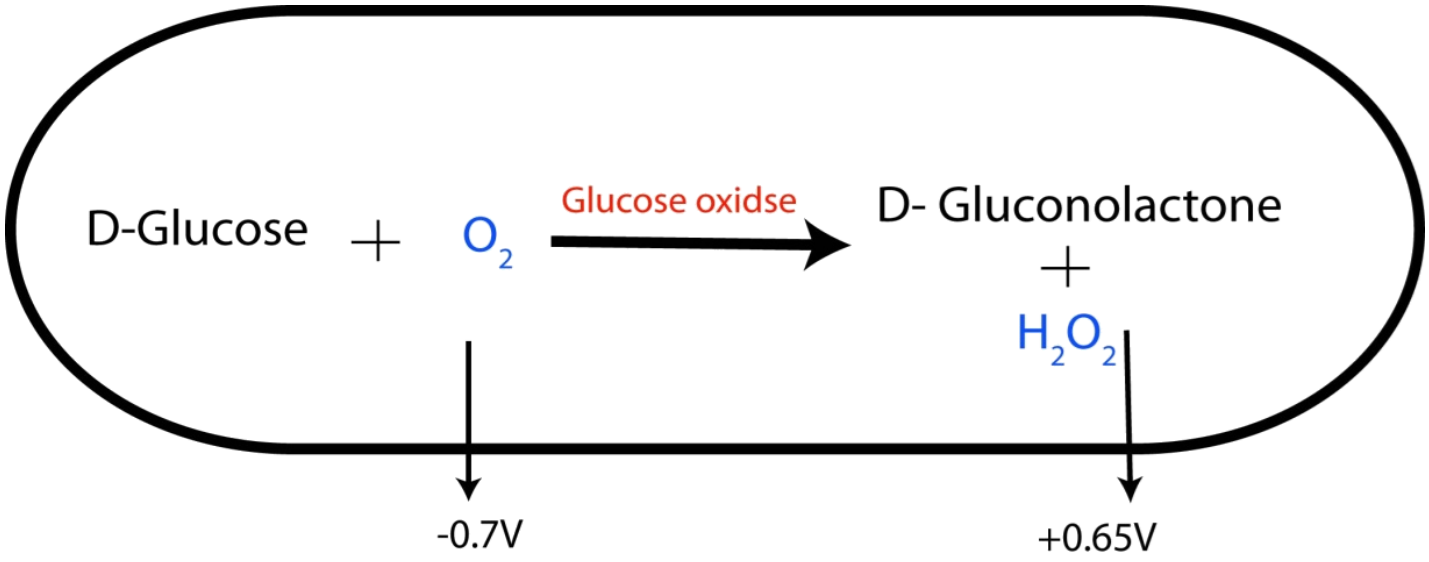
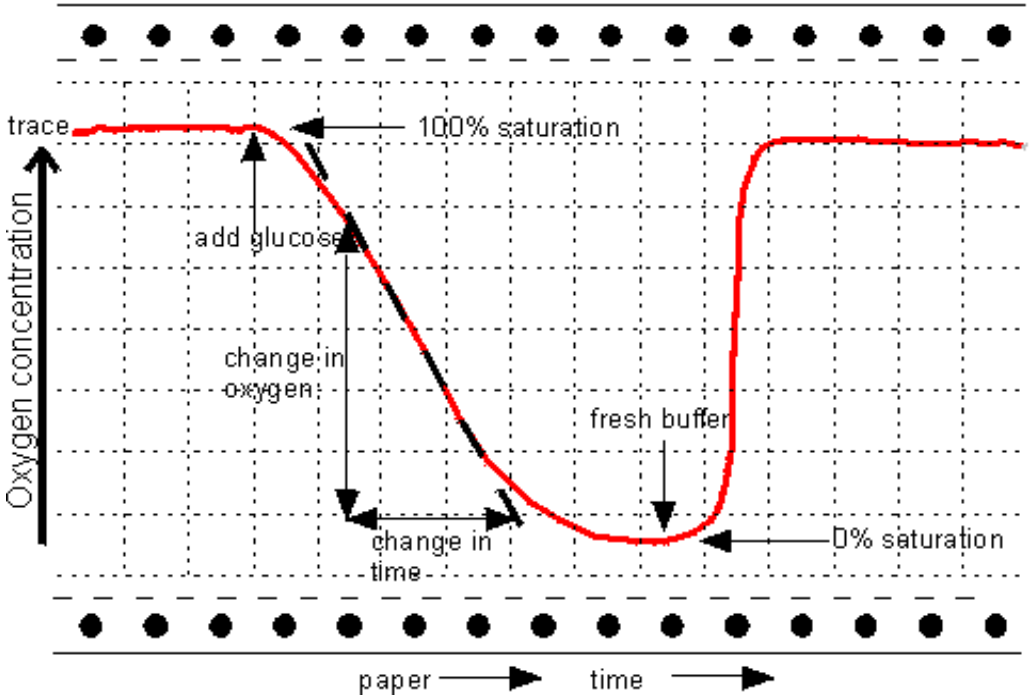
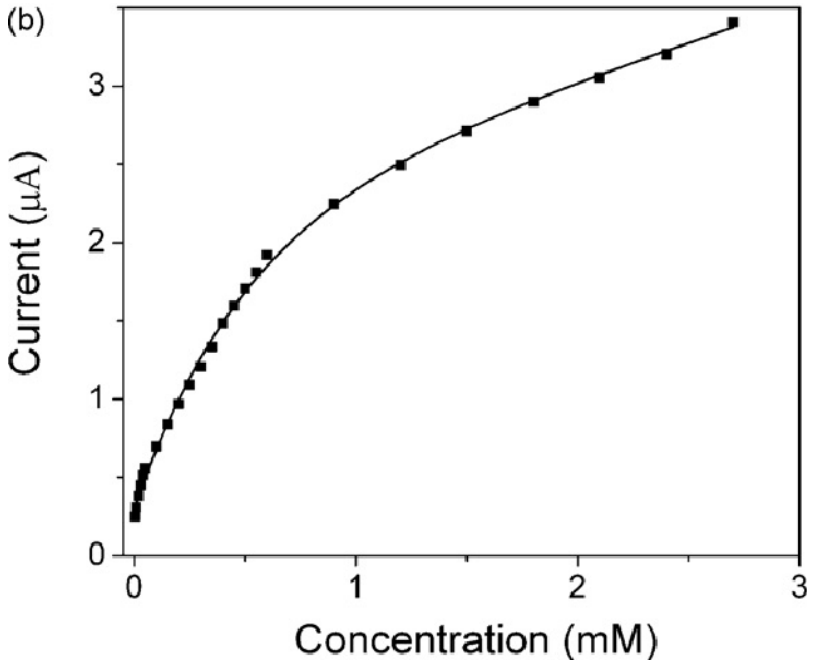
How to identify the redox potential of a compound?

Our previous example





O_2 as redox entity



H_2O_2 as redox entity

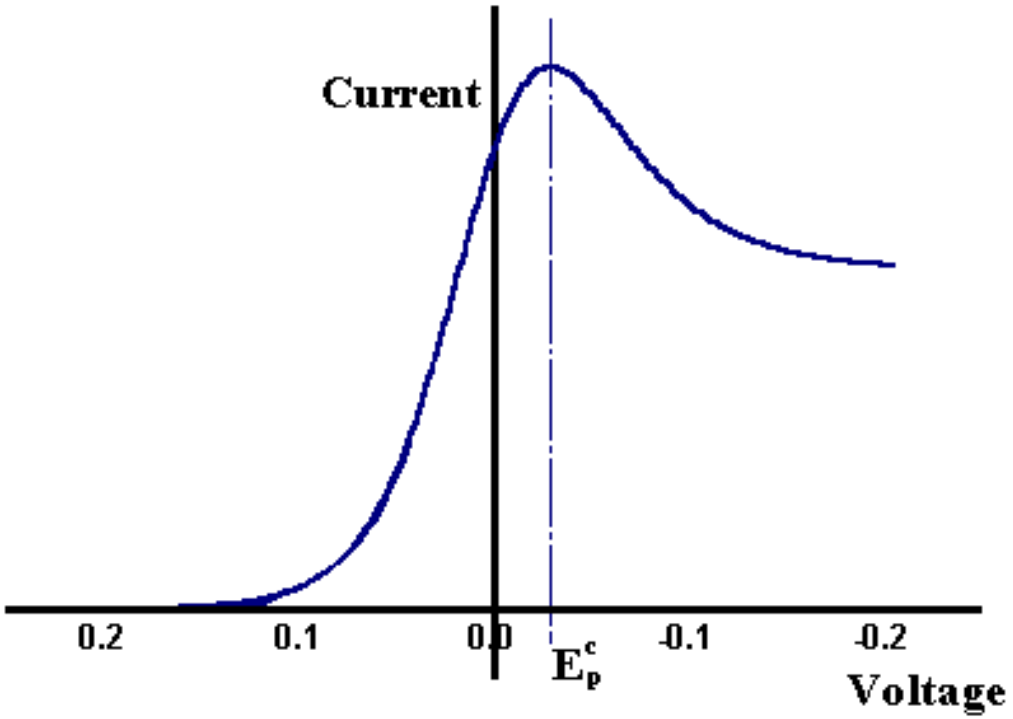
Common voltammetry techniques:

- 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:

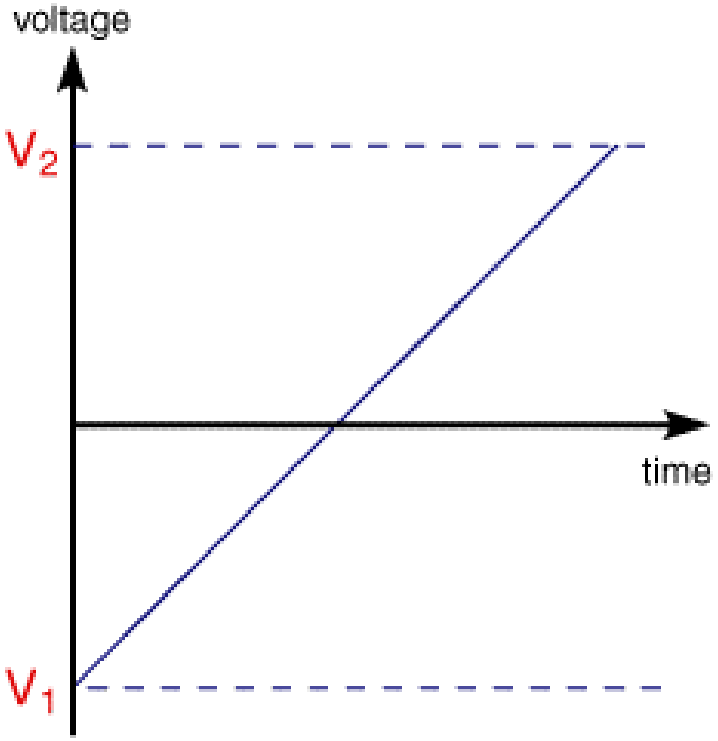


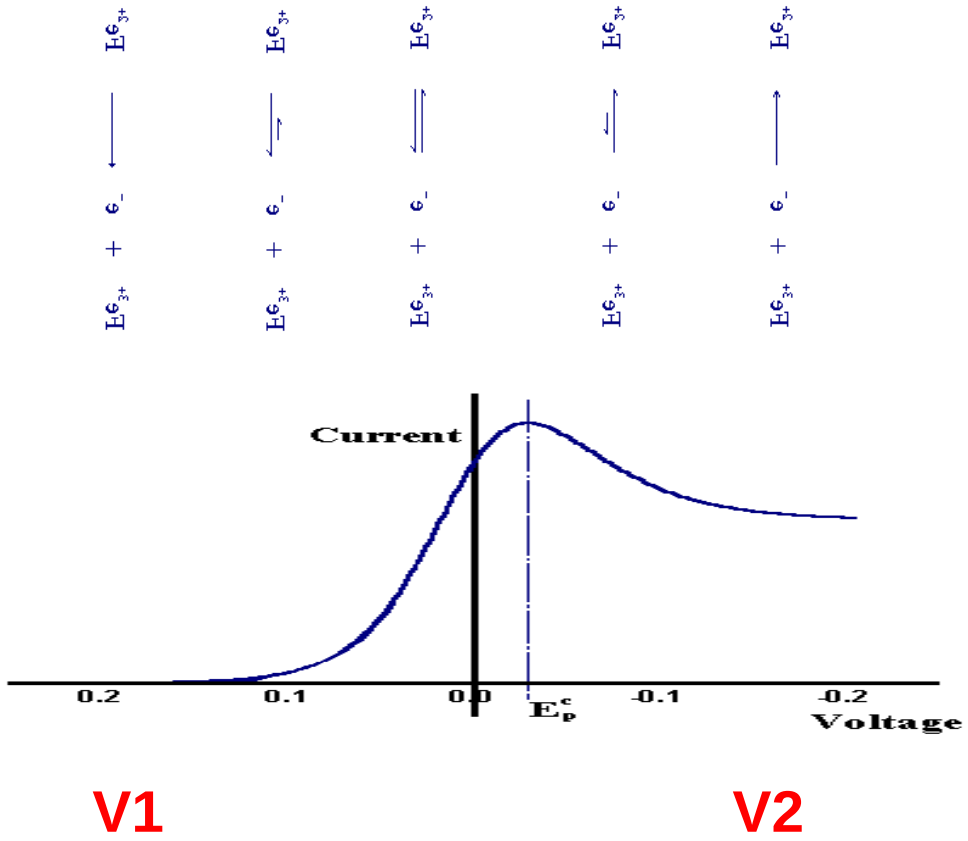
The characteristics of the linear sweep voltammogram recorded depend on a number of factors including:

*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 sweept 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 Nernst equation can be used to determine the relative concentration of Fe^{3+} to Fe^{2+} at the electrode at every electrode potential (E) encountered on the sweep (if the wave is reversible). The requirement that the electron transfer be reversible (fast) is to ensure that electrons are transferred rapidly and equilibrium is always maintained at the electrode. In other words, the concentrations of Fe^{3+} to Fe^{2+} at the electrode change immediately as the electrode potential changes

The **Nernst equation** predicts the relationship between concentration and voltage (potential difference), where **E** is the applied potential difference and $\mathbf{E^{\ominus}}$ is the standard electrode potential.

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

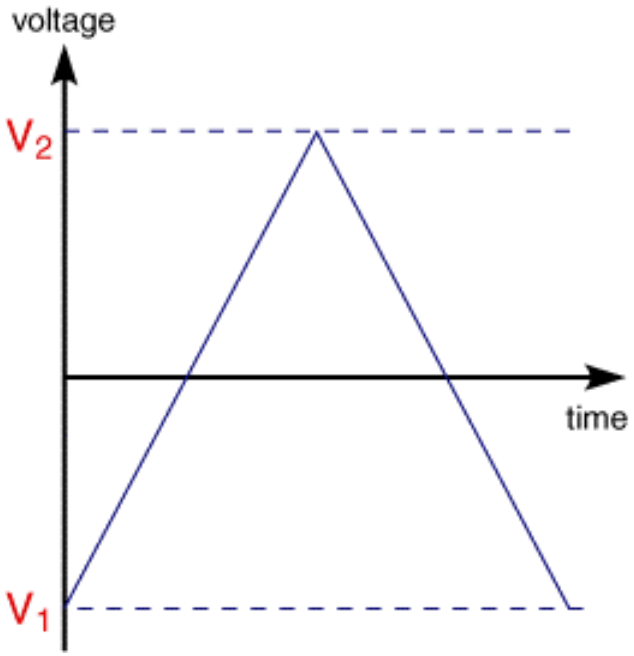
Cyclic Voltammetry

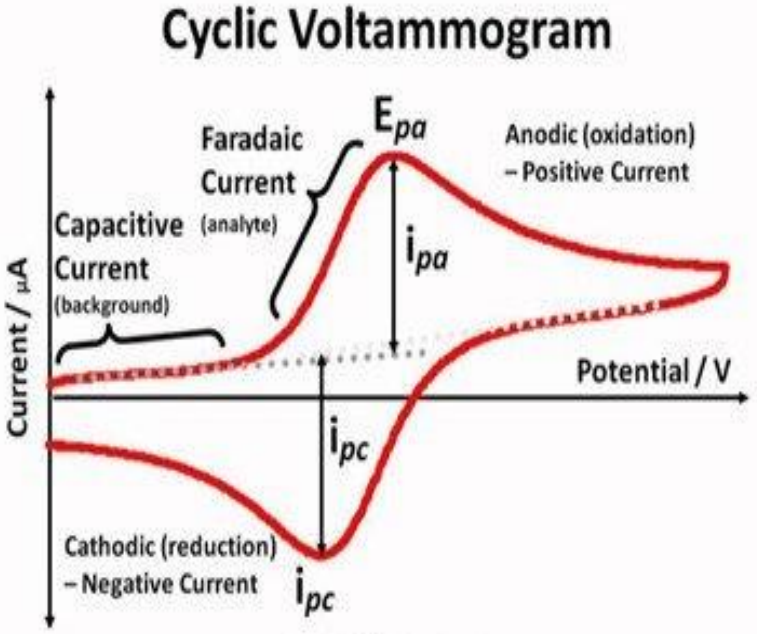
In addition to forward scan as in LSV, a reverse scan is also done.

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.

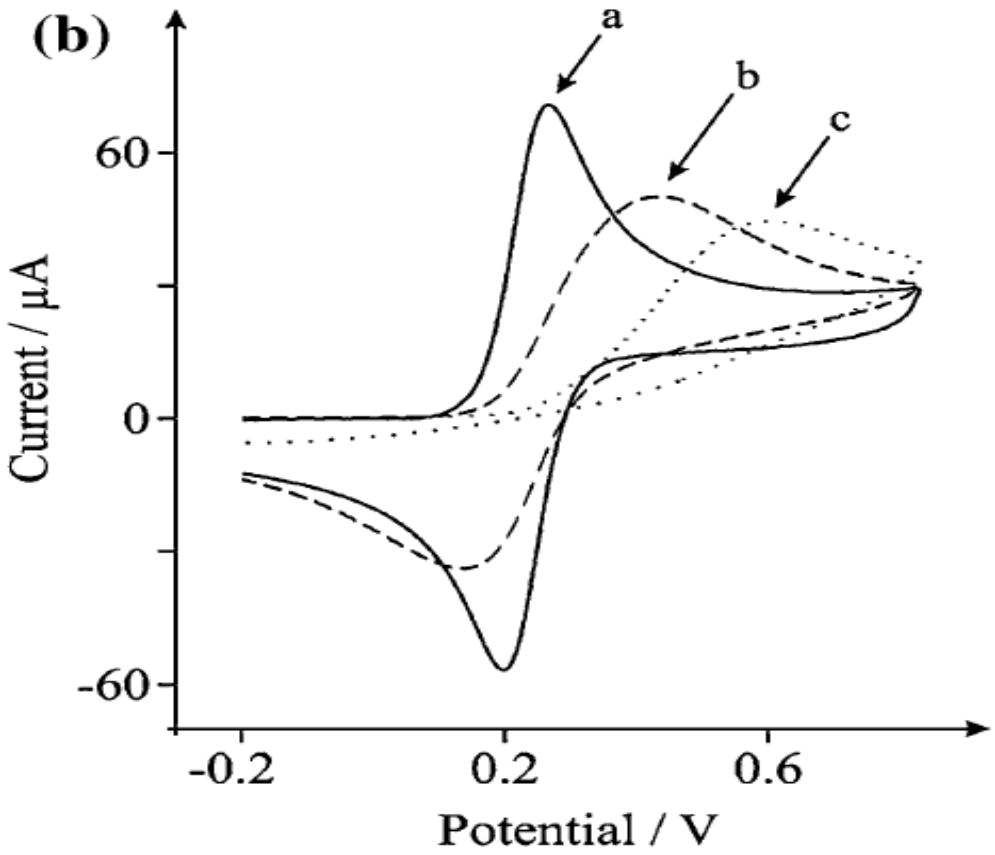




a Typical cyclic voltammogram depicting the peak position E_P and peak height I_P.

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

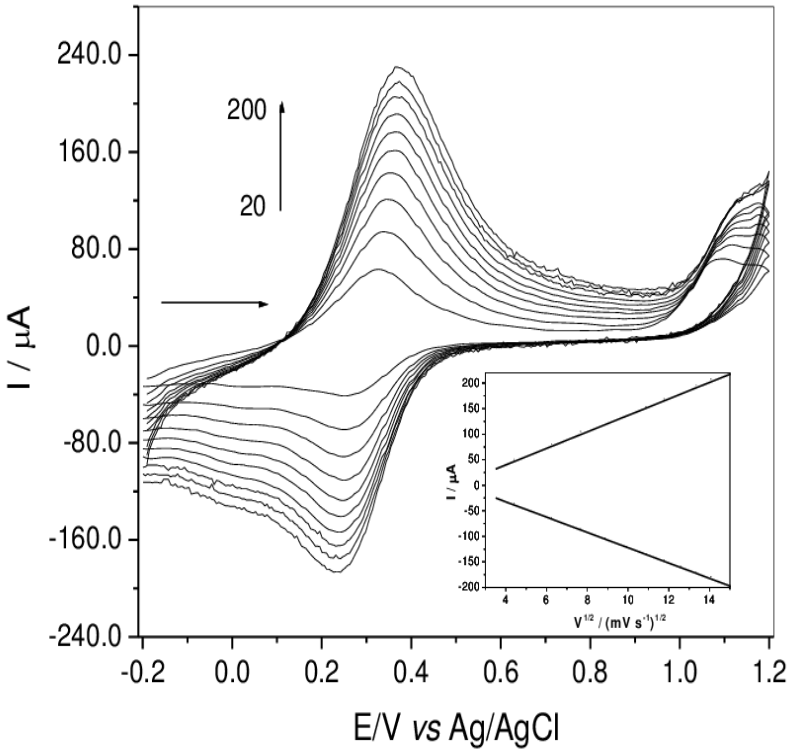
Formal potential (an approximation to the standard potential) of the species is $(E_{p(ox)}+E_{p(red)})/2$



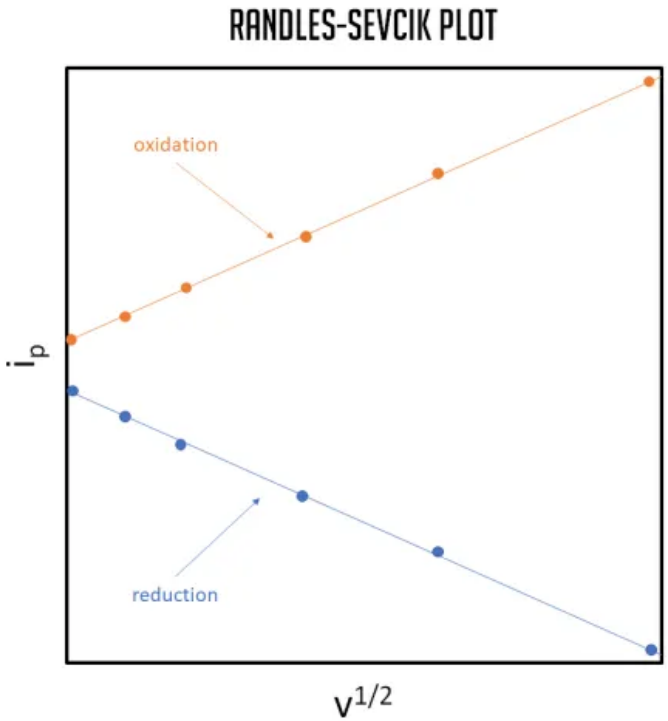
b Cyclic voltammograms for reversible (*a*), quasi-reversible (*b*) and irreversible (*c*) electron transfer

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)

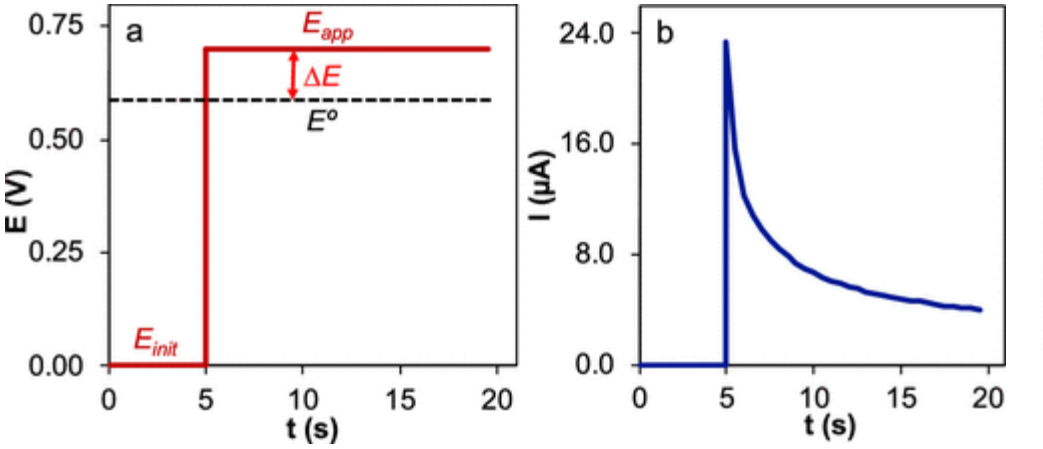


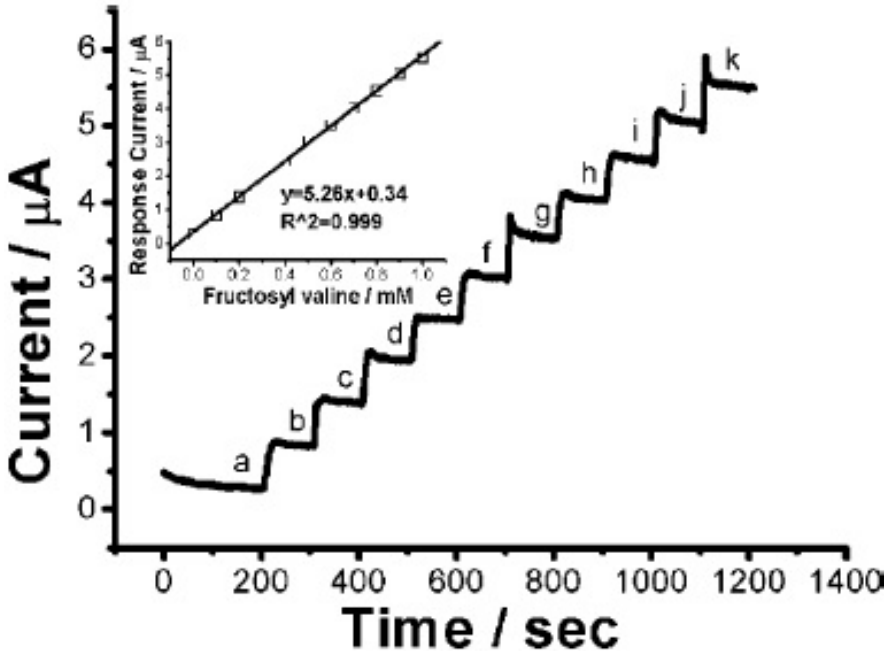
Randles-Sevcik Plot, displays the peak currents of the redox reactions versus the square root of the scan-rate.
It can be used to calculate the electrochemical active area and diffusion coefficient.



Chronoamperometry:

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





First, the electrode is poised at E_{init}, well negative with respect of $E^{0'}$ (for the redox couple), so only Red is presented in solution.

At time 5 s the potential is stepped to a value significantly positive for the redox couple (E_{appl}), so all Red in the vicinity of the electrode is immediately converted to Ox, showing an exponential current decay

Valid for reversible reaction limited by diffusion (no stirring)

Cottrell equation

$$i = \frac{nFAc_j^0\sqrt{D_j}}{\sqrt{\pi t}}$$

$$i = kt^{-1/2}$$

i = current, in unit A

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

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;

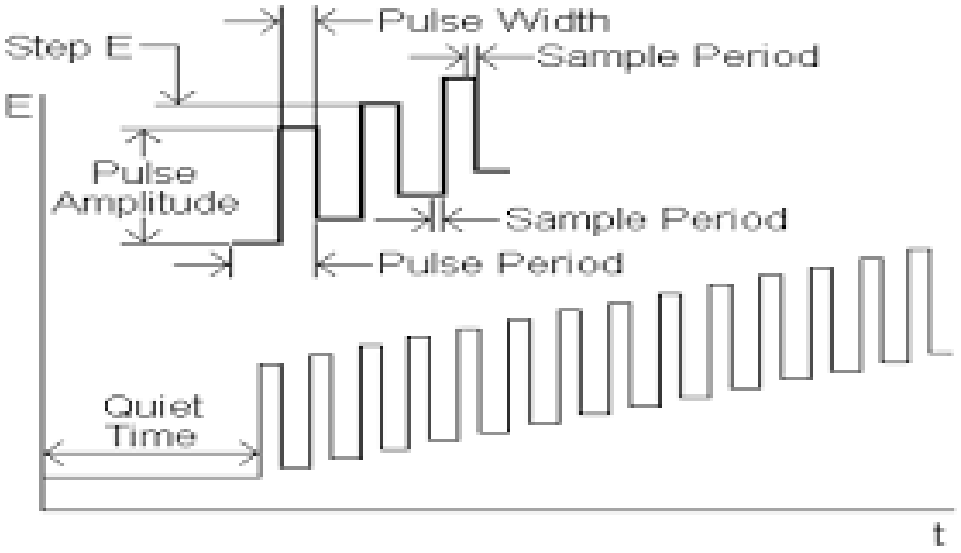
D = diffusion coefficient for species in cm^2/s

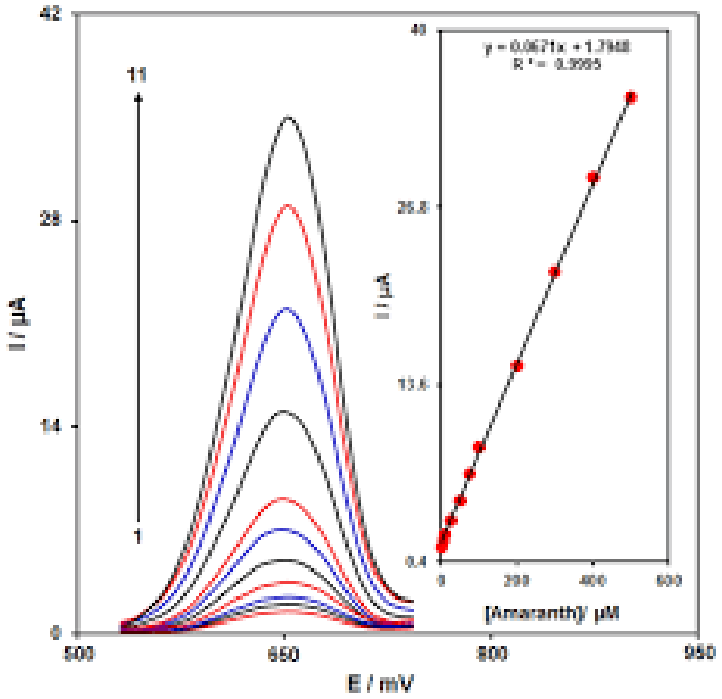
t = time in s.

- Describes the change in *i* with respect to *t* in a controlled step potential experiment, such as chronoamperometry.
- The *i* response shows a dependence with the $t^{-1/2}$.
- describes the case for a planner electrode

DPV - Differential pulse voltammetry

(just to show you a technique that uses pulses) (next slide one example of an immunobiosensor using this method).





In DPV, a base potential value is chosen at which there is no faradaic reaction and is applied to the electrode. The base potential is increased between pulses with equal increments. The current is immediately measured before the pulse application and at the end of the pulse, and the difference between them is recorded. It gives better signal to noise ratio in comparison to other amperometric technique.

Magnetic beads combined with carbon black-based screen-printed electrodes for COVID-19: A reliable and miniaturized electrochemical immunosensor for SARS-CoV-2 detection in saliva.
doi.org/10.1016/j.bios.2020.112686

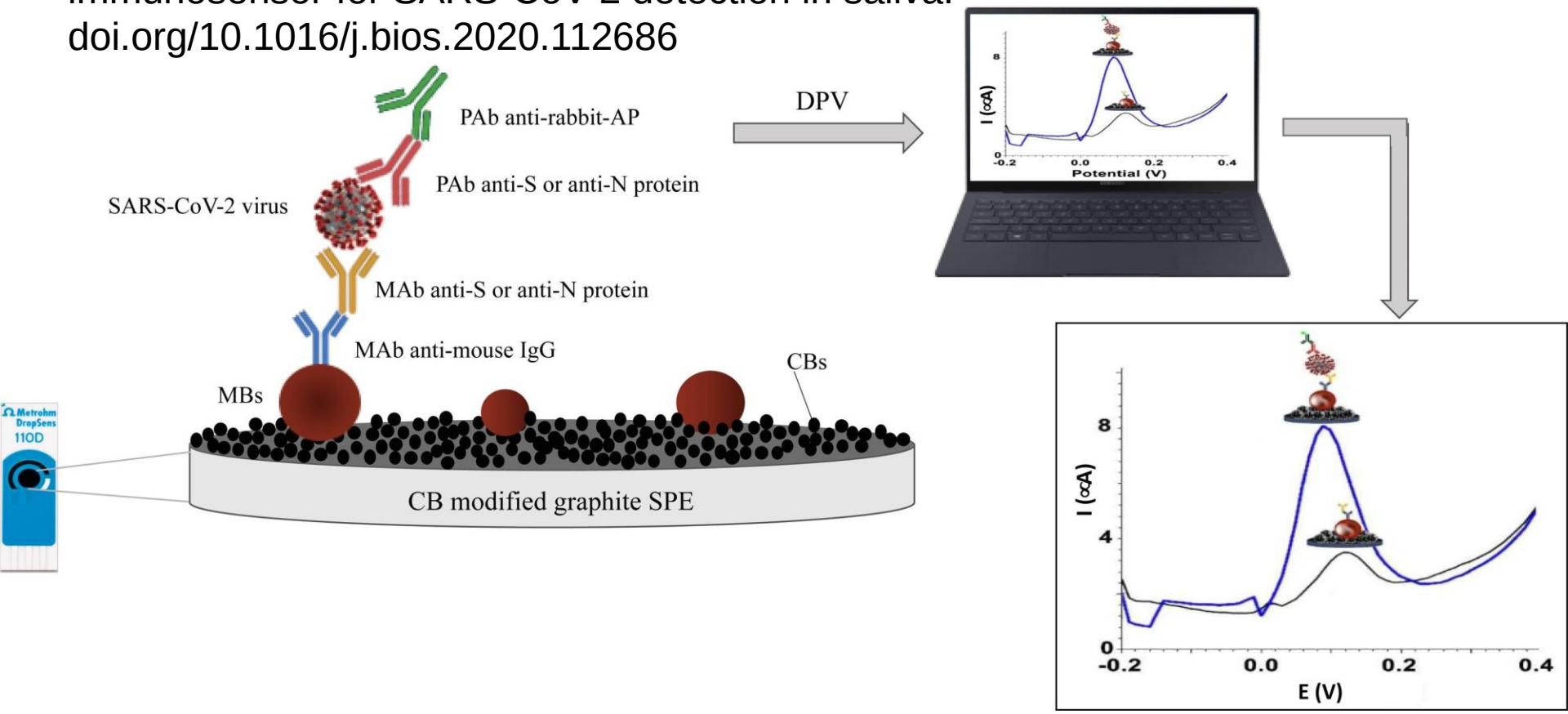


Fig. 2. Schematic representation of the electrochemical immunosensors for SARS-CoV-2 detection proposed by Fabiani et al. [32]. List of abbreviations: CB = carbon black; SPE = screen printed electrode; MBs = magnetic beads; MAb = monoclonal antibodies; PAb = polyclonal antibodies anti-S = antibodies against Spike protein; anti-N = antibodies against Nucleocapsid protein; AP = alkaline phosphatase. AP as the label of enzyme-linked bioassays- (with 4-nitrophenyl phosphate as substrate)

J. Munoz, R. Montes, M. Baeza. Trends in electrochemical impedance spectroscopy involving nanocomposite transducers: characterization, architecture surface and Bio-Sensing

TrAC, Trends Anal. Chem., 97 (2017), pp. 201-215, 10.1016/j. trac.2017.08.012