

## CYCLIC Voltammetry

⇒ read more:

- C.M.A. Brett & A.M.O. Brett, “Electrochemistry”, Oxford University Press, Oxford, 1993 → **chapter 9**
  
- E. Gileadi, “Electrode Kinetics for Chemists, Chemical Engineers and Materials Scientists”, VCH, Weinheim, 1993 → **chapter 25**

## Different ways to do voltammetry:

- **Potential step**
- **Linear sweep**
- **Cyclic Voltammetry (CV)**

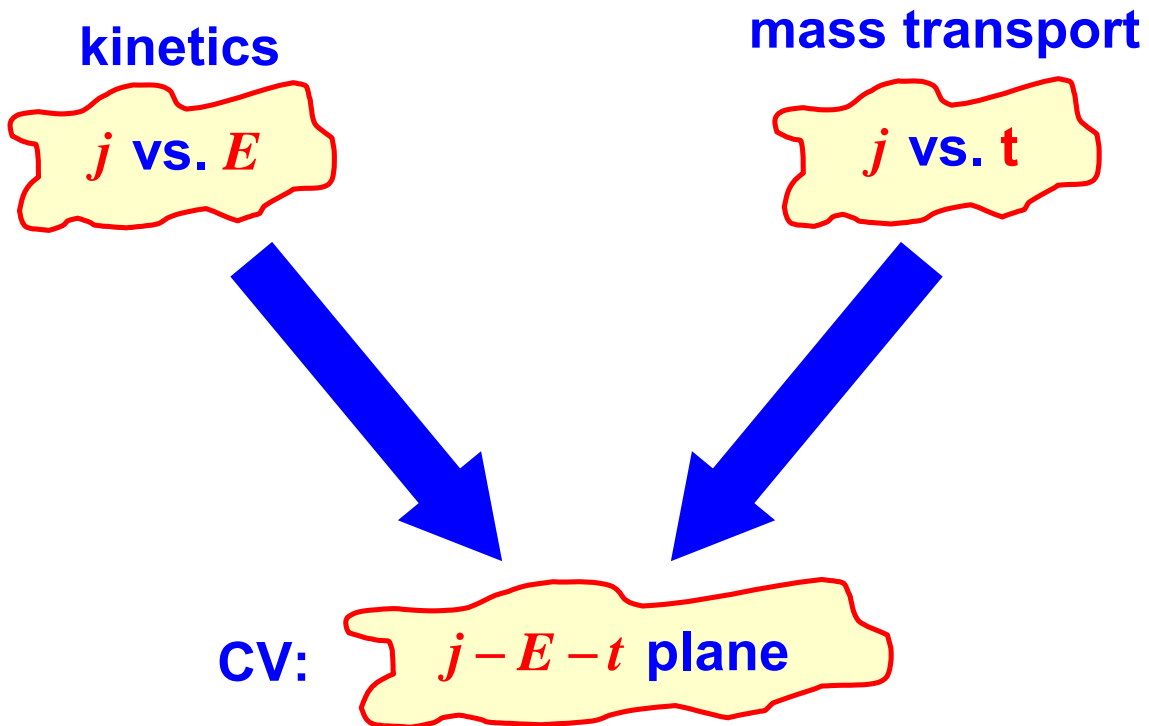
**CV: widely used technique for studying electrode processes (particularly by non-electrochemists)**

**Principle of CV: Apply continuous cyclic potential  $E$  to working electrode**

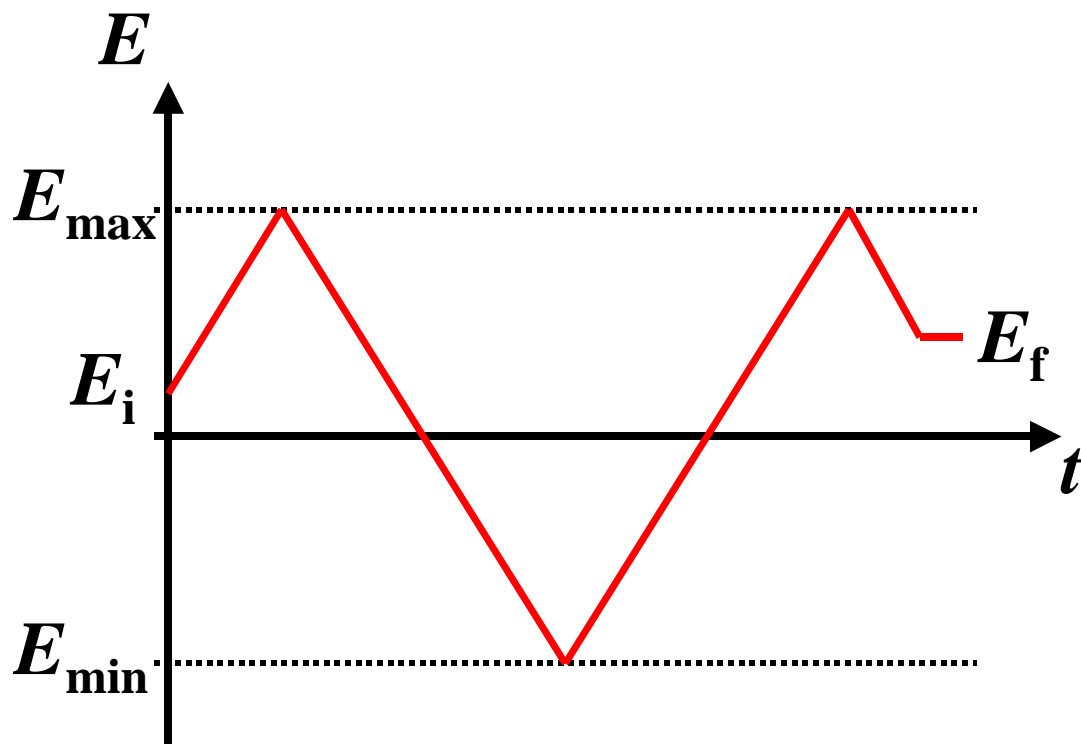
⇒ **Effects**

- **Faradic reactions: oxidation/reduction of electroactive species in solution**
- **Adsorption/desorption due to  $E$**
- **Capacitive current: double layer charging**

⇒ **deviations from steady state, i.e.  $\frac{dc}{dt} \neq 0$**



- Potential changed at a constant sweep rate,  $v = \left| \frac{dE}{dt} \right|$
- Cycled forward and backward between fixed values
- Current plotted as a function of potential



In principle: useful...

- **Unknown electrochemical system**

- start analysis with CV

- survey over processes, kinetics

- identify involved species and mechanisms

- ⇒ **qualitative understanding**

- **Semi-quantitative analysis**

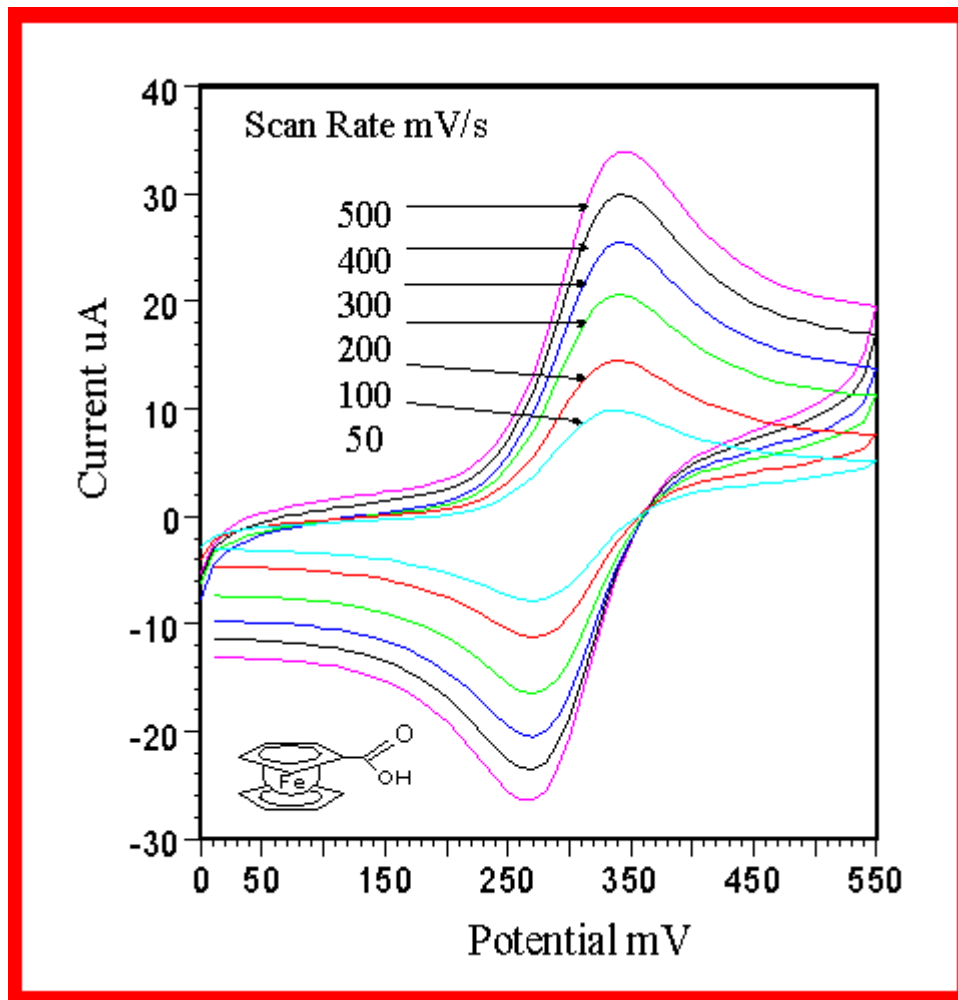
- **diagnostic capabilities**

... but difficult to understand and analyze

- **a lot of information**

- **difficult to discern!!!**

How do typical cyclic voltammograms look like?



## Measured Current

faradaic current

+

capacitive current



electrode reaction



double layer charging

→ total current density:

$$j = j_F + j_C$$
$$= j_F + C_d \frac{dE}{dt}$$

$$j = j_F + \nu C_d$$

rate constants

double layer correction

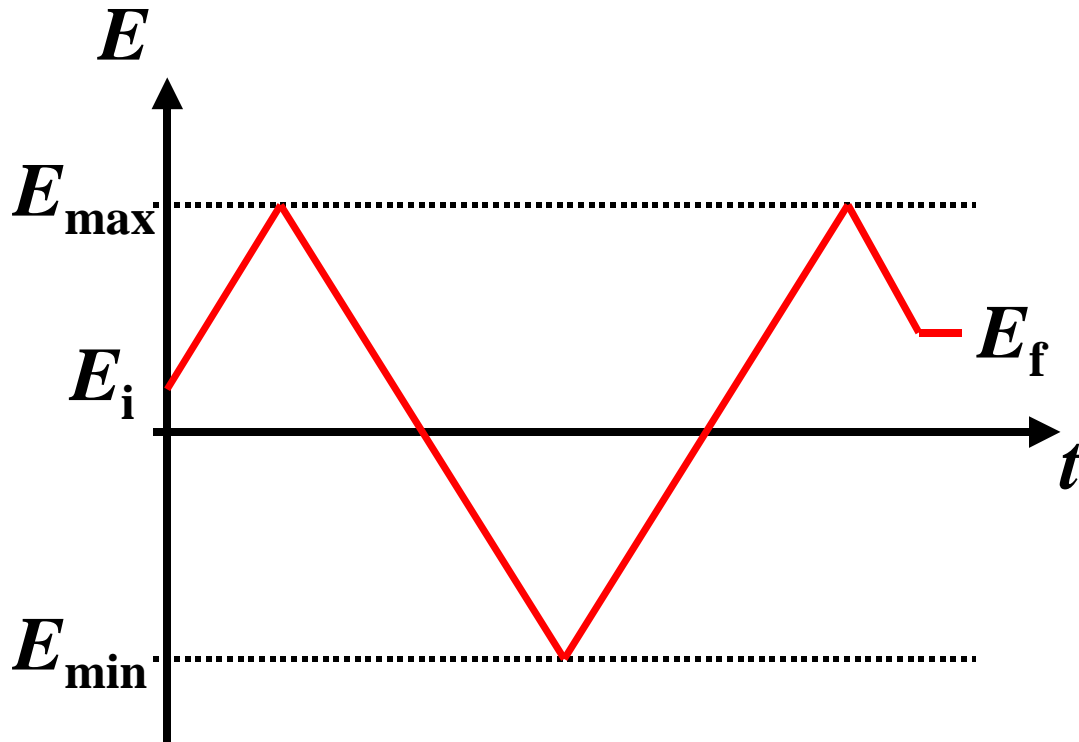
Double layer correction important if  $\nu$  is large!

What do we need?

- Nernst-equation → equilibrium
  - Butler-Volmer equation → kinetics
  - Diffusion equation → mass transport
  - Double layer charging
  - Adsorption
- ⇒ anything new??

## What is controlled in CV?

### Variation of applied potential with time



### Important parameters:

- Initial potential,  $E_i$
- Initial sweep direction
- Sweep rate,  $\nu$  [ $\text{mV s}^{-1}$ ]  $\implies$   $\sim \text{mV s}^{-1}$  to  $10^3\text{-}10^4 \text{ V s}^{-1}$
- Maximum potential,  $E_{\max}$
- Minimum potential,  $E_{\min}$   $\implies$  solvent stability
- Final potential,  $E_f$

## Sweep rate: 3 ranges of operation

(1) very slow sweeps (→ nothing new!)

$$\nu = 0.1 - 2 \text{ mV s}^{-1}$$

quasi-steady state conditions

sweep rate and reversal: no effect on  $j/E$  relationship

- corrosion
- passivation
- fuel cell reactions

(2) Oxidation or reduction of species in the bulk

$$\nu = 0.01 - 100 \text{ V s}^{-1}$$

measurement  
time (10-50 s)  
(mass transport)

- double layer charging
- uncompensated  
solution resistance

(3) Oxidation/reduction of species on surface

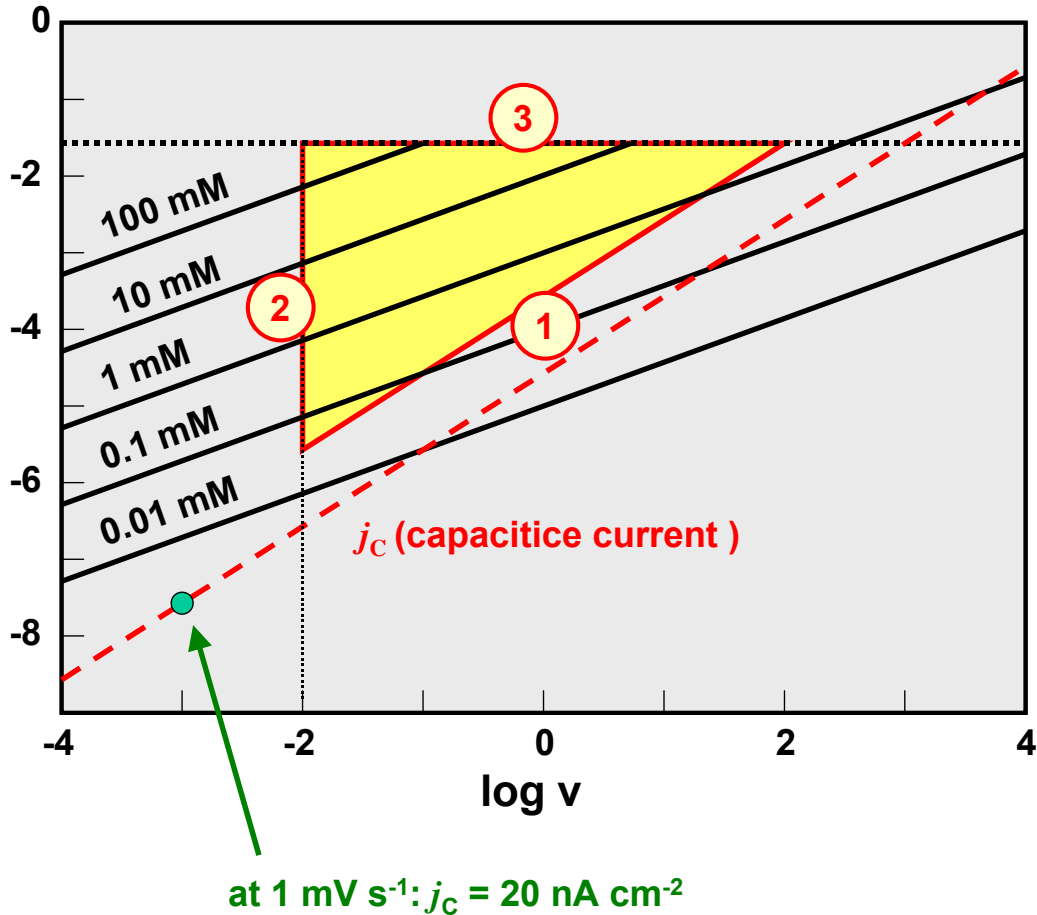
$$\nu = 0.01 - 100 \text{ V s}^{-1}$$

background currents,  
impurities

- double layer charging
- uncompensated  
solution resistance



## Optimum range of concentration and sweep rate



(1)  $j_F$  (at peak)  $\geq 10j_c$

(2)  $v > 10 \text{ mV s}^{-1}$  (avoid convection)

(3)  $j_F$  (at peak)  $< 20 \text{ mA cm}^{-2}$

(minimize effect of uncompensated solution resistance)

(4)  $c^b \leq 100 \text{ mM}$

(permit addition of supporting electrolyte)

but:  $c^b > 0.1 \text{ mM}$  (double layer charging)

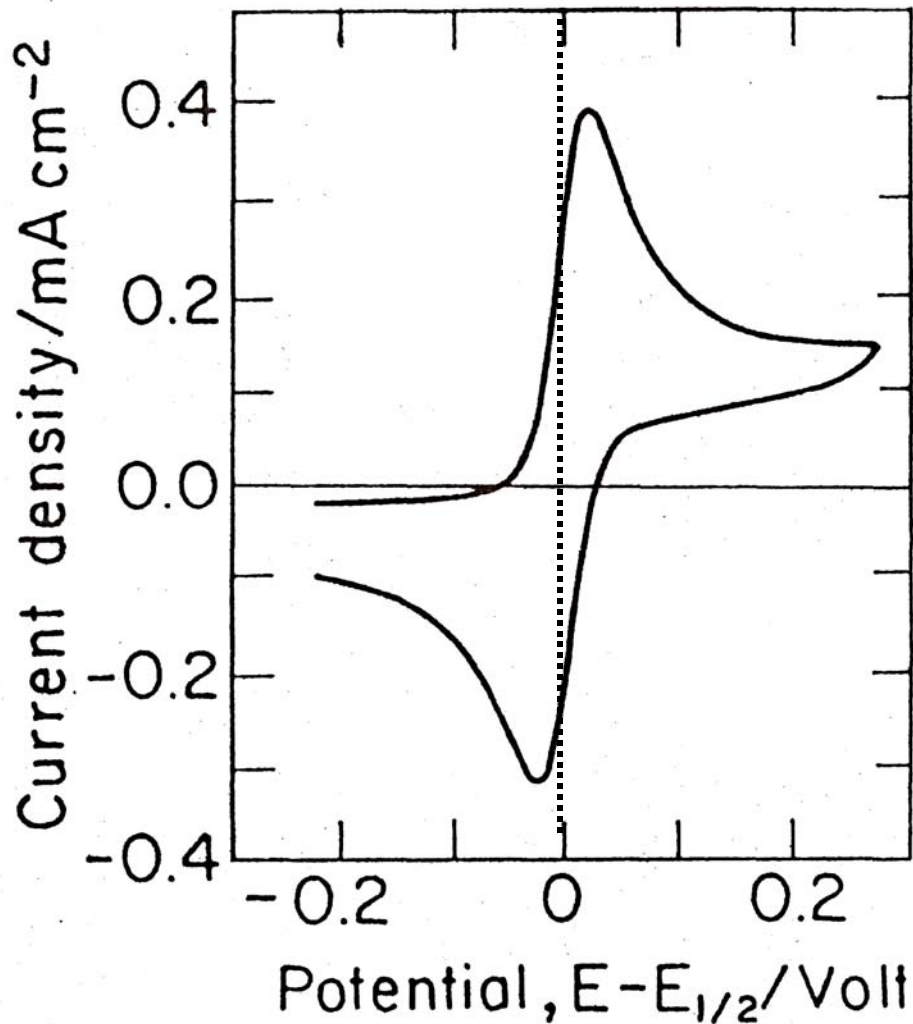
What about porous (rough) electrodes? Would they help improving the range of sweep rates?

Let's look at some typical CVs

Consider CV for simple **electron transfer process**

e.g.  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^- (\text{M})$  (anodic) – which quadrant?

$\text{Fe}^{3+} + \text{e}^- (\text{M}) \rightarrow \text{Fe}^{2+}$  (cathodic) – which quadrant?



Why is a peak observed in this plot?

Why is  $j=0$  at  $E < E^{\text{eq}}$  (or why is CV asymmetric)?

Let's start in ...

□ **Lower left corner** (cathodic region):

$E < E^{eq} \Rightarrow$  cathodic current ( $< 0$ )

$c_{ox}$  consumed (depleted near electrode)

$c_{red}$  produced (enhanced near electrode)

$\Rightarrow j = 0$  at  $E < E^{eq}$  (remember Nernst equation!)

□  $E$  increases  $\rightarrow$  towards **upper right corner** (anodic)

$c_{red}$  depleted

$c_{ox}$  produced

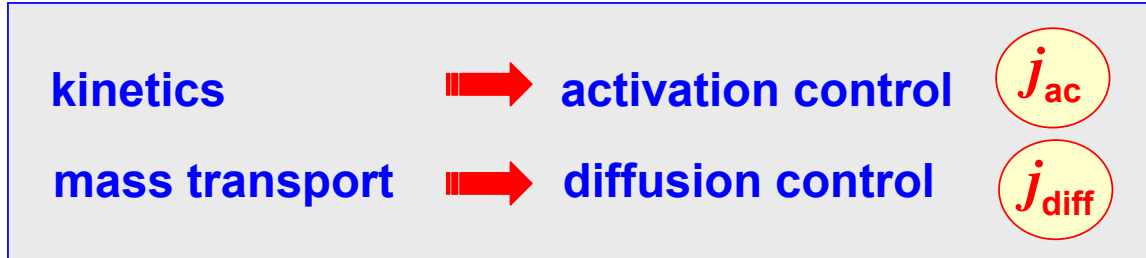
$\Rightarrow$  peak is reached at  $j = j_p$ ,  $E = E_p$

What causes occurrence of peak?

???

**Of course: Interplay of diffusion and mass transport!**

**Consider: simple phenomenology**



**Resulting current:**

$$\frac{1}{j} = \frac{1}{j_{ac}} + \frac{1}{j_{diff}}$$

□ **initially:**

$$j_{ac} \ll j_{diff} \Rightarrow j = j_{ac}$$

→  $j$  increases with  $E$  (and  $t$ )

□  $t$  proceeds,  $E$  grows →  $j_{ac}$  ↗ and  $j_{diff}$  ↘

until  $j_{ac} \approx j_{diff}$  → **MAXIMUM  $t$**

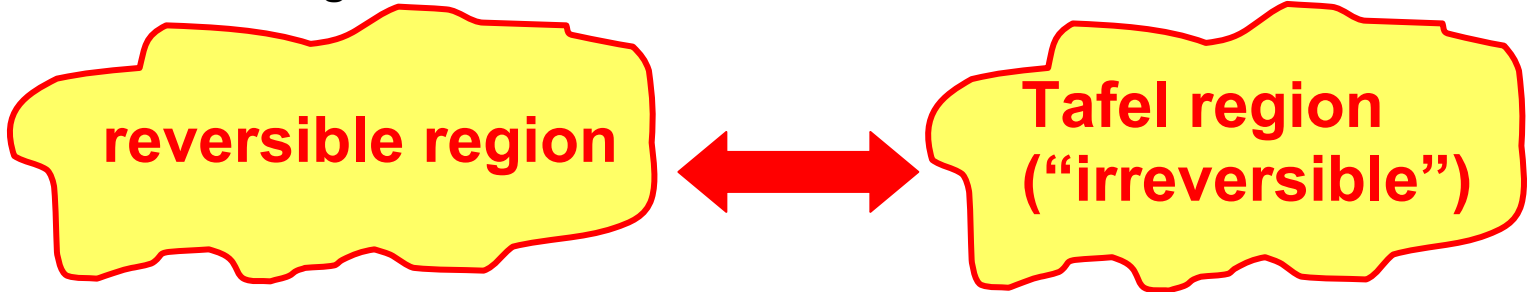
□ **further progress:**  $j_{ac} \gg j_{diff} \Rightarrow j = j_{diff}$

→  $j$  decreases with  $E$  (and  $t$ )

**You see: Same phenomena (and equations) as before!**

**Now: More detail!**

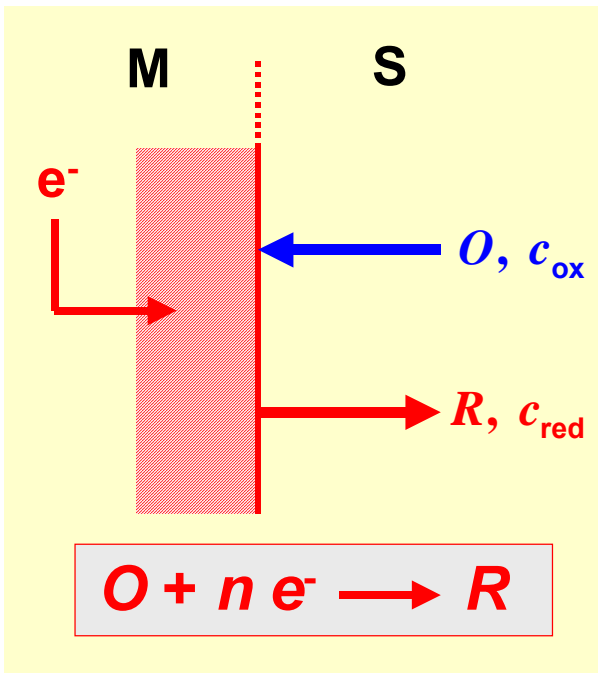
**Distinguish:**



**Which fundamental parameter is this distinction related to?**

## Semi-quantitative treatment of CV

### (1) Simple, reversible electron transfer planar electrode



Diffusion equations (both species):

$$\frac{\partial c_{ox}}{\partial t} = D_o \frac{\partial^2 c_{ox}}{\partial x^2}$$

$$\frac{\partial c_{red}}{\partial t} = D_R \frac{\partial^2 c_{red}}{\partial x^2}$$

#### Initial and boundary conditions:

$$t = 0, x = 0 \text{ (interface): } c_{ox}^s = c_{ox}^b \text{ (1), } c_{red}^s = c_{red}^b = 0 \text{ (2)}$$

$$t > 0, x \rightarrow \infty \text{ (bulk): } c_{ox} \rightarrow c_{ox}^b \text{ (3), } c_{red} \rightarrow 0 \text{ (4)}$$

Mass balance:

flux of "ox" (reaching surface) = flux of "red" (leaving surface)

$$D_o \frac{\partial c_{ox}}{\partial x} + D_R \frac{\partial c_{red}}{\partial x} = 0 \text{ (5)}$$

(careful: provided that both species are soluble!)

One condition is missing! – "The reversible case"

What does “reversibility” mean in this context?

Concentrations at the surface,  $c_{\text{ox/red}}^s$ , and potential  $E$  are related via (6)

□ Nernst-equation

$$E(t) = E^0 + \frac{RT}{nF} \ln \frac{c_{\text{ox}}^s(t)}{c_{\text{red}}^s(t)}$$

□ linear Tafel region (high overpotentials)

$$nFk^0 c_{\text{ox}}^s \exp\left(\frac{(1-\alpha^c)F|E - E^0|}{RT}\right) = nFD_o \frac{\partial c_{\text{ox}}}{\partial x} \Big|_{x=0}$$

Potential is externally controlled function of time:

cathodic scan:  $E = E_i - vt$ , for  $0 < t < t_{\text{rev}}$

anodic scan:  $E = E_i - vt_{\text{rev}} + v(t - t_{\text{rev}})$ , for  $t_{\text{rev}} < t$

Overall:

Well-defined problem! Diffusion equations can be solved with given conditions in Laplace-domain – however, back-transformation into time-domain has to be done numerically

Don't go through this!

Let's consider instead some important parameters!

## Quantitative parameters for reversible CVs

### Peak potential:

$$E_p(\text{rev}) = E_{1/2} \pm 1.1 \frac{RT}{nF}$$

+ : anodic sweep

- : cathodic sweep

Here:  $E_{1/2}$  is the half-wave potential at which  $j = \frac{1}{2} j_{\text{diff}}$

$$E_{1/2} = E^0 - \frac{RT}{nF} \ln \left( \frac{D_O}{D_R} \right)^{1/2}$$

usually:  $E_{1/2} \approx E^0$  since ( $D_O \approx D_R$ )

### Note:

- $E_p(\text{rev})$  is independent of  $\nu$   
(criterion for reversibility!!!)
- $E_p(\text{rev})$  is independent of concentration!



## Peak current density:

$$j_p(\text{rev}) = 0.446nF \left( \frac{nFD_o}{RT} \right)^{1/2} c_{\text{ox}}^b v^{1/2}$$

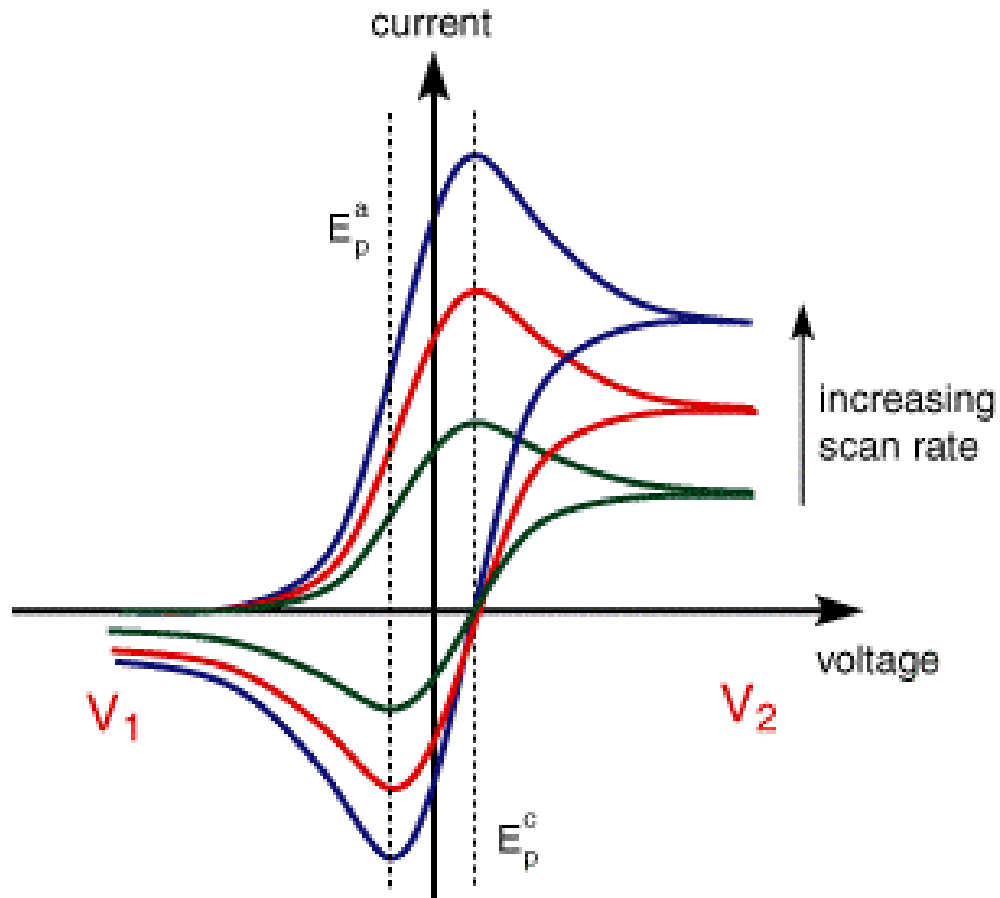
e.g.:  $n = 1$ ,  $D_o = 2.0 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ,  $c_{\text{ox}}^b = 10^{-4} \text{ mol cm}^{-3}$

$$j_p(\text{rev}) = 0.12 \text{ A cm}^{-2} v^{1/2} [\text{in V s}^{-1}]$$

at room T:

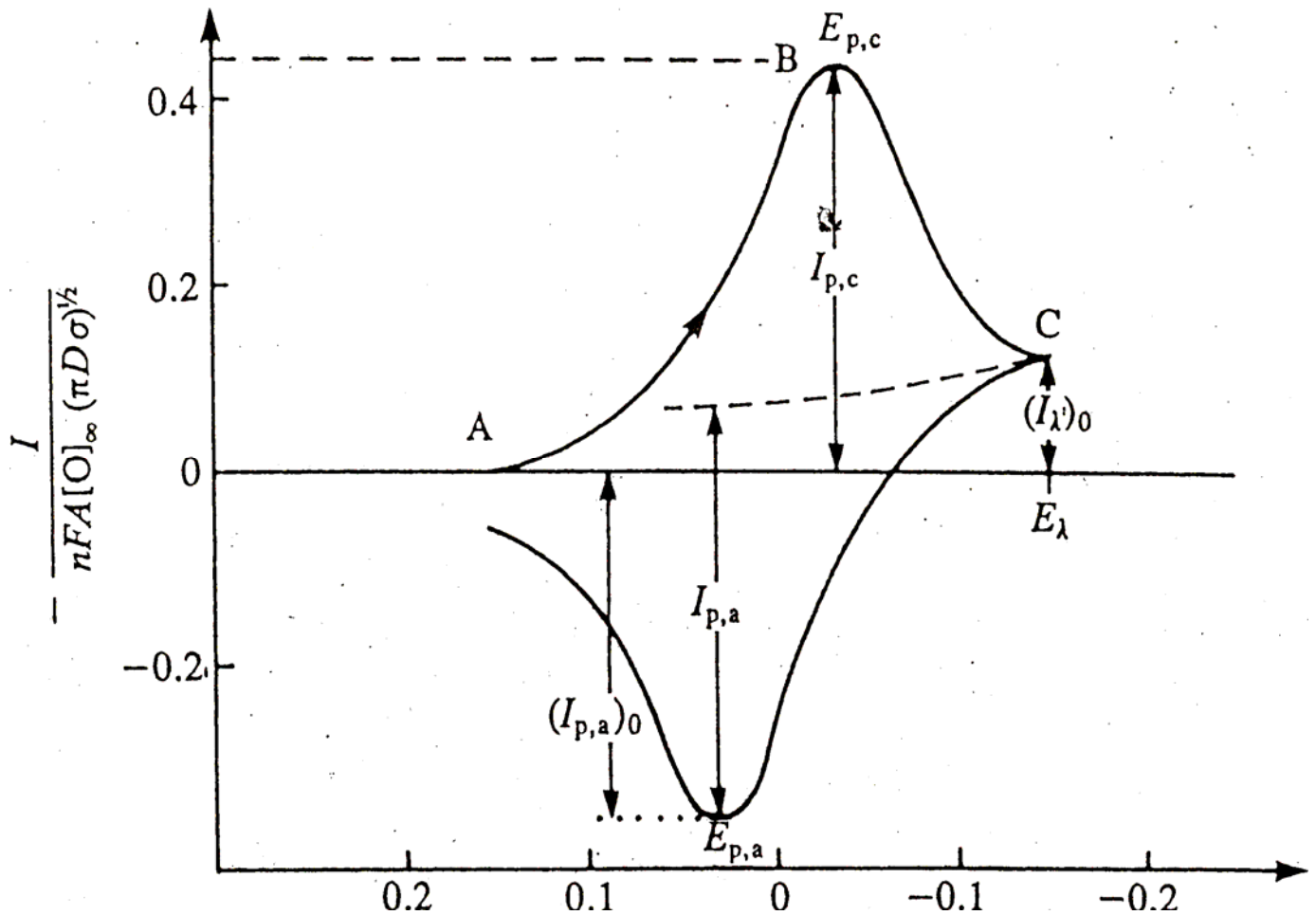
$$j_p(\text{rev}) = \left[ 2.72 \cdot 10^5 n^{3/2} D_o^{1/2} c_{\text{ox}}^b \right] v^{1/2}$$

$\left[ \frac{\text{A}}{\text{cm}^2} \right]$        $\left[ \frac{\text{cm}^2}{\text{s}} \right]$      $\left[ \frac{\text{mol}}{\text{cm}^3} \right]$      $\left[ \frac{\text{V}}{\text{s}} \right]$

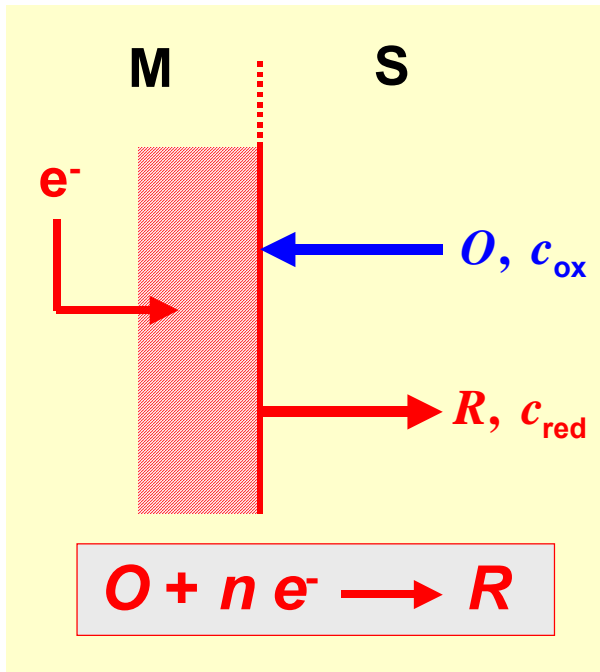


## Diagnostic information in reversible CV:

- $j_p \propto \nu^{1/2}$
- $E_p$  independent of  $\nu$
- $|E_p - E_{p/2}| = \frac{56.6}{n} \text{ mV}$ , where  $E_{p/2} = E(I = I_p/2)$
- $E_{p,a} - E_{p,c} = \frac{57}{n} \text{ mV}$
- $|I_{p,a}/I_{p,c}| = 1$



(2) Irreversible ET at planar electrode, linear Tafel region



linear sweep and CV lead to the same voltammetric profile, no inverse peak appears on inverting the scan direction

Reduction as an example

$$nFD_O \left. \frac{\partial c_{ox}}{\partial x} \right|_{x=0} = nFk^0 c_{ox}^s \exp \left( - \frac{(1-\alpha^c)F(E-E^0)}{RT} \right)$$

$$= nFk^0 c_{ox}^s \exp \left( - \frac{(1-\alpha^c)F(E_i-E^0)}{RT} \right) \times \exp(-\beta t)$$

where  $E = E_i - vt$  and  $\beta = \frac{(1-\alpha_c)F}{RT} v$

## Peak potential:

$$E_p(\text{irrev}) = E^0 - \frac{RT}{(1-\alpha_c)F} \left[ 0.780 + \frac{1}{2} \ln \left( \frac{(1-\alpha_c)FD_o}{RT(k^0)^2} \right) \right] + \frac{1}{2} \ln v$$

i.e. depends on  $\ln v$

## Peak current density:

$$j_{p,c}(\text{irrev}) = -2.99 \cdot 10^5 n (1-\alpha_c) c_{\text{ox}}^b D_o^{1/2} v^{1/2}$$

$\left[ \frac{\text{A}}{\text{cm}^2} \right]$        $\left[ \frac{\text{mol}}{\text{cm}^3} \right]$     $\left[ \frac{\text{cm}^2}{\text{s}} \right]$     $\left[ \frac{\text{V}}{\text{s}} \right]$

e.g.:  $\alpha_c = 0$ ,  $n = 1$ ,  $D_o = 2.0 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ,  $c_{\text{ox}}^b = 10^{-4} \text{ mol cm}^{-3}$

$$j_p(\text{irrev}) = -0.134 \text{ A cm}^{-2} v^{1/2} [\text{in V s}^{-1}]$$

Alternative expression for  $j_{p,c}(\text{irrev})$ :

$$j_{p,c}(\text{irrev}) = -0.227 n F k^0 c_{\text{ox}}^s \exp \left( -\frac{(1-\alpha_c)F(E_p(\text{irrev}) - E^0)}{RT} \right)$$

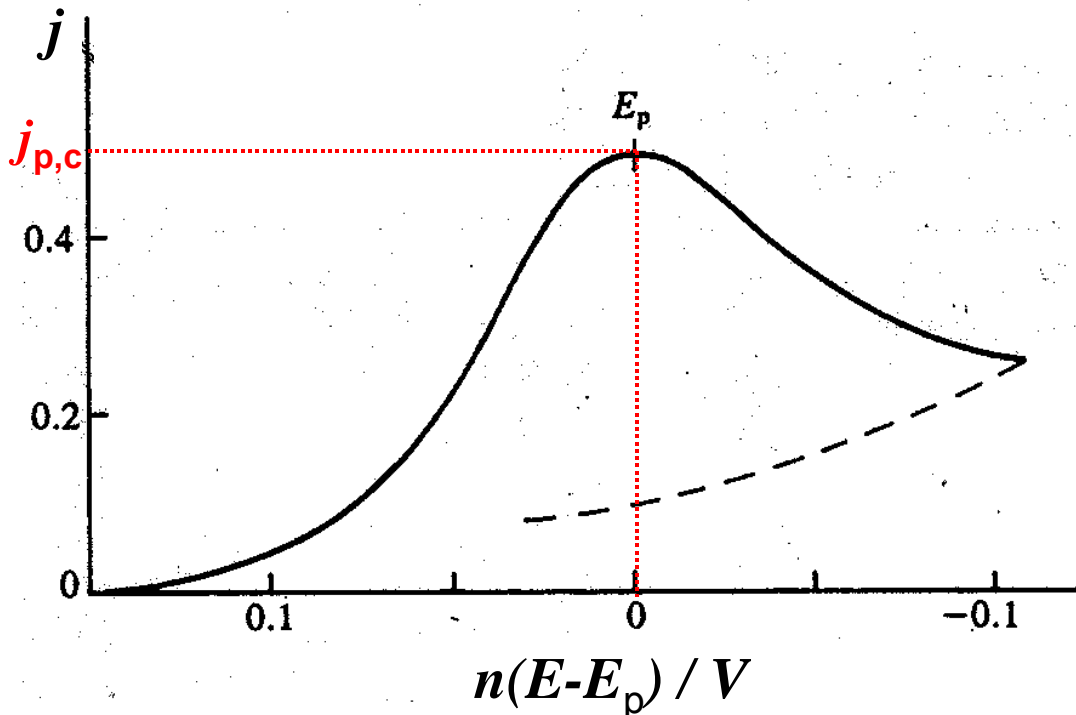
↑ effect of mass transport!

## Ratio of peak current densities (simple ET)

$$\left| \frac{j_p(\text{irrev})}{j_p(\text{rev})} \right| = 1.107 \left( \frac{1-\alpha_c}{n} \right)^{1/2}$$

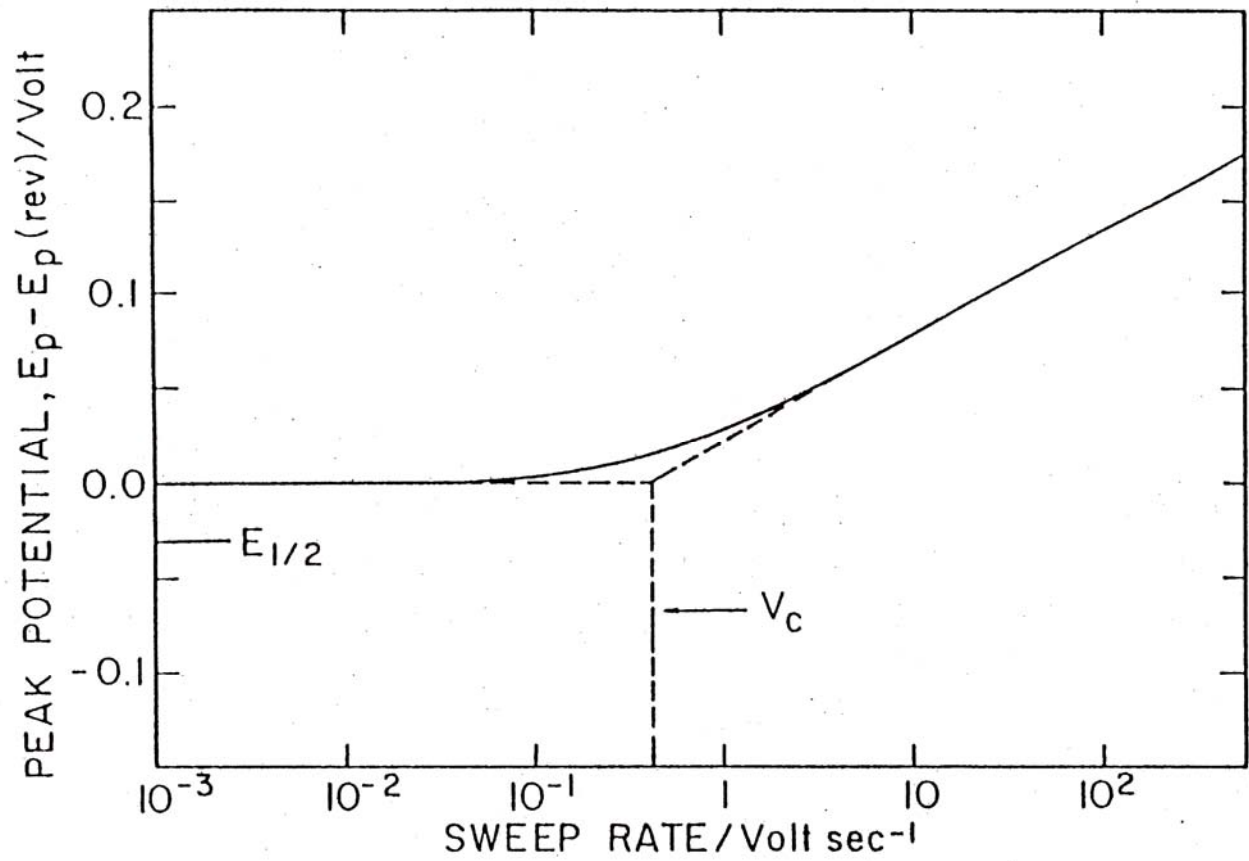
e.g.  $\alpha_c = 0.5$ ,  $n = 1 \Rightarrow \left| \frac{j_p(\text{irrev})}{j_p(\text{rev})} \right| = 0.78$  (usually < 1)

## Linear sweep voltammogram for irreversible system



- well-separated anodic and cathodic peak (independent)
- current decay upon inverting sweep direction
- peaks at larger (over)potentials compared to reversible system
- $E_p$  (irrev) depends on sweep rate
- larger  $\nu$   $\rightarrow$  broader and lower peaks, i.e. more irreversible

## Peak potential as a function of sweep rate



Reversibility is controlled by sweep rate  $\nu$  !

## Quasi-reversible systems

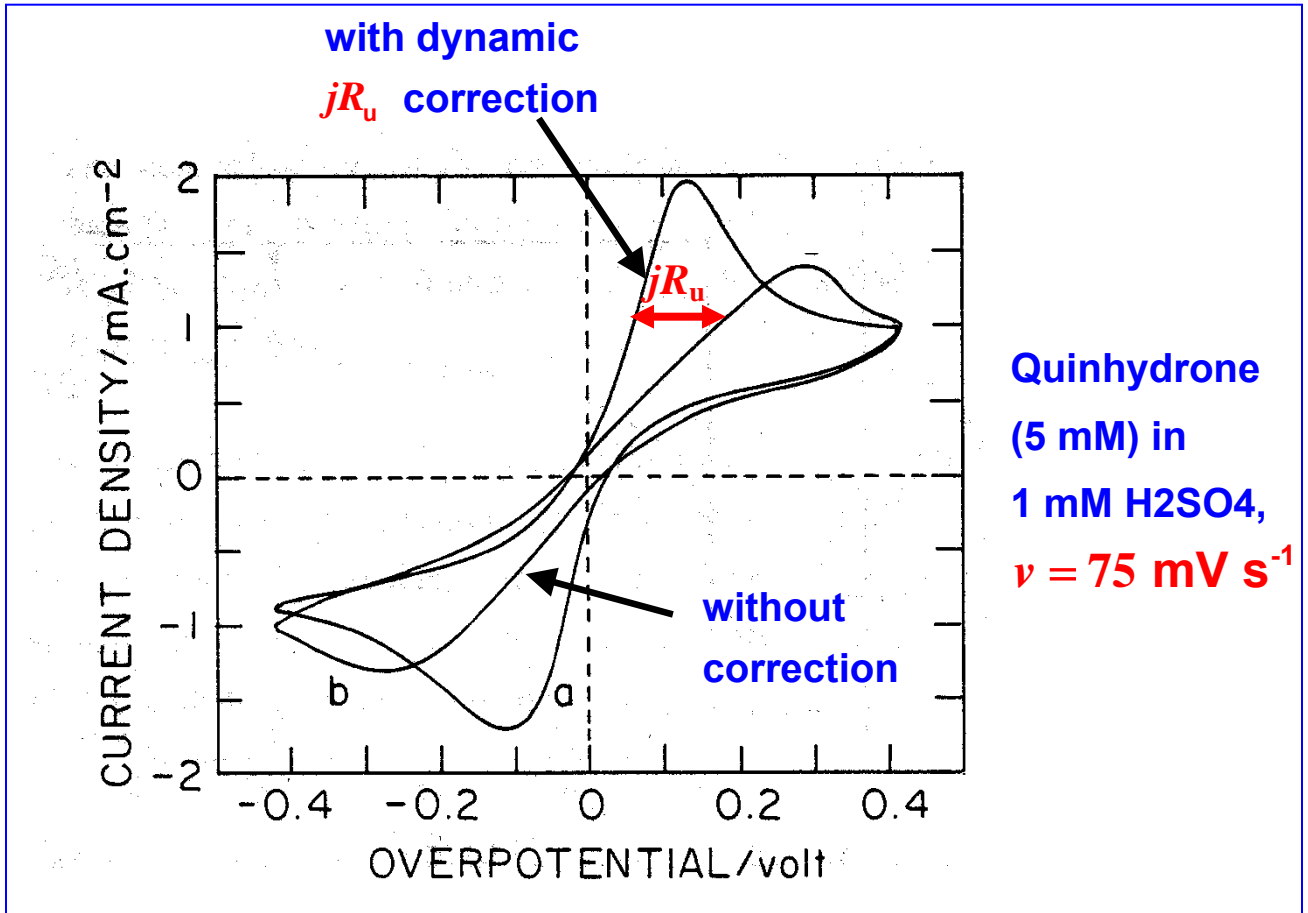
**General rule: “irreversibility” increases with increasing sweep rate  $\nu$**

### Extent of “irreversibility”:

- large sweep rates
- widely separated anodic and cathodic peaks
- decrease in peak current relative to the reversible case

**CV: technique with potential control!!! – Problematic!**

- ❑ **Problem:** potential drop  $jR_u$  due to uncompensated solution resistance
- ❑ Actual **interfacial potential** is smaller than controlled potential (between -WE and CE),  $|E_{int}| = |E_f| - jR_u$
- ❑ Effect: **reduced current peak** (flattened CV) at apparently higher potential

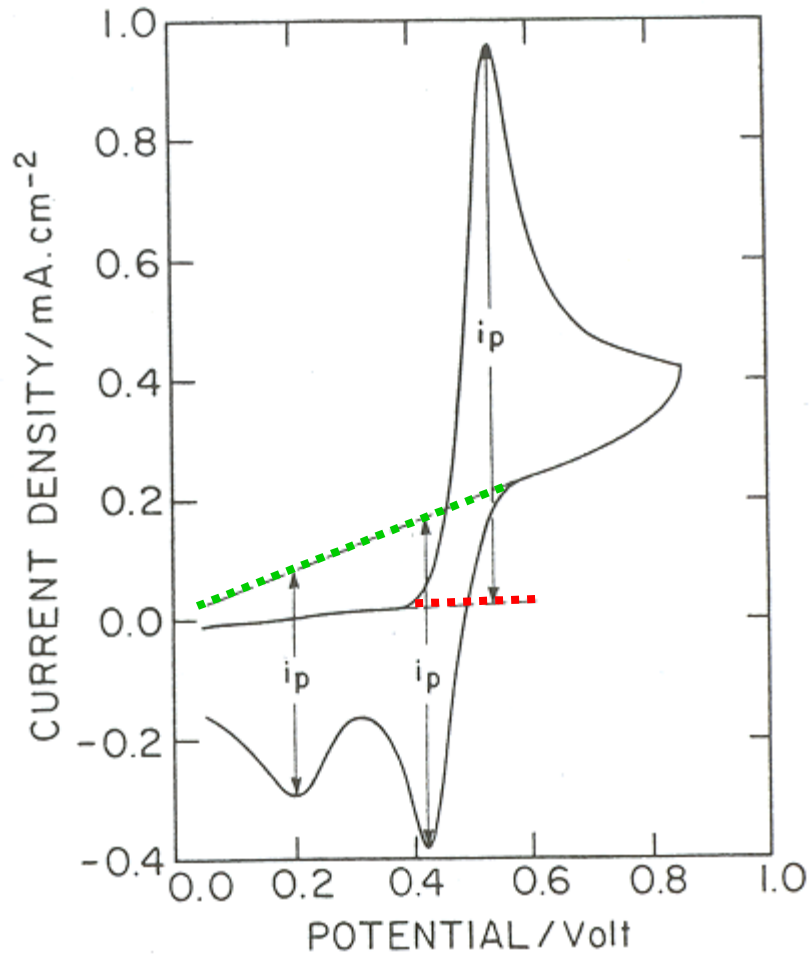


**Distorted shape of CV in particular in vicinity of peak:  
effectively reduced sweep rate at the interface near peak!**



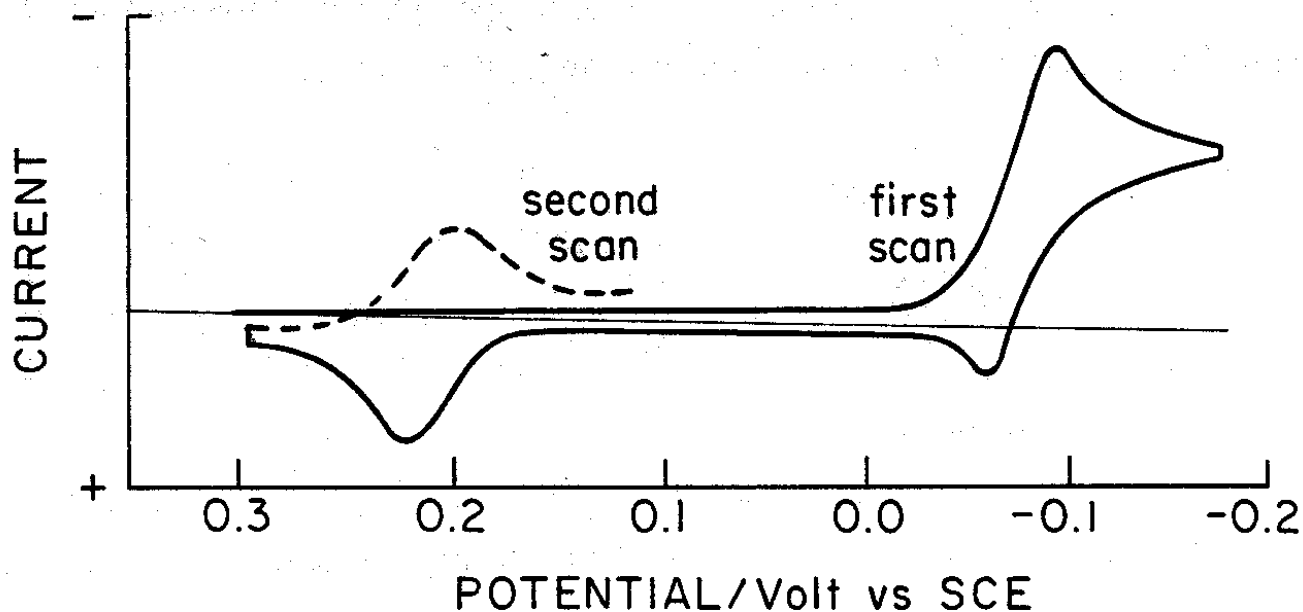
## Determine peak current density in CV

- ❑ **extrapolate baseline** (no theoretical basis for this – imaginative extrapolation)
- ❑ **weakness of CV** when used as a **quantitative** tool

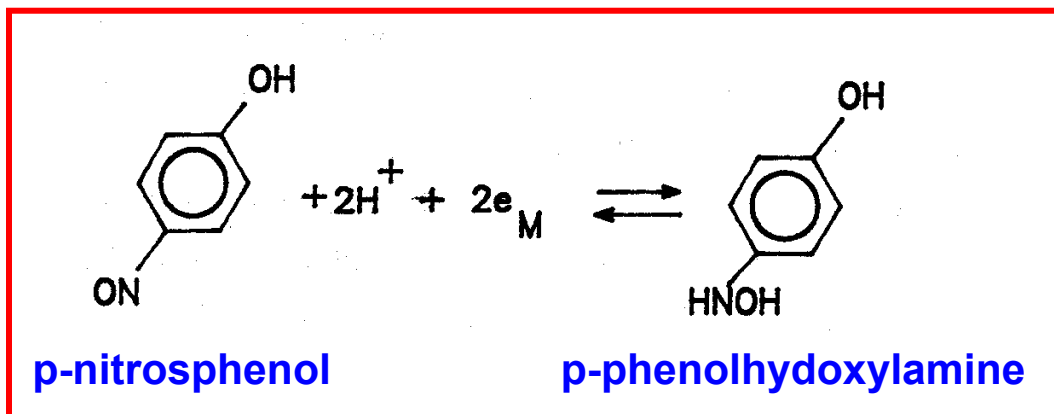


Use of CV: qualitative studies of reactions in certain potential range

Example 1: CV of dropping mercury electrode (DME) in solution of p-nitrosphenol in acetate buffer



- Start at **0.3 V vs. SCE** in **cathodic direction**:  
**first reduction peak at -0.1 V**



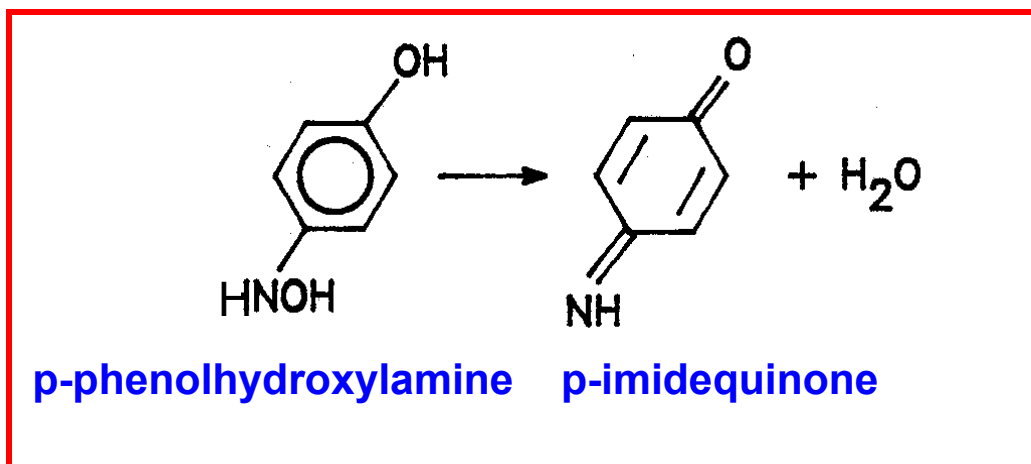
- **anodic return sweep**: reverse reaction → **peak at -0.05 V**, position as expected, but **suppressed**
- **another unexpected anodic peak at +0.22V**, corresponds to **cathodic peak not seen in first scan!**

**What is going on?**

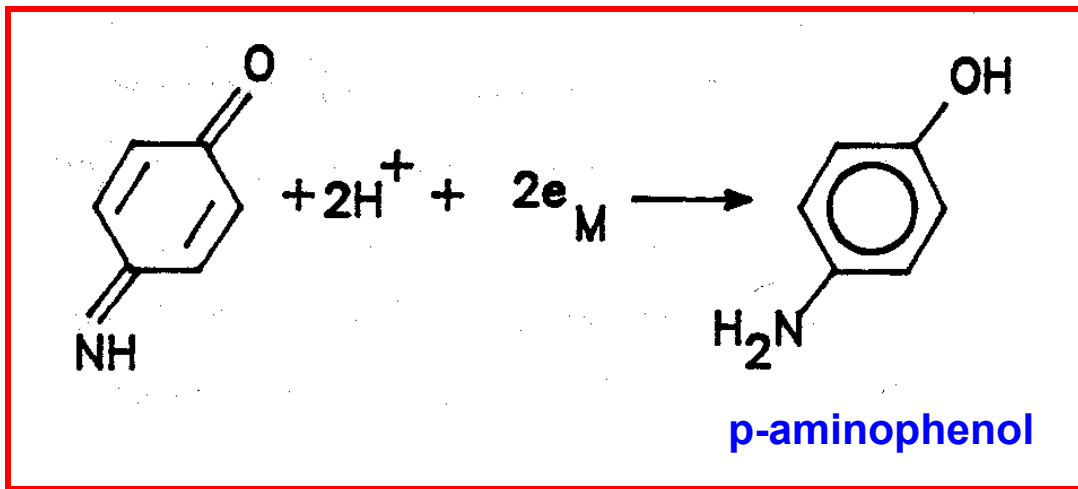
**Chemical reaction following charge transfer**

**Producing new redox couple!**

**Decomposition of p-phenohydroxylamine**



New redox couple:

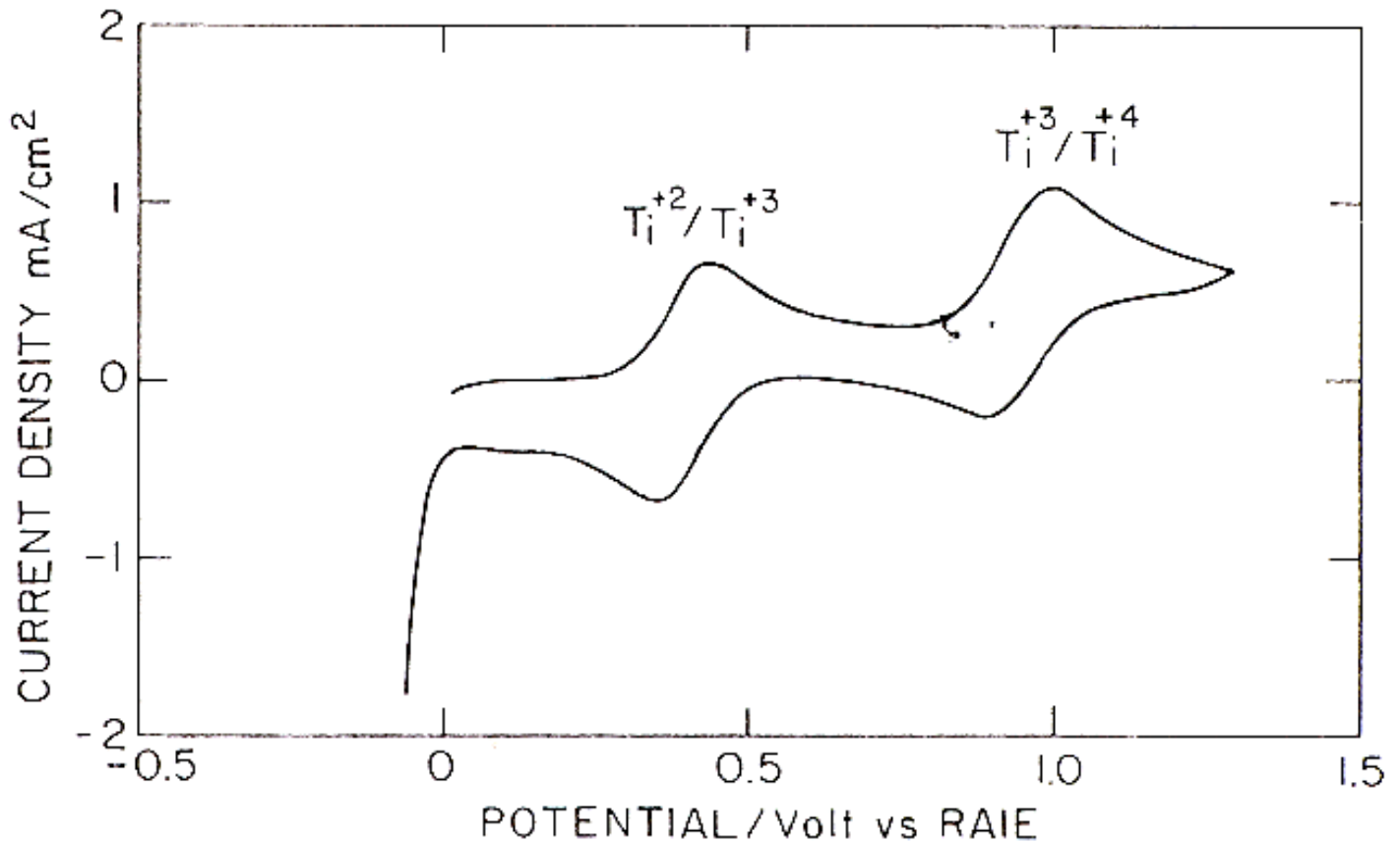


Reaction sequence: **ECE** mechanism

(**electrochemical** – **chemical** – **electrochemical**)

**Example 2:** reduction of  $Ti^{4+}$  in 1:2 NaCl/ $AlCl_3$ ,  $Ti^{2+}$  from anodic dissolution of Ti, Al-wire as reference electrode (separate compartment)

Sweep rate (or scan rate):  $\nu = 100 \text{ mV s}^{-1}$



**Two reduction steps, separated by ~0.5 V.**

**Reversible or irreversible steps? Which step has the higher rate constant?**

~ 60 mV

