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Study of the Electrodeposition of Rhodium on Polycrystalline Gold Electrodes by Quartz Microbalance and Voltammetric Techniques

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The electrodeposition of rhodium on different polycrystalline gold substrates from $Na_3RhCl_6 \cdot 12H_2O + NaCl$ solutions was investigated by electrochemical quartz crystal microbalance and voltammetric techniques. A study of the electrodeposition of rhodium from the concentrated chloride solutions used in this work show several features that are associated with potentiostatic transients with growth of the clusters controlled by mixed kinetics, charge transfer and diffusion. The results in this paper offer a clear warning against the blind interpretation of potentiostatic transients with models based on simple diffusion controlled growth. At low overpotentials the electrodeposition of rhodium is characterized by very slow charge transfer kinetics and starts with the formation of a submonolayer. Even at more negative potentials current transients and massograms recorded at constant potential exhibit an apparent induction time, indicating that growth initially is controlled by mixed kinetics, charge transfer and diffusion. Bulk deposition of rhodium is shifted to more negative potentials compared with other solutions, *e.g.*, H₂SO₄-based electrolytes, but the exact influence of rhodium speciation in the plating solutions remains unknown.

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Information on the initial stages of the electrodeposition of rhodium is relatively scarce. Some groups studied the electrodeposition of rhodium on platinum,¹⁻³ vitreous carbon,⁴ and copper⁵ electrodes. Kibler *et al.*⁶ reported the results of an *in situ* scanning tunneling microscope (STM) study of the initial stages of rhodium electrodeposition on Au(111). Arbib *et al.*⁷ investigated the nucleation and growth kinetics of rhodium on polycrystalline gold and on Au(100) single crystal electrodes. Recently, de Dios *et al.*⁸ studied the preparation of Rh-adlayers on Pt(100) electrodes and their electrocatalytic activity for the reduction of nitrous oxide. Baraka *et al.*⁹ investigated the electrodeposition of rhodium metal on oxidized titanium electrodes. Interest in the electrodeposition of thin layers of rhodium has been stimulated by the high activity of this metal for the conversion of automotive exhaust fumes in three-way catalysts.¹⁰⁻¹³

This work reports a study of the nucleation and growth of rhodium on polycrystalline gold electrodes by means of voltammetry and electrochemical quartz crystal microbalance (EQCM). The advantage of the combined use of massograms and voltammograms for the study of different types of electrochemical reactions was illustrated recently by several authors.¹⁴⁻¹⁶ It is shown that the nucleation and growth of rhodium on polycrystalline gold from concentrated chloride solutions is a typical example of the effect of slow electrode kinetics on the morphology of potentiostatic transients.

Experimental

The plating solution was prepared from Na₃RhCl₆·12H₂O (Alfa Aesar), NaCl and HCl (Fisher Chemicals), and double distilled water. The pH of the solutions, aged for at least six months before use, was 3-3.4 to avoid interference of the hydrogen evolution reaction. Aquation is the principal reaction of the hexachlorocomplex in water and aqueous solutions contain a mixture of Rh(H₂O)₃Cl₃, Rh(H₂O)₄Cl₂⁺ and, on ageing, Rh(H₂O)₅Cl²⁺. Higher chlorocomplexes can exist in solutions with a sufficient large excess of chloride anions.^{17,18}

A home build quartz microbalance and oscillator were used for EQCM experiments. The voltammetric measurements were performed with a modified PAR model 174 polarographic analyzer with the working electrode at hard ground and a resistor in series with the platinum counterelectrode connection.¹⁹ A Hewlett-Packard HP53132a instrument was used for frequency measurements with a

precision of 0.1 Hz. A personal computer with GPIB and data acquisition boards (National Instruments) was used for the simultaneous measurement of frequency and current (voltage drop across the series resistor) with a minimum sample time of 10 ms. EQCM measurements were performed with polished AT-cut gold-coated 10 MHz quartz crystals (Elchema, Potsdam, N.Y.) of 14 mm blank diam (mass sensitive area: 0.196 cm²). The sensitivity factor in the Sauerbrey equation $\Delta f = -k\Delta m^{19}$ (Δf : the observed frequency change; Δm : mass change per area) was determined by galvanostatic copper deposition and is very close to the theoretical value (k = 0.226 Hz cm² ng⁻¹).

Rhodium metal cannot be dissolved anodically and therefore the number of EQCM experiments had to be restricted because a (rather expensive) quartz crystal could be used only once. Gold evaporated on a silicon wafer [further indicated as Au(Si)] was used as the disposable working electrode for other voltammetric experiments. The wafer was cut into 2×2 cm squares which fitted into an electrochemical cell, constructed to ensure linear diffusion, with a circular area of 0.35 cm² exposed to the solution and a new working electrode was used for each experiment. Electrochemical experiments were performed with Ecochemie Autolab PSTAT10 and Autolab PGSTAT12 instruments. Before each experiment the solution was thoroughly deoxygenated with purified, water-saturated nitrogen. All experiments were performed at room temperature (20 $\pm 2^{\circ}$ C).

Potentials were measured *vs.* a mercury-mercurous sulfate reference electrode but were converted ($E^0 + E_j = 0.658 \text{ V}^{20}$) to standard hydrogen electrode (SHE) to facilitate a comparison with the results reported in other papers.

Results and Discussion

A typical cyclic voltammogram (CV) and the corresponding massogram for a 2 mM rhodium salt solution are shown in Fig. 1. The potential was scanned from the conditioning potential, 0.450 V, in the negative direction at a rate of 0.020 V s^{-1} . The cyclic voltammogram shows a very sharp cathodic peak for rhodium deposition at about -0.050 V in the forward scan and a very pronounced nucleation loop in the reverse scan. The position of this peak shifts to slightly more positive values when the concentration of the metal ion is increased. A slight increase of the current is observed at 0.150 V, *i.e.*, before the main peak in the CV. The voltammetric behavior is essentially the same for the two types of gold substrates used in this work. Anodic dissolution of rhodium has not been observed, in agreement with earlier reports,⁴⁻⁷ because a passivating oxide layer is formed on the metal at positive potentials.

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Figure 1. Cyclic voltammogram and massogram for rhodium deposition from 2 mM $Na_3RhCl_6 \cdot 12H_2O + 0.1$ M NaCl on a polycrystalline gold electrode (conditioning and initial potential: 0.45 V; scan rate: 0.020 V s⁻¹).

The massogram shows a very small frequency decrease, Δf \simeq -1.5 Hz, in the potential region before the main peak in the CV. In the background electrolyte containing no rhodium salt, a frequency increase, $\Delta f \simeq 1$ Hz, is observed over the same potential interval. The formation of a monolayer of rhodium on an atomically flat Au(111) surface corresponds with $\Delta f = -54$ Hz (667 μ C cm^{-2}). Therefore, if the small current before the peak corresponds to rhodium deposition, then the observed frequency response corresponds to the formation of only 5-6% of a monolayer. Evidently it is dangerous if not impossible to draw definite conclusions from such CV experiments and this point is better investigated by constant potential methods where the frequency response can be monitored over longer time intervals. A comparison of the voltammogram and the massogram for the main peak in the voltammogram shows rather large deviations from the Sauerbrey equation. Thus, the frequency decrease is much larger than expected on basis of the integrated current and this point is addressed further in this paper (see Appendix).

At this point it is already interesting to make some comparisons with the results of earlier reports. Pletcher and Urbina⁴ studied the deposition of rhodium from $10 \text{ mM Na}_3\text{RhCl}_6 + 1 \text{ M NaCl}$ (pH 3.9) on vitreous carbon electrodes. Kibler *et al.*⁶ (Fig. 2) studied rhodium deposition on Au(111) from 0.1 mM Na₃RhCl₆ in $0.1 \text{ MH}_2\text{SO}_4 + 10 \text{ mM} \text{ HCl.}$ Arbib *et al.*⁷ (Fig. 1) recorded CVs for the deposition of rhodium from 10 mM Na₃RhCl₆ · 12H₂O in 0.1 M HClO₄ on polycrystalline and (100)Au substrates. However, the value of $i_p/cv^{1/2}$ (where i_p is the peak current density of the main peak in the CVs (vide infra), c is the concentration, and v the scan rate) estimated from these different papers is practically the same as the value determined in this work. This shows that all the rhodium species in solution, whatever the ionic speciation, can participate in the deposition process as noted already by Pletcher and Urbina.⁴ However it remains unknown whether the different complexes undergo charge transfer directly or the reduction process involves chemical reaction steps.

It is also interesting to make a comparison with the results obtained by other workers on gold electrodes. Kibler *et al.*⁶ reported that rhodium deposition on Au (111) from 0.1 mM Na₃RhCl₆ in 0.1 M H₂SO₄ + 10 mM HCl starts at about 0.440 V. The peak in cyclic voltammetry (scan rate: 0.010 V s⁻¹) occurs at about 0.340 V



Figure 2. (a) Potentiostatic transients for rhodium deposition from 2 mM Na₃RhCl₆·12H₂O + 0.1 M NaCl on Au(Si) electrodes at different electrode potentials (conditioning and initial potential: 0.450 V). (b) Dimensionless plots of $(i/i_{max})^2$ vs. t/t_{max} for the transients of Fig. 2a. The solid lines are the theoretical lines for instantaneous respectively progressive 3D nucleation with diffusion controlled growth.

for deposition on a well-ordered Au(111) crystal, with a small shoulder at 0.420 V; on a stepped crystal a single peak is observed at 0.410 V. They reported that there is no indication for underpotential deposition (of course, the meaning of "upd" is not clear, because the equilibrium potential is not known with certainty, *vide infra*). Kibler *et al.*⁶ studied the deposition of rhodium by *in situ* STM at 0.430 V, choosing this potential in order to slow down the deposition rate. At this potential a rhodium bilayer is formed first, but the deposition process is very slow (as expected at this potential) and it took about 20 min for completion of the bilayer. Further deposition on top of the bilayer proceeds via a Stranski-Krastanov growth mode and is accompanied by a strong roughening of the surface.

Arbib *et al.*⁷ observed the start of rhodium deposition from $Na_3RhCl_6 \cdot 12H_2O$ in 0.1 M HClO₄ on a Au(100) single crystal electrode in a CV (scan rate: 0.020 V s⁻¹) at about 0.400 V, in essence the same value as reported by Kibler *et al.*⁶ (taking into account the different scan rates). However, Arbib *et al.*⁷ found only a rather small peak at 0.325 V, which on the basis of the integrated charge

was attributed to the formation of a (sub)monolayer of rhodium. After this small first peak the current drops practically sharply and a second much larger peak for rhodium deposition is observed at about 0.050 V. Similar results were also reported for rhodium deposition on polycrystalline gold electrodes. Chronoamperometric transients on Au(100) showed two clearly distinct sections with two current maxima. These transients were analyzed with a model that associates the first peak at short times to 2D nucleation and growth of the first two monolayers, followed at longer times by 3D nucleation and growth of the metal on top of the first monolayer. However, Arbib et al.7 did not consider the well-documented fact that rhodium or rhodanized electrodes are good catalysts for the elec-troreduction of perchlorate ions to chloride.²¹⁻²⁵ The reduction of perchlorate starts at about 0.300 V^{24} in 0.1 M HClO₄ and the reduction rate follows the sequence Rh(100)>Rh(poly)>Rh(111) under transient conditions.^{23,24} Reduction of perchlorate is a pH-dependent multistep reaction and accumulation of the reduction intermediates and chloride can block the further reduction of this anion.²³⁻²⁵ Therefore it seems quite plausible that the deposition of rhodium starts at 0.400–0.450 V in 0.1 M HClO₄ but that the further growth of the rhodium islands is blocked by the intermediates of perchlorate reduction and chloride. Chloride and intermediates are desorbed at about 0.100 V and 3D nucleation occurs at slightly more negative potentials. Such a scheme explains that the relative height of the two peaks is not only a function of the rhodium concentration in solution but also of the perchloric acid concentration.²⁶ The reduction of perchlorate on rhodium requires contact adsorption of this anion^a and is suppressed in HClO₄ solutions containing millimolar concentrations of chloride or sulfate.²³⁻²⁵ However, when rhodium is freshly deposited on a foreign substrate perchlorate reduction and adsorption of other anions are competitive processes. Anyway, perchloric acid seems not to be well suited as a supporting electrolyte for the fundamental study of rhodium deposition because of the possible interference of perchlorate reduction on the deposited metal.

The formal standard potential of the couple $RhCl_6^{3-}/Rh$ has been given as 0.500 V,²⁷ but this value is based on a rather uncertain estimate of the stability constant of the hexachlorocomplex in HCl solutions. Nevertheless, the potential where rhodium deposition starts according to Kibler et al.⁶ and Arbib et al.⁷ is only slightly more negative than this value of the standard which may indicate rather facile electrode kinetics. The peak maximum in cyclic voltammetry found in this work is shifted by about 0.400 V to more negative potentials. The position of the peak maximum found in this work corresponds well with the value reported by Pletcher and Urbina⁴ for the deposition of rhodium from 10 mM Na₃RhCl₆ + 1 M NaCl (pH 3.9) on vitreous carbon electrodes. This correspondence between the positions of the peak maxima may be simply accidental. In fact, the potential at which electrodeposition starts (corresponding to the "critical overpotential") normally depends on a set of experimental conditions (electrode material, pretreatment of the electrode, surface roughness, ...). However, a limited number of experiments with different electrode materials (gold, platinum, vitreous carbon, ...) shows that the peak maximum occurs in a very narrow region of potentials. This seems to indicate that a kinetic factor associated with the speciation of the rhodium complexes in chloride solutions (pH \simeq 3.5-4) is a dominating factor that determines the onset of rhodium deposition.

Chronoamperometric transients recorded at different potentials for nucleation on Au(Si) are shown in Fig. 2a. The corresponding dimensionless plots of $(i/i_{max})^2 vs. t/t_{max}$, which are customary used for the characterization of nucleation transients, are shown in Fig.



Figure 3. (a) AFM surface morphology of the bare Au(Si) substrate (area: $2 \times 2 \mu m^2$), which reveals some sputtering imperfections. (b) Surface morphology after recording a transient for 10 s at -0.125 V (2 mM Na₃RhCl₆·12H₂O + 0.1 M NaCl).

2b, together with the theoretical lines for the limiting cases of instantaneous and progressive 3D nucleation with diffusion-controlled growth.²⁸⁻³⁰ At short times there is an important contribution of charging current which masks the initial rising part of the nucleation transient. In the dimensionless plots, the experimental points after the current maximum fall between the theoretical lines for both limiting cases which may suggest slow nucleation with diffusioncontrolled growth.

In fact the current/time transients shown in Fig. 2a actually fit quite well to a theoretical model for 3D nucleation on active sites with purely diffusion-controlled growth (the fitting used the nonlinear least square procedure based on the Levenberg-Marquardt algorithm described previously²⁹). This fitting yields seemingly "normal" values of the nucleation site density N_0 , the nucleation rate constant A, and the diffusion coefficient. For example, analysis of the transient recorded at E = -0.125 V yields $N_0 = 7.2 \times 10^6$ cm⁻², A = 8.1 s⁻¹, and $D = 7.70 \times 10^{-6}$ cm²s⁻¹. Then, the expected number of nuclei equals the site density and the average radius of a nucleus is calculated from the charge, which corresponds roughly to the deposition of 10 monolayers, as 200 nm. However, a scanning electron microscope did not reveal anywhere on the surface nuclei of this anticipated size. Figure 3 shows an atomic force microscope image of the sputtered gold electrode before and after recording the transient.

The bare gold has a nanofibrous structure and the average depth of the surface features R_a is a few nm. The surface after recording the transient exhibits a strong increase of R_a and roughness. Evidently, it is somewhat ambiguous to count nuclei sized in the na-

^a As pointed out recently by Lang and Horányi,²⁶ the reduction of perchlorate on rhodium electrodes is better not described as a reaction of adsorbed CIO_4^- with adsorbed H atoms. Instead the reduction process corresponds to a slow decomposition of adsorbed perchlorate followed by fast reduction steps. This conclusion is based on the fact that reduction of perchlorate already proceeds at a measurable level in a potential range where the surface concentration of adsorbed H atoms is negligible.



Figure 4. (a) Potentiostatic current transient and corresponding massogram for rhodium deposition from 2 mM Na₃RhCl₆·12H₂O + 0.1 M NaCl on a polycrystalline gold electrode at E = -0.025 V (conditioning and initial potential: 0.45 V). (b) Plot of $-\Delta f vs$. time for the initial stages of rhodium deposition on polycrystalline gold electrodes: (open circles) -0.025 V and (solid circles) 0 V.

nometer range on a sputtered substrate like used in this work. But a rough estimate indicates a nucleus number density in the range 10^{9} - 10^{10} cm⁻², at least three orders of magnitude higher than expected on the basis of the fitting results for 3D nucleation and growth. This clearly shows that analysis of nucleation transients with theoretical models for simple diffusion-controlled growth can lead to erroneous interpretations.

Some potentiostatic transients were also recorded with the EQCM. A typical current transient (-0.025 V) and the corresponding massogram are shown in Fig. 4a. The initial part of the gravimetric data is shown in Fig. 4b (for -0.025 V resp. 0 V). Both the current and the EQCM results clearly show kind of an induction time. Thus, it appears that rhodium deposition can start at quite positive potentials but is kinetically very slow. The induction time depends strongly on the applied potential and this explains why the deposition of the initially formed submonolayer is hardly seen in the cyclic voltammetric experiments described earlier. A plot of $(i/i_{max})^2$ *vs.* t/t_{max} for the transient recorded at -0.025 V is shown in Fig. 5.



Figure 5. Dimensionless plot of $(i/i_{max})^2 vs. t/t_{max}$ for the transient of Fig. 4a. The solid lines are the theoretical lines for instantaneous resp. progressive 3D nucleation with diffusion controlled growth.

The experimental points fall below the theoretical line for progressive nucleation with diffusion-controlled growth for all times (except of course for $t/t_{max} = 1$, which is the reference point). Such behavior has also been observed by other authors, for example by J. C. Ziegler³¹ (copper deposition on a n-Si(111):H surface from 0.1 mM CuSO₄ + 0.1 MH₂SO₄ solutions) and Schrebler *et al.*³² (nucleation of rhenium on gold).

It thus is evident that the experimental results can not be described by a model for 3D nucleation with simple diffusion controlled growth (i.e., growth controlled by diffusion from the moment the nuclei are born, vide infra). Such apparently "anomalous" plots of $(i/i_{\text{max}})^2$ vs. t/t_{max} can be explained by a combination of slow nucleation and slow charge transfer, i.e., kinetically hindered deposition and growth. Cao and West³³ described a numerical algorithm to investigate the effect of slow charge transfer on potentiostatic transients for 3D-nucleation and growth. The same problem was investigated by Langerock et al.³⁴ using an extension of the concept of planar diffusion zones. In this context it is important to remember that the growth of a nucleus initially is always controlled by pure charge transfer.³⁵⁻³⁷ Growth controlled by diffusion will occur only after an apparent induction time $t_0 \simeq 0.2 Dc/V_{\rm m} v_{\rm f}^2$, ³⁸ where D is the diffusion coefficient, c is the concentration of electroactive species, $V_{\rm m}$ is the molar volume of the deposit, and $v_{\rm f}$ = $(i_0/zF)\exp(-\alpha z f \eta)$ is the rate of the charge transfer reaction per unit area. However, for this discussion it is nevertheless useful to consider instantaneous nucleation with growth controlled purely by diffusion at all times t as a reference to compare the effect of slow nucleation or growth controlled by mixed kinetics, keeping other factors as the site density, concentration, electrode potential, etc. constant. In a plot of $(i/i_{\text{max}})^2$ vs. time, this hypothetical situation corresponds to the upper theoretical line shown in Fig. 5. Then one can consider the effect of slow nucleation while still supposing growth controlled purely by diffusion. The slower formation of nuclei results in a slower increase of the current and for the limiting case of progressive nucleation (high value of the site density N_0 , very low value of the nucleation rate constant A) the lower theoretical line in Fig. 5 is obtained. For intermediate values of N_0/A the points of $(i/i_{\text{max}})^2$ vs. t/t_{max} will fall between these two theoretical limits and this is the basis to determine the values of N_0 and A from experimental transients if growth is supposed to be purely controlled by diffusion. Now consider the case of instantaneous nucleation with growth controlled by mixed kinetics. Again there is a retardation of the current increase, compared with diffusion controlled



Figure 6. Plot of the ratio $(d\Delta f_{exp}/dt)/(d\Delta f_{dep}/dt)$ vs. time for the transient shown in Fig. 4a. The quantity $(d\Delta f_{exp}/dt)$ was obtained from the experimental frequency vs. time response. The quantity $(d\Delta f_{dep}/dt)$ is calculated from the current vs. time curve, using the Sauerbrey equation $\Delta f_{dep} = -k\Delta m_{dep}$ with the experimentally determined value of the proportionality factor.

t/s

growth, because initially the growth is controlled by pure charge transfer. This means that qualitatively the effect of slow nucleation or mixed kinetics on a potentiostatic transient cannot be distinguished. For the case of instantaneous nucleation with growth controlled by mixed kinetics the experimental points in a plot of $(i/i_{max})^2 vs. t/t_{max}$ will also fall between the theoretical lines for the limiting cases with diffusion controlled growth.^{33,34,38} In the case of progressive nucleation and a sufficiently low value of $v_f = (i_0/zF)\exp(-\alpha z f \eta)$, the experimental points in a plot of $(i/i_{max})^2 vs. t/t_{max}$ show the behavior seen in Fig. 6. Thus, the experimental results described earlier can be explained by the combination of progressive nucleation and growth controlled by mixed kinetics. It is important however to realize that any other factor that causes an apparent induction time, for example site birth effects as considered by Milchev,^{39,40} will have the same effect on a potentio-static transient.

Again, remember that the case of so called progressive nucleation corresponds to very high values of the ratio N_0/A so that the maximum number of clusters is not limited by the number of active sites. This is akin to saying that the limiting case of progressive nucleation corresponds to nucleation on a homogeneous surface $(N_0/A \rightarrow \infty)$. Most theories of the potentiostatic transient for 3D nucleation with diffusion controlled growth are based on the concept of planar diffusion/exclusion zones.^{28,29} An exclusion zone is a circular area spreading around a growing cluster where the formation of new nuclei is impossible because of the depletion of electroactive material. For diffusion-controlled growth the radius of the zones increases with $t^{1/2}$ and the overlap of the zones will result in a finite number of observable clusters, i.e., the nucleus saturation density $N_{\rm S}$.⁴¹ If the growth is controlled by mixed kinetics the zones initially grow at a much smaller rate (compared with the diffusion controlled case). This can result in a value of $N_{\rm S}$ that can be several orders of magnitude higher than would be estimated on the basis of a model that is based on purely diffusion controlled growth, specially when the nucleus saturation density is not limited by the availability of active sites. This behavior has been observed in this work and similar findings have been reported over the years by several other workers.42-4

Conclusions

The electrodeposition of rhodium on different polycrystalline gold substrates from Na₃RhCl₆·12H₂O + NaCl solutions was investigated by EQCM and voltammetric techniques. A study of the electrodeposition of rhodium from the concentrated chloride solutions used in this work show several features that are associated with potentiostatic transients with growth of the clusters controlled by mixed kinetics, charge transfer, and diffusion. The results in this paper offer a clear warning against the blind interpretation of potentiostatic transients with models based on simple diffusion controlled growth. At low overpotentials the electrodeposition of rhodium is characterized by very slow charge transfer kinetics and starts with the formation of a submonolayer. Even at more negative potentials, current transients and massograms recorded at constant potential exhibit an apparent induction time, indicating that growth initially is controlled by mixed kinetics, charge transfer, and diffusion. Kibler et al.⁶ reported that rhodium deposition on Au(111) from 0.1 mM Na_3RhCl_6 in $0.1 M H_2SO_4 + 10 mM HCl$ at low overpotentials starts with the formation a bilayer and that further deposition proceeds via a Stranski-Krastanov growth mode, accompanied by a strong roughening of the surface. This conclusion was based upon in situ STM measurements with well-defined electrode surfaces. The results of this study with polycrystalline gold substrates agree well with the findings of Kibler et al. Bulk deposition of rhodium is however shifted to more negative potentials compared with other solutions, e.g., H₂SO₄-based electrolytes. The effect of rhodium speciation in the plating solutions on charge transfer kinetics remains however unknown and may explain eventually the divergent experimental observations made by different workers.

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Appendix

The expression for the experimental frequency response $\Delta f_{\rm exp}$ during an EQCM experiment can be quite generally written as 45,46

$$\Delta f_{\exp} = -k(\Delta m_{\rm dep} + \Delta m^*) + \Delta f_{\rm m} + \Delta f_{\rm r} \cdots$$
 [A-1]

The first term on the right is the Sauerbrey term which accounts for the frequency shift due to mass changes on the electrode ($\Delta m_{\rm dep}$ is the mass change due to faradaic deposition/dissolution of electroactive material and Δm^* includes the contributions of adsorption, trapping of solvent molecules ...). Other possible contributions to the frequency shift include changes of viscosity, roughening of the surface, ... etc. If only the mass changes corresponding with deposition/dissolution are considered, then

$$\Delta f_{dep} = -k\Delta m_{dep} \qquad [A-2]$$

Evidently $\Delta m_{\rm dep}$, hence $\Delta f_{\rm dep}$, can be calculated from the measured current, assuming a 100% current efficiency. A typical plot of $(d\Delta f_{\rm exp}/dt)/(d\Delta f_{\rm dep}/dt)$ vs. time during the recording of a potentiostatic transient for deposition of rhodium on gold is shown in Fig. 6 (this kind of plot has the advantage over a plot of $\Delta f_{\rm exp}/\Delta f_{\rm dep}$ vs. time that it shows deviations of the Sauerbrey equation as a transient phenomenon).

The frequency shift is much higher than anticipated on the basis of the Eq. A-2 but only during the initial stages of electrodeposition. Similar results were obtained for cyclic voltammetry. Large deviations from the "simple" Sauerbrey equation were reported previously by other authors⁴⁷⁻⁵² but the interpretation of these deviations may be highly case sensitive. A simple explanation for the observed behavior could be that the development of surface roughness is accompanied by trapping of solvent molecules. However it seems unlikely that the contribution of roughening and water trapping can explain the observed deviations because the average depth of the surface features is too small.⁵² Stress caused by the large lattice misfit between the rhodium deposit and the gold substrate (the lattice constants are 3.8043 and 4.0786 Å, respectively) is the most likely cause for the excess frequency shift.⁵¹ This would explain that the "simple" Sauerbrey equation applies after the deposition of the first 4-5 monolayers. To test this hypothesis more results are needed, including a complete impedance analysis of the EQCM response during the initial stages of deposition, and experiments in this direction are planned for the near future.

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