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Electrodeposition of rhenium species onto a gold surface in sulfuric acid media

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Abstract It has been shown that the chemical nature of electrodeposited rhenium species depends on the H_2SO_4 concentration in the supporting electrolyte from which the deposition takes place. In dilute H_2SO_4 , mostly ReO_2 and ReO_3 and traces of Re_2O_5 are deposited. With the increase of H_2SO_4 concentration, Re_2O_5 becomes the principal deposit; in H_2SO_4 solution in higher concentration than 10 M, solely Re_2O_5 is deposited. From highly dilute H_2SO_4 solutions ($\text{pH} \approx 0.9$), Re^0 is deposited, which oxidizes at 0.7 V. If the current density of deposition is higher than 80 mA/cm^2 , thermodynamically two types of Re^0 are deposited and oxidized at 0.7 V and 0.95 V.

Keywords Electrodeposition · Rhenium · Sulfuric acid

Introduction

Since the application of rhenium in catalysts for motor fuel reforming [1], and as a protecting material against heat corrosion on the inner surface of gas turbines [2], knowledge of its redox properties has become more and more important. In spite of its importance, however, the redox equilibria of rhenium are still hardly known.

One of the unusual properties of rhenium is the dependence of the chemical nature of the electrodeposited rhenium species on the sulfuric acid concentration in the supporting electrolyte. From various technically applied plating solutions, Re^0 can be deposited [3]. With

the increase of H_2SO_4 concentration, however, different rhenium oxides may also be deposited [4, 5, 6, 7].

The aim of our paper is to demonstrate how the chemical nature of the deposited material depends on the conditions of deposition, what potential sweep (or cyclic voltammetric) curves can be expected in the course of oxidation of the deposited material, and finally what the oxidation state of the deposited rhenium can be. In order to avoid the complication caused by the adsorbed material, we chose smooth gold as the substrate material for the study of rhenium electrodeposition [7, 8].

Experimental

A conventional three-compartment cell with working, reference and auxiliary electrodes was used, as described in our previous papers [7, 9]. The volume of the main compartment of the cell was about 50 mL. The H_2SO_4 supporting electrolyte was prepared from Merck p.a. grade reagent with triply distilled water, as described earlier [9]. The cell solutions were deoxygenated and agitated by bubbling purified nitrogen through the cell.

A smooth Au electrode with about 2 cm^2 apparent surface area was used as a working electrode. In order to eliminate organic impurities and traces of rhenium, the gold electrode was anodized with about 0.5 A for 10–15 s in 0.5 M H_2SO_4 before every rhenium deposition experiment.

All measurements were carried out at room temperature. The potential of the working electrode was measured with respect to a hydrogen electrode immersed in the same supporting electrolyte that was poured into the main compartment of the cell.

Merck p.a. grade Re_2O_7 was used in the experiments and it was added to the supporting electrolyte in the form of Re_2O_7 . Occasionally a stock solution was made (10 mg $\text{Re}_2\text{O}_7/\text{mL}$ water) and this solution was pipetted into the main compartment of the cell in the required quantity, and then Re deposition started at 0.6–0.65 V.

Except for Re^0 deposition, rhenium was deposited from a HReO_4 solution containing H_2SO_4 and then the potential sweep of the rhenium-covered electrode was measured in the same solution with a 2 mV/s sweep rate.

Results and discussion

Based on the dependence of the run of potential sweep curves of rhenium-covered electrodes on H_2SO_4

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concentration, the dependence of Re deposition on H_2SO_4 concentration can be divided into four groups. In each group the chemical nature of the deposited material and the run of potential sweep curves show significant differences from the other groups. The oxidation potential peaks of different rhenium species, however, very often overlap one another. Another disturbing phenomenon is some interaction between different rhenium species deposited onto a substrate surface. This interaction results in some deviation of the peak potentials from the theoretical redox potential values, in scattering or shifting of the potential peaks, depending on the amount of deposited material.

In study of Re electrodeposition, important questions concern the chemical nature of the deposited material and the reproducibility of the measurements. Despite the above-mentioned complications, under strict and appropriate experimental conditions, reproducible measurements can of course be carried out. On the basis of peak potentials and the chemical behavior of the deposited material, as well as on the results of earlier studies [4, 5, 6, 7, 11], the chemical composition of the deposit can also be established.

Rhenium deposition from 0.1–3 M H_2SO_4 solutions

The first experiment was Re deposition for 20 h with 0.02 mA current in 0.1 M H_2SO_4 solution, in the presence of 0.4 g/L Re_2O_7 . The potential sweep of the rhenium-covered electrode is shown in Fig. 1 and it is similar to the curves published in our earlier paper (fig. 4 in [10]). In spite of somewhat different conditions, the run of the curves and the peak potentials are almost the same (the reproducibility is good).

The next experiment was Re deposition in 2 M H_2SO_4 in the presence of 1.0 g/L Re_2O_7 with polarization by 0.05 mA. The times of the polarizations were increased from 0.5 h to 17 h while the end potentials of the polarization decreased from 4 mV to -30 mV. Potential sweeps of the Re-covered electrode are shown in Fig. 2. A similar curve (curve 1 in Fig. 3) was measured in 3 M H_2SO_4 by polarization with 0.02 mA for 20 h at 0.4 g/L Re_2O_7 concentration.

On the basis of the results published in earlier papers [4, 5, 6, 7], it can be stated that the peak at about 0.38 V is the oxidation of bulk ReO_2 while at 0.7 V the oxidation of ReO_3 takes place [7]. A peak at about 0.45–0.5 V can be observed in Figs. 2 and 3 (curve 1), but the

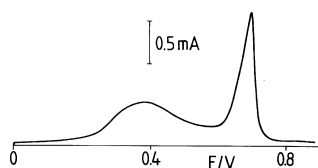


Fig. 1 Potential sweep of the Au electrode covered with rhenium by polarization with 0.02 mA in 0.1 M H_2SO_4 containing 0.4 g/L Re_2O_7 for 20 h. Sweep rate: 2 mV/s

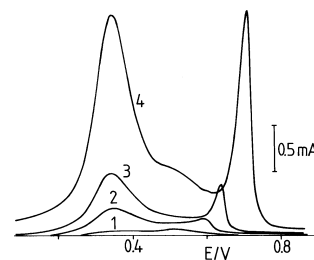


Fig. 2 Potential sweep of the Au electrode covered with rhenium species by polarization with 0.05 mA in 2 M H_2SO_4 containing 1 g/L Re_2O_7 for 0.5 h (1), 2.0 h (2), 5.0 h (3) and finally 17.0 h (4). Sweep rate: 2 mV/s

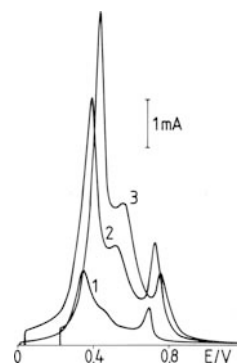


Fig. 3 Potential sweep of the Au electrode covered with different rhenium species by polarization with 0.02 mA for 20 h in 3.0 M H_2SO_4 (1), 4.0 M H_2SO_4 (2) and finally in 5.0 M H_2SO_4 (3) containing 0.4 g/L Re_2O_7 . Sweep rate: 2 mV/s

rhenium compound oxidized at this potential has not been identified so far. Our further experiments, however, show that this compound may be Re_2O_5 .

Rhenium deposition from 3–5 M H_2SO_4 solutions

A series of electrodeposition experiments was carried out to demonstrate the effect of sulfuric acid concentration on Re deposition, increasing the H_2SO_4 concentration from 3 M to 5 M. In this series, the Re_2O_7 concentration was 0.4 g/L, the polarization current was 0.02 mA and the time of polarization was 20 h (Fig. 3). During Re deposition the potential decreased to 17 mV (3 M H_2SO_4), to 42 mV (4 M H_2SO_4) and then to 225 mV (5 M H_2SO_4).

The most important effect of H_2SO_4 on Re deposition is the increase of the reaction rate with the increase of H_2SO_4 concentration (the end potential is shifted from 17 mV to 225 mV). From 3 M H_2SO_4 to 5 M H_2SO_4 the rate increase is about threefold (Fig. 3). It follows from this experimental observation that H_2SO_4 plays some catalytic role in the electroreduction of Re from HReO_4 solutions.

The experiment depicted by curve 3 in Fig. 3 was repeated under somewhat different conditions (Fig. 4). The Re_2O_7 concentration was increased to 1.0 g/L, the

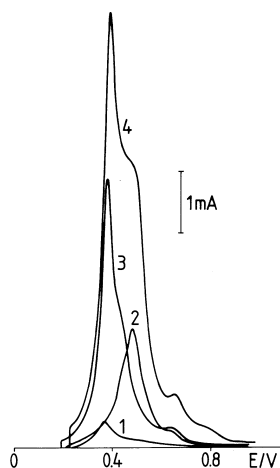


Fig. 4 Potential sweep of the Au electrode covered with rhenium species deposited by polarization with 0.05 mA in 5.0 M H_2SO_4 containing 1 g/L Re_2O_7 for 0.5 h (1), 2.0 h (2), 3.5 h (3) and finally 8.5 h (4). Sweep rate: 2 mV/s

current to 0.05 mA, and the duration of the Re electrodeposition was 0.5 h (Fig. 4, curve 1), 2.0 h (curve 2), 3.5 h (curve 3) and 8.5 h (curve 4). At the end of polarization the electrode potentials were 0.18 V (after 0.5 h), 0.19 V (after 2 h), 0.195 V (after 3.5 h) and 0.216 V (after 8.5 h).

The predominant potential peaks in Figs. 3 and 4 appear at about 0.4 V. At this potential, oxidation of ReO_2 takes place [4, 5, 6, 7]. The next peak between 0.47 and 0.55 V results from the oxidation of an unidentified rhenium compound, presumably Re_2O_5 . Between 0.7 V and 0.75 V the oxidation of ReO_3 can be expected [7]. According to Figs. 3 and 4, the material oxidized at more positive potentials than 0.6 V is of minor importance, e.g. traces of ReO_3 may be in the deposit.

Rhenium deposition from 8–12 M H_2SO_4 solutions

With a further increase of sulfuric acid concentration in the supporting electrolyte, the depositing oxide composite is simplified and the deposition of only one oxide can be observed (Figs. 5 and 6). According to earlier papers, this oxide is Re_2O_5 [7, 11].

Rhenium deposition from 8 M H_2SO_4 is depicted by the potential sweep curve in Fig. 5. This experiment was carried out in the presence of 0.4 g/L Re_2O_7 with 0.01 mA for 20 h. On the basis of Fig. 5 it can be stated that ReO_2 deposition could not take place, and the deposited material is composed thermodynamically of two kinds of Re oxides. The dominating sharp peak at 0.49 V (the central peak in Figs. 1, 2, 3, 4) is presumably the oxidation of Re_2O_5 , because its oxidation can be expected at this potential [11]. There is a smaller peak (the tailing) at about 0.7 V, which is the result of oxidation of a small amount of ReO_3 [7].

After polarization of the Au electrode in 10 M H_2SO_4 supporting electrolyte at 0.4 g/L Re_2O_7 concentration

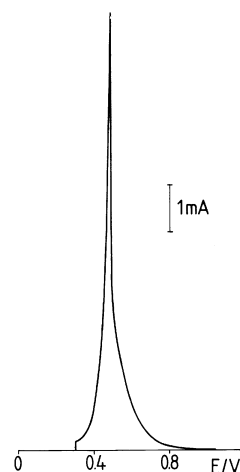


Fig. 5 Potential sweep of the Au electrode covered probably with Re_2O_5 by polarization with 0.01 mA in 8.0 M H_2SO_4 containing 0.4 g/L Re_2O_7 . Sweep rate: 2 mV/s

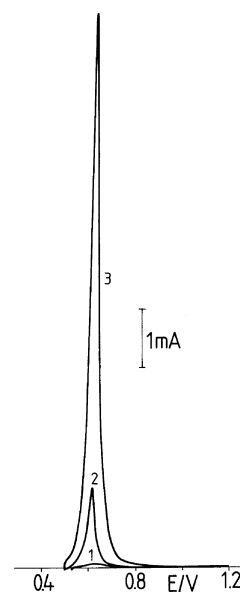


Fig. 6 Potential sweep of the Au electrode covered with Re_2O_5 by polarization with 0.05 mA in 12 M H_2SO_4 containing 1.0 g/L Re_2O_7 for 1.0 h (1), 2.0 h (2) and finally for 4.0 h (3). Sweep rate: 2 mV/s

with 0.02 mA for 13 h, its potential sweep is similar to the sweep in Fig. 5. The peak potential, however, is shifted to 0.58 V and the peak at 0.7 V is hardly noticeable.

According to Fig. 6, in 12 M H_2SO_4 solution only one oxide (Re_2O_5) was deposited [7, 11]. In the course of the measurements (see Fig. 6), the Re_2O_7 concentration was 1.0 g/L and the polarization current was 0.05 mA. Before the sweep the Au electrode was polarized for 1.0 h (curve 1), for 2.0 h (curve 2) and for 4.0 h (curve 3 in Fig. 6). After 1 h polarization the electrode potential decreased to 0.526 V, after 2 h polarization to 0.507 V and after 4.0 h polarization to 0.504 V.

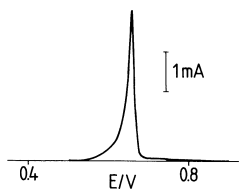


Fig. 7 Potential sweep of the Au electrode covered with Re_2O_5 crystallized onto the electrode surface from the repeatedly used 12 M H_2SO_4 containing 1.0 g/L Re_2O_7 . Sweep rate: 2 mV/s

After repeated use for rhenium deposition studies of the same 12 M H_2SO_4 solution containing 1.0 g/L Re_2O_7 , the solution turns blue upon the effect of dissolved Re_2O_5 . This dissolved material could crystallize onto the Au electrode surface. After this spontaneous process the potential sweep is given in Fig. 7. On the basis of the peak potential it can be stated that by electrodeposition, and by spontaneous crystallization, the same material (i.e. Re_2O_5) is deposited [7, 11].

Rhenium deposition from a plating solution

Finally, the results for Re^0 deposition are given. The composition of the plating solution used for formation of an electroplated Re^0 layer on an Au surface was taken from the literature of the electroplating industry [3]. The composition of the electroplating bath was 11 g/L Re_2O_7 in 3.3 g/L H_2SO_4 , with the temperature ranging from 25 to 45 °C and the current density from 100 to 140 mA/cm^2 [3].

In a separate cell, in the above-mentioned plating bath, a 2.0 cm gold wire (diameter 1.0 mm) was polarized with 100.0 mA for different times and the rhenium-covered Au wire was placed in the cell for potential sweep measurements. The sweeps were measured in 0.5 M H_2SO_4 supporting electrolyte. The sweep after 0.25 min rhenium deposition is depicted by curve 1 in Fig. 8. After 1.0 min deposition the sweep is given by curve 2 and after 2.0 min deposition by curve 3 in Fig. 8.

In Fig. 8, only one predominant peak can be observed and the peak potential is about 0.68 V; moreover, every curve has a tail between 0.72–0.97 V. If we assume that the oxidation of Re^0 gives ReO_4^- , then the 0.68 V peak potential seems to be very high, since the E° value for the ReO_4^-/Re redox couple is only 0.34 V [12]. Another question is the process concerns the tailing.

In order to obtain further information on the tailing, we carried out a series of Re^0 deposition experiments with increasing current densities from 6.4 mA/cm^2 to 320 mA/cm^2 . For the experiments a 1 cm Au wire (diameter 1.0 mm) was used as the substrate metal. Re^0 deposition was carried out in the same plating bath as in earlier experiments [3], and the Re^0 -covered electrode was studied also in 0.5 M H_2SO_4 (Fig. 9).

The very first Re^0 deposition was carried out in this case with 2.0 mA for 3 min (for the sake of simplicity, however, this sweep has been omitted from Fig. 9). The

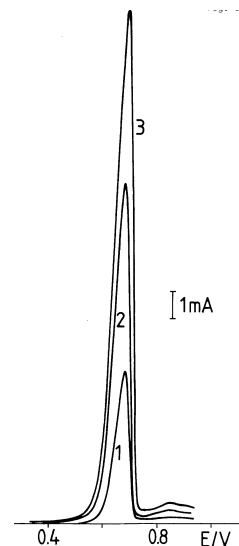


Fig. 8 Potential sweep of a 2-cm long Au wire electrode in 0.5 M H_2SO_4 after Re^0 deposition in a separate cell, in a plating bath with 100 mA plating current for 0.25 min (1), 1.0 min (2) and finally for 2.0 min (3). Sweep rate: 2 mV/s

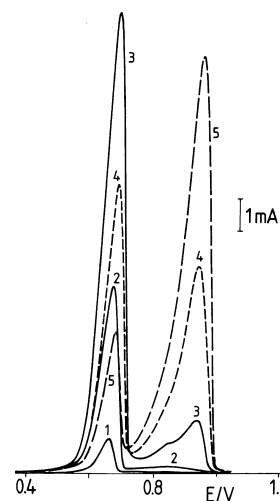


Fig. 9 Potential sweep of a 1-cm long Au wire electrode in 0.5 M H_2SO_4 after Re^0 deposition in a separate cell, in a plating bath by polarization for 3.0 min with 5 mA (1), 25 mA (2), 62.5 mA (3), 75.0 mA (4) and finally with 100.0 mA (5) plating current. Sweep rate: 2 mV/s

peak potential of the oxidation of the small amount of deposit was 0.67 V; therefore, in fact, Re^0 was deposited even at this relatively low current density.

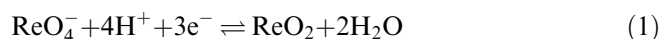
After the above experiment, maintaining the other variables at constant values, we gradually increased the deposition current and studied the Re^0 -covered Au wire in 0.5 M H_2SO_4 (Fig. 9). The potential sweeps after Re^0 deposition with 5.0 mA (curve 1), with 25 mA (curve 2), with 62.5 mA (curve 3), with 75 mA (curve 4) and finally with 100.0 mA (curve 5) are depicted in Fig. 9.

The most remarkable result in this series of experiments is that the material which can be oxidized between

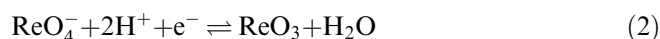
0.73–1.0 V increases considerably at higher current densities. Up to about 80 mA/cm² (curve 2 in Fig. 9) the amount of this material in the deposit is negligible, but in the case of 320 mA/cm² current density (curve 6 in Fig. 9), most of the deposited material is oxidized between 0.73 V and 1.0 V.

Conclusions

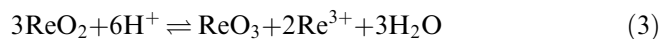
In the course of electrodeposition of rhenium species onto a smooth gold surface, different electrode reactions take place simultaneously. Above all, the deposition of ReO₂ must be taken into account (Figs. 1, 2, 3, 4) [4, 5, 6, 7]:



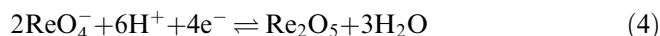
In addition to ReO₂ deposition, ReO₃ formation also takes place on a gold surface (Figs. 1, 2, 3) [7]:



Instead of direct reduction of the ReO₄⁻ ion, ReO₃ formation can take place via disproportionation of the deposited ReO₂ [7]:

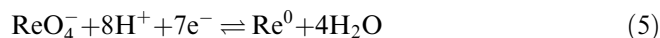


An important result of this paper is the conclusion that some Re₂O₅ deposition must be taken into account, even in dilute H₂SO₄ solutions (Figs. 2, 3, 4):



With increasing sulfuric acid concentration, reaction 4 will gradually be the predominant reaction and in 10–12 M H₂SO₄ solutions this will be the only electrode reaction [7, 11]; consequently, the deposited material will be solely Re₂O₅ (Figs. 5 and 6).

From the chosen plating bath, only Re⁰ was deposited [3]; therefore, the reaction for Re⁰ formation (Figs. 8 and 9):



must be taken into consideration. A seven-electron surface reaction must be the result of a complicated reaction mechanism, which is almost entirely unknown. We have experienced the surprising effect of an unknown reaction mechanism in the course of reoxidation of the deposited Re⁰ layer. Two unexpected

results have been observed. First, oxidation of the Re⁰ layer takes place at 0.67–0.7 V, which is far above the standard potential ($E^\circ = 0.34$ V [12]) of reaction 5. Another surprising result is that the oxidation of the Re⁰ layer deposited with higher than 80 mA/cm² current density results in two peaks, one at 0.7 V and another at 0.95 V.

On the basis of these observations it may be stated that during the oxidation of the Re⁰ layer the surface reaction is probably not reaction 5. According to redox potential tables, the standard potential of reaction 3 ($E^\circ = 0.768$ V [12]) is near the observed value; therefore it may be assumed that the final oxidation step is reaction 3 or that some unknown redox process accounts for the unexpected oxidation potentials (Figs. 8 and 9).

An even more difficult question is the interpretation of the second peak at 0.95 V in Fig. 9. Since the peak size is somewhat sensitive to the type of substrate metal, it may be assumed that the second peak is the result of some strong interaction between the substrate metal and the deposited Re⁰. In the interpretation of the second peak at 0.95 V in Fig. 9, we supposed a substrate deposit interaction. It can be some internal interaction, however, also in the deposited material, because using a Pt substrate, similar results could be observed, proving that the results depicted in Figs. 8 and 9 are somewhat independent of the nature of the substrate metal.

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