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Effect of the solution composition and the applied potential on the kinetics of roughness relaxation at gold electrodes in slightly acid electrolytes

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Abstract

The roughness relaxation of thin columnar Au electrodeposits at constant potential and 25°C in 0.05 M NaF, 0.05 M KCl and 0.05 M K_2SO_4 has been studied. These measurements were taken in the -0.6 to 0.8 V (vs Hg/Hg_2SO_4 reference electrode) potential range. The kinetic data were obtained from the roughness factor decay over 5×10^4 s. The value of the surface diffusion coefficient D_s of Au atoms was derived from the roughness decay law at constant potential and pH. At any potential, the value of D_s increases in the order $NaF < K_2SO_4 < KCl$. This sequence correlates with the specific adsorption of anions on Au. In K_2SO_4 and NaF solutions, as the electroformation of AuOH species takes place, the effect of SO_4^{2-} and F^- ions is no longer observed. In contrast, in 0.05 M KCl solution, the value of D_s increases steadily as the applied potential is increased positively.

INTRODUCTION

Surface roughness relaxation phenomena on metals in the range 273–325 K offer the possibility of deriving quantitative information about the mobility of surface atoms either in vacuo or at metal–aqueous solution interfaces [1–3].

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Knowledge of these phenomena becomes of particular interest, for instance, for understanding those surface processes which determine the stability and duration of large metal area catalysts and the mechanisms of metallic corrosion processes, such as stress corrosion cracking.

Recent investigations on electrodispersed metal electrodes, based on scanning tunnelling microscopy (STM) combined with scanning electron microscopy (SEM), have shown that these electrodes, which can be described as columnar-like structures, exhibit roughness relaxation, implying the radial growth of columns at a practically constant height [2]. The kinetics of this process can be followed through the time dependence of the surface roughness factor R , followed by electroadsorption measurements, employing appropriate molecules or atoms as references. The roughness relaxation of electrodispersed metal electrodes obeys the rate equation [2]

$$R^{-1} = (3/\pi h)(Bt + r_0^4)^{1/4} \quad (1)$$

where $B = (2\gamma a^4 D_s / kT)$, γ is the surface tension (surface Gibbs energy) of the metal, a is the corresponding lattice parameter, D_s is the surface diffusion coefficient of metal atoms at temperature T , k is Boltzmann's constant, r is the instantaneous average radius of columns and r_0 is the value of r for $t = 0$. Equation (1) for $t \rightarrow \infty$ and $r \gg r_0$ becomes

$$R^{-1} = (3/\pi h) B^{1/4} t^{1/4} \quad (2)$$

and, for $t \rightarrow 0$, it gives

$$R^{-1} = 3r_0/\pi h \quad (3)$$

Thus, from the slope of the R^{-1} vs. $t^{1/4}$ linear plots (eqn. (2)), D_s can be evaluated. This method has allowed us to measure, for the first time, values of D_s and E_s , the activation energy for surface diffusion, for polycrystalline Au and Pt in aqueous, acid electrolytes [2]. For Au at 298 K, the values $D_s \cong 1 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ and $E_s \cong 58 \text{ kJ mol}^{-1}$ were reported [2]. These numbers are close to $D_s = 2 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ and $E_s = 50 \text{ kJ mol}^{-1}$, which very recently were reported for the surface mobility of Au(111) in HClO_4 at room temperature through pit radii measurements by in situ STM imaging [4]. The reasonable coincidence of these numbers supports the validity of the present method of estimating D_s and E_s .

Au is widely recognized as a suitable metal for surface diffusion studies, owing to its relatively high surface atom mobility at room temperature [5]. Recently, roughness relaxation measurements of electrodispersed Au electrodes, made in the presence of either Cl^- or SO_4^{2-} ions under open circuit conditions [3], demonstrated that Cl^- ion adsorption increases markedly the value of D_s , whereas SO_4^{2-} ion adsorption produces only a slight increase in D_s [3] with respect to those values reported for Au in vacuo or in air [2]. However, the comparison of D_s values determined in different electrolytes with an open circuit potential becomes rather uncertain, because the open circuit potential values change with the electrolyte composition. It is clear that, if anion adsorption affects D_s , and with anion

adsorption changing with the applied potential, according to the adsorption isotherm, a marked effect of the applied potential on D_s should be expected. Thus, it is important to study the roughness relaxation of these electrodes under potentiostatic conditions. Despite the fact that Au also exhibits a potential-dependent surface reconstruction for well-defined, single-crystal faces [6-8], this reconstruction involves small changes in R (of the order of 2-1), which are much smaller than the changes in R (of the order of 100-10) resulting from particle growth phenomena [2].

The present paper is devoted to investigating the roughness relaxation of electrodispersed Au electrodes in 0.05 M NaF, 0.05 M KCl and 0.05 M K_2SO_4 at pH 5.0 under potentiostatic conditions, covering a wide potential range in the absence of interfering faradaic processes.

EXPERIMENTAL

The electrochemical runs were performed with a conventional cell, involving an electrodispersed Au working electrode (EDAuE), a large-area Au counterelectrode, and an Hg/Hg₂SO₄/K₂SO₄(sat.) (MSE) reference electrode. All the potential values given in the text refer to the MSE scale. The entire experiments were performed under purified N₂ at 298 K.

The in situ preparation of EDAuEs has been described extensively elsewhere [9,10]. Briefly, a polycrystalline Au wire electrode immersed in 0.5 M H₂SO₄ at room temperature was anodized at 2.0 V for a preset time to accumulate a certain amount of hydrous Au oxide. The amount of hydrous Au oxide can be controlled through the duration of the anodization time. Subsequently, the hydrous Au oxide layer was electroreduced by applying a potential sweep from 1.0 to -0.6 V at 0.1 V s⁻¹. The resulting EDAuEs exhibited average thickness values ranging between 4×10^{-6} and 3×10^{-4} cm, depending on the amount of Au oxide accumulated on the Au substrate.

The roughness relaxation of the EDAuEs immersed in the deaerated working solution under a constant applied potential E_g was followed by stepwise evaluation of the electrode roughness factor R in the range $-0.6 \leq E_g \leq 0.8$ V, using the following aqueous solutions: 0.05 M NaF, 0.05 M K₂SO₄ and 0.05 M KCl at pH 5. The value of R was determined voltammetrically from the ratio of the O adatom monolayer electrodesorption charge from the EDAuE at a given time to the O adatom monolayer electrodesorption charge from the untreated Au electrode. For this purpose, voltammograms were carried out in 1 M H₂SO₄ at 0.1 V s⁻¹ between -0.6 and 1.1 V. After each determination of R , which lasted less than 3 min, the EDAuE was returned into the cell containing the working solution to continue the roughness relaxation. Similar voltammograms recorded between -0.6 and 1.1 V on smooth Au wires or stabilized (100 h) EDAuEs show no changes in R . Thus, the observed decay in R cannot be assigned to the oxide formation and removal produced during the voltammetric measurements to estimate R . This fact agrees with in situ STM results for Au(111) in HClO₄, showing that cycles to potentials, at

Fig. 1. Voltammograms for polycrystalline Au electrodes ($R = 1$) recorded at 0.01 V s^{-1} in (a) 0.05 M NaF , (b) $0.05 \text{ M K}_2\text{SO}_4$ and (c) 0.05 M KCl at 25°C .

which no more than an oxide monolayer is formed, do not result in changes in the surface roughness [11].

RESULTS AND DISCUSSION

The voltammograms of the Au electrodes ($R \approx 1$) recorded at 0.01 V s^{-1} in slightly acid (pH 5.00) 0.05 M NaF , $0.05 \text{ M K}_2\text{SO}_4$ and 0.05 M KCl are shown in Fig. 1. In 0.05 M NaF and $0.05 \text{ M K}_2\text{SO}_4$, the voltammograms exhibit the broad anodic and cathodic current peaks related to the electroformation and the electroreduction of Au oxide layers. In contrast, in KCl aqueous solutions, a remarkable increase in the anodic current occurs at potentials more positive than 0.37 V , owing to the electrodisolution of Au in the solution. Previous results [12] on the electrochemical behaviour of Au in solutions containing Cl^- ions show that Au dissolves anodically at potentials more positive than 0.3 V . However, the extrapolated anodic current, even at 0.4 V , is smaller than $10^{-7} \text{ A cm}^{-2}$ [13]. Accordingly, 0.4 V was fixed as the upper potential limit for the roughness relaxation in 0.05 M KCl . No difference in the voltammograms, except for the increase in the voltam-

Fig. 2. Typical $1/R$ vs. $t^{1/4}$ plots at different E_g values: (a) 0.05 M K_2SO_4 , $E_g = -0.6$ V ($\circ$), -0.45 V ($\bullet$), 0.4 V ($\times$); (b) 0.05 M NaF, $E_g = 0.4$ V ($\times$), -0.6 V ($\circ$), 0.2 V ($\blacktriangle$); (c) 0.05 M KCl, $E_g = -0.6$ V ($\circ$), -0.45 V ($\bullet$), 0.2 V ($\blacktriangle$) at 25°C .

metric charge, could be observed when the R values of the EDAAuEs were increased from 1 to 100.

Typical R vs. $t^{-1/4}$ plots obtained for EDAAuEs in 0.05 M NaF, 0.05 M KCl and 0.05 M K_2SO_4 solutions at different E_g values are depicted in Fig. 2. By using the value of R^{-1} for $t = 0$ and eqn. (3), r_0 is determined to be close to 5×10^{-7} cm. Otherwise, from the slopes of the straight lines, the D_s values at different E_g values can be calculated through eqn. (2), taking $a = 4.07 \times 10^{-8}$ cm, $r_0 = 5 \times 10^{-7}$ cm, values of h obtained from eqn. (3) and values of γ derived from the electrocapillary curves. To evaluate the effect of the change of γ ($\Delta\gamma$) on D_s , the γ vs. E plot was determined for each electrolyte solution (Fig. 3). The electrocapillary curves were obtained following the method of Grahame et al. [14], using the following integration constants; the metal charge density, $\sigma^m = 14 \mu\text{C cm}^{-2}$ at $E = -1.1$ V and $\gamma = 900 \text{ erg cm}^{-2}$ ($1 \text{ erg} = 10^{-7} \text{ J}$) at $E = E_{\text{pcz}}$, the potential of zero charge.

The values $\Delta\gamma$, D_s and D_{sc} , the corrected values of D_s , at different potentials for the three electrolyte solutions used in the present work are shown in Table 1. One can observe that the shift of γ caused by the applied potential affects the D_s

Fig. 3. Plot of γ vs. E for a smooth polycrystalline Au electrode in 0.05 M NaF (■), 0.05 M K_2SO_4 (▲) and 0.05 M KCl (●).

TABLE 1

Values of $\Delta\gamma$, D_s and D_{sc} obtained for polycrystalline Au in different electrolyte aqueous solutions and applied potential conditions at 25°C.

E/V	$\Delta\gamma/\text{erg cm}^{-2}$	$D_s \times 10^{14}/\text{cm}^2 \text{ s}^{-1}$	$D_{sc} \times 10^{14}/\text{cm}^2 \text{ s}^{-1}$
<i>0.05 M NaF</i>			
-0.6	2.4	4.4	4.4
-0.45	0.0	8.1	8.1
-0.30	2.6	5.6	5.6
0.0	24.5	8.5	8.7
0.20	53.1	31	33
<i>0.05 M K_2SO_4</i>			
-0.6	1.0	8.1	8.1
-0.45	1.0	13	13
-0.30	6.4	23	23
0.0	34.0	28	29
0.20	68.0	44	47
<i>0.05 M KCl</i>			
-0.6	0.5	63	63
-0.45	5.0	92	92
-0.30	17.7	110	110
0.0	75.0	220	240
0.2	140	350	410

Fig. 4. Plots of D_s vs. E_g in different electrolyte solutions: $\blacktriangle$, 0.05 M NaF; $\bullet$, 0.05 M K_2SO_4 ; $\blacksquare$, 0.05 M KCl.

values by less than 10%, as calculated with $\gamma = 900 \text{ erg cm}^{-2}$, even at the most positive potentials. It should be noted that values of γ in the range 900–1480 erg cm^{-2} are reported in the literature for polycrystalline Au [15]. The use of the highest γ value would decrease all the reported values of D_s by a factor of 1.5. Nevertheless, at present, there is no conclusive argument to decide which is the most reliable value of γ to be used in the calculations.

This fact introduces a certain limitation to the method of obtaining absolute D_s values, although the comparison of D_s values for different electrolyte solutions and applied potentials remains valid. Furthermore, concerning the question of whether the effective surface tension of small crystallites is similar to the bulk value, it should be mentioned that some γ values higher than the bulk value have been measured for small metal crystallites, using the Gibbs–Kelvin equation [16]. These results, however, were probably due to a systematic error in the measurements [16]. Also, small Ag crystallites in photographic emulsions exhibit normal γ values with respect to the bulk Ag [16].

The D_s vs. E_g plots for the different aqueous solutions are shown in Fig. 4. In 0.05 M NaF, the value of D_s increases from $5 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ at $E_g = -0.6 \text{ V}$ to a maximum value $D_s = 2.5 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ at $E_g \approx 0.2 \text{ V}$. Likewise, for $E_g > 0.2 \text{ V}$, D_s decreases to a value similar to that obtained at $E_g = -0.6 \text{ V}$. In 0.05 M K_2SO_4 , the same trend can be observed, although, in this case, the D_s values become slightly higher than those obtained in NaF aqueous solution. Thus, D_s

increases from $E_g = -0.60$ V to attain a maximum value $D_s = 4.5 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ at $E_g = 0.2$ V and, finally, decreases to a value close to that observed at $E_g = -0.6$ V. Otherwise, in 0.05 M KCl, D_s increases as E_g increases, so that $D_s = 8 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ at $E_g = 0.4$ V. As already mentioned, in 0.05 M KCl at potentials greater than 0.4 V, the proper Au electrodisolution reaction takes place. This fact restricts our roughness relaxation measurements up to $E_g \leq 0.4$ V.

The present results indicate that, at a constant potential, the mobility of Au surface atoms increases with the solution composition, according to the order $\text{NaF} < \text{K}_2\text{SO}_4 < \text{KCl}$. This sequence agrees with the specific adsorption ability of anions on Au [17]. Therefore, the effect of the applied potential on D_s can be explained through the potential dependence of anion specific adsorption.

In 0.05 M KCl, the surface mobility of Au is enhanced, as the applied potential is shifted positively and the Cl^- ion concentration in solution is increased [3]. In this case, it appears that the strong interaction of Cl^- ions with Au surface atoms leads to a faster displacement of the metal atoms. This conclusion agrees with in situ STM data of Au single crystals in acid solutions containing Cl^- ions [11,18], which indicates an increase in the step motion induced by Cl^- adsorption. However, it was also observed that a correlation exists between the surface mobility of metal atoms and the melting temperature T_m of the metal [1]. The formation of surface metal compounds with melting temperatures T_{ms} lower than T_m induces surface mobility. This assumption is based on the empirical relationships [1]

$$D_s \propto \exp(-KT_m) \quad (4)$$

$$D_s \propto \exp(-KT_{ms}) \quad (5)$$

where K is a proportionality constant. Accordingly, for AuCl_3 , a possible surface compound at the Au-Cl aqueous solution interface at sufficiently high positive potentials, $T_{ms} = 256^\circ\text{C}$ [19], i.e. a value which is much lower than $T_m = 1063^\circ\text{C}$ for Au. Considering that, for Au surface atoms in vacuo, $D_s \approx 10^{-15} \text{ cm}^2 \text{ s}^{-1}$, eqns. (4) and (5) predict that at the Au/ AuCl_3 / Cl^- interface $D_s \approx 10^{-11} \text{ cm}^2 \text{ s}^{-1}$, i.e. a value which is in good agreement with that obtained from the D_s vs. E_g plot in 0.05 M KCl (Fig. 4) at high positive potentials. Hence, the observed increase in the surface mobility of Au in 0.05 M KCl can be reasonably justified throughout the formation of the AuCl_3 surface compound.

In 0.05 M NaF and 0.05 M K_2SO_4 , the surface mobility of Au increases as E_g is increased. This effect can also be assigned to anion adsorption. However, in this case, D_s reaches a maximum value at 0.2 V, i.e. a potential where the electroformation of AuOH species begins [20], and decreases markedly for $E_g > 0.2$ V. These results indicate that, at potentials greater than 0.2 V, both SO_4^{2-} ions, which are adsorbed on Au, and F^- ions, which are very weakly adsorbed on Au, participate in the following displacement reactions:

where the braces denote adsorption sites at the Au surface and the parentheses denote adsorbed species. According to the present results, the effect of SO_4^{2-} ions on the surface mobility of Au atoms is greater than that of F^- ions.

This fact also can be understood through the interaction between the SO_4^{2-} ions and Au surface atoms. The effect of the specific adsorption of SO_4^{2-} ions on Au in acid solution has been observed [21] over the same potential range, where the value of D_s increases with potential. The adsorption of SO_4^{2-} on low index, single-crystal planes produces an overlay lattice of anions with holes, in which OH species can be adsorbed [21]. The decrease in the mobility of the Au surface atoms induced by AuOH electroformation is seemingly in contrast to recent in situ atomic force microscopy observations for the Au surface in 0.5 M H_2SO_4 [22]. However, in this case, the annealing of the surface Au was observed at potentials where the Au oxide electroformation takes place, changing the properties of the surface. Therefore, no reliable quantitative comparison of surface mobility data is possible.

The value of $D_s = 8 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ for polycrystalline Au in solutions containing F^- ions at $E_g \approx 0.0 \text{ V}$ is slightly higher than $D_s = 2 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$, as given in ref. 4 for Au(111) in 0.1 M HClO_4 at a similar potential, using in situ STM. It should be noted that, although both D_s values are obtained in solutions containing weakly adsorbable anions, they refer to different pH values and crystallographic surface conditions.

Finally, it should be noted that, even at the most negative potentials, an effect of the solution composition is still observable. In this case, this effect cannot be explained in terms of anion adsorption, but should be assigned to the proper electrolyte structure at the electrochemical interface. The structure of the solution in contact with the Au surface atoms depends on the nature of the anions in the solution [23] and, in particular, on the size of the anions and their capability for hydrogen bonding interaction with water. The effect of the solution structure on the electrochemical characteristics of the metal–solution interface should be reflected over the entire potential range covered by the present work.

CONCLUSIONS

Previous results provide valuable information about the kinetics and mechanism of roughness decay at metal–solution interfaces and the effect of anion adsorption on the decay process. They offer basic information for predicting the stability and duration of rough metal electrodes of interest in electrocatalytic reactions.

However, data reported in this work become particularly interesting for a comprehensive approach to metal corrosion processes, such as stress corrosion cracking. As already mentioned [19], the lack of D_s values for electrochemical systems and their dependence on the applied potential and electrolyte composition are the relevant problems to test stress corrosion cracking models. The present results show that, even in dilute aqueous solutions containing Cl^- ions, the surface Au atom mobility at high positive potentials becomes about three orders of magnitude greater than that resulting in aqueous solutions containing weakly

adsorbed anions or organic adsorbates [3]. For the latter solutions, the D_s values are similar to those reported for Au surfaces in vacuo [1]. The increased surface mobility of Au in solutions containing Cl^- ions can explain the susceptibility to corrosion of Au alloys in FeCl_3 [24]. Otherwise, at potential values where the Au oxide layer formation commences, the Au atom surface mobility induced by weakly adsorbed anions is considerably diminished. All these facts agree with the predictions of the surface diffusion theory of stress corrosion cracking [19], concerning the protective properties of oxide and organic inhibitors, and the beneficial role of Cl^- anions and the applied potential on this type of corrosion.

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