Lecture 12

Introduction to modelling of chemical power sources

Goal of the Lecture

The goal of this lecture is to introduce students to the fundamental principles of modelling chemical power sources, including batteries, fuel cells, and electrochemical capacitors. The lecture provides a unified framework linking thermodynamics, kinetics, and mass transport to cell voltage, efficiency, and performance prediction. Students will learn how these principles form the basis of computational models used in advanced energy-storage simulations.

Lecture Objectives

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

1. ***Classify** major types of chemical power sources and describe their energy conversion principles.*
2. ***Explain** the thermodynamic basis of cell voltage using Gibbs free energy and the Nernst equation.*
3. ***Apply** Butler–Volmer and Tafel kinetics to model electrode reaction rates.*
4. ***Describe** mass transport phenomena (diffusion, migration, convection) using the Nernst–Planck equation.*
5. ***Analyze** how polarization losses (activation, ohmic, concentration) reduce cell voltage under load.*
6. ***Interpret** the coupled thermodynamic–kinetic–transport model that forms the backbone of chemical power source simulations.*

Chemical power sources are devices that convert chemical energy into electrical energy through electrochemical reactions. They are the foundation of modern energy systems — from portable electronics and electric vehicles to grid-scale storage and renewable energy integration.

Main types include:

- Galvanic cells / Batteries
- Fuel cells
- Supercapacitors (electrochemical capacitors)

Modelling these systems is essential for:

- Predicting performance and degradation,
- Optimizing design and materials,
- Scaling from lab cells to industrial modules,
- Integrating with power electronics and control systems.

Type	**Energy Conversion Principle**	**Example Systems**	**Key Modeling Focus**
Primary batteries	Irreversible chemical → electrical	Zn–MnO_2, Li–$SOCl_2$	Discharge kinetics, internal resistance
Secondary (rechargeable) batteries	Reversible redox processes	Li-ion, NiMH, Pb-acid	Charge/discharge cycling, degradation
Fuel cells	Continuous reactant supply	H_2/O_2 PEMFC, SOFC	Reaction–transport coupling, steady operation
Supercapacitors	Electrostatic or pseudocapacitive storage	EDLC, RuO_2	Double-layer formation, transient response

The maximum theoretical energy of a chemical power source is determined by the Gibbs free energy change:

$$\Delta G = -nFE_{eq}$$

The theoretical energy density (Wh/kg) is:

$$E_{spec} = \frac{-\Delta G}{M\ 3600}$$

where M is molar mass of reactants.

At any moment, the electrical power delivered by a cellis:

$$P = IV$$

and the energy efficiency:

$$\eta = \frac{V}{E_{eq}}$$

However, the actual voltage V is lower than E_{eq} due to polarization losses (activation, ohmic, concentration).

Modelling a chemical power source involves coupling three main submodels and each submodel contributes to voltage–current–time predictions, forming the core of full-system modelling.

Model	**Physics Represented**	**Typical Equations**
Thermodynamic model	Reaction potentials and equilibrium	Nernst equation
Kinetic model	Reaction rates at electrodes	Butler–Volmer equation
Transport model	Ionic and electronic transport	Nernst–Planck & Ohm's law

Electrode reactions are described by Butler-Volmer kinetics:

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

In high overpotential limits, this simplifies to Tafel kinetics:

$$\eta = a + b log(j)$$

Mass transport ensures reactants reach and products leave the electrode. Described by the Nernst–Planck equation including diffusion, migration and convection as following:

$$J_i = -D_i \nabla c_i - z_i u_i c_i \nabla \phi + v c_i$$

However, in some cases transport limitations can create concentration polarization:

$$\eta_{conc} = \frac{RT}{nF} ln\left(\frac{c_{bulk}}{c_{surface}} \right)$$

In general, the cell voltage under load is:

$$V = E_{eq} - \eta_{act} - \eta_{ohm} - \eta_{conc}$$

Modelling of chemical power sources bridges electrochemistry, thermodynamics, transport phenomena, and electrical engineering.
A clear understanding of each process level enables:

- Design of efficient and durable energy systems,
- Accurate performance prediction, and

- Intelligent control and optimization in real-world applications.

Learning Outcomes

Learning Outcome (LO)	**Indicator of Achievement (ID)**	**Description**
LO 4: Describe the key structures and performance criteria of chemical and electrochemical energy storage systems.	**ID 4.1:** Introduction to modelling chemical power sources.	Students will explain and apply the conceptual framework of thermodynamic, kinetic, and transport modelling for electrochemical energy devices.

Questions for Self-Examination

1. What distinguishes a primary battery from a secondary (rechargeable) battery in terms of modelling requirements?
2. How is Gibbs free energy related to the theoretical cell voltage and energy density?
3. Write the Nernst equation. What information does it provide for cell modelling?
4. Under what conditions can the Butler–Volmer equation be simplified to the Tafel form?
5. What types of polarization losses cause the actual cell voltage to deviate from the equilibrium potential?
6. Explain how diffusion, migration, and convection contribute to mass transport in chemical power sources.
7. Write the full Nernst–Planck expression. Which term dominates in a highly concentrated electrolyte?

Self-Study Assignment
Assignment Title:

Development of a Unified Electrochemical Model for a Simple Battery Cell in COMSOL Multiphysics

Objective:

To build a simplified chemical power source model integrating thermodynamics, kinetics, and mass transport, and to observe how each component affects the cell's voltage–current behavior.

Tasks

1. Geometry and Physics Setup

- Construct a **1D model** of a simple electrochemical cell with:
    - Anode region
    - Electrolyte separator
    - Cathode region

Include the physics:

- **Transport of Diluted Species (tds)** → Nernst–Planck transport
- **Electrostatics (es)** or **Secondary Current Distribution** → ionic/electronic conduction
- **Electrode Surface Reactions** → Butler–Volmer kinetics

2. Thermodynamic Model

- Define equilibrium potentials for the anode and cathode using the **Nernst equation**.
- Compute theoretical OCV using:

$$E_{\text{eq}} = -\frac{\Delta G}{nF}$$

3. Kinetic Model

- Apply Butler–Volmer kinetics on both electrodes:

$$i = i_0\left[e^{\alpha_a F\eta/RT} - e^{-\alpha_c F\eta/RT}\right]$$

Explore two regimes:

- Near equilibrium → BV linearization
- Large overpotential → Tafel behavior

4. Transport Model

- Implement the full Nernst–Planck equation for ions:

$$\mathbf{N}_i = -D_i \nabla c_i - z_i u_i F c_i \nabla \phi$$

Perform simulations with:

- **Diffusion only**
- **Diffusion + migration**

Compare concentration profiles and voltage response.

5. Polarization and Discharge Simulation

- Apply a range of discharge currents (e.g., 0.5, 1.0, 2.0 A/m²).
- Extract the cell voltage:

$$V = E_{\text{eq}} - \eta_{\text{act}} - \eta_{\text{ohm}} - \eta_{\text{conc}}$$

Plot:

- V(t) curves
- Concentration profiles
- Overpotential contributions

6. Performance and Efficiency Analysis

- Compute instantaneous power:

$$P = V \cdot I$$

- Estimate energy efficiency at different loads.
- Identify when concentration polarization becomes dominant.

References

1. Bard, A. J., Faulkner, L. R., Electrochemical Methods, 2nd edition, 2001.
2. Newman, J., Thomas-Alyea, K., Electrochemical Systems, 3rd edition.
3. COMSOL Application Library: Lithium-Ion Battery, Fuel Cell, Electrochemical Capacitor examples.