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Experimental Conditions for the Electrochemical Activation of an Electrodeposited Ruthenium Electrode

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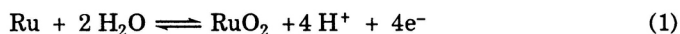
Several types of electrodeposited ruthenium electrodes on a platinum substrate have been studied. The first type was prepared by a galvanostatic deposition using 40 mA cm^{-2} current density and varying deposition time from 1 to 60 min. A porous layer was obtained which exhibited passive behaviour during potentiodynamic polarization at positive potentials before commencement of the oxygen evolution reaction. This layer has been electrochemically activated to a second type of electrode by square wave pulses between -0.2 and $+0.85 \text{ V vs. SCE}$. The complete reduction of the oxide is a necessary condition for the activation process. A potentiostatic electro-deposition and a galvanostatic electrodeposition using low current density and short deposition time produced electrodes whose voltammetric behaviour was similar to a bulk ruthenium electrode in acid solution.

INTRODUCTION

The electrochemical activation of an electrode (*i.e.* the enhancement of the electrocatalytic efficiency of electrode reaction) is a well known phenomenon. It was intensively investigated from both the fundamental and applied aspects of electrocatalysis. For example, the potentiodynamic cycling of noble metals, iridium¹⁻³ and rhodium^{4,5}, induces growth of a hydrous oxide film at a metal/electrolyte interface. It was found that the activated oxide film exhibited an enhanced electrocatalytic effect in the oxygen evolution reaction (OER) on iridium in acid^{6,7} and rhodium in alkaline solution.⁸

The ruthenium electrode, which exhibits, next to RuO_2 , the lowest overpotential in OER,⁹ can also be activated by potentiodynamic and/or square wave (SQW) pulsing. Conway and coworkers reported an enhancement of chlorine and oxygen evolution on the cycled ruthenium electrode in an acid solution.¹⁰ In an recent paper from our laboratory¹¹ it was shown that an enhanced oxygen evolution on activated ruthenium electrode was accompanied to some extent by the enhanced ruthenium dissolution, but the process was more than 80% truly electrocatalytic due to the formation of a more effi-

cient oxide film. The present work shows the experimental conditions necessary to achieve this activation. As far as the hydration of the oxide film is concerned, we usually deal with two main types of noble metal oxides: anhydrous and hydrous. For example, an anhydrous oxide, ruthenium dioxide, prepared by calcination from various precursors, mostly RuCl_3 on titanium, began to be used in 1965 on an industrial scale in chloralkali industry.¹² The hydrous type of RuO_2 is formed by electrochemical oxidation in an aqueous solution. The first oxidation state¹³ is Ru_2O_3 and its oxidation proceeds further to RuO_2 , thermodynamically the most stable ruthenium oxide species. The overall reaction proceeds *via* a proton exchange mechanism¹⁴



RuO_3 and RuO_4 are formed by the increase of positive potentials.^{15,16} They are unstable and decompose evolving oxygen. Hydrous oxide films have a more open structure and allow water molecules and electrolyte ions to enter their pores. Their electrochemistry is of interest in many branches of chemistry, such as corrosion science, electrocatalysis and colloid chemistry.¹⁷

EXPERIMENTAL

The ruthenium electrode was prepared by a galvanostatic and/or potentiostatic electrodeposition on a platinum wire substrate (1.6 cm length, 0.05 cm diameter) from a stirred solution of 1 g dm^{-3} $(\text{NH}_4)_2\text{RuCl}_6$ in 0.1 mol dm^{-3} HCl (FLUKA *puriss. p.a.*) at 25°C . Some comparative experiments were carried out using a bare ruthenium electrode (Johnson & Matthey) of elliptical shape and fixed by epoxy resin into a glass tube.

A EG&G 273 potentiostat was used for electrochemical measurements. The ruthenium electrode was activated by SQW pulses from -0.2 V to $+0.85 \text{ V}$ *vs.* saturated calomel electrode (SCE) with 40 s as holding time. This time was sufficient to reduce the oxide formed at a positive potential.

Scanning electron microscopy (SEM) was carried out using a Cambridge Stereo Scan 600 instrument.

A three compartment electrochemical cell thermostated at 25°C , with platinum foil as a counter electrode and a SCE as a reference, was used. A solution was prepared from sulphuric acid (FLUKA *p.a.*) and quadruply distilled water. Purified nitrogen was used for solution deaeration.

RESULTS

The typical voltammetric characteristics of an electrodeposited ruthenium electrode are shown in Figure 1. In the positive direction, after hydrogen ionization at 0.1 V *vs.* SCE, the surface oxidation starts with a broad but rather featureless range between 0 V and $+0.6 \text{ V}$ followed by the main oxidation peak at $+0.9 \text{ V}$. The current decreases until the potential reaches $+1.15 \text{ V}$, when oxygen evolution commences. In the negative direction, the oxide is reduced only to a small extent before its complete reduction at -0.2 V , where hydrogen deposition and evolution take place.

The deposition time in the electrode preparation characterized by the cyclic voltammogram in Figure 1 was 1 min at 40 mA cm^{-2} current density. When the deposition time was extended to 60 min using the same current density, the cyclic voltammogram shown in Figure 2 was obtained. Its main difference from that in Figure 1 is a much sharper decrease of current in the positive direction after the oxidation peak at $+0.7 \text{ V}$. In the negative direction, a smaller amount of oxide is reduced before high negative potentials at -0.2 V .

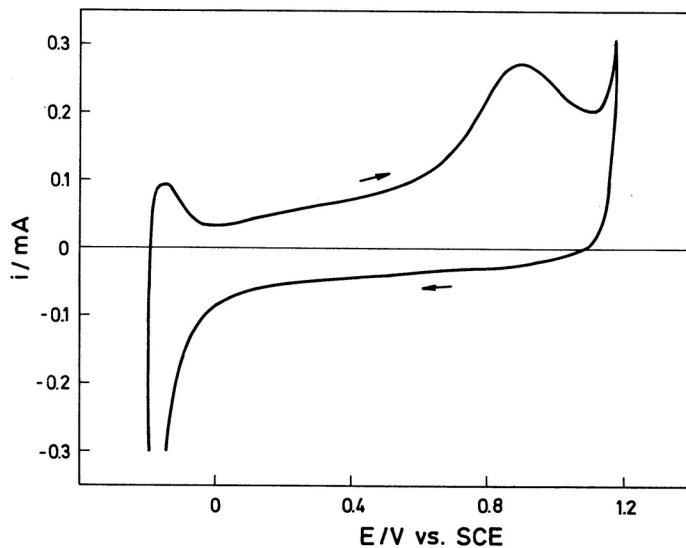


Figure 1. Cyclic voltammogram at a 50 mV s^{-1} sweep rate in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ of a galvanostatically electrodeposited (40 mA cm^{-2} current density) ruthenium electrode on platinum substrate. Deposition time 1 min.

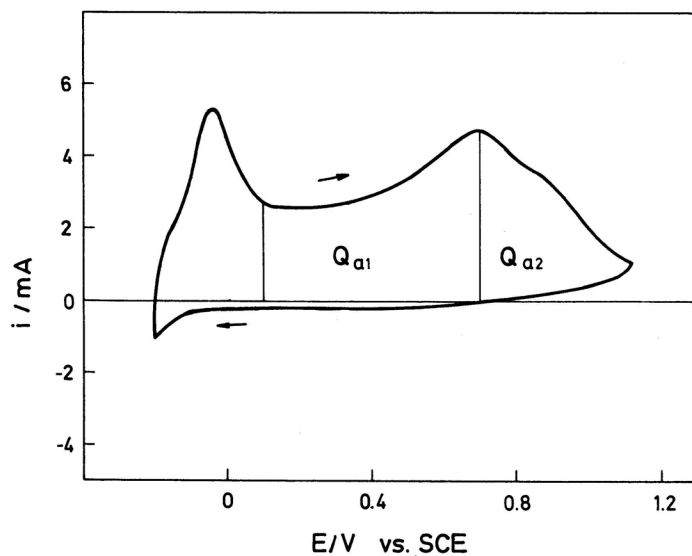


Figure 2. Same as Figure 1 but 60 min deposition time

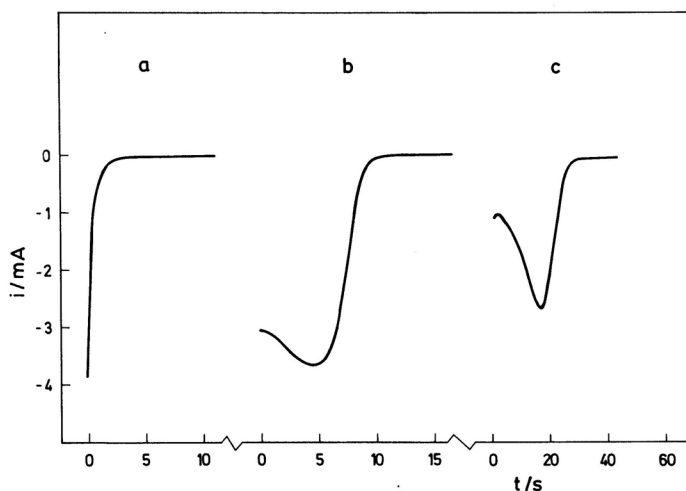


Figure 3. Current-time curves at -0.2 V vs. SCE when the potentiodynamic scan was reversed from (a) $+0.8$ V; (b) 1.0 V and (c) 1.18 V, respectively.

The kinetics of the oxide reduction depends upon the switching potentials, as illustrated in Figure 3. The current-time curves were recorded at -0.2 V after reversing the positive direction of potentiodynamic sweep at $+0.8$; 1.0 and 1.18 V, respectively. The oxide was reduced after 5 s when the positive potential limit was $+0.8$ V, after 10 s while switching the potential at $+1.0$ V and after 30 s while reversing the potential from $+1.18$ V.

The family of cyclic voltammograms shown in Figure 4 was obtained by multicycling the potential from -0.2 V to $+0.85$ V using SQW pulses at 0.0125 Hz frequency for different numbers of SQW pulses. By increasing the number of SQW pulses, the voltammograms change in the positive direction in that the main oxidation peak merges into the current of the OER without a sharp decrease of current. In the negative direction, a small peak at $+0.9$ V shows up and the oxide is reduced more easily. The cyclic voltammogram No. 1 in Figure 4 will be referred to in the following text as a Type A electrode while that obtained by 40 SQW pulses (No. 4) will be referred to as a Type B electrode.

The experimental conditions necessary to obtain the Type B electrode behaviour using a time program of SQW pulsing are shown in Table I. It is evident that it is necessary hold the potential at -0.2 V for at least 10 s to obtain Type B electrode.

Figure 5 shows the total anodic voltammetric charge as a function of deposition time. The relationship is linear up to 11 min and as the charge increases further, there is a deviation from linearity. The anodic voltammetric charge was divided into two parts: Q_{a1} , from the very beginning of the oxide formation at 0 V to the main oxidation peak at $+0.8$ V and, Q_{a2} , from this peak to the potential of the OER. The ratio Q_{a2}/Q_{a1} is shown in Table II.

An attempt was made to prepare the electrodeposited ruthenium electrode in different experimental conditions in order to figure out which type of ruthenium electrode-Type A or Type B- could be obtained. Figure 6 shows the cyclic voltammograms

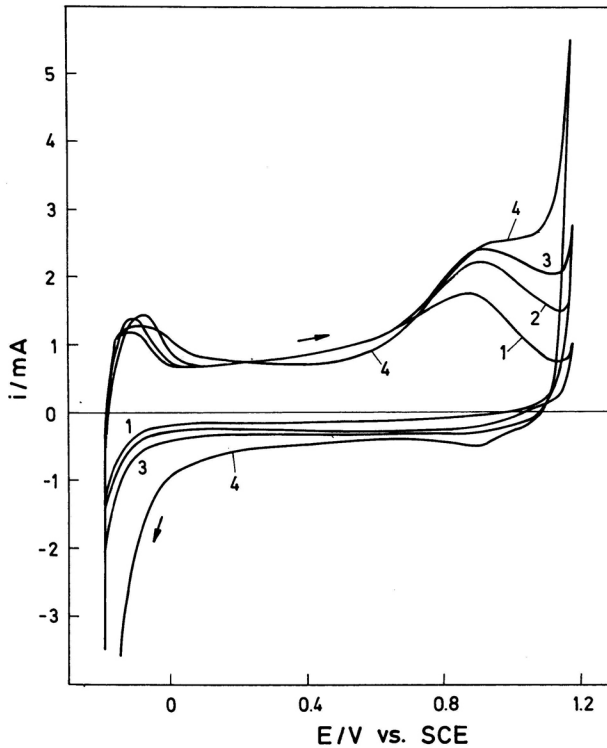


Figure 4. Cyclic voltammograms at a 50 mV s^{-1} sweep rate in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ of the galvanostatically electrodeposited (40 mA cm^{-2}) ruthenium electrode after (1) 5; (2) 10; (3) 20 and (4) 40 SQW cycles from -0.2 V to $+0.85 \text{ V vs. SCE}$. The potential was held for 40 s at each potential value.

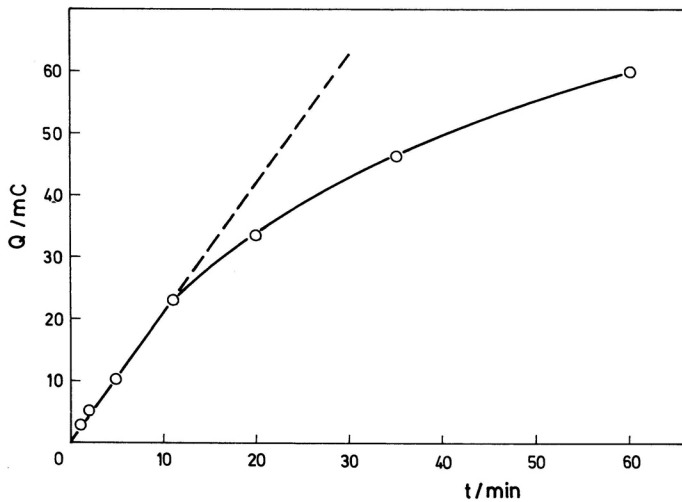


Figure 5. Anodic voltammetric charge from $+0.1 \text{ V}$ to $+1.12 \text{ V}$ of galvanostatically electrodeposited (40 mA cm^{-2}) ruthenium electrode as a function of deposition time.

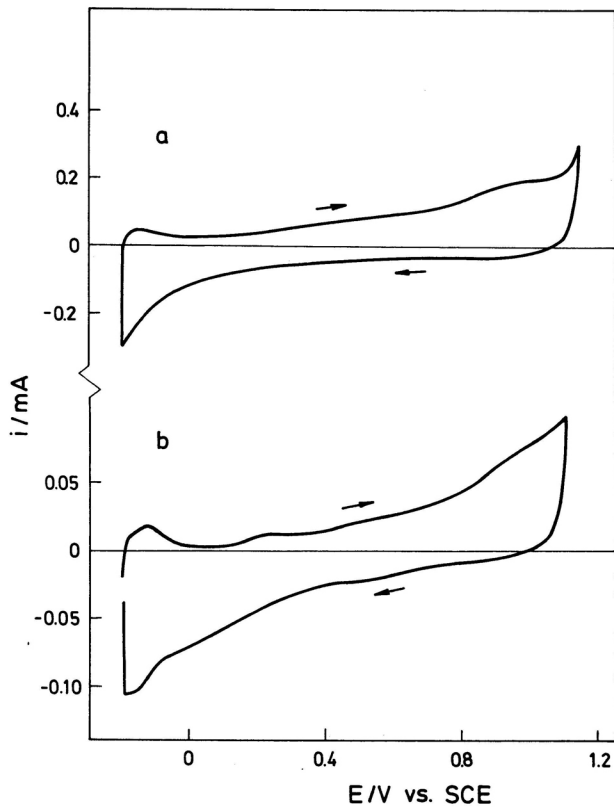


Figure 6. Cyclic voltammograms of the (a) potentiostatically electrodeposited (-0.2 V 15 min) and (b) galvanostatically deposited (4 mA cm^{-2} ; 10 s deposition time) ruthenium electrodes. Sweep rate 50 mV s^{-1} .

TABLE I

Experimental conditions in terms of a time program of the SQW pulsing in obtaining Type A and/or Type B electrode behaviour

Holding at -0.2 V (s)	Holding at $+0.85$ V (s)	Type of electrode
1	1	A
10	1	A
1	10	B(A)
10	10	B

TABLE II

The voltammetric charge, Q_{a1} and Q_{a2} (see Figure 2) for the galvanostatically electrodeposited ruthenium electrode (40 mA cm^{-2} current density) at different deposition times

Deposition time	Q_{a1}	Q_{a2}	Q_{a2}/Q_{a1}
min	mC	mC	
1	0.94	2.08	2.21
2	1.76	3.24	1.84
5	4.20	6.30	1.50
11	13.4	10.0	0.75
20	16.6	10.5	0.63
60	38.0	22.8	0.60

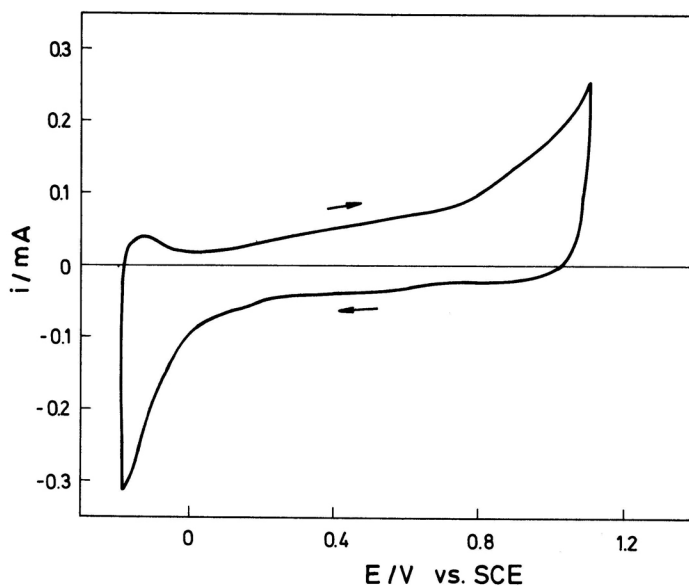


Figure 7. Cyclic voltammogram at a 50 mV s^{-1} sweep rate of the bulk ruthenium electrode in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$.

obtained when the ruthenium was electrodeposited potentiostatically at -0.2 V for 15 min (Figure 6a). By carrying out deposition at -0.2 V , intensive hydrogen coevolution was avoided (it commences just at -0.2 V) while during galvanostatic electrodeposition at 40 mA cm^{-2} current density, the working potential is -0.4 V . Figure 6b shows the cyclic voltammogram of the galvanostatically electrodeposited ruthenium but the deposition time and current density, were considerably smaller (10 s deposition time; 4 mA cm^{-2} current density) than those used in the Type A/Type B electrodes preparation (40 mA cm^{-2} current density; 15 min deposition time; Figure 4). In both cases in Figure 6, in potentiostatic and low current-short time galvanostatic electrodeposition,

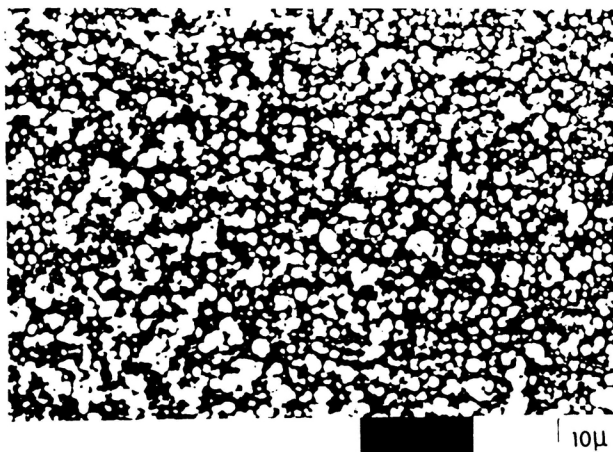


Figure 8. SEM micrographs of the Type A ruthenium electrode.

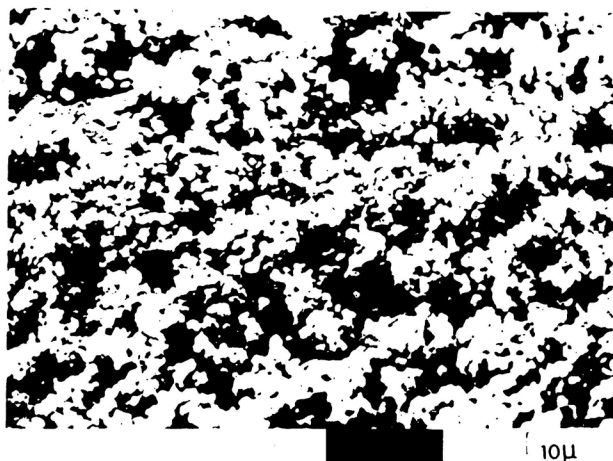


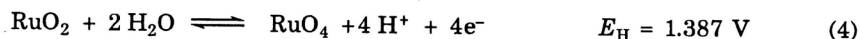
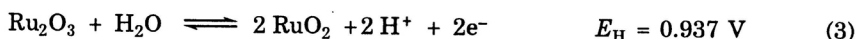
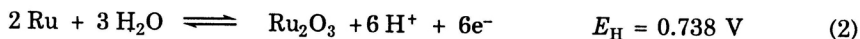
Figure 9. SEM micrographs of the Type B ruthenium electrode.

the Type B electrode behaviour was obtained. In order to compare the voltammetric behaviour of the electrodeposited ruthenium electrodes with that of the bulk ruthenium electrode, the voltammogram of the latter is shown in Figure 7. It is evident that its potentiodynamic profile is that of the Type B electrode.

The surfaces of the Type A and Type B electrodes, respectively, were examined by the scanning electron microscopy and the corresponding SEM micrographs are shown in Figures 8 and 9. The porous surface without cracks of the Type A electrode is evident. The Type B electrode, however, exhibits a more porous surface.

DISCUSSION

The galvanostatically electrodeposited ruthenium electrode, either on the platinum substrate used in the present work or on the titanium, is porous.^{18,19} This means that the voltammetric charge of the oxide formation is much higher than it would correspond to the geometrical area of the substrate if the layer was smoothly electrodeposited. The porosity is evidenced by the increase of the voltammetric charge with deposition time (Figure 5). The linear increase of the voltammetric charge up to 11 min indicates that this might even be the case that at shorter deposition times the whole deposit was available for electron transfer. The surface oxidation proceeds according to equation 1 and it means that the structure is available for the proton transfer as well. After 11 min, the deposit is obviously too thick and a deviation from linearity takes place although the voltammetric charge is still increasing. The quantity of the electrodeposited ruthenium after 15 min deposition time was calculated from the data in our recent publication¹⁹ and by using the same current density in the present work. This quantity is $3.6 \times 10^{-5} \text{ g cm}^{-2}$. The voltammetric behaviour of electrodeposited ruthenium is well documented²⁰⁻²⁴ and in the present work we shall put emphasis only on the behaviour of the main oxidation peak at +0.8 V and its dependence on the deposition time. The following redox couples of ruthenium oxidation/reduction processes and equilibrium potentials at pH = 0 are available from the Pourbaix diagram,¹³ although the stability of Ru₂O₃ was questioned by Barral *et al.*²⁵:



The Q_{a2}/Q_{a1} charge separation line in Figure 2 corresponds to the first appearance of the passivation process, *i.e.* a sharp decrease of current rather than to various redox couples. What goes on when the RuO₂ layer is formed is a passivation of the surface. The RuO₂ layer prevents further oxidation of ruthenium atoms. This blocking is less pronounced at the electrode prepared at shorter deposition times (Figure 1) than at longer times (60 min, Figure 2). The decrease of the Q_{a2}/Q_{a1} ratio with deposition time (Table II) is also an indication of increased passivating process. The passive layer on ruthenium is not, however, of the same nature as on iron or nickel, for example.²⁶ The passive layer on these metals prevents their dissolution at high positive potentials where oxygen is evolved, or at least reduces it to a very small rate. In the case of ruthenium, the highest oxidation state is +8 (Eq. 4). The RuO₄ species dissolves while releasing oxygen.

The passive layer, however, changes while activating the electrode by potentiodynamic and/or SQW cycling. The activated layer is more efficient in the OER as well as in the chlorine evolution reaction.¹⁰ The transition from the non-activated (Type A) electrode to the activated (Type B) electrode is illustrated in Figure 4 and the data in Table I show that a complete reduction of the oxide at -0.2 V (see Figure 3) is a necessary condition for this transition. When the potential was held only 1 s at -0.2 V, there was an »in-between« state of the Type A/Type B behaviour. The oxide was not reduced completely, as shown by a current-time curve in Figure 3. The model

proposed in this paper is the opening of the structure of the passive layer while activating the layer with potential pulsing.

During the reduction process, the protons (*i.e.* hydronium ions) have to react with the rather compact RuO_2 layer when the penetration of water or hydronium ions is hindered to a greater extent than in the case of Ru_2O_3 . This is the reason for the various induction periods for oxide reduction shown by current-time curves in Figure 3. Rishpon and Gottesfeld²⁷ were able to distinguish two charging modes on the electrodeposited ruthenium. The first was attributed to the charging of the grain boundaries and the second mode to the charging of the bulk of the metal deposit. Blocking of the oxidation by the RuO_2 layer in the case of higher metal loading at different deposition times (Table II) is also a reason for the decrease of the Q_{a2}/Q_{a1} ratio. The activation of the electrode changes this ratio in the Type A/Type B transition (Figure 4). During this activation, hydrogen was evolved on the negative potential (-0.2 V), but this process did not disturb the formation or reduction of the oxide layer, as it was shown by Breiter²⁸ using AC measurements on the ruthenium foil electrode. The model proposed by Jung *et al.*²⁹ for the change of the RuO_2 layer, prepared by thermal decomposition on titanium during continuous potentiodynamic cycling, can be used here with some differences. The differences arise from the hydrous nature of the oxide layer in the present case. These authors observed a 25–35% increase in the voltammetric charge after 24 hours of continuous cycling and explained it as an opening of the structure of the RuO_2 layer. Ruthenium dioxide, formed by the thermal decomposition of RuCl_3 on titanium at 450°C , is anhydrous without any water present. We deal with anodically formed hydrous RuO_2 , where there is always some water present in the pores. We can consider the activation during continuous cycling between Ru/RuO_2 states as a process of continuous making and breaking of ruthenium/oxygen bridges assisted by a proton exchange. This exchange *via* a Grotthuss mechanism of proton transfer is more easily achieved in the case of the hydrous oxide film and the anodic charge increases more rapidly than it was the case with thermal RuO_2 . On the other hand, there is a main difference in the reduction routes of two oxides. The thermally prepared RuO_2 reduces only to a Ru(II) state³⁰ at the negative potential limit of the potentiodynamic scan while the hydrous RuO_2 is reduced to metal. In the thermally prepared RuO_2 , the voltammetric charge was increasing during the whole potentiodynamic scan, and in the case of hydrous oxide it was only in the $\text{Ru}_2\text{O}_3/\text{RuO}_2$ transition. In the case of the hydrous ruthenium oxide, all the atoms are probably available for the electron transfer in the $\text{Ru}/\text{Ru}_2\text{O}_3$ transition. Therefore, in the Type B electrode more metal atoms are available for oxidation to RuO_2 state at potentials more positive than $+0.8$ V. Potentiostatically prepared ruthenium layers, as well as these prepared galvanostatically at low current density and short deposition time (Figure 6), are less porous and, in fact, in the potentiodynamic profiles more similar to the bulk ruthenium electrode evidenced by a relatively low voltammetric charge and by the absence of the passive behaviour typical of the Type A electrode. The similarity of potentiodynamic profiles of potentiostatically deposited and bulk ruthenium electrodes with the profile of the Type B electrode is, therefore, only due to the absence of passive behaviour. The electrode called Type B is obtained only when a highly porous Type A electrode has been electrochemically activated. The RuO_2 bridges in this case prevent further oxidation of ruthenium atoms below the passive layer. The porous nature of the Type A electrode is also visible on the SEM micrograph in Figure 8. After activation period, the surface looks more swollen, as evidenced by the SEM micrograph in Figure 9, due to the penetration of water into the pores.

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SAŽETAK**Ekperimentalni uvjeti za elektrokemijsko aktiviranje elektrodeponirane rutenijeve elektrode***M. Vuković*

Istraživano je nekoliko vrsta elektrodeponirane rutenijeve elektrode na podlozi od platine. Galvanostatskom elektrodepozicijom s gustoćom struje od 40 mA cm^{-2} i vremenima depozicije od 1 do 60 min dobivena je porozna presvlaka koja pokazuje pasivna svojstva za vrijeme potenciodinamičke polarizacije na pozitivnim potencijalima prije izlučivanja kisika. Ta je presvlaka elektrokemijski aktivirana u drugi tip elektrode kvadratnim pulsevima potencijala između -0.2 V i $+0.85 \text{ V}$ prema zasićenoj kalomelovoj elektrodi. Potpuna redukcija oksida uvjet je za tu aktivaciju. Potenciostatskom elektrodepozicijom kao i galvanostatskom elektrodepozicijom kod nižih gustoća struje i kraćih vremena depozicije dobivene su presvlake čije su voltametrijske karakteristike bile slične karakteristikama čvrste rutenijeve elektrode.