Voltammetry (stirred)

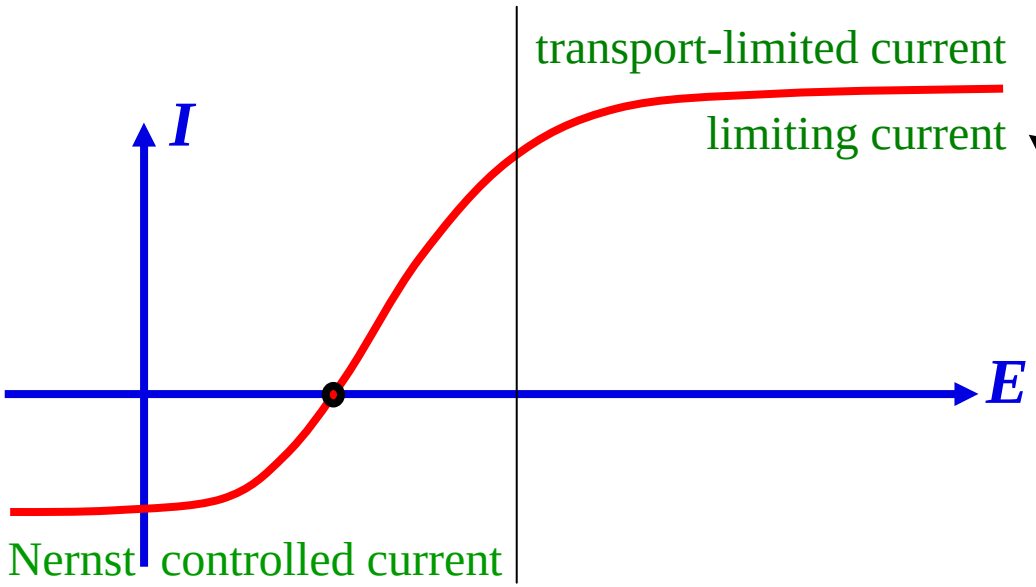
- Stationary electrode
- Stirred = mass transport by convection
- Vary potential linearly with time
- Measure current vs time

Theory

assume $Ox + n\,e^- \leftrightarrow Red$

- both Ox and Red are soluble
- reversible reaction (electrochemically)
- potential varies

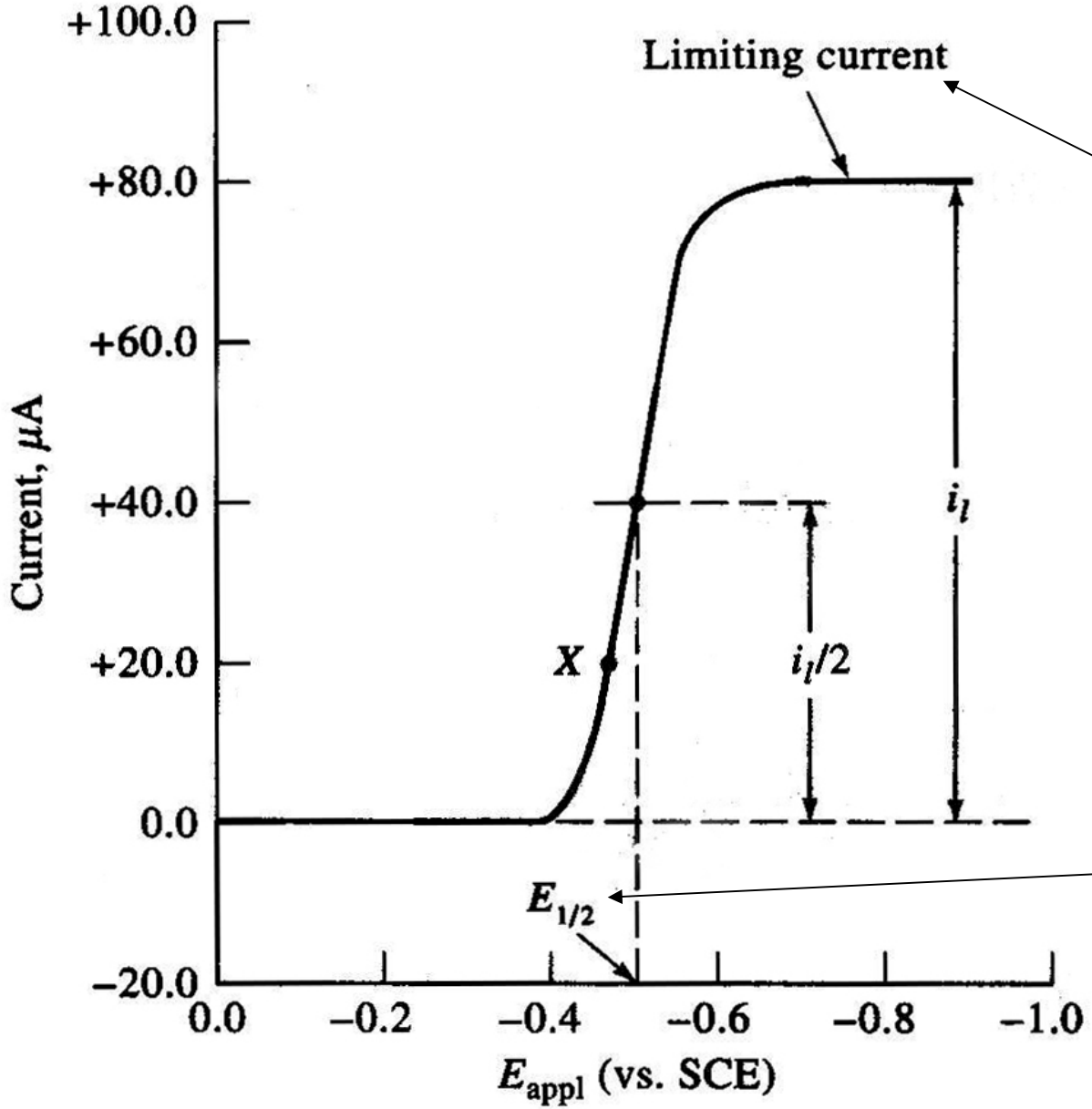
Define - Limiting Current as steady state current when [Ox] = 0 at electrode surface i.e., applied potential is sufficiently cathodic such that all Ox is reduced at electrode



$$I = \frac{nFADC_{bulk}}{\delta}$$

Gives quantitative information

$$E = E^{o} - \frac{RT}{nF} \ln \frac{[Red]}{[Ox]}$$

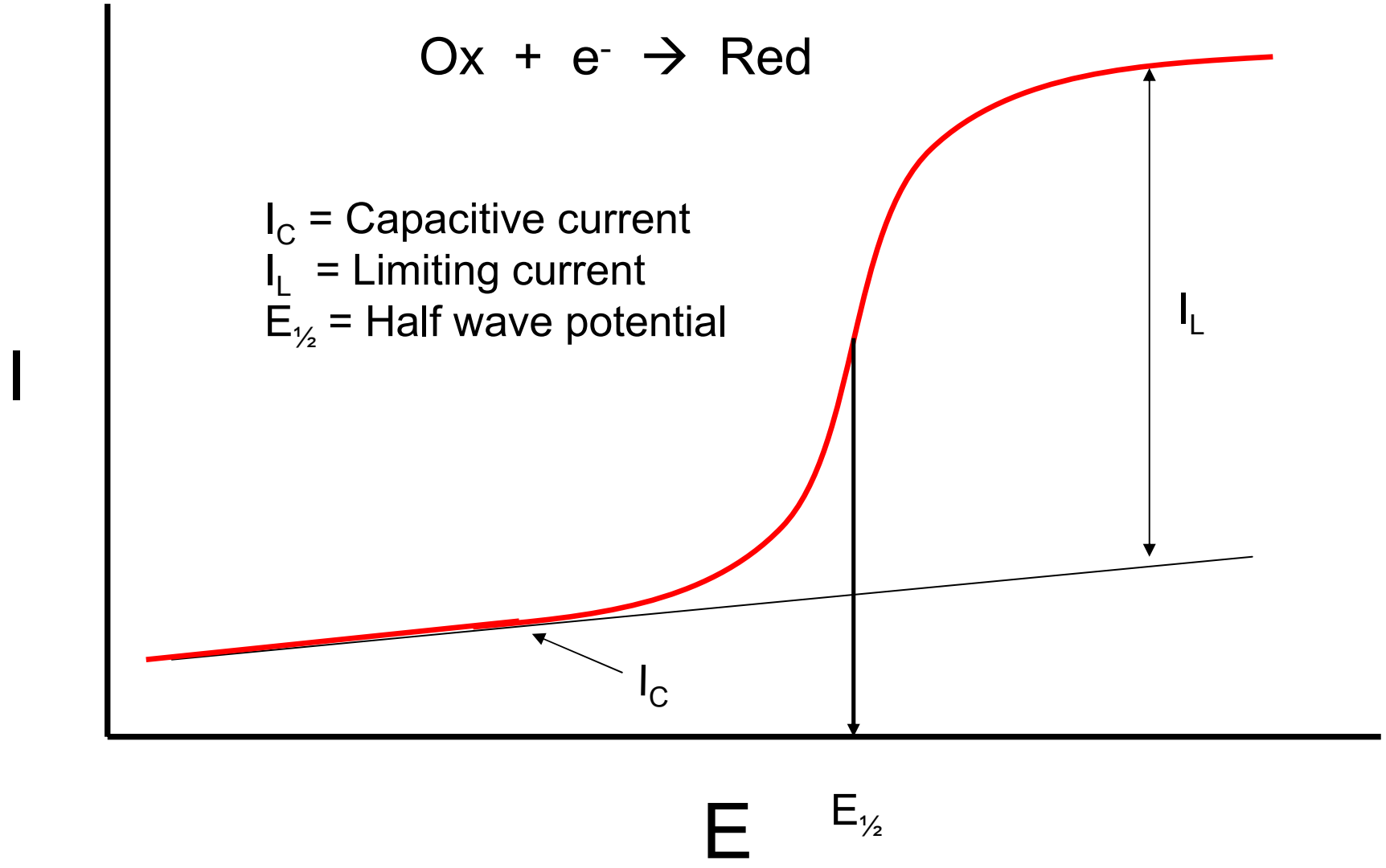


quantitative information

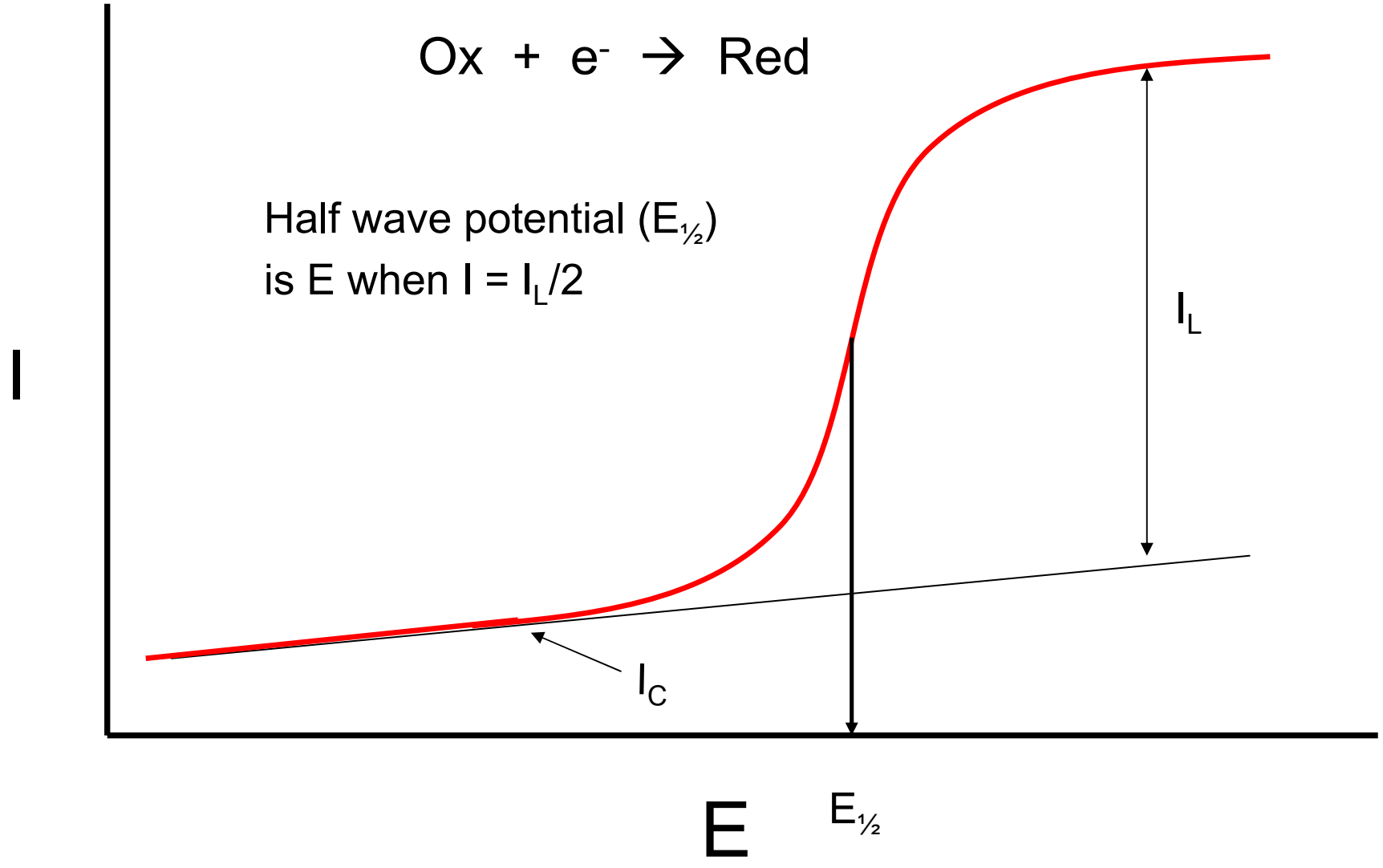
qualitative information

Linear-scan voltammogram → for stirred solution

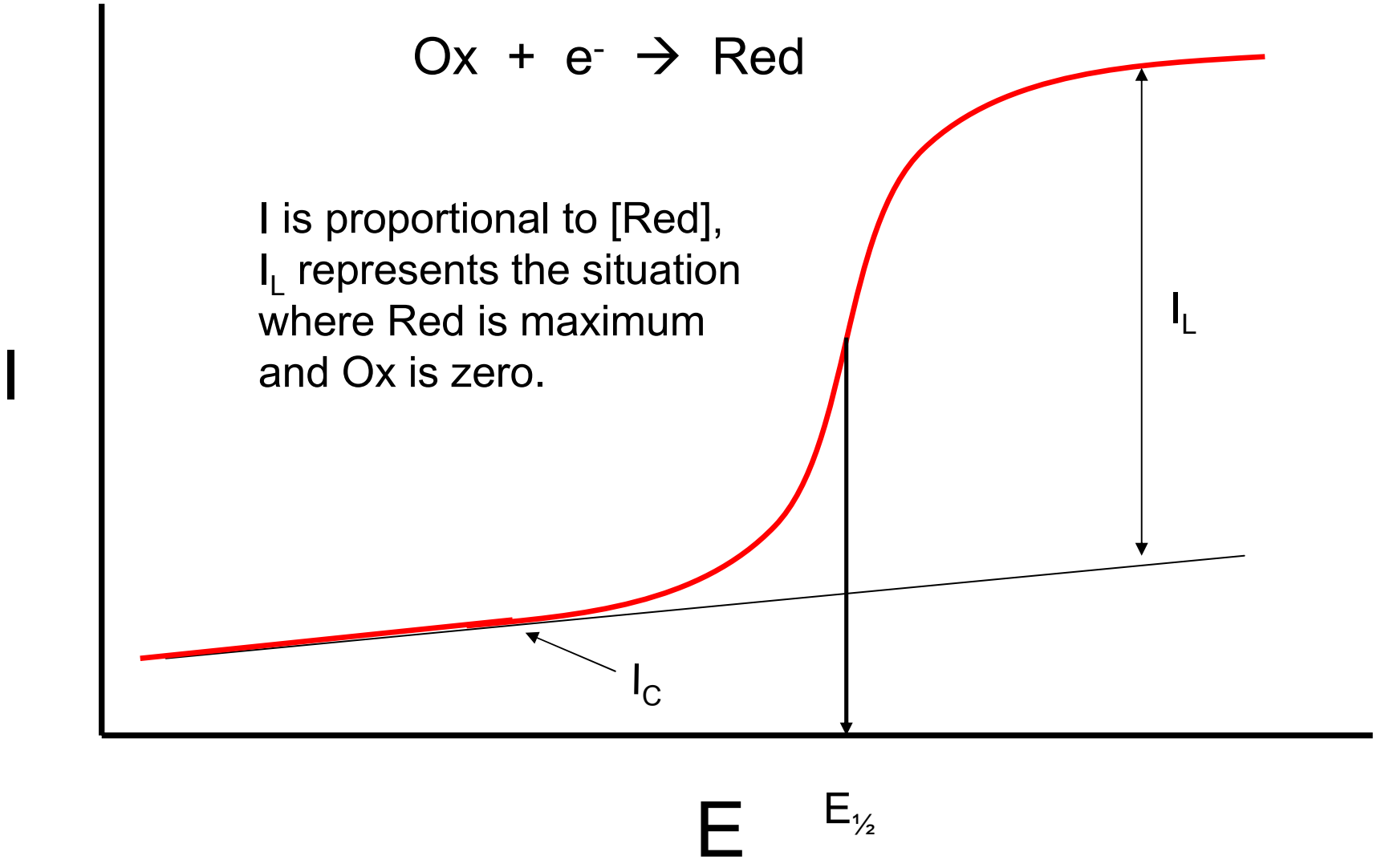
Linear Scan Voltammetry (stirred)



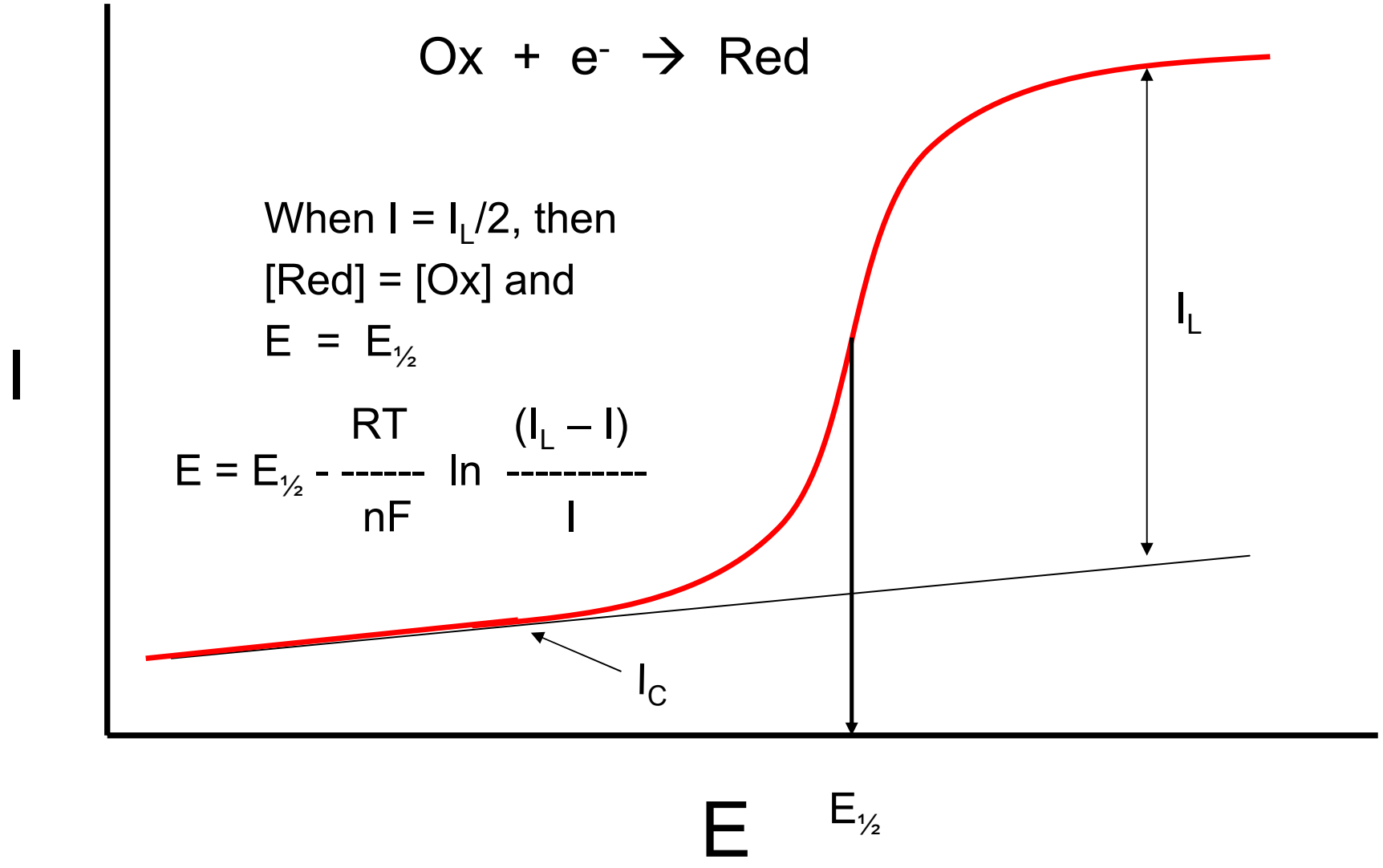
Linear Scan Voltammetry (stirred)



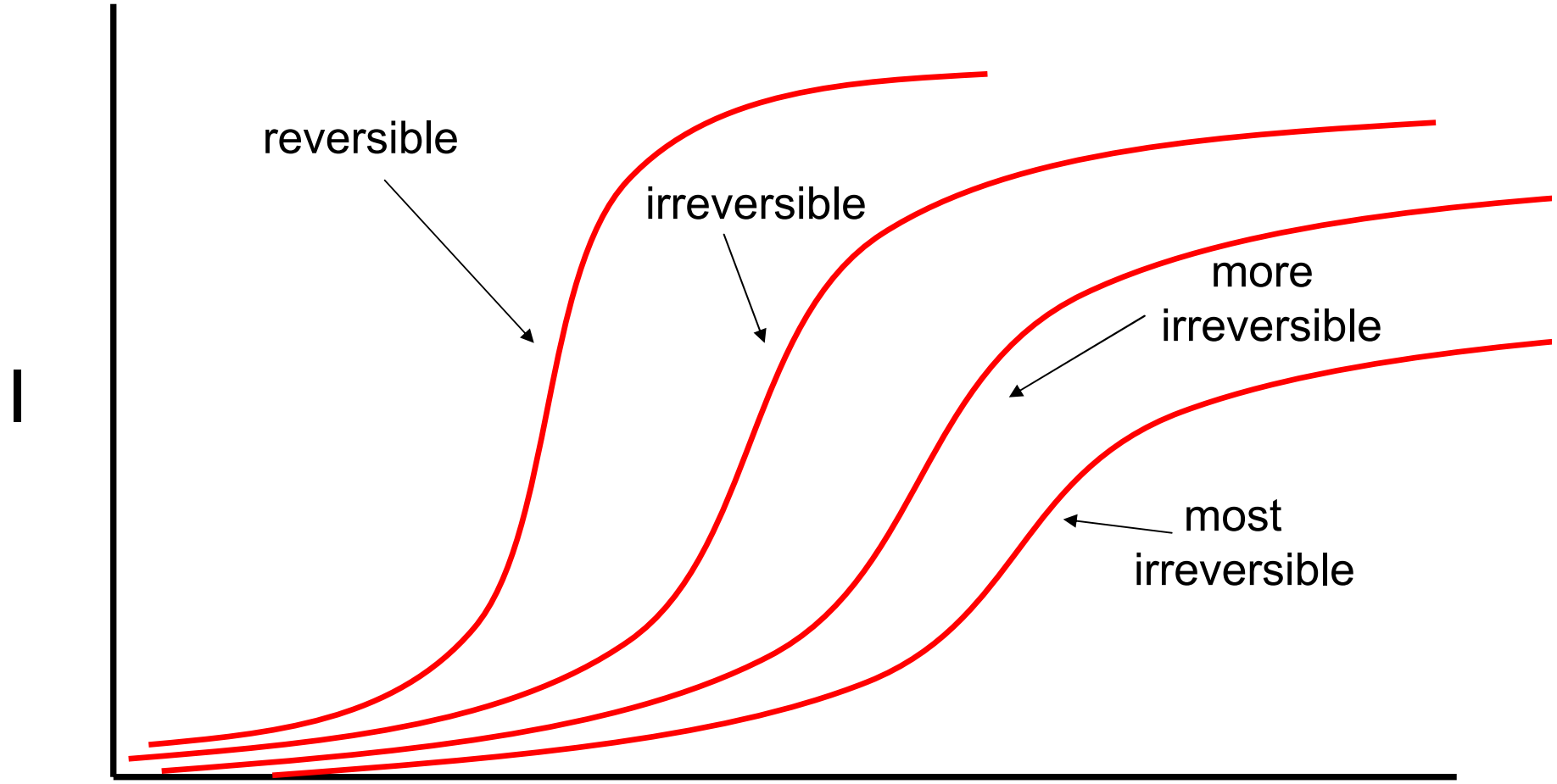
Linear Scan Voltammetry (stirred)



Linear Scan Voltammetry (stirred)

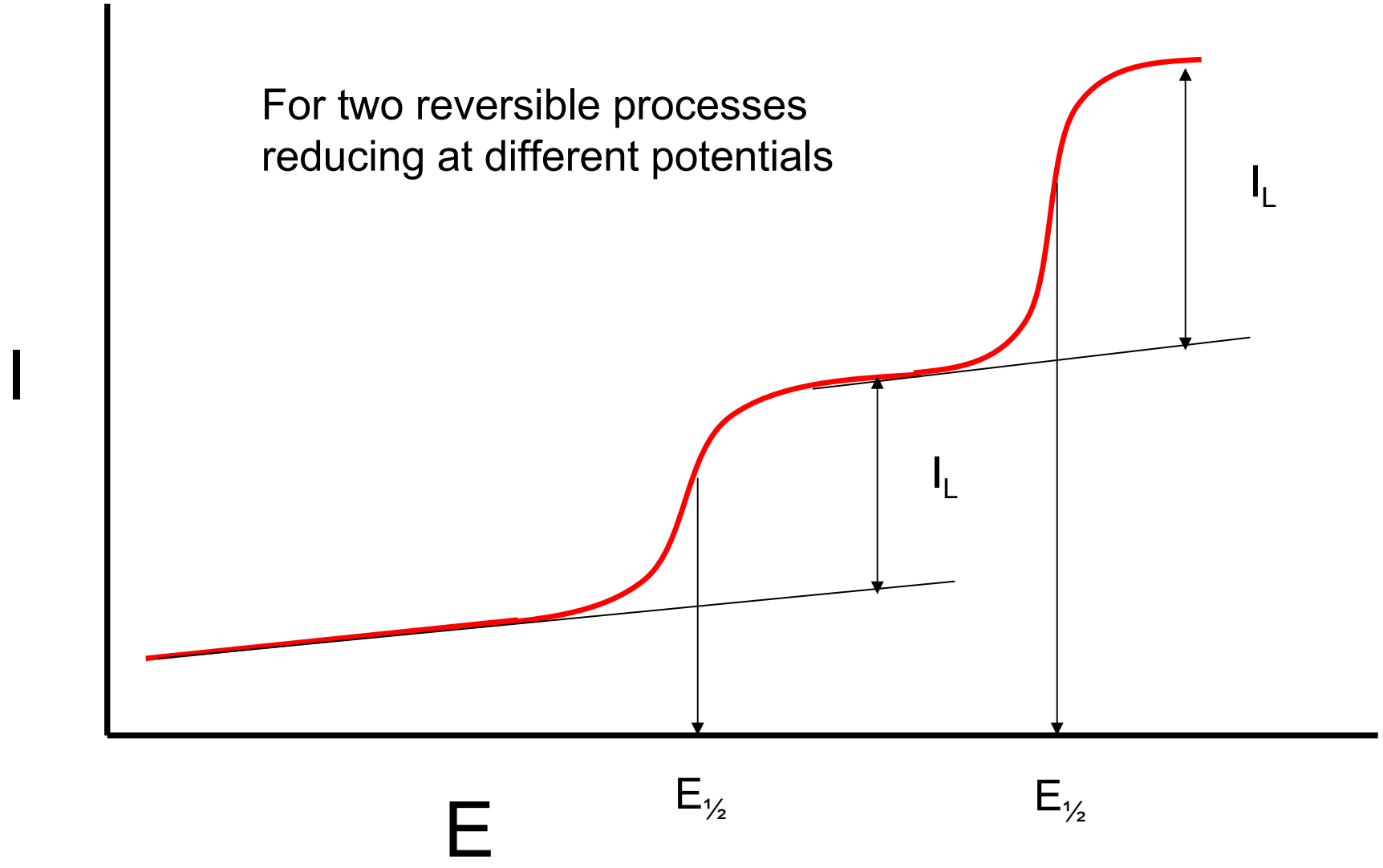


Linear Scan Voltammetry (stirred)



Can assign rate constants (k) for irreversible processes

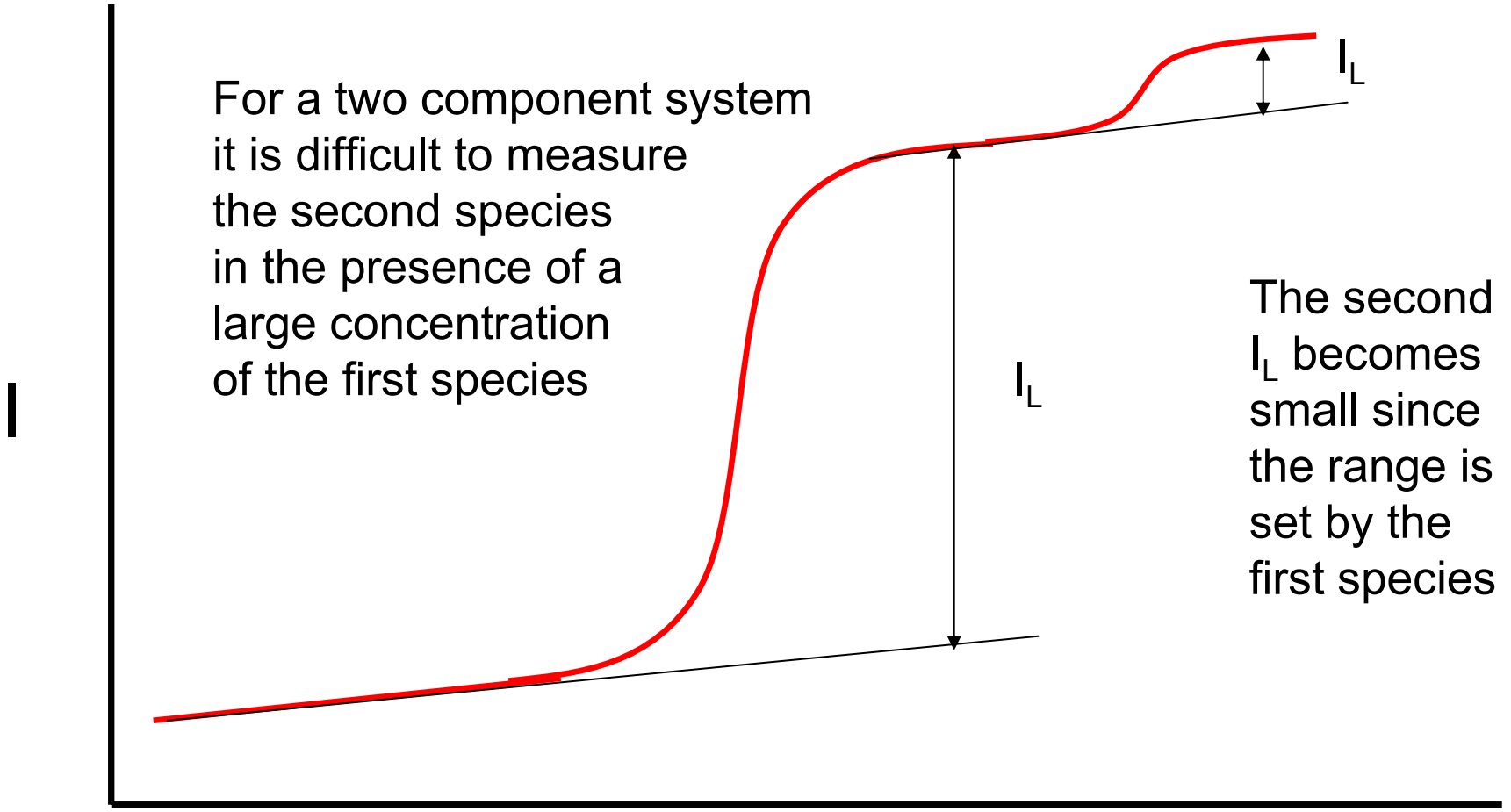
Linear Scan Voltammetry (stirred)



Linear Scan Voltammetry (stirred)

- Normally use Pt or C (graphite) electrodes
- Better to use rotating electrode than stir bar
- LSV can be used for quantitative analysis
- Can measure many metal ions & organics
- Fairly sensitive due to convective mass transport, i.e., I_F is large
- The output signal in the form of a wave is considered a drawback
  - can be difficult to perform data analysis
  - multiple components gives stacked waves

Linear Scan Voltammetry (stirred)



This problem is inherent for techniques that produce waves

Voltammetry (unstirred)

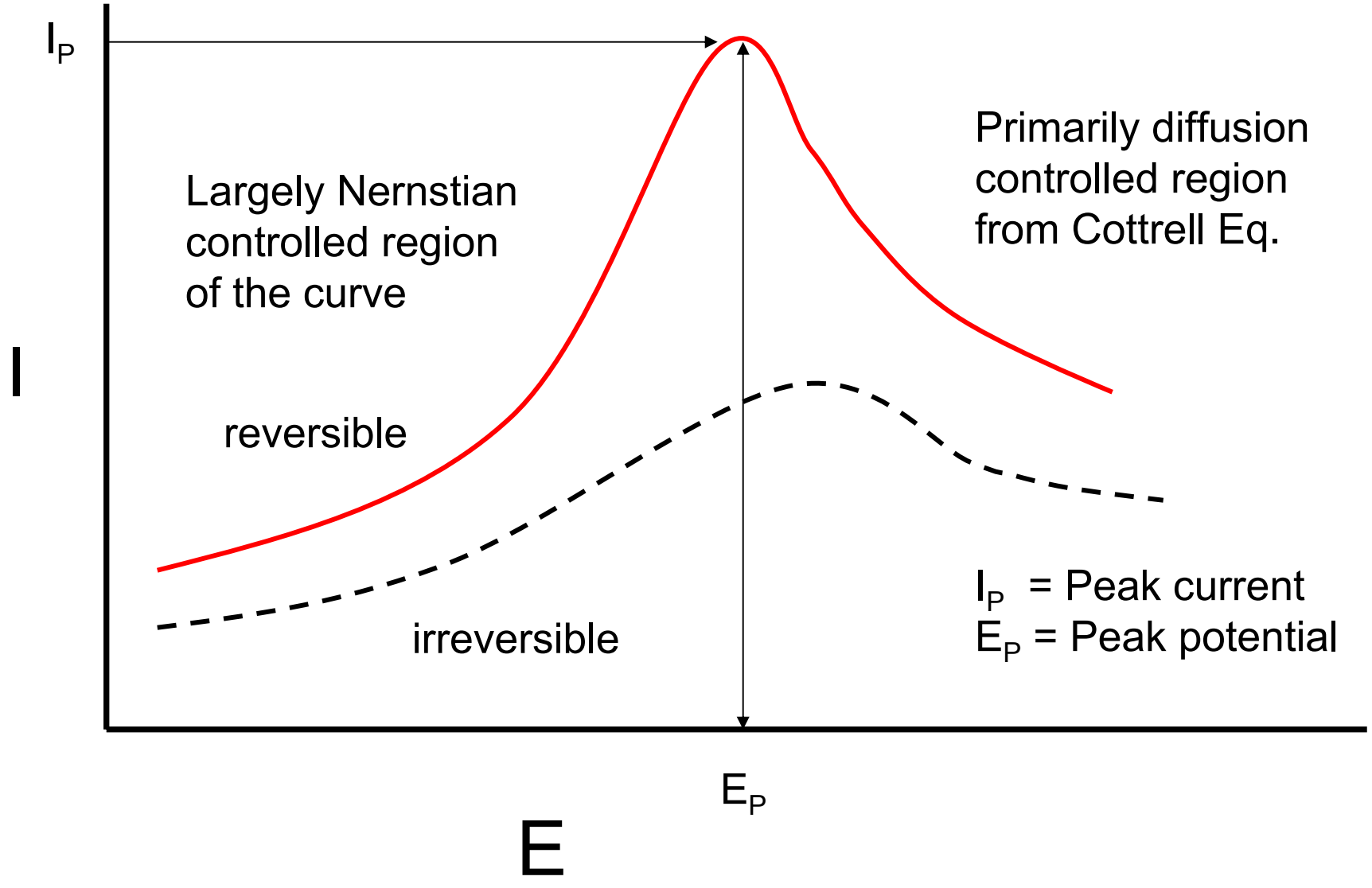
- Stationary electrode
- Unstirred solution = mass transfer by diffusion
- Vary potential linearly with time
- Measure current vs time

Theory

assume $Ox + n\,e^- \leftrightarrow Red$

- both Ox and Red are soluble
- reversible reaction (electrochemically)
- potential varies

Linear Scan Voltammetry (unstirred)



Voltammetry (unstirred) - Theory

$$I_P = 0.452 \frac{n^{3/2} F^{3/2}}{R^{1/2} T^{1/2}} A D^{1/2} C_{bulk} \nu^{1/2}$$

New term ν = scan rate

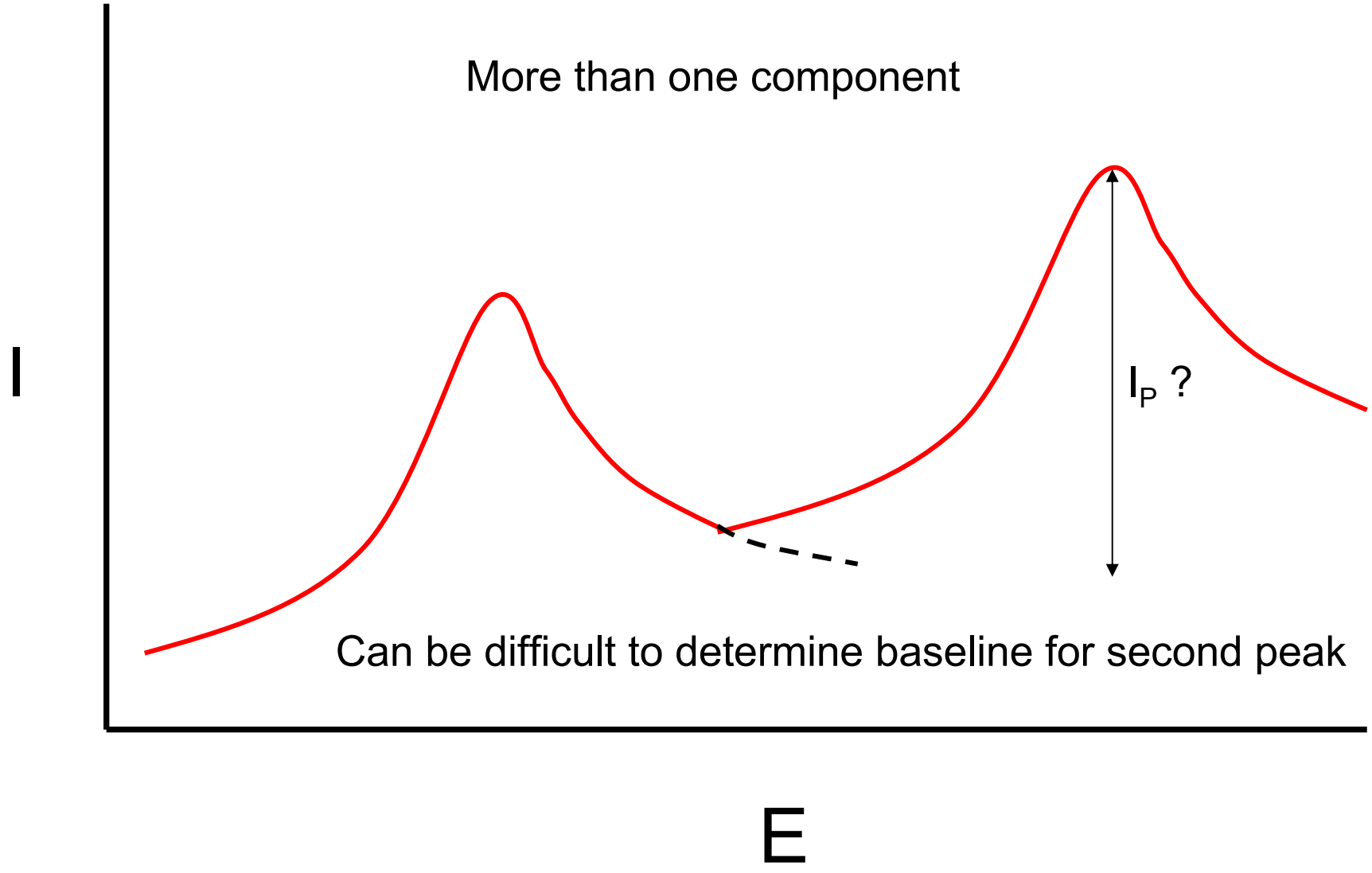
Increase scan rate & I_P increases, however,

I_C is directly proportional to ν

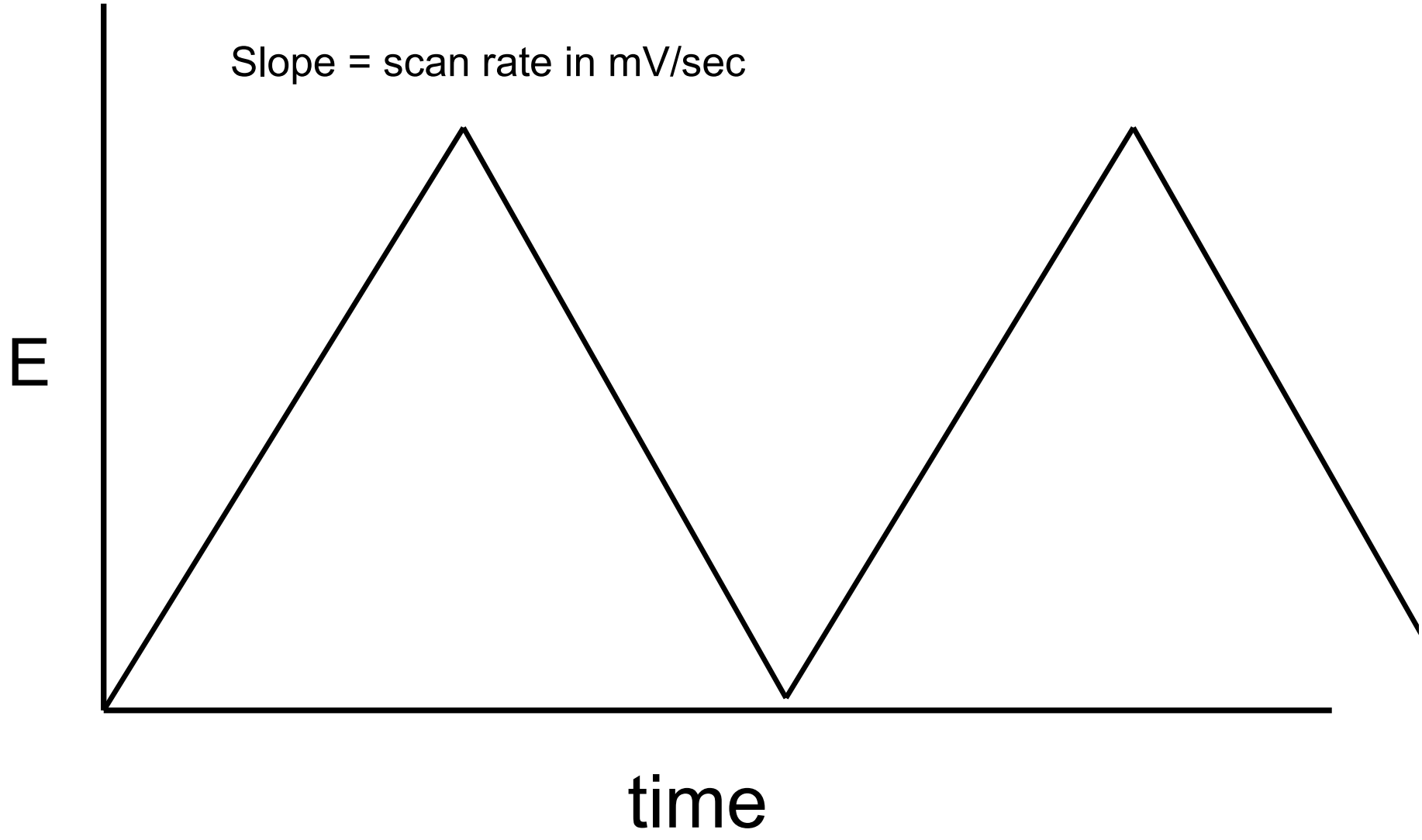
Ratio I_F/I_C is greatest at slow scan rates

$$E_P = E_{1/2} - 1.1 \frac{R\ T}{n\ F}$$

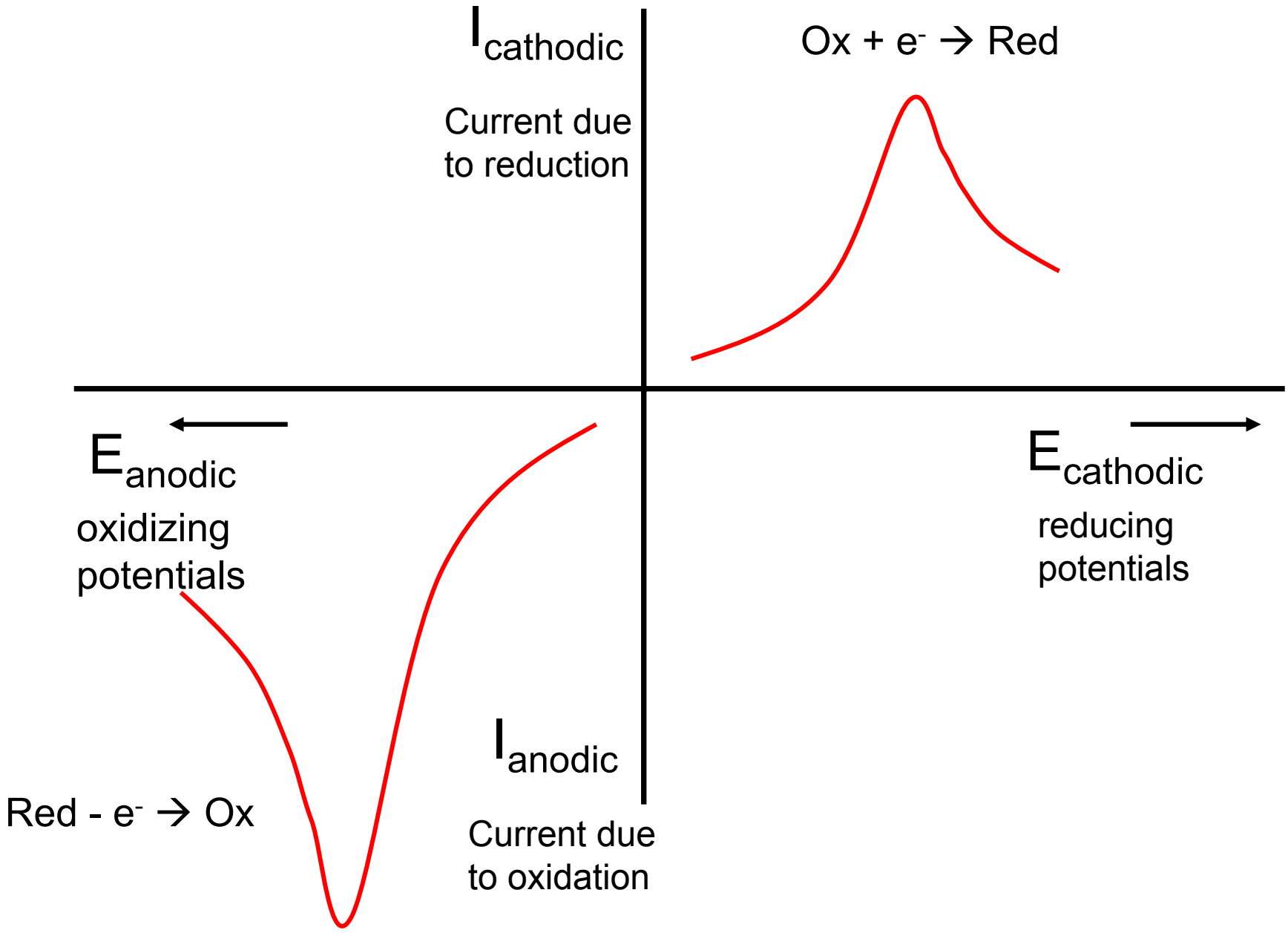
Linear Scan Voltammetry (unstirred)



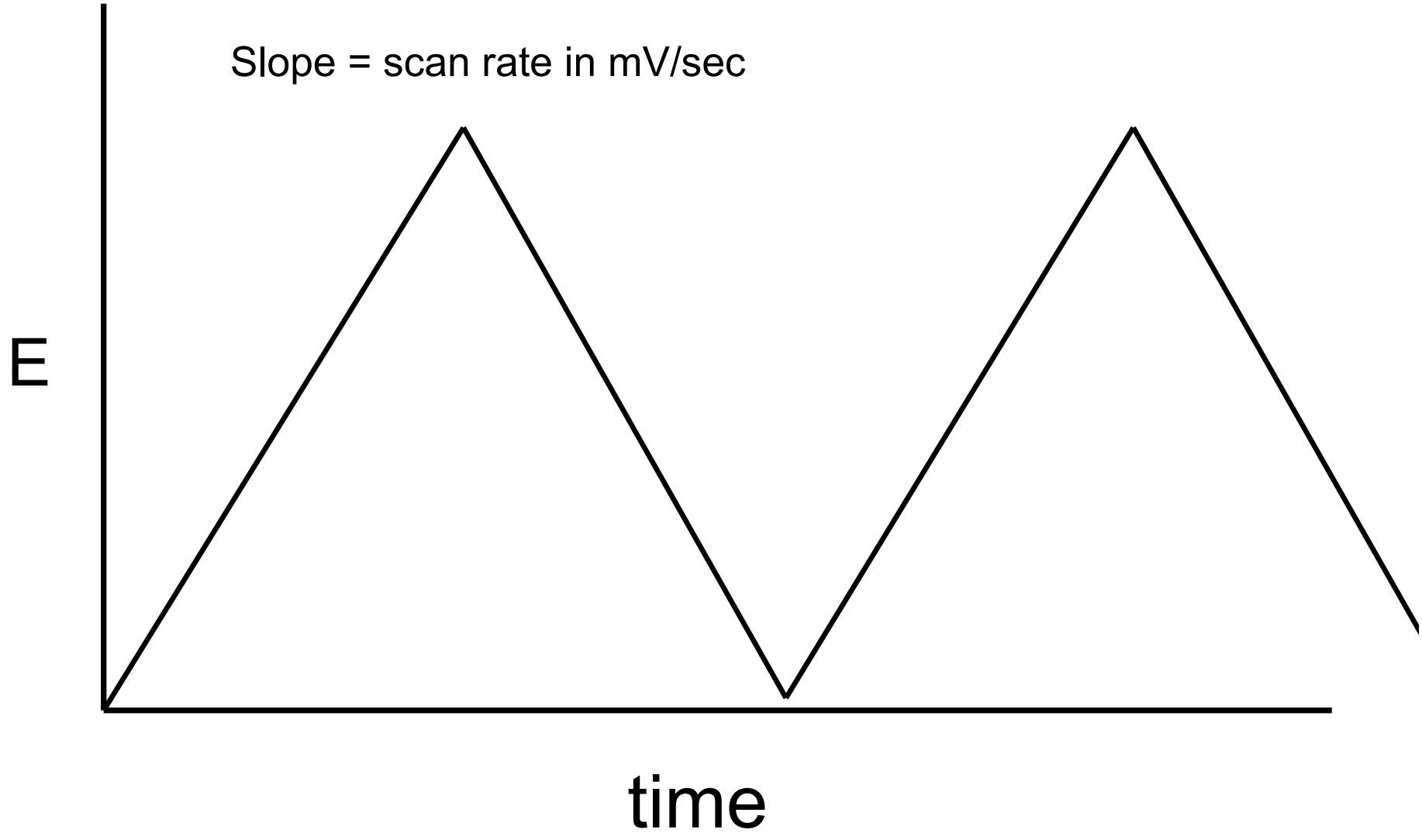
Applied Signal for Linear Scan Voltammetry



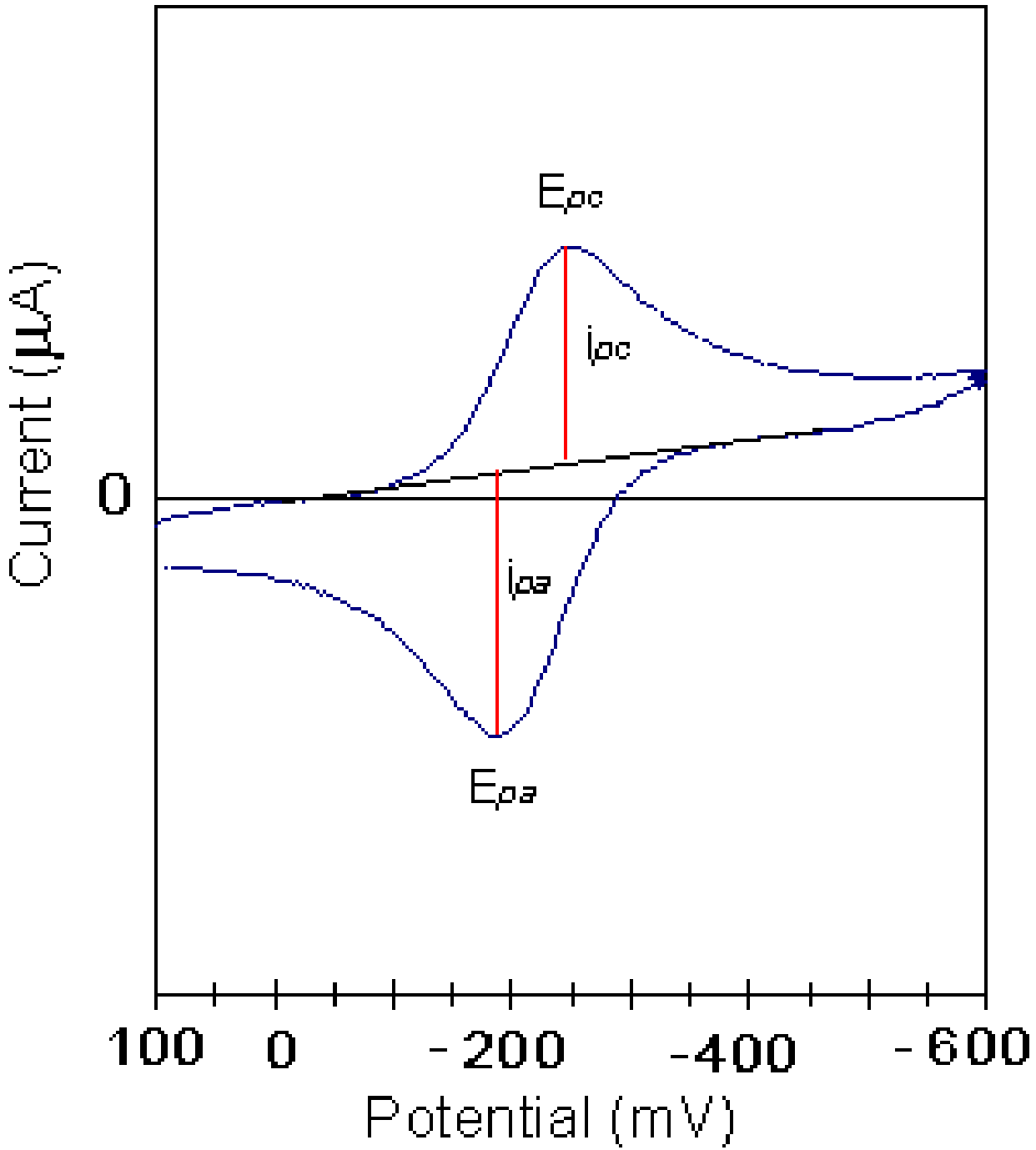
Convention for plotting current & potential



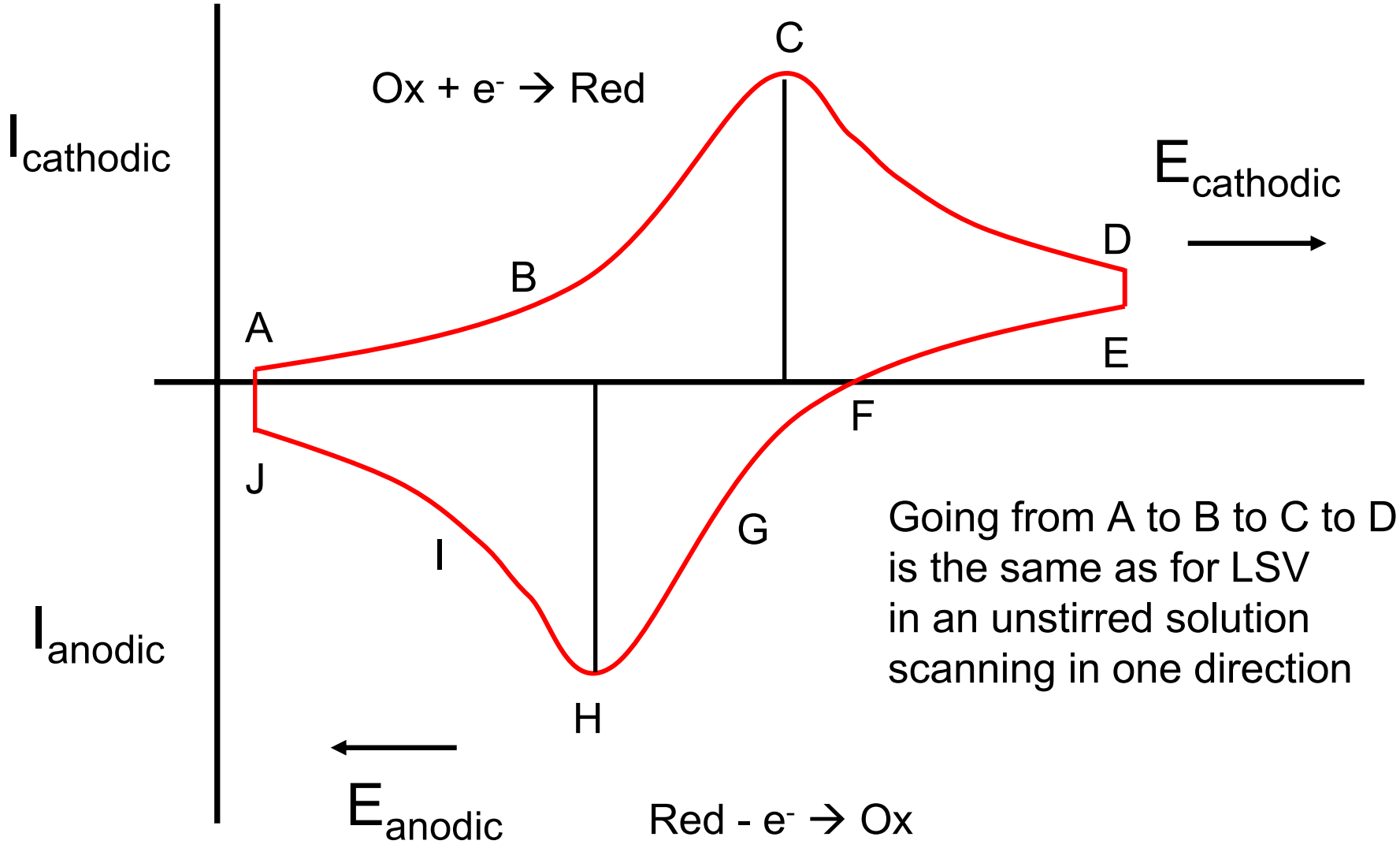
Applied Signal for Linear Scan Voltammetry



Cyclic Voltammetry

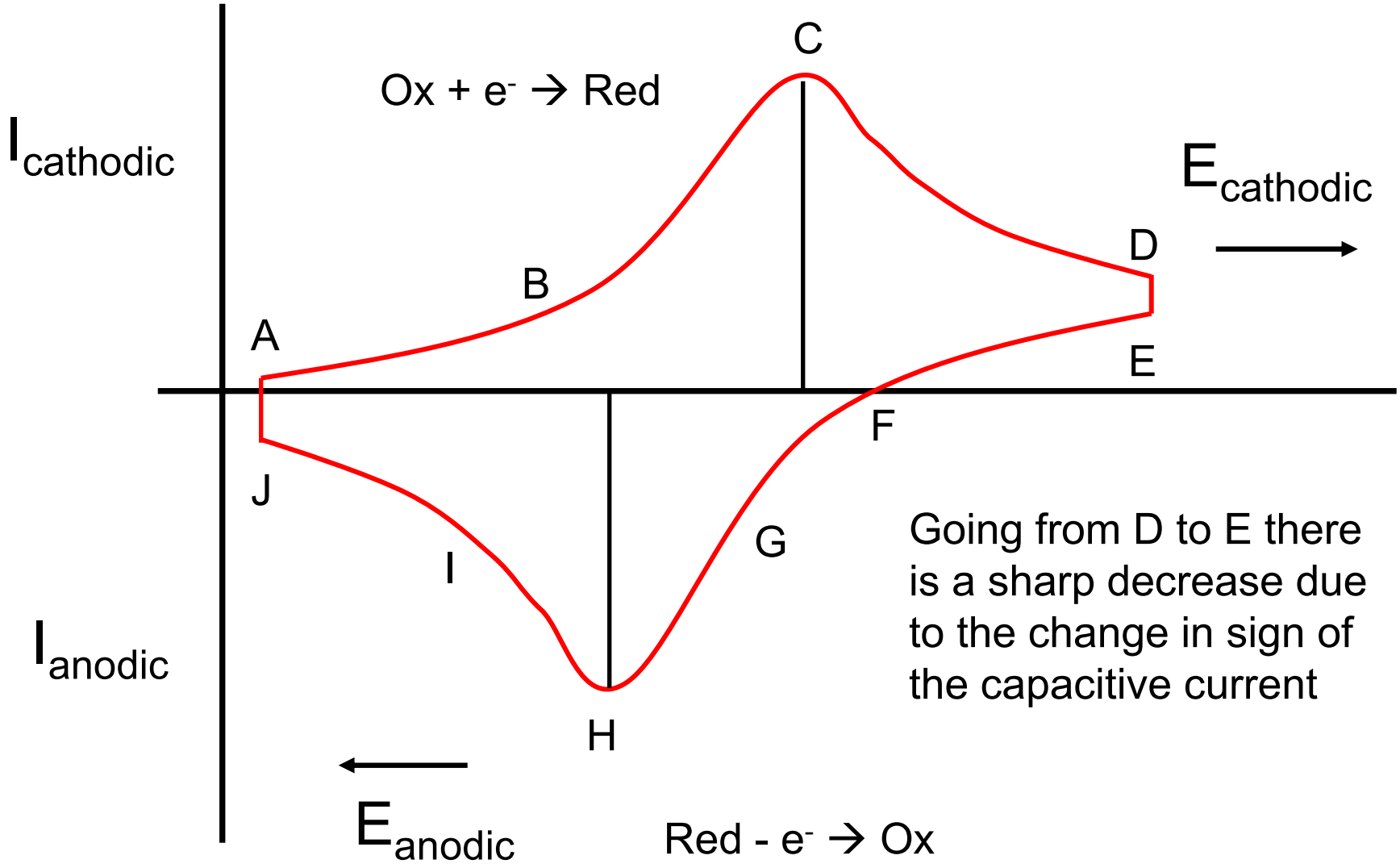


Convention for plotting current & potential



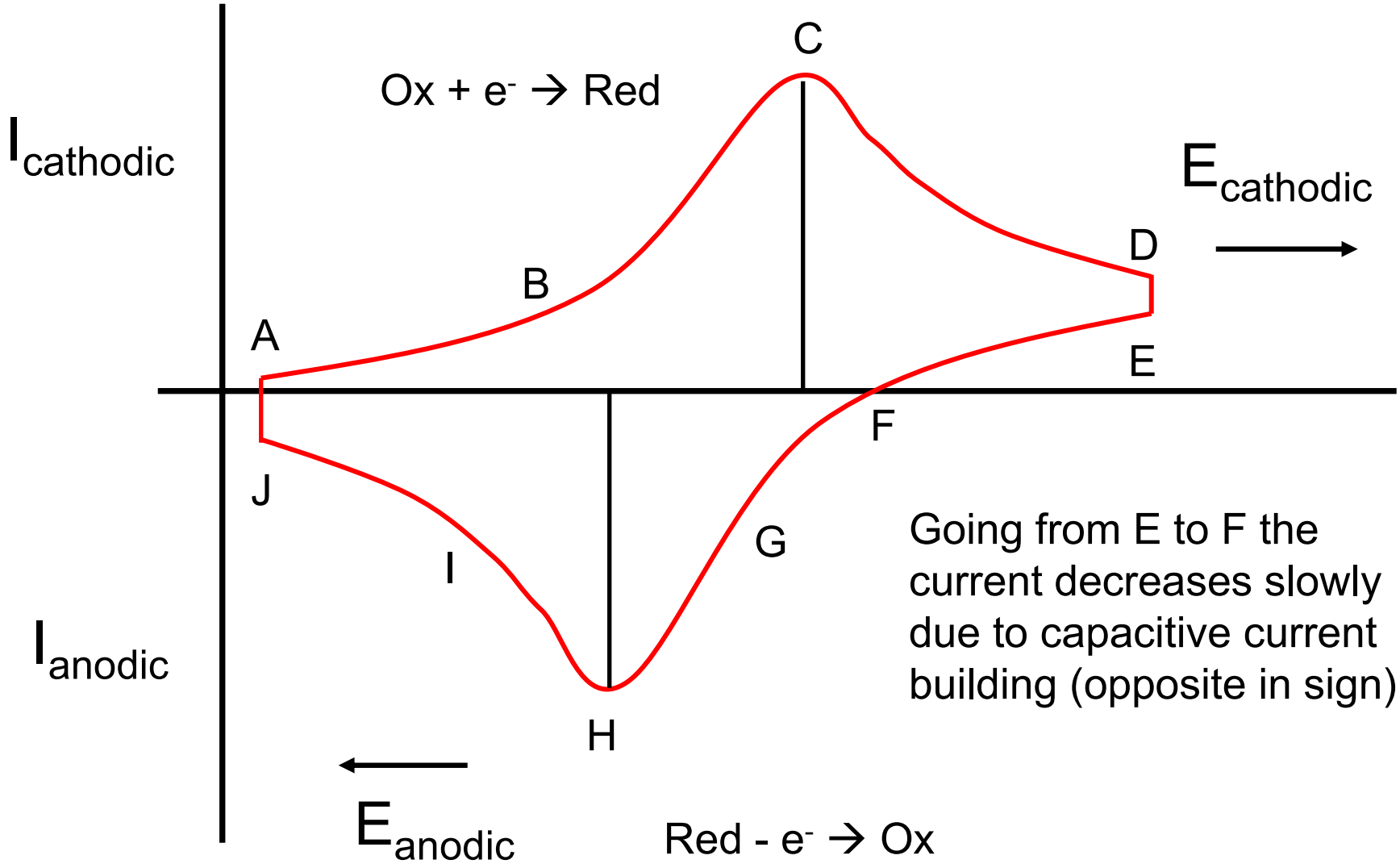
Going from A to B to C to D
is the same as for LSV
in an unstirred solution
scanning in one direction

Convention for plotting current & potential

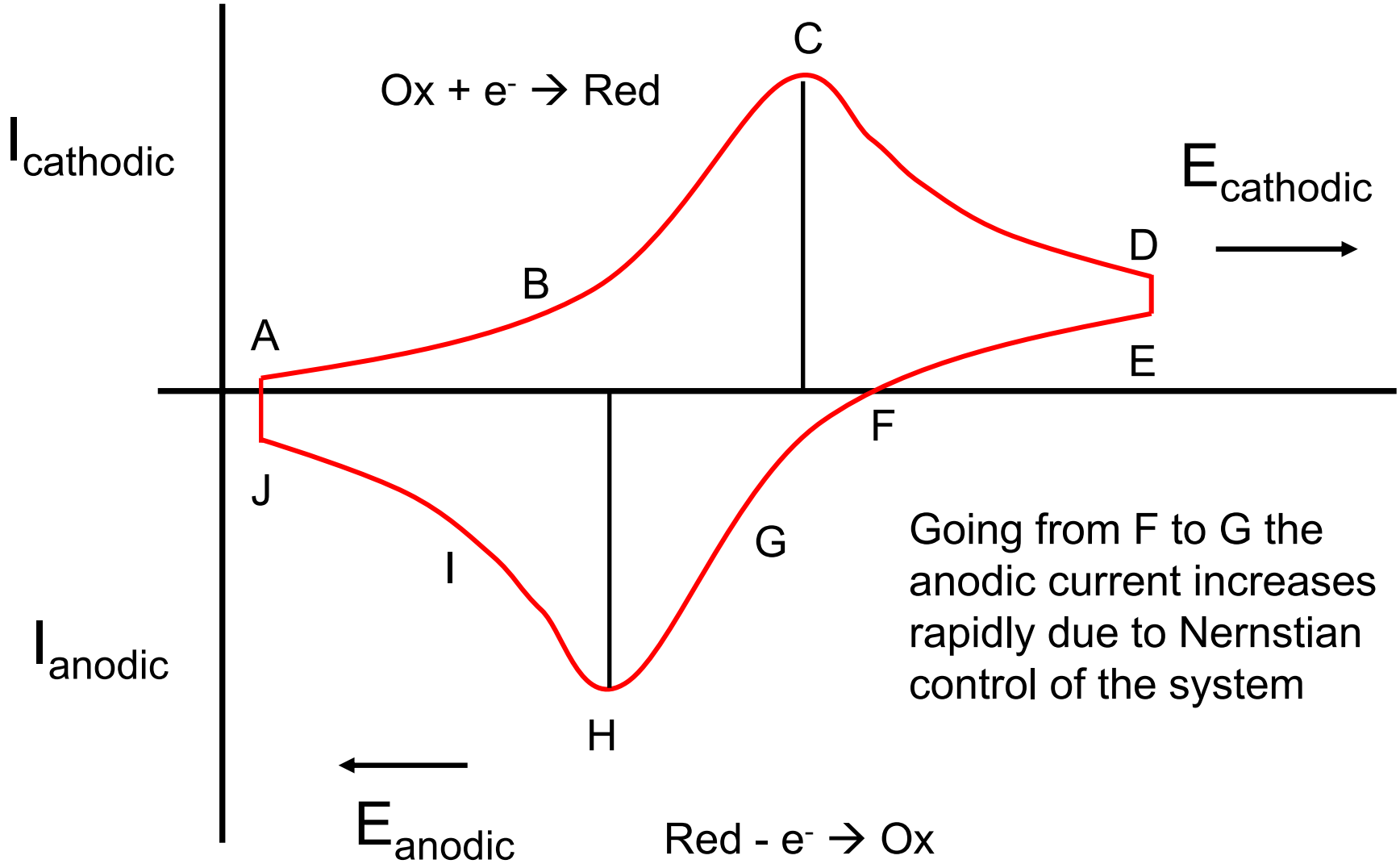


Going from D to E there is a sharp decrease due to the change in sign of the capacitive current

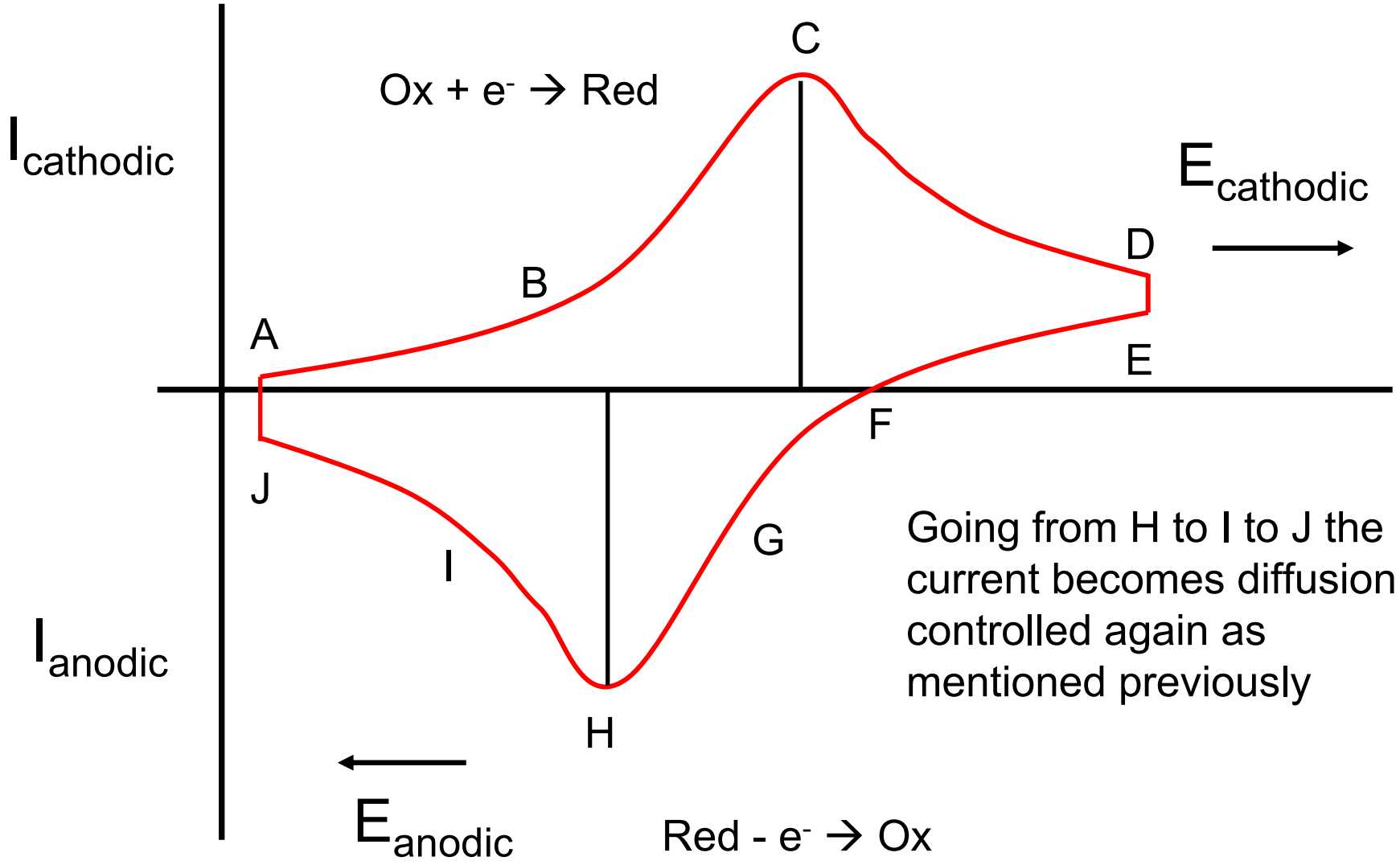
Convention for plotting current & potential



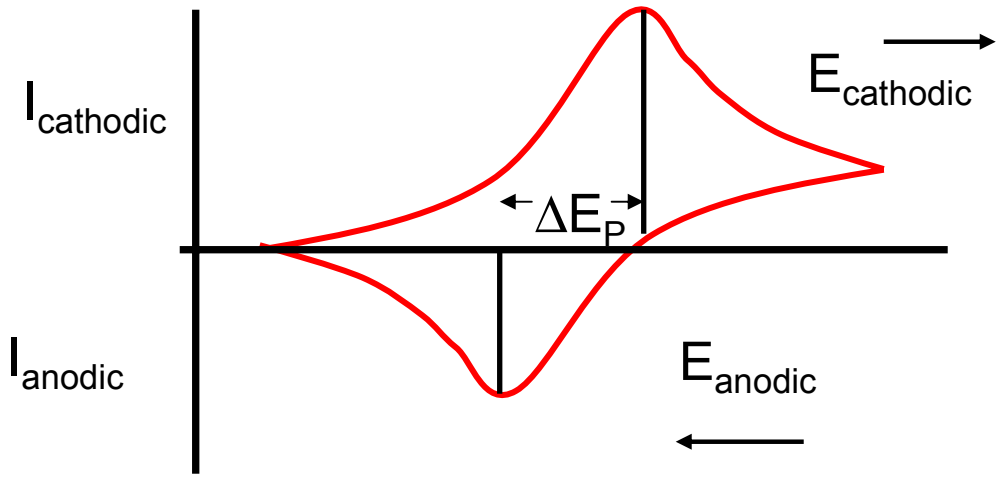
Convention for plotting current & potential



Convention for plotting current & potential

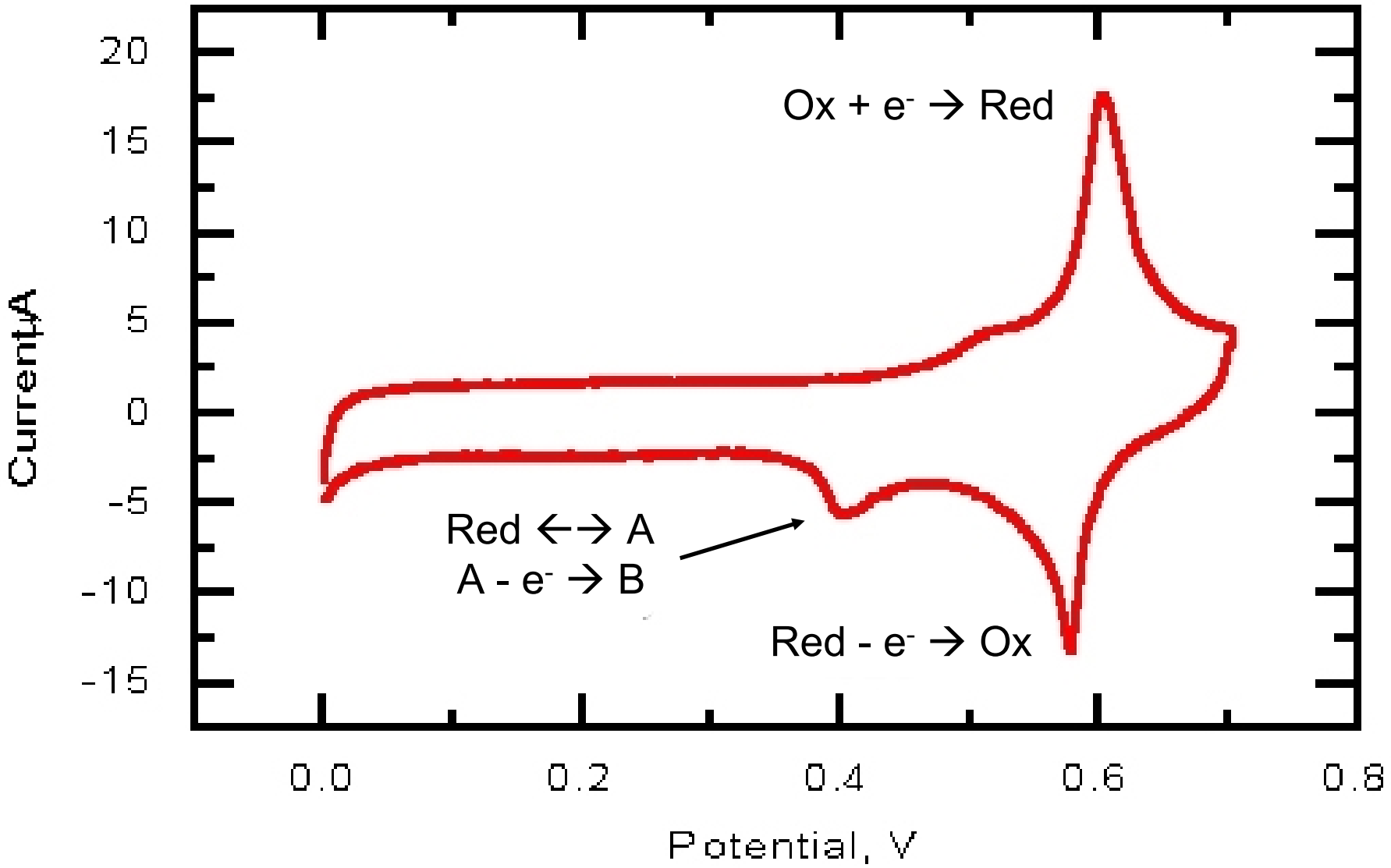


Going from H to I to J the current becomes diffusion controlled again as mentioned previously



CV Diagnostics	$\mathbf{I_P/\nu^{1/2}}$	$\mathbf{I_{anodic}/I_{cathodic}}$	$\mathbf{\Delta E_P/2}$
Reversible Charge Transfer	Constant with ν	1	Constant with ν
Irreversible Charge Transfer	Not constant with ν	< 1	$\Delta E_P/2$ increase with ν

Cyclic Voltammetry of Complex Systems



Cyclic Voltammetry

- Powerful technique for elucidating mechanisms of oxidation & reduction
- Good for studying electrode kinetics
- http://www-biol.paisley.ac.uk/marco/Enzyme_Electrode/Chapter1/Cyclic_Voltammetry1.htm