Lecture #8. **Modeling of electrochemical processes**

Goal

This lecture introduces students to the principles of electrochemical process modeling, integrating thermodynamics, reaction kinetics, and mass transport. Electrochemical modeling is essential for analyzing and optimizing systems such as batteries, fuel cells, corrosion processes, electroplating, and electrochemical sensors. Students will learn how classical equations—Nernst, Butler–Volmer, and Fick's laws—are combined to simulate the performance of electrochemical systems, with a focus on lithium-ion batteries as a key example.

Electrochemical processes involve chemical reactions that occur at the interface between an electrode and an electrolyte, leading to the transfer of electrons.

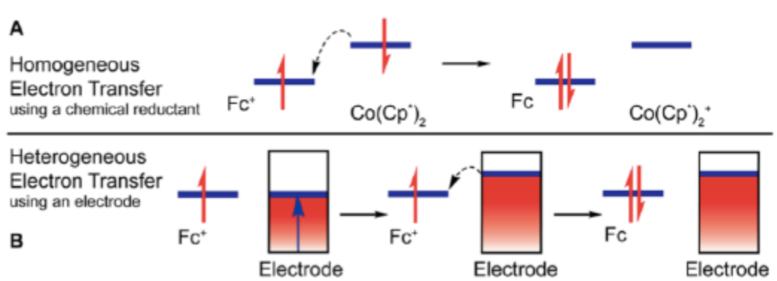
Electrochemical processes are fundamental in batteries, fuel cells, electroplating, corrosion studies, and sensors.

Modeling electrochemical processes is essential for understanding and optimizing systems like batteries and fuel cells. It integrates thermodynamics, kinetics, and mass transport, providing valuable insights for innovation in energy storage and conversion technologies.

Key Components of Electrochemical Modeling

Electrode Reactions:

Oxidation and Reduction: The basic reactions involve the transfer of electrons from one species to another.



Nernst Equation describes the relationship between the concentration of reactants/products and the electrode potential:

$$E=E^0-(RT/nF)\ln Q$$

where E is the electrode potential, E^0 is the standard potential, R is the gas constant, T is the temperature, n is the number of electrons, F is Faraday's constant, and Q is the reaction quotient.

Thermodynamic Models:

- Used to calculate equilibrium potentials and understand the feasibility of electrochemical reactions.

Kinetic Models:

- Focus on the rates of electron transfer and mass transport. The Butler-Volmer equation is often used to describe current density (lecture#5):

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

  where j_0 is the exchange current density, α_a and α_c are the anodic and cathodic transfer coefficients, η is the overpotential of the reaction (η=E-E_{eq}), and E_{eq} is the equilibrium potential.

Transport Models:

- Describe the diffusion and migration of ions in the electrolyte, often modeled using Fick's laws.

Modeling a Lithium-Ion Battery

Lithium-ion batteries are widely used in portable electronics and electric vehicles, making their modeling crucial for performance optimization.

Goal of Modeling: To predict battery performance metrics like capacity, voltage, and efficiency under various operating conditions (temperature, charge/discharge rates).

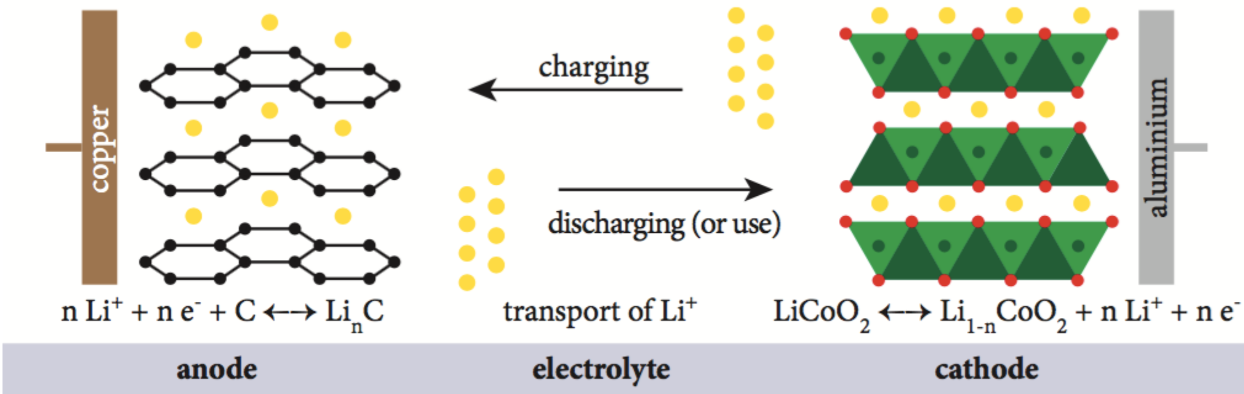
Impact of Modeling: Helps in the design of batteries with improved cycle life, energy density, and safety.

Electrode Reactions:

At the anode: $Li^{+}+e^{-}\leftrightarrow Li$

At the cathode: $CoO_2+Li^{+}+e^{-}\leftrightarrow LiCoO_2$

In a battery, lithium ions are oxidized at the anode and reduced at the cathode.



Modeling Approach:

Kinetic Models: Use the Butler-Volmer equation to describe charge transfer kinetics at the electrode surfaces.

Transport Models: Implement Fick's laws to model lithium ion diffusion in the electrolyte and within the electrodes.

Thermodynamic Models: Apply the Nernst equation to predict the cell voltage under different operating conditions.

Learning Outcomes

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

1. Explain the fundamental components of electrochemical process modeling (thermodynamics, kinetics, mass transport) (related to LO 4, ID 4.3–4.4).

2. Apply the Nernst equation to calculate electrode potentials under non-standard conditions (related to LO 4, ID 4.3).

Questions and Self-Study Assignments

1. Explain the difference between oxidation and reduction in an electrochemical system.

2. Write the Butler–Volmer equation and explain the meaning of each term.

3. Describe how concentration gradients near the electrode influence electrochemical kinetics.

4. For a lithium-ion battery, explain why diffusion inside the solid electrode can be a rate-limiting step.

5. Sketch qualitatively the voltage vs. state-of-charge curve for a Li-ion battery and explain its shape.

6. Read one recent article (last 3 years) on battery modeling and summarize:

- which equations were used;

- main assumptions;

- key findings about performance or degradation.

References

1. Chemical Reaction Engineering Module User's Guide. – COMSOL, 2020.

2. Ghasem N. Modeling and Simulation of Chemical Process Systems. - CRC Press, 2015. – 518 p.