

Lecture#2 Fundamental Concepts of Modeling in Chemical Engineering with a Focus on Electrochemical Processes

Goal

This lecture aims to develop a deeper understanding of the fundamental principles that form the basis of modeling in chemical engineering, with a particular focus on electrochemical processes. Students will explore different types of models (empirical, mechanistic, and stochastic), the general steps in process modeling, and how these principles are applied to electrochemical systems such as electrolysis, batteries, and fuel cells. The lecture also emphasizes governing equations (Nernst, Butler–Volmer, and Nernst–Planck) that describe electrochemical kinetics and transport phenomena.

Types of Models

1. Empirical Models

- Derived from experimental data.
- Focus on fitting data to mathematical functions without necessarily capturing the underlying physical principles.
- Useful for systems where detailed mechanisms are not fully understood.

2. Mechanistic (Deterministic) Models:

- Based on fundamental principles like mass, energy, and momentum balances.

- Governed by equations such as:

- Conservation of Mass: $\frac{d(\text{mass})}{dt} = \text{Rate of mass in} - \text{Rate of mass out} + \text{Generation}$

- Conservation of Energy: $\frac{d(\text{energy})}{dt} = \text{Energy in} - \text{Energy out} + \text{Heat generated}$

- Momentum Balances: Used for flow systems (fluid dynamics).

3. Stochastic Models:

- Incorporate randomness or uncertainties.
- Useful in processes with inherent variability, such as particle processes or biological systems.

Key Steps in Process Modeling

1. Define the System: Identify the boundaries, inputs, outputs, and state variables.
2. Formulate the Governing Equations: Based on conservation laws (mass, energy, momentum) and empirical relationships (reaction kinetics, thermodynamics).
3. Simplify and Assumptions: Assumptions are necessary to simplify complex systems (e.g., steady-state, ideal gas behavior, isothermal conditions).
4. Solve the Equations: Analytical or numerical methods are used, depending on the complexity.
5. Validate the Model: Compare model predictions with experimental data to ensure accuracy.

Electrochemical Processes in Chemical Engineering

What are Electrochemical Processes?

Electrochemical processes involve chemical reactions that are driven by an electric current or produce electricity. These processes are widely used in areas such as energy storage (batteries), electrolysis (e.g., hydrogen production), electroplating, and corrosion prevention.

Electrochemical systems are unique in that they couple chemical reactions with electron transfer at interfaces, typically between an electrode and an electrolyte. Modeling these systems is crucial for optimizing their performance and efficiency.

Key Electrochemical Systems

Electrolysis:

- Uses electrical energy to drive a non-spontaneous chemical reaction.
- Common applications include water electrolysis (hydrogen production) and chlor-alkali processes.

Batteries:

- Energy storage devices that convert chemical energy into electrical energy.

- Lithium-ion batteries are widely used in portable electronics and electric vehicles.

Fuel Cells:

- Devices that convert the chemical energy of a fuel (usually hydrogen) directly into electricity.

- The most common type is the proton exchange membrane (PEM) fuel cell, which is used in clean energy applications.

Governing Equations in Electrochemical Modeling

Electrochemical processes are governed by coupled transport and reaction phenomena. The main principles involved include:

1. Butler-Volmer Equation:

- Describes the relationship between current density and the electrochemical reaction rate at the electrode surface.

- The equation takes into account both anodic and cathodic reactions:

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

Where: j – current density; j_0 – exchange current density; η – overpotential (deviation from equilibrium voltage); F – Faraday's constant; R – gas constant; T – temperature; α_a and α_c – anodic and cathodic transfer coefficients.

2. Nernst Equation:

- Provides the equilibrium potential for an electrochemical reaction.

- It accounts for the effect of ion concentrations in the electrolyte on the cell potential:

$$E = E^0 + \frac{RT}{nF} \ln \left(\frac{[Ox]}{[Red]} \right)$$

Where: E^0 – standard electrode potential; n – number of electrons transferred; $[Ox]$ and $[Red]$ – concentrations of oxidized and reduced species.

3. Mass Transport in Electrochemical Systems:

- Transport of ions in the electrolyte plays a key role in the overall performance of the system.

- The Nernst-Planck equation describes the flux of ions due to diffusion, migration, and convection:

$$\mathbf{J}_i = -D_i \nabla c_i + z_i u_i c_i \mathbf{E} + c_i \mathbf{v}$$

Where: D_i – diffusion coefficient; c_i – concentration of species; z_i – charge number; u_i – mobility of species; \mathbf{E} – electric field; \mathbf{v} – velocity of the fluid (if convection is present).

Example: Modeling Water Electrolysis

Water electrolysis is a crucial process in the production of hydrogen, which is a clean fuel. The electrolysis process involves splitting water molecules into hydrogen and oxygen using electricity. The overall reactions are:

Anode (oxidation): $2\text{H}_2\text{O} = \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$

Cathode (reduction): $4\text{H}^+ + 4\text{e}^- = 2\text{H}_2$

The key challenges in modeling water electrolysis include:

- Reaction Kinetics: Predicting the rate of hydrogen and oxygen generation, which is influenced by the electrode material and the overpotential.
- Mass Transport: Modeling the movement of protons and hydroxide ions in the electrolyte to ensure efficient electrolysis.
- Energy Efficiency: Understanding the voltage efficiency and energy losses due to overpotentials at the electrodes.

By solving the Nernst and Butler-Volmer equations, coupled with mass transport equations, engineers can optimize the efficiency of electrolyzers, reducing energy consumption and maximizing hydrogen production.

Challenges and Advances in Electrochemical Process Modeling

Challenges

- Multiphysics Complexity: Electrochemical systems involve complex interactions between chemical kinetics, charge transfer, and mass transport, often requiring multi-scale models.
- Parameter Estimation: Many parameters, such as exchange current density or diffusivity, are difficult to measure directly and require accurate estimation techniques.

- Nonlinear Behavior: Electrochemical systems exhibit nonlinear behavior, which complicates the solution of governing equations.

Advances

- Computational Methods: The development of advanced computational tools (e.g., **COMSOL Multiphysics**) enables more accurate simulation of complex electrochemical processes.
- Data-Driven Models: Machine learning techniques are increasingly being applied to model electrochemical systems, using experimental data to improve predictions without requiring detailed mechanistic understanding.
- Hybrid Models: Combining empirical and mechanistic models can provide greater flexibility and predictive power.

Conclusion

Modeling in chemical engineering, particularly in electrochemical processes, is a fundamental tool for process design, optimization, and innovation. Whether in fuel cells, batteries, or electrolysis, understanding the key principles and applying mathematical models allows engineers to enhance the efficiency, scalability, and sustainability of these systems. However, electrochemical processes present unique challenges, particularly in terms of complex interactions between reaction kinetics, charge transfer, and mass transport. Despite these challenges, advances in computational methods and hybrid modeling approaches continue to push the boundaries of what is possible in the field.

Learning Outcomes

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

- 1. Explain the types of models used in chemical engineering (empirical, mechanistic, and stochastic) and identify their applications and limitations (related to LO 2, ID 2.1).*
- 2. Describe the key steps in developing a process model — system definition, formulation, assumptions, solution, and validation (related to LO 2, ID 2.2).*
- 3. Understand the fundamental equations governing electrochemical processes (Butler–Volmer, Nernst, and Nernst–Planck equations) and their physical meaning (related to LO 4, ID 4.3–4.5).*

Questions and Self-study Assignments

1. Define and differentiate between empirical, mechanistic, and stochastic models. Provide one example for each.
2. Write the general mass and energy balance equations for a continuous-flow reactor and explain each term.
3. What are the main steps in developing a process model? Give an example where each step plays a critical role.
4. Explain how the Butler–Volmer equation describes the kinetics of electrochemical reactions.
5. Discuss how mass transport phenomena (diffusion, migration, and convection) influence electrochemical reaction rates.
6. Prepare a short summary (1 page) of a recent journal article (within the last 3 years) that applies modeling to batteries, electrolysis, or fuel cells. Identify:
 - the type of model used;
 - the governing equations;
 - main findings related to process optimization or efficiency.
7. Reflect on how hybrid or machine-learning-based models can complement classical modeling approaches in electrochemical research.

References

1. Finlayson B.A. Introduction to Chemical Engineering Computing. Second Edition. - John Wiley & Sons, 2012. ISBN 9781118309599, DOI: 10.1002/9781118309599
2. Pryor R.W. Multiphysics Modeling Using COMSOL5 and MATLAB. - Mercury Learning and Information, 2015. – 700 p. ISBN 1938549988