

HYDROGEN EVOLUTION REACTION ON RuO₂·3SiO₂ ELECTRODES PREPARED BY THE SOL-GEL PROCESS

The hydrogen evolution reaction (HER) on RuO₂·3SiO₂ electrodes in 1N H₂SO₄ at the room temperature was studied by the galvanostatic method and the properties of the formed layers by voltammetry measurements. Layers of RuO₂·3SiO₂ electrodes were prepared by the sol-gel process by dipping wires or rods of a carrier material in a solution of a sol-gel precursor. The formed film was fired at 300°C. The weight of the film varied between 7.0 – 70 · 10⁻⁵ g cm⁻². The activity of freshly prepared electrodes, expressed by the current density at the overvoltage $\eta = -0.2$ V of the electrodes prepared on gold and titanium carriers was significantly greater than that on thermally prepared RuO₂ electrodes. Long term hydrogen evolution (several hours) caused a decrease in the activity of the HER. The voltammetry of layers showed that RuO₂·3SiO₂ layers were less stable than conventionally prepared layers as the reduction of RuO₂ or the incorporation of hydrogen in RuO₂·3SiO₂ layers occurred.

In recent years, conductive oxide materials have been the subject of noticeable attention within the field of electrochemical applications, moreover a considerable number of studies have been dedicated to them, including those focusing on the hydrogen evolution reaction (HER). In this respect, the most suitable materials for active electrodes for hydrogen evolution are mainly RuO₂ [1–9] and IrO₂ or their mixtures prepared in various ratios. The electrocatalytic activity of RuO₂ was studied devoting attention to hydrogen evolution from both acidic and alkaline environment. Several studies were also dedicated to hydrogen evolution from a solution typical for chlorate production [2,10]. The studies carried out so far imply that RuO₂ electrodes are relatively active in regard to the HER and surprisingly even sufficiently stable against reduction [1,10,11]. In comparison to active metallic electrodes, commonly prepared on a platinum or nickel basis, oxide electrodes are significantly more resistant to surface contamination by electrocatalytic poisons such as Fe, Cu, Cd, which are often present in an electrolyte [1].

The overvoltage for hydrogen evolution on RuO₂ cathodes, as implied in the majority of published studies, is low even in regard to technologically interesting current densities. The reason is not only that these electrodes commonly have a large surface, but also to the fact that the Tafel slope usually has a low value ranging around 40 mV/dec. ESCA electrode measurements after cathodic loading showed that no significant reduction of RuO₂ to metallic ruthenium occurs during electrochemical hydrogen evolution, even though certain incorporation of hydrogen into the RuO₂ layer occurred [7,10,12].

RuO₂ and IrO₂ electrodes are usually prepared by spreading a solution of a pertinent chloride in a thin layer on a suitably modified support (usually titanium) and then the chloride is decomposed at higher temperatures and the layer is heated at 300 – 550°C. The operation is repeated several times in order to achieve the required thickness. By this way, layers with a marked porosity and a corresponding factor of roughness f ranging between the values $f = 30 - 600$ [2,9] were acquired. Recently, the sol-gel method (SG) has been used to acquire controlled porosity and suitable electrode properties in electrochemical applications. This method was originally developed as a method, which would allow the preparation of glass and ceramics with lower energy consumption for their production. The innovative utilisation of this process consisted in enabling the mixing of all the needed components on a molecular basis. Consequently, the gelatination process allowed the preparation of single- or double-component-oxide networks containing a significant part of water and remains of organic components. These components can be separated by using apposite drying techniques, while amorphous materials can often be produced with a high degree of porosity. Gels can be formed to fibers, powders or they can be easily spread on various bases. The SG technique can be well used for the preparation of simple single-component oxide materials or even for the preparation of more complicated oxide materials containing a network made of e.g. SiO₂ or TiO₂ film.

In this work, we have mainly studied the reaction of hydrogen evolution on the layers of RuO₂/3.SiO₂ produced by the SG, dip coating, technique. We selected the a RuO₂/3.SiO₂ layer composition to find out whether a SiO₂ network with incorporated active centres of RuO₂ would have an activity comparable to common RuO₂ layers. Furthermore, our concern was whether possible interactions of RuO₂/3.SiO₂ with a support would have any effect upon electrode activities and whether the SiO₂ network would have an impact upon

Author address: I. Paseka, Institute of Inorganic Chemistry,
Academy of Sciences of the Czech Republic, 250 68 Rez near
Prague, Czech Republic

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the stability of layers during long-term cathodic polarisation or after RuO_2 reduction to metallic ruthenium by hydrogen at higher temperatures. Three materials were studied as the supports – gold, titanium and glassy carbon.

EXPERIMENTAL

$\text{RuO}_2/3.\text{SiO}_2$ layers (further referred to as SG RuO_2) were prepared by the dip – coating, technique applied on the above mentioned supports. The sol – gel solution for the preparation of layers was prepared from $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, which was dissolved in ethanol. Ethylene glycol was added to this solution by drops under intensive stirring. Afterwards the temperature of the solution was increased to 338 K. Then, the calculated and weighted amount of tetraethoxysilane was slowly added dropwise to the heated solution and the produced mixture stirred at this temperature until a homogeneous solution was obtained. The electrodes were in the form of a wire, or as in the case of the glassy carbon support in the form of a rod with a diameter of 4 mm. The wire diameter was 1 mm and the length was approx. 6 cm. The rate of stretching of the supports from SG solutions was always constant, i.e. 11.5 cm/min. The produced sol gel film was heated to constant weight in a furnace at 300°C for a period of 1 hour. After this heating, the active area was limited by covering the remaining area with a teflon tube. By one dipping and subsequent heating a layer of $\text{RuO}_2/3.\text{SiO}_2$ with an average weight of $7.1 \times 10^{-5} \text{ g cm}^{-2}$ was produced. Thicker layers were produced by repeated spreading of the layers and their heating.

The reaction of hydrogen evolution was studied by the galvanostatic method. The polarisation properties of the electrodes were measured in 1N H_2SO_4 at room temperature. The acidic solution was prepared from 3 times distilled water and 96% H_2SO_4 . The solution was further purified by adding approx. 5g of platinum black to approx. 1.5 L of the acid saturated by hydrogen and subsequently stirring for several days. The potentials of the electrodes were measured against a hydrogen electrode in the same solution. Their values are also refereed against the hydrogen electrode in the same solution. All the data and curves provided on the figures were corrected for iR ohmic drop between the reference and the working electrode. The electrode capacitances were measured by the decay method. An A/D transmitter, Advantech 711/S, connected with a PC computer was used for this measurement. The acquired E–t digital data were approximated by the least squares method to the curve $E(t) = -b \ln(t + a) - b \ln c$, where t represents time, a, b, c, are constants. The capacitance values were calculated using the equation $C^0 = [j/(dE/dt)]_{t=0}$. The roughness factors f were calculated using the equation $f = C^0/C_{dl}$, where the value of $10 \mu\text{F cm}^{-2}$ was used for the specific capacitance of the electrode double layer C_{dl} of the oxide electrode.

Within the range of potentials +0.05 – +1.0 V, the voltammetric curves were used for the characterisation of the prepared layers. The measurement was performed using a Wenking ST 72 potentiostat and a Unipan 711 pulse generator. Simultaneously, $E \div t$ and $I \div t$ curves were digitally recorded with using an A/D transmitter, Advantech 711/S, and a PC computer. The potential sweep rate was 100 mV s^{-1} . The oxidation charges Q_{ox} were calculated from the recorded $I \div E$ values at the potential increase in the direction to higher positive potentials and the reduction charges Q_{red} at the opposite direction of the potential increase. Then, these values were used for an approximate determination of the electrode surface or rather for the roughness factor f. The value published by Burke et al [13] for RuO_2 electrodes 1.51 C m^{-2} for $\Delta E = 0.95 \text{ V}$ was used for this purpose.

RESULTS

The results characterising the polarisation properties of the electrodes during the measurement of the first polarisation curve after the preparation, together with the values of the measured roughness factors, are summarised in Table 1. Figures 1 and 2 show some of the cases of the influence of supports of the RuO_2 layers. The data in Table 1 conspicuously indicate the significant influence of the supports of the RuO_2 layer upon the polarisation properties of these electrodes. It is apparent that regardless of the significant differences in the activity of both electrodes A and B, obviously, the layers deposited on the golden support are the most active. The low value of the slope of the polarisation curve of this electrode allows hydrogen evolution even with high current densities at a low overvoltage. For

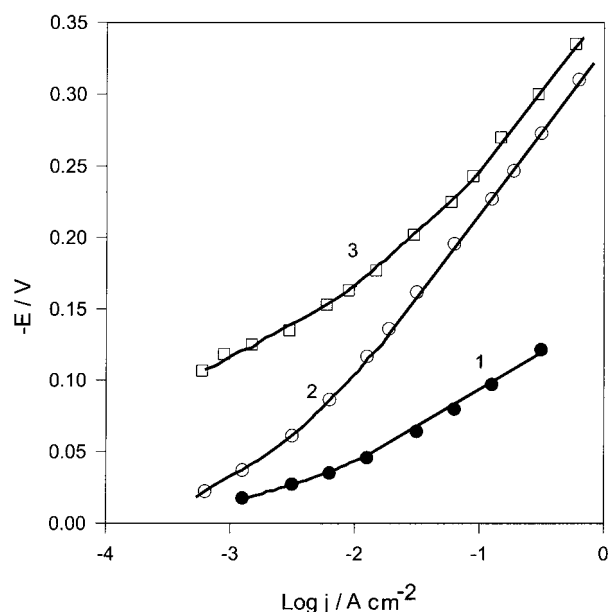


Figure 1. Polarisation curves for the HER on a freshly 1 time deposited layer of $\text{RuO}_2.3\text{SiO}_2$ on various supports 1 – gold, 2 – titanium, 3 – glassy carbon.

Table 1. Kinetic parameters of the hydrogen evolution reaction on various $\text{RuO}_2 \cdot 3\text{SiO}_2$ electrodes. (Specification of electrodes – numbers in parentheses is represent the number of deposited layers; f – roughness factor evaluated from the current interruption, f' – from voltammetric measurements).

Electrode	$j_{-0.2\text{V}}/\text{mA cm}^{-2}$	b V/dec.	f	f'	remark
RuO_2/Au (1)x A	*1360	0.077	7.8	9.5	
(1)x B	440	0.085	5.8		
(1+1)x A	*2700	0.080	13.3	12.6	
(1+1)x B	626	0.083		9.9	
(1+1+3)x A	*1490	0.090	12.6	15.8	
(1+1+3)x B	*9000	0.090	88	17.9	
(5)x A	200	0.080	12	13.4	
(5)x B	140	0.105	10	13.4	
(5+5)x	707	0.095		22.4	
RuO_2/Ti (1)x	70 ± 76	0.104 ± 0.013	17.8	5.5	
(1+1)x	110 ± 79	0.107 ± 0.004	17.0	8.7	
(1+1+3)x	400 ± 300	0.118 ± 0.013	16.5	19.4	
(5+5)x	680 ± 270	0.120 ± 0.015		38.9	
(10)x	400	0.104	38.7	68.9	
RuO_2/GC (1)x	35	0.110	6.6	21.9	
(1+1)x	30	0.114	10.4	18.8	
(1+1+3)x	105	0.090	19	21.0	
(5x)	155	0.065	10.6	21.5	
RuO_2/Ti TD	55	0.240			ther. decom. [8]
	80*	0.240			ther. decom. [1]
	3.5+				ther. decom. [7]

* Extrapolated values, + values without the correction of the ohmic drop.

instance, in regard to electrode A, the current density was $j \approx 0.130 \text{ A cm}^{-2}$ at $E = -0.1 \text{ V}$, which was more than one order more than the current density on RuO_2/Ti or RuO_2/GC electrodes. The curves shown on the figures

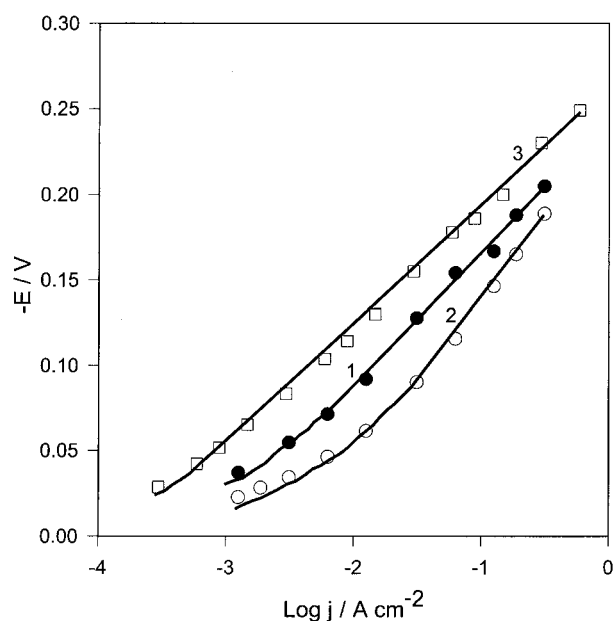


Figure 2. Polarisation curves for the HER on 5 times freshly deposited layers of $\text{RuO}_2 \cdot 3\text{SiO}_2$ on various supports. 1 – gold, 2 – titanium, 3 – glassy carbon.

were acquired on electrodes measured immediately after inserting them into the measuring vessel, while the polarisation curves were measured in the direction from the lowest to the highest current densities. During consecutive measurement in the opposite direction, the overvoltage of the electrodes decreased, especially in the range of low current densities ($j \leq 0.1 \text{ A cm}^{-2}$). This behaviour was well in concordance with the behaviour of the RuO_2/Ti electrodes described in works [3,4,7].

As apparent from Fig. 2, the influence of a support upon the polarisation properties of electrodes is not so relevant any more in the case of electrodes containing several RuO_2 layers (5 or more). This figure as well as Fig. 1 shows polarisation curves of hydrogen evolution on electrodes with 5 RuO_2 layers again measured on electrodes immediately after their insertion into a measurement vessel during measurement from the lowest to the highest densities. It is apparent from the pertinent curves in Fig. 1 and 2 that the activity of the RuO_2/Ti and RuO_2/GC electrodes with 5 layers significantly increased in comparison to electrodes with one RuO_2 layer, while the activity of RuO_2/Au electrodes with 5 layers significantly decreased in comparison to one-layered RuO_2/Au electrodes.

The data provided in Table 1 imply that the electrodes, especially those with fewer RuO_2 layers, have very varied properties, and thus the electrodes will

be described and discussed especially according to their kind of the support.

RuO₂/Au electrodes

High values of $j_{-0.2V}$ are typical for these electrodes, which reach values usually higher than 1 A cm^{-2} and low values of the slope of the polarisation curve b . (Table 1 shows $j_{-0.2V}$ values marked with *, which were extrapolated from the area of lower current densities, since the experimental device did not allow measurement at such high current densities). With most electrodes, the slope of polarisation curve b reached values between $0.08 - 0.09 \text{ V/dec}$. As already mentioned, the activity of electrodes with 5 and more layers is significantly lower (5 – 10x) than of those electrodes containing less layers. Nevertheless, the roughness factor f does not change so notably with the number of layers and if, then in the opposite direction, although electrodes with more layers have higher f values. The roughness factor with one layer is around 6–7 and electrodes containing 5 – 10 layers reach the value $f \approx 10 - 12$. (Only one electrode with 5 RuO₂ layers had an outstandingly large surface with the roughness factor $f = 88$ and correspondingly high activity $j_{-0.2V}$, regardless of having been prepared using the same procedure as the others).

RuO₂/Ti electrodes

Values of $j_{-0.2V}$ of electrodes with 1–2 RuO₂ layers ranged from $10 - 200 \text{ mA cm}^{-2}$ and the values of the slopes b of the polarisation curves of these electrodes ranged from $0.095 - 0.110 \text{ V/dec}$. Electrodes with 5 up to 10 RuO₂ layers are significantly more active than electrodes with less RuO₂ layers. The surfaces of these electrodes, determined from the capacitance values of electrode double layers, deposited once or two times, are approximately the same and their roughness factor ranges from 17 – 18. A more significant increase in the roughness factor was observed in the case of 5 and 10 layers, in which f values of around 40–70 were measured.

RuO₂/GC electrodes

RuO₂/GC electrodes were the least active of the studied objects. The value b around 0.110 V/dec and the value $j_{-0.2V} \approx 30 \text{ mA cm}^{-2}$ are characteristic for polarisation curves of electrodes with 1–2 RuO₂ layers. For electrodes with 5 and more RuO₂ layers, polarisation curves with a lower slope of $b \approx 0.065 - 0.090$ and observably higher values of $j_{-0.2V} \approx 105 - 150 \text{ mA cm}^{-2}$ are typical. The roughness factor of RuO₂/GC electrodes does not significantly change with the number of layers (the measured values of f maximally changed 3x and the values of f were approximately the same for all electrodes – ranging from 6.6 – 11).

Effect of long-term cathodic polarisation

The duration of cathodic polarisation has two different effects. Short polarisation for a period of several minutes of current densities of a couple of units to tens of units of mA cm^{-2} generally caused a slight increase in the activity of most electrodes, especially RuO₂/GC electrodes. This behaviour is in good agreement with the behaviour of RuO₂/Ti electrodes, which were thoroughly described and explained in the work of Chen and others [7]. During longer polarisation (hours to tens of hours loaded with current densities around 100 mA cm^{-2}), the opposite effect occurs – a significant decrease in the activity of these electrodes. Fig. 3 shows an example of an effect of long-term loading upon the activity of RuO₂/Ti (5x) (i.e. 5x layers) electrodes. During the loading, an increase of the overvoltage (during loading by a constant current) and deactivation of the electrodes occurred gradually. This deactivation of RuO₂ electrodes was observed on RuO₂ electrodes deposited on all supports. The decrease in the activity, expressed by the value $j_{-0.2V}$, ranged in a broad interval of 2 – 200. Generally, it can be said that the higher the initial activity of these electrodes, the more significant was the decrease in their activity during long-term polarisation. It is interesting that even a short break in loading by the cathodic current (several minutes) causes a partial re-activation of the electrodes (see Fig. 3). Short-term oxidation of the electrodes to a potential around 1.0 V showed an even more efficient mode of re-activation. The re-activation of electrodes has, however, no long-lasting effect and the gradual deactivation

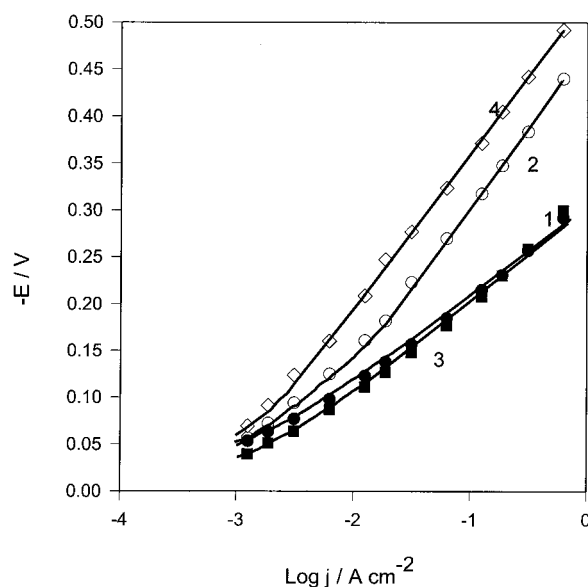


Figure 3. Polarisation curves for the HER on 5 times freshly deposited layers of RuO₂.3SiO₂/Ti. The influence of long term hydrogen evolution. 1 – freshly prepared electrode, 2 – after 46 hours of hydrogen evolution at $j = 0.186 \text{ A cm}^{-2}$, after the previous procedure and then after the currentless condition ($E_{j=0} = 0.015 \text{ V}$) for 20 minutes, 4 – after a further 22 hours of hydrogen evolution at $j = 0.186 \text{ A cm}^{-2}$.

proceeds much faster during cathodic loading than during the initial cycle. Deactivation of the electrodes is accompanied by a slight increase in the roughness factor of the electrodes – even up to 1.2 to 2 times higher. During loading longer than 50 – 70 hours by current densities of $j \geq 100 \text{ mA cm}^{-2}$, significant structural changes, observable even visually, occurred in regards to some electrodes (e.g. RuO_2/Ti (5x)). After the described long-lasting loading, the initial layer, visually observed as homogenous and dark-brown, changed its colour to dark black and it was apparent that the ruthenium layer had partially peeled off from the Ti support.

The influence of heating of RuO_2 electrodes in hydrogen

The above text implies that the surface stage of the electrodes significantly influences the polarisation properties and the activity of the electrodes. E.g. the reduction of RuO_2/Au electrodes by hydrogen at 300°C caused a very significant increase in the activity of these electrodes, characterised by an increase in the values $j_{-0.2\text{V}}$ and a decrease in the slope b of the polarisation curve to values of 0.035 – 0.045. Reduced RuO_2 layers, especially those on a Ti support, have deteriorated mechanical properties. During hydrogen evolution, the layers quickly undergo a dust removal or a peeling off. Consequently, even after a short-term (in an extent of several hours) hydrogen evolution, a significant decrease of the activity and a decrease of the roughness factor by 2–5 times occurred. More reproducible measurements were possible only with the golden support with one or two RuO_2 layers. The layers deposited several times or layers deposited on other than golden supports were so fragile after the reduction by hydrogen that the heated layers were unstable and brought no reproducible results.

Voltammetry of RuO_2 electrodes

Fig. 4 shows typical voltammograms of freshly prepared RuO_2 SG(1x) layers plotted directly after inserting them into the solution in the measuring vessel at the potential $E = 0.045 \text{ V}$. The conspicuous asymmetry of the voltammetric curves, apparent from the figures, shows that the oxidation charge Q_{ox} , acquired by an integration of the $j - E$ curves at the E increase in a positive direction, is markedly higher than the reduction charge Q_{red} , acquired by the same way at the potential increase in the opposite direction. The voltammetric curves read after the measurement of the polarisation curve showed that after the polarisation curve measurement, an observable increase in the red-ox charges occurred on all electrodes, however Q_{ox} was higher, and thus, the asymmetry of the values of the oxidation and reduction charges was even higher. The values Q_{ox} and Q_{red} change with the number of layers, furthermore the $j - E$ curves rather change their shape in

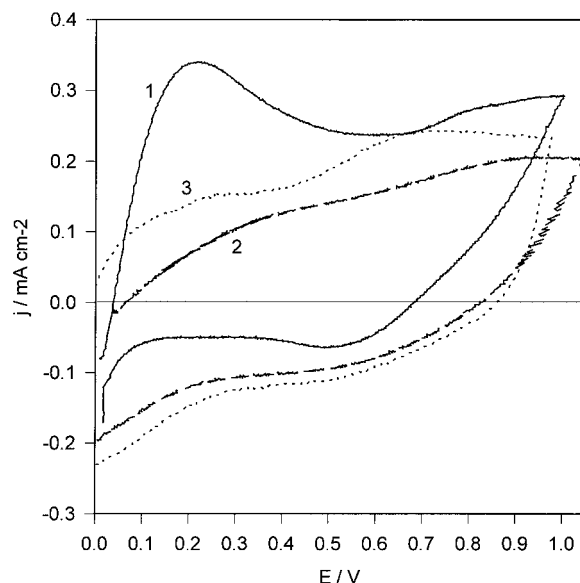


Figure 4. Voltammograms of $\text{RuO}_{2.3}\text{SiO}_2$ electrodes with 1 deposited layer on various supports. 1 – gold, 2 – titanium, 3 – glassy carbon.

such a sense that the difference in the values of Q_{ox} and Q_{red} is decreased. This is more apparent in the case of RuO_2/Au electrodes than in the remaining types of electrodes. The shape of the $j - E$ curves shows that it is difficult to exactly determine the values of Q_{ox} and Q_{red} needed for the determination of the roughness factor. Therefore, in order to calculate the average values of Q_{ox} and Q_{red} , we proceeded as such that the current densities were read from the voltammetric curves in the area of the potentials $E = 0.4 - 0.5 \text{ V}$, where $j_+ \approx j_-$ (on RuO_2 SG layers, before their cathodic polarisation) and it was assumed that these current densities were approximately constant in the area of potentials 0.05 – 1.0 V. Thus, $Q_{\text{ox}} \approx Q_{\text{red}} \approx j \cdot t$. The comparison of values f and f' (see Table 1), which were acquired by using completely different methods, shows that the agreement of these values is with most of the electrodes rather surprisingly good and, therefore, such acquired electrode values of the roughness represent real values.

The shape of the voltammetric curves shows that the red-ox processes on RuO_2 SG electrodes are slow, and thus proceed irreversibly even during a relatively slow sweep rate ($v = 10 - 100 \text{ mV s}^{-1}$). Consequently, even after the change of the direction of the potential increase, red-ox processes proceed in the previous direction for a certain period of time (e.g. during polarisation at $E = 1.0 \text{ V}$, the anodic current continues up to values of $E \approx 0.9 - 0.7 \text{ V}$, i.e. the values $\Delta E \approx 0.1 - 0.3 \text{ V}$ less positive than the potential inflection point). It was unambiguously demonstrated that irreversibility, characterised as the value ΔE , at $j = 0$, is the highest for the golden support and the lowest for the glassy carbon. As mentioned above, the general shape of the voltammetric curves significantly changes with an

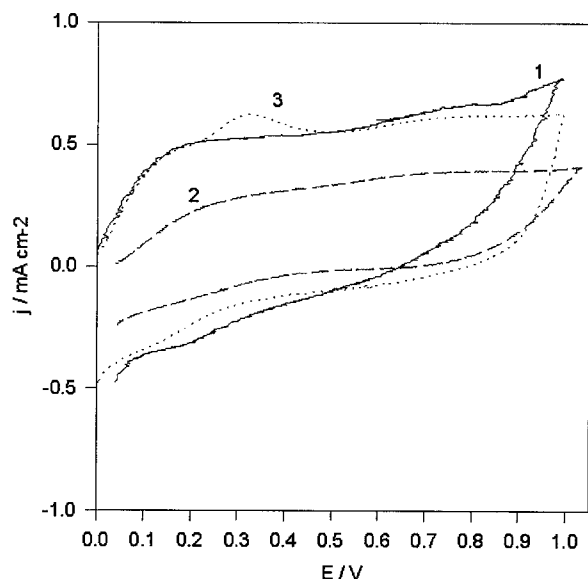


Figure 5. Voltammograms of $\text{RuO}_2.3\text{SiO}_2$ electrodes with 5 deposited layer on various supports. 1 – gold, 2 – titanium, 3 – glassy carbon.

increasing number of deposited RuO_2 SG layers. The oxidation and reduction currents increase with an increasing number of layers, however the red-ox processes rate also increases, since the values of ΔE decrease (e.g. ΔE decreased by 15 (GC) to 33% (Au) with 5 layers compared to 1 layer) (see Fig. 5). The time of cathodic polarisation has the most significant effect on the shape of the voltammetric curves, as apparent from Fig. 6, where the voltammetric curve of RuO_2 SG /

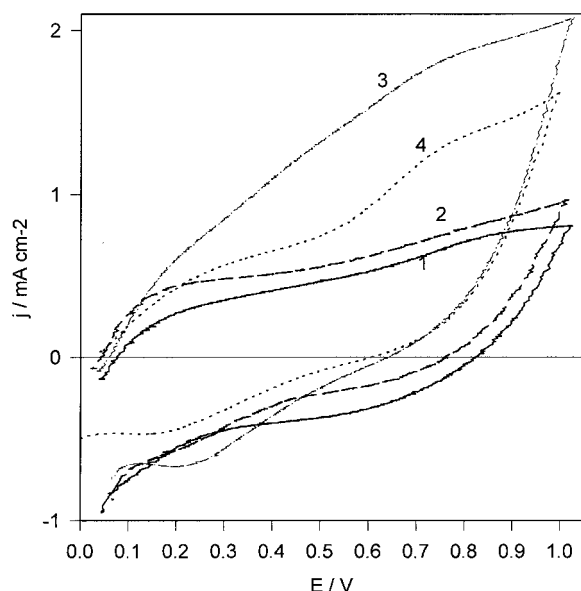


Figure 6. Voltammograms of $\text{RuO}_2.3\text{SiO}_2/\text{Ti}$ electrodes with 5 deposited layers. Influence of history of layers. 1 – immediately after the preparation, 2 – after the measurement of the polarisation curve, 3 – after 22 hours of hydrogen evolution at $j = 0.186 \text{ A cm}^{-2}$, 4 – the 3. course of the voltammogram after the voltammogram depicted by curve 3.

Ti (5x) is shown. The figure conspicuously shows that the properties of RuO_2 SG layers have changed during cathodic polarisation. These changes are manifested in the HER activity of the electrodes as well as in the values of Q_{ox} . Furthermore, it is apparent from this figure that already after the first measurement of the cathodic polarisation curve, Q_{ox} slightly increased, however mainly after long-term polarisation during hydrogen evolution. Additionally, the figure shows that after measuring the voltammetric curve, the repeated voltammetric curve Q_{ox} has a lower value. Nevertheless, even after the third repetition of the voltammetric curve, Q_{ox} does not fall to the initial value, i.e. before cathodic polarisation.

The described behaviour of RuO_2 SG electrodes is in many ways markedly different from the behaviour of RuO_2 electrodes prepared by the thermal decomposition (TD) of ruthenium chloride. This is related to both the electrocatalytic properties of these two types of electrodes and their voltammetric characteristics. The increase in the electrode activity during the HER after longer-term (tens of minutes to hours) cathodic polarisation is typical for RuO_2 TD electrodes, whereas the opposite behaviour is rather typical for RuO_2 SG electrodes, i.e. a slight increase in the activity after a short-lasting period of polarisation and a significant decrease in the activity after long-term cathodic loading. Different cathodic behaviour during voltammetry also corresponds to different electrocatalytic behaviour. The shape of the voltammetric curves shows that the red-ox processes are carried out faster on RuO_2 TD electrodes and the ratio of reduction and oxidation charge values are near to one and do not alter with the time of cathodic polarisation [7]. The increase in the electrode activity is accompanied by only a slight increase in the red-ox charges (around 1.5 times). On the other hand, an asymmetry in the values of oxidation and reduction charges is characteristic for SG electrodes, which increases with polarisation time, while values of Q_{ox} significantly exceed values of the reduction charge Q_{red} . In the case of RuO_2 TD electrodes, both direct XPS measurements [9,10,11] as well as indirect voltammetric measurements [7,9,12] showed that no reduction of ruthenium oxide to metallic ruthenium occurred in the course of hydrogen evolution. On the contrary to the RuO_2 TD electrodes, the behaviour of RuO_2 SG electrodes implies that significant reduction occurs. The decrease in the oxidation degree of ruthenium in RuO_2 SG electrodes in the course of cathodic hydrogen evolution is accompanied by a decrease in the electrode activity, which comes to effect by an outstanding increase in the reaction overvoltage of hydrogen evolution. The consecutive activation of electrodes by their resting in currentless state or polarizing them under positive potential or unloading of the voltammetric curve leads to a reactivation of the electrodes to the HER. The low resistance of the

reduced layers against mechanical stress during hydrogen evolution, as well as a colour change of the layer after long-lasting loading during hydrogen evolution rather advocate for a change in a valence of the ruthenium in the oxide accompanied by a change of crystalline structure than for H-chemisorption taking place in the inner structure of ruthenium oxide without the reduction of ruthenium oxide (as assumed in the case of RuO₂ TD electrodes 7,12).

Compared to RuO₂ TD electrodes, the relatively high activity of new RuO₂ SG electrodes for the HER and their relatively easy reducibility advocate for strong interaction between RuO₂ and SiO₂ particles, and even for the strong interaction of these particles with the support, on which the relevant layers are deposited. It is evident that the kind of support influences both the electrode activity for the HER reaction, as well as the red-ox processes rate during voltammetry in the measured area of potentials.

CONCLUSION

The hydrogen evolution rate on RuO₂ SG electrodes, especially on those with a smaller number of deposited layers, considerably depend on the kind of support. Except for RuO₂/GC layers, the initial activity of these electrodes, expressed by the value $j_{-0.2V}$, is significantly higher than the activity of TD electrodes. After long-term hydrogen evolution, the activity of RuO₂ SG electrodes substantially decreases. Contrary to RuO₂ TD electrodes, RuO₂ SG electrodes not only loose their activity during long-term hydrogen evolution, but also involve significant structural changes during which

either the substantial incorporation of hydrogen to RuO₂ SG layers occurs or probably even partial ruthenium reduction.

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Ivo Paseka

Ivo Paseka born in 1933 in Prerov, Czech (previously Czechoslovak) Republic. Between 1952 and 1957 study at the Prague Institute of Chemical Technology, Institute of Inorganic Technology. Ph.D. study at the Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences. Ph.D. obtained at that Institute in 1961 on the subject "The influence of poisons on the decomposition of alkali amalgams". Since that year he worked at that Institute as a scientist in the group of technical electrochemistry, since 1977 as the head of this group until 1995. Since 1996 until now he has worked as Senior scientist in the Department of Solid State Chemistry of the Institute of Inorganic Chemistry of the Academy of Sciences of the Czech Republic, now situated in a research centre in Rež near Prague.

Main research activities: electrocatalytic materials for hydrogen and oxygen evolution, electroreduction of nitric oxide, non-metallic materials for alkali amalgam decomposition, hydrogenation and electroreduction of unsaturated compounds, electrochemical methods in the characterisation of some precious metal (Pt, Pd, Ru) catalysts, properties of amorphous electrocatalysts, synthesis of special magnetic materials.

