


CHE 729

Electrochemistry

Lecture 2

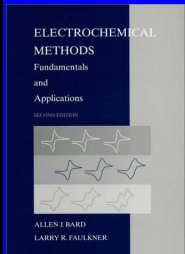
Voltammetry



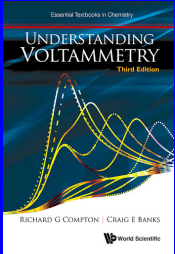
Dr. Wujian Miao
THE UNIVERSITY OF
SOUTHERN MISSISSIPPI

1

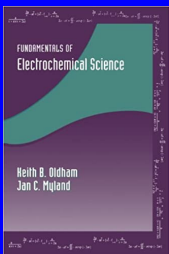
Reference Books



ELECTROCHEMICAL METHODS
Fundamentals and Applications
2nd Edition
ALLEN J. BARD
LARRY R. FAULKNER



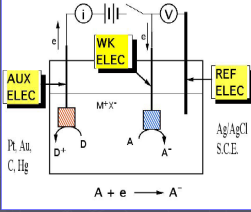
Understanding VOLTAMMETRY
3rd Edition
RICHARD G. COMPTON | CRAIG E. BANKS
World Scientific



FUNDAMENTALS OF Electrochemical Science
Keith B. Oldham
Jan C. Njolund

2

Electrochemical Cell



- ▶ **Working electrode:** place where redox occurs, surface area few mm² to limit current flow.
- ▶ **Reference electrode:** constant potential reference
- ▶ **Counter (Auxiliary) electrode:** inert material, plays no part in redox but completes circuit

•**Supporting electrolyte:** alkali metal salt does not react with electrodes but has conductivity

3

Electrochemical Instrumentation

4

Voltammetry

- ▶ Electrochemistry techniques based on **current (i)** measurement as function of **voltage (E_{app})**
- ▶ Voltammetry — Usually when the working electrode is solid, e.g., Pt, Au, GC.
- ▶ Polarograph — A special term used for the voltammetry carried out with a (liquid) **MURCURY electrode**.
- ▶ Voltammogram — The plot of the electrode current as a function of potential.

5

Linear sweep voltammetry

- ▶ The potential is varied linearly with time with sweep rates v ranging from 10 mV/s to about 1000 V/s with conventional electrodes and up to 10^6 V/s with ultramicroelectrodes (UMEs).
- ▶ It is customary to record the current as a function of potential, which is equivalent to recording current versus time.
- ▶ Linear sweep voltammetry, linear scan voltammetry (LSV), or linear potential sweep chronoamperometry.

6

Linear Diffusion to a Planar Electrode

(a)

$x = \infty$ ("bulk")
 at $x=0$, rate constant k^0 (cm/s)
 by diffusion

Electrode reaction: $A + e \rightleftharpoons A^-$
 (Ox + ne \rightarrow Red) (reversible)

In solution: $A_{\text{bulk}} \rightarrow A_{x=0}$

7

Linear Sweep/Scan Voltammetry

Peak-shaped $i \sim E$ profile

(a)

(b)

(c)

8

For $A + e = A^-$ reversible reaction, $E^0(A/A^-) = E^0$

- (1) $E \gg E^0, i \sim 0$
- (2) $E = E^0 + dE, i \gg 0$, increases
- (3) $E = E^0, i \gg 0, [A] = [A^-] = [A^*]/2$
- (4) $E = E^0 - 28.5 \text{ mV}, i \rightarrow \text{maximum}, [A]_{x=0} \sim 0.25[A^*]$
- (5) $E \ll E^0, i \gg 0$, decreases, as the depletion effect

$$A + e = A^-$$

$$E = E^0 + \frac{RT}{nF} \ln \frac{[A]}{[A^-]}$$

where $E = E^0, [A] = [A^-]_{x=0}$

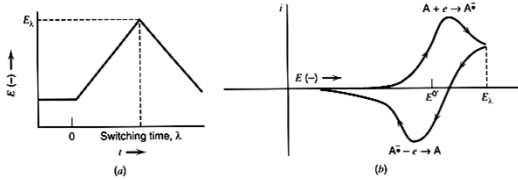
Digisim demonstration

9

Cyclic Voltammetry (CV)

➤ Potential: $E(t) = E_i - vt (V), 0 < t \leq \lambda$

$E(t) = E_i - 2v\lambda + vt (V), t > \lambda$



→ CV is not an ideal method for quantitative evaluation of system properties. It is powerful in qualitative and semi-quantitative reaction behavior.

[DigiSim demonstration](#)

10

Cyclic Voltammetry- i vs time

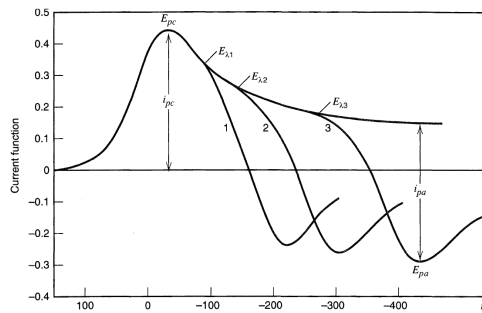
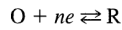


Figure 6.5.1 Cyclic voltammograms for reversal at different E_1 values, with presentation on a time base.

[DigiSim demonstration](#)

11

NERNSTIAN (REVERSIBLE) SYSTEMS



Semi-infinite linear diffusion, only O exist initially

LSV: potential changes linearly at a sweep rate of v (V/s)

$$E(t) = E_i - vt$$

➤ Nernst equation

$$\therefore E(t) = E^{0'} + \frac{nF}{RT} \ln \frac{C_O(0,t)}{C_R(0,t)}$$

$$\therefore \frac{C_O(0,t)}{C_R(0,t)} = \exp \left[\frac{nF}{RT} (E_i - vt - E^{0'}) \right] = S(t) \cdot \theta$$

$$S(t) = e^{-\sigma t}, \quad \sigma = (nF / RT)v; \quad \theta = \exp \left[(nF / RT)(E_i - E^{0'}) \right]$$

12

Mass Transfer/Transport

Modes of Mass Transport

1. *Migration* – movement of charged body under influence of an electric field.
2. *Diffusion* – movement of species under the influence of a concentration gradient.
3. *Convection* - stirring or hydrodynamic transport.

For a *Nernst* process:

$$v_{\text{rxn}} = v_{\text{mt}} = i / nFA \rightarrow \text{flux } (J)$$

v_{rxn} : net rate of electrode reaction

v_{mt} : rate of mass transfer

i : current; A : area of electrode

J unit: mole $\text{cm}^{-2} \text{s}^{-1}$

$$i_{\text{total}} = i_{\text{d}} + i_{\text{m}} + i_{\text{c}}$$

If use short times ($< 10 \text{ s}$) and don't stir (quiescent), then $i_{\text{total}} = i_{\text{d}} + i_{\text{m}}$

13

Figure 4.3.1 shows three diagrams illustrating mass transport to an electrode during reduction. Each diagram shows a vertical electrode on the left with a negative sign (-) and a reactant species moving towards it from the right. Arrows indicate the direction of mass transfer (i_m) and migration (i_d).

- (a) Positively charged reactant: $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$. Both migration and diffusion contribute to the total current: $i = i_d + |i_m|$.
- (b) Negatively charged reactant: $\text{Cu}(\text{CN})_2^{2-} + 2e^- \rightarrow \text{Cu} + 4\text{CN}^-$. Migration opposes diffusion, so the total current is the difference: $i = i_d - |i_m|$.
- (c) Uncharged reactant: $\text{Cu}(\text{CN})_2 + 2e^- \rightarrow \text{Cu} + 2\text{CN}^-$. Only diffusion contributes to the current: $i = i_d$.

Figure 4.3.1 Examples of reduction processes with different contributions of the migration current: (a) positively charged reactant, (b) negatively charged reactant, (c) uncharged reactant.

14

Nernst-Planck Equation (governing the mass transport to an electrode)

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} + \frac{-z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x)$$

Diffusion

Migration

Convection

$J_i(x)$ = flux of species i at distance x from electrode (mole $\text{cm}^{-2} \text{s}^{-1}$)
 D_i = diffusion coefficient (cm^2/s)
 $\partial C_i(x)/\partial x$ = concentration gradient at distance x from electrode
 $\partial \phi(x)/\partial x$ = potential gradient at distance x from electrode
 $v(x)$ = velocity at which species i moves (cm/s)

"-": flux direction opposes the concentration gradient change

15

If We Use High Concentration of Good Electrolyte in Quiescent Solution...

Nernst-Planck Equation reduces to...

Fick's First Law

- Flux of substance is proportional to its concentration gradient:

$$-J_o(x,t) = D_o \frac{\partial C_o(x,t)}{\partial x} = -\frac{i}{nFA}$$

i.e., flux \propto concentration gradient

16

LSV Reversible System

After the *Laplace transformation* and a series of mathematical treatments of the diffusion equations:

$$i = nFAC_o^*(\pi D_o \sigma)^{1/2} \chi(\sigma t)$$

$$(\sigma = (nF / RT)v)$$

where $\chi(\sigma t)$ is a pure number at any given point and can be solved *numerically*.

χ ["kai"]

17

Excel Calculation of $\chi(\sigma t)$

TABLE 6.2.1 Current Functions for Reversible Charge Transfer (3)^{a,b}

$\frac{nE - E_{1/2}}{RT/F}$	$\frac{nE - E_{1/2}}{mV \text{ at } 25^\circ C}$	$\pi^{1/2} \chi(\sigma t)$	$\phi(\sigma t)$	$\frac{nE - E_{1/2}}{RT/F}$	$\frac{nE - E_{1/2}}{mV \text{ at } 25^\circ C}$	$\pi^{1/2} \chi(\sigma t)$	$\phi(\sigma t)$
4.67	120	0.009	0.008	-0.19	-5	0.400	0.548
3.89	100	0.020	0.019	-0.39	-10	0.418	0.596
3.11	80	0.042	0.041	-0.58	-15	0.432	0.641
2.34	60	0.084	0.087	-0.78	-20	0.441	0.685
1.95	50	0.117	0.124	-0.97	-25	0.445	0.725
1.75	45	0.138	0.146	-1.109	-28.50	0.4463	0.7516
1.56	40	0.160	0.173	-1.17	-30	0.446	0.763
1.36	35	0.185	0.208	-1.36	-35	0.443	0.796
1.17	30	0.211	0.236	-1.56	-40	0.438	0.826
0.97	25	0.240	0.273	-1.95	-50	0.421	0.875
0.78	20	0.269	0.314	-2.34	-60	0.399	0.912
0.58	15	0.298	0.357	-3.11	-80	0.353	0.957
0.39	10	0.328	0.403	-3.89	-100	0.312	0.980
0.19	5	0.355	0.451	-4.67	-120	0.280	0.991
0.00	0	0.380	0.499	-5.84	-150	0.245	0.997

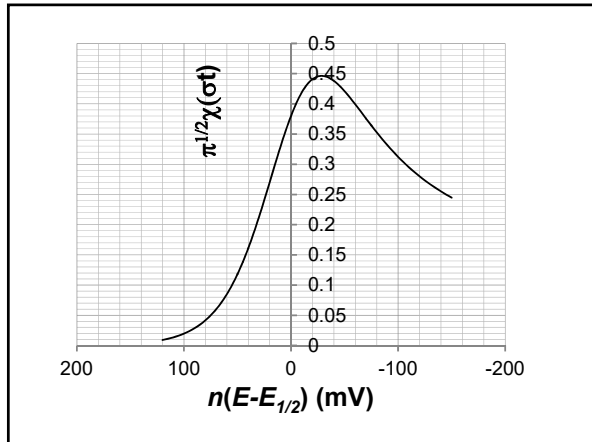
My Excel calculation
0.446295

^aTo calculate the current:

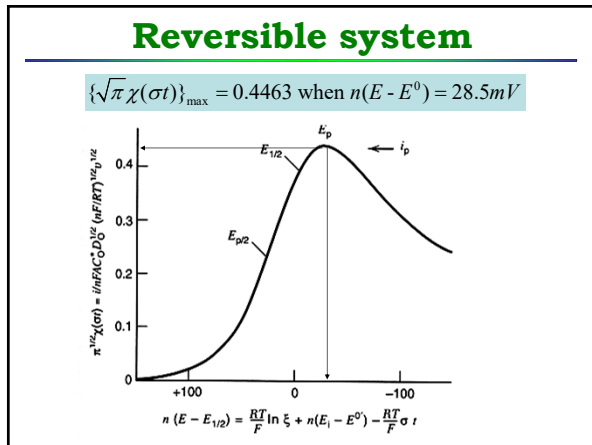
- $i = i(\text{plane}) + i(\text{spherical correction})$.
- $i = nFAD_o^{1/2} C_o^* \pi^{1/2} \chi(\sigma t) + nFAD_o C_o^* \phi(\sigma t) / r_o$.
- $i = 602n^{1/2} AD_o^{1/2} C_o^* \pi^{1/2} [\pi^{1/2} \chi(\sigma t) + 0.168(D_o^2 / v) \phi(\sigma t)]$ at 25°C with quantities in the following units: i , amperes; A , cm²; D_o , cm²/s; v , V/s; C_o^* , M; r_o , cm.

^b $E_{1/2} = E^\ominus + (RT/nF) \ln(D_R/D_O)^{1/2}$.

18



19



20

Peak current and potential

➤ Peak current i_p

$$i_p = 0.4463 \left(\frac{F^3}{RT}\right)^{1/2} n^{3/2} AC_o^* D_o^{1/2} \nu^{1/2}$$

$$= (2.69 \times 10^5) n^{3/2} AC_o^* D_o^{1/2} \nu^{1/2} \text{ at } 25^\circ \text{C.}$$

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

Units: Amperes, cm^2 , cm^2/s , mol/cm^3 , V/s

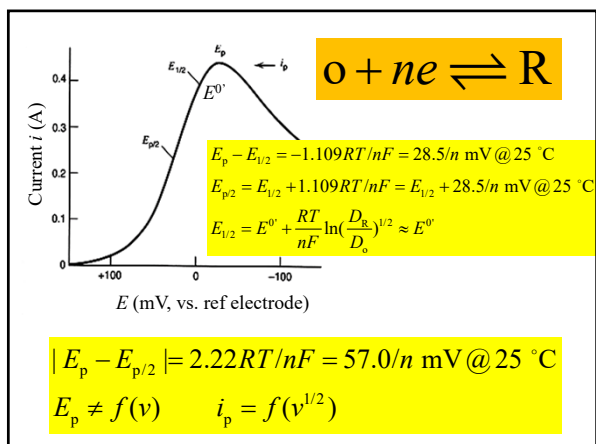
➤ Peak potential E_p

$$E_p = E_{1/2} - 28.5 / n \text{ (mV) at } 25^\circ \text{C}$$

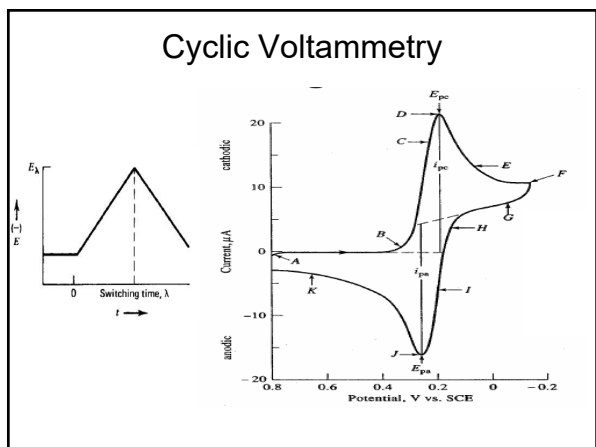
$$E_{1/2} \equiv E^0 + (RT/nF) \ln(D_R / D_O)^{1/2}$$

→ E_p is independent of scan rate.

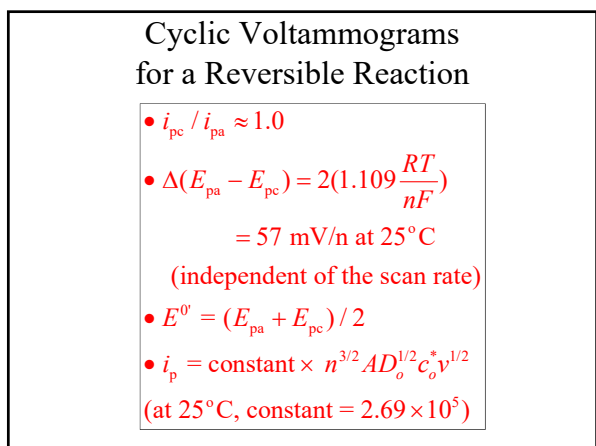
21



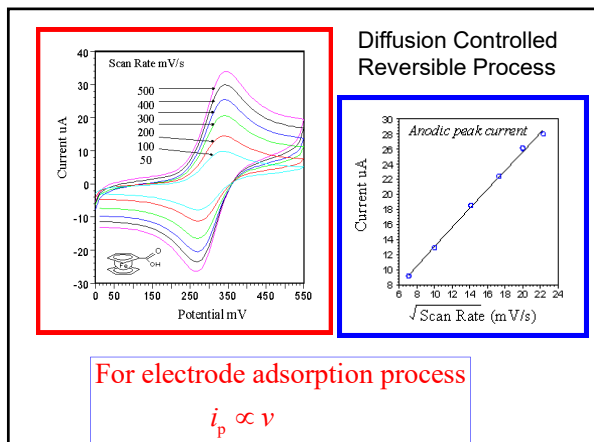
22



23



24



25

Peak separation potentials, although close to 57 mV, are slightly a function of switching potentials.

Table 6.5.1 Variation of ΔE_p with E_λ for a Nernstian System at 25°C (3)

$n(E_{pc} - E_\lambda)$ (mV)	$n(E_{pa} - E_{pc})$ (mV)
71.5	60.5
121.5	59.2
171.5	58.3
271.5	57.8
∞	57.0

26

Reversibility of Electrochemical System Can be Changed via the Change of Scan Rate

Reversible (Nernstian)	$\Lambda \geq 15; k^0 \geq 0.3\nu^{1/2}$ cm/s
Quasireversible	$15 \geq \Lambda \geq 10^{-2(1+\alpha)}; 0.3\nu^{1/2} \geq k^0 \geq 2 \times 10^{-5} \nu^{1/2}$ cm/s
Totally irreversible	$\Lambda \leq 10^{-2(1+\alpha)}; k^0 \leq 2 \times 10^{-5} \nu^{1/2}$ cm/s

$$\Lambda = \frac{k^0}{(D_O^{1-\alpha} D_R^\alpha f \nu)^{1/2}}$$

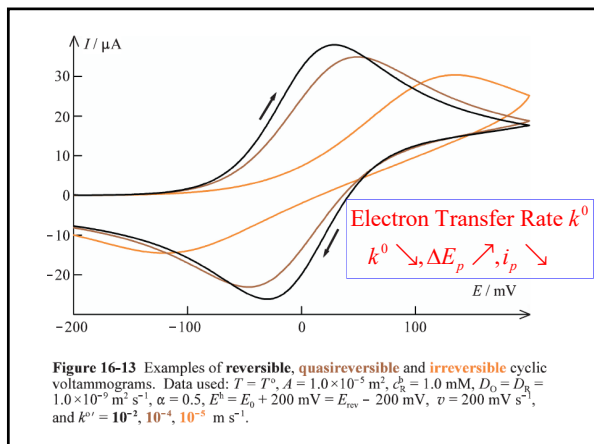
$$\Lambda = \frac{k^0}{(D f \nu)^{1/2}}$$

Λ/λ lamda

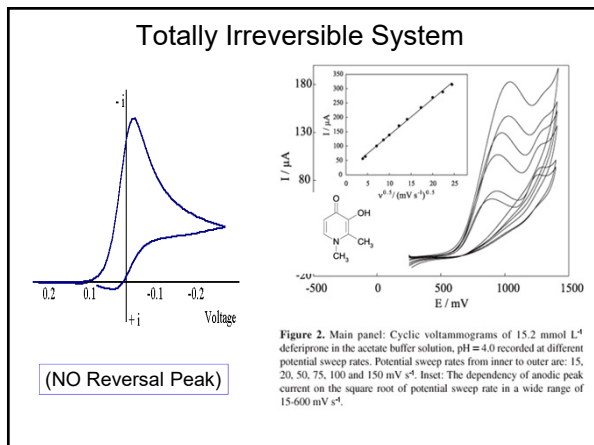
At small ν (or long times), systems may yield reversible waves, while at large ν (or short times), irreversible behavior is observed.

$f = nF/RT$

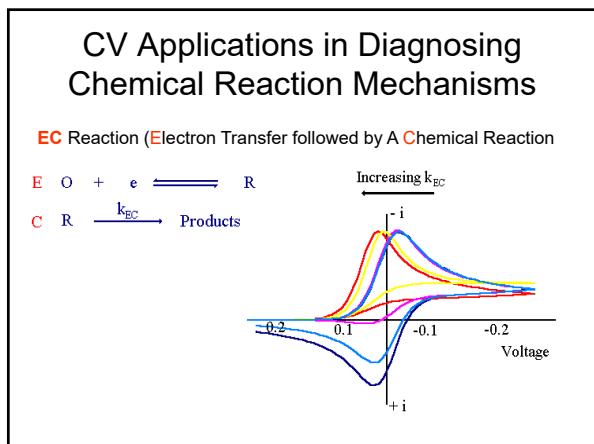
27



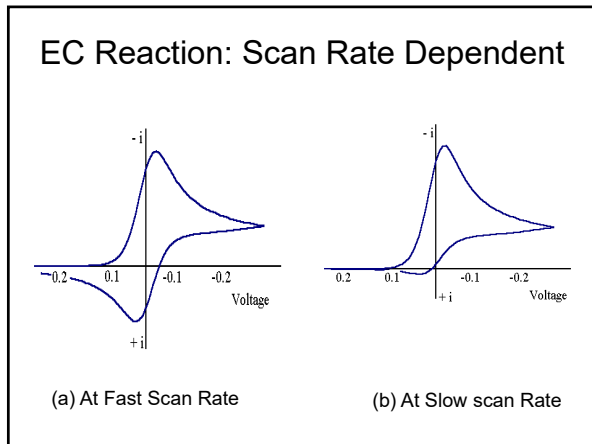
28



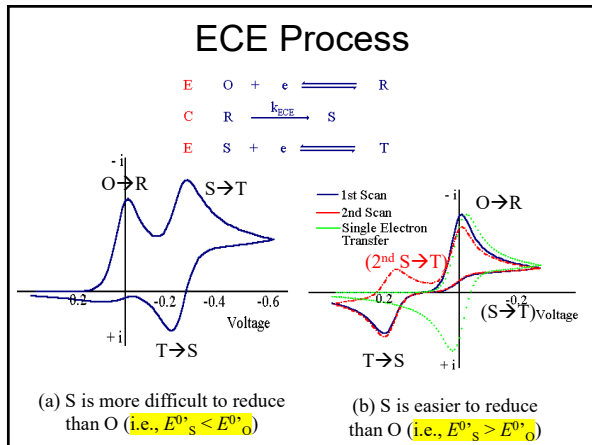
29



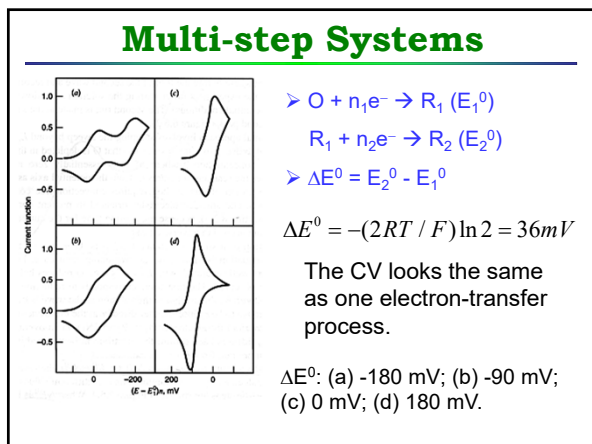
30



31



32

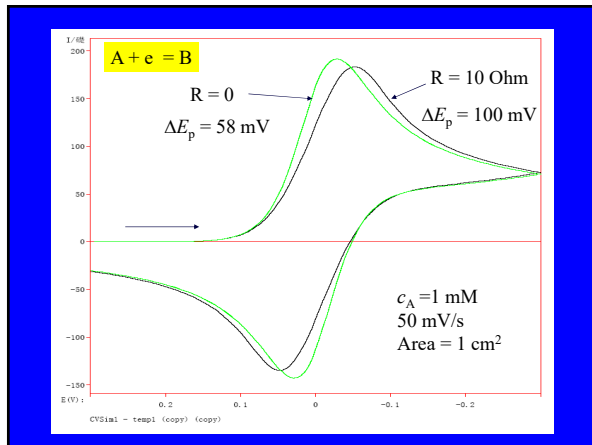


33

Ohmic Potential, IR Drop

- Potential change (drop) due to electrochemical solution resistance
- $E_{ir} = IR$
I—current of the electrochemical cell,
R—resistance of the electrolyte solution.
- $E_{cell} = E_{cathode} - E_{anode} - IR$
- Question: In electrochemical study, an inert electrolyte is always added to the analyte solution. Why?

34



35

Faradaic and Nonfaradaic Processes

Faradaic

- Charges or electrons are transferred across the electrode|electrolyte interface as a result of electrochemical reactions
- Governed by Faraday's law

$$Q = nFN_A \quad \text{where } n = \# \text{ of } e \text{ transferred}$$

$$F = \text{Faraday constant (96,485 C/mol)}$$

$$N_A = \# \text{ of moles of electroactive species}$$

$$i = \frac{dQ}{dt} = nF \frac{dN_A}{dt}$$

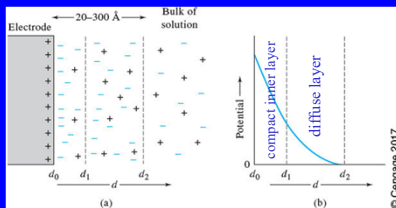
36

Nonfaradaic Process

- Charges associated with movement of electrolyte ions, reorientation of solvent dipoles, adsorption/desorption of species, etc. at the electrode|electrolyte interface.
- Changes with changing potential and solution composition
- Charges do not cross the interface but external currents can still flow
- Regarded as "background current"

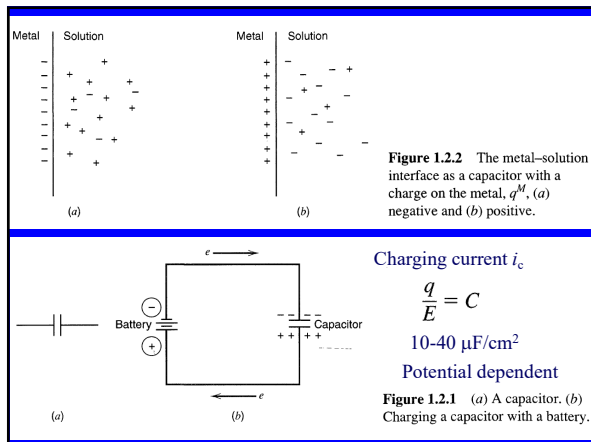
37

Nonfaradaic Processes and the nature of electrode|electrolyte interface; the Double layer



- Electrons transferred at electrode surface by redox reactions occur at liquid/solid interface (heterogeneous)
- (1) A compact inner layer ($d_0 \rightarrow d_1$)
- (2) a diffuse layer ($d_1 - d_2$)

38



39

Equivalent Circuits of Electrochemical Cell

Series Capacitances

$$C_{\text{total}} = \frac{1}{\frac{1}{C_1} + \frac{1}{C_2} + \dots + \frac{1}{C_n}}$$

Figure 1.2.5 Left: Two-electrode cell with an ideal polarized mercury drop electrode and an SCE. Right: Representation of the cell in terms of linear circuit elements.

⁵Actually, the capacitance of the SCE, C_{SCE} , should also be included. However, the series capacitance of C_d and C_{SCE} is $C_T = C_d C_{\text{SCE}} / [C_d + C_{\text{SCE}}]$, and normally $C_{\text{SCE}} \gg C_d$, so that $C_T \approx C_d$. Thus, C_{SCE} can be neglected in the circuit.

40

RC Circuit-Voltage Ramp (Potential Sweep)

$i_c = f(v)$

Figure 1.2.10 Current-time behavior resulting from a linear potential sweep applied to an RC circuit.

Figure 1.2.11 Current-time and current-potential plots resulting from a cyclic linear potential sweep (or triangular waves) applied to an RC circuit.

$$E = vt = E_{R_s} + E_{C_d}$$

$$vt = R_s (dq / dt) + q / C_d$$

if $q = 0$ at $t = 0$

$$i = vC_d [1 - \exp(-t / R_s C_d)]$$

41

General Equivalent Circuit

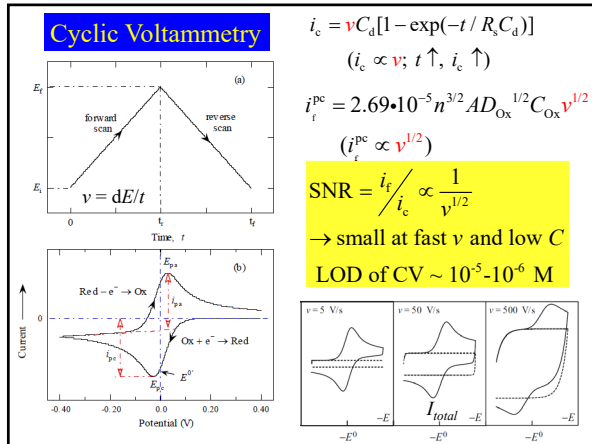
E : Potential applied to WE
 C_d : Double layer capacitance
 Z_f : Impedance (Faradaic reaction)
 i_c : Charging current ("noise")
 i_f : Faradaic current ("signal")
 I : Total measured current

Overall current $I = i_c + i_f$

Signal-to-noise ratio (SNR) = i_f / i_c

SNR \uparrow , limit of detection (LOD) \downarrow

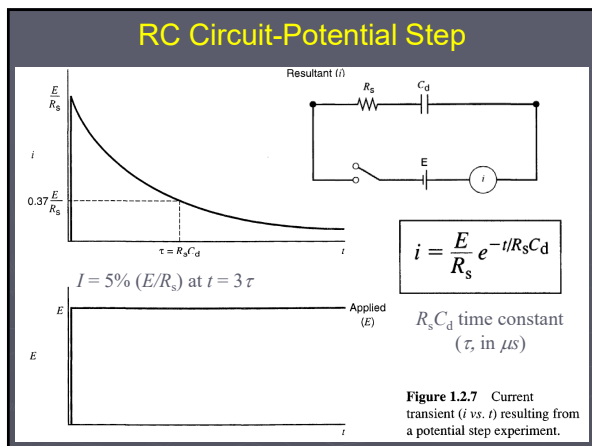
42



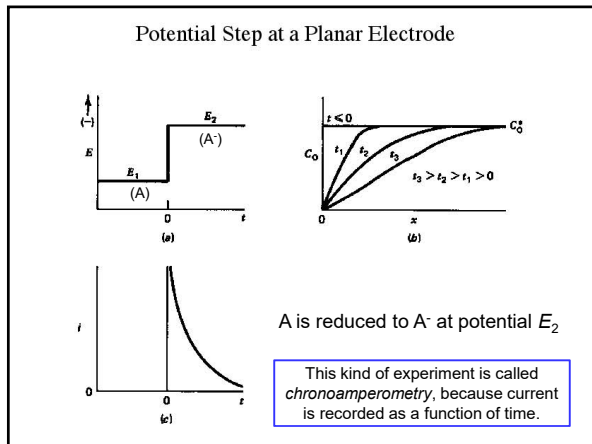
43

How do we eliminate the charging current so that electrochemical techniques could be used in quantifying low concentrations of redox species?
 (Pulse Voltammetry)

44



45



46

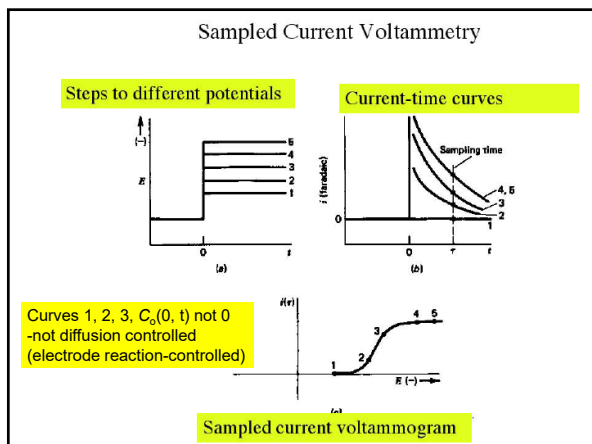
Cottrell Equation

$$\frac{i}{nFA} = D_o \left(\frac{\partial c_o}{\partial x} \right)_{x=0} = D_o \left(\frac{\Delta c_o}{\delta} \right)_{x=0}, \quad \delta = \sqrt{\pi Dt}$$

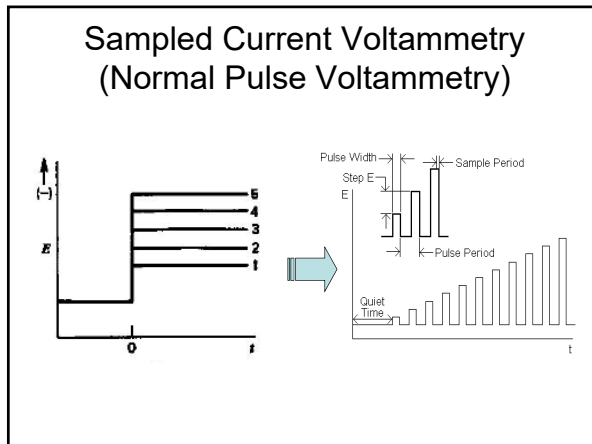
$$= D_o \left(\frac{c_o^* - 0}{\delta} \right) = D_o \left(\frac{c_o^* - 0}{\delta} \right) = \frac{D_o c_o^*}{\sqrt{\pi Dt}}$$

$$i = nFA \frac{D_o c_o^*}{\sqrt{\pi Dt}} = \frac{nFAD_o^{1/2} c_o^*}{\pi^{1/2} t^{1/2}}$$

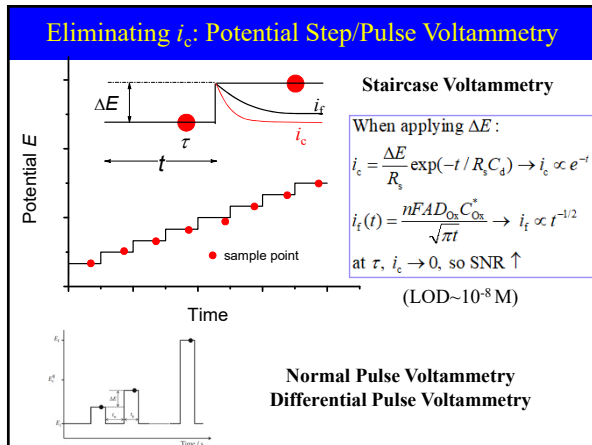
47



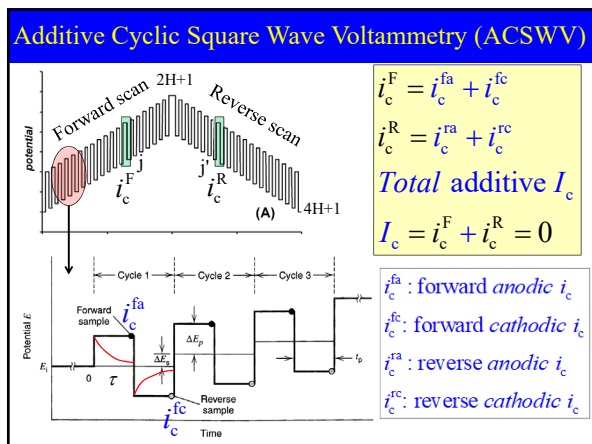
48



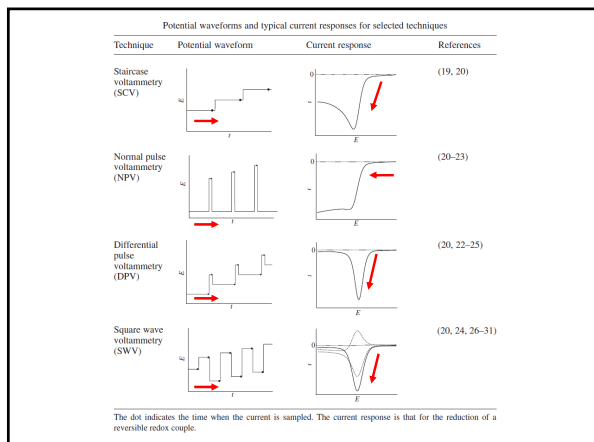
49



50



51



52

Pulse Voltammetric Techniques

- All pulse techniques are based on the difference in the rate of the decay of the charging and the faradaic currents following a potential step (or "pulse").

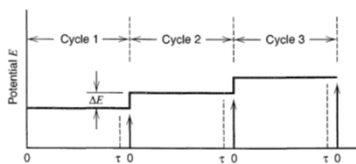
$$i_{ch} = -\frac{\Delta E}{R_s} \exp\left(-\frac{t}{R_s C_d}\right); i_f = \frac{nFA\sqrt{DC^*}}{\sqrt{\pi t}} \text{ (Cottrell Eq.)}$$

- The rate of decay: i_{ch} much faster than i_f -- i_{ch} is negligible at a time of $5R_s C_d$ (time constant, $\sim \mu s$ to ms) after the potential step.
- The sampled i consists solely of the faradaic current.

53

Important parameters

- **Pulse amplitude:** the height of the potential pulse. This may or may not be constant depending upon the technique.
- **Pulse width:** the duration of the potential pulse.
- **Sample period:** the time at the end of the pulse during which the current is measured.



54

Staircase Polarography/Voltammetry

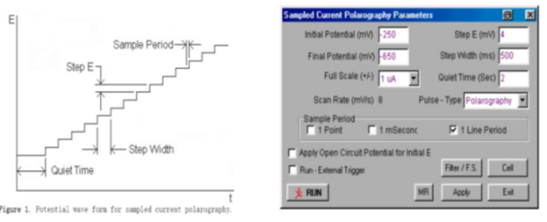
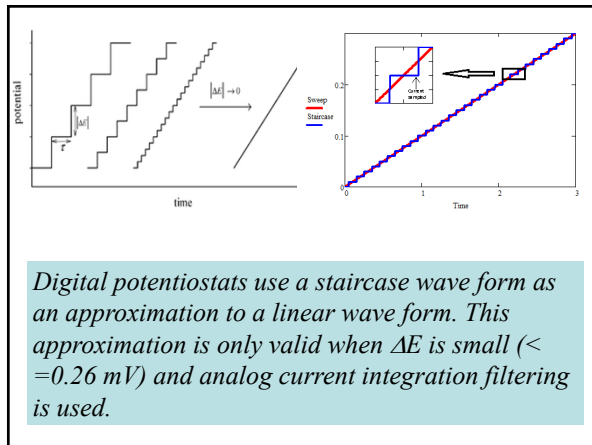


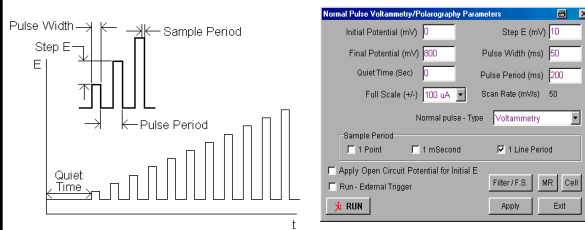
Figure 1. Potential wave form for sampled current polarography.

55

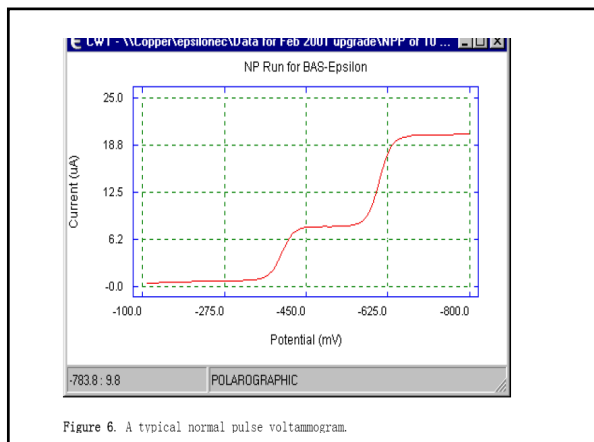


56

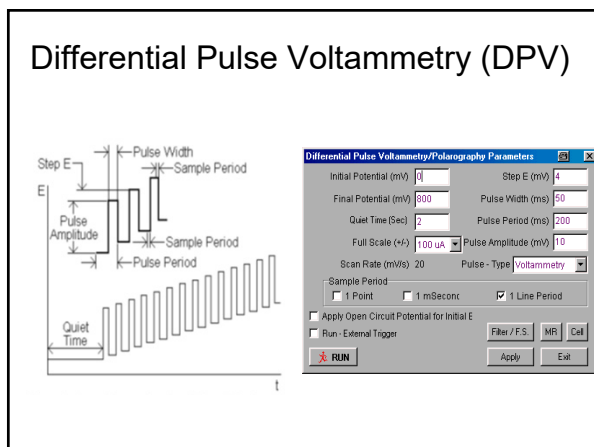
Normal Pulse Polarography/Voltammetry



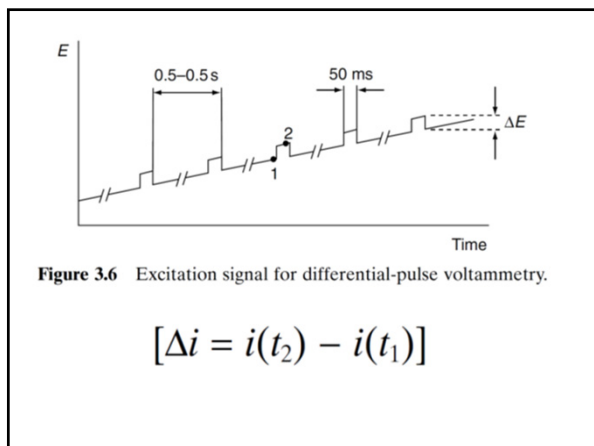
57



58

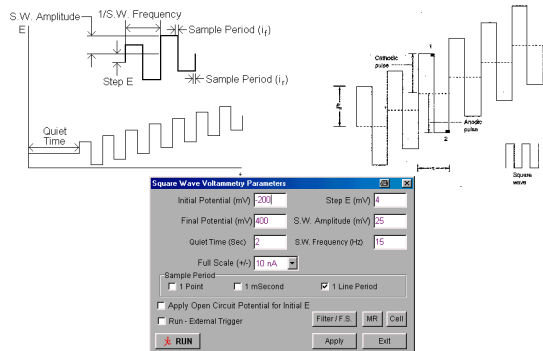


59



60

Square Wave Voltammetry (SWV)



61

Peak Current:
$$i_p = \frac{nFAD^{1/2}C}{\sqrt{\pi t_m}} \left(\frac{1-\sigma}{1+\sigma} \right)$$

where $\sigma = \exp[(nf/RT)(\Delta E/2)]$ (ΔE is the pulse amplitude)

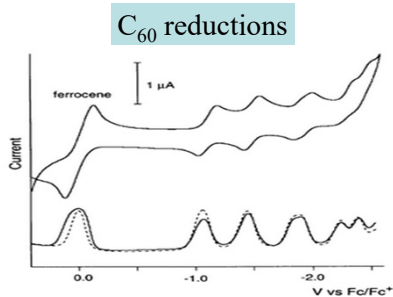
$\left(\frac{1-\sigma}{1+\sigma} \right) = 1$ for large pulse amplitudes

The peak potential (E_p) can be used to identify the species.

$$E_p = E_{1/2} - \Delta E/2$$

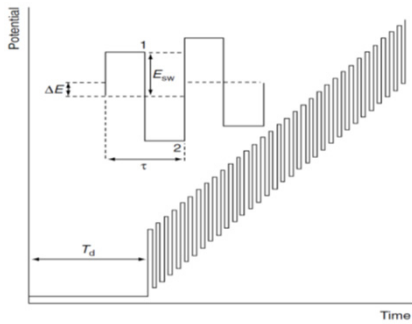
62

Charging current (smaller more than an order of magnitude than that of NPV) with LOD 10 nM.



63

Square Wave Voltammetry (SWV)



64

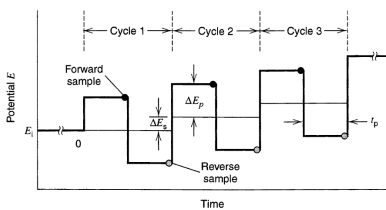
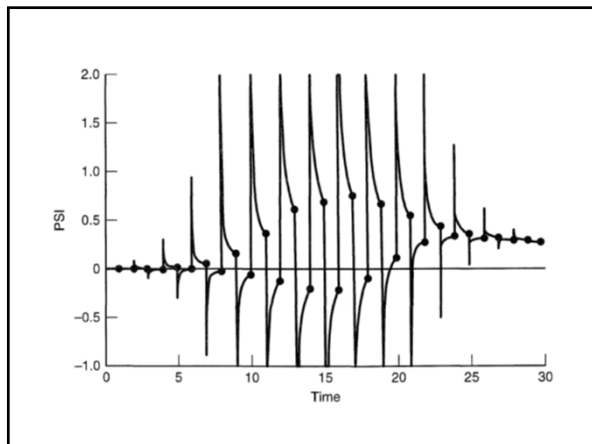


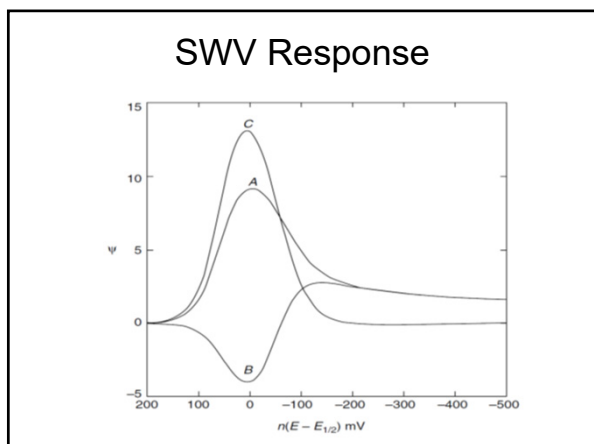
Figure 7.3.13 Waveform and measurement scheme for square wave voltammetry. Shown in bold is the actual potential waveform applied to the working electrode. The light intervening lines indicate the underlying staircase onto which the square wave can be regarded as having been superimposed. In each cycle, a forward current sample is taken at the time indicated by the solid dot, and a reverse current sample is taken at the time marked by the shaded dot.

$$E_m = E_i - \left[\text{Int} \left(\frac{m+1}{2} \right) - 1 \right] \Delta E_s + (-1)^m \Delta E_p \quad (\text{for } m \geq 1)$$

65



66



67

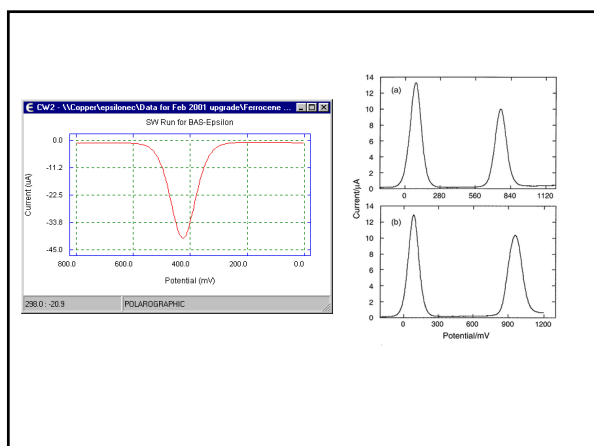
$$\Delta i_p = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t_p^{1/2}} \Delta\psi_p$$

TABLE 7.3.2 Dimensionless Peak Current (ψ_p) vs. SWV Operating Parameters^a

$n\Delta E_p/mV$	$n\Delta E_s/mV$			
	1	5	10	20
0 ^b	0.0053	0.0238	0.0437	0.0774
10	0.2376	0.2549	0.2726	0.2998
20	0.4531	0.4686	0.4845	0.5077
50	0.9098	0.9186	0.9281	0.9432
100	1.1619	1.1643	1.1675	1.1745

^aData from reference 50.
^b $\Delta E_p = 0$ corresponds to staircase voltammetry.

68



69

Comparison between SWV and CV

SWV Strengths

- Low electrochemical background.
- Much low detection limit.
- Much less distortion of voltammogram—easy to fit theoretical data.
- Better for evaluating quantitative parameters.

CV Strengths

- More intuitively in chemical terms for most practitioners.
- Reversal of CV covers a large span of E —more readily highlights linkages b/w processes occurring at widely separated potentials.
- Wider range of time scales.

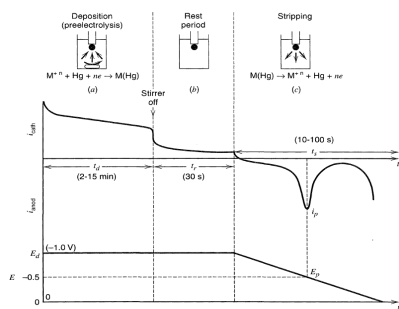
70

Applications of Voltammetry

- Dopamine detection in mice brains
- Au or Si NPs redox behavior
-
-

71

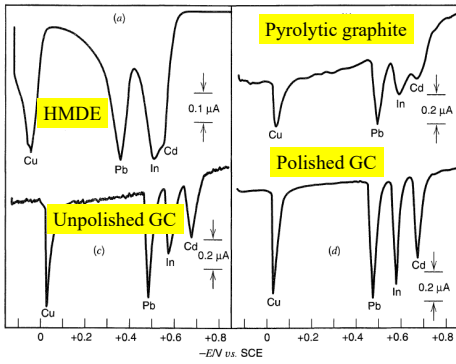
Anodic Stripping Voltammetry (ASV)



Principle of anodic stripping. (a) Preelectrolysis at E_d ; stirred solution, (b) Rest period; stirrer off. (c) Anodic scan.

72

ASV-Electrode Dependence



73

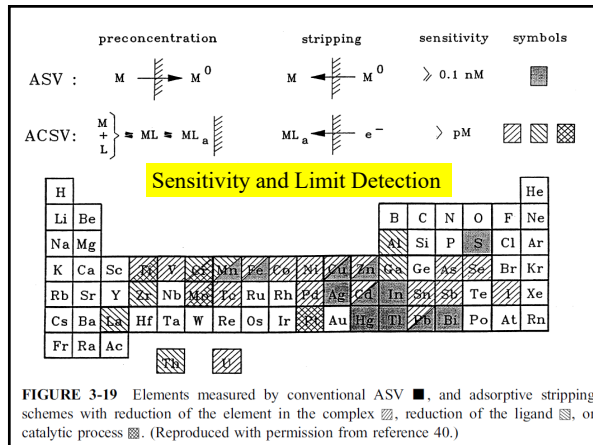


FIGURE 3-19 Elements measured by conventional ASV ■, and adsorptive stripping schemes with reduction of the element in the complex ▨, reduction of the ligand ▩, or catalytic process ▪. (Reproduced with permission from reference 40.)

74

