Study of Silver Electrodeposition in Deep Eutectic Solvents using Atomic Force Microscopy

Andrew P. Abbott,^a Muhammad Azam,^{a,b} Karl S. Ryder^a and Saima Saleem^{a,c}

^a Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK

^b Institute of Chemistry, University of the Punjab, Lahore, Pakistan

^c Institute of Quality & Technology Management, University of the Punjab, Lahore, Pakistan.

E-mail: apa1@le.ac.uk

Abstract

The electrodeposition of metals in ionic liquids and deep eutectic solvents leads to deposits with significantly different morphologies to those seen with aqueous solutions. The classical methods of fitting amperometric data to nucleation and growth mechanisms do not fit the data well in ionic systems and tend to focus on the short time-scale aspects of nucleation. In the current study, *ex-situ* AFM was used to model crystallite sizes and distributions by digitising and modelling the images. The deposition of silver from a deep eutectic solvent was chosen as it has been studied by several groups with a variety of techniques. The crystallite size data obtained from AFM and chronoamperometry for long time-scale deposition studies are compared and it is shown that the trends are similar but there is a discrepancy in the nuclear number density of approximately an order of magnitude. The nuclear number density was found to be consistent with aqueous nucleation studies once differences in concentration and mass transport were accounted for.

Introduction

The electrodeposition of metals using ionic liquids and deep eutectic solvents has become a popular topic because it enables the deposition of water sensitive metals and can lead to novel morphologies.¹ The origin of these different crystallite structures has not been studied in detail but it is generally the case that the crystallite sizes are smaller in ionic media than in aqueous solutions and the crystallite size distribution is relatively uniform.

The morphology and grain structure are generally thought to be strongly dependent on the early stages of the metal deposition. The most common approach to studying nucleation and growth involves analysis of current-time transients and fitting these data to theoretical models. To test the validity of the theoretical, microelectrode studies, computer simulation and direct visual monitoring of the growth of the nuclei have been applied using a variety of microscopic methods.^{2,3,4,5,6} Microscopic studies allow a direct comparison between the parameters extracted from analysis of current transients and the actual processes observed on the electrode surface. Studies of the number, size and spatial distribution of the developing nuclei have been made in aqueous solutions but none have been performed in ionic liquids.

Markov and Stoycheva⁷ made the first *ex-situ* attempt to observe a growing droplet of mercury on platinum using a double potential step technique using an optical microscopy. Milchev⁸ used the same procedure with an improved double potential step technique. Serruya *et al.*⁹ deposited lead on glassy carbon for a long period and quantified the distribution of nuclei on the surface again using optical microscopy.

Scanning probe microscopy (SPM) enables measurements to be performed with higher resolution than optical spectroscopy.^{10,11} Initially *ex-situ* AFM and SEM studies were used for the investigation of the spatial and size distribution and the morphology of the deposit and gave a reliable atomistic description of nucleation and growth for precise control of metal on metal homoepitaxy and heteroepitaxy.^{12,13}

Sonnenfeld and Hasma¹⁴ were the first to use STM to image highly oriented pyrolytic graphite (HOPG) in solution under potential control. The first effort to use SPM for an *in situ* study was made by Gewirth and Niece¹⁵ but they focused on the atomic scale appearance of electrochemically deposited adatoms rather than the determination of

nucleation parameters. Mao *et al.*¹⁶ used AFM to image a single growing silver nucleus on a carbon micro-electrode and studied the nucleation dimensions. In 2002, Hyde *et al.*¹⁷ used *in-situ* AFM to observe directly the appearance and growth of individual nuclei. We have previously used *in-situ* AFM coupled with electrochemical quartz crystal microbalance (EQCM) to explore the early stages of Zn deposition from deep eutectic solvents (1:2 ChCl: ethylene glycol).¹⁸ Higher resolution images have been obtained using TEM.¹⁹ The authors noted differences between the growth kinetics for nanoclusters and that obtained by chronoamperometric measurements. They postulated the differences could be due to the way in which the TEM experiment was carried out (small volume of electrolyte) or the competition for copper ions between clusters, although neither idea explained the magnitude of the difference in growth kinetics.

In the current study, *ex-situ* AFM was used to study silver deposition from 1:2 ChCl: ethylene glycol. This process has been extensively studied previously using different silver salts and different eutectic mixtures.²⁰ The novelty of the current approach is that the AFM images were digitised to determine the area and volume changes of individual nuclei as a function of time. The ensemble of nuclei were then fitted to predict charge time transients and these were compared to measured current-time transients obtained through chronoamperometric experiments. The aim is to study crystallite growth at semi-infinite time-scales in the typical concentrations used for ionic liquid studies.

Experimental

Choline chloride [$\text{HOC}_2\text{H}_4\text{N}(\text{CH}_3)_3\text{Cl}$] (ChCl) (Aldrich 99%) was recrystallised from absolute ethanol, filtered and dried under vacuum. Ethylene glycol (EG) (Aldrich 99+) was used as received. The Deep Eutectic Solvent (DES) was formed by stirring ChCl and EG together in a 1:2 molar ratio at 50 °C until a homogeneous, colourless liquid formed. Chronoamperometry was carried out using Echo Chemie Autolab PGSTAT12 potentiostat controlled with GPES (v 4.9) software. A three-electrode system was used consisting of a platinum working electrode (1 mm diameter, made in-house), a platinum counter electrode and a silver wire quasi reference electrode. The working electrode was polished with 0.3 μm alumina paste, rinsed and dried prior to all measurements. A silver wire quasi-reference electrode was used in all electrochemical experiments, which has been shown to have a stable reference potential under the given conditions.

The potential window of the DES was reported previously and encloses the electrochemical regions discussed in this work.¹⁸

The silver is deposited potentiostatically at -35 mV for times ranging from 10 to 6000 seconds. After each deposition, the electrode was removed from the solution and thoroughly washed with deionised water followed by ethanol to ensure the complete removal of the residual solvents.

Surface analysis was carried out using an atomic force microscope. Atomic force micrographs were acquired using a Digital Instruments (DI) Nanoscope IV, Dimension 3100 instrument using resonant tapping mode and nanoscope version 6.13 software. AFM images (20 μm x 20 μm) at five randomly selected locations were obtained after each deposition experiment. The micrographs obtained from AFM were analysed and the island volume and the projected area of all the islands were calculated by the commercial image analysis software 'Digimizer' developed by MedCalc Software.

Results

When metals are electrodeposited using over-potential control, Volmer-Weber growth usually occurs producing three dimensional islands.²¹ The nucleation over-potential usually controls the kinetics of island growth.²² When under-potential deposition does not occur, several hundred millivolts are usually required to be in the nucleation over-potential region such that island growth occurs via mixed diffusion/kinetic control.^{23,24}

The island growth kinetics for silver on a platinum electrode in the deep eutectic solvent 1:2 ChCl: EG containing 0.1 mol dm⁻³ AgNO₃ has been studied. The island growth kinetics are determined by analysing the projected area and height of all the islands at different deposition times using scaling analysis.²⁵ Analysis of the island dimensions and the distribution of nearest neighbour distances is studied using *ex-situ* AFM micrographs.

First, the platinum electrode surface was characterized. **Figure 1** shows the surface morphology of the bare platinum electrode. These micrographs show the typical polishing lines (scratches) on the whole surface of the substrate due to the mechanical polishing of the platinum electrode with alumina. These scratches are about 20-30 nm deep and about 70-100 nm wide. Occasional pits (1.2 μm in diameter) are also observed and arise due to air entrapped during the manufacturing of the electrode. The images

also reveal that the electrode surface consists of nodule-like features with an average diameter of 30-50 nm and the surface is also enriched with several surface features. However, the surface is smooth enough to be used for the investigation of the early stages of silver deposition.

Figure 1: *AFM images of the polished bare platinum electrode surface with typical morphological characteristics showing regions characteristic of “smooth” left panel and “rough regions” right panel*

Topographic characterization of deposited silver

The topographic AFM images of silver deposited on the platinum electrode surface obtained at different time intervals ranging from 10 to 6000 s are shown in **Figure 2**. It should be stressed at this point that this timescale is considerably longer than that traditionally considered for metal nucleation and growth studies. The time taken to reach a current maximum in the chronoamperogram in a DESs is traditionally 5 to 10 times longer than that found in aqueous solutions due to the high viscosity, however the overpotential required is considerably smaller than that found in classical nucleation studies due to the high metal ion concentration. A misleading assertion in the literature when comparing aqueous and ionic liquid studies assumes that the high viscosity of the latter yields differences in metal deposition rates and morphologies. A recent study comparing nickel deposition in aqueous solutions and deep eutectic solvents showed that the deposition rate was the same in both despite a 100-fold difference in the viscosity.²⁶ Nickel deposited from DESs showed different XRD responses to that deposited under the same conditions using aqueous solutions resulting in harder deposits.

Figure 2: *AFM topography images of electrodeposited silver at 0.35V obtained at different time intervals as mentioned*

Figure 2 shows AFM images of silver deposition at different timescales, demonstrating the evolution of crystallites. The silver deposits through the formation of 3D hemispherical islands with random spatial distribution over the substrate surface although some of the nuclei have aligned along the polishing line. The silver islands grow individually, both vertically and laterally with an aspect ratio of 0.5. After 100 s the individual nuclei start to interact resulting in the formation of large silver clusters and this phenomenon continues until these clusters coalesce.

Charge density

The current transients for the deposition of silver (**Figure 3a**) show the characteristics of diffusion limited growth having a t_{max} of about 10 s. The decay of current after t_{max} is slow which may be due to the small nucleation over-potential resulting in a not purely diffusion limited growth and mixed growth kinetics. The AFM images were digitised to determine the volume and hence mass of material deposited. The aim was to show that the AFM images are a true representation of the whole surface, by making a comparison between the charge density obtained from the integration of the whole current transients and the charge density obtained from all the islands in AFM images. The mass of silver deposited was calculated from the sum of the volume of each island and charge density is calculated using Faraday's law;

$$Q = \frac{nmF}{M} \quad (1)$$

where Q is the charge, n is the number of electrons involved in the process, m is the mass of silver deposited, F is the Faraday's constant and M is the molar mass of the substance.

Figure 3:

(a) Current transients for silver deposited on a platinum surface at -35 mV from a solution containing 0.1 mol dm^{-3} AgNO_3 at different time-lengths (b) Comparison of the global charge density ($\square$) and the charge density calculated from the AFM images ($\circ$).

The calculated charge density was averaged over five separate AFM images ($20 \text{ } \mu\text{m} \times 20 \text{ } \mu\text{m}$) randomly selected over the surface. Figure 3b shows a very good agreement between the global charge density and the charge density calculated from the digitised AFM images confirming that the island distribution is uniform across the surface and the AFM images are representative of the whole substrate surface.

Nuclear number density

Figure 4a shows dimensionless graphs of the current transients for the deposition of silver for deposition after 10, 20, 50 and 100 s. It shows a good agreement with the progressive nucleation and growth mechanism. This is consistent with analysis of the AFM images presented in **Figure 2** which shows the island size distribution. The time dependence of the island density for the deposition of silver before interactions of the individual nuclei is shown in **Figure 4b**. The nuclear number density increases sharply up to 20 s and then remains roughly constant up to 100 s and reaches approximately $3.25 \times 10^7 \text{ cm}^{-2}$.

Figure 4: (a) The dimensionless graphs of the current transients presented in figure 3 for different time lengths: 10 s ($\square$), 20 s ($\circ$), 50 s (Δ), 100 s ($\times$) (b) The nuclear number density calculated from the AFM images ($\diamond$), calculated from t_m and J_m Equation 4 ($\circ$) and the Heermann model, as expressed by Equations (6-8) non-linear best fit (Δ).

The graph also shows the nuclear number densities, N_0 , calculated from the maximum time and current density coordinates (t_m and J_m) using the growth law for progressive nucleation followed by diffusion limited growth (equation 2 and 5) and values ranges from 2.01 to $3.03 \times 10^6 \text{ cm}^{-2}$. This is higher than that observed for silver deposition from aqueous solutions²⁷ due to the differences in silver concentration, however, it is 2 to 3 orders of magnitude smaller than that observed using copper in the same concentration in aqueous solution.¹⁹ This suggests that nucleation in DESs is just a function of concentration and viscosity

The current maximum occurs at a time

$$t_m = \left(\frac{4.67}{AN_0\pi KD} \right)^{1/2} \quad (2)$$

With a maximum current density

$$J_m = 0.462zFD^{3/4}C(AN_0K)^{1/4} \quad (3)$$

The product $J_m^2 t_m$ yields

$$J_m^2 t_m = 0.2598 (zFC_{Ag(I)})^2 D_{Ag(I)} \quad (4)$$

$$N_s = \left(\frac{AN_0}{2KD} \right)^{1/2} \quad (5)$$

Where D is the diffusion coefficient, C is the concentration, z is the ionic charge. The N_0 values obtained from the non-linear best fit of the whole current transients using the Heermann *et al.* model (equation 6) are also compared.

$$J_{theoretical} = k_1 \exp(-k_2 t) + zFc \left(\frac{D}{\pi} \right)^{1/2} \left(\frac{\phi}{\Theta t^{1/2}} \right) [1 - \exp(-\pi k N_0 D t \Theta)] \quad (6)$$

where $k_1 \exp(-k_2 t)$ is the contribution due to the double layer charging can be quantitatively calculated using the approach proposed by Holzle and co-workers²⁸ and based on a Langmuir type adsorption-desorption equilibrium where;

$$k = \left(\frac{8\pi Mc}{\rho} \right)^{1/2} \text{ and } \phi = 1 - \frac{\exp(-At)}{At^{1/2}} \int_0^{(At)^{1/2}} \exp \lambda^2 d\lambda, \text{ known as Dawson's integral.}$$

The value of Dawson's integral can be approximated by a rational function²⁹

$$F(x) \equiv e^{-x^2} \int_0^x e^{\lambda^2} d\lambda \cong \frac{0.0513 + 0.4791x}{1 - 1.207x + 1.186x^2} \quad (7)$$

and the product $\frac{\phi}{\Theta t^{1/2}}$ in **equation 6** becomes³⁰

$$\frac{\phi}{\Theta t^{1/2}} = \frac{0.5214At^{1/2} - 1.207A^{3/2}t + 1.1864A^2t^{3/2} - 0.0513A^{1/2}}{[At - 1 + \exp(-At)](1 - 1.207A^{1/2}t^{1/2} + 1.186At)} \quad (8)$$

This reduces the equation to a relatively simple mathematical form.

The fitting of current transients is done by a 'non-linear best fitting' method using **equations 6** by varying the parameters k_1 and k_2 for charging the double layer and A , N_0 and D for the nucleation contribution. The simulation of data is conducted by a macro written in Microsoft Excel using Visual Basic. The values are in the range of 3.2 to 4.8 x 10⁶ cm⁻². Details of the fitting process are given in more detail elsewhere.³¹

The nuclear number densities calculated from the AFM images are about one order of the magnitude larger than the values calculated from the analysis of the current transients. Similar discrepancies have also been observed for other systems e.g. copper on TiN from pyrophosphate solution,³² lead on glassy carbon,³³ gold on GaAs,³⁴ Au on Si³⁵ and Cu on Au.¹⁹ The exact reason is unknown but Radisic et al. proposed that it was due, in part, to surface adsorption and diffusion which control the early stages of

nucleation.¹⁹ The applicability of fitting nucleation current-time transients has recently been questioned due primarily to the irreproducibility of the data as nucleation is a random process and these data fit poorly to the rigid models of such as those described above.³⁶ Harniman described the use of lateral molecular force microscopy to study nucleation with an improved spatiotemporal resolution.³⁶ The major discrepancy in all these models appears to be the assumption that crystallites growing in 3D hemispherical islands. It is quite clear that the timescale of the experiment affects the validity of this model. Figure 2 shows that at $t < 10$ s most islands are hemispherical but as they grow the diffusion fields overlap and the models break down. This is the advantage of a 3D imaging technique like AFM as opposed to a 2D technique.

Spatial distribution

The local environment around a growing island has a very strong influence on its growth. The analysis of the islands' spatial distribution can provide an insight into the kinetics of nucleation and growth. The spatial distribution may be random, cluster or dispersed. The key feature of the models proposed for the nucleation and growth of the islands is complete spatial randomness (CSR).²⁵ CSR assumes that the probability of nucleation occurring at a position on the surface is the same for all positions.

Analysis of the nearest neighbour distance (NND) is a useful tool to characterise the spatial distribution.³⁶ The spatial correlation between islands are examined using point pattern analysis which looks at the 2D distribution of nuclei as they grow.³⁷ **Figure 5** shows the probability distribution of islands for NNDs at different times up to 100 seconds, the data were obtained from the five AFM images ($20\ \mu\text{m} \times 20\ \mu\text{m}$) and a total of 140 nuclei are analysed in each case. At short times, between 10 and 20 s, the spatial distribution is narrow but it broadens at longer times due to the coalescence of nuclei resulting in adatom depletion zones around the islands which suppresses nucleation in these regions. This phenomenon is consistent with surface diffusion-mediated lateral island growth. The solid lines in **Figure 5** correspond to the fitted Poisson distribution for complete spatial randomness. The experimental data fits well to the Poisson distribution i.e. the probability of finding ' n ' particles in any arbitrary region of area, A , follows a Poisson distribution,³⁸

$$f(n) = \frac{(\rho A)^n}{n!} e^{-\rho A} \quad (9)$$

Where ρ is the number of particles per unit area and corresponds to the island density if islands are considered as zero-volume particles.

These results indicate there is no statistically significant spatial correlation between islands even after long times, suggesting that they are randomly distributed over the surface. These data contrast with those found by Serruya et al.³¹ who studied silver deposition in aqueous ammonia and chloride solutions. They found that nucleation exclusion zones occurred around nuclei and this increased the nearest neighbour nucleation distance. This was also found for the deposition in nitrate based electrolytes. It should be stressed that both studies were performed at much higher over-potentials (100 – 200 mV) in solutions with much lower metal ion concentrations (2.2 mM).

(10 s)

(20 s)

(50 s)

(100 s)

Figure 5: *Nearest-neighbour distance distributions at different times of deposition obtained after spatial analysis of 140 islands from the five randomly selected AFM images. The solid lines corresponds to the fitted Poisson distributions for complete spatial randomness indicating the good fit of the experimental data.*

Island growth kinetics

The island growth kinetics are determined using scaling analysis²⁵ based on the evolution of island sizes and shapes which are determined from the volume and projected areas of each island in five AFM micrographs. **Figure 6** shows plots of the volume versus the projected area of the islands. Solid lines show the isotropic growth of ideal hemispherical islands according to the relationship in equation 10,

$$V = \frac{2}{3\sqrt{\pi}} A^{3/2} \quad (10)$$

where V is the volume of the island and A is the projected area of the island and $3/2$ is the scaling exponent (m).

The graphs exhibit a broad distribution in both volume and area due to their different birth times (progressive nucleation). It is assumed that each nucleus grows independently due to spatial random distribution of the growing nuclei and hence all the nuclei obey the same growth power law from which geometric information can be extracted.

The scaling exponent (m) is determined by the slope of a plot of $\log V$ vs $\log A$ (which should be 1.5 (eqn 10)) and was found to be 1.48 which indicates that the island growth is isotropic. This shows that growth of the islands is not diffusion controlled and the high viscosity of the DES does not affect the uniformity of island growth. At 50 and 100 s a slight deviation from the power law is observed which is probably due to the onset of coalescence as shown in Figure 2.

Figure 6: Plot of volume vs. projected area of silver hemispherical islands (120 islands at each time interval). The solid line shows isotropic island growth.

Conclusion

The electrodeposition of Ag(I) from a deep eutectic solvent has been investigated using *ex-situ* AFM to probe the nucleation and growth mechanism. This technique gives a more representative measure of the nuclear number density which is independent of assumptions made for the nucleation and growth rates. It is shown that the discrepancy between the mechanisms reported in aqueous solutions and ionic liquids arises from the different experimental conditions used in the two liquids. The high metal ion concentrations typically used in ionic liquids results in high nucleation number densities, small nuclei sizes and a relatively narrow distribution of crystallite sizes. Comparing the nuclear number density with values obtained using aqueous solutions at similar metal concentrations, smaller values are obtained in the DES due to the higher viscosity and lower diffusion coefficients. The nucleation and growth in DESs appears

to fit with standard models and the resultant morphology differences compared to aqueous solutions result from differences in mass transportation.

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