Chapter 1

Introduction

The work described in this thesis deals with the study of thin films formed by four different techniques namely; Langmuir-Blodgett method, self-assembled monolayer formation, layer-by-layer assembly and electrochemical formation of metal-conducting polymer nanocomposite films. The main focus of the study is on the nature of these films with special emphasis on the electron transfer and electrocatalytic properties.

The thesis consists of three major parts; the first part deals with the synthesis and characterization of ultrathin films prepared by using different methods namely, Langmuir-Blodgett (LB) method, self-assembled monolayer (SAM) and layer-by-layer assembly (LbL). The LB approach of film formation relies on the physical adsorption, which is weaker in terms of adhesion to the substrate but possesses the advantage of the possibility of multilayers formation. In this work we have analyzed the LB films of cholesterol on two different SAM systems.

The SAM formation, on the other hand is a typical example of chemisorption which is essentially a strong adsorption but limited to the single layer of the molecules. In the present work we have studied a composite film system composed of cyclodextrin and thiocholesterol that shows a high electron transfer blocking property towards the redox couples in aqueous medium. The film exhibits regions of hydrophilic and hydrophobic properties on the modified surface, which was imaged using lateral force microscopy (LFM).

The LbL film formation is quite different from both the above mentioned methods. In this case the adhesion of material to the substrate is relatively stronger than the LB method. It is possible to form multilayer films using LbL method, where the stability of the layers is essentially due to the electrostatic interactions. Therefore the LbL method possesses the virtues of both LB and SAM methods. In this work we describe the LbL film formed by two oppositely charged polyelectrolytes namely; polystyrenesulfonate (PSS) and polyallylamine hydrochloride (PAH).

The second part of the thesis deals with the synthesis of conducting polymer polyaniline (PANI) by using electrochemical technique and the formation of nanocomposites from PANI and a porphyrin derivative. These nanocomposites are essentially the J-aggregates of porphyrin and
they form diverse nanostructures ranging from disc like nanostructures to nanofibers. We have shown that these nanostructures find useful applications in sensors and exhibit interesting linear and nonlinear optical properties.

The third part of the thesis deals with the synthesis, characterization and the study of the electrocatalytic property of conducting polymer and metal nanocomposites. We have proposed a new and simple one step electrochemical method for the synthesis of metal and conducting polymer nanocomposite films. We have studied four conducting polymers namely; polyaniline (PANI), polypyrrole (PPY), polythiophene (PTP) and polyethylenedioxythiophene (PEDOT). Noble metals gold and palladium were used to form nanocomposites with these conducting polymers. The nanocomposite films were characterized systematically by using various electrochemical, spectroscopic and microscopic techniques, which include cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), FTIR spectroscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray analysis (EDAX) among many others.

These nanocomposite films find useful applications as an electrocatalyst material for the electro-oxidation of small organic molecules such as methanol, ethanol and formic acid. This makes the present study useful for direct fuel cells (DFCs).

The present chapter provides a concise description of the methods and materials used in the thesis work.

1.1 Ultrathin films

The LB films, SAMs and LbL films are three major types of the ultrathin films of organic compounds which can be formed on variety of substrates. In the following section we will discuss all the above three films in some detail. Nanoscale films produced with the above techniques have opened up interesting possibilities in organic electronics, electrocatalysis, bioelectrochemistry and electroanalysis. In addition to the fabrication of nanomaterials and uses in the molecular electronics, fundamental processes such as charge transfer mechanisms involving biomolecules can be investigated at the molecular level. In our work we have focused mainly on how a thin film modified surface affect the electron transfer process in some of the common redox systems and also how this behavior varies in different types of films.
1.1.1 Langmuir-Blodgett (LB) film

A single layer of amphiphilic molecules spread at air-water interface is termed as the Langmuir monolayer. The necessary condition for the formation of Langmuir film is that the compound should be amphiphilic in nature so that it can be spread on water surface [1,2]. An amphiphilic compound or amphiphile is the one which has both hydrophilic and hydrophobic groups. Figure 1.1 shows a typical amphiphilic molecule and its Langmuir film at air-water interface. The Langmuir monolayer can be transferred onto a solid surface by LB technique. In Figure 1.1 the polar part may refer to any functional group which has affinity towards water, which is also called the hydrophilic part. Some such groups are \(-\text{COOH}, -\text{OH}, -\text{CONH}_2\) etc. Nonpolar parts typically contain a hydrophobic group like a hydrocarbon chain. These molecules form a single molecule thick assembly on the water surface. The overall effect of a Langmuir film on water surface is the reduction in the surface energy or the surface tension of water.

![Schematic representation of the amphiphilic molecule and Langmuir monolayer at air-water interface](image)

**Fig. 1.1 Schematic representation of the amphiphilic molecule and Langmuir monolayer at air-water interface**

The LB film can be formed on a solid surface when a solid substrate is dipped upwards and downwards through the Langmuir monolayer at air-water interface. The polar parts of the molecules adsorb on the substrate during the upward motion and hydrophobic parts of the molecules adsorb on the substrate during the downward motion. The process is shown in Figure 1.2. Depending on the nature of the substrate i.e. hydrophilic or hydrophobic, different kinds of LB films are possible, which are named as X-type, Y-type and Z-Type as shown in Figure 1.2. The first layer of the molecules can only be deposited on hydrophilic substrates during up stroke whereas on hydrophobic substrates the initial layer can be deposited during the down stroke. However the monolayer formation can take place during both up and down stroke (Y-type...
deposition). Deposition can also occur during only down stroke (X-type deposition) or only up stroke (Z-type deposition). During the LB film formation the surface area of the Langmuir monolayer decreases due to the continuous removal of the molecules from the surface onto the solid substrate. A parameter called the transfer ratio \( r \) is defined as the ratio of the decrease in the Langmuir monolayer area to the total surface area of the substrate to be coated. A unit value of the transfer ratio reflects the ideal LB deposition.

![Diagram of LB deposition process](image)

**Fig. 1.2** Schematic representation of the LB deposition process during the upward and downward motions and different types of LB deposition on different substrates

### 1.1.2 Self-assembled monolayers (SAMs)

Self-assembled monolayers (SAMs) are the molecular assemblies of organic films of a few nanometers thickness. These films are formed by the spontaneous chemisorption of organic molecules on a substrate when it is immersed into a dilute solution containing organic molecules. In contrast to the LB films the bonding between the substrate and organic molecules is much stronger in SAMs due to the chemical adsorption process.

The self-assembly phenomenon is known for the past many years, yet the significant progress in the field has emerged only in recent times. A variety of studies can be carried out with the help of SAMs such as studying electron transfer reactions, single molecule electron tunneling, sensors and molecular electronics etc. There are many examples of SAM formation
Introduction

with different organic molecules and substrate combinations. Alkanethiols and dithiols on gold [3,4], silver [5] and copper [6], dialkyl sulphides and disulphides on gold [7], alcohols and amines on platinum [8] and carboxylic acids on aluminum oxides [9] and silver [10] are the main examples of SAM. The process of self-assembly is mainly divided into three steps as shown in Figure 1.3, the first step is the chemisorption of the head group onto the substrate, which is an exothermic process.

![Figure 1.3 Schematic representation of the self-assembled monolayer formation process on gold substrates](image)

The very strong molecule-substrate interactions result in the pinning of the head group to a specific site on the surface through a chemical bond. The bonding can be covalent but slightly polar for alkanethiol monolayers on gold or ionic bond for carboxylic acids on AgO/Ag. The energy associated with the adsorption of carboxylic acid on Ag/AgO is of the order of tens of kcal/mol [11,12] and in the case of thiolate on gold it is 40-50 kcal/mol. As a result of the exothermic process during the first step, organic molecules try to occupy every available bonding site on the surface and in this process they compete with the molecules that have been already adsorbed. The second step is the inter chain van der Waals interactions among the alkyl groups. The energy associated with this process is only a few kcal/mol. The third and final step is the reorientation of the terminal groups. In the case of simple alkanethiol, methyl group is the terminal group. The thermal disorder at room temperature of the surface groups is evident from
the helium diffraction [13] and FTIR studies on monolayers [14]. The energy associated with this process is of the order of a few $k_B T$.

Both the alkanethiols and disulphides adsorb onto gold substrate to form the same thiolate ($RS^-$) species. The reaction of dialkyl disulphides with gold is an oxidative addition reaction as shown below.

$$RS - SR + Au^0_n \rightarrow 2R - S^- + Au^+ + Au_{n-2}^0$$

In the case of alkanethiol, the reaction may be considered as an oxidative addition of the thiol (S-H) bond to the gold surface, followed by a reductive elimination of hydrogen. When a clean gold surface is used for the monolayer preparation, the protons may probably end as H$_2$ molecule. The chemical reaction occurs in this case can be expressed as below:

$$R-S-H + Au^0_n \rightarrow R-S^- - Au^+ + Au_{n-1}^0 + \frac{1}{2}H_2$$

The combination of hydrogen atoms at the gold surface to form H$_2$ molecule is an important exothermic step in the process of self-assembly. During the chemisorption process, the thiolate species has been formed, as can be seen from the equation represented above, which is verified by XPS [4,15,16], FTIR spectroscopy [17], FT-mass spectrometry [18], electrochemistry [19] and Raman spectroscopy [20].

1.1.3 Layer-by-layer (LbL) assembly

Figure 1.4 shows the schematic diagram of the typical LbL assembly process with two oppositely charged polyelectrolytes namely; polystyrenesulfonate (PSS) and polyallylamine hydrochloride (PAH). In the beginning of the LbL film formation, we need a charged substrate which, in the case of metals can be achieved by forming a charged SAM on metals such as a SAM of 4-mercaptopropane sulfonate (negative charge) or cysteamine (positive charge). The simplest mechanism of LbL adsorption can be described as a sequential adsorption of oppositely charged species by dipping the substrate into the respective solutions alternatively. Recent results show that the film formation takes place due to the charge overcompensation and this can only take place till a threshold value of surface charge density beyond which film formation will no longer take place [21-24].

Over the past few years the LbL deposition technique has become an efficient method for producing organized films of oppositely charged molecules. There are several advantages
associated with the LbL method such as simplicity, versatility, low cost, and precise control of film thickness. In addition LbL film formation has the advantage of multilayer film formation with variety of materials. The nanostructured films prepared by the use of LbL method have tremendous advantages especially to fabricate new devices whose properties can be tuned by carefully choosing the desired polyelectrolytes. These films find several applications in the field of electrochromism, bioelectrocatalysis, electroanalysis and electrocatalysis.

![Diagram of layer-by-layer film formation process on solid substrates](image)

**Fig. 1.4 Schematic representation of the layer-by-layer film formation process on solid substrates**

The alternate dipping of such charged surface into a solution of oppositely charged polyelectrolyte yield a film of that polyelectrolyte on the surface which after cleaning in Millipore water can be immersed into the solution of another polyelectrolyte to form a bilayer of polyelectrolyte. This process can be repeated many times to obtain required thickness of the film until a threshold value of surface charge density comes into the picture.

**1.1.4 Electron transfer barrier properties of a thin film modified electrode**

In the literature there has been a detailed and comprehensive study on the structure and properties of aliphatic thiols on gold surface [3,4,19]. The ultimate aim in the area of SAM is to obtain a completely blocking and almost defect free structure of the monolayer.
Main effect of the blocking SAMs is the suppression of simple redox reactions across metal-solution interface by acting as a dielectric spacer. This phenomenon is due to the blocking of redox ions due to the presence of a close packed domain of hydrocarbon chains. Several factors such as the heterogeneous rate constant for the electron transfer reaction, the size and charge of the redox species, mechanism of electron transfer (inner-sphere or outer-sphere) affect the apparent blocking properties of the SAMs. These factors complicate the interpretation of suppressed faradaic current in terms of pinholes, defects and electron tunneling across the monolayer. The electron transfer blocking properties of a thin film modified electrode can easily be studied with the help of cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The current due to faradaic reactions at pinholes is limited by mass transfer at relatively low overpotentials compared to kinetically controlled currents due to tunneling. Hence the factors that affect the mass transfer should affect the observed currents if they are dominated by pinhole currents. This point of mass transfer controlled or kinetically controlled process for the electron transfer reactions can be resolved by using electrochemical impedance spectroscopic studies.

1.1.5 Applications of ultrathin films

Ultrathin film modified substrates find a variety of applications in several fields such as in corrosion protection, molecular electronics, memory storage, supercapacitors, sensors, photolithography, wetting behavior and surface patterning for various uses. Apart from this the thin film modified electrodes also act as an electron transfer barrier for several redox species between the metal surface and the solution. These films act as an insulating layer between the metal and the electrolyte and obstruct the further reaction, which can find potential applications in corrosion inhibition. Ultrathin films have also been used for the studies of single molecular electronic properties using either scanning tunneling microscopy or scanning tunneling spectroscopy. With the help of these two methods, a single molecule can be addressed on the surface and the electronic properties of the molecule can be studied. Using the SAM of dithiols, two metal surfaces can be interconnected resulting in a molecular wire between two electrodes. It has been shown that the wetting properties of the surface can be tuned by using molecules that have different terminal functional groups. For example, carboxyl terminal group provides a
hydrophilic film surface while methyl group in the terminal position results in highly hydrophobic surface.

These films also influence the orientation of the water molecules at the film/water interface and it has been shown that the long chain alkanethiol SAMs form a hydrophobic gap at the interface [25,26]. This hydrophobic gap reduces the interfacial capacitance in alkanethiol SAMs to a large extent, while for SAMs with polar functional groups the capacitance decreases only to a small extent. Ultrathin films have been widely used for the synthesis of monolayer protected nanoparticles especially gold nanoparticles [27]. The functionalization of the nanoparticles yields a highly stable coating on them which prevents the agglomeration of nanoparticles and such nanoparticles have good solution processability for further studies.

One of the main advantages of the SAMs is the possibility for further functionalization of the surface through terminal functional groups like carboxyl, amino or other derivative groups at the terminal positions. Such groups can be easily attached with different organic molecules, redox probes, enzymes, proteins or other biomaterials [28-30]. Such biofunctionalized monolayers have been widely used for the sensor applications [31-33]. One of the recent advancement in the ultrathin film study is the lithography, where different patterns can be formed on the metal surface using the different organic molecules [34,35]. In this thesis, we have focused our studies on the electron transfer barrier properties of different types of ultrathin films. We have used electrochemical, FTIR and scanning probe techniques for the characterization of these monolayers.

1.2 Nanocomposites

Nanocomposites, by plain definition are the materials having more than one phase and at least one of the phases should have one dimension less than 100 nanometers [36]. Of late the definition of nanocomposite materials has become wider notably to include a large range of systems for example one, two and three-dimensional materials, made of distinctly dissimilar components and mixed at the nanometer scale. In the broad sense this definition includes mesoporous materials, colloids, copolymers, organic-inorganic hybrid materials and multiphase nanostructures etc. The physical and chemical properties for example the electronic, mechanical, thermal, optical, electrochemical, catalytic properties of the nanocomposite are strikingly different from that of the component materials.
From ancient prehistoric times the human kind has been associated with nanostructures or nanocomposites either in the natural form like bones or the fascinating artificial ones like the Maya Blue. Ancient Romans had used colloidal gold (gold nanoparticles) to color glass with shades of violet or red. A fascinating class of hybrid materials can now be prepared by the mixing of different organic and inorganic materials. For last few years a rapid growth is noticed in the understanding and controlling of the chemistry of these nanocomposite materials to design and shape them for various applications.

In the present thesis, we have studied the electrochemical synthesis of organic-inorganic hybrid nanocomposite of conducting polymers and noble metals as a porous film on conducting substrates and their intriguing catalytic activity.

1.2.1 Conjugated (conducting) polymers

The plastics which we use daily are essentially the polymers, which are large molecules with a repeating structural unit. In fact the electrical wires are coated with plastics (polymers) as insulating material to protect them from short-circuits. The polymers are known to be insulators. A.J. Heeger, A.G. MacDiarmid and H. Shirakawa have discovered a new class of polymers which are electrically conducting almost like a metal. They were awarded the Noble prize in chemistry in the year 2000 for their discovery.

Polyacetylene was the first polymer in which the electrical conductivity was first detected. This polymer was already known as a black powder since 1974. Polyacetylene was prepared by Shirakawa and co-workers from acetylene, using a Ziegler-Natta catalyst. Despite its metallic appearance it was not known to be a conductor until 1977 when Shirakawa, MacDiarmid and Heeger discovered that the polyacetylene can be made 10⁹ times more conductive by oxidation with chlorine, bromine or iodine vapors. The oxidation by halogens is called the doping of the polymer.

The doped form of the polyacetylene has the conductivity about 10⁴ to 10⁵ S m⁻¹, which can be compared with the conductivity of metals (10⁸ S m⁻¹). Figure 1.5 shows the conductivity chart of different materials, the conducting polymers are somewhere in between semiconducting to conducting zone. The conductivity in conducting polymers arises due to the presence of highly conjugated structure (the presence of alternate double bonds). It is known that conjugated double
Introduction

bonds show entirely different behavior than isolated double bonds. These conjugated double bonds act in a group, as if they know that the next-nearest bond is also double.

![Conjugated Polymers]

**Fig. 1.5** Conductivity chart showing different materials including the conducting polymers

Huckel’s theory for aromaticity predicts that π electrons are delocalized over the entire length of the molecule, which makes the band gap very small especially for a long chain i.e. in the case of a polymer. The conductivity of a conducting polymer depends on both its ability to transport charge carriers along the polymer backbone and for the carriers to hop between polymer chains. Most of the conducting polymers do not have good electrical conductivity in their native state and therefore they need to be doped with suitable dopant in order to achieve high conductivity [37].

The high sensitivity of polyacetylene to air and insolubility in many of the solvents impose a barrier on the use and processability of polyacetylene. This has led researchers to look for another class of conjugated polymers. Polyaniline (PANI), polypyrrole (PPY), polythiophene (PTP) and polyethylenedioxythiophene (PEDOT) are the four most commonly used conducting polymers. These polymers can be prepared either by a chemical method or an electrochemical method. A chemical synthesis approach involves the addition of an oxidant such as ammonium peroxydisulfate (APS) into the solution of the monomer (aniline in case of polyaniline). The oxidizing agent initiates the polymerization reaction to yield the polymer. On the other hand in the case of electrochemical method, mineral acids such as sulfuric acid, hydrochloric acid and other strong acids are commonly used for the synthesis of conducting polymers. Table 1.1 shows some of the important conducting polymers and their conductivities.
### Introduction

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Conductivity (S m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacetylene</td>
<td>10³ to 10⁵</td>
</tr>
<tr>
<td>Polyphenylene</td>
<td>1000</td>
</tr>
<tr>
<td>Poly(p-phenylene sulfide)</td>
<td>100</td>
</tr>
<tr>
<td>Poly(p-phenylene vinylene)</td>
<td>1000</td>
</tr>
<tr>
<td>Polypyrroles</td>
<td>100</td>
</tr>
<tr>
<td>Polythiophenes</td>
<td>100</td>
</tr>
<tr>
<td>Polyaniline</td>
<td>10</td>
</tr>
</tbody>
</table>

*Table 1.1 Some of the important conducting polymers and their conductivities*

#### 1.2.2 Applications of conjugated polymers

A large volume of research is being carried out worldwide on structural modifications and functionalization for making conducting polymers potentially attractive materials for device applications. Since, conducting polymers with proper functionality respond to gaseous vapors at room temperature itself and can be deposited on a wide variety of substrates ranging from metallic to polymeric, they can find applications that prove to be difficult for conventional gas sensors which often require high-temperature operation. For this purpose one can take advantage of the conductivity of these polymers which includes the fascinating ability of these polymers to undergo a transition from insulating to conducting form.

The conducting polymers are easy to be prepared in nanostructured form such as nanorods, nanofibers etc. An improvement in the sensing ability was observed in the case of nanofibers of PANI than the conventional PANI [38]. Most of the polymers are insulators, a small addition of conducting polymer increases the conductivity and eliminates electrostatic charge. Conducting polymers can also be used as antistatic devices, using them as electricity dissipative additives. In contrast to carbon and inorganic metals, conducting polymers can preserve transparency and homogeneity when mixed with other polymers. The antistatic properties of conducting polymers prevent possible explosions during the movement of combustible fuels through polymeric transport lines. The static dissipation also eliminates data loss or device malfunction caused by sparks in electronic equipment. Conducting polymers also find important applications in modern optical devices such as organic light emitting diodes.
(OLEDs) [37]. There are many advantages of conducting polymers based OLEDs i.e. wide angle of visibility, reduced power consumption, high image quality, low operational temperatures and smaller size. Conducting polymer electrodes can also be used for electromechanical actuators that allow the transformation of the electrical signal into the mechanical movement [37]. The idea of artificial muscles can be realized using PANI, PPY and other conducting polymers. Electromechanical actuators have numerous applications, for example, a device may control small orifice in a drug delivery reservoir implanted in human body. Conducting polymers can also be applied for electromagnetic shielding in the microwave frequency range. This application requires highly conducting conjugated polymers [37].

1.2.3 Metal and conducting polymer nanocomposites

PANI is a conducting polymer with multiple, switchable inherent oxidation states (Figure 1.6). There are several reports in the literature about conducting polymers based inorganic–organic nanocomposites because the inclusion of inorganic materials into the polymer matrix can introduce entirely new properties to the polymer. This can lead to new functional materials with the advantages of both the inorganic and the organic components. For example, metal-PANI [37,39-42] and inorganic-PANI [37,43-46] nanocomposites have been found to be useful for sensors, catalysts, photovoltaic devices, and magnetic materials.

Different metal particles e.g., Au [47,48], Ag [49,50], Pt [41,50] and Pd [49,50] can be directly deposited on the polymer by direct chemical or electrochemical redox reactions between polymer and metal cations.

![Different oxidation states of polyaniline](image)

**Fig. 1.6 Different oxidation states of polyaniline**
Introduction

As shown in Figure 1.7, two types of structures are most commonly proposed in the literature for metal-conducting polymer nanocomposites [37], the first one is the dot-ON-wire structure and second one is the dot-IN-wire structure. In the former structure the metal nanoparticles are adsorbed (physical or chemical) or attached by a chemical bond on the surface of the polymer while in the latter the metal particles are impinged into the matrix of the polymer.

In this work we have synthesized metal-conducting polymer nanocomposites by using a novel electrochemical method. Palladium and gold were the metals used in this study. The nanocomposites were formed as a thin film on conducting substrates. We have studied the electrocatalytic activity of these nanocomposite films for electro-oxidation of small organic molecules such as ethanol, methanol and formic acid and also for hydrogen evolution reaction (HER). Such a study is useful in the development of fuel cell technology to meet the next generation energy demands.

1.3 Electrocatalysis for fuel cells

Electrocatalysis plays an important role in the context of energy conversion and storage. The electrocatalysis of fuel-cell reactions is a prominent area of research for both academics and in
industries. A simple definition of electrocatalysis, could be that "It expresses the enhancement of electrochemical reaction rates by surface modifications of various kinds at the electrochemical active surface". An electrocatalyst is basically a catalyst, which participates in an electrochemical reaction and modifies or increases the rate of chemical reactions without being consumed in the process. In other words electrocatalyst in the context of the electrode process reduces the overpotential for the electrochemical reaction, bringing it closer to the thermodynamic equilibrium potential.

For any electrochemical reactions, the voltage applied across an electrolytic cell (∆V) can be written as the following:

\[ ∆V = ∆E + η + ∆Ω, \]

where ∆E is the thermodynamic cell voltage depending on the electrode characteristics. η is the total overpotential which represents the additional energy required to carry out the reaction at practical rate and ∆Ω is the ohmic drop in the cell circuit. An electrocatalyst works in a way to bring down the overpotential (η) required for the reaction. An increase in the rate of the reaction brought about by just enhancing the surface area is not the true electrocatalytic effect unless there is a modification of the nature of the surface active sites.

There are two basic parameters which determine the rate of an electrochemical reaction, for a given electrocatalyst. These parameters are linked with the geometric and electronic structure of the electrocatalyst. The geometrical effects determine how the geometrical structure of the catalyst material is responsible in bringing out the catalytic activity of the material. For example, the atoms on the primary surfaces of palladium metal <100>, <110>, and <111> are different, which causes an entirely different kind of interaction with reactant molecules at each plane [51].

As shown in Figure 1.8 (Source: Osada et al. reference 51) there is huge variation in the electrocatalytic activity on different planes of Pd for formic acid electro-oxidation. This can be understood because the bonding energy of reactant will be different in a molecule and on the metal surface atoms depending on the exposed metal surface geometry. In addition, if a metal is used in conjunction with another metal there will be a change in the surface structure and the catalytic activity will be affected.
Another noteworthy parameter that plays a crucial role in electrocatalysis is the electronic structure of the catalyst material. The electronic structure is described by the electronic orbitals of the catalyst atoms, especially the outer or valence electrons, which influence the catalytic properties most on the interaction with neighboring atoms. A majority of the electrocatalytic materials utilized for fuel cells are metals or more specifically the noble metals. These catalysts include platinum, iridium, ruthenium, palladium, gold and silver. Few of the non-noble elements have also demonstrated catalytic activity, often in combination with the noble elements, and they include nickel, iron, cobalt, chromium, vanadium, molybdenum, tin, tungsten and others. The most common electrocatalytic material is platinum metal because of its ability to function close to the thermodynamic potential.

There is huge interest in identifying the new catalytic materials which are cheaper and relatively more abundant. Volcano plots have been studied in the literature in order to understand the properties of any catalytic material. These are plots which show the maximum in the activity of a series of catalytic materials for a given value of any property for example the heat of adsorption of the intermediate on the electrode surface with a linear decrease in either side of the plots. Figure 1.9 shows a typical volcano plot of electrocatalysis of hydrogen reaction. The property studied here is the enthalpy of hydrogen adsorption. From the figure we can see that Pt group metals have intermediate value of enthalpy of hydrogen adsorption and a high activity. This suggests that an intermediate value of enthalpy of hydrogen adsorption is required for
achieving high catalytic activity [52-54]. On Pt group metals, the chemisorption of hydrogen on the metal surface can easily remove the adsorbed oxygen with the formation of water.

Fig. 1.9 Volcano plot for the hydrogen evolution reaction (HER) for various pure metals (Source: Conway et al.[53])

Nanomaterials offer unique properties either used as electrodes or electrolytes in fuel cell devices. In the case of nanomaterials, which have very high surface area with small particle size the electronic structure of the surface atoms changes drastically and the catalytic properties improve. Nanomaterials of Pd, Au in combinations with other low cost materials have the potential to emerge as a substitute for Pt.

Fuel cell is basically an electrochemical device that converts chemical energy to electrical energy. In principle fuel cells operate in a way different from a battery in the sense that it does not run down or require recharging after use. However it produces electrical energy as long as the fuel is supplied. In a fuel cell, the fuel constantly flows into the cell so the cell never seizes, as long as the flow of fuel is maintained into the cell the electricity flows. A typical fuel cell consists of an electrolyte medium sandwiched between two electrodes. The first electrode or the anode is the place where electrochemical oxidation of fuel occurs while at other electrode or the cathode electrochemical reduction of oxidant takes place. Ionic species generated after the oxidation of the fuel are transported from anode to cathode through the ionically conducting but electronically insulating electrolyte membrane. This membrane also acts as a barrier between the fuel and oxidant. Electrons generated at the anode during oxidation have to pass through the
external circuit on their way to the cathode, where the reduction reaction occurs. This movement of electrons essentially creates the current. Since the fuel and oxidant do not mix at any point and no combustion takes place, the fuel cells are not limited by the Carnot efficiency and theoretically can yield 100% efficiency. However there are certain other issues which determine the efficiency of a fuel cell. Fuel cells are primarily classified according to the electrolyte material used. The choice of electrolyte material also governs the operating temperature of the fuel cell.

The most common type of a fuel cell is hydrogen-oxygen fuel cell. The chemical reaction in hydrogen oxygen fuel cell involves the following half-cell reaction schemes with the production of water.

\[
\begin{align*}
\text{Anode:} & \quad \text{H}_2 \quad \longrightarrow \quad 2\text{H}^+ + 2\text{e}^- \quad \text{E}_0 = 0 \text{ V} \\
\text{Cathode:} & \quad \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \quad \longrightarrow \quad \text{H}_2\text{O} \quad \text{E}_0 = 1.23 \text{ V} \\
\text{Overall reaction:} & \quad \text{H}_2 + \frac{1}{2}\text{O}_2 \quad \longrightarrow \quad \text{H}_2\text{O} \quad \text{E} = 1.23 \text{ V}
\end{align*}
\]

Even though the efficiency of a fuel cell is not limited by the Carnot efficiency, the operating efficiencies of the fuel cells are always lower than the theoretical values due to the overpotentials caused by activation, ohmic, and mass transport phenomena. All the available energy from the above reaction can be converted to electrical energy in an ideal process.

1.3.1 Electro catalysis of small organic molecules

Due to the problems related to the processability, transmission and storage small chain alcohols such as methanol and ethanol, which are liquid at normal temperatures, have been used as the alternatives to hydrogen in fuel cells. The fuel cell devices that use these alcohols as fuel are called direct alcohols fuel cells (DAFCs). Direct methanol fuel cell (DMFCs) is the most common among the DAFCs. Methanol remains in liquid form from -97.0°C to 64.7°C at atmospheric pressure, which is good enough to be used under all conditions. With higher energy density than hydrogen, methanol has become the most attractive fuel for fuel cell technology.

The half cell reactions in DMFC are following:

\[
\begin{align*}
\text{Anode:} & \quad \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad \longrightarrow \quad 6\text{H}^+ + 6\text{e}^- + \text{CO}_2 \\
\text{Cathode:} & \quad \frac{3}{2}\text{O}_2 + 6\text{H}^+ + 6\text{e}^- \quad \longrightarrow \quad 3\text{H}_2\text{O} \\
\text{Overall reaction:} & \quad \text{CH}_3\text{OH} + \frac{3}{2}\text{O}_2 \quad \longrightarrow \quad 2\text{H}_2\text{O} + \text{CO}_2
\end{align*}
\]
A great amount of work can be found on metal based catalytic materials for electrocatalysis [55-77]. For example the combination of different metal catalyst for methanol electrocatalysis have been studied [55-59]. Methanol oxidation reaction always yields carbon monoxide (CO), which strongly adsorbs on the platinum catalyst and reduces the catalytic surface area, which eventually deteriorates the performance of the cell. The addition of another metal for example ruthenium or gold is always useful in order to achieve CO tolerant catalytic material. According to the well known theory these metals produce hydroxyl ions which get adsorb on the catalyst and react with CO to form CO$_2$ [55-57]. Shukla et al. have studied the effect of tungsten on the electrocatalytic activity of Pt towards methanol electro-oxidation [58]. Interestingly in a recent report it was observed that Pt in combination with Ti and W is an excellent CO tolerant material [59].

Ross et al. have studied the effect of alloy on the electro-oxidation of methanol [60-62] in particular tin modified Pt electrode [61]. The effect of temperature on the activity of the Pt-Ru alloy was also studied [62]. Different aspects of the electrocatalysis were also studied by many researchers especially the poisoning of the electrode [63,64] and the synergistic effect in the electrocatalysis of methanol on Pt-Pd electrode [65].

In addition there are reports on the use of conjugated polymers and metal combinations for methanol electro-oxidation [66-71]. One of the early reports on the use of conjugated polymers appeared in a classic work by Kost et al. [69] wherein the Pt microparticles were dispersed in conducting polyaniline matrix and the modified electrode was found to be a good catalyst for hydrogen reduction and methanol electro-oxidation.

A majority of the electrocatalysis work is carried out with Pt as an electrocatalyst. However the high price of Pt has forced researchers to work on the alternate catalytic materials. In the present thesis we have studied the synthesis and applications of two different metals (Au and Pd) and conducting polymers combinations as the electrocatalyst materials for possible applications in fuel cell.

1.3.2 Alkaline fuel cells (AFCs)

Alkaline fuel cells (AFCs) are fuel cells which use alkaline electrolytes separating the anode and cathode. Although fuel cells based on acidic electrolytes using Nafion, a perfluorinated polymer containing sulfonic acid side groups as a proton exchange membrane have received lot of
attention in the literature. However, alkaline electrolytes based fuel cells nevertheless have plenty of scope since fuel cells based on acidic electrolytes function mainly with Pt based catalysts and this dependency makes them more expensive [80-88]. However the AFCs can function with relatively less expensive metals such as Au, Ag and Ni too. In a report by Vercoe et al. it was observed that higher energy density fuel such as ethanol yields better results in AFCs than methanol [83,84]. There are many advantages associated with the AFCs which make them cost effective to manufacture than acidic electrolytes based fuel cells [81-84]. In AFCs a liquid alkaline electrolytes such as metal hydroxides e.g., potassium hydroxide is used, which reacts with CO₂ to form metal bicarbonates or carbonate salts. A sufficient amount of these salts can precipitate and irreversibly block the cathode thus acting as a poison and decreasing its electrolyte conductivity, which eventually results in a decline in the electrocatalytic performance. To avoid such problems, polymers with attached organic cations have been used as alkaline anion exchange membranes (AAEMs) because their cations can not aggregate with anions to form a crystal lattice [83,84]. This approach therefore is extremely useful for operation under alkaline conditions in the presence of CO₂.

Figure 1.10 shows the schematic of an alkaline fuel cell where the charge carriers are hydroxyl ions which migrate from cathode to anode where the reaction with hydrogen produces water and electrons.

The reactions at both the electrodes can be written as following:

Anode: \[ 2 \text{H}_2 + 4 \text{OH}^- \rightarrow 4 \text{H}_2\text{O} + 4 \text{e}^- \quad E_0 = 0.828 \text{ V} \]

Cathode: \[ \text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 4 \text{OH}^- \quad E_0 = 0.401 \text{ V} \]

Overall reaction: \[ 2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O} \quad E = 1.229 \text{ V} \]

In the case of methanol as a fuel the reaction can be written as following:

\[ 2 \text{CH}_3\text{OH} + 3 \text{O}_2 + 4 \text{OH}^- \rightarrow 2 \text{CO}_3^{2-} + 6 \text{H}_2\text{O} \]

It is clear from the reaction above that not only oxygen and methanol are consumed in the reaction but two hydroxyl ions are used per methanol molecule. This requires a procedure of electrolyte replenishment, which can be achieved by adding electrolyte with the consumption of the methanol [67].
1.4 Aims and scope of the present thesis

The first part of the thesis deals with the electron transfer properties of ultrathin films formed by self-assembled monolayer, Langmuir-Blodgett films and layer-by-layer films. The thesis contains the study of the electron transfer properties of different composite films such as the LB film with a SAM or an LbL film in conjunction with SAM. We believe that the studies carried out during the course of this research investigation lead to a better understanding of the processes occurring during the electron transfer in different types of ultrathin films. The phenomenon of electron transport through composite thin films is very important not only from the commercial point of view but also in fundamental studies of electrochemical reactions especially in biological systems.

In the second part of the thesis we have explored electrocatalytic applications of the nanocomposite thin films of noble metals with conducting polymers. Different combinations of metals (gold and palladium) were studied with different conducting polymers. In the thesis work we have shown that the conducting polymers are a suitable matrix for the dispersion of the electrocatalyst material. The nanocomposites of metals and conducting polymers are shown as an efficient electrocatalyst material for oxidation of small organic molecules. The potential
application of the small organic molecules ranging from methanol and ethanol to formic acid as fuel in direct fuel cells have been explored and discussed in the thesis. We have focused more on the electrocatalysis in alkaline medium for potential applications in alkaline fuel cells. The alkaline fuel cells are relatively less explored by researchers but they have enormous applications as they can be used with relatively less expensive metal catalysis, which makes them cheaper to manufacture.
Bibliography


24
Introduction


