Lecture 1 | Principles of electrochemical measurements

MODERN RESEARCH METHODS IN ELECTROCHEMISTRY

Educational program: 7M05301 Chemistry

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Purpose, expected results & learning outcomes

What students should understand and be able to do

PURPOSE

Establish the physical and instrumental basis of modern electrochemical measurements.

EXPECTED RESULT

Explain how controlled electrical perturbations reveal equilibrium, kinetics and transport.

LEARNING OUTCOMES

Identify WE / RE / CE; interpret E–i and i–t data; distinguish potentiostat from galvanostat; estimate Nernst potential and iR error.

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Lecture trajectory: from principles to applications

Concept → instrument → signal → interpretation → research decision

01 Redox thermodynamics

02 Three-electrode cell

03 Variables & perturbations

04 Current–potential response

05 Instrumentation & iR

06 Practical electroanalysis

Why it matters: reliable potentials, interpretable kinetics, reproducible measurements, and applications in sensing, corrosion, batteries and electrocatalysis.

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Redox reactions and electrode equilibrium

Thermodynamics determines the equilibrium potential

- Reduction: $Ox + ne^- \rightleftharpoons Red$; oxidation is the reverse process.
- Nernst equation: $E = E^{\circ\prime} + (RT/nF)\ \ln(aOx/aRed)$.
- At 25 °C: $E = E^{\circ\prime} + (0.05916/n)\ \log_{10}(aOx/aRed)$ V.
- Use activities for rigorous thermodynamics; concentrations are an approximation.

WORKED EXAMPLE

For n = 1, aOx/aRed = 10 at 25 °C: $E - E^{\circ\prime}$ = +59.2 mV.

Potential must be stated versus a reference electrode.

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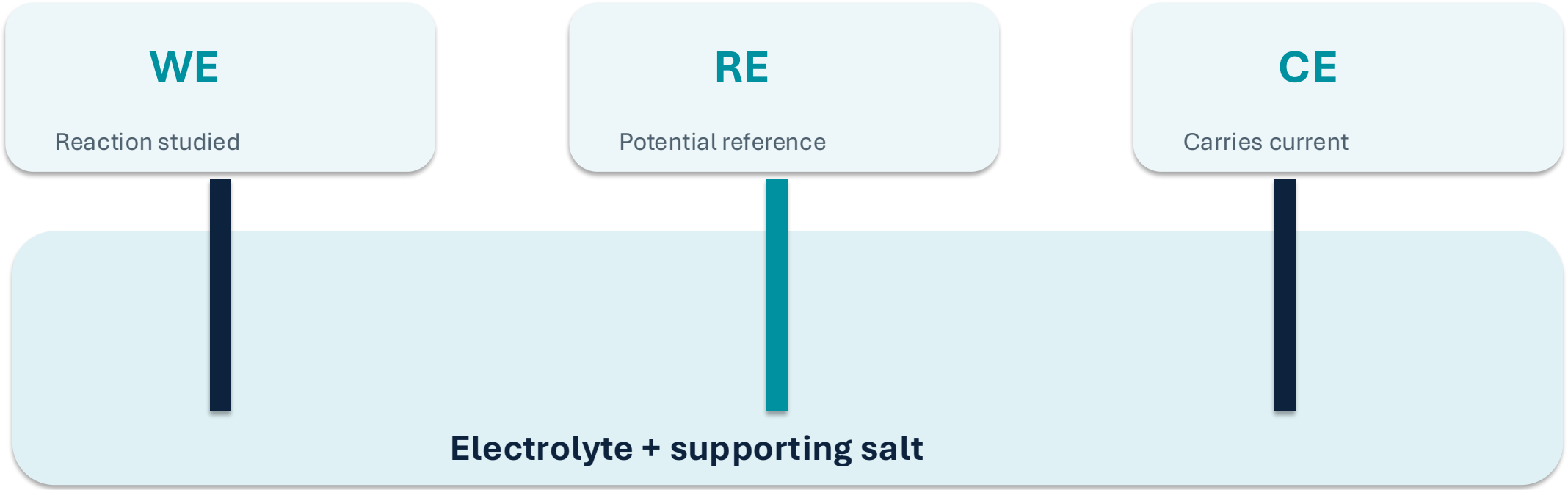
The three-electrode electrochemical cell

Separate current delivery from potential sensing



RE tip close to WE reduces uncompensated resistance; keep CE products away from WE (separator when needed).

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Controlled variables and experimental design

A measurement is an input–output experiment

CONTROL / INPUT

Potential E(t) → potentiostatic

Current i(t) → galvanostatic

Concentration, temperature, hydrodynamics and geometry must be specified.

OBSERVE / OUTPUT

i(t), E(t), charge Q = ∫i dt, impedance Z(ω).

A valid interpretation requires an appropriate physical model.

Typical experiment: potential step ΔE → transient current i(t). A diffusion-controlled planar electrode often shows $i \propto t^{-1/2}$ (Cottrell regime).

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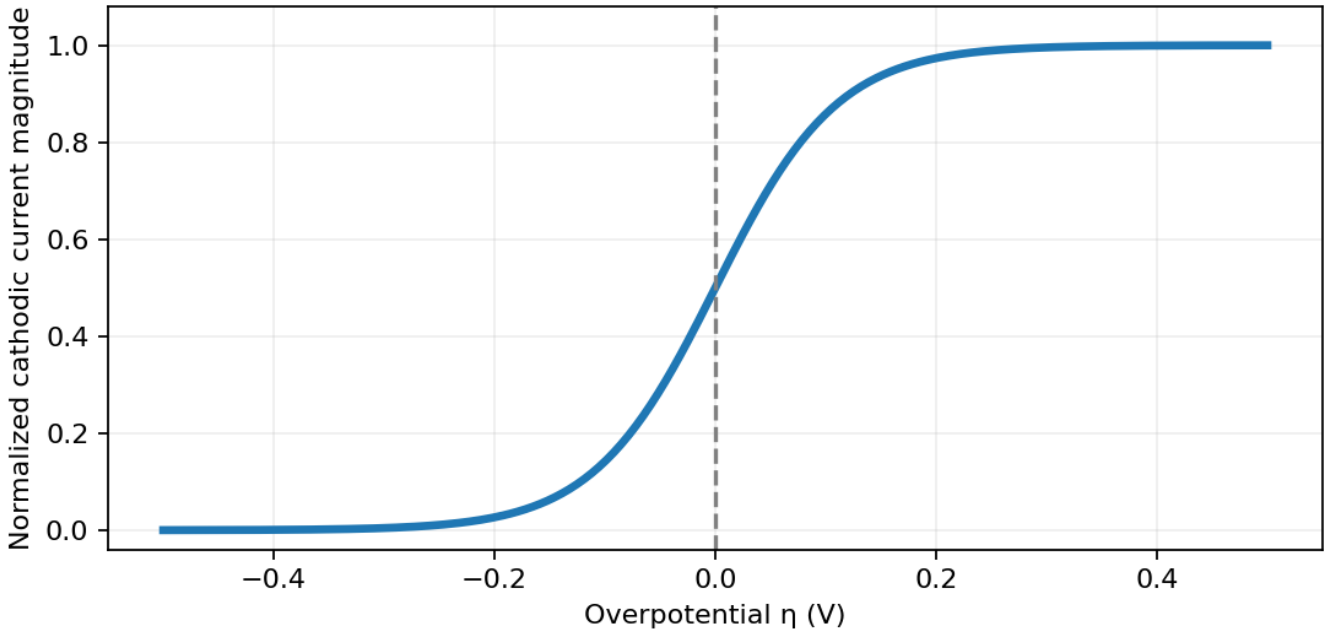
Polarization and current–potential curves

Thermodynamics, charge transfer and mass transport



INTERPRETATION

η = E − Eeq is the overpotential.

Small |η|: kinetic sensitivity.

At large driving force: mass-transfer limitation may produce a limiting current.

Curve is illustrative, not experimental data.

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Potentiostat, galvanostat and measurement signals

Feedback maintains the commanded experimental variable

POTENTIOSTAT

Controls EWE − ERE by adjusting current through WE–CE.

Records i(t), E(t).

Used for CV, LSV, chronoamperometry and EIS.

GALVANOSTAT

Controls current i(t) by adjusting the cell voltage.

Records E(t), i(t).

Used for battery cycling, deposition and chronopotentiometry.

Core signal path: waveform generator → feedback controller → electrochemical cell → acquisition → data analysis.

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Ohmic drop and impedance: avoiding artefacts

Electrode potential accuracy depends on cell design

- Uncompensated resistance Ru causes a potential error: $\Delta E\Omega = iRu$.
- Example: $i = 2$ mA and $Ru = 50\ \Omega \rightarrow |\Delta E\Omega| = 0.10$ V.
- Reduce Ru using supporting electrolyte, appropriate cell geometry and RE placement.
- Simplified interfacial model: Ru in series with (Rct ‖ Cdl); real interfaces may require CPE/diffusion terms.
- Check electrode cleanliness, RE stability, gas bubbles, background signal and instrument limits.

Practical implication: a 100 mV iR error can strongly distort apparent reaction kinetics.

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Conclusions

Five ideas to retain

- Electrochemical experiments connect redox thermodynamics with measurable signals.
- The three-electrode cell enables independent potential measurement and current flow.
- Input–response analysis reveals equilibrium, kinetics and mass transport.
- Potentiostats and galvanostats use feedback to control E or i, respectively.
- Good practice requires reference calibration, iR assessment and reproducibility.

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Homework and quantitative problems

Prepare short calculations and explain your assumptions

- 1 Nernst: calculate $E - E^{\circ\prime}$ at 298 K for n = 2 and aOx/aRed = 100.
- 2 Ohmic drop: calculate $\Delta E\Omega$ for i = 5 mA and Ru = 35 Ω; suggest two remedies.
- 3 Cell design: draw WE, RE and CE; explain the RE position and CE separator.
- 4 Experimental choice: select CV, chronoamperometry or chronopotentiometry for studying diffusion after a potential step; justify.
- 5 Critical thinking: explain why a current plateau alone does not prove slow electron-transfer kinetics.

Suggested reading: Bard, Faulkner & White, Electrochemical Methods: Fundamentals and Applications (3rd ed., 2022).

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