Lecture 12

Introduction to modelling of chemical power sources

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:

$$\eta = a + blog(j)$$

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.