Lecture 6 | Cyclic Voltammetry: Theory, Simulation, and Parameter Estimation

Al-Farabi Kazakh National University

Department of Analytical, Colloidal Chemistry and Technology of Rare Elements

Discipline: Modeling in Electrochemistry

Educational program: 7M07103 Chemical Engineering

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Purpose and Expected Learning Outcomes

PURPOSE

Build a quantitative understanding of cyclic voltammetry: theory, simulation, and parameter estimation.

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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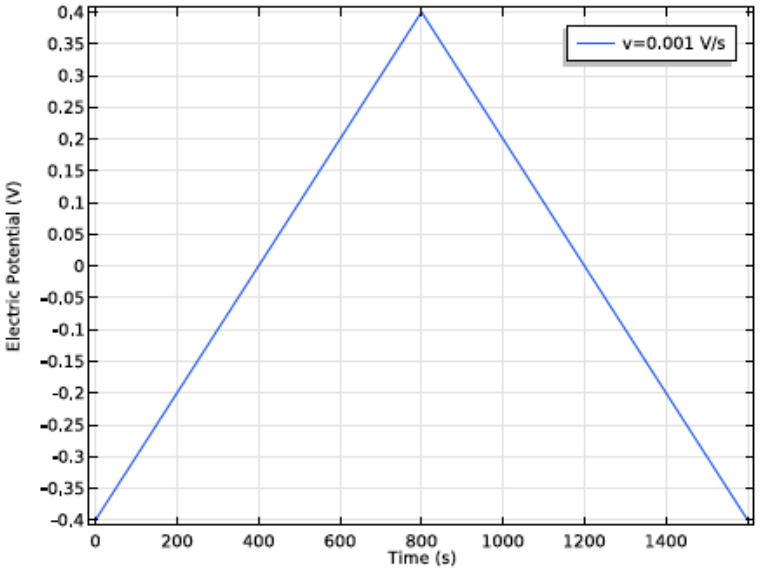
Triangular potential waveform

$$E(t) = Ei \pm vt$$

Potential is swept between two vertex potentials.

Scan rate v (V s^{-1}) controls experiment duration.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

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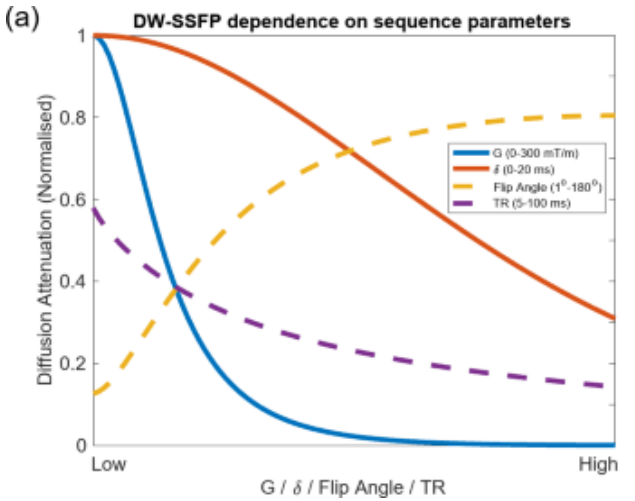
Time-dependent diffusion

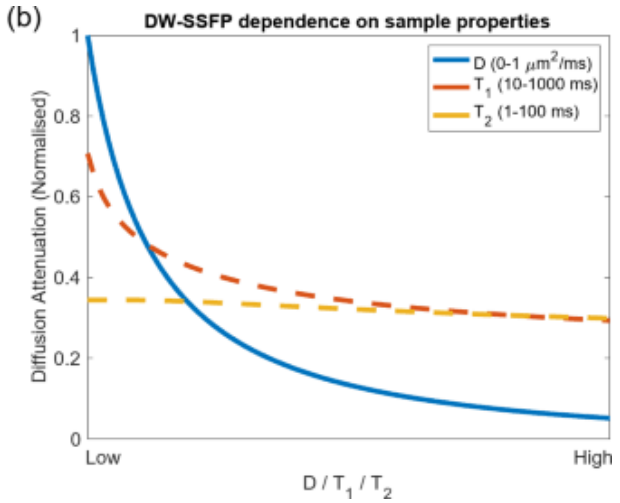
$$\partial c_i/\partial t = D_i \partial^2 c_i/\partial x^2$$

Solve oxidized and reduced species concentrations.

Large planar electrodes permit a one-dimensional approximation.

MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE





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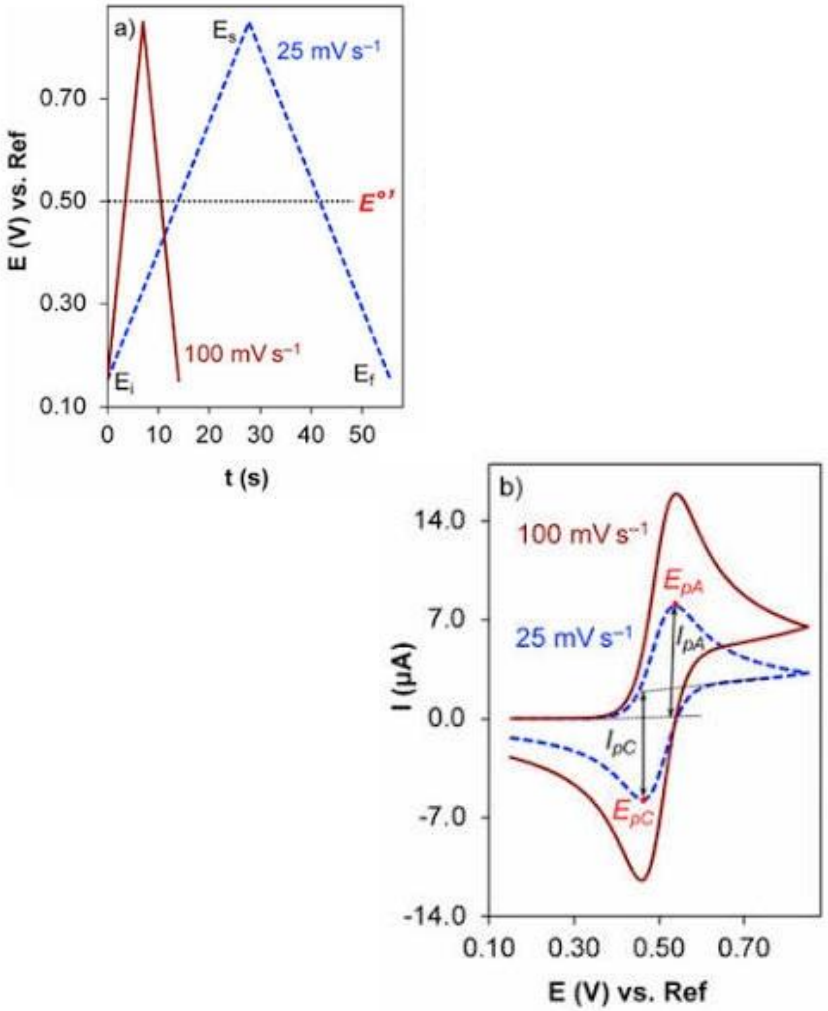
Reversible peak-current scaling

$$ip = 0.4463\, nFAc^*\sqrt{(nFDv/RT)}$$

At 298 K, Randles–Ševčík predicts $ip \propto v^{1/2}$.

Assumes planar semi-infinite diffusion and reversible electron transfer.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

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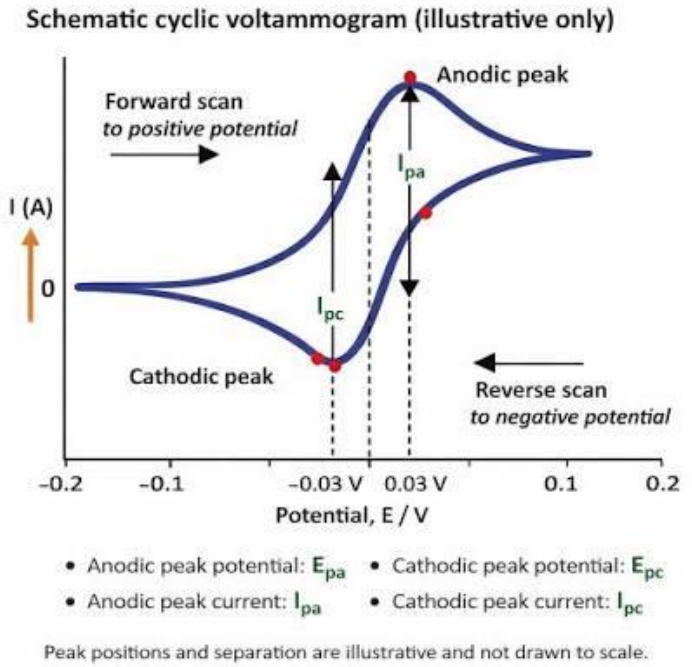
Peak separation and reversibility

ΔEp ≈ 59 mV/n at 298 K

Ideal reversible one-electron CV gives ~59 mV separation.

Kinetic limitations, resistance, and coupled chemistry increase separation.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

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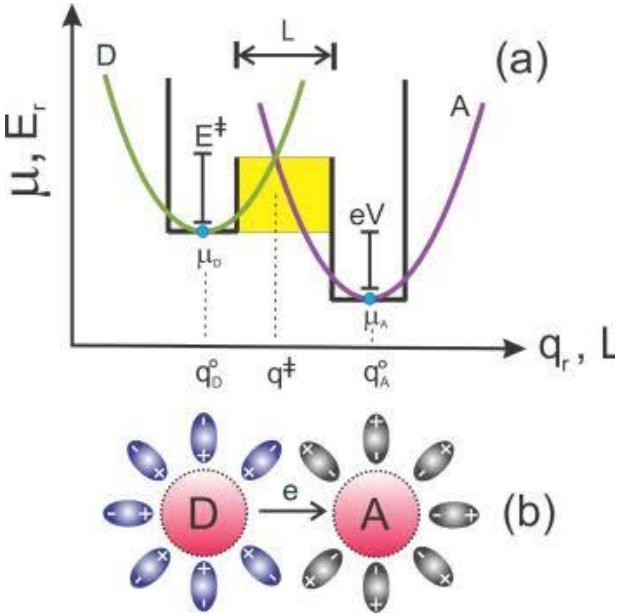
Finite-rate electron transfer

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

Couple diffusion to Butler–Volmer electrode kinetics.

Compare simulations over scan rate to estimate k0 and α.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

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Inverse modeling and validation

$$\min_{\theta} \Sigma_k [i_{meas,k} - i_{model,k}(\theta)]^2$$

Fit physically identifiable parameters across multiple scan rates.

Check residuals, uncertainty, and capacitive baseline.

MODEL – SOLVE – VALIDATE

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Conclusions: From Physical Mechanisms to Predictive Models

1. Triangular potential waveform

$E(t) = Ei \pm vt$

2. Time-dependent diffusion

$\partial ci/\partial t = Di\partial^2 ci/\partial x^2$

3. Reversible peak-current scaling

$ip = 0.4463\ nFAc^*\sqrt{(nFDv/RT)}$

4. Peak separation and reversibility

$\Delta Ep \approx 59\ mV/n$ at 298 K

5. Finite-rate electron transfer

$j = j0[\exp(\alpha aF\eta/RT) - \exp(-\alpha cF\eta/RT)]$

6. Inverse modeling and validation

$\min\theta\ \Sigma k[imeas,k - imodel,k(\theta)]^2$

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Homework: Quantitative and Research-Oriented Problems

CONCEPTUAL Compare the assumptions underlying “Triangular potential waveform” and “Reversible peak-current scaling”.

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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