Lecture 3 | Charge Transfer Across the Electrical Double Layer

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 charge transfer across the electrical double layer.

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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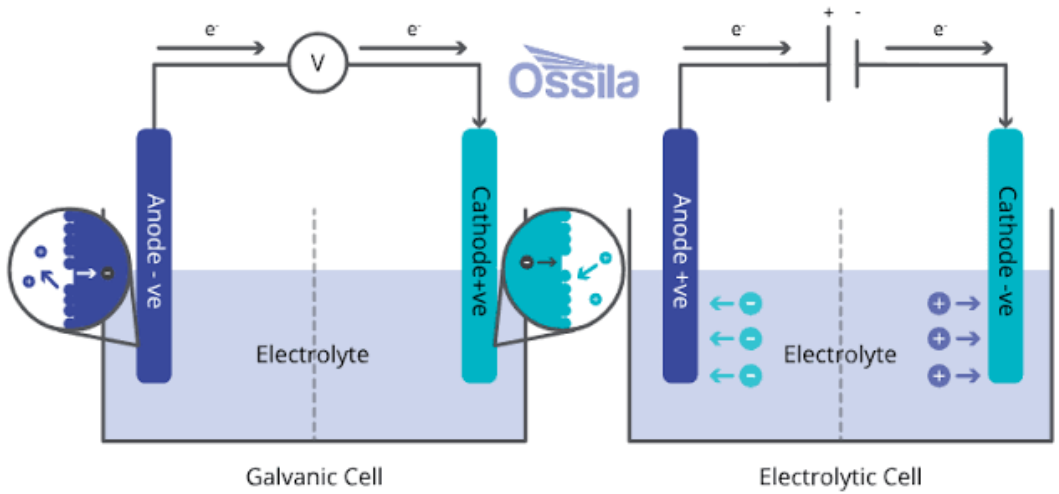
One-dimensional electrochemical cell

$$Me^{n+} + ne^- \rightleftharpoons Me(s)$$

A 1D electrolyte domain connects two reactive electrodes.

The interfacial reaction couples ionic flux to current.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

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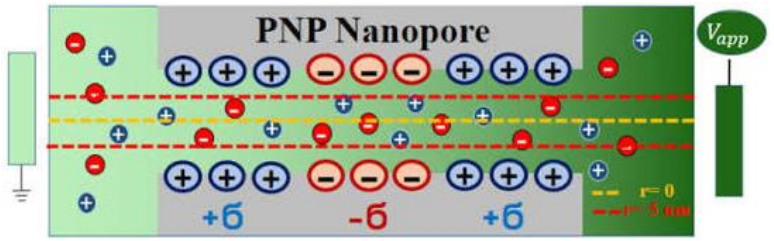
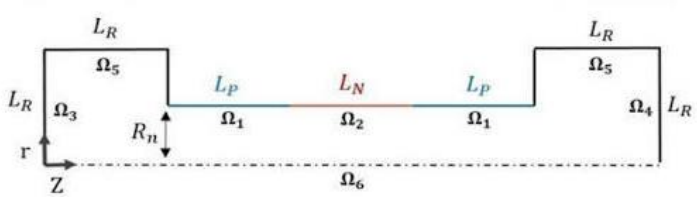
Transport and space-charge coupling

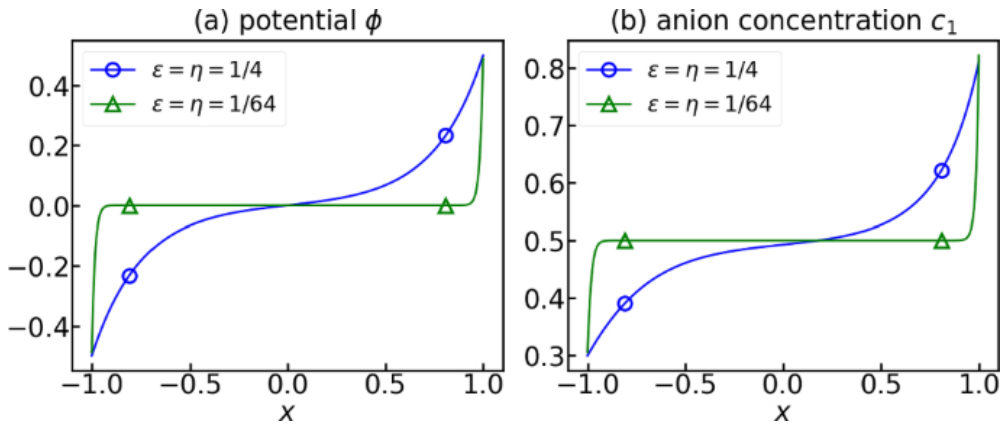
$$N_i = -D_i \nabla c_i - (z_i F D_i / RT) c_i \nabla \phi$$

The PNP model resolves concentration and electric-potential profiles.

Local electroneutrality may fail inside nanometer-scale double layers.







MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

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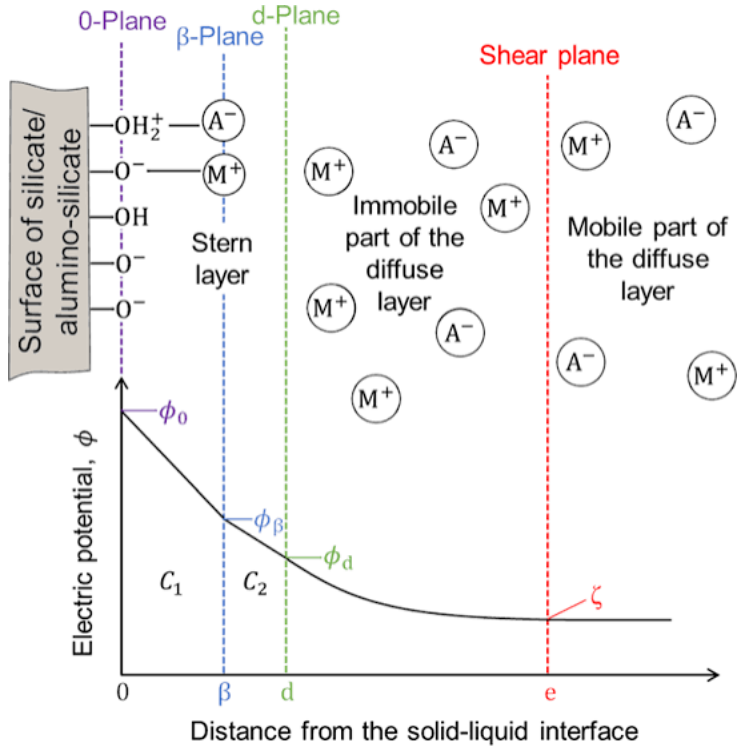
Stern-layer boundary condition

$$\phi + \lambda S(n \cdot \nabla \phi) = \phi M$$

A Robin boundary condition represents the compact-layer potential drop.

Effective Stern length incorporates compact-layer dielectric response.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

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

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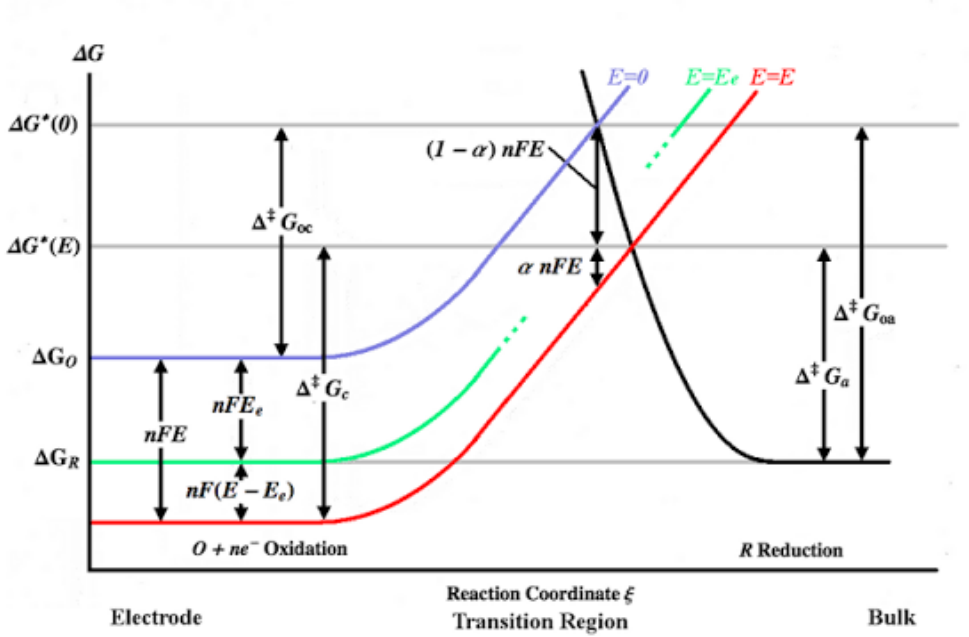
Butler–Volmer boundary kinetics

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

Reaction-plane potential determines activation overpotential.

Use consistent sign conventions for anodic/cathodic flux.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

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

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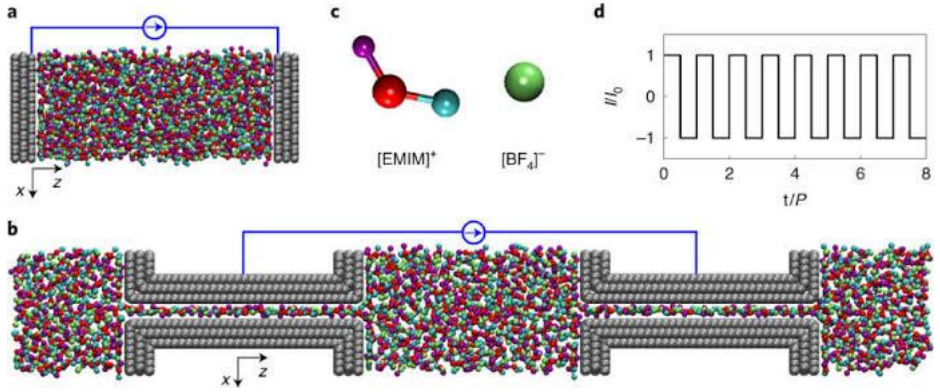
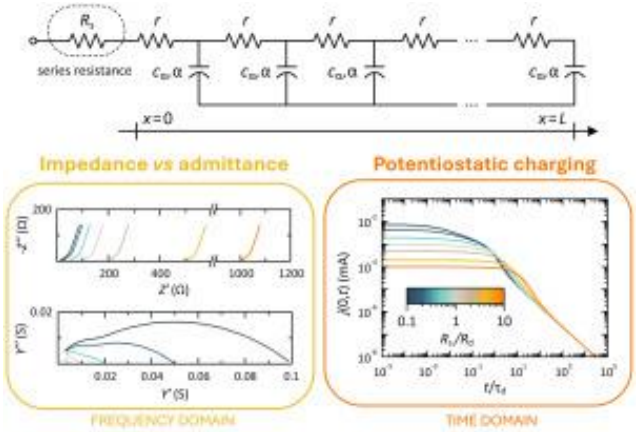
Flux conservation and galvanostatic control

$$-n \cdot N_i = v_i \, j/(nF)$$

Stoichiometry connects each ionic species flux to current density.

Galvanostatic models solve electrode voltage as an unknown.





MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

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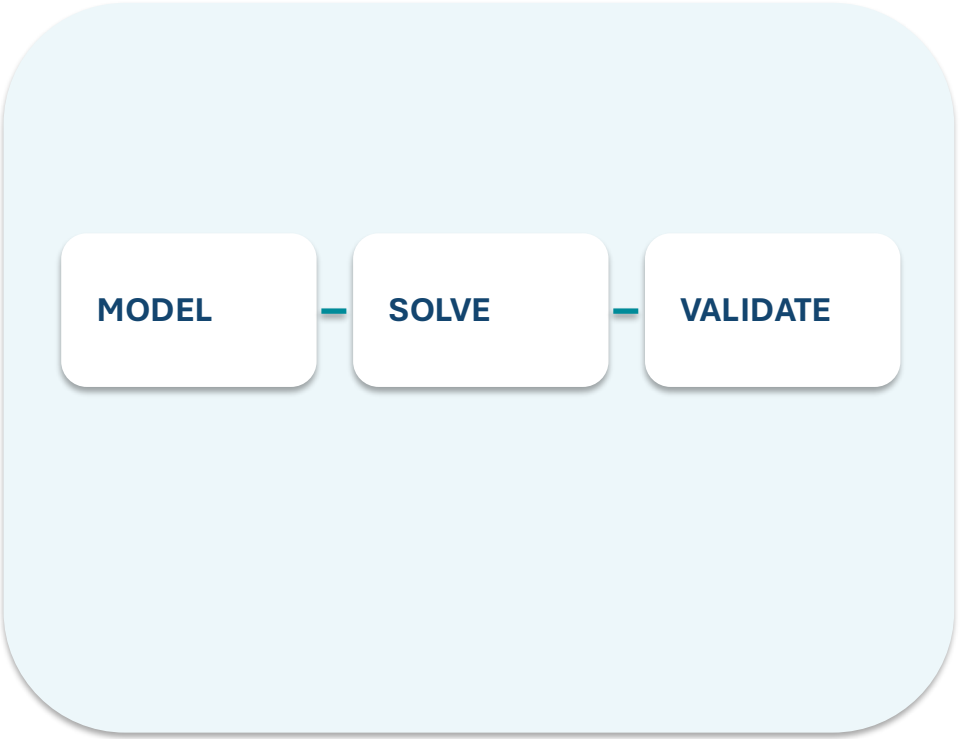
Model limitations and numerical checks

$$\int \Omega c_i \, dV = \text{prescribed inventory}$$

Check species conservation and electrode boundary orientation.

Highly concentrated electrolytes need activity and steric corrections.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

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Conclusions: From Physical Mechanisms to Predictive Models

1. One-dimensional electrochemical cell

$$M^{n+} + ne^- \rightleftharpoons M(s)$$

2. Transport and space-charge coupling

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

3. Stern-layer boundary condition

$$\phi + \lambda_S (n \cdot \nabla \phi) = \phi_M$$

4. Butler–Volmer boundary kinetics

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

5. Flux conservation and galvanostatic control

$$-n \cdot N_i = \nu_i j / (nF)$$

6. Model limitations and numerical checks

$$\int_\Omega c_i \, dV = \text{prescribed inventory}$$

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Homework: Quantitative and Research-Oriented Problems

CONCEPTUAL Compare the assumptions underlying “One-dimensional electrochemical cell” and “Stern-layer boundary condition”.

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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