Lecture 5 | Mechanisms of Electrochemical Reactions

Modern research methods in electrochemistry

Educational program: 7M05301 Chemistry

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Purpose and expected learning outcomes

Purpose

Explain how electron transfer and coupled chemical steps shape experimental cyclic voltammograms.

By the end, students can

Identify E, EE, EC, CE and EC' mechanisms from reaction schemes and CV features.

Interpretation

Assess peak separation, reverse peak suppression, scan-rate dependence and catalytic current.

Research competence

Propose scan-rate and concentration tests, and distinguish mechanistic evidence from ambiguity.

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Lecture trajectory: from a CV to a mechanism

1 · Reference

Reversible and slow electron transfer

2 · Coupled chemistry

EC and CE mechanisms

3 · Multiple electrons

EE wave merging and splitting

4 · Catalysis

EC' response and diagnostic tests

Application: molecular electrocatalysis, redox mediators, reaction intermediates and catalyst screening.

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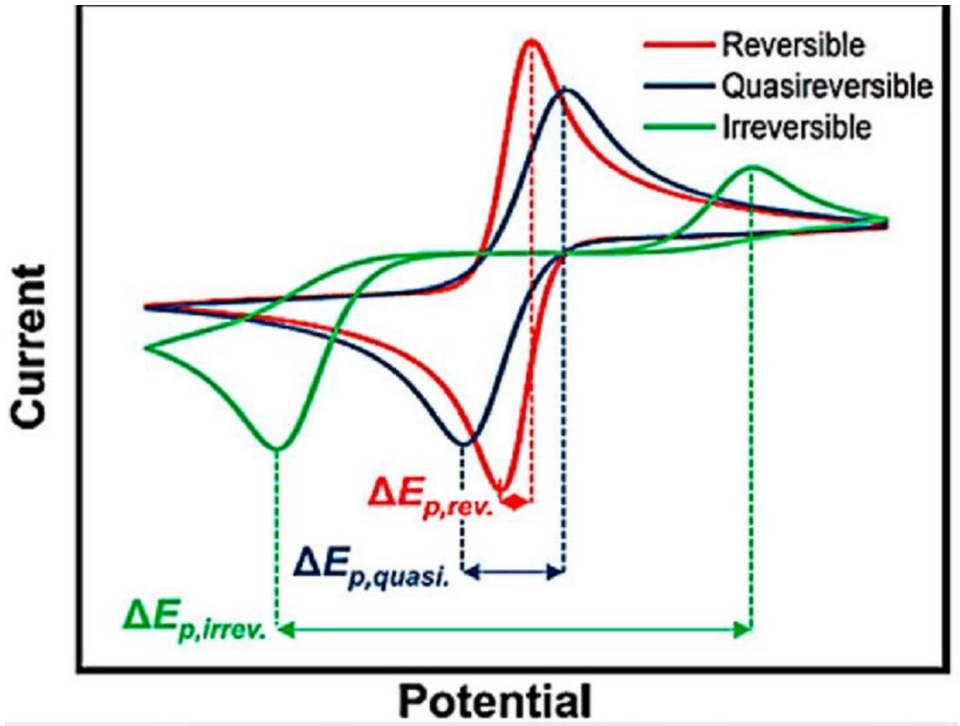
Electrochemical reversibility is a kinetic concept

E: Ox + e^- ⇌ Red; schematic CVs (not fitted experimental data)



Reversible: surface concentrations follow Nernst equilibrium.

Quasi-reversible: finite electron-transfer kinetics increase peak separation.

Irreversible: reverse electron transfer is too slow on the CV timescale.

At 298 K, ideal ΔEp ≈ 59 mV for a reversible one-electron, diffusion-controlled couple.

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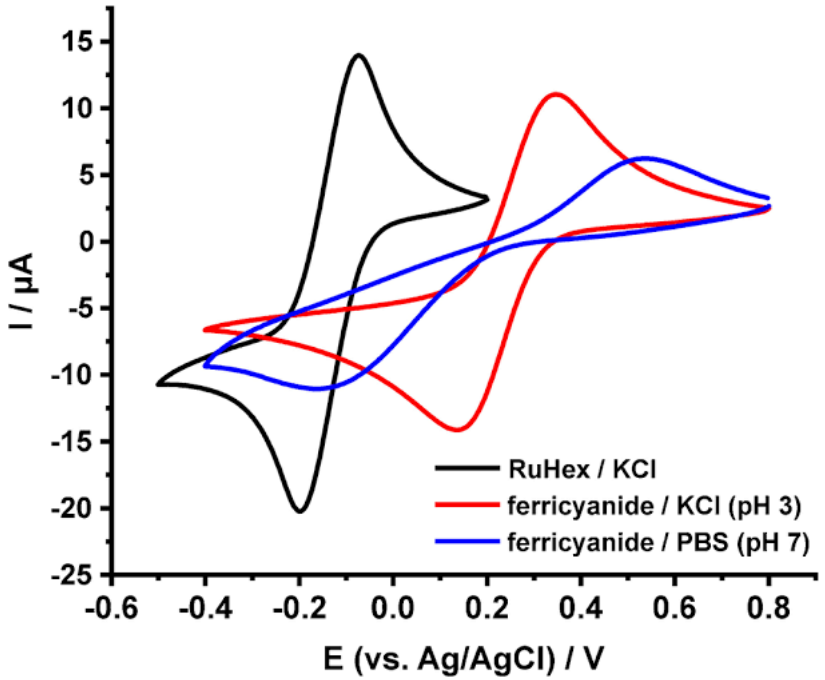
EC mechanism: electron transfer followed by chemistry

E: Ox + e^- ⇌ Red C: Red → Z



The chemical step consumes Red before it can be reoxidized.

As k × experimental timescale increases, the reverse anodic peak decreases.

Peak suppression alone is not unique proof of EC chemistry.

Diagnostic: change scan rate, substrate concentration, and potential window; compare simulations.

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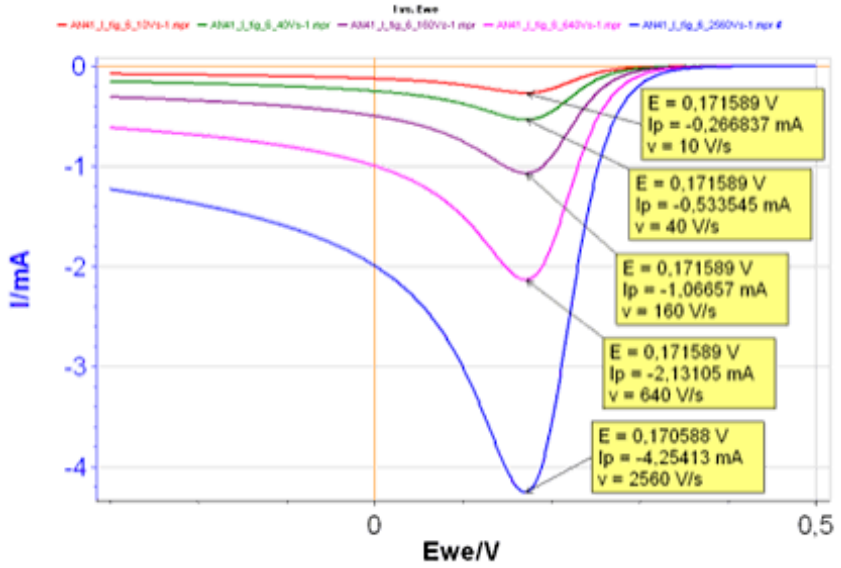
Scan rate is a mechanistic clock

Faster scans leave less time for a following chemical reaction



Characteristic time near a voltammetric wave scales approximately with RT/(nFv).

Slow scan: Red is consumed; reverse peak weakens.

Fast scan: more Red survives; reverse peak recovers.

Illustrative comparison only: the traces show qualitative trends, not a numerical EC simulation.

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CE mechanism: chemical pre-equilibrium before E

C: $Z \rightleftharpoons Ox$ E: $Ox + e^- \rightleftharpoons Red$

Chemical supply

The concentration of electroactive Ox depends on equilibrium and interconversion rates.

Experimental observation

Scan rate and concentration can reveal whether Ox is replenished during the voltammetric scan.

Important correction

The reduced product must be Red, not Z, unless an additional step is explicitly specified.

Interpretation caveat

A single CV is rarely sufficient to establish a CE pathway uniquely.

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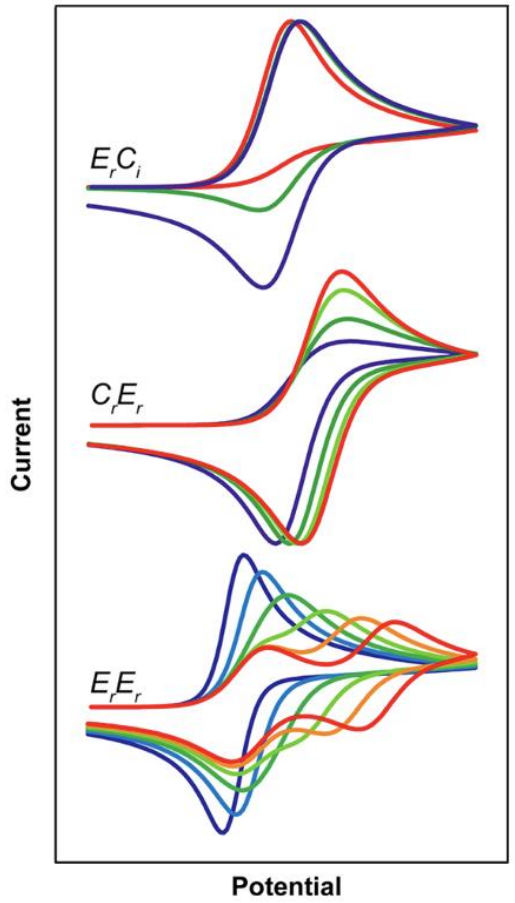
Sequential electron transfers: EE mechanism



$Ox + e^- \rightleftharpoons Red; Red + e^- \rightleftharpoons Q$

Separated formal potentials: two resolvable redox waves.

Overlapping potentials: merged or distorted waves.

Peak separation and shape also depend on kinetics, diffusion and interactions.

Do not assign electron count from peak spacing alone: use charge, standards, spectroscopy or modeling.

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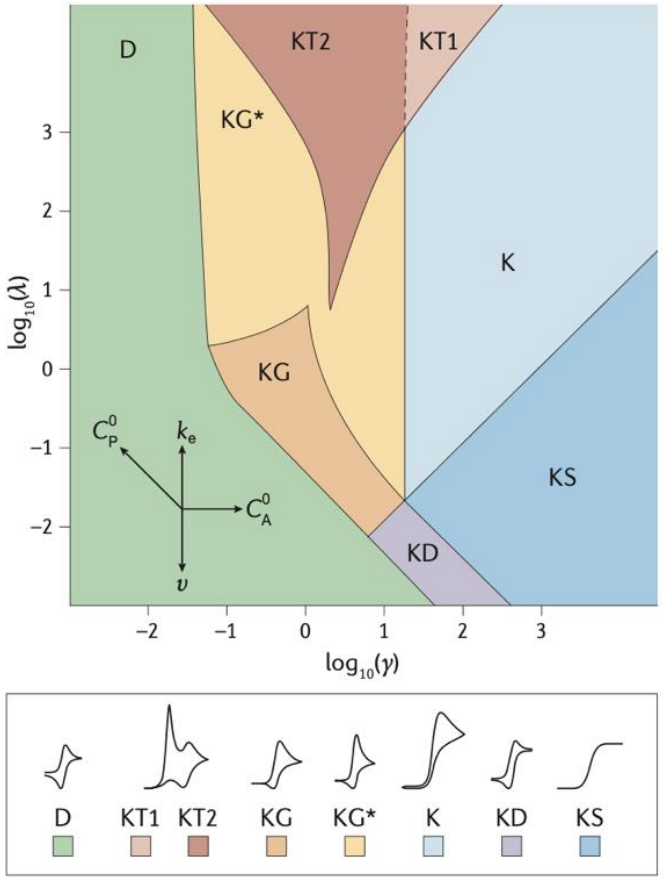
EC' electrocatalysis: regeneration amplifies current

E: Cat + e^- ⇌ Cat^- C': Cat^- + S → Cat + P



The chemical step regenerates Cat, allowing repeated electron transfer.

Substrate addition may produce an enhanced catalytic wave.

The response depends on catalyst/substrate concentrations, scan rate and reaction kinetics.

Application: compare blank and substrate-containing CVs; confirm products and catalyst stability.

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Conclusions: mechanisms are hypotheses to test

E

Electron-transfer kinetics control reversibility and peak separation.

EC

Following chemistry can suppress the return peak; fast scans may recover it.

CE / EE

Chemical pre-equilibria and sequential electrons reshape voltammograms.

EC'

Catalyst regeneration increases current, but requires independent mechanistic validation.

Suggested reading: Elgrishi et al., J. Chem. Educ. 95 (2018) 197–206; Lee et al., Nat. Rev. Chem. 1 (2017) 0039.

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Homework and research problems

1. Explain why ΔEp increases as heterogeneous electron transfer slows.

2. For EC (Red → Z), predict the change in reverse peak when scan rate rises from 0.1 to 10 V s^{-1}.

3. Sketch two CVs for an EE mechanism with $\Delta E^{\circ\prime}$ = 0.05 and 0.30 V; discuss wave overlap.

4. Propose three control experiments to distinguish EC' catalysis from electrode fouling or substrate reduction.

5. Research task: select a published molecular catalyst, propose its E/C mechanism and justify it with at least two independent observations.

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