Fundamentals of Mass Transfer in Electrochemical Reactions

Modern research methods in electrochemistry

Al-Farabi Kazakh National University

Department of Analytical, Colloidal Chemistry and Technology of Rare Elements

Educational program: 7M05301 Chemistry

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Purpose and expected learning outcomes

PURPOSE

Explain how diffusion, migration and convection determine the flux of electroactive species and the measured electrode current.

BY THE END OF THE LECTURE, STUDENTS CAN:

- Distinguish the three mechanisms of mass transport.
- Apply Fick’s laws and interpret concentration profiles.
- Use the Nernst–Planck equation and predict limiting-current behavior.
- Select experimental conditions to isolate diffusion or control convection.

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Lecture trajectory: from mechanisms to applications

01 PHYSICS

What drives ions and molecules through solution?

02 EQUATIONS

How do gradients and fluid flow determine flux?

03 EXPERIMENTS

How can current reveal transport parameters?

APPLICATIONS • Cyclic voltammetry • Chronoamperometry • Rotating disk electrodes • CO_2 electroreduction • Electrodeposition

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Three pathways of mass transport

DIFFUSION

Concentration gradient

High C → low C

MIGRATION

Electric field drives charged species

CONVECTION

Bulk liquid flow transports dissolved species

Physical picture: a reactant can reach an electrode because its concentration is depleted at the surface, because it experiences an electric field, or because the liquid itself moves. All three contributions may coexist.

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Diffusion: Fick's first and second laws

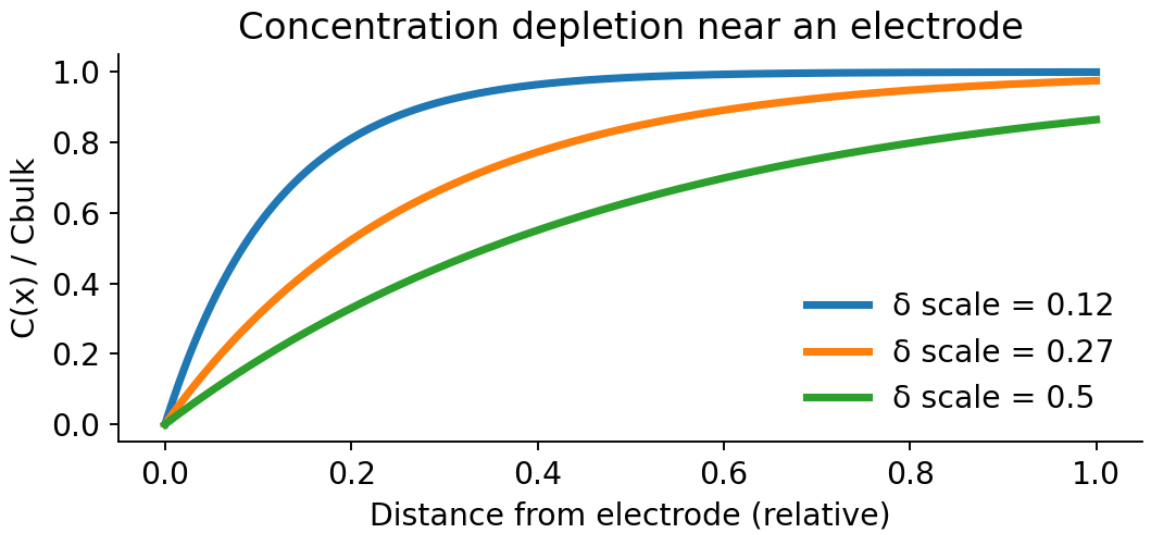
$$J_{diff} = -D\left(\frac{\partial C}{\partial x}\right)$$

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2}\right)$$

J: mol m^{-2} s^{-1}; D: m^2 s^{-1}

The minus sign points toward decreasing concentration.

Second law assumes constant D and one-dimensional diffusion without reaction in solution.



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Migration: charged species in an electric field

$$J_{mig} = -(zFD/RT)\, C\, (\partial\phi/\partial x)$$

- z = ion charge number; ϕ = solution electric potential.
- Cations and anions migrate in opposite directions under the same field.
- Excess supporting electrolyte usually suppresses the migration contribution of a dilute electroactive analyte.
- Migration cannot always be neglected in low-conductivity media, concentrated electrolytes or membrane systems.

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Convection: hydrodynamics and the diffusion layer

NATURAL

Density gradients caused by temperature or composition

FORCED

Stirring, pumping, rotation, gas-induced flow

EFFECT

Thinner boundary layer → greater reactant flux

At a rotating disk electrode (RDE), rotation creates reproducible laminar flow. The diffusion-layer thickness scales approximately as $\delta \propto \omega^{-1/2}$ under Levich conditions.

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Nernst–Planck equation: one unified framework

$$J_i = -D_i \partial C_i/\partial x - (z_i F D_i / RT)\, C_i\, \partial \phi/\partial x + C_i v_x$$

$-D \nabla C$

Diffusion: chemical concentration gradient

$-zFDC\nabla\phi/RT$

Migration: electric potential gradient

$C\, v$

Convection: movement with the liquid

For dilute ideal solutions; flux is measured relative to the laboratory frame. Consistent units are essential.

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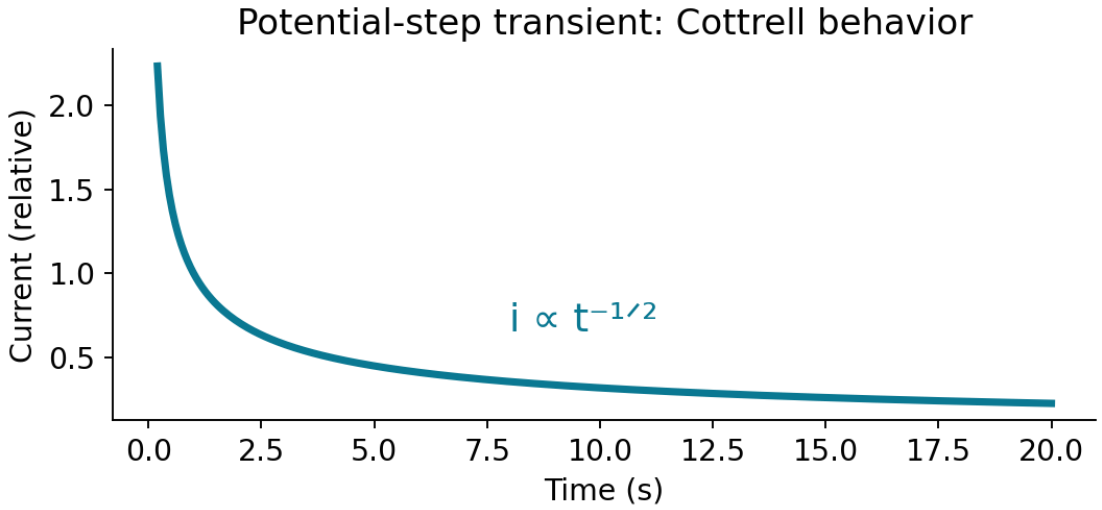
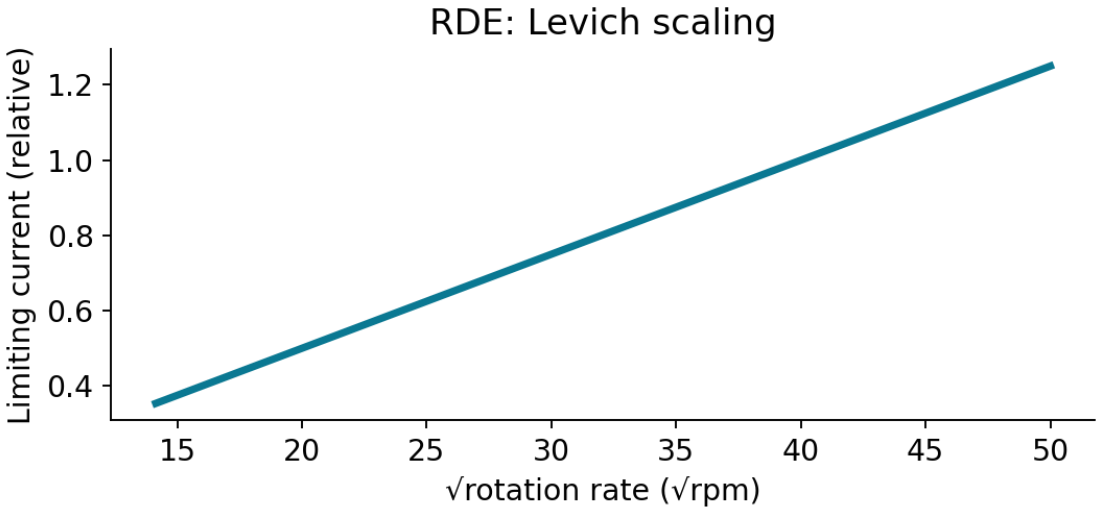
From mass transfer to measurable current





Cottrell: $i(t) = nFAD^{1/2}C^* / (\pi t)^{1/2}$

Planar, semi-infinite diffusion after a potential step.

Levich: $iL = 0.620\ nFAD^{2/3}\nu^{-1/6}\omega^{1/2}C^*$

Steady-state transport at an RDE (ω in rad s^{-1}).

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Conclusions: controlling transport controls current

- Diffusion is driven by concentration gradients; migration by electric fields; convection by liquid flow.
- Fick’s laws describe diffusion, while Nernst–Planck combines all three contributions.
- Supporting electrolyte and quiescent solutions help isolate diffusion in suitable systems.
- Potential-step and RDE experiments provide quantitative transport information.
- Mass-transfer limitations are central to electroanalysis, electrosynthesis and CO_2 reduction.

Suggested reading: Bard, Faulkner & White, Electrochemical Methods: Fundamentals and Applications (2022).

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Homework and quantitative problems

- 1. Explain why increasing supporting-electrolyte concentration can reduce analyte migration.
- 2. Fick: $D = 1.0 \times 10^{-9}$ m² s⁻¹; $\Delta C = 2$ mol m⁻³ across 100 µm. Calculate $|J|$.
- 3. Cottrell: predict $i(4\ s)/i(1\ s)$ for diffusion-controlled chronoamperometry.
- 4. Levich: by what factor does limiting current change when RDE rotation rate quadruples?
- 5. Research: compare diffusion limitations in CO_2 reduction at planar and gas-diffusion electrodes.

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