CHAPTER I
1. INTRODUCTION

Electrochemical surface science has become an emerging area in electrochemistry that concerns with studies to understand the nature of the electrode surface and its modification at the molecular level [1]. Tailoring of electrode interface is the manifestation of such studies and an active area of research. Modifications of electrochemical interface are being effected employing a variety of techniques. This area has been dedicated to imparting desirable properties such as molecular recognition, electron transfer, electrocatalysis, etc. to the electrode surface [2-3].

Attempts are being made to evolve simple and elegant methodologies for making custom built modified interface that is highly sensitive to the required specifications. Chemically modified electrodes (CMEs) fulfil these requirements with suitable modifying agents. Chemically modified electrodes are generally defined as a deliberate control of molecular structure of the electrode surface aimed at tailoring the electrode to meet specific applications. The choice and nature of the modifying agent depends on the applications namely, electrocatalysis [4-6], biosensors [7-9], electrochemical sensors [10,11], electrosynthesis of inorganic, organic and biochemical component [12]. The resulting modified interface can have both desirable and deleterious effect. It can either accelerate or retard the electrode reaction that leads to passivation of the electrodes on the contrary to promote electrochemical reactions [13].

1.1. Preparative Methods for Chemically Modified Electrodes

The principal routes for the modifications of electrodes are

1. Chemisorption

2. Langmuir–Blodget method (L-B method)
3. Self-Assembled Monolayers (SAM)

4. Covalent bonding

5. Film deposition

1.1.1. Chemisorption

Chemisorption refers to adsorption of electroactive material onto the electrode surface. Several contributions on modification of electrodes by chemisorption have appeared recently after the pioneering work by Hubbard and Lane [14,15] describing the chemisorption of electroactive organic compounds on platinum electrodes.

Gao et. al. recently reported chemisorption of thiols and disulphides on gold surface that leads to the formation of stable modified surface [16]. This kind of modification paved the way for the spontaneous chemisorption process that produces highly ordered monolayer films of thiols and disulphides. A detailed description is dealt in the subsequent section.

1.1.2. Langmuir–Blodget Method

Langmuir and co-workers developed a methodology for the formation of ultra thin film in the order of molecular dimensions onto solid substrates by transferring the preformed monolayers from the air/water interface. They identified two preparative methods for the effective transfer of thin films onto the substrates namely, Langmuir-Blodgett and Langmuir-Saffer (L-B and L-S) [17,18]. Amphiphilic molecules that contain both hydrophobic tail and a hydrophilic polar heads are employed for the formation of monolayer in a LB trough. A variety of substitutions in the hydrophobic tail with the incorporation of redox species of interest have been carried out in this regard.
The LB method is precise and multilayers can be built in a systematic fashion with required orientation. However, the films are not very stable over a period of time.

Numerous research workers presented the preparation, description and applications of LB films [19-21]. Slowinski et al. verified the probability of transferring the monolayer of hydroxy alkane thiol from the water/air interface onto the gold electrode using the LB and LS methods [22].

Highly ordered redox modified ultra thin films have been developed by Forster and Faulkner [23]. LB and SAM techniques have an attractive feature of allowing fabrication of a molecular assembly with a controlled thickness. Hetero deposited LB films develop artificial photosynthesis and molecular devices. Recently, polymer LB films gained much importance because of its excellent stability and applications [24,25].

1.1.3. Self-Assembled Monolayer (SAM)

Molecular self-assembly is the spontaneous association of molecules under equilibrium conditions into structurally stable and well-defined aggregates as reported by Whitesides and co-workers [26]. Monolayer self-assembly chemistry is a most promising strategy for constructing stable and well-defined monolayers onto electrode surfaces. Monolayer self-assembly via thiols, disulphides, silanes, silicon dioxides, fatty acids and metal oxides on various metal electrodes like gold and platinum have been reported by several research workers [27-29].

A novel self-assembled monolayer employing electrochemically active triruthenium (III) complex on gold electrode surface has been reported recently by Sasaki et al. [30]. Similarly, majority of SAM electrochemistry has been largely based on surface attachment of organic and biological molecules as well as simple mononuclear
metal complexes [26,31-33]. Various research groups reported, electrodes modified with SAM on gold surfaces for different applications [34-37]. Bharathi and co-workers demonstrated the potential dependant opening and closing of the self-assembled monolayer of 2-mercapto benzene thioazole on gold surface [38].

Folkers et. al. studied the formation of composite self-assembled monolayer of alkaline thiolates on gold [39]. Mixed self-assembled monolayer composed of ferrocene thiol and alkene thiol onto gold electrode was recently reported by Rowe and Creager [40]. Thioamide self-assembly with tricarboxylate receptor on gold electrode for the electrochemical detection of protonated amines have been reported for ion sensing application [34,41].

1.1.4. Covalent Bonding

Covalent bond formation between specific functional groups such as hydroxyl group, amino group, carboxylic acid group generated on the electrode surface with the organic, silyl, inorganic modifiers provide useful applications. Excellent protocols were evolved for the reproducible generation of hydroxy and acid functional groups onto carbon substrates [42,43]. This was derivatised through ester/amide bond formation with organic redox molecules. Recently, several research groups modified the silicon surfaces by covalent bonding [44,45]. The modified electrodes thus obtained are stable in variety of solvents. Substituted benzoquinones and naphthoquinones are prosthetic groups in a number of redox enzymes and hence modification of electrode surface with quinones is of prime importance. Solvev et. al. has effected the modification of electrode surface employing amino silanes as the modifying reagent [46]. Similarly, Wrington and Bookbinder have carried out the modification with siloxane polymer [47]. Covalent
immobilisation of an optically active molecule onto carbon substrate was studied by Watkins et. al. [48].

Schiffrin et. al. reported the chemical modification of indium tin oxide (ITO) and gold substrate electrodes with dithiozole via covalent linkage. These modified electrodes were found to be effective for metal ion chelation that lead to the ion sensing applications of transition metal ions, such as Copper (II) and Lead (II) ions [49].

1.1.5. Film Modified Electrodes

Modification of electrode surface with thin films has been an intensive area of research. Film deposition refers to the formation of electroactive substances onto the electrode surfaces as many molecular layers as possible. According to the film forming agents used, the film deposition is presented under the following heads.

1. Modification with organic polymer films
2. Modification with inorganic films

For convenience, the details of the modification with organic and inorganic films are discussed as separate sections.

1.2. Modification with Organic Polymer Films

Modification of electrode surface has been carried out with ionically conducting polymers and electronically conducting polymers. The former includes polymers such as NAFION, polysulphonic acids, polyethylene oxides etc. Electronically conducting polymers such as polyaniline (PAN) [50,51], polypyrrole (PPY) [50,52], polythiophene [53], polyphenylene [54] have been largely investigated. Among these polymers PAN has been extensively studied because of its potential applications in biosensors [55], electrochromic devices [56], rechargeable batteries [57] and electrocatalysis [58].
The formation of polymer films onto electrode surfaces gains an importance since last decade. This is because of the application of polymer modified electrodes in very many areas of analytical chemistry. Electrodes modified with polymers as modifying agents in recent times contains electrochemically or chemically reactive centres. The electrochemically active centres can exchange electron with the substrate electrodes. Electrochemically active polymer films form chemical bond with the electrode, which produces electrochemical responses and they are more easily observed than those of immobilised molecular layer [59-61].

The polymers formed onto electrode surfaces can be classified as redox polymers, electronically conducting polymers and ion exchange polymers. Ion exchange polymer has got excellent electrostatic binding with the electrode surfaces. The redox polymer has the electroactive site on the polymer chain backbone itself. Electronically conductive polymers are more efficient conductors than the redox polymers because of their highly delocalised electronic structure.

Tremendous advancement has been made in the understanding of chemistry/electrochemistry, structure, electrical and optical phenomena, processing and application of several polymers and their derivatives. Nowadays very great attention is being paid to polyaniline, polypyrrole and their derivative [50].

Polyaniline is probably the oldest known synthetic organic polymer obtained by the chemical or electrochemical oxidative polymerisation of aniline. PAN was reported in 1862 by Lethbye [62]. Various researchers regenerated the current phase of PAN research during last decade [63,64].
PAN has been known as a promising electroactive polymer for secondary batteries [65-67]. An important step in the formation of PAN modified electrodes to produce transparent and flexible electrodes used in light emitting diodes were developed by Gustafsson et. al. [68]. Among the conducting polymers PAN is of special interest because it can be polymerised in aqueous solution under various experimental conditions to get the desirable thickness and morphology [69,70].

Santos et. al. studied the corrosion inhibition of steel by PAN films [71]. Soluble polyaniline is an excellent corrosion inhibitor [72,73]. Polyaniline film formed on electroactive surfaces has good adhesion, electrical, electrochromic and electroactive properties [51,56,74,75]. These types of properties make them interesting for their potential application as chemically modified electrode for specific reactions. Polyaniline modified electrodes are better candidate for the immobilisation of redox mediators on the electrochromic surfaces. Polyaniline coatings on iron appear to be promising for metal anodic protection in corrosive aqueous media was studied by Sazou and Georgelious [76]. The electrocatalytic effect of polyaniline modified electrode for hydroquinone/benzoquinone and $\text{Fe}^{2+}/\text{Fe}^{3+}$ was observed by Yano et. al. [77]. Recently, the strong electroactive effect with a poly methyl aniline-coated electrode with polyaniline towards the redox system hydroquinone/benzoquinone was studied by the same authors [78]. Joseph et. al. studied the application of polyaniline coated electrodes for selective electro oxidation of hydroquinone and o-phenylene diamine [79].

Holze and Malinauskas recently studied on the \textit{in-situ} spectroscopy and electrochemical study of redox reactions at polyaniline modified Indium Tin Oxide(ITO) electrode [80]. The ratio of reduced and oxidised form on the electrochemically active
polymer is measured using UV-Visible spectroscopy. The redox interactions between polymers and redox species in the electrolyte are also followed.

Impedance spectroscopic study of polyaniline film in aqueous and organic solutions was reported by Pistoia and Firdiponti [81]. The authors showed that the charge transfer resistance is rather low at intermediate oxidation levels which is in quiet agreement with the metallic behaviour reported at these potentials. Trojanowicz has reported the amperometric sensing of ammonia in aqueous solutions using a polyaniline modified electrode in flow injection system. This electrode was utilised for designing amperometric biosensor for urea [82].

In 1968 Dall'olio reported the electrochemical polymerisation of polypyrrole [83]. Since then the research activity in this particular polymer has continued to proceed at a constantly increasing pace. The electrochromic performance of the polypyrrole films prepared on the electrode plate in an electrolysis cell. The effects on the film thickness, the anion species and the electrolyte solution on the redox reaction, as well as the electrochromism are reported by Chiu et. al. [84].

Pei et. al. reported that the poly pyrrole film on platinum electrode responded to the change in the solution pH quite slowly due to the slow protonation and deprotonation process of the polypyrrole chains [85]. Jovanovic et. al. showed that the polypyrrole doped with bisulphate ions can serve as effective pH sensor [86].

Ugo et. al. recently modified the glassy carbon electrode with Poly[1-methyl - 3-(pyrrol - 1-yl methyl) pyridinium] by electrochemical oxidation of suitable monomer in acetonitrile solution. The electrodes are powerful tools for the determination of traces
of mercury in chloride containing media. They have also used the modified electrodes for the analysis of sediment pore water [87].

Sadik developed a new electrode material made of electroactive polymers to have remarkable sensing application through their ability to reversibly oxidise or reduce by applying electrical potentials. This antibody immobilised electroactive polypyrrole can be used in biosensing applications [88]. Sun and Fitch developed a nitrate sensor based on electrochemically prepared conducting polypyrrole films [89].

Michalska and Maksymiuk studied the electrochemical behaviour of polypyrrole doped with chloride and dodecyl sulphate ions as well as poly (N-methyl pyrrole) doped with perchlorate anions [90]. Reports published by Yang and Dong indicates that the polypyrrole prepared has been changed from an electronically conducting polymer to a redox polymer after immersion in sodium chloride solution [91].

Yu and co-workers fabricated a polyglycine modified electrode on glassy carbon electrode. The electrode shows excellent electrocatalytic activity towards the oxidation of ascorbic acid, reducing the overpotential by 350 mV [92].

NAFION-glucose oxidase ferrocene electrodes were used to study electron transfer in electrochemical and enzymatic reactions. The ferrocene mediators were incorporated by either soaking platinum/NAFION and platinum/NAFION glucose oxidase electrode in an aqueous solutions. The research paper also details the electrocatalytic oxidation of glucose at NAFION-glucose oxidase electrode loaded with ferrocene derivative [93]. Similarly, Koide and Yokoyama reported on the electrochemical characterisation of an enzyme electrode based on ferrocene containing redox polymer [94]. An attempt has been made to crosslink polyallylamine with
glutaraldehyde and modified successively with ferrocene carboxylic acid on glassy carbon substrate. The catalytic electrochemistry of the modified enzyme electrode was also discussed in detail along with the biosensing application of the electrode.

Bonazzola and Calvo investigated the complex electrochemical behaviour of electrodes modified with polypyrrole-flavin mononucleotide composite film by cyclic voltammetry, electrochemical impedance spectroscopy and visible spectro electrochemistry with optically transparent electrode [95]. The photoelectrochemical and electrochemical behaviour of gold electrodes modified with bilayers of polypyrrole and polyaniline has been studied by Upadyay et. al. [96]. Polypyrrole modified electrodes and their composite modified electrodes for a variety of applications such as electrocatalysis, electrochemical analysis and sensor developments have been reported by various research groups [84,91, 97-99].

Measurement of cations by polymer modified films coated with NAFION membrane was investigated by Brett et. al. These modified electrodes were used in trace metal analysis of environmental sample [100].

1.2.1. NAFION Film Coated Electrodes

Ion exchange membranes play a vital role in life sciences and engineering technology [101], batteries [102,103], fuel cell [104] and electrochemical sensors [105-107]. NAFION is a fluorinated polymer bearing sulphonic acid in the polymeric network. NAFION 117 is at present manufactured by Dupont de Nemous and Co. Great deal of research work is being carried out on NAFION coated electrodes. Thin film of NAFION can be coated from the alcoholic solution by conventional methods such as dip coatings and evaporation techniques. NAFION membrane shows excellent properties
such as thermal stability, chemical stability, mechanical strength, electrical conductivity and above all it has high selectivity to the desired ionic species [108-111]. NAFION possesses SO$_3^-$ group in the polymer matrix and has the tendency to form hydrophilic molecular dimension pores in the NAFION membrane and hence the ion transports characteristics.

Gierke proposed the molecular level structure for NAFION, and the membrane is a series of clusters of inverted micelles interconnected by small pores [112]. Lakshminarayanaiah studied the ion exchange characteristics and water transport properties of NAFION membranes employing a variety of techniques [113,114].

Lehmani et. al. identified the electrophoretic mobilities of sodium, nickel, and silver ions in NAFION membrane and in conclusion the super selectivity of NAFION membrane for different cations have been demonstrated [115].

Shi and Anson proposed the procedure for cation electrodes with a film of NAFION that are saturated with [Os(bpy)$_3$]$^{2+}$ ion. The internal structures of both the forms such as fully hydrated or dehydrated are proposed for the observed behaviour [116]. NAFION membranes are widely used as a proton exchange membrane in fuel cells [104,117]. Maruyama et. al. reported the influences of NAFION film on the electrode kinetics of anodic hydrogen oxidation on NAFION coated platinum electrodes. The same research group also studied the mass transport of hydrogen on partially immersed NAFION coated electrode in the proton exchange membrane fuel cells [118].

Several other research groups reported on the oxygen reduction at NAFION coated electrodes and showed that the presence of NAFION film significantly enhances the electrode kinetics of oxygen reduction [119-121]. Ramaraj and Gopi reported on the
electrocatalytic reduction of oxygen at NAFION coated and clay modified electrodes in presence of tetraaza macrocyclic cobalt III complexes. They have observed that the yield of $H_2O_2$ and the rate of $H_2O$ production were higher at clay coated electrodes than at NAFION coated electrodes [122]. The research paper also details that the reduction of oxygen takes place at more negative potential in the case of NAFION coated electrode when compared with the clay modified electrodes.

Toniolo et. al. have evolved methodologies for the fabrication of NAFION membrane coated electrochemical sensors for specific substrates. The results observed shows that the sensor is effective in electrolyte free liquid samples [123]. Jordan et. al. studied the sensor characteristics of NAFION coated gold electrode in presence of ethylene and showed that the sensor characteristics increases with surface area of the electrode and decreases with humidity, which adversely affect the sensor's performance [124].

The NAFION polymer often serves as a matrix for electrode modification and provides exclusion and cation permeation selectivity. NAFION film coating on modified surfaces prolonged the stability and lifetime of the modified electrodes. Covering a modified electrode with a NAFION film could protect the mechanical loss of the modified film from the electrode surfaces and also from the interference of anions present in the sample solution [113].

Electrodeposition of catalytic platinum onto NAFION coated glassy carbon electrode was studied by Ye and Fedkiw [125]. High surface area catalytic platinum deposition in NAFION has been achieved either by chemical [126,127] or by electrochemical [128,129] routes.
Langmaier and co-workers demonstrated the ferric/ferrous electron transfer reactions on the NAFION coated gold and platinum electrode in perchloric acid solution. The order of the reaction is almost similar to that observed for polycrystalline electrodes of platinum and gold. The NAFION film prevent the flow of trace anion present in perchloric acid and thereby influences the ferric/ferrous electron transfer reaction via the inner sphere catalysis [130].

Analysis of trace metals whose reduction potential are rather negative and which do not form amalgams can be effected by thin mercury film electrodes coated with NAFION was described by Ugo et. al. [131,132]. Daniele et. al. recently reported and characterised the mercury microelectrode prepared by depositing mercury onto platinum electrode by electrochemical method coated with NAFION by dip coating [133].

The thin film deposited electrochemically onto a conductive surface can be used as a rechargeable battery electrode. Lee et. al. [134] described PAN/NAFION composite film deposited on ITO. This type of rechargeable battery was similar to PB-NAFION composite battery formed by sandwiching NAFION between two thin layers of PAN-NAFION composites. The useful features of the composite polymer modified electrodes assure a good contact between electroactive material and the electrolyte. They also possess improved mechanical properties [135].

The performance of conducting polymer-coated electrodes can be improved by incorporating NAFION into the polymer matrix. NAFION exhibits some degree of phase segregation, which leads to unusual stability towards the dissolution [136,137].

Premkumar and Ramaraj reported the preparation of poly o-phenylene diamine incorporated into a NAFION film coated electrode. The modified electrode shows
excellent electrocatalytic behaviour. which reduces oxygen couple with the permeation of the oxygen through the NAFION [138].

Orata and Buttry reported the virtues of composite structures in electrode modification by studying the preparation and properties of polyaniline/NAFION deposited on gold and glassy carbon substrate electrode. The study revealed that the charge transport characteristics of the modified film improves to a greater value. They discussed the thermodynamic view of the kinetic process involved in these modified electrodes [139].

The redox performance of the polypyrrole/NAFION composite electrode was investigated by Momma et. al. in polyethylene oxide-LiClO₄ electrolyte. These kind of modified polypyrrole/NAFION composite film shows an excellent charge discharge characteristics. which suit as battery electrode for the future [99].

The result observed by Wang and Adzic demonstrates that the NAFION coatings are suitable over a larger potential range. They are also suitable for studying surface properties and ion distribution on electrode surfaces [140]. Recently, Bidan and co-workers reported that the nitrous oxide sensor based on carbon fibre electrode modified by poly N-methyl pyrrole in iron substituted Keggin-type hetero polyanion coated by a NAFION external layer [141].

1.3. Modification with Inorganic Films

Electrodes modified with inorganic films have excellent electron transfer characteristics and stability during electrolytic applications when compared to organic modifying agents [142,143]. Modified electrodes with thin inorganic films attract electrochemists for specific applications. Polynuclear metal complexes, polynuclear
metal oxides, zeolites, clays, etc. are being used as modifiers for the modification of electrode surfaces. These inorganic modifiers provide three-dimensional network to the electrode surface that imparts special characteristics to the modified surface. These electrodes have ion-exchange properties, electrocatalytic properties, electrochromic properties etc. Hence the modified electrodes act as ion sensors, amperometric detectors, for the electrolysis of the targeted species etc. In addition to this in recent years the inorganic modifiers can also protect the metal surfaces against corrosion [144-147].

1.3.1. Metal Hexacyanoferrate (MHCF) Modified Electrodes

1.3.1.1 Prussian Blue (PB)

Metalhexacyanoferrates are polynuclear metal complexes that have a zeolitic structure with channel diameter of about 3.2 Å. Ferric ferrocyanide also known as prussian blue (PB) has been manufactured as an important pigment for paints and printing inks [148]. PB exist in two forms viz, “water insoluble PB” and “Water soluble PB” [149,150], which was established by spectral studies [151,152]. This oldest pigment undergoes redox reaction that leads to prussian white and prussian green respectively [153]. The Chemical modification of electrode surface with thin films of PB was reported by Neff, by simply immersing the electrode in a ferric-ferricyanide solution [154]. Platinum and gold substrate electrodes employed for the deposition of thin films of PB under non-electroplating condition and the driving force is autocatalytic-reduction of ferric-ferricyanide [155]. Similarly, Ellis and co-workers have deposited PB film by chemical method [156]. Gomathi and Rao have reported the modification of glassy carbon electrode surface with thin films of PB employing Potential Sweep Method (PSM). These method scores over the other method by virtue of its simplicity and well
o - Outer Sphere transition metal ion
• - Iron Centre of hexacyanoferrate centre

Fig. 1.1 Structure of Metal hexacyanoferrate
defined experimental conditions [157]. PB modified electrodes have been investigated for their applications in electrochromic display devices [158], ion selective electrodes [142,159], signalling devices [160] and solid state energy storage devices [161,162].

Prussian blue film has a well-defined crystal building that makes the system an interesting one for studying the charge transport processes through electroactive films. Soluble prussian blue, KFeFe(CN)$_6$ films can be reduced to a colourless form called Everitt’s salt, K$_2$FeFe(CN)$_6$ (ES) or well oxidised to prussian yellow, KFeFe(CN)$_6$Cl (PY). The role of potassium and hydrogen ions during the Prussian blue $\Leftrightarrow$ Everitt’s salt process is very critical. Potassium ions act as a stoichiometric reactant and the hydrogen ions play a very important role in the kinetics of electron-hopping process [155].

$$K_2FeFe(CN)_6 \rightleftharpoons KFitFe(CN)_6 + K^+ \quad \ldots \ldots \ldots \ldots (1)$$

$$K_4Fe_4[Fe(CN)_6] \rightleftharpoons 4Fe[Fe(CN)_6]_3 + 4K^+ \quad \ldots \ldots \ldots \ldots (2)$$

$$KFeFe(CN)_6 - e \rightleftharpoons FeFe(CN)_6 + K^+ \quad \ldots \ldots \ldots \ldots (3)$$

Prussian blue was found to be a good catalyst for both hydrogen peroxide and oxygen reduction [163,164]. However, as was shown by Karyakin et. al. the deposition of Prussian blue under certain conditions led to the electrosynthesis of a completely selective electrocatalyst for hydrogen peroxide reduction in the presence of oxygen [165]. The development of amperometric biosensors on the basis of prussian blue modified electrodes was first reported by Karyakin et. al. [166]. Selective detection of H$_2$O$_2$ by electroreduction in the presence of O$_2$ allows a substantial decrease in the electrode working potential avoiding the influence of so called reductants. The later is present in real samples and affect the biosensor selectivity dramatically producing parasitic anodic currents [167]. Selective electrocatalysis of hydrogen peroxide reduction results in a
complete stabilisation of the inorganic polycrystal on the electrode surface at negative potentials. The kinetics of hydrogen peroxide reduction on electrodes modified with specially deposited prussian blue were investigated using a wall-jet cell with continuous flow [168].

Prussian blue and related metal cyanometalate compounds belong to a family of polymeric complexes that have been studied extensively for many years. Interesting properties, which have led to the continuous interest in these compounds, include the non-daltonian stoichiometry and ionic as well as electrical conductivity through zeolite molecular pores. Prussian blue was mechanically attached to carbon electrodes using a technique initially developed by Scholz and co-workers [169,170]. The method provides an array of microcrystalline particles on the electrode surface rather than the traditional thin film. Because of this feature a large range of solid insoluble materials may be investigated by electrochemical methods [171,172]. The applicability of the voltammetric investigation of solid microcrystalline particles mechanically attached to electrode surfaces to ion-conducting and electrically semiconducting materials, such as prussian blue has been demonstrated in conjunction with in situ quartz crystal microbalance experiments [173].

PB colloids can be extracted from aqueous solution by an organic solvent containing some cationic surfactants. The extracted PB solution is coated on a transparent electrode by casting technique. The electrochemical, analytical and photoelectrochemical characteristics of the cast PB film was compared with the electrodeposited PB film. [156]
Neff devised a chemical method to deposit thin films of PB onto platinum and
gold electrode and where the first to investigate the electrochemistry of the film [154].
Itaya et. al. modified the Neff's preparation method that reported on the spectroscopic
and electrochemical properties of these films prepared electrochemically on a number of
substrate electrodes [174].

Kuhnhardt studied the nucleation and growth of prussian blue film on glassy
carbon electrode. The time dependency of the current and the charge, confirms a three-
dimensional nucleation and growth mechanism by the surface diffusion of PB particles to
kinks at growing nuclei.[175].

The analytical importance of the PB modified electrode have been reported by
several research groups[142,158-161]. Bocarsly and co-workers reported a shift in the
redox potential of the $\text{Fe}^{3+/2+}$ in the case of PB [176,177]. The analogues of prussian blue
have been reported repeatedly for their excellent electrocatalytic properties [163].

Murray and Masui recently reported that the PB exhibits two different redox
characteristics. Reduction of PB leads to Prussian white and the oxidation leads to
prussian yellow which are ionically conductive, and hence can be used as diode-like
material [178].

The PB film deposited onto glassy carbon electrode brings about the
electrocatalytic oxidation of hydrazine was demonstrated by Scharf and Grabner in which
the oxidation process occurs at about 0.7 V vs Ag/AgCl. The charge transfer step of the
process was explained as one-electron process [179].

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1.3.1.2. Electrochemistry of Prussian Blue

The metal hexacyanometallates has the general formula $M_k^A[M^B(CN)_6]_i \cdot xH_2O$ where $M^A$ and $M^B$ are transition metal ions with different formal oxidation numbers. Even though the oldest compound of this type has been extensively studied earlier the other analogues and its electrochemical characterisation gains momentum recently [180].

These hexacyanoferrates are the compounds from transition metals which have got stability towards dissolution over oxidation and reduction reactions. More over these compounds exhibit both ionic conductivity as well as redox properties. They possess zeolytic structure and charge neutrality has to be maintained during redox processes that makes PB useful for many applications [10,142-144].

Solid metal hexacyanometallates have attracted considerable interest during the last decade because of their potential application in electrocatalysis, electrochromism, electrochemical sensors, energy storage devices and electroanalytical applications [145.158-160]. Hence, these compounds have got both ionic conductivity as well as redox properties. The stability of these compounds upon oxidation and reduction are another reason for its impeccable importance in the field of electrochemistry. The zeolytic structure of these compounds along with charge neutrality on diffusion, makes these compounds very useful for many applications.

The characterisation of these insoluble film can be carried out by voltammetry and other electroanalytical techniques. Since these compounds possess zeolytic structure the percolation of ions with smaller size than the pore size is possible
1.3.1.3. Prussian Blue/Polymer Composite Modified Electrodes

NAFION is a cation exchanger and good proton conductor with unusual swelling properties whose water uptake and proton conductivity are strongly dependent on pre-treatment [181,182]. The electrochemical properties of the platinum electrodes modified with prussian blue (PB), polyaniline (PAN) and inner PB/outer PAN films have been examined using in situ fourier transform infrared spectroscopy [99,134,139].

PAN is one of the most studied conducting polymer and is an attractive material for many applications including electrocatalysis, sensors, and batteries [55-58,67]. The modified electrodes with various anionic iron(II) complexes were used as a mediator of electrochemical reduction of CO$_2$ by the mediated electrode was investigated with a detailed charge-compensating scheme by means of the in situ Fourier transform infrared spectroscopic method. The products generated in the electrochemical reduction of CO$_2$ on these modified electrodes were identified by taking in situ spectra during anodic stripping [183].

Solid state electrochromic windows (ECWs) were made by incorporating PAN-PB multilayers by electrochemical deposition of PAN and PB. This enhances the stability and solar light modulation of the ECWs. ITO glass plates were immersed in solution consisting of PAN and PB forming chemicals at different concentrations for the preparation of the modified electrodes [184].

Recently, Karayakin and co-workers developed a prussian blue/conducting polypyrrole composite electrode. The electroactivity of the electrode enhanced due to the presence of the polymeric film and this electrode can be successfully utilised for the detection cytochrome C [185].

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1.3.2. Nickel Hexacyanoferrate (NiHCF)

Modification of electrode surface with nickel hexacyanoferrate (NiHCF) has been carried out by a number of research groups by chemical and electrochemical routes. Thin films of nickel hexacyanoferrate can readily be prepared by repetitive potential cycling in a number of conducting substrates like nickel [186,187], graphite [188] and gold [189,190]. Sinha et. al. [191,192] has demonstrated the formation of NiHCF thin films onto nickel surface by simple anodisation in ferricyanide solution. Joseph et. al. reported potential sweep method for the deposition of NiHCF from acidic medium employing a solution comprising of nickel chloride and ferricyanide mixture [193]. Besides exhibiting good electrochemical activity, such films have revealed a redox character that suggests the cation incorporation into the film structure. Surface derivatisation leading to reversible nickel hydroxide is seen to unique with these films when treated with alkali.

Casella and co-workers [194] demonstrated the formation of thin films of mixed nickel hydroxide and oxyhydroxide micro particles on gold electrode substrate modified by electrochemical deposition and characterised by electrochemical methods. Joseph et. al. also reported electrochromic nickel hydroxide on platinum, graphite and glassy carbon [195]. Electroless deposition of nickel hexacyanoferrate on the aluminium surface was developed by Azar and Nerbin [196].

1.3.3. Cobalt Hexacyanoferrate (CoHCF)

Joseph et. al. reported the preparation and characteristics of the CoHCF modified electrodes for the first time by potential sweep method [197]. Gao et. al. reported cobalt hexacyanoferrate (CoHCF) modified electrode has been the new addition in the
analogue of PB, and demonstrated the electrochromic properties [198,199]. The authors reported on the method of preparing thin films of cobalt hexacyanoferrate on glassy carbon and platinum electrode surfaces. The CoHCF film on the surface of the electrode has been characterised by IR, Mossbauer and XPS spectroscopic techniques. Recently, Cai et al. reported the formation of cobalt hexacyanoferrate thin film on the surface of a microband gold electrode [200]. Kulesza and co-workers studied the electrochromism of CoHCF modified electrode in presence of different cations [201,202]. Studies on electrochromism of CoHCF indicate that the behaviour is analogous to that of nickel analogue. Zaldivar and co-workers investigated the structure and property of cobalt hexacyanoferrate complex immobilised on Sn IV oxide coated on silica gel surface [203,204].

1.3.4 Other Modified Hexacyanoferrate Electrodes

Other PB analogue modified electrodes such as on chromium hexacyanoferrate(CrHCF) [205], titanium hexacyanoferrate(TiHCF) [206], palladium hexacyanoferrate(PdHCF) [10], cadmium hexacyanoferrate(CdHCF) [207], molybdenum hexacyanoferrate(MoHCF) [208], silver hexacyanoferrate(AgHCF) [209], vanadium hexacyanoferrate(VHCF) [210], copper hexacyanoferrate(CuHCF) [159,211] were prepared and studied extensively by various research groups.

Joseph et al. reported the modification of carbon substrates with thin films of zinc hexacyanoferrate(ZnHCF) for the first time [212]. Dong and Jinn, Kulesza and Faszynska reported the electrochemical deposition and characterisation of indium hexacyanoferrate(InHCF) film modified electrodes [213-215].

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1.3.5. Composite and Mixed Metal Hexacyanoferrate (MM'HCF) Modified Electrodes

There is a growing interest in transition metal hexacyanoferrate and polynuclear inorganic materials, for modifying the electrode surfaces. The cyanometallate materials can also be viewed as analogues of prussian blue, which is, from the electronic point of view, a semiconductor or more precisely, a class II mixed-valance system with electrons and unoccupied states for them to move on [180].

Kulesza et. al. presented a reasonable approach in devising novel polynuclear silver cross-linked nickel hexacyanoferrate microstructures. This type of mixed transition metal systems through which one could exploit available information on highly insoluble bulk material precipitates and produce microstructures with novel physicochemical properties [216]. Very recently, during the preparation of this thesis, Kulesza et. al. have reported the preparation of powders of hybrid Co/Ni HCF by chemical route and have characterised the stoichiometry of the material. Further they have reported the preliminary results on the modification of the electrode surface with the hybrid hexacyanoferrate modified electrodes. The mixed analogues of iron and nickel/cobalt have been prepared employing potential sweep method to get the Ni/Fe HCF and Co/Fe HCF modified electrodes [217,218].
1.4. Ion-Selective Electrodes (ISE)

Selectivity is perhaps the single most important characteristics of any chemical sensor, which determines the application of the sensor. Research into ion selective electrodes gains importance for the selection of suitable ions. Over the past fifty years the best ion selective electrode identified is pH glass electrode. After this invention, there are excellent cation and anion selective electrodes for suitable purposes[11,142,159].

Ion selective electrode finds useful in the field of agriculture and fertilisers for analysing the nitrate, chloride, potassium, and ammonium ions in the soil and fertiliser samples. They are also used in the area of electroplating, food processing and environmental monitoring where the samples of hazardous chemicals can be identified by these type of electrodes. Ion selective electrodes are of two types depending on the sensing characteristics viz, cation and anion selective electrodes. Ion selective electrodes are simple to use efficient and sensing process little quicker. The adaptability of these electrodes are excellent and the analysis of samples cover a wide range of concentrations.

Measure of ion selectivity involves measuring the electrode response to a varying activity of primary ions in the presence of a fixed background of an interfering ion or vice versa. Diamond and Forster demonstrated that the ion selective electrodes predict the concentration of sodium, calcium and potassium ion in blood plasma and mineral water samples using dip and flow injection analysis measurements [219].

Ion selective electrodes have emerged as a powerful tool for monitoring a variety of samples. These electrodes can be effectively used to study heavy metals and toxic chemicals. These electrodes have excellent ability to monitor the selectivity and activity of a particular ion in a solution. These electrodes were used as sensors in potentiometric
determinations, potentiometric titrations, chemical and biochemical kinetic studies [142.156.180].

Nitrate doped polypyrrole films on a glassy carbon substrate have been prepared electrochemically in aqueous acetonitrile and propylene carbonate solution as nitrate sensors [89]. The effect of solvent, electrolyte and plasticiser on the sensitivity, selectivity and lifetime of polypyrrole sensors for the determination of nitrate were also discussed.

The selective membrane electrodes are of two types viz, solid membrane electrodes and ion-selective liquid membranes. Solid membrane electrodes are made of homogeneous, sparingly soluble crystalline substances or single crystals. Where as the liquid membranes are generally polymer based with an organic mediator immiscible with water and an active substance sensitive for the ion of interest [220].

Thin films of these materials deposited on conducting substrate behaves like electrodes of the second kind in the sense that the cell potential depends on the activity of certain ions in the electrolytic solution phase. It is apparent from this class of compounds that they can be used as a good candidates for practical application as ion selective electrodes. The use of thin films of prussian blue and heterogeneous prussian blue membranes as potassium ion selective electrode was investigated by Krishnan et. al [221].

During the redox reactions of smaller pore size than the zeolytic structure of the hexacyanoferrates can freely diffuse in and out of the lattice structure, which has become the basis for developing ion selective electrode for the determination of cation in solution
The basic theme underlying the various experimental approach for electrode modification is to introduce redox groups that can be easily oxidised and reduced onto the surface of a substrate electrode of a metal or semiconductor, which there after acts as a better candidate electrode for desired applications.

In the development of this subject, attention has been paid largely onto the development of novel and efficient routes for the surface modification. There is yet another fact that the nature and origin of the modified film also gain importance.

Modifying the substrate electrode via, inorganic metal salts and complexes can effect modification of electrode surface. Electrodes modified with organic modifiers possess some stability problems and thus they can not be used in application based on promotion of charge transfer characteristics. On the other hand the electrodes modified with inorganic species promise to subside the stability problem [164].

1.5. Electrocatalysis

Modified electrodes have the ability to catalyse redox reactions at lower potential when compared with that of the unmodified electrodes which reduces the problem of over potential and brings about desired reactions [4,5,164]. The selectivity and sensitivity of these electrodes provide specific application pertaining to the electrochemical detection of species in liquid chromatography [222]. Scholz and Narayanan compared the electrocatalytic activities of electrodes modified with metal hexacyanoferrates on to the surface of paraffin impregnated graphite electrodes for the oxidation of hydrazine [223]. The catalytic activities of these modified electrodes were compared based on the ratio of the total current required for the catalytic oxidation of hydrazine with that of the bare
electrodes. The authors identified that the hexacyanoferrates of manganese, zinc and indium possesses the highest catalytic activity.

Hexacyanoferrate modified electrodes are widely used for electrocatalysis in both ionic and non-ionic forms in biosensors [224]. Labuda and Hudakova prepared hexacyanoferrate modified carbon paste electrodes for the catalysis of ascorbic acid. The sensors used are synthetic hyerotalcite as solid resin and tris-octyl amine as pasting liquid for the anion exchange behaviour attached with hexacyanoferrate film on the carbon substrate [225].

Azar and Nerbin have reported the electrocatalytic property of aluminium electrode modified with NiHCF film towards the oxidation of ascorbic acid over the pH range 4-10 that found suitable for the ascorbic acid determination [196].

Chen recently reported the oxidation and reduction of thiosulphate by iron II, indium III, nickel II, and cobalt II hexcayanoferrate film modified on platinum and glassy carbon substrates [226]. The catalytic reaction was very rapid in the case of indium and iron hexacyanoferrate whereas the nickel and cobalt hexacyanoferrate exhibit different mechanism with the oxidation occur at more positive potential than the earlier two modified electrodes developed by Azar and Nerbin [196].

Catalti and co-workers investigated the enhanced stability and electrocatalytic activities of ruthenium modified cobalt hexacyanoferrate formed on a glassy carbon substrate electrode. The author utilised the catalytic ability of the modified electrode by the oxidation of hydrazine, thiosulphate and p-chloro phenol in acid medium [227,228]. The same research group have also showed that the ruthenium III hexacyanoferrate and
Iron II, III hexacyano ruthenate film can be used in solid state and electrocatalytic applications as sensing electrodes [229].

Electrocatalytic oxidation of methanol at a nickel hydroxide/glassy carbon modified electrode in alkaline medium and the electroxidation of alcohol and sugar catalysed on the nickel oxide modified glassy carbon electrode was studied extensively [189,230]. The electrocatalytic oxidation of glucose on nickel hydroxide modified gold electrode in alkaline medium was investigated by Casella et al. [194]. Similarly, Bocarsly et al. illustrated the electrocatalytic oxidation of ascorbic acid using NiHCF derivatised on nickel electrode [231].

Various research groups reported on the electrocatalytic oxidation of NADH at electrodes modified with conducting polymers [232-234]. The electrocatalytic oxidation of NADH at cobalt hexacyanoferrate modified on gold electrode was investigated for the first time by Chen et al. [200].

Bharathi et al. attempted the preparation of modified electrodes with multiple redox centres greatly increases their scope in the area of electroanalytical applications such as electrocatalysis, sensors, etc. [235]. Thin film of nickel hexacyanoferrate on glassy carbon electrode was prepared and the effect of alkaline hydroxide solution on the modified electrode was also discussed by Cataldi and co-workers [236].

1.6. Sensors

Metal hexacyanoferrate compound shows excellent ion exchange characteristics used in the cleaning up of radioactive waste in the nuclear waste storage basin [237]. Haight and co-workers reported the in situ determination of oxidation state profiles in
nickel hexacyanoferrate derivatised electrodes under potential control in an electrochemical cell using line image Raman spectroscopy [238].

Svitel et. al. investigated the possibilities of water insoluble hexacyanoferrate complexes as mediator [239], instead of classical potassium hexacyanoferrate [240]. The water–insoluble salts of hexacyanoferrate III and cationic surface-active agents were synthesised and used as electron-mediator for sulphite oxidase.

Joseph et. al. reported the modification of electrode surface with ZnHCF. The facile entry of potassium ion over the other metal cations such as sodium, lithium and ammonium is also reported [212]. In another reports published by Jan and Lin showed that the cobalt hexacyanoferrate modified glassy carbon electrode can be utilised for the detection of hydrogen peroxide [241].

Composite electrodes made of graphite, paraffin along with metal hexacyanoferrate as the active material were prepared by Scholz et. al. [242]. The PB analogues of copper, silver, nickel and cadmium viz, CuHCF, AgHCF, NiHCF and CdHCF have been employed and the electrodes were evaluated for the determination of $H^+$, $Li^+$, $Na^+$, $K^+$, $Rb^+$. Cs$^+$. NH$_4^+$, Mg$^{2+}$, Ca$^{2+}$ and Ba$^{2+}$.

Tani and co-workers have developed a selective electrode based on CuHCF and NiHCF for cations belonging to alkali, alkaline earth group, heavy metals and ammonium ions [243]. Bocarsly et. al. has employed nickel surface modified with NiHCF for the determination of alkali metal cations in solution [244]. The same research group also developed ferric hexacyanoferrate and cupric hexacyanoferrate modified electrodes for the detection of simple cations in flow systems. Trace analysis of cesium ions in
presence of large excess of sodium ion was studied by employing NiHCF modified electrode [176,244].

Joseph et. al. have reported the electrochemical characteristics of the CoHCF modified electrodes. The effectiveness of alkali metal cations on the cyclic voltammetric behaviour was also discussed in detail [197]. The indium hexacyanoferrate films modified on glassy carbon substrate electrode can serve as a model system to test the convolution method for cation exchange [214,245]. The changes in the surface of the indium hexacyanoferrate films deposited on platinum or glassy carbon electrodes in different applied potential were reported by Cataldi et. al. [246].

Presence of Iron III ions in a solution can be identified by reactive electrodes made up of silver hexacyanoferrate, graphite and paraffin have been developed by Scholz and Kahlert [209].

The hexacyanoferrate modified electrodes are useful sensors for both electroactive and non-electroactive cations. This investigation was made by Thomsen and Baldwin who prepared nickel and cupric hexacyanoferrate on different substrate electrodes for the application of non-electroactive species of alkali and alkaline earth cations and ammonium ions in a flow injection systems [247].

CuHCF modified electrode has been evaluated for the determination of potassium and ammonium ions under flow conditions by the number of researchers [211,248]. Siperko and kuwana prepared cupric hexacyanoferrate thin films on glassy carbon substrate for the detection of potassium and ammonium ions [211].

The reversible redox behaviour of the transition metal hexacyanoferrates has also been used for developing chemically modified electrodes for analytical applications.
These modified electrodes are successfully used in the determination of compounds of biological and environmental importance [12].

1.7. Electrochromism

Modified electrodes as electrochromic materials attracted much research interest in recent years [156, 158, 180, 249, 250]. Kulesza and co-workers studied the electrolyte cation dependent colouring, electrochromism and thermochromism of cobalt hexacyanoferrate modified electrodes on glassy carbon disk substrate [251]. VHCF modified electrodes showed electrochromic properties with sensitive colour switches were reported by Liu and Dong [252]. Spectroelectrochemical and electrochemical investigations of CoHCF film prepared on gold covered foil substrate electrode in potassium salt electrolyte by Kulesza and co-workers for electrochromic applications [202].

1.8. State of the Art and Scope of the work

In the previous sections detailed literature survey has been presented on the chemically modified electrodes with special reference to PAN modified electrodes, NAFION coated electrodes and MHCF modified electrodes. The survey reveals that the electrochemical route is simple and elegant for the modification of electrodes with organic and inorganic modifiers.

The detailed literature survey has also been made on the application of the modified electrodes in electrocatalysis, electrosynthesis, biosensors, electrochemical sensors, energy storage devices and electrochromic devices. It is seen from the current literature that the modification of electrodes with prussian blue and its analogues gaining importance because of their three dimensional structure that is capable of accommodating
metal ions in their channelled structure. It has been brought out clearly that PB has two iron centres, namely, the outer sphere iron centres (Fe^{2+/3+}) and the inner sphere HCF. Huge volume of reports are available replacing the outersphere iron centres by other transition metal ions to form the analogues of PB, via., NiHCF, CoHCF, ZnHCF, InHCF, etc. Except AgHCF, majority of the MHCFs has similar structural features. Hence it is possible to replace part of the outer sphere transition metal ion with other metal ion of interest to have a mixed analogues that may possess special characteristics. The present work deals with evolving protocols for the modification of such mixed analogues.

In the present work, the cobalt/nickel hexacyanoferrate thin films were employed for the modification of the electrode surfaces. The main reason being both nickel and cobalt have similar atomic radii and physicochemical characteristics. In addition to this their modification protocols are clearly similar. The CoHCF modified electrodes possess ion selective characteristics, electrochemical characteristics and magnetic properties. The NiHCF modified electrodes possess excellent electrochemical reversibility, derivatisation to oxy hydroxy electrode, etc. Hence, the mixed electrode of Co/Ni HCF may possess interesting electrochemical characteristics when compared to the individual analogues. The present work aims at evolving protocols/methodologies for the modification of glassy carbon electrode with thin films of Co/Ni HCF varying the extent of Co to Ni incorporation in a reproducible fashion. Further, the work also attempts to characterise the modified electrodes employing electrochemical, spectral and other chemical methods. It is well established that metal hexacyanoferrate modified electrodes are excellent electrocatalytic electrodes for a variety of substrates. An attempt has been made for the
evaluation of the modified electrodes for the electrocatalytic oxidation of ascorbic acid, thiosulphate, monitoring of biochemical reaction and also for the evaluation as potassium sensor.

In addition to this work, the present work aims at the modification of GC surface with bilayer membranes of NAFION and polyaniline. Both these polymers have their own domains of importance and the present work attempts to study the change in the electrochemical characteristics of the bilayer modified electrodes.

The thesis comprises of six chapters that discusses the outcome of this investigations, detailing the procedures, experimental data and discussion with conclusion.

1. Chapter 1
   - Gives a detailed account of the literature survey.
   - Provides the scope of the present work.

2. Chapter 2
   - Gives the experimental conditions and equipments employed.
   - Describes the materials employed in the present work.

3. Chapter 3
   - Discusses the details of electrode modification with thin films of Co/Ni HCF using GC as well as ITO electrodes along with specific experimental conditions and methods employed.
   - The details of the electrochemical characterisation of the modified electrodes are given. The CV data, derivatisation of Co/Ni HCF modified electrodes, impedance characteristics and spectral studies are also given.
- The data are discussed with reference to the feed ratio of the Co/Ni HCF modified electrodes and the nature of the thin film.

4. Chapter 4
- Provides information on the electrocatalytic oxidation of ascorbic acid and thiosulphate.
- Gives an account of the evaluation of these modified electrodes for sensing potassium ion.
- The details of the study employing glucose oxidase using the modified electrodes are provided.

5. Chapter 5
- The methodology of modification of electrode surface with bilayer of NAFION and polyaniline (PAN) is discussed.
- The electrochemical characterisation and the spectral characterisation of the bilayer layer modified electrodes are given.
- The mechanistic pathway of aniline oxidation on NAFION coated electrode is also discussed.

6. Chapter 6
- This chapter deals with the overall conclusion of the present study and also provides the future scope of this work.

In addition to the specific points all the chapters comprise of the experimental part specific to the particular study and also conclusion of the particular chapter.