LECTURE 10

Modeling Electrochemical Processes and Research Methods

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: use one physical model to interpret CV and EIS data, and turn measurements into parameters with known uncertainty.

SIMULATE

A cyclic voltammogram from diffusion equations and electrode kinetics.

EXTRACT

D from Randles–Ševčík analysis and k^0 from peak separation (Nicholson).

MODEL

Impedance spectra with a Randles circuit and a Warburg element.

CONNECT

Circuit elements (R_{ct}, σ, C_{dl}) to physical parameters k^0, D, c.

FIT

Data by complex nonlinear least squares and judge models by residuals.

DESIGN

Experiments with controls, replicates and reported uncertainty.

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From an electrochemical experiment to a defensible result

01 Physical model

$E^{\circ\prime}$, k^0, α, D, C_{dl}, R_u

02 Cyclic voltammetry

Simulation, scan-rate series

03 CV analysis

Randles–Ševčík, Nicholson

04 Impedance

Randles circuit, Warburg

05 Fitting

CNLS, residuals, uncertainty

06 Research practice

Controls, replicates, reporting

Running example: 5 mM $K_3[Fe(CN)_6]$ / $K_4[Fe(CN)_6]$ in excess KCl on a 3 mm glassy-carbon disk

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A unified model of an electrode reaction

One set of parameters must explain every experiment on the same system.

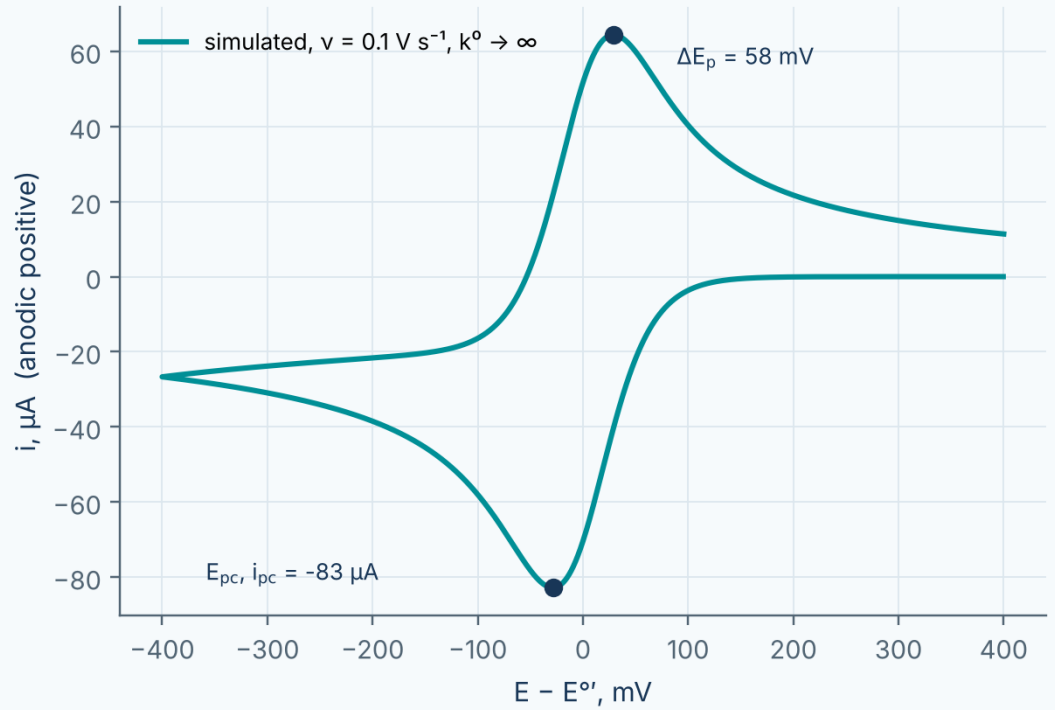
$$O + e^- \rightleftharpoons R, \quad \partial c_i/\partial t = D\,\partial^2 c_i/\partial x^2$$

$$j = Fk^0[c_O e^{-\alpha f(E-E^{\circ\prime})} - c_R e^{(1-\alpha)f(E-E^{\circ\prime})}]$$

MODEL CONDITIONS 3 mm disk, 5 mM ferricyanide, $D_O = D_R = 7.6 \cdot 10^{-10}$ $m^2\,s^{-1}$, fast kinetics; implicit finite-volume simulation, 0.5 mV steps.

EXAMPLE $v = 0.1\ V\,s^{-1}$: $\Delta E_p = 58$ mV, $i_{pc} = 83$ µA (Randles–Ševčík: 82.9 µA). $i_{pa}/i_{pc} = 0.78$ from zero current; ≈ 1 with the correct baseline.

EXAMPLE · SIMULATED REVERSIBLE CYCLIC VOLTAMMOGRAM



ENGINEERING INTERPRETATION CV probes the time domain and EIS the frequency domain of the same parameters $E^{\circ\prime}$, k^0, D and C_{dl}.

Further reading: Bard, Faulkner & White, Electrochemical Methods, 3rd ed. (2022), ch. 6–7; Elgrishi et al., J. Chem. Educ. 95 (2018) 197–206; Nicholson, Anal. Chem. 37 (1965) 1351.

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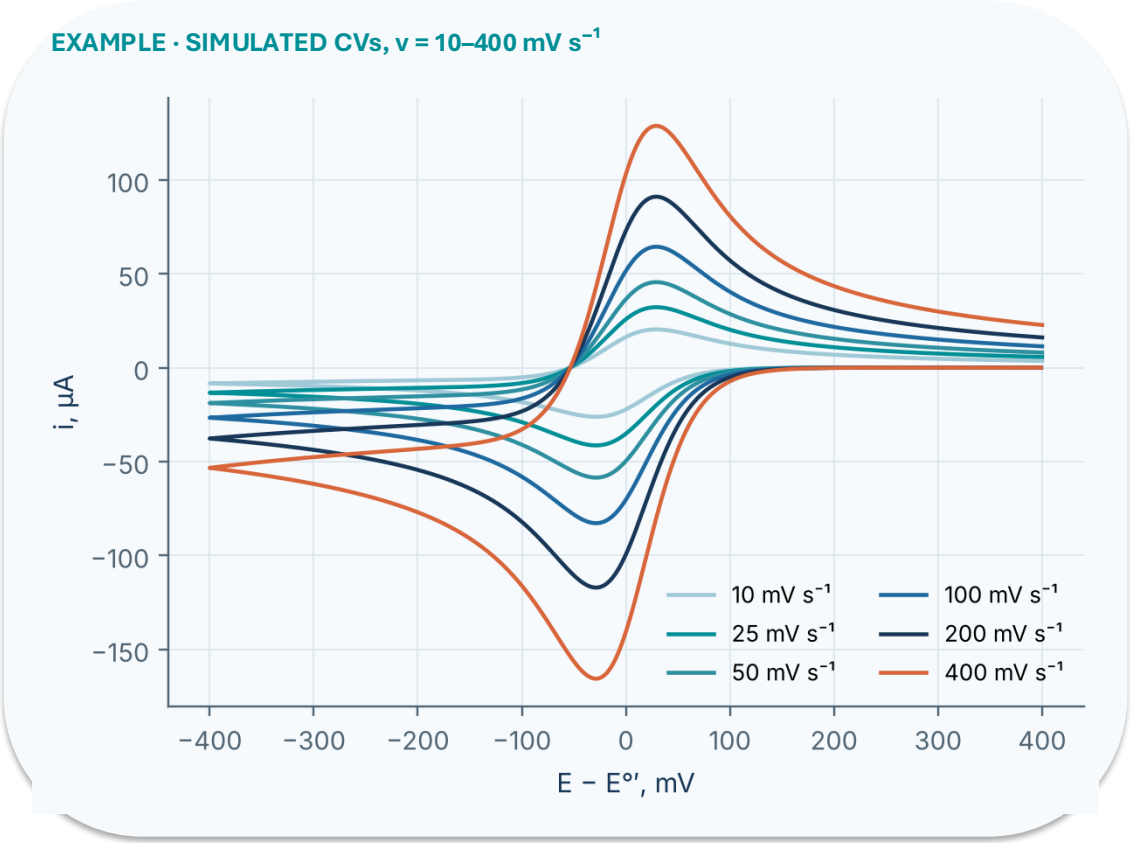
Cyclic voltammetry protocol and scan rate

A triangular potential waveform produces forward and reverse peaks.

$$E(t) = E_i - vt \quad \text{(forward)}$$
$$i_c = C_{dl}Av \quad \text{(charging)}$$

MODEL CONDITIONS Six scan rates 10–400 mV s^{-1}, same electrode and solution; potential window ±400 mV around E°'.

EXAMPLE Charging current at 0.1 V s^{-1}: 20 µF cm^{-2} × 0.0707 cm^2 × 0.1 V s^{-1} = 0.14 µA ≪ 83 µA. On a porous electrode with 1000× area it dominates.



ENGINEERING INTERPRETATION Peak potentials independent of v indicate fast kinetics; shifting peaks indicate kinetic or IR limitation.

Further reading: Bard, Faulkner & White, Electrochemical Methods, 3rd ed. (2022), ch. 6–7; Elgrishi et al., J. Chem. Educ. 95 (2018) 197–206; Nicholson, Anal. Chem. 37 (1965) 1351.

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Randles–Ševčík analysis

For diffusion control the peak current grows with the square root of scan rate.

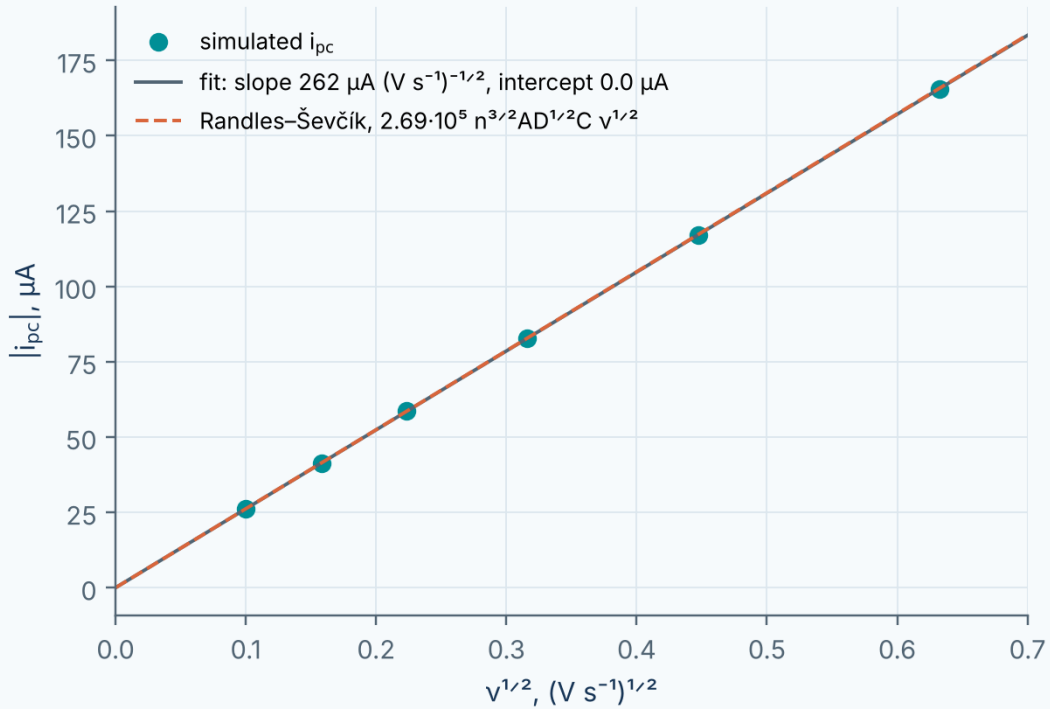
$$i_p = 2.69 \cdot 10^5 \, n^{3/2} \, A \, D^{1/2} \, C \, v^{1/2}$$

(25 °C; A cm^2, D cm^2 s^{-1}, C mol cm^{-3})

MODEL CONDITIONS Reversible electron transfer, planar semi-infinite diffusion, peak current measured from zero baseline on the forward scan.

EXAMPLE Slope 262 µA (V s^{-1})$^{-1/2}$ gives D = 7.59·10^{-6} cm^2 s^{-1}, within 0.2 % of the 7.60·10^{-6} used in the simulation (code verification).

EXAMPLE · i_{pc} VS $v^{1/2}$



ENGINEERING INTERPRETATION A linear plot supports, but does not prove, diffusion control; adsorbed species give $i_p \propto v$.

Further reading: Bard, Faulkner & White, Electrochemical Methods, 3rd ed. (2022), ch. 6–7; Elgrishi et al., J. Chem. Educ. 95 (2018) 197–206; Nicholson, Anal. Chem. 37 (1965) 1351.

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Peak separation and electron-transfer kinetics

Slow kinetics widen the peak separation as the scan rate increases.

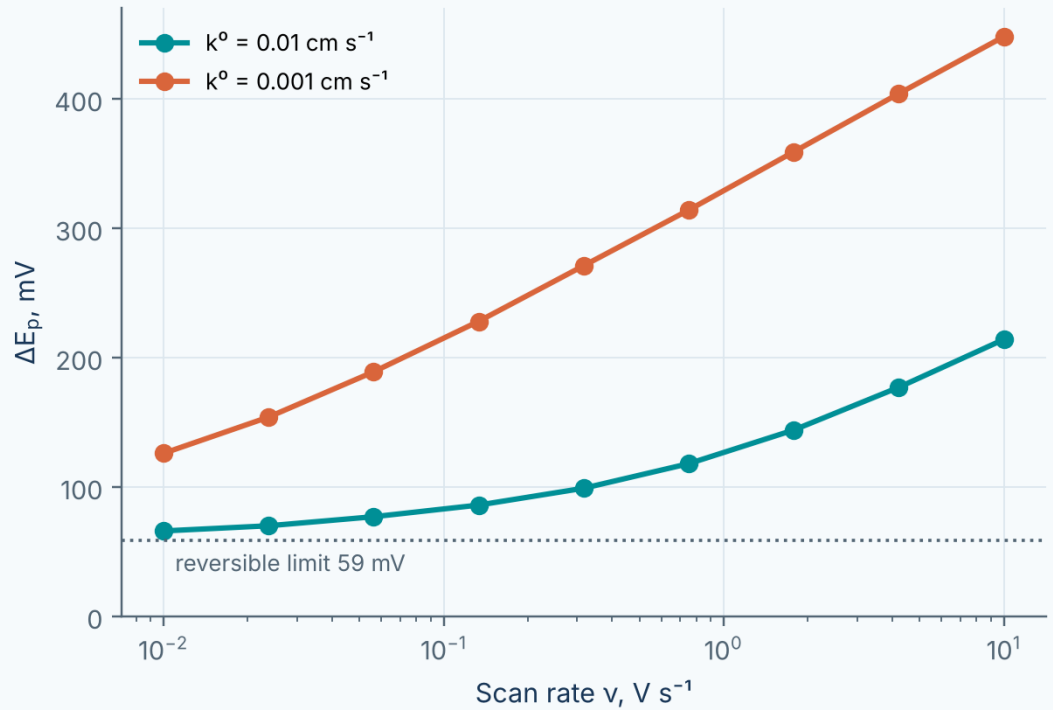
$$\psi = k^0 / (\pi D n F v / RT)^{1/2}$$

$$\Delta E_p \approx 59/n \text{ mV} \quad \text{(reversible, 25 °C)}$$

MODEL CONDITIONS $\alpha = 0.5$, $D_O = D_R$, no uncompensated resistance; simulated ΔE_p compared with Nicholson's working curve.

EXAMPLE $k^0 = 0.01$ cm s^{-1}: $\Delta E_p = 66$ mV at 10 mV s^{-1} and 86 mV at 0.13 V s^{-1} ($\psi = 0.90$; Nicholson: 84 mV at $\psi = 1$). $k^0 = 0.001$ cm s^{-1}: 126–448 mV.

EXAMPLE · ΔE_p VS SCAN RATE FOR TWO k^0



ENGINEERING INTERPRETATION Uncompensated resistance also widens ΔE_p; vary c to tell them apart (iR grows with c, kinetics does not).

Further reading: Bard, Faulkner & White, Electrochemical Methods, 3rd ed. (2022), ch. 6–7; Elgrishi et al., J. Chem. Educ. 95 (2018) 197–206; Nicholson, Anal. Chem. 37 (1965) 1351.

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Impedance and the Randles circuit

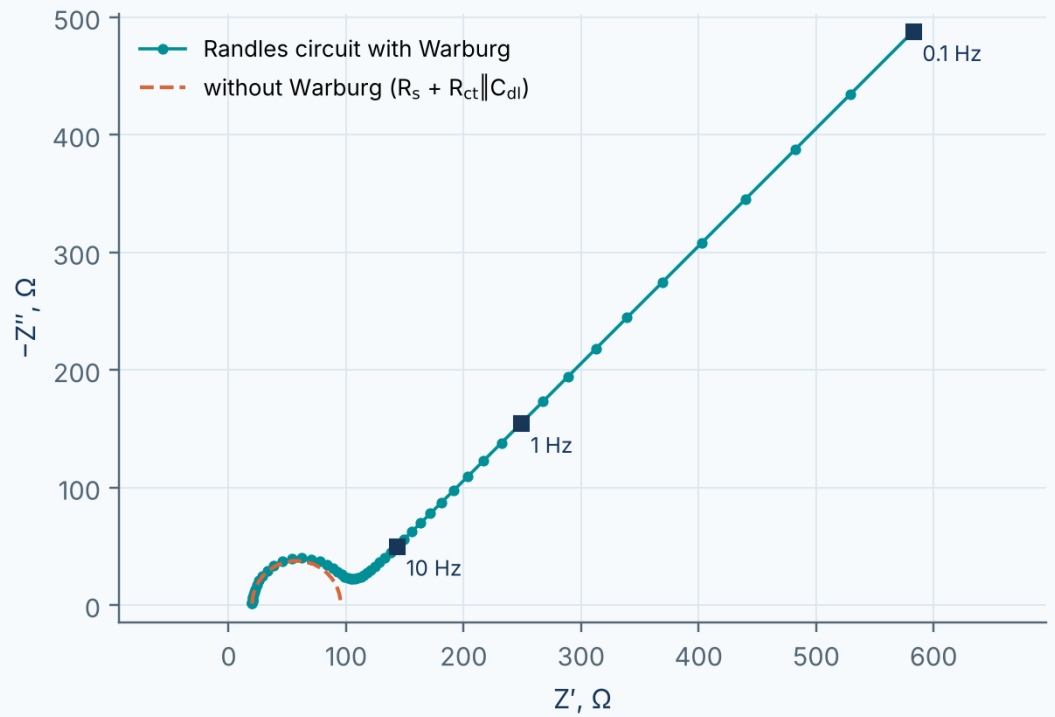
Small-signal impedance separates resistive, capacitive and diffusive responses.

$$Z = R_s + 1 / [j\omega C_{dl} + 1/(R_{ct} + Z_W)]$$
$$R_{ct} = RT / (n^2F^2Ak^0c)$$

MODEL CONDITIONS Equimolar 5 mM ferri/ferrocyanide, $k^0 = 0.01$ cm s^{-1}, $\alpha = 0.5$, $C_{dl} = 20$ µF cm^{-2}, $R_s = 20$ Ω, small amplitude (linear response).

EXAMPLE $R_{ct} = 75$ Ω; the arc apex lies at $f = 1/(2\pi R_{ct}C_{dl}) = 1.5$ kHz. Below ~10 Hz diffusion (45° line) dominates.

EXAMPLE · NYQUIST PLOT, 100 kHz – 0.1 Hz



ENGINEERING INTERPRETATION Each circuit element must map to a physical process; otherwise the fit is only a curve description.

Further reading: Orazem & Tribollet, Electrochemical Impedance Spectroscopy, 2nd ed. (2017); Lazanas & Prodromidis, ACS Meas. Sci. Au 3 (2023) 162–193.

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Diffusion impedance and Bode representation

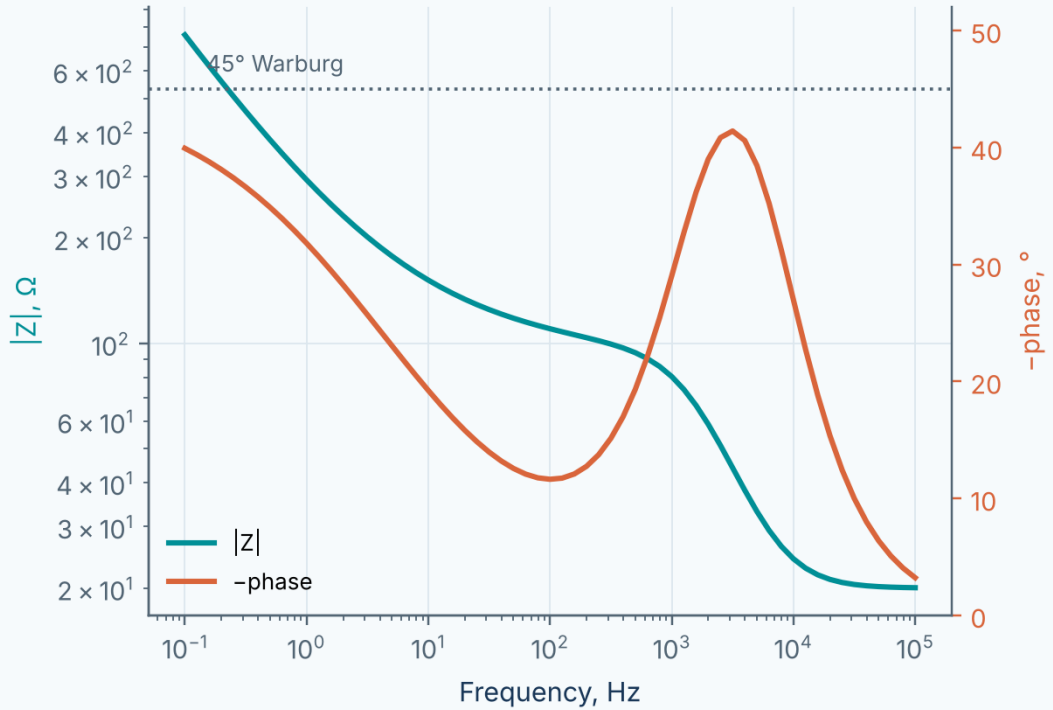
Semi-infinite Warburg impedance has equal real and imaginary parts.

$$Z_W = \sigma(1 - j) / \omega^{1/2}$$
$$\sigma = RT/(n^2F^2A\sqrt{2})\cdot[1/(c_O\sqrt{D_O}) + 1/(c_R\sqrt{D_R})]$$

MODEL CONDITIONS Same system as slide 8; planar semi-infinite diffusion, $D_O = D_R = 7.6\cdot10^{-10}$ m^2 s^{-1}.

EXAMPLE $\sigma = 386\ \Omega\ s^{-1/2}$. $|Z|$ tends to $R_s = 20\ \Omega$ at high frequency; the phase approaches 45° at 0.1 Hz where Z_W dominates.

EXAMPLE · BODE PLOT OF THE RANDLES CIRCUIT



ENGINEERING INTERPRETATION Thin films or a rotating electrode give finite-length diffusion: the 45° line bends at the lowest frequencies.

Further reading: Orazem & Tribollet, Electrochemical Impedance Spectroscopy, 2nd ed. (2017); Lazanas & Prodromidis, ACS Meas. Sci. Au 3 (2023) 162–193.

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Fitting and model discrimination

A good model gives random residuals and well-determined parameters.

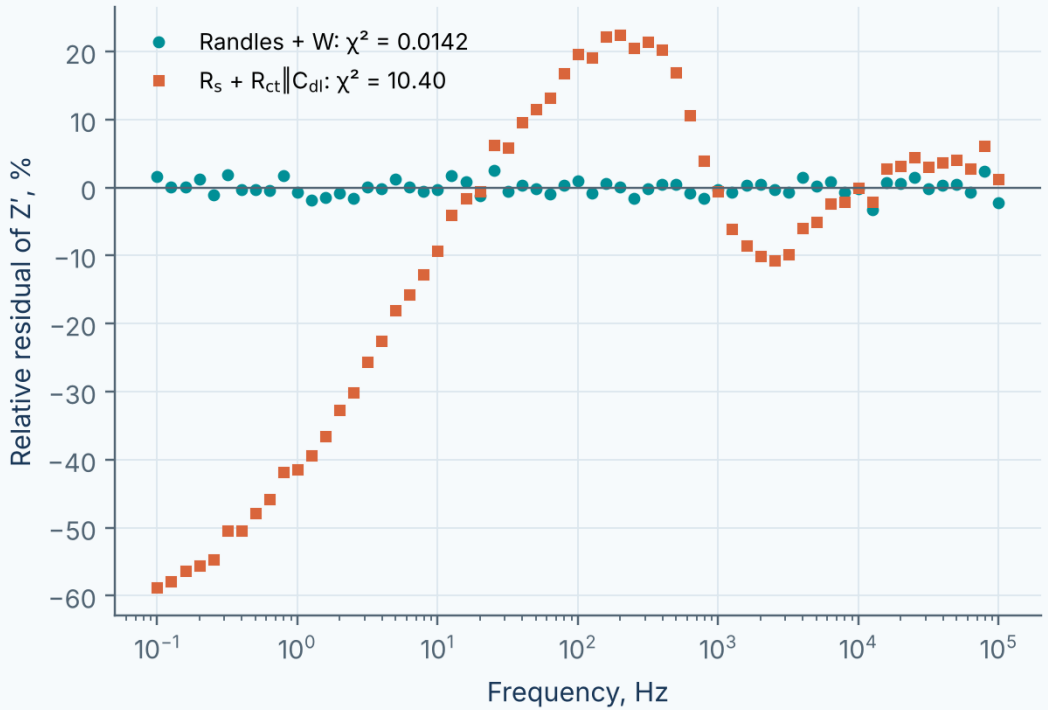
$$\chi^2 = \Sigma\, |Z_{exp} - Z_{model}|^2 / |Z_{exp}|^2$$

complex nonlinear least squares

MODEL CONDITIONS Synthetic data from slide 8 with 1 % random noise; modulus weighting; standard errors from the Jacobian.

EXAMPLE Randles + W recovers R_s = 19.94 ± 0.06 Ω, R_{ct} = 75.5 ± 0.3 Ω, C_{dl} = 1.409 ± 0.008 µF, σ = 385 ± 1 Ω $s^{-1/2}$. Without W, χ^2 is 700× larger and residuals are systematic.

EXAMPLE · RESIDUALS OF TWO CANDIDATE MODELS



ENGINEERING INTERPRETATION Check data with Kramers–Kronig first; then compare models by residuals and uncertainty, not by eye.

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Research practice: from measurement to a defensible result

HYPOTHESIS

State which parameter (D, k^0, R_{ct}) is expected to change, and why.

CONTROLS

Blank electrolyte, bare electrode and a known redox probe (ferri/ferrocyanide).

REPLICATES

At least three independent electrodes; report mean ± standard deviation.

IR AND REFERENCE

Measure R_u, compensate or correct; report the reference electrode and its check.

UNCERTAINTY

Propagate fit errors and electrode-area uncertainty to the final parameters.

REPORTING

Share raw data, scripts and model files so that others can reproduce the analysis.

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Conclusions: a verified model is a useful model

MODEL

Diffusion + Butler–Volmer kinetics explains both CV and EIS.

CV

$i_p \propto v^{1/2}$ gives D; $\Delta E_p(v)$ gives k^0 through ψ.

EIS

R_s, R_{ct}, C_{dl} and σ map to resistance, kinetics, interface and diffusion.

VERIFICATION

Simulations reproduce Randles–Ševčík and Nicholson benchmarks.

FITTING

Use residuals and confidence intervals to choose between models.

PRACTICE

Controls, replicates, IR correction and open data make results reliable.

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Homework: calculations, interpretation and research

1. THEORY Explain why ΔE_p grows with scan rate for a quasi-reversible couple but not for a reversible one. Use the parameter ψ.

2. CALCULATION 2 mM ferrocenemethanol ($n = 1$, $D = 7.8 \cdot 10^{-6}$ cm^2 s^{-1}) on a 2 mm disk at 50 mV s^{-1}: find i_p. Find R_{ct} for $k^0 = 0.005$ cm s^{-1} in an equimolar 2 mM solution.

3. DATA Fit the file L10_eis_dataset.csv with $R_s + R_{ct} \| C_{dl}$ and with the Randles circuit. Report parameters ± standard error and plot residuals.

4. CODE Write a CV simulator (implicit finite differences) and reproduce three points of Nicholson's working curve.

5. RESEARCH Design an experiment that separates slow kinetics from uncompensated resistance in CV. List variables, controls, replicates and expected results.

Constants: $F = 96485$ C mol^{-1}; $R = 8.314$ J mol^{-1} K^{-1}; $T = 298.15$ K; $RT/F = 25.69$ mV.

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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.