LECTURE 02

Fundamental Concepts of Modeling with Electrochemical Processes

Department of Analytical, Colloidal Chemistry and Technology of Rare Elements

Modeling of chemico-technological processes | 6B07102 Chemical Engineering

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Purpose and expected learning outcomes

Purpose: develop physically grounded models that connect measurable chemical-engineering behavior to governing equations and reliable predictions.

EXPLAIN

Identify governing phenomena and state assumptions.

CALCULATE

Apply equations using consistent physical units.

COMPARE

Evaluate alternative model formulations.

INTERPRET

Read simulated curves and measured responses.

EVALUATE

Test limitations, uncertainty and validity.

APPLY

Propose a reproducible modeling workflow.

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From physical system to engineering decisions

01 Define system

Boundaries, outputs

02 Formulate physics

Balances and kinetics

03 Specify parameters

Units and assumptions

04 Solve equations

Analytical or numerical

05 Validate outputs

Experiment and errors

06 Optimize process

Design and control

Industrial relevance: reactors • separations • electrolysis • energy storage • environmental treatment

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Fundamental Electrochemical Equations

Electrochemical models are based on fundamental relationships between electrode potential, current, and reaction kinetics.

1. Faraday's Law

The amount of substance transformed during electrolysis is proportional to the electric charge passed through the system.

$$m = MIt / nF$$

where:

- m — mass of the deposited or consumed substance.
- M — molar mass.
- I — electric current.
- t — electrolysis time.
- n — number of electrons transferred.
- F — Faraday constant (96,485 C/mol).

Butler–Volmer Equation

The relationship between current density and electrode overpotential is described by:

$$j = j_o [\exp(\alpha_a nF\eta/RT) - \exp(-\alpha_c nF\eta/RT)]$$

where j_o is the exchange current density and η is the electrode overpotential.

Mass Transport in Electrochemical Systems

Mass transport determines how electroactive species move from the bulk electrolyte to the electrode surface.
Three main mechanisms are involved:

1. Diffusion — movement of species due to concentration gradients.
2. Migration — movement of charged species under an electric field.
3. Convection — transport caused by fluid movement.

Fick's First Law:

$$J = -D(\partial C/\partial x)$$

where:

- J — diffusion flux.
- D — diffusion coefficient.
- C — concentration.
- x — spatial coordinate.

The Nernst–Planck equation combines diffusion, migration, and convection:

$$J_i = -D_i \nabla C_i - (z_i D_i F/RT) C_i \nabla \phi + C_i v$$

where z_i is the ionic charge number, ϕ is the electric potential, and v is the fluid velocity.

Balances and electrochemical interfaces

Electrode reactions couple electron flow to species consumption.

$$Cu^{2+} + 2e^{-} \rightarrow Cu(s)$$

MODEL CONDITIONS A current density j (A m^{-2}) sets molar reaction flux through Faraday's law.

ENGINEERING INTERPRETATION Battery, electroplating and electrolyzer models share interface balances.

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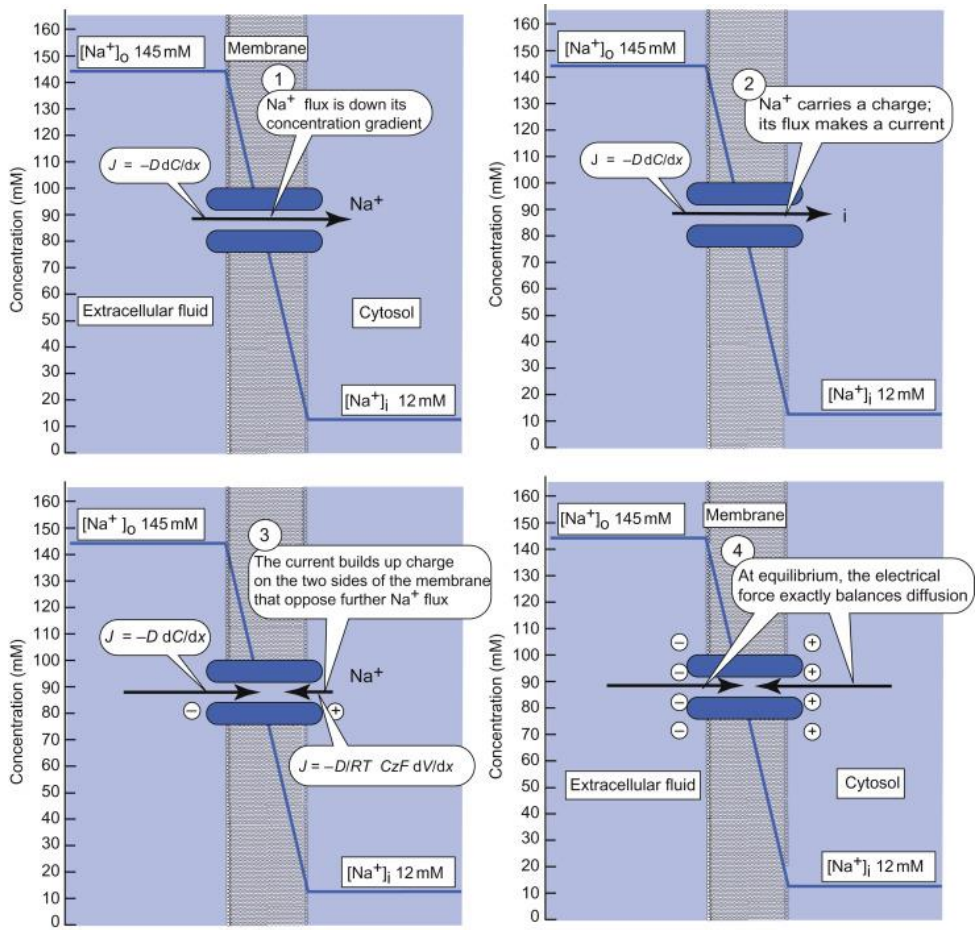
Thermodynamics: equilibrium potential

The Nernst equation describes equilibrium, not reaction speed.

$E_{eq} = E° - (RT/nF) \ln Q$

MODEL CONDITIONS Q uses dimensionless activities; n is electrons per reaction; T in K.



ENGINEERING INTERPRETATION Electrolyte composition changes reversible cell voltage.

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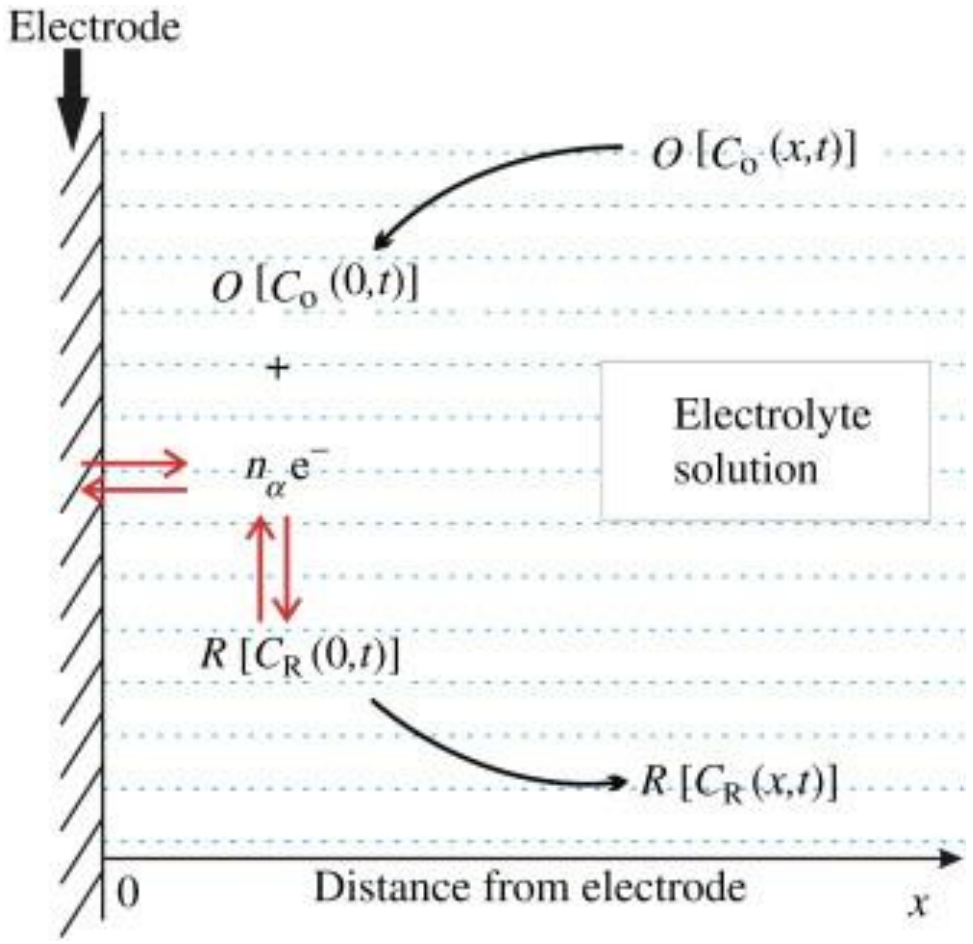
Electrode kinetics

Butler–Volmer describes activation-controlled interfacial current.

$$j = j_0[\exp(\alpha_a nF\eta/RT) - \exp(-\alpha_c nF\eta/RT)]$$

MODEL CONDITIONS $\eta = E - E_{eq}$; j_0 is exchange current density; α values are transfer factors.



ENGINEERING INTERPRETATION **Tafel slopes approximate sufficiently large |η| without transport limits.**

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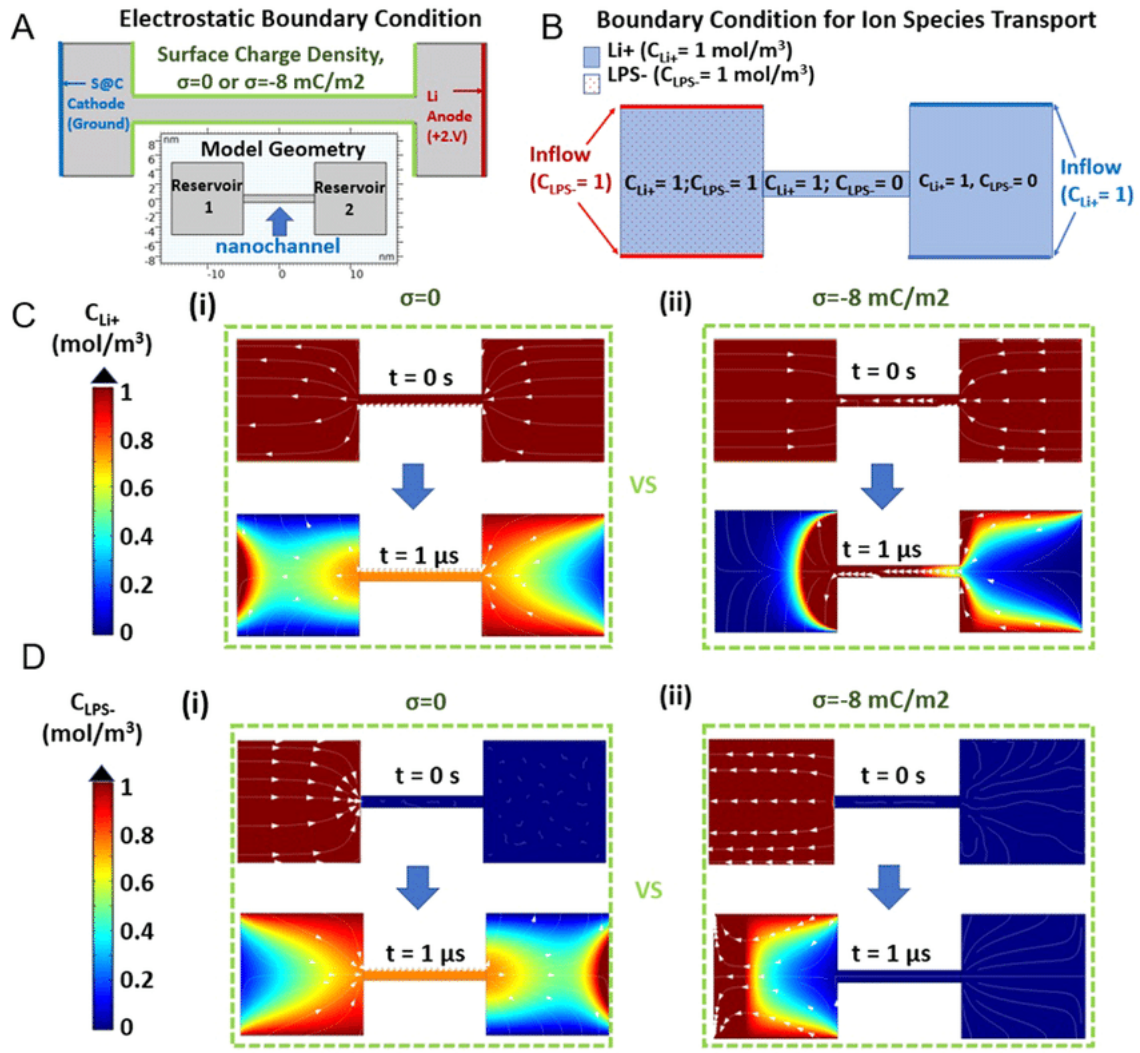
Transport of charged species

Diffusion, migration and convection combine in ionic flux.

$$N_i = -D_i \nabla c_i - z_i (D_i F/RT) c_i \nabla \phi + c_i v$$

MODEL CONDITIONS Ideal dilute-solution Nernst–Planck; c_i mol m^{-3}, N_i mol m^{-2} s^{-1}.



ENGINEERING INTERPRETATION **Supporting electrolyte can suppress migration of dilute analytes.**

DOI:10.1038/s41467-021-27861-w

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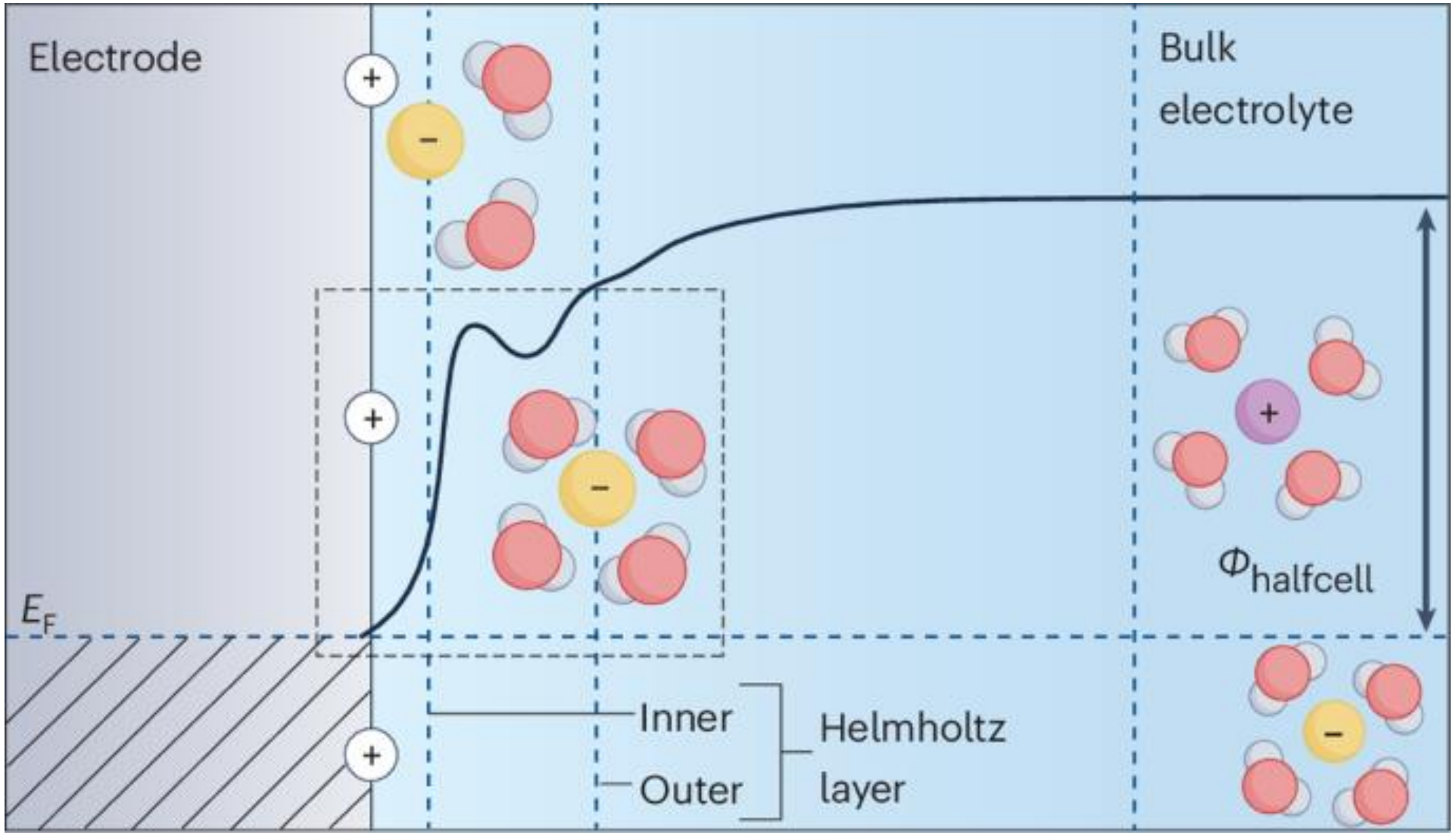
First-principles approaches and concepts to simulate electrochemical interfaces

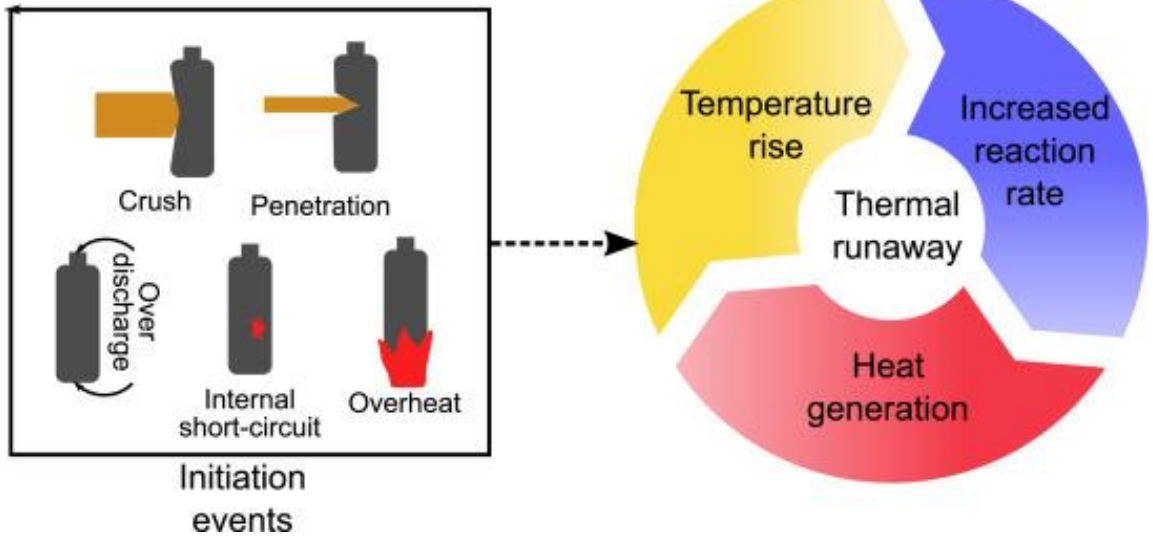


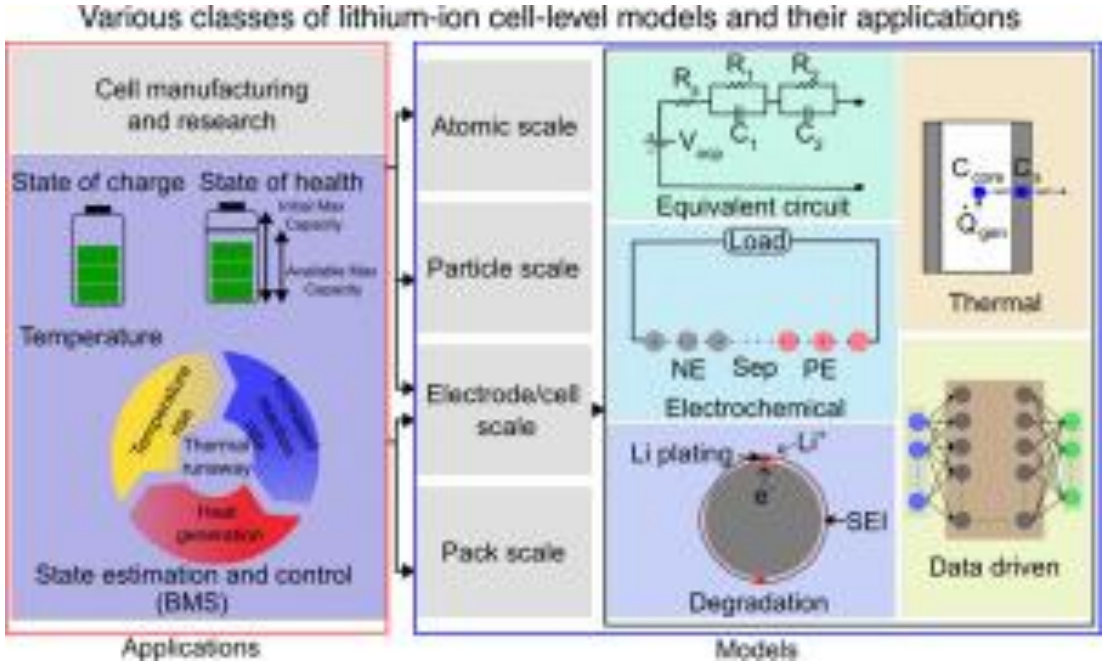
Todorova, M., Wippermann, S. & Neugebauer, J. First-principles approaches and concepts to simulate electrochemical interfaces. *Nat Rev Chem* **10**, 133–146 (2026). https://doi.org/10.1038/s41570-025-00792-6

Applications and Modeling Workflow

Applications of electrochemical modeling:

- Batteries and fuel cells.
- Electrochemical sensors.
- Metal electrodeposition and electrorefining.
- Corrosion protection.
- Water electrolysis and hydrogen production.
- Electrochemical wastewater treatment.





Rohit Mehta, Amit Gupta Mathematical modelling of electrochemical, thermal and degradation processes in lithium-ion cells—A comprehensive review // Renewable and Sustainable Energy Reviews 192 (2024) 11426

Conclusions: a verified model is a useful model

PHYSICS

Identify dominant conservation and transport laws.

EQUATIONS

State variables, signs, units and assumptions.

PARAMETERS

Determine measurable coefficients and uncertainty.

NUMERICS

Check stability, convergence and physical balances.

EXPERIMENT

Validate predictions with independent observations.

APPLICATION

Use models for design, control and optimization.

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Homework: calculations, interpretation and research

1. THEORY Explain the assumptions behind "$Cu^{2+} + 2e^{-} \rightarrow Cu(s)$" and identify when they fail.

2. CALCULATION For $C_0 = 2.0$ mol m^{-3}, $k = 0.020$ s^{-1} and $t = 60$ s, calculate $C = C_0 \exp(-kt)$ and conversion.

3. DATA Simulated normalized outputs at $t = 0, 20, 40, 60$ s are 1.00, 0.67, 0.45, 0.30. Estimate a first-order rate constant.

4. CRITIQUE Explain how transport limitations or nonideal mixing could invalidate a simple rate model.

5. RESEARCH Design a two-condition validation experiment for fundamental concepts of modeling with electrochemical processes; report measured variables, units and uncertainty.

Constants when needed: $F = 96485$ C mol^{-1}; $R = 8.314$ J mol^{-1} K^{-1}; $T = 298.15$ K.

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Recommended Literature

1. Fogler, H. S. *Elements of Chemical Reaction Engineering*. 5th ed., Pearson, 2016.
2. Himmelblau, D. M., Riggs, J. B. *Basic Principles and Calculations in Chemical Engineering*. 8th ed., Pearson, 2012.
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5. Bequette, B. W. *Process Control: Modeling, Design, and Simulation*. Prentice Hall, 2003.