Basic Concepts of Potentiostatic Measurement

Al-Farabi Kazakh National University

Department of Analytical, Colloidal Chemistry and Technology of Rare Elements

Discipline: Modern research methods in electrochemistry

Educational program: 7M05301 Chemistry

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Purpose and expected learning outcomes

PURPOSE • Understand controlled-potential experiments and extract quantitative information from current–time transients.

- Explain feedback control of the working-electrode potential.
- Connect potential steps to diffusion profiles and current transients.
- Apply the Cottrell equation to estimate diffusion coefficients.
- Recognize charging, kinetic, nucleation and convection artifacts.

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Lecture trajectory: from potential to material properties

01 CONTROL

Three-electrode potentiostat

02 PERTURB

Potential-step waveform

03 RESPOND

Transient current and diffusion

04 QUANTIFY

Cottrell plot and D

05 VALIDATE

Indium deposition; CA vs EIS

APPLICATIONS • Metal electrodeposition • Battery electrodes • Corrosion • Electrocatalysis

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How a potentiostat controls potential

POTENTIOSTAT

WE	Reaction and measured current
RE	High-impedance potential sensing
CE	Carries balancing current

Feedback changes the WE–CE voltage to maintain the programmed WE–RE potential.

Important: the reference electrode should carry negligible current; solution resistance causes uncompensated iR drop.

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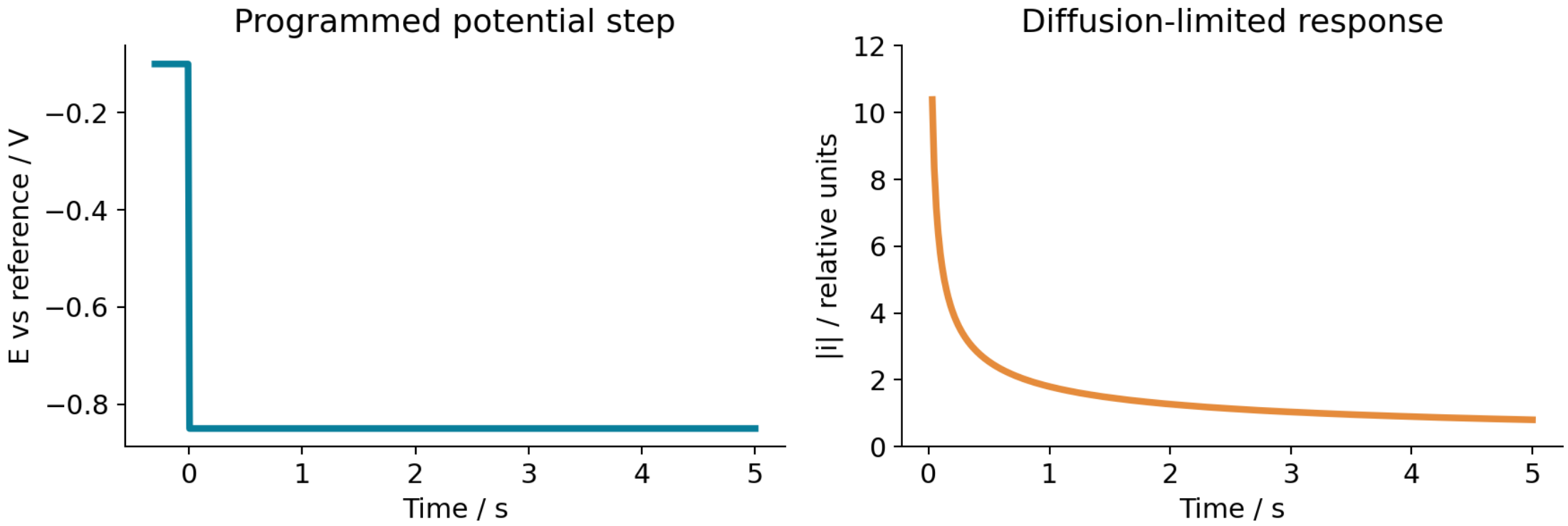
Potential step → a current transient



Example: anthracene + e^- → anthracene radical anion in deoxygenated DMF (from the lecture notes).

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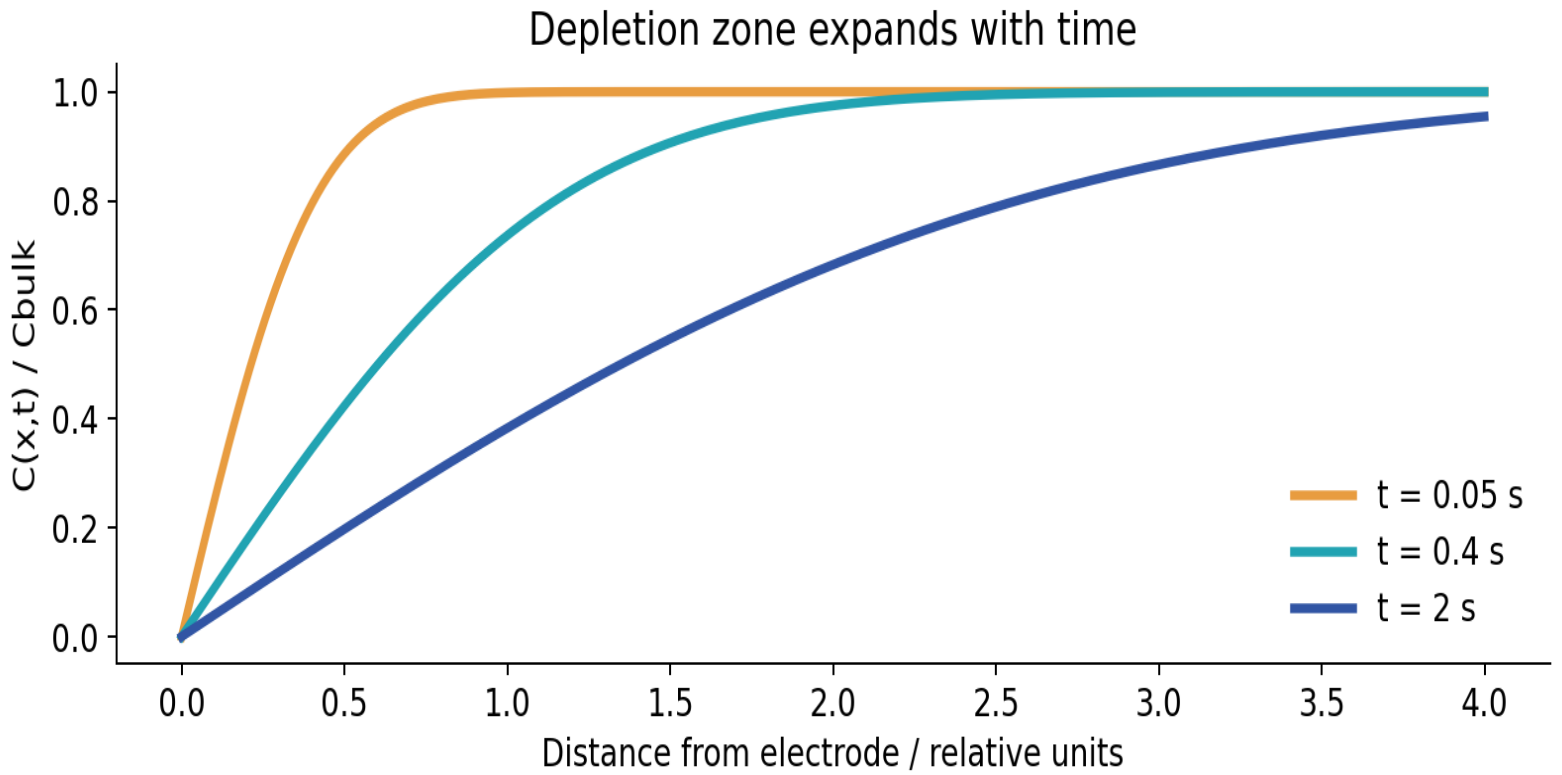
Why the current decays: growing diffusion layer



At the electrode surface:

$C(0,t) \approx 0$

As t increases, the depletion region grows ($\sim\sqrt{Dt}$) and the surface concentration gradient becomes smaller.

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Cottrell equation: quantify diffusion

$$|i(t)| = n\,F\,A\,C^{*}\,\sqrt{[D / (\pi t)]}$$

- Conditions: planar electrode; semi-infinite linear diffusion; rapid electron transfer; negligible convection.
- A: electrode area; C*: bulk concentration; D: diffusion coefficient; n: electron number.
- Plot |i| versus $t^{-1/2}$: slope $m = n\,F\,A\,C^{*}\,\sqrt{(D/\pi)}$.
- Therefore $D = \pi\,[m / (n\,F\,A\,C^{*})]^{2}$. Use consistent SI or cgs units.

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Cottrell plot: from data to diffusion coefficient

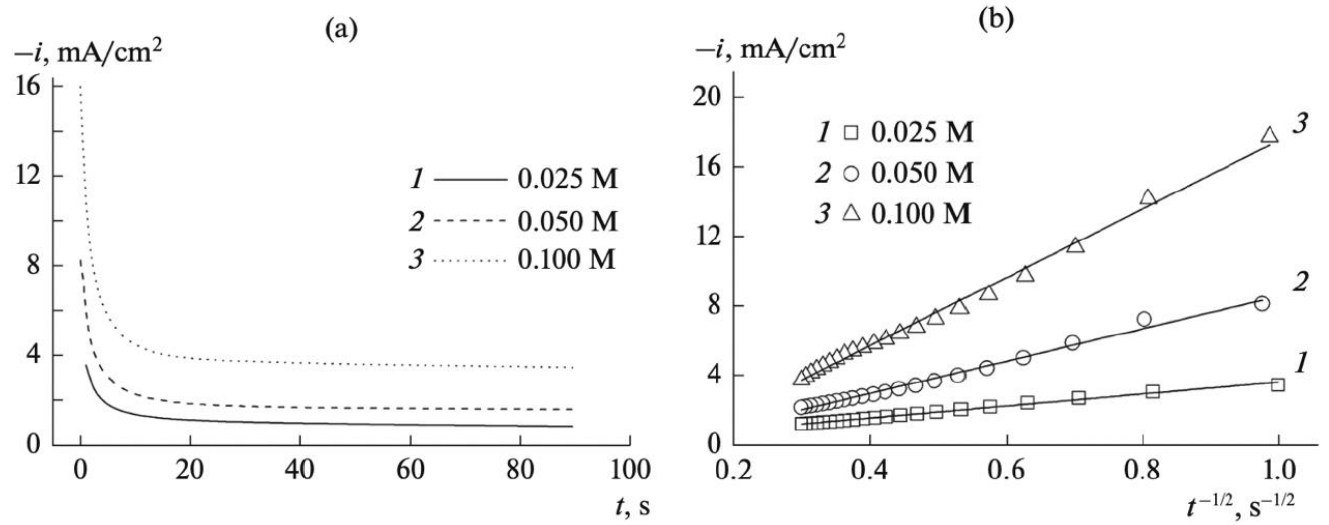

Figure 3. (a) Chronoamperograms of indium electrodeposition at 25°C on indium electrode from 2.0 M NaCl solution with different content of $In(ClO_4)_3$ at E = –0.9 V; (b) the dependence i - $t^{-1/2}$ [2].

Protocol

1. Correct baseline and select diffusion-controlled times.
2. Fit $|i| = m\, t^{-1/2} + b$.
3. Determine D from m.
4. Inspect residuals; b ≠ 0 can indicate artifacts.

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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Research case: indium electrodeposition in chloride media

From Avchukir et al. (2018): indium electroreduction at −0.9 V, 25 °C, in 2.0 M NaCl with varying $In(ClO_4)_3$ concentrations.

Table 1. Diffusion coefficient of indium ions and effective mass-transfer constant for electroreduction of indium in 2.0 M NaCl solution obtained by chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS) methods [2].

$c_{In^{3+}}$, M	$D_{In^{3+}}$, 10^{-6} cm^2/s		m_{eff}, 10^{-4} cm/s
	CA	EIS	CA
0.025	0.69	0.71	1.04
0.500	1.13	1.04	1.12
0.100	1.98	2.42	1.30

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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Conclusions

- A potentiostat maintains a prescribed WE potential versus RE by controlling current through CE.
- A potential step creates a concentration gradient; diffusion-limited current decays as $t^{-1/2}$.
- The Cottrell slope provides D only when its assumptions are satisfied.
- CA and EIS provide complementary transport and kinetic information; compare models and uncertainty.

References: Bard, Faulkner & White, Electrochemical Methods (2022); Avchukir et al., Russian Journal of Electrochemistry 54 (2018), 1096–1103.

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Homework and problems

- 1 Derive the Cottrell relationship from Fick's second law and state all boundary conditions.
- 2 Calculate $|i|$ at $t = 1.0$ s for $n = 1$, $A = 0.0707\ \mathrm{cm}^2$, $C^* = 1.0$ mM and $D = 1.0 \times 10^{-5}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$.
- 3 A Cottrell slope doubles at fixed n, A and C*. By what factor does D change?
- 4 Sketch charging current and diffusion current on the same log–log i–t plot.
- 5 Explain why indium electrodeposition may deviate from ideal planar diffusion (nucleation, surface growth, speciation).

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