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

Goal

This lecture introduces students to the fundamentals of numerical modeling in chemical and electrochemical systems using the example of copper electrochemical deposition. Students will learn how to formulate, discretize, and solve the governing equations describing mass transport, potential distribution, and electrode kinetics. The focus is on understanding the interplay of physical phenomena and the numerical methods—such as the Finite Difference Method (FDM) and Finite Element Method (FEM)—used to obtain quantitative solutions for process optimization and analysis.

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.

Learning Outcomes

By the end of this lecture, students will be able to:

1. *Explain the importance of numerical modeling in simulating electrochemical processes such as copper electrodeposition (related to LO 4, ID 4.1).*
2. *Formulate the governing equations for electrochemical deposition, including the Nernst–Planck, Poisson, and Butler–Volmer equations (related to LO 4, ID 4.3–4.4).*
3. *Define and implement appropriate boundary conditions for electrochemical systems to ensure accurate numerical solutions (related to LO 4, ID 4.3–4.5).*
4. *Interpret simulation results — including concentration gradients, potential profiles, and current distributions — to evaluate process efficiency and uniformity (related to LO 4, ID 4.4–4.5).*
5. *Discuss how numerical modeling can optimize industrial electrochemical deposition processes, reducing experimental time and cost (related to LO 4, ID 4.6).*

Questions and Self-study Assignments

1. Define numerical modeling and explain why it is particularly useful for studying electrochemical deposition processes.
2. Write the Nernst–Planck equation for ion transport and describe the physical meaning of each term (diffusion, migration, and convection).
3. Explain the Poisson equation and its role in determining electric potential within the electrolyte.
4. Derive the Butler–Volmer equation and describe how it relates current density to electrode kinetics and overpotential.
5. Using the finite difference approximation, express the one-dimensional diffusion term from Fick's Law and explain how it is used in discretizing the mass transport equation.
6. Describe typical boundary conditions used for electrochemical modeling at (a) the electrode surface and (b) the bulk solution.
7. Discuss the difference between direct and iterative solvers used in solving the algebraic systems resulting from discretization.
8. Review one recent research article (within the last 3 years) where numerical modeling was applied to copper or other metal electrodeposition. Summarize:
-which equations were modeled;
- which numerical methods were used;
- what conclusions were drawn about process optimization or morphology control.

References

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2. Pryor R.W. Multiphysics Modeling Using COMSOL5 and MATLAB. - Mercury Learning and Information, 2015. – 700 p. ISBN 1938549988