

Mathematical Modeling of Cyclic Voltammogram Curves of Copper Deposition ^[1,2,3]



Shuvodeep De, Qiang Huang

Chemical and Biological Engineering, University of Alabama

Motivation

- Manufacturing of interconnects and packaging of integrated circuits are usually achieved by electrodeposition of Cu and other metals
- Electrolytes, additives, and processes are to be developed and optimized to improve defectivity, topography, and manufacturing throughput
- Numerical simulation finds important application in chemistry and process development for variety of dimensions and layout-outs of the structure
 - Process simulation / prediction requires determination of kinetic parameters (of Cu and additives)
- Use CVs to determine such parameters.
 - Example: Cu with suppressor alone.

Model Assumptions

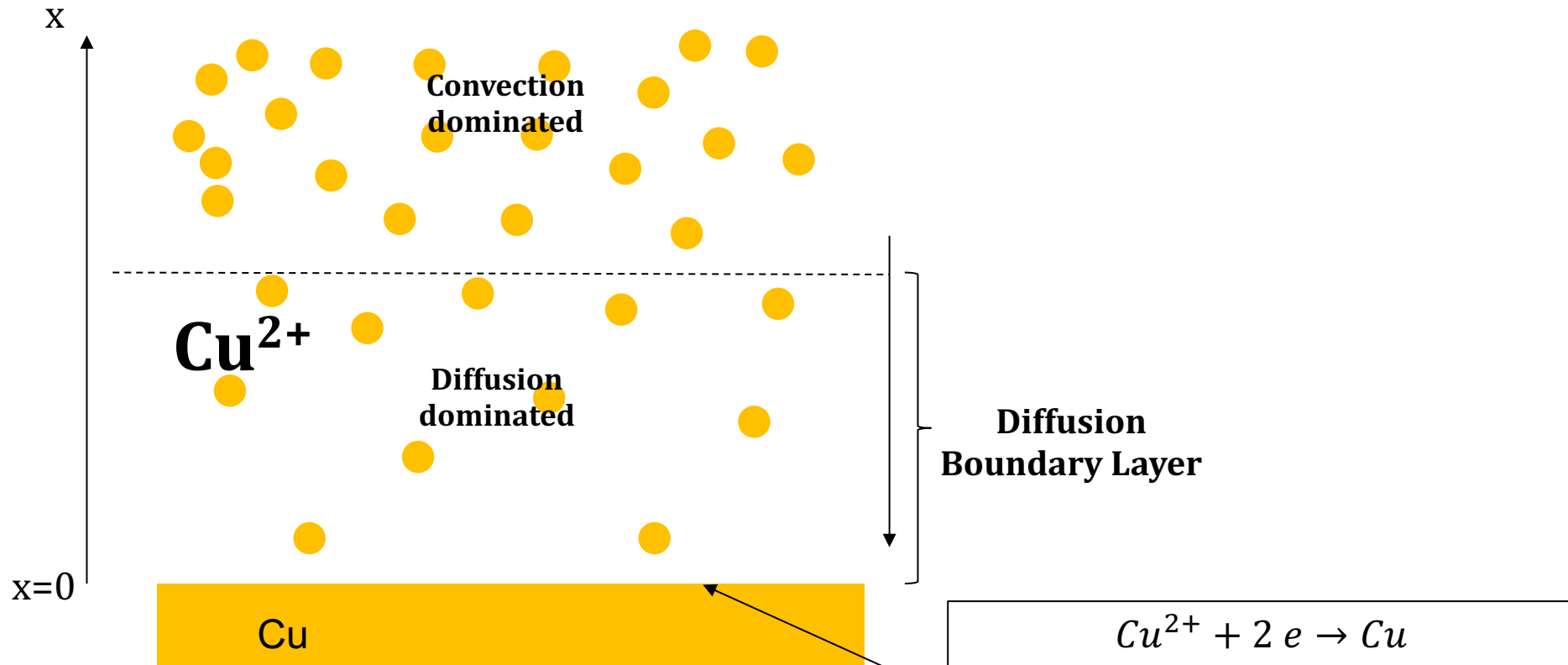
- **System**

- 1-D
- Steady state
- Rotating disc electrode (vicinity surface)

- **Chemistry**

- Cu deposition follows Tafel approximation, no anodic component considered.
- Suppressor functions through and only through a surface adsorbate species, and the adsorbate shifts the Cu over-potential but does not change the Tafel slope
- Adsorbed suppressors desorbs from the surface or gets incorporated into film
- The adsorption, desorption, and incorporation are all potential dependent, following a similar Tafel relationship
- No bulk chemical interaction between Cu and additive, they are only coupled through boundary condition at the electrode surface.

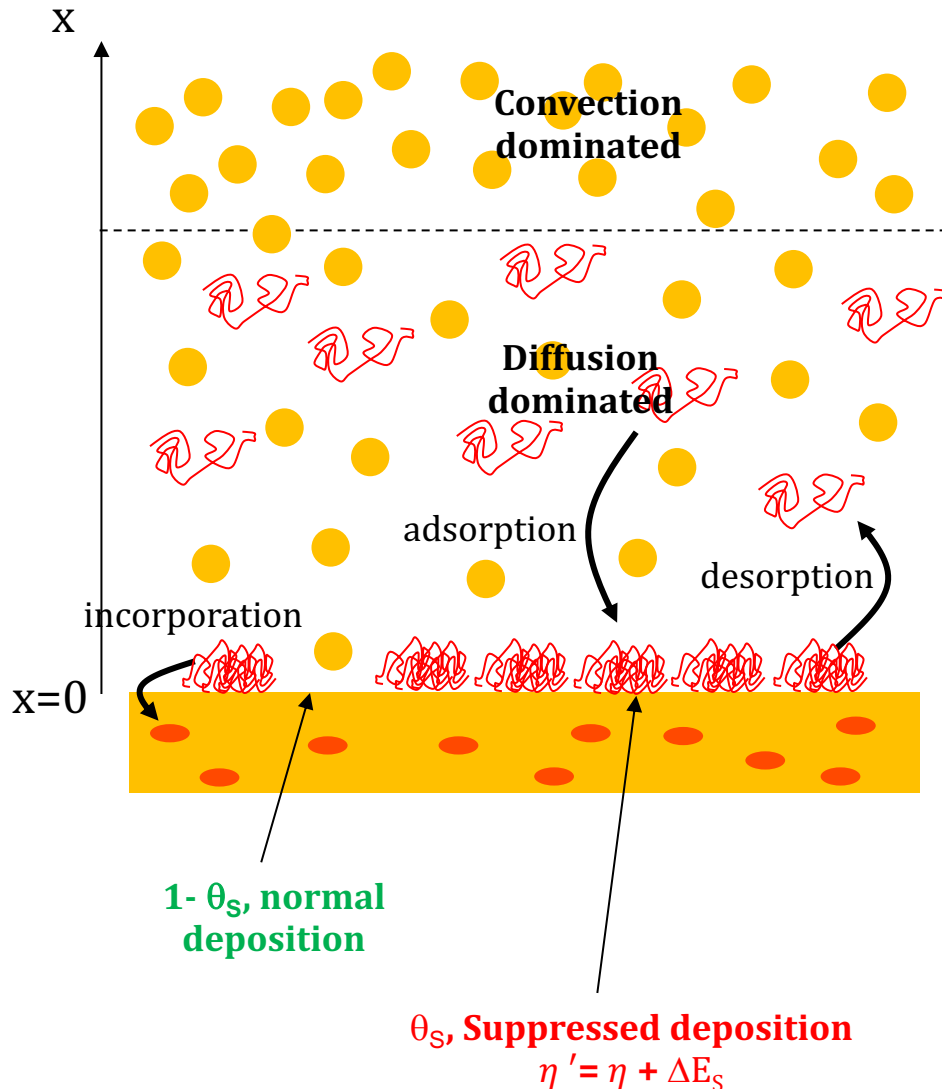
Physiochemical Model (Cu without additives)



- Tafel equation is used for cathodic deposition only
- Applicable for RDE (one dimensional problem)

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

Physiochemical Model (with Suppressor)



- Suppressor molecule
- Cu^{2+} ion
- Diffusion Boundary Layer**
- 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

Numerical Model

➤ Governing Differential Equation (steady state):

$$\frac{d^2 C_{Cu}}{dx^2} - \frac{V}{D_{Cu}} \frac{dC_{Cu}}{dx} = 0$$

C_{Cu}^* : Cu concentration at infinity

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

C_S^* : Suppressor concentration at infinity

V : Velocity function of fluid

$$V = -0.51023 \omega^{\frac{3}{2}} \nu^{\frac{-1}{2}} x^2$$

➤ Boundary conditions:

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

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

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

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

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

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

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

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

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

$$\theta_{eq} = \theta_S(1 - e^{-b_{Cu}\Delta E_S})$$

Analytical Solution and Determination of Parameters

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

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

$$\frac{dC_{Cu}}{dx} = \frac{3^{\frac{2}{3}} \alpha^{\frac{1}{3}} \beta C_{Cu}^*}{\beta \Gamma(0.333, 0) + 3^{\frac{2}{3}} \alpha^{\frac{1}{3}}} \quad C_S^* : \text{Suppressor concentration at infinity}$$

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

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

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

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

➤ **Measurable quantity - current (parameter dependent, used to fit parameters):**

$$\begin{aligned} \text{Current Density} &= 2 * 96485 * \frac{1}{1000} * D_{Cu} \frac{dC_{Cu}}{dx} (x = 0) \\ &= 2 * 96485 * \frac{1}{1000} * D_{Cu} \frac{3^{\frac{2}{3}} \alpha^{\frac{1}{3}} \beta C_{Cu}^*}{\beta \Gamma(0.333, 0) + 3^{\frac{2}{3}} \alpha^{\frac{1}{3}}} \end{aligned}$$

Particle Swarm Optimization Algorithm

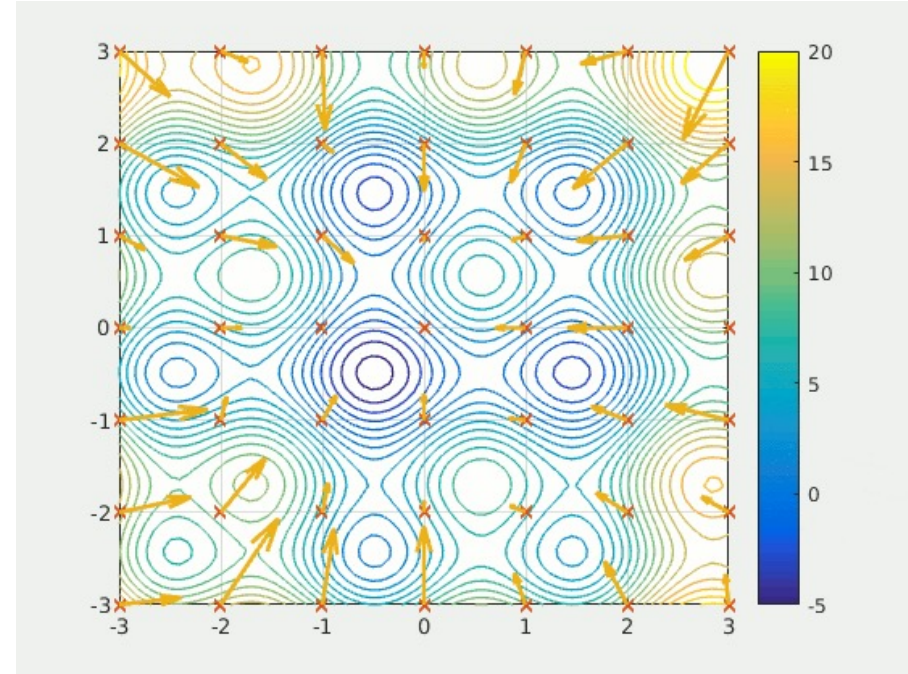
- Set of random *particles* (Points) defined over full domain
- *Objective function* is evaluated for every particle
- *Design variable* of the particles are *improved* based on a particle's *own best value* and the *global best value* in the entire swarm
- Discovery of *improved positions* become a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

$$- v_{k+1}^i = w v_k^i + \frac{r_1(p^i - x_k^i)}{\Delta t} + \frac{r_2(p_k^g - x_k^i)}{\Delta t}$$

$$- x_{k+1}^i = x_k^i + v_{k+1}^i \Delta t$$

Where,

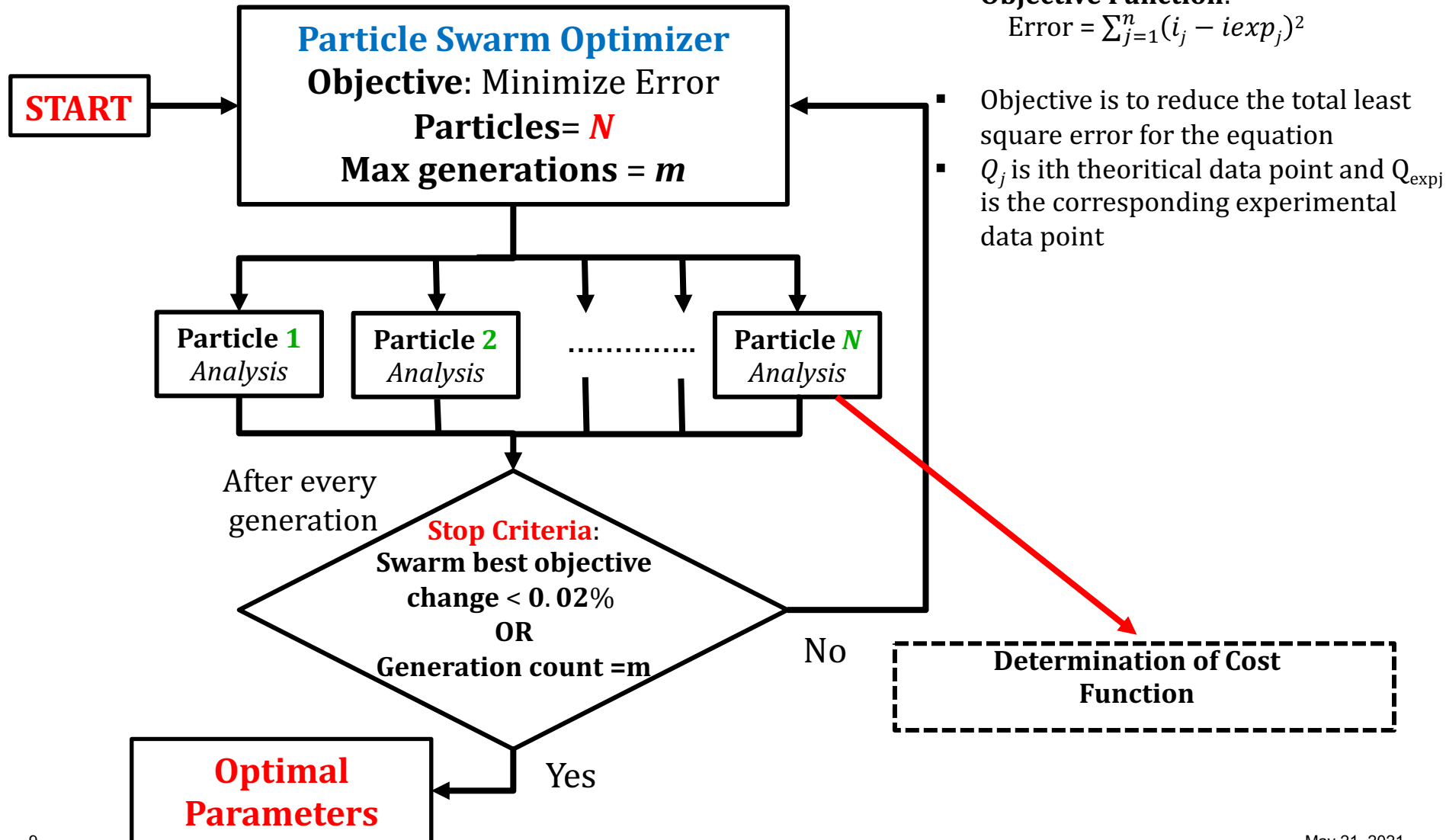
- w , weighting parameter, balance between local and global search
- r_1 and r_2 are random numbers varying from 0 to 1
- Δt , time step is generally taken unity
- p^i and p_k^g are particle's own best position and best swarm position



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

Particle Swarm Optimization Algorithm

For Each Particle

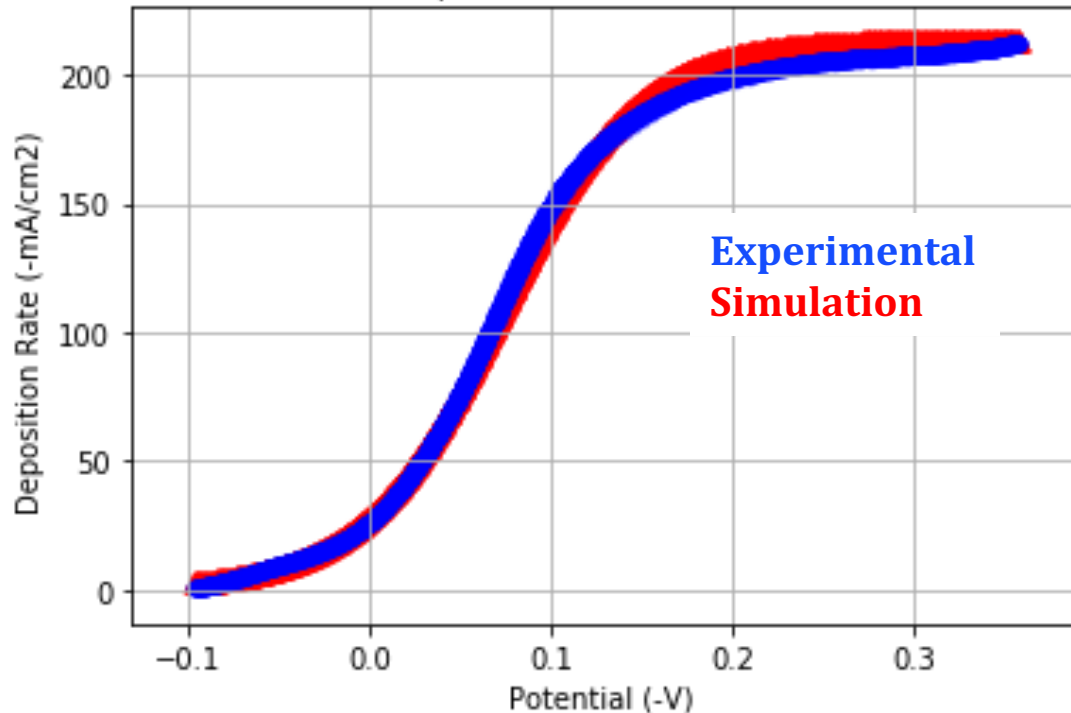


- **Objective Function:**

$$\text{Error} = \sum_{j=1}^n (i_j - i_{\text{exp}j})^2$$
- Objective is to reduce the total least square error for the equation
- Q_j is i th theoretical data point and $Q_{\text{exp}j}$ is the corresponding experimental data point

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

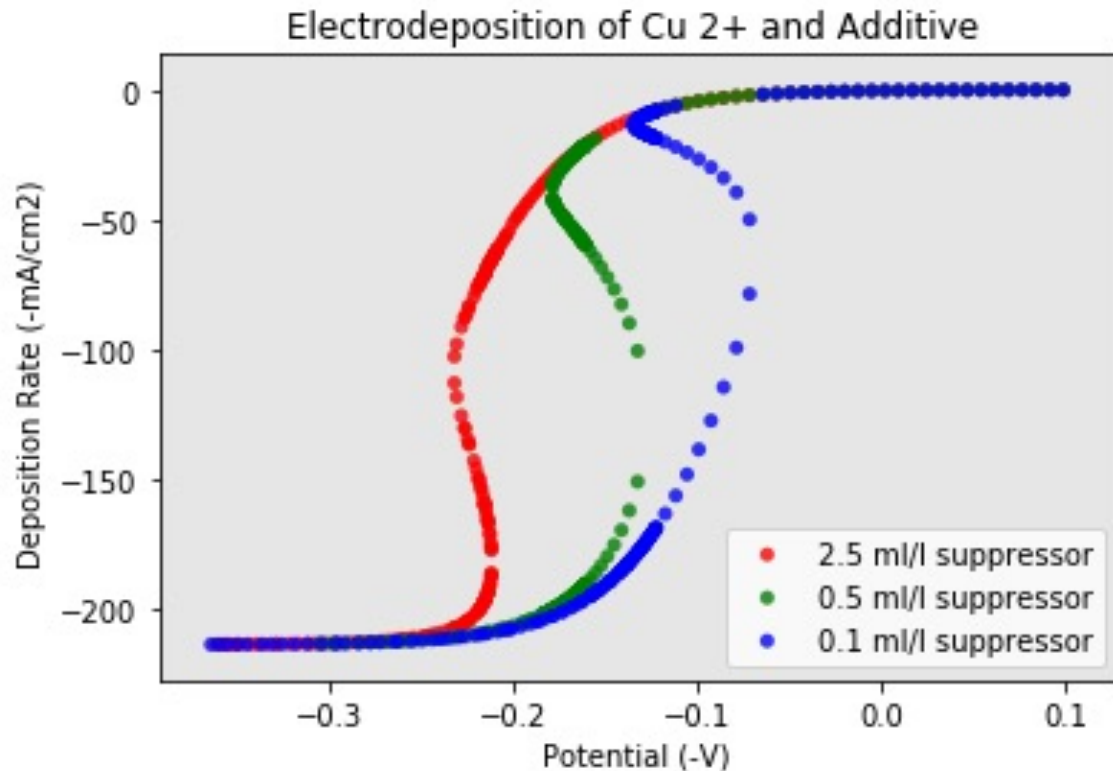
Electrodeposition of Cu^{2+} at 100 RPM



Fitting exp and theoretical CV curves

- $k_{\text{Cu}}, b_{\text{Cu}}$ 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

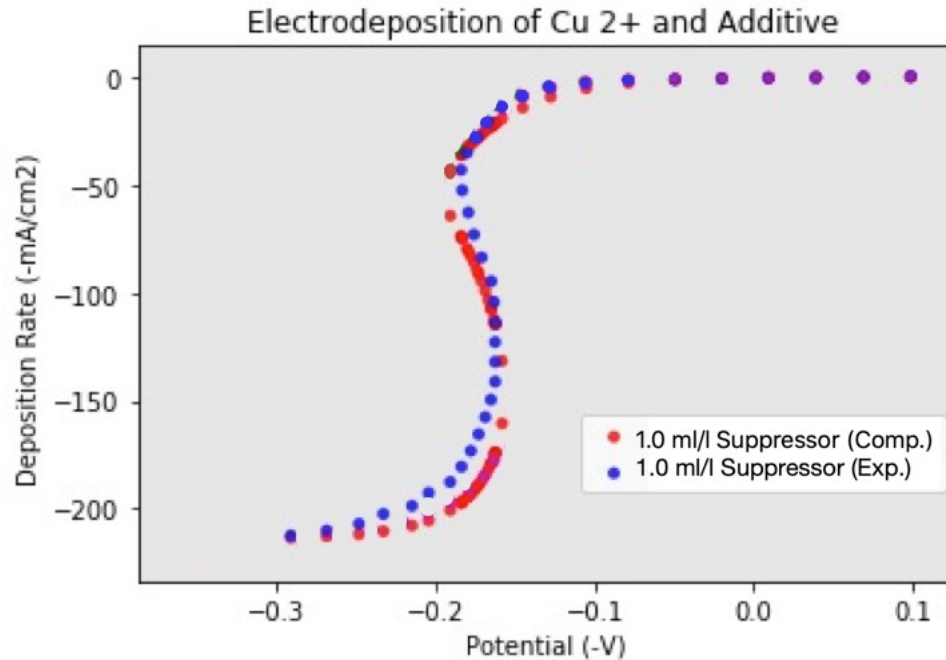
- Mass balance equation is numerically solved for different Suppressor concentrations
- For a certain range of V multiple solutions of θ_s obtained
- This results the S-shaped negative resistance curves for the current
- This is consistent with the Negative Differential Resistance (NDR) features found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

- On the surface, the concentrations are related as:

Consumption = Adsorption - Desorption

$$C_s(0)(1 - \theta_s)A_{SAD} = A_{SD}\theta_s + k_{\theta}A_{Cu}C_{Cu}(0)\theta_s(1 - \theta_{eq})$$

Fitting Experimental and Theoretical CV Curves (Suppressor included)



Fitting exp. and theoretical CV curves

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

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

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

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

- k_{Cu} and b_{Cu} used as obtained from fitting Cu-case
- $k_{S,D}$, $b_{S,D}$, $k_{S,AD}$, $b_{S,AD}$, k_{θ} , b_{θ} 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 adsorption – desorption – consumption physiochemical model is proposed used 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
 - Experimentally observed NDR region in CV can be successfully simulated
- 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
- [3] De, S., Sides, W. D., Brusuelas, T., & Huang, Q. (2020). Electrodeposition of superconducting rhenium-cobalt alloys from water-in-salt electrolytes. *Journal of Electroanalytical Chemistry*, 860, 113889.
- [4] De, S., White, J., Brusuelas, T., Patton, C., Koh, A., & Huang, Q. (2020). Electrochemical behavior of protons and cupric ions in water in salt electrolytes with alkaline metal chloride. *Electrochimica Acta*, 338, 135852.
- [5] Huang, Q., Sides, W. D., De, S., & Hu, Y. (2019, September). Electrodeposition of Cu, Co and Re from Water in Salt Electrolytes. In ECS Meeting Abstracts (No. 46, p. 2116). IOP Publishing.