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# Electrocrystallization of Au nanoparticles on glassy carbon from HClO<sub>4</sub> solution containing [AuCl<sub>4</sub>]<sup>-</sup>

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#### ABSTRACT

The mechanism and kinetics of electrocrystallization of Au nanoparticles on glassy carbon (GC) were investigated in the system GC/1 mM KAuCl<sub>4</sub> + 0.1 M HClO<sub>4</sub>. Experimental results show that the gold electrodeposition follows the so-called Volmer–Weber growth mechanism involving formation and growth of 3D Au nanoparticles on an unmodified GC substrate. The analysis of current transients shows that at relatively positive electrode potentials ( $E \ge 0.84$  V) the deposition kinetics corresponds to the theoretical model for progressive nucleation and diffusion-controlled 3D growth of Au nanoparticles. The potential dependence of the nucleation rate extracted from the current transients is in agreement with the atomistic theory of nucleation. At sufficiently negative electrode potentials ( $E \le 0.64$  V) the nucleation frequency becomes very high and the nucleation occurs instantaneously. Based on this behaviour is applied a potentiostatic double-pulse routine, which allows controlled electrodeposition of Au nanoparticles with a relatively narrow size distribution.

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### 1. Introduction

Gold nanoparticles exhibit interesting size-dependent electronic, optical and chemical properties and are very attractive for various technological applications in nanoelectronics, sensorics, optics and catalysis [1–3]. A powerful technique for modification of electrodes with metal nanoparticles is the electrodeposition since the driving force and the rate of the deposition process can be easily controlled by the electrode potential and the current density [4-8]. The key to electrodeposition of nanoparticles with controlled shape and size is the knowledge of the kinetics and mechanism of initial electrocrystallization stages in the particular electrochemical system. Electrodeposition of isolated metal nanoparticles can be achieved successfully in systems with weak metal-substrate interaction. No underpotential deposition (UPD) takes place in such systems and the electrocrystallization process starts in the overpotential deposition (OPD) range with the formation and growth of 3D metal nanoparticles on an unmodified foreign substrate (Volmer-Weber growth mechanism) [6]. This growth mechanism operates on electrode substrates with low surface energy and has been observed most frequently by

electrodeposition of metals on glassy carbon (GC) [9–20], highly oriented pyrolytic graphite (HOPG) [4,21–26] and H-terminated *n*-Si [27–38]. Detailed studies of nucleation and growth kinetics by gold electrodeposition have been performed on GC and *n*-Si substrates in the systems  $GC/[Au(NH_3)_2]^+ + 1 M NH_4Cl$  [10],  $GC/[AuCl_4]^- + 6 M LiCl$  [11] and *n*-Si/[Au(CN)\_2]^- + 0.2 M KCN(pH 14) [33–35]. Several groups have used as electrolytes for electrodeposition of Au nanoparticles [AuCl\_4]^--containing acidic HClO\_4 or H\_2SO\_4 aqueous solutions as well as room-temperature ionic liquids and investigated the influence of deposition conditions on the size, structure, morphology and electrochemical properties of electrodeposited nanoparticles [14–20,39–41]. However, in these systems detailed studies of involved nucleation and growth phenomena are absent, which are important for the optimization of polarization routines for controlled electrodeposition of Au nanoparticles.

In this paper, we report a study of the kinetics and mechanism of electrocrystallization of Au nanoparticles in the system  $GC/1 \text{ mM}[\text{AuCl}_4]^- + 0.1 \text{ M HClO}_4$  by means of cyclic voltammetry, chronoamperometry and scanning electron microscopy (SEM). It is shown that the electrodeposition of Au nanoparticles follows the theoretical model for nucleation and 3D growth controlled by hemispherical diffusion. The potential dependences of the nucleation rate and the size of critical nuclei were determined from the analysis of initial parts of current transients at relatively positive electrode potentials. A double-pulse polarization routine was applied to deposit Au nanoparticles with a narrow size distribution.



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#### 2. Experimental

Electrochemical measurements were carried out at room temperature (T=294 K) in a conventional three-electrode cell using an Autolab Potentionstat/Galvanostat PGSTAT30 (Eco Chemie, The Netherlands). The electrodeposition of Au nanoparticles was performed from a solution consisting of 1 mM KAuCl<sub>4</sub> and 0.1 M HClO<sub>4</sub>. The electrolyte solution was prepared from suprapur chemicals and Millipore<sup>®</sup> water and was deoxygenated prior to each measurement with pure nitrogen. A saturated mercury sulfate electrode (SMSE) was used as reference electrode. All electrode potentials *E* given in this report are referred to the potential of the standard hydrogen electrode (SHE).

The GC substrates  $(0.6 \text{ cm} \times 0.6 \text{ cm})$  were polished with diamond paste (up to 0.3  $\mu$ m) and subsequently cleaned ultrasonically for 10 min in ethanol and 10 min in Millipore<sup>®</sup> water. The morphology and the size of electrodeposited Au nanoparticles were characterized by SEM using a Leo 1550 SEM equipment with electron beam energy of 20 keV.

#### 3. Results and discussion

The cyclic voltammogram shown in Fig. 1 illustrates the electrochemical behaviour of the system  $GC/1 \text{ mM}[AuCl_4]^- + 0.1 \text{ M HClO}_4$ . In this system the active gold species in the electrolyte solution are the  $[AuCl_4]^-$  complex ions and the overall deposition reaction can be expressed by

$$[AuCl_4]^- + 3e^- \Rightarrow Au + 4Cl^- \tag{1}$$

The absence of cathodic current at potentials more positive than 1 V in the initial cathodic scan of the cyclic voltammogram in Fig. 1 shows that an Au UPD does not occur in this system and the deposition process follows the Volmer–Weber growth mechanism. The sharp increase of the cathodic current at potentials below 1 V indicates the onset of gold electrodeposition. The constant current observed during the reversed anodic scan shows that the deposition process becomes diffusion limited. The higher cathodic current observed during the reversed scan for E > 0.97 V indicates that the deposition of gold on gold is easier than the nucleation of gold on GC. A crossover of reverse current and zero current line is observed at a potential  $E \approx 1.13$  V, which is more positive than the standard equilibrium potential  $E_{Au(III)/Au(0)}^0 = 1.00$  V corresponding to the reaction (1) [42]. This behaviour could be related to a reaction mechanism proposed previously for gold electrodeposition from



**Fig. 1.** Cyclic voltammogram recorded in the system  $GC/1 \text{ mM}[\text{AuCl}_4]^- + 0.1 \text{ M}$ HClO<sub>4</sub>. The potential scan is initiated at E = 1.32 V in the cathodic direction. Scan rate: |dE/dt| = 1 mV/s.



Fig. 2. Current transients for electrocrystallization of gold at different electrode potentials in the system  $GC/1 \, mM[AuCl_4]^- + 0.1 \, M \, HClO_4$ .

[AuCl<sub>4</sub>]<sup>-</sup>-containing electrolytes with low concentration of free Cl<sup>-</sup> ions [43,44]. According to this mechanism the overall deposition reaction (1) involves two charge transfer steps coupled with a preceding chemical reaction:

$$[\operatorname{AuCl}_4]^- \Leftrightarrow [\operatorname{AuCl}_2]^+ + 2\operatorname{Cl}^- \tag{2}$$

$$[\operatorname{AuCl}_2]' + 2e \Rightarrow [\operatorname{AuCl}_2] \tag{3}$$

$$[\operatorname{AuCl}_2]^- + e^- \Rightarrow \operatorname{Au} + 2\operatorname{Cl}^- \tag{4}$$

The cyclic voltammogram in Fig. 1 shows that the anodic dissolution of the gold deposit is strongly inhibited. This inhibition can be assigned to the low chloride concentration in the electrolyte solution and/or to the formation of a passivating film of "adsorbed oxygen" or oxide on the gold surface, which starts in the same potential range and can impede significantly the gold dissolution reaction [45,46].

The nucleation and growth phenomena in the initial stages of gold deposition were investigated by potentiostatic transient measurements. Fig. 2 shows current transients obtained at different electrode potentials in the range  $0.64 \text{ V} \le E \le 0.94 \text{ V}$ . The transients exhibit an initial current decay in the range 0.001-1 s, which cannot be related to the double-layer charging. Such falling currents in the initial parts of transients have been often observed in various electrodeposition systems and were related to different processes such as adsorption [47,48], multistep charge transfer reactions [49] and redox-processes influencing the state of the substrate surface [50]. After the initial current decay, the transients in Fig. 2 show the characteristic current increase due to the nucleation and growth of gold nanoparticles. The current maximum observed at high cathodic potentials results from the overlap of growing particles and/or their diffusion zones [5–9]. According to the model including diffusion-controlled growth of hemispherical particles proposed by Scharifker and Hills [9] the deposition transients for progressive and instantaneous nucleation can be described by the equations:

$$\left(\frac{i}{i_{\text{max}}}\right)_{\text{prog}}^{2} = 1.2254 \left(\frac{t_{\text{max}}}{t}\right) \left\{1 - \exp\left[-2.3367 \left(\frac{t}{t_{\text{max}}}\right)^{2}\right]\right\}^{2}$$
(5)

$$\left(\frac{i}{i_{\max}}\right)_{inst}^{2} = 1.9542 \left(\frac{t_{\max}}{t}\right) \left\{1 - \exp\left[-1.2564 \left(\frac{t}{t_{\max}}\right)^{2}\right]\right\}^{2} \quad (6)$$

Experimental current transients for 0.84 V and 0.64 V are represented in Fig. 3 in a non-dimensional  $(i/i_{max})^2$  vs.  $t/t_{max}$  plot and are compared with the theoretical curves given by Eqs. (5) and (6). It is clearly seen, that the experimental current transient at



**Fig. 3.** Non-dimensional  $(i/i_{max})^2$  vs.  $(t/t_{max})$  plots of current transients for electrocrystallization of gold at E = 0.84 V and E = 0.64 V compared to the theoretical curves corresponding to the models for progressive nucleation (solid line) and instantaneous nucleation (dashed line).

0.84 V corresponds to the model involving progressive nucleation. The transient at 0.64 V fits relatively well with the theoretical curve for instantaneous nucleation. In this case the deviation of experimental points from the theoretical curve at short times ( $t < t_{max}$ ) can be connected with the contribution of the initial falling current discussed above to the total current. Assuming that at  $t = t_{max}$  this contribution is negligible the number density  $N_0$  of growing nanoparticles generated instantaneously on the active nucleation sites can be estimated from the coordinates of the maximum  $i_{max}$  and  $t_{max}$ , which are coupled according to the theoretical model by [9]:

$$(i_{\max}t_{\max})_{inst}^2 = 0.065(zF)^2 \left(\frac{c^3}{8\pi V_m N_0^2}\right)^{1/2}$$
(7)

where z=3 is the number of electrons involved in the overall deposition reaction, *F* is the Faraday constant,  $c=10^{-6} \text{ mol cm}^{-3}$  is the concentration of gold ions in the bulk electrolyte and  $V_{\rm m} = 10.19 \text{ cm}^3 \text{ mol}^{-1}$  is the molar volume of gold. A value of  $N_0 = 3 \times 10^6 \text{ cm}^{-2}$  was estimated with Eq. (7) from the coordinates of the maximum of experimental current transient at 0.64 V.



**Fig. 4.** Current transient for electrocrystallization of gold at E=0.54 V. The inset shows the *i* vs.  $t^{-1/2}$  plot of the transient.



**Fig. 5.**  $i^{2/3}$  vs. *t* plots of the initial rising parts of the transients shown in Fig. 2.

Fig. 4 presents a current transient measured at a relatively low electrode potential E = 0.54 V. The inset of the figure shows that the current transient follows the Cottrell relation [51]:

$$i = zFc \left(\frac{D}{\pi}\right)^{1/2} t^{-1/2} \tag{8}$$

where *D* is the diffusion coefficient of gold ions in the electrolyte. From the slope of the linear  $i - t^{-1/2}$  dependence in Fig. 4 and Eq. (8) was estimated a value for the diffusion coefficient of  $D = 1.1 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>, which is close to the values reported previously [13,25].

Information about the nucleation kinetics was obtained by analyzing the initial rising parts of current transients obtained in the potential range  $0.84 \text{ V} \le E \le 0.94 \text{ V}$ , where the nucleation is progressive. The transient analysis was performed at relatively short times, i.e. before the overlapping of the diffusions zones of growing gold nanoparticles. Fig. 5 shows the initial rising parts of current transients from Fig. 2 as  $i^{2/3}$  vs. *t* plots. The observed linear dependences are in agreement with the model for progressive nucleation and diffusion-controlled growth and can be expressed by [9]

$$i^{2/3} = -1.53Dc(\pi JzF)^{2/3} V_{\rm m}^{1/3}(t-t_0)$$
<sup>(9)</sup>

where  $t_0$  represents the induction period. The nucleation rate *J* was extracted from the slopes of the straight lines in Fig. 5 using Eq. (9) and the value for the diffusion coefficient  $D = 1.1 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup> estimated above. The obtained data for the nucleation rate at different electrode potentials were analyzed on the basis of atomistic theory of electrochemical nucleation [5–7,11]. According to this theory the nucleation rate *J* is given by

$$J(E) = A(n_{\rm crit}) \exp\left[-\frac{(1 - \alpha + n_{\rm crit})zeE}{kT}\right]$$
(10)

where  $n_{crit}$  is the number of atoms in critical nucleus for a given potential range,  $(1 - \alpha)$  is the cathodic charge transfer coefficient and *e* is the elementary charge. Eq. (10) predicts a change of the slope of the ln *J* vs. *E* plot of experimental data if clusters with different size  $n_{crit}$  are critical nuclei in neighbouring potential ranges.

Fig. 6 represents the experimental data for the nucleation rate at different electrode potentials obtained from the linear  $i^{2/3} - t$  dependences in Fig. 5. The ln *J* vs. *E* plot of the experimental data shows two distinct linear regions in good agreement with the predictions of the atomistic nucleation theory. From the slopes of the straight lines in Fig. 6 using Eq. (10) with  $\alpha$ =0.5 were



**Fig. 6.** Potential dependence of the nucleation rate obtained from the linear  $i^{2/3} - t$  plots in Fig. 5.

estimated values of  $n_{\rm crit} = 1$  and  $n_{\rm crit} = 0$  for the potential ranges 0.94 V > E > 0.91 V and 0.91 V > E > 0.84 V, respectively. These values indicate that a single Au adatom is critical nucleus in the potential range  $0.94 \text{ V} \ge E \ge 0.91 \text{ V}$ , whereas at potentials more negative than 0.91 V each nucleation site plays the role of critical nucleus and the single Au atom adsorbed on a nucleation site represents a supercritical cluster, which can grow spontaneously. The results are in agreement with previous studies on gold electrodeposition in the system GC/5 mM HAuCl<sub>4</sub> + 6 M LiCl, where values of  $n_{\rm crit}$  below 1 were reported for relatively low electrode potentials (E < 0.84 V) [13].

Information on the shape, size and number density of electrodeposited gold nanoparticles was obtained by SEM observations. Fig. 7 shows a typical SEM image of Au nanoparticles deposited under conditions of instantaneous nucleation at E = 0.64 V and t = 100 ms. The nanoparticles have an approximately hemispherical shape in accordance with the theoretical model applied above for the analysis of current transients. However, the analysis of SEM images shows  $N_0$ -values ranging between  $2 \times 10^8$  cm<sup>-2</sup> and  $5 \times 10^8$  cm<sup>-2</sup>, which are about two orders of magnitude higher than the value  $(N_0 = 3 \times 10^6$  cm<sup>-2</sup>) estimated from the coordinates of the current maximum of the transient at E = 0.64 V (cf. Fig. 2) using Eq. (7). This result indicates that the theoretical model does not describe realistically the interaction between the growing particles in the advanced deposition stages giving rise to the maximum of cur-



Fig. 7. SEM image of Au nanoparticles electrodeposited at E = 0.64 V for t = 100 ms.

rent transients. Such disagreement between the theoretical model and experimental results has been reported also for other electrodeposition systems [34,47,48,52-57]. It should be noted that an agreement between particle number densities obtained from analysis of current transients and from microscope images has been reported for systems involving a single charge transfer step [58,59], whereas a disagreement is observed particularly in systems involving multiple charge transfer steps [47,48,53-56] or single charge transfer step coupled with a preceding chemical reaction step [34,52]. However, a clarification of the exact reason for the observed disagreement is still missing and requires further experiments and improved theoretical modelling of involved processes taking into account the above discussion. Therefore, at present reliable information for the real number density of electrodeposited nanoparticles can be obtained by microscopic imaging.

The instantaneous nucleation observed in the potential range  $E \le 0.64$  V offers the possibility for electrodeposition of Au nanoparticles with uniform size. However, at relatively long deposition times the particles deposited under conditions of instantaneous nucleation are characterized by a relatively broad size distribution. As demonstrated by Penner [4], the broadening of size distribution results from the so-called "interparticle diffusion coupling" (IDC), which leads to a dispersion in the growth rates of individual particles. This IDC effect can be minimized applying a double-pulse polarization technique [4,5]. In this technique the first short pulse with duration  $\tau_1$  to a sufficiently low potential  $E_1$  generates small Au nanoclusters under conditions of instantaneous nucleation. This pulse is followed by a second pulse to a potential  $E_2$ , which is more positive than the critical potential for nucleation. Under these conditions the probability for formation of new nuclei becomes practically zero and the Au nanoclusters generated during the first nucleation pulse grow slowly under kinetic or mixed control. The particle diameter can be varied easily by the duration  $\tau_2$  of the second growth pulse.



**Fig. 8.** SEM image of Au nanoparticles electrodeposited by the double-pulse technique ( $E_1 = 0.64$  V,  $\tau_1 = 1$  ms;  $E_2 = 1.02$  V,  $\tau_2 = 120$  s). The corresponding particle size histogram is shown at the bottom of the image.

Basically, the double-pulse technique separates the nucleation and growth processes in time and has been developed originally for experimental studies of electrocrystallization [5-7]. In the last decade this technique has been successfully applied for electrodeposition of nanoparticles [4,24,60-62], nanowires [4,63] and compact metal films [32,35]. Fig. 8 represents a SEM image of Au nanoparticles deposited by the double-pulse method in the system investigated in this work. The corresponding particle diameter histogram shows that this technique can be successfully applied for deposition of Au nanoparticles with a relatively narrow size distribution.

#### 4. Conclusions

The results of this study show that electrocrystallization of gold in the system GC/1 mM[AuCl<sub>4</sub>]<sup>-+0.1 M HClO<sub>4</sub> fol-</sup> lows the Volmer-Weber growth mode. In the potential range 0.84 V < E < 0.94 V the electrocrystallization kinetics corresponds to the theoretical model for progressive nucleation and diffusioncontrolled growth of 3D nanoparticles. The potential dependence of nucleation rate obtained from the initial parts of current transients is analyzed on the basis of the atomistic theory of nucleation and the size of critical nuclei in this potential range is determined. The results indicate that at more negative electrode potentials (E < 0.64 V) the process of electrocrystallization occurs under conditions of instantaneous nucleation. It is demonstrated that gold nanoparticles with a uniform size can be deposited applying the double-pulse technique involving an instantaneous nucleation pulse followed by a slow growth pulse.

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