Chapter-I

Introduction and Overview of Cyclic Voltammetry and Its Theoretical Considerations.
1.1 Introduction

The fundamental process in electrochemical reactions is the transfer of electrons between the electrode surface and molecules in the interfacial region either in solution or immobilized at the electrode surface. The kinetics of this heterogeneous process can be significantly affected by the microstructure and roughness of the electrode surface, the blocking of active sites on the electrode surface by adsorbed materials, and the nature of the functional groups (e.g., oxides) present on the electrode surface [1, 2]. Hence chemically modified electrodes (CMEs) have evolved as a recently emerging field and much study of interest have been shown by many researchers in this field. In detail, the chemically modified electrodes comprise an approach to electrode system design that finds the use in a wide spectrum of basic electrochemical investigations, including the relationship of heterogeneous electron transfer and chemical reactivity of electrode surface chemistry, electrostatic phenomena at electrode surface, and electron as well as ionic transport phenomena in polymers, and the design of electrochemical devices and systems for applications in chemical sensing, energy conversion and storage, molecular electronics, electrochromic displays and electro-organic synthesis. The applicability of these CMEs is wide-ranging, but one important application is biomolecule sensing.

There has been an increasing interest in the creation of modified electrode surfaces that differ from the corresponding bare surfaces and produce an electrode surface that generates reproducible result, which has a vast application in biological and chemical sensing. The focus of the work covered in this thesis is to controllably alter the properties of carbon surfaces, so that the surfaces can be used for desired sensor applications. Carbon was the chosen surface, as it is highly conducting with a wide potential window, structurally stable, relatively inexpensive and stable layers of modifiers can attach to the surface in a controllable manner. There are many different forms of conducting carbon materials including glassy carbon (GC), highly oriented pyrolytic graphite (HOPG), pyrolysed photoresist film,(PPF), carbon nanotubes, carbon powder, screen printed carbon, carbon fibres, carbon nanocapsules, Fullerene and carbon composites [3].
In this thesis carbon powder was selected and was applied to study the electrochemical properties of the selected neurotransmitters and the process taking place across the interface of the electrode surface and the electrolyte. A species capable of undergoing electron transfer process is called an electroactive species. In order to carry out electron transfer process with the electrode, the electroactive species comes from the bulk solution and approaches the electrode surface. Hence the electron transfer plays a fundamental role in governing the pathways of chemical reactions. Measurement of speed of the electron transfer process and the number of electrons involved are difficult in traditional experimental methods like spectroscopy [4]. Hence the knowledge of the driving force for many reactions remains elusive. Electrochemical methods offer the potential to investigate this process directly by determination of number of electrons involved. Electrochemical studies of biologically active compounds serve to elucidate biological processes and their inter-relationship that are involved in living organisms [5-8]. For any series of interrelated processes within a system, it is normally necessary to study the component part of the system. An attempt has been made to study the electrochemical properties and behaviour of compounds, which plays an important role in biochemical redox reactions in various organisms.

Electrochemical techniques provide efficient tools for surface modifications. Very simple experiments can be performed where species from solution can be physically adsorb, electropolymerised, or covalently attached onto the electrode surface at certain controlled potential. The aim of the work covered in this thesis was to study the effect of modified carbon paste electrodes on the oxidation properties of dopamine, serotonin, norepinephrine, epinephrine, ascorbic acid and uric acid in biological buffer solution. This work searches for alternatives to counter, the major problem associated with the voltammetric detection of dopamine (DA), norepinephrine (NE), epinephrine (EP) and serotonin (5-HT) in real samples which is the coexistence of interfering compounds such as ascorbic acid (AA) and uric acid (UA) which results in their overlapped voltammetric response at bare electrode. [9-11]. Moreover, the bare electrodes very often suffer from the fouling effect due to the accumulation of oxidized products on the electrode surface, which results in rather poor selectivity and sensitivity.
Advances since the mid-1980s, including the development of ultramicroelectrodes, the design of tailored interfaces and molecular monolayers, the coupling of biological components and electrochemical transducers, the synthesis of ionophores and receptors containing cavities of molecular size, the development of ultratrace voltammetric techniques or of high-resolution scanning probe microscopies, and the microfabrication of molecular devices or efficient flow detectors, have led to a substantial increase in the popularity of electroanalysis and to its expansion into new phases and environments. Indeed, electrochemical probes are receiving a major share of the attention in the development of chemical sensors.

1.2. Voltammetry

Historically, the branch of electrochemistry we now call voltammetry developed from the discovery of polarography in 1922 by the Czech chemist Jaroslav Heyrovsky, for which he received the 1959 Nobel Prize in Chemistry. Voltammetry refers to the measurement of current that result from the application of potential. Unlike potentiometric measurements, which employ only two electrodes, voltammetric measurements utilise a three electrode electrochemical cell. The use of three electrodes (working, auxiliary and reference) along with the potentiostat instrument allows accurate application of potential functions and measurement of the resultant current.

Analytical chemists routinely use voltammetric techniques for the quantitative determination of a variety of dissolved inorganic and organic substances. Inorganic, physical, and biological chemists widely use voltammetric techniques for a variety of purposes, including fundamental studies of oxidation and reduction processes in various media, adsorption processes on surfaces, electron transfer and reaction mechanisms, kinetics of electron transfer processes, and transport, speciation, and thermodynamic properties of solvated species. Voltammetric methods are also applied to the determination of compounds of pharmaceutical interest and, when coupled with HPLC, they are effective tools for the analysis of complex mixtures.
1.2.1. Voltammetric Techniques and Their Theoretical Aspects

The different voltammetric techniques that are used are distinguished from each other primarily by the potential function that is applied to the working electrode to drive the reaction, and by the material used as the working electrode. These can be described as follows.

1.2.1.1. Linear Sweep Voltammetry (LSV)

Linear sweep voltammetry involves applying a linear potential sweep to the working electrode (the electrode under study) while monitoring simultaneously the current flowing in the circuit. A signal generator produces a voltage sweep from \(E_i\) to \(E_f\) and a potentiostat applies this potential wave to the electrode under study. The scan direction can be positive or negative and in principle, the sweep rate can possess any constant value:

\[
\text{Sweep rate} = \frac{dE}{dt}
\]

This method of analysis is commonly employed in polarography whereby under well-defined conditions, the limiting current derived from a redox process in solution during LSV may be used to quantitatively determine the concentration of electroactive species in solution.

1.2.1.2. Square Wave Voltammetry (SWV)

Among the various voltammetric techniques, exceptional versatility is found in a method called square wave voltammetry, which was invented by Ramaley and Krause, and developed extensively by the Osteryoungs and their co-workers [12]. Its a differential technique in which potential waveform composed of a symmetrical square wave of constant amplitude is superimposed on a base staircase potential [13, 14]. It is the plot of the difference in the current measured in forward \((i_f)\) and reverse cycle \((i_r)\), plotted against the average potential of each waveform cycle. In this technique, the peak potential occurs at the \(E_{1/2}\) of the redox couple because the current function is symmetrical around the potential [15, 16]. The main advantages of SWV are excellent peak separation and high sensitivity.
1.2.1.3. Anodic Stripping Voltammetry (ASV)

Anodic stripping voltammetry is an electrolytic method in which a mercury electrode is held at a negative potential to reduce metal ions in solution and form an amalgam with the electrode. The solution is stirred to carry as much of the analyte metal to the electrode as possible for concentration into the amalgam. After reducing and accumulating the analyte for some period of time, the potential on the electrode is increased to reoxidize the analyte and generate a current signal. The current produced by anodic stripping depends on the particular type of mercury electrode, but is directly proportional to the concentration of analyte concentrated into the electrode.

1.2.1.4. Normal Pulse Polarography (NPP)

Pulse polarographic techniques are voltammetric measurements which are variants of the polarographic measurement which try to minimise the background capacitive contribution of current by eliminating the continuous varying potential ramp, and replacing it with a series of potential steps of short duration. In normal pulse polarography, each potential step begins at the same value (a potential at which no faradaic electrochemistry occurs), and the amplitude of each subsequent steps increases in small increments. When the mercury drop is dislodged from the capillary, the potential is returned to the initial value in preparation for a new step. The polarogram is obtained by plotting the measured current vs. the potential to which the step occurs. As a result the current is not followed during the mercury drop growth, and normal pulse polarogram has the typical shape of a sigmoid. After the initial potential step, the capacitive current decays exponentially while the faradaic current decays as the square root of time. The diffusion current is measured just before the drop is dislodged, allowing excellent discrimination against the background capacitive current.

1.2.1.5. Differential Pulse Polarography / Voltammetry (DPP/ DPV)

This technique was proposed by Barker and Gardner [17]. DPV can provide greater sensitivity and more efficient resolution and differentiation of various species. This technique differs from NPP because each potential pulse is fixed, of small amplitude (0.01 to 0.1). Current is measured at two points from each pulse, just before the
application of the pulse and at the end of the pulse. The difference between the current measurements at these points for each pulse is determined and plotted against the base potential. At potentials around the redox potential, the difference in current reaches a maximum and decreases to zero as the current becomes diffusion controlled. The current response is therefore a symmetric peak.

1.2.1.6. Fast Scan Cyclic Voltammetry

Fast scan cyclic voltammetry (FSCV) is a linear sweep voltammetry technique in which the background subtracted voltammogram gives additional information about the electrolyzed species. The current response over a range of potentials is measured, making it a better technique to discern additional current contributions from other electroactive species. FCV is a relatively fast technique with single scans typically recorded every 100 ms, however, the fast scan rates decrease the signal to noise ratio.

1.2.1.7. Cyclic Voltammetry (CV)

Cyclic voltammetry is a method for investigating the electrochemical behaviour of a system. It was first reported in 1938 and described theoretically by Randles [18]. Cyclic voltammetry is the most widely used technique for acquiring qualitative information about electrochemical reactions. The power of cyclic voltammetry results from its ability to rapidly provide considerable information on the thermodynamics of redox processes, on the kinetics of heterogeneous electron-transfer reactions, and on coupled chemical reactions or adsorption processes. Cyclic voltammetry is often the first experimental approach performed in an electroanalytical study, since it offers rapid location of redox potentials of the electroactive species and convenient evaluation of the effect of media upon the redox process [17,19-22].

1.2.1.7a. Basic principles of Cyclic Voltammetry

A cyclic voltammogram is obtained by applying a linear potential sweep (that is, a potential that increases or decreases linearly with time) to the working electrode. As the potential is swept back and forth past the formal potential, \( E^0 \), of an analyte, a current flows through the electrode that either oxidizes or reduces the analyte. The magnitude of
this current is proportional to the concentration of the analyte in solution, which allows
cyclic voltammetry to be used in an analytical determination of concentration.

The equipment required to perform cyclic voltammetry consists of a conventional
three-electrode potentiostat connected to three electrodes (working, reference and
auxiliary) immersed in a test solution. The potentiostat applies and maintains the
potential between the working and reference electrode while at the same time measuring
the current at the working electrode. Charge flows between the working electrode and the
auxiliary electrode. A recording device (such as a computer or plotter) is used to record
the resulting cyclic voltammogram as a graph of current versus potential.

1.2.1.7b. Fundamentals of Cyclic Voltammetry

Voltammetry is a collection of electroanalytical techniques in which information
about the analyte is derived from the measurement of current as a function of applied
potential. It is widely used by chemists for non-analytical purposes including
fundamental studies on redox processes, adsorption processes on surfaces, electron
transfer mechanisms and electrode kinetics.

Electrochemistry affords some of the most sensitive and informative analytical
techniques. Electroanalytical methods such as CV, stripping voltammetry and differential
pulse voltammetry are not only capable of assaying trace concentrations of an
electroactive analyte, but supply useful information concerning its physical and chemical
properties. Quantities such as oxidation potentials, diffusion coefficients, electron transfer
rates and transfer numbers are readily obtained using electroanalytical methods, which are
difficult to obtain using other techniques. Moreover, electroanalytical methods can be
combined with spectroscopy in situ to provide information concerning molecular
structures and reaction mechanisms of transient electroactive species.

CV is a potential sweep technique. It involves sweeping the electrode potential
between potential limits $E_1$ and $E_2$ at a known sweep rate (also called scan rate). On
reaching limit $E_2$ the sweep is reversed to $E_1$ to obtain a cyclic scan. The CV scan is a
plot of current verses potential and indicates the potential at which redox process occur.
The potential axis is also a time axis that is related to scan rate [23]. The excitation signal
for CV is a linear potential scan with triangular waveform as shown in Fig. 1.1. This triangular potential excitation signal sweeps the potential of an electrode between two values, sometimes called the switching potential.

The current measured during this process is often normalised to the electrode surface area and referred to as the current density. The current density is then plotted against the applied potential, and the result is referred to as a cyclic voltammogram. A peak in the measured current is seen at a potential that is characteristic of any electrode reaction taking place. The peak width and height for a particular process may depend on the sweep rate, electrolyte concentration and the electrode material [24, 25].

To carry out an oxidation process, a positive potential ramp is applied and the electroactive species loses an electron at the electrode giving rise to an anodic peak current ($i_{pa}$) which usually gives an oxidation peak at a given potential ($E_{pa}$). Cathodic currents ($i_{pc}$) are observed when the potential is applied in the negative direction leading to a reduction process, typically giving a reduction peak at a given potential ($E_{pc}$). The CV is usually initiated at a potential where species are not electroactive.

1.3. Theory

In theory, any atom or molecule can be oxidized or reduced if enough energy can be provided. However, the range of energies that can be applied is limited by the experimental conditions. So we need only consider molecules that are said to be electrochemically active. Therefore there is a very wide range of electrochemically active. The molecules which have lone pairs of electrons or multiple bonds are electrochemically active. Therefore, there is a very wide range of electrochemically active organic compounds, including important classes of molecules such as pharmaceuticals, biochemicals, herbicides, pesticides, food additives, dyes and explosives.

In cyclic voltammetry, a species that undergoes a reduction during a cathodic polarization of working electrode in unstirred solution is reoxidised by applying a reverse (anodic) scan. The correlation of the cathodic and anodic peak currents and differences in cathodic and anodic peak potentials with the voltage scan rates has been studied
mathematically for different electrochemical reactions [26, 27]. The sweep rates in cyclic voltammetry can be about the same as in single sweep voltammetry.

Cyclic voltammetry makes possible the elucidation of the kinetics of electrochemical reactions taking place at electrode surfaces [28, 29]. In a typical voltammogram, there can be several peaks. From the sweep-rate dependence of the peak amplitudes, widths and potentials of the peaks observed in the voltammogram, it is possible to investigate the role of adsorption, diffusion, and coupled homogeneous chemical reaction mechanisms [30].

The important parameters of a cyclic voltammogram are the magnitudes of anodic peak current ($i_{pa}$), the cathodic peak current ($i_{pc}$), the anodic peak potential ($E_{pa}$) and cathodic peak potential ($E_{pc}$). The basic shape of the current verses potential response for a cyclic voltammetry experiment is shown below (Fig. 1.2). At the start of the experiment, the bulk solution contains only the reduced form of the redox couple (R) so that at potentials lower than the redox potential, i.e. the initial potential, there is no net conversion of R into O, the oxidised form (point A). As the redox potential is approached, there is a net anodic current which increases exponentially with potential. As R is converted into O, concentration gradients are set up for both R and O, and diffusion occurs down these concentration gradients. At the anodic peak (point B), the redox potential is sufficiently positive that any R that reaches the electrode surface is instantaneously oxidised to O. Therefore, the current now depends upon the rate of mass transfer to the electrode surface and so the time dependence is $qt$ resulting in an asymmetric peak shape. Upon reversal of the scan (point C), the current continues to decay with a $qt$ until the potential nears the redox potential. At this point, a net reduction of O to R occurs which causes a cathodic current which eventually produces a peak shaped response (point D). If a redox system remains in equilibrium throughout the potential scan, the electrochemical reaction is said to be reversible. In other words, equilibrium requires that the surface concentrations of O and R are maintained at the values required by the Nernst Equation. Under these conditions, the following parameters characterize the cyclic voltammogram of the redox process. The peak potential separation ($E_{pa} - E_{pc}$) is equal to $57/n$ mV for all scan rates where n is the
number of electron equivalents transferred during the redox process. The situation is very
different when the redox reaction is not reversible, when chemical reactions are coupled
to the redox process or when adsorption of either reactants or products occurs. In fact, it
is these "non-ideal" situations which are usually of greatest chemical interest and for
which the diagnostic properties of cyclic voltammetry are particularly suited. This is
helpful in understanding the fundamentals of the technique. As shown in Fig.1.3,
scanning the potential in the negative direction makes the electrode a stronger reductant,
whereas scanning the potential in the positive direction makes it a better oxidant.

1.4. Applications of Cyclic Voltammetry

CV has become a very popular technique for electrochemical studies of new
systems, and has proved as a sensitive tool for obtaining information about fairly
complicated electrode reactions [31, 32]. CV methods have found to have extensive
applications for the evaluation of thermodynamic and kinetic parameters such as number
of electrons change (n), heterogeneous rate constant (k0), entropy (S), Gibb's free energy
(G) and diffusion coefficient (D0) etc., of a number of redox reactions and associated
chemical reactions. These methods are especially useful in both oxidation and reduction
process and to study the multiple electron transfer in an electrochemical reaction [33].

The primary objective of developing these CV techniques was analytical, both
qualitative as well as quantitative. As the peak current is proportional to concentration,
this method can be used for the estimation of a number of inorganic, organic and
organolmetallic compounds.

Much intensive research is in progress with the additional regular analytical
applications. CV studies in rat brain [34], in vivo studies in animals [35], bacteria [36]
and even plants [37, 38] are picking up. With the introduction of newer electrode material
of very small size [39], these methods of chemical analysis in living systems might grow
even faster. CV studies of fused salts and solid electrolyte [40] might prove very useful
for trace analysis.

Background-subtracted cyclic voltammetry can be employed for measuring lower
concentration. In particular fast-scan (1000 Vs⁻¹) background-subtracted cyclic
voltammetry is seeing increased use for the in-vivo monitoring in neurotransmitters (such as dopamine or serotonin) in the brain. Such coupling of digital background subtraction and fast voltammetric measurements provides the subsecond temporal resolution necessary for detecting dynamic concentration changes in the micromolar range occurring in the extracellular environment of the brain.

The good temporal and chemical resolution of such in-vivo cyclic voltammetric experiment offers improved understanding of the chemistry of the brain. These repetitive scanning in-vivo experiments generate large quantities of data that are best represented as three-dimensional (potential, current, time) color contour images. For example, the temporal release of dopamine following electrical stimulation is evidenced from the rapid interferences from adsorption processed and chemical reactions that are coupled to the primary oxidation reaction of catecholamines neurotransmitters.

Voltammetric detectors may also find increasing applications in chromatography [41, 42]. This is an example of situation where an analytical tool of great importance also supplements the applicability of another analytical tool of great scope.

Industrial corrosion processes are being monitored using rotating disk electrodes. Voltammetric amazingly low detection limits are being used to monitor lead levels in the bloodstream. Electrodes coated with special polymers find use as glucose detectors for diabetics.

Oxidative bursts of reactive oxygen species are used by cells to fight bacteria and viruses, such oxidative bursts produced by human fibroblasts can be followed electrochemically by using a carbon fibre platinized ultra microelectrode place within a few microns of a single living cell, when membrane is punctured with a micrometer sized sealed pipette. In spite of experimental difficulties, it has been possible to obtain electric signals indicating that the oxidative bursts of a mixture of cytotoxic chemicals: H_{2}O_{2}, NO, ONO_{2}^{-} and NO_{2}^{-}. The cell survived the puncture and performs a similar burst after a couple of hours [43]

Coatings for cars that would not change in appearance after years of service might be discovered, along with repulsion systems for electric vehicles and methods to remove
toxic materials selectively from streams of H$_2$O$_2$, the scientific basis of this has already been demonstrated.

Recent advances in instrumental techniques, however, promise access to molecular-level information about electrochemical systems. This exciting development opens up important new opportunities in fundamental and applied science.

1.5. The Solvent

A number of physicochemical properties must be considered while choosing a solvent for electrochemical work [44]. The solvent used for the electrochemical process must be a liquid at room temperature, it must have sufficient solubility for ionic substances to form conducting electrolyte, it must be able to dissolve the electroactive species of interest, it must have a wide enough potential region for the study of the redox process of interest, that is, solvent itself must not undergo oxidation or reduction in this potential region and it must possess the required acid-base properties. The dielectric constant is one of the important parameter.

The cheapest solvent is water, which possesses many physico-chemical properties. It can dissolve ionic components and form highly conducting solutions. Many compounds of electrochemical interest dissolve easily in this solvent. It is acid-base properties are well understood. However, the solvent itself gets reduced or oxidized to H$_2$ and O$_2$ very easily. Hence it only possesses region of 2.0 V for the study of other processes. Water also easily forms oxide films on solid electrodes hence affects reactivity and reproducibility. Some organic reactants are less soluble in water. This defect is normally overcome by using alcoholic mixed solvents or alcohol stock solution of reactants.

Acetonitrile is perhaps a solvent with inert electrochemical properties. It has +3.0 V (verses SCE) anodic and -3.0 V cathodic limits. Even these limit are probably set by the supporting electrolyte oxidation and impurity (water) reduction. If impurities are absent, radical ion chemistry may be studied very well. However this solvent has very poor solubility for ionic species. Salts containing organic ions such as tetra alkyl ammonium salts must be employed.
Dimethyl formamide (DMF) is one of the aprotic solvents which have very good dissolving power of ionic species. It has a cathodic limit up to -0.3 V for anion radicals. Hence this is the solvent of choice for studies on anion radicals and dianions. In the positive potential regions above +1.0 V, the solvent itself decomposes. Cation radicals are less stable in this medium.

Dimethyl sulfoxide (DMSO) has electrochemical properties similar to DMF in the cathodic region. It has somewhat a better cathodic potential limits. Since it is not as basic as DMF, cation radicals are somewhat stable in this medium.

Methylene chloride is the solvent of choice for organic oxidation studies. It is stable up to +3.0 V as acetonitrile. Cation radicals and dications are quite stable in this medium. Electrolytes are easily soluble in methylene chloride when compared with acetonitrile. Even large organic molecules and polymers are soluble in this medium. However, at negative potentials of -1.0 V, the solvent decomposes. The anionic species are less stable in this medium.

Even totally non-polar solvents such as benzene and other hydrocarbons may be used to study the solution phase [45] as well as surface [46, 47] processes. A few detailed discussions on the solvents used in electrochemistry [48-50] are available. Most of the solvents with required purity levels for voltammetric studies are commercially available.

Water deionised and repeatedly distilled with alkaline KMnO₄ is usually considered as pure. The purity is checked by conductivity measurements. However, this water might still contain some volatile impurities [51]. These may be removed by passing the distilled water vapour through a column containing Pt catalyst at about 800 °C over which oxygen also simultaneously passed. The organic impurities are oxidized completely by this procedure.

The main impurity present in non-aqueous solvents is water. This is usually removed by refluxing with anhydrous copper sulphate, aluminium chloride, P₂O₅ etc and distilling many times and collecting the proper fraction. The distillation is normally conducted at reduced pressure to avoid decomposition of the solvents. Some aprotic solvents may easily absorb moisture. In such cases vacuum lines must be employed.
during purification, storage and use in voltammetric work [52]. An easier procedure would be to employ a dehydrating agent such as anhydrous alumina as an internal addition [53] It must, however, be ensured that these materials do not interfere in the voltammetric behaviour in the other ways.

1.6. Supporting Electrolytes

All ionic salts or ionisable compounds in a solvent are defined as supporting electrolytes. It is very important to realise that they can influence the electrochemical processes in a number of ways. These electrolytes impart conductivity to the solvent and hence enable continuous current flow in solution. The salient features of supporting electrolyte are, they must remain electroactive in the potential region of interest, the concentration of the supporting electrolyte should be very high, in order that they do not form space charges near the surface and hence the space charge potential do not influence the charge transfer kinetics. They should not get adsorbed on the surface, in which case they can catalyse or inhibit other reactions. They should neither form ion pairs with anion radicals formed in the electrode process nor form complexes with the reactants or products.

H₂SO₄, HClO₄ and HCl are normally employed for studies in acidic aqueous solutions and NaOH or KOH are employed for alkaline media. In neutral region, if buffering is important, acetate, citrate, pyrophosphate and phosphate buffers are usually employed. B-R buffer is used over a wide pH range. If the redox process does not involve acid-base reactions, no buffer are needed and any electrolyte may be used.

Solubility is the main consideration in selecting supporting electrolyte for aprotic solvent. A number of tetra-ethyl ammonium (TEA) salts show good solubility in aprotic media. Tetra-ethyl ammonium (TEA) salts and more recently tetra-n-butyl ammonium (TBA) salts are widely employed for this purpose. TEA salts are frequently available in the form of halides. The perchlorates or fluroborates may be easily obtained by double decomposition of these salts with the corresponding sodium salts. The precipitated TAACIO₄ or TAABF₄ may be recrystallised twice or thrice [53]. Hygroscopic electrolytes dehydrated in an oven and stored in desiccators. Care must be exercised in
handling explosive salts such as NaClO₄. They must neither be overheated nor ground in mortar with force.

1.7. Electrodes

The advent of modern electrochemistry created the need for new electrodes and electrode setups. The most common arrangement today is the electrochemical cell with three different electrodes:

- Working electrode (WE)
- Reference electrode (RE)
- Counter electrode (CE)

1.7.1. Working Electrode.

The ideal working electrode is very clean metal surface with a well defined geometry that is in direct contact with an electrochemical test solution. Working electrodes intended for general purpose work are usually made from a metal that is electrochemically inert over a wide range of potentials. The most widely used metals are mercury, platinum, gold, and various forms of carbon. Solid metals are typically fashioned into disks surrounded by a chemically inert shroud made from Teflon, glass, or epoxy. Mercury, being a liquid, tends to be used as a spherical droplet in contact with the solution.

The size and shape of the electrode surface also has an effect on the voltammetric response of the electrode. The overall current observed at an electrode is directly related to its surface area, and disk shaped electrodes with diameters greater than 100 mm, or macroelectrodes, generally produce easily measured currents in the microamp to milliamp range. Electrodes with dimensions less than 100 mm are generally referred to as microelectrodes, and these typically produce currents in the picoamp to nanoamp range. Although the overall currents observed at microelectrodes are small enough to require specialized electrochemical equipment, these electrodes enjoy a greater signal to-background ratio and, being small, find uses in applications where the sample size is quite small.
1.7.1.1. Mercury Electrode

This is the most popular electrode [54] makes use of liquid mercury as a working electrode. In most common incarnation, the dropping mercury electrode, a reservoir of mercury is allowed to slowly drain through a vertical capillary tube immersed in the electrochemical test solution. As the mercury slowly exits from the capillary; it forms a small drop with a nearly spherical shape that is in contact with the test solution. Electroactive analytes in the test solution undergo oxidation or reduction reactions at the surface of the drop.

This electrode configuration enjoys quite a few advantages including a very long history of use and an electrode surface that is easily reproducible. Indeed, in the event that the surface of the mercury drop becomes fouled, the drop is simply allowed to fall into the test solution, and a fresh drop is allowed to form at the capillary tube's exit. In aqueous solutions, the mercury electrode can be used at more negative potentials than other metals without interference from the reduction of hydronium ion. Finally, the mercury electrode plays an important role in stripping voltammetry-a technique which relies on preconcentrating one or more analytes into a mercury electrode and then separately electrolyzing (or stripping) each individual analyte out of the electrode.

1.7.1.2. Platinum Electrode

Despite the expense associated with these precious metal, platinum is one of the most widely used materials for fabricating working electrodes. Platinum has the advantage of being an easily machined metal that is electrochemically inert. In aqueous solvent systems, the platinum working electrode is a good choice when working with positive potentials, but at negative potentials, interference from the reduction of hydronium ion is a problem. In rigorously anhydrous organic solvent systems, platinum is the best and most popular choice for the working electrode material due to its wide potential window in both the positive and negative directions.

Large diameter platinum macroelectrodes are generally fabricated by welding a thick platinum disk to the end of a brass rod, machining the platinum disk and brass rod so that they are concentric, and then placing a Teflon shroud around the entire assembly.
The platinum surface is then ground to a mirror quality finish using a polishing paste that contains sub-micron alumina particles. As with all solid metal electrodes, the surface must occasionally be repolished to remove surface contaminants picked up during experiments.

Smaller diameter platinum disk electrodes and platinum microelectrodes are usually fabricated by shrouding a short length of platinum wire in soft glass. The diameter of the resulting platinum disk is the same as the diameter of the wire used. Because of the hardness of the glass shroud, these electrodes are usually polished to a mirror finish using polishing paste that contains sub-micron diamond particles.

Of the solid metal electrodes, it is definitely the most popular due to its applicability to a wide range of electrochemical systems, durable and long lasting. Its primary disadvantage is that it has a limited use at negative potentials in aqueous solutions.

1.7.1.3. Gold Electrodes

Gold working electrodes are designed along the same lines as platinum working electrodes. Gold is usually less expensive than platinum, but it is not as electrochemically inert. The surface of a gold electrode is subject to oxidation at moderately positive potentials, and so it is not as generally useful as platinum.

1.7.1.4. Carbon Electrodes

Various forms of carbon are used as working electrode materials [55, 56]. Carbon electrodes are useful over a fairly wide potential window in both the positive and negative directions, and their principle advantage over platinum electrodes is the ability to work at more negative potentials in aqueous solutions. Solid carbon electrodes are usually made from glassy carbon or pyrolytic graphite, both of which are fairly expensive materials that are more difficult to machine than platinum or gold. The surface of a carbon electrode usually needs to be polished quite frequently, and the surface sometimes has to be “activated” by various empirical methods in order to obtain maximal performance from the electrode.
A less expensive carbon electrode can be fashioned using carbon paste [57]. A cylindrical recess is drilled into a Teflon shroud, and an electrical contact is placed in the back of the recess. Each time the electrode is to be used, the recess is packed with a paste that contains carbon particles, and then the paste is carefully polished to a smooth disk-shaped surface. Working with a carbon paste electrode is technically more demanding because the paste can be gouged inadvertently after being polished.

1.7.1.5. Rotated Electrodes

A special class of electrochemical techniques, known as hydrodynamic methods, actually involve the use of spinning working electrodes. Typically, a specially designed glassy carbon or platinum disk electrode is attached to the end of a rigid shaft, and then this shaft is mounted on a high speed motor. These electrodes are immersed in a test solution and rotated at several thousand rotations per minute. A characteristic “vortex-like” solution flow pattern emerges as a result of the electrode’s motion.

Because the solution is constantly stirred, fresh analyte solution is always being conveyed to the region near the surface of the electrode. This steady flow of analyte allows what is known as a “steady-state current” to flow at the rotating electrode as analyte are either oxidized or reduced. Steady-state currents are generally quite easy to measure because they remain constant with respect to time. In most other electrochemical methods, currents tend to decay with time as the supply of analyte near the electrode is depleted.

When using a rotating electrode, it is important that the cell volume be large enough to sustain a rapidly spinning solution flow. Also, the opening at the top of the cell must be large enough for the shaft of the rotating electrode. This means that the cell contents are open to the air, making oxygen removal difficult. A strong flow of inert gas is required to blanket the solution whenever a rotating electrode is being used to study an air-sensitive electrochemical system. Electrical contact to a rotating electrode is usually made with brushes that are in mechanical contact with the rotating shaft.
1.7.2. Reference Electrode

The potential of a working electrode in a voltammetry experiment is always controlled with respect to some standard, and that standard is the reference electrode. While the thermodynamic scale of half-reaction potentials found in most textbooks measures electrode potentials against the "standard hydrogen" reference electrode (SHE), in actual practice the SHE is much too cumbersome to use. For this reason, a number of other reference electrodes have been developed. Experimental measurements of potential are made against these alternate reference electrodes, and then the potentials are "corrected" by simple addition or subtraction and reported against the SHE.

One of the most generally available reference electrodes for work in aqueous solutions is the saturated calomel electrode (SCE). The half reaction that occurs inside of an SCE reference is given below.

\[
\text{Hg}_2\text{Cl}_2(s) + 2e^- \leftrightarrow 2 \text{Hg}(l) + 2 \text{Cl}^-(aq)
\]

At 25°C, the formal potential for the SCE half reaction lies 0.2415 volts more positive than the SHE reference electrode. A potential measured against using an SCE can be reported versus the SHE simply by adding 0.2415 volts to it.

The SCE electrode must be constructed in an appropriate piece of glassware that can keep a small amount of mercury in direct contact with solid calomel (Hg_2Cl_2) paste while at the same time keeping the paste in contact with a saturated aqueous solution of potassium chloride. The short hand notation for the SCE half cell is as follows:

\[
\text{Pt}(s) / \text{Hg}(l) / \text{Hg}_2\text{Cl}_2(s) / \text{KCl} (aq, \text{sat'd}) //
\]

Electrical contact is made by immersing a platinum wire into the liquid mercury, and the potassium chloride solution maintains ionic contact with the test solution in the electrochemical cell via a salt bridge or porous glass frit. Such electrodes can be "home made" or purchased from a variety of manufacturers.

Other useful reference electrodes are based on half reactions involving a silver electrode. For work in aqueous systems, the "silver-silver chloride" or "Ag/AgCl" reference is quite popular. The half reaction for this reference electrode is as follows:
\[
\text{AgCl}(s) + e^- \rightleftharpoons \text{Ag}(s) + \text{Cl}^-(aq)
\]

The actual potential assumed by an Ag/AgCl reference depends only on the activity of the chloride anion. (The other two species appearing in the half reaction are solids which always have unit activity.). To serve as a reference, the chloride activity needs to be held constant. To accomplish this, a silver wire (coated with a layer of silver chloride) is immersed in an internal solution saturated with potassium chloride. The chloride ion concentration remains fixed at the saturation limit. The short hand notation for this reference electrode half cell is given below:

\[
\text{Ag(s)} / \text{AgCl}(s) / \text{KCl (aq, sat'd), AgNO}_3(aq) //
\]

Electrical contact is made by direct connection to the silver wire, and the internal electrode solution is placed in ionic contact with the test solution via a salt bridge or porous glass frit.

1.7.3. The Auxiliary Electrode

In traditional two electrode cells that have only a working electrode and a reference electrode, current is necessarily forced to flow through the reference electrode whenever a measurement is made. If enough current flows through a reference electrode, its internal chemical composition may be significantly altered, causing its potential to drift away from the expected standard value. For this and other reasons, it is desirable to make electrochemical measurements without current flowing through the reference electrode. Modern three and four electrode potentiostats use a feedback circuit to prevent this from happening, but this feedback circuit requires that an additional auxiliary electrode be introduced into the electrochemical cell. This auxiliary (or counter) electrode provides an alternate route for the current to follow, so that only a very small current flows through the reference electrode.

The auxiliary electrode can be made from just about any material using any desired electrode geometry. Design choices are usually based on finding a material that is chemically inert in the particular test solution being studied, and it is generally a good idea for the auxiliary electrode to have a large surface area. In most cases, a coil of platinum wire is used, but stainless steel, copper or aluminium wire may work in non-
corrosive solutions where metal cation interference is not a concern. If the electrochemical cell is made of metal, then the cell itself might be used as the auxiliary.

Because current flows at the auxiliary electrode, electrochemical processes will also occur there. If the working electrode is reducing something, then the auxiliary electrode must oxidize something, and vice versa. The products generated at the auxiliary electrode, if allowed to diffuse to the working electrode, may interfere with the experimental measurement. When this is a problem, the auxiliary electrode is placed in a separate compartment containing an electrolyte solution that is in ionic contact with the main test solution via a glass frit. In most cases, however, the auxiliary can be placed right in the test solution along with the reference and working electrodes.

1.8. A Brief Literature Survey of Cyclic Voltammetric Investigations

Research interests involve the study of reactive intermediates that are formed when compound are reduced or oxidized electrochemically. The application of the chemically modified electrodes in electroanalysis offer several advantages due to their unique electrode surface properties. Therefore, there has been an increasing interest in the creation of chemically modified electrode surfaces that differ from the corresponding bare surfaces. These chemically modified electrodes can lower the over potential, increase the reaction rate and improve the selectivity of some bioactive molecules. The literature survey reveals the following prominent references.

Ren et al [58] investigated the electrocatalytic behaviour of electrodeposited film of caffeic acid on a glassy carbon (GC) electrode under neutral conditions (pH 7.4) in 0.15 M phosphate buffer solution (PBS) using CV. They observed a high electrocatalytic activity of the poly (caffeic acid) modified GC electrode towards the oxidation of epinephrine (EP) a component of neural transmission of nerve impulse.

Jin et al [59] explored the electrochemical behaviour of a poly rutin modified paraffin impregnated graphite electrode towards the electrocatalytic oxidation of adrenalin, serotonin and ascorbic acid in 0.1 M PBS (pH 7.0) as supporting electrolyte using CV and differential pulse voltammetry (DPV). They observed that as compared with bare electrode the poly rutin modified electrode displayed strong electrocatalytic
activity for the oxidation of adrenalin serotonin and ascorbic acid. It resolved the overlapped voltammetric response of adrenalin and AA into two well defined voltammetric peaks of about 172 mV by DPV.

Yongxin and Xiangquin [60] evaluated a poly (vinyl alcohol) modified GC electrode for the selective and sensitive determination of of DA, AA and UA and simultaneously in their mixture by using CV and DPV. They observed well separated peaks of the three compounds with potential difference of 140, 140 and 280 mV in CV and 180, 130 and 310 mV in DPV between DA and AA, DA and UA and AA and UA respectively in 0.1 M PBS (pH. 7.0).

Cheng et al [61] studied the electropolymerisation of o-Amino benzoic acid as a modifier to fabricate a poly (o-ABA) modified GC electrode towards the oxidation of epinephrine in the presence of ascorbic acid in 0.1 M PBS (pH 7.0). They observed that the polymeric film modified GC electrode has excellent electrocatalytical activity on the oxidation of epinephrine by using CV and DPV.

Aslanoglu et al [62] performed CV and DPV studies to investigate the electrochemical determination of DA in the presence of AA using a poly (3-Acetythiophene) modified GC electrode in 0.1 M PBS (pH 7.2). They observed that the poly (3-Acetythiophene) modified GC electrode accelerated the rate of electron transfer reaction of DA.

The electrochemical properties of DA, EP and their simultaneous determination at a poly (L-Methionine) modified GC electrode in 0.1 M PBS (pH 7.5) by using CV have been discussed by Ma and Sun [63]. They demonstrated that the poly (L-Methionine) modified GC electrode can be applied for the simultaneous measurement of DA and EP in the presence of high concentration of UA and AA in urine samples.

Zhao et al [64] developed a poly (sulfosalycyclic acid) modified GC electrode for the electrochemical studies of DA in neutral pH using CV. They observed that the polymer film modified GC electrode exhibited high electrocatalytic activity to DA oxidation.
Roy et al [65] studied the electropolymerisation of N, N, dimethylaniline (DMA) on the surface of GC electrode in 0.2 M PBS (pH 7.0) by CV. They demonstrated that the poly (N,N,diniethylaniline) film coated GC electrode can simultaneously detect AA and DA which coexisted in a homogenous solution and the separation of the oxidation peak potentials for AA and DA was about 300 mV which was large enough for the simultaneous determination of these two species in their mixture solution.

Simultaneous determination of DA and AA at a poly (toluidine blue) modified GC electrode in 0.1 M PBS (pH 6.6) has been studied by Chen et al [66] They observed that the resulting polymer film modified GC electrode can remarkably catalyse the electrochemical oxidation DA and AA. Zhang et al [67] reported the use of poly (styrene sulphone acid) sodium salt / single wall carbon nanotube film modified GC electrode to fabricate a biosensor for the detection of DA in the presence of AA.

A poly (3,4-ethylenedioxy) thiophene film modified GC electrode (PEDOT) for the simultaneous determination of various combinations of DA and AA in 0.1 M PBS (pH 7.0) using CV and square wave voltammetry has been developed by Vasantha and Chen [68] They used the PEDOT modified GC electrode to study the electrocatalytic activity of DA and AA. The also studied the mechanism for the electrochemical oxidation of DA and AA using a rotating ring disk electrode method at the PEDOT film modified GC electrode.

Yao et al [69] studied the electrochemical characterisation of poly (eriochrome black T) and its application to simultaneous determination of DA, AA and UA in 0.05 M PBS (pH 4.0) using CV. They observed that the polymer film modified GC electrode conspicuously enhanced the redox current of DA, AA and UA and could separately determine DA at its low concentration in the presence of higher concentration of AA and UA. Chen et al [70] developed a poly (4-(2-pyridyl-azo) resorcinol modified GC electrode and used it for the electrocatalytic oxidation and determination of DA in the presence of AA and UA in PBS (pH 4.0) using CV. They demonstrated that the film modified electrode showed excellent electrocatalytic activity towards the oxidation of DA, AA and UA individually and simultaneously.
Zhang et al [71] reported a novel polymerised film of acid chrome K on the surface of GC electrode by electropolymerisation method and its application for the simultaneous determination of DA, AA, and UA in 0.05 M PBS (pH 4.0) using CV. Hou et al [72] investigated a polymerised film 3, 5, dihydroxy benzoic acid (DBA) on the surface of GC electrode in neutral solution by using CV and applied it for the electrochemical determination of DA and AA.

Lin et al [73] developed a nano-composite of DNA / poly (p-aminobenzenesulphonic acid) bilayer modified GC electrode as a biosensor by electrodeposition method in 0.1 M PBS (pH 7.0) using CV. They demonstrated that the fabricated electrode showed a good electrocatalytic activity towards the oxidation of DA, UA and AA and separated the originally overlapped voltammetric signals of DA, UA and AA at bare GC electrode into three well defined peaks with large potential separation in neutral pH.

The electrochemical polymerisation of 4-amino-1-1-azobenzene-3,4-disulphonic acid (acid yellow 9 dye) onto the surface of GC electrode and indium tin oxide coated electrode from acidic solution containing acid yellow 9 dye (AY) monomer using CV has been studied by Kumar et al [74]. They observed that the poly (AY) film coated electrode exhibited excellent electrocatalytic activity towards the oxidation of DA in 0.1 M PBS (pH 7.0). They also demonstrated that the poly (AY) modified electrode was found to be a good sensor for the selective and sensitive determination of DA without any interferences.

Li and Lin [75] developed a gold nanocluster/overoxidized-polypyrrole composite modified glassy carbon electrode by electrodeposition of gold nanoclusters on insulating overoxidized-polypyrrole (PPyox) film modified glassy carbon electrode (GCE). They demonstrated that the nano-Au/PPyox composite-coated exhibited stable and sensitive current responses toward DA and 5-HT oxidation.

Jin et al [76] fabricated a novel poly rutin (Ru) modified paraffin-impregnated graphite electrode (WGE) by electrochemical method. They observed that Ru/WGE displayed strong catalytic function for the oxidation of adrenalin (EP), serotonin (5-HT),
and ascorbic acid (AA) and resolved the overlap voltammetric response of EP and AA into two well-defined voltammetric peaks of about 172 mV with DPV.

Sun et al. [77] developed an electrochemical sensor based on carbon nanotubes (CNTs)-ionic liquid (IL) composite for the simultaneous determination of serotonin (5-HT) and dopamine (DA). They observed that the CNTs-IL composite modified electrode presents excellent selectivity and sensitivity towards 5-HT and DA and eliminates the interference of ascorbic acid.

Goyal et al. [78] reported the simultaneous voltammetric determination of serotonin and 5-hydroxyindole acetic acid using single walled carbon nanotube modified glassy carbon electrode and gold nanoparticles modified indium tin oxide electrode. They demonstrated that this method was fast, simple, accurate with low detection limits for 5-hydroxytryptamine (5-HT) at single-walled carbon nanotube modified glassy carbon electrode and 5-hydroxyindole acetic acid (5-HIAA) at gold nanoparticles modified indium tin oxide electrode.

Wu et al. [79] developed a chemically modified electrode based on the carbon nanotube film–coated glassy carbon electrode (GCE) for the simultaneous determination of dopamine (DA) and serotonin (5-HT). They explored that the multiwall carbon nanotube (MWNT) film–coated GCE exhibits a marked enhancement effect on the current response of DA and 5-HT and lowers oxidation overpotentials. The responses of DA and 5-HT merge into a large peak at a bare GCE, but they yield two well-defined oxidation peaks at the MWNT film–coated GCE.

1.9. Residual Current in Voltammetry

On applying a potential sweep, the current that flows through the cell before the charge transfer takes place, is called the residual or background current. It is composed of the following components. [80]

1.9.1. Faradaic Current

It is generated from the faradaic process which is a non-adsorptive process arising from electron transfer across the metal or electrolyte interface. The redox reaction of solution species that takes place is controlled by Faraday’s laws [81], that is, the amount
of electricity which is passed (charge) is proportional to the number of moles of reactant converted. Electrode process where Faradaic process takes place are classified as charge transfer electrodes, since the extent of reaction depends on the measured charge passing through the electrode surface.

1.9.2. Non-Faradaic Current

It arises when the adsorption and desorption of ions from the electrode surface results in an electric current due to charging of double layer. The interface between the electrolyte and the working electrode acts like a capacitor. Therefore, a current is required to change the potential applied to the working electrode and this is referred to as non-faradaic current. Since the potential in a CV experiment is constantly changing, there is an approximately constant charging current, which makes a major contribution to the background current. As there is no charge transfer across the double layer, it is not governed by Faraday’s laws and hence is called non-faradaic current. The charging current is directly proportional to the sweep rate whereas the faradaic current is directly proportional to the square root of scan rate.

1.10. Polarisable and Non-Polarisable Interfaces

All electrode-solution interfaces can be classified as polarisable or non-polarisable. An electrode for which an electron can pass easily across the interface is called non-polarisable. In this case, external application of a change of potential may result in more electrons passing rapidly across the interface. Thus, there is a negligible build-up of excess charge on the electrode surface, i.e. the interface does not polarise. Platinum in contact with hydrochloric acid is a non-polarisable interface. In contrast, when the transfer of electrons is difficult, a potential change from outside will induce a substantial build-up of excess charges at the interface, hence, the electrode is termed polarisable. When a potential is applied externally to the electrode, the transfer of electrons through the interface is negligible. That is, a small change in current flow causes a large change in electrode potential. An ideally polarisable interface is one which can allow the passage of current without causing a change in the potential difference across it. In addition, when the current associated with charging the electrode-electrolyte interface arises purely from capacitive effects; such an interface is termed an ideally polarisable interface.
polarisable electrode (IPE) [82]. While no real electrode behaves ideally over the entire potential range, some electrode-solution systems, over limited potential ranges, can show behaviour which is approximately, ideal, for instance, a mercury electrode in contact with a de-aerated potassium chloride solution which behaves as an IPE at potentials in excess of 1.5 V.

1.11. Electrodes Processes

The reaction taking place between the electrode surface and species within the solution can proceed through a series of steps that causes the conversion of the dissolved oxidised species (O) to reduced species (R) in solution (Fig. 1.4). The electrode reaction rate is governed by the reaction rates such as.

i. Mass transfer

ii. Electron transfer of non-adsorbing species.

iii. Chemical reactions preceding or following the electron transfer which could be homogeneous such as protonation or dimerization’ or heterogeneous ones like catalytic decompositions on the electrode surfaces.

iv. Other surface reactions such as adsorption, desorption, crystallisation etc.

The simplest reaction involves only mass transfer of reactant to the electrode, heterogenous electron transfer involving non adsorbed species and the mass transfer of the product to the bulk solution. More complex reaction sequence involving a series of electron transfer, protonations, branching mechanisms, parallel paths or modifications of the electrode surfaces are quite common. When a steady state current is obtained, the rates of all reactions steps are the same. The magnitude of this current is often limited by the inherent sluggishness of one or more reactions called rate determining steps. The more facile reactions are then held back from maximum rates by the slowness with which such steps disposes of their products or create their participants [83, 84].
1.11.1. Mass Transfer Processes

Whenever an electrochemical charge transfer process takes place at the electrode surface, the electroactive material gets depleted and a concentration gradient is set up. Under such conditions the reactant diffuses towards the electrode surface and the corresponding product of the electrode reaction diffuses away from the electrode surface. Mass transfer in electrochemistry illustrates the movement of electroactive species from one location in solution to another arising from differences in electrical or chemical potential at the two locations. There are three forms of mass transport which can influence an electrolysis reaction (Fig. 1.5):

i. Diffusion

ii. Migration

iii. Convection.

1.11.1a. Diffusion

Diffusion is the movement of a species down a concentration gradient and it must occur whenever there is a chemical change at a surface. Diffusion arises due to the depletion of the electroactive ion near the electrode surface; this depletion is only due to the charge transfer occurring at the electrode surface. The diffusion processes are named after the detailed study of geometry of the electrodes viz, planar diffusion (to a plane electrode), spherical diffusion (to a spherical electrode i.e. mercury electrode) and cylindrical diffusion (to a wire electrode). The diffusion is characterized and governed by Fick's laws of diffusion [85].

Fick's Laws of Diffusion

Consider a stationary planar electrode-electrolyte interface. If a species O is reduced to R at the interface, its concentration $C_0$ at the surface is lowered when compared with its bulk concentration. Hence O from the bulk will move towards the electrode. After a long interval of time, a steady rate of flow of O towards the surface (called the flux, J) would be established. This rate is given by Fick's first law [86].

$$J = -D_{ox} \delta C_{ox}(x,t) / \delta x$$
where, \( D_{ox} \) is the diffusion coefficient at the electroactive ion (in \( \text{cm}^2\text{s}^{-1} \)).

The rate of change of concentration with time is given by Fick’s second law of diffusion [86]

\[
\frac{\partial C_{ox}(x,t)}{\partial x} = D_{ox} \frac{\partial^2 C_{ox}(x,t)}{\partial x^2}
\]

In this equation, the concentration is written as \( C_{ox}(x,t) \) to specifically indicate that its value depends on both distance \( x \) from the planar interface and time \( t \). Similar equations may also be written for \( C_R \). These two equations will take different forms depending upon geometry [86, 87] of the electrode. The value of \( D \) varies from system to system.

1.11.1b. Migration

Migration involves the movement of charged ions under the influence of electric field. Since migration is nonspecific in nature, migration due to the electroactive ion cannot be distinguished from the migration of other charged species present in the solution. Therefore, it becomes necessary to add a large excess of inert electrolyte to the cell solution, in order to eliminate the migration of the electroactive ions of interest. The inert electrolyte, which is generally called the supporting electrolyte, neutralizes the electrostatic forces of attraction acting between the working electrode and electroactive ion by suppressing the transport number of the reactants. To achieve this inert electrolyte is added to the electrolytic solution (at least 50 to 100 times in excess of the electroactive ions). Inert or indifferent supporting electrolyte contains ions that do not take part in the electrolysis [85]

1.11.1c. Convection

Convection is the movement of ions due to mechanical forces. Natural convection arises due to the difference in density and temperature at different parts of the solution and natural convection cannot be duplicated or reproduced. Sometimes convection is forced by stirring the solution in a known fashion. The forced convection can be reproduced and treated mathematically. The natural convection because of its non-reproducible nature complicates the electrode process. It is imperative to eliminate it.
This can be achieved by carrying out the electrolysis in a thermostat in the absence of stirring or vibrations. Care should be taken to restrict the electrolysis time to a few minutes otherwise the natural convection sets in and reproducible results may not be achieved [85].

1.11.2. Electron Transfer (ET) or Charge Transfer Process

The electron transfer at the interface between the electrode and electrolyte is central to an electrode reaction. Electroactive species having moved from the bulk of the solution by either diffusion or under forced convection enters in the electrical double layer, which is under direct influence of the electrode. On entering the double layer the species undergoes a structural orientation so that it can take up or give up electrons from or to the electrode surface respectively with the least activation energy when a suitable potential is applied and macroscopically, we observe current. This state of the reactant species is known as transition state. Being unstable the species is in transit state converts itself to the final product by release of activation energy and gets reduced or oxidized. This final product after undergoing suitable reorientation either gets deposited on the electrode surface or moves away from the electrode surface into the bulk solution. The transfer of electrons to or from the substrate is an activated process. The electron transfer process can be

i. Reversible process

ii. Irreversible process and

iii. Quasi-reversible process

1.11.2a. Reversible Electron Transfer Process

For a reversible process, oxidation and reduction peak is observed as shown in Fig.1.6. Reversibility can be defined as chemical or electrochemical. In an electrochemically reversible process the electron transfer is not rate limiting. For a chemically reversible process, both forms of redox couple (O for oxidized form and R for reduced form) are stable in the time scale of measurement. The rate of electron transfer is fast compared to the rate of mass transport and does not control the overall rate. In this process the rate of reaction is fast enough to maintain equal concentration of the oxidized
and reduced species at the surface of electrode. The concentration $C_{ox}$ and $C_{red}$ of oxidized and reduced forms of the redox couple respectively follow the Nernst equation

$$E = E^0 + \frac{RT}{nF} \ln \frac{C_{ox}}{C_{red}}$$

Where, $n$ = no. of electrons transferred, $F$= Faraday constant, $R$= Gas constant and $T$=temperature. If the system is diffusion controlled then the Fick’s law of diffusion holds for both oxidation and reduction. Under these conditions, peak current given by Randles Sevcik equation;

$$i_p = (2.69 \times 10^5)n^{3/2}A D^{1/2}C_0 \nu^{1/2}$$

where $n$ is the stoichiometric number of electrons involved in the electrode reaction, $A$ is the area of electrode in cm$^2$, $D_0$ is the diffusion coefficient of the species O in cm$^2$s$^{-1}$, $C_0$ is the concentration of the species O in mol/cm$^3$ and $\nu$ is the scan rate in Vs$^{-1}$.

**Diagnostic tests for cyclic voltammograms of reversible system at 25 °C**

i. $\Delta E_p = E_{pa} - E_{pc} = \frac{59}{n}$ mV, where $n$ is number of electrons change

ii. $i_{pc}/i_{pc} = 1$

iii. $i_p \propto \nu^{1/2}$

iv. $E_p$ is independent of $\nu$

**1.11.2b. Irreversible Electron Transfer Process**

For an irreversible process, only forward oxidation or reduction peak is observed but at times with a weak reverse peak (Fig. 1.7). This process is usually due to slow electron exchange or slow chemical reactions at the electrode surface [31]. In an irreversible electrode process, the mass transfer step is very fast as compared to the charge transfer step.

For an Irreversible reaction, the peak current is given by [88]

$$i_p = 2.99 \times 10^5 n (\alpha n)^{1/2} A D_0^{1/2} \nu^{1/2} C_0^{*}$$

$$(\alpha n_a) = 47.7/E_p \cdot E_{pc}^{1/2}$$
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The value of $E_p$, the difference between the cathodic and anodic peak is of the order of 59 mV/n is given by equation. The peak separation $E_p$ is a factor determining the reversibility or irreversibility of an electrode reaction. The equation by Nicholson is normally used to calculate electron transfer rate constants.

**Diagnostic tests for cyclic voltammograms of irreversible system at 25 °C**

i. no reverse peak

ii. $i_p \propto v^{1/2}$

iii. $E_p$ shifts = $30/\alpha n_a$ mV, where $\alpha$ is charge transfer coefficient

iv. $[E_p-E_p/2] = 47.7/\alpha n_a$ mV

1.11.2c. Quasi Reversible Electron Transfer process.

This is a class of electrode reactions in which the rates of charge transfer and mass transfer are comparable or competitive. Quasi-reversible process is intermediate between reversible and irreversible systems (Fig.1.8). The current due to quasi-reversible processes is controlled by both mass transport and charge transfer kinetics.[2, 22] The process occurs when the relative rate of electron transfer with respect to that of mass transport is insufficient to maintain Nemst equilibrium at the electrode surface. In the quasi-reversible region both forward and backward reactions make a contribution to the observed current.

**Diagnostic tests for cyclic voltammograms of quasi-reversible system at 25 °C**

i. $i_p$ increases with scan rate, but is not proportional to scan rate.

ii. $i_{pc}/i_{pa} = 1$, provided $\alpha_c=\alpha_a = 0.5$

iii. $\Delta E_p$ is greater than 59/n mV and its increases with increasing scan rate

iv. $E_{pc}$ shifts negatively with increasing $v$
1.12. Objectives and Scope of the Thesis

The focus of the work covered in this thesis is to controllably alter the properties of carbon surfaces by electropolymerisation method, modifiers, immobilization using cyclic voltammetric technique, so that the surfaces are useful for desired sensor applications.

Alongside the primary goal, the research carried out promotes knowledge at many levels relevant to the interests of the academic community in the field of sensor fabrication, such as the employment of a number of different monomers and their electrosynthesis.

The present work is also aimed at investigating the electrochemical studies and elucidation of the sequence of electron transfer and chemical reactions that occur at or near the electrode surface. Research interests involve the study of reactive intermediates that are formed when compounds are reduced or oxidised electrochemically.

The aspects investigated are reversible/irreversible or coupled nature of electron transfer, number of electrons involved, kinetic and diffusion controlled processes, effect of concentration of electroactive species on the redox pathways, effect of pH, nature of the products formed etc.

More emphasis has been given not only to the electrochemical behaviour of dopamine ascorbic acid and uric acid but also the versatility of use of carbon paste electrode. The preparation and characterisation of bare and chemically modified carbon paste electrode surface has been studied. Thorough characterisation of carbon paste electrode before modification has been studied. The electrochemical properties, carbon composition and surface roughness of both the surfaces are examined.

Present work is also aimed at the development of neurotransmitter voltammetric sensors for the detection of DA, UA, NE, EP, 5-HT and AA which are neurotransmitters present in the extracellular fluid of the central nervous system. It is generally believed that the direct redox reactions of these species at bare electrodes are irreversible and high over potential are usually required for their amperometric detection. Moreover, the direct redox reaction of these species takes place at very similar potentials and often suffers
from pronounced fouling effects, which results in rather poor selectivity and reproducibility. Hence there is need for the development of polymer modified electrodes because of its high selectivity and sensitivity due to the film homogeneity in electrochemical deposition, strong adherence to the electrode surface and chemical stability of the film. The electrochemical studies of these biologically active species serve to elucidate their biological process and their interrelationship that are involved in living organisms. In addition to analytical aspects, CV has been used to establish the electrochemical behaviour of the given molecules through mechanistic studies.

Starting with simple carbon pastes, improving their performances by chemical modification implies its versatility. Exploring the advantage of the modified, an attempt has been made to explore its applications to real life situations.
Fig. 1.1. Variation of the applied potential as a function of time in a cyclic voltammetry experiment.

Fig. 1.2. A typical cyclic voltammogram of current verses potential.
Cathodic Current

Electrode becomes stronger reductant

0

Anodic Current

Electrode becomes stronger oxidant

(+) 0 (-)

Potential, vs Reference Electrode

Fig. 1.3. Potential-Current axes for Cyclic Voltammetry

Electrode Electrode surface region Bulk solution

Electrode - Electrolyte Interface

Chemical reaction O' \rightleftharpoons O'_{surf}

Mass transfer O_{bulk} \rightleftharpoons O_{surf}

Electron transfer

Adsorption O'_{ads}

Desorption

O_{ads}

Chemical reaction R' \rightleftharpoons R'_{surf}

Mass transfer R_{bulk} \rightleftharpoons R_{surf}

Fig. 1.4. General pathway of electrode-mediated processes of oxidized (O) and reduced (R) electroactive species.
Fig. 1.5. Modes of mass transport

Fig. 1.6. Typical voltammogram for a reversible process
Fig. 1.7. Typical voltammogram for an irreversible process.

Fig. 1.8. Typical voltammogram for a quasi-reversible process
1.13. References


