Journal of Electroanalytical Chemistry 880 (2021) 114880

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Electrochemistry and spectroelectrochemistry of perrhenates in sulfuric acid solutions

M. Chotkowski [a,b,*], D. Połomski [a,b]

[a] University of Warsaw, Faculty of Chemistry, Pasteura 1, 02-093 Warsaw, Poland
[b] University of Warsaw, Biological and Chemical Research Centre, Żwirki i Wigury 101, 02-089 Warsaw, Poland

ARTICLE INFO

Article history:
Received 24 June 2020
Received in revised form 27 October 2020
Accepted 20 November 2020
Available online 23 November 2020

Keywords:
Perrhenate
Rhenium species
UV–Vis spectroelectrochemistry

ABSTRACT

The spectroscopic and electrochemical behavior of perrhenate ions was examined in aqueous solutions containing concentrated sulfuric acid. The chronopotentiometric results show a multi-electron reduction process. Additional hydrodynamic experiments reveal generation of an ionic form of Re(V) that undergoes oxidation on the ring electrodes. Reduced rhenium species are transformed in 12 M H_2SO_4 into soluble species characterized by an absorption band at 366 nm.

1. Introduction

Rhenium and its compounds are increasingly used in many areas of science and industry. Various rhenium compounds are important components of radiopharmaceuticals, e.g. oxocomplexes of Re [1,2], and catalysts [3,4]. Some of the rhenium containing catalysts, for example ReNi [4], are prepared electrochemically by the reduction of perrhenates. A detailed knowledge of the electrochemical processes involving rhenium compounds, especially ReO_4^-, is therefore required, but the literature data on the subject are ambiguous and often contradictory.

A critical review considering the electroreduction of perrhenate ions in acidic media was published in 2003 [5]. It describes the electroreduction of perrhenates in aqueous sulfuric acid solutions as a process strongly dependent on the experimental conditions, especially on the concentration of the acid. Later on, Szabó and Bakos [6] have shown that in moderate concentrated H_2SO_4 solutions (0.1 M – 3 M), the main product of the perrhenates reduction is a non-soluble ReO_2, while in highly concentrated H_2SO_4 solutions, mainly Re_2O_5 and ReO_3 precipitates forming a non-soluble deposit. These authors also suggested [7] that in strongly acidic media rhenium (III) is produced as a result of rhenium dioxide disproportionation. Much earlier works of Wehner and Hindman [8,9] were devoted to examination of the electrolytic reduction of perrhenates in mineral acids solutions. These authors stated that for all examined systems Re(V) was generated is concentrated acid solutions (>8 M HCl, and >12 M H_2SO_4) as an insoluble deposit on the electrode or as a colloidal suspension. Lower acidity, e.g. 4 M HCl, promotes generation of Re(IV). The dark blue or black deposit of Re (V) slowly dissolves and decomposes in concentrated H_2SO_4 leading to obtain unstable Re(VI). Based on an analysis of UV–Vis spectra, these authors suggested that oxidation of Re(IV) may lead to formation of a mixture of Re (V)-Re(VI) (λ = 545 nm) while pure Re(V) can be observed at ca. 410 nm although both forms had not been identified definitely. Identification of the Re(V,VI) species is additionally complicated by the fact that Re(V) may be observed in various forms that differ spectroscopically. A disproportionation reaction of Re(V,VI) as well as their various forms are also known for Tc(V,VI) species [10].

More recent electrochemical investigations were focused on the characterization of metallic rhenium in acidic solutions and on studies on hydrogen evolution reaction on this type of the surface [11,12].

The perrhenates generate an absorption band in UV–vis spectrum (λ_{max} = 230 nm) [13] and therefore the UV–vis spectroscopy is especially suitable for studying reactions involving the rhenium ions. This technique is particularly useful for determining the mechanism of electrochemical processes with participation of species dissolved in the solution [14,15]. It has been demonstrated [15] that for reversible systems the spectroscopic signal (dA/dt vs. E) recorded in an OTTL-RVC (Optically Transparent Thin Layer electrode - Reticulated Vitreous Carbon) cell is an equivalent to the electrochemical voltammetric current vs. potential curve (j vs. E).

Our earlier work was focused on the mechanistic aspects of the pertechnetates electroreduction in aqueous solutions [16]. One may expect that rhenium, which is a technetium analogue, should reveal some similar

---

[*] Corresponding authors at: University of Warsaw, Faculty of Chemistry, Pasteura 1, 02-093 Warsaw, Poland.
E-mail addresses: mchotk@chem.uw.edu.pl (M. Chotkowski), dpolomski@chem.uw.edu.pl (D. Połomski).

http://dx.doi.org/10.1016/j.jelechem.2020.114880

aspects of chemistry and electrochemistry of the latter. For both elements, the multi-step process of their ions, MO_4^- (M: Tc or Re), electroreduction is observed.

The simultaneous use of spectroscopic and electrochemical methods (spectroelectrochemical technique) in examination of the rhenium compounds has been applied mainly in investigations of the rhenium complex compounds [17–19] and for non-aqueous media. Only few papers are devoted to characterization of inorganic rhenium species in aqueous solutions. For example Hahn et al. [20] examined spectroelectrochemically mixed-valent rhenium oxides at pH 1.5. These authors investigated Re/ReO_x on ITO at 480 nm and proposed the following reaction of disproportionation of unstable Re(III) oxides, Eq. (1):

$$2\ Re2O3 + 6H2O \rightleftarrows Re^0 + 3(ReO2{\cdot}2H2O) \qquad (1)$$

The purpose of this work is to investigate the electrochemical and spectroelectrochemical behavior of perrhenate ions in concentrated sulfuric acid solutions. It is shown that the use of the OTTLE-RVC technique in conjunction with cyclic voltammetry allows for the determination of the mechanism related to the generation and stability of rhenium species on the electrode and dissolved in solution.

2. Experimental

All measurements were performed at 298 K. The solutions were prepared using high purity distilled water (Millipore®) and high purity chemicals: $KReO_4$ (Alfa Chemicals), H_2SO_4 (POCh). Before each experiment the solution was deoxygenated with Ar (4 N) for 30 min.

The electrochemical experiments were carried out under stationary and hydrodynamic conditions and were performed using a Pine Research Instrumentations rotating gold ring disc electrode (RRDE AFER8AUAU with 22% collection efficiency and an Autolab electrochemical analyzer (PGSTAT128N) [21]. These experiments were carried out in a three electrode system with a Pt mesh and $Hg,Hg_2SO_4 \mid 0.5\ M\ H_2SO_4$ serving as counter and reference electrode, respectively. All potentials given in the text are referred to the SHE electrode.

The spectroelectrochemical measurements were carried out in a home made optically transparent thin layer electrochemical cell in which a reticulated vitreous carbon – RVC was a working electrode. This cell has been described in detail in our previous paper [22]. The reference spectrum has been taken from the measurements carried out in 12 M H_2SO_4. The voltammetric and spectroscopic measurements that were carried out in this cell were performed simultaneously using a CHI604 (CH Instruments) electrochemical analyzer and a MultiSpec 1500 (Shimadzu) spectrophotometer, respectively. The diffusion coefficient of ReO_4^- and the liquid junction potential between the reference electrodes and the H_2SO_4 solutions have been were calculated using a previously described approach [23].

3. Results and discussion

Fig. 1 presents the influence of the acid concentration on cyclic voltammograms recorded in 0.5, 4 and 12 M H_2SO_4 solutions containing 1 mM $KReO_4$. An increase in the acid concentration significantly affects peaks in cathodic branch of the CVs. The curves recorded in 4 and 12 M H_2SO_4 reveal a well developed reduction peak. This peak is sharper in 12 M H_2SO_4 as compared to 4 M H_2SO_4. Moreover, its potential is shifted toward more positive values when the acid concentration increases: from ca. 0.12 V to 0.5 V for 4 and 12 M H_2SO_4, respectively. This shift is much greater than for a simple reversible redox couple. In 0.5 M H_2SO_4 the currents related to ReO_4^- ions reduction are poorly visible.

An analysis of the above mentioned acid concentration influence on the reduction currents must include the aspects related to both the structure of the reacting Re species as well as their chemical stability. The chemical form of the Re(VII) species present in the concentrated sulfuric acid solutions is not fully explained. This point can be clarified if we assume, that rhenium may be regarded as an analogue to technetium. Poineau et al. [24,25] reported that the pertechnetates transform into $[TcO_3(HSO_4)_3(H_2O)(OH)]^-$, $[TcO(HSO_4)_2(H_2O)_3]^+$ in 12 M H_2SO_4. Therefore, we may assume that the rhenium exists in concentrated H_2SO_4 solutions as a tetrahedral ReO_4^- which can transform into octahedral complexes. The second aspect of the discussed process is related to the stability of the reduced Re forms electrogenerated at the early stages of the process. In the less acidic solutions these forms are extremely unstable and decompose to Re(IV), but are stabilized at high H^+ concentrations. Such behavior results in a strong separation of the cathodic peaks observed on the voltammetric curve (Fig. 1). The charges related to these transitions calculated for 4 M H_2SO_4 are greater than those obtained for 12 M H_2SO_4. This effect is also related to changes in the mechanism of the ReO_4^- reduction. According to the theory of the multistep electrochemical-chemical reactions, the disproportionation of electrogenerated reduced species leads to an increase in the height of respective voltammetric peaks [26]. The disproportionation may involve not only Re(V) but also Re(VI). This effect strongly affects the measured charges.

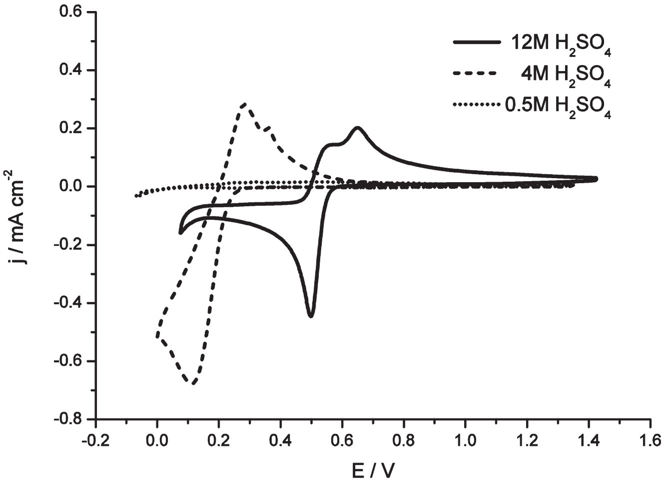

Fig. 1. Cyclic voltammograms recorded in 1 mM $KReO_4$ and various concentration of H_2SO_4 on Au electrode, $v = 0.05\ V\ s^{-1}$, $E_{start} = 0.8$ V.

Anodic branches of CVs also reveal significant differences related to the acidity of the solutions. For 4 and 12 M H_2SO_4 two anodic waves are observed. Their evolution depends on H^+ concentration. In less concentrated sulfuric acid solutions the first oxidation peak is higher than the second one while in strongly concentrated acid this relation is reversed. Most probably, the first oxidation peak is related to an oxidation of lower-valent rhenium species, e.g. metallic rhenium, Re(III,IV) to perrhenates while the second one shows transformation of Re(V or VI) to perrhenates and/or (as an analogue to technetium) electrooxidation of especially resistant to oxidation polymeric forms of Re(III,IV) to perrhenates.

The CVs recorded for the perrhenates reveal similarities to CVs characteristic of the pertechnetates [21]. Although both elements, Re and Tc, are in the same group of the peridoc table and the rhenium is considered as the technetium analogue, the redox reactions of the latter does not simply reflects those of rhenium. In 12 M H_2SO_4 the pertechnetates are reduced in two well separated main steps. The first one leads to formation of Tc (V) and the second one results in formation of polymeric species or oxides of Tc(IV) and Tc(III) Deeper reduction of the latter may lead to formation of a metallic technetium deposit. The evolution of the shape of CV curves induced by variation in the acid concentration indicates not only stabilization of the ionic forms of the reduced Re species but also suggests changes in the mechanism of the perrhenic ions electroreduction. The general scheme of the processes of reduction of the latter ions is similar to that observed for the respective ions containing Tc In concentrated acidic solutions one may consider the following scheme, Eq. (2):

$$Re(VII) \rightarrow Re(V) \rightarrow \ldots \rightarrow Re^0 \qquad (2)$$

while in less acidic solutions Re(V) transforms immediately to Re(IV), Eq. (3):

$$\mathrm{Re(VII)} \rightarrow (\mathrm{unstable\ \ Re(V)}) \rightarrow \mathrm{Re(IV)} \rightarrow \ldots \rightarrow \mathrm{Re}^0. \qquad (3)$$

The electrooxidation of the reduced Re species leads to formation of two anodic peaks which are sensitive to the acid concentration. This observation indicates a multistep electrooxidation process of the perrhenic ions. For 4 M H_2SO_4 the first oxidation peak at 0.28 V is stronger than the second one observed at 0.38 V. This is in contrast to the behavior of the appropriate signals in much more concentrated acid solutions where a reverse sequence is observed. It seems that the second oxidation peak describes the electrooxidation of reduced Re species stabilized or generated with higher efficiency in 12 M H_2SO_4 than in 4 M H_2SO_4.

A significant influence of the electrode material on the process of the perrhenates electroreduction in acidic solutions is observed (S1). Gold electrodes reveal well-shaped current peaks due to Re redox reactions only in very strongly acidic solutions. These are a very strong reduction wave and two oxidation signals (Fig. 1). In turn, the electrochemical signals of ReO_4^- reaction on a platinum electrode reveal adsorption on the electrode surface and formation of rhenium(IV, V and VI) oxides during the perrhenates electroreduction. These oxides are ReO_2, Re_2O_5 and/or ReO_3, depending on the acid concentration. Currents due to the oxidation and reduction of Re on glassy carbon (GC), which was the third type of the electrode material studied, are much less developed as compared to Pt but in this context are similar to those observed for the Au substrate.

Additional information on the mechanism of the perrhenate ions electroreduction is delivered from chronopotentiometric measurements. Fig. 2 presents chronopotentiometric curves recorded in 12 M H_2SO_4 and 1 mM $KReO_4$. The results clearly show that the discussed process occurs in two main stages. The first one is observed at ca. 0.5 V and the second one at a lower potential of ca. 0.25 V.

The respective relation between the square root of the transition time ($\tau^{1/2}$) and the reciprocal current, j^{-1} is shown in Fig. 3. A good linearity observed for the first transition time, τ_1, strongly suggests reversibility of the electroreduction of perrhenates in 12 M H_2SO_4. For this type of the process the measured potential, E, is a logarithmic function of time, t, at 25 °C, according to Eq. (4) [26]:

$$E = E_{1/2} + \frac{0.059}{n}\ \log\left(\frac{\tau^{1/2} - t^{1/2}}{t^{1/2}}\right) \qquad (4)$$

The other terms in Eq. (4) have their usual meaning.

The plot of $E = f(\log(\frac{\tau^{1/2}-t^{1/2}}{t^{1/2}}))$ reveals a slope of 0.028 ± 0.003 which enabled calculation of the number of the electrons involved in this process (n_e = 2.1 ± 0.2). The obtained results are in line with those of Bakos, Szabo [6,7] and Wehner, Hindman [8]. The potential determined at ~~in~~ ¼τ equals 0.518 V. This value represents the half-wave potential, $E_{1/2}$, for the Re(VII)/Re(V) couple. Assuming that the reduced and the oxidized forms of Re have almost the same value of the diffusion coefficients, we may conclude that the $E_{1/2}$ is equal to E^0. Taking into account that Re is an analogue to Tc, one may suggest that ReO^{3+} could be the core of the ionic form of Re(V) [27].

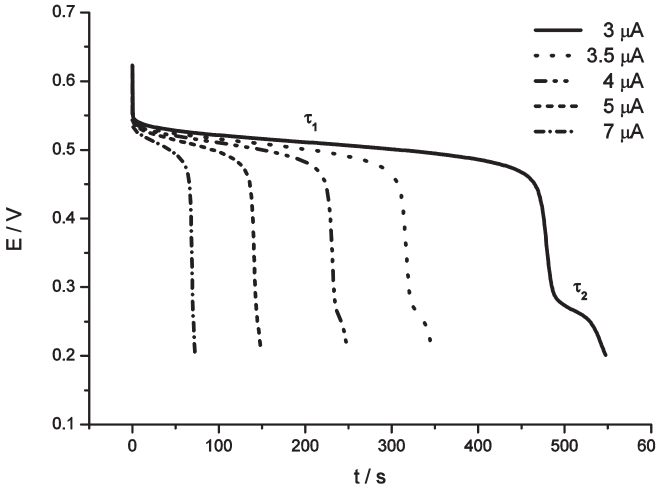

Fig. 2. Chronopotentiometric curves recorded in 1 mM $KReO_4$ + 12 M H_2SO_4 for an Au electrode and for various applied currents.

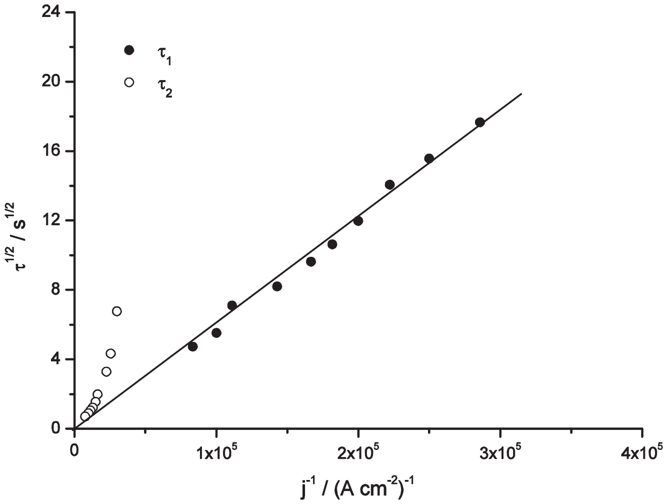

Fig. 3. Transition time (τ) vs. reciprocal current (j^{-1}) for chronopotentiometric reduction of 1 mM $KReO_4$ in 12 M H_2SO_4 on a gold electrode.

In opposite to the first reduction step the second step in not reversible. For the latter the linear relation between $\tau^{1/2}$ and j^{-1} does not hold. The section of the potential change vs. time relationship located within the region of the second transition time was analyzed using Eq. (5) [26] which is applicable for irreversible processes. The terms in Eq. (5) have their usual meaning.

$$E = \frac{0.059}{\alpha n_\alpha}\ \log\left(\tau^{1/2} - t^{1/2}\right) - \frac{0.059}{\alpha n_\alpha}\ \log\left(\frac{\pi^{1/2} D_{ox}^{1/2}}{2k_{fh}^0}\right) \qquad (5)$$

The αn_α parameter equaled 2.35 ± 0.35. The electron transfers occur sequentially, and multistep reaction with reversible, quasi- and/or irreversible stages must be taken into account. Thus, the analysis of the αn_α value may also lead to the conclusion that initially obtained Re(V) species are reduced even to Re^0.

The reversibility of the first step of the perrhenates electroreduction in concentrated sulfuric acid solution (12 M H_2SO_4) is revealed also by cyclic voltammograms recorded under hydrodynamic experiments (Fig. 4). An analysis of RRDE ring currents allows concluding that ReO_4^- reduction is accompanied by formation of soluble species in 4 M H_2SO_4 and especially in 12 M H_2SO_4. The limiting currents are possible to record only for the highest acid concentration studied. For this solution the ratio of i(ring): i (disc) equals 0.21 and is very close to the nominal collecting efficiency (0.22) of this system. A decrease in the acid concentration significantly affects the electrochemical signals. For 0.5 M H_2SO_4 the ring electrode does not reveal any current resulting from the oxidation of the soluble rhenium species which indicates generation of insoluble rhenium deposit on the disc electrode.

Fig. 5 presents cyclic voltammograms recorded at a scan rate of 0.2 mVs^{-1} for a RVC-OTTL electrode in 0.5, 4 M and 12 M H_2SO_4 with the addition of 1 mM $KReO_4$. The reduction of ReO_4^- ions in 12 M H_2SO_4 results in formation of two signals: a small peak at ca. 0.8 V and a peak at 0.4 V (c2)

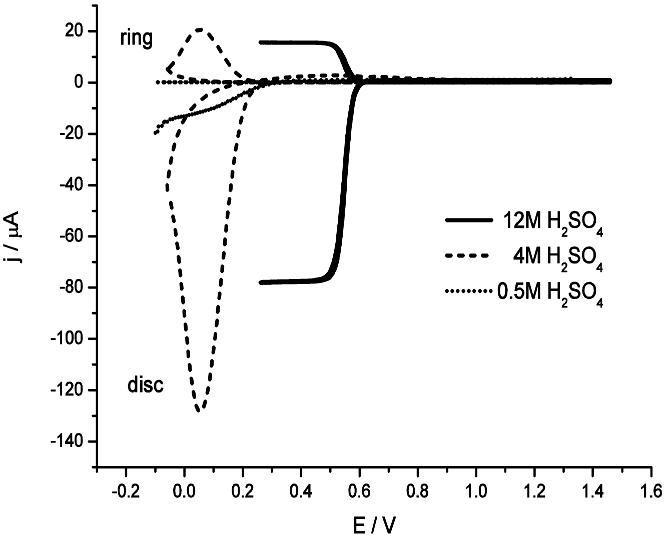

Fig. 4. Cyclic voltammograms of a gold disc electrode of a RRDE recorded with rotation speed of 1600 rpm in 1 mM $KReO_4$ and various concentration of H_2SO_4, $v = 1\ Vs^{-1}$. Ring electrode currents measured simultaneously with CV of a disc electrode for potential of 0.7 V.

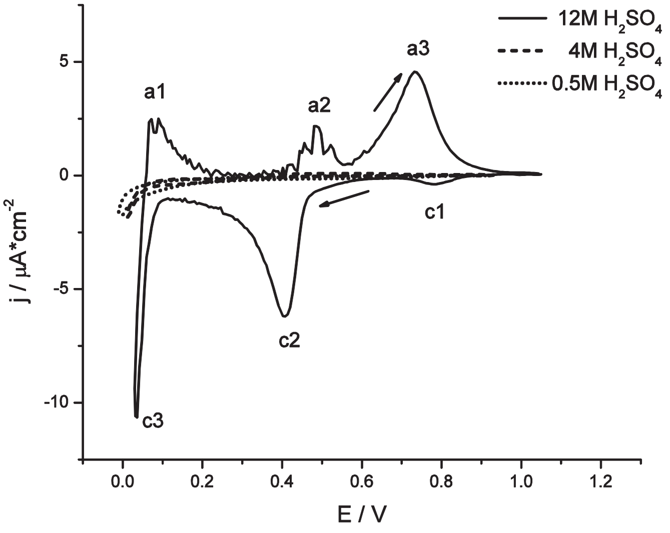

Fig. 5. Cyclic voltammograms of a OTTL-RVC electrode in 0.5 M, 4 M and 12 M H_2SO_4 + 1 mM $KReO_4$, $E_{start} = 1$ V, $v = 0.2\ mVs^{-1}$.

and is accompanied by a significant increase in the current at the potentials lower than 0.1 V. The peak (c1) is probably connected with the electroreduction of perrhenate(VII) ions to rhenium oxides at lower oxidation state, i.e. ReO_3. ReO_4^-/ReO_3 system is the only rhenium redox couple for which so high value of the redox potential is reported [28]. It is given by Eq. (6) [28]:

$$E = 0.732 - 0.1182 \cdot pH + 0.0591 \cdot \log\left(a_{ReO_4^-}\right) \qquad (6)$$

Taking into account the extremely high acid concentration (pH < 0) one may conclude that this peak shows reduction of Re(VII) to Re(VI). The main reduction peak (c2) appears above 0.42 V and most likely represents the reduction of ReO_4^- initially to Re(V) and later to other insoluble reduced Re species.

The strong cathodic current observed at 0.05 V is related to the electroreduction of the rhenium oxides to the metallic rhenium. This cathodic current is also attributed to the reduction of H^+ ions [15]. As it was suggested by Schrebler et al. [29], the H adatoms adsorbed at the surface of the electrode may participate in the reduction of the rhenium species to the metallic rhenium. Indeed, an anodic wave (a1), characteristic of desorption of the hydrogen from the metallic rhenium surface is recorded at potential of 0.05 V.

The origin of the two anodic waves (a2 and a3) seen (Fig. 5) at potentials of 0.5 V and 0.75 V is unclear. Two anodic waves, apparently similar to these discussed above, were observed by Szabó and Bakos [6] during the electrooxidation of rhenium deposit in an acidic solution (5 M H_2SO_4). These signals, however, were reported to appear at different potentials located between c.a. 0.47 V and 0.55 V vs. RHE. The presence of these peaks was explained by the electrooxidation of ReO_3 and Re_2O_5 to ReO_4^- ions. The same authors reported that only a single wave connected with the electrooxidation of rhenium(V) oxide to perrhenate ions is observed in 12 M H_2SO_4 solution. Likely, the third anodic wave (a3) is related to the electrooxidation of rhenium of a mixed oxidation state forms to perrhenate ions. In comparison to the thin layer conditions, the experiments carried out under semi infinite conditions at Au electrode reveal two overlapped and weakly separated waves at ca. 0.55 and 0.65 V (SI 2). Such electrochemical characteristic of the oxidation of the reduced rhenium species in the latter conditions (semi infinitive) shows participation of perrhenate ions in the oxidation reactions.

An analysis of UV–Vis spectra recorded simultaneously to cyclic voltammograms provides additional information on the discussed process (Fig. 6). In order to preserve the thin layer conditions, a low polarization scan rate was used here. The electroreduction of perrhenates at potentials lower than ca. 0.7 V leads to a significant decrease in their concentration. The decrease in the intensity of the wave characteristic of the perrhenates (λ_{max} = 230 nm) is accompanied by formation of a weak band with the maximum at ca. 370 nm (S3). Low intensity of the latter signal indicates that an additional chemical reaction occurs between ionic form of the reduced Re and the perrhenates. The evolution of the absorption bands characteristic of perrhenates, Re(reduced) and one in Vis region (700 nm) from Vis region is shown in Supporting information (S4). Lack of a significant increase in the absorbance in Vis region (700 nm) indicates that the product of this reaction must be deposited on the electrode surface. When concentration of

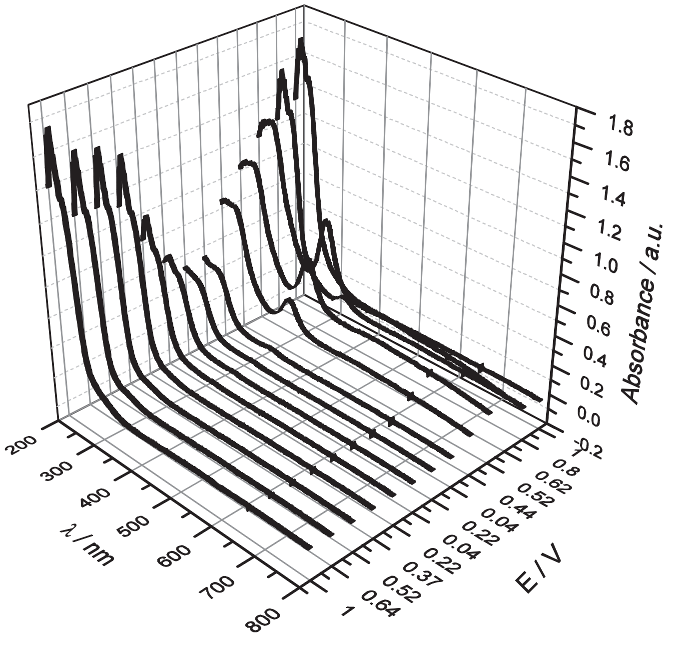

Fig. 6. UV–Vis spectra recorded during cyclic voltammetry experiment in 1 mM $KReO_4$ + 12 M H_2SO_4, $v = 0.2\ mVs^{-1}$.

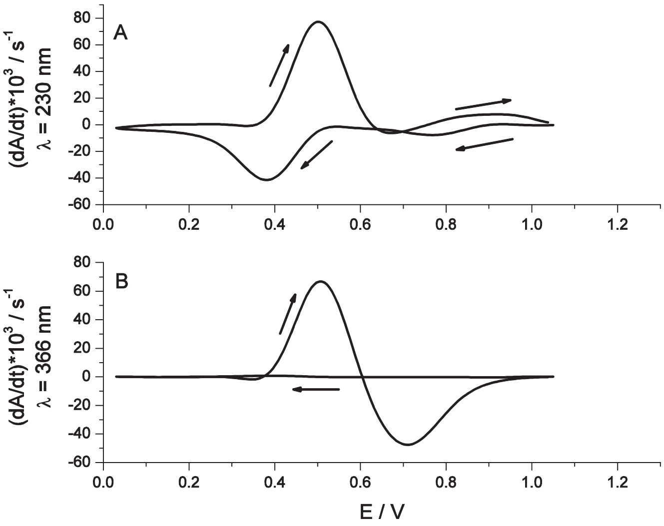

Fig. 7. A–B. Derivative voltabsorptograms for wavelengths of 230 nm (Fig. 7A) and 366 nm (Fig. 7B) of a OTTL-RVC electrode in 12 M H_2SO_4 + 1 mM $KReO_4$, v = 0.2 mV·s^{-1}, E_{start} = 1 V.

the perrhenates is significantly reduced by their electroreduction, the electrooxidation of the above mentioned rhenium deposit leads to formation of an ionic form of Re characterized by a wave with a maximum at ca. 370 nm. This time, however, this signal is much more intense as compared to the one recorded during the reduction of perrhenates.

We assume that the wave at 366 nm is most likely to be assigned to soluble rhenium(III) (or eventually Re(IV)) species present in the solution. Simultaneously to this band an increase in the absorbance in the whole Vis region is observed. This indicates instability of ionic reduced forms of Re that may hydrolyze in the solution and/or undergo additional chemical reactions.

An analysis of the derivative voltabsorptograms for 230 and 366 nm presented in Fig. 7A and B, respectively, provides more information about the mechanism discussed above.

Fig. 7A and B show the derivative voltabsorptograms (dA/dt vs. E) recorded for the OTTL-RVC electrode in 12 M H_2SO_4 + 1 mM $KReO_4$ solution at wavelengths of 230 nm and 366 nm, respectively. The voltabsorptograms are sensitive to the concentration of the rhenium species in the solution, while the simultaneously recorded CVs refer to the composition of the rhenium compounds adsorbed at the electrode surface. As discussed earlier, the voltammetric reduction of the perrhenate ions results in formation of a weak electrochemical reduction signal at potential of 0.8 V (Fig. 5). An analysis of the spectroscopic signal from the derivative voltabsorptogram calculated for 230 nm, i.e. the value characteristic of the presence of ReO_4^- in the solution (Fig. 7A), reveals a weak negative wave which evidences a decrease of the concentration of these ions in the solution. At this potential, c.a. 0.75–0.8 V, formation of the rhenium(VI) deposit on the RVC electrode (Fig. 5) may occur, according to Eq. (7).

$$ReO^{4-} + 2H^+ + e \rightleftarrows ReO_3 + H_2O \qquad (7)$$

The main negative wave calculated for 230 nm (Fig. 7A) which corresponds to the main cathodic peak c2 from the voltammetric curve (Fig. 5; c2) is connected with the electroreduction of perrhenate ions to rhenium according to the scheme (2). All rhenium species obtained during the electroreduction of perrhenate ions in 12 M H_2SO_4 are present close to the surface of the electrode. At potentials lower than 0.2 V, no changes in the derivative voltabsorptograms for 230 nm and for 366 nm are observed and therefore no changes in the solution composition are expected in this potential region. This result supports our earlier conclusion that the signals recorded by the electrochemical system below 0.1 V (Fig. 5) are connected only with the changes in the structure of the rhenium deposit present at the surface and adsorption/ desorption of the hydrogen at/from it.

The anodic branch of on the derivative voltabsorptogram for 230 nm reveals maxima at potentials of 0.5 V and 0.9 V. The first wave is connected with the electrooxidation of metallic Re and ReO_2 to ReO_4^-. The derivative voltabsorptogram calculated for the wavelength of 366 nm reveals a maximum at potential of 0.5 V which is the same value as the one at which the oxidation peak appears in the cyclic voltammograms presented in Fig. 5. This conclusion could confirm previous literature suggestions about the existence of soluble Re species with +III or + IV oxidation states. A partial disproportionation of rhenium dioxide may explain this effect [6], Eq. (8).

$$ReO^2 + 6H^+ + 4e^- \rightleftarrows ReO_3 + 2\ Re(III)_{aq} + 3H_2O \qquad (8)$$

On the other hand, the formation of some polymeric Re(III,IV) species, in an analogy to Tc(III,IV), could not be excluded (Eq. 9).

$$Re(III) + \ Re(IV) \rightleftarrows Re^{III} - Re^{IV} \qquad (9)$$

Moreover, a synproportionation reaction between Re(III) and Re(VII) can also take place, according to Eq. (10):

$$Re(III) + \ Re(VII) \rightleftarrows \ Re(IV) \qquad (10)$$

The Eq. (10) may explain formation of the weak wave characteristic of reduced Re species observed during the electroreduction of perrhenates. The aforementioned chemical reactions of reduced Re species additionally complicate precise description of the process of perrhenates electroreduction.

Our previous article devoted to the oxidation of $[Tc_2O_2]^{3/4+}$ species revealed that these forms are much more difficult to oxidize than monomeric reduced Tc species [22]. Such behavior is manifested by unusually high potential required to their oxidation in CV experiments. In an analogy to Tc one may expect that the reduced Re(III,IV) species may also form polymeric forms resistant to oxidation. At potentials higher than 0.6 V, the Re(III or IV) soluble species disappear and the perrhenate ions are regenerated in the solution. The second positive wave for 230 nm is due to the oxidation of the reduced Re soluble species to the perrhenate ions. A negative value of dA/dt vs. E obtained for 366 nm above 0.6 V indicates that the Re(III or IV) species disappear from the solution. An additional analysis of the derivative voltabsorptogram revealed that the reduced ionic form of rhenium is almost completely (ca. 96%) converted to the perrhenates. Only a small fraction of the most probably insoluble rhenium dioxide remained in the solution.

4. Conclusions

A highly efficient electroreduction of the perrhenate ions takes place only in strongly acidic media. In the first step of this process, the ReO_4^- ions are reduced to rhenium (V). The latter form is subsequently reduced to other reduced rhenium forms which also includes metallic rhenium. The UV–vis results show that the electrooxidation of the rhenium deposit proceeds with the formation of soluble Re(III and/or IV) species. The latter form may react with the perrhenates. The ionic form of reduced rhenium is relatively stable in strongly acidic media. The anodic peak observed on cyclic voltammetric curves at the potentials higher than 0.7 V can be connected with the electrooxidation of rhenium(III or IV) species to perrhenates.

CRediT authorship contribution statement

M. Chotkowski: Conceptualization, Methodology Supervision, Project administration, Writing - original draft preparation, Review and editing;

D. Połomski: Conceptualization, Data curation, Formal analysis, Investigation, Visualization, Writing - original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was partially financially supported by the University of Warsaw (501-D112-01-1120000 (Zlec.5011000357)). The contribution of Damian Połomski was realized within Project No POWR.03.02.00-00-I009/17-00 (Operational Project Knowledge Education Development 2014-2020 co-financed by European Social Fund).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jelechem.2020.114880.

References

[1] M.F. Cerda, E. Mendez, G. Obal, C. Kremer, J.S. Gancheff, A.M.C. Luna, Voltammetric studies of the interaction between Re(V) complexes and proteins, J. Inorg. Biochem. 98 (2004) 238–244.

[2] J. Xia, Y. Wang, G. Li, J. Yu, D. Yin, Synthesis of pyridyl derivatives for the future functionalization of biomolecules labeled with the fac-$[^{188}\text{Re(CO)}_3(\text{H}_2\text{O})_3]^+$ precursor, J. Radioanal. Nucl. Chem. 279 (2009) 245–252.

[3] M. Parlinska-Wojtana, E. Drzymała, G. Gruzeł, J. Depciuch, M. Donten, A. Kowal, Ternary Pt/Re/SnO_2 nanoparticles for ethanol oxidation reaction: understanding the correlation between the synthesis route and the obtained material, Appl. Catal. A: General 570 (25) (2019) 319–328.

[4] V.V. Kuznetsov, Yu.D. Gamburg, V.V. Zhulikov, V.M. Krutskikh, E.A. Filatova, A.L. Trigub, O.A. Belyakova, Electrodeposited NiMo, CoMo, ReNi, and electroless NiReP alloys as cathode materials for hydrogen evolution reaction, Electrochim. Acta (2020) 136610 available online 18 June. (in press).

[5] E. Ménez, M.F. Cerdá, A.M. Castro Luna, C.F. Zinola, C. Kremer, M.E. Martins, Electrochemical behavior of aqueous acid perrhenate-containing solutions on noble metals: critical review and new experimental evidence, J. Colloid Interface Sci. 263 (2003) 119–132.

[6] S. Szabó, I. Bakos, Electrodeposition of rhenium species onto a gold surface in sulfuric acid media, J. Solid State Electrochem. 8 (2004) 190–194.

[7] S. Szabó, I. Bakos, Electroreduction of rhenium from sulfuric acid solutions of perrhenic acid, J. Electroanal. Chem. 492 (2000) 103–111.

[8] P. Wehner, J.C. Hindman, Electrolytic reduction of perrhenate. II. Studies in sulfuric acid, J. Am. Chem. Soc. 75 (12) (1953) 2873–2877.

[9] J.C. Hindman, P. Wehner, Electrolytic reduction of perrhenate. I. Studies in perchloric, ethanesulfonic, trifluoroacetic and hydrochloric acids, J. Am. Chem. Soc. 75 (12) (1953) 2869–2872.

[10] J.A. Rard, M.H. Rand, G. Anderegg, H. Wanner, Chemical Thermodynamics of Technetium, Elsevier, New York, 1999.

[11] R. Garcia-Garcia, G. Ortega-Zarzosa, M.E. Rincón, et al., The hydrogen evolution reaction on rhenium metallic electrodes: a selected review and new experimental evidence, Electrocat. 6 (3) (2014) 263–273.

[12] R. Garcia-Garcia, J.G. Rivera, R. Antaño-Lopez, Impedance spectra of the cathodic hydrogen evolution reaction on polycrystalline rhenium, Int. J. Hydrog. Energy 41 (2016) 4660–4669.

[13] V.G. Solomonik, A.V. Marenich, Isomerism and vibrational spectra of alkali metal perrhenates: Ab initio CISD + Q calculations, J. Struct. Chem. 42 (2001) 914–919.

[14] W.R. Heineman, F.M. Hawkridge, H.N. Blount, in: J. Bard (Ed.), Electroanalytical Chemistry, vol. 13, Marcel Deker, 1984 , Ch. 1.

[15] S. Zapomni, A. Czerwinski, R. Marassi, Thin-layer derivative cyclic voltabsorptometry, J. Electroanal. Chem. 266 (1989) 37–46.

[16] M. Chotkowski, B. Wrzosek, M. Grdeń, Intermediate oxidation states of technetium in concentrated sulfuric acid solutions, J. Electroanal. Chem. 814 (2018) 83–90.

[17] H. Hartmann, T. Scheiring, J. Fiedler, W. Kaim, Structures and spectroelectrochemistry (UV–vis, IR, EPR) of complexes $[(\text{OC})_3\text{ClRe}]_n$(abpy), $n = 1, 2$; abpy = 2,2′-azobispyridine, J. Organomet. Chem. 604 (2000) 267–272.

[18] J.R. Kirchhoff, W.R. Heineman, E. Deutsch, Technetium Electrochemistry. 4.1 11Electrochemical and Spectroelectrochemical Studies on the Bis(tertiary phosphine or arsine (D))rhenium(III) Complexes trans-$[\text{ReD}_2\text{X}_2]^+$ (X = Cl, Br). Comparison with the Technetium(III) Analogues, Inorg. Chem. 26 (1987) 3108–3113.

[19] S.K. Strubing, I. Wen Sun, W.E. Cleland, C.L. Hussey, Electrochemistry and spectroelectrochemistry of polynuclear rhenium(III) chloride cluster complexes and their one-electron-reduction products in a basic room-temperature chloroaluminate molten salt, Inorg. Chem. 29 (1990) 993–999.

[20] B.P. Hahn, R.A. May, K.J. Stevenson, Electrochemical deposition and characterization of mixed-Valent rhenium oxide films prepared from a Perrhenate solution, Langmuir 23 (2007) 10837–10845.

[21] M. Chotkowski, A. Czerwinski, Electrochemical and spectroelectrochemical studies of pertechnetate electroreduction in acidic media, Electrochim. Acta 76 (2012) 165–173.

[22] M. Chotkowski, Z. Rogulski, A. Czerwiński, Spectroelectrochemical investigation of MnO_2 electro-generation and electro-reduction in acidic media, J. Electroanal. Chem. 651 (2) (2011) 237–242.

[23] M. Chotkowski, A. Czerwiński, Thin layer spectroelectrochemical studies of pertechnetate reduction on the gold electrodes in acidic media, Electrochim. Acta 121 (2014) 44–48.

[24] F. Poineau, P.F. Weck, K. German, A. Maruk, G. Kirakosyan, W. Lukens, D.B. Rego, A.P. Sattelberger, K.R. Czerwinski, Speciation of heptavalent technetium in sulfuric acid: structural and spectroscopic studies, Dalton Trans. 39 (2010) 8616–8619.

[25] F. Poineau, K. German, P.F. Weck, A. Maruk, W. Lukens, G. Kirakosyan, A.P. Sattelberger, D.B. Rego, K.R. Czerwinski, Speciation and reactivity of technetium in sulfuric acid, Nucl. Med. Biol. 37 (6) (2010) 686.

[26] Z. Galus, Fundamentals of Electrochemical Analysis, Halsted Press, 1976.

[27] F. Poineau, P.F. Weck, B.P. Burton-Pye, I. Denden, E. Kim, W. Kerlin, K.E. German, M. Fattahi, L.C. Francesconi, A.P. Sattelberger, K.R. Czerwinski, Reactivity of $HTcO_4$ with methanol in sulfuric acid: Tc-sulfate complexes revealed by XAFS spectroscopy and first principles calculations, Dalton Trans. 42 (13) (2013) 4348–4352.

[28] N. de Zubov, in: M. Pourbaix (Ed.), Atlas of Electrochemical Equilibria in Aqueous Solutions, Pergamon Press, Oxford 1966, pp. 300–306.

[29] R. Schrebler, P. Cury, M. Orellana, H. Gómez, R. Córdova, E.A. Dalchiele, Electrochemical and nanoelectrogravimetric studies of the nucleation and growth mechanisms of rhenium on polycrystalline gold electrode, Electrochim. Acta 46 (2001) 4309–4318.