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

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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)

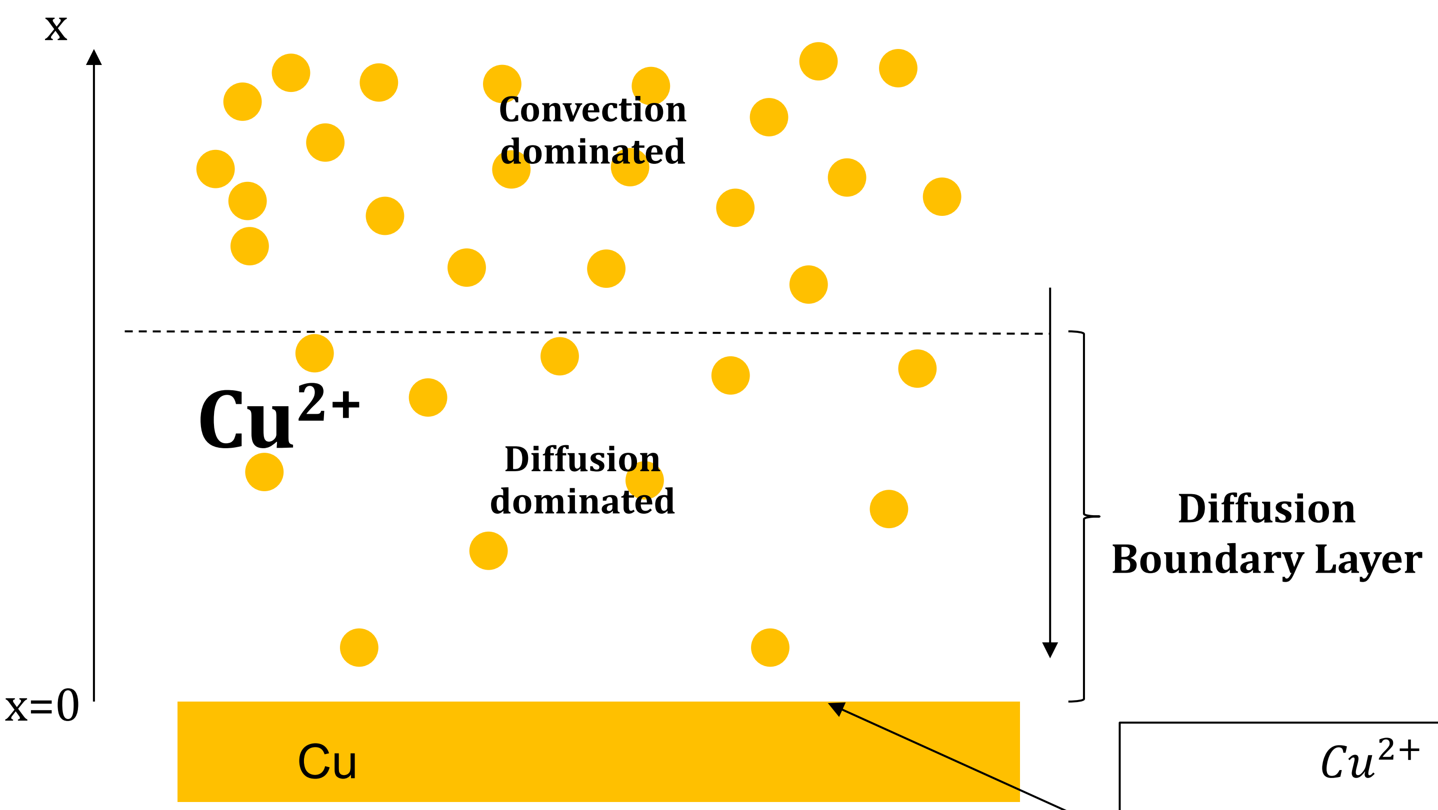
- Use CVs to determine such parameters.
  - Example: Cu with suppressor alone.

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)



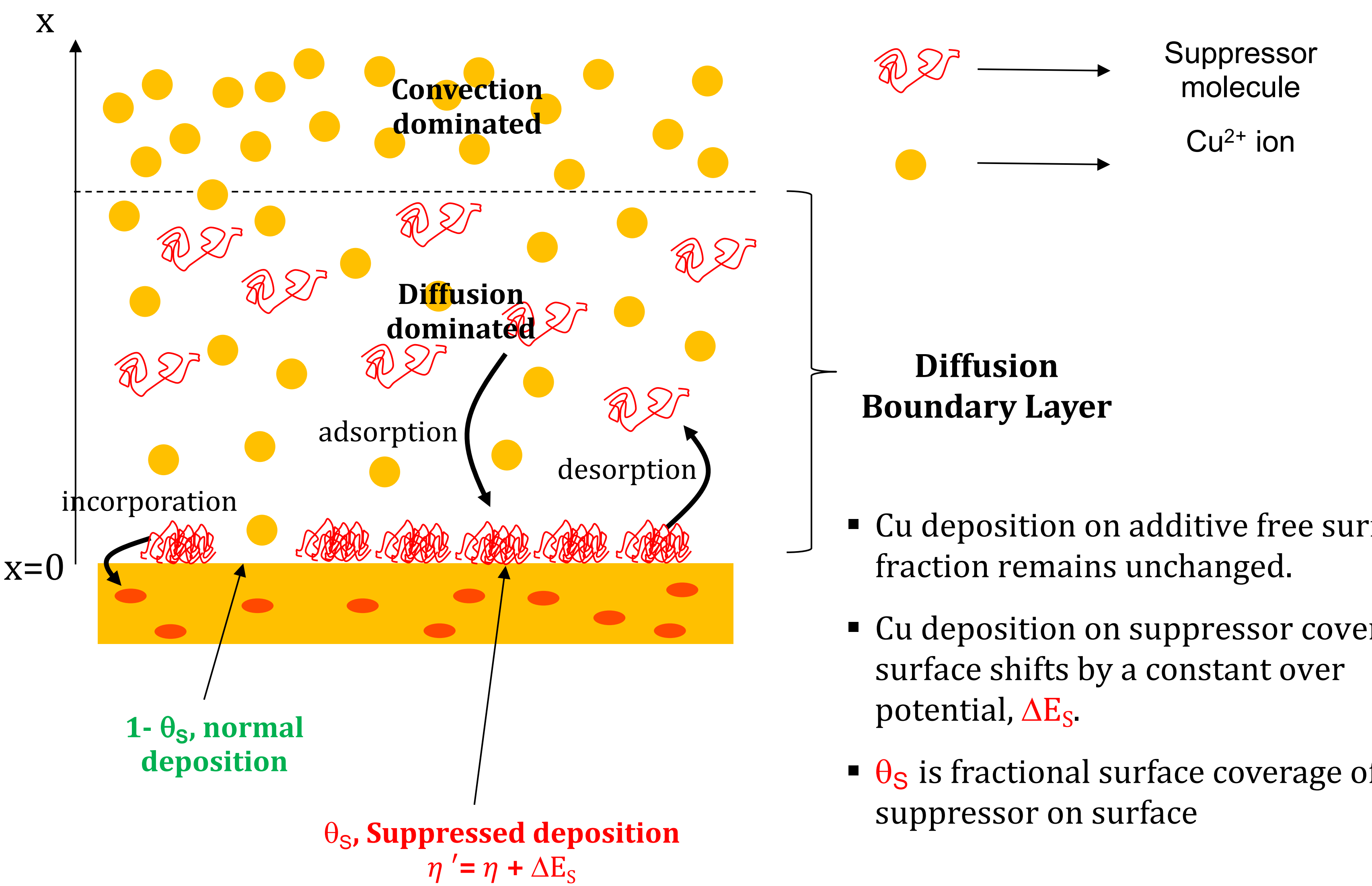
$$Cu^{2+} + 2\,e \rightarrow Cu$$

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

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



- 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

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Numerical Model

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

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

$$\frac{d^2C_s}{dx^2} - \frac{V}{D_s}\frac{dC_s}{dx} = 0$$

$$V = -0.51023\,\omega^{\frac{3}{2}}\,\upsilon^{\frac{-1}{2}}\,\mathrm{x}^2$$

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

$C_S *$: Suppressor concentration at infinity

V : Velocity function of fluid

- **Boundary conditions:**

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

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

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

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

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

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

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

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

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

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

Analytical Solution and Determination of Parameters

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

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

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

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

$C_S *$: 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

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

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

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

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

Particle Swarm Optimization Algorithm

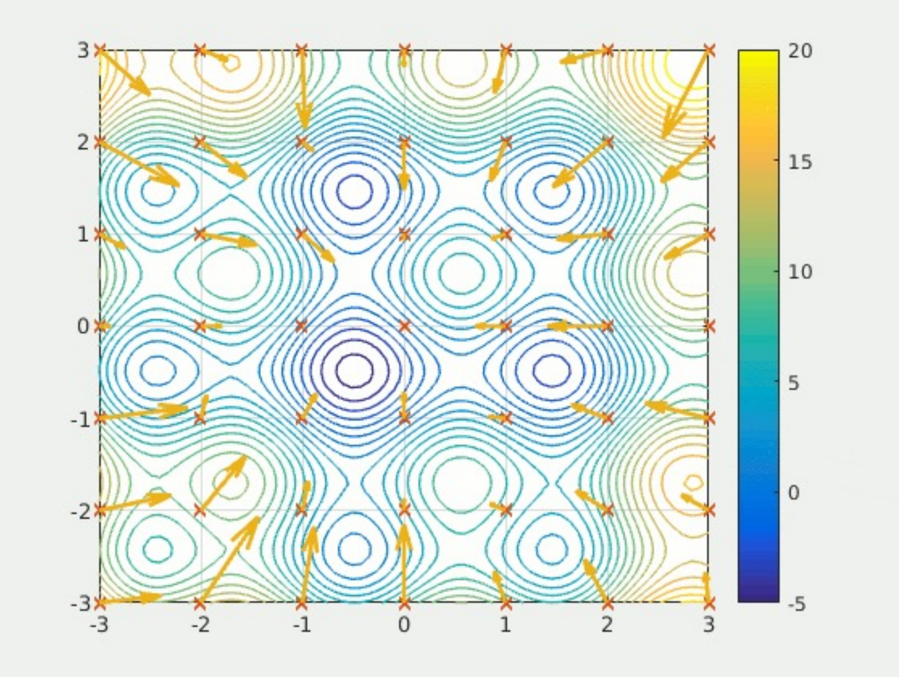
- Set of random *particles* (Points) defined over full domain
- *Objective function* is *evaluated* for every particle
- *Design variable* of the particles are *improved based on* a particle's *own best value* and the *global best value* in the entire swarm
- Discovery of *improved positions* become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

  – $v_{k+1}^{i} = w\, v_{k}^{i} + \frac{r_1\left(p^{i} - x_{k}^{i}\right)}{\Delta t} + \frac{r_2\left(p_{k}^{g} - x_{k}^{i}\right)}{\Delta t}$

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

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



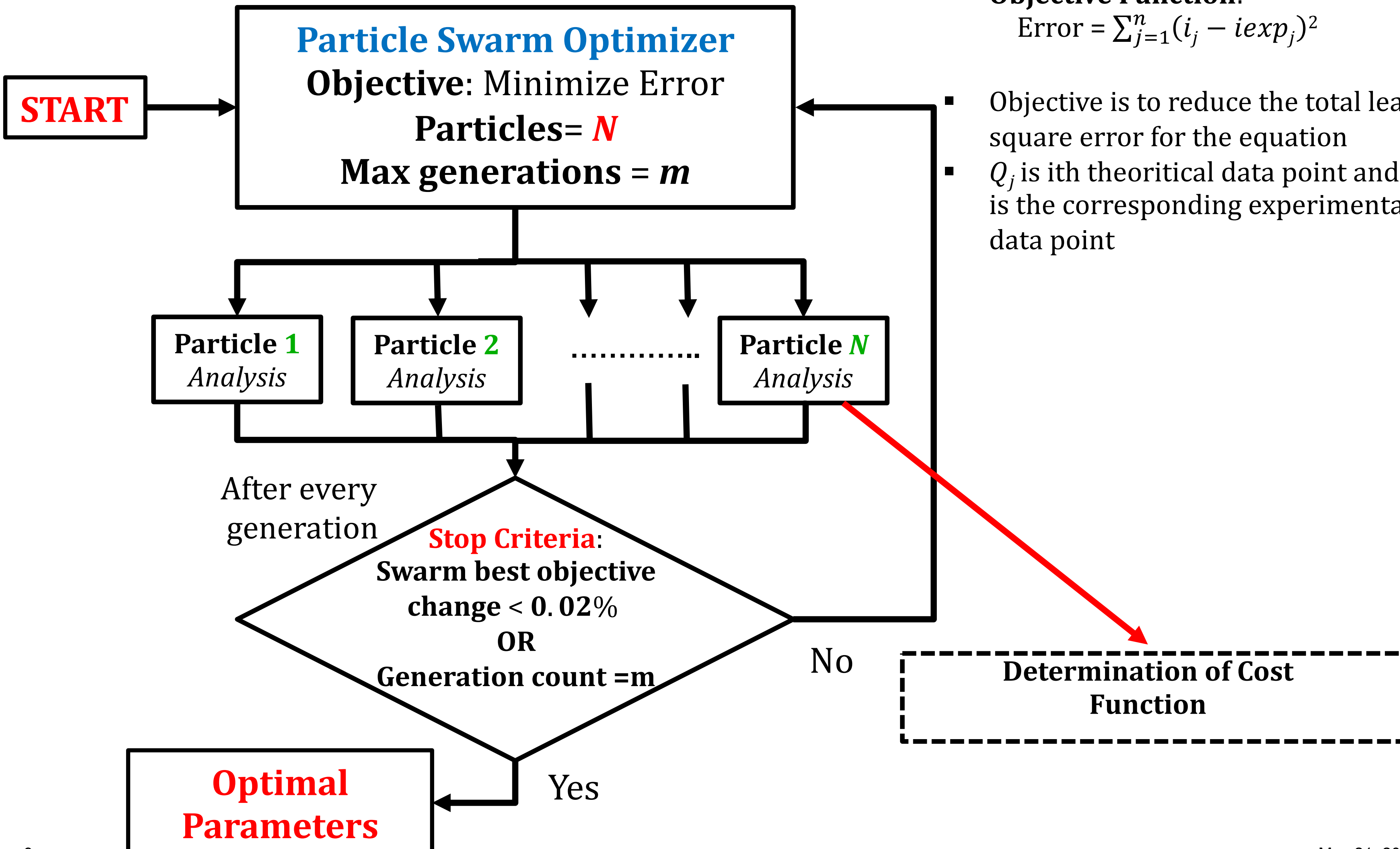
A particle swarm searching for the global minimum of a function
**IMAGE CREDIT: Wikipedia*

Particle Swarm Optimization Algorithm

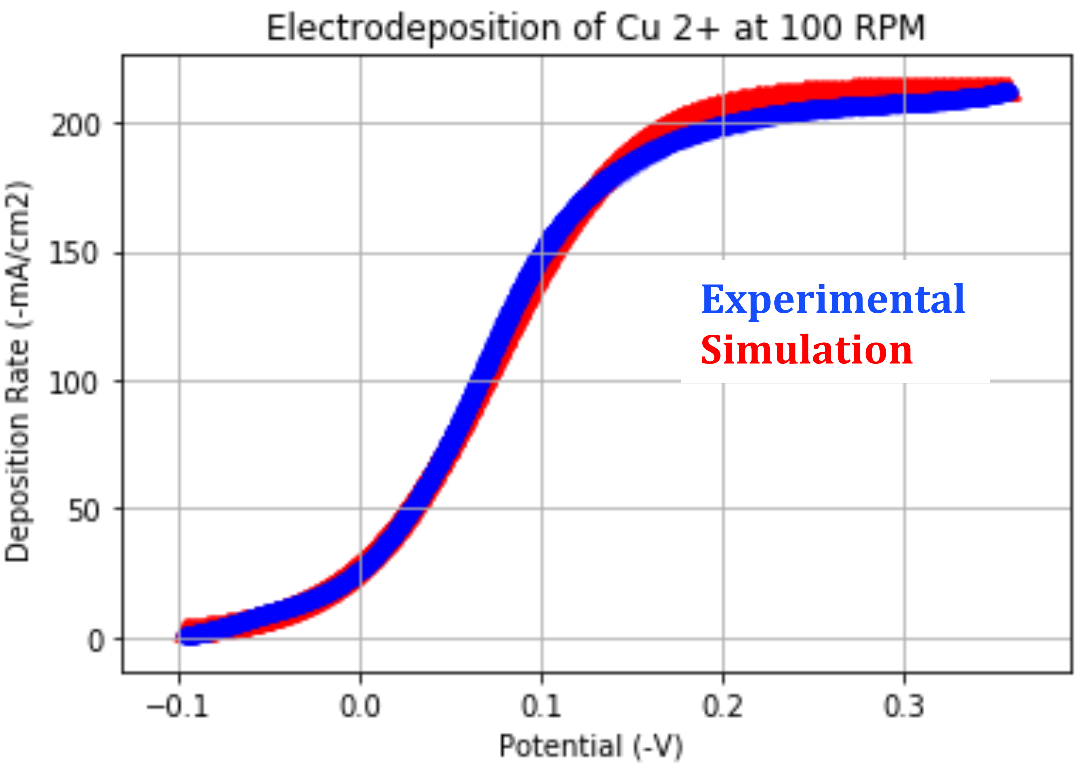
For Each Particle

- **Objective Function**:
  Error = $\sum_{j=1}^{n}(i_j - iexp_j)^2$

- 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



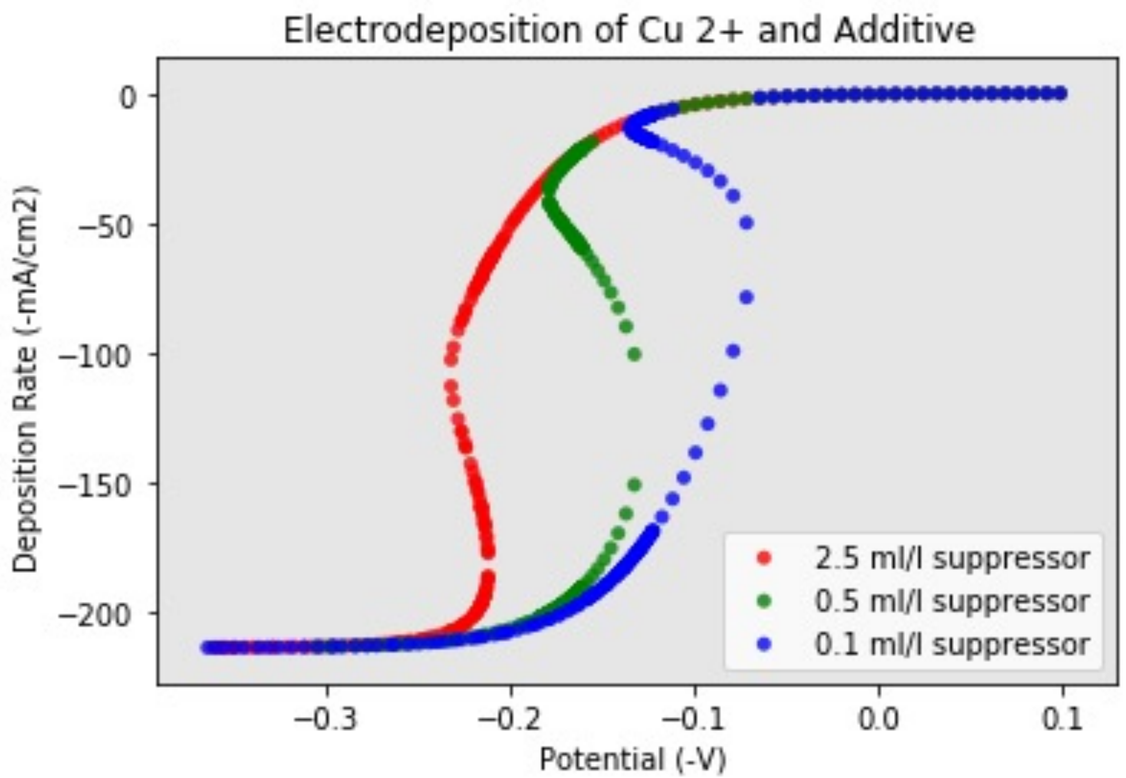
Fitting CV Curve for Cu^{2+} reduction (without Suppressor)



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

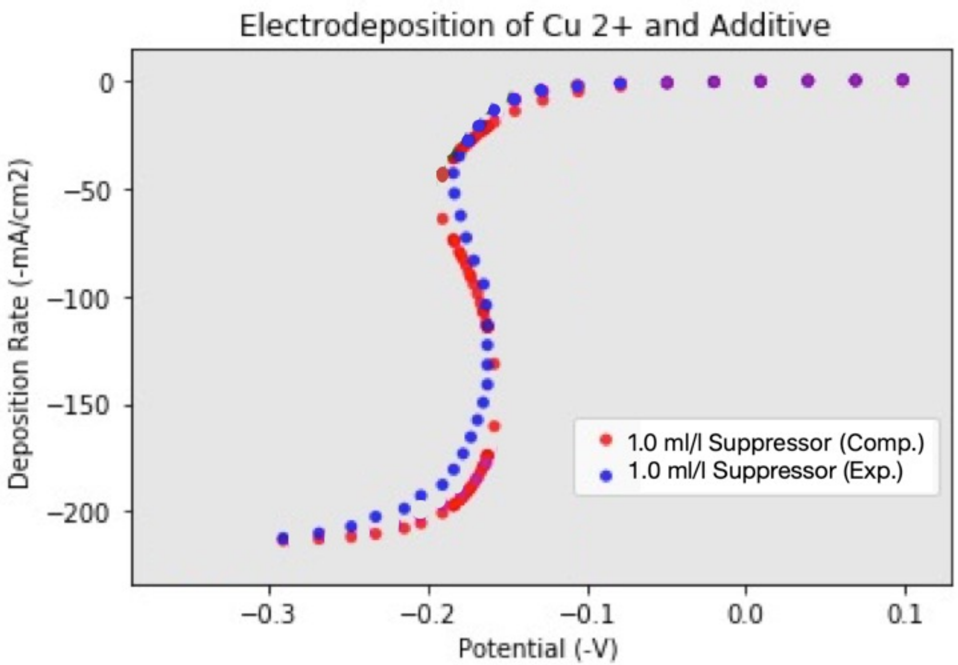
- Mass balance equation is numerically solved for different Suppressor concentrations
- For a certain range of V multiple solutions of θ_S obtained
- This results the S-shaped negative resistance curves for the current
- This is consistent with the Negative Differential Resistance (NDR) features found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

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

Consumption = Adsorption - Desorption

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

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 form 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.