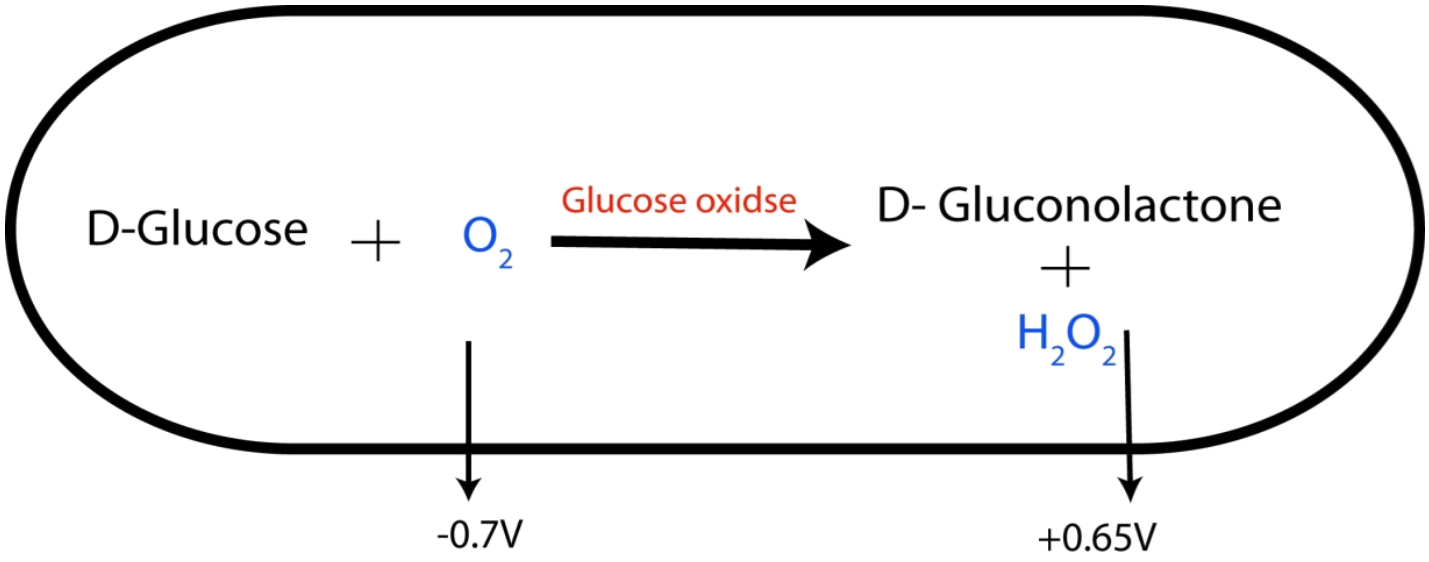
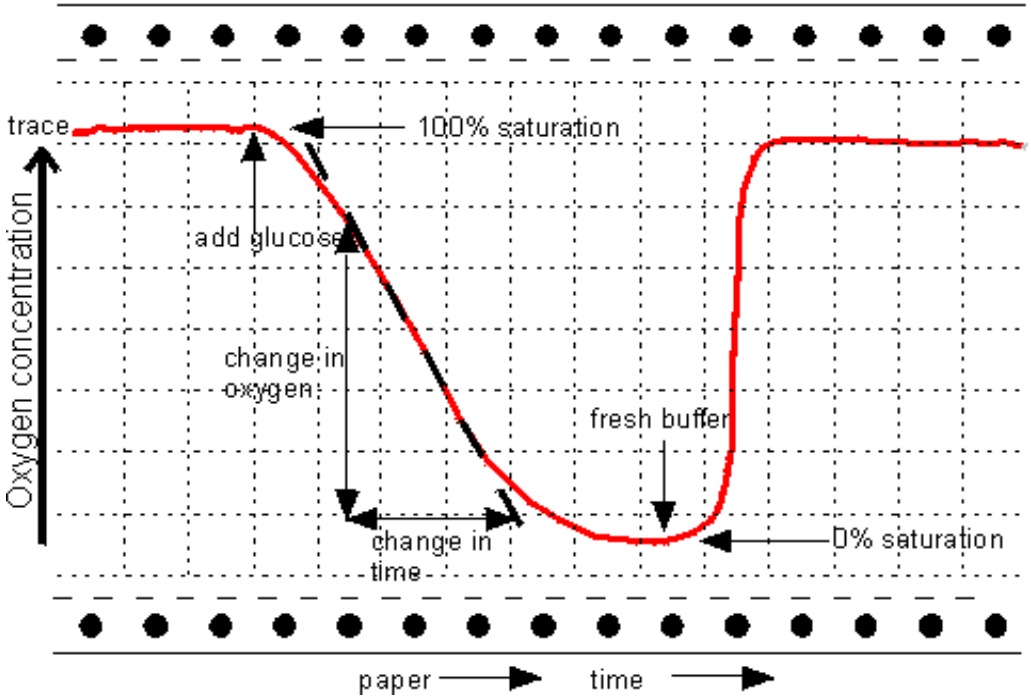
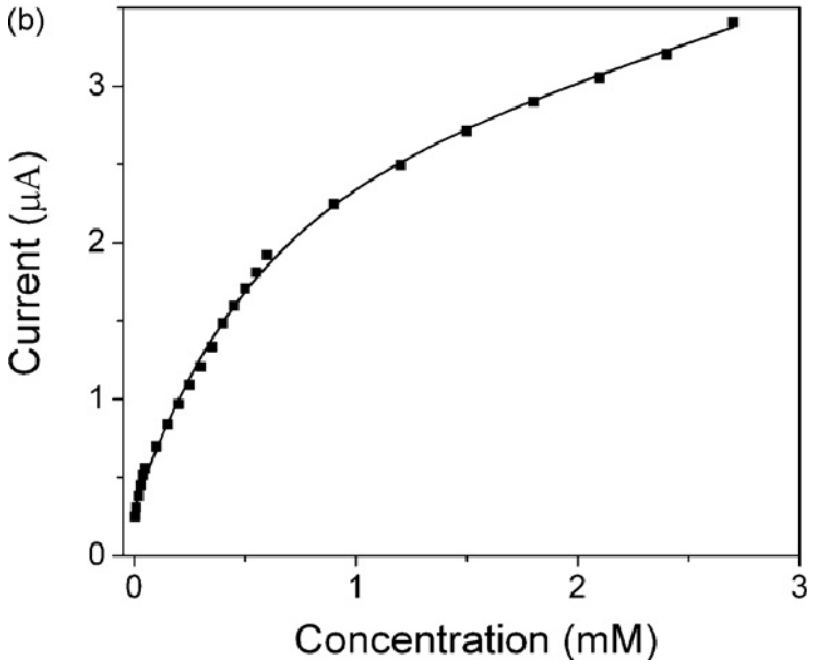
How to identify the redox potential of a compound?

Our previous example





O_2 as redox entity



H_2O_2 as redox entity

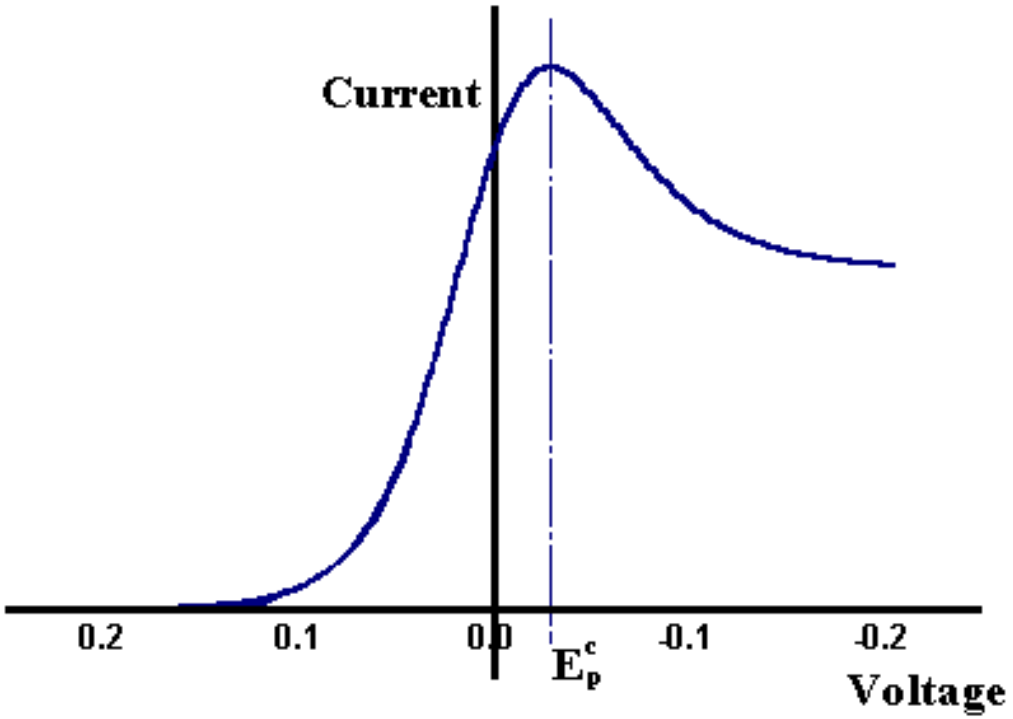
Common voltammetry techniques:

- Linear Sweep Voltammetry (LSV)
- Cyclic Voltammetry (CV)

Some other Voltammetric techniques used in developing biosensors are Differential pulse voltammetry, Square wave voltammetry etc.
In voltammetry, information about an analyte is obtained by measuring the *current* as the *potential* is varied.

Linear Sweep Voltammetry:

A fixed voltage range is scanned from a lower to an upper limit:

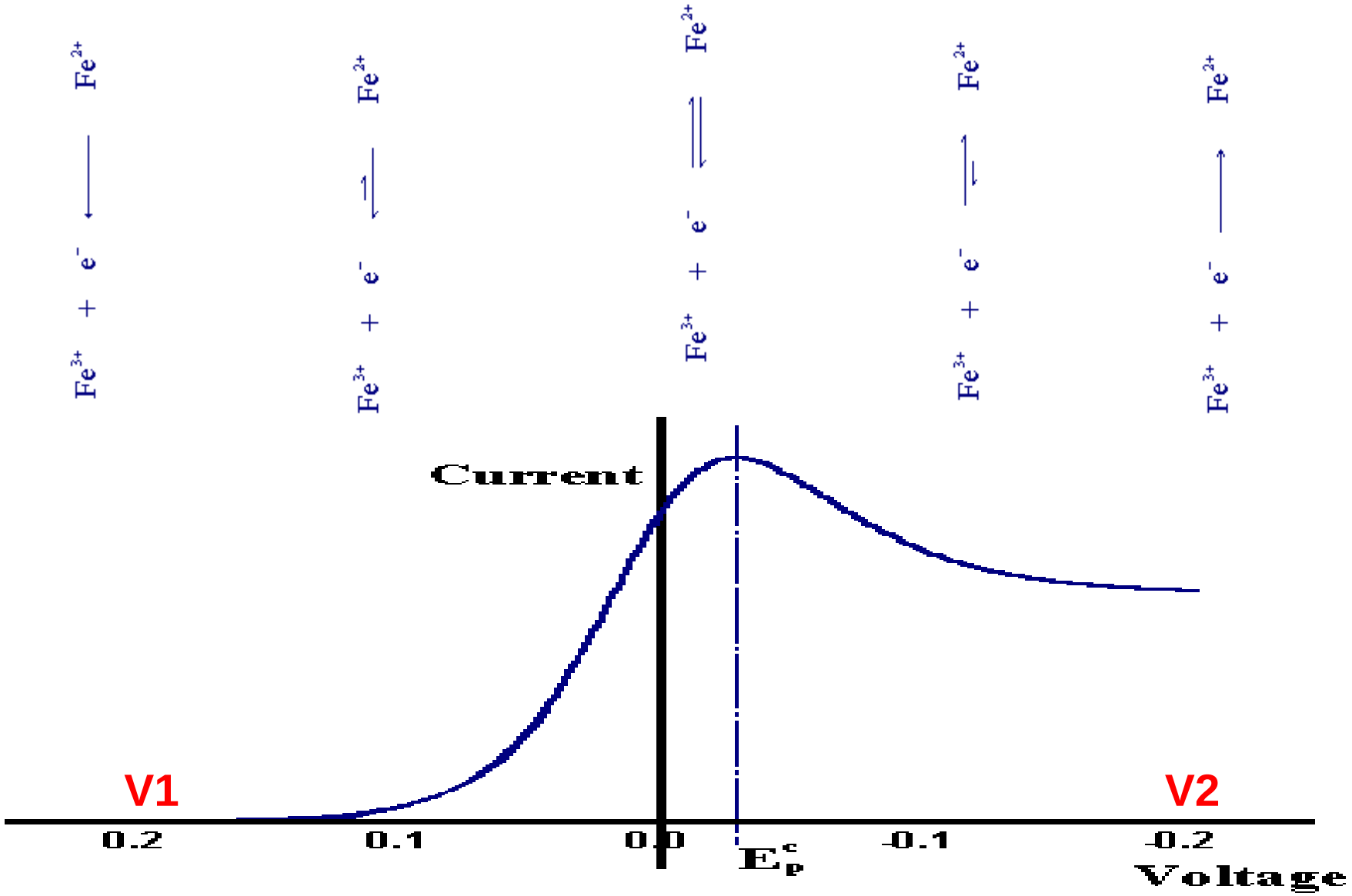


The characteristics of the linear sweep voltammogram recorded depend on a number of factors including:

*The rate of the electron transfer reaction(s)
*The chemical reactivity of the electroactive species
*The voltage scan rate

Let us consider the Fe^{3+}/Fe^{2+} system:

Following voltammogram would be seen for a single voltage scan using an electrolyte solution containing only Fe^{3+} resulting from a voltage sweep.



As the voltage is swept from $\mathbf{V_1}$ to $\mathbf{V_2}$ the equilibrium position shifts from no conversion at $\mathbf{V_1}$ to full conversion at $\mathbf{V_2}$ of the reactant at the electrode surface.

As the voltage is swept to the right (to more reductive values) a current begins to flow and eventually reaches a peak before dropping.

The rate of electron transfer is faster in comparison to the voltage sweep rate.

At the electrode surface equilibrium is established identical to that predicted by thermodynamics.

The **Nernst equation** predicts the relationship between concentration and voltage (potential difference), where **E** is the applied potential difference and **E°** is the standard electrode potential.

$$E = E^{\theta} + \frac{RT}{nF} \ln \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

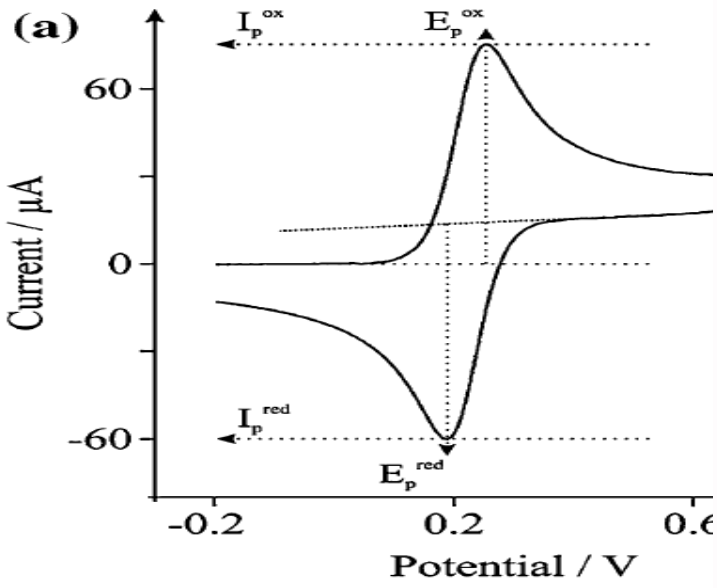
Cyclic Voltammetry

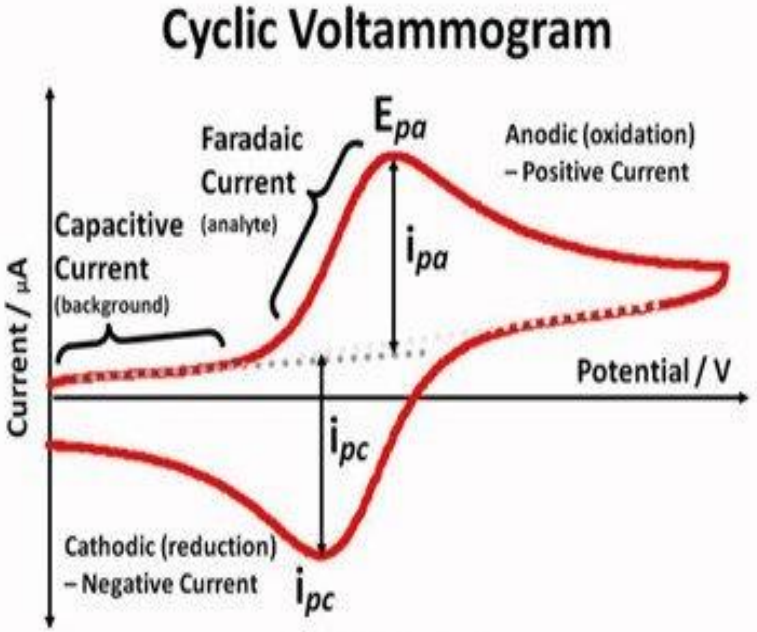
In addition to forward scan as in LSV, a reverse scan is also done.

The direction of the potential scan is reversed at the end(often referred to as a switching potential).

The same potential window is scanned in the opposite direction, **hence the term cyclic**.

Hence, the species formed by oxidation on the first (forward) scan can be reduced on the second (reverse) scan.

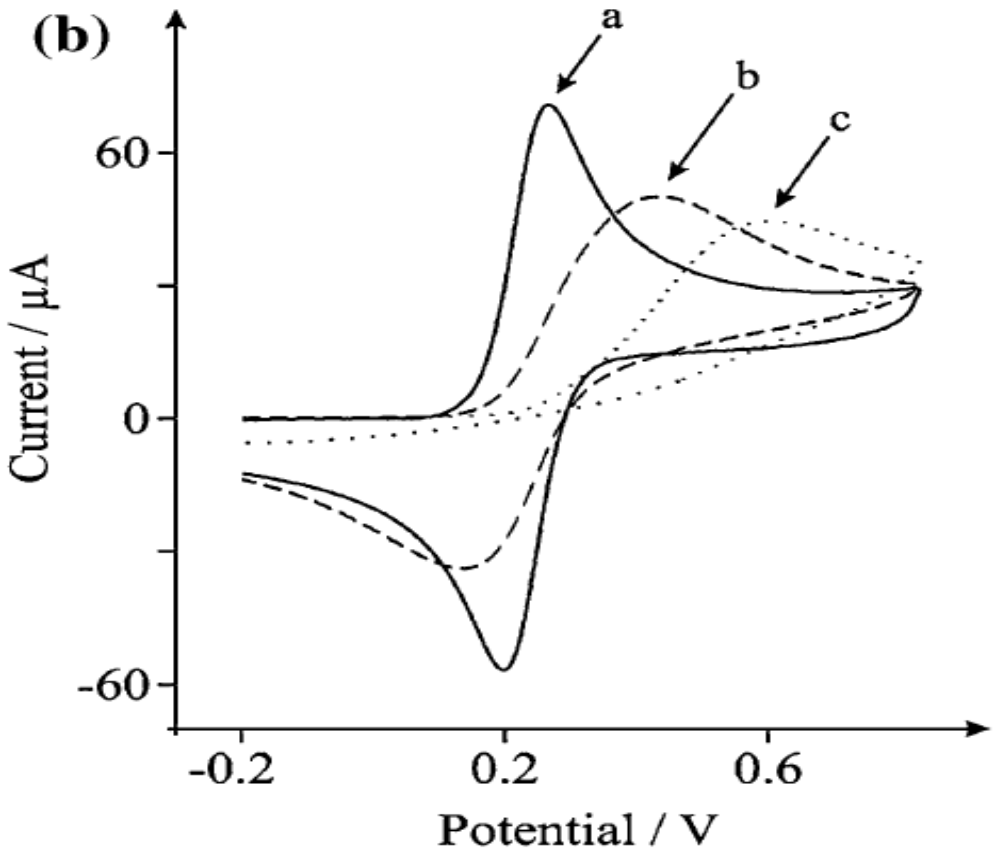




a Typical cyclic voltammogram depicting the peak position E_P and peak height I_P.

The reverse scan is simply move back through the equilibrium positions gradually converting electrolysis product (e.g. $\mathbf{F^{2+}}$ back to reactant $\mathbf{Fe^{3+}}$).

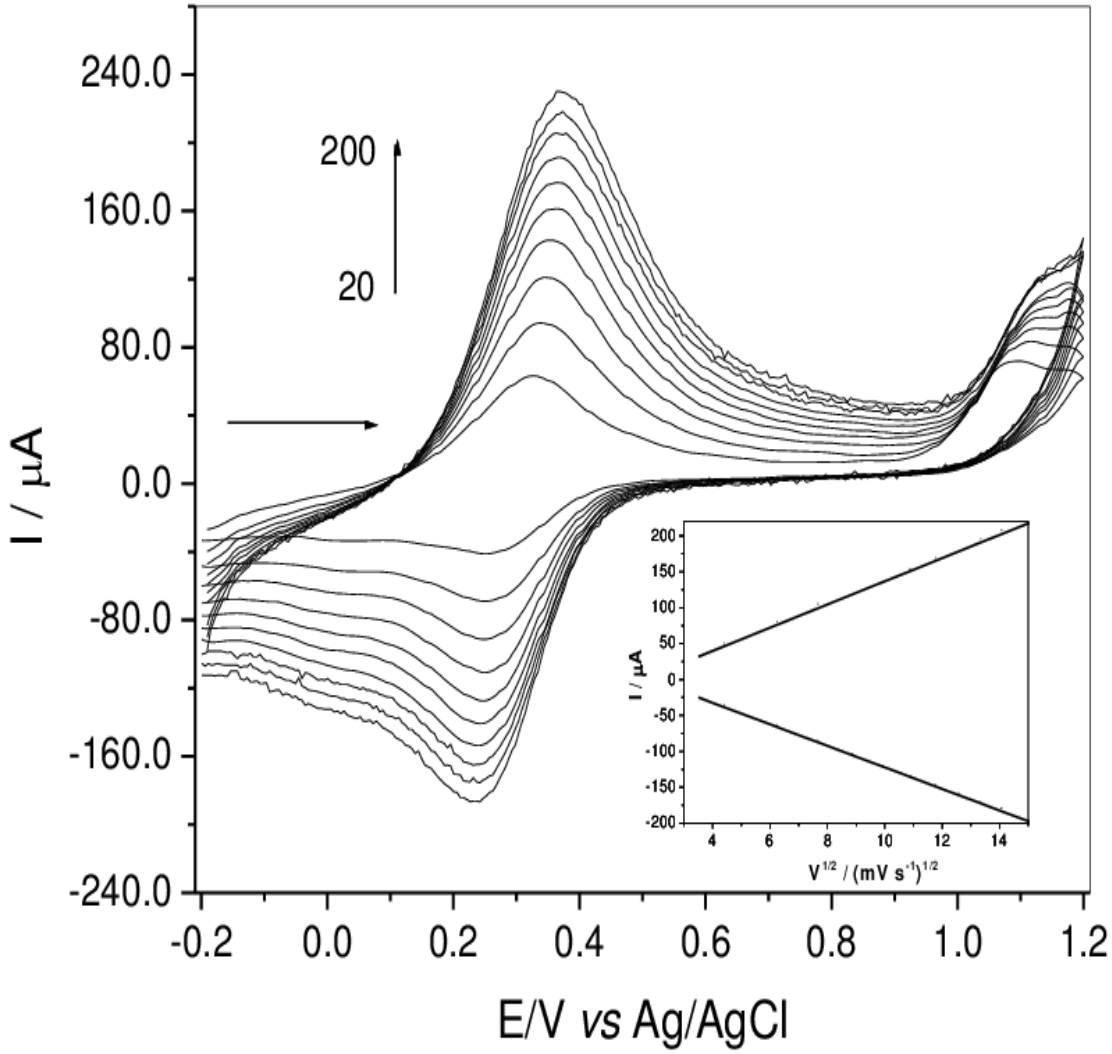
Formal potential of the species is $(E_{p(ox)}+E_{p(red)})/2$



b Cyclic voltammograms for reversible (*a*), quasi-reversible (*b*) and irreversible (*c*) electron transfer

Randles–Sevcik equation (effect of scan rate on the peak current i_p).

$$i_p = 2.68 \times 10^5 \; n^{3/2} A D^{1/2} C v^{1/2}$$ (If the solution is at 25 °C)



i_p = current maximum in amps

n = no. of electrons transferred i

the redox event

A = electrode area in cm^2

D = diffusion coefficient in cm^2/s

C = concentration in mol/cm^3

ν = scan rate in V/s

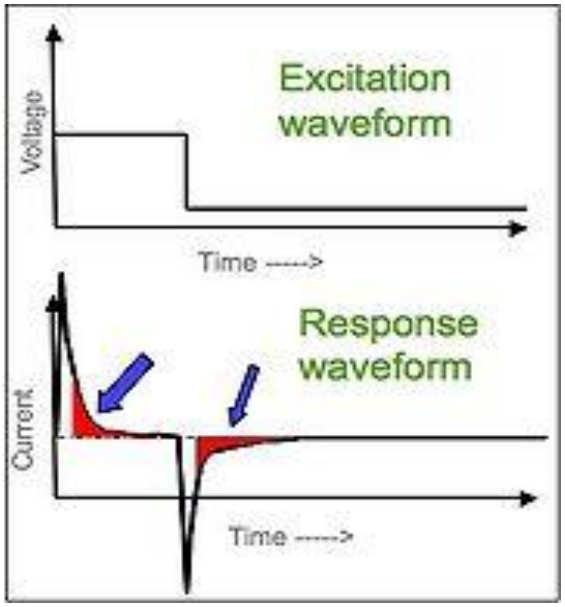
R = Gas constant in J K^{-1} mol^{-1}

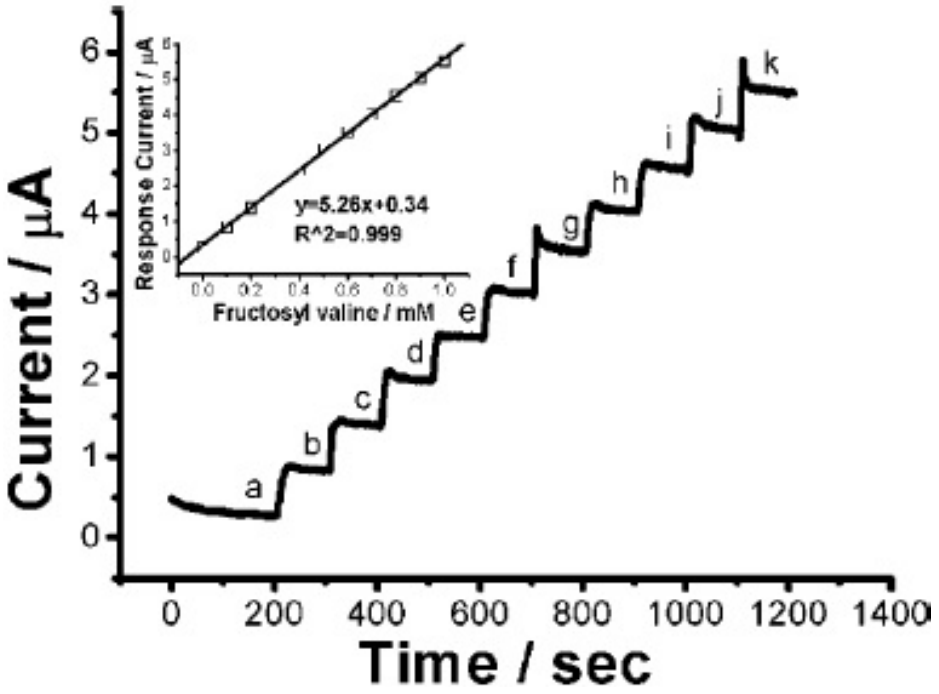
T = temperature in K

F = Faraday Constant in C mol^{-1}

Chronoamperometry:

The potential of the working electrode is stepped, and the resulting current from faradic processes occurring at the electrode (caused by the potential step) is monitored as a function of time.





This pulsed techniques generates high charging currents, which decay exponentially with time. To measure the faradic current (the current that is proportional to the concentration of the analyte), current in the last 70-80% of each scan is integrated (when charging current has dissipated).

It gives better signal to noise ratio in comparison to other amperometric technique.

Cottrell equation

$$i = \frac{nFAc_j^0\sqrt{D_j}}{\sqrt{\pi t}} \qquad i = kt^{-1/2}$$

i = current, in unit A

n = number of electrons (to reduce/oxidize one molecule of analyte , for example)

F = Faraday constant, 96485 C/mol

A = area of the (planar) electrode in cm^2

C^0_j = initial concentration of the reducible analyte in mol/cm^3;

D = diffusion coefficient for species in cm^2/s

t = time in s.

- Describes the change in *i* w.r.t. to *t* in a controlled potential experiment, such as chronoamperometry.
- describes the *i* response when the V is a step function in *t*.
- describes the case for a planner electrode