LECTURE 05

# Introduction to Numerical Modeling: Copper Electrodeposition

Department of Analytical, Colloidal Chemistry and Technology of Rare Elements

Modeling of chemico-technological processes | 6B07102 Chemical Engineering

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# Purpose and expected learning outcomes

Purpose: build the first complete numerical model of a real electrochemical process and learn to judge whether its answer can be trusted.

### EXPLAIN

Why Cu deposition couples ion transport, charge transfer and a moving metal surface.

### FORMULATE

The 1D diffusion PDE with a Faraday flux condition and a consistent sign convention.

### DISCRETIZE

Diffusion by explicit finite differences and state the stability limit $\lambda \leq 1/2$.

### CALCULATE

Limiting current, Sand time and film growth rate from measurable parameters.

### VERIFY

A code against Cottrell/erf solutions, grid refinement and a global copper balance.

### VALIDATE

Predictions with chronoamperometry, coulometry and profilometry data.

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# From an electroplating bath to a verified numerical model

## 01 Define system

0.10 M $CuSO_4$ + 1 M $H_2SO_4$, planar cathode, 1D domain

## 02 Formulate physics

Mass balance, Faraday flux, Butler–Volmer kinetics

## 03 Specify parameters

$D = 7.2 \cdot 10^{-10}$ $m^2$ $s^{-1}$, $c_0 = 0.10$ M, $n = 2$

## 04 Solve equations

Analytical benchmarks, then FTCS finite differences

## 05 Verify and validate

Grid convergence, mass balance, experiment

## 06 Use the model

Current limits, deposition time, film thickness

**Industrial relevance: PCB and through-hole plating • Cu interconnects (damascene) • electrorefining • electrowinning**

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# Copper deposition as a multiphysics problem

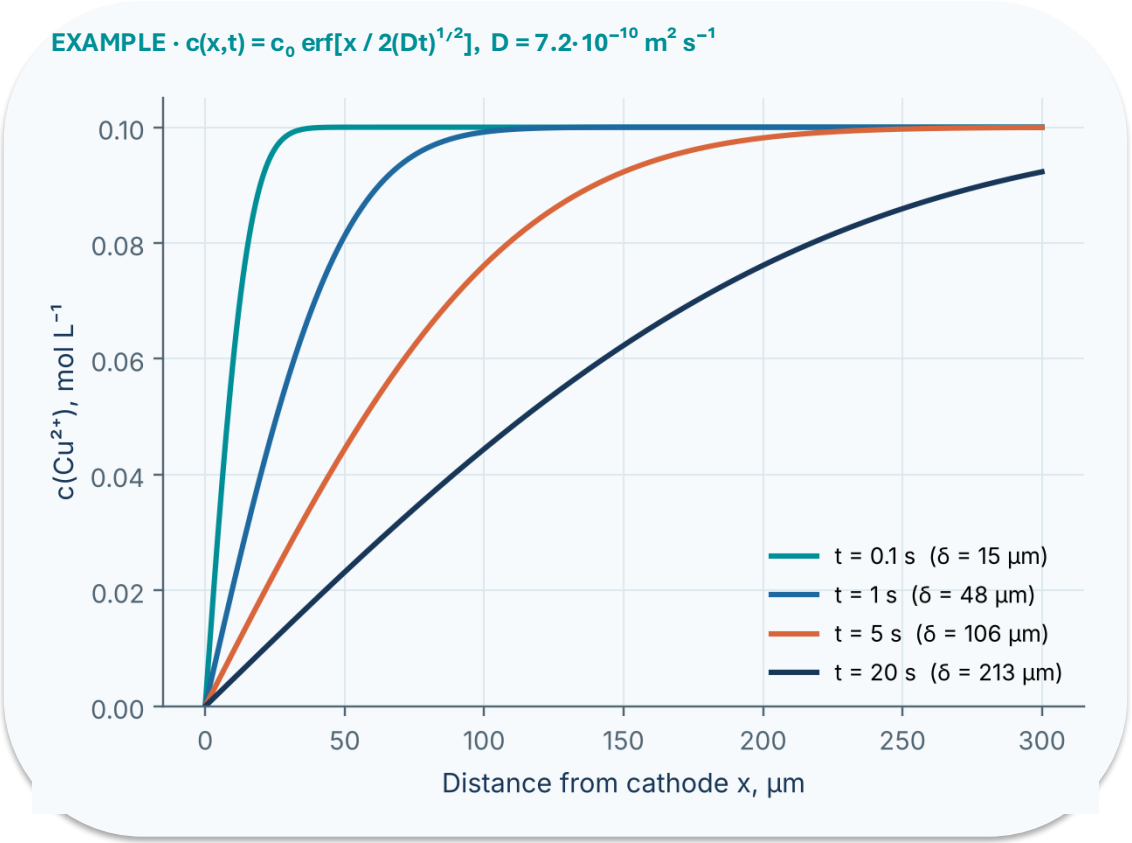
Ion depletion, solution potential and charge transfer interact at the cathode.

**$Cu^{2+} + 2e^- \rightarrow Cu(s)$**

**$E° = +0.34$ V vs SHE**

**MODEL CONDITIONS** 1D planar cathode at x = 0; excess $H_2SO_4$ suppresses migration; stagnant layer, no convection; isothermal 25 °C.

**WORKED EXAMPLE** Potential step to the limiting region (c(0,t) = 0) in 0.10 M $Cu^{2+}$: the depleted zone reaches about 48 µm after 1 s and 213 µm after 20 s.




**ENGINEERING INTERPRETATION** Model outputs are current density, surface concentration and film thickness; each one can be measured.

Further reading: Bard, Faulkner & White, Electrochemical Methods, 3rd ed. (2022), ch. 1, 6, 9; Newman & Balsara, Electrochemical Systems, 4th ed. (2021), ch. 11–12, 17.

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# Transport equation and flux

Species conservation turns the ionic flux into a time-dependent concentration field.

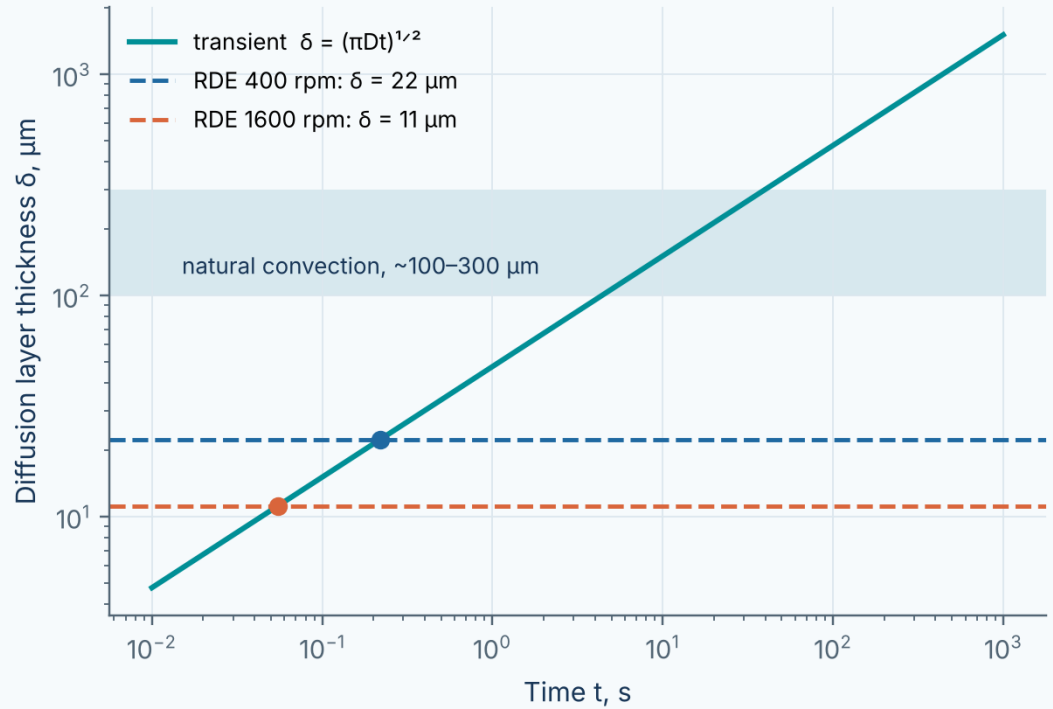
$$\partial c_i/\partial t + \nabla \cdot N_i = R_i$$

$$N_i = -D_i \nabla c_i - z_i u_i F c_i \nabla \phi + c_i u$$

**MODEL CONDITIONS** With supporting electrolyte ($H_2SO_4 \gg CuSO_4$) and u = 0 the Nernst–Planck flux reduces to Fick's law, $\partial c/\partial t = D\, \partial^2 c/\partial x^2$.

**WORKED EXAMPLE** Transient layer $\delta = (\pi D t)^{1/2}$ grows until convection caps it. For a rotating disk (Levich) δ = 22 µm at 400 rpm and 11 µm at 1600 rpm, reached after 0.22 s and 0.05 s.

**EXAMPLE · DIFFUSION LAYER VS CONVECTIVE LAYER ($v = 1 \cdot 10^{-6}$ m$^2$ s$^{-1}$)**




**ENGINEERING INTERPRETATION** Without excess acid, $Cu^{2+}$ migration matters: solve full Nernst–Planck with electroneutrality.

Further reading: Bard, Faulkner & White, Electrochemical Methods, 3rd ed. (2022), ch. 1, 6, 9; Newman & Balsara, Electrochemical Systems, 4th ed. (2021), ch. 11–12, 17.

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# Electrode boundary condition and sign convention

Faraday's law converts the electrode current into an ionic flux.

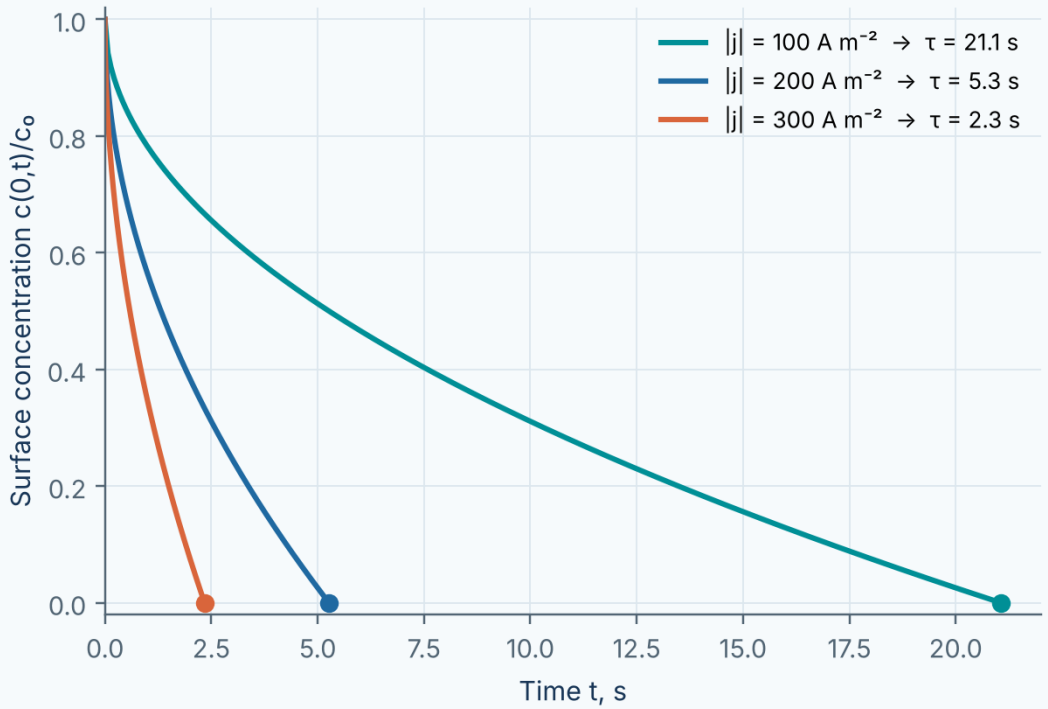
$$N_x(0,t) = j_c / (nF)$$

$$\tau_{Sand} = \pi D(nFc_0)^2 / (4j^2)$$

**MODEL CONDITIONS** x points into the solution; cathodic $j_c < 0$, so the $Cu^{2+}$ flux at x = 0 is negative (toward the metal). The far boundary keeps c = $c_0$.

**WORKED EXAMPLE** Galvanostatic |j| = 200 A $m^{-2}$ (20 mA $cm^{-2}$): N = $-1.04 \cdot 10^{-3}$ mol $m^{-2}$ $s^{-1}$. Surface $Cu^{2+}$ is exhausted after τ = 5.3 s; at 100 A $m^{-2}$, τ = 21 s.

EXAMPLE · GALVANOSTATIC DEPLETION, $c_0$ = 0.10 M




**ENGINEERING INTERPRETATION** Beyond τ the imposed current cannot be carried by $Cu^{2+}$ alone: $H_2$ evolution and powdery deposits begin.

Further reading: Bard, Faulkner & White, Electrochemical Methods, 3rd ed. (2022), ch. 1, 6, 9; Newman & Balsara, Electrochemical Systems, 4th ed. (2021), ch. 11–12, 17.

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# Charge-transfer kinetics with mass-transport limitation

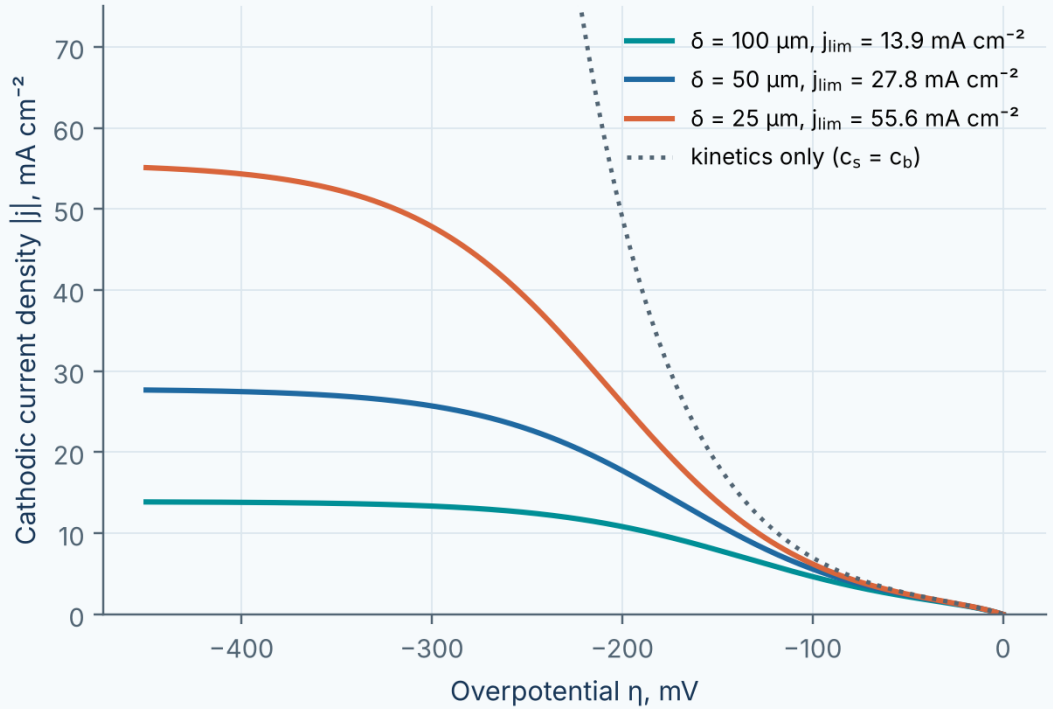
Butler–Volmer kinetics sets the current until diffusion takes over.

$$j = j_0[(c_s/c_b)\exp(-\alpha_c f\eta) - \exp(\alpha_a f\eta)]$$
$$j_{lim} = nFDc_b / \delta, \quad f = F/RT$$

**MODEL CONDITIONS** Assumed $j_0 = 10\ A\ m^{-2}$, $\alpha_c = 0.5$, $\alpha_a = 1.5$; $c_s/c_b = 1 - j/j_{lim}$ from a Nernst layer of thickness δ.

**WORKED EXAMPLE** δ = 50 µm gives $j_{lim} = 278\ A\ m^{-2}$ (27.8 mA $cm^{-2}$). Halving δ to 25 µm doubles the plateau; the kinetic branch below −100 mV is unchanged.

**EXAMPLE · POLARIZATION CURVES, $c_b$ = 0.10 M**




**ENGINEERING INTERPRETATION** Compact Cu is plated at 20–50 % of $j_{lim}$; near the plateau deposits turn rough or dendritic.

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# Finite differences in space and time (FTCS)

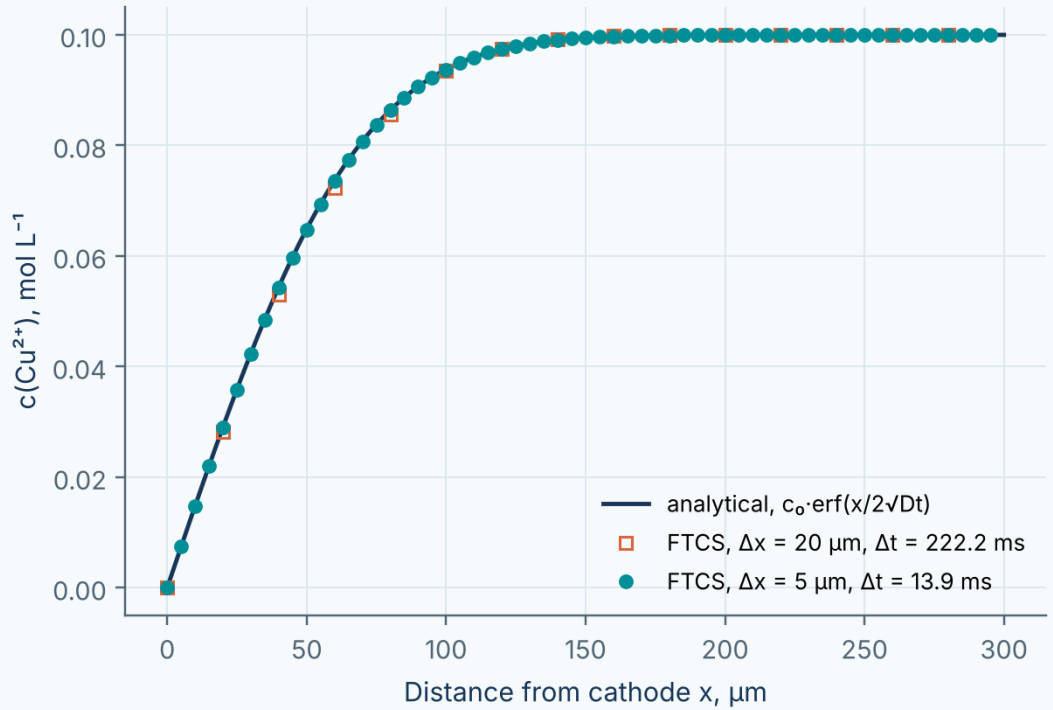
Replace derivatives by differences on a grid $x_i = i\Delta x$, $t^k = k\Delta t$.

$$c_i^{k+1} = c_i^k + \lambda(c_{i+1}^k - 2c_i^k + c_{i-1}^k)$$
$$\lambda = D\Delta t/\Delta x^2$$

**MODEL CONDITIONS** Forward Euler in time, centred second difference in space. Truncation error $O(\Delta t) + O(\Delta x^2)$; with $\lambda$ fixed the scheme converges as $O(\Delta x^2)$.

**WORKED EXAMPLE** $\Delta x = 5$ µm and $\lambda = 0.4$ give $\Delta t = 13.9$ ms; 144 steps reach t = 2 s. A 20 µm grid already reproduces the erf profile within a few %.

EXAMPLE · FTCS VS ANALYTICAL PROFILE AT t = 2 s




**ENGINEERING INTERPRETATION** Always test a new code on a problem with a known exact solution before trusting it on a new one.

Further reading: Britz & Strutwolf, Digital Simulation in Electrochemistry, 4th ed. (2016); Crank, The Mathematics of Diffusion (1975); LeVeque, Finite Difference Methods (2007).

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# Stability of the explicit scheme

The explicit update is stable only for small enough time steps.

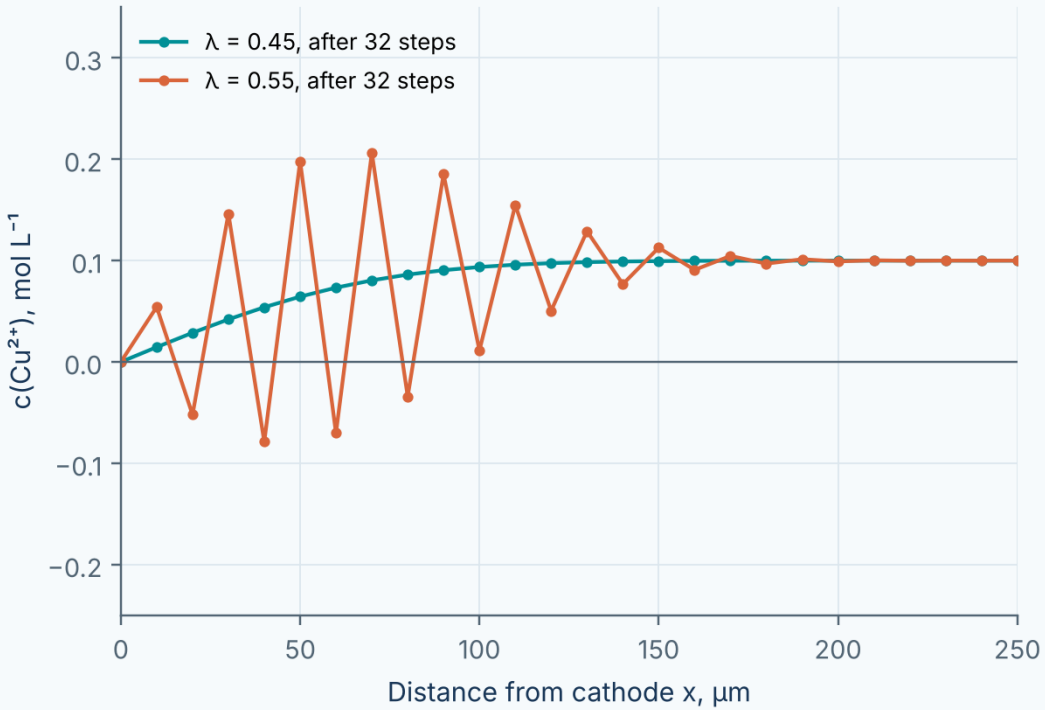
$$\lambda = D\Delta t/\Delta x^2 \leq 1/2$$

$$\Delta t_{max} = \Delta x^2 / (2D)$$

**MODEL CONDITIONS** Von Neumann analysis: the shortest grid mode is multiplied by $(1 - 4\lambda)$ per step; for $\lambda > 1/2$ it grows without bound.

**WORKED EXAMPLE** $\Delta x = 10$ µm: $\lambda = 0.55$ produces negative concentrations after 32 steps. For $\Delta x = 1$ µm, $\Delta t_{max} = 0.69$ ms, so 20 s needs ≈ 29 000 steps.

EXAMPLE · λ = 0.45 (STABLE) VS λ = 0.55 (UNSTABLE)




**ENGINEERING INTERPRETATION** Implicit schemes (backward Euler, Crank–Nicolson) are unconditionally stable but need a linear solve per step.

Further reading: Britz & Strutwolf, Digital Simulation in Electrochemistry, 4th ed. (2016); Crank, The Mathematics of Diffusion (1975); LeVeque, Finite Difference Methods (2007).

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# Simulating a chronoamperometric step

Solve c(x,t) numerically and recover the current from the surface gradient.

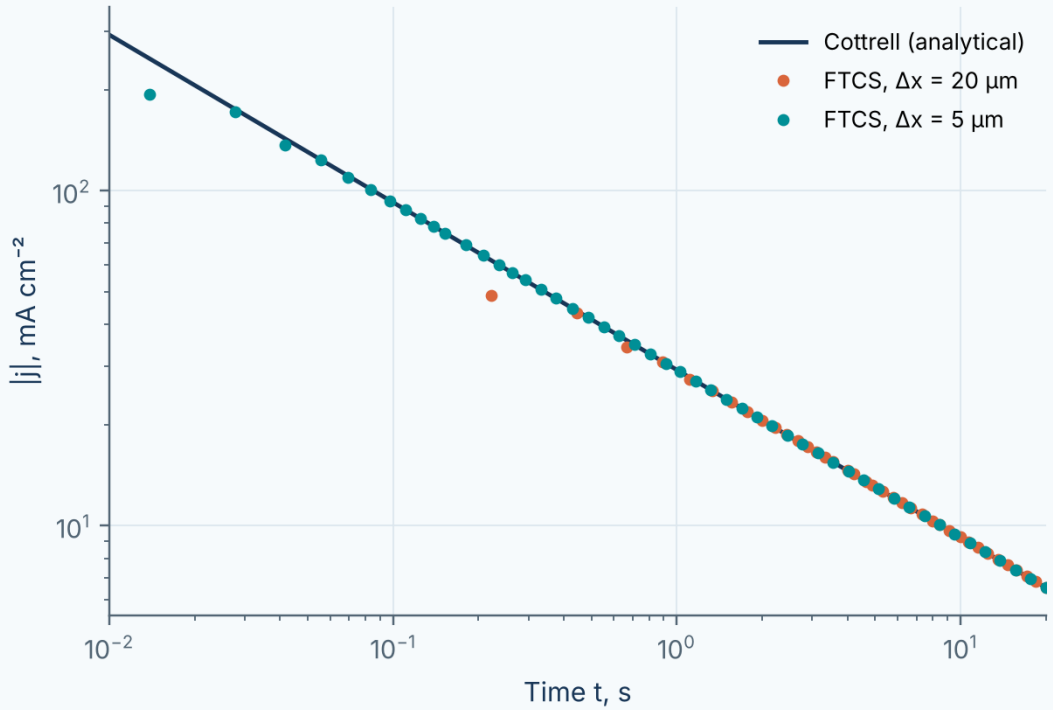
$$j(t) = -nFD\,(\partial c/\partial x)|_{x=0}$$

$$\text{Cottrell: } |j| = nFc_0(D/\pi t)^{1/2}$$

**ALGORITHM** 1) grid 0…800 µm; 2) c = $c_0$ everywhere; 3) $c_0$ = 0 at x = 0; 4) FTCS update; 5) j from a second-order one-sided gradient; 6) repeat to 20 s.

**RESULT** At t = 1 s the Cottrell current is 292 A $m^{-2}$ (29 mA $cm^{-2}$). Δx = 5 µm matches it from 0.05 s on; Δx = 20 µm fails at short times.

EXAMPLE · NUMERICAL TRANSIENT VS COTTRELL EQUATION




**ENGINEERING INTERPRETATION** Early-time error: a layer thinner than a few Δx is not resolved. Refine where gradients are steep.

Further reading: Britz & Strutwolf, Digital Simulation in Electrochemistry, 4th ed. (2016); Crank, The Mathematics of Diffusion (1975); LeVeque, Finite Difference Methods (2007).

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# Film growth from the passed charge

The deposit thickness follows from Faraday's law and the metal density.

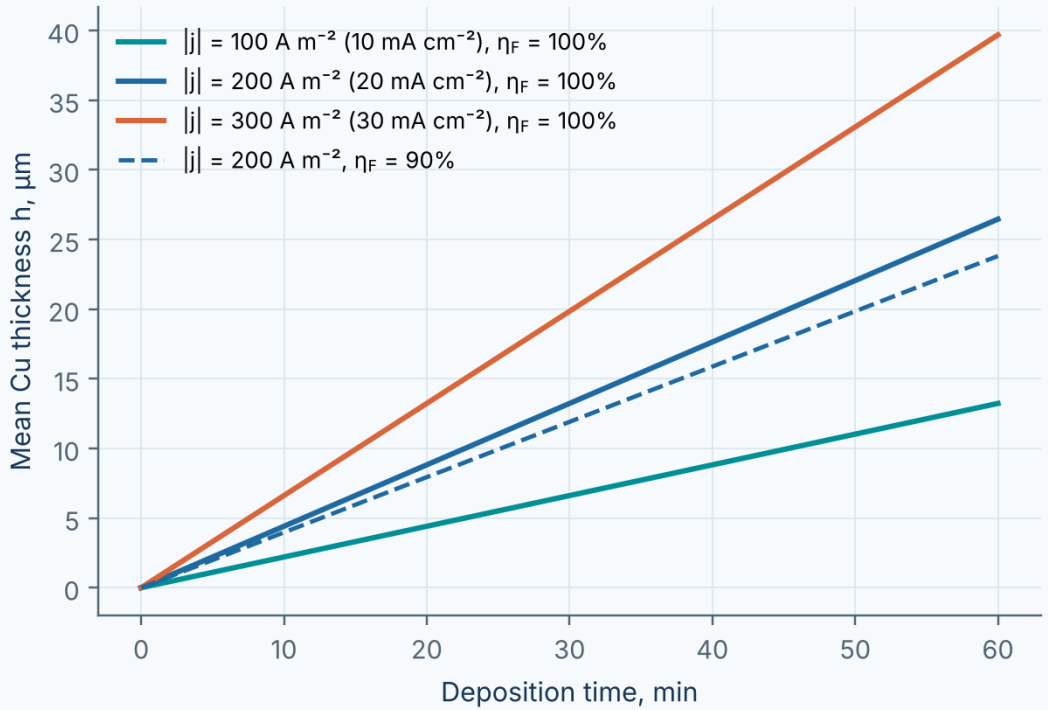
$$\frac{dh}{dt} = -\eta_F \, M \, j_c \,/\, (nF\rho)$$

$$M = 63.55 \text{ g mol}^{-1}, \quad \rho = 8.96 \text{ g cm}^{-3}$$

**MODEL CONDITIONS** Uniform current, compact deposit, current efficiency $\eta_F$; side reactions ($H_2$ evolution, $Cu^+$ formation) lower $\eta_F$.

**WORKED EXAMPLE** $|j| = 200$ A m$^{-2}$: $dh/dt = 7.35$ nm s$^{-1}$ = 26.5 µm h$^{-1}$. With $\eta_F = 90$ % the 1 h thickness drops to 23.8 µm.

EXAMPLE · MEAN THICKNESS VS TIME




**ENGINEERING INTERPRETATION** Local thickness differs from the mean wherever the current distribution is non-uniform (edges, recesses).

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# Verification: grid convergence

A verified code converges to the exact solution at its theoretical rate.

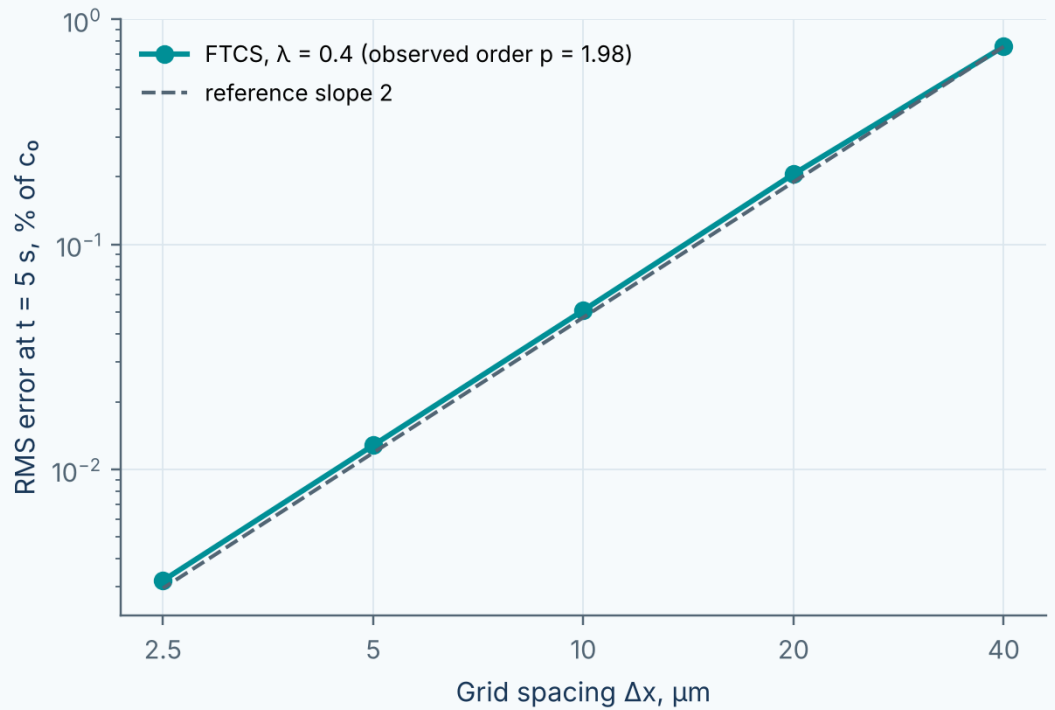
$$p = \ln(e_1/e_2) \,/\, \ln(\Delta x_1/\Delta x_2)$$

$$e = \|c_{num} - c_{exact}\| \,/\, c_0$$

**MODEL CONDITIONS** $\lambda = 0.4$ held constant, so $\Delta t$ shrinks with $\Delta x^2$; error measured at t = 5 s against the erf solution.

**WORKED EXAMPLE** Halving $\Delta x$ from 40 to 2.5 µm cuts the RMS error from 0.76 % to 0.003 %; the observed order p = 1.98 matches the expected 2.

**EXAMPLE · OBSERVED ORDER OF ACCURACY**




**ENGINEERING INTERPRETATION** If p falls well below the theoretical order, look for an error in boundary conditions or in the time stepping.

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# Verification: global copper conservation

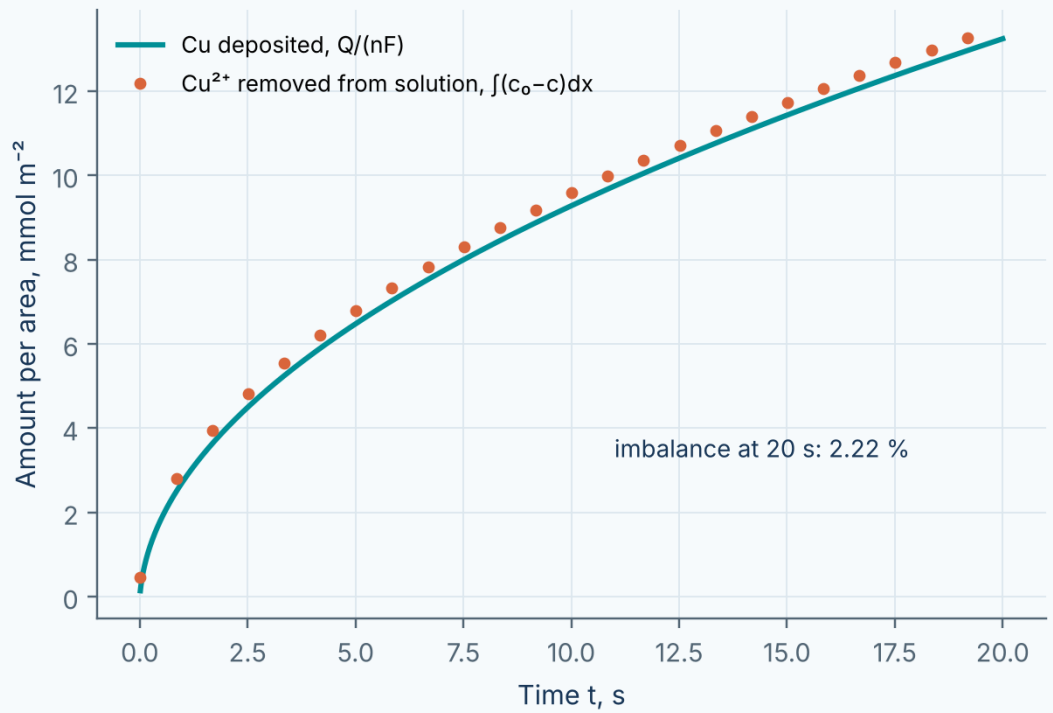
Copper lost from the solution must equal copper deposited on the electrode.

$$\int_0^L (c_0 - c)\,dx = (1/nF) \int_0^t |j|\,dt$$

**MODEL CONDITIONS** Both sides are evaluated independently from the same simulation ($\Delta x = 5$ µm, $\lambda = 0.4$, 0–20 s).

**WORKED EXAMPLE** The imbalance is 9.0 % at $\Delta x = 20$ µm, 4.5 % at 10 µm, 2.2 % at 5 µm and 1.1 % at 2.5 µm. First-order decay points to the boundary-flux evaluation as the weakest step.

**EXAMPLE · COPPER BALANCE, $\Delta x = 5$ µm**




**ENGINEERING INTERPRETATION** Verification asks “are the equations solved correctly?”; validation asks “are they the right equations?”

Further reading: Britz & Strutwolf, Digital Simulation in Electrochemistry, 4th ed. (2016); Crank, The Mathematics of Diffusion (1975); LeVeque, Finite Difference Methods (2007).

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# Validation: comparing the model with experiment

A model is validated only against data that were not used to fit its parameters.

## CHRONOAMPEROMETRY

Plot $|j|$ vs $t^{-1/2}$: the slope gives $nFc_0(D/\pi)^{1/2}$ and therefore D. Compare with the value used in the model.

## POLARIZATION CURVE

Measured plateau gives $j_{lim}$ and δ; the low-η region gives $j_0$ and $\alpha_c$ by Tafel analysis.

## COULOMETRY / MASS

Weigh the cathode: $m = \eta_F \cdot Q \cdot M/(nF)$. The ratio of weighed to predicted mass is the current efficiency.

## PROFILOMETRY / SEM

Measure thickness and roughness at centre and edges; a 1D model predicts only the mean value.

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# Conclusions: a verified model is a useful model

## PHYSICS

Cu deposition is limited by charge transfer at low η and by $Cu^{2+}$ diffusion near $j_{lim}$.

## EQUATIONS

Fick's law + Faraday flux + Butler–Volmer; keep signs and units consistent.

## PARAMETERS

D, $j_0$, α and δ are measurable; each carries an uncertainty that propagates to the result.

## NUMERICS

FTCS is simple but conditionally stable ($\lambda \leq 1/2$); refine the grid where gradients are steep.

## VERIFICATION

Exact benchmarks, observed order of accuracy and global mass balance.

## APPLICATION

Estimate plating time, safe current density and expected thickness.

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# Homework: calculations, interpretation and research

**1. THEORY** State every assumption that reduces the Nernst–Planck equation to Fick's second law for $Cu^{2+}$ in 0.1 M $CuSO_4$ + 1 M $H_2SO_4$. Which one fails first in a pure 0.1 M $CuSO_4$ bath?

**2. CALCULATION** For $c_0$ = 0.25 M, D = $7.2 \cdot 10^{-10}$ $m^2$ $s^{-1}$ and |j| = 300 A $m^{-2}$: find the Sand time, the Cottrell current at t = 2 s and the film thickness after 45 min at 100 % efficiency.

**3. CODE** Implement FTCS for the potential-step problem ($\Delta x$ = 10 µm, $\lambda$ = 0.4). Plot j(t) against the Cottrell equation and report the error at t = 0.1, 1 and 10 s.

**4. CRITIQUE** Repeat task 3 with $\lambda$ = 0.51 and with a flux of the wrong sign. Describe how each error shows up in the copper balance.

**5. RESEARCH** Find a published chronoamperogram for Cu deposition. Extract D from the $t^{-1/2}$ plot and compare it with the value used in this lecture.

Constants: F = 96485 C $mol^{-1}$; R = 8.314 J $mol^{-1}$ $K^{-1}$; T = 298.15 K; M(Cu) = 63.55 g $mol^{-1}$; $\rho$(Cu) = 8.96 g $cm^{-3}$.

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**Recommended Literature**


1. Fogler, H. S. *Elements of Chemical Reaction Engineering*. 5th ed., Pearson, 2016.
2. Himmelblau, D. M., Riggs, J. B. *Basic Principles and Calculations in Chemical Engineering*. 8th ed., Pearson, 2012.
3. Bird, R. B., Stewart, W. E., Lightfoot, E. N. *Transport Phenomena*. 2nd ed., John Wiley & Sons, 2002.
4. Levenspiel, O. *Chemical Reaction Engineering*. 3rd ed., John Wiley & Sons, 1999.
5. Bequette, B. W. *Process Control: Modeling, Design, and Simulation*. Prentice Hall, 2003.