Fundamentals of Polarization Methods

Discipline: Modern research methods in electrochemistry

Educational program: 7M05301 Chemistry

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Purpose and expected learning outcomes

Purpose: understand potential-sweep experiments and interpret i–E responses.

- Explain potential polarization and scan-rate control
- Distinguish LSV, CV, corrosion polarization and pulse techniques
- Identify peak potentials, currents and reversibility indicators
- Use scan-rate dependence to evaluate diffusion vs kinetics
- Design an experiment and identify common artifacts

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Lecture trajectory: from excitation to interpretation

01

Control

Potential waveform

02

Measure

Current response

03

Interpret

Peaks and slopes

04

Quantify

D, kinetics, corrosion

05

Apply

Electrodeposition / sensors

Practical benefit: select a waveform that reveals reaction mechanism, mass transport, electrode stability, or analytical concentration.

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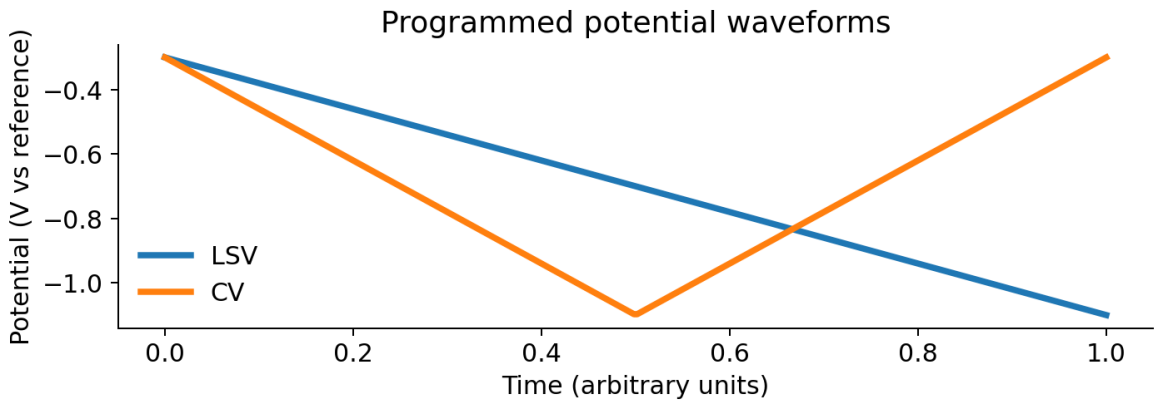
Polarization: what the instrument controls

Potentiostat maintains E(WE − RE); current passes between WE and CE.

- Overpotential: $\eta = E - E_{eq}$ (with consistent reference)
- Faradaic current depends on charge-transfer kinetics and mass transfer
- Charging current: $i_C \approx C_{dl} \cdot A \cdot dE/dt$
- Observed current = faradaic + capacitive + background



The scan rate $v = |dE/dt|$ sets the experimental timescale.

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Linear sweep voltammetry (LSV)

One-direction ramp: E(t) = Ei + vt; a peak occurs for planar diffusion-limited depletion.

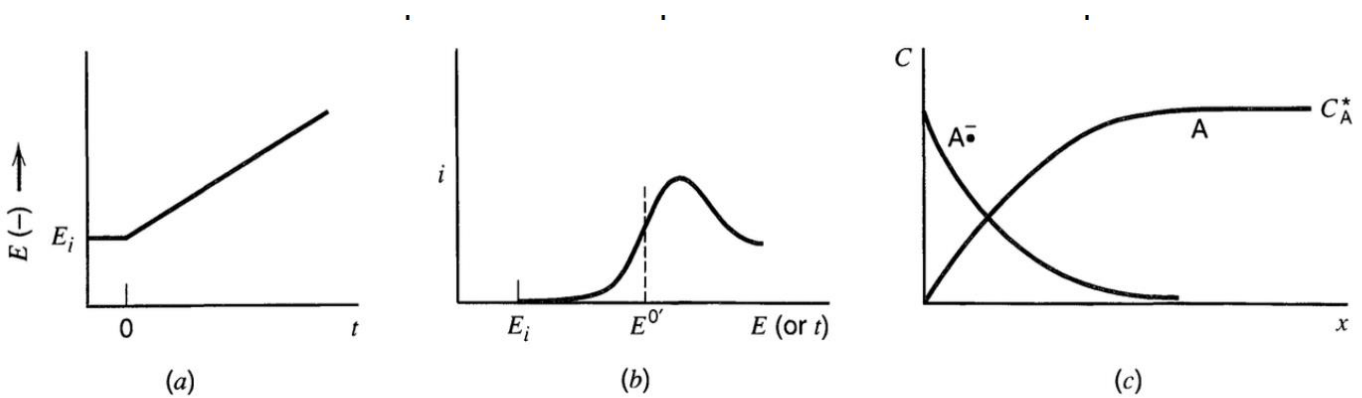

Figure 1. (a) Linear potential sweep or ramp starting at E_i (b) Resulting i-E curve, (c) Concentration profiles of A and A^* for potentials beyond the peak [1].

- Peak current increases with concentration and √scan rate for reversible diffusion control
- Peak potential shifts with kinetics, resistance and coupled chemistry
- A steady limiting plateau is possible with convective or microelectrode transport
- Use supporting electrolyte to suppress migration

Bard, Allen J., Larry R. Faulkner, and Henry S. White. Electrochemical methods: fundamentals and applications. John Wiley & Sons, 2022.

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Cyclic voltammetry (CV): scan reversal

Forward reduction creates Red; the reverse scan can reoxidize it.

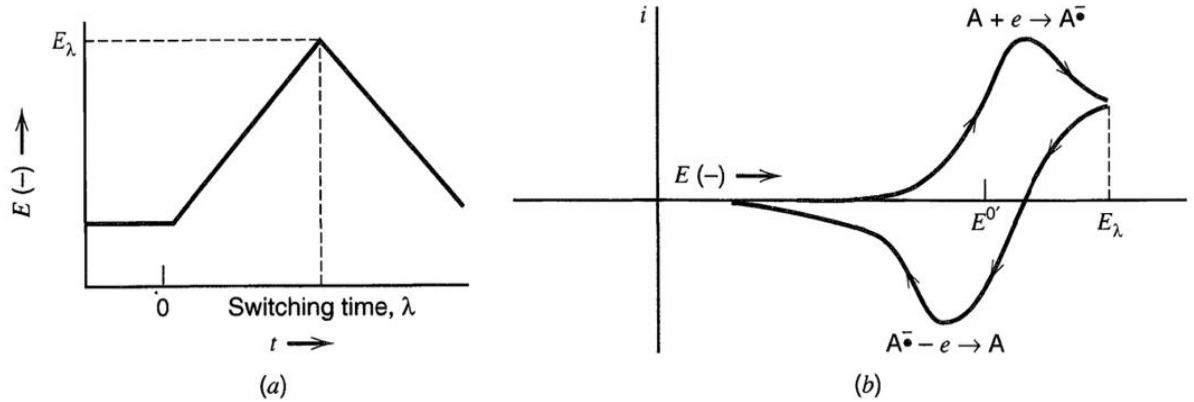

Figure 2. (a) Cyclic potential sweep, (b) Resulting cyclic voltammogram.

- For a reversible 1e⁻ couple at 25 °C: ΔEp ≈ 59 mV under ideal conditions
- Formal potential: E°' ≈ (Epa + Epc)/2 when assumptions apply
- Peak-current ratio and scan-rate effects probe follow-up chemistry
- Large ΔEp alone does not uniquely identify slow electron transfer

Bard, Allen J., Larry R. Faulkner, and Henry S. White. Electrochemical methods: fundamentals and applications. John Wiley & Sons, 2022.

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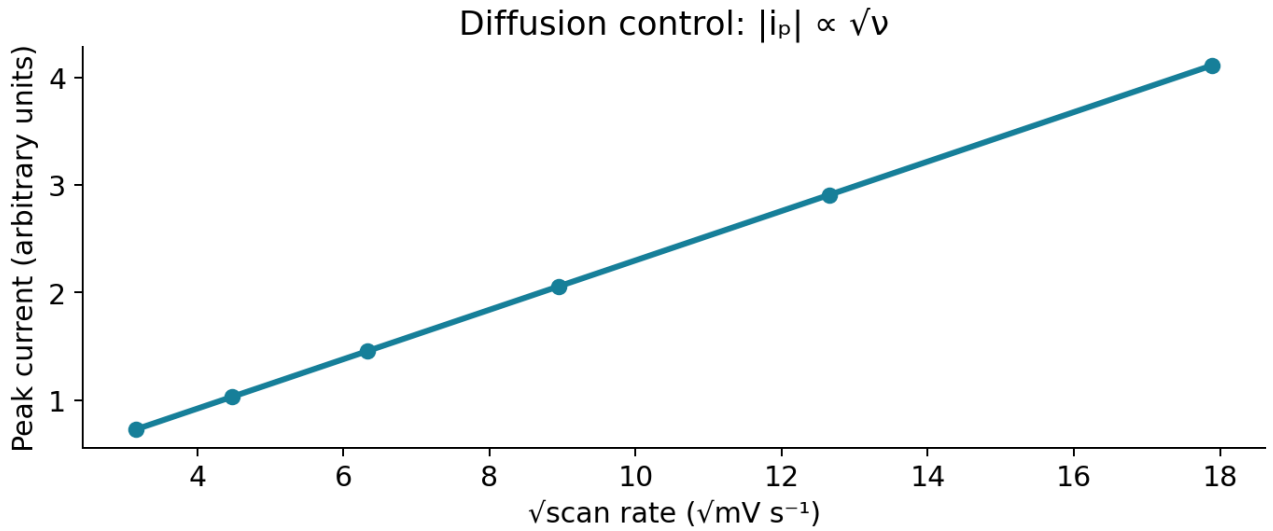
Quantitative interpretation: Randles–Ševčík

Reversible, diffusion-controlled planar electrode at 25 °C

$$ip = 2.69 \times 10^5 \, n^{3/2} \, A \, D^{1/2} \, C \, v^{1/2} \quad (A, cm^2, cm^2/s, mol/cm^3, V/s)$$



- Linear |ip| vs √v supports diffusion control, but is not conclusive alone
- Check baseline subtraction and capacitive background
- Verify scan-rate range, solution resistance and electrode area

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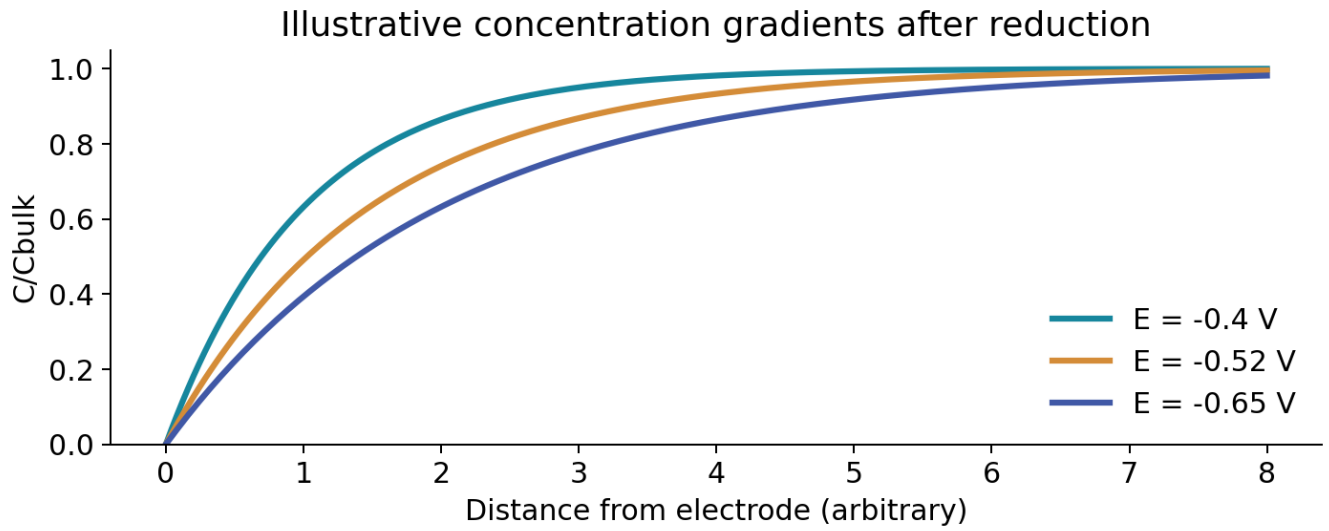
Why peaks appear: depletion and diffusion layers

Planar electrode: the reactant concentration at the surface decreases as reduction accelerates.



- Near the peak, surface reactant becomes strongly depleted
- Diffusion-layer growth reduces flux at later scan times
- Reverse scan reoxidizes product accumulated near the interface
- Peak shape depends on geometry, diffusion and kinetics

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Applications: corrosion and indium electrodeposition

Interpretation must match the specific electrochemical system and experimental conditions.

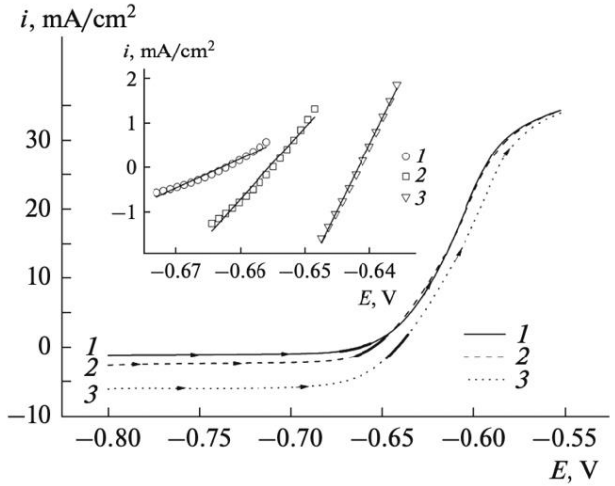

Figure 3. Polarization curves of indium discharge-ionization on indium electrode at 25°C, v = 5 mV/s in 2.0 M NaCl solution with different content of $In(ClO_4)_3$: (1) 0.025 M; 2) 0.050 M; (3) 0.100 M.
Insert: linear segment, region of low overpotentials.

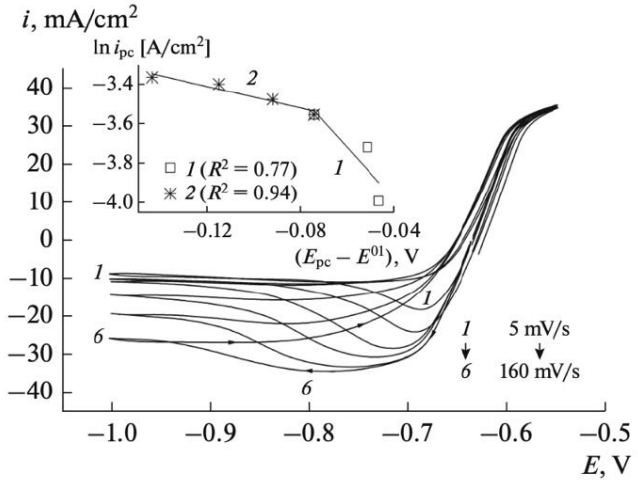

Figure 4. Cyclic voltammograms of indium at 25°C on indium electrode in 0.1 M $In(ClO_4)_3$+ 2.0 M NaCl solution at different polarization rates.
Insert: dependence of $ln(i_{pc})$ on $(E_{pc}-E^{o'})$ at different potential sweep rates: (1) low (5–20 mV/s), (2) high (20–160 mV/s).

- Corrosion polarization: Ecorr, icorr and Tafel slopes require appropriate fitting regions
- Indium in chloride electrolyte: compare concentration and scan-rate effects
- Avchukir K. et al. study reports LSV/CV of In electroreduction in 2.0 M NaCl
- Avoid interpreting illustrative curves as original experimental data

Avchukir et al., Russian Journal of Electrochemistry 54 (2018), 1096–1103.

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Conclusions: choose the method for the question

- LSV maps onset, peaks and limiting-current behavior
- CV tests reversibility, reaction pathways and product stability
- Scan-rate studies help separate diffusion, kinetics and chemical follow-up
- Polarization curves are shaped by faradaic + capacitive currents, iR drop and mass transfer
- Corrosion analysis and electrodeposition demand system-specific interpretation

Core references: Bard, Faulkner & White (2022); Avchukir et al. (2018).

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Homework and research problems

- 1. Sketch LSV and CV waveforms and explain why a reverse peak forms.
- 2. For n=1, A=0.0707 cm^2, D=1.0×10^{-5} cm^2/s, C=1.0 mM, v=0.10 V/s: calculate ip.
- 3. A reversible CV gives Epa=0.120 V and Epc=0.058 V. Calculate ΔEp and E°'; discuss ideality.
- 4. Explain why increasing v raises both diffusion peak current and capacitive current.
- 5. Propose a scan-rate series to investigate indium reduction and identify necessary controls.

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