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Original Scientific Paper

Electrochemical Investigation of an Electrodeposited and Thermally Treated Ruthenium Electrode in Alkaline Solution*

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The oxygen evolution reaction has been studied on ruthenium electrodeposited on a titanium substrate in 1 mol dm^{-3} sodium hydroxide solution. A Tafel slope of 40 mV per decade was obtained, but the electrode dissolved under anodic polarization. Thermal treatment of the bare ruthenium electrode at 450 °C in air stabilized the electrode surface. The service life test within four days did not show any dissolution of the electrode layer. Anodic oxidation of the electrode treated at 250 °C has shown the presence of a duplex oxide film, hydrous at the outer layer of the electrode and more compact closer to the titanium surface. Impedance measurements in the frequency range from 0.1 Hz—20 kHz show two parallel processes on the electrode surface.

INTRODUCTION

The invention of a dimensionally stable anode (DSA) by Beer[1] in 1965 initiated intensive fundamental work in the electrochemistry of ruthenium and ruthenium oxide films[2–4]. Low overvoltage in chlorine and oxygen evolution reactions, good electrical conductivity and stability against corrosion are the most important characteristics of DSA electrodes. These electrodes are usually prepared by thermal decomposition of $RuCl_3$ on a titanium substrate[5]. An alternative way of preparation of electrodes in the form of a thin film of noble metal is the method of electrodeposition on some cheaper, conductive metallic substrate. The electrodeposited ruthenium electrode has also been investigated in various ways[6]. It exhibits the lowest overvoltage in the oxygen evolution reaction (OER). Its disadvantage, however, is the low stability gainst corrosion. This is a problem with electrodeposited ruthenium electrodes[7,8]. This problem also arises with other noble metals, as it was recently reviewed by Kolotyrkin *et al.*[9]. In the alkaline solution, most of the research was carried out using thermally prepared RuO_2 electrodes[10–16]. The electrodeposited ruthenium electrode corrodes under anodic polarization in the alkaline[10] as well as in the acidic solutions[17–21], and the dissolution rate increases with the concentration of hydroxyl ions[8].

It is the aim of the present work to investigate the electrochemical properties of electrodeposited ruthenium on a titanium substrate in alkaline

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solution with the emphasis on its stability in the electrocatalysis of the OER. In several papers from this laboratory the anodic stability of iridium, ruthenium and rhodium oxide films has been reported. The electrolytically grown hydrous oxide film on iridium[22] and the electrodeposited ruthenium on titanium[6] dissolve under anodic polarization in sulfuric acid. The electrodeposited rhodium electrode, however, is much more stable in both acidic[23] and alkaline solutions[24].

EXPERIMENTAL

Titanium wire (Goodfellow Metals, 0.25 cm^2 geometrical area), sealed into glass, served as substrate for electrodeposition. It was polished with emery paper and 1 μm alumina powder, washed with quadruply distilled water and subjected to a potentiodynamic polarization from -1.0 V to +0.25 V vs. SCE at 2 Hz for 2 min in 1 mol dm^{-3} NaOH. The electrodeposition was carried out galvanostatically from a stirred solution of 1 g dm^{-3} $(NH_4)_2RuCl_6$; 0.1 mol dm^{-3} HCl (puriss. Fluka) at 40 ma cm^{-2} 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 cyclic voltammogram from —1.1 V to +0.2 V vs. SCE, in order to characterrize it potentiodynamically. The reverse scan was terminated at -1.1 V and the electrode was, therefore, in its reduced state.

The quantity of electrodeposited ruthenium was 9.0×10^{-6} g. It was determined using a titanium plate of 2 cm^2 area. The electrodeposition was carried out by the same current density as on the wire electrode. The plate was weighed before and after electrodeposition and the difference was 3.6×10^{-5} g cm^{-2} i. e. 9.0×10^{-6} g on the titanium wire electrode of 0.25 cm^2 area.

The cell, instrumental set-up for electrodeposition, potentiostatic and potentiodynamic measurements have been described elsewhere[23]. The potentials are

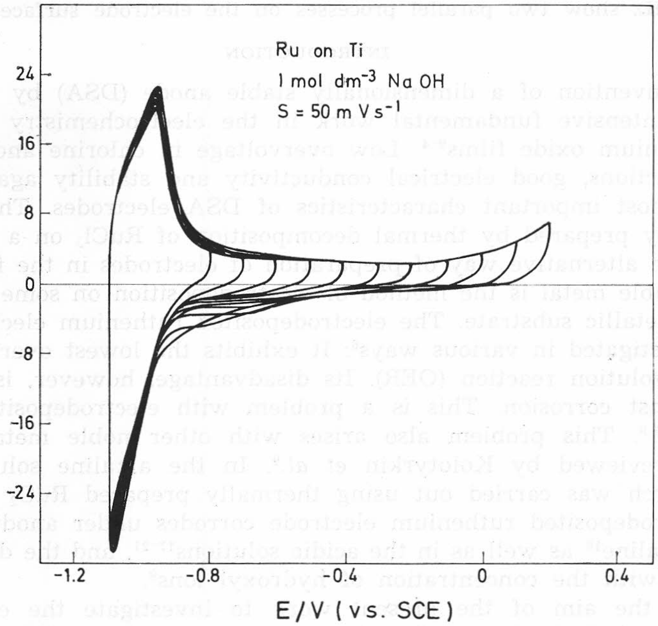

Figure 1. Cyclic voltammograms at a sweep rate of 50 mVs^{-1} of a electrodeposited ruthenium electrode on a titanium substrate in 1 mol dm^{-3} NaOH (100 mV increments in anodic direction).

referred to the saturated calomel electrode (SCE) and the currents are expressed for the geometrical area of titanium substrate.

The ac impendance measurements were carried out using a frequency response analyzer Solartron 1250 and an electrochemical interface Solartron 1286. The amplitude of the ac signal was 5 mV, and data were collected over the frequency range 0.1 Hz—20 kHz. The ac equipment was controlled by Hewlet Packard 9816 computer which was also used for subsequent data manipulation.

RESULTS

Figure 1. shows surface oxidation/reduction processes of the electrodeposited ruthenium on titanium in 1 mol dm^{-3} NaOH solution. After the hydrogen ionization peak from -1.1 V to -0.9 V vs. SCE there is a broad range of surface oxidation up to the potential of OER at +0.2 V. In the reverse scan there is an irreversible reduction of the oxide; the peak overlaps with that of the hydrogen deposition process from —0.9 to —1.1 V.

The potentiostatic polarization plot of the OER of the electrodeposited, thermally untreated ruthenium electrode exhibits the Tafel slope of 40 mV dec^{-1} at the potentials up to +0.3 V (Figure 2). Further polarization in anodic direction causes a sharp decrease of current. It seems that passivation phenomena take place. The brown colour of the solution clearly indicates the dissolution of the ruthenium layer. The thermal treatment at 450 °C in air for one hour stabilizes the surface. The Tafel slope is also 40 mV dec^{-1} at lower current densities and increases at higher current densities, without decreases of current.

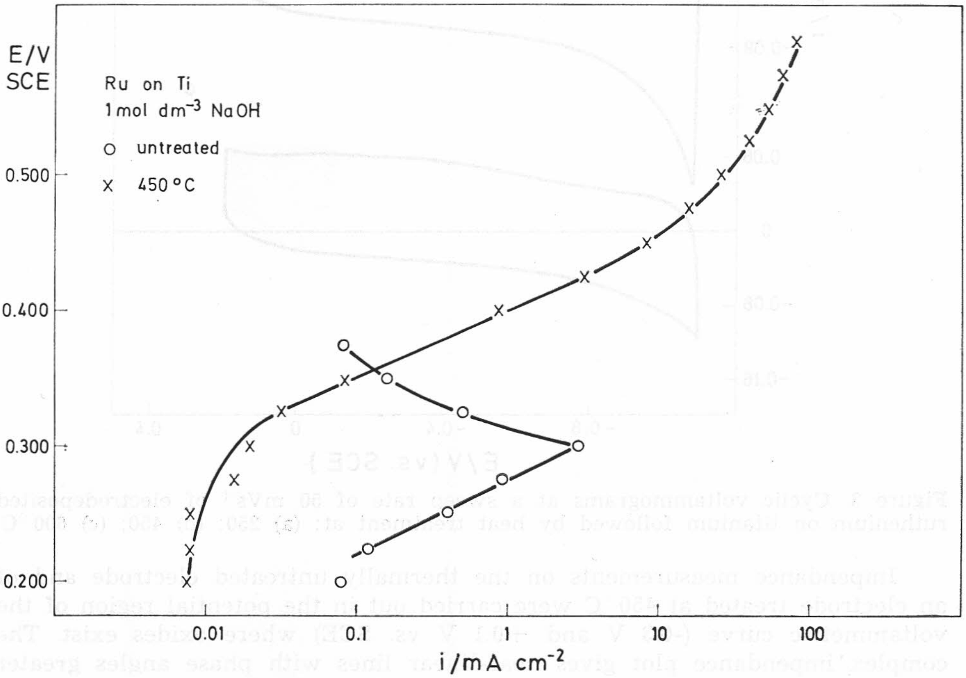

Figure 2. Potentiostatic polarization curves for OER on electrodeposited ruthenium on titanium substrate in 1 mol dm^{-3} NaOH (O) and on electrodeposited ruthenium electrode followed by heat treatment at 450 °C (X). Data were taken after 2 min at each potential value, corrected for IR drop.

The effect of thermal treatment on the potentiodynamic response of the electrodeposited ruthenium is illustrated in Figure 3. The hydrogen peaks and the total voltammetric charge decrease with an increase of the treatment temperature from thermally untreated electrode (Figure 1) to electrodes treated thermally at 250 °C, 450 °C and 600 °C (Figure 3).

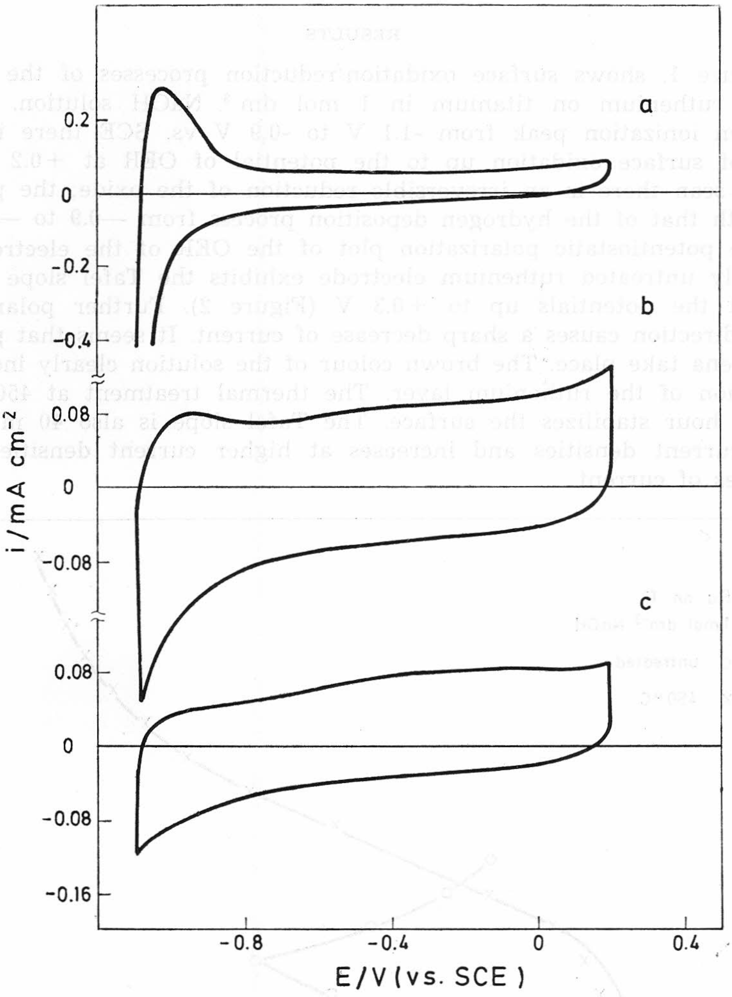

Figure 3. Cyclic voltammograms at a sweep rate of 50 mVs^{-1} of electrodeposited ruthenium on titanium followed by heat treatment at: (a) 250; (b) 450; (c) 600 °C.

Impendance measurements on the thermally untreated electrode and of an electrode treated at 450 °C were carried out in the potential region of the voltammetric curve (-0.3 V and +0.1 V vs. SCE) where oxides exist. The complex impendance plot gives near-linear lines with phase angles greater than $\pi/4$, indicating a large capacitive impendance. Values for electrode impendance were converted to its equivalent components of the electrode admittance y' and y".

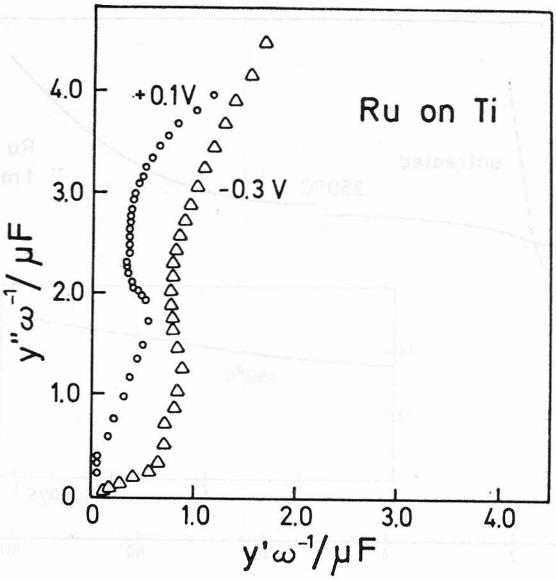

Figure 4. Complex plane admittance plot for electrodeposited ruthenium electrode in 1 mol dm^{-3} NaOH solution.

Figures 4. and 5. show the complex admittance data. The first circle in the high frequencies range is followed by the linear line in the low frequency range, typical of the admittance response for two processes going on at the electrode surface[25].

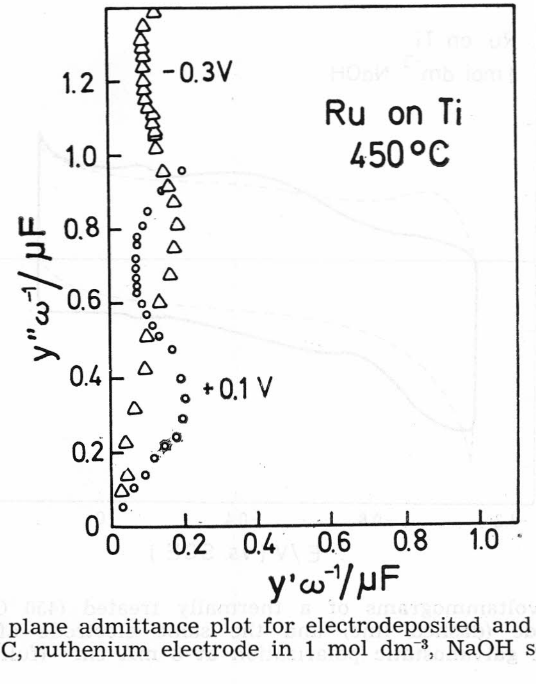

Figure 5. Complex plane admittance plot for electrodeposited and thermally treated, at 450 °C, ruthenium electrode in 1 mol dm^{-3}, NaOH solution.

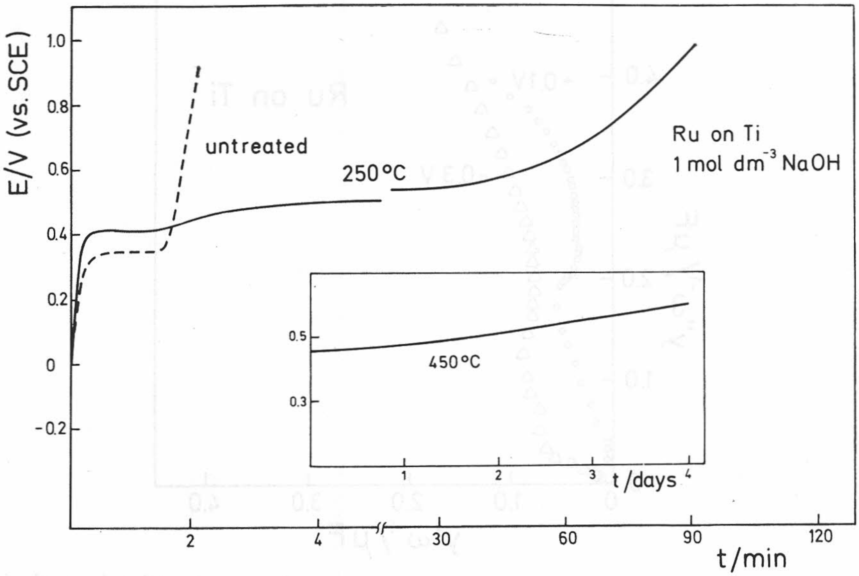

Figure 6. Potential vs. time curves during anodic galvanostatic polarization at 8 mA cm^{-2} of a thermally untreated electrodeposited ruthenium electrode in 1 mol dm^{-3} NaOH and on the thermally treated electrodes, at 250 and 450 °C, respectively.

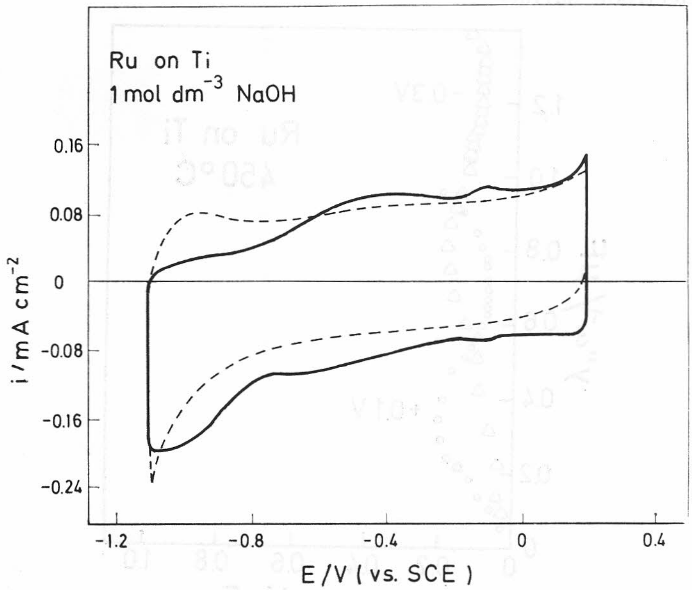

Figure 7. Cyclic voltammograms of a thermally treated (450 °C) electrodeposited ruthenium electrode (dashed line) and the same electrode after four days of anodic galvanostatic polarization at 8 mA cm^{-2} (full line).

The stability of the oxide film has been investigated by monitoring the potential during galvanostatic polarization of the electrodeposited ruthenium layer. Thermally untreated electrode showed a sharp increase in the potential after 1.5 min (Figure 6). Using galvanostatic polarization of 8 mA cm^{-2} over 1.5 min. and taking into account 8 electrons exchanged in the electrode reaction of ruthenium oxidation and 100% efficiency, calculation shows that the quantity of dissolved ruthenium is 9.3 × 10^{-5} g cm^{-2}. The amount of electroplated ruthenium was 3.6 × 10^{-5} g cm^{-2} (see Experimental Section), the rest of the current was consumed in the OER. The electrode treated at 250 °C showed a stable potential for 1 min, then an increase of potential for about 100 mV, followed by slowly changing potentials for one hour when the potential increased more rapidly. The electrode treated at 450 °C exhibited a slow but continuous increase of potential within four days of polarization when the experiment was terminated. Cyclic voltammograms, recorded before and after this experiment, show little difference in their potentiodynamic profiles and corresponding voltammetric charges (Figure 7.). In fact, there was a small increase of the voltammetric charge in the anodic region after -0.6 V and during the whole cathodic scan.

DISCUSSION

The oxygen evolution reaction on noble metals proceeds on oxide covered electrodes. It is accompanied by the dissolution of the oxide layer and the search for optimal conditions between stability and efficiency is of current interest in electrocatalysis. Cyclic voltammetry is a very useful method in the characterization of metal and metal oxide electrodes, particularly when there are small increments in potential (50-100 mV) into anodic direction. The potentiodynamic behaviour of the electrodeposited ruthenium on a titanium substrate in 1 mol dm^{-3} NaOH (Figure 1.) exhibits some differences in comparison with the voltammetric behaviour of ruthenium in sulfuric acid[6]. In both cases the electrodes were prepared under the same experimental conditions and on the same substrate, titanium. Therefore, a direct comparison is possible. In the alkaline solution (Figure 1.) the peak of hydrogen ionization is higher than in the sulfuric acid: this phenomenon was also observed by Entina *et al.*[26] using ruthenized platinum. Surface oxidation is, however, more pronounced in the sulfuric acid where the proton transfer is involved in the redox processes in the oxide film[19,20,27,28]. In the alkaline solution[16] oxyhydrated rutheniums species are involved in the redox processes including also the proton transfer. Surface oxidation starts both in acidic and in alkaline solutions immediately after hydrogen ionization, in contrast to platinum or rhodium[29] where the surface oxidation is distinguished from hydrogen ionization by a double layer region. The OER proceeds with the Tafel slope of 40 mV per decade (Figure 2.) *i. e.* 2RT/3F and remains unchanged after heat treatment at 450 °C. Tafel slopes of ruthenium electrodes prepared by different procedures are about 40 mV per decade and this value indicates the second electron transfer as a rate determining step (ref. 2, p. 530). The most significant experimental data shown in Figure 2. are the decrease of the current at the thermally untreated electrode and the absence of the current decrease during potentiostatic polarization at the thermally treated electrode. The current at the thermally treated electrode is lower (on the same potential) than at the untreated one. This is due to the decrease of the electrode area, and to the loss of activity. This is also the reason for the decrease of the voltammetric charge with an increase of the treatment temperature (Figure 3), a well known phenomenon when hydrous oxide films are thermally treated (ref. 2, p. 557). The OER at a thermally untreated electrode occurs at the hydrous surface on which ruthenium is in +8 oxidative state[16,28] and dissolves into solution as RuO_4 releasing oxygen. Thermal treatment oxidizes ruthenium to anhydrous RuO_2. Oxygen is released also from oxyhydrated species without dissolution of ruthenium. The impedance data with a high capacitive component indicate the porous nature of the oxide film, and complex processes on the electrode. The behaviour of the curves in Figures 4. and 5. shows that formation of an oxide film by faradaic process is accompanied by adsorption of hydroxyl intermediates.

One of the most important factors in electrocatalysis is the stability of the active electrode layer. The service life test (Figure 6.) shows that the thermally untreated electrode dissolves after 1.5 min with a sharp increase of potential when titanium surface is expossed to the solution. When this happens, the poorly conducting film of titanium oxide is formed on the titanium surface. The sharp increase of potential at the thermally untreated electrode (Figure 6.) could also be due to passivation of titanium which can passsivate below the RuO_2 layer as it was pointed out by Loučka[30]. In our opinion, however, this is not the case in this work where the electrodeposited layer of ruthenium is very unstable under anodic polarization. This conclusion is supported by the cyclic voltammogram recorded after the sharp increase of potential. It shows a featureless profile typical of a titanium wire electrode before the electrodeposition is carried out. The electrode treated at 250 °C exhibits interesting behaviour during galvanostatic polarization. The potential is stable within 1 min and then increases by about 100 mV. When the anodic galvanostatic current is switched on and the oxygen starts to evolve, we suggest the following processes. The last few layers of the electrodeposited ruthenium (those exposed to the solution) are more porous than the inner ones, and therefore more hydrated. They are unstable chemically but active electrocatalytically exhibiting the lowest overvoltage. Oxygen is evolved on the highly hydrated layers which quickly dissolve. Then more compact, more stable and less active layers are exposed to the solution. They also dissolve, accompanied by a slow increase of overpotential until the first islands of titanium show up. This is followed by a sharp increase of potential. It is still unclear why all of the electrodeposited and during OER oxidized layers are not hydrated to the same extent as the outer ones, but the galvanostatic transient indicates that the presence of the duplex oxide film might be the reason. A similar increase of potential during anodic galvanostatic polarization was observed with the electrodeposited iridium electrode and with the iridium electrode where a hydrous oxide film was grown electrolytically by potential pulsing in sulfuric acid[31]. In the case of iridium and gold the presence of a duplex oxide film (more hydrous in the outer layers and more compact closer to the bulk metal surface) was already suggested[32–35].

Thermal treatment at 250 °C was not sufficient to oxidize ruthenium metal to compact anhydrous RuO_2. The most stable surface resulted from heating the electrode at 450 °C, which is the temperature of DSA preparation[5] and also the temperature at which ruthenium is oxidized to RuO_2[36]. At this temperature the bulk hydrous RuO_2 was stabilized for OER as shown by Iwakura *et al.*[37]. This was also the case in this work with the electrodeposited ruthenium thermally treated at 450 °C. Within four days of galvanostatic polarization of the electrode, treated at 450 °C, the potential was increasing rather slowly without a sharp increase which would indicate exposure of the titanium surface (Figure 6.). The ruthenium oxide layer is undoubtedly still present and the increase of potential can be ascribed to some deactivation rather than to dissolution. This is supported by cyclic voltammograms in Figure 7. which show the potentiodynamic curves before and after this experiment. There is not much difference in their potentiodynamic profiles. Thermally treated electrodes exhibit rather featureless shapes, but what is important is that the voltammetric charge is not smaller. Actually, it increased slightly after four days showing the absence of any significant electrode dissolution.

The voltammetric charge as a surface process cannot be taken, generally, as a measure of the quantity of electrode material. In the case of such porous electrodes, in certain experimental conditions, it can serve, however, as a measure of electrocatalyst loading. The voltammetric charge of oxide formation (Figure 1.) increases with deposition time and, therefore, in the opposite direction it would decrease with dissolution of the ruthenium layer.

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SAŽETAK

Elektrokemijsko razvijanje kisika na elektrodeponiranoj rutenijevoj elektrodi

M. Vuković i D. Čukman

Istraživano je elektrokemijsko razvijanje kisika na elektrodeponiranoj rutenijevoj elektrodi na nosaču od titana u 1 mol dm^{-3} otopini natrijevog hidroksida. Izmjeren je Tafelov nagib od 40 mV po dekadi, ali se elektroda otapa za vrijeme anodne polarizacije. Termalnim tretiranjem na 450 °C stabiliziran je elektrodni sloj. Pokus trajnosti elektrode unutar četiri dana nije pokazao otpanje elektrode. Termalno tretiranje na 250 °C pokazalo je prisustvo dvije vrste oksidnog sloja, hidratizirani vanjski sloj i kompaktniji sloj bliže površini titanijevog nosača. Impedantna mjerenja izvršena su u rasponu frekvencija 0.1 Hz—20 KHz i pokazuju dva paralelna procesa na površini elektrode.