Electrode kinetics and the slow-discharge theory

Modern research methods in electrochemistry

Educational program: 7M05301 Chemistry

Department of Analytical, Colloidal Chemistry and Technology of Rare Elements

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Purpose and expected learning outcomes

PURPOSE • Connect electrode reaction rates with measurable current–overpotential relationships.

- Define exchange current density, overpotential and activation control.
- Derive limiting forms of Butler–Volmer: linear polarization and Tafel laws.
- Distinguish charge-transfer limitation from diffusion and catalytic EC’ regimes.
- Interpret polarization curves and select a valid kinetic analysis.

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Lecture trajectory: from mechanism to measurement

01 Equilibrium

i_o and η

02 Activation control

Butler–Volmer

03 Tafel analysis

Extract slopes

04 Transport limits

Identify plateaus

05 Catalytic EC’

Interpret CV shapes

06 Research decisions

Avoid false kinetics

APPLICATIONS • Electrocatalysis • Corrosion • Electrodeposition • Energy conversion

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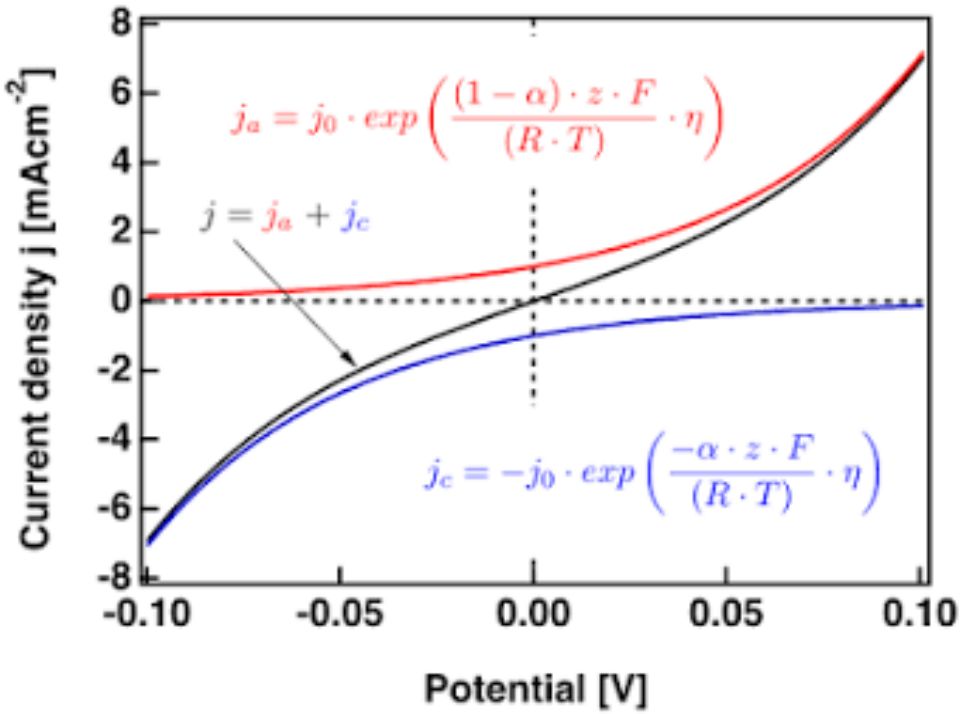
Dynamic equilibrium and slow electron transfer

$Ox + ne^- \rightleftharpoons Red$

At equilibrium: $|i_a| = |i_c|$, so $i_{net} = 0$.

Overpotential: $\eta = E - E_{eq}$.

Small i_o means slow exchange and larger activation losses.



KEY IDEA • A zero net current does not mean electron transfer stops.

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Butler–Volmer: the master kinetic relation

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

- i_0: exchange current density (A cm^{-2}); η: overpotential (V).
- α_a and α_c: anodic and cathodic transfer coefficients; n: electrons in the kinetic expression.
- Positive η favors oxidation; negative η favors reduction (anodic-positive convention).
- Assumptions: activation-controlled charge transfer, constant surface composition, negligible iR drop.

Caution: α and n must match the selected elementary-step kinetic model.

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Near equilibrium: polarization resistance

$|\eta| \ll RT/F$

$i \approx i_o(\alpha_a + \alpha_c)nF\eta/RT$

$R_p = (d\eta/di)\eta \to 0$

$= RT/[nFi_o(\alpha_a + \alpha_c)]$

Linearized i–η curve near equilibrium

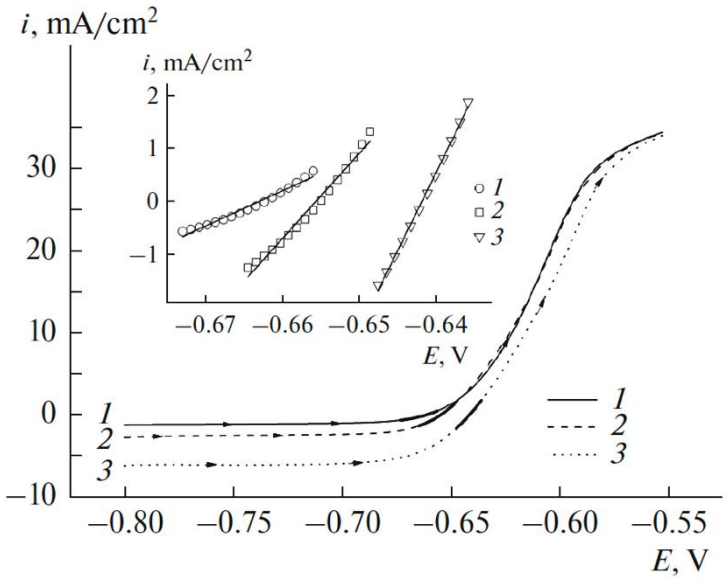

Fig. 3. Polarization curves of indium discharge-ionization on indium electrode at 25°C, v = 5 mV/s in 2.0 M NaCl solution with different content of $In(ClO_4)_3$: (*1*) 0.025 M; (*2*) 0.050 M; (*3*) 0.100 M. Insert: linear segment, region of low overpotentials.

Practical use: estimate i_o from a small-signal polarization measurement, after correcting solution resistance.

Avchukir, Kh, et al. "The kinetics of indium electroreduction from chloride solutions." *Russian Journal of Electrochemistry*54.12 (2018): 1096-1103.

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Large overpotential: Tafel kinetics

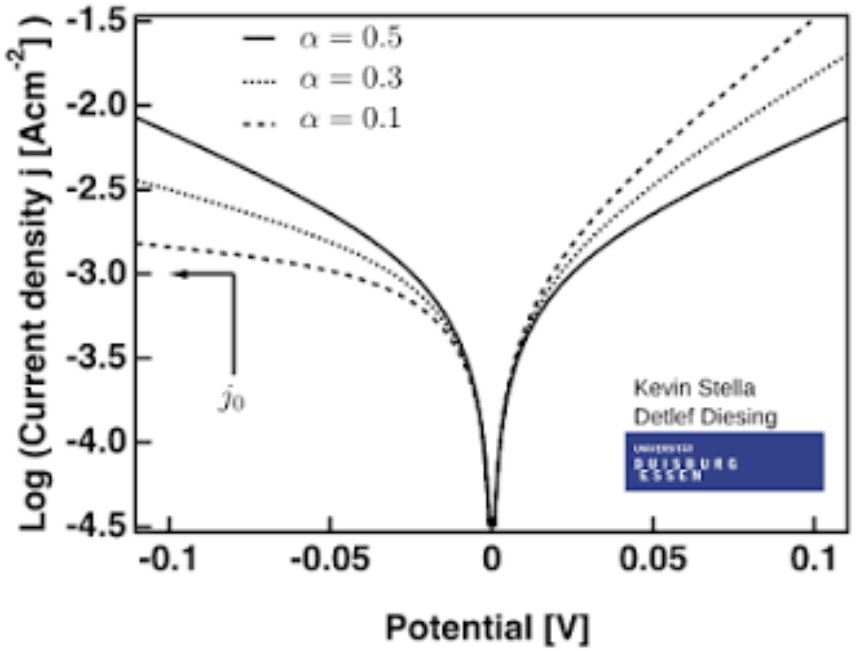
$$\eta = a + b \log_{10}|i|$$

Anodic slope: $b_a = 2.303RT/(\alpha_a nF)$

Cathodic magnitude: $|b_c| = 2.303RT/(\alpha_c nF)$

At 298 K, $\alpha n = 0.5$ gives ≈118 mV dec^{-1}.

Tafel region: η versus $\log_{10}|i|$



Fit only a genuine activation-controlled region; exclude mass transport, capacitive current and uncompensated iR.

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From activation control to mass-transfer limitation

Two different bottlenecks

ACTIVATION: interfacial electron transfer is slow.

TRANSPORT: reactant supply is slow.

A diffusion-limited plateau is not a kinetic plateau.

Koutecký–Levich: $1/i = 1/i_k + 1/i_l$ (under applicable conditions).

Saturating current under transport limitation

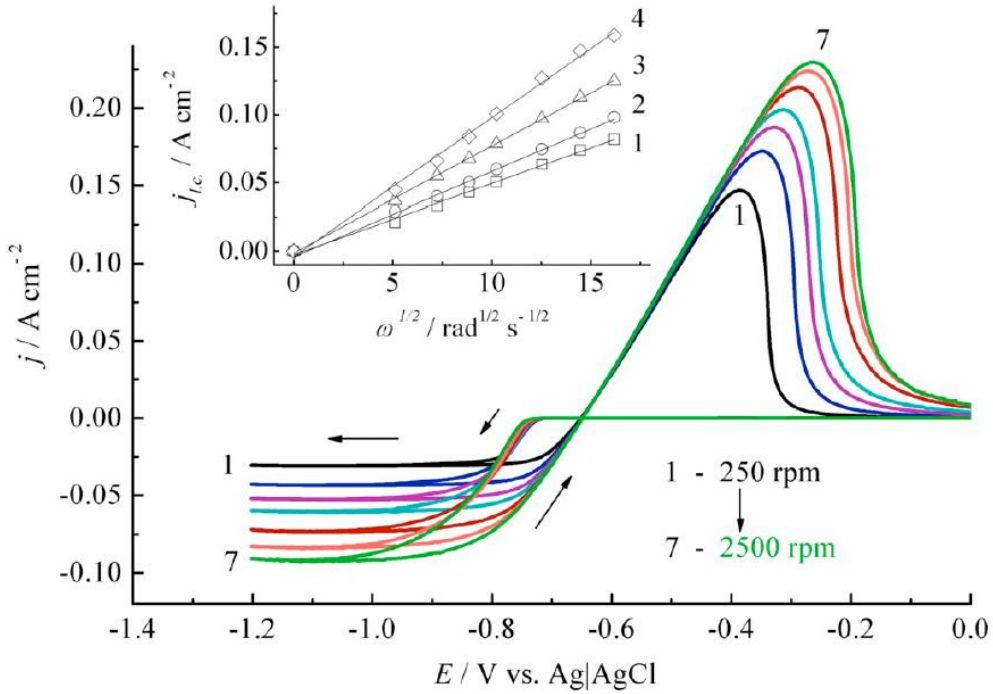

Fig. 2. Cyclic voltammograms obtained at 25 °C on GC electrode in 0.05 M $InCl_3$ + 2 M NaCl solution for various rotating rates (250, 500, 750, 1000, 1500, 2000 and 2500 rpm). Scan rate of 10 mV s^{-1}. Inset: Levich plot performed at various temperatures: 1–25 °C; 2–35 °C; 3–45 °C; 4–55 °C.

Avchukir, Khaisa, et al. "Influence of tetrabutylammonium chloride on the electrodeposition of indium from chloride solution on a glassy carbon electrode." Journal of Electroanalytical Chemistry 842 (2019): 176-183

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Catalytic EC′ mechanisms and voltammetric regimes

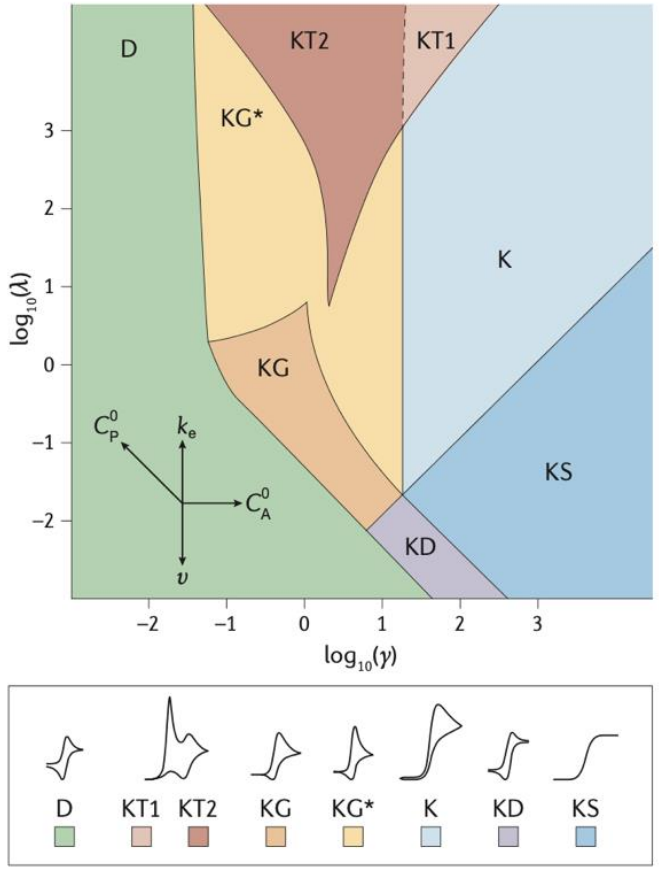
E: Ox + e⁻ ⇌ Red | C′: Red + S → Ox + P

D
Diffusion-controlled peak

K
Kinetic catalytic response

KT / KG
Transition and growth regimes

KD / KS
Mixed / steady-state catalytic waves



Source lecture: D → KT → KG → K → KD → KS (Lee et al., 2017). These catalytic CV regimes are distinct from the classical slow-discharge concept.

Lee, Katherine J., et al. "Electrochemical and spectroscopic methods for evaluating molecular electrocatalysts." Nature Reviews Chemistry 1.5 (2017): 0039.

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Conclusions: diagnose the controlling process

- Exchange current density and overpotential describe interfacial charge-transfer kinetics.
- Butler–Volmer connects equilibrium, linear polarization and Tafel regimes.
- A Tafel slope is meaningful only in a verified activation-controlled region.
- Diffusion plateaus and catalytic steady-state waves require different mechanistic models.
- Combine CV, polarization, scan-rate tests and hydrodynamic control for robust interpretation.

Reading: Bard, Faulkner & White, Electrochemical Methods (2022); Lee et al., Nat. Rev. Chem. 1, 0039 (2017).

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Homework and research problems

- 1 Derive the linearized Butler–Volmer equation for $|\eta| \to 0$.
- 2 Calculate the anodic Tafel slope at 298 K for $\alpha_a = 0.50$ and $n = 1$.
- 3 If $i_o = 10^{-6}$ A cm^{-2}, estimate R_p for $\alpha_a + \alpha_c = 1$, $n = 1$, $T = 298$ K.
- 4 Sketch activation-controlled and diffusion-limited polarization curves; annotate the differences.
- 5 Explain how scan rate and substrate concentration can distinguish a catalytic EC’ wave from a diffusion peak.

Submit calculations with units and a short mechanistic justification.

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