Lecture 1 | Introduction to Mathematical Modeling of Electrochemical Processes

Al-Farabi Kazakh National University

Department of Analytical, Colloidal Chemistry and Technology of Rare Elements

Discipline: Modeling in Electrochemistry

Educational program: 7M07103 Chemical Engineering

Lecturer: Khaisa Avchukir, PhD, Associate Professor

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Purpose and Expected Learning Outcomes

PURPOSE

Build a quantitative understanding of introduction to mathematical modeling of electrochemical processes.

01 Explain the physical assumptions and governing electrochemical equations.

02 Calculate relevant kinetic, transport, and interfacial parameters.

03 Interpret simulated responses and compare them with measurements.

04 Evaluate model limitations and propose a reproducible validation plan.

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Lecture Trajectory and Practical Relevance



Scientific value: link measurable current, potential, concentration, or impedance to mechanistic parameters.

Applications: electroanalysis • energy conversion • electrodeposition • corrosion • process engineering

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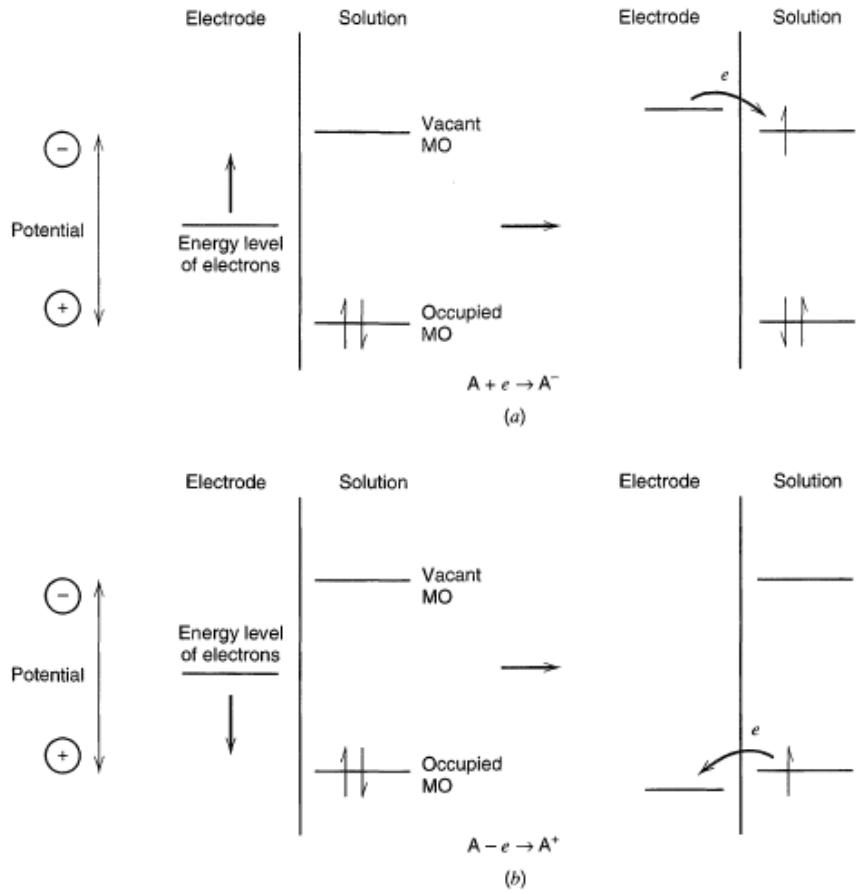
Electrode potential and electron-transfer energetics

$$\Delta G = -nFE$$

A negative potential increases electron energy; reduction transfers electrons to solution species.

A positive potential favors oxidation; equilibrium depends on redox activities.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

Reference: Bard, Faulkner & White, Electrochemical Methods (3rd ed.)

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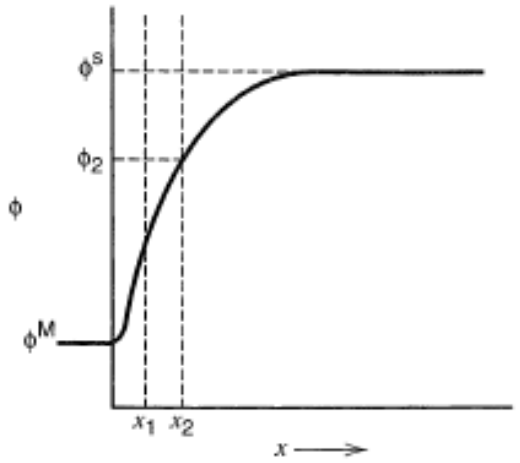
Thermodynamic equilibrium: the Nernst equation

$$E = E^\circ + (RT/nF)\ \ln(aOx/aRed)$$

Activities, not concentrations, determine the exact equilibrium potential.

At 298 K, $2.303RT/F \approx 0.05916$ V.



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Faradaic versus nonfaradaic response

$$i = i_F + i_C \; ; \; i_C = C_{dl}(dE/dt)$$

Faradaic current involves electron transfer and chemical transformation.

Charging current reflects double-layer charge redistribution.

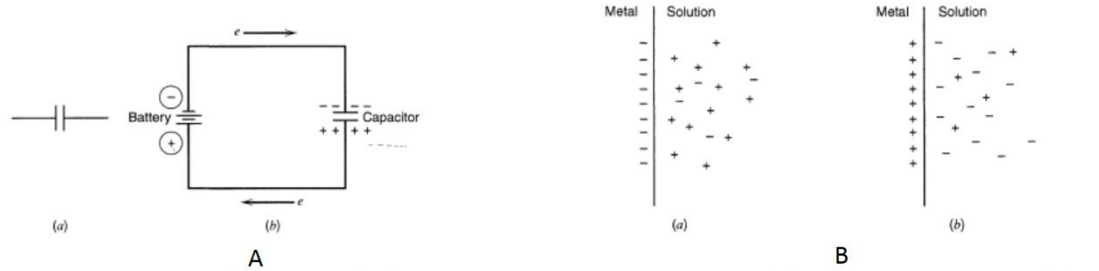

Figure 2. A) (a) A capacitor, (b) Charging a capacitor with a battery. B) The metal-solution interface as a capacitor with a charge on the metal, q^M, (a) negative and (b) positive [1].

MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

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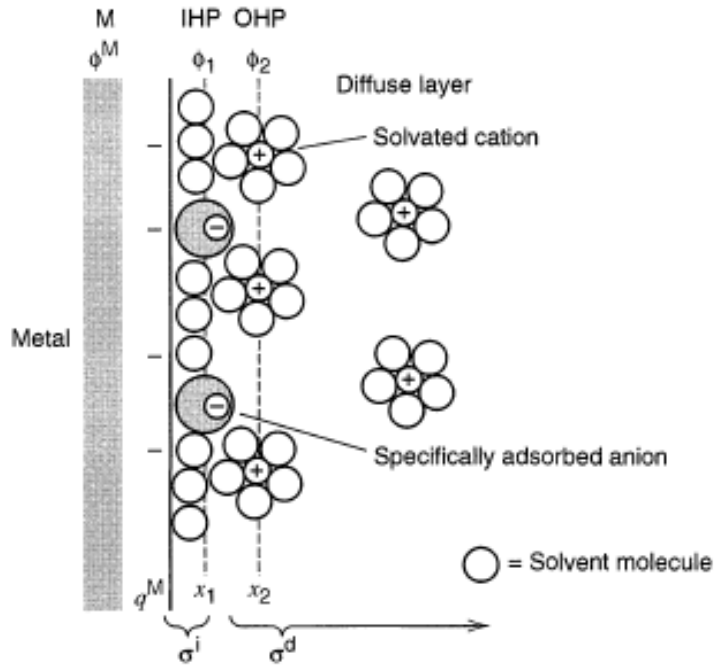
Electrical double layer and interfacial charge

Cdl = dQ/dE

Compact and diffuse regions screen the electrode surface charge.

Capacitance depends on potential, adsorption, and electrolyte composition.



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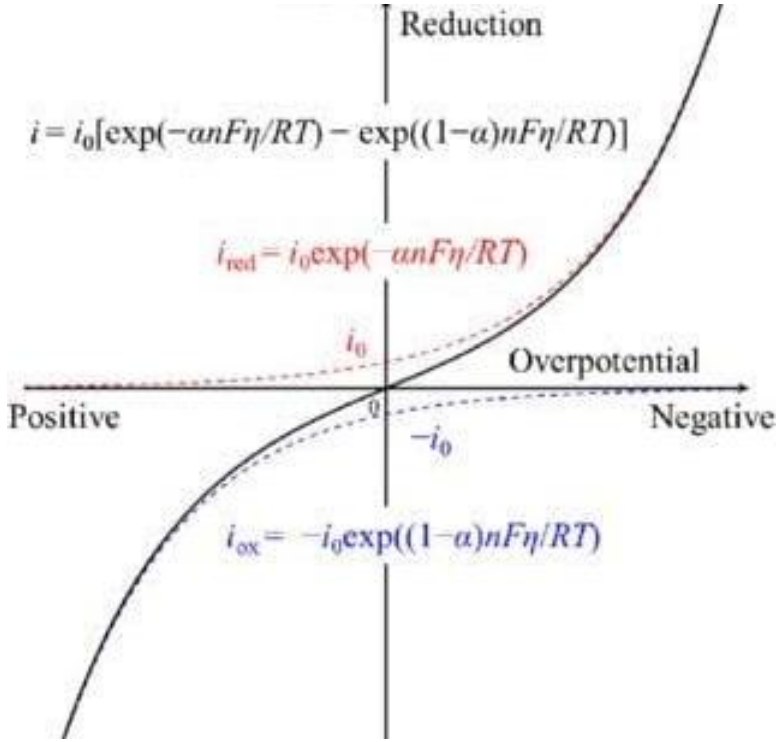
Reaction kinetics and overpotential

$$i = i_0[\exp(\alpha_a F\eta/RT) - \exp(-\alpha_c F\eta/RT)]$$

Butler–Volmer relates net current to activation overpotential.

Exchange current i_0 and transfer coefficients characterize interfacial kinetics.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

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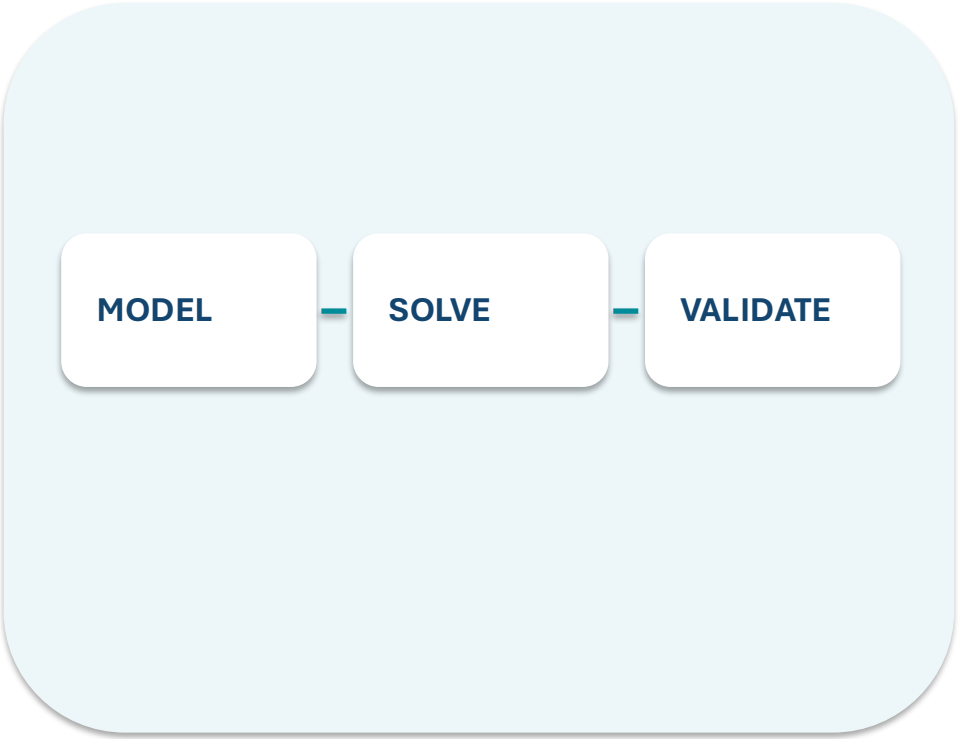
A coupled modeling workflow

$$\partial c/\partial t = \nabla\cdot(D\nabla c)$$

Specify geometry, governing equations, initial/boundary conditions, and parameters.

Solve numerically; compare predicted currents with measurements and test sensitivity.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

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Conclusions: From Physical Mechanisms to Predictive Models

1. Electrode potential and electron-transfer energetics

$\Delta G = -nFE$

2. Thermodynamic equilibrium: the Nernst equation

$E = E^\circ + (RT/nF)\ \ln(a_{Ox}/a_{Red})$

3. Faradaic versus nonfaradaic response

$i = i_F + i_C\ ;\ \ i_C = C_{dl}(dE/dt)$

4. Electrical double layer and interfacial charge

$C_{dl} = dQ/dE$

5. Reaction kinetics and overpotential

$i = i_0[\exp(\alpha_a F\eta/RT) - \exp(-\alpha_c F\eta/RT)]$

6. A coupled modeling workflow

$\partial c/\partial t = \nabla\cdot(D\nabla c)$

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Homework: Quantitative and Research-Oriented Problems

CONCEPTUAL Compare the assumptions underlying “Electrode potential and electron-transfer energetics” and “Faradaic versus nonfaradaic response”.

CALCULATION Given T = 298.15 K, F = 96485 C mol^{-1}, R = 8.314 J mol^{-1} K^{-1}, D = 1.0×10^{-9} m^2 s^{-1}, c = 1.0 mol m^{-3}, A = 1.0 cm^2, n = 1, compute a relevant transport or kinetic prediction and state assumptions.

DATA INTERPRETATION For simulated normalized signals (t/s, response): (0.2,0.82), (0.5,0.61), (1.0,0.44), (2.0,0.30), identify the trend and test a plausible physical model.

CRITICAL THINKING Predict how a tenfold change in the controlling kinetic or transport parameter changes the response; distinguish hypotheses.

RESEARCH TASK Design a COMSOL or Python model with geometry, boundary conditions, mesh-convergence test, and an experimental validation plan.

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