Lesson# 5. Introduction to Numerical Modeling (Example: Copper Electrochemical Deposition)

Numerical modeling is particularly useful in simulating electrochemical deposition processes like copper deposition, where multiple physical phenomena (such as mass transport, charge transfer, and electrochemical kinetics) interact. In this section, we'll delve deeper into numerical modeling, explaining its components with equations using copper electrochemical deposition as an example.

1. Governing Equations in Copper Electrochemical Deposition

In copper electrochemical deposition, copper ions (Cu^{2+}) in an electrolyte are reduced at the cathode to form solid copper (Cu) according to the reaction:

$$Cu^{2+} + 2e^{-} = Cu\ (s)$$

The numerical model needs to account for various physical processes, including:

i. Nernst-Planck Equation for Mass Transport:

Mass transport of copper ions in the electrolyte occurs due to diffusion, migration, and convection. The Nernst-Planck equation governs this transport:

$$\frac{\partial C_{Cu^{2+}}}{\partial t} = -\nabla N_{Cu^{2+}}$$

Here, $N_{Cu^{2+}}$ represents the flux of copper ions, which is composed of:

- Diffusion: Due to concentration gradients, governed by Fick's Law:

$$N_{diff} = -D_{Cu^{2+}} \nabla C_{Cu^{2+}}$$

where $D_{Cu^{2+}}$ is the diffusion coefficient, and $C_{Cu^{2+}}$ is the concentration of copper ions.

- Migration: Movement under the influence of an electric field:

$$N_{mig} = -z_{Cu^{2+}} + \mu_{Cu^{2+}} + C_{Cu^{2+}} + \nabla\phi$$

where $z_{Cu^{2+}}$ is the charge number (+2 for Cu^{2+}), $\mu_{Cu^{2+}}$ is the mobility, and $\nabla\phi$ is the gradient of the electric potential.

- Convection: Transport due to bulk movement of the solution (if applicable):

$$N_{conv} = vC_{Cu^{2+}}$$

where v is the fluid velocity.

ii. Poisson Equation for Electric Potential:

The electric potential distribution, ϕ, in the system is determined by the Poisson equation, which relates the potential field to the charge distribution:

$$\nabla^2\phi = -\frac{\rho}{\epsilon}$$

where ρ is the charge density, and ϵ is the permittivity of the medium. This equation is important for understanding the electric field in the electrolyte that drives the migration of ions.

iii. Butler-Volmer Equation for Electrode Kinetics:

At the electrode surface, the current density j depends on the overpotential η (the difference between the applied potential and equilibrium potential) through the Butler-Volmer equation:

$$j = j_0\left(exp\left(\frac{\alpha_a F\eta}{RT}\right) - exp\left(\frac{-\alpha_c F\eta}{RT}\right)\right)$$

where: j_0 is the exchange current density; α_a and α_c are the anodic and cathodic charge transfer coefficients; F is the Faraday constant; R is the gas constant, and T is the temperature.

This equation captures the rate of electron transfer at the copper-electrolyte interface.

2. Discretization: Finite Difference or Finite Element Method

Numerical methods, like Finite Difference Method (FDM) or Finite Element Method (FEM), are used to discretize these equations. Discretization breaks the continuous space into small grid points, approximating derivatives at these points.

Finite Difference for Diffusion (1D Example):

The diffusion term from Fick's Law, $\frac{\partial C_{Cu^{2+}}}{\partial t}$, can be approximated using finite differences as:

$$\frac{C_{i+1} - C_i}{\Delta x}$$

where $C_{i+1}\ and\ C_i$ are the concentrations at points i and i+1, and Δx is the distance between the points.

Finite Element for Poisson Equation:

For a 2D or 3D domain, FEM can be used to solve the Poisson equation for the potential field ϕ. The domain is divided into small elements (e.g., triangles or tetrahedrons), and the solution is approximated by piecewise functions (basis functions) within each element.

3. Numerical Solution:

Once the equations are discretized, the next step is to solve the resulting algebraic system of equations. This can be done using:

- Iterative methods: Methods like Gauss-Seidel or Jacobi can be used to iteratively solve the system.

- Direct solvers: These solve the algebraic system directly, though they can be computationally expensive for large systems.

4. Boundary Conditions:

Numerical modeling requires appropriate boundary conditions to ensure that the solution is well-posed:

- At the electrode (cathode): The concentration of Cu^{2+} changes due to electrochemical reactions, which can be expressed as a flux boundary condition:

$$D_{Cu^{2+}} \frac{\partial C_{Cu^{2+}}}{\partial t} = \frac{j}{2F}$$

where *j* is the current density, and *F* is Faraday's constant.

- At the bulk solution: The concentration is typically assumed constant or zero flux.

5. Post-Processing:

After solving the system of equations, the solution is analyzed by plotting the concentration profiles, potential distributions, or current densities over time. For instance:

- Copper deposition rate: Can be visualized by plotting the growth of the deposited copper layer over time.

- Concentration gradients: Showing how the concentration of copper ions evolves during deposition.

6. Example Results:

Numerical simulations of copper electrochemical deposition could show how the concentration of copper ions depletes near the electrode surface as deposition progresses, and how the electric potential influences the deposition rate. These models can also predict the uniformity of the copper layer, helping optimize deposition conditions in industrial applications.

Conclusion:

Numerical modeling in electrochemical deposition involves solving complex sets of partial differential equations (PDEs) governing mass transport, potential distribution, and reaction kinetics. Using methods like FDM or FEM, these equations are discretized and solved iteratively, providing valuable insights into the electrochemical system's behavior. This approach allows researchers to optimize deposition processes and predict outcomes before performing experiments.