

Scientific paper

Electrochemical Reduction of Perchlorate Ions on Ruthenium

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Abstract

The reduction of perchlorate ions at ruthenium electrodes was investigated by voltammetry, chronoamperometry, impedance spectroscopy, and by measuring changes of interfacial stress changes using the cantilever bending method as functions of electrode potential, and concentrations of perchloric acid and HCl. The cyclic voltammograms recorded at a rotating (Ru) disc electrode were highly asymmetric with respect to the electrode potential axis, and a negative current could be observed even during the positive sweep. Chloride ions decrease the interfacial stress and exert an inhibiting effect on the reduction process indicating the role of competitive adsorption. The desorption rate of Cl⁻ depends strongly on the hydrodynamic conditions, probably through desorption/diffusion coupling. These results serve as a warning that in perchlorate-containing solutions in contact with Ru the adsorption of chloride ions may also influence the rate of other electrochemical processes.

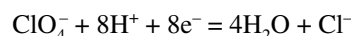
Keywords: Perchlorate reduction; Chloride adsorption; Interfacial stress change; Bending beam method

1. Introduction

Investigation of electrochemical and electrocatalytic properties of ruthenium came to the fore during the last decades^{1,2} especially the ruthenium dioxide electrode has attracted considerable practical interest due to its applications in technical electrochemical processes. Relatively less study was devoted to the investigation of phenomena occurring at non-oxidized ruthenium surfaces.³ It is known that among noble metals, ruthenium is very important in electrocatalysis and fuel cells, especially for CO tolerant, methanol or formic acid fuel cells^{4,5} and for direct ethanol solid oxide fuel cells.⁶ Recently there has also been some interest in measuring surface stress changes at the ruthenium–perchloric acid interface⁷ in connection with CO oxidation experiments.

Perchlorate containing solutions are widely used as supporting electrolytes in electrochemical studies with various electrodes. In many studies it has been assumed that the adsorption of perchlorate ions on noble metal electrodes is very weak and the reduction of perchlorate ions is not taking place under the actual experimental conditions. However, evidence for the occurrence of the reduction of

perchlorates has been reported for many electrodes^{8–9,10,11,12} including the ruthenium–aqueous perchloric acid system.^{13,14} In ref.¹³ electrodeposited Ru layers in contact with 1 mol·dm⁻³ HClO₄ solution were investigated at 50 °C. Considerable amounts of chloride ions have been detected in the solution after holding the electrode potential at $E = -200$ mV vs. saturated calomel electrode (SCE) for 4 h. In addition, the adsorption and reduction of ions could be clearly demonstrated by the ‘distortion’ of the cyclic voltammograms. The reduction process was assumed to proceed through the overall reaction



i.e., with the transfer of eight electrons. (It should be noted that the overall reaction does not contain any information on the mechanism. E.g., one could write the overall reaction with equal right without any electrons as $\text{HClO}_4 + 4\text{H}_2 = 4\text{H}_2\text{O} + \text{HCl}$.)

Results of radiotracer measurements presented in ref. confirmed the finding that perchlorate ions suffer a slow reductive transformation at Ru even under “mild” experimental conditions. It has also been shown in ref.¹⁴

that significant adsorption of Cl^- ions occurs even at very low concentrations and the adsorbability of Cl^- ions surpasses that of ClO_4^- , H_2PO_4^- and SO_4^{2-} or HSO_4^- (the latter case is quite evident as the measurements were carried out in the presence of H_2SO_4 supporting electrolyte). It was a very important observation that Cl^- ions exert an inhibiting effect on the reduction process, indicating the role of the competitive adsorption that should exist between ClO_4^- and Cl^- ions. Preliminary interfacial stress measurements also indicated that the formation of chloride ions cannot be neglected in electrochemical investigations¹⁵.

All these results should be taken as a warning to be very cautious when studying the electrochemical/electrocatalytic properties of ruthenium in electrolyte solutions containing perchlorate ions.

The aim of this communication is to present new results concerning the electrochemical reduction of perchlorate ions in the {Ru | aqueous HClO_4 solution} system, with special attention to interfacial stress changes due to the adsorption of chloride ions.

2. Experimental

2. 1. Preparation of Rotating Disc Electrodes

Ruthenium layers for rotating disc electrode (RDE) experiments have been prepared by using a 5 mm diameter Au cylinder embedded in a Teflon rod (diameter 15 mm). Before electrodeposition of Ru, the gold disc was polished with water based diamond suspensions of 1 μm and 0.25 μm particle size (Struers), rinsed in water and ethanol, and cleaned ultrasonically in water. After this treatment it was electrochemically cleaned in 1 M sulfuric acid solution, rinsed in water and immersed in the plating solution. A ruthenium layer (thickness \approx 50 nm) was deposited galvanostatically on the gold layer in a conventional three-compartment cell from a 0.1 M HCl + 10 g/dm³ RuCl_3 solution prepared from p.a. hydrochloric acid (Merck, 37%), $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ (Reagent Plus® Aldrich), and ultrapure water (Millipore). The solution was purged with oxygen-free argon (Linde 5.0) before use and an inert gas (argon) blanket was maintained throughout the deposition process. The reference electrode was a NaCl saturated calomel electrode in contact with the cell electrolyte solution via an electrolyte bridge, the counter electrode was a carbon rod. After the electrochemical plating process, the Ru layer was electrochemically cleaned in 0.5 M sulfuric acid solution by continuous potential cycling between -0.2 and $+0.2$ V vs. SSCE at a scan rate of 0.05 V/s, and rinsed in ultrapure water.

2. 2. RDE Experiments

The perchloric acid solutions used for rotating disc (RDE) measurements were prepared with ultra-pure water and perchloric acid (Merck Suprapur®). Special attention

was paid to remove traces of dissolved oxygen. Therefore, the electrochemical cell and the solutions have always been purged with high purity, oxygen-free argon gas (Linde 5.0) before use and an inert (argon) gas blanket was maintained throughout the experiments.

All electrochemical experiments were performed in gas-tight cells made of Pyrex glass. The temperature was maintained at the required temperature by a thermostated water jacket; the stability of temperature was better than ± 0.2 °C. The RDE/cyclic voltammetric and impedance measurements were carried out with an Autolab PGSTAT20 potentiostat (Eco Chemie). A conventional three-electrode configuration was used, with a rotating working electrode, a counter electrode (a cylindrical gold plate in contact with the electrolyte solution), and an aqueous sodium chloride saturated calomel reference electrode (SSCE). The rotating disc electrode was driven by a Pine RDE rotator controlled by a MSR speed control system (Pine Instrument Co.). The SSCE reference electrode was in contact with the cell electrolyte solution via an electrolyte bridge. Unless otherwise stated, potentials in this paper are quoted with respect to this electrode.

2. 3. The Electrochemical Bending Beam Method

The “electrochemical bending beam” method^{16–25} can be effectively used in electrochemical experiments, since the changes of the interfacial stress ($\Delta\gamma$) of an electrode consisting of a thin metal film on one side of an insulating plate in contact with an electrolyte solution can be estimated from the changes of the radius of curvature of the strip. If the thickness of the film t_f is sufficiently smaller than that of the plate t_s , i.e. $t_s \gg t_f$, the change of ($\Delta\gamma$) can be obtained by an expression based on Stoney's equation^{26,19,27,28}

$$\Delta\gamma = \frac{E_s t_s^2}{6(1-\nu_s)} \cdot \Delta(1/R) = k_i \Delta(1/R) \quad (1)$$

where E_s , ν_s and R are Young's modulus, Poisson's ratio and radius of curvature of the plate, respectively. According to Equation (1), for the calculation of $\Delta\gamma$ the changes of the reciprocal radius of curvature $\Delta(1/R)$ (or simply the changes of the curvature, ΔR^{-1}) of the plate must be known.

The values of $\Delta(1/R) = \Delta\gamma/k_i$ can be calculated, if the changes of the deflection angle of a laser beam mirrored by the metal layer on the plate are measured using an appropriate experimental setup (Figure 1), and the following approximate equation can be derived for large R and s , and small deflection angles.^{29,30}

$$\Delta\gamma \approx k_i \frac{\Delta b}{2n_{s,d} s w} = k_i \Delta R^{-1} \quad (2)$$

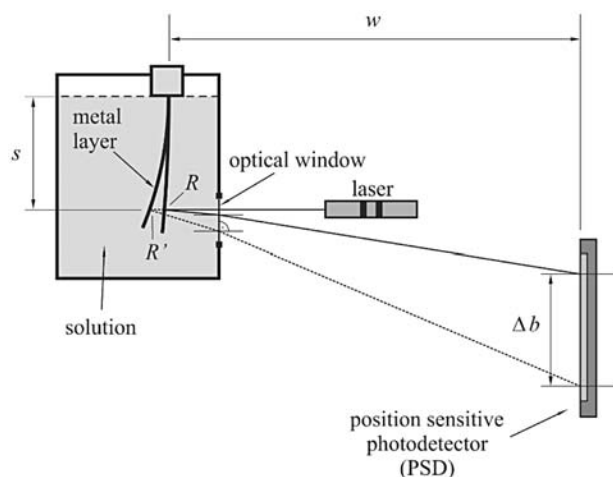


Figure 1: Schematic picture of the experimental setup for bending beam experiments. s is the distance between the level of the solution in the cell (practically the lower end of the electrode holder) and the reflection point of the laser beam on the glass plate covered by a thin metal layer; w is the distance between the electrode and the position sensitive photo-detector (PSD), Δb is the change of the position of the light spot on the PSD, R , R' radii of cantilever curvature at a different electrode potentials.

where s is the distance between the level of the solution in the cell (practically the lower end of the electrode holder) and the reflection point of the laser beam on the glass plate covered by a thin metal layer; w is the distance between the electrode and the position sensitive photo-detector (PSD) and Δb is the change of the position of the light spot on the PSD. Since the laser beam is reflected inside the solution, and the deflection is measured outside the cell (in the air), the refractive index $n_{s,i}$ of the solution must also be taken into account.^{19,29,31} If the actual values of k_1 (or t_s , E_s , v_s), w , s , and $n_{s,i}$ are known, for the calculation of $\Delta\gamma$ only the experimental determination of Δb is necessary.

2. 4. Preparation of the Cantilevers

Cantilever beams used for the measurement of surface stress changes were made by evaporating a 100 nm thick gold layer on a very thin layer of titanium evaporated on one side of a glass plate (supplier: Matsunami Glass Ind., Ltd., Japan, total length: $l_s = 60.0$ mm, width: $w_s = 5.0$ mm, thickness: $t_s = 147$ μm , $n_g = 1.522$) after carefully cleaning the surface of the substrate. A ruthenium layer (thickness ≈ 40 nm) was deposited galvanostatically on the gold layer in the same cell that was used for the preparation of the Ru RDE. The geometric area of the electrode was $A = 4.0$ cm \cdot 0.50 cm = 2.0 cm². A constant current density of 10 mA cm⁻² was applied for 360 s. After the electrochemical plating process, the Ru layer was electrochemically cleaned in 0.5 M sulfuric acid solution by continuous potential cycling between -0.2 and $+0.2$ V vs. SSCE at a scan rate of 0.05 V/s, and rinsed in ultrapure water. Selected samples were aged in argon atmosphere

at room temperature for 2 months in order to reduce intrinsic stress in the film. The morphology of the samples was studied with a multimode atomic force microscope instrument (Park System, XE-100, South Korea) in non-contact mode. The thickness of the ruthenium layer could also be measured this way. A Quanta™ 3D FEG high-resolution, low-vacuum SEM/FIB instrument was used for SEM analysis. According to EBSD (Electron Backscatter Diffraction) measurements the electrodeposited Ru films showed no preferred crystallographic orientation.

2. 5. Bending Beam Experiments

A battery-powered potentiostat (Jaisle Model 1001 T-NC) was used for the interfacial stress measurements. Control voltage was supplied by a function generator (Hewlett–Packard 3314A) or by a data acquisition card. A National Instruments 6034E DAC was used for the computer-based acquisition of the analog output signals of the PSD and the potentiostat. The software for controlling and data acquisition was developed in the National Instruments LabVIEW® environment. A position-sensitive detector (Hamamatsu Inc., S1300) attached to a signal processing unit (Hamamatsu C4757), the He-Ne laser (Melles Griot 05-LHP-151) and the electrochemical cell (gas-tight cell made of Pyrex® glass) were assembled on an optical bench in order to avoid vibrations. The changes of output dc signals of the PSD were converted into the changes of position of the reflected beam on the PSD, that is, Δb . The distance between the level of the solution in the cell and the reflection point of the laser beam (s) was measured with the help of a cathetometer (type KM-6). The value of constant k_1 ($= 331.6$ N) can be calculated according to Equation (2) with $t_s = 147$ μm , $E_s = 7.09 \cdot 10^{10}$ N m⁻², $v_s = 0.230$.

All electrochemical bending beam experiments were performed in gas-tight cells made of Pyrex glass equipped with an optical window (made of optical crown glass). The electrochemical cell and the perchloric acid solution (prepared with ultra-pure water and Merck Suprapur® perchloric acid) have been purged with high purity, oxygen-free argon gas (Linde 5.0) before use and an argon gas blanket was maintained throughout the experiments. A conventional three-electrode configuration was used, with a cantilever working electrode, a counter electrode (a cylindrical gold plate in contact with the electrolyte solution), and an aqueous sodium chloride saturated calomel reference electrode (SSCE).

Refractive indexes were measured at 25.0 °C with a Zeiss PR 2 refractometer. The refractive index of 0.1 M HClO₄ solution at 632.8 nm ($n_{s,i} = 1.3318$) was calculated using Cauchy's formula. This value is important, since the He-Ne Laser operates at this wavelength. The temperature was maintained at the required temperature by a thermostated water jacket; the stability of temperature was better than ± 0.2 °C.

3. Results and Discussion

3. 1. Rotating Disc Electrode Experiments

3. 1. 1. Cyclic Voltammetry

In Figure 2 cyclic voltammograms obtained with a rotating Ru disc (rotation rate: ω_{RDE}) in contact with a perchloric acid solution ($c_{\text{HClO}_4} = 1 \text{ M}$) are shown. There is a distinct difference between curves recorded at stagnant electrodes and those recorded at the RDE. At $\omega_{\text{RDE}} = 0 \text{ rpm}$ only a slight asymmetry of the “stationary” cyclic voltammogram recorded at a sweep rate of $\nu = 5 \text{ mV s}^{-1}$ can be observed (Figure 2, curve 1).

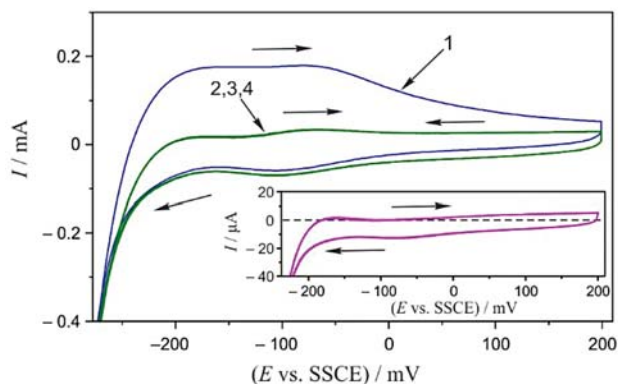


Figure 2: Cyclic voltammograms of a rotating Ru disc electrode in $1 \text{ mol} \cdot \text{dm}^{-3}$ aqueous perchloric acid solution. I : current; E : electrode potential. Curve 1–4: sweep rate $\nu = 5 \text{ mV s}^{-1}$, RDE rotation rates 1: 0 rpm; 2–4: 2000 rpm. Insert: sweep rate $\nu = 1 \text{ mV s}^{-1}$, RDE rotation rate: 1000 rpm.

On the contrary, when the electrode was rotated the shape of the CV became highly asymmetric with respect to the electrode potential axis (Figure 2, curve 2–4), and a negative current could be observed even during the positive-going scan at low sweep rates (Figure 2, insert). A similar effect was observed when the electrolyte solution was continuously stirred by argon gas. As a matter of fact, in a certain potential range the CV recorded under such conditions shows a potential independent limiting rate of reduction superimposed by double layer charging. Comparison of perchloric acid with sulphuric acid solution³ shows that in Figure 2 it is reduction of perchlorate ions.¹³ The dependence of the reduction current on the RDE rotation rate indicates that the desorption rate of Cl^- ions generated during the reduction process is significantly influenced by the hydrodynamic conditions, most probably through desorption/diffusion coupling.³² It should be noted that in case of cyclic voltammograms recorded at higher sweep rates the reduction process cannot be readily discerned from the shape of the response curves alone due to the high charging current.

3. 1. 2. Chronoamperometry

Chronoamperometric measurements were carried out in $0.5 \text{ M H}_2\text{SO}_4$ and 1 M HClO_4 solutions. The curves obtained at $T = 25 \text{ }^\circ\text{C}$ are presented in Figure 3. During these experiments the current was recorded as a function of time at constant electrode potential and at different RDE rotation rates. It can be seen in Figure 3 that in the case of the H_2SO_4 solution the limiting currents are low and practically independent of the rpm value. In contrary to this, in the 1 M HClO_4 solution more or less well-defined negative stationary currents were observed at all rotation rates. This also supports the suggestion that perchlorate ions are reduced to chloride ions at the Ru surface and desorption of the Cl^- ions from the active sites plays a key role in the electrode process.

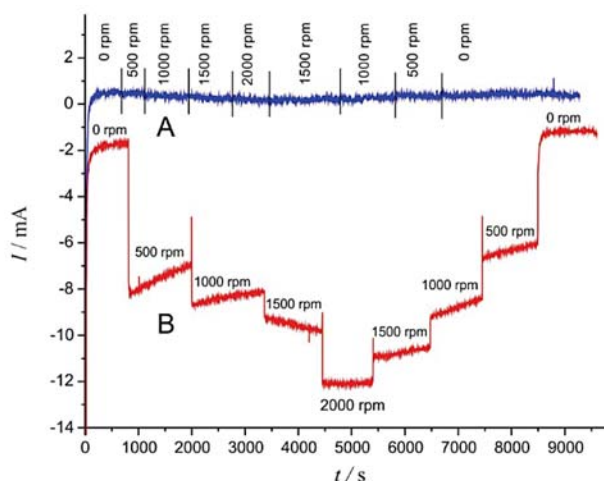


Figure 3: Chronoamperometric measurements. The current (I) as a function of time (t) at constant electrode potential ($E = -0.15 \text{ V}$) and at different electrode rotation rates. A: Ru in $0.5 \text{ mol} \cdot \text{dm}^{-3} \text{ H}_2\text{SO}_4$ solution, B: Ru in $1 \text{ mol} \cdot \text{dm}^{-3} \text{ HClO}_4$ solution. (Geometric surface area of the electrode: $A = 0.196 \text{ cm}^2$, temperature: $T = 25.0 \text{ }^\circ\text{C}$).

3. 1. 3. Impedance Measurements

In Figure 4 (complex) immittance diagrams and Bode plots ($\log |Z|$ (magnitude) vs. $\log f$ and φ (phase angle) vs. $\log f$ plots) of Ru in $1 \text{ mol dm}^{-3} \text{ HClO}_4$ solution are shown. The impedance of the electrode was measured at different rotating rates of the RDE at the electrode potential of $E = -0.2 \text{ V}$ versus SSCE ($T = 25 \text{ }^\circ\text{C}$). The impedance measurements were started as soon as stationary conditions were reached (e.g., about 20 min after changing the rotation rate of the RDE). The first observation is that the plots are very similar to what is expected qualitatively for the case of a single charge transfer step coupled with diffusion. In all the spectra obtained for the rotating Ru disc| $1 \text{ mol dm}^{-3} \text{ HClO}_4$ solution system, only one time constant can be identified in the high-frequency range,

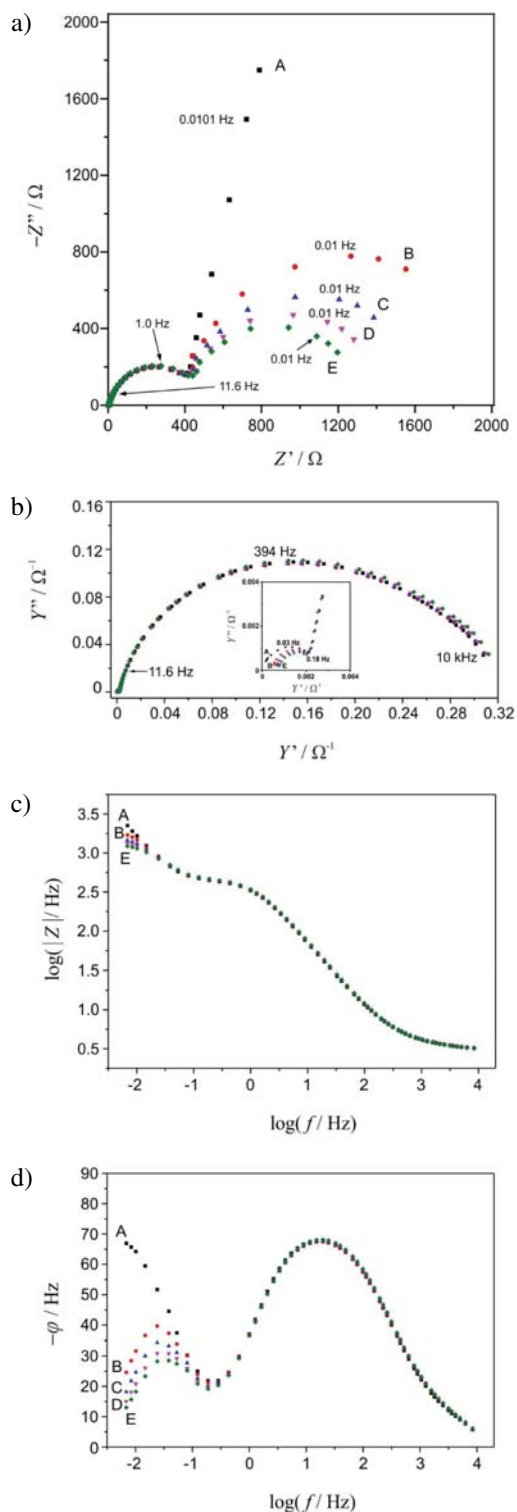


Figure 4: a) Impedance (complex plane plot) recorded on Ru in 1 mol dm³ HClO₄ solution. The impedance of the electrode was measured at different rotating rates of the RDE at the electrode potential of $E = -0.2\text{V}$ vs. SSCE.

b) The corresponding complex plane admittance diagrams (Y'' vs. Y' plots) and c) – d) Bode diagrams ($\log |Z|$ vs. $\log f$ and ϕ vs. $\log f$ plots). Geometric surface area of the electrode: $A = 0.196\text{ cm}^2$, temperature: $T = 25.0\text{ }^\circ\text{C}$. Rotation rates (ω): (A) 0 rpm (■); (B) 500 rpm (●); (C) 1000 rpm (▲); (D) 2000 rpm (▼); (E) 3000 rpm (◆).

which suggests that the measured impedance response is dominated by a single (rate determining) charge transfer step. This means that the assumption that the $\text{ClO}_4^- \rightarrow \text{ClO}_3^-$ transformation is the rate-determining step¹⁰ seems to be a relevant and acceptable interpretation of the observed impedance response. Research on this issue is ongoing and will be the topic of forthcoming papers.

3. 2. Electrochemical Bending Beam Measurements

On the basis of the results of the previous sections we can reasonably expect that the interfacial stress curves also indicate the effect of adsorption of Cl^- ions, i.e. the reduction of perchlorate ions. In order to test this hypothesis the ruthenium coated cantilever in contact with 0.1 M HClO₄ solution was subjected to a series of triangular potential sweeps from -0.25 V to 0.2 V vs. SSCE at a sweep rate of $\nu = 50\text{ mV s}^{-1}$ (Figures 5 and 6). Prior to the first potential cycle, the solution was vigorously stirred with Ar. In Figure 5 the curvature changes are shown as a function of time. The change in curvature was about -0.0065 m^{-1} in the potential range from -0.25 V to 0.2 V vs. SSCE, which corresponds to about 2.15 Nm^{-1} . Since the surface of the electrodeposited layers is not perfectly smooth, the calculated $\Delta\gamma$ values can be inaccurate,³³ therefore only the $\Delta(1/R)$ values are given in the relevant figures. According to the figure the corresponding $\Delta(1/R)$ values recorded during subsequent potential cycles are slightly shifted in the negative direction with respect to the first curve. At the end of the 4th potential cycle the solution was stirred again with argon for $\sim 20\text{ s}$. As it can be seen in Figure 5 the shapes (and position) of curve 1 and 6 (curves 1 and 6 were recorded immediately after stir-

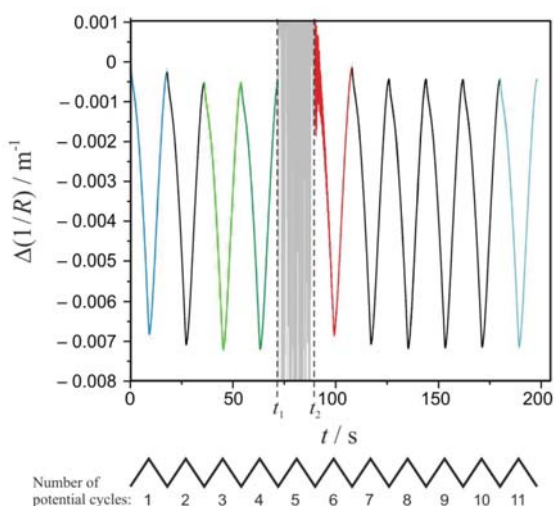


Figure 5: Electromechanical responses of a ruthenium coated cantilever to consecutive potential cycles (-0.25 V to 0.2 V vs. SSCE). Changes of the reciprocal radius of curvature $\Delta(1/R)$ with time (t). t_1 to t_2 : stirring with Ar gas.

ring of the solution) are almost identical. The difference between the curves recorded before and after stirring is clearly noticeable also in Figure 6a, which shows the dependence of $\Delta(1/R)$ on the electrode potential E (“volt-deflectograms”).

The corresponding cyclic voltammograms are presented in Figure 6b. In accordance with the results of the RDE measurements, there is only a slight difference between the curves recorded before and after stirring, namely that during the first anodic scan after stirring the solution, the current between $E \approx -0.050$ V and $E = 0.2$ V seems to be somewhat lower than the current in subsequent scans. This is consistent with the occurrence of perchlorate reduction once the adsorbed hydrogen is largely removed. On the other hand, the effect of perchlorate reduction is not so significant for the subsequent potential cycles, since the continued reduction of perchlorate will be inhibited by the adsorption of the chloride product.

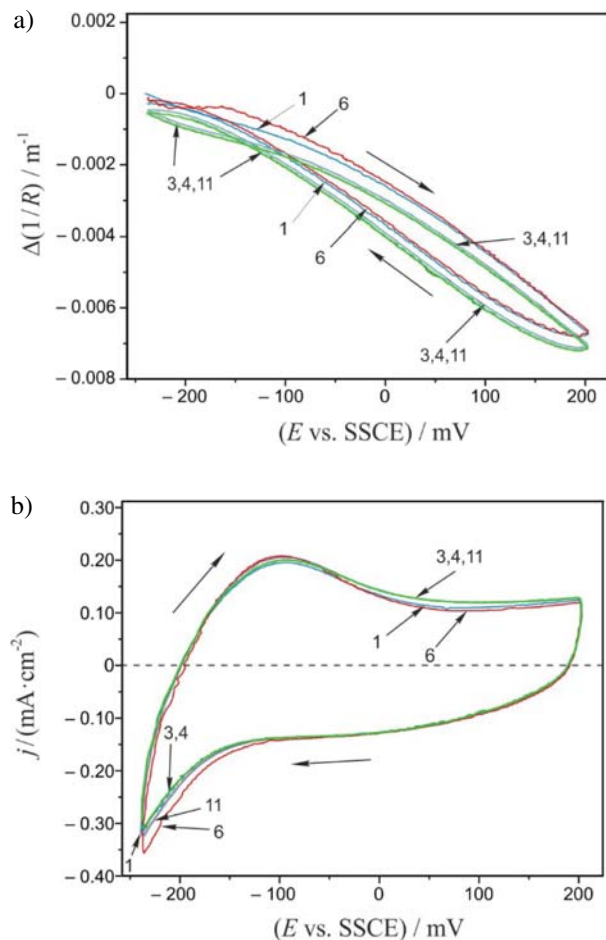


Figure 6: Electrochemical and electromechanical responses of a ruthenium coated cantilever to consecutive potential cycles (–0.25 V to 0.2 V vs. SSCE). (a) Changes of the reciprocal radius of curvature $\Delta(1/R)$ with the electrode potential (E). (b) Selected cyclic voltammograms, j : current density, E : electrode potential. The numbering of the curves corresponds to that in Fig.5.

The shift of the $\Delta(1/R)$ values in the negative direction, i.e. the decrease of the interfacial stress during potential cycling can be explained as follows: After (at least partially) removing the adsorbed Cl^- ions from the electrode surface (“cleaning of the surface”) by stirring the solution (or by rotation of the electrode as in rotating disc voltammetry), strongly adsorbed “new” chloride ions are produced during the first potential cycle, causing the decrease of the interfacial stress.

The effect of chloride ions on the interfacial stress could be demonstrated by adding different amounts of HCl to the 0.1 M perchloric acid solution in the electrochemical cell while holding the electrode potential at $E = 8$ mV vs. SSCE. The results are shown in Figure 7. After the addition of oxygen free HCl solution (resulting concentration: $0.0005 \text{ mol} \cdot \text{dm}^{-3}$) a decrease of the interfacial stress could be observed. The total change in $1/R$ was about 0.00045 m^{-1} . The interfacial stress decreased further ($\Delta(1/R) = -0.00015 \text{ m}^{-1}$) when the concentration of HCl was increased to $0.001 \text{ mol} \cdot \text{dm}^{-3}$.

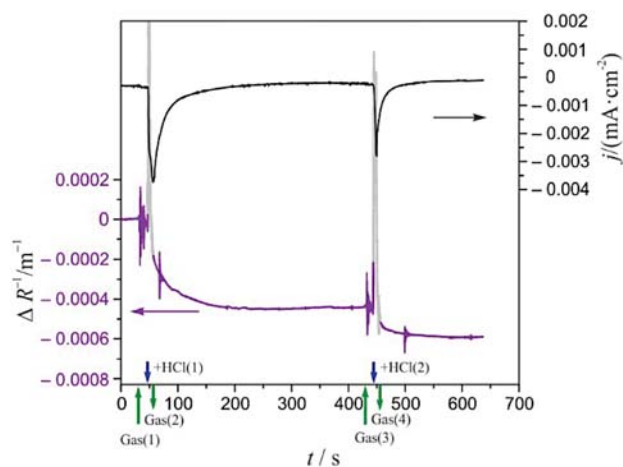


Figure 7: Curvature change ($\Delta(1/R)$) vs. time (t) and current density (j) vs. time curves obtained following the addition of HCl to a solution of 0.1 mol dm^{-3} perchloric acid. First run: Gas(1): start of the stirring (with Ar gas), +HCL(1): addition of HCl (Cl^- concentration: $0.0005 \text{ mol dm}^{-3}$). Second run: Gas(2): stop of stirring. Second run: Gas(3): start of stirring (with Ar gas), +HCL(2): addition of HCl (Cl^- concentration: $0.001 \text{ mol dm}^{-3}$), Gas(2): stop of stirring.

4. Conclusions

On the basis of the above results we can conclude that both the addition of chloride ions as well as the cycling of the electrode potential lead to the change of the interfacial stress in the same direction. This observation can be considered as an additional proof of the formation of Cl^- from perchlorate ions on ruthenium during voltammetric experiments.

The most important conclusion of this study is that it is practically impossible to record interfacial stress chan-

ge vs. electrode potential curves characterizing the “true” adsorption properties of the ruthenium|perchloric acid solution interface, since in the potential range where the reduction of perchlorate ions occurs the metal surface is always covered, at least partially, by chloride ions. The presence of Cl⁻ ions on the surface may significantly influence the electrocatalytic activity of ruthenium in solutions containing perchlorate ions.

Evidently the same issues have to be taken into account when testing the electrocatalytic activity of Ru-containing alloys in perchlorate solutions. In such cases, it is usually assumed that the results obtained are characteristic of a chloride-free system. However, as we showed above, Ru is also an excellent catalyst for the reduction of perchlorate ions to Cl⁻, i.e. chloride ions can easily be formed during the experiments. Consequently, the results of such tests may be misleading and of little or no practical use.

5. Acknowledgements

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Povzetek

Redukcijo perkloratnih ionov na površini rutenijevih elektrod smo proučevali z voltometrijo, kronoamperometrijo, impedančno spektroskopijo in z merjenjem spremembe površinske napetosti na osnovi metode upogibne ročice kot funkcije elektrodnega potenciala ter koncentracije perklorove kisline in HCl. Ciklični voltamogrami, posneti na rotirajoči (Ru) disk elektrodi, so bili izrazito asimetrični glede na elektrodo potencialno os, poleg tega smo izmerili negativne tokove celo pri pozitivnem preletu potenciala. Kloridni ioni zmanjšujejo površinsko napetost in delujejo inhibirajoče na redukcijske procese, kar nakazuje na kompetitivno adsorpcijo. Hitrost desorpcije Cl^- je močno odvisna od hidrodinamskih pogojev, najverjetneje preko desorpcijsko/difuzijske sklopitve. Rezultati opozarjajo na možnost, da lahko v perkloratnih raztopinah kloridni ioni vplivajo tudi na hitrost drugih elektrokemijskih procesov, ki potekajo na rutenijevi elektrodi.