacijskim krivuljama normalizirane na te vrijednosti. Rutenij je na temelju najmanjeg Tafelova nagiba od 30 mV po dekadi i najveće normalizirane struje pokazao najveću elektrokatalitičku aktivnost. Anodnom galvanostatskom polarizacijom s gustoćama struje od 0.016 A cm^{-2} i 1 A cm^{-2} nađeno je da je rodijeva prevlaka najstabilnija.