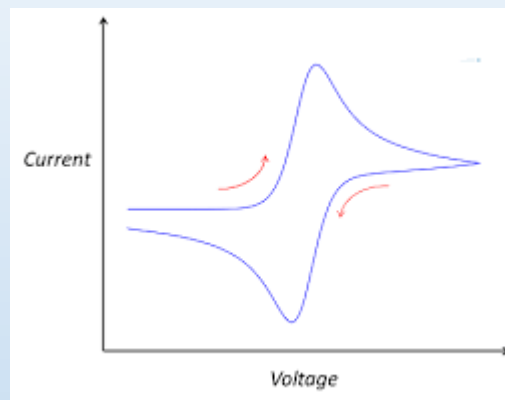# Fundamentals of Electrochemistry

Course: CSO 203

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Introduction to the Nernst Equation

Consider the equilibrium between ferrocenium (Fc^+) and ferrocene (Fc), this equilibrium is described by the **Nernst equation**

The Nernst equation relates the potential of an electrochemical cell (E) to the standard potential of a species (E^0) and the relative activities of the oxidized (Ox) and reduced (Red) analyte in the system at equilibrium

$$E = E^0 + \frac{RT}{nF}\ln\frac{(Ox)}{(Red)} = E^0 + 2.3026\frac{RT}{nF}\log_{10}\frac{(Ox)}{(Red)}$$

F is Faraday's constant, R is the universal gas constant, n is the number of electrons, and T is the temperature

In application of the Nernst Equation to the one-electron reduction of Fc^+ to Fc, the activities are replaced with their concentrations, which are more experimentally accessible, the standard potential E^0 is replaced with the formal potential $E^{0\prime}$, and n = 1

$$E = E^{0\prime} + \frac{RT}{F}\ln\frac{[Fc^+]}{[Fc]} = E^{0\prime} + 2.3026\frac{RT}{F}\log_{10}\frac{[Fc^+]}{[Fc]}$$

Introduction to the Nernst Equation

The formal potential is specific to the experimental conditions employed and is often estimated with the experimentally determined $E_{1/2}$ (V)

The Nernst equation provides a powerful way to predict how a system will respond to a change of concentration of species in solution or a change in the electrode potential

If the potential of $E = E°' \approx E_{1/2}$ is applied to Fc^+ solution, the Nernst equation predicts that Fc^+ will be reduced to Fc until $[Fc^+] = [Fc]$, and equilibrium is achieved.

What are the two points in the curve where concentrations of Fc^+ and Fc at the electrode surface are equal in order to follow the Nernst equation, $E = E_{1/2}$?
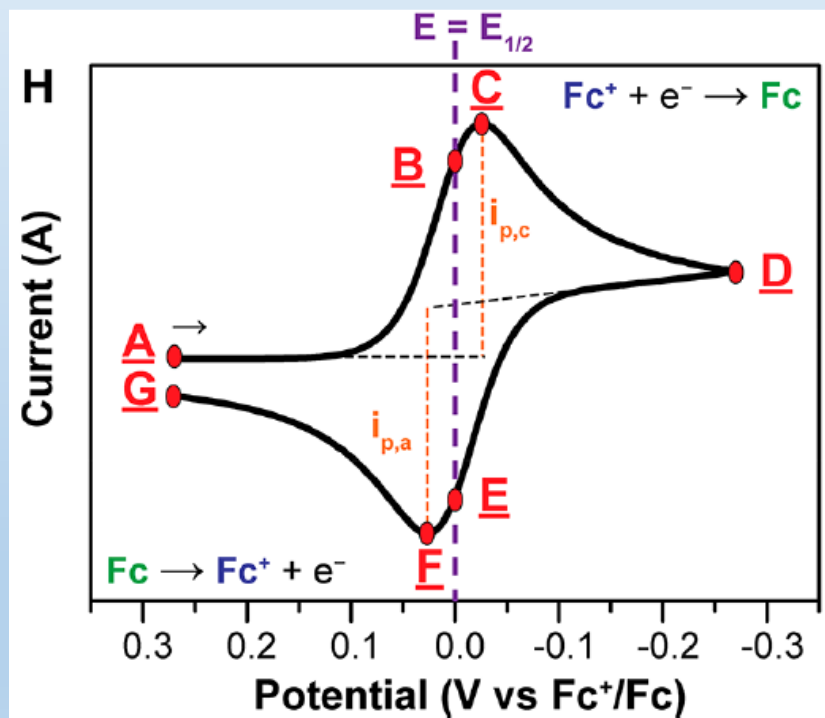
# *Understanding peak-to-peak separation in voltammogram*

Why do we observe peak-to-peak separation in cyclic voltammogram?
The two peaks are separated due to the diffusion of the analyte to and from the electrode

If the Faradaic process is chemically and electrochemically reversible, the difference between the anodic and cathodic peak potentials, called peak-to-peak separation (ΔEp), is 59 mV at 25 °C (2.22 RT/F) for one electron transfer process
Electrochemical reversibility is used to denote whether the analyte is stable upon reduction and can subsequently be re-oxidized
Ideally, the full width at half max (FWHM) on the forward scan of the peak is 59 mV
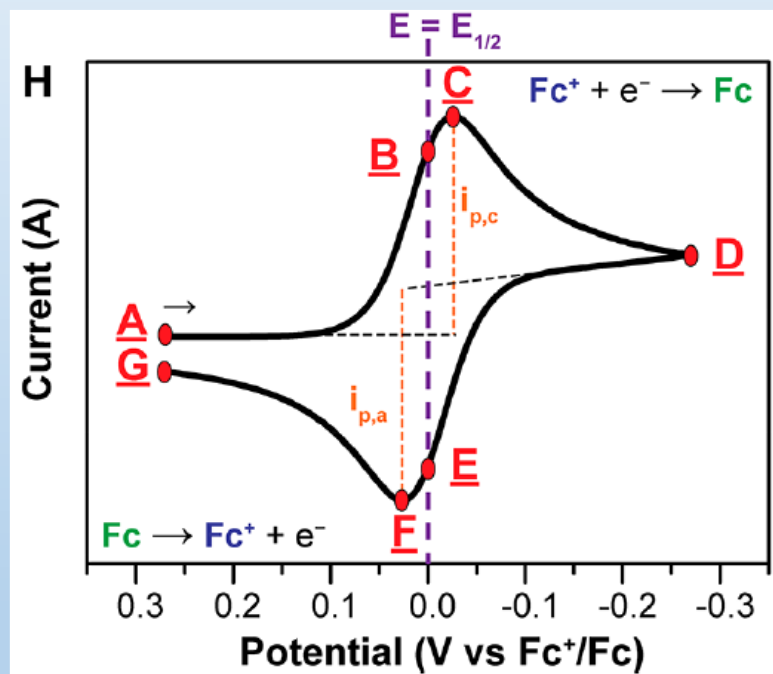
How to deduce experimentally?

4

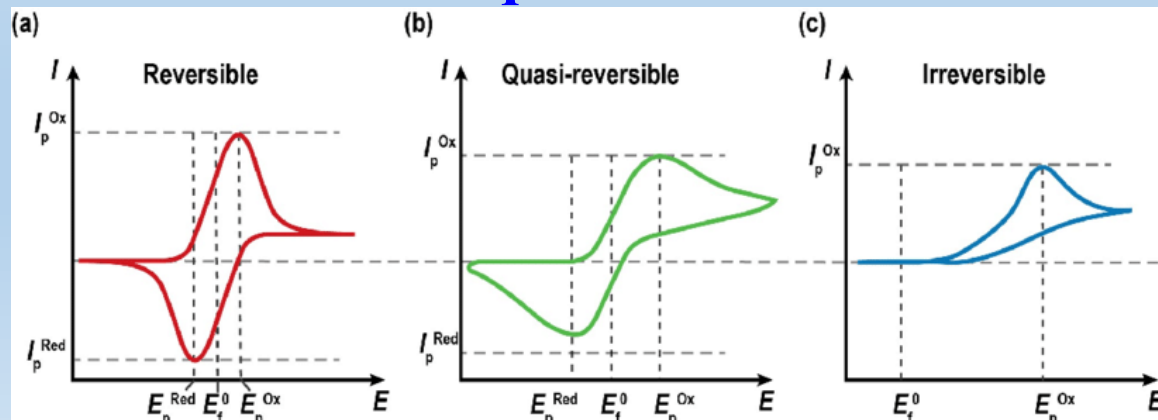# *Reversible, quasi-reversible and irreversible cyclic voltammogram*

In case of **irreversible process,** analytes that react in homogeneous chemical processes upon reduction/oxidation such as ligand loss or degradation occur

Electrochemical reversibility refers to the electron transfer kinetics between the electrode and the analyte

When there is a low energy barrier to electron transfer (electrochemical reversibility), the Nernstian equilibrium is established immediately upon any change in applied potential

By contrast, when there is a high energy barrier to electron transfer (electrochemical irreversibility), electron transfer reactions are sluggish and more negative (positive) potentials are required to observe reduction/oxidation process that produces larger ΔEp

Often electrochemically reversible processes, where the electron transfers are fast, and the processes follow the Nernst equation are referred to as "Nernstian."

Diagnostic criteria for a reversible, quasi-reversible and irreversible CV

Reversible	Quasi-reversible	Electrochemical irreversible
$\Delta E_p = (E_{p,a}-E_{p,c}) = 59$ mV/z (298K)	$\Delta E_p = (E_{p,a}-E_{p,c}) = f(v)$	E_p shift about 30 mV/αz (298 K) with tenfold higher v (α = unknown factor)
$E^{0'} = 0{,}5\ (E_{pa}+E_{pc})\ (D_{Ox}=D_{Red})$	$E^{0'} = 0{,}5\ (E_{pa}+E_{pc})\ (D_{Ox}=D_{Red})$	-
$I_{p,a} \propto v^{1/2}$ $I_{p,a} = \text{const}_1\ v^{1/2}$	-	$I_{p,a} \propto v^{1/2}$ $I_{p,a} = \text{const}_2\ v^{1/2}$
$I_{p,a}/I_{p,c} = 1$ for all v	$I_{p,a}/I_{p,c} = 1$ for all v	One peak current ($I_{p,c}$) missing

An irreversible system has, as mentioned before, either an anodic or cathodic peak. Examples of this are catalytic processes.
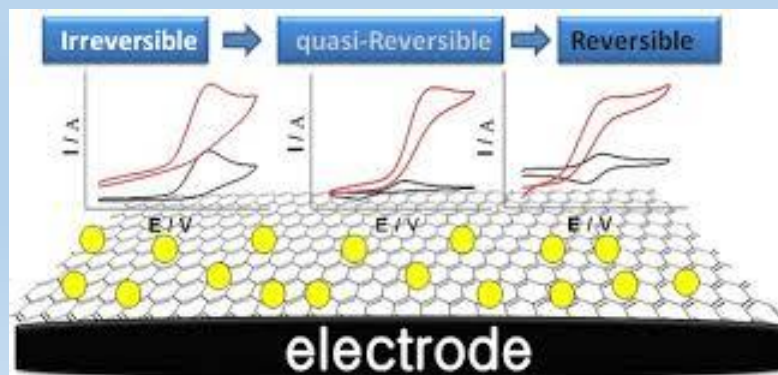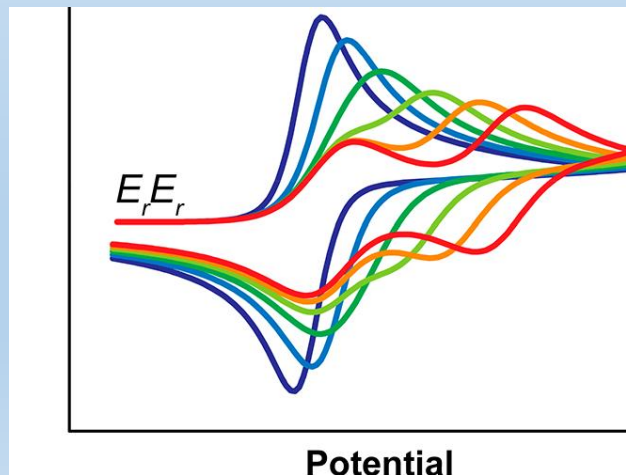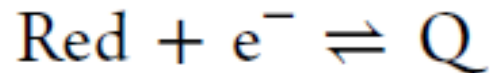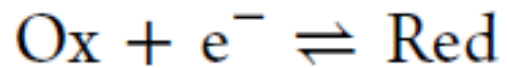
Beyond simple one-electron (1e⁻) reversible voltammogram

➢ **Understanding voltammograms more complicated than the data seen for simple, reversible, one-electron transfer reactions**

➢ **Slow electron transfer or multielectron transfers process can be investigated by cyclic voltammetry measurements**

➢ **When electron transfers are coupled to chemical reactions, cyclic voltammetry can provide kinetic and mechanistic information**

➢ **The notations used to describe various coupled reactions: *E* indicates an electron transfer step, *C* indicates a homogeneous chemical reaction (a chemical step)**

➢ **The subscript *r* indicates reversibility, and subscript *i* indicates irreversibility**

➢ **Each reaction is described for the reduction of the analyte *Ox* to *Red*. The same concepts can be readily extended to oxidative reactions (*Red* to *Ox*)**

➢ **When electron transfer at the electrode surface is slow compared to mass transport, the process is termed electrochemically "*irreversible*."**

➢ **Slow electrode kinetics compel significantly more negative applied potentials for appreciable current to flow. As a result, peak-to-peak separation is larger than the 59 mV anticipated for a reversible one-electron redox couple**

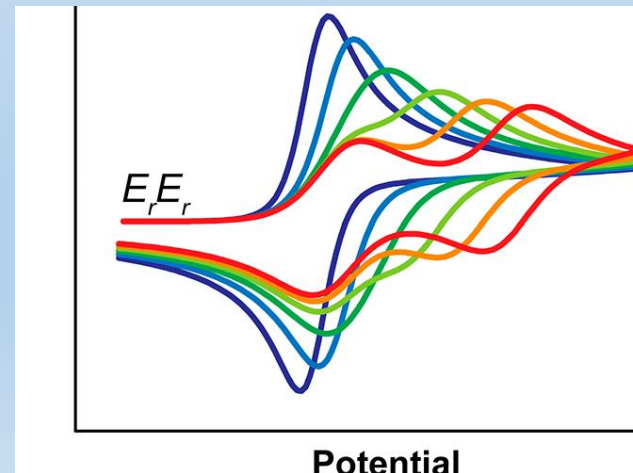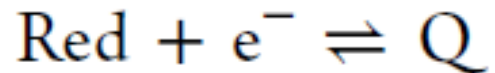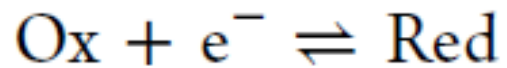# *Two Sequential Electron Transfer Reversible Process E_rE_r*

➢ **Many complexes can undergo multiple reversible redox processes**

➢ **For simplicity, we will only consider two electrochemical steps**

➢ **The voltammogram appearance is dependent upon the difference in formal potential of the two electrochemical steps**

➢ **If the second electrochemical step is thermodynamically more favorable than the first, the voltammogram appears identical to a Nernstian two-electron transfer, and the peak-to-peak separation (ΔEp) will be ~ 29.5 mV instead of the 59 mV**

➢ **If the second electron transfer becomes less thermodynamically favorable, ΔEp grows until it reaches a maximum value of just over 140 mV**

$$Ox + e^- \rightleftharpoons Red$$

$$Red + e^- \rightleftharpoons Q$$

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E_rE_r

Potential

# *Voltammograms modelled using DigiElch simulation software*
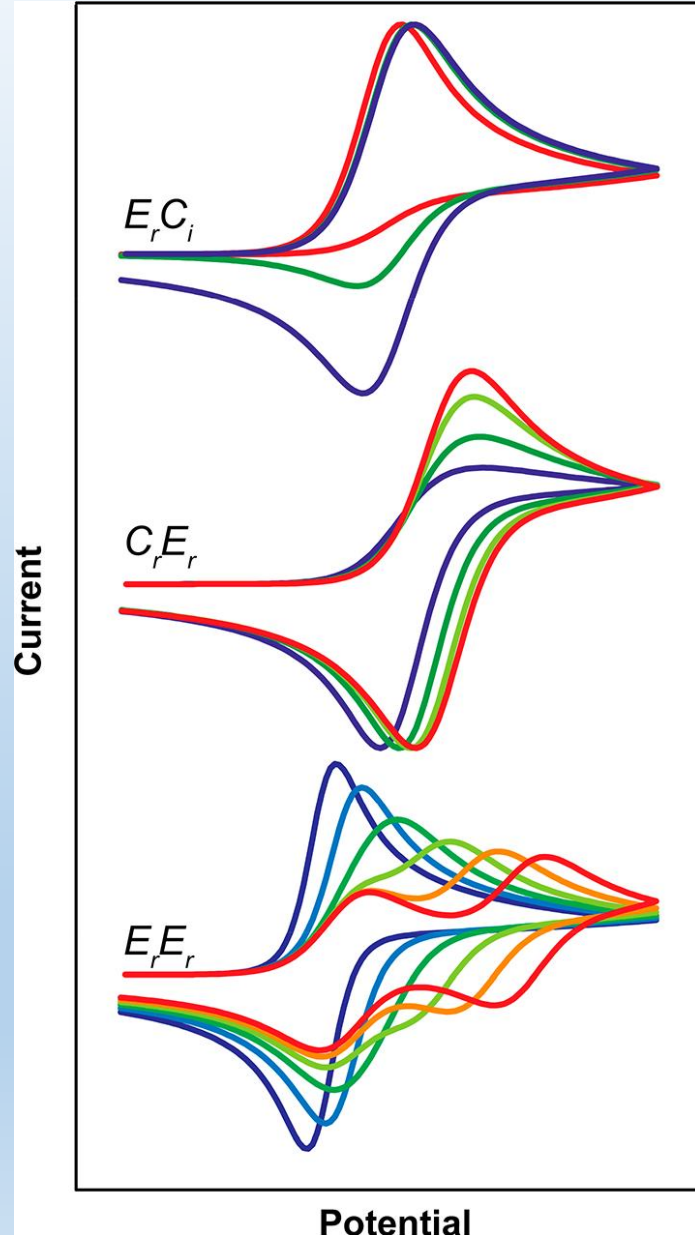
➢ **ErCi mechanism**: increasing the scan rate (from $\upsilon = 0.1$ (**red**) to 1 (**green**) to 10 V s^{-1} (**dark blue**)) restores reversibility (rate constant for the Ci step k = 5 s^{-1}).

$$Ox + e^- \rightleftharpoons Red$$

$$Red \xrightarrow{k} Z$$
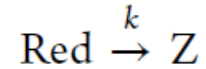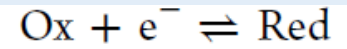
➢ **CrEr mechanism**: the faster the forward rate constant of the Cr step, the more reversible the voltammogram ($K_{eq} = 0.1$, $k_f = 1$ (**blue**), 10 (**dark green**), 100 (**lime green**), 1000 s^{-1} (**red**)).

$$Z \rightleftharpoons Ox$$

$$Ox + e^- \rightleftharpoons Red$$
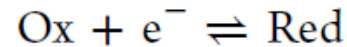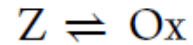
➢ **ErEr mechanism**: as the separations between the two reduction potentials decreases, the peaks merge to become a single two-electron peak. $\Delta E_p = -0.05$ (**dark blue**), 0 (**light blue**), 0.05 (**dark green**), 0.1 (**lime green**), 0.15 (**orange**), and 0.2 V (**red**).

$$Ox + e^- \rightleftharpoons Red$$

$$Red + e^- \rightleftharpoons Q$$
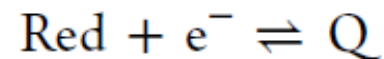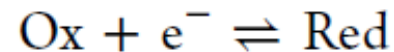
Importance of the Scan Rate in Electrochemistry

➢ *The scan rate of the experiment controls how fast the applied potential is scanned*

You get higher current at faster scan rate, do you know why is it so?

➢ *Faster scan rates lead to a decrease in the size of the diffusion layer; as a consequence, higher currents are observed*

*How does the current correlate with scan rate?*

For electrochemically reversible electron transfer processes involving freely diffusing redox species, the Randles−Sevcik equation describes how the peak current i_p (A) increases linearly *with the square root of the scan rate v (V s^{-1})*

$$i_p = 0.446 nFAC^0 \left(\frac{nFvD_o}{RT} \right)^{1/2}$$

where n is the number of electrons transferred in the redox event, A (cm^2) is the electrode surface area (usually treated as the geometric surface area), D_o (cm^2 s^{-1}) is the diffusion coefficient of the oxidized analyte, and C^0 (mol cm^{-3}) is the bulk concentration of the analyte

Importance of the Scan Rate in Electrochemistry

➢ *The Randles−Sevcik equation can give indications as to whether an analyte is freely diffusing in solution*

➢ *As analytes can sometimes adsorb to the electrode surface, it is essential to assess whether an analyte remains homogeneous in solution prior to analyzing its reactivity*

➢ *In addition to verifying that the analyte is freely diffusing, the Randles−Sevcik equation may be used to calculate diffusion coefficients*
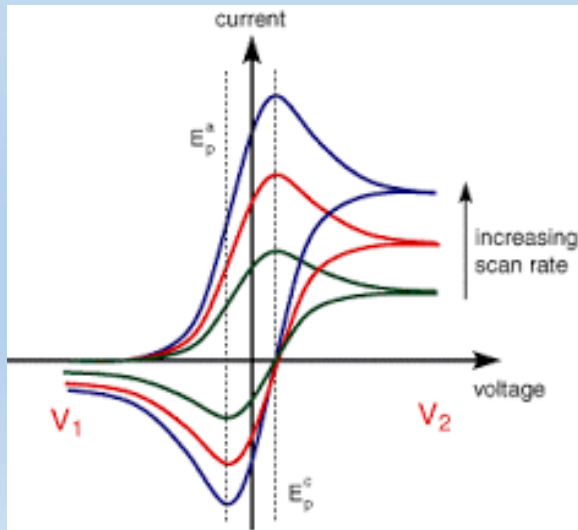
$$i_p = 0.446nFAC^0\left(\frac{nFvD_o}{RT}\right)^{1/2}$$
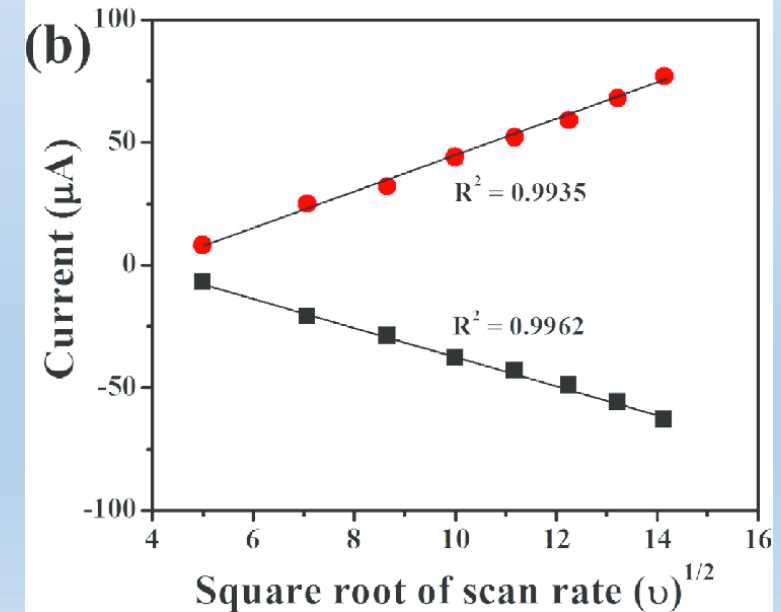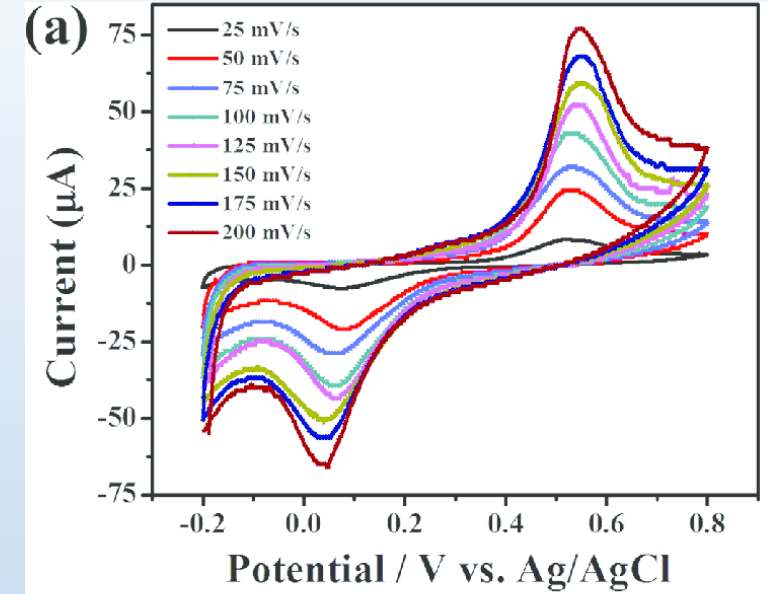
How to distinguish between diffusion-controlled and an adsorbed process?

➤ *For a diffusion controlled reversible electrochemical process, peak current (i_p) is a function of square root of scan rate ($v^{1/2}$).*

➤ *However, for an electrode-adsorbed species, the peak current (i_p) linearly dependent on scan rate (v).*

$$i_p = \frac{n^2 F^2}{4RT} v A \, \Gamma^*$$

I* is the surface coverage of the adsorbed species (mol cm^{-2})

*What if analyte does not obey Randles-Sevcik equaition?*

The electrochemical process is either quasi-reversible or electron transfer may be occurring via surface-adsorbed species.

How to distinguish then?

i.   *Check peak-to-peak separation*

ii. *Linear dependent of peak current on scan rate*

iii. *For a quasi-reversible process, ΔEp shift with the scan rates*

iv. *For a surface-adsorbed species, small ΔEp is observed and does not change much upon varying the scan rates*
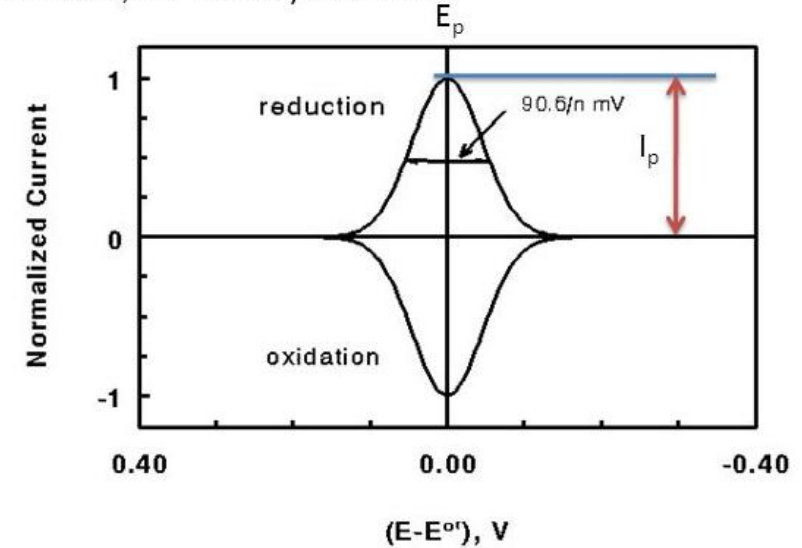
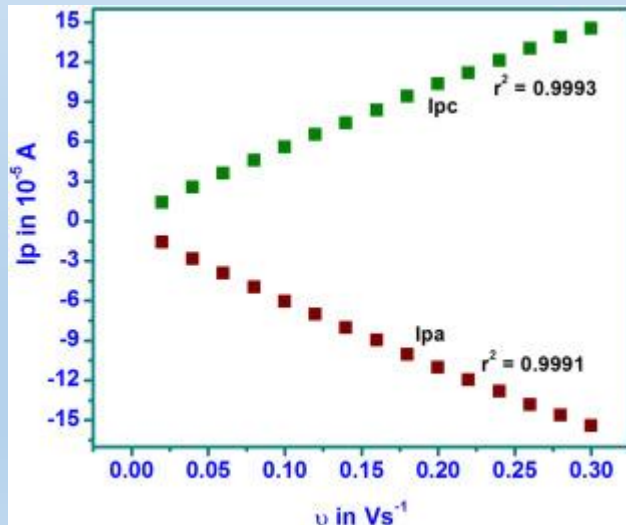# *Cyclic Voltammograms of electrode-adsorbed species*
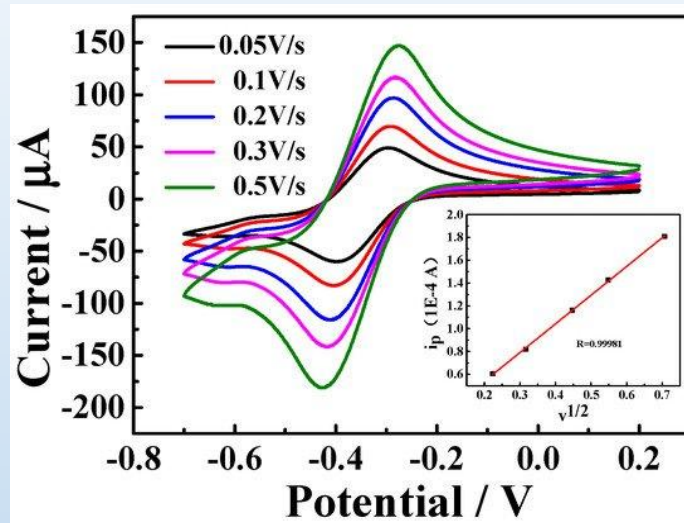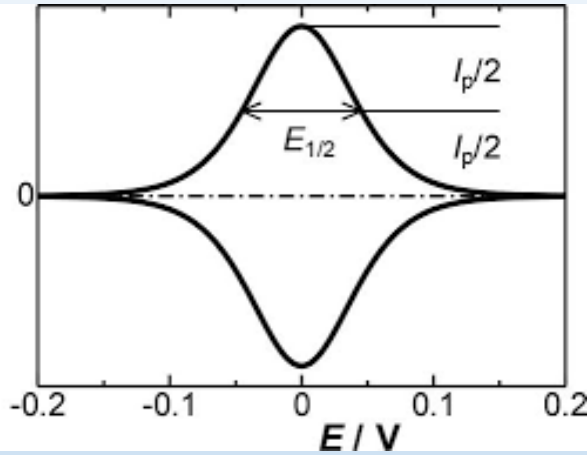
Ideal, reversible thin layer cyclic voltammogram

Example cobalt complex: $LCo^{III} + e^- \longleftrightarrow LCo^{II}$

$Q = nFA\Gamma_T$ Γ_T = total surface concentration of electroactive species
A = electrode area, F = Faraday's constant

reversible peak current I_p increases linearly as scan rate (v) is increased; And $\Delta E_p = 0$. Rate constants can be obtained by increasing v to drive the CV into a kinetically limited situation where $\Delta E_p > 0$. Q = area under reduction curve

A simple way to polish electrodes is with figure-eight motions on a cloth polishing pad in a water-alumina slurry. When using circular motions, the polishing is often uneven, and the surface can become slanted.

Alumina-water slury

Polishing pad

✓ Figure-eight polishing motion

✗ Circular polishing motion