Cyclic Voltammetry (An Introduction)

- An Introduction to Cyclic voltammetry
- Applications of Cyclic voltammetry

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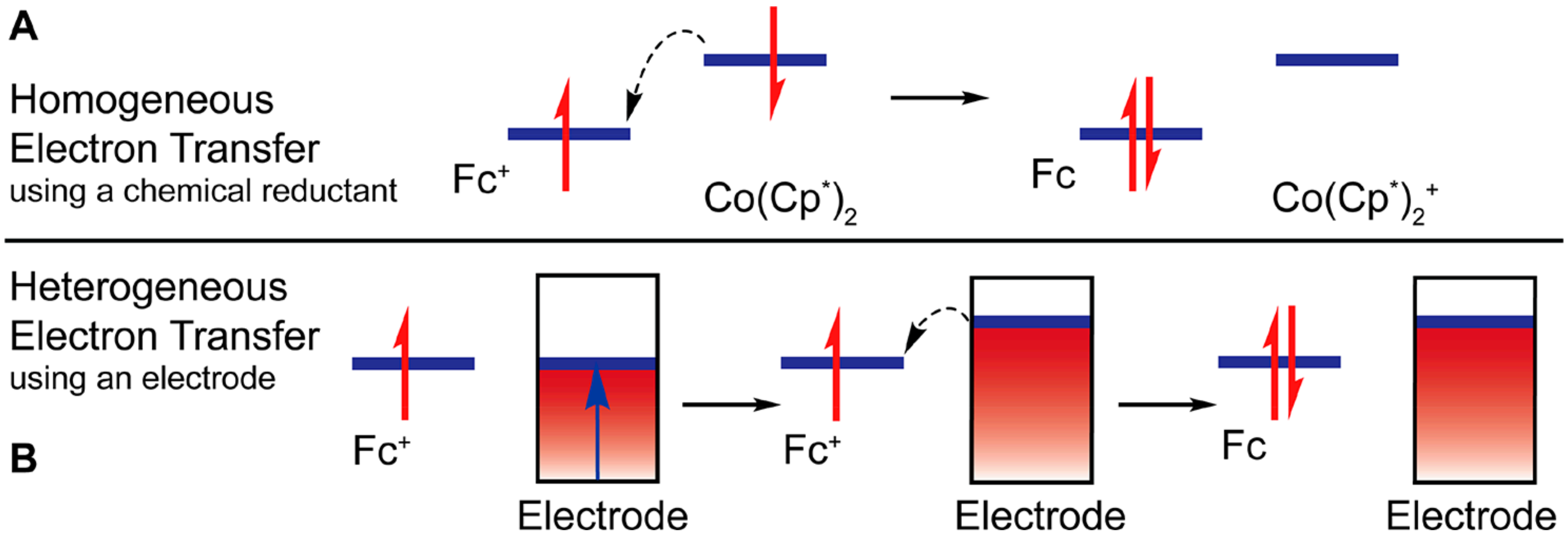
Electron Transfer

Before we begin to understand cyclic voltammetry (CV), we must first understand the types of electron transfers:

Homogeneous: This is usually a chemical process that utilizes a chemical reductant

Heterogeneous: This is usually electrochemical electron transfer wherein the electron transfer occurs to/from electrode



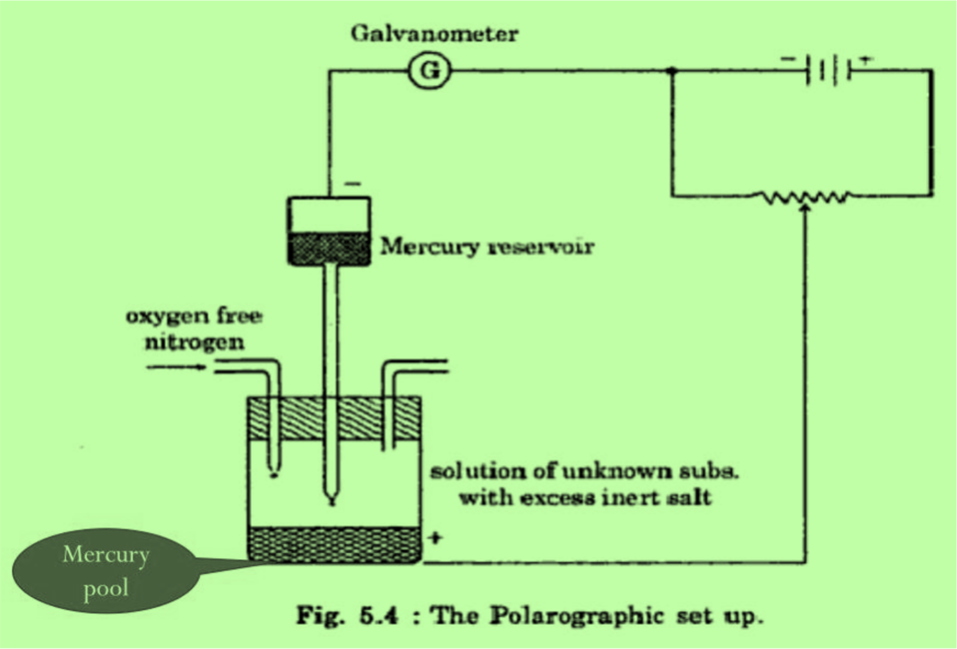
Ferrocene/Ferrocenium as redox couple

Elgrishi et. al., J. Chem. Educ. 2018, 95, 197–206

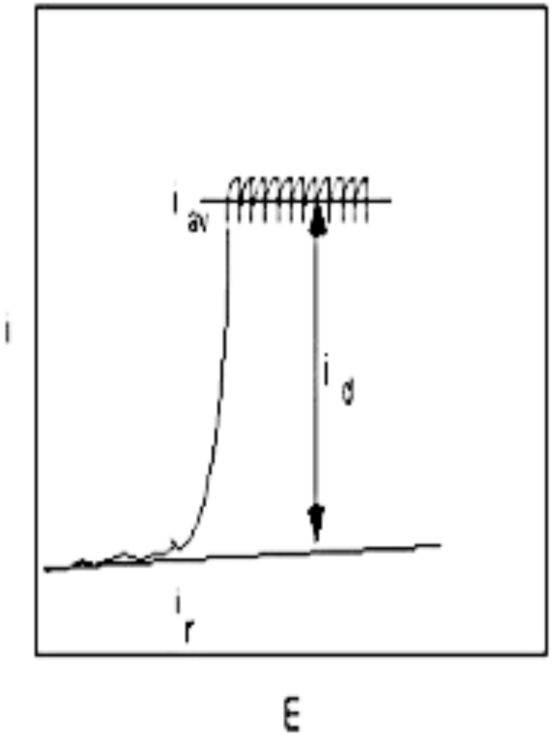
Polarography

Polarography: It is considered as the Granddaddy of the modern cyclic voltammetry: In polarography, the electrical potential/ voltage of a growing drop of mercury in an electrolyte solution is varied as a function of time and current due to the ongoing electrochemical reaction is measured.

Mercury is used because:
(1) Since it is liquid a fresh metal surface is generated as the drop changes,
(2) It shows a wide potential window,
(3) Many metals can be reversibly reduced on mercury.



A typical polarography setup



i_r: Residual current: Current obtained when no electrochemical change takes place

i_d: diffusion current: Current due to the diffusion of electroactive species to the electrode surface

i_{av}: Average or limiting current: Average current through out the life of drop

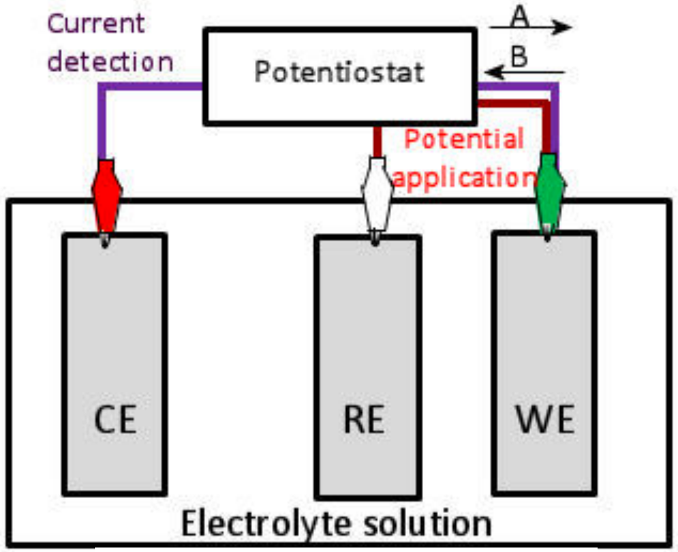
V. Lakshminarayanan, Resonance Sep 2004

Cyclic Voltammetry (An Introduction)

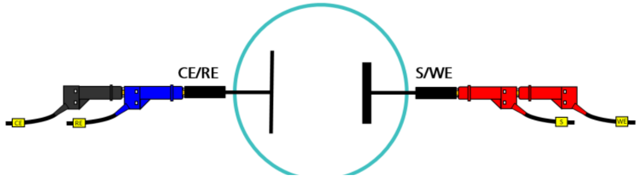
Two and three electrode setups: Electrochemical experiments can be carried out either in 2 or 3-electrodes setup. 3-electrode Setup being the more common and accurate.

Requirements for a 3-electrodes electrochemical cells

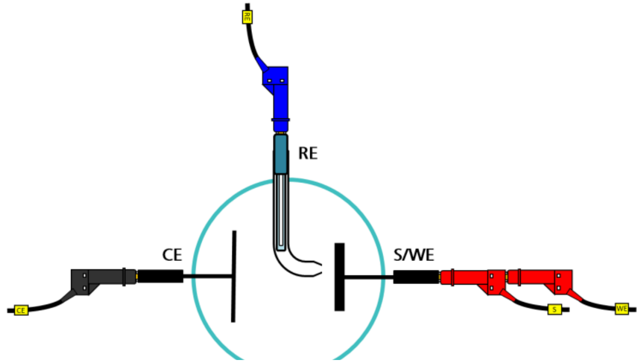
(1) Working, reference, and counter electrodes
(2) Cell and Electrolyte solution
(3) Potentiostat
(4) Connecting cables
(5) Redox couple e.g., Ferrocene/Ferrocenium
(6) Personal computer for data recording



3-electrode setup



onnections for 2-electrode setup



Connections for 3-electrode setup

A. Bard, L. Faulkner, *Electrochemical Methods – Fundamental and Applications,* 2nd Edition, John Wiley and sons

Cyclic Voltammetry (An Introduction)

Different types of electrodes:

(1) **Working Electrode:** This is the electrode of interest, where the electrochemical reaction is occurring. A potentiostat is used to control the applied potential of the working electrode as a function of the reference electrode potential. The electrode must be such that it should not have any redox properties on its own.
Typical examples of working electrodes are Gold electrode, Platinum electrode, Glassy carbon electrode, Graphite electrode, etc.

(2) Reference Electrode: A reference electrode is an electrode whose electrode potential is stable and it is also a non-polarizable electrode. It is used as a reference against which the potential of other working electrodes can be measured in an electrochemical cell.
Typical examples of reference electrodes are Calomel electrode, Ag/AgCl electrode, Ag/$AgNO_3$ electrode, Graphite electrode, etc.

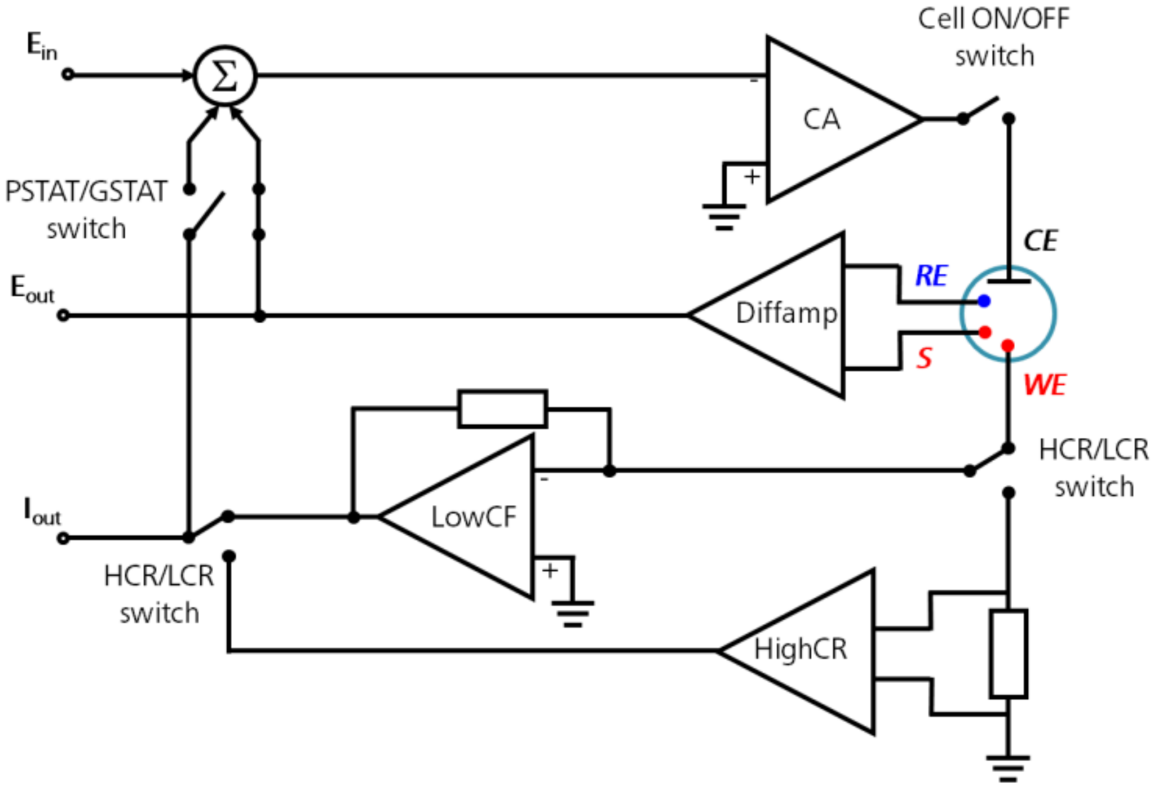
(3) Counter electrode: The counter electrode is used in an electrochemical cell to complete the electrical circuit. Current is recorded between the working and counter electrode.
Typical examples of counter electrodes are large area Pt electrode, mesh type Pt electrode.

Potentiostat

Potentiostat: This is the machine that we require in order to perform a cyclic voltammetry experiment.

- The main function of the machine is to keep the potential difference of the working electrode constant with respect to the reference electrode.
- In galvanostatic mode, the machine can control the current flow between the working electrode and counter electrode.
- The basic diagram of the potentiostat is shown in the figure below.

A typical potentiostat machine from Solartron Analytical Versastat-4



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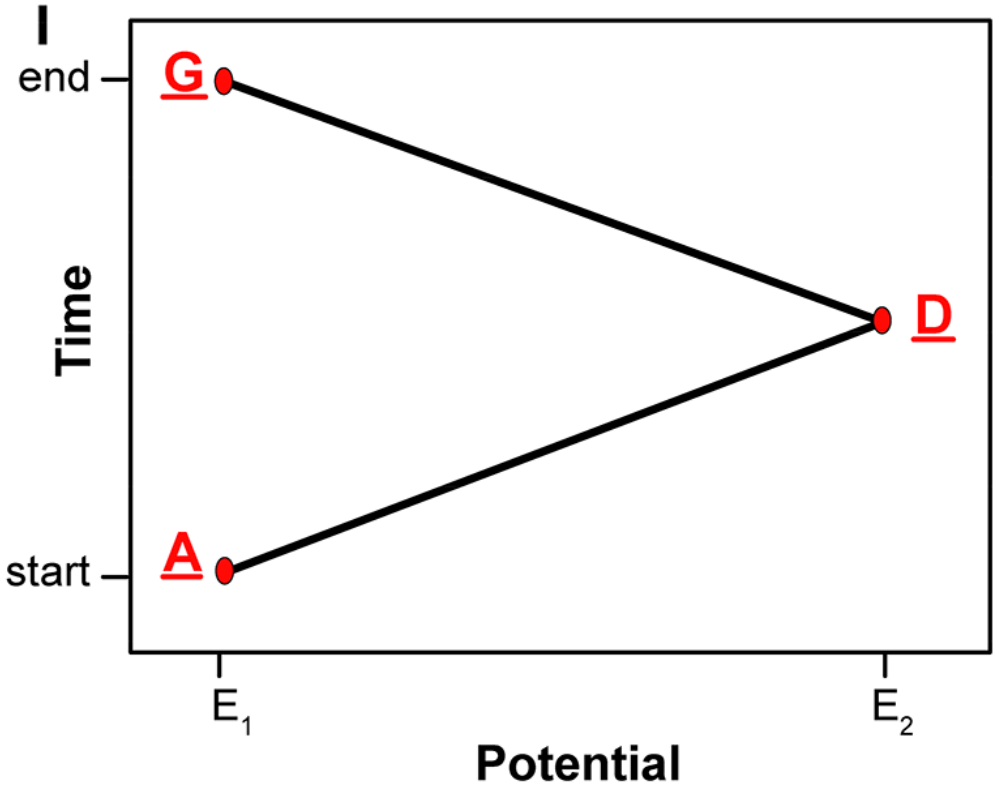
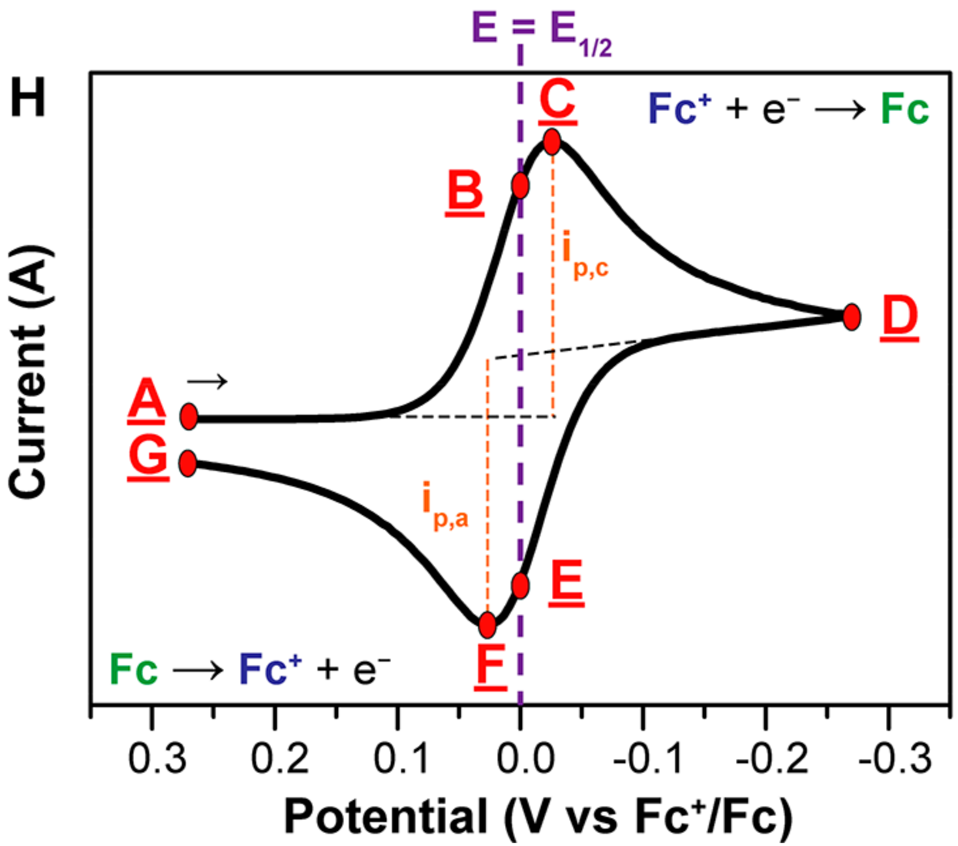


Typical input of a CV experiment:
Potential is scanned from A (E1) to D and then back to original position G (E1)

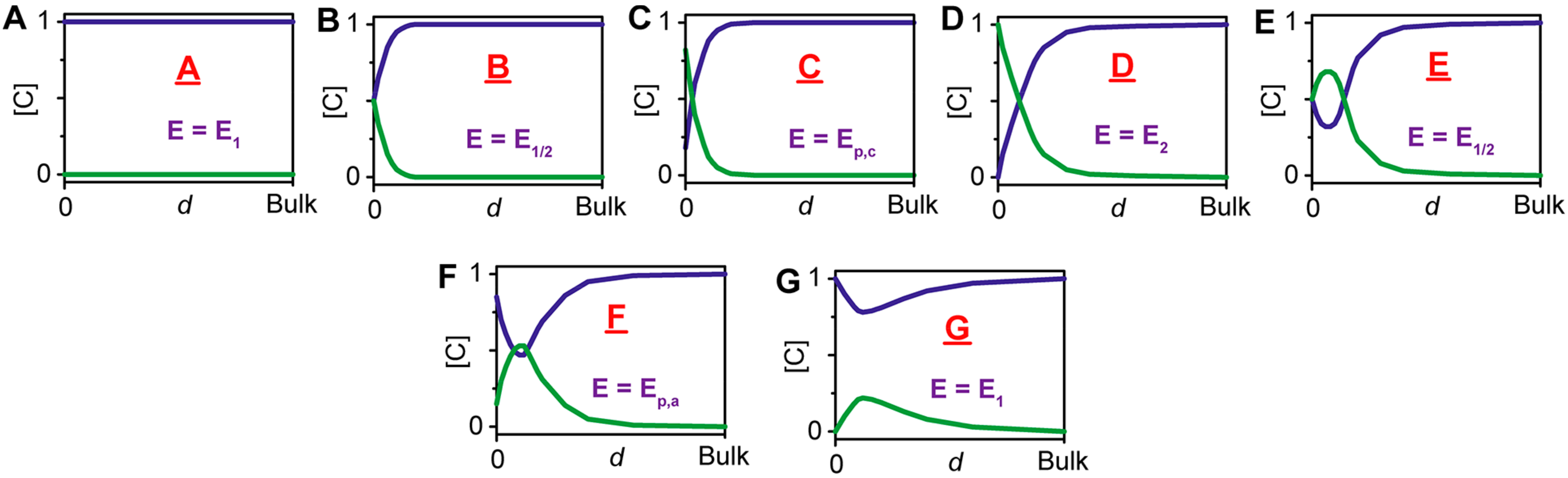


Typical output of a CV experiment in terms of I vs V plot
Measured for a well-known redox couple (Ferrocene/Ferrocenium)

Elgrishi et. al., J. Chem. Educ. 2018, 95, 197–206

Cyclic Voltammetry (An Introduction)

Concentration profiles (mM) for Fc^+ (blue) and Fc (green) as a function of the distance from the electrode



Elgrishi et. al., J. Chem. Educ. 2018, 95, 197–206

Cyclic Voltammetry (An Introduction)

- The concentrations of the redox species at the electrode surface are defined by the Nernst equation

$$E = E^0 - RT/nF\ ln\ (C_{Red}/C_{Ox})$$

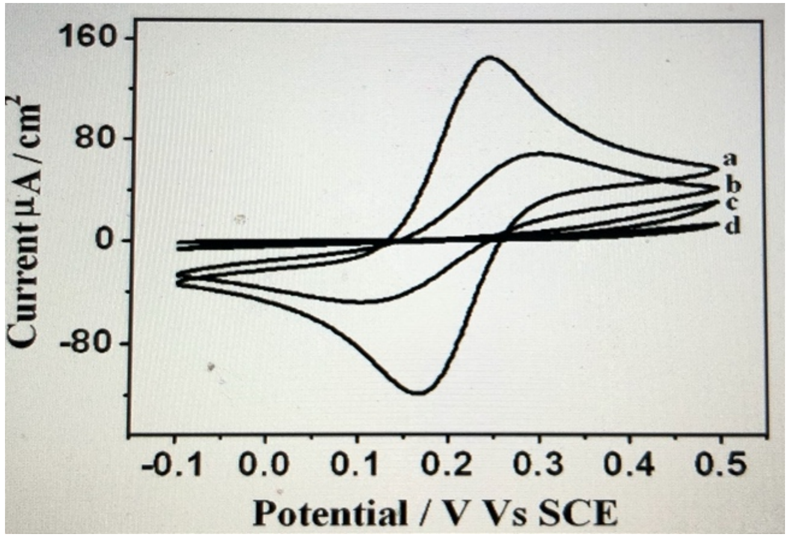
- Reversibility: In the case of an electrochemically reversible process:

- The difference between the anodic and cathodic peak potentials also called peak-to-peak separation (ΔEp), is 57 mV at 25 °C (2.22 RT/F).

- The concentration is related to the peak current by the Randles-Sevcik equation

$$i_p = 2.69 \times 10^5 n^{3/2} A C_o D^{1/2} v^{1/2}$$

Where i_p: peak current
A: Area of the electrode
D: Diffusion coefficient (cm^2/s)
C_o: concentration
V: scan rate



Reversibility order for the 4 plots a-d are a > b > c > d

R.K. Pandey et al. / Journal of Colloid and Interface Science 315 (2007) 528–536

Cyclic Voltammetry (Applications)

- Cyclic voltammetry (CV) is arguably the most important electroanalytical technique for various analytical purposes
- Study of useful reaction mechanisms: e.g., oxidation of aniline, dopamine oxidations etc.
- Some useful quantitative measurements such as determination of diffusion coefficient.
- Studying the reversibility of electrochemical reactions.
- Various useful applications in energy storage and energy conversion reactions e.g., electrocatalysis in fuel cells, battery, supercapacitors studies etc.
- Study of corrosion phenomenon of metals
- Electrochemical synthesis of useful substances e.g., conducting polymers such as polyaniline, nanoparticle films on electrodes etc.

References

1) *Elgrishi et. al., J. Chem. Educ. 2018, 95, 197–206*

2) *V. Lakshminarayanan, Resonance Sep 2004*

3) *A. Bard, L. Faulkner, Electrochemical Methods – Fundamental and Applications, 2nd Edition, John Wiley and sons*

4) *R.K. Pandey et al. / Journal of Colloid and Interface Science 2007, 315, 528–536*