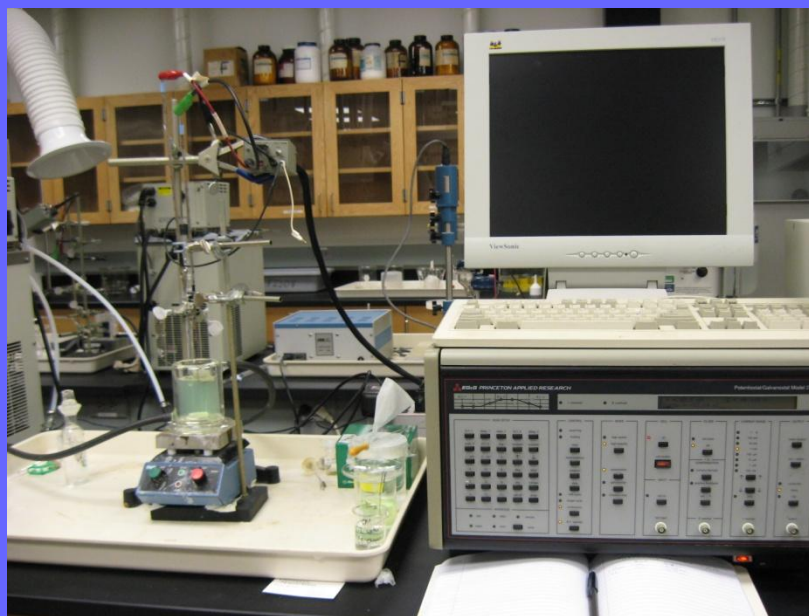
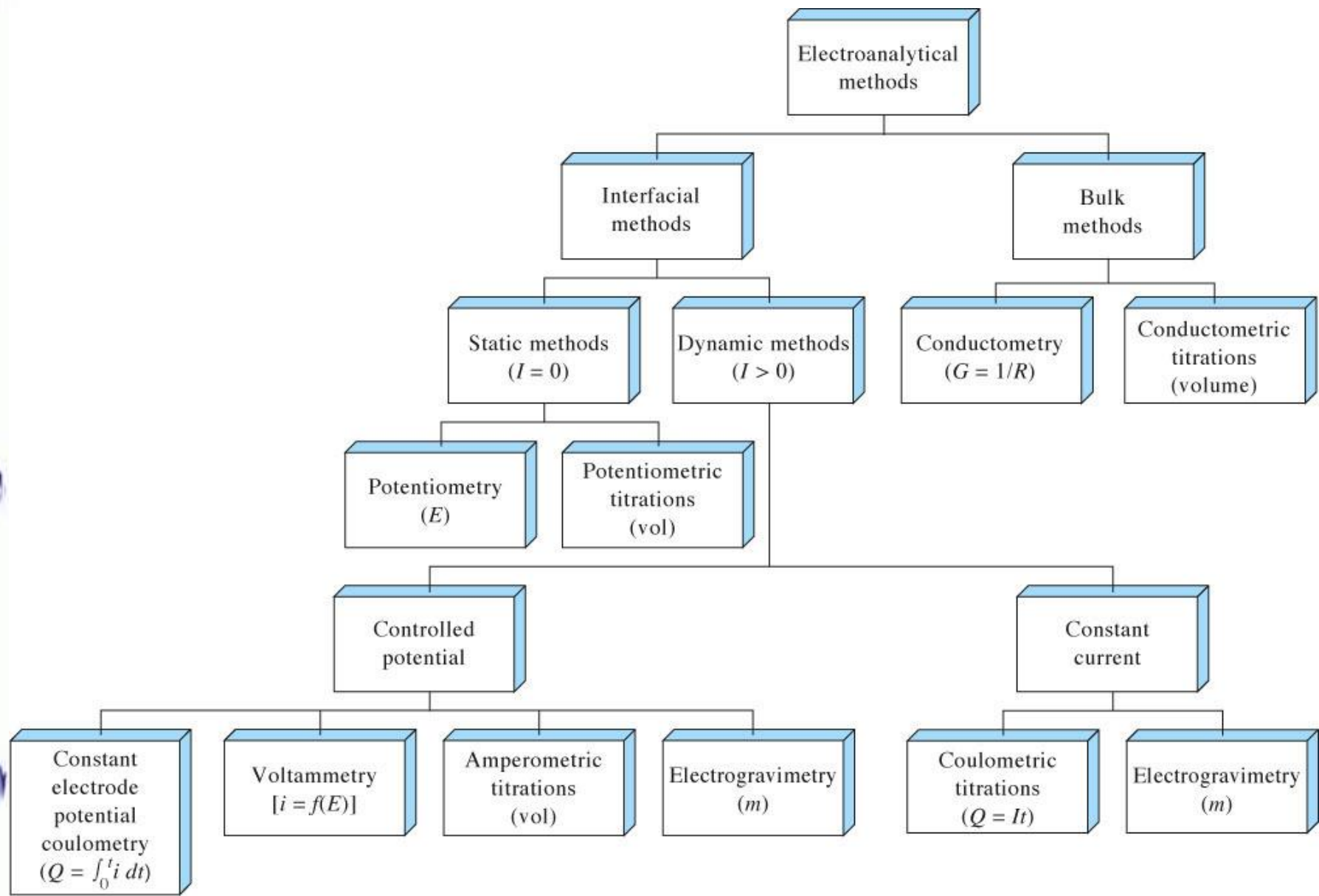


Chemistry 4631

Instrumental Analysis Lecture 23





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Voltammetry

Voltammetry – measurement of current as a function of applied potential using working electrode.

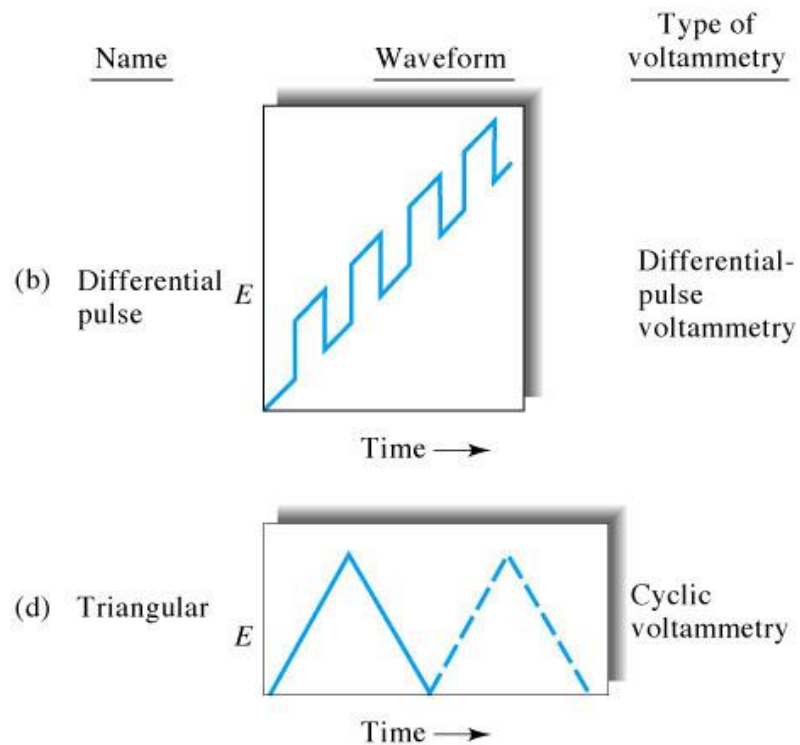
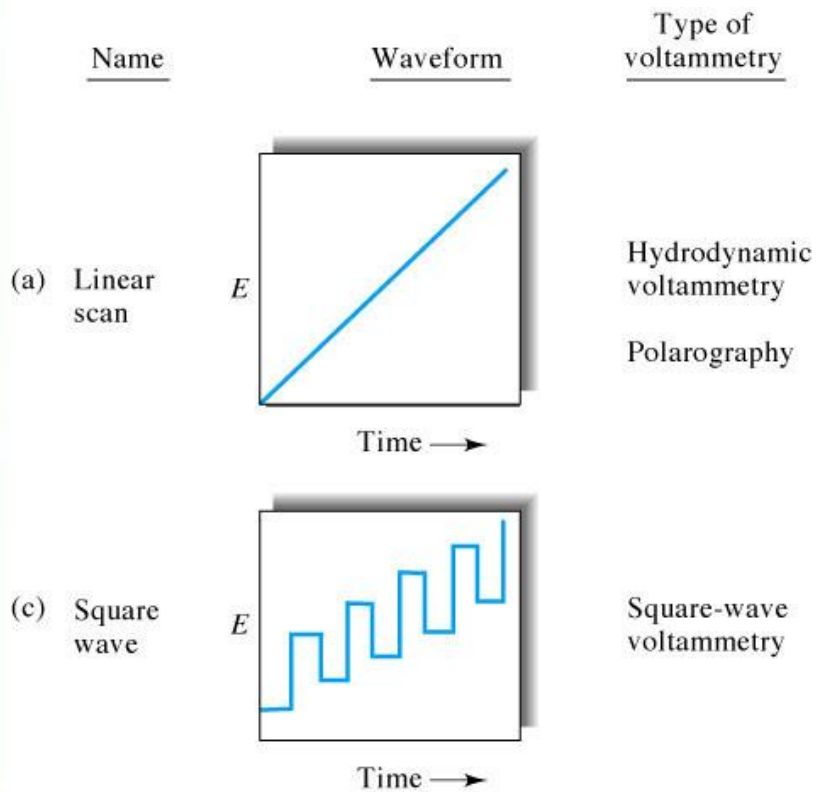
Historically – 1st voltammetry was polarography developed by Heyrovsky in 1921.

Voltammetry

Excitation signal

A variable potential excitation signal is applied to an electrochemical cell.

The excitation signal has a distinctive waveform, from linear to triangular.



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Voltammetry

Waveform can be a step:

Chronoamperometry – current as a function of time with respect to applied potential

Chronocoulometry – charge as a function of time with respect to applied potential

Differential Pulse Voltammetry - small pulses added to a linear ramp to measure current changes

Voltammetry

Waveform can be a sweep:

Linear Sweep Voltammetry – current as a function of time and applied potential

Cyclic Voltammetry – current as a function of applied potential in two directions

Anodic Stripping Voltammetry – current as a function of applied potential after deposition.

Voltammetry

Instrumentation

Potentiostat is an instrument capable of applying a controlled potential to a working electrode and measuring the resulting current from a redox reaction.

Connected to a cell with 3 electrodes in a solution.

Voltammetry

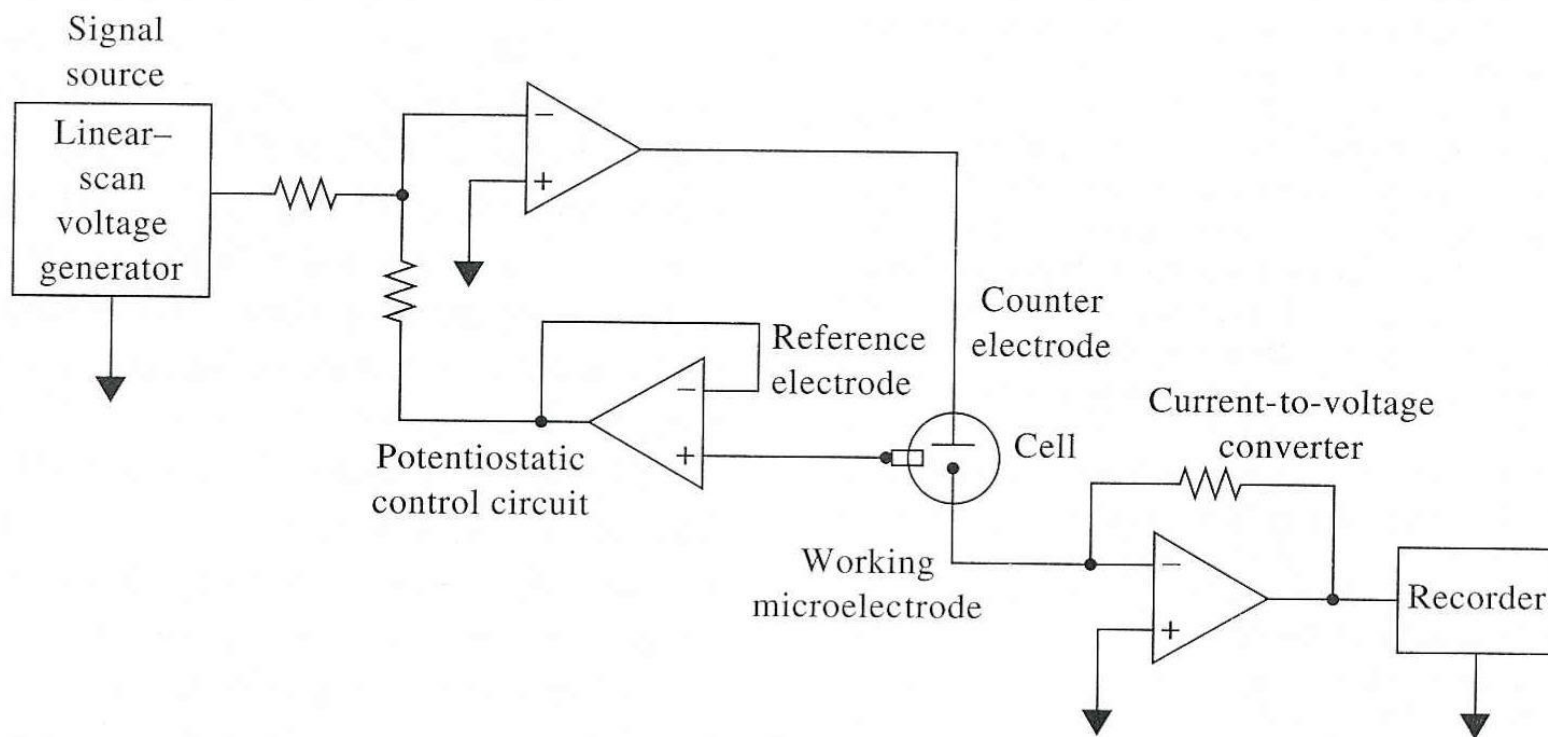


Figure 25-2 A system for potentiostatic three-electrode linear-scan voltammetry.

Voltammetry

Instrumentation

Electrochemical cell consist of three electrodes immersed in a solution of supporting electrolyte.

Working electrode – potential varies linearly with time, usually very small

Reference electrode – potential is constant with time – SCE or Ag/AgCl common

Counter (auxiliary) electrode – conducts current from source through solution – Pt wire common

Voltammetry

Working Electrodes

Come in a variety of shapes, compositions, and sizes.

Working electrodes have a potential window.

This window determines the range of potentials the working electrode can be used.

The window is limited on the positive side by the oxidation of water to $O_2(g)$ and on the negative side by the reduction of water to $H_2(g)$.

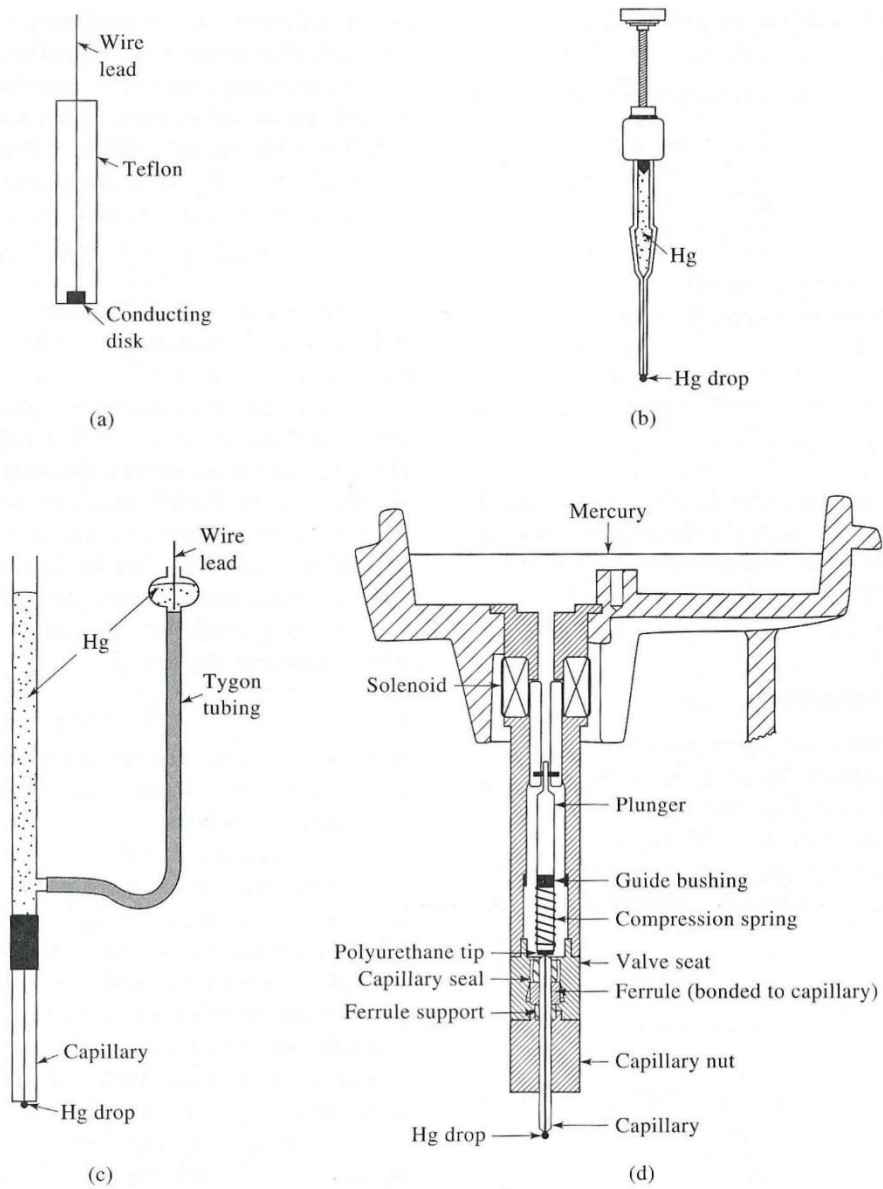
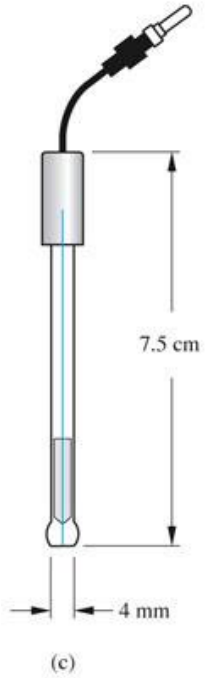
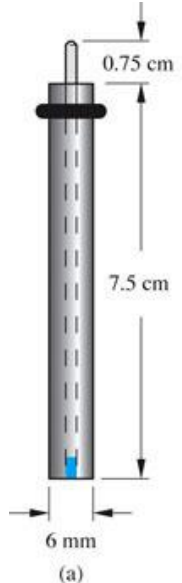


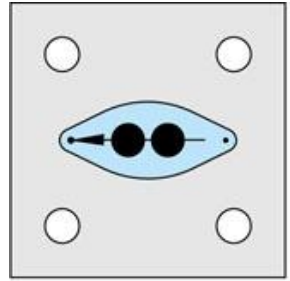
Figure 25-3 Some common types of microelectrodes: (a) a disk electrode, (b) a hanging mercury drop electrode, (c) a dropping mercury electrode, (d) a static mercury drop electrode.



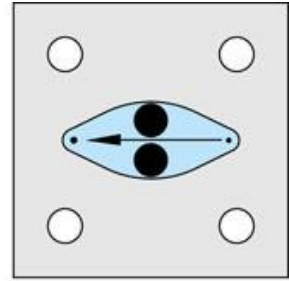
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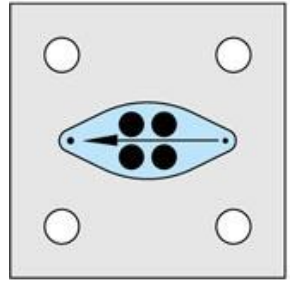
(d)



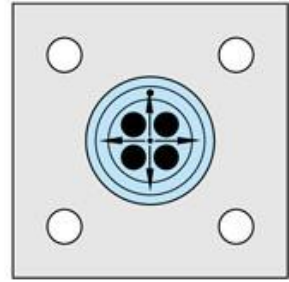
Dual, series crossflow



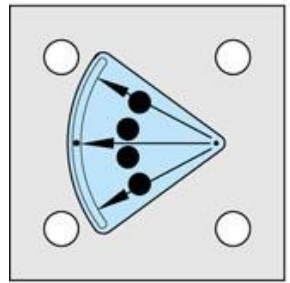
Dual, parallel crossflow



Quad square crossflow



Quad square radialflow



Quad arc crossflow

(c)

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Voltammetry

Working Electrodes

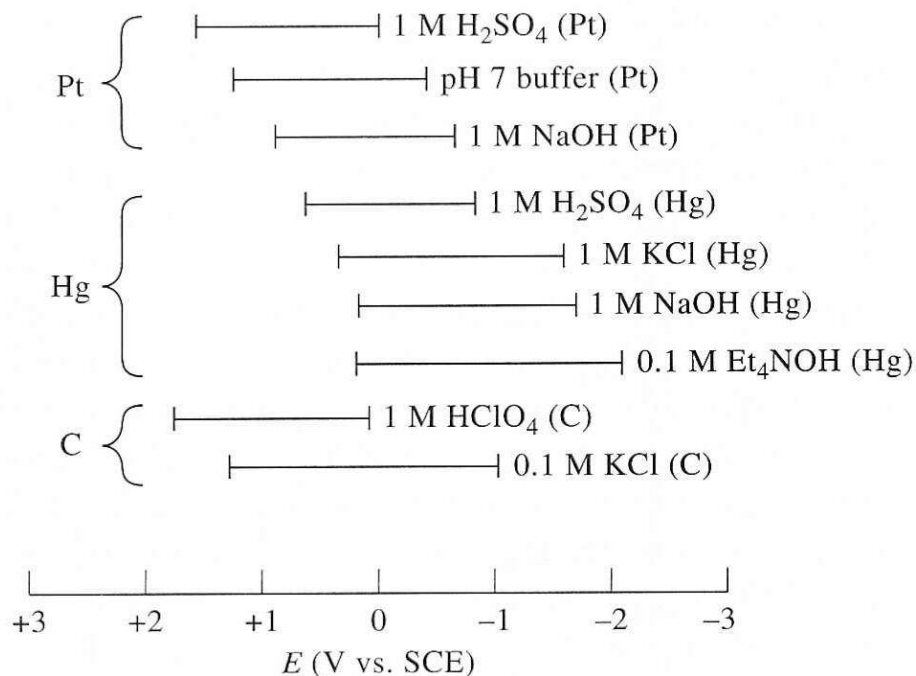


Figure 25-4 Potential ranges for three types of electrodes in various supporting electrolytes. (Adapted from A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, back cover. New York: Wiley, 1980. Reprinted by permission of John Wiley & Sons, Inc.)

Voltammetry

Working Electrodes

Working electrode material:

Metals: Ag, Au, Pt, Ni, SS, etc...

Carbon

Mercury

Voltammetry

Working Electrodes

Carbon

More complex than the metal electrodes.

The sp^2 carbon varies in conductivity, stability, hardness and porosity.

Voltammetry

Carbon

Common carbon electrodes:

Polycrystalline graphite electrodes

Carbon paste electrodes (CPE)

Control porosity of graphite material by filling pores with inert liquid carbon paste is graphite mixed with Nujol (heavy hydrocarbon) or hexadecane.

Paste is then packed into shallow well.

CPE's are easily modified (i.e., steric acids, zeolites, complexing agents).

Voltammetry

Carbon

Common carbon electrodes:

Polycrystalline graphite electrodes

Glassy Carbon

High MW carbanaceous polymer (polyacrylonitrile, phenol/formaldehyde resin). Polymer is heated to 400-800°C then heated under pressure at 1000-3000°C. Hard and highly disordered.

Voltammetry

Carbon

Common carbon electrodes:

Polycrystalline graphite electrodes

Carbon Fibers

Made from polyacrylonitrile (PAN)
drawn into filaments during curing.

Voltammetry

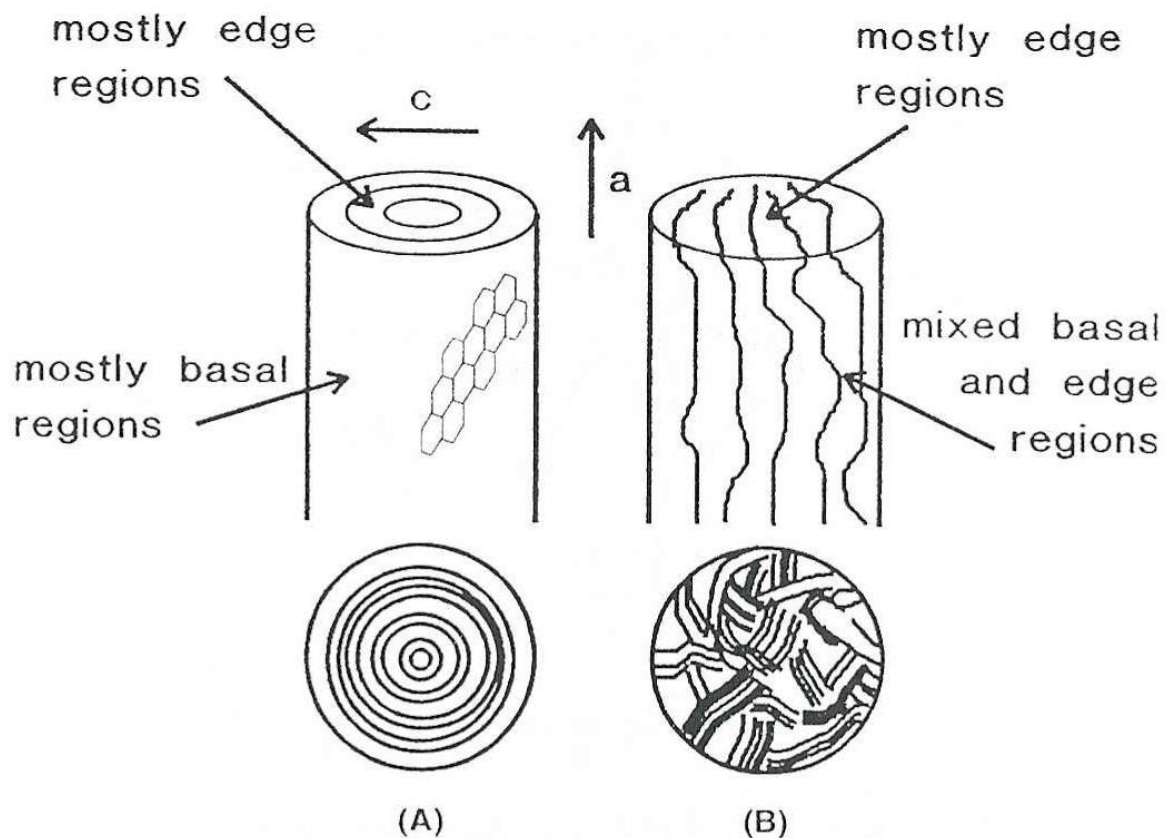


Figure 10.14 Illustration of carbon fibers, side and end views: (A) ordered "onion" fiber; (B) disordered "random" fiber.

Voltammetry

Working Electrodes

Modified Electrodes

- Irreversible adsorption
- Covalent bonding
- Coatings (i.e. polymers)
- Enzymes
- Self-assembled monolayers

Voltammetry

Voltammograms

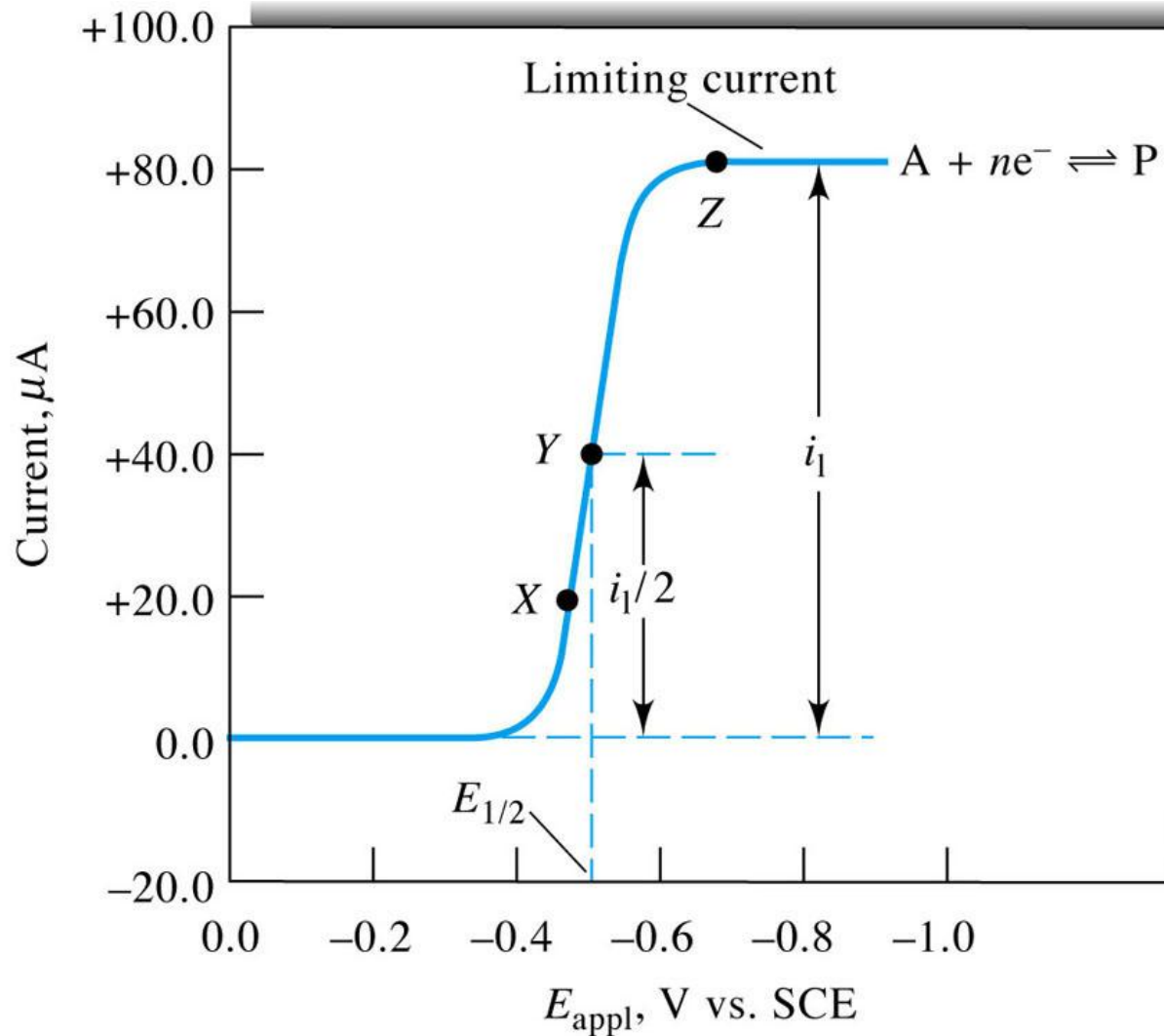
When a linear-scan voltammogram is taken in a moving solution, the experiment is called hydrodynamic voltammetry. The resulting curve is a voltammetric wave with a sigmoidal shape. Working electrode can also be rotated.

Polarography

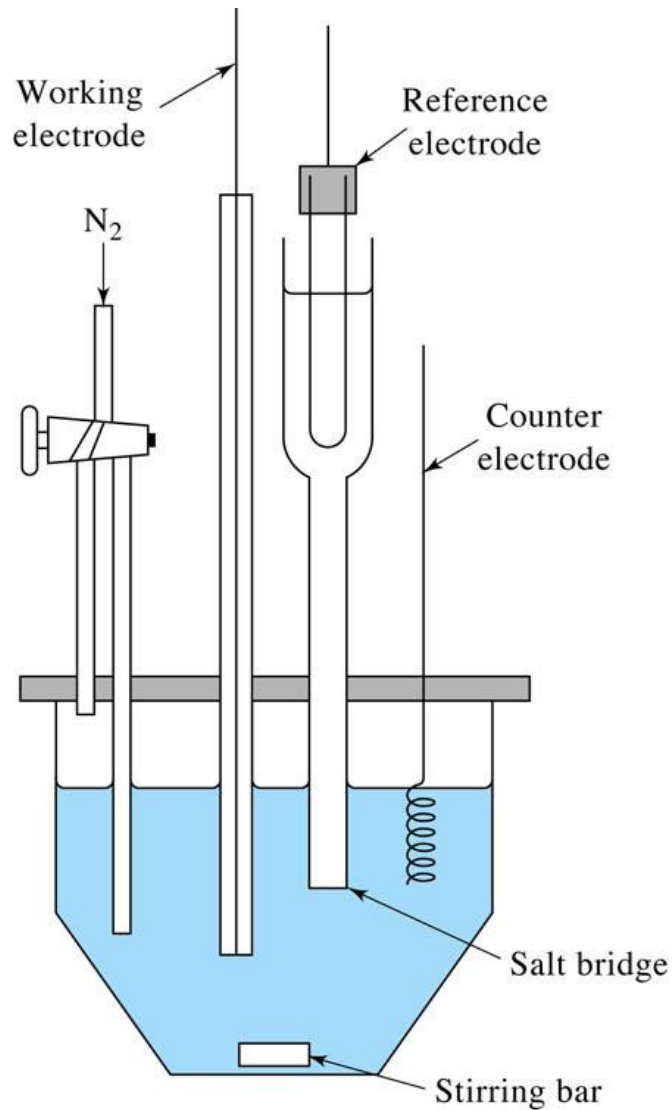
Voltammetry using a dropping Hg electrode.

Voltammetry

Voltammograms



Voltammetry



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Voltammetry

Concentration Profiles

For the following equation



$$E_{\text{appl}} = E^\circ_A - 0.0592/n \log c_p^0/c_A^0 - E_{\text{ref}}$$

E_{appl} – potential between WE and Ref

c_p^0 and c_A^0 – molar concentration of P and A
at the electrode surface.

Voltammetry

Profiles in Unstirred Solution

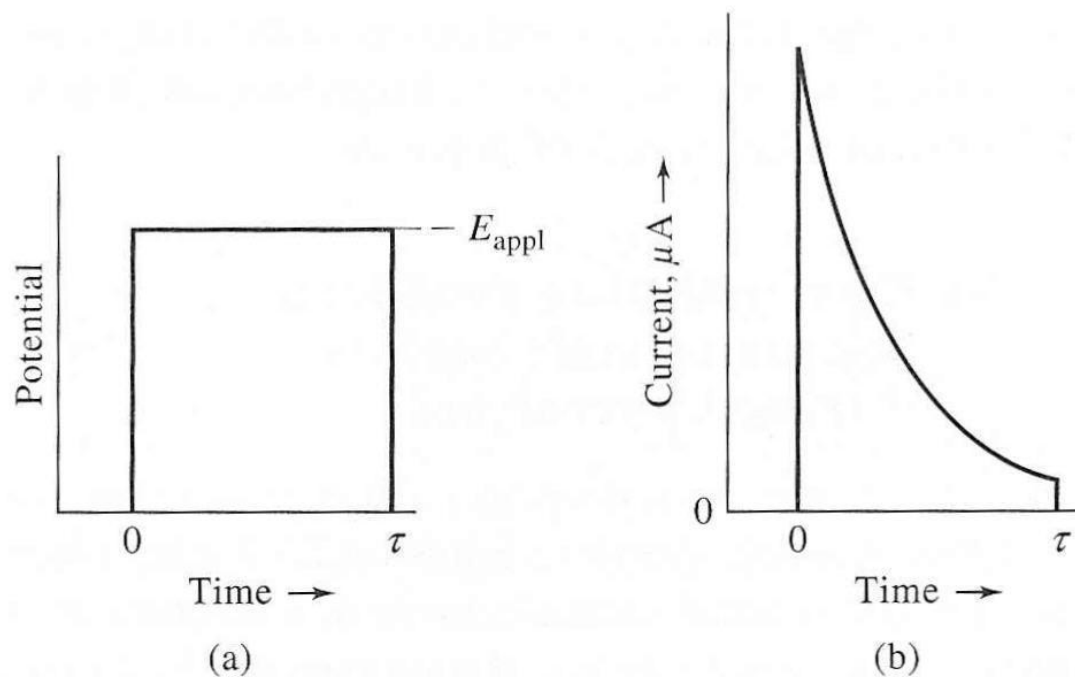
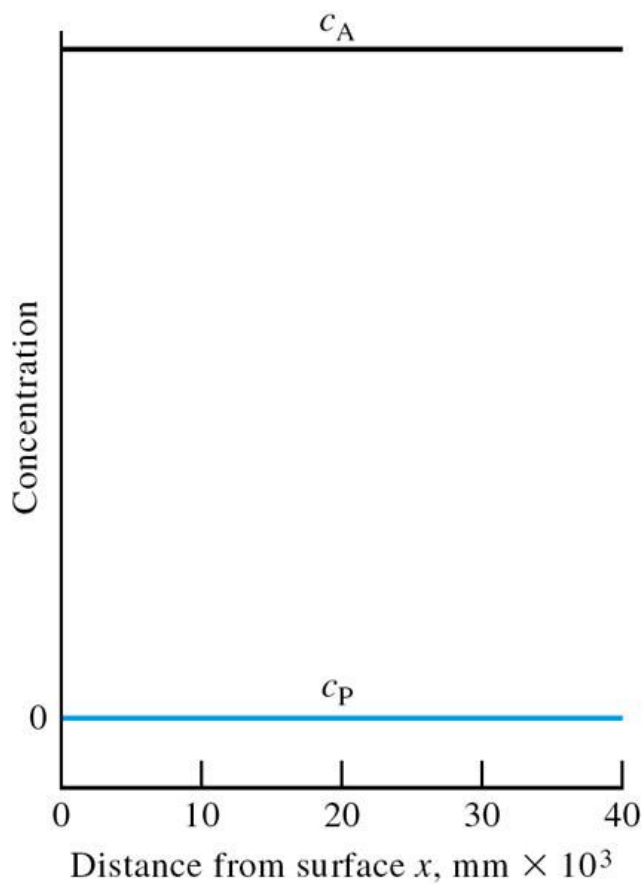


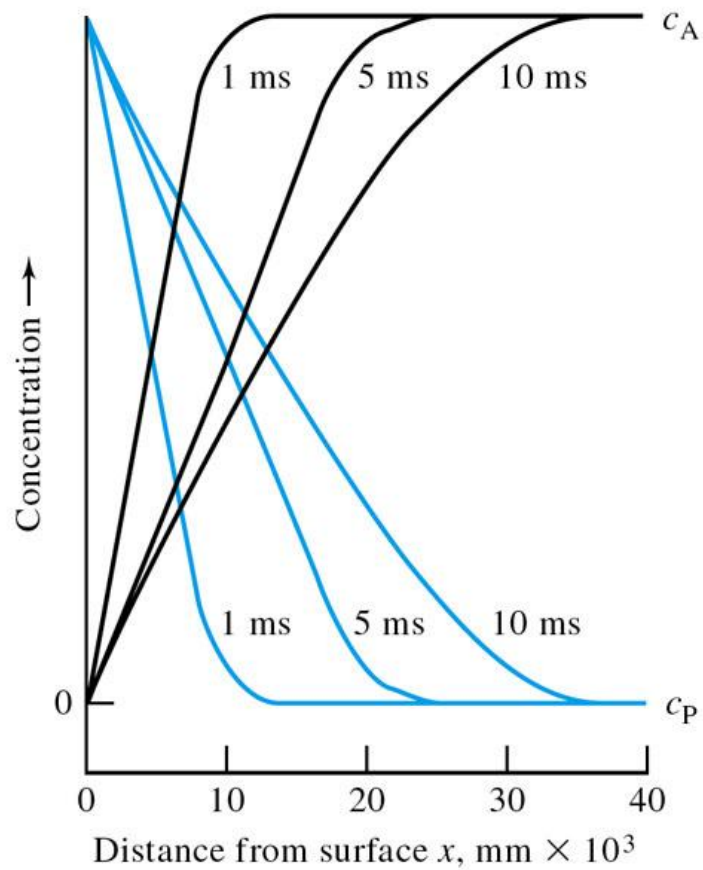
Figure 25-7 Current response to a stepped potential for a planar microelectrode in an unstirred solution. (a) Excitation potential. (b) Current response.

Voltammetry

Profiles in Unstirred Solution



(a)



(b)

Voltammetry

Cyclic Voltammetry

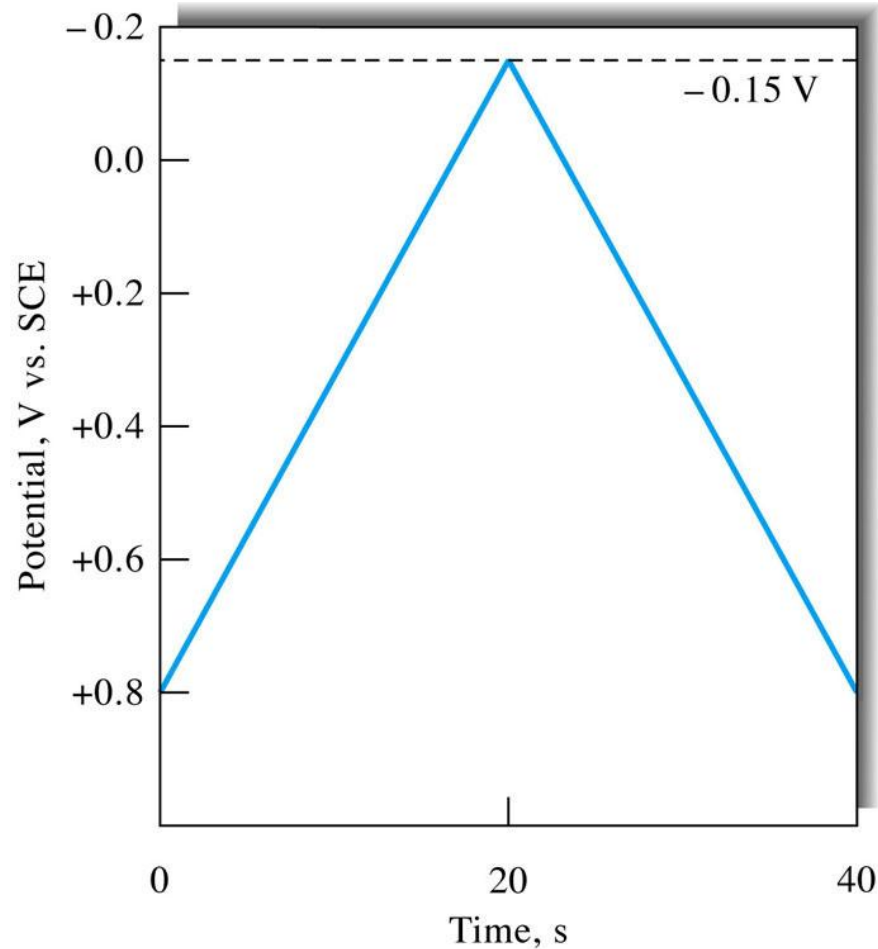
In CV, current response in unstirred solution is excited by triangular waveform.

Potential varies linearly, scan direction is reversed.

CV important for studying mechanism and kinetics (rates).

Voltammetry

Cyclic Voltammetry



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Cyclic Voltammetry

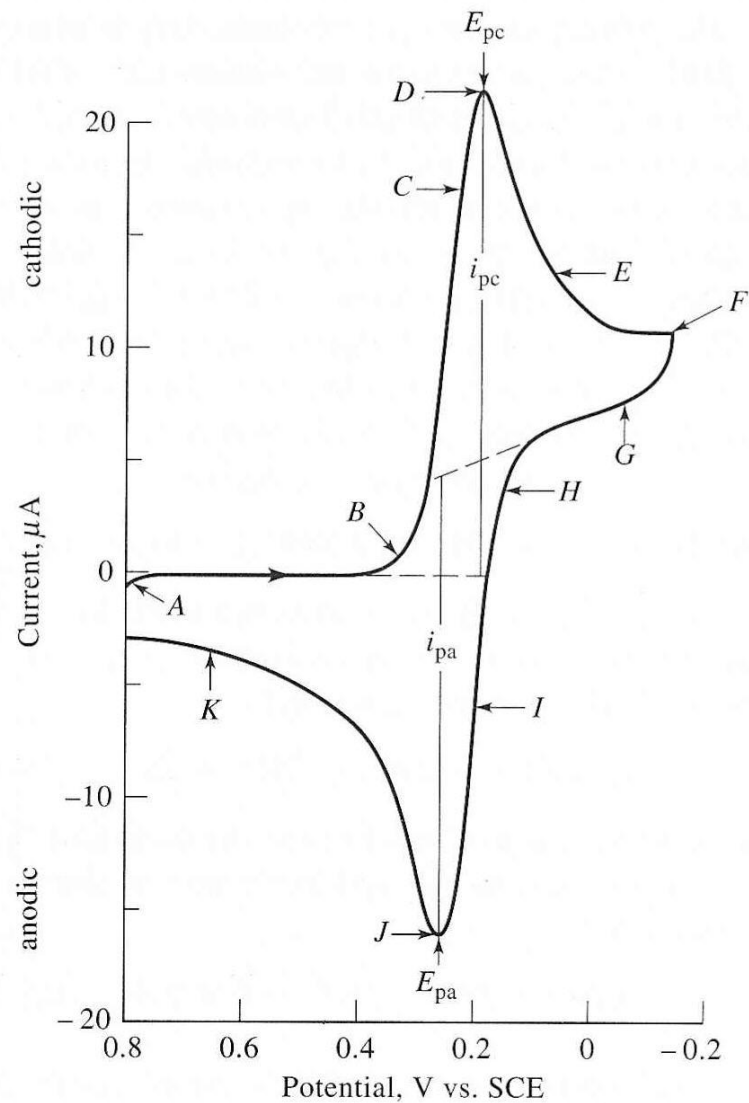


Figure 25-20 Cyclic voltammogram for a solution that is 6.0 mM in $\text{K}_3\text{Fe}(\text{CN})_6$ and 1.0 M in KNO_3 . (From P. T. Kissinger and W. H. Heineman, *J. Chem. Educ.*, **1983**, 60, 702. With permission.)

Voltammetry

Cyclic Voltammetry

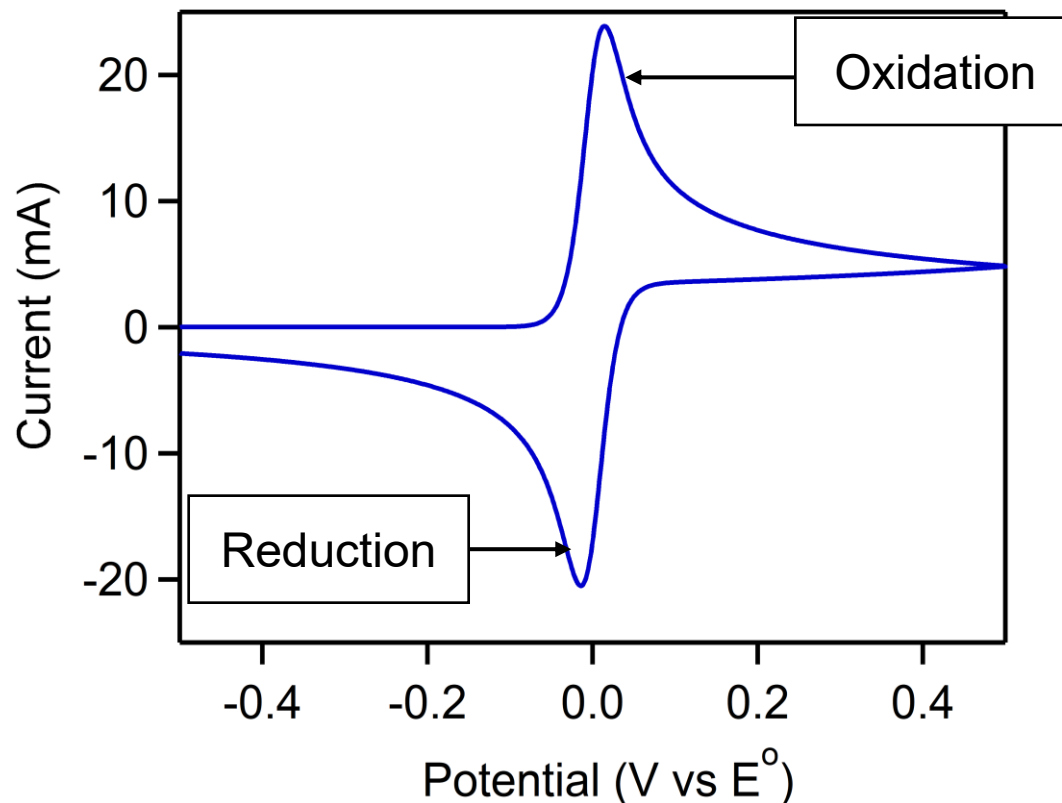
You control the potential (energy of electrons at the working electrode surface), and measure the current.

- A current peak in a CV indicates electron transfer is happening**
- Oxidation happens at more positive potentials, reduction happens at more negative potentials**

Voltammetry

Cyclic Voltammetry

- Oxidation happens at more positive potentials, reduction happens at more negative potentials



Voltammetry

Cyclic Voltammetry

Applied potential vs the reference electrode.

Note that there is nothing special about 0.0 V, because it's all relative to the reference.

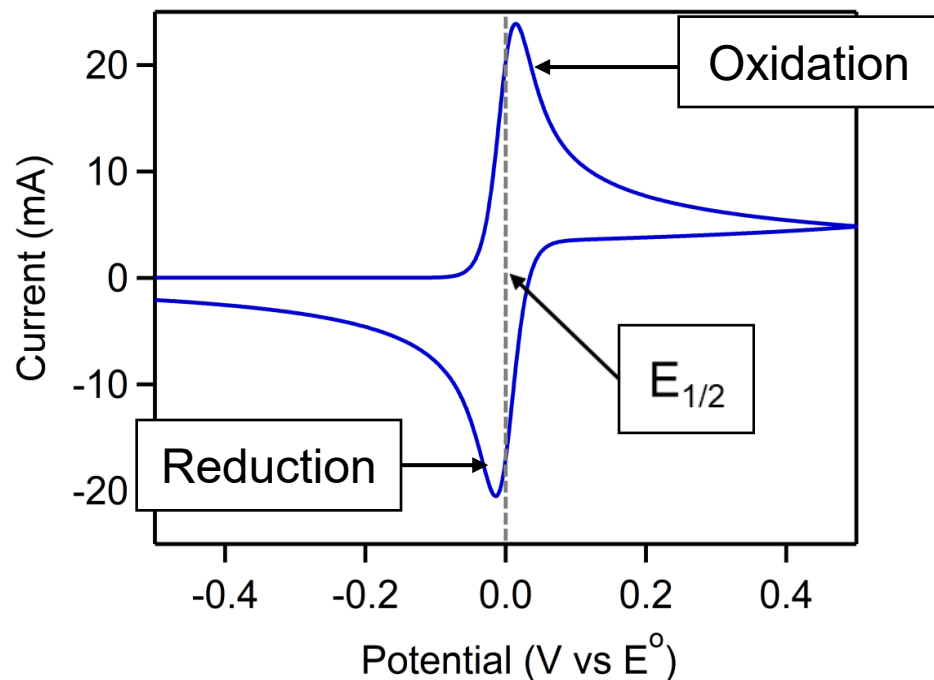
More positive potentials are more oxidizing, but that does not necessarily mean they are greater than 0 V.

Voltammetry

Cyclic Voltammetry

The shape of the CV is determined only by thermodynamics (E^0 and the Nernst equation).

Nernst equation: $E = E^0 - (0.059/n)\ln([\text{reduced species}]/[\text{oxidized species}])$



$E_{1/2}$ = potential that is halfway in between oxidation and reduction peaks

Voltammetry

Cyclic Voltammetry

Nernstian Systems

For a planar electrode at 25°C,

$$i_p = (2.69 \times 10^5) n^{3/2} A D_O^{1/2} C^* \nu^{1/2} \text{ (Randles-Sevcik equation)}$$

$$A - \text{cm}^2$$

$$D_O - \text{cm}^2/\text{s}$$

$$C_O^* - \text{mol}/\text{cm}^3$$

$$\nu - \text{V}/\text{s}$$

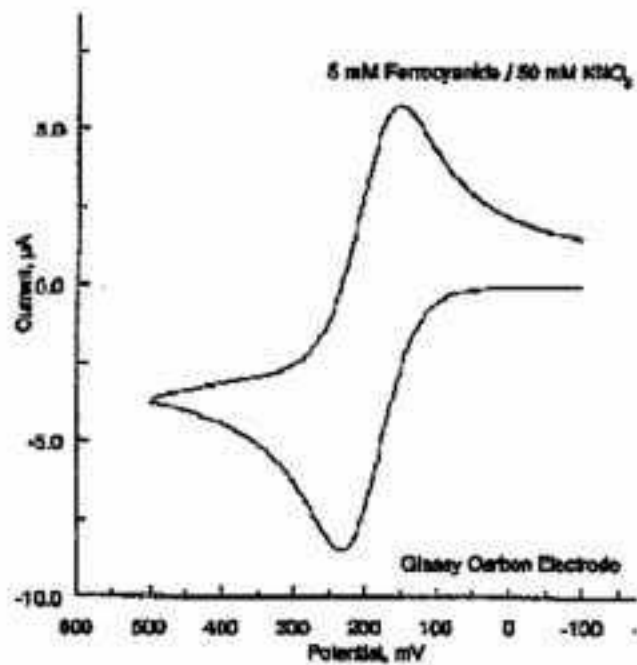
$$i_p - \text{Amps}$$

$$i_p \propto \nu^{1/2}$$

Plot of i_p versus $\nu^{1/2}$ gives a straight line for reversible systems

Voltammetry

Cyclic voltammetry



Reversible reaction

Glassy carbon electrode

5mM Ferrocyanide
in 50mM KNO₃

Scan rate 100mV/sec

Voltammetry

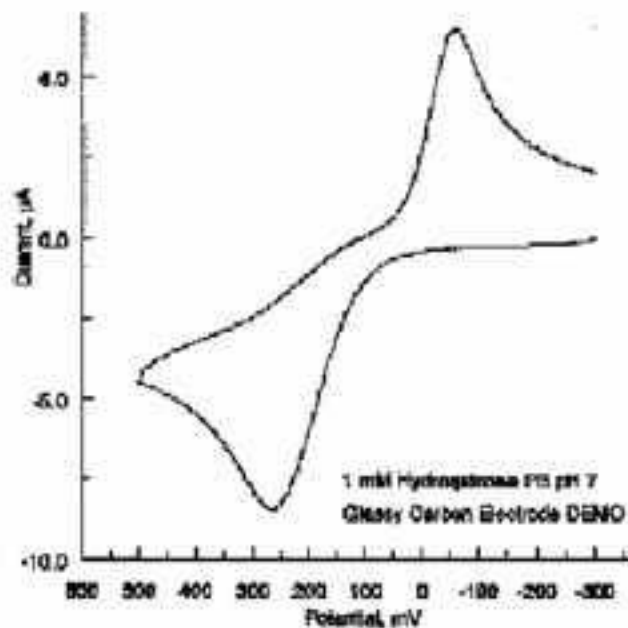
Cyclic voltammetry

Quasi-reversible reaction.

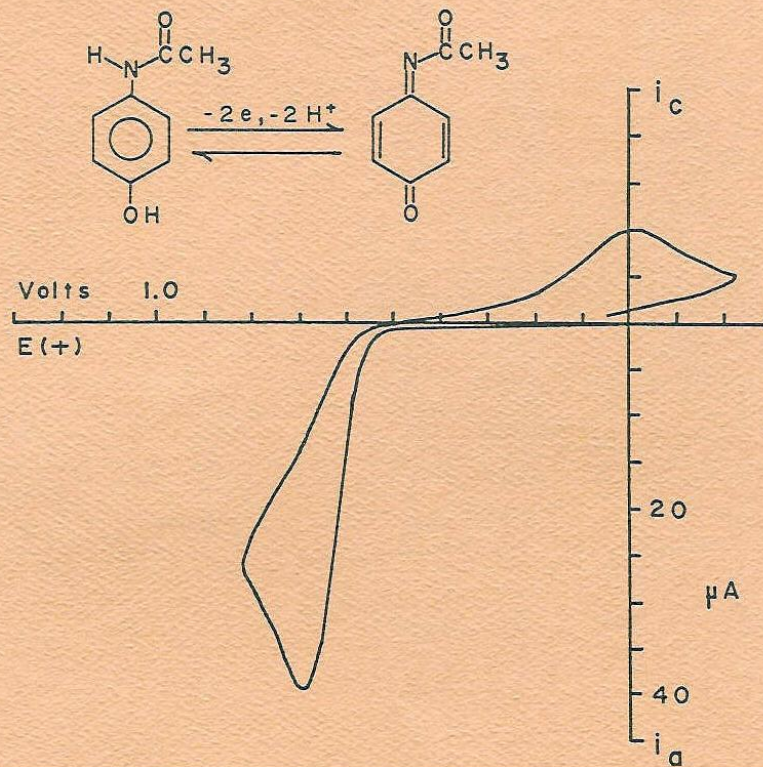
As the reaction approaches irreversibility the peak separation becomes greater.

1 mM hydroquinone
in pH 7 phosphate buffer

Scan rate of 500mV/sec



Voltammetry



SAMPLE: Acetaminophen

MEDIUM: 25% methanol in pH 4.0 citrate (0.1 M)

CONC: 1 mM

RATE: 150 mV/s

ETRODE: GC

REF: RE-1, Ag/AgCl

MODEL: CV-1A

Acetaminophen (Tylenol) is a widely consumed aspirin substitute. As a monosubstituted

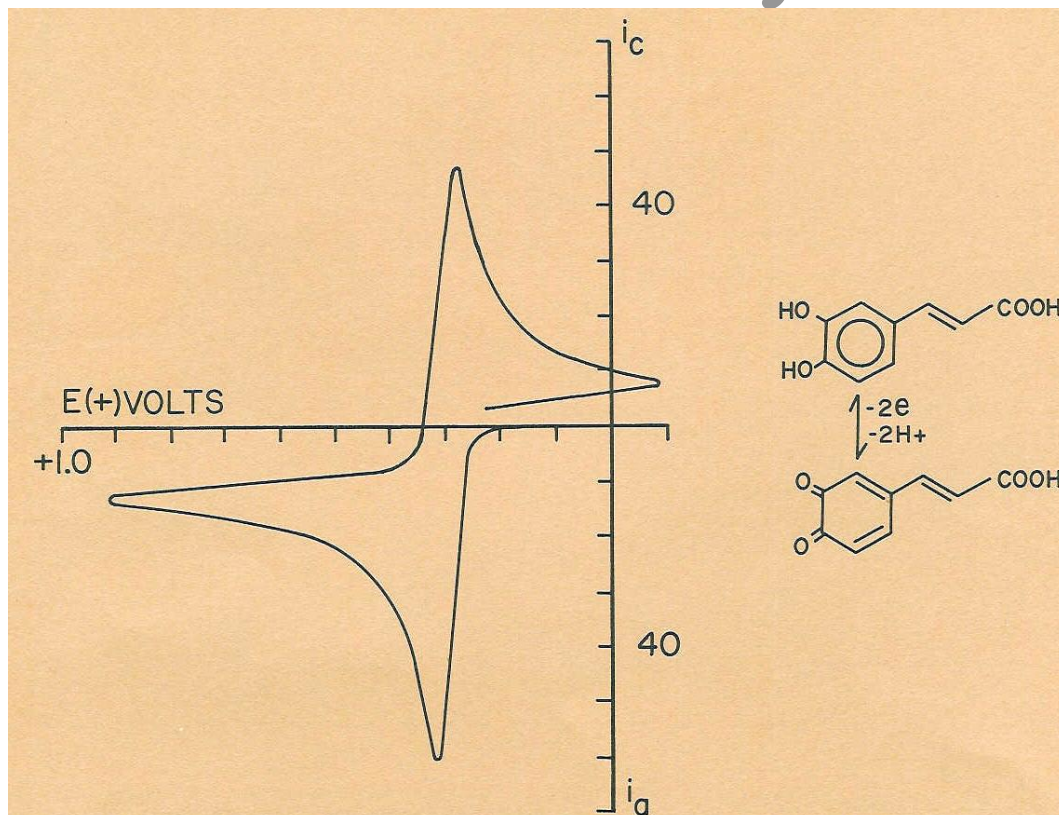
aminophenol it is electrochemically active.

The voltammetric behavior indicates a

2-electron oxidation at moderate potential

with significant but not ideal reversibility.

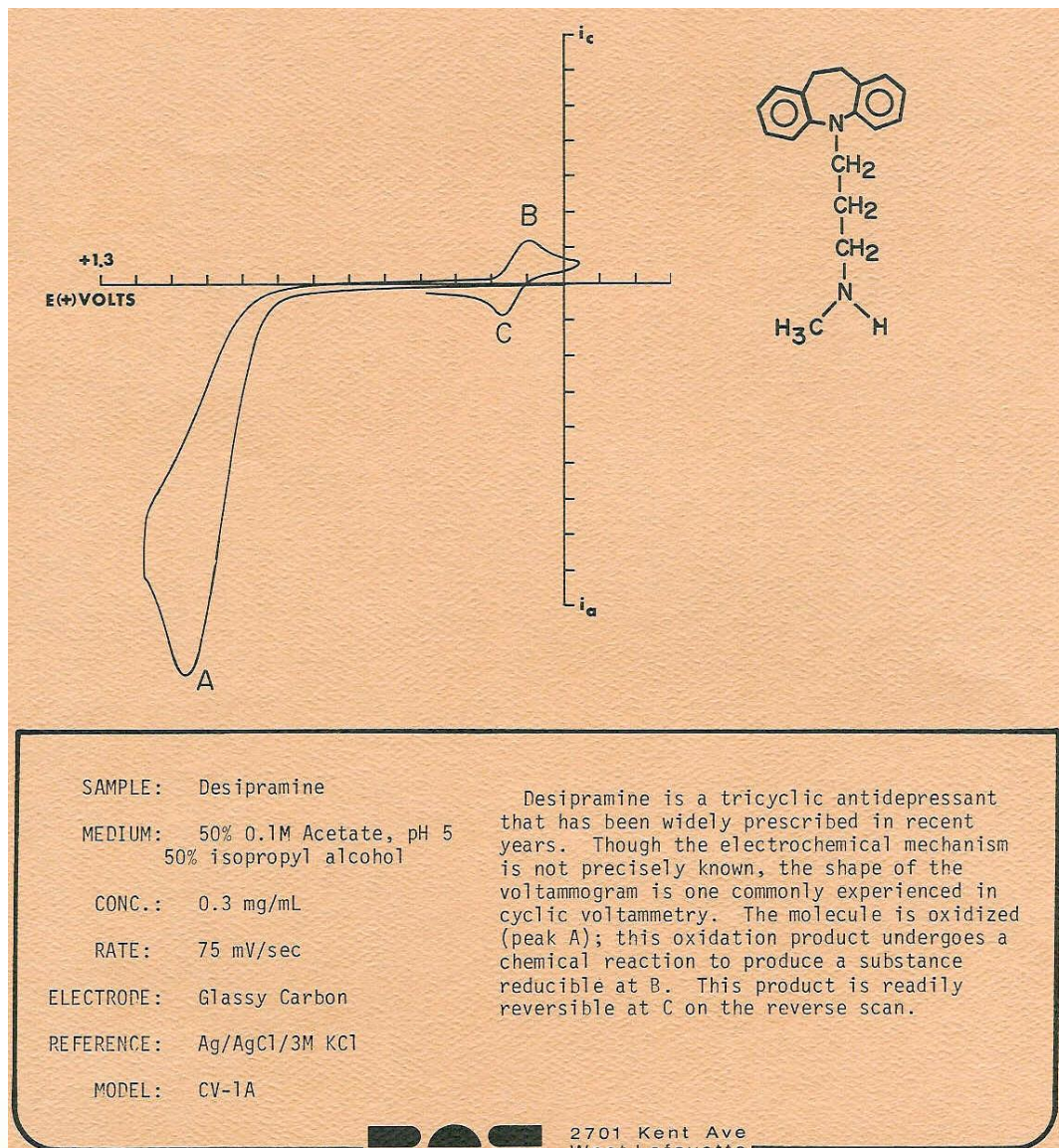
Voltammetry



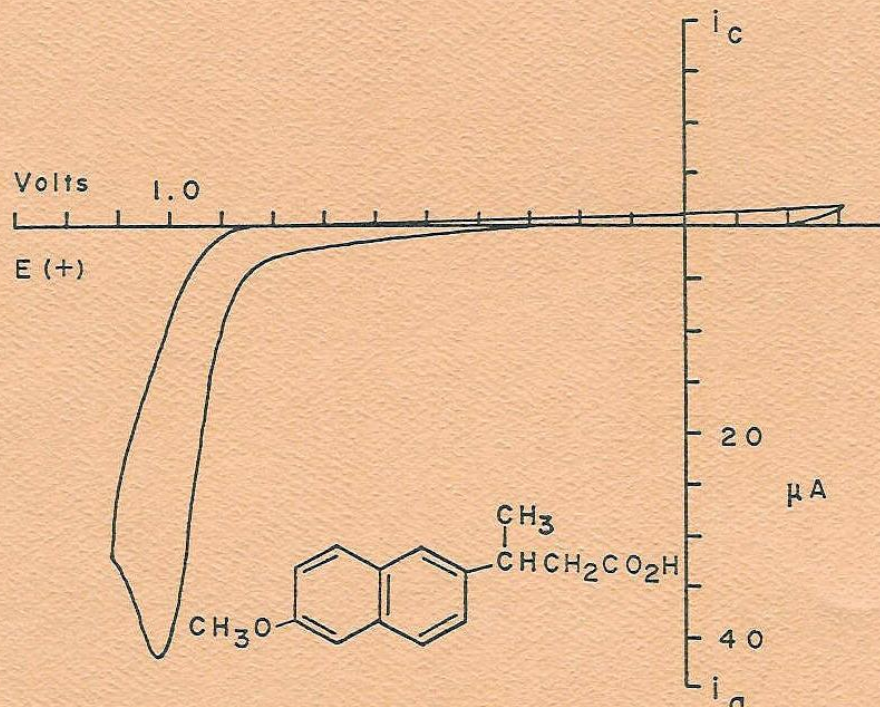
SAMPLE: caffeic acid
MEDIUM: 1 M acetate buffer, pH 4.6
CONC: 1 mM
RATE: 300 mV/s
ETRODE: CPE
REF: RE-1, Ag/AgCl
MODEL: CV-1A

Caffeic acid is unique among catechol natural products. The double bond conjugated with the ring lowers the oxidation potential and enhances the heterogeneous electron transfer rate. Contrast this beautiful voltammogram with the less ideal behavior of catechin or epinephrine. Chlorogenic acid (the quinic acid ester of caffeic acid) also exhibits a nearly ideal voltammogram. Both molecules are candidates for very selective LCEC due to their ease of oxidation.

Voltammetry



Voltammetry



SAMPLE: Naproxen

MEDIUM: 40% methanol in pH 5.0
acetate (0.1 M)

CONC: 2 mM

RATE: 150 mV/s

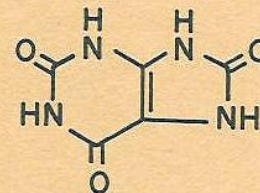
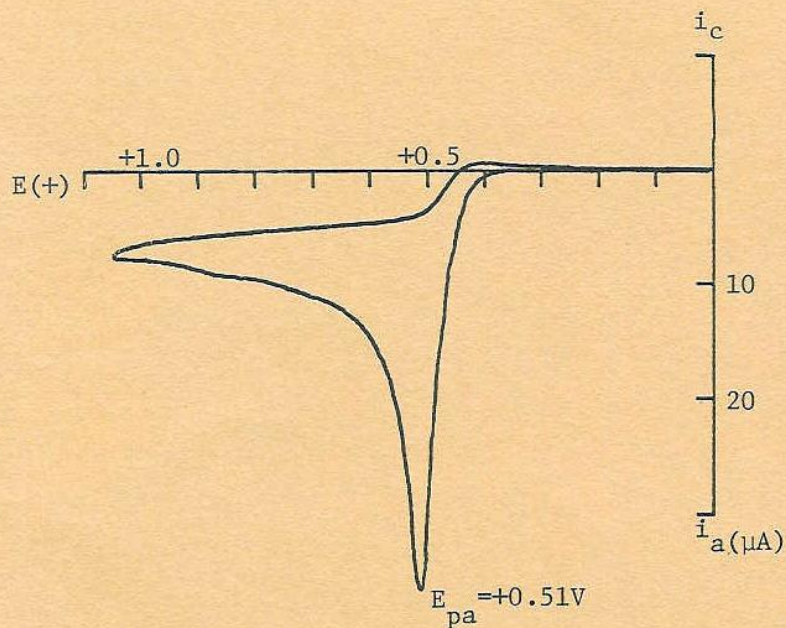
ETRODE: GC

REF: RE-1, Ag/AgCl

MODEL: CV-1A

Naproxen is a potent non-steroidal anti-inflammatory, analgesic, and antipyretic drug in widespread clinical use for rheumatism and osteoarthritis. Although it is a hydroxy-substituted naphthol rather than a simple phenol it has similar CV properties. The readily attainable oxidation potential is probably due to the extended conjugation and may be enhanced by the ring alkyl substitution as well.

Voltammetry



SAMPLE: uric acid

MEDIUM: 0.1 M acetate buffer (pH 5.25)

CONC: 43.7 mg/50 ml

RATE: 250 mV/s

ETRODE: CPE

REF: RE-1, Ag/AgCl

MODEL: CV-1A

The oxidation of uric acid at a carbon electrode is the basis for one of the most successful LCEC methods. Trace uric acid can be conveniently detected with great specificity in microliter clinical samples of urine and blood and in food products. Uric acid contamination in foods is an excellent indicator of insect infestation. This is a classic example of a chemically irreversible process.

Voltammetry

UMEs

Application

Carbon-fiber electrodes for detection of catecholamine and indoleamine neurotransmitters and metabolites.

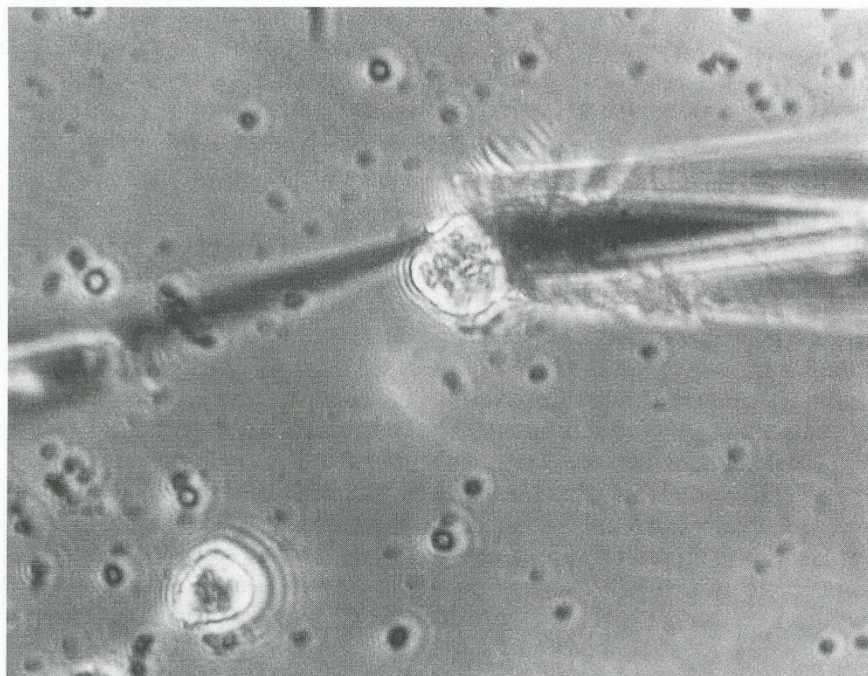


Figure 12.8 Light micrograph of a bovine adrenal medullary cell in culture with etched and glass-encased carbon-fiber electrodes ($r = 5 \mu\text{m}$) placed adjacent to it. Magnification is 450 \times . [From Ref. 88, reproduced with permission of the copyright holder.]

Voltammetry

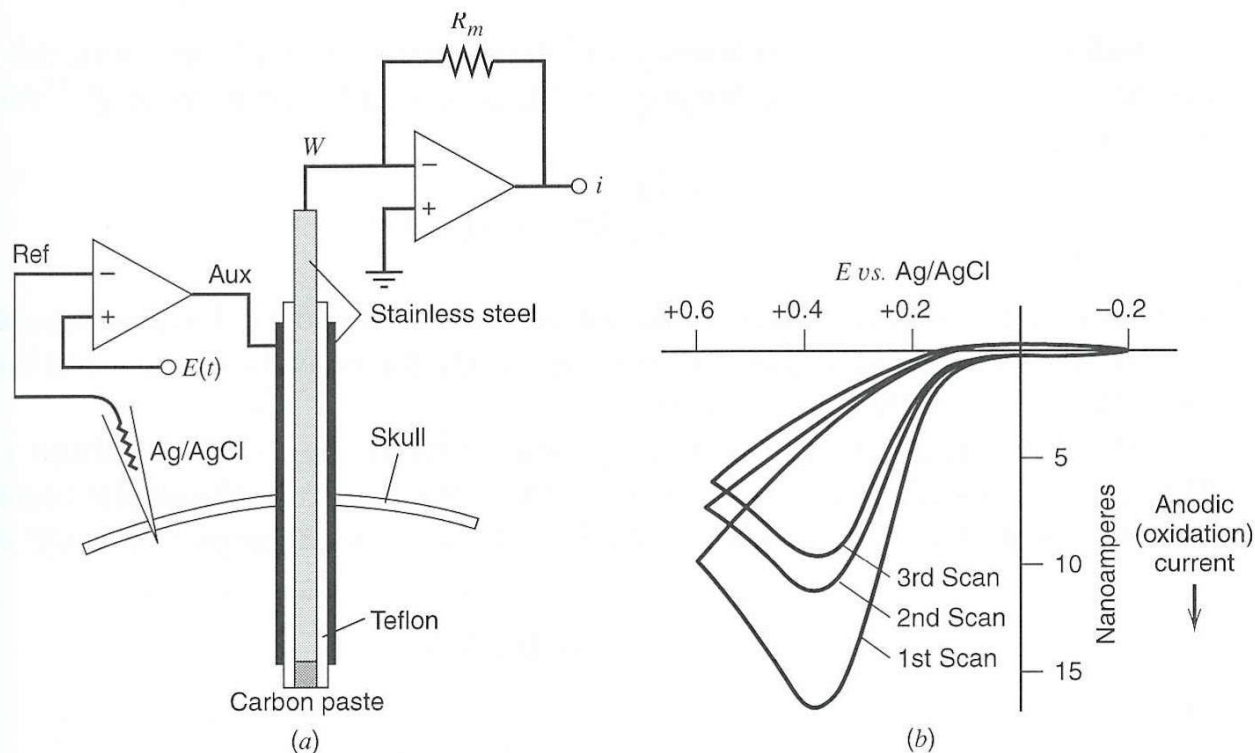


Figure 6.6.5 Application of cyclic voltammetry to *in vivo* analysis in brain tissue. (a) Carbon paste working electrode, stainless steel auxiliary electrode (18-gauge cannula), Ag/AgCl reference electrode, and other apparatus for voltammetric measurements. (b) Cyclic voltammogram for ascorbic acid oxidation at C-paste electrode positioned in the caudate nucleus of an anesthetized rat. [From P. T. Kissinger, J. B. Hart, and R. N. Adams, *Brain Res.*, **55**, 20 (1973), with permission.]

Assignment

- Read Chapter 22
- HW12 Chapter 22: 1, 5, 7, 9, and 11
- HW12 Due Today

- Read Chapter 23
- HW13 Chapter 23: 2, 4, 7, 8, and 11
- HW13 Chapter 23 Due 3-27

- Read Chapter 25
- HW14 Chapter 25: 1-8 and 10
- HW14 Chapter 25 Due 3-27

Electroanalytical Chemistry

Electrochemical Example

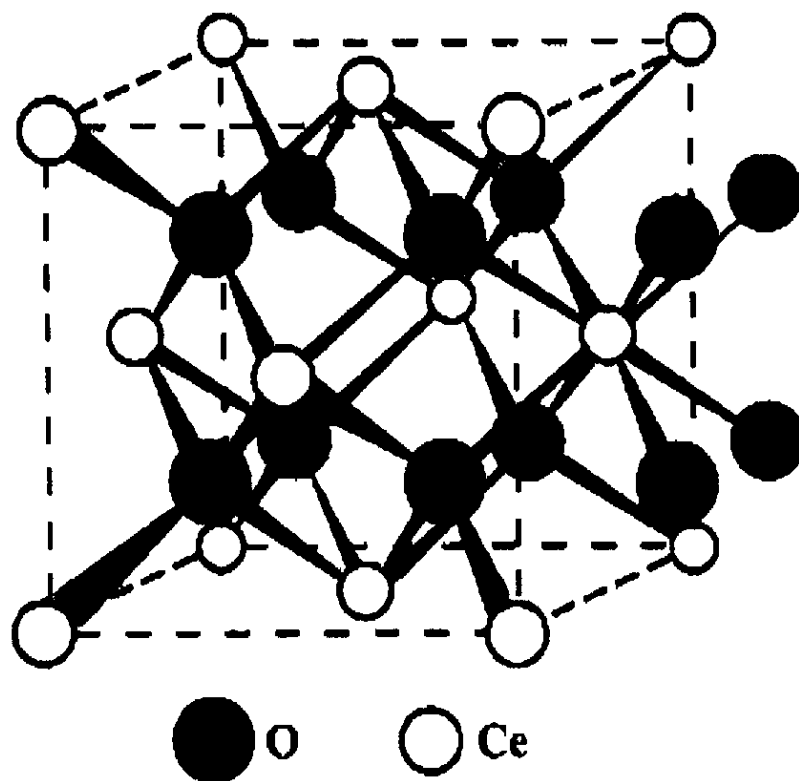


FIG. 1. The fcc cell of CeO_2 with the fluorite structure.

Electroanalytical Chemistry

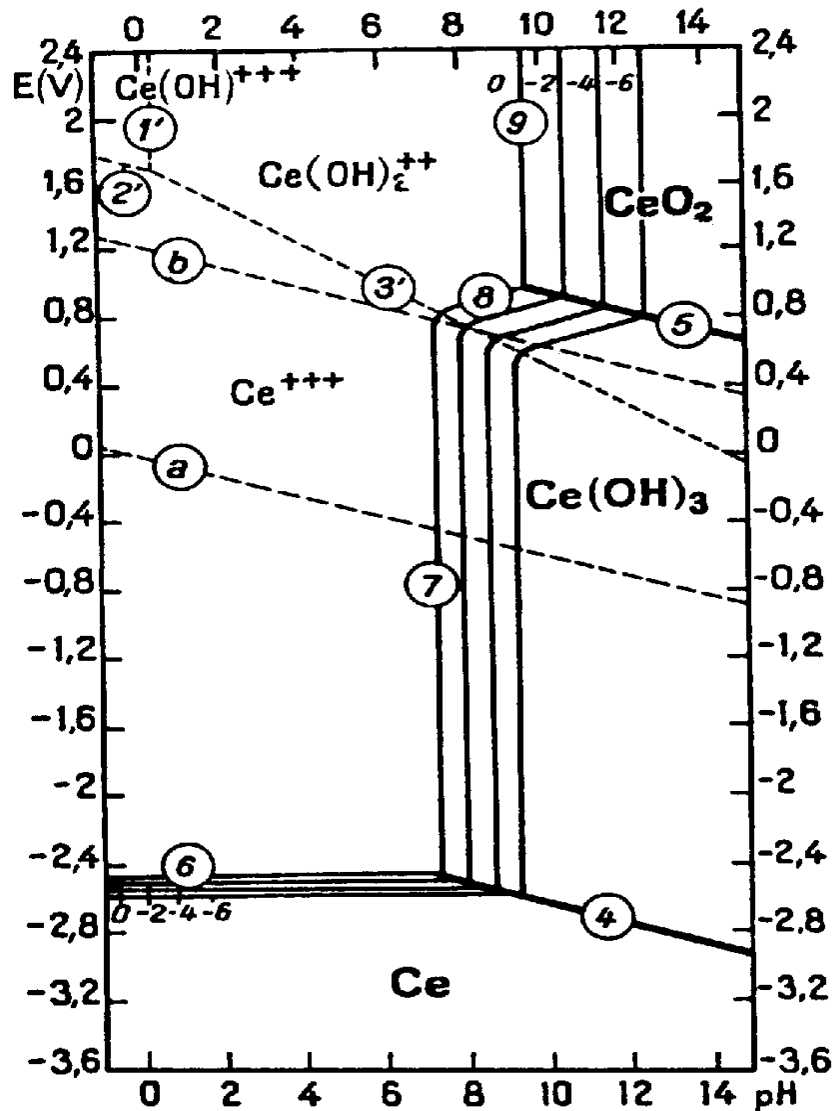
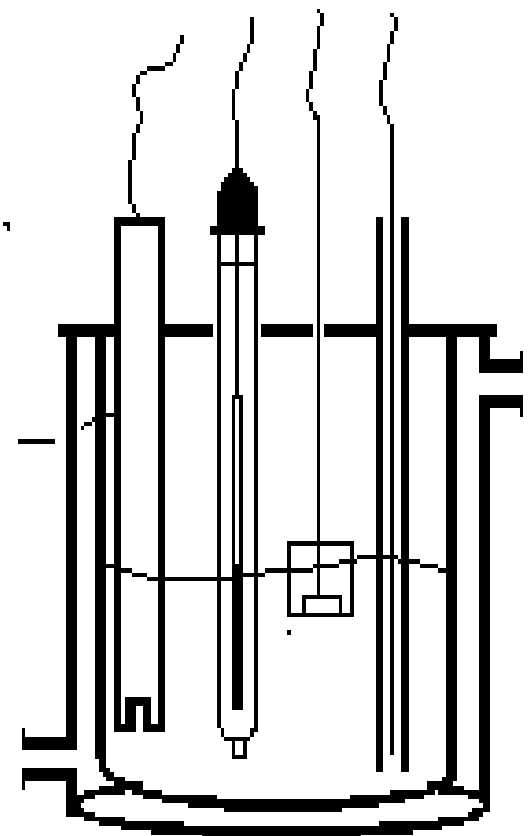


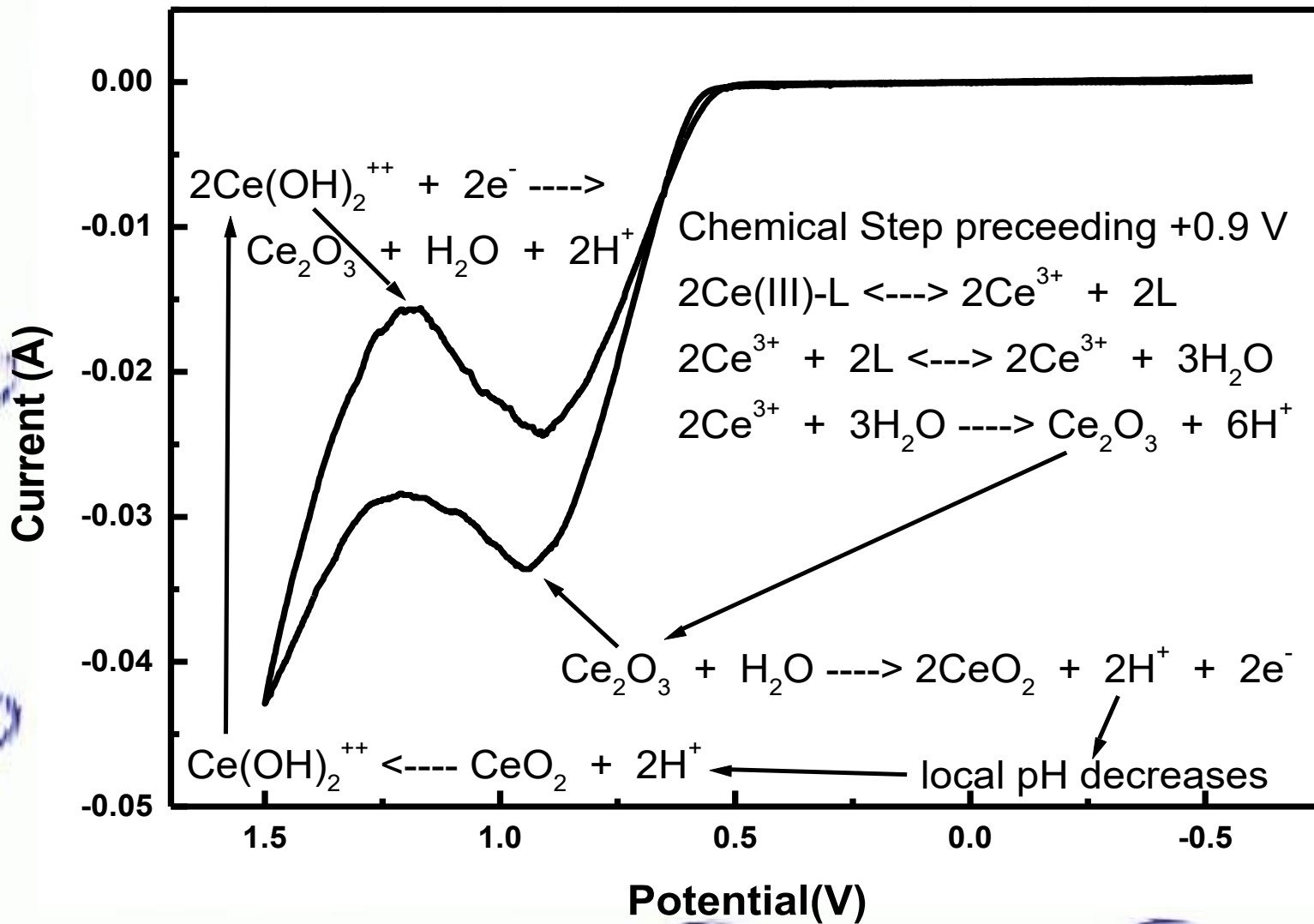
FIG. 5. Cerium-water.

Electroanalytical Chemistry

Electrochemical Cell



Electroanalytical Chemistry



Electroanalytical Chemistry

The oxidation peak, at ~ 0.9 V is preceded by a chemical reaction as follows:



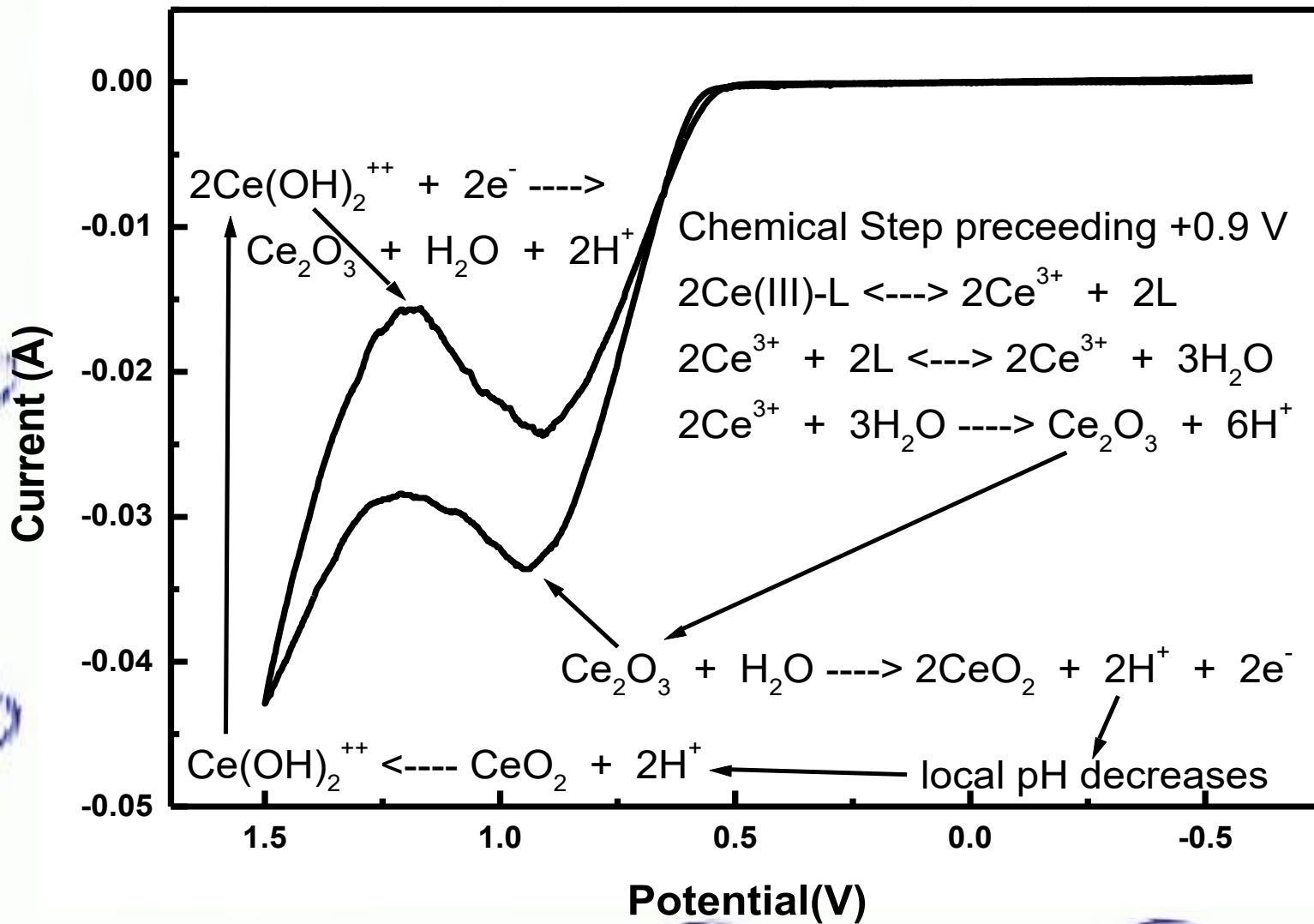
Since the formation constant for the cerium-ligand complex in eq 1 is relatively small, then free metal ions in solution are available at the higher pH to form Ce_2O_3 , this species can oxidize to CeO_2 at voltages above ~ 0.8 V vs. SHE.



The thermodynamic voltage calculated for the reaction in eq. 2 is:

$$E = 1.559 - 0.0591\text{pH} = 0.85 \text{ V vs. SHE or } 0.61 \text{ V vs. SCE.}$$

Electroanalytical Chemistry



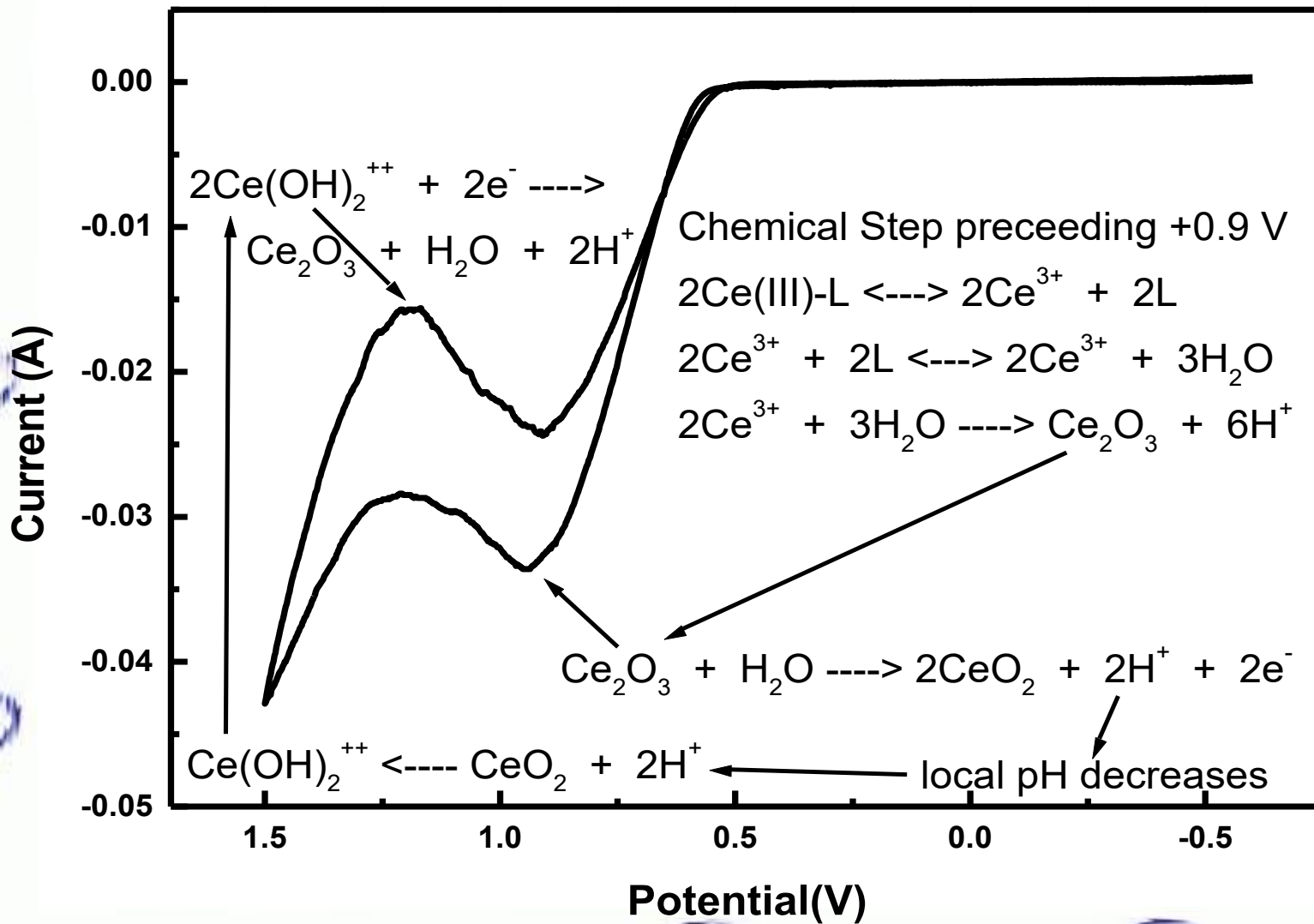
Electroanalytical Chemistry

On the reverse scan of the CV, a reduction peak positive of the anodic peak is seen in the CV. The CeO_2 produced at the electrode during the anodic scan (eq. 2) also produces hydrogen ions, which lowers the local pH at the electrode surface. A chemical reaction can then form Ce(OH)_2^{++} ions at the immediate vicinity of the electrode, which can then be reduced to Ce_2O_3 .



The thermodynamic potential for eq. 4 can be calculated as 1.13 V vs. SHE or 0.89 V SCE.

Electroanalytical Chemistry



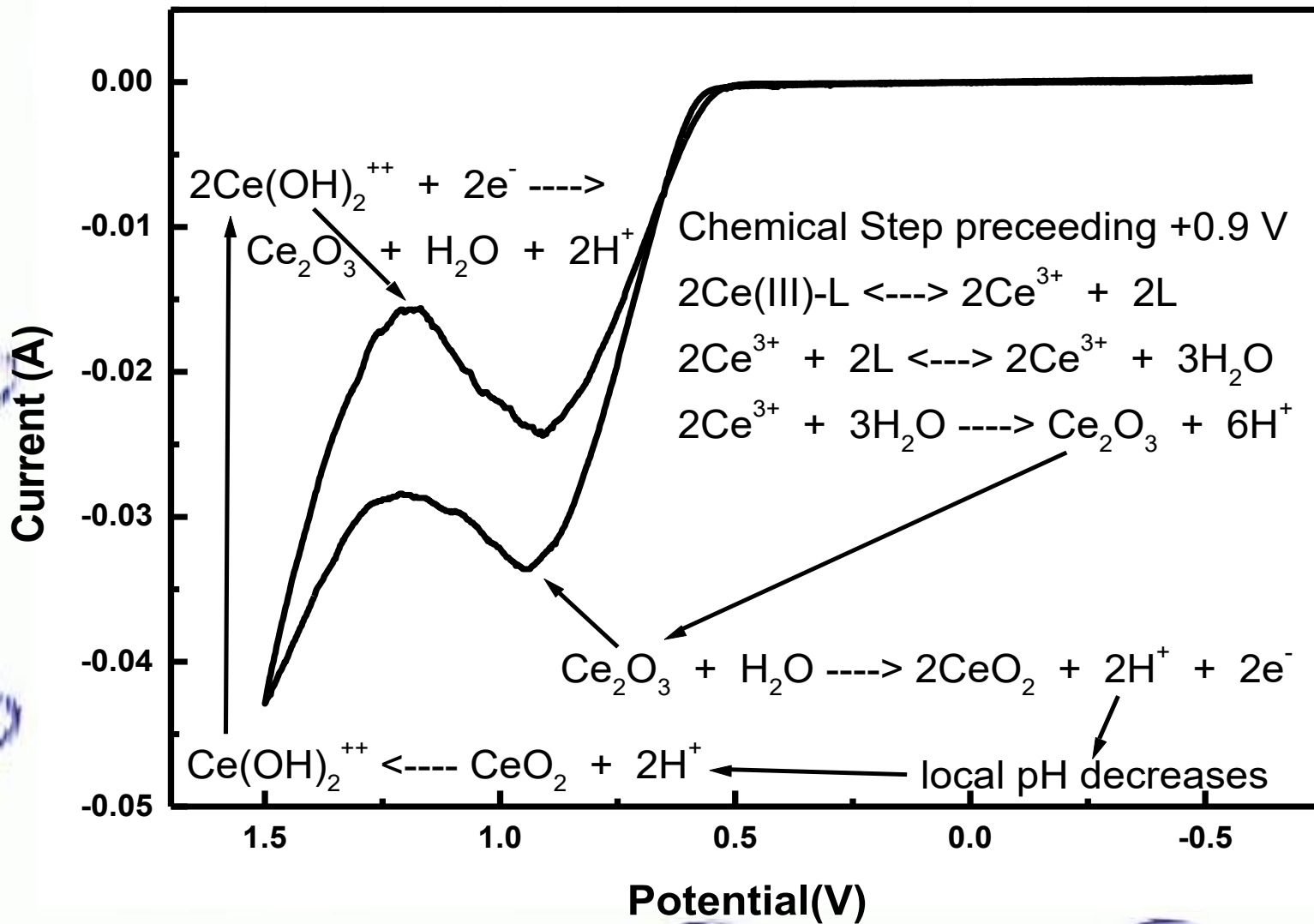
Electroanalytical Chemistry

The calculated thermodynamic potentials are 0.28 V apart.

The ΔV between the two peaks in the CV is ~ 0.25 V, which corresponds to the calculated thermodynamic potential difference for the equations above.

Experimentally, two powder products, Ce_2O_3 and CeO_2 , form in this solution. (X-ray Diffraction).

Electroanalytical Chemistry



Voltammetry

Profiles in Stirred Solution

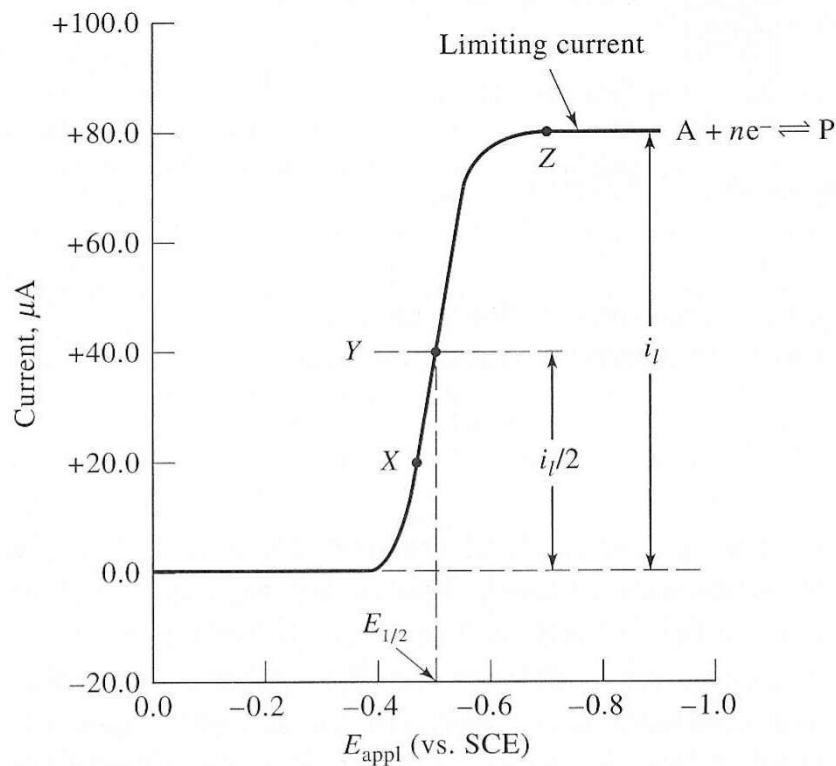


Figure 25-5 Linear-scan voltammogram for the reduction of a hypothetical species A to give a product P.

Voltammetry

Profiles in Stirred Solution

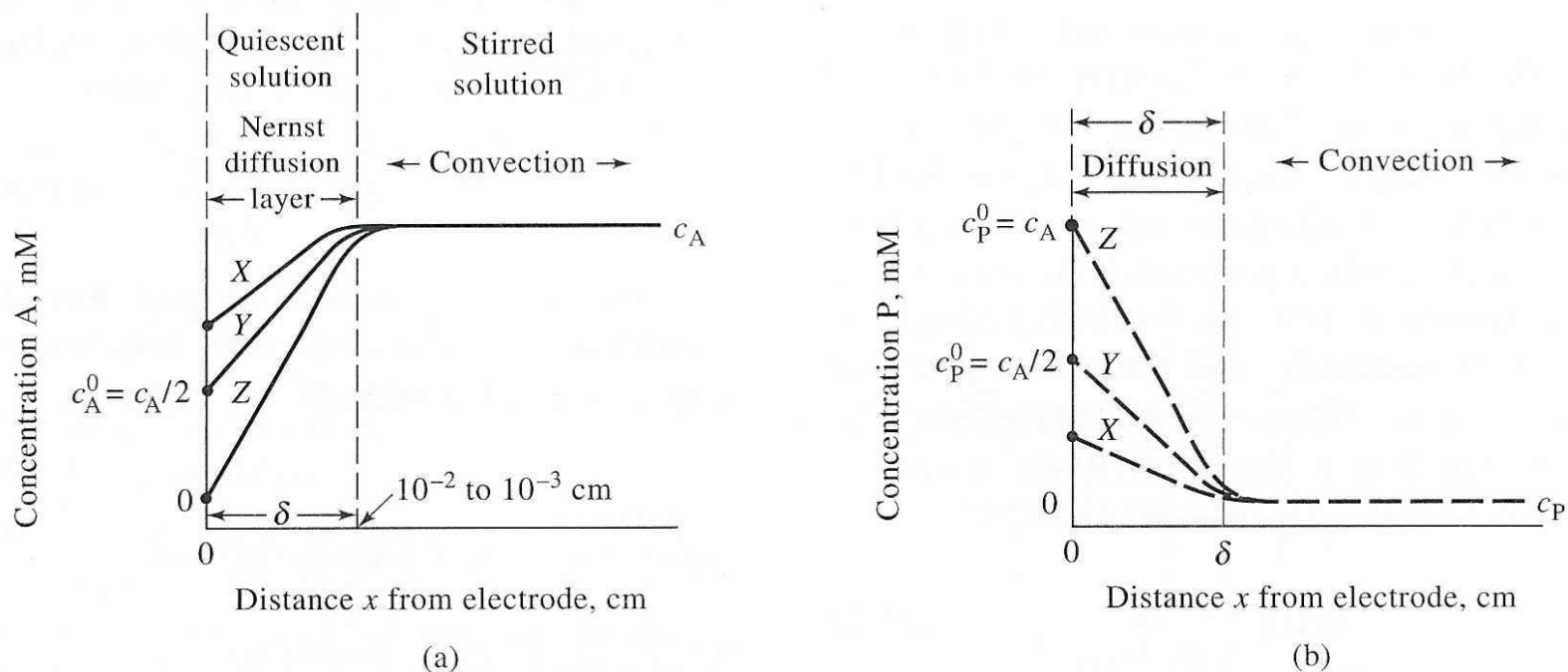


Figure 25-10 Concentration profiles at an electrode/solution interface during the electrolysis $A + ne^- \rightarrow P$ from a stirred solution of A. See Figure 25-5 for potentials corresponding to curves X, Y, and Z.

Voltammetry

Carbon Microstructure

Single-crystal graphite is inherently anisotropic.

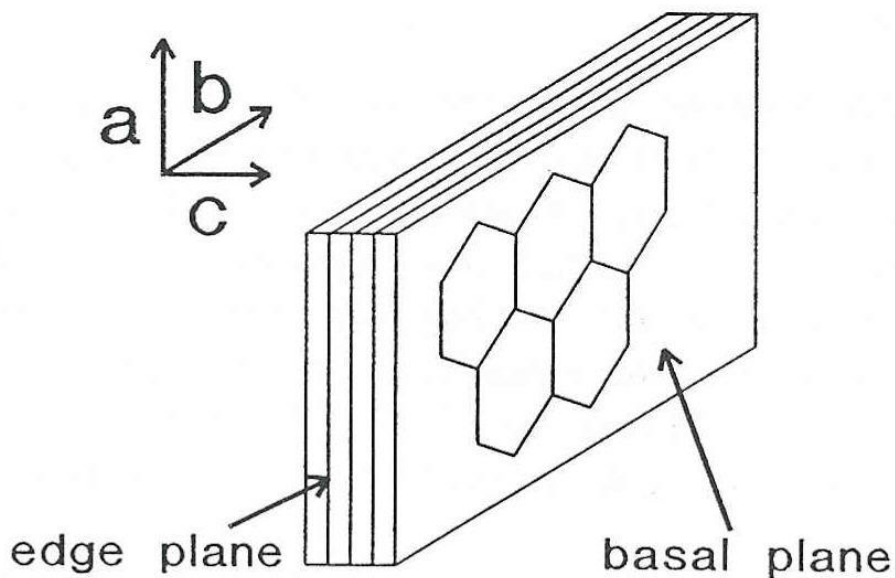


Figure 10.3 Structure of highly ordered pyrolytic graphite.

Voltammetry

Carbon Microstructure

Electrochemical properties for the two planes vary greatly.

Table 10.1 Anisotropic Electrochemical Properties of HOPG

	Basal Plane	Edge Plane
Capacitance, $\mu\text{F}/\text{cm}^2$	< 1.0	$\sim 50\text{--}70$
Adsorption of anthraquinone disulfonate, pMol/cm^2	< 1	> 150
k° for $\text{Fe}(\text{CN})_6^{3-/4-}$, cm/sec	$< 10^{-6}$	$0.06\text{--}0.10$

Source: Data from References 2, 9, and 10.

Voltammetry

Carbon

Common carbon electrodes:

1) HOPG-highly ordered pyrolytic graphite

Made by pyrolysis of light hydrocarbons at $\sim 800^{\circ}\text{C}$ then treated at high temperature and pressure annealed at 3000°C .

HOPG has weak interplanar bonding so can be renewed with adhesive tape.

Voltammetry

Carbon

Common carbon electrodes:

2) Polycrystalline graphite electrodes

c. Graphite Composite Electrodes

Mix graphite powder with suitable filler that hardens.

Voltammetry

Carbon

Common carbon electrodes:

1) Polycrystalline graphite electrodes

b. Spectroscopic Graphite Electrodes

Rods with low metal impurity used in emission spectroscopy. Can immerse in molten wax (ceresin or paraffin) then place in a vacuum, polish end of rod.