

Cyclic Voltammetry

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Cyclic voltammetry (CV) is used extensively by electrochemists to obtain the potential at which the chemical processes occur, and to obtain information about coupled homogeneous chemical reactions or the role of adsorption and diffusion of solution species. CV is a technique that allows one to scan the potential of a working electrode in one direction (anodic or cathodic) to observe the peaks due to (oxidation or reduction) of the substrate/analyte, and then in the opposite direction (cathodic or anodic) to observe peaks due to (reduction or oxidation) of the **intermediate formed** in the forward scan. Using this electro-analytical technique one can record the current (*i*) of a redox active species as a function of applied potential.

Current

The current (*i*) is controlled by the following processes.

- mass transfer (occurs by diffusion, migration and convection).
- electron transfer at the electrode surface.
- chemical reactions preceding or following the electron transfer.
- other surface reactions, *e.g.*, adsorption, desorption, or crystallization.

Electrodes

Generally, voltammetry requires only two electrodes but, practically it is difficult to maintain a constant potential along with current. The cell used in cyclic voltammetry consists of three electrodes, namely **working electrode**, **counter electrode** (auxiliary electrode), and **reference electrode**. A three-electrode system can conveniently balance the current and the applied potential.

The **working electrode** behaves as an anode or cathode depending on the applied potential. Generally, this electrode has a metallic surface with a well-defined area where the reactions of interest take place. Most common working electrodes are made of inert material

such as platinum, gold, graphite, and glassy carbon.

The **reference electrode** is used to measure the potential of the working electrode. The potential of the reference electrode is a constant value, and which should not change with the redox process taking place in the electrolyte. In other words, the reference electrode is used to keep the potential between itself and the working electrode constant. Examples of reference electrodes and their potentials (in volts) with respect to primary reference electrode, Standard Hydrogen Electrode (SHE), are given in Table 1.

Table 1. Potentials of reference electrodes

Name	Half-Cell Reaction	Potential
SCE	$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Hg} + 2\text{Cl}^-$	+0.2415
SSC(0.1M)	$\text{AgCl} + \text{e}^- \rightleftharpoons \text{Ag} + \text{Cl}^-$	+0.2881
SSC(sat)	$\text{AgCl} + \text{e}^- \rightleftharpoons \text{Ag} + \text{Cl}^-$	+0.2224
SHE	$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$	0.0000

Saturated/standard calomel electrode (SCE), silver-silver chloride electrode (SSC) and glass electrode are some examples of common **secondary reference electrodes**.

The silver-silver chloride reference electrode SSC (sat) is composed of a silver wire immersed in a solution that is **saturated** with potassium chloride and silver chloride.

The **counter electrode** can complete the circuit and balance the charges. The current does not pass through either working electrode or reference electrode. The potential is measured between the reference and working electrodes, and the current (*i*) is measured between the working and counter electrodes. Common counter electrodes are made of platinum or graphite.

Potentiostat is the external power source in cyclic voltammetry process which applies a potential across the electrodes, while simultaneously measuring the current or the change of potential across the multiple electrodes. For the reaction $\text{Ox} + \text{e}^- \rightleftharpoons \text{Red}$,

$$E = E^\circ - (RT/nF)\ln\{[\text{Red}]/[\text{Ox}]\}.$$

Electrolytes

Electrolyte is a conducting solution which does not undergo any redox reactions in the applied potential range. Li_2CO_3 , NaCl, KCl, KClO_4 , K_2SO_4 , KNO_3 , mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC), poly(methacrylate) (PMA) and poly(ethylene glycol) (PEG) are used as electrolytes depending on the solubility, reaction mechanisms and conductivity. Ammonium salts such as R_4NPF_6 , R_4NBF_4 , and R_4NClO_4 , ($\text{R} = \text{Me, Et, Pr and Bu}$) are the common electrolytes used with organic solvents such as acetone, acetonitrile, DMF, CH_2Cl_2 , etc. Normally, the concentration of the electrolyte is about 0.1 M with an analyte or sample concentration of 1-2 mM.

Most radical cations/anions formed during cyclic voltammetry are very reactive and can react with moisture and oxygen present in the solution. Thus, solvents and electrolytes are dried and kept in an inert atmosphere. The electrolyte solution is deaerated by bubbling nitrogen or argon just before the experiment.

To perform the cyclic voltammetry, the electrolyte solution is first added to an electrochemical cell along with a reference electrode, working electrode and counter electrode (Figure 1).

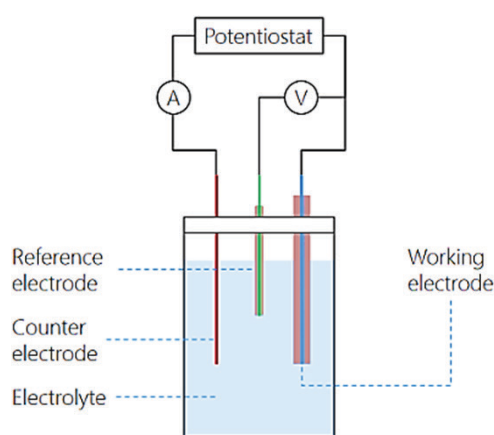


Figure 1. Three-electrode cell used in CV

A linear sweep of the potential of the working electrode is carried out until it reaches a preset limit, at this point, it is swept back in the opposite direction as in Figure 2.

The resulting graph/plot of current as a function of applied potential and is called the cyclic voltammogram.

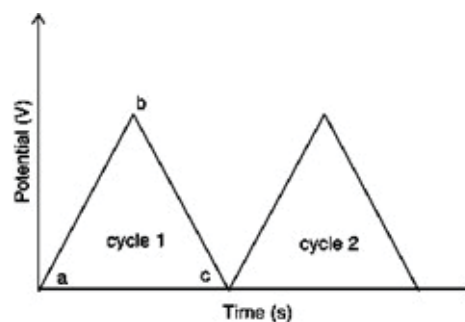


Figure 2. Potential vs time

Normally, a reversible cyclic voltammogram consists of a characteristic duck-shaped plot as shown in Figure 3. The shape of the graph may change with the scan rate, applied potentials, adsorbed species, electrolyte, and type of electrodes.

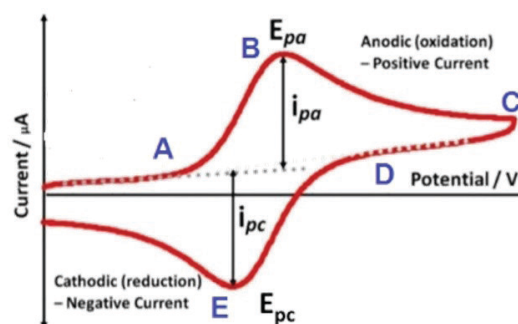


Figure 3. Current vs potential; duck-shaped cyclic voltammogram

The x-axis represents the applied potential while y-axis is the resulting current (i).

The cyclic voltammogram depicted in Figure 3 starts with more negative (-) potential and increases up to a previously set positive value ($A \rightarrow C$). At point A, the rate of oxidation is limited by the migration of the substrate or analyte. In this initial process oxidation of the substrate takes place by releasing electrons. Then the potential is switched back with the time ($C \rightarrow E$), during this process oxidized substrate is reduced back to the starting substrate.

From $A \rightarrow C$, oxidation takes place at the anode and the maximum **anodic** potential reached at point B is called E_{pa} , and the maximum current is i_{pa} , where p refers to the "peak". At point B, the migration rate of substrate equals the diffusion rate of oxidized substrate. At point C, the electrode surface is saturated with the oxidized substrate. Thus, the substrate approach to the electrode surface is hindered. The rate of oxidation is limited by

the diffusion of oxidized substrate.

When the potential is switched back, the reduction of the intermediate formed takes place and the current increases gradually. The highest **cathodic** potential is reached at point E and it is called E_{pc} and the maximum current is i_{pc} .

The peak current (i_p) is calculated by the **Randles-Sevcik** equation.

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

$$= K C_A$$

n = number of electrons in the redox reaction

A = area of the working electrode, cm^2

D = diffusion coefficient for the electroactive species, $\text{cm}^2 \text{s}^{-1}$

ν = scan rate, V s^{-1}

C_A = concentration of the electroactive species at the electrode, mol cm^{-3}

$E_{1/2}$ is the midway between anodic and cathodic peak potentials, $E_{1/2} = (E_{pa} + E_{pc})/2$.

The noteworthy features of the cyclic voltammogram shown in Figure 3 are (i) the peak separation ($\Delta E_p = 57 \text{ mV}$), (ii) the peak current is proportional to square root of the scan rate (*i.e.*, $i_p \propto \nu^{1/2}$), and (iii) area under the anodic curve equals to the charge passed for oxidation.

Non-reversible Systems

Many redox reactions are quasi-reversible or non-reversible. CV of a non-reversible process is shown in Figure 4.

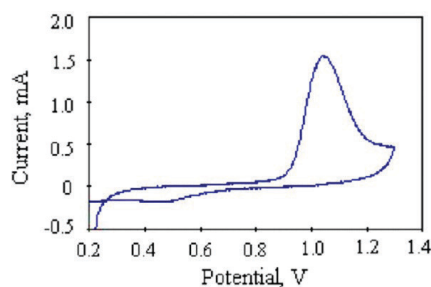


Figure 4. Non-reversible cyclic voltammogram

Non-reversibility is due to the subsequent chemical reactions of the reactive intermediate formed involving adsorption, deposition, dimerization, isomerization, dissociation, decomposition, *etc.*

Applications of Cyclic Voltammetry

Cyclic voltammetry has many applications. For example,

- studying reaction mechanisms.
- determining diffusion coefficients.
- studying the nature of electrochemical reactions.
- applications in energy storage and energy conversion reactions *e.g.*, electrocatalysis in fuel cells, battery, supercapacitors studies, *etc.*
- studying of corrosion phenomenon of metals.
- electrochemical synthesis of useful substances *e.g.*, conducting polymers such as polyaniline, electroactive films on electrodes, *etc.*
- *in vivo* and *in vitro* analysis.

Cyclic voltammetry can also be used to prepare polymer-modified electrodes by repetitive scanning of a solution containing monomers.

CV of Modified Electrodes

Electrode surface can be modified by (i) chemical bonding of electroactive groups or molecules (ii) electro-polymerization or depositing insoluble polymeric materials, and (iii) adsorption of electroactive species or molecules. These adsorbed electroactive groups give simple symmetrical voltametric curves at slow scan rates (Figure 5).

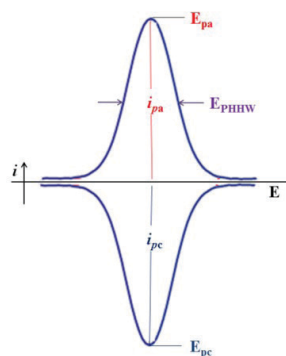


Figure 5. CV of an adsorbed species

The noteworthy features are (i) $i_{pa} = i_{pc}$ and $E_{pa} = E_{pc}$, (ii) there is no peak separation ($\Delta E_p = 0 \text{ V}$), (iii) the half-height width (ΔE_{pHHW}) is about 90 mV for a one-electron redox couple, (iv) area under the anodic curve and cathodic curve are equal, and (v) the peak current is proportional to scan rate (*i.e.*, $i_p \propto \nu$), which proves that the redox species are immobilized. Stability of the adsorbed layer can be examined by repetitive scanning of the electrode.