

Supporting Information

Electrochemical Nucleation and Growth Kinetics: Insights from Single Particle Scanning

Electrochemical Cell Microscopy Studies

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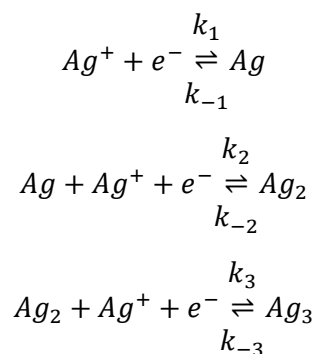
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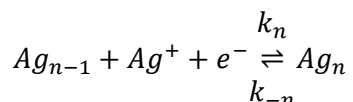
Theoretical Framework

Basic Assumptions

The nucleation and growth of Ag particles can be assumed to follow a reaction scheme of the form:



which can be more compactly expressed as:



where Ag_n is a particle consisting of n atoms and k_n/k_{-n} are forward/reverse rate constants for the formation of Ag_n . These rate constants can be assumed to adopt the standard expressions for a one-electron reduction or oxidation:

$$\begin{aligned} k_n &= a_{Ag^+} k^0 e^{-\frac{\alpha \Delta G_{n-1 \rightarrow n}}{k_b T}} \\ k_{-n} &= k^0 e^{-\frac{(1-\alpha) \Delta G_{n-1 \rightarrow n}}{k_b T}} \end{aligned}$$

Here, k^0 is a rate constant (s^{-1}) reflecting the general facility of Ag^+ reduction, α is the corresponding transfer coefficient, a_{Ag^+} is the activity of Ag^+ ions in solution, $k_b T$ is Boltzmann's constant times the absolute temperature, and $\Delta G_{n-1 \rightarrow n}$ represents the change in free energy associated with the reaction. This free energy change is:

$$\Delta G_{n-1 \rightarrow n} = \Delta G_{f,n} - \Delta G_{f,n-1}$$

where the free energy of formation is given by:

$$\Delta G_{f,n} = \Delta G^0 n + \sum A_i \gamma_i$$

Here, ΔG^0 is the standard free energy change associated with the deposition of an atom onto bulk silver, A_i is the area of the i -th interface involved in the deposition process, and γ_i is its corresponding surface energy. This equation assumes that the stability of the particles can be treated in a defined way as a function of size, which while a good first approximation, is not appropriate for very small clusters. The A_i can be expressed in terms of n by introducing geometric factors, B_i :

$$B_i = \frac{A_i^3}{V^2} = \frac{A_i^3}{V_a^2 n^2}$$

Here, V is the particle volume, A_i is the area of the i -th interface, and V_a is the atomic volume of the particle material (here Ag). Incorporating these expressions make the free energy of formation:

$$\Delta G_{f,n} = \Delta G^0 n + V_a^{2/3} n^{2/3} \sum B_i^{1/3} \gamma_i$$

This equation would include terms from each relevant interface in the particle deposition process, of which there would usually be three: substrate-electrolyte, particle-electrolyte, and substrate-particle. More conveniently, these could be implicitly described in terms of an “effective” surface energy using based on the particle-electrolyte interface, where it is assumed:

$$B_{p-e}^{1/3} \gamma_{eff} = B_{p-e}^{1/3} \gamma_{p-e} + B_{s-e}^{1/3} \gamma_{s-e} + B_{s-p}^{1/3} \gamma_{s-p}$$

In the discussion in the main text, we assume $B = B_{p-e}$ and $\gamma = \gamma_{eff}$. Although it is not a focus of the present work, the observed difference in the effective particle surface energy would therefore represent (assuming similar particle geometries):

$$\gamma_{eff,C} - \gamma_{eff,ITO} = \frac{B_{s-e}^{1/3} (\gamma_{C-H_2O} - \gamma_{ITO-H_2O}) + B_{s-p}^{1/3} (\gamma_{C-Ag} - \gamma_{ITO-Ag})}{B_{p-e}^{1/3}}$$

I.e., if the surface energies of the substrate-electrolyte interfaces were known, the difference in the surface energies of the substrate-particle interfaces could be determined.

Ignoring these subtleties, the free energy of formation can be expressed more simply as:

$$\Delta G_{f,n} = \Delta G^0 n + B^{1/3} V_a^{2/3} \gamma n^{2/3}$$

$\Delta G_{n-1 \rightarrow n}$ is then given by:

$$\Delta G_{n-1 \rightarrow n} = \Delta G^0 + B^{1/3} V_a^{2/3} \gamma [n^{2/3} - (n-1)^{2/3}]$$

It's instructive to recognize that as $n \rightarrow \infty$ $\Delta G_{n-1 \rightarrow n} \rightarrow \Delta G^0$. This expression can be simplified somewhat by making the following substitutions:

$$\eta = \frac{q(E - E^0)}{k_b T} = \frac{\Delta G^0}{k_b T} \qquad \chi = \frac{B^{1/3} V_a^{2/3} \gamma}{k_b T}$$

where E is the applied potential, E^0 is the standard reduction potential. η and χ are dimensionless constants representing the applied electrochemical driving force and surface energy, respectively. The rate constants can then be expressed more simply as:

$$k_n = a_{Ag} k^0 e^{-\alpha\chi[n^{2/3}-(n-1)^{2/3}]} e^{-\alpha\eta}$$

$$k_{-n} = k^0 e^{(1-\alpha)\chi[n^{2/3}-(n-1)^{2/3}]} e^{(1-\alpha)\eta}$$

The critical nucleus size, where $\Delta G_{f,n}$ reaches a maximum, can be found in terms of η and χ as:

$$\left. \frac{\partial \Delta G_{f,n}}{\partial n} \right|_{n=n_c} = 0 \quad \Rightarrow \quad n_c = -\frac{8}{27} \frac{\chi^3}{\eta^3}$$

Quasi-equilibrium Kinetic Models

Traditional models employed to model the electrochemical nucleation of small particles rely on an assumption of quasi-equilibrium. Following this approach, one assumes the densities of particles below a certain critical size and of vacant nucleation sites on the electrode surface are effectively constant. While details can be found elsewhere,^{1,2} this ultimately predicts a nucleation rate of the form:

$$J_{nuc} \approx Z\Gamma_0 k_{n_c} e^{-\frac{\Delta G_{f,c}}{k_b T}} = k_{nuc} \Gamma_0$$

Here, Z is a numerical factor which depends on the geometry of the particle, k_{n_c} has the definition provided above, and $\Delta G_{f,c}$ is the free energy of formation of a cluster of critical size, n_c . Γ_0 is the surface density of vacant nucleation sites on the electrode surface. J_{nuc} therefore represents the formation rate ($\text{cm}^{-2} \text{s}^{-1}$) of stable nuclei on the electrode.

Following these assumptions, the generation of nuclei on the electrode surface would follow:

$$\frac{d\Gamma_{nuc}}{dt} = k_{nuc} \Gamma_0 = (\Gamma^0 - \Gamma_{nuc}) k_{nuc}$$

$$\Gamma_{nuc}(t) = \Gamma^0 (1 - e^{-k_{nuc} t})$$

Here, Γ^0 is the total number of possible nucleation sites on the surface. The probability of a particle nucleating in the vicinity of a particular time can be generated from this expression via:

$$P_n(t) = \frac{d\Gamma_{nuc}}{dt} \frac{1}{\Gamma^0} = k_{nuc} e^{-k_{nuc} t}$$

This implies that the nucleation times observed for a system following the quasi-equilibrium approximation should be exponentially distributed with a timescale dictated by k_{nuc} . If one adopts a more stringent view of the quasi-equilibrium condition, requiring $\Gamma_{nuc} \ll \Gamma^0$, this becomes:

$$P_n(t) \approx k_{nuc} (1 - k_{nuc} t)$$

which predicts an even or linear distribution of nucleation times. As described in the main text, neither assumption does an appropriate job of modeling the nucleation times observed in our SECCM studies.

Time-Dependent Kinetic Model

Here, we have modeled the nucleation and growth of particles by generating explicit solutions to the set of coupled differential equations:

$$\frac{d\Gamma_0}{dt} = -k_1\Gamma_0 + k_{-1}\Gamma_1$$

$$\frac{d\Gamma_1}{dt} = k_1\Gamma_0 - (k_{-1} + k_2)\Gamma_1 + k_{-2}\Gamma_2$$

$$\frac{d\Gamma_2}{dt} = k_2\Gamma_1 - (k_{-2} + k_3)\Gamma_2 + k_{-3}\Gamma_3$$

...and so on. This can be generically represented (making appropriate exceptions for Γ_0) as:

$$\frac{d\Gamma_n}{dt} = k_n\Gamma_{n-1} - (k_{-n} + k_{n+1})\Gamma_n + k_{-(n+1)}\Gamma_{n+1}$$

While the generation of explicit solutions to this set of differential equations is infeasible, they can be straightforwardly solved numerically. To do so, consider a set of $N + 1$ differential equations of the above form (where N is significantly larger than n_c) written in matrix form as:

$$\mathbf{K}\boldsymbol{\Gamma} = \mathbf{D}$$

where the matrices are defined via:

$$\mathbf{K} = \begin{pmatrix} -k_1 & k_{-1} & 0 & \dots & 0 & 0 & 0 \\ k_1 & -(k_{-1} + k_2) & -k_2 & \dots & 0 & 0 & 0 \\ 0 & k_2 & -(k_{-2} + k_3) & \dots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \dots & -(k_{-(N-2)} + k_{(N-1)}) & k_{-(N-1)} & 0 \\ 0 & 0 & 0 & \dots & k_{N-1} & -(k_{-(N-1)} + k_N) & k_{-N} \\ 0 & 0 & 0 & \dots & 0 & k_N & -k_{-N} \end{pmatrix}$$

$$\boldsymbol{\Gamma} = \begin{pmatrix} \Gamma_0 \\ \Gamma_1 \\ \vdots \\ \Gamma_N \end{pmatrix} \quad \mathbf{D} = \begin{pmatrix} \frac{d\Gamma_0}{dt} \\ \frac{d\Gamma_1}{dt} \\ \vdots \\ \frac{d\Gamma_N}{dt} \end{pmatrix}$$

Solutions to the resulting differential equations can be found through analysis of \mathbf{K} to find its corresponding eigenvalues (λ_i 's) and eigenvectors ($\boldsymbol{\psi}_i$). Solutions can then be found via:

$$\boldsymbol{\Gamma}(t) = \boldsymbol{\psi}\boldsymbol{\lambda}\mathbf{X}$$

Here, $\boldsymbol{\psi}$ is a square matrix composed of the obtained eigenvectors and $\boldsymbol{\lambda}$ is a diagonal matrix of the form:

$$\boldsymbol{\lambda} = \begin{pmatrix} e^{\lambda_0 t} & 0 & \dots & 0 & 0 \\ 0 & e^{\lambda_1 t} & \dots & 0 & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \dots & e^{\lambda_{N-1} t} & 0 \\ 0 & 0 & \dots & 0 & e^{\lambda_N t} \end{pmatrix}$$

\mathbf{X} is a vector consisting of constants which accounts for the initial values of Γ_n through:

$$\boldsymbol{\psi X} = \boldsymbol{\Gamma}(t = 0) = \begin{pmatrix} \Gamma^0 \\ 0 \\ \vdots \\ 0 \end{pmatrix}$$

The vector resulting from these calculations, $\boldsymbol{\Gamma}(t)$, can be used to calculate nucleation rates by differentiating the total surface coverage of particles above a critical size:

$$P_n = \frac{1}{\Gamma^0} \frac{d}{dt} \sum \Gamma_{n > n_c}$$

The P_n distributions displayed in the main text were calculated following this procedure, varying χ and k^0 in the rate constant expressions to achieve good agreement with experimental data. In these calculations, n_c was chosen to be that where $\Delta G_{f,n} = 0$, $n_c = -(\chi/\eta)^3$, which was found to yield more consistent results in the Monte Carlo simulations described below.

Monte Carlo Simulations of Particle Nucleation Kinetics

Nucleation time distributions can also be generated through a Monte-Carlo type simulation. To illustrate this, consider that the lifetime of a particle of size n (τ_n) can be described via:

$$\tau_n = \frac{1}{k_{-n} + k_{n+1}}$$

where k_{-n} and k_{n+1} have the same definitions. The time spent at this size (Δt_n) would be expected to follow an exponential distribution:

$$P_{\Delta t} = \frac{1}{\tau_n} e^{-\frac{\Delta t}{\tau_n}}$$

The probability of the particle increasing in size at the next reaction step is:

$$p_+ = \frac{k_{n+1}}{k_{n+1} + k_{-n}} = 1 - p_-$$

With this in mind, the random nucleation trajectory of an individual particle can be generated through a simple algorithm where:

1. A time-step is generated by sampling an exponential distribution. A random number, x , between 0 and 1 is generated and used to calculate a time step via:

$$\Delta t_n = -\tau_n \ln(1 - x)$$
2. The direction (forward or backward) is determined by comparing another random number to p_+ . If $x < p_+$, n is increased by 1. If $x > p_+$, it is decreased by 1.
3. If $n > n_c$, the simulation is terminated. Otherwise, the process is repeated from 1.

Additional Experimental Data

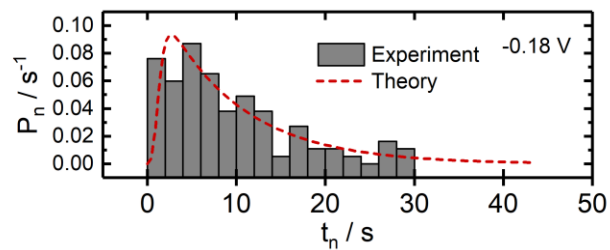


Figure S1: Rescaled data from **Figure 4** in the main text depicting probability density of Ag nucleation times on ITO at -0.18 V vs. Ag QRCE.

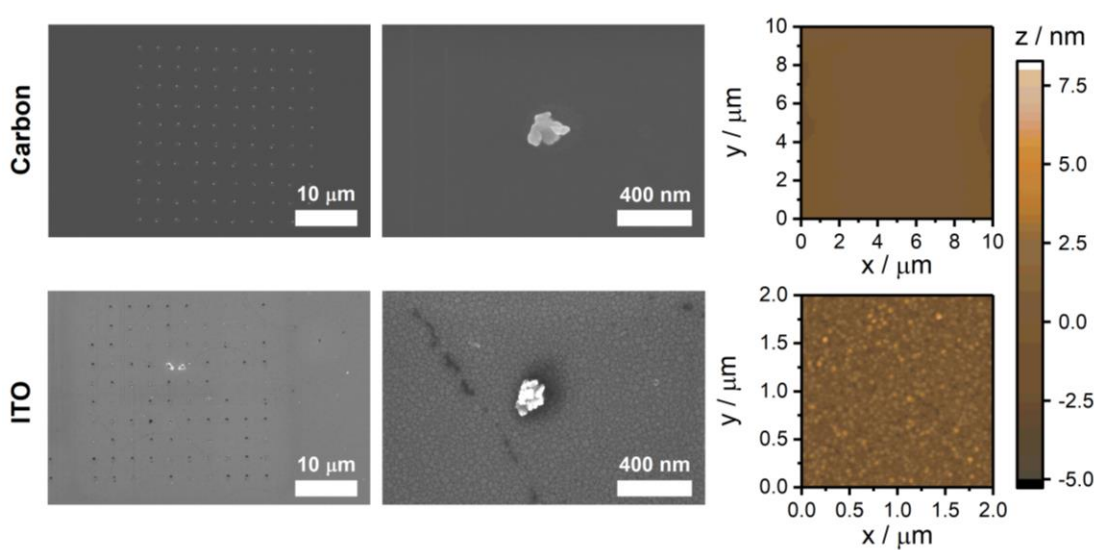


Figure S2: SEM images of Ag nanoparticle arrays deposited on C and ITO electrodes (left) and atomic force microscopy images of bare C and ITO electrodes (right).

References

- 1 A. Milchev, *ChemTexts*, 2016, **2**, 1–9.
- 2 E. Budevski, G. Staikov and W. J. Lorenz, *Electrochemical Phase Formation and Growth*, DOI:10.1002/9783527614936.