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Mathematical Modeling of Cyclic Voltammogram Curves of Copper Deposition [1,2]

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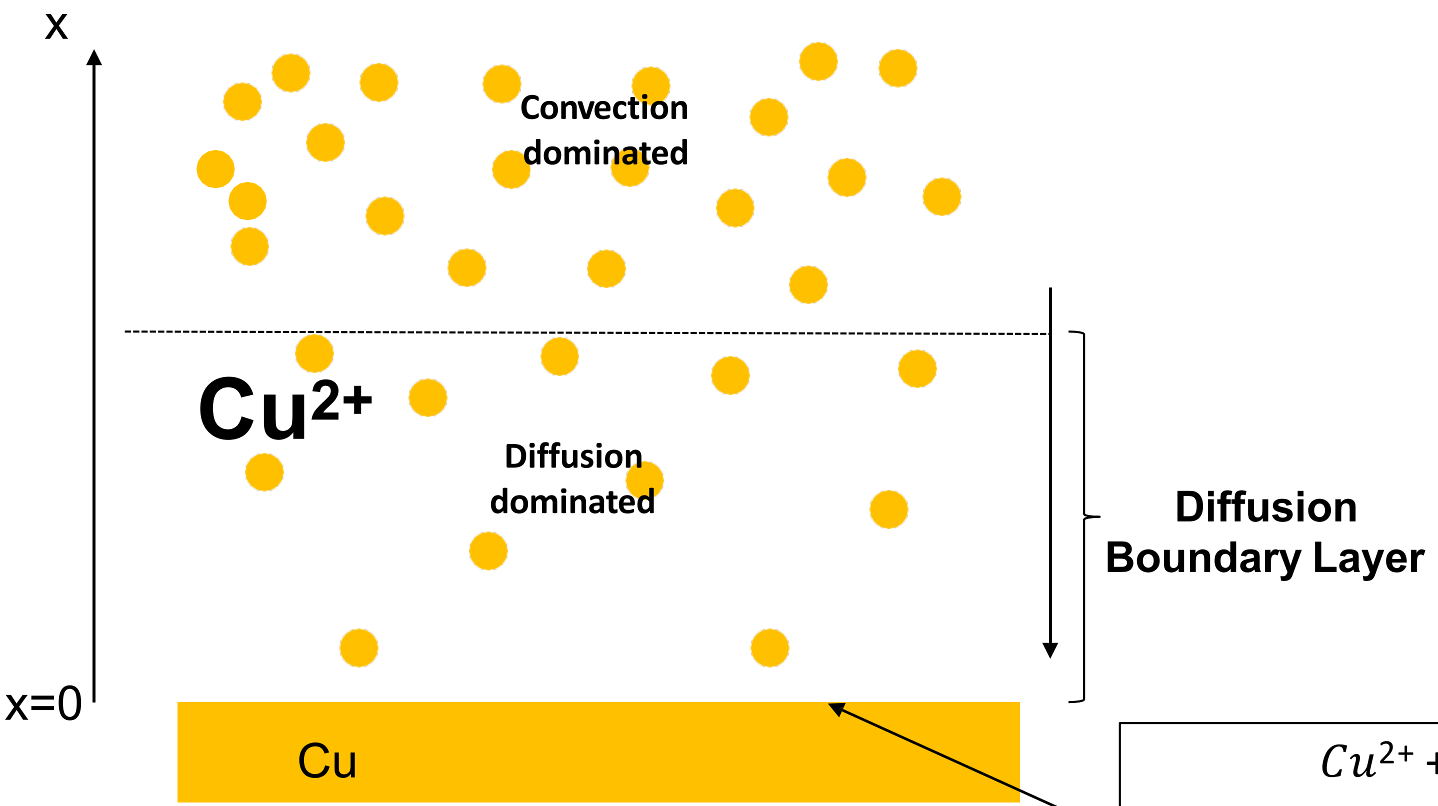
Motivation

- Manufacturing of interconnects and packaging of integrated circuits are usually achieved by electrodeposition of Cu and other metals
- For large features in packaging like Cu micro bumps forced convection is provided
- Forced convection reduces deposition time, but results in non-uniform deposition
- Special additives are added to modify deposition profile and tune nucleation and growth of metal
- Simulation of Cu deposition in the presence of additives can be very much beneficial to the semi-conductor manufacturing industry
- Simulation requires determination of the kinetic parameters of additives
- A semi-analytical method to extract kinetic parameters of additives (suppressor) is discussed

Process for extract Kinetic Parameters of Suppressor

- The process involves solving simultaneous one-dimensional convection-diffusion equation for Copper and Suppressor
- The boundary condition of suppressor includes terms for 'adsorption' and 'desorption'.
- The current is a convoluted function of surface coverage of the additive; hence the differential equations are coupled.
- The surface coverage is solved from the following mass balance equation:
  - **Consumption = Adsorption – Desorption**
- Adsorption, Desorption and Consumption terms are dependent on kinetic parameters.
- The solution is obtained over a range of voltage to generate the theoretical CV curve.
- For a given additive (suppressor) dosage, the loss function is computed between the theoretical and experimental CV curves.
- The loss function is minimized using **Particle Swarm Optimization** algorithm considering the kinetic parameters of the additives as variables

Physiochemical Model (Cu without additives)



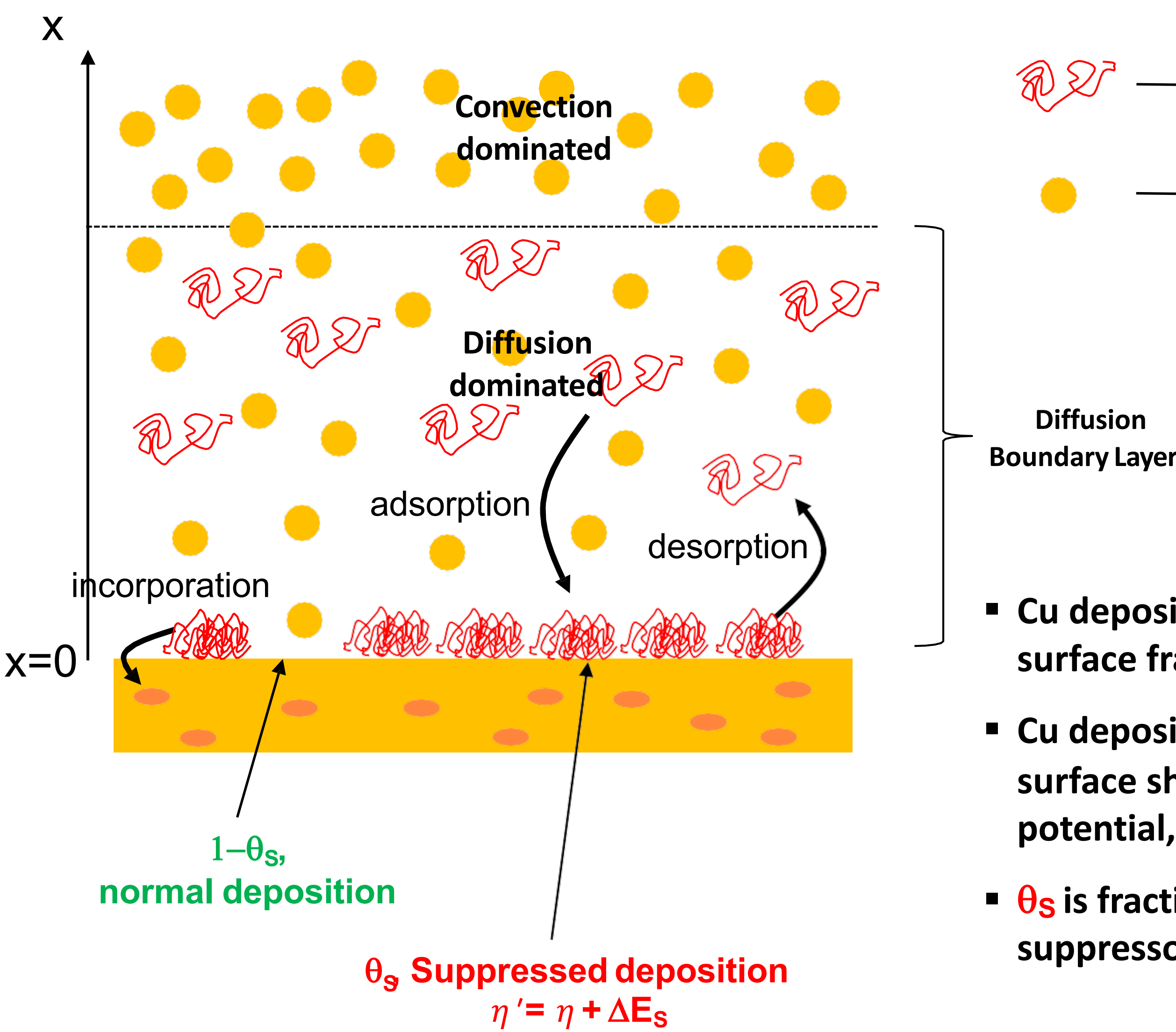
$$Cu^{2+} + 2\,e \rightarrow Cu$$

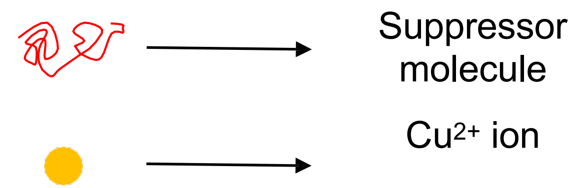
$$r = k_{Cu} \cdot exp(-b_{Cu} \cdot \eta) \cdot C_{Cu^{2+},x=0}$$

- **Tafel equation** is used for cathodic deposition only
- Applicable for RDE and 3D geometry

k_{Cu} : Reaction rate constant
b_{Cu} : Tafel slope
η : Over potential for deposition (after the correction of ohmic drop)

Physiochemical Model (with Suppressor)





- **Cu deposition on additive free surface fraction remains unchanged.**
- **Cu deposition on suppressor covered surface shifts by a constant over potential, ΔE_S.**
- **θ_S is fractional surface coverage of suppressor on surface**

Analytical Solution and Determination of Parameters

- **Governing Differential Equation (steady state):**

$$\frac{d^2 C_{Cu}}{dx^2} - \frac{N}{\square} \frac{dC_{Cu}}{dx} = 0$$

$$\frac{d^2 C_S}{dx^2} - \frac{N}{D_S} \frac{dC_S}{dx} = 0$$

$$N = -0.51023\, \omega^{\frac{3}{2}} \nu^{\frac{-1}{2}}$$

$C_{Cu}*$: Cu concentration at infinity

C_S*: Suppressor concentration at infinity

- **Boundary conditions:**

$$@\ x = 0,\ D_{\square} \frac{dC_{Cu}}{\square} = A_{\square} (1 - \theta_S) C_{\square}$$

$$@\ x = \infty,\ C_{Cu} = C_{\square}^{*}$$

$$A_{Cu} = k_{Cu}\, e^{-b_{Cu}\eta}$$

$$@\ x = 0,\ D_S \frac{dC_S}{dx} = A_{S,\square} (1 - \theta_S) C_S - \theta_S A_{S,D}$$

$$@\ x = \infty,\ C_S = C_S*$$

$$\eta' = \eta + \Delta E_S$$

$$A_{S,D} = k_{S,D} e^{-b_{S,D}\eta'}$$

$$A_{S,\square} = k_{S,\square}\, e^{-b_{S,AD}\eta'}$$

$$@\ x = 0,\ A_{S,AD} C_S (1 - \theta_S) = A_{S,D}\theta_S + A_8 \theta_S A_{Cu} C_{Cu} (1 - \theta_{eq})$$

$$A_8 = k_8\, e^{-b_8\eta'}$$

$$\theta_{eq} = \theta_s e^{-b_8\eta'}$$

Analytical Solution and Determination of Parameters

- **Solution (after applying boundary conditions):**

C_{Cu}^* : Cu concentration at infinity

C_S*: Suppressor concentration at infinity

$$C_{Cu}(0) = C_{Cu}^*\left[1 - \frac{\beta\Gamma(0.333,0)}{\Gamma(0.333,0) + 3^{\frac{2}{3}}\alpha^{\frac{1}{3}}}\right]$$

$$\frac{dC_{Cu}}{dx} = \frac{3^{\frac{2}{3}}\alpha^{\frac{1}{3}}\beta C_{Cu}^*}{\beta\Gamma(0.333,0) + 3^{\frac{2}{3}}\alpha^{\frac{1}{3}}}$$

Where, $\alpha = \frac{N}{D_{Cu}}$, $\beta = \frac{k_{Cu}(1-\theta_{eq})e^{-b_{Cu}\eta}}{D_{Cu}}$, and Γ is the incomplete Gamma function

$$C_S(0) = C_S^*\frac{(\theta_S A_{S,D} - (1-\theta_S)A_{S,AD})\Gamma(0.333,0)}{A_{S,AD}(1-\theta_S)\Gamma(0.333,0) + 3^{\frac{2}{3}}\left(\frac{N}{D_S}\right)^{\frac{1}{3}}} + C_S^*$$

$$A_{S,D} = k_{S,D}\, e^{-b_{S,D}\eta'}$$
$$A_{S,AD} = k_{S,AD}\, e^{-b_{S,AD}\eta'}$$

- **Measurable quantity (deposition rate) :**

$$Current\ Density = 2 * 96485 * \frac{1}{1000} * D_{Cu}\frac{dC_{Cu}}{dx}(x=0)$$

$$= 2 * 96485 * \frac{1}{1000} * D_{Cu}\frac{3^{\frac{2}{3}}\alpha^{\frac{1}{3}}\beta C_{Cu}^*}{\beta\Gamma(0.333,0) + 3^{\frac{2}{3}}\alpha^{\frac{1}{3}}}$$

Analytical Solution and Determination of Parameters

- **Concentrations at the surface:**

$$C_S(0) = C_S^* \frac{(\theta_S A_{SD} - (1-\theta_S) A_{SAD})\,\Gamma(0.333,0)}{A_{SAD}(1-\theta_S)\,\Gamma(0.333,0) + 3^{\frac{2}{3}}\left(\frac{N}{D_S}\right)^{\frac{1}{3}}} + C_S^*$$

$$C_{Cu}(0) = C_{Cu}^*\left(1 - \frac{\beta\,\Gamma(0.333,0)}{\Gamma(0.333,0) + 3^{\frac{2}{3}}\alpha^{\frac{1}{3}}}\right)$$

- **On the surface, the concentrations are related as:**

Consumption = Adsorption - Desorption

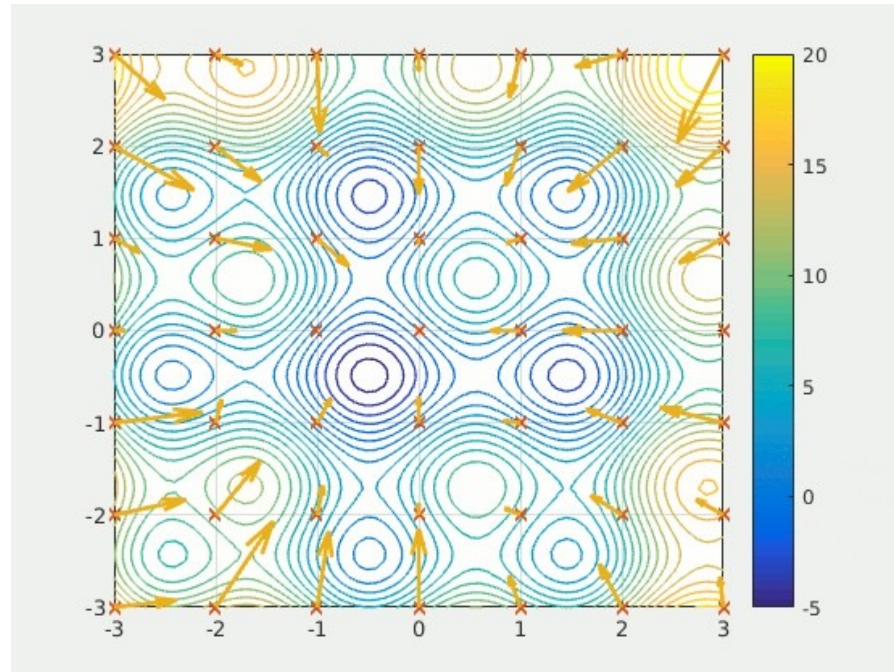
$$C_S(0)(1-\theta_S)A_{SAD} = A_{SD}\theta_S + k_0 A_{Cu} C_{Cu}(0)\,\theta_S(1-\theta_{eq})$$

Particle Swarm Optimization Algorithm

- Set of random *particles* (Points) defined over full domain
- *Objective function* is *evaluated* for every particle
- *Design variable* of the particles are *improved based on* a particle's *own best value* and the *global best value* in the entire swarm
- Discovery of *improved positions* become a *guide* for movements of the swarm
- **After each iteration, new values are found using:**

  – $v^i_{k+1} = w\, v^i_k + \frac{r_1\left(p^i - x^i_k\right)}{\Delta t} + \frac{r_2\left(p^g_k - x^i_k\right)}{\Delta t}$

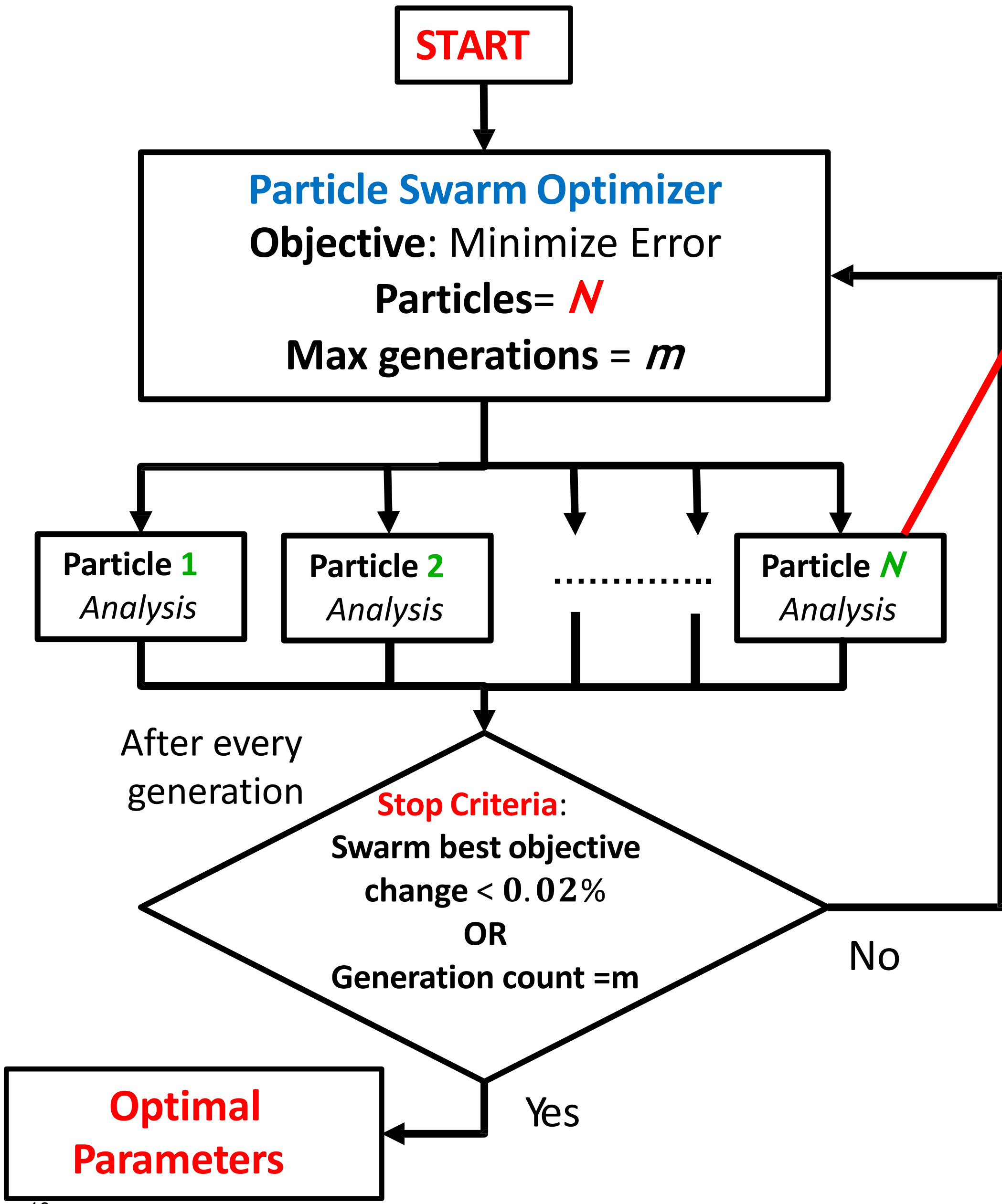
  – $x^i_{k+1} = x^i_k + v^i_{k+1}\,\Delta t$



A particle swarm searching for the global minimum of a function
**IMAGE CREDIT: Wikipedia*

Where,

- w, weighting parameter, balance between local and global search
- r_1 and r_2 are random numbers varying from 0 to 1
- Δt, time step is generally taken unity
- p^i and p^g_k are particle's own best position and best swarm position

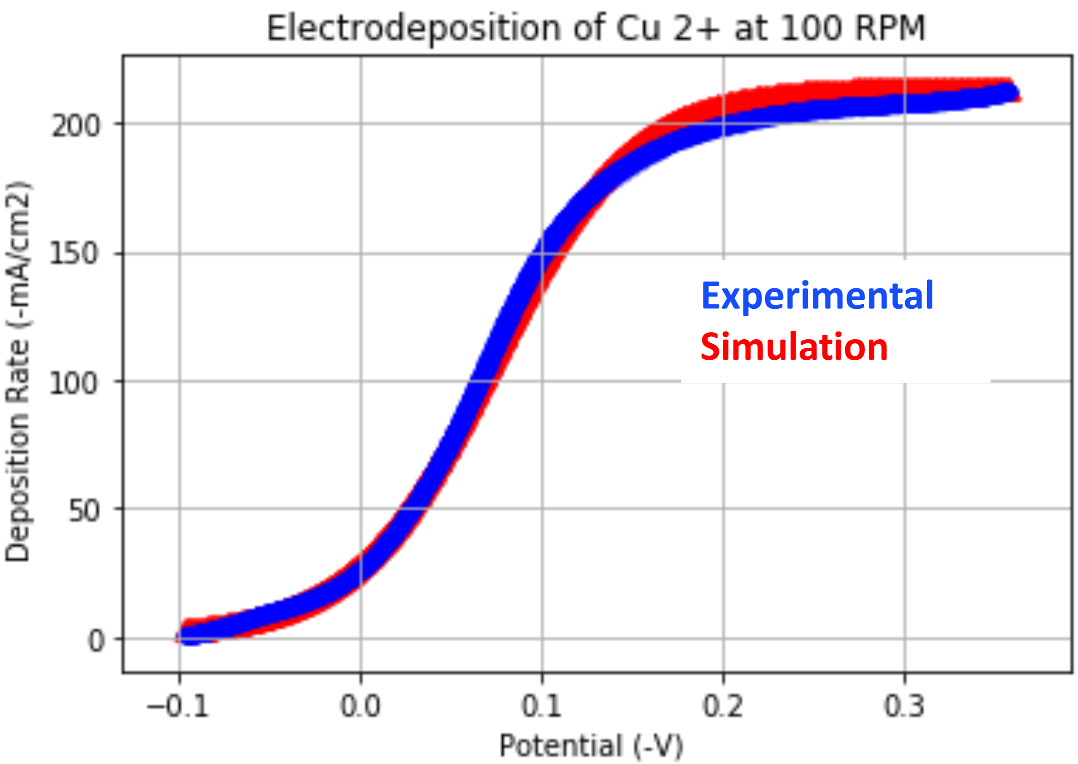


For Each Particle

Determination of Cost Function

- **Objective Function:**
  - $\text{Error} = \Sigma^{n}_{j=1} (Q_j - Q_{expj})^2$
- Objective is to reduce the total least square error for the equation
- Q_j is ith theoritical data point and Q_{expj} is the corresponding experimental data point

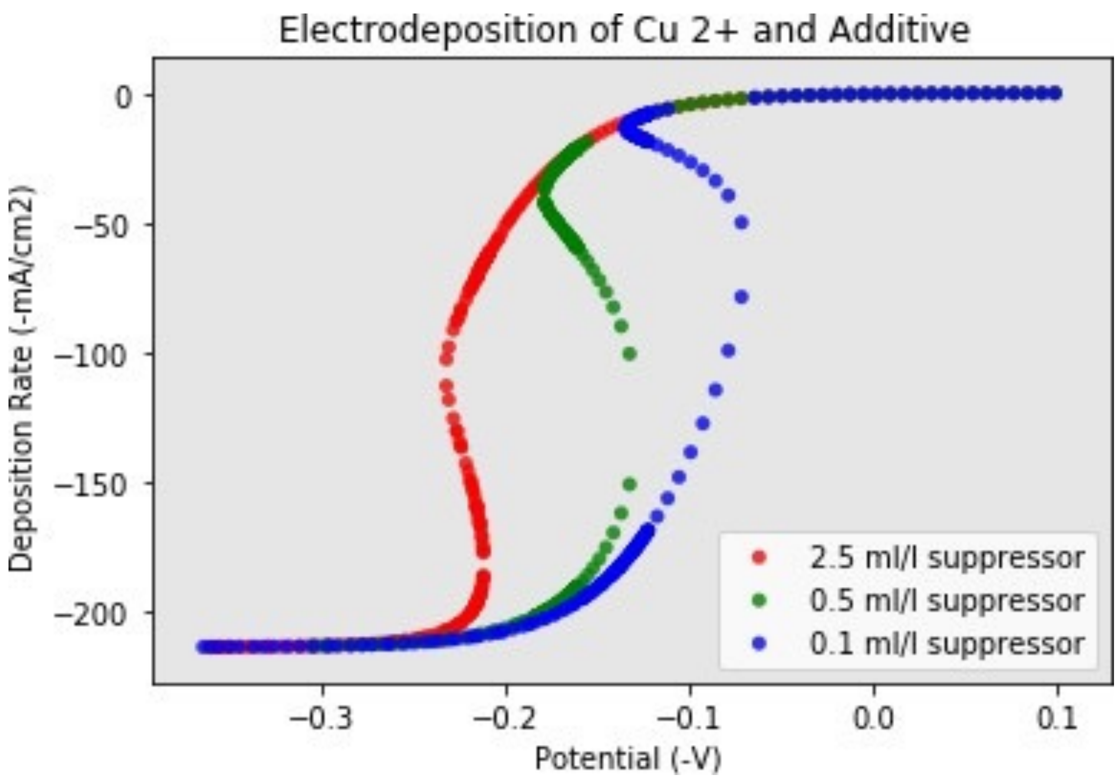
Fitting CV Curve for Cu^{2+} reduction (without Suppressor)



Fitting exp and theoretical CV curves

- k_{Cu}, b_{Cu} considered design variable
- Objective function is sum of square of difference between experimental and theoretical current over the range of voltage
- Particle Swarm Optimization applied to minimize Obj function
- Convergence achieved when Obj function didn't change for several iterations

Example of Simulation of CV Curve for different Suppressor Concentrations



Fitting exp and theoretical CV curves

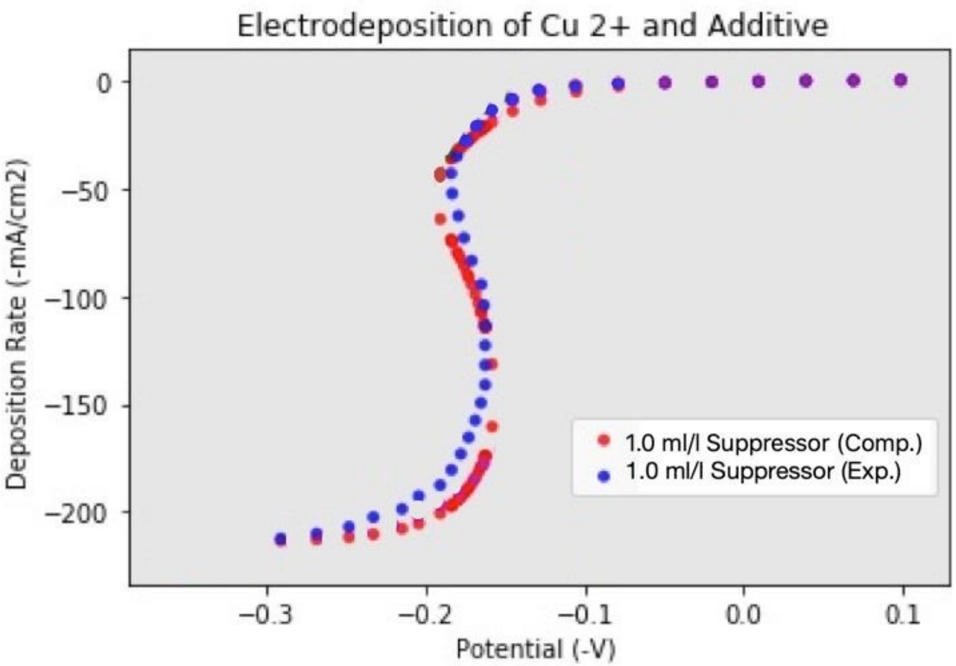
- Mass balance equation is numerically solved for different Suppressor concentrations
- For a certain range of V multiple solutions of θ_S obtained
- This results the S-shaped negative resistance curves for the current
- This is consistent with the Negative Differential Resistance (NDR) features found in experiment

- **On the surface, the concentrations are related as:**

Consumption = Adsorption - Desorption

$$C_S(0)(1-\theta_S)A_{SAD}=A_{SD}\theta_S+k_8A_{Cu}C_{Cu}(0)\theta_S(1-\theta_{eq})$$

Fitting Experimental and Theoretical CV Curves (Suppressor included)



Fitting exp and theoretical CV curves

$$A_{Cu} = k_{Cu} \quad e^{-b_{Cu}\eta}$$

$$A_{S,D} = k_{S,D} e^{-b_{S,D}\eta'}$$

$$A_{S,AD} = k_{S,AD} \quad e^{-b_{S,AD}\eta'}$$

$$A_8 = k_8 \quad e^{-b_8\eta'}$$

- k_{Cu} and b_{Cu} used as obtained form fitting Cu-case
- $k_{S,D}$, $b_{S,D}$, $k_{S,AD}$, $b_{S,AD}$, k_8 , b_8 are design variables
- Experimental curves may or may not show NDR region (depending on additive concentration)
- k_{Cu}, b_{Cu} considered design variable
- Objective function is sum of square of difference between experimental and theoretical current over the range of voltage
- Particle Swarm Optimization applied to minimize Obj function
- Convergence achieved when Obj function didn't change for several iterations

Conclusion

- A physiochemical model is proposed for Cu electrodeposition in presence of suppressor
- A semi-analytical method to solve set of differential equations describing one-dimensional Cu electrodeposition with additive (suppressor) is developed
- The semi-analytical model showed the existence of multiple solution of surface coverage of suppressor over a range of Voltage for certain suppressor concentrations
- Theoretical S-shaped curve of current density is consistent with NDR region observed experimentally
- The kinetic parameters of Cu and suppressor are optimized using PSO algorithm to fit the semi-analytical solution of current density to experimental data

References

[1] De, S., & Huang, Q. Estimation of Kinetic Parameters of Additives By Semi-Analytical Solution. In *PRiME 2020 (ECS, ECSJ, & KECS Joint Meeting)*. ECS.

[2] De, S., & Huang, Q. Mathematical Modeling of Cyclic Voltammogram Curves of Copper Deposition Involving Multiple Additives. In 240th ECS Meeting. ECS

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