Lecture 7 | Electrochemical Impedance Spectroscopy and Equivalent-Circuit Modeling

Al-Farabi Kazakh National University

Department of Analytical, Colloidal Chemistry and Technology of Rare Elements

Discipline: Modeling in Electrochemistry

Educational program: 7M07103 Chemical Engineering

Lecturer: Khaisa Avchukir, PhD, Associate Professor

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Purpose and Expected Learning Outcomes

PURPOSE

Build a quantitative understanding of electrochemical impedance spectroscopy and equivalent-circuit modeling.

01 Explain the physical assumptions and governing electrochemical equations.

02 Calculate relevant kinetic, transport, and interfacial parameters.

03 Interpret simulated responses and compare them with measurements.

04 Evaluate model limitations and propose a reproducible validation plan.

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Lecture Trajectory and Practical Relevance



Scientific value: link measurable current, potential, concentration, or impedance to mechanistic parameters.

Applications: electroanalysis • energy conversion • electrodeposition • corrosion • process engineering

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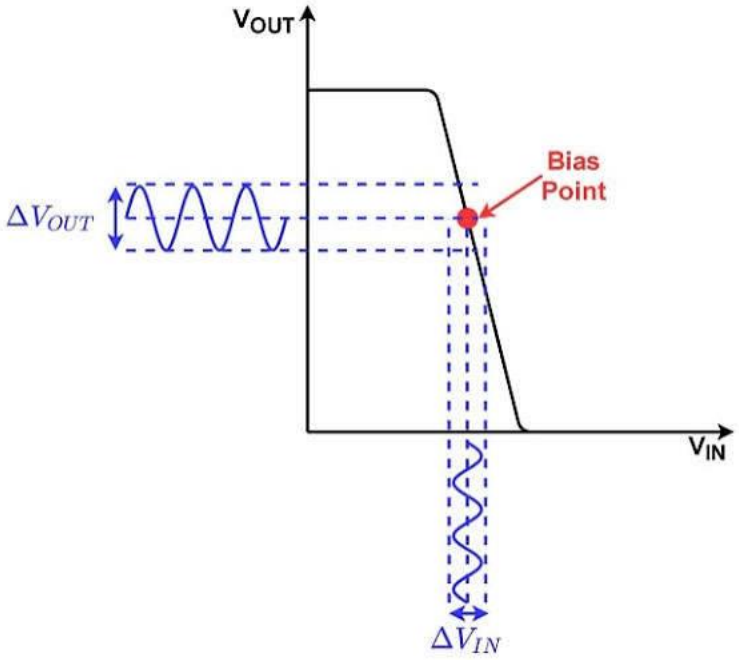
Small-signal linear response

$$Z(\omega) = \hat{E}(\omega)/\hat{I}(\omega)$$

Apply a small sinusoidal perturbation around steady state.

Use frequency-dependent complex impedance to separate timescales.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

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Complex impedance and plots

$$Z = Z' + jZ'' \; ; \; \omega = 2\pi f$$

Nyquist plots commonly show −Z" against Z'.

Bode plots show Z and phase against log frequency.

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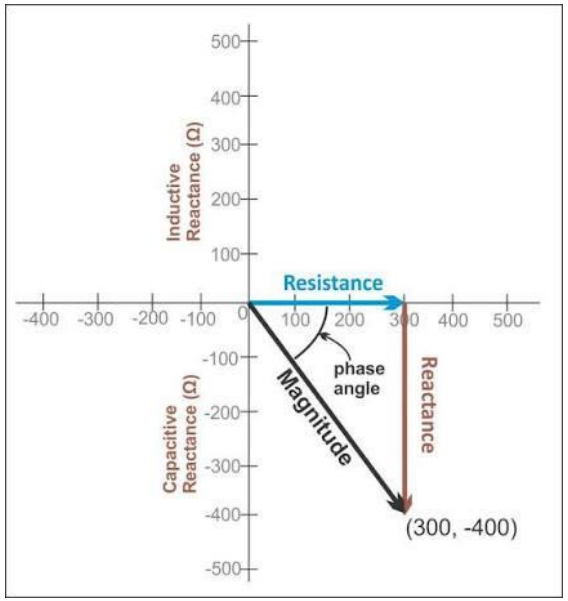

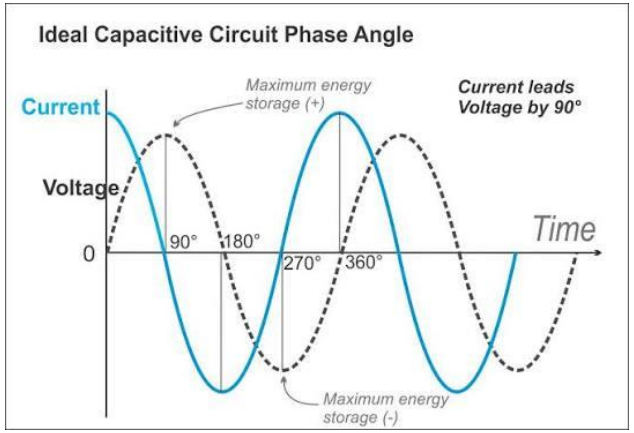

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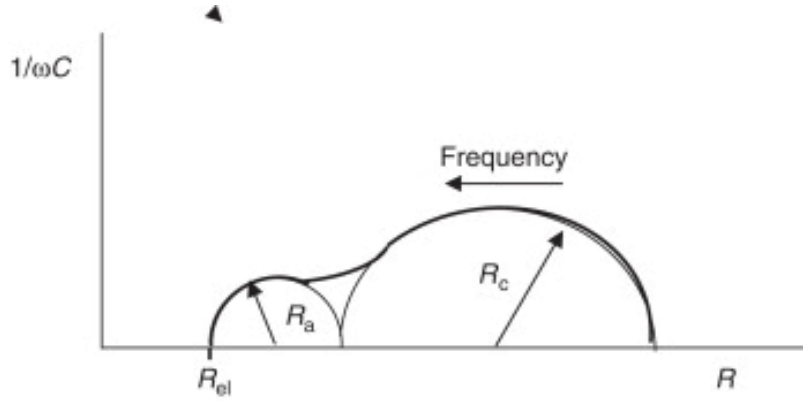
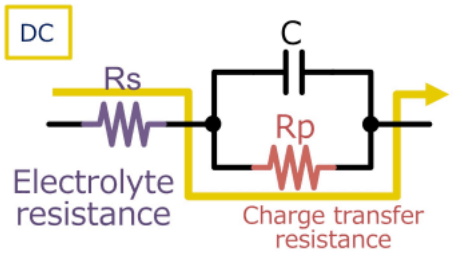
Charge-transfer resistance

Rct = RT/(nFi0) (BV with nFη exponent)

Near equilibrium, slope of current–overpotential defines Rct.

For n-electron BV written with nF in exponent, $Rct=RT/(nFi_0)$.





$R_{DC} \fallingdotseq Rs+Rp$

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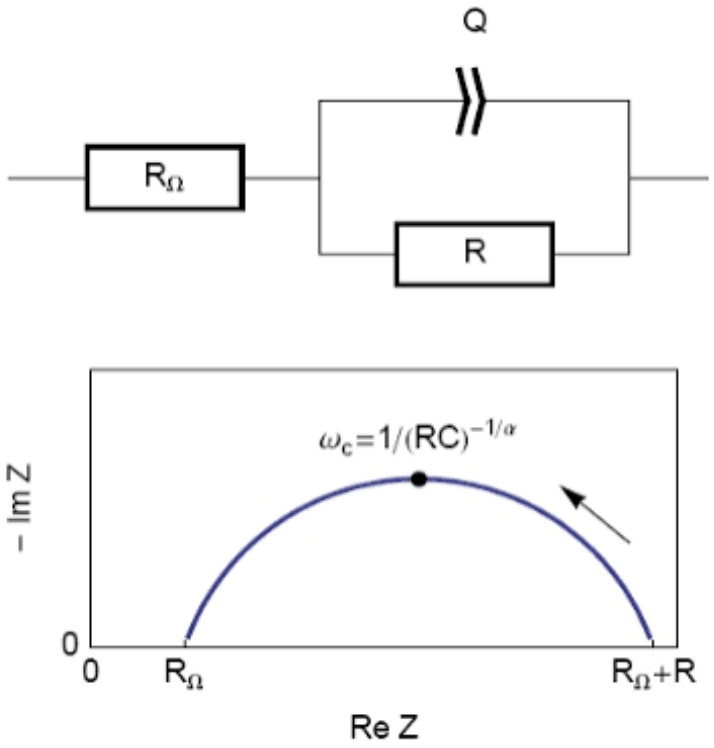
Double-layer capacitance

ZC = 1/(jωCdl)

Ideal capacitance gives −90° phase and a frequency-dependent reactance.

CPE behavior reflects distributed relaxation or heterogeneity.



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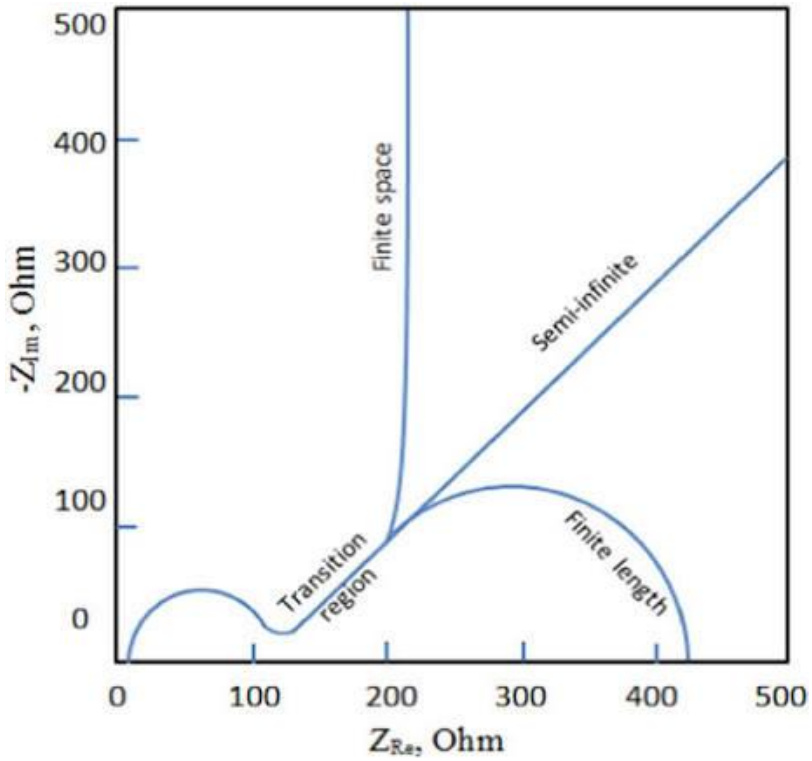
Diffusion impedance

$$Z_W = \sigma(1-j)/\sqrt{\omega}$$

Semi-infinite diffusion produces a 45° Nyquist tail.

Finite-length transport produces different low-frequency behavior.



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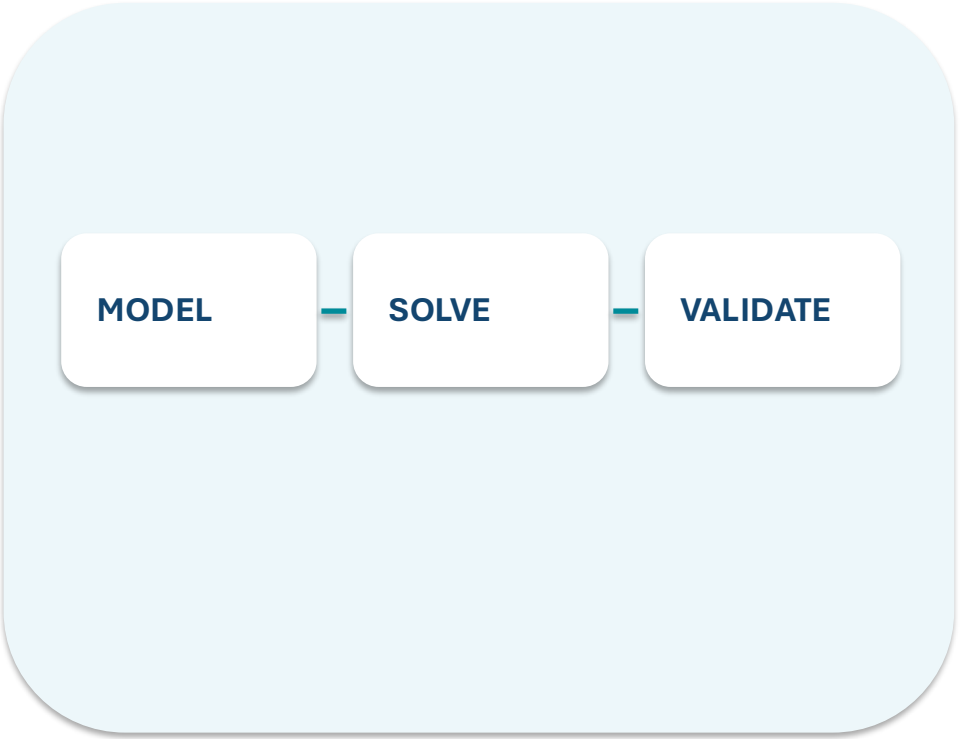
Equivalent circuits and identifiability

$$Z = R_s + [1/(1/R_{ct} + j\omega C_{dl})]$$

A Randles-type circuit combines solution resistance and interfacial kinetics.

Fit complex data and test Kramers–Kronig consistency.



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Conclusions: From Physical Mechanisms to Predictive Models

1. Small-signal linear response

$Z(\omega) = \hat{E}(\omega)/\hat{I}(\omega)$

2. Complex impedance and plots

$Z = Z' + jZ''$; $\omega = 2\pi f$

3. Charge-transfer resistance

$R_{ct} = RT/(nFi_0)$ (BV with $nF\eta$ exponent)

4. Double-layer capacitance

$Z_C = 1/(j\omega C_{dl})$

5. Diffusion impedance

$Z_W = \sigma(1-j)/\sqrt{\omega}$

6. Equivalent circuits and identifiability

$Z = R_s + [1/(1/R_{ct} + j\omega C_{dl})]$

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Homework: Quantitative and Research-Oriented Problems

CONCEPTUAL Compare the assumptions underlying “Small-signal linear response” and “Charge-transfer resistance”.

CALCULATION Given $T = 298.15$ K, $F = 96485$ C mol^{-1}, $R = 8.314$ J mol^{-1} K^{-1}, $D = 1.0 \times 10^{-9}$ m^2 s^{-1}, $c = 1.0$ mol m^{-3}, $A = 1.0$ cm^2, $n = 1$, compute a relevant transport or kinetic prediction and state assumptions.

DATA INTERPRETATION For simulated normalized signals (t/s, response): (0.2,0.82), (0.5,0.61), (1.0,0.44), (2.0,0.30), identify the trend and test a plausible physical model.

CRITICAL THINKING Predict how a tenfold change in the controlling kinetic or transport parameter changes the response; distinguish hypotheses.

RESEARCH TASK Design a COMSOL or Python model with geometry, boundary conditions, mesh-convergence test, and an experimental validation plan.

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