

## Electrochemical reduction of perchlorate ions

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### Abstract

The electrochemical reduction of perchlorate ions is surveyed in the light of experimental results. The indications of the occurrence of perchlorate reduction in voltammetry, chronoamperometry, and in experiments applying the radiotracer method, the electrochemical bending beam technique and impedance spectroscopy are presented. Some possible mechanisms of the complicated reduction processes are discussed. Environmental aspects and some methods for perchlorate removal and wastewater treatment are briefly summarized.

### Keywords

Corrosion; Electrochemical reduction; Environmental contamination; Electrochemical impedance spectroscopy; Radiotracer technique; Electrochemical bending beam method; Perchlorate ions; Perchlorate stability; Reduction mechanism; Voltammetry; Wastewater treatment;

## 1. Introduction

From thermodynamic point of view  $\text{ClO}_4^-$  ions are expected to be unstable against reductive attacks in a wide potential range at the metal/(acidic or neutral) solution interface (i.e. at electrodes). This clearly follows from the standard electrode potential values presented in Table 1.

**Table 1.** Standard potential values of reaction steps potentially involved in the reduction of  $\text{ClO}_4^-$  ions\*

Reaction	$E^\circ / \text{V}$
$\text{ClO}_2 + e = \text{ClO}_2^-$	0.93
$\text{ClO}_3^- + 2\text{H}^+ + e = \text{ClO}_2 + \text{H}_2\text{O}$	1.15
$\text{ClO}_4^- + 2\text{H}^+ + 2e = \text{ClO}_3^- + \text{H}_2\text{O}$	1.19
$\text{ClO}_2 + \text{H}^+ + e = \text{HClO}_2$	1.27
$\text{HClO} + \text{H}^+ + 2e = \text{Cl}^- + \text{H}_2\text{O}$	1.50
$\text{HClO}_2 + 2\text{H}^+ + 2e = \text{HClO} + \text{H}_2\text{O}$	1.64

\*Selected constants. Charlot, G.; Collumeau, A.; Marchon, M.J.C. *Oxidation-Reduction Potentials of Inorganic Substances in Aqueous Solution*, Butterworths, London, 1971.

Based on thermodynamics alone, perchlorate is expected to be a powerful oxidizer. Perchloric acid, for example, should be able to oxidize water to oxygen in aqueous solutions. In contrary to this, perchlorate ions are usually considered as stable anions in electrochemistry therefore perchloric acid and its salts are often used as supporting electrolytes in different experiments (e.g. investigation of dissolution, deposition, or corrosion of metals and semiconductors) and many observations revealed that perchlorate salts show considerable stability in electrochemical environment. This behavior can be explained by the concept of "kinetic stability" i.e. the stability of perchlorate in aqueous solutions is governed by kinetics and not a result of thermodynamics.

Nevertheless, evidence for the occurrence of the reduction process has been reported for Rh [1-5], Pt [6-9], WC [10], Al [11], Ti [12], Ir [13], Ru [14], Re [15], Tc [16] and Sn [17] electrodes.

Butula and Butula[18] found already in 1971 that using Pd/BaSO<sub>4</sub> and Rh/C catalysts in acetic acid at 60 °C, HClO<sub>4</sub> could be reduced with hydrogen to HCl. In the seventies of the last century the hydrogenation of perchlorate ions has been studied at different

temperatures, perchlorate and hydrogen ion concentrations. It was demonstrated that  $\text{ClO}_4^-$  ions dissolved in acidic aqueous solutions could be reduced to  $\text{Cl}^-$  ions by molecular hydrogen in the presence of powdered platinum black catalyst [9].

Considering the link between the liquid (aqueous) phase heterogeneous catalytic hydrogenation and electrocatalytic reduction [19] the conclusion was drawn that electrocatalytic/electrochemical reduction of  $\text{ClO}_4^-$  ions can be performed at electrodes prepared from materials which are identical with the material of catalyst powders used in the catalytic hydrogenation. By 1990 it became evident that the contradictory results obtained during a decade could be explained if one assumes that the reduction occurs not only on rough surfaces having high areas but also for smooth polycrystalline surfaces and well-defined crystal faces [3-5]. These observations prompt us to keep in mind the possibility of the occurrence of the reduction process at any electrode used in acid aqueous media containing perchlorate ions.

Besides the significance of perchlorate reduction for the fundamental electrochemistry nowadays a very practical reason, the so called perchlorate contamination challenge, came into foreground orienting the attention towards the reductive elimination of perchlorate ions. Perchlorates are used as oxidizer component and primary ingredient in solid propellants for rockets, missiles, and fireworks. Therefore dissolved ammonium, potassium, magnesium, or sodium salts are present as contaminant in groundwater and surface waters originating from improper disposal of the solid propellants and from the wastewaters of the manufacturing plants. Perchlorate salts are also used in optoelectronics [20], electronic tubes, car air bags and leather tanning.

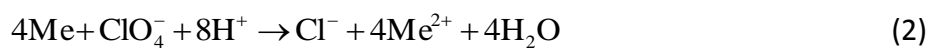
As the sorption or natural chemical reduction of perchlorate in the environment is not significant, perchlorates are exceedingly mobile in aqueous systems and can persist for many decades under typical ground and surface water conditions. A large number of water sources in the United States have been contaminated with perchlorate [21-27]. However, the perchlorate problem is not located to the US only. This type of contamination constitutes a major problem in China [28-30], as well as many other countries in the world [31-33]. E.g. in Israel, an ammonium-perchlorate manufacturing plant that disposed of untreated wastewater in four unlined ponds for 25 years caused extensive perchlorate contamination in the underlying aquifer. The perchlorate migration in the deep vadose zone

has been found very low under natural recharge conditions in the semiarid region [34]. The perchlorate contamination is also present in fruits and vegetables [35]. One of the main health hazards is connected with the very fact that perchlorate interferes with iodide uptake in the thyroid gland [36, 37]. In large doses, it has been linked to anemia and fetal brain damage [30, 36]. The development and implementation of water treatment technologies have been comprehensively summarized in recent reviews [38, 39].

According to the above considerations, the problem of perchlorate reduction constitutes an intersection of several branches of science, such as electrochemistry (anodic dissolution of metals, discharge of oxonium ions), (electro)catalysis, corrosion science (passivity of metals, coupling of cathodic and anodic processes), civil, environmental and medical sciences, etc., however, in this brief review, the discussion is focused mainly on the electrochemical reduction of  $\text{ClO}_4^-$  ions.

## 2. The overall reaction

The interaction of a metal with dissolved perchlorate ions should be considered as a corrosion process i.e. the overall transformation is composed of at least two or three reactions



From electrochemical point of view this formulation involves three charge transfer processes



This last step should be a very complex one composed of several elementary steps. The equations given above involve the coupling of the anodic dissolution of the metal with two cathodic processes: discharge of protons and reduction of  $\text{ClO}_4^-$  ions.

In principle the reduction of  $\text{ClO}_4^-$  ion could occur through a “catalytic mechanism” via the interaction with hydrogen atoms adsorbed on the metal surface.

In series communications [40-42] it was demonstrated that the reduction of  $\text{ClO}_4^-$  ions takes place during the corrosion of Cu, Al, Zn, Ni and Fe in deoxygenated  $\text{HClO}_4$  solutions and it was emphasized that for the interpretation of the results of corrosion or anodic dissolution studies in the  $\text{HClO}_4$ /metal systems this fact cannot be left out of consideration.

### 3. Indications of the occurrence of perchlorate reduction

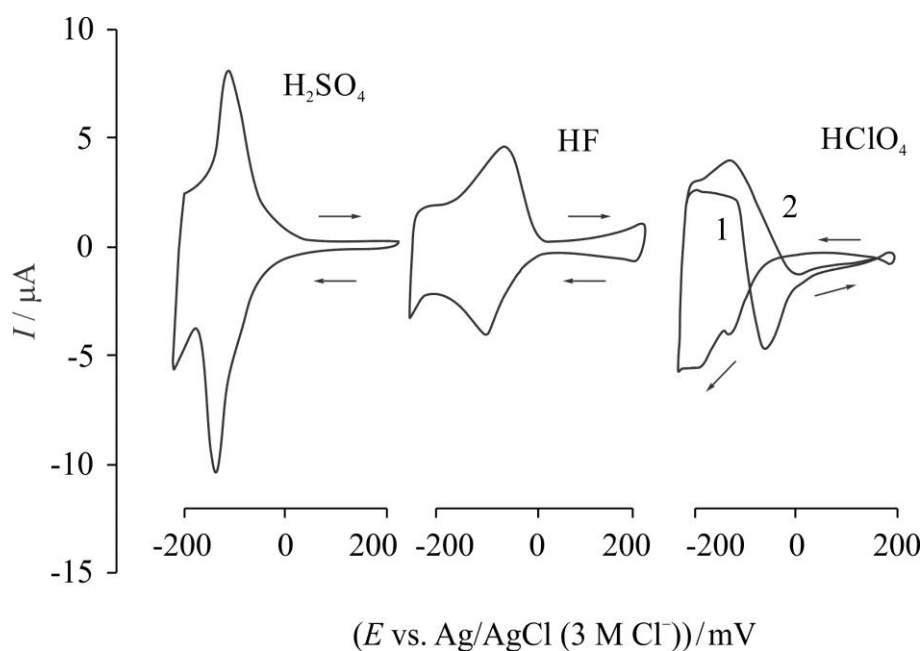
As it has been mentioned in the introduction, during electrochemical experiments perchlorate reduction may occur unexpectedly [43]ide tettem a Visnja cikkét. In a recent work sodium pechlorate was used as electrolyte for the study of Prussian blue analogue cathode materials, and the formation of  $\text{NaMnCl}_3$  was observed. It has been concluded that the chloride ions could be originated only from the  $\text{ClO}_4^-$  ions in the electrolyte, because no other chloride source were present [44]. Nevertheless, instead of examining the phenomenon many electrochemists have ignored the possible complications that should be ascribed to the occurrence of a reduction process involving perchlorate ions in experiments carried out in the presence of  $\text{HClO}_4$  supporting electrolyte [45-47]. Detailed mechanistic conclusions were drawn from EQCM and electrochemical impedance spectroscopy (EIS) studies of anodic dissolution and corrosion of various metals in perchloric acid solutions, for instance, in the case of nickel [48] and iron [49, 50] without taking into account the possible reduction of  $\text{ClO}_4^-$  ions under the applied experimental conditions.

In the following some examples are presented to illustrate the impact of perchlorate reduction on the results from different experimental techniques such as voltammetry, chronoamperometry, radiotracer method, electrochemical-mechanical testing, and impedance spectroscopy.

#### 3.1. Voltammetry

The apparent consequence of the reduction of  $\text{ClO}_4^-$  ions is the distortion of the voltammetric curves. [Figure 1](#) shows cyclic voltammetric curves obtained in  $1 \text{ mol dm}^{-3}$   $\text{H}_2\text{SO}_4$ , HF and  $\text{HClO}_4$  supporting electrolytes using rhodized electrodes [51]. In the case of  $\text{H}_2\text{SO}_4$  and HF, although there is some difference between them, the voltammetric curves behave “normally” as expected. In contrast to this, the voltammetric curve obtained in the presence of perchloric acid is distorted. The negative peak in the course of the positive

sweep clearly indicates the occurrence of a cathodic process, namely the reduction of perchlorate ions. Similar voltammetric curves were obtained with single- and polycrystalline smooth Rh and platinized Pt[8] surfaces [3, 4]. Electrochemical behavior of Ir(100) in perchloric acid solutions has also been characterized [52]. The asymmetry of the cyclic voltammograms recorded in the double layer region could be attributed to a slow reduction process, e.g. the reduction of perchlorate ions.



**Figure 1:** Voltammograms obtained for rhodized electrodes in different electrolytes; acid concentration  $1 \text{ mol dm}^{-3}$ , sweep rate =  $5 \text{ mV s}^{-1}$ . Adapted from [53].

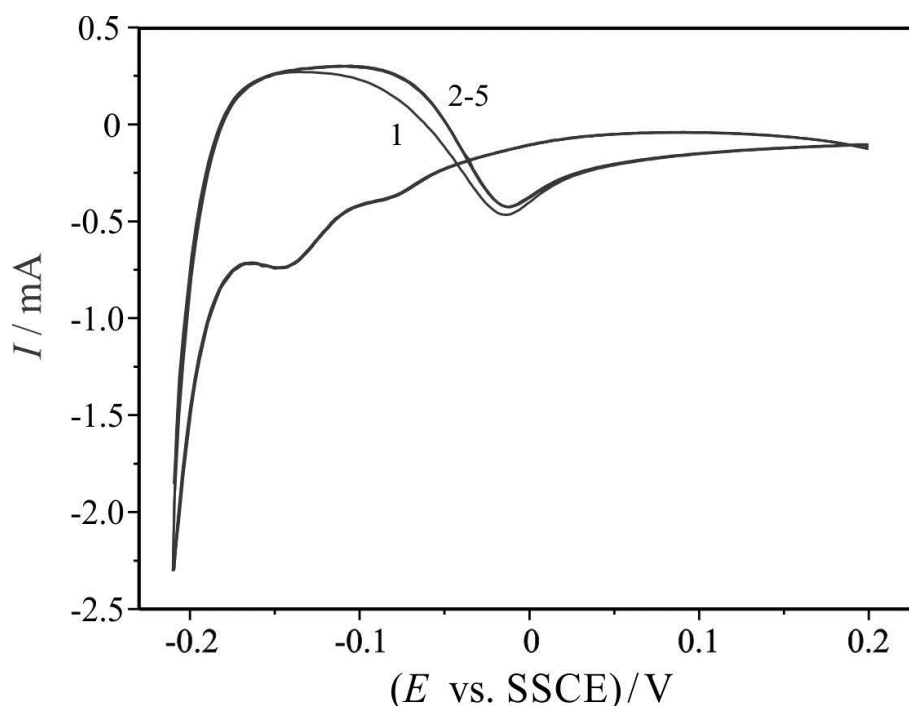
The characteristic features common to these systems are as follows:

- the reduction process occurs, almost exclusively, during the positive sweep of the cyclic voltammogram,
- generally, no reaction can be observed on the negative sweeps, but the shape, height and position of the corresponding hydrogen peak differ significantly from those expected,
- there is general agreement in the literature that the rate of reduction of  $\text{ClO}_4^-$  ions at noble metal and catalytic electrodes should be very low at both ends of the potential scale; consequently the  $I$  vs.  $E$  curve should go through a minimum,
- the distortion of the anodic peak gradually disappears during subsequent cycles, but the anodic and cathodic peaks remain asymmetric,

- (e) the only reduction product in the solution is  $\text{Cl}^-$ ,
- (f) the very rapid decrease in the electrocatalytic activity with respect to  $\text{ClO}_4^-$  reduction can be explained by self-inhibition, namely by the inhibiting action of  $\text{Cl}^-$  ions formed during reduction and adsorbed on the electrode surface. The higher the  $\text{Cl}^-$  concentration, the more pronounced is its inhibitive effect,
- (g) the desorption of  $\text{Cl}^-$  ions from the metal surface is a very slow process. For instance, no measurable desorption of  $\text{Cl}^-$  ions were detected until several minutes after switching the electrolyte solution from  $1 \text{ mol}\cdot\text{dm}^{-3} \text{ HF} + 10^{-4} \text{ mol}\cdot\text{dm}^{-3} \text{ HCl}$  to  $1 \text{ mol}\cdot\text{dm}^{-3} \text{ HF}$  [54, 55].

Almeida et. al. [17] studied the electrochemical behavior of tin in deaerated sodium perchlorate using potentiodynamic and potentiostatic techniques. The behavior of Sn in sodium perchlorate was unexpectedly complicated by the reduction of the perchlorate anion. It was shown that the reduction process takes place within a potential region comprising the negative side of the double layer region and the positive side of the hydrogen region ( $-0.7 \leq E \leq -1.3 \text{ V}$ ). It was stated that the presence of oxide on the electrode surface favors the reduction reaction, which may occur in two steps: the formation of basic tin(II) chloride followed by its reduction, producing chloride.

In [Figure 2](#) cyclic voltammograms obtained for a Rh rotating disc electrode in contact with a  $3 \text{ mol}\cdot\text{dm}^{-3} \text{ HClO}_4$  solution are shown [54].



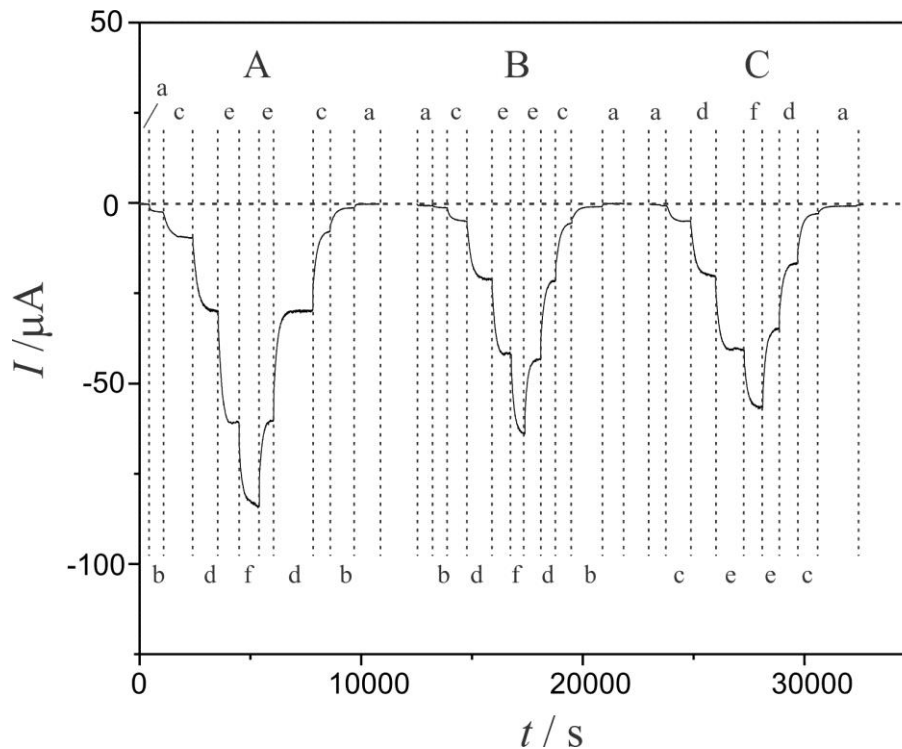
**Figure 2:** Cyclic voltammograms obtained for a Rh rotating disc electrode in contact with a  $3 \text{ mol}\cdot\text{dm}^{-3} \text{ HClO}_4$  solution (geometric surface area of the electrode:  $A = 0.196 \text{ cm}^2$ , rotation rate:  $\omega_r = 950 \text{ rpm}$ , temperature:  $T = 25.0 \text{ }^\circ\text{C}$ ) (SSCE: sodium saturated calomel electrode). Adapted from [54].

There is a distinct difference between curves recorded at stagnant electrodes and the curves obtained with the RDE. In case of stationary electrodes the distortion of the anodic peak gradually disappears during subsequent potential cycles, i.e. the negative current during the positive sweep is continuously decreasing over the consecutive scans. In contrast to this, in case of rotating disc electrodes the shape of the voltammogram does not change after the second or third cycle, and a negative current can be always observed during the positive sweep. It means that the desorption rate of  $\text{Cl}^-$  ions generated during the reduction process is significantly influenced by the hydrodynamic conditions, probably through desorption/diffusion coupling. This conception is supported by the results of chronoamperometric measurements carried out at different temperatures. The curves obtained at  $T = 45 \text{ }^\circ\text{C}$  are presented in Figure 3 [54].

### 3.2. Chronoamperometry

During chronoamperometric experiments the current was recorded on rhodium as a function of time at constant electrode potentials and at different electrode rotation rates. Well-defined stationary cathodic currents were observed in all cases. The values of the stationary currents depend on the rotating rate of the RDE, the electrode potential, and the temperature.





**Figure 3:** Chronoamperometric measurements. The current ( $I$ ) as a function of time ( $t$ ) at constant electrode potentials and at different electrode rotation rates. Electrode potentials: A: 0.01 V vs. SSCE; B: 0.06 V vs. SSCE; C: 0.11 V vs. SSCE. Rotation rates ( $\omega_r$ ): a: 0 rpm; b: 500 rpm; c: 1000 rpm; d: 2000 rpm; e: 3000 rpm; f: 4000 rpm. (geometric surface area of the electrode:  $A = 0.196 \text{ cm}^2$ , temperature:  $T = 45.0 \text{ }^\circ\text{C}$ ) [54]

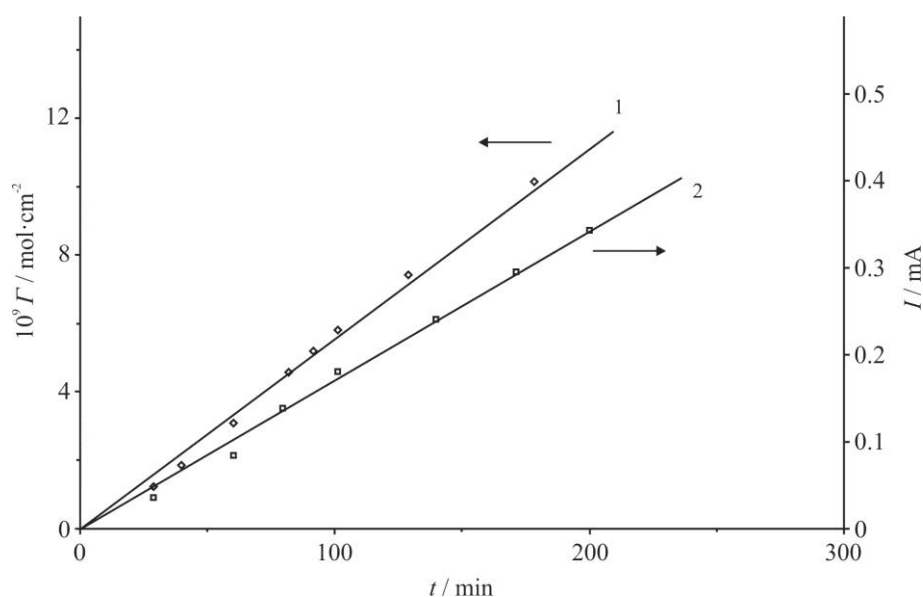
It should be pointed out, that the above measurements were carried out at potentials where the surface concentration of adsorbed H is very low, if any; consequently it is unlikely that it can play any role. Thus it should be assumed that the rate-determining step is the decomposition of adsorbed  $\text{ClO}_4^-$  ions.

### 3.3. Combined electrochemical-radiotracer technique

Electrocatalytic activity in perchlorate reduction was found also in the case of some non-noble metals: Tc [16], Re [15], Sn [1] and Ti [12, 56]. Considering the very fact that Tc is an artificial element, emitting  $\beta$ -radiation, the coupled electrochemical and radiochemical study of electrodeposition of Tc species from  $\text{HClO}_4$  supporting electrolyte gave an interesting insight in the reduction of  $\text{ClO}_4^-$  ions.

It was found that under potentiostatic conditions during the deposition of Tc species the increase in the radiation intensity, i.e. the increase of the amount of deposited material is accompanied by a continuous increase of a cathodic current as shown by Figure 4 (the

amount of the electrodeposited Tc species was determined directly by the measurement of the intensity of the radiation coming from the electrodeposited layer).



**Figure 4:**  $\Gamma$  vs. time (1) and (absolute value) current vs. time (2) curves obtained in the course of a simultaneous radiometric and electrochemical measurement of the deposition of Tc species ( $c_{\text{TcO}_4^-} = 8 \times 10^{-4} \text{ mol dm}^{-3}$ ) from a  $1 \text{ mol dm}^{-3} \text{ HClO}_4$  supporting electrolyte at  $E = 50 \text{ mV}$ , (geometric surface area,  $13 \text{ cm}^2$ ) Adapted from [53].

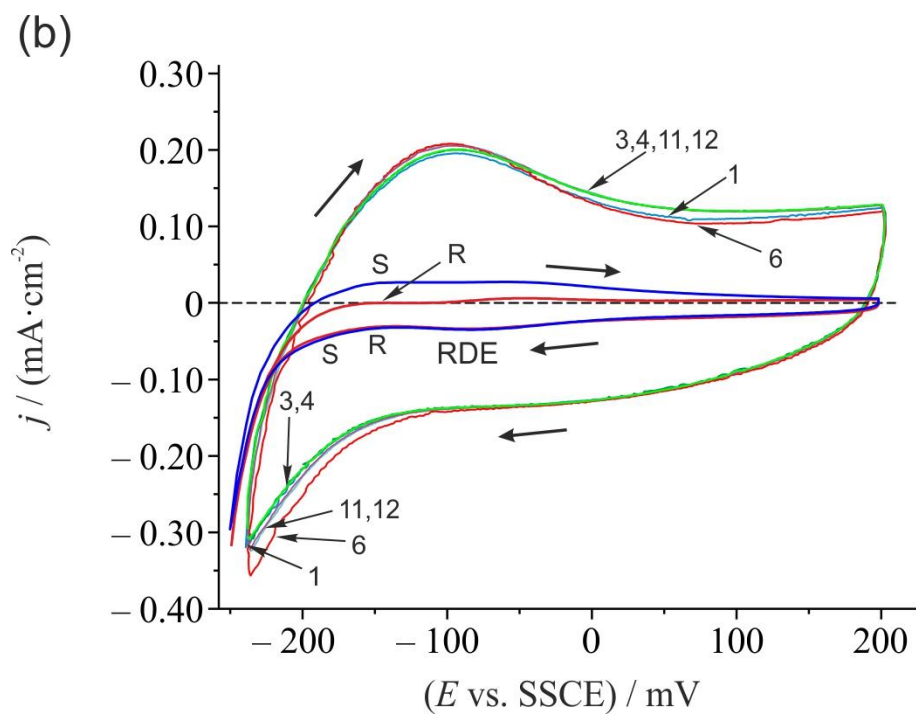
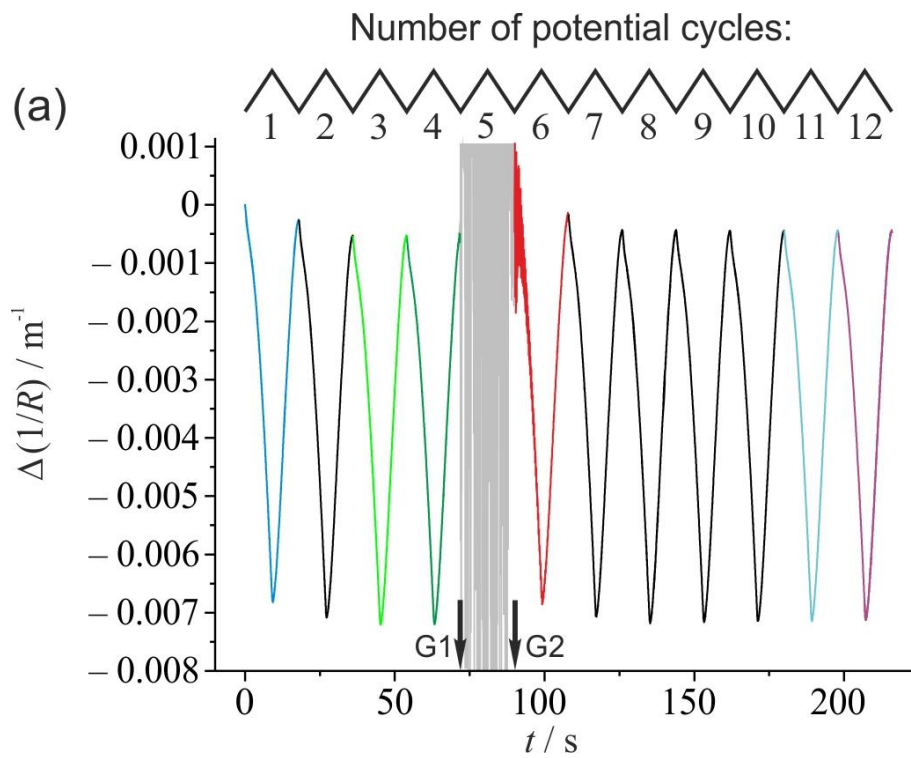
Till now only the occurrence of  $\text{ClO}_4^-$  reduction has been suggested as acceptable explanation [16]. Indeed, the voltammetric study of the system furnished unambiguous evidence proving the validity of this assumption. It is well known from the literature [57] that the electrochemical behavior and properties of technetium and rhenium and those of their various ions are very similar. Considering the similarity of Tc and Re it was no wonder that the behavior found in the case of Tc can also be observed for Re and vice versa.

### 3.4. Electrochemical-mechanical measurements

The change of the interface stress of electrodes during polarization can be followed e.g. by the electrochemical bending beam method (details of this and similar methods are described in the chapter entitled “Interface stress measurements in an electrochemical environment” of this Encyclopedia). The reduction of perchlorate ions on ruthenium is presented as an illustrative example [58, 59]. A ruthenium coated cantilever in contact with

0.1 M HClO<sub>4</sub> 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 5a - 5c). Prior to the first potential cycle, the solution was vigorously stirred with Ar. According to Figures 5a the corresponding  $\Delta(1/R)$  values recorded during subsequent potential cycles are slightly shifted in the negative direction with respect to the first curve. (Note that the changes of the interface (surface) stress ( $\Delta\gamma_s$ ) for a thin metal film on one side of an insulator (e.g. glass) strip or a metal plate, one side of which is coated with a thin insulator layer, in contact with an electrolyte solution can be estimated from the changes of the radius of curvature of the strip by an expression according to the equation **Error! Objects cannot be created from editing field codes.** where  $k_i$  is a sensitivity constant.) After the 4<sup>th</sup> potential cycle the solution was stirred again with argon for ~20 s. As it can be seen in Figures 5a the shapes (and position) of curves 1 and 6 (which were recorded immediately after stirring of the solution) are almost identical. The difference between the curves recorded before and after stirring is clearly noticeable also in Figure 5c, which shows the dependence of  $\Delta(1/R)$  on the electrode potential  $E$  ("voltdeflectograms").

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<sup>-</sup> 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.



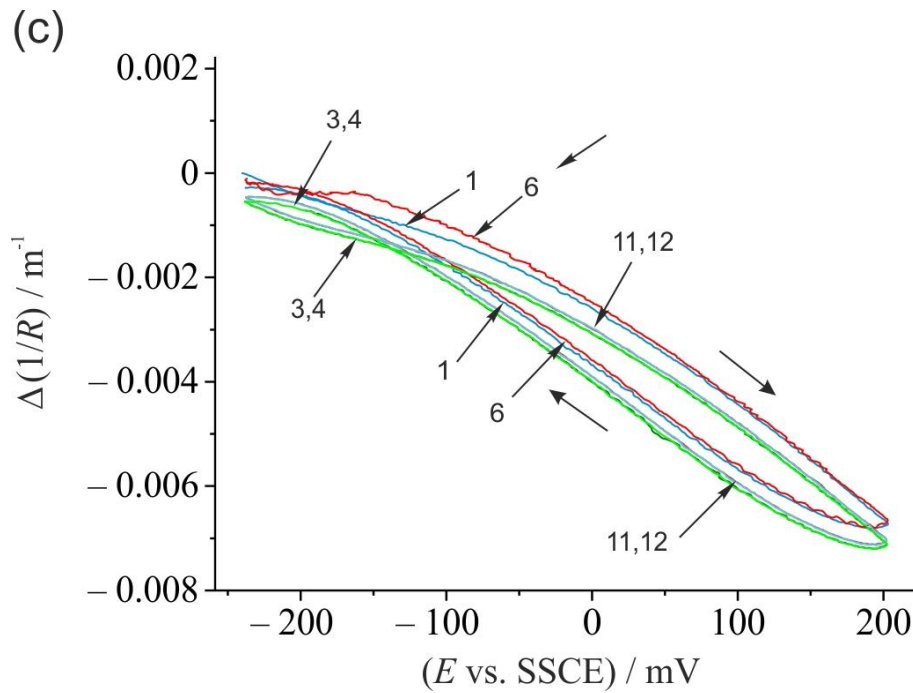


Figure 5: Electrochemical and electromechanical responses of a ruthenium coated cantilever to consecutive potential cycles (-0.25 to 0.2 V vs. SSCE, sweep rate: 50 mVs<sup>-1</sup>). (a) Changes of the reciprocal radius of curvature  $\Delta(1/R)$  with time ( $t$ ). (b) Curves 1,3,4,6,11,12: selected cyclic voltammograms from the experiment in (a); (c) Changes of the reciprocal radius of curvature  $\Delta(1/R)$  with the electrode potential ( $E$ ), curves 1,3,4,6,11,12 correspond to those of (b). G1: the stirring with Ar started, G2: stirring stopped. RDE (S and R): cyclic voltammograms ( $j$ : current density,  $E$ : electrode potential) obtained for the rotating Ru disc in contact with  $C_{HClO_4}=0.1$  M  $HClO_4$  solution (rotation rates: S: stationary electrode, R: 1000 rpm; sweep rate  $v=5$  mV s<sup>-1</sup>), for better visibility the current density is multiplied by a factor of 2 [58].

### 3.5 Electrochemical impedance spectroscopy (EIS)

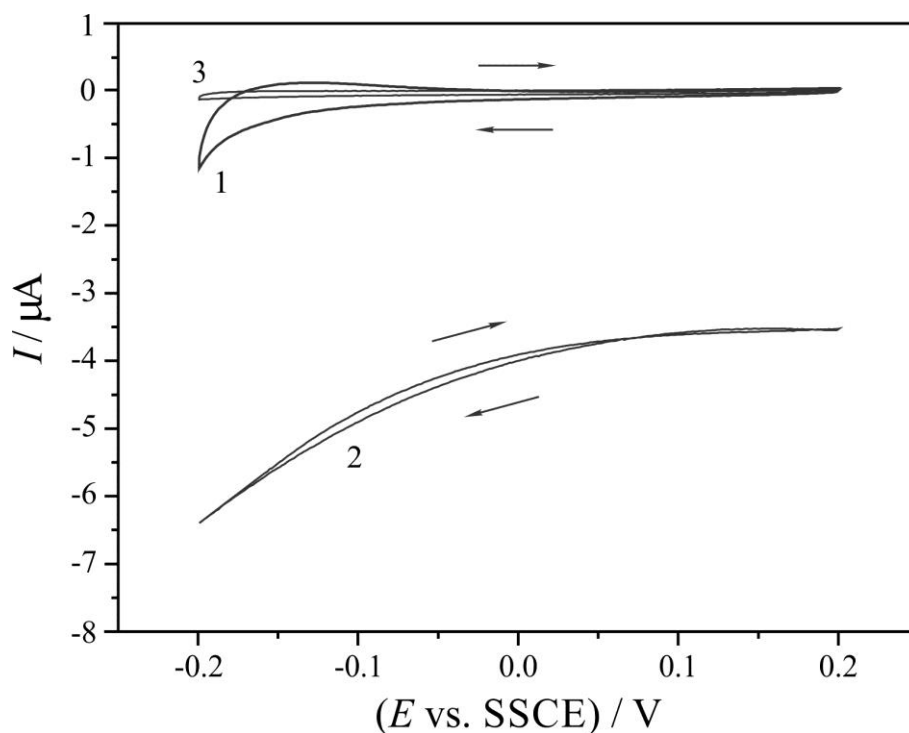
The reduction reaction may have an impact on the electrochemical impedance spectra recorded in solutions containing perchlorate ions. In refs. [54, 59, 60] impedance spectra were recorded on rotating ruthenium and rhodium disc electrodes in perchloric acid solutions at different potentials, rotation rates and temperatures. 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 [61]. On the basis of the kinetic model of the perchlorate reduction a theoretical expression was derived for the impedance which fits the experimental data quite well [60].

For all the spectra obtained on ruthenium and rhodium, only one time constant could be identified in the high frequency range, suggesting that the measured impedance response is dominated by a single (rate determining) charge transfer step. In the case of the reduction of perchlorate ions the assumption that the  $\text{ClO}_4^- \rightarrow \text{ClO}_3^-$  transformation is the rate determining step seems to be a relevant and acceptable interpretation of the phenomena observed. Experiments with  $\text{ClO}_3^-$  ions strongly support this hypothesis [54].

#### 4. Mechanistic investigations

##### 4.1. Experiments with chlorate ions

Figure 6 shows cyclic voltammograms obtained for Rh in contact with a solution containing  $0.49 \text{ mol}\cdot\text{dm}^{-3} \text{ NaClO}_4 + 0.01 \text{ mol}\cdot\text{dm}^{-3} \text{ HClO}_4$ , and for the same electrode in contact with a solution containing  $0.49 \text{ mol}\cdot\text{dm}^{-3} \text{ NaClO}_3 + 0.01 \text{ mol}\cdot\text{dm}^{-3} \text{ HClO}_4$ . It can be clearly seen from the figure, that in this potential range the negative current is at least 2 orders of magnitude higher in the presence of  $\text{ClO}_3^-$  ions than the current measured in the other solution. For comparison, the voltammetric curve obtained in  $1 \text{ mol}\cdot\text{dm}^{-3} \text{ HClO}_4$  solution is also given in the figure.



**Figure 6:** Cyclic voltammograms obtained for Rh (1): in contact with a solution containing  $0.49 \text{ mol}\cdot\text{dm}^{-3} \text{ NaClO}_4 + 0.01 \text{ mol}\cdot\text{dm}^{-3} \text{ HClO}_4$ , and (2): for the same electrode in contact with a solution containing  $0.49 \text{ mol}\cdot\text{dm}^{-3} \text{ NaClO}_3 + 0.01 \text{ mol}\cdot\text{dm}^{-3} \text{ HClO}_4$ . (3): voltammetric curve obtained 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:  $T = 25.0 \text{ }^\circ\text{C}$ ) Adapted from [54].

Similar mechanistic conclusions were drawn in the case of titanium electrode. It was reported [12] that perchlorate ion is electrochemically reduced to chloride ion at an active titanium electrode in aqueous  $1.0 \text{ M HClO}_4$ . It is assumed that the reduction occurs by direct reaction at the surface rather than a pathway involving catalysis by soluble titanium corrosion products. The reaction occurs by oxygen atom transfer to the titanium surface, and the implications of this mechanism for the surface composition of active titanium electrodes are discussed. Chlorate ion is also reduced at titanium, and the rate coefficient for chlorate reduction is at least  $10^5$  times greater than that for the perchlorate reduction.

Presence of chlorate and perchlorate ions leads to passivity breakdown and pitting corrosion of iron in sulfuric acid solutions [62]. The origin of the pitting has been attributed to  $\text{Cl}^-$  produced via the reduction of  $\text{ClO}_3^-$  and  $\text{ClO}_4^-$  ions by  $\text{Fe}^{2+}$ . Similar results were obtained for Al[63]. The XPS experiments detected perchlorate and chloride ions on the surface. Both of these ions may play role in the passivity breakdown.

#### 4.2 Effect of chloride ions formed in the course of the reduction process

According to the electrochemical literature [15], in contrast to the behavior of platinized platinum electrodes, the catalytic activity of “rhenized” electrodes can be observed under potentiostatic or galvanostatic conditions for relatively long periods of time, although no real steady state can be attained in the case of a potentiostatic experiment.

The continuous decrease in the reduction current can be explained by two important effects:

- i) the self-inhibition of the process by the adsorption of  $\text{Cl}^-$  ions formed in the reduction, (the current efficiency with respect to the formation of  $\text{Cl}^-$  ions is above 90 %). The effect of  $\text{Cl}^-$  ions was demonstrated in separate experiments by adding HCl in low concentration to the solution phase in the course of the reduction,
- ii) deactivation of the electrode surface owing to the chemical transformation of the surface layer participating in the reaction.

The effect of chloride ions on the interface stress of ruthenium in contact with 0.1 M  $\text{HClO}_4$  solution 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  $E = 8 \text{ mV vs. SSCE}$  [58, 59]. 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  $0.00045 \text{ m}^{-1}$ . The interfacial stress decreased further ( $\Delta(1/R) = -0.00015 \text{ m}^{-1}$ ) when the concentration of HCl was increased to  $0.001 \text{ mol} \cdot \text{dm}^{-3}$ .

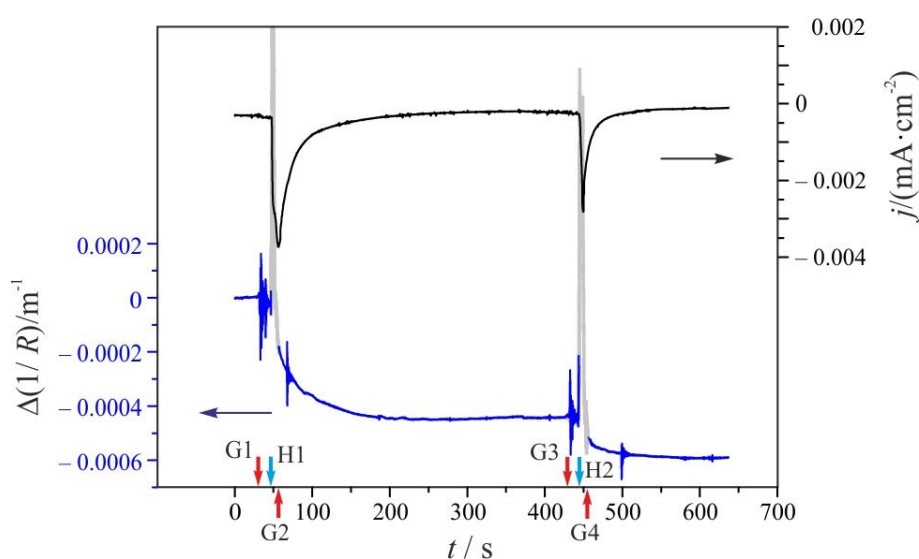


Figure 7: Curvature change ( $\Delta(1/R)$ ) vs. time ( $t$ ) and current density ( $j$ ) vs. time curves obtained following the addition of HCl to a solution of  $0.1 \text{ mol dm}^{-3}$  perchloric acid. First run: Gas(1): start of the stirring (with Ar gas), +HCl(1): addition of HCl ( $\text{Cl}^-$  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 ( $\text{Cl}^-$  concentration:  $0.001 \text{ mol dm}^{-3}$ ), Gas(4): stop of stirring [58].

The XPS studies of the electrodeposition of Cu on Ru(0001) in perchlorate media [64] show that  $\text{ClO}_4^-$  dissociates into adsorbed  $\text{Cl}^-$  and  $\text{ClO}_x^-$  species. Similar findings were reported if the composition of the passive layers formed on Zn electrode in naturally aerated and deaerated  $0.1 \text{ M KClO}_4$  solution were studied using chronopotentiometry, electrochemical impedance, and X-ray photoelectron spectroscopic measurements (XPS):  $\text{Cl}^-$  ions from the perchlorate reduction reaction was detected in the solutions during electrode polarization [65, 66].



Due to the strong adsorption of the  $\text{Cl}^-$  ions they often occupy the active sites of the surface and inhibit the perchlorate reduction. But in cases in which pitting corrosion takes place chloride ions also help the formation of metal ions which can reduce the perchlorate ions, so chloride ions play a dual role in such cases.

Investigating the electrodisolution of Al in perchloric acid solutions [67] current oscillations occurred over a large range of  $\text{HClO}_4$  concentration and over a wide scale of applied potential. During the anodic dissolution of the Al electrode in  $\text{HClO}_4$  solutions, perchlorate ions were reduced to chloride ions, which induced pitting corrosion.

## 5. Possible mechanisms of the reduction of perchlorate ions

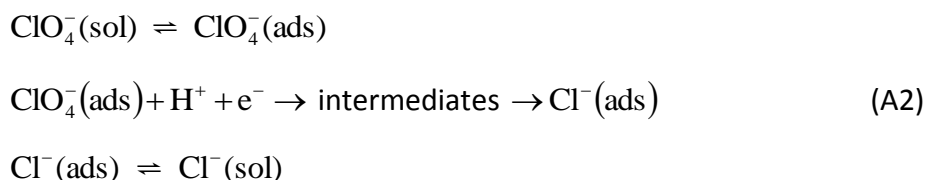
The reduction process leading to the formation of  $\text{Cl}^-$  ions should be a very complicated reaction as eight electrons are involved in the overall process. It is difficult to believe that it can be performed without the formation of any stable intermediates or products of side-reactions, etc. Analogous to the reduction of perchlorate in homogeneous solution, the reduction of perchlorate at an electrode (or any surface) must involve oxygen atom transfer. Therefore, it is not surprising that there is a controversy in the literature regarding the mechanism of the reduction of  $\text{ClO}_4^-$  ions on rhodium. According to the "classical" view, the rate-determining step in the electrocatalytic process can be described as a reaction of adsorbed  $\text{ClO}_4^-$  species with adsorbed H atoms [1, 13, 51, 54, 55, 68]. In contrast, according to the suggestions made in [69] the reduction process can be considered as a slow decomposition of  $\text{ClO}_4^-$  species on the surface followed by fast reduction steps. The latter approach is based on the view that the reduction rate attains a measurable level at potentials where the surface concentration of H is very low; consequently it is unlikely that it can play any role. Thus it should be assumed that the rate-determining step is the decomposition of adsorbed  $\text{ClO}_4^-$  ion with the participation of a free adsorption site in its neighborhood.

In accordance with the above considerations, three fundamental types of possible mechanisms are distinguished in the literature for the electrocatalytic reduction of  $\text{ClO}_4^-$  ions [13, 51, 53-55, 69-71], namely the mechanism (A) involving protons and/or adsorbed hydrogen, the serial mechanism (B) and the mechanism (C) involving free-metal sites.

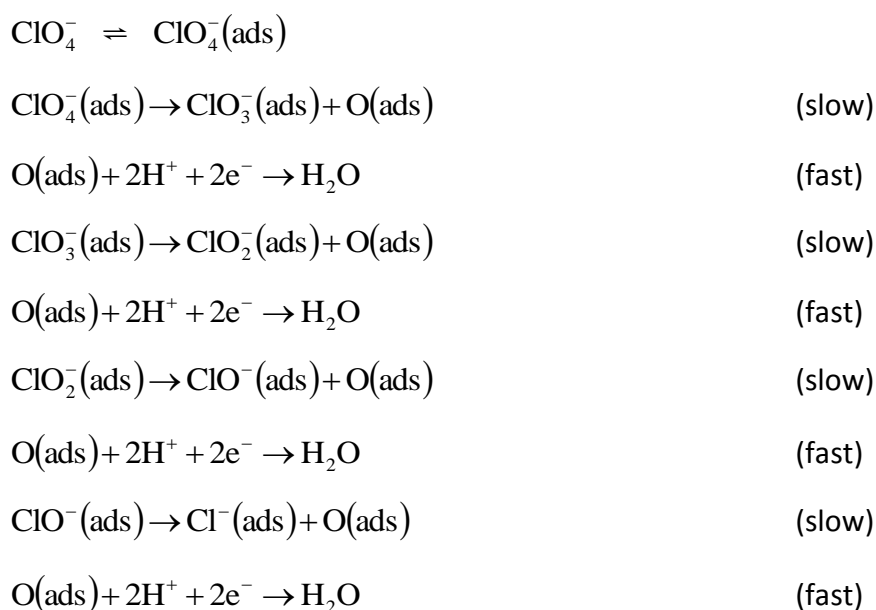
*Mechanism (A)* can follow two alternative paths:



or



*Mechanism (B):*



where “(ads)” denotes that the species is adsorbed, while “(sol)” refers to components in the solution phase. According to this scheme, the whole process starting from perchlorate ion occurs on the surface and the role of desorption of intermediates can be neglected, i.e. their desorption rate is very low compared with the rate of the chemical transformation.

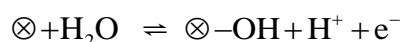
*Mechanism (C):*

According to this mechanism it should be assumed that the rate-determining step is the decomposition of adsorbed perchlorate ion if a free "active" site ( $\otimes$ ) is in its neighbourhood. This assumption is the same as that made in [72] in connection with the reduction of  $\text{N}_2\text{O}$ .

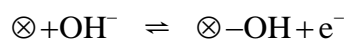
The decomposition reaction can be written as:



On the other hand, it can be assumed that the surface concentration of active sites is determined by the following reactions:



or



In this case the potential dependence of the surface concentration of free active sites plays an important role.

It can be seen, that in the reaction schemes proposed in the literature the adsorption of perchlorate ion is an elementary step of the overall reduction. The decomposition of the adsorbed perchlorate ion is assumed to be a slow, however, there are only speculations about the rates of the subsequent steps. For instance, in mechanism (B) all decomposition steps are assumed to be slow, however, the rate of the decomposition of chlorate ions is much more greater than that of the perchlorate reduction.

## 6. Water treatment technologies and electrochemistry

Although there are still no effective water treatment & perchlorate removal technologies today that are based exclusively on electrochemical methods, there are practical applications in which electrochemical processes play an important role.

For example, during electrochemical hydrogenation electrochemical reduction and catalytic hydrogenation happens simultaneously. Combining this technique with adsorption the perchlorate reduction efficiency in a model system containing 10 mg/L perchlorate can be over 70% [73].

Titanium in the zero-valent state has a high thermodynamic potential to reduce perchlorates. However, metallic titanium ( $\text{Ti}^0$ ) is not an effective reductant due to the spontaneous formation of a thick oxide film on the surface. On the other hand  $\text{Ti(II)}$  and  $\text{Ti(III)}$  ions are sufficiently strong reductants, which have the thermodynamic ability to reduce  $\text{ClO}_4^-$  ions. In experiments with Ti in contact with perchlorate and nitrate solutions  $\text{Ti}^{3+}$  or  $\text{Ti}^{2+}$  were generated by applying anodic current [56] and kinetical experiments were carried out in synthetic perchlorate, nitrate solutions and in tap water media at different perchlorate and nitrate concentrations. The results reported in [74, 75] clearly demonstrate that zero valent titanium undergoing pitting corrosion has the capability to chemically

reduce perchlorate by producing dissolved Ti(II) and therefore, it has the potential to be applied in treatment systems. Unfortunately, although perchlorate is effectively reduced during electrochemically induced corrosion of Ti, this process may not be immediately applicable to perchlorate treatment due to the high potentials needed to produce active reductants, the amount of titanium consumed, the inhibition of perchlorate removal by chloride, and the possible oxidation of chloride ions to chlorine.

It is also worth to mention that if in a biological electrochemical system some specific microorganisms are attached to the cathode, so called microbial cathode (biocathode) is formed. These microorganisms can accept electrons from a solid surface (cathode) and bioreduce the nitrate, nitrite or perchlorate through biocatalysis. This is also a promising method for perchlorate removal from groundwater and wastewater [76].

## Nomenclature

### Symbols and Units

$A$	surface
$c$	concentration ( $\text{mol dm}^{-3}$ )
$E$	electrode potential
$\gamma_s$	interface (surface) stress
$\Gamma$	surface excess concentration ( $\text{mol cm}^{-2}$ )
$I$	current
$j$	current density
$k_i$	sensitivity constant
$R$	radius of curvature of the cantilever
$t$	time
$T$	temperature
$v$	sweep rate ( $\text{mV s}^{-1}$ )
$\omega$	angular frequency

### Abbreviations and Acronyms

EIS	electrochemical impedance spectroscopy
EQCM	electrochemical quartz crystal microbalance

RDE	rotating disc electrode
SSCE	NaCl-saturated calomel electrode
XPS	X-ray photoelectron spectroscopy

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