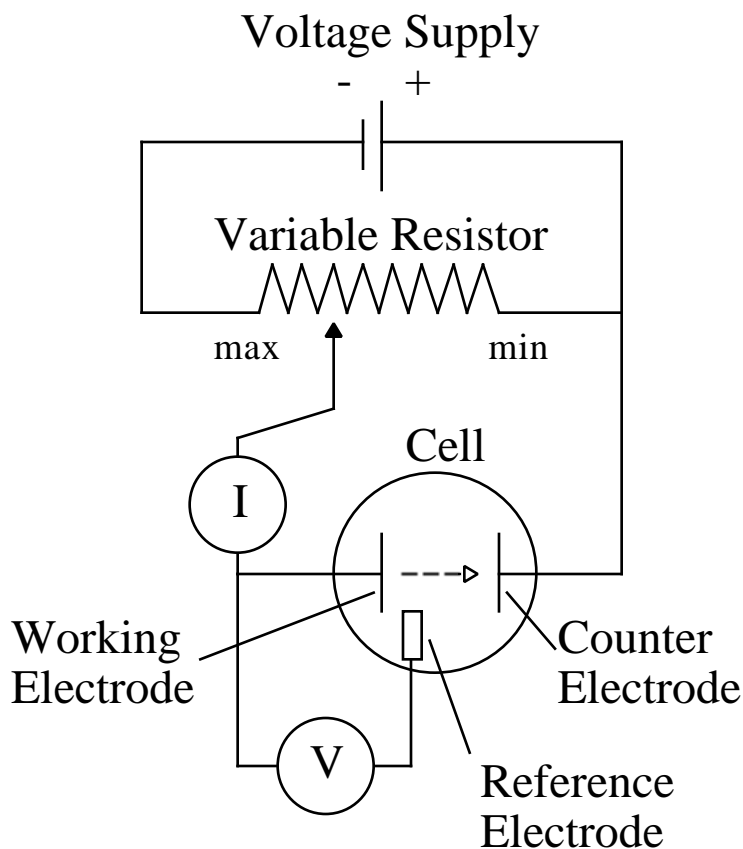


Voltammetry (Chapter 25)

Electrochemistry techniques based on **current** (i) measurement as function of **voltage** (E_{appl})



Working electrode	(microelectrode) place where redox occurs surface area few mm^2 to limit current flow
Reference electrode	constant potential reference (SCE)
Counter electrode	inert material (Hg, Pt) plays no part in redox but completes circuit
Supporting electrolyte	alkali metal salt does not react with electrodes but has conductivity

Why not use 2 electrodes?

OK in potentiometry - very small currents.

Now, want to measure current (larger=better) but

- potential drops when current is taken from electrode (IR drop)
- must minimize current withdrawn from **reference** electrode surface

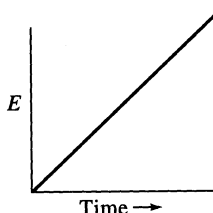
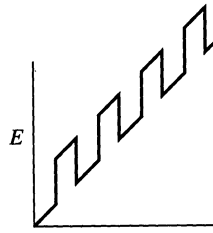
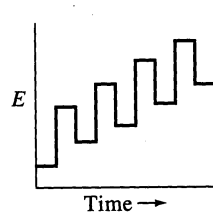
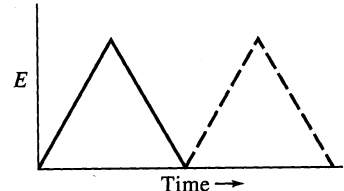
Potentiostat (voltage source) drives cell

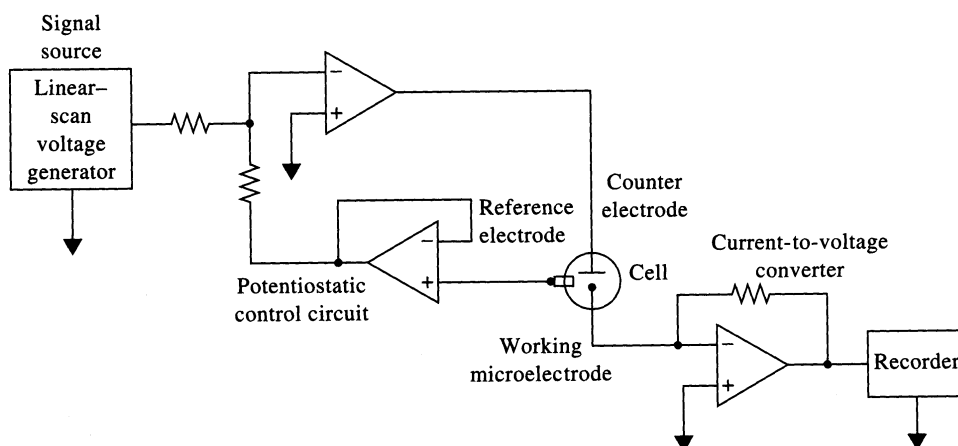
- supplies whatever voltage needed between **working** and **counter** electrodes to maintain specific voltage between **working** and **reference** electrode

NOTE:

- Almost all **current carried between working and counter** electrodes
- Voltage measured between **working** and **reference** electrodes
- Analyte dissolved in cell not at electrode surface!

Excitation signals (Fig 25-2)

Name	Waveform	Type voltammetry
(a) Linear scan		Polarography Linear-scan voltammetry
(b) Differential pulse		Differential pulse polarography
(c) Square wave		Square-wave voltammetry
(d) Triangular		Cyclic voltammetry



Microelectrodes

C, Au, Pt, Hg each useful in certain solutions/voltage ranges

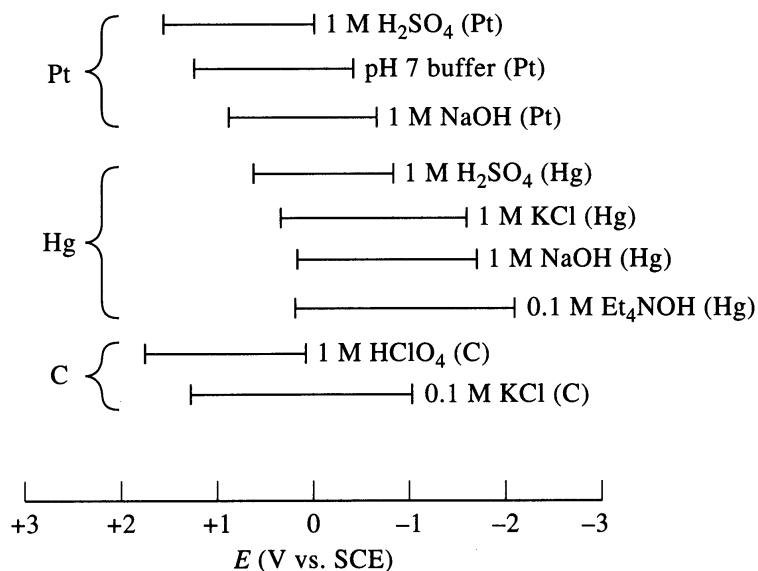
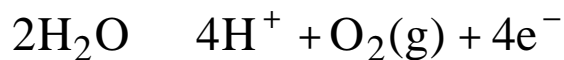
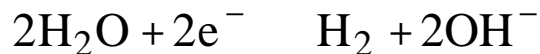


Fig 25-4

At -ve limit, **oxidation** of water



At +ve limit, **reduction** of water



Varies with material/solution due to different **overpotentials**

Overpotential always reduces theoretical cell potential when current is flowing

$$= E_{\text{current}} - E_{\text{equilibrium}}$$

Overpotential (overvoltage) develops as a result of electrode **polarization**:

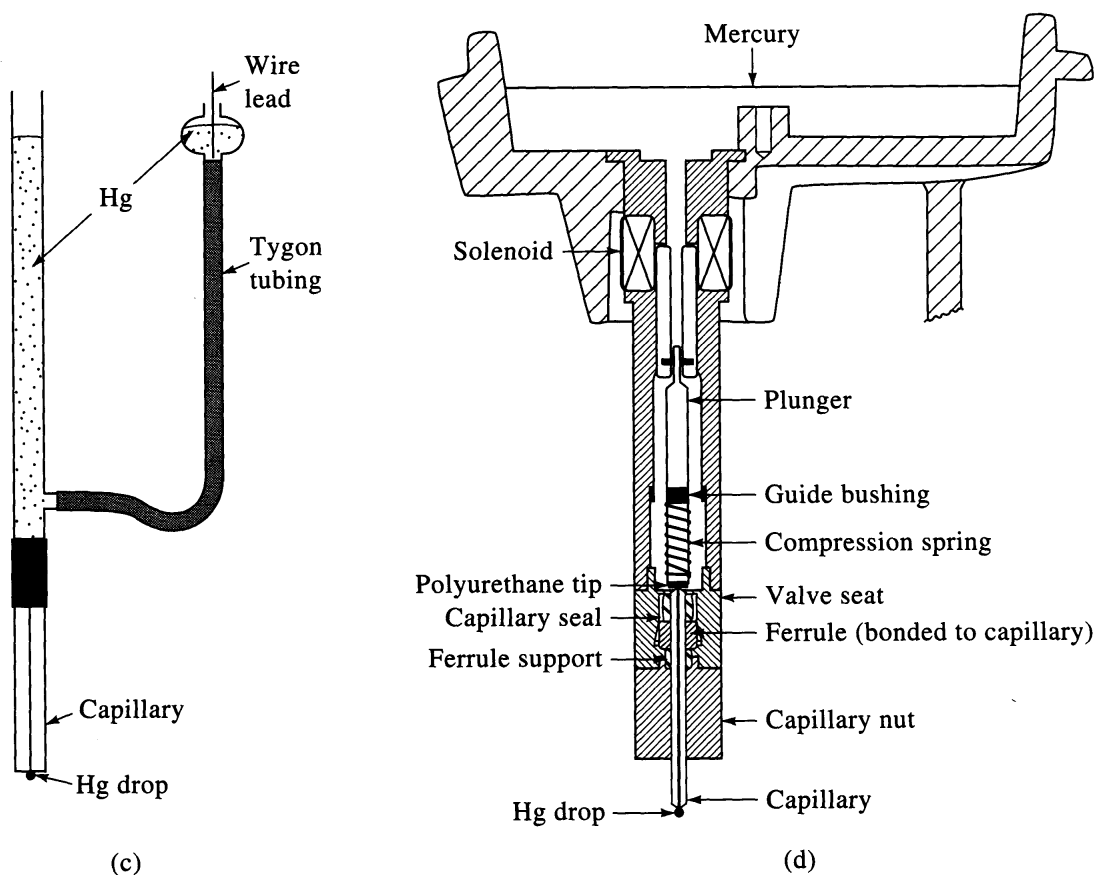
- **concentration** polarization - mass transport limited
- **adsorption/desorption** polarization - rate of surface attach/detachment
- **charge-transfer** polarization - rate of redox reaction
- **reaction** polarization - rate of redox reaction of intermediate in redox reaction

Overpotential means **must apply greater potential** before redox chemistry occurs

Hg particularly useful

- (i) high overpotential at -ve limit
- (ii) easy to prepare clean surface

Hg Microelectrodes: (Fig 25-3)



Voltammograms (voltammetric waves) are graphs of current (i) vs. applied voltage (E_{appl})

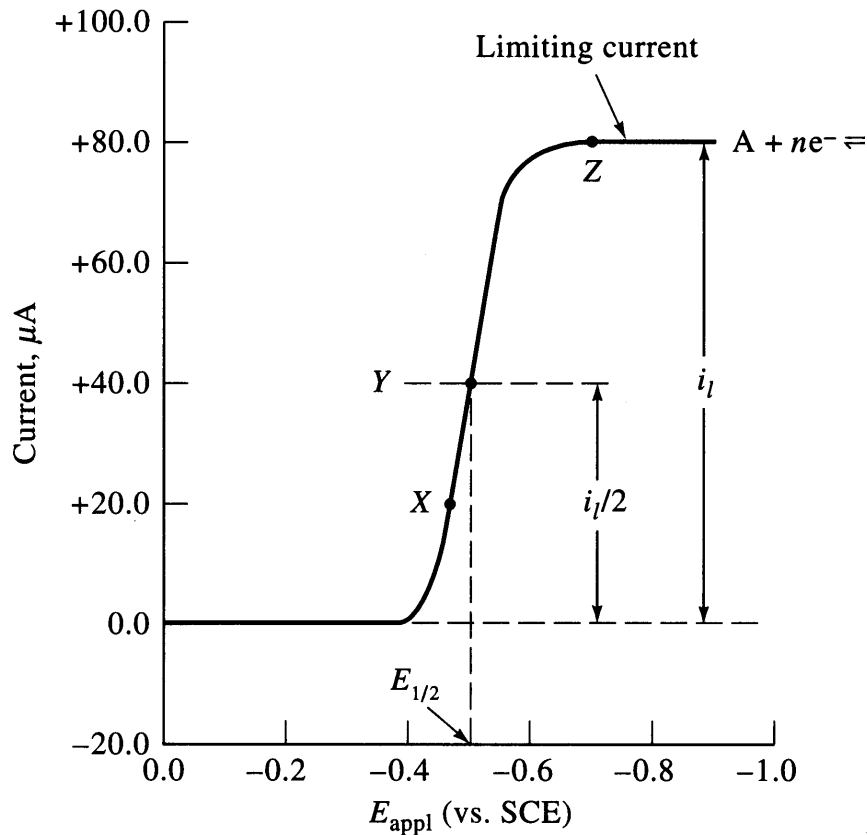


Fig 25-5

Hg microelectrode is cathode -ve terminal in above



Increase in current at potential at which A can be reduced (reaction demands electrons, supplied by potentiostat)

Two important points

- **Half wave potential** ($E_{1/2}$) is close to E^0 for reduction reaction

$$E_{1/2} = E^0 - E_{\text{ref}}$$
$$-0.50 = E^0 - 0.24 \quad \text{for SCE}$$
$$E^0 = -0.26 \text{ V}$$

- **Limiting current** (i_l) proportional to analyte **concentration** (really, activity)

$$i_l = k c_A$$

Current is just measure of **rate** at which species can be brought to electrode surface

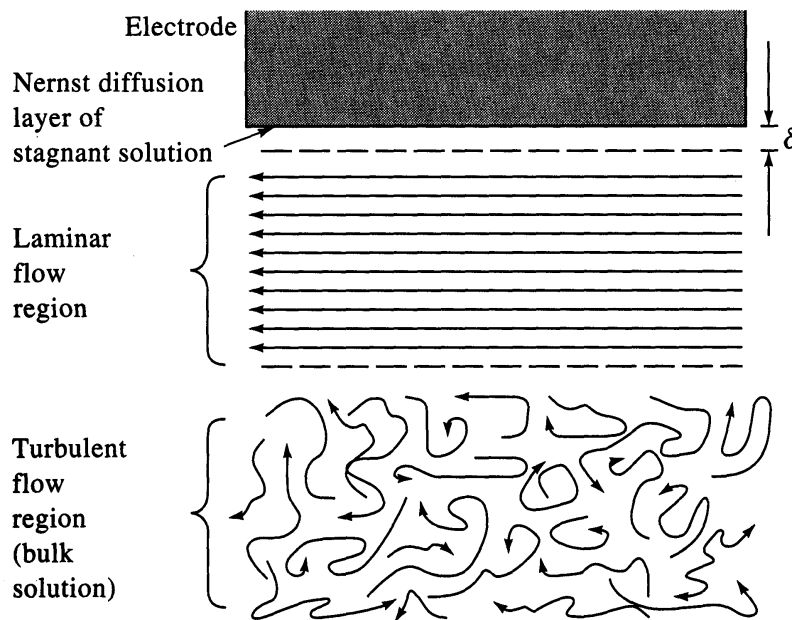
Two methods:

Stirred - hydrodynamic voltammetry

Unstirred - polarography (dropping Hg electrode)

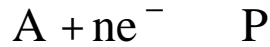
Hydrodynamic Voltammetry

In stirred solution, diffusion layer (**Nernst layer** 0.1-0.01 mm) forms near electrode (Fig 25-9)



- Three transport mechanisms (i) migration (ii) convection (iii) diffusion

In general



$$E_{\text{cell}} = E_A^0 - \frac{E_{\text{ind}}}{n} \log \frac{c_P}{c_A} - E_{\text{ref}}$$

but what are c_P and c_A near electrode surface (c_P^0 and c_A^0) ?

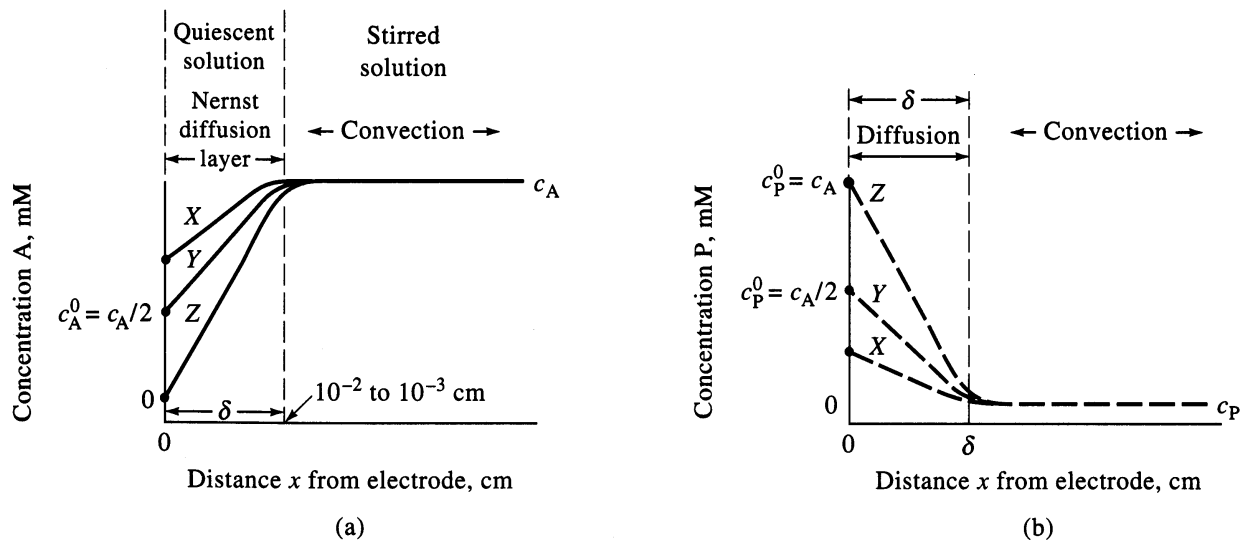


Fig 25-10

Convection dominates in stirred solution

Current is a measure of how fast A is brought to electrode surface

$$i = nFAD_A \underbrace{\frac{c_A}{x}}_{\text{rate of change of [A] with } x}$$

Faraday (C·mol⁻¹)

Electrode Area (cm²)

Diffusion Coefficient (cm²·s⁻¹)

Rate can be rewritten

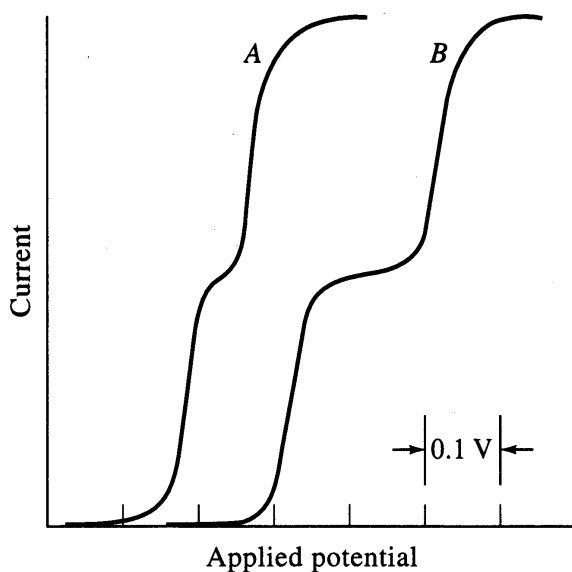
$$\begin{aligned} i &= \frac{nFAD_A}{\delta} (c_A - c_A^0) \\ &= k_A (c_A - c_A^0) \end{aligned}$$

At maximum current, $c_A^0 = 0$ so

$$i_l = k_A c_A$$

Applications of Hydrodynamic Voltammetry

Single voltammogram can quantitatively record many species provided enough separation between waves (Fig 25-11)



Problems with dissolved O_2 - must **purge** (sparge) **solutions**

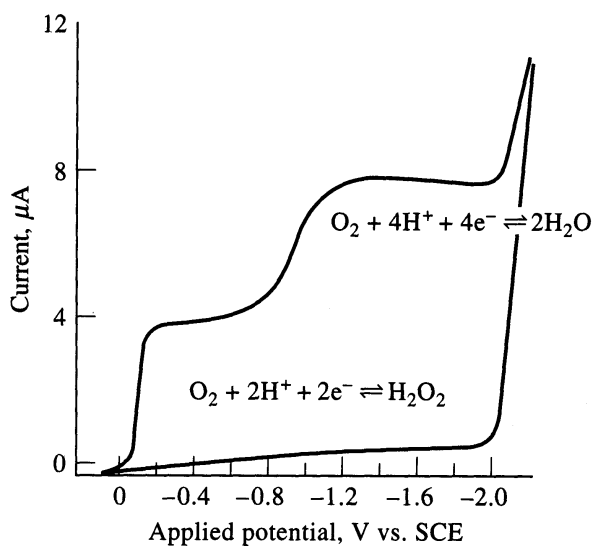


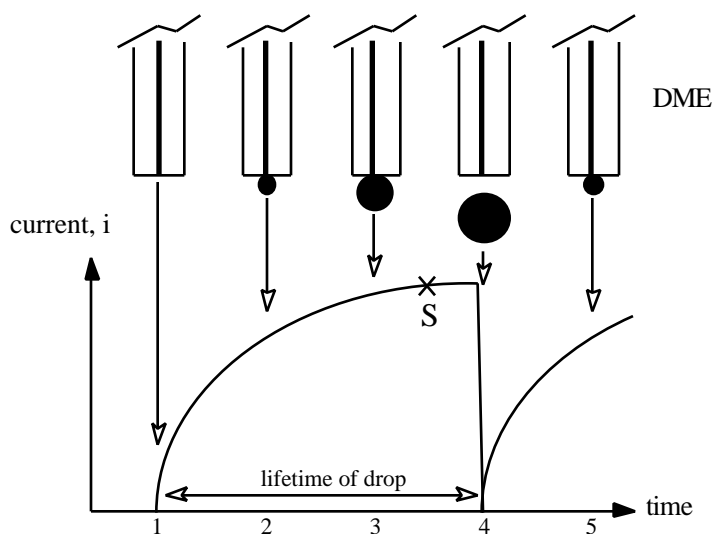
Fig 25-13

Polarography

First voltammetric technique

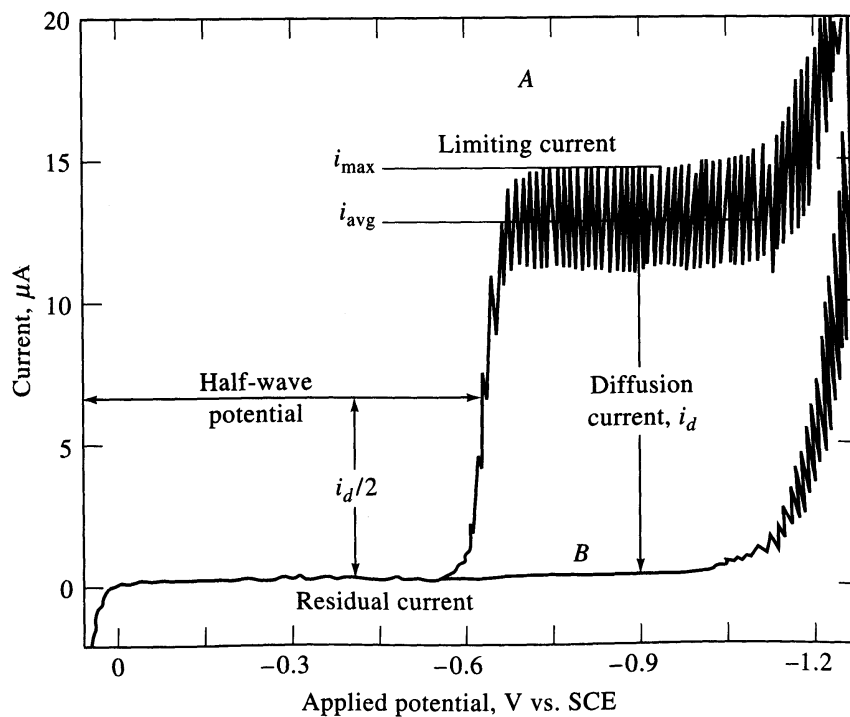
Differs from hydrodynamic

- **unstirred** (diffusion dominates)
- **dropping Hg electrode (DME)** is used as working electrode
current varies as drop grows then falls off

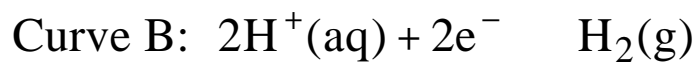
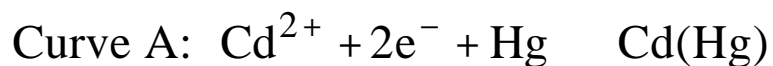


Linear Scan Polarography:

Fig 25-23



$$i_{\text{ave}} = \frac{6}{7} i_{\text{max}}$$



Unstirred - only diffusion - currents **smaller**

Diffusion Current (Ilkovic Equation)

$$i_{d \max} = 706 nD^{1/2} \underbrace{m^{2/3} t^{1/6}}_{\substack{\text{electrode} \\ \text{dependant} \\ \text{capillary} \\ \text{constant}}} c_A$$

number of electrons

analyte conc (mM)

diffusion coefficient ($\text{cm}^2 \cdot \text{s}^{-1}$)

drop time (s)

flow rate of Hg (mg/s)

Residual Current

- redox reactions of impurities in solution
- charging of Hg drop
(non-faradaic current/non-redox current)

Advantages of DME (compared to planar electrodes):

- **clean surface** generated
- **rapid** achievement of constant current during drop growth
- **remixing** of solution when drop falls
- high Hg **overvoltage** means even metals with high -ve E^0 can be measured without H_2 formation

Disadvantages of DME:

- Hg easily **oxidized**, limited use as anode ($E < +0.4$ V)



- **nonfaradaic residual currents** limit detection to $>10^{-5}$ M
- **cumbersome** to use (toxic mercury)
- sometimes produce **current maxima** for unclear reasons (use maxima suppressor) (Fig 25-25)

Current Sampled Polarography

- Drop knocker used to detach drop slightly before natural drop time for **reproducible drop times**
- Near **end of drop life**, current is measured (sampled)
- Current **held** at this value until next drop
- Sampled polarogram consists of short steps with **less fluctuation** than "raw" polarogram

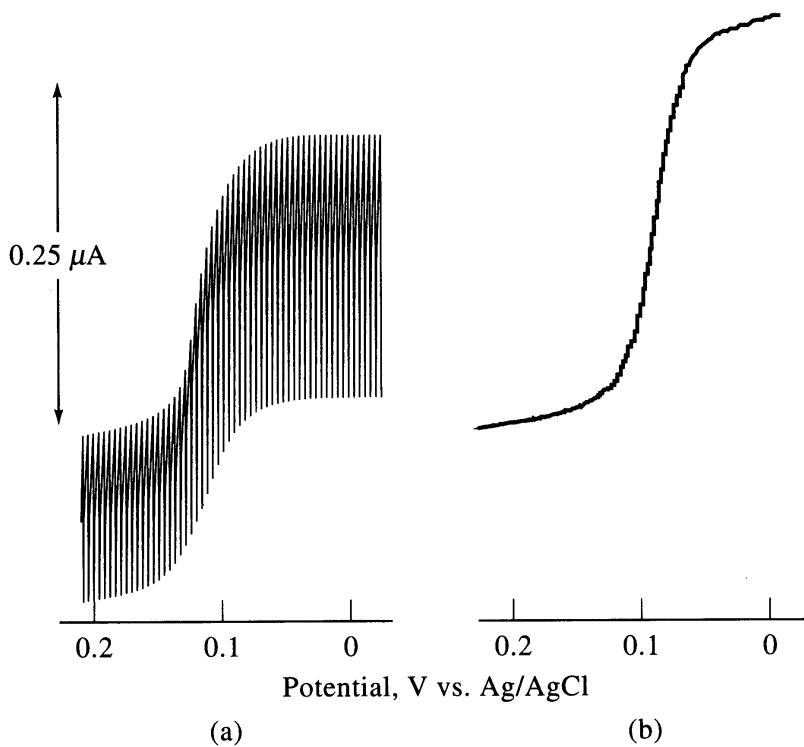


Fig 25-26

Pulse Polarography: Differential Pulse Polarography

Conventional polarography somewhat limited by nonfaradaic currents

DPP relies on two measurements when difference between **faradaic** and **nonfaradaic** currents are largest

Detection limits 10^{-7} - 10^{-8} M (compare with 25-27)

- Small, short voltage pulses applied to linear ramp near end of drop lifetime
- Initial V rise, causes Hg drop to charge up (non faradaic current) but **quickly returns to zero**
- In presence of reducible species, faradaic current also present (**decays less slowly**)
- Past reduction potential, small voltage pulse doesn't make much difference, already at diffusion limit

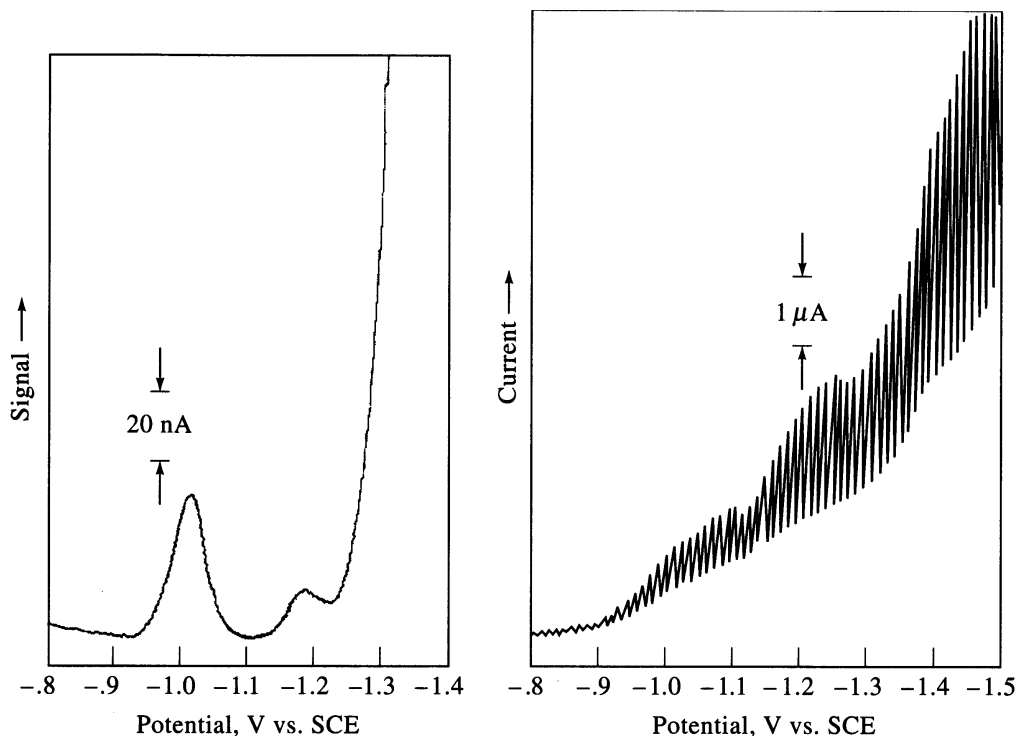


Fig 25-29

