Electrochemical studies of PEDOT: microscopy, electrooxidation of small organic molecules and phenol, and supercapacitor studies

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by

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April 2009
Dedicated to my parents and Dr. Balai Chand Kundu
DECLARATION

I hereby declare that the matter embodied in this thesis entitled “Electrochemical studies of PEDOT: microscopy, electrooxidation of small organic molecules and phenol, and supercapacitor studies” is the results of investigations carried out by me in the Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India under the supervision of Prof. N. Munichandraiah and it has not been submitted for the award of any degree or diploma or membership, etc.

In keeping with the general practice of reporting scientific observations, due acknowledge has been made wherever the work described is based on the finding of other investigators. Any omission, which might have occurred by oversight or error in judgment, is regretted.

Snehangshu Patra
CERTIFICATE

This is to certify that the thesis entitled “**Electrochemical studies of PEDOT: microscopy, electrooxidation of small organic molecules and phenol, and supercapacitor studies**” by Snehangshu Patra is a record of original bonafide work carried out under my guidance and has not been submitted in any university or Institute.

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6.1. Introduction.......................................................................................196
Following the discovery of electronic conductivity in doped polyacetylene, various studies on conducting polymers have been investigated. These polymers are essentially characterized by the presence of conjugated bonding on polymer backbone, which facilitates formation of polarons and bipolarons as charge carriers. Poly(3,4-ethylenedioxythiophene) (PEDOT) is an interesting polymer because of high electronic conductivity, ease of synthesis and high chemical stability. Electrochemically prepared PEDOT is more interesting than the polymer prepared by chemical routes because it adheres to the electrodes surface and the PEDOT coated electrodes can directly be used for various applications such as batteries, supercapacitor, sensors, etc. A majority of the studies described in the thesis are based on PEDOT. Studies on polyanthanilic acid and reduction of hydrogen peroxide on stainless steel substrate are also included.

Chapter 1 provides an introduction to conducting polymers with a focus on synthesis, electrochemical characterization and applications of PEDOT.

In Chapter 2, microscopic and impedance spectroscopic characterization of PEDOT coated on stainless steel (SS) and indium tin oxide (ITO) coated glass substrates are described. Electrosynthesis of PEDOT is carried out on SS electrodes by three different techniques, namely, potentiostatic, galvanostatic and potentiodynamic techniques. The SEM images of PEDOT prepared by the galvanostatic and potentiostatic routes indicate globular morphology. However, it is seen that porosity increases by increasing the current or the potential. In the cases of both galvanostatic and potentiostatic routes, the oxidation of EDOT to form PEDOT takes place continuously during preparation. However, in the case of potentiodynamic experiment between 0 and 0.9 V vs. SCE (saturated calomel electrode), the formation of PEDOT occurs only when the potential is greater than 0.70 V. During multicycle preparation to grow thicker films of PEDOT, formation of PEDOT takes place layer by layer, a layer of PEDOT being formed in each potential cycle. PEDOT prepared in the potential ranges 0-0.90 V and 0-1.0 V show globular morphology similar to the morphology of the galvanostatically and potentiostatically prepared polymer. If prepared in the potential ranges 0-1.1 V and 0-1.2 V, the PEDOT films have rod-like and fibrous
morphology. This is attributed to larger amount of PEDOT formed in each cycle in comparison with lower potential ranges and also to partial oxidation of PEDOT at potentials $\geq 1.10$ V. PEDOT is also electrochemically prepared on ITO coated glass substrate. Preparation is carried out under potentiostatic conditions in the potential range between 0.9 and 1.2 V. Atomic force microscopy (AFM) studies indicate a globular topography for PEDOT films prepared on ITO coated glass plates. The height and width of globules increase with an increase in deposition potential. The PEDOT coated SS electrodes are subjected to electrochemical impedance spectroscopy studies in 0.1 M H$_2$SO$_4$. The Nyquist plot of impedance consists of a depressed semicircle, which arises due to a parallel combination of the polymer resistance and double-layer capacitance ($C_{dl}$). Impedance data are analyzed.

Studies on electrooxidation of methanol, formic acid, formaldehyde and ethanol on nanocluster of Pt and Pt-Ru deposited on PEDOT/C electrode are reported in Chapter 3. Studies on electrooxidation of small molecules are important in view of their promising applications in fuel cells. Films of PEDOT are electrochemically deposited on carbon paper. Nanoclusters of Pt and bimetallic Pt-Ru catalysts are potentiostatically deposited on PEDOT/C electrodes. Catalysts are also prepared on bare carbon paper for studying the effect of PEDOT. The presence of PEDOT film on carbon paper allows the formation of uniform, well dispersed nanoclusters of Pt as well as Pt-Ru catalysts. TEM studies suggest that the nanoclusters of about 50 nm consist of nanoparticles of about 5 nm in diameter. Electrooxidation of methanol, formic acid, formaldehyde and ethanol are studied on Pt-PEDOT/C and PtRu-PEDOT/C electrodes by cyclic voltammetry and chronoamperometry. The data for oxidation of these small organic molecules reveal that PEDOT imparts a greater catalytic activity for the Pt and Pt-Ru catalysts. Results of these studies are described in Chapter 3.

In Chapter 4, PEDOT is coated on SS substrate to investigate phenol oxidation. Studies on electrochemical oxidation of phenol are interesting because it is important to remove phenol from contaminated water or industrial effluents. Deactivation of the anode due to the formation and adsorption of polyoxyphenylene on its surface is a common problem for a variety of electrode materials, during phenol oxidation. Investigations on suitable anode materials, which can undergo no or moderate poisoning by
polyoxyphenylene, are interesting. In the present study, it is shown that the electrooxidation rate of phenol is greater on PEDOT/SS electrodes than on Pt. Deactivation of PEDOT/SS electrode is slower in relation to Pt. The oxidation of phenol on PEDOT/SS electrode occurs to form both polyoxyphenylene and benzoquinone in parallel. Cyclic voltammetry of phenol oxidation is studied by varying the concentration of phenol, sweep rate and thickness of PEDOT. Ac impedance studies indicate a gradual increase in polymer resistance due to adsorption of polyoxyphenylene during multi-sweep cyclic voltammetry. This investigation reveals that PEDOT coated on a common metal or alloy such as SS is useful for studying electrooxidation of phenol, which is generally studied on a noble metal based electrodes.

Electrochemically prepared PEDOT is used for supercapacitor studies and the results are presented in Chapter 5. Generally, electronically conducting polymers possess high capacitive properties due to pseudo-faradaic reactions. PEDOT/SS electrodes prepared in 0.1 M H$_2$SO$_4$ are found to yield higher specific capacitance (SC) than the electrodes prepared from neutral aqueous electrolyte. The effects of concentration of H$_2$SO$_4$, concentration of SDS, potential of deposition and nature of supporting electrolytes used for capacitor studies on SC of the PEDOT/SS electrodes are studied. Specific capacitance values as high as 250 F g$^{-1}$ in 1 M oxalic acid are obtained during the initial stages of cycling. However, there is a decrease in SC on repeated charge-discharge cycling. Spectroscopic data reflect structural changes in PEDOT on extended cycling.

Self-doped PANI is expected to possess superior electrochemical characteristics in relation to PANI. The self-doping is due to the presence of an acidic group on the polymer chain. However, self-doped PANI is soluble in acidic solutions against insolubility of PANI. In the present study, poly(anthranilic acid), PANA, is encapsulated in porous Nafion membrane by chemical and a novel electrochemical methods. PANA present in solid form in Nafion membrane does not undergo dissolution in acidic solutions. The methods of preparation and various electrochemical, optical and spectroscopic characterizations studies of PANA-Nafion are described in Chapter 6.

Electroreduction of H$_2$O$_2$ is studied on sand-blasted stainless steel (SSS) electrode in an aqueous solution of NaClO$_4$ and the details are reported in Chapter 7. The cyclic voltammetric reduction of H$_2$O$_2$ at low concentrations is characterized by a cathodic peak at
Synopsis

-0.40 V versus standard calomel electrode (SCE). Cyclic voltammetry is studied by varying the concentration of \( \text{H}_2\text{O}_2 \) in the range from 0.2 mM to 20 mM and the sweep rate in the range from 2 to 100 mV s\(^{-1}\). Cyclic voltammograms at concentrations of \( \text{H}_2\text{O}_2 \) higher than 2 mM or at high sweep rates consist of an additional current peak, which may be due to the reduction of adsorbed species formed during the reduction of \( \text{H}_2\text{O}_2 \). Amperometric determination of \( \text{H}_2\text{O}_2 \) at -0.50 V vs. SCE provides the detection limit of 5 \( \mu \)M \( \text{H}_2\text{O}_2 \). A plot of current density versus concentration has two linear segments suggesting a change in the mechanism of \( \text{H}_2\text{O}_2 \) reduction at concentrations of \( \text{H}_2\text{O}_2 \geq 2 \) mM. From the rotating disc electrode study, diffusion co-efficient of \( \text{H}_2\text{O}_2 \) and rate constant for reduction of \( \text{H}_2\text{O}_2 \) are evaluated. Thus, stainless steel, which is inexpensive and a common alloy, is useful for studying electrochemical reduction of \( \text{H}_2\text{O}_2 \) and also for analytical application. This work is initiated to study the reduction of \( \text{H}_2\text{O}_2 \) on PEDOT/SS electrodes. As a result of preliminary experiments, it is found that PEDOT does not exhibit any influence on the kinetics of \( \text{H}_2\text{O}_2 \) reduction. Therefore studies conducted using bare stainless steel are included in this chapter.

Results of the above studies are described in the thesis.
Chapter 1

Introduction

ABSTRACT

There has been growing scientific and technological interest on electronically conducting polymers such as polyaniline (PANI), polypyrrole (PPY), polythiophen (PTH), poly (3,4-ethylenedioxythiophene) (PEDOT) etc., in recent years. General characteristics of conducting polymers, in particular PEDOT, are briefly described in this chapter. Studies reported in the thesis are highlighted.
1.1. GENERAL ASPECT OF CONDUCTING POLYMERS

The discovery in the late seventies that certain types of polymers, though intrinsically poor conductors, acquire (following chemical or electrochemical treatment) electrical conductivity approaching that of metals, opened up an exciting new area of material research [1]. The essential structural property needed by polymers to attain significant conductivity is a conjugated $\pi$-system over a large number of monomer units, a feature common to polyacetylene (PA) and polyheterocycle such as polypyrrole (PPY) and polythiophene (PTH), polyaniline (PANI), etc.

Although PA, $(\text{CH})_x$ was first synthesized in late 1950s [2], it remained for about 20 years as a material of interest only to spectroscopists and theroreticians [3]. During the course of these studies, it became clear that electronically PA was best viewed as a wide-bandgap semiconductor with a low intrinsic conductivity [4]. In 1968, however, Berets and Smith showed that the conductivity of pressed pellets of PA could be varied over the range $10^{-9}$ to $10^{-2}$ S cm$^{-1}$ by exposure to various Lewis acids and bases [5]. By exposing PA films to strong oxidizing or reducing agents, the groups of Shirakawa, Macdiarmid and Heeger obtained higher conductivities of the order of $10^2$ to $10^3$ S cm$^{-1}$ [6] followed by conductivity close to that of copper metal [7]. For a perfect single crystal of PA, theory even predicts a room temperature conductivity of $2 \times 10^6$ S cm$^{-1}$ and also an exponential increase on decreasing the temperature [8]. These significant results have tended to focus much of the subsequent research on physical and electrical properties of these doped materials [9]. A knowledge of the chemical nature of interactions between PA and various dopants is fundamental to understand properties of these fascinating materials. Developments in the field of conducting polymers have been reviewed in recent literature by many authors [10-
Polymers with special properties have been of increasing scientific and technological interest, thus offering opportunities to polymer and organic chemists to synthesize a variety of promising new materials. Poly (3,4-ethylenedioxythiophene) (PEDOT) belongs to this class of polymers, which can be synthesized conveniently by both chemical and electrochemical routes. Furthermore, PEDOT possesses good chemical as well as environmental stability, and does not require any special precautions to handle.

1.2. CONDUCTION MECHANISM

The processes that switch conjugated polymer from the insulating to the conducting state are redox reactions, which are chemically or electrochemically driven. They are called doping processes, p-doping or n-doping in relation to the positive or negative sign of the injected charge in the polymer chain. Examples of both types are as follows [13]:

\[
\begin{align*}
\left[ \begin{array}{c}
\text{S} \\
\hline \\
\text{S}
\end{array} \right]_n + n_yA^- & \underset{\text{p-doping}}{\overset{\text{undoping}}{\longrightarrow}} \left[ \begin{array}{c}
\text{S} \\
\hline \\
\text{S}
\end{array} \right]_n y^+ \left[ A^- \right]_y + n_y \text{e}^- \quad A^- = \text{ClO}_4^- \ldots \\

\left[ \begin{array}{c}
\text{S} \\
\hline \\
\text{S}
\end{array} \right]_n + n_yM^+ & \underset{\text{n-doping}}{\overset{\text{undoping}}{\longrightarrow}} \left[ \begin{array}{c}
\text{S} \\
\hline \\
\text{S}
\end{array} \right]_n y^- \left[ M^+ \right]_y - n_y \text{e}^- \quad M^+ = (C_2H_5)_4^+ \ldots
\end{align*}
\]

The electrolyte ions involved in these processes are called the dopant anion and the dopant cation, respectively, while \( y \), which represents the ratio between the dopant ion and the polymer repeat unit, is commonly referred to as the doping level of the polymer. The fact that conjugated polymers repeatedly undergo electrochemical doping-undoping processes involving a relatively large amount of electronic charge makes these conjugated polymers attractive electroactive material. Much effort has been devoted to their use in advanced...
electrochemical devices, where the replacement of the conventional electrode materials with these polymers can lead to substantial improvements in design, versatility, reliability and cost efficiency [14]. Conjugated polymers have an electronic band structure with the energy gap between the highest occupied $\pi$-electron valence band and the lowest unoccupied conduction band determining the intrinsic electrical and optical properties of the polymer. Doping processes modify the polymer’s electronic band structure by generating new electronic states in the energy gap which causes an increase in conductivity.

When an electron is removed from the valence band of conjugated polymer, a hole or a radical cation is created that does not delocalize completely as would be expected from the classical band theory. Partial delocalization occurs, extending over several monomeric units and causing them to deform structurally. Energy of this radical cation that is partially delocalized over some polymer segments is called polaron [15]. Formation of polaron in PA is shown below:

![Polaron Diagram]

If another electron is removed from the already oxidized polymer, two situations can arise. The second electron may come from different segment of the polymer creating another independent polaron. Or, the electron may be removed from the first polaron (the unpaired electron) to create a dication, which is referred to as bipolaron as shown below:
The two positive charges of a bipolaron are not independent, but act as a pair. Polaron and bipolarons are mobile, and they move along the polymer chain by rearrangement of conjugation in an electric field. When the doping level increases, two polarons interact with each other. The neutral defects are gradually pulled from the charged defects, approach each other, and finally recombine, leaving two charged solitons [15].
There are different ways by which doping in PA can be carried out. These methods are broadly classified as solution doping, vapor phase doping and electrochemical doping. PA has been doped by exposing to vapors of electron-attracting compounds such as iodine, bromine, AsF₅ and SbF₅ [16]. With many other dopants [17], conductivity increases rapidly through semi-conducting regime to metallic regime. Doping can be terminated at any degree of conductivity. Electrochemical doping offers some distinct advantages. Doping level can be precisely controlled by the amount of charge passed. The charge–voltage characteristics can be determined easily.

1.3. LIST OF CONDUCTING POLYMERS

A list of molecular structures and approximate conductivity values of some important conjugate polymers is given in Fig. 1.1 [14].

1.4. SYNTHESIS OF PEDOT

Poly(3,4-ethylenedioxythiophene) (PEDOT) represents a class of conjugated polymers that can be potentially used as active materials for flexible organic electronics because of their superior conductivity, transparency and thermal stability [14,19,20]. Its unique optoelectronic properties make PEDOT an excellent material for various applications such as in electrochromics [21-28], light emitting diodes [29-31], solar cell [32-34], sensors and actuators [35-41], etc. However, since pure PEDOT bulk material is insoluble and infusible, much research attention has been focused on the development of a solution-processable PEDOT formulation. Currently, a commercially available aqueous dispersion solution of PEDOT and poly(styrenesulfonate) (PEDOT-PSS, trade name Baytron1) was developed by the Bayer AG Company of Germany. PSS serves as charge balancing dopant during polymerization [42].
Fig. 1.1. Molecular structures and approximate conductivity values in S cm$^{-1}$ of some conjugate polymers [14].

1.4.1. Chemical synthesis: For mass production of PEDOT, chemical oxidative polymerization is a promising process. Dai et al. synthesized PEDOT-PSS composite by using emulsion polymerization method [43]. The conductivity increased by the addition of poly[2-(3thienyl)-ethoxy-4-butylsulfonate] (PTEB). Addition of PTEB in the PEDOT-PSS matrix also increased the thermal stability and added higher crystallinity to PEDOT matrix. An attempt was also made to synthesize PEDOT-s-SBC (poly(styrene-b-butadiene-b-
styrene)) composite by chemical polymerization while the sulfonation level of s-SBC was varied [44]. The DC conductivity found to increase with increasing sulfonation level. Among various chemical oxidative polymerization procedures, emulsion polymerization is one of the most promising [44]. However, the monomer, 3,4-ethylenedioxythiophene (EDOT) is relatively insoluble in water, thienyl cation radicals formed during polymerization react in water. A typical oil-in water emulsion polymerization of EDOT results in low yields of PEDOT with poor conductivity. To circumvent this problem, it has recently been suggested that addition of surfactant such as sodium dodecyl sulfate (SDS) [45], poly (styrenesulfonate) (PSS), etc., to an aqueous solution of EDOT significantly improves polymerization yield [43]. The advantage of using a surfactant containing sulfonate functional group is that the surfactant stabilizes the synthesized colloids and also allows doping to take place in one step by which the prepared PEDOT possess a high electrical conductivity. In general, the conductivity increases with increasing doping level of PEDOT from the sulfonate groups of the surfactant. However, with excess amount of the nonconductive surfactants on the outer surface of conductive particles, the conductivity reaches a maximum and then decreases with increasing surfactant amount. To overcome this problem, oil-in-water emulsion polymerizations of PEDOT in the presence of water soluble conductive oligomers or polymers as surfactants may be useful.

Chemical synthesis of nanomaterials draws a great attention in the literature in last decade [46-51]. Hain et al., synthesized PEDOT nanorods with varying morphology [46]. The morphology can be varied by controlling monomer concentration and alcohol concentration in aqueous phase. PEDOT and mesoporous carbon composites were
synthesized by simple polymerization method [47] and properties like electronic conductivity and electrochemical performances were also investigated.

1.4.1.1. Mechanism of polymerization: Although the overall polymerization of EDOT to PEDOT appears as a simple oxidative polymerization, the detailed mechanism is rather complex. The reaction of EDOT with iron (III) tosylate is summarized in Fig. 1.2 [52]. The overall polymerization reaction can be separated into two principal steps: (1) oxidative polymerization of the monomer to the neutral polythiophene and (2) oxidative doping of the neutral polymer to the conductive polycation. The reaction starts with the slowest, rate determining step, oxidation of EDOT to the radical cation followed by the dimerization of the free radicals. End group oxidation of oligomers, beginning with dimers, is faster than the monomer oxidation and leads to the formation of higher oligomers. At the end, oligomers or polymers are doped by further oxidation.

Fig. 1.2. Proposed reaction mechanism of EDOT oxidation to conductive PEDOT [52].
1.4.2. Electrochemical synthesis

The electrochemical polymerization (ECP) of conducting polymer is more interesting than the chemical polymerization because of the following advantages[53]: (i) ECP produces conducting polymer, which adheres to the electrode surface, (ii) as the kinetics of polymerization reactions are controlled by the potential applied (or charge passed) to the working electrode, ECP offers a great deal of controllability during the synthesis and oxidation (doping) of conducting polymer, and (iii) the conducting polymer deposited electrodes can directly be used for various applications such as batteries, supercapacitors, fuel cells, etc.

The electrochemical methods generally employed for polymerization of conducting polymer are as follows:

(i) **Constant current or galvanostatic method**: This method essentially consists of electrodes dipped in an acidic electrolyte solution containing EDOT monomer. Passing a current density in the range 1 - 10 mA cm\(^{-2}\) through the anode leads to the deposition of PEDOT film on its surface [54]. In a non-aqueous solution, a higher value of current density was used for polymerization on Al electrodes [54]. The study showed that the p- and n-doping behaviour of PEDOT can be experimentally probed by in situ FTIR and resonance Raman spectroscopy.

(ii) **Constant potential or potentiostatic method**: In this method, a constant potential in the range 0.8-1.2 V vs. saturated calomel electrode (SCE) is applied to the working electrode in monomer containing aqueous solution [55]. In nonaqueous solution, the potential is more than what was used for aqueous solution polymerization. Cho et al., electropolymerized PEDOT on ITO coated glass under an applied magnetic field, which increased the
polymerization rate [55]. SEM data showed a change in morphology under applied magnetic field.

(iii) Potential sweep or potentiodynamic method: In this method, the working electrode is cycled between predetermined potential values. This method produces a uniform polymeric film, which adheres strongly to the electrode surface [56]. Thicker films can be produced by this method by using lower scan rates, and they can be peeled off from the electrodes to yield free-standing, electrically conducting polymer films. As these films are in an oxidized state, they represent PEDOT cations, and their overall charge balance is achieved by incorporation of counter ions from the electrolyte solution. The copolymerization of PEDOT and 5-cyanoindole (CNI\textsubscript{n}) was successfully performed potentiodynamically in acetonitrile by direct oxidation of monomer mixtures in the potential range of -0.25 to 2.0 V vs. SCE [57]. The mechanism of formation of radical cation and polymerization to produce PEDOT are shown in Fig. 1.3 [58].

Fig. 1.3. Mechanism of chain reaction [58].
1.5. APPLICATIONS OF PEDOT

1.5.1. Antistatic coatings: An antistatic agent is a compound used for treatment of materials or their surfaces in order to reduce or eliminate static charges generally generated by the triboelectric effect. The role of antistatic agent is to make the surface slightly conductive, either by being conductive itself, or by absorbing moisture from the air. The molecules of an antistatic agent often have both hydrophilic and hydrophobic areas, similar to those of a surfactant; the hydrophobic side interacts with the surface of the material, while the hydrophilic side interacts with moisture present in air and binds the water molecules. The requirement for antistatic layers are typically [59]: (i) a surface conductivity of $10^5$ up to $10^9 \ \Omega$ per square; (ii) a transparent, practically colourless appearance; and (ii) good adhesion and hardness.

The first introduction of PEDOT–PSS into an industrial product was done by Agfa. This company was stimulated by its high conductivity, colour, stability, processability and the moisture independent antistatic effect [59,60]. The antistatic layer in a photographic film is needed to avoid electrostatic discharges within the photographic layers during the processing of the film.

In an another application, PEDOT–PSS was used as an outer surface antistatic layer on cathode ray tubes to avoid contamination by dust. In addition, the optical properties of PEDOT–PSS seem to be beneficial for the optical contrast. The technical profile of an antistatic layer for optical applications comprises a low content of large particles, sufficient hardness and adhesion on glass as well as a surface resistance of about $10^6 \ \Omega$ per square.

15.2. Electroluminescent devices: An electroluminescent (EL) devices consists of two transparent conducting layers contacting a composite layer consisting of a zinc sulfide
emitter and a dielectric (e.g., barium titanate). When an AC voltage of approximately 100 V, 400 Hz is applied, the zinc sulfide starts emitting light. The light intensity can be tuned by doping agents. Due to the relatively high voltage, the specific resistance is less critical as for low voltage applications like liquid crystal-display panels. Therefore it is possible to replace the state-of-the-art transparent conductor indium tin oxide (ITO) by a conducting polymer [61,62]. Although the polymer still has a lower specific conductance compared to ITO a large benefit is obtained from the fact that all layers can be processed by printing techniques while usually ITO has to be coated by tedious sputtering techniques. Besides low process costs an additional advantage is the flexibility of the contact layer. Because ITO is a brittle material, it is not ideally suited to destruction-free thermal deformation. Devices fabricated with transparent, conductive PEDOT–PSS layers can be shaped three-dimensionally.

1.5.3. Batteries: PEDOT has several advantages as cathode active material: (i) a high electronic conductivity [19], (ii) it is one of the most stable conducting polymer available at present [20], and (iii) the electron donating properties of oxygen reduces the oxidative potential of polythiophene main chain and promotes the reduction reaction of the cathode. Hence, it is an interesting material which can be used for good cathode material. Novak and Dietrich reported that PEDOT was utilized as cathode material in 0.1 M Bu₄NPF₆/PC and 0.1 M Bu₄NF₆/CH₂Cl₂. A high specific capacity of 140 mAh g⁻¹ was obtained. This value is higher than that of other conducting polymers, such as PANI, PPY, PPP, PT etc. [63,64]. PEDOT was used in a cathode as an electrocatalyst to accelerate redox reaction of DMcT [65-68]. It was also used as a host of organic-inorganic hybrid materials for lithium batteries [69-71]. Zhan et al., synthesized PEDOT chemically and studied as cathode
material for lithium battery application [72]. A high specific capacity of 691 mA h g\(^{-1}\) was obtained.

1.5.4. Solar cells: Polymeric photovoltaic cells and sensors are related to polymeric light emitting diodes (LEDs) [73]. In a polymeric LED, injected holes and electrons recombine to generate photons. In a study consisting of a semiconducting polymer layer combined with a HIL/PEDOT layer, photons generate charges and subsequently a voltage. In this process a positive and negative charges are generated simultaneously. In order to prevent the recombination of these two charges, which would result in a decreased efficiency, a quick charge separation is necessary. This can be achieved by introduction of efficient electron conductors into the semiconducting polymers. While the task of photovoltaic cells is to generate energy, photo sensors just detects light. In this case the resistance of the transparent conductor is less crucial. Hence in addition to the electronic function, it is also possible to use PEDOT to replace ITO [74]. It is advisable to use highly conducting formulations of PEDOT–PSS or pristine PEDOT for this purpose [74,75]. Eom et al., described solar cell device configuration of ITO/PEDOT-PSS/P3HT-PCBM/ZnO/Ag, in which Ag cathode was prepared by the inkjet printing method using silver ink [34]. Dye-sensitized solar cells (DSSCs) were made by depositing composite films of graphene and polystyrene doped PEDOT (grapheme/PEDOT-PSS) on ITO substrate by spin coating method [33]. Chang et al., demonstrated a polymer solar cell with a conductive PEDOT anode on glass substrate [32].

1.5.5. Sensors: A sensor is a device that measures a physical quantity and converts it into a signal, which can be read by an observer or by an instrument. Applications of sensor include cars, machines, aerospace, medicine, manufacturing and robotics. Pigani et al.,
described that nanoparticles of Au and Pt modified PEDOT electrodes were useful amperometric blind analysis of white wines [35]. Electrochemical glucose biosensor based on conducting microtubes of PEDOT was constructed by Park et al., [36]. Cholin oxidase (ChOx) immobilized into conductive PEDOT film was described to detect cholin [40]. Dopamine and 4-nitrophenol was detected simultaneously on sensor based on Pt modified PEDOT and poly(3-[CE]-2-azulene-1-yl) vinyl thiophene) [41]. PEDOT incorporated gold nanoparticles were synthesized through a sequence of chemical and electrochemical routes for detection of dopamine and uric acid in presence of ascorbic acid [39]. Zaiudeen et al., demonstrated actuators based on PEDOT and PPY free standing film [37].

1.5.6. Electrochromic devices: Electrochromic devices change light transmission properties in response to voltage and thus control the amount of light and heat passing through. In electrochromic windows, the electrochromic material changes its opacity: it changes between a coloured, translucent state (usually blue) and a transparent state.

Ma et al., fabricated PEDOT/TiO₂ nanocomposite electrode-based electrochromic devices, where TiO₂ films were introduced to enhance the interfacial adhesion of the polymer to the substrate [21]. A dual type electrochromic devices were assembled by using different thickness of TPD films, (N, N-diphenyl - N, N-bis(3-methylphenyl )-1, 1’-biphenyl-4,4’-diamine), ITO/TPD/PU-LiClO₄/PEDOT/ITO, in which the colour contrast of the device increases with increasing TPD film thickness [22]. Polyelectrolyte multilayer films composed of a polycation (poly(allylamine hydrochloride) and polyanion (PEDOT:PSS) were prepared by a spin self-assembly method, and their electrochemical and electrochromic properties were investigated [23]. All-solid-state electrochromic windows, which have complementary color transition, were assembled by employing
poly(aniline-N-butylsulfonate)s, photopolymerizable electrolyte and PEDOT in sequence [24]. Electrochromic devices based on complementary layers of PEDOT and Prussian blue were fabricated by use of a free-standing proton conducting polymer electrolyte as a transport medium [25]. A dual type electrochromic device based on poly(5-(4-tert-butylphenyl)dipyrromethane) was constructed with PEDOT [26]. Fabretto et al., investigated the mechanism of conductivity enhancement in PEDOT-PSS using linear-diol additive [27]. PEDOT layer was grown on the Si nanowire of diameter 138 nm and its electrochromic properties were investigated [28].

1.5.7. Electrocatalysis: One of the most fascinating properties of conducting polymer is their ability to catalyze some electrode reactions. Electrocatalysis on a conducting polymer modified electrode consists of a few processes as follows [76]; (i) heterogeneous electron transfer between the electrode and conducting polymer layers, (ii) diffusion of solution species to the reaction zone, where the electrocatalysis conversion occurs, (iii) a chemical reaction takes place between solution species and conducting polymer and (iv) diffusion of reaction products out of a polymer layer in to the bulk solution.

Interpretation of the kinetic behaviour and voltammetric response, is a subject of several reviews [76-78]. Thus electrocatalysis on a conducting polymer modified electrode is a complex process. On a conducting polymer modified electrode, electron transfer can occur at (i) outer conducting polymer/electrolyte interface if the charge transfer is faster than that of mass transfer and their electrochemical conversion; (ii) inner substrate electrode/conducting polymer interface if the mass transfer and their electrochemical reaction proceeds at faster rate than that of charge transfer assuming the permeability of a porous conducting polymer layer is sufficiently high to penetrate the reacting species and
solution ions; and also (iii) inside the polymer layer if both the above processes occur at a comparable rate.

Electrocatalytic reduction of benzoquinone was reported to occur at outer polyaniline/electrolyte interface in an acidic solution whereas reduction occurs within the polyaniline film in an alkaline solution [79]. Mandic et al., reported the occurrence of electrocatalytic process of hydroquinone/benzoquinone and $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couples either at an outer surface or inside the polyaniline film, depending on the electrode potential [80].

Vasanth et al., studied electrocatalytic activity and simultaneous detection of neurotransmitter dopamine and ascorbic acid using thin film of PEDOT modified glassy carbon electrode [81]. Su et al., reported electrocatalysis and sensitive determination of cystine at PEDOT modified screen printed electrode where a detailed study of reaction mechanism and catalytic response was shown [82]. A detailed study on electrocatalytic oxidation of NADH at gold nanoparticles loaded PEDOT-PSS films was reported [83]. A synergistic effect of catechin, immobilized on PEDOT surface, was observed for electrocatalytic oxidation and detection NADH, ascorbic acid and uric acid [84]. The electrocatalytic behavior of PEDOT was investigated by Bello et al., with respect to detection of ascorbic acid [85].

1.6. ELECTRODEPOSITION OF METAL NANOPARTICLE ON CONDUCTING POLYMER SURFACE

The activity of noble metal based electrocatalyst metal particles depends on their dispersity [86]. For catalytic applications, a high degree of dispersity and a large surface area are desirable. Conducting polymers are often considered to be useful for supporting catalyst particles. Porous and high surface area of conducting polymers favour for
supporting electrocatalytic materials. Electrochemical formation of bi-metal (Cu-Pd) electrocatalyst on PEDOT surface was reported [51]. The presence of Cu-stabilized species in the PEDOT layer has a positive effect by impeding hydrogen reduction. Electrocatalytic oxidation of methanol is one of the most studied processes on conducting polymers and dispersed metal composites, because of its importance in methanol-oxygen fuel cells. Electrocatalytic oxidation of formic acid was studied on nanocatalyst (Pt, Pt-Pd) impregnated PTH electrodes [87]. Electrocatalytic oxidation of methanol on a novel Pt-dispersed PEDOT-PSS was reported [88]. Nanoparticles of Pt/H3MoO3 electrodeposited on PEDOT-PSS were studied as an electrocatalyst for methanol oxidation [89].

1.7. ELECTROCHEMICAL REDOX SUPERCAPACITORs

Electrochemical energy conversion is considered occurring in different ways: (i) in a battery [90] or a fuel cell, the chemical energy associated with electrode materials is converted into electrical energy through Faradaic oxidation and reduction processes, and (ii) in an electrochemical capacitor [91,92], the energy associated with electrostatic charges is converted into electrical energy through non-Faradaic processes.

An important difference exists between the reversibility of Faradaic and non-Faradaic systems. In energy conversion by capacitors, an excess or a deficiency of electric charges is established on the capacitor plates during charging and the reverse process occurs during discharging. On the other hand, electrochemical energy conversion in batteries takes place through Faradaic reactions, which cause chemical conversions of the electrode materials. The cycle-life of batteries is usually restricted to a few hundreds of cycles. By contrast, a capacitor has infinite cycle-life, as there are no occurrence of chemical or phase changes during charging and discharging processes. But the amount of
charge stored in an ordinary capacitor is limited by the size of the capacitor plates and usually it is small. The capacitance of a charged electrode/electrolyte interface is about 20-50 \( \mu \text{F cm}^{-2} \). This value can be increased to more than 200 F g\(^{-1}\) by using large accessible electrode areas, which are realized with high-area carbon powders, felts and aerogels.

An interesting intermediate situation arises between batteries and double-layer capacitors, where electrochemical processes involve chemical changes in electroactive materials with Faradaic charge transfer, but the charging and discharging processes resemble more closely to a capacitor than that of a battery. The variation of voltage (V) with the charge withdrawn or added to the system is nearly linear. This type of electrical energy storage system is known as a supercapacitor \([91]\).

Figure 1.4 shows the plot of specific energy versus specific power (Ragone plot) for various types of energy storage systems. It can be seen in Fig. 1.4 that the supercapacitors have higher specific power and lower specific energy compared to batteries and fuel cells. Because of high power density, interest in capacitors has arisen in recent years for using in high-power pulse applications. Additionally, capacitors are expected to be useful in a hybrid device \([93]\) together with batteries or fuel cells, in electric vehicle propulsion systems. While the battery supplies energy during normal power requirements, the capacitor supplements energy when high power requirements during starting, acceleration, change of gear, hill climbing, etc., with a duration of only a few minutes. Supercapacitors are more reliable and faster working backup power sources than batteries. Small low voltage capacitors are used for this purpose in a variety of products such as CD players, cameras, computers, telephones, electronic toys, etc. Supercapacitors, especially those using non-aqueous electrolytes, are less sensitive to low temperatures than batteries. The
fuel economy of automobiles can be significantly improved by recovering energy during breaking. The quantity of energy recovered from each breaking event is small but the rate of recovery (power) is high. Hence supercapacitors with their high power capability are ideal for this application.

![Specific power versus specific energy for capacitors, supercapacitors, batteries, and fuel cells.](image)

**Fig. 1.4.** Specific power versus specific energy for capacitors, supercapacitors, batteries, and fuel cells.

Different materials used as electrodes for supercapacitors are listed below [91,94]:

*Carbon:* Carbon in various modifications is the most frequently used material for electrochemical capacitors. Reasons for using carbon include (i) low cost, (ii) high porosity and hence large surface area, (iii) availability in large scales and (iv) established electrode production technologies. Carbons are available with a specific surface area of up to 2500 m² g⁻¹ in various forms such as powders, woven cloths, felts, fibers, etc. Charge storage in
carbon electrodes is predominantly capacitive in the electrochemical double-layer. There are, however, contributions to pseudocapacitance from surface functional groups which are generally present on activated carbons. The use of carbon as active electrode material for electrochemical capacitors has been reviewed by Sarangapani et al. [95] and recently by Gamby et al. [96].

(2) Metal oxides: Hydrated ruthenium oxide is a well-known example of this category of capacitor materials [97]. Cyclic voltammograms of RuO$_2$ electrodes have almost rectangular shape with good capacitive behaviour. In aqueous acidic electrolytes, the charge storage process is proton insertion into bulk oxide materials. Zheng et al. [98] have demonstrated that RuO$_2$.xH$_2$O prepared by a sol-gel process at low temperatures is highly amorphous, electrically conductive and with a specific capacitance over 720 F g$^{-1}$. The high specific capacitance in combination with low resistance has resulted in very high specific powers. But RuO$_2$ is expensive. Several investigations have been reported on alternate low cost metal oxides [99].

(3) Conducting polymers: Electronically conducting polymers are useful as material for electrochemical faradic capacitor because of their high capacitance and low cost. Mermilliod et al. [100] have demonstrated a large capacitance background current associated with the cyclic voltammogram of PANI electrode. The possibilities of employing conducting polymers such as PPY, PANI and PTH have been suggested by Rudge et al., [101].

Frackowiak et al., [102] studied different types of multi-walled and single-walled carbon nanotubes, which were functionalized by deposition of conducting PPY. The value of capacitance obtained from these modified nanotubes was about 170 F g$^{-1}$. This value was
nearly twice to that obtained from unmodified nanotubes (≈80 F g⁻¹) or from pure PPY
(≈90 F g⁻¹). Yamamoto et al., [103] studied a solid state capacitor, in which an Al-Zr alloy
was one of the electrodes and a composite consisting of PANI doped with a carboxylic acid
was the other electrode. Fabio et al., [104] studied chemically synthesized PTH and
polyparafluorophenylthiophene (PFPT) as active materials for supercapacitors. Specific
capacitance values of 260 F g⁻¹ and 110 F g⁻¹ were obtained for PTH and PFPT,
respectively.

Among all the substituted polythiophene, PEDOT is interesting as a good capacitor
material [105-119]. Lee et al. reported a facile synthesis of PEDOT nanotube and its
application in high powered supercapacitor [105]. A potentiostatically grown thick films of
microporous PEDOT were investigated as capacitor materials which produce practically
accessible capacitance, approaching 5 F cm⁻² measured by both cyclic voltammetry (CV)
and electrochemical impedance spectroscopy (EIS) [106]. Composite materials like other
conducting polymers [107,108], inorganic oxides framework [109], metal oxides [110-
113], carbon nanotubes/nanofibers [114-117], etc., are widely reported in the literature. Xu
et al., prepared PEDOT/PPY composite electrode material by galvanostatic polymerization
and showed a capacitance value of 200 F g⁻¹ with a very good cycling performance
[107,108]. Oxide materials like MnO₂ [110,111], RuO₂ [112], V₂O₅ and MoO₃ [113] etc.
also formed good composite capacitor material with PEDOT. A composite with carbon
nanotube/PEDOT/PSS/PANI was shown to have high specific capacitance as well as high
cyclability [117]. Ionic liquids also act as solvents for preparation as well as capacitor
studies of PEDOT [118,119].
1.8. FUEL CELLS

In the context of fast depletion of fossil fuel resources as well as the increase in atmospheric pollution, research and development activities on batteries and fuel cells have occupied great importance in recent years. A fuel cell is an electrochemical device that combines hydrogen and oxygen (H$_2$–O$_2$ fuel cell) to produce electrical energy, with water and heat as its by-products. As long as the fuel is supplied, the fuel cell will continue to generate power. Since the conversion of the fuel to energy takes place via an electrochemical process (not combustion), the process is clean, quiet and highly efficient. There are several types of fuel cells categorized as (i) phosphoric acid fuel cell, (ii) proton exchange membrane or solid polymer fuel cell, (iii) molten carbonate fuel cell, (iv) solid oxide fuel cell, (v) alkaline fuel cell, (vi) direct methanol fuel cell, and (vii) regenerative fuel cell.

Among several types of fuel cells, polymer electrolyte direct methanol fuel cells (DMFCs) are being projected for a variety applications ranging from micro-power to mega-power [120]. This is primarily because of feeding of a liquid fuel to the anode in a convenient way. Rapid miniaturization of electronic devices and expansion of their utility are likely demand for further potential applications of DMFCs. The catalyst of choice in DMFCs, which operate in medium-low temperature, are generally based on Pt metal for both the anodic and cathodic reactions. Decrease of efficiency of catalyst in DMFC is greatest concern in the last few decades. The byproducts of methanol oxidation cause fouling of catalysts. Highly dispersed nanometric catalyst particles are expected to increase efficiency. For good dispersion of the catalyst, generally carbon support is used despite a recent debate on carbon corrosion [121-123]. However, a thin film of an electronically
conducting polymer acts as a good dispersing material for Pt particles and also it improves the interfacial properties between the electrode and the electrolyte. The conducting polymer can allow a facile flow of electronic charge during the electrochemical oxidation of methanol on Pt. There are a few reports in the literature where PEDOT was used as a catalyst support [124-126]. Arbizzani et al., reported facile oxidation of methanol by PtRu catalyst with the metals support of PEDOT-PSS [124]. PEDOT was used to decrease methanol crossover by polymerizing PEDOT in the pores of commercial Nafion membrane [125]. PEDOT was also used for an anode catalyst for biological fuel cell [126].

1.9. SCOPE OF THE THESIS STUDIES

Poly(3,4-ethylenedioxythiophene) (PEDOT) is an interesting polymer because of high electronic conductivity, ease of synthesis and high chemical stability. Electrochemically prepared PEDOT is more interesting than the polymer prepared by chemical routes because it adheres to the electrodes surface and the PEDOT coated electrodes can directly be used for various applications such as batteries, supercapacitor, sensors, etc. A majority of the studies described in the thesis are based on PEDOT. Studies on polyanthanilic acid and reduction of hydrogen peroxide on stainless steel substrate are also included. In brief, the contents of the thesis are as follows:

Chapter 1 provides an introduction to conducting polymers with a focus on synthesis, electrochemical characterization and applications of PEDOT.

In Chapter 2, microscopic and impedance spectroscopic characterization of PEDOT coated on stainless steel (SS) and indium tin oxide (ITO) coated glass substrates are described. The SEM images of PEDOT prepared by the galvanostatic and potentiostatic routes indicate globular morphology. However, in the case of potentiodynamic experiment
between 0 and 0.9 V vs. SCE (saturated calomel electrode), the formation of PEDOT occurs only when the potential is greater than 0.70 V. PEDOT prepared in the potential ranges 0-0.90 V and 0-1.0 V show globular morphology similar to the morphology of the galvanostatically and potentiostatically prepared polymer. If prepared in the potential ranges 0-1.1 V and 0-1.2 V, the PEDOT films have rod-like and fibrous morphology. This is attributed to larger amount of PEDOT formed in each cycle in comparison with lower potential ranges and also to partial oxidation of PEDOT at potentials ≥ 1.10 V. Atomic force microscopy (AFM) studies indicate a globular topography for PEDOT films prepared on ITO coated glass plates. The height and width of globules increase with an increase in deposition potential. The Nyquist impedance plot of PEDOT/SS electrode consists of a depressed semicircle, which arises due to a parallel combination of the polymer resistance and double-layer capacitance ($C_d$). Impedance data are analyzed.

Studies on electrooxidation of methanol, formic acid, formaldehyde and ethanol on nanocluster of Pt and Pt-Ru deposited on PEDOT/C electrode are reported in Chapter 3. Nanoclusters of Pt and bimetallic Pt-Ru catalysts are potentiostatically deposited on PEDOT coated carbon electrodes. The presence of PEDOT film on carbon paper allows the formation of uniform, well dispersed nanoclusters of Pt as well as Pt-Ru catalysts. TEM studies suggest that the nanoclusters of about 50 nm consist of nanoparticles of about 5 nm in diameter. Electrooxidation of methanol, formic acid, formaldehyde and ethanol are studied on Pt-PEDOT/C and PtRu-PEDOT/C electrodes by cyclic voltammetry and chronoamperometry. The data for oxidation of these small organic molecules reveal that PEDOT imparts a greater catalytic activity for the Pt and Pt-Ru catalysts.
In Chapter 4, PEDOT is coated on SS substrate to investigate phenol oxidation. It is shown that the electrooxidation rate of phenol is greater on PEDOT/SS electrodes than on Pt. Deactivation of PEDOT/SS electrode is slower in relation to Pt. The oxidation of phenol on PEDOT/SS electrode occurs to form both polyoxyphenylene and benzoquinone in parallel. Cyclic voltammetry of phenol oxidation is studied by varying the concentration of phenol, sweep rate and thickness of PEDOT. This investigation reveals that PEDOT coated on a common metal or alloy such as SS is useful for studying electrooxidation of phenol, which is generally studied on a noble metal based electrodes.

Electrochemically prepared PEDOT is used for supercapacitor studies and the results are presented in Chapter 5. PEDOT/SS electrodes prepared in 0.1 M H₂SO₄ are found to yield higher specific capacitance (SC) than the electrodes prepared from neutral aqueous electrolyte. The effects of concentration of H₂SO₄, concentration of SDS, potential of deposition and nature of supporting electrolytes used for capacitor studies on SC of the PEDOT/SS electrodes are studied. Specific capacitance values as high as 250 F g⁻¹ in 1 M oxalic acid are obtained during the initial stages of cycling.

Soluble poly(anthranilic acid), PANA, is encapsulated in porous Nafion membrane by chemical and a novel electrochemical methods. PANA present in solid form in Nafion membrane does not undergo dissolution in acidic solutions. The methods of preparation and various electrochemical, optical and spectroscopic characterizations studies of PANA-Nafion are described in Chapter 6.

Electroreduction of H₂O₂ is studied on sand-blasted stainless steel (SSS) electrode in an aqueous solution of NaClO₄ and the details are reported in Chapter 7. The cyclic voltammetric reduction of H₂O₂ at low concentrations is characterized by a cathodic peak at
-0.40 V versus standard calomel electrode (SCE). Cyclic voltammograms at concentrations of \( \text{H}_2\text{O}_2 \) higher than 2 mM or at high sweep rates consist of an additional current peak, which may be due to the reduction of adsorbed species formed during the reduction of \( \text{H}_2\text{O}_2 \). Amperometric determination of \( \text{H}_2\text{O}_2 \) at -0.50 V vs. SCE provides the detection limit of 5 \( \mu \text{M} \) \( \text{H}_2\text{O}_2 \). From the rotating disc electrode study, diffusion co-efficient of \( \text{H}_2\text{O}_2 \) and rate constant for reduction of \( \text{H}_2\text{O}_2 \) are evaluated. Thus, stainless steel, which is inexpensive and a common alloy, is useful for studying electrochemical reduction of \( \text{H}_2\text{O}_2 \) and also for analytical application. This work is initiated to study the reduction of \( \text{H}_2\text{O}_2 \) on PEDOT/SS electrodes. As a result of preliminary experiments, it is found that PEDOT does not exhibit any influence on the kinetics of \( \text{H}_2\text{O}_2 \) reduction. Therefore studies conducted using bare stainless steel are included in this chapter.

1.10. REFERENCES


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ABSTRACT

Polyethylenedioxythiophene (PEDOT) is electrochemically prepared as a film on stainless steel (SS) substrate by galvanostatic, potentiostatic and potentiodynamic method. The oxidation of EDOT to PEDOT takes place at potentials $\geq 0.75$ V vs. SCE (saturated calomel electrode). The growth of PEDOT is continuous during galvanostatic and potentiostatic modes of preparation. On the other hand, the preparation is discontinuous during multicycle potentiodynamic method. This route leads to layer by layer formation, each layer being formed in a potential cycle. The morphology of PEDOT prepared at low current densities, low potentials and low potential ranges during cycling is essentially globular. The globules develop porosity at high current densities and high potentials in the case of galvanostatic and potentiostatic routes, respectively. In the case of high potential range of potentiodynamic deposition, however, the morphology becomes rod-like and fibrous. This is attributed to discontinuous, layer by layer formation of PEDOT and also to its oxidation. For atomic force microscopy (AFM) study, PEDOT was deposited potentiostatically on indium tin oxide (ITO) coated glass substrate. AFM studies indicate that a globular topography for PEDOT films prepared on ITO coated glass plates. The height and width of globules increase with an increase in deposition potential. The PEDOT coated SS electrodes are subjected to electrochemical impedance spectroscopy studies in 0.5 M H$_2$SO$_4$. The Nyquist plot of impedance consists of a depressed semicircle, which arises due to a parallel combination of the polymer resistance and double-layer capacitance ($C_{dl}$).

2.1. INTRODUCTION

Polyethylenedioxythiophene (PEDOT) is useful as an active material for applications such as batteries [1,2], sensors [3], electrochromic devices [4], etc., because of its high electronic conductivity. PEDOT is generally prepared by electrooxidation of its monomer, namely, ethylenedioxythiophene (EDOT), and the polymer forms as a coating on the anode surface. Morphological characterization of PEDOT films is important because their properties depend on surface characteristics. In order to study the surface properties of conducting polymers, several techniques such as scanning electron microscopy (SEM) [5], atomic force microscopy (AFM) [6-8], scanning tunneling microscopy (STM) [9-12], etc., are employed. Surface morphology of polypyrrole (PPY) was studied using SEM [5]. PPY was deposited on rotating disc electrode (RDE) made of stainless steel (SS) and morphology of PPY was studied by SEM. Morphology of PPY was found to vary with speed of rotation [5]. Naoi et al., used SEM and AFM to study the growth of a PPY film on indium tin oxide (ITO) coated glass in presence of different surfactants [13]. Perpendicularly oriented columnar structure was observed for electrochemically deposited PPY films from micellar solutions of anionic surfactants. Hernandez-Perez et al., reported the effect of electrosynthesis of PPY films on their surface morphology [6]. They studied the distribution of roughness and size of PPY globules using ex-situ AFM by preparing PPY with different electrochemical methods [6]. Li and Wang studied a relationship between the PPY surface morphology and its thermal stability, as well as its ionic conductivity using AFM and STM [11]. It was found that the topography of thick films of PPY on various substrates was similar although surface morphology of the substrates was different. The microstructure of these films was found to transform from disordered,
amorphous and flocculent particles to ordered, homogeneous and oriented particles on exposure to air. On the basis of AFM and STM studies, Dietler et al., demonstrated that the transport properties at the surface of PPY were very inhomogeneous [9].

Surface characterization studies of PEDOT coatings are reported [14,15]. Yang et al., investigated ion transport into and out of PEDOT films by scanning electrochemical microscopy (SECM) [14]. Cho and Park studied the surface morphology of PEDOT-metal nanoparticles by ex-situ current sensing AFM [15]. It was found that an electrical contact was established between noble metal particles and polymer surface, and that the interaction of particles with the polymer could be either physical or chemical. Au and Ag nanoparticles were easily deposited from the respective colloidal solutions on PEDOT because of the presence of S atoms in the polymer.

In the present work, PEDOT is electrochemically deposited on ITO coated glass plates and SS substrates by different deposition techniques. The electrodes are subjected to SEM, AFM and electrochemical impedance spectroscopy (EIS) studies.

2.2. EXPERIMENTAL

The monomer EDOT was purchased from Aldrich and analytical grade H₂SO₄ from Merck. Reagent grade sodium dodecylsulphate (SDS, C₁₂H₂₅NaOSO₃) from Merck was used as the surface-active agent. A high purity commercial 304 grade SS foil (thickness: 0.2 mm). All solutions were prepared in doubly distilled water. A glass cell of about 70 ml capacity with suitable ground glass joints to introduce a working electrode, Pt foil auxiliary electrodes, and a saturated calomel reference electrode (SCE) was used for electrochemical deposition of PEDOT and also for impedance studies. All potential values are reported against SCE.
Preliminary experiments using a polished and cleaned SS substrate indicated poor adherence of electrodeposited PEDOT coatings. In order to improve the adherence, SS sheet was subjected to sand blasting to generate a noticeable rough surface and washed copiously using a detergent followed by a mild etching in dilute H$_2$SO$_4$. A foil of 7 mm wide and 6 cm long was sectioned out of a sandblasted SS sheet, 1.4 cm$^2$ area at one of the ends was exposed to the electrolyte and the rest of its length was used as a tag for taking electrical contact. The SS substrate was again washed thoroughly, rinsed with acetone and dried in vacuum at ambient temperature for about 30 min. An electrolyte of 0.1 M H$_2$SO$_4$ + 0.01 M EDOT + 0.01 M SDS was used for PEDOT deposition. The electrodeposition was carried out by galvanostatic, potentiostatic and potentiodynamic methods. For AFM studies, PEDOT was electrodeposited by potentiostatic method on ITO coated glass using the same procedure as it was deposited on SS. The quantity of PEDOT deposited on SS increased with an increase in the charge passed. Thus, charge was considered as a measure of mass of PEDOT. Charge density used for deposition of PEDOT was 1.4 C cm$^{-2}$ unless otherwise specified.

A Digital Instruments atomic force microscope model Nanoscope IV was used for the surface characterization studies of PEDOT films under ambient laboratory conditions. AFM images were recorded in tapping mode using silicon nitride probes. Surface characteristics of PEDOT coatings were evaluated using the software package received from the supplier.

Electrochemical deposition of PEDOT by various routes was carried out using EG&G PARC potentiostat/galvanostat model Versastat. Electrochemical impedance
measurements were performed using Solartron impedance analyzer model 1286 with an ac excitation signal of 5 mV (peak to peak) in frequency range from 100 kHz to 10 mHz. The scanning electron microscope (SEM) images were recorded using FEI scanning electron microscope model Quanta 200 or Sirion. All experiments were conducted in an air-conditioned room at 22 ± 1 °C.

2.3. RESULT AND DISCUSSION

2.3.1. Preparation of PEDOT film: The electrochemical preparation of PEDOT involves oxidation of EDOT molecule at the electrode surface:

\[
\begin{array}{c}
\text{EDOT} \\
\begin{array}{c}
\text{O} \\
\text{S} \\
\text{O} \\
\text{O}
\end{array}
\end{array}
\rightarrow
\begin{array}{c}
\text{PEDOT} \\
\begin{array}{c}
\text{O} \\
\text{S} \\
\text{O} \\
\text{O}
\end{array}
\end{array} + 2nH^+ + 2ne^-
\]  \hspace{1cm} (2.1)

The reaction occurs through the formation of cation free-radicals of the monomer, the combination of them resulting in the formation of dimer, further oxidation of dimer, etc., eventually resulting in the formation of the polymer, PEDOT [17]. The polymer is insoluble in aqueous and many common non-aqueous solvents, and therefore forms as a film on the electrode used for oxidation.

Electrochemical polymerization of EDOT and other derivatives of thiophene require generally anhydrous organic media [18]. The difficulties for electrooxidation of these monomers in aqueous media include [19]: (i) the monomers are weakly soluble in water, (ii) the oxidation potential of these molecules are close to or higher than the potential of oxygen evolution and (iii) the electropolymerization process is inhibited by water, because
of the formation of thienyl cation radicals which react rapidly in water. To solve these problems, anionic surfactants such as SDS were added to aqueous solutions of thiophene derivatives [19]. In the presence of SDS, the solubility of the monomers increased and their oxidation potential lowered. Sakmeche et al. [20] electrodeposited PEDOT in the presence of SDS in 0.1 M LiClO₄ aqueous solutions consisting of 0.05 M EDOT on a Pt electrode. It was shown that there was an increase in solubility of EDOT due to SDS and also the oxidation mechanism in aqueous solutions was different from acetonitrile solutions.

Strong electrostatic interaction between EDOT •* radical cation and SDS anion were reportedly explained the effect of SDS, which resulted in strongly bonded complex between these ions. Furthermore, well-organized and adherent films of PEDOT were formed on Pt at lower potentials than in the absence of SDS in the aqueous medium. PEDOT nanoparticles were also prepared in an aqueous solution in presence of dodecylbenzene sulfonic acid as a surfactant. Vasantha and Phani [21] employed hydroxylpropyl-β-cyclodextrin (HP-β-CD) as solubilizing agent for EDOT. The cyclic HP-β-CD has a hydrophobic interior and hydrophilic outer side, and it forms an inclusion compound with EDOT. Potentiostatic cycling of a Pt electrode in 0.1 M LiClO₄ aqueous electrolyte consisting of 0.05 M HP-β-CD and 0.026 M EDOT produced homogenous and adherent PEDOT films on Pt surface. Neutral aqueous media were employed for preparation of PEDOT in most of the reports in the literature. As low concentration of aniline produced highly porous polyaniline films due to low rate of oxidation [18], 0.01 M was used in the present study although a maximum solubility of 0.05 M EDOT was obtained in aqueous neutral media consisting of SDS [19].

2.3.2. Electrochemistry of PEDOT formation: In preparation of electrodeposited films, the nature of growth can affect the properties of the resulting films. The potential step
chronoamperometric technique, where the change in current is followed with time after stepping the potential to a desired value, is useful for studying phase formation kinetics and the growth mechanism [23]. A series of current-time transients were recorded for a Pt electrode at different stepping potentials, as shown in Fig. 2.1. The transients are found to have three regions. When the potential is stepped up, there is an increase in current due to double-layer charging (region I in Fig. 2.1). The current decreases with time in the II region where the electron-transfer process starts occurring. The pattern of the current variation in this region depends on the mechanism of charge-transfer step. The nature of the current-time curve in this region corresponds to nucleation and growth of the electrodeposits. There is a steady flow of current in the III region due to the growth of electrodeposited polymer. The relationship between current and time in the II region is different for different mechanisms of growth [16]. By establishing the power-law relationship of the current and time corresponding to this region (Fig. 2.1), the respective mechanism can be predicted:

\[ I_t = Z F D^{1/2} c A / ( \pi t )^{1/2} \]  

(2.2)

where \( ZF \) is the molar charge of the depositing species, \( D \) is the diffusion coefficient, \( c \) is the concentration of the species of interest in solution, \( A \) is the geometric surface area of the electrode, \( t \) is time, \( I_t \) is the current obtained in the experiments.

For determination of the value of \( n \), Eq. (2.2) is rewritten as:

\[ \log I = \log k -0.5 \log t \]  

(2.3)
For the data presented in Fig. 2.1, log I vs. log t plots were constructed and shown in Fig. 2.2. The plots are linear for the data recorded in the potential range 0.9 to 1.2 V and the value of slope (equal to -0.5 in Eq. (2.3)) is about -0.5. This value suggests that the electrocrystalization of PEDOT involves three-dimensional growth of the nuclei [24].

Fig. 2.1. Current transients for electrodeposition of PEDOT on Pt electrode at 0.9 (1), 1.0 (2), 1.1 (3) and 1.2 V vs. SCE (4) in 0.1 M H₂SO₄ + 0.01 M EDOT + 0.01 M SDS.
During galvanostatic deposition, potential of the electrode was measured at a constant current density. The data corresponding to initial stages of preparation at different current densities (C.ds.) are shown in Fig. 2.3. The deposition of PEDOT occurs at about 0.75 V when C.d is 0.5 mA cm$^{-2}$ and the potential increases with an increase of c.d., as expected. The growth of PEDOT films was continued for a total charge of 1.4 C cm$^{-2}$ for each electrode.
Fig. 2.3. Potential transients for electrodeposition of PEDOT on SS electrode at 0.5 (i), 1.0 (ii), 1.5 (iii) and 2.0 (iv) mA cm$^{-2}$ in 0.1 M H$_2$SO$_4$ + 0.01 M EDOT + 0.01 M SDS.

Fig. 2.4 shows cyclic voltammograms record during potentiodynamic deposition of PEDOT on SS at a sweep rate of 10 mV s$^{-1}$ in various potential ranges. The increase in current at about 0.70 V is due to oxidation of EDOT resulting in the formation of PEDOT. When the upper potential limit is 0.90 or 1.0 V (Fig. 2.4(A) and (B)), a current peak is not observed. However, when the potential is extended to 1.10 V (Fig. 2.4 (C)), a current peak (P$_a$) at 0.95 V is clearly observed. This indicates that the oxidation of EDOT to PEDOT is diffusion controlled. On further increasing the potential limit to 1.20 V, an additional
Fig. 2.4. Voltammograms of Potentiodynamic deposition of PEDOT on SS in 0.01 M EDOT + 0.01 M SDS + 0.1 M H₂SO₄ in the potential range of (A) 0 to 0.90, (B) 0 to 1.00, (C) 0 to 1.10 and (D) 0 to 1.20 V. The arrow sign indicate the direction of the scan. The area of the SS electrode is 1.4 cm².
Fig. 2.5. Cyclic voltammograms of SS in 0.01 M EDOT + 0.01 M SDS + 0.1 M H₂SO₄ at sweep rate of (A) 2, (B) 5, (C) 10, (D) 20, (E) 50 and (F) 100 mV s⁻¹.
oxidation peak (Pₐ₁) is present (Fig. 2.4(D)) at 1.15 V. This current peak is attributed to the oxidation of PEDOT [18].

In order to examine the effect of sweep rate on the oxidation of EDOT, cyclic voltammograms were recorded with various sweep rates ranging from 2 to 100 mV s⁻¹ in the potential range from 0 to 1.10 V (Fig. 2.5). The peak current density of Pₐ varies linearly with the square root of the sweep rate as shown in Fig. 2.6. This data further supports that the oxidation of EDOT is diffusion controlled.

2.3.3. SEM studies: SEM micrographs of PEDOT/SS electrodes prepared galvanostatically at different c.ds. ranging from 0.5 to 2 mA cm⁻² are shown in Fig. 2.7. The polymer prepared at 0.5 and 1.0 mA cm⁻² has globular morphology (Fig. 2.7(A) and (B)). On
increasing the c.d. of preparation, the polymer surface becomes porous and a spongy-like morphology is observed as shown in Fig. 2.7(C) and (D).

**Fig. 2.7.** Scanning electron micrographs of PEDOT/SS electrode prepared by galvanostatic method at a fixed current of (A) 0.5, (B) 1.0, (C) 1.5, and (D) 2.0 mA cm$^{-2}$. The charge of the electrode is 1.4 C cm$^{-2}$.

SEM micrographs of the samples deposited at different potentials are presented in Fig. 2.8. At 0.90 V (Fig. 2.8(A)), a compact, globular morphology is observed. At higher magnifications, the large size globules (about 1 μm size) seen in Fig. 2.8(A) were found to consist of several smaller globules of about 100 nm size. As the potential of deposition is increased to 1.0 V, there is an increase in porosity of the sample (Fig. 2.8(B)). A spongy nature of the surface is observed at higher potentials (Fig 2.8(C) and (D)).
Fig. 2.8. The Scanning electron micrographs of PEDOT/SS electrode deposited potentiostatically at (A) 0.90, (B) 1.00, (C) 1.10, and (D) 1.20 V vs. SCE. The charge of the electrode is 1.4 C cm$^{-2}$.

Several PEDOT/SS electrodes were prepared at 0.90 V for various deposition charges. Mass of PEDOT increases linearly with an increase in charge. Changes occurring in morphology when PEDOT films grow in thickness are shown Fig. 2.9. The polymer prepared for 0.29 C cm$^{-2}$ charge does not uniformly cover the substrate (Fig. 2.9(A)).
When the film of PEDOT grows thicker for 0.7 C cm$^{-2}$ (Fig. 2.9(B)), the polymer surface possesses globular morphology. On further increase in thickness (Fig. 2.9(C), (D) and (E)), it is seen that smaller globules of PEDOT tend to grow on bigger globules, due to three dimensional growth. SEM micrographs of PEDOT/SS electrodes prepared
potentiodynamically at a sweep rate of 10 mV s\(^{-1}\) by varying the potential range are presented in Fig. 2.10. Morphology changes by increasing the upper limit of potential range. Surface of the polymer prepared in the potential range of 0 to 0.90 V (Fig. 2.10 (A)) consists of well separated globules.

**Fig. 2.10.** Scanning electron micrographs of PEDOT/SS electrode prepared by cyclic voltammetry with sweep rate of 10 mV s\(^{-1}\) in the potential range of (A) 0 to 0.90 V, (B) 0 to 1.00 V, (C) 0 to 1.10 V, and (D) 0 to 1.20 V vs. SCE. The charge of the electrode is 1.4 C cm\(^{-2}\).
The size of globules decreases with increasing the potential limit to 1.0 V (Fig. 2.10(B)). On further increasing of the upper potential limit to 1.10 V, the globular morphology changes to rod-like morphology (Fig. 2.10(C)). The average diameter of the rods is about 0.5 \( \mu \text{m} \). This rod like morphology changes to fibrous morphology on further increasing the potential to 1.20 V. The average diameter of the fibers is less than 100 nm.

In preparation of electrodes films, the relative rates of nucleation and growth of the film largely influence the morphology of the surface. The potential step chronoamperometric technique (2.3.2. Electrochemistry of PEDOT formation), where the change of current is followed with time after stepping the potential to a desired value, is useful for studying phase formation kinetics and the growth mechanism [16]. It is shown that the electrocrystallization of PEDOT involves diffusion limited three-dimensional growth of the nuclei. The SEM images of PEDOT prepared by the galvanostatic and potentiostatic routes (Fig. 2.7-2.9) indicates globular morphology. However, it is seen that porosity increases by increasing the current (Fig. 2.7) or the potential (Fig. 2.8). Furthermore, porosity does not develop substantially, if PEDOT is deposited with increasing mass (or thickness) at 0.90 V of potentiostatic deposition (Fig. 2.9). In the cases of both galvanostatic and potentiostatic routes of preparation, the oxidation of EDOT to form PEDOT takes place continuously during the time of preparation. However, in the case of potentiodynamic deposition, the formation of PEDOT occurs only when the potential is greater than 0.70 V. During multicycle preparation to grow thicker films of PEDOT, the oxidation of EDOT occurs discontinuously. This means, the formation of PEDOT takes place layer by layer, a layer of PEDOT being formed in each potential cycle. Thus, the preparation condition of the potentiodynamic route are different from the conditions of
potentiostatic and galvanostatic routes. In spite of this, PEDOT prepared in the potential ranges 0-0.90 V and 0-1.0 V show globular morphology (Fig. 2.10(A) and (B)) similar to the morphology of the galvanostatically (Fig. 2.7) and potentiostatically (Fig. 2.8 and 2.9) prepared polymer. In the case of PEDOT prepared in the potential ranges 0-1.1 V and 0-1.2 V, the PEDOT films change to rod-like and fibrous morphology (Fig. 2.10(C) and (D)). This is attributed to larger amount of PEDOT formed in each cycle in comparison with lower potential ranges and also to partial oxidation of PEDOT at potentials ≥ 1.10 V [25].

2.3.4. AFM studies: AFM image of bare ITO coated glass surface is presented in Fig. 2.11. The image (Fig. 2.11) reveals that the thin film of ITO consists of nano-sized globules. From analysis of the image, the topographic parameters obtained are as follows: average globule height - 4 nm; average width - 30 nm and root mean square roughness (R_{rms}) - 1.5 nm. In Fig. 2.12, AFM image of PEDOT deposited on ITO at 0.9 V is presented. The image reveals that the PEDOT surface consists of spherical globules with an average width of 120 nm; average height - 21 nm and R_{rms} - 100 nm. A comparison of Figs. 2.11 and 2.12 reveals that a PEDOT globule occupies the area equivalent to 3-4 globules of ITO surface.

AFM images of PEDOT films deposited at 1.0, 1.1 and 1.2 V are shown in Figs. 2.13, 2.14 and 2.15, respectively. As the potential of deposition increases from 0.9 V (Fig. 2.9), there is an increase in the size of globules. Average height and average width versus deposition potential are shown in Fig. 2.16. There is an increase in globules height from about 21 nm for PEDOT prepared at 0.9 V to about 40 nm for the film.
prepared at 1.2 V (Fig. 2.16 (A)). In a similar way width of globules also increases from 120 nm to 255 nm (Fig. 2.16 (B)). The rate of formation of PEDOT film increases with increasing potential from 0.9 to 1.2 V. The increase in height and width of PEDOT globules with increasing potential of preparation is attributed to the increase in rate of its formation. Variation of $R_{\text{rms}}$ with deposition potential is shown in Fig. 2.17. It is seen that $R_{\text{rms}}$ of the PEDOT film prepared at 0.9 V is as high as 100 nm, and it decreases sharply to 30 nm for the film deposited at 1.0 V. Above 1.0 V, there is a gradual decrease in $R_{\text{rms}}$. In an

Fig. 2.11. AFM image of bare ITO coated glass surface in (A) 2D and (B) 3D.
Fig. 2.12. AFM image PEDOT deposited on ITO at 0.9 V in (A) 2D, (B) 3D and (C) cross sectional view. The charge for PEDOT preparation in all cases is 2.5 mC cm$^{-2}$.

electrocrystallization process [23], it is known that nucleation rate of the deposit and its growth rate are important in deciding roughness of the deposit. If the growth rate exceeds
the nucleation rate, the electrodeposited films grow rough. On the other hand, if the growth rate is less than the nucleation rate, smooth deposits are obtained. As there is a decrease in

Fig. 2.13. AFM image PEDOT deposited on ITO at 1.0 V in (A) 2D, (B) 3D and (C) cross sectional view.
$R_{\text{rms}}$ of PEDOT with increasing deposition potential (Fig. 2.17), it is inferred that nucleation rate of PEDOT is greater than its growth rate, and that the nucleation rate increases with deposition potential.

Fig. 2.14. AFM image PEDOT deposited on ITO at 1.0 V in (A) 2D, (B) 3D and (C) cross sectional view.
Fig. 2.15. AFM image PEDOT deposited on ITO at 1.2 V in (A) 2D, (B) 3D and (C) cross sectional view.
Fig. 2.16. Dependence of (A) average globule height and (B) average globule width of PEDOT on potential of deposition.

Fig. 2.17. Dependence of root mean square roughness of PEDOT film on potential of deposition.
2.3.5. AC impedance studies: Electrochemical impedance spectra of PEDOT/SS electrodes prepared at different potentials ranging from 0.9 to 1.2 V are shown in Fig. 2.18. These measurements were carried out in 0.1 M H₂SO₄. The Nyquist plot of the electrode prepared at 0.9 V consists of high frequency intercept on the real axis, a broad semicircle followed by low frequency linear data. The high frequency intercept on the real axis corresponds to the ohmic resistance, which is due to the electrolyte, current collecting substrates, current leads, etc. The broad semicircle arises due to parallel combination of polymer resistance and double layer capacitance.

The linear low frequency data are nearly parallel to the imaginary axis, instead of making 45° to the real axis. Hence this part of impedance is considered to be due to the polymer capacitance. By increasing the preparation potential, it is seen in Fig. 2.18 that the diameter of the semicircle increases. An equivalent circuit shown in Fig. 2.19 is used to analyze the impedance spectra of PEDOT/SS electrodes (Fig. 2.19). The circuit elements are explained as follows: $R_Ω$ is ohmic resistance, $R_p$ is resistance of polymer chain, $Q_1$ is constant phase elements (CPE) used in place of double layer capacitance ($C_{dl}$) and $Q_2$ is another CPE used in place of polymer capacitance ($C$). $Q_1$ is employed in place of $C_{dl}$ because the semicircles in Fig. 2.19 are broad, and $Q_2$ is employed in place of $C$ because of the linear low frequency data make an angle less than 90° on the real axis. The need for using CPEs instead of pure electrical elements arises because of non-homogeneous, fractal nature of electrode/electrolyte interfaces [26].
Fig. 2.18. Nyquist impedance spectra of PEDOT/SS electrodes in 0.5 M H$_2$SO$_4$ at 0.26 V. PEDOT was deposited at 0.9 (i), 0.95 (ii), 1.0 (iii), 1.05 (iv), 1.1 (v) and 1.2 (vi) V. Theoretical curves generated from the fit results are shown as solid curves and experimental data are shown as symbols. Some frequency values are shown in Hz. The charge of PEDOT was 100 mC cm$^{-2}$. 
Fig. 2.19. The equivalent circuit used for fitting the impedance data of PEDOT/SS electrodes. Impedance elements are explained in the text.

The impedance data in Fig. 2.18 were subjected to non-linear least squares (NLLS) fitting procedure employing the equivalent circuit (Fig. 2.19) [27]. The solid curves in Fig. 2.18 are simulated spectra generated from the fit parameters, and the experimental data are shown as different symbols. Overlap of the theoretical spectra with experimental spectra and also low values of $\chi^2$ parameter ($<1 \times 10^{-2}$) obtained in NLLS procedure indicated a good quality of fitting. The impedance parameters are given in Table 2.1. There is a small scatter in the values of $R_\Omega$ due to variations in positioning the electrodes in the electrochemical cell from experiment to experiment. The average value of $R_\Omega$ obtained is $1.22 \, \Omega$. The variation of $R_p$ of PEDOT with deposition potential is shown in Fig. 2.20.

Table 2.1. The electrochemical impedance parameters of PEDOT/SS electrodes prepared at various potentials

<table>
<thead>
<tr>
<th>Preparation potential (V)</th>
<th>$R_\Omega$ (Ohm)</th>
<th>$R_p$ (Ohm)</th>
<th>$Q_1$</th>
<th>$n_1$</th>
<th>$Q_2$</th>
<th>$n_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>0.91</td>
<td>1.24</td>
<td>$5.5 \times 10^{-4}$</td>
<td>0.865</td>
<td>$3.4 \times 10^{-2}$</td>
<td>0.950</td>
</tr>
<tr>
<td>0.95</td>
<td>1.17</td>
<td>5.43</td>
<td>$3.8 \times 10^{-4}$</td>
<td>0.869</td>
<td>$1.9 \times 10^{-2}$</td>
<td>0.948</td>
</tr>
<tr>
<td>1.0</td>
<td>1.75</td>
<td>7.65</td>
<td>$2.6 \times 10^{-4}$</td>
<td>0.870</td>
<td>$2.0 \times 10^{-2}$</td>
<td>0.960</td>
</tr>
<tr>
<td>1.05</td>
<td>0.99</td>
<td>28.00</td>
<td>$2.8 \times 10^{-4}$</td>
<td>0.871</td>
<td>$2.1 \times 10^{-2}$</td>
<td>0.950</td>
</tr>
<tr>
<td>1.1</td>
<td>1.36</td>
<td>76.00</td>
<td>$4.4 \times 10^{-4}$</td>
<td>0.873</td>
<td>$1.6 \times 10^{-2}$</td>
<td>0.911</td>
</tr>
<tr>
<td>1.2</td>
<td>1.14</td>
<td>106.50</td>
<td>$4.7 \times 10^{-4}$</td>
<td>0.875</td>
<td>$1.7 \times 10^{-2}$</td>
<td>0.894</td>
</tr>
</tbody>
</table>
Fig. 2.20. Resistance of the polymer ($R_p$) versus potential of deposition of PEDOT/SS

The value of $R_p$ for PEDOT prepared at 0.90 V is as low as 1.24 $\Omega$. There is an increase in $R_p$ with an increase in potential, the increase being gradual between 0.9 and 1.0 V and then rapid from 1.0 to 1.2 V (Fig. 2.20). In order to understand the increase in $R_p$, the electrodes prepared at different potentials were subjected to cyclic voltammetry. Voltammograms of PEDOT/SS electrodes prepared at 0.9 and 1.2 V are typically shown in Fig. 2.21. Low currents flow at the electrodes between 0 and 0.9 V, and current peaks appear between 0.9 and 1.2 V. The current is attributed to oxidation of PEDOT [25]. The oxidative degradation leads to an increased resistance to charge transport on the polymer chain. As the starting potential of the current peak is 0.9 V (Fig. 2.21), the resistance of PEDOT prepared at 0.9 V is the least (Table 2.1 and Fig. 2.20).
Fig. 2.21. Cyclic voltammograms recorded during the first sweep in 0.1 M H₂SO₄ of PEDOT/SS electrode prepared at (i) 0.9 V and (ii) 1.2 V. The charge of preparation of PEDOT was 100 mC cm⁻².

However, the polymer undergoes partial oxidation during its preparation if the deposition potential is 0.95 V and greater. When the deposition potential is higher, the proportion of oxidized PEDOT and therefore its resistance are greater. Accordingly, $R_p$ varies with potential of deposition as shown in Fig. 2.20.

2.4. CONCLUSIONS

PEDOT was synthesized from an aqueous electrolyte of 0.01 M EDOT + 0.01 M SDS + 0.1 M H₂SO₄ on SS electrode by galvanostatic, potentiostatic and potentiodynamic methods. Thin film of PEDOT was characterized by SEM, AFM and impedance
spectroscopy. The morphology of PEDOT prepared at low current densities, low potential and low potential range during cycling was essentially globular. The globules developed porosity at higher current densities and higher potentials in the case of galvanostatic and potentiostatic routes, respectively. In case of higher potential range of potentiodynamic deposition, however, the morphology became rod-like and fibrous. For AFM studies, PEDOT was coated potentiostatically on ITO coated glass. AFM studies indicate that a globular topography. PEDOT coated SS electrodes were further characterized by impedance spectroscopy. The Nyquist plots of impedance consist of depressed semicircle which arises due to parallel combination of the polymer resistance and double layer capacitance. Impedance data suggested that the polymer resistance increased with potential of deposition. The increase in resistance was attributed to the irreversible oxidation of the polymer.

2.5. REFERENCES


Nanoclusters of Pt and bimetallic Pt-Ru deposited on PEDOT for electrooxidation of methanol, formic acid, formaldehyde and ethanol

ABSTRACT

Nanoclusters of Pt and bimetallic Pt-Ru electrodeposited on PEDOT exhibit a high catalytic activity for electrooxidation of small organic molecules, namely, methanol, formic acid, formaldehyde and ethanol. Electrodeposition of the catalyst particles is carried out in an acidic electrolytes consisting of chloroplatinic acid and ruthenium chloride on PEDOT coated carbon paper. A thin layer of PEDOT on the carbon substrate facilitates the formation of uniform, well-dispersed, small clusters of catalysts that consist of nanosize particles. The cyclic voltammetry studies suggest that peak currents of oxidation of the small organic molecules are several times greater for Pt-PEDOT/C and PtRu-PEDOT/C electrodes than Pt/C and PtRu/C electrodes, respectively. Chronoamperometry studies suggest good stability of Pt-PEDOT/C and PtRu-PEDOT/C electrodes for electrooxidation of methanol, formic acid, formaldehyde and ethanol.

A paper based on this chapter has appeared in Langmuir 25 (2009) 1732.
3. 1. INTRODUCTION

Fuel cells are considered for a variety of applications because they have high energy efficiency and low pollutants [1-3]. H₂-fed polymer electrolyte fuel cell (PEMFCs) and direct methanol fuel cells (DMFCs) are important choices [4-7]. Despite of intensive research over many years in these technologies, inherent limitations still remain. The H₂-PEMFC is limited by the problem associated with hydrogen storage and transport. For DMFCs, decrease of catalyst efficiency with usage [8] and methanol crossovers [9] are main problems. In recent years, interest has arisen in other small molecule fuel cells (formic acid, ethanol, formaldehyde, etc.) [10-14].

Formic acid, used in direct formic acid fuel cells (DFAFCs), is a liquid at room temperature and safe. Dilute formic acid is used as a food additive (recommended by US Food and Drug Administration [15]). Formic acid exhibits a smaller cross-over flux through Nafion membrane than methanol [16,17], thus, allowing the use of a high concentration of HCOOH and a thin membrane in DFAFCs. The major disadvantage of formic acid as a fuel is that its volumetric energy density is only 2104 WhL⁻¹, which is considerably lower than that of methanol (4900 WhL⁻¹).

Formaldehyde is often used as a model molecule to study the electrocatalytic activity of electrodes. HCHO was identified as the main product of methanol oxidation by high performance liquid chromatography (HPLC) and other technique [18]. However, HCHO oxidation is of fundamental and technical importance. Therefore, HCHO is important in the formulation of a mechanism for methanol oxidation [19]. Due to its hazardous and toxic properties, HCHO is studied much less than methanol.
Ethanol is safer, non-toxic, more convenient and has greater energy density (8.01 kWh kg\(^{-1}\) versus 6.09 kWh Kg\(^{-1}\)) than methanol [20]. Furthermore, ethanol can be easily produced in large quantities through fermentation of sugar-containing raw materials. Therefore, it is attractive and appears to fulfill most of the requirements of a fuel for low temperature fuel cells. Thus, direct ethanol fuel cell (DEFC) is another promising low-temperature fuel cell.

For electrooxidation of small organic molecules, the electrocatalyst must break C-H bond and enable the reaction intermediates (namely, CO, H\(_2\)CO, HCOOH, etc.) to produce the final product, namely, CO\(_2\) at low potential [21]. In the case of ethanol oxidation, the catalyst must also break the C-C bond, which is tougher than breaking C-H bond [22-24].

Noble metal catalysts such as Pt, Pd, Rh, etc., are employed to oxidize CH\(_3\)OH [4-7], HCOOH [25-27], HCHO [28-30] and C\(_2\)H\(_5\)OH [31]. Adsorption of carbon monoxide (CO\(_{ads}\)) on the catalyst takes place in all these oxidation processes. Hence, the efficiency of the catalyst decrease due to CO\(_{ads}\). A successful route to decrease the poisoning effect of CO\(_{ads}\) is the addition of another element to Pt, the most frequently employed element being Ru [31-33]. There are reports where Ir [34,35], Bi [36], Au [37], Pb [38], Ni [39, 40] and Sn [41, 42] were also employed to study the electrooxidation reactions on bimetallic catalyst.

There are large number of reports on chemical routes for the preparation of catalysts for fuel cell studies [43-47]. Electrochemical process is an efficient process to prepare metal catalysts on preferred electrode surfaces [48]. Generally, carbon and carbon related materials are chosen for supporting catalysts for fuel cell application [48-54], but corrosion of carbon over prolonged use of the catalyst is a concern. Some oxide materials
are also employed for supporting catalysts [55-57]. In this direction, conducting polymers are interesting. A thin film of an electronically conducting polymer (CP) acts as a good dispersing material for Pt particles and also it improves the interfacial properties between the electrode and the electrolyte. The CP can allow a facile flow of electronic charge during the electrochemical oxidation of methanol on Pt. Generally, an electrochemically deposited CP grows three dimensionally on a substrate. Hence, it introduces a high porosity and roughness, which generate a large surface area for electrochemical reactions. Additionally, the CP provides a low ohmic drop across the electrode. A number of polymeric films, such as, polypyrrole (PPY), polyaniline (PANI), poly(3-methylethiophene) (PMT), poly(3,4-ethylenedioxythiophene) (PEDOT), etc., have been investigated as conducting catalyst supports for small molecule oxidation [58-68]. Kitani et al., [58] prepared Pt modified PANI on carbon electrodes by electrochemical deposition and studied catalytic activity for methanol oxidation. From cyclic voltammetry and chronoamperometry studies, they showed greater catalytic activity for Pt/PANI/C electrodes than Pt/C electrodes. The remarkable effect of PANI was attributed to greater dispersion of Pt particles on PANI. Liu et al., [59] studied the effect of preparation conditions of PANI on dispersion of Pt for methanol oxidation. Galvanostatically prepared PANI consisted of porous and interconnected nanowires and therefore Pt particles were dispersed more uniformly than on potentiostatically prepared PANI. The former electrode was shown to have greater catalytic activity for methanol oxidation. Similar to these studies, Kost et al., [60] studied Pt particles dispersed in a three-dimensional array in fibril-type PANI film electrodes; Rajesh et al., [61] prepared Pt nanoparticle-supported PPY nanotubules; Wu et al., [62] dispersed Pt particles into PANI/single wall carbon nanotubes; Selvaraj and Alager [63]
studied Pt and Pt-Ru nanoparticle in PPY/multiwall carbon nanotubes. Selvaraj et al., studied the oxidation of formic acid and formaldehyde on Pt and Pt-Pd decorated PPY-CNT composites [28]. Electrocatalytic oxidation of formaldehyde was investigated on polyaniline prepared in an ionic liquid, 1-ethylimidazolium trifluoroacetate (PAN-HEImTfa) [64]. Jiang et al., reported that the electrocatalytic formaldehyde oxidation on Pt nanoparticles decorated poly(N-acetylaniline)/MWNTS nanocomposites [65]. Swathirajan and Mikhail [66] investigated poly(3-methylthiophene) as the Pt support for methanol oxidation. PEDOT was employed as a dispersion medium for Pt particles in only a few studies [67,68]. Kuo et al., [67] prepared PEDOT-poly(styrene sulfonic acid) (PSS) coated indium tin oxide (ITO) electrode by spin coating of a commercial polymer composite Pt particles onto PEDOT-PSS were deposited by cyclic voltammetry in a H2PtCl6 solution. The catalytic activity of Pt-PEDOT-PSS/ITO electrode for ethanol oxidation was studied by cyclic voltammetry and chronoamperometry. However, the cyclic voltammetry did not produce current peaks corresponding to methanol oxidation. Instead, the data indicated a linear increase of current. Chronoamperometry data indicated a rapid decrease of current. In another study, Drillet et al., [68] polymerized a monomer solution to PEDOT powder by chemical oxidation using Na2S2O8 as the oxidizing agent. Pt particles were deposited on to PEDOT powder by reducing H2PtCl2 using formaldehyde. Electrodes as well as membrane electrode assemblies (MEA) were prepared on carbon and electrochemical studies using half-cells as well as DMFC model cells were performed. The catalytic activity and long-term stability of Pt-PEDOT/C electrodes were evaluated at Pt loading level of 1 mg cm−2. A thin film of PEDOT helps catalyst to disperse on the surface very homogenously which in turn enhance the rate of electrooxidation for the same amount of catalyst loading [68].
In the present study, PEDOT was electrochemically deposited on a carbon paper and then nanoparticles of Pt and bimetallic PtRu were electrodeposited onto PEDOT by potentiostatic electrodeposition. Acidic solutions consisting of chloroplatinic acid and ruthenium chloride at low concentrations were used. The loading levels of Pt and PtRu studied were in the range of a few µg cm\(^{-2}\). The experimental results indicate high catalytic activity of Pt in terms of mass specific peak current and also the ratio of peak currents of cyclic voltammograms for electrooxidation of methanol, formic acid, formaldehyde and ethanol. The experimental results evidently suggest beneficial effect of PEDOT on electrooxidation of these small organic molecules.

3.2. EXPERIMENTAL

3, 4-ethylenedioxythiophene (EDOT) monomer was purchased from Aldrich and analytical grade H\(_2\)SO\(_4\) from Merck. Reagent grade sodium dodecylsulphate (SDS, C\(_{12}\)H\(_{25}\)NaOSO\(_3\)) from Merck was used as the surface-active agent. Analytical grade methanol, Formaldehyde, Formic acid and ethanol were also purchased from Merck. H\(_2\)PtCl\(_6\) and RuCl\(_3\), xH\(_2\)O were purchased from Kemie Lab. A Toray carbon paper foil (thickness: 0.2 mm) was used as the substrate for electrodeposition of PEDOT and Pt. All solutions were prepared in doubly distilled water. A glass cell of about 50 ml capacity with suitable ground–glass joints to introduce a working electrode, Pt foil auxiliary electrodes, and a saturated calomel reference electrode (SCE) was used for electrochemical deposition and characterization of PEDOT and Pt-PEDOT electrodes. All potential values are reported against SCE.

A foil of 7 mm in width and 3 cm in length was sectioned out of a carbon sheet, 1.4 cm\(^2\) area at one of the ends was exposed to the electrolyte and the rest of its length was used
to take electrical contact through a Cu wire. An electrolyte of 0.1 M H₂SO₄ + 0.01 M EDOT + 0.01 M SDS was used for PEDOT deposition. The electrodeposition was carried out at a constant potential of 0.9 V, as reported in Chapter 2. The quantity of PEDOT deposited on the substrate increased with an increase in charge passed. Thus, the charge was considered as a measure of mass of PEDOT. Experiments were carried out using PEDOT/C electrodes prepared with 0.07 C cm⁻², unless otherwise specified. After the electrochemical deposition of PEDOT, the electrode was separated from the cell, washed repeatedly in 0.1 M H₂SO₄ solution under stirring for about 30 min. While Pt particles were potentiostatically deposited at 0.1 V in an aqueous electrolyte consisting of 0.002 M H₂PtCl₆ + 0.1 M H₂SO₄, PtRu particles were deposited at 0.0 V in 0.002 M H₂PtCl₆ + 0.002M RuCl₃ + 0.1 M H₂SO₄ electrolyte. Several preliminary experiments were conducted to arrive at suitable potential values for deposition of Pt and Pt-Ru nanoparticles. Current was monitored for the intended duration of deposition and the charge was calculated for estimation of the quantity of Pt and Pt-Ru. The atomic ratios of Pt and Ru in the bimetallic coatings were estimated by analysis of X-ray photoelectron spectra (XPS). Geometric area of carbon substrate was used for calculation current density.

Potentiostatic deposition of PEDOT, Pt, Pt-Ru, Ru as well as cyclic voltammetry experiments were carried out using an EG&G PARC potentiostat/galvanostat model Versastat or a Solartron electrochemical interface model SI 1287. Electron microscopic images were recorded using FEI Company scanning electron microscope (SEM) model Sirion and transmission electron microscope (HRTEM) model TECNAI F30. X-ray diffraction (XRD) patterns were recorded using Philips diffractometer model X’PERT PRO using CuKα (λ = 1.5418 Å) as the source. X-ray photoelectron spectroscopy was recorded
using SPECS photoelectron spectrometer with Mg as the source and data were analyzed by Casa XPS software. All experiments were conducted in an air-conditioned room at 22±1 °C.

3.3. RESULTS AND DISCUSSIONS

3.3.1. Electrooxidation of methanol on Pt-PEDOT/C electrode

3.3.1.1. Preparation of PEDOT and Pt: PEDOT was electrochemically deposited on Carbon paper, as detailed in chapter 2. While 0.07 C cm⁻² was the charge used for PEDOT preparation for most of the experiments, electrodes were also prepared by varying the charge for the experiments to study the effect of PEDOT quantity. The mass (M) of PEDOT in was calculated from charge (Q) using Eq. (3.1):

\[
M = \frac{Q \times MW}{2 \times F \times A}
\]

where A is the electrode area and MW is the molecular mass of EDOT monomer. The value of charge 0.07 C cm⁻² corresponds to 53 µg cm⁻² of PEDOT.

For deposition of Pt nanoparticles on PEDOT, several experiments were carried out by varying the concentration of H₂PtCl₆, potential of deposition and time followed by examining their microstructure. As a result of these experiments, a solution of 0.002 M H₂PtCl₆ in 0.1 M H₂SO₄ and a potential of 0.10 V were chosen for deposition of well dispersed Pt nanoparticles on PEDOT. The specific mass of Pt was calculated from the charge using an equation similar to Eq. (3.1). The specific mass of Pt was varied from about 10 µg cm⁻² to 300 µg cm⁻², for several experiments.
3.3.1.2. Physical characterization: Crystalline nature of Pt-nanoparticles was investigated by X-ray diffraction studies. Figure 3.1, curve (i) shows XRD pattern of Pt-PEDOT/C with Pt loading of 289 µg cm$^{-2}$. The XRD pattern is indexed to fcc unit cell of Pt (JCPDS file no.7440-06-4). The peak at 2θ = 39.86, 46.28, 67.80 and 81.60° are assigned to (111), (200), (220) and (311) planes, respectively. The peaks observed at 2θ = 42.67, 54.55, 77.49 and 86.76° are also present in XRD patterns of carbon (Fig. 3.1, curve (iii)) as well as PEDOT/C (Fig. 3.1 curve (ii)) electrodes. The patterns of carbon paper (curve (iii)) and
PEDOT coated carbon paper (curve (ii)) are identical suggesting amorphous nature of PEDOT. The peaks at $\theta = 42.67, 54.55, 77.49$ and $86.76^\circ$ are attributed to carbon.

![SEM images of Pt-PEDOT/C](image)

**Fig. 3.2.** SEM images of Pt-PEDOT/C with Pt loading level of 10 $\mu$g cm$^{-2}$. Magnifications: (A) 50,000 X and (B) 2,00,000 X

3.3.1.3. **Microscopy:** SEM images of Pt deposited on PEDOT/C electrode are shown in Fig. 3.2. Agglomerated Pt particles are uniformly distributed on the electrode surface. The size of agglomerates is in the range of 30-50 nm. In order to examine the effect of PEDOT on
morphology of the electrodes, Pt was deposited on bare carbon paper and examined by SEM. Micrographs of Pt-PEDOT/C and Pt/C electrodes, prepared by identical conditions are shown in Fig. 3.3. Finer agglomerates and more uniform distribution of Pt are seen on PEDOT (Fig. 3.3(A)) than on bare carbon paper (Fig. 3.3(B)). The Pt aggregates on PEDOT are composed of smaller particles, which is evident from TEM image (Fig. 3.4(A)). The size of Pt particles is in the range of 2-3 nm. The EDAX data (Fig. 3.4(B)) confirm the presence of Pt. The HRTEM micrograph (Fig. 3.4(C)) provides lattice fringes with a separation of 1.24 Å. The value corresponds to (311) plane of fcc lattice of Pt.

It is known that electrochemically deposited Pt nanoparticles tend to agglomerate instead of dispersing as individual isolated nanoparticles on the surface of the substrate [69-71]. Maillard et al., [69] electrochemically deposited Pt in 0.007 M H₂PtCl₆ + 0.01M HCl on a glassy carbon electrode by potential sweep technique. TEM images provided evidence for agglomerated nanograined Pt structures, and not for isolated nanoparticles. The aggregates ranged in size from 25 to 100 nm, which consisted of Pt nanoparticles of 6-7 nm diameters. The formation of Pt aggregates was attributed to 3D nucleation and growth mechanism. Primary nucleation of Pt deposit was followed by secondary nucleation on predeposited Pt surface. This was due to the fact that pre-deposited Pt surface possessed higher concentration of nucleation centers compared to the bare substrate. As a result, the growth of Pt electrodeposits lead to the formation of aggregated structures. If the substrate is smooth like highly ordered pyrolytic graphite, formation of particle agglomerates was also considered to occur through migration and coalescence of Pt nanoparticles favoured by weak interaction of Pt with the substrate.
Fig. 3.3. SEM image of (A) Pt-PEDOT/C and (B) Pt/C with Pt loading level of 10 µg cm$^{-2}$. The scale bar in both figures corresponds to 5 µm.

3.3.1.4. X-ray photoelectron spectroscopy: The Pt-PEDOT/C electrode was investigated by recording XPS spectra. Figure 3.5(A) shows the Pt 4f region of the XPS spectrum of Pt-PEDOT/C, which could be deconvoluted into two pairs of doublets. For each doublet, the binding energy (BE) of Pt 4f$_{5/2}$ is about 3.2-3.3 eV higher than that of Pt 4f$_{7/2}$ [72]. The most intense doublet appearing at 71.5 and 74.8 eV is the signature of metallic Pt. The relatively
Fig. 3.4. (A) TEM image, (B) EDAX spectrum and (C) HRTEM image of Pt-PEDOT/C with Pt loading level of 10 µg cm$^{-2}$. 
large shift of these values from 70.8 eV for the bulk Pt suggests that there is significant metal-support interaction, or it can be due to small cluster size [73,74]. The weaker doublet at higher BEs at 73.1 and 76.5 eV, is attributed to a small amount of Pt (iv) residue on the surface [78]. Figure 3.5(B), (C) and (D) show the XPS data for C1s, O1s and S2p regions, respectively. By deconvolution of C1s data (Fig. 3.5(B)), two peaks are observed. The peak at 284.7 eV is attributed to carbon conducting substrate [75,76] and the peak at 285.9 eV is due to the carbon back bone of the polymer. The S 2p core-level high resolution XPS spectrum (Fig. 3.5(C)) corresponds to single sulfur bonding environment in PEDOT with a spin-split doublet, S 2p_{1/2} and S 2p_{3/2} [77-79]. The asymmetric tail to higher binding energy is related to the doping process, in which the delocalized π-electrons in thiophene ring broaden the binding energy spectrum of the S atom. In O1s core-level XPS spectrum (Fig. 3.5(D)), a peak at 532.7 eV corresponds to the sole oxygen binding environment in PEDOT and peak at 531.1 eV is due to loosely bound surface oxygen [77].

3.3.1.5. Electrochemistry: Cyclic voltammogram of a Pt-PEDOT/C electrode in 1 M H₂SO₄ at a sweep rate of 50 mV s⁻¹ is shown in Fig. 3.6. Typical behavior of polycrystalline Pt is similar to this voltammogram [80]. The current peaks appearing between -0.2 and 0.0 V are due to adsorption and desorption of hydrogen atoms on Pt surface. Although the current peaks are not well separated, two pairs of peaks are noticed. The pair appearing at less positive potentials is due to weakly adsorbed hydrogen and the other pair at more positive potentials is due to strongly adsorbed hydrogen. Adsorbed oxygen is reflected in the increase in oxidation current at about 0.60 V and its reduction by a cathodic current peak at about 0.55 V in the reverse sweep. These features of the voltammograms (Fig. 3.6), which
are similar to those of Pt metal [80] suggest that agglomerated Pt nanoparticles deposited on PEDOT are electrochemically active.

Shown in Fig. 3.7(A), curve (i) is cyclic voltammetry of oxidation of methanol on Pt-PEDOT/C in 0.1 M H₂SO₄ consisting of 1 M CH₃OH at a sweep rate of 5 mV s⁻¹. A forward oxidation peak (Pᶠ) appears at 0.60 V and the backward oxidation peak (Pᵇ) at 0.50
Fig. 3.6. Cyclic voltammetry of Pt-PEDOT/C recorded in 1 M H₂SO₄ at a sweep rate of 50 mV s⁻¹. Pt loading level: 289 µg cm⁻².

V. The interest on methanol oxidation for fuel cell application arises due to the fact that it yields six electrons per methanol molecules [81,82].

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \quad (3.2)
\]

However, the reaction proceeds via formation of several intermediates such as CO, CHₓOH (0 < x < 2), CH₃O, HCOO⁻, etc. Several intermediate steps of CH₃OH oxidation to CO₂, as well as secondary reaction products such as HCOOH, HCHO, etc., are proposed [82]. The reaction intermediates undergo adsorption on the catalyst surface. CO is identified as the
Fig. 3.7. Cyclic voltammograms of (A) Pt-PEDOT/C electrode (i) and Pt/C electrode (ii) with Pt loading level (both electrodes) of 10 µg cm\(^{-2}\); and (B) Pt foil in 1 M CH\(_3\)OH + 0.1 M H\(_2\)SO\(_4\) at a sweep rate of 5 mV s\(^{-1}\).

species primarily responsible for poisoning of Pt catalyst. The forward current peak is attributed to the oxidation of CH\(_3\)OH molecule and the backward current peak to the oxidation of adsorbed intermediates. The relative magnitude of the backward peak is an
indication of the amount of oxidizable intermediates adsorbed on the catalyst surface. For reliability of the catalyst, it is desirable that the backward current peak is minimal in comparison with the forward current peak. Fig. 3.7(A), curve (ii) shows cyclic voltammogram of Pt/C without PEDOT in 0.1 M H₂SO₄ + 1 M MeOH at a sweep rate of 5 mV s⁻¹. In this case, the forward oxidation peak current for methanol oxidation is only about 50% when compared to the electrode with PEDOT. The Pt nanoparticles are uniformly deposited as smaller aggregates in Pt-PEDOT/C compared to Pt/C (Fig. 3.3). Consequently higher current density is obtained for Pt-PEDOT/C.

The magnitude of backward peak current reflects the quantity of still oxidizable reaction intermediates after completing forward sweep of the cyclic voltammogram. The ratio of forward peak current (Iₚ) to backward peak current (Iₛ) is a measure of the efficiency of Pt catalyst. Raghuveer et al., reported the value of Iₚ/Iₛ ratio of commercial ETEK catalyst as 1 [83]. Pt and Pt-Ru decorated polypyrrole/multiwalled carbon nanotubes show maximum Iₚ/Iₛ ratio as 1.2 [63]. Heat treated Pt and Pt₅₂Ru₄₈ supported by carbon showed the Iₚ/Iₛ ratio are 0.87 and 2.30 respectively [84]. Potentiodynamically or pulse galvanostatically deposited Pt on polyaniline micro-fiber shows the value of Iₚ/Iₛ ratio is 1.7 [85]. In the present study, the Pt-PEDOT/C exhibit the ratio of Iₚ/Iₛ is 1.8, which is a very high value. The electrocatalytic behavior of this electrode is also understood by comparing with a Pt foil electrode (Fig. 3.7 (B)). The forward peak potential for methanol oxidation on Pt-PEDOT/C (Fig. 3.7(A), curve (i)) is almost 50 mV less and peak current is about 50 times greater than that of bare Pt (Fig. 3.7(B)). The mass specific peak current (mA mg⁻¹) is another parameter useful for measuring the efficiency of the catalyst. The mass specific peak current obtained for Pt catalyst grown in mesoporous carbon is 215 mA mg⁻¹ [83].
Mesoporous carbon with high surface area and large pore diameter was synthesized by a soft colloidal template route. A higher value of mass specific peak current was measured for Pt catalyst supported on mesoporous carbon in comparison with commercially available carbon [83]. About 160 mA mg\(^{-1}\) was obtained for Pt loaded on carbon nanotubes [86]. About 26 mA mg\(^{-1}\) was reported for Pt deposited on PANI coated on glassy carbon.
electrode for methanol oxidation [87]. Rajesh et al., [61] electrochemically deposited Pt by square wave pulse technique Pt on conductive PPY nanotubes, which were synthesized by Al₂O₃ nano-porous template. The PPY nanotubes provided a very high surface area to Pt nanoparticles for methanol oxidation and mass specific peak current of about 2500 mA mg⁻¹ was reported [61]. In the present study, mass specific peak current for methanol oxidation obtained on Pt-PEDOT/C electrode is as high as 614 mA mg⁻¹.
The stability of Pt-PEDOT/C electrodes was studied by repeated cycling of the electrode in 0.1 M H₂SO₄ consisting of 1 M CH₃OH. There was a gradual decrease of cyclic voltammetric peak currents in about 10 cycles and thereafter reproducible stable voltammograms were recorded (Fig. 3.8). Chronoamperometry data recorded at three different potentials for several hours in a stirred solution are shown in Fig. 3.9. The measured current is nearly stable for about 6 hours tested. It is thus concluded that Pt-PEDOT/C electrodes are stable for methanol oxidation.

![Graph](image)

Fig. 3.10. Variation of mass specific peak current of Pt-PEDOT/C electrode with mass of PEDOT. Data obtained from the cyclic voltammetry in 1 M CH₃OH + 0.1 M H₂SO₄ at a sweep rate of 5 mV s⁻¹ with the Pt loading level of 10 µg cm⁻².
3.3.1.6. Influence of specific mass of PEDOT: Because PEDOT has pronounced effect on catalytic activity of Pt, it was intended to examine the effect of mass of PEDOT on mass specific peak current for methanol oxidation. Fig. 3.10 shows the data of Pt-PEDOT for methanol oxidation with PEDOT mass. With an increase in mass of PEDOT, initially there is an increase in specific peak current and it decreases thereafter. Thus the appropriate mass of PEDOT for achieving a high specific mass current for methanol oxidation is 53 µg cm\(^{-2}\), which corresponds to the charge of 0.07 C cm\(^{-2}\) used for its deposition.

![Graph showing the variation of mass specific peak current of Pt-PEDOT/C electrode with mass of Pt. Data obtained from the cyclic voltammetry in 1 M CH\(_3\)OH + 0.1 M H\(_2\)SO\(_4\) at a sweep rate of 5 mV s\(^{-1}\).]
3.3.1.7. **Influence of mass of Pt:** It was intended to examine the influence of mass of Pt on specific peak current for methanol oxidation. Fig. 3.11 shows that the data of Pt-PEDOT/C electrode with mass of Pt. A continuous decrease in specific peak current with mass of Pt is seen. With an increase of mass of Pt, nanoparticles tend to form a smooth layer and consequently, surface area as well as material utilization decrease.

![Graph showing the variation of mass specific peak current of Pt-PEDOT/C electrode (i) and Pt/C electrode (ii) with concentration of H₂SO₄ with Pt loading level of 10 µg cm⁻². Data obtained from the cyclic voltammetry in 1 M CH₃OH + 0.1 M H₂SO₄ at a sweep rate of 5 mV s⁻¹.]

3.3.1.8. **Influence of concentration of electrolyte during oxidation:** To study the influence of concentration of the supporting electrolyte during oxidation, several electrodes were
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prepared with constant PEDOT mass (charge = 0.07 C cm\(^{-2}\)) as well as Pt loading (10 µg cm\(^{-2}\)) and cyclic voltammograms were recorded in H\(_2\)SO\(_4\) of varying concentrations containing 1 M MeOH. The specific peak current versus concentration of H\(_2\)SO\(_4\) is shown in the Fig. 3.12, curve (i). A decrease in specific peak current with concentration of H\(_2\)SO\(_4\) is observed. Similar to this data, a decrease in peak current density with an increase in H\(_2\)SO\(_4\) concentration was also reported in the literature [74]. With an increase in concentration, the hindering effect of sulfate ions increased and also surface area increased, the optimum concentration of H\(_2\)SO\(_4\) was found to be 0.2 M for a Pt-PANI/GC electrode. But experiments were not conducted to examine whether this effect was due to PANI, Pt or both. In the present study, electrodes were also prepared without PEDOT and mass specific peak current is presented in Fig. 3.12, curve (ii). Curve (ii) is substantially lower than curve (i).

3.3.2. Electrooxidation of methanol on PtRu-PEDOT/C electrode

3.3.2.1 Preparation of Pt-Ru: For the deposition of Pt-Ru bimetallic particles, a mixed solution of 0.002 M H\(_2\)PtCl\(_6\) and 0.002 M RuCl\(_3\) in 0.1 M H\(_2\)SO\(_4\) was generally used. Some experiments were also conducted by increasing the concentration of RuCl\(_3\) up to 0.010 M, but keeping the concentration of H\(_2\)PtCl\(_6\) at 0.002 M. The deposition was carried out at 0.0 V. The atomic ratio of Pt and Ru was estimated by XPS spectra as detailed later. The amounts if Pt and Ru in the bimetallic particles were calculated from the charge passed for the deposition and the atomic ratio.

In preparation of electrodeposited nanoparticles, chronoamperometry, where the variation in current is followed with time after stepping the potential to a desired value, is useful for studying kinetics and growth mechanism [88]. The current–time transients
recorded during deposition of Pt and Pt-Ru are presented in Fig. 3.13(A). Current increases to a high value immediately after stepping the electrode to the deposition potential. Then, it

![Graph of current transients for electrodeposition of Pt and Pt-Ru](image)

**Fig. 3.13.** (A) Current transients for electrodeposition of Pt from aqueous solution of 0.1 M H₂SO₄ + 0.002 M H₂PtCl₆ at 0.1 V vs, SCE (i) and Pt-Ru from aqueous solution of 0.1 M H₂SO₄ + 0.002 M H₂PtCl₆ + 0.002 M RuCl₃ at 0.0 V vs. SCE on PEDOT/C electrode (ii); and (B) A log-log plot of current transient’s data shown in Fig. 3.13(A).
decreases gradually, obviously due to very low concentrations of Pt and Ru salts. The relationship between current and time in this region is given as [89].

\[ I = \frac{Z \cdot F \cdot D^{1/2} \cdot c \cdot A}{(\pi \cdot t)^{1/2}} \]  

where ZF is the molar charge of the depositing species, D is the diffusion coefficient, c is the concentration of the species of interest in solution, A is the geometric surface area of the electrode, t is time, I is the current measured in the experiments.

Eq. (3.3) can be approximated as in Eq. (3.4)

\[ I = \frac{K}{t^{0.5}} \]  

where K is constant for a given concentration, c.

Or,

\[ \log I = \log K - 0.5 \log t \]  

log I versus log t plot is expected to be linear with a slope of -0.5 for diffusion controlled three dimensional growth of electrodeposits. The I-t data shown in Fig. 3.13(A) are replotted in log-log scales and shown in Fig. 3.13(B). Linear plots with slopes of -0.30 and -0.46 for Pt and Pt-Ru depositions, respectively. These values, which are close to -0.50, indicate diffusion controlled three dimensional growth of electrodeposited particles.

3.3.2.2. XRD study: XRD patterns of carbon paper, PEDOT/C, Pt-PEDOT/C, Ru-PEDOT/C and PtRu-PEDOT/C electrodes are shown in Fig. 3.14. The XRD pattern of Pt-PEDOT/C (Fig. 3.14, curve (iv)) is indexed to fcc unit cell of Pt (JCPDS file no.7440-06-4). The peak at \( \theta = 39.95, 46.32, 67.84 \) and 81.34° are assigned to (111), (200), (220) and (311) planes,
Fig. 3.14. X-ray diffraction patterns of C (i), PEDOT/C (ii), Ru-PEDOT/C (iii), Pt-PEDOT/C (Pt loading level is 289µg/cm²) (iv), and PtRu-PEDOT/C electrodes (v).

respectively. The peaks observed at 2θ = 42.67, 54.55, 77.49 and 86.76° are also present in the XRD patterns of carbon (Fig. 3.14, curve (i)) as well as PEDOT/C (Fig. 3.14, curve (ii)) electrodes. The patterns of carbon paper (curve (i)) and PEDOT coated carbon paper (curve
(ii)) are identical suggesting amorphous nature of PEDOT. The peaks at $\theta = 42.67, 54.55, 77.49$ and $86.76^\circ$ are attributed to carbon paper used in the present work.

The XRD pattern of Ru-PEDOT/C (Fig. 3.14, curve (iii)) shows no peaks related to crystalline Ru, thus, indicating that the electrodeposited Ru is amorphous. Furthermore, the XRD patterns (Fig. 3.14, curve (v)) of PtRu-PEDOT/C prepared in $0.002\ M\ H_2PtCl_6 + 0.002\ M\ RuCl_3$ electrolyte is similar to the pattern of Pt-PEDOT/C. Thus, Ru remains amorphous in bimetallic state also. PtRu-PEDOT/C electrodes prepared in solutions of higher RuCl$_3$ concentration also exhibited similar XRD patterns. The amorphous nature of Ru in Pt-Ru bimetallic particles remains for all compositions studied in the present work. Broad diffraction peaks of Pt-PEDOT/C and PtRu-PEDOT/C indicate small crystal size.

3.3.2.3. Microscopy: SEM images of PtRu-PEDOT/C electrode prepared in $0.002\ M\ H_2PtCl_6 + 0.002\ M\ RuCl_3$ solution are shown in Fig. 3.15 in different magnifications. Agglomerated particles are uniformly distributed on the electrode surface. The size of agglomerates is in the range of 30-50 nm. Study on the effect of PEDOT on morphology (3.3.1.3. Microscopy) of electrodeposited Pt reveals that fine agglomerates of Pt are uniformly distributed on PEDOT coated carbon paper than on bare carbon paper. The thin layer of PEDOT possesses surface defects uniformly distributed on its surface, and each defect act as nucleation center for the formation of metal atoms. Growth of these metal atoms occurs on continuing the electrolysis, while results in the formation of nanosize clusters. The average size of Pt-Ru clusters seen in Fig. 3.15(B) is about 50 nm. The Pt-Ru aggregates on PEDOT are composed of small particles, which is evident from TEM images. TEM image (Fig.
Fig. 3.15. SEM images of PtRu-PEDOT/C with total metal loading level of 23 µg cm⁻². Magnifications: (A) 25,000 X and (B) 1,00,000 X.

3.16(A)) shows a particle size is in the range of 4~6 nm. The ideal size of Pt-Ru particles used as catalyst for electrooxidation of methanol reported in literature is also about 4-6 nm [60]. The HRTEM micrograph (Fig. 3.16(B)) provides lattice fringes with a separation of
1.24 and 2.19 Å. These values correspond to (311) and (111) plane, respectively, of fcc lattice of Pt. The EDAX data (Fig. 3.16(C)) confirm the presence of Pt and Ru.

Fig. 3.16. (A) TEM image, (B) HRTEM and (C) EDAX spectrum image of PtRu-PEDOT/C.

It is known that electrochemically deposited Pt based metal nanoparticles tend to agglomerate instead of dispersing as individual isolated nanoparticles on the surface of the substrate. A spontaneous deposition of Pt on Ru surface reveals a 3D globular agglomerated
nanocluster which was evident from scanning tunneling microscopy study [90]. An average diameter of 25-30 nm was reported for the nanoclusters. The SEM and TEM images of electrochemically deposited Pt-Ru on carbon cloth fiber also revealed an agglomerated deposit [90].

3.3.2.4. X-ray photoelectron spectroscopy: PtRu-PEDOT/C electrodes were investigated by recording XPS spectra. For these experiments, several electrodes were prepared by varying the concentration of RuCl₃ in the range from 0.002 M to 0.010 M while maintaining the concentration of H₂PtCl₆ at 0.002 M. The charge used for electrodeposition was about 1.4 C cm⁻². The electrodes are listed in Table 3.1. Figure 3.17(A) shows the Pt 4f region of the XPS spectrum of PtRu-PEDOT/C (electrode # 1 in Table 3.1), which could be deconvoluted into two pairs of doublets. For each doublet, the binding energy (BE) of Pt 4f₅/₂ is higher than that of Pt 4f₇/₂ by 3.3 eV [72]. The most intense doublet appearing at 71.5 and 74.8 eV is the signature of metallic Pt. The relatively large shift of these values from 70.8 eV for the bulk Pt suggests that there is a significant metal-support interaction, or it can be due to small cluster size [73,74]. The weaker doublet at higher BEs at 74.8 and 78.1 eV, is attributed to a small amount of Pt⁴⁺ residue on the surface [75]. Figures 3.17(B), (C), (D) and (E) show the XPS data for Ru 3p, C1s, O1s and S2p regions, respectively. Ru 3p peak could be deconvoluted into two peaks. The broad peak (Fig. 3.17(B)) at 462.6 eV indicates the presence of Ru⁰ and peak at 467.8 eV Ru²⁺ states, respectively [91]. By deconvolution of C1s data (Fig. 3.17(C)), two peaks are observed. The peak at 283.8 eV is attributed to carbon conducting substrate [75,76] and the peak at 289.0 eV is due to the carbon of the polymer back bone. The S2p core-level high resolution XPS spectrum (Fig.
Fig. 3.17. XPS spectra of (A) Pt 4f, (B) Ru 3p (C) O 1s, (D) C 1s and (E) S 2p regions of PtRu-PEDOT/C electrode.

3.17(E)) corresponds to single sulfur bonding environment in PEDOT with a spin-split doublet, S 2p1/2 and S 2p3/2 [76-78]. The asymmetric tail to higher binding energy is related to the doping process, in which the delocalized π-electrons in thiophene ring
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broaden the binding energy of the S atom. In O1s core-level XPS spectrum (Fig. 3.17 (E)), a peak at 533.2 eV corresponds to the sole oxygen binding environment in PEDOT and peak at 532.0 eV is due to loosely bound surface oxygen [77].

XPS spectra of the other electrodes (Table 3.1) were similar to the spectrum of electrode # 1 as discussed above. In order to estimate the atomic ratio of Pt and Ru in the bimetallic deposits, spectral peaks corresponding to Pt 4d5/2 at 315 eV and Ru 3d3/2 at 285 eV were employed. From relative intensities of these two peaks, the atomic ratio of Pt to Ru was estimated and given in Table 1 for all electrodes. Although equal concentrations of (0.002 M) H2PtCl6 and RuCl3 were employed for electrode # 1, the atomic ratio of Pt to Ru obtained is 1:1.3. With an increase in concentration of RuCl3 in the electrolyte, Ru content in the bimetallic deposits increases. Thus, the XPS studies confirm codeposition of Pt and Ru from H2PtCl6 and RuCl3 electrolytes on PEDOT/C electrodes.

Table 3.1. Details of electrodes used for XPS studies.

<table>
<thead>
<tr>
<th>Electrode No.</th>
<th>Concentration of RuCl3 in 0.002 M H2PtCl6 (M)</th>
<th>Charge passed (C cm⁻²)</th>
<th>Atomic Ratio of Pt: Ru</th>
<th>Mass of Pt (μg cm⁻²)</th>
<th>Mass of Ru (μg cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.002</td>
<td>1.45</td>
<td>1:1.3</td>
<td>127.4</td>
<td>165.50</td>
</tr>
<tr>
<td>2</td>
<td>0.004</td>
<td>1.43</td>
<td>1:1.5</td>
<td>115.4</td>
<td>173.14</td>
</tr>
<tr>
<td>3</td>
<td>0.006</td>
<td>1.44</td>
<td>1:1.7</td>
<td>107.9</td>
<td>183.51</td>
</tr>
<tr>
<td>4</td>
<td>0.008</td>
<td>1.48</td>
<td>1:2.4</td>
<td>87.80</td>
<td>210.83</td>
</tr>
<tr>
<td>5</td>
<td>0.010</td>
<td>1.43</td>
<td>1:3</td>
<td>72.14</td>
<td>216.43</td>
</tr>
</tbody>
</table>

3.3.2.5. Electrochemical studies: Cyclic voltammograms of Pt-PEDOT/C and PtRu-PEDOT/C electrodes in 1 M H₂SO₄ at a sweep rate of 50 mV s⁻¹ are shown in Fig. 3.18. The feature of cyclic voltammogram of Pt-PEDOT/C electrode (Fig. 3.18, curve (i)) is similar to typical behavior of polycrystalline Pt [80]. The current peaks appearing between -
0.2 and 0.0 V are due to adsorption and desorption of hydrogen on Pt surface. Although the current peaks are not well separated, two pairs of peaks are noticed. The pair appearing at less positive potentials is due to weakly adsorbed hydrogen and the other pair at more positive potentials is due to strongly adsorbed hydrogen. The charge associated with hydrogen adsorption desorption is a measure of active surface area [92,93]. Using 210 μC cm\(^{-2}\) as the basis for calculation of surface area [93], approximate value of surface area

![Cyclic voltammetry of Pt-PEDOT/C (Pt loading level: 289 μg cm\(^{-2}\)) (i) and PtRu-PEDOT/C (PtRu loading level: 289 μg cm\(^{-2}\)) (ii) electrodes recorded in 1 M H\(_2\)SO\(_4\) at a sweep rate of 50 mV s\(^{-1}\).](image)

Fig. 3.18. Cyclic voltammetry of Pt-PEDOT/C (Pt loading level: 289 μg cm\(^{-2}\)) (i) and PtRu-PEDOT/C (PtRu loading level: 289 μg cm\(^{-2}\)) (ii) electrodes recorded in 1 M H\(_2\)SO\(_4\) at a sweep rate of 50 mV s\(^{-1}\).
calculated from the charge of desorption of hydrogen in -0.02 to 0.10 V region is 20 m² g⁻¹ of Pt. This value is comparable to reported values [92,94] for Pt particles. Adsorbed oxygen is reflected in an increase in oxidation current at about 0.60 V and its reduction by a cathodic current peak at about 0.55 V in the reverse sweep. These features of the voltammograms (Fig. 3.18, curve (i)), which are similar to those of Pt metal [80] suggest that agglomerated Pt nanoparticles deposited on PEDOT are electrochemically active. Cyclic voltammogram (Fig. 3.18, curve (ii)) of PtRu-PEDOT/C electrode prepared in 0.002 M H₂PtCl₆ + 0.002 M RuCl₃, but with double the amount of charge in relation to Pt-PEDOT/C electrode used for recording cyclic voltammogram shown in Fig. 3.18, curve (i), also indicates hydrogen adsorption/desorption peaks in -0.20 to 0.10 V region. Between 0.10 and 0.80 V, double –layer charging current is greater for PtRu-PEDOT/C electrode than for Pt-PEDOT/C electrode. The charging current of PtRu-PEDOT/C electrode increases with potential in the anodic sweep, and there is no clear separation of double layer and oxygen adsorption regions. The charge associated with hydrogen adsorption/desorption region is smaller for PtRu-PEDOT/C electrode than Pt-PEDOT/C electrode suggesting decreased amount of Pt or decreased Pt active surface on the former electrode. It was found that Ru-PEDOT/C electrode did not produce similar voltammograms.

3.3.2.6. Electrooxidation of methanol: Figure 3.19(A) shows cyclic voltammograms of Pt-PEDOT/C (curve (i)) and PtRu-PEDOT/C (curve (ii)) electrodes in 0.1 M H₂SO₄ + 1.0 M CH₃OH solution at a sweep rate of 5 mV s⁻¹. In the inset of Figure 3.19(A), a cyclic voltammogram of Ru-PEDOT/C electrode in 0.1 M H₂SO₄ + 1.0 M CH₃OH is presented. Charges used for deposition of metal particles in Pt, Ru and Pt-Ru electrodes are 0.057,
0.057 and 0.114 C cm$^{-2}$, respectively. No current peaks (Fig. 3.19(A) inset) corresponding to methanol oxidation suggested that Ru does not have a direct role in oxidation of methanol. Pt-PEDOT/C electrode exhibits two oxidation peaks, P$_1$ and P$_2$ which correspond to the oxidation of methanol during the forward sweep and the oxidation of intermediates during the reverse sweep at 0.61 and 0.46 V, respectively. The formation of reactive intermediates occurs due to incomplete oxidation of methanol during the forward sweep,

\[ \text{Fig. 3.19. (A) Cyclic voltammograms of Pt-PEDOT/C (i) and PtRu-PEDOT/C (ii) electrode with Pt loading level of 10 µg cm}^{-2} \text{ in 1 M CH}_3\text{OH} + 0.1 \text{ M H}_2\text{SO}_4 \text{ at a sweep rate of 5 mV s}^{-1}; \text{ (B) Cyclic voltammogram of Pt-Ru/C without PEDOT. The cyclic voltammery of Ru-PEDOT/C in 1 M CH}_3\text{OH} + 0.1 \text{ M H}_2\text{SO}_4 \text{ is shown in the inset.} \]
and gets adsorbed on the catalyst. In the case of PtRu-PEDOT/C electrode, these peaks appear at potentials, 0.46 and 0.36 V, respectively. The shape of the curves and the range of peak potentials are in accordance with previous work [46,95]. The onset potential of methanol oxidation on Pt-PEDOT/C electrode is about 0.30 V, whereas it is about 0.15 V on PtRu-PEDOT/C electrode. The mechanism of electrooxidation of methanol on Pt-Ru bimetallic catalyst includes the following important stages [96].

\[
\text{Pt-Ru + CH}_3\text{OH} \rightarrow (\text{Pt – CO}) –\text{Ru + 4 H}^+ + 4 e^- \quad (3.6)
\]

\[
(\text{Pt – CO}) –\text{Ru + H}_2\text{O} \rightarrow (\text{Pt-CO})- (\text{Ru-OH}) + \text{H}^+ + e^- \quad (3.7)
\]

\[
(\text{Pt-CO})- (\text{Ru-OH}) \rightarrow \text{Pt-Ru + CO}_2 + \text{H}^+ + e^- \quad (3.8)
\]

Reaction (3.6) occurs in four different steps, each step involves single electron transfer process. Thus several intermediate species of the type CH\textsubscript{x}O (0<x<4) are expected to be formed. Adsorption of CO intermediate occurs on Pt sites (reaction 3.6). Oxidation of H\textsubscript{2}O (reaction 3.7) leading to the formation of adsorbed OH takes place on Ru sites. Adsorbed CO and OH on adjacent sites of Pt and Ru, respectively, combine resulting in the final reaction product, CO\textsubscript{2} (reaction 3.8). While the formation of adsorbed OH takes place on Ru sites in the case of Pt-Ru bimetallic catalyst, this process as well as the formation of adsorbed CO occurs only on Pt sites alone in the case of Pt catalyst. Pt-Ru, thus, is a better catalyst for methanol oxidation. The lower onset potential as well as lower peak potentials on PtRu-PEDOT/C electrode than on Pt-PEDOT/C electrode support greater catalytic activity of the former electrode.

The effect of PEDOT as support for Pt-Ru catalyst is evident by comparing cyclic voltammograms in Fig. 3.19. Voltammogram in Fig. 3.19(B) was recorded for Pt-Ru/C electrode (in the absence of PEDOT). Although the peak potentials are nearly the same in
Fig. 3.20. The ratio of $I_f/I_b$ versus cycle number of (■) Pt- PEDOT/C, (●) Pt$_{1}$Ru$_{1.3}$-PEDOT/C, (▲) Pt$_{1}$Ru$_{1.5}$-PEDOT/C, (▼) Pt$_{1}$Ru$_{1.7}$-PEDOT/C, (♦) Pt$_{1}$Ru$_{2.4}$-PEDOT/C and (◄) Pt$_{1}$Ru$_{3}$-PEDOT/C electrode.

In the absence and presence of PEDOT, the current values are substantially smaller. This is due to the fact that the bimetallic catalyst particles tend to grow into non-uniformly distributed, large agglomerates on bare carbon paper. Thus, a thin layer of PEDOT as a support for uniform distribution of electrodeposited Pt-Ru, favours for achieving a high catalytic efficiency. Mass specific peak current (on the basis of Pt mass) for methanol oxidation obtained on PtRu-PEDOT/C electrode is as high as 657 mA mg$^{-1}$.

Furthermore, $I_f/I_b$ ratios calculated for ten repetitive voltammograms for Pt-PEDOT/C and PtRu-PEDOT/C electrodes are shown in Fig. 3.20. The data for PtRu-
PEDOT/C electrodes include for different atomic ratios of Pt and Ru. For Pt-PEDOT/C electrodes, the $I_r/I_b$ ratio is about 1.5. However, this ratio is greater than 3.0 for all PtRu-PEDOT/C electrodes. These data indicate that PtRu-PEDOT/C electrodes possess greater tolerance to adsorption of reaction intermediate species, which poison the catalyst particles.
Fig. 3.22. The Current-time data of PtRu-PEDOT/C at 0.70 (i), 0.75 (ii), 0.8 (iii), 0.85 (iv) and 0.90 V vs. SCE (v) in 1 M CH₃OH + 0.1 M H₂SO₄.

The stability of PtRu-PEDOT/C electrodes was studied by repeated cycling of the electrode in 0.1 M H₂SO₄ consisting of 1 M CH₃OH (Fig. 3.21). There is a small decrease of cyclic voltammetric peak currents on repeated cycling Chronoamperometry data recorded at five different potentials for an hour in a stirred solution are shown in Fig. 3.22. The measured current is steady for about 1 h tested. It is thus concluded that PtRu-PEDOT/C electrodes are stable for methanol oxidation.
It was intended to examine the influence of mass of Pt on specific peak current for methanol oxidation. Fig. 3.23 shows that the data of PtRu-PEDOT/C electrode with mass of Pt. A continuous decrease in specific peak current with mass of Pt is seen. With an increase of mass of Pt, nanoparticles tend to form a smooth layer and consequently, surface area as well as material utilization decrease.

**Fig. 3.23.** The variation of mass specific current (mA mg\(^{-1}\)) versus mass of Pt in PtRu-PEDOT/C electrode. The data obtained from cyclic voltammetric study of PtRu-PEDOT/C in 1M MeOH + 0.1 M H\(_2\)SO\(_4\) at a sweep rate of 10 mV s\(^{-1}\).

3.3.3. Electrooxidation of formic acid

3.3.3.1. Reaction mechanism: As in the case of polymer electrolyte membrane fuel cells, the direct formic acid fuel cell also uses an air cathode. Oxygen reduction through a 4-electron
transfer reaction at the cathode is usually facilitated by a platinum based catalyst. At the anode, direct oxidation of formic acid releases two electrons per molecule. The cathode, anode and overall reaction of a direct formic acid fuel cell in acidic media are given below:

\[
\text{Anode: } \text{HCOOH} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \quad E^0 = -0.25 \text{ V (vs. SHE)} \quad (3.9)
\]

\[
\text{Cathode: } \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O} \quad E^0 = 1.23 \text{ V (vs. SHE)} \quad (3.10)
\]

\[
\text{Overall: } \text{HCOOH} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad \text{OCV} = 1.48 \text{ V} \quad (3.11)
\]

The mechanism of electrooxidation of HCOOH is a subject of several studies [97-99]. The most commonly accepted mechanism is known as parallel or dual-path mechanism [69]. Direct oxidation (pathway 1) occurs without formation of CO as an intermediate:

\[
\text{Pathway 1: } \text{HCOOH} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \quad (3.12)
\]

In the second reaction pathway (pathway 2), CO\text{ads} forms as a reaction intermediate by dehydrogenation, which is followed by oxidation to CO\text{2}.

\[
\text{Pathway 2: } \text{HCOOH} \rightarrow \text{CO}_{\text{ads}} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \quad (3.13)
\]

In reaction pathway 2, formic acid first undergoes adsorption on the catalyst surface forming CO\text{ads}, which is then oxidized to CO\text{2} as the end product. For direct formic acid fuel cells, pathway 1 is preferable to enhance overall cell efficiency by avoiding poisoning of the catalyst. Hence, a selection of an appropriate catalyst is pivotal in formic acid oxidation to proceed via reaction pathway 1.
3.3.3.2. Electrochemistry: Cyclic voltammogram for Pt-PEDOT/C electrode in 0.1 M H$_2$SO$_4$ + 0.5 M HCOOH at a scan rate of 10 mV s$^{-1}$ in the potential range of 0 to 0.9 V is shown in Fig. 3.24. In the forward direction of the potential sweep, Pt-PEDOT/C electrode exhibits two anodic current peaks, which are in agreement with those reported in the literature for polycrystalline Pt [68]. The first anodic peak (P$_{a1}$) (at 0.3 V) is due to
direct oxidation of HCOOH to CO₂, whereas the second peak (P₂) at 0.6 V is ascribed to the oxidation of COₐds generated from the dissociative adsorption step [68]. Oxidation of COₐds releases the surface sites for the subsequent direct oxidation of HCOOH. In the reverse direction, a large oxidation peak (Pₜ) due to oxidation of formic acid is observed. A noticeable fact in the voltammogram of Pt-PEDOT/C electrode is that the current density of peak P₂ is higher compared to peak P₁. Cyclic voltammogram recorded on a Pt foil are similar to the data of Pt-PEDOT/C electrode (Fig. 3.24), but for lower current values.

Fig. 3.25. Cyclic voltammograms of PtRu-PEDOT/C (i) and PtRu/C (without PEDOT) (ii) (Mass of Pt = 6.3 μg cm⁻²) in 0.1 M H₂SO₄ + 0.5 M HCOOH at a sweep rate of 10 mV s⁻¹.
Cyclic voltammogram of PtRu-PEDOT/C electrode in 0.1 M H₂SO₄ + 0.5 M HCOOH is shown in Fig. 3.25. The shape of the voltammogram is distinctly different from that of Pt-PEDOT/C (Fig. 3.24). A single peak at 0.40 V is only present. This indicates that the formic acid oxidation on the PtRu-PEDOT/C electrode follows the dehydrogenation branch or pathway 1. This catalytic behavior is similar to that of Pd/C electrode, where Pd facilitates the formic acid oxidation via the dehydrogenation step without forming the strongly adsorbed intermediates (CO_ads) [49]. Kristian et al., designed a submonolayer of Pt-decorated Au, which exhibits improved activity towards oxidation of formic acid by suppressing the formation of CO_ads via the “ensemble” effect [70].

Cyclic voltammogram of Pt/C is shown in Fig. 3.24, (curve (ii)) to through light on the effect of PEDOT on electrooxidation of HCOOH. The shape of cyclic voltammogram is similar to that of Pt-PEDOT/C electrode (Fig. 3.24, curve (i)). However the maximum peak current density (P_b) of Pt/C is almost 8 times smaller than the value of Pt-PEDOT/C. In the case of Pt-Ru electrode, the maximum oxidation peak current density (P_b) of PtRu/C (Fig. 3.25, curve (ii)) electrode is 4 times smaller than that of electrode with PEDOT (Fig. 3.25, curve (i)). Hence, a clear beneficial effect of PEDOT towards electrooxidation of HCOOH is observed.

Mass specific current of Pt-PEDOT/C is obtained by dividing the peak current density of peak P_b by mass of Pt in the electrode. A mass specific current of 250 mA mg⁻¹ is obtained for the oxidation of HCOOH on Pt-PEDOT/C electrode (Fig. 3.26, curve (i)) where as it is 400 mA mg⁻¹ for PtRu-PEDOT/C electrode (Fig. 3.26, curve (ii)) at low
Fig. 3.26. Mass specific current versus mass of Pt-PEDOT/C (i) and PtRu-PEDOT/C (ii) electrodes. The data obtained from cyclic voltammetric study of Pt-PEDOT/C and PtRu-PEDOT/C in 0.5 M HCOOH + 0.1 M H2SO4 at a sweep rate of 10 mV s⁻¹.

loading levels. There is a decrease in mass specific current with an increase in loading level of the catalysts.

In order to examine the stability, Pt-PEDOT/C and PtRu-PEDOT/C electrodes were subjected to amperometry studies in 0.5 M HCOOH + 0.1 M H2SO4. Chronoamperometry
data were recorded at 6 different potentials by keeping the electrolyte under stirring and shown in Figs. 3.27 and 3.28. The current densities are nearly stable for an hour. It is thus concluded that Pt-PEDOT/C and PtRu-PEDOT/C electrodes are stable for HCOOH oxidation.
Fig. 3.28. Current-time data of PtRu-PEDOT/C (Pt loading level = 14 µg cm\(^{-2}\)) at 0.3 (i), 0.4 (ii), 0.5 (iii), 0.6 (iv), 0.7 (v) and 0.8 V vs. SCE (vi) in 0.5 M HCOOH + 0.1 M H\(_2\)SO\(_4\).

3.3.4. Electrooxidation of formaldehyde

3.3.4.1. Reaction mechanism: Formaldehyde in aqueous solutions exists mainly in the hydrated form CH\(_2\)(OH)\(_2\), according to the equilibrium for the solvation reaction [71]: 
Electrooxidation of formaldehyde was recently studied on basal planes of Pt single crystals [72] and it was found that the dissociative adsorption of HCHO occurs at potentials as low as 0.05 V. Adsorption was found to be fast at Pt(1 0 0) and Pt(1 1 0) planes, and relatively slow at Pt(1 1 1) plane. A complex scheme of parallel reactions involving adsorbed intermediates, such as CO$_{ad}$ and H$_2$COO$_{ad}$ was suggested (Scheme 3.1)[72].

![Chemical Reaction](image)

**Scheme 3.1**

The analysis of products using FTIR spectroscopy revealed that reaction steps II–V involving HCOOH as the main product, play a main role at Pt(1 1 1) electrodes. It was suggested that CO$_{ad}$ acts as a catalyst poison, while H$_2$COO$_{ad}$ is the intermediate of a fast reaction pathway forming HCOOH as soluble intermediate product. The existence of a fast
reaction pathway, which is inhibited due to a surface blockage by CO\textsubscript{ad}, suggests the possibility of enhancing the reaction rate by using PtRu, which can oxidize CO\textsubscript{ad} at relatively low potentials.

![Cyclic voltammogram of Pt-PEDOT/C electrode](image)

**Fig. 3.29.** Cyclic voltammogram of Pt-PEDOT/C (Pt loading level = 14 µg cm\(^{-2}\)) (i) and Pt/C (without PEDOT) (ii) in 0.1 M H\(_2\)SO\(_4\) + 0.5 M HCHO at a sweep rate of 10 mV s\(^{-1}\).

3.3.4.2. Electrochemistry: Electrooxidation of HCHO was studied by cyclic voltammetry in 0.1 M H\(_2\)SO\(_4\) and shown in Fig. 3.29. Cyclic voltammogram of Pt-PEDOT/C electrode (Fig. 3.29) with Pt loading of 14 µg cm\(^{-2}\) in 0.1 M H\(_2\)SO\(_4\) + 0.5 M HCHO electrolyte shows
an oxidation peak at 0.56 V in the forward scan. Cyclic voltammogram of Pt foil is shown in Fig. 3.30 for comparison. According to the mechanism proposed for formaldehyde oxidation on a smooth Pt electrode [100], the 0.56 V peak is due to the oxidation of CO$_{ads}$, formed during the oxidation of HCHO and Pt [28,100]. In the reverse direction, the current peak is due to the oxidation of formaldehyde [28,100]. The slow increase in current at lower potentials on the forward sweep results from poisoning of the electrode by reaction

![Cyclic voltammogram of commercial Pt foil in 0.1 M H$_2$SO$_4$ + 0.5 M HCHO at a sweep rate of 10 mV s$^{-1}$](image)

*Fig. 3.30. Cyclic voltammogram of commercial Pt foil in 0.1 M H$_2$SO$_4$ + 0.5 M HCHO at a sweep rate of 10 mV s$^{-1}$*
intermediate formed during HCHO oxidation (Scheme 3.1, step (i)). At higher oxidation potentials, a quick increase in current during the forward sweep is due to transformation of poisonous intermediates to carbon dioxide (Scheme 3.1, step (iii)). The surface CO$_{\text{ad}}$ poison formed in step i (scheme 3.1) can be removed by reaction with OH$_{\text{ad}}$ formed by dissociation of water molecules on Pt surface. But activation of H$_2$O on Pt is a difficult process and it

![Fig. 3.31. Cyclic voltammogram of PtRu-PEDOT/C (Pt loading level = 6.3 µg cm$^{-2}$) (i) and Pt/C (without PEDOT) (ii) in 0.1 M H$_2$SO$_4$ + 0.5 M HCHO at a sweep rate of 10 mV s$^{-1}$.](image)
occurs only at high potential (>0.5 V). Due to high potential required for oxidation of CO\textsubscript{ad} on Pt, the electrode surface is blocked by large quantity of CO\textsubscript{ad} species thereby hindering the adsorption of HCHO molecules. Thus an overall retarding effect is observed on Pt-PEDOT/C electrode.

Cyclic voltammogram of PtRu-PEDOT/C electrode with Pt loading level of 6.3 \( \mu \text{g cm}^{-2} \) is shown in Fig. 3.31. The peak currents of formaldehyde oxidation are comparable for the Pt-PEDOT/C and PtRu-PEDOT/C electrodes. In the case of Pt-Ru catalyst, Ru helps in increasing the rate of oxidation to a considerable extent. Ru facilitates the reaction to proceed through a direct pathway mechanism without formation of surface poison (Scheme 3.1, steps ii-v). Oxidation of HCHO on Pt surface takes place \textit{via} dehydrogenation reaction as shown in Scheme 3.1 (step ii).

\[
\text{HCHO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}^+ + 4e^- \tag{3.15}
\]

This process involves the transfer of four electrons and occupation of one Pt active surface site. Because HCHO is directly converted to CO\textsubscript{2} through dehydrogenation reaction without the formation of CO in the presence of Ru, the rate of oxidation is higher in PtRu-PEDOT/C electrodes. Selvaraj et al., also reported a similar observation with PtPd-PPY-CNT/graphite electrode, where Pd helps HCHO to oxidize through the step ii (Scheme 3.1) directly to CO\textsubscript{2} [28].

Cyclic voltammogram of Pt/C electrode in 0.5 M HCHO + 0.1 M H\textsubscript{2}SO\textsubscript{4} is presented in Fig. 3.29, curve (ii) to show the effect of PEDOT on electrooxidation of HCHO. The higher current density of Pt-PEDOT/C for HCHO oxidation compared to Pt/C
is due to the greater dispersion of Pt over the PEDOT surface [46]. The beneficial effect of PEDOT is also clear in case of Pt-Ru electrode also (Fig. 3.31, curve (ii)).

Mass specific current versus mass of Pt of both Pt-PEDOT/C and PtRu-PEDOT/C electrode are given in Fig. 3.32. Mass specific current was calculated from forward peak current of cyclic voltammogram and mass of Pt present in the electrode. The highest mass

![Graph](image)

**Fig. 3.32.** Mass specific current versus mass of Pt in Pt-PEDOT/C (Pt loading level = 14 µg cm\(^{-2}\) (i) and PtRu-PEDOT/C (Pt loading level = 6.3 µg cm\(^{-2}\))(ii) electrodes. The data obtained from cyclic voltammetric study of Pt-PEDOT/C and PtRu-PEDOT/C electrodes in 0.5 M HCHO + 0.1 M H\(_2\)SO\(_4\) at a sweep rate of 10 mV s\(^{-1}\).
specific currents for HCHO oxidation are 134 (Pt-PEDOT/C) and 340 (PtRu-PEDOT/C) mA mg$^{-1}$ for Pt-PEDOT/C and PtRu-PEDOT/C electrodes, respectively.

Pt-PEDOT/C and PtRu-PEDOT/C electrodes are subjected to chronamperometry. Chronoamperometry data are presented in Figs. 3.33 and 3.34 different potentials in stirred electrolyte. The steady oxidation current densities of the electrodes are suggested that electrodes are stable for HCHO oxidation.

![Current-time transients of Pt-PEDOT/C](image)

**Fig. 3.33.** The current-time transients of Pt-PEDOT/C at 0.65 (i), 0.7 (ii), 0.75 (iii), 0.8 (iv), 0.85 (v) and 0.9 V vs. SCE (vi) electrodes in 0.5 M HCHO + 0.1 M H$_2$SO$_4$.

3.3.5. Electrooxidation of ethanol

3.3.5.1. Reaction mechanism: The anodic oxidation of ethanol, reduction of oxygen and over all reactions of DEFC are presented as follows:
Anodic reaction:

\[ \text{CH}_3\text{CH}_2\text{OH} + 3 \text{H}_2\text{O} \rightarrow 2 \text{CO}_2 + 12 \text{H}^+ + 12 \text{e}^- \quad (E_a = 0.084 \text{V vs. SHE}) \quad (3.16) \]

Cathodic reaction:

\[ 3\text{O}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow 6\text{H}_2\text{O} \quad (E_c= 1.229 \text{ V vs. SHE}) \quad (3.17) \]

Overall reaction:

\[ \text{CH}_3\text{CH}_2\text{OH} + 3\text{O}_2 \rightarrow 2 \text{CO}_2 + 3 \text{H}_2\text{O} \quad (E_{\text{cell}}= 1.145 \text{ V vs. SHE}) \quad (3.18) \]

The complete oxidation of ethanol involves releasing of 12 electrons per ethanol molecule. The cleavage of C-C bond plays an important role in ethanol oxidation and consequently determines the fuel cell efficiency.

![Fig. 3.34. The current-time transients of PtRu-PEDOT/C at 0.65 (i), 0.7 (ii), 0.75 (iii), 0.8 (iv), 0.85 (v) and 0.9 V vs. SCE (vi) electrodes in 0.5 M HCHO + 0.1 M H_2SO_4.](image-url)
3.3.5.2. Electrochemistry: Cyclic voltammogram for ethanol electrooxidation on the Pt-PEDOT/C electrode (Fig. 3.35) is similar to the characteristic current-voltage features reported for ethanol oxidation on polycrystalline Pt electrode [23,101]. Cyclic voltammogram of commercial Pt foil (Fig. 3.36) is also given for comparison. Ethanol oxidation current peak appears at 0.63 V. On reversing the potential sweep, re-oxidation of
ethanol begins at approximately 0.62 V and becomes a peak at about 0.43 V. Cyclic voltammogram of PtRu-PEDOT/C electrode is shown in Fig. 3.37. The shape of the 

![Cyclic voltammogram of commercial Pt foil in 0.1 M H₂SO₄ + 0.5 M C₂H₅OH at a sweep rate of 10 mV s⁻¹](image)

*Fig. 3.36. Cyclic voltammogram of commercial Pt foil in 0.1 M H₂SO₄ + 0.5 M C₂H₅OH at a sweep rate of 10 mV s⁻¹*

voltammogram is similar to the shape of Pt-PEDOT/C electrode (Fig. 3.35). Forward oxidation peak appears at 0.60 V, which is lower in comparison with Pt-PEDOT/C electrode indicating a greater catalytic activity of PtRu-PEDOT/C electrode. According to the literature [43,33,104], there are relatively narrow ranges of monometallic, bimetallic or trimetallic compositions that present a high activity for ethanol oxidation. Spinace et al.,
[43] found that the catalytic activity for the ethanol oxidation increases with an increase in Ru content up to Pt-Ru ratio of 1:3. Neto et al., [33] observed that the catalytic activity increases with an increase in Ru content in PtRu composition up to 3:2. Chetty et al., [102] reported an optimum ratio of Pt and Ru as 1:1. Compositions of PtSn, PtRuW and PtRuNi were also studied for ethanol oxidation [102]. The presence of the third metal (Ni) in the PtRu catalyst increased the activity of ethanol electrooxidation [102]. PtSn catalyst was

![Cyclic voltammogram of PtRu-PEDOT/C (i) and PtRu/C (without PEDOT) (ii) electrode (Pt loading level = 6.3 µg cm⁻²) in 0.1 M H₂SO₄ + 0.5 M C₂H₅OH at a sweep rate of 10 mV s⁻¹.](image)

*Fig. 3.37. Cyclic voltammogram of PtRu-PEDOT/C (i) and PtRu/C (without PEDOT) (ii) electrode (Pt loading level = 6.3 µg cm⁻²) in 0.1 M H₂SO₄ + 0.5 M C₂H₅OH at a sweep rate of 10 mV s⁻¹.*
prepared by modified polyl process and ethanol electrooxidation was performed [42]. PtRuNi/C electrocatalyst exhibited greater current and higher stability than PtRu/C in the potential range of interest for direct ethanol fuel cell [40].

![Graph showing mass specific current versus mass of Pt-PEDOT/C and PtRu-PEDOT/C electrodes.](image)

**Fig. 3.38.** Mass specific current versus mass of Pt-PEDOT/C (Pt loading level = 14 µg cm⁻²) (i) and PtRu-PEDOT/C (Pt loading level = 6.3 µg cm⁻²) (ii) electrodes. The data obtained from cyclic voltammetric study of Pt-PEDOT/C and PtRu-PEDOT/C electrode in 0.5 M C₂H₅OH + 0.1 M H₂SO₄ at a sweep rate of 10 mV s⁻¹.

Cyclic voltammogram of Pt/C is shown in Fig. 3.35, curve (ii). Current values measured for Pt/C electrode are lower in relation to Pt-PEDOT/C electrode. Similar
observation on the effect of PEDOT is also made in the case of PtRu electrodes (Fig. 3.37, curve (ii)).

Mass specific current versus mass of the Pt is presented in Fig. 3.38. The maximum specific forward current densities of Pt-PEDOT/C and PtRu-PEDOT/C electrodes are 90 and 350 mA mg$^{-1}$, respectively.

*Fig. 3.39. The current-time data of Pt-PEDOT/C electrode (Pt loading level = 14 µg cm$^{-2}$) at 0.65 (i), 0.7 (ii), 0.75 (iii), 0.8 (iv), 0.85 (v) and 0.9 V vs. SCE (vi) in 0.5 M C$_2$H$_5$OH + 0.1 M H$_2$SO$_4$.***
Pt-PEDOT/C and PtRu-PEDOT/C electrodes were stirred electrolyte in 0.5 M C₂H₅OH + 0.1 M H₂SO₄ were subjected to chronoamperometry. Chronoamperometry at different potentials and the data are shown in Fig. 3.39 and 3.40. The current densities are nearly stable for an hour. It is thus, concluded that Pt-PEDOT/C and PtRu-PEDOT/C electrodes are stable for HCOOH oxidation.

Fig. 3.40. The current-time transients of PtRu-PEDOT/C electrode (Pt loading level = 14 µg cm⁻²) at 0.65 (i), 0.7 (ii), 0.75 (iii), 0.8 (iv), 0.85 (v) and 0.9 V vs. SCE (vi) in 0.5 M C₂H₅OH + 0.1 M H₂SO₄.
3.4 CONCLUSIONS

Nanoclusters of Pt and bimetallic Pt-Ru electrodeposited on PEDOT exhibit a high catalytic for electrooxidation of small organic molecules, namely, methanol, formic acid, formaldehyde and ethanol. A thin layer PEDOT on the carbon substrate facilitates the formation of uniform, well-dispersed, small clusters of catalysts that consist of nanosize particles. The cyclic voltammetry studies suggest that peak currents of oxidation of the small organic molecules are several times greater for Pt-PEDOT/C and PtRu-PEDOT/C electrodes than Pt/C and PtRu/C electrodes, respectively. Chronoamperometry studies suggest good stability of Pt-PEDOT/C and PtRu-PEDOT/C electrodes for electrooxidation of methanol, formic acid, formaldehyde and ethanol.

3.5. REFERENCES
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Electrooxidation of phenol on PEDOT deposited stainless steel electrodes

ABSTRACT

Studies on electrochemical oxidation of phenol are interesting because it is important to remove phenol from contaminated water or industrial effluents. Deactivation of the anode due to the formation and adsorption of polyoxyphenylene on surface is a common problem for a variety of electrode materials, during phenol oxidation. Investigations on suitable anode materials, which can undergo no or moderate poisoning by polyoxyphenylene, are interesting. In this study, PEDOT coated SS electrodes are investigated. The electrooxidation rate of phenol is greater on PEDOT/SS electrode than on Pt. Deactivation of PEDOT/SS electrode is slower in relation to Pt. The oxidation of phenol on PEDOT/SS electrode occurs to form both polyoxyphenylene and benzoquinone in parallel. Cyclic voltammetry of phenol oxidation is studied by varying the concentration of phenol, sweep rate and thickness of PEDOT. Ac impedance studies indicate a gradual increase in polymer resistance due to adsorption of polyoxyphenylene during multi sweep cyclic voltammetry.

4.1. INTRODUCTION

Several chemical plants generate waste water with high concentrations of phenol and substituted phenols. These compounds do not undergo biological degradation and they can react with chlorine during water treatment [1]. Phenolic impurities in water are toxic and therefore are hazardous to human health as well as aquatic life. Electrochemical treatment of waste water or industrial effluents, which are contaminated with phenols, is an important and convenient route for removal of these compounds.

Electrooxidation of phenols has been studies on a variety of anode materials, which include noble metals such as Pt [2-9], Au [10-12], etc., metal oxides such as RuO$_2$ [13-14], IrO$_2$ [15], SnO$_2$ [15-18], PbO$_2$ [19-23], etc., and also non-metallic materials such as carbons [24-27], boron doped diamond [28-29], etc. One common problem persistent in almost all studies of electrooxidation of phenol is deactivation of the anode during extended periods of electrolysis. One of the oxidation products of phenol, namely, poloxyphenylene forms as a film on the anode thereby making the anode electrochemically inactive. It is important to investigate anode materials, which are resistant to fouling by poloxyphenylene.

Electrooxidation of organic molecules is generally considered to occur by a hydroxyl radical (OH$^\bullet$) that is formed from water and adsorbed on the anode surface [30].

\[
S[ \cdot ] + \text{H}_2\text{O} \rightarrow S[\text{OH}^\bullet] + \text{H}^\text{+} + \text{e}^\text{-}
\]  \hspace{1cm} (4.1)

where S[ \cdot ] stands for an adsorption site on anode surface. The adsorbed hydroxyl radical (S[OH$^\bullet$]) can initiate oxidation of organic molecules. Phenol oxidation mechanism involves the formation of phenoxy radical (\text{C}_6\text{H}_5\text{O}^\bullet) as the primary oxidation product [22].

\[
S[ \cdot ] + \text{C}_6\text{H}_5\text{OH} \rightarrow S[\text{C}_6\text{H}_5\text{O}^\bullet] + \text{H}^\text{+} + \text{e}^\text{-}
\]  \hspace{1cm} (4.2)
Further oxidation of phenoxy radical takes place in two different pathways [22]. One pathway leads to the total oxidation of phenoxy radicals to CO₂ via formation of several intermediates, as follows:

\[ S \left[ C_6H_5O^\cdot \right] + S[OH^\cdot] \rightarrow S[ ] + C_6H_4O_2 + 2H^+ + 2e^- \]  
(benzoquinone) \hspace{1cm} (4.3)

\[ C_6H_4O_2 + 6S[OH^\cdot] \rightarrow 6S[ ] + C_4H_4O_4 + 2CO_2 + 6H^+ + 6e^- \]  
(maleic acid) \hspace{1cm} (4.4)

\[ C_4H_4O_4 + 4S[OH^\cdot] \rightarrow 4S[ ] + 4CO_2 + 8H^+ + 8e^- \] \hspace{1cm} (4.5)

The complete oxidation of phenoxy radical to CO₂ as the final product is the most desirable reaction. In the other pathway, however, phenoxy radical undergoes polymerization as,

\[ S \left[ C_6H_5O^\cdot \right] \rightarrow S[\text{dimer}] \rightarrow S[\text{polymer}] \] \hspace{1cm} (4.6)

The polymer, namely, polyoxyphenylene, covers the anode surface as an insulating film. As a result, the anode undergoes fouling and becomes less efficient for further oxidation of phenol. The experimental conditions such as phenol concentration, acidity, potential, the nature of the anode, etc., influence the electrooxidation of phenol to take either of the pathways or both simultaneously. Complete oxidation of phenol to CO₂ in the first pathway is expected at high current densities and low phenol concentrations [22]. On the other hand, low current densities and high concentrations of phenol produce the insulating polymer film.

A study on electrooxidation of phenol on Pt surface, which is modified by a conducting polymer, is reported [31]. There is an improvement in the stability of the modified Pt electrode with respect to fouling. The fouling of the modified Pt electrode is slower when compared with the bare Pt electrode. In recent years, several reversible reactions as well as irreversible oxidation processes on polyaniline (PANI) modified SS
Electrooxidation of phenol…

Electrodes were studied [32-34]. A common metal or alloy such as SS is used as a current collecting substrate, because it is inexpensive and convenient for extending the investigations for practical applications. In this context, it is anticipated that oxidation of phenol on a conducting polymer, which is coated on a non-platinum metal, is interesting. To the best of author’s knowledge, there are no studies of electrooxidation of phenol on a common metal surface, which is modified by an electronically conducting polymer. In the present work, electrooxidation of phenol on SS modified with PEDOT in aqueous acid solution is investigated.

4.2. EXPERIMENTAL

Electrodeposition of PEDOT on SS substrates was carried out at 0.90 V in an electrolyte of 0.1 M H₂SO₄ + 0.01 M EDOT + 0.01 M SDS, as described in 2.2 Experimental section. The quantity of PEDOT deposited on a SS increases with an increase in charge passed. Thus, the charge is considered as a measure of thickness of PEDOT. A majority of the experiments were carried out using PEDOT/SS electrodes prepared with 0.7 C cm⁻², unless otherwise specified. After the electrochemical deposition of PEDOT, the electrode was separated from the cell, washed repeatedly in 0.1 M H₂SO₄ under stirring for about 30 min. Electrodes were also made by varying the charge passed for deposition of PEDOT with varying mass. For the purpose of weighing the deposited PEDOT, the SS substrate was dried and weighed before immersing in the electrolyte. After passing the intended charge, the electrode was removed from the electrolyte, washed, dried at 50 °C under vacuum for 12 h and again weighed. The difference in the two weights was considered as the mass of PEDOT. Geometric area of sandblasted SS substrate was used for calculation of current density and charge density. Some experiments were also carried out
on a Pt foil (area: 1.4 cm$^2$) electrode. Other experimental details are as described in Section 2.2

4.3. RESULT AND DISCUSSION

4.3.1. Cyclic voltammetry: When a non-platinum metal is employed for an electrooxidation reaction, anodic corrosion of the metal is a common concern. In the present study, SS substrate was subjected to cyclic voltammetry in 0.1 M H$_2$SO$_4$ + 0.01 M EDOT + 0.01 M SDS electrolyte, which was used for the deposition of PEDOT. The data are presented in Fig. 4.1, curve (i) together with cyclic voltammogram (curve ii) measured in blank solution (absence of EDOT monomer). No current peaks corresponding to the oxidation of SS are observed in the voltammograms (Fig. 4.1, curve (i) and (ii)). A current peak due to oxidation of EDOT is present at about 0.9 V (Fig. 4.1, curve (i)). Formation of PEDOT was visually noticed at this stage. Stability of SS in this electrolyte might be due to mild acidic conditions of the electrolyte and also due to adsorption of SDS molecules on the surface of SS. Once a layer of PEDOT was formed, it provided further corrosion resistance to SS surface. PEDOT/SS electrodes were free from the problems associated with corrosion and anodic oxidation of the SS substrate.
Cyclic voltammetric data of PEDOT/SS electrode in 0.5 M H2SO4 (curve (i)) and in 0.01 M C6H5OH + 0.5 M H2SO4 (curve (ii)) in the potential range from 0 to 1.05 are shown in Fig. 4.2(A). There is an increase of current in 0.5 M H2SO4 (Fig. 4.2(A) curve (ii)) at 0.9 V. In contrast to curve (i), current starts increasing at 0.75 V (Fig. 4.2(A) curve (ii)) in 0.01 M C6H5OH + 0.5 M H2SO4 due to the beginning of oxidation of C6H5OH. The current peak (P_{a1}) appearing at 0.96 V is attributed to the C6H5OH oxidation. The peak current (Fig.
4.2(A), curve (ii)) is several times greater than the current (Fig. 4.2(A), curve (i)) present at 0.96 V in 0.5 M H₂SO₄, thus suggesting the occurrence of C₆H₅OH oxidation on the PEDOT/SS electrode.

Fig. 4.2. (A) Cyclic voltammograms in 0.5 M H₂SO₄ (i) and 0.01 M C₆H₅OH + 0.5 M H₂SO₄ (ii) at 10 mV s⁻¹ of PEDOT/SS electrodes; and (B) successive cyclic voltammograms in 0.01 M C₆H₅OH + 0.5 M H₂SO₄ at 10 mV s⁻¹ of PEDOT/SS electrode. Arrows on the curves indicate increasing sweep numbers (charge passed for PEDOT deposition = 0.7 C cm⁻²).

Successive cyclic voltammograms of a PEDOT/SS electrode recorded in 0.01 M C₆H₅OH + 0.5 M H₂SO₄ at 10 mV s⁻¹ are shown in Fig. 4.2(B). Voltammograms of bare Pt electrode was also recorded under similar conditions for comparison (Fig. 4.3). In the first sweep of PEDOT/SS electrode, very pronounced anodic peak (Pa₁) appeared at 0.96 V in the forward potential sweep (Fig. 4.2(B)). As stated previously (Fig. 4.2(A)), this peak is attributed to the oxidation of phenol resulting in the formation of phenoxy radical [13]. There is an
increase in current at potentials 1.0 V due to the oxidation of H₂O, and S[OH•] (Reaction 4.1).

Fig. 4.3. Cyclic voltammetry of Pt electrode in 0.5 M H₂SO₄ + 0.01 M phenol at sweep rate of 10 mV s⁻¹.

is expected to be formed at this stage. It is noticed that corresponding to Pₐ₁, there is no cathodic peak during the reverse sweep. It is likely that phenoxy and hydroxyl radicals generated by electron-transfer steps (Reactions 4.1 and 4.2, respectively) combine rapidly to produce the products shown in Reactions 4.3 to 4.6. As a result, a cathodic current peak corresponding to the anodic peak Pₐ₁ is absent. However, a small cathodic peak (Pₑ) appears
at about 0.38 V. In the second cycle, a new anodic peak (P_a) starts developing at about 0.45 V, the peak P_a1 decreases in height and the peak P_c increases. On further repetition of the potential sweeps, there is a gradual decrease in peak current of P_a1, and a gradual increase in currents of both P_a and P_c peaks (Fig. 4.2(B)). These features were completely absent when a bare SS electrode was cycled in 0.01 M C_6H_5OH + 0.5 M H_2SO_4 electrolyte. In the case of Pt electrode, the peak P_a1 appeared at 0.93 V due to the formation of phenoxy radical in the first sweep. In the subsequent sweep, there was a substantial decrease in current of peak P_a1 and the other peaks P_a and P_c did not evolve clearly, unlike the data of PEDOT/SS electrode (Fig. 4.2(B)). These results suggest that the electrooxidation of phenol occurs on PEDOT coated on SS substrate.

A comparison of cyclic voltammetric data of PEDOT/SS (Fig. 4.2(B)) and Pt electrodes (Fig 4.3) clearly reveals the superiority of the PEDOT/SS electrode over the Pt electrode towards electrooxidation of phenol. Firstly, the peak current of P_a1 of the first sweep is nearly 60 times greater for the PEDOT/SS electrode than the Pt electrode. Secondly, there is a sudden collapse of peak height of P_a1 for the Pt during the second sweep. On the other hand, there is a gradual decrease of height of P_a1 for the PEDOT/SS electrode on repeated potential cycles. Failure of Pt for continuous faradaic oxidation of phenol due to surface passivation is also reported by Al-Maznai and Conway [35]. Similar to the comparison made in the present study between Pt and PEDOT/SS electrodes for oxidation of phenol, comparative studies are reported by Heras et al. [31] between Pt and PEDOT/Pt electrodes. The behavior of Pt is identical in both studies. However, the fouling effect is less for PEDOT/SS electrode than for PEDOT/Pt electrode [31]. There is about 70% decrease in peak current between the first and second sweeps for PEDOT/Pt electrode.
[35], whereas it is only 18% for PEDOT/SS electrode in the present study (Fig. 4.2(B)). Other electrode materials also experience fast fouling due to the formation of polyoxyphenylene. In cyclic voltammograms of boron doped diamond electrode in 0.0025 M C₆H₅OH + 1 M HClO₄, for instance, an anodic peak corresponding to the oxidation of C₆H₅OH was observed [28]. As the number of cycles increased, the anodic current peak decreased, the anodic current peak decreased until almost zero after about five cycles [28]. Another significant feature in the present study is that the peaks Pₐ and Pₖ increase on repeated cycling of the PEDOT/SS electrode, whereas such a feature is absent in the case of Pt electrode. The variations of peak currents (I) of Pₐ₁, Pₐ and Pₖ of the PEDOT/SS electrode with cycle number are shown in Fig. 4.4. There is a gradual decrease of Iₚₐ₁ during the first six potential sweeps and thereafter there is a marginal decrease. Similarly Iₚₖ and Iₚₐ increase noticeably during the first six sweeps followed by a marginal increase thereafter.

The greater peak current of Pₐ₁ on the PEDOT/SS electrode in comparison with the Pt electrode suggest that PEDOT surface as well as its porous nature are favorable for formation of phenoxy radical, which undergoes adsorption (Reaction 4.2). A sudden decrease in Iₚₐ₁ for Pt indicates that the Pt surface is covered with polyoxyphenylene film in the first sweep itself. This result suggests that the Pt surface favors oxidation of phenoxy radical through the pathway shown in Reaction (4.6). However, a gradual decrease of Iₚₐ₁, as well as a gradual increase of Iₚₐ and Iₚₖ (Fig. 4.4) for the PEDOT/SS electrode suggest that the oxidation of phenoxy radical proceeds via both routes shown in Reactions (4.3) and (4.6). The pair of peaks Pₐ and Pₖ is attributed to the quasi-reversible behavior of hydroquinone/benzoquinone (H₂Q/Q), Q being formed in Reaction (4.3).
Fig. 4.4. Variation of peak currents of phenol oxidation ($I_{pa1}$), reduction of benzoquinone ($I_{pc}$) and oxidation of hydroquinone ($I_{pa}$) on PEDOT/SS electrode in 0.01 M $C_6H_5OH + 0.5 M H_2SO_4$ (charge passed for PEDOT deposition = 0.7 C cm$^{-2}$).

The presence of the $H_2Q/Q$ redox couple was confirmed by the addition of $H_2Q$ externally to the electrolyte of 0.01 M $C_6H_5OH + 0.5 M H_2SO_4$. Cyclic voltammograms of PEDOT/SS electrode recorded after adding $H_2Q$ in different concentrations are presented Fig. 4.5. For recording these voltammograms, PEDOT/SS electrode was first subjected to 10 cycles in 0.01 M $C_6H_5OH + 0.5 M H_2SO_4$ in the potential range 0 to 1.05 V to get the data shown in Fig. 4.2(B), followed by cycling in the range from 0 to 0.85 V after the addition of required...
quantity of H₂Q. There is a linear increase of I_{pa} and I_{pc} with concentration of H₂Q, which was added to the electrolyte (not shown). This study confirms the formation of benzoquinone.

![Cyclic voltammograms of PEDOT/SS electrode in 0.01 M C₆H₅OH + 0.5 M H₂SO₄ at 2 mV s⁻¹ with different concentrations of hydroquinone added to the electrolyte after ten sweeps (charge passed for PEDOT deposition = 0.7 C cm⁻²).](image)

*Fig. 4.5. Cyclic voltammograms of PEDOT/SS electrode in 0.01 M C₆H₅OH + 0.5 M H₂SO₄ at 2 mV s⁻¹ with different concentrations of hydroquinone added to the electrolyte after ten sweeps (charge passed for PEDOT deposition = 0.7 C cm⁻²).*

In another experiment, subsequent to cycling of the PEDOT/SS electrode in 0.01 M C₆H₅OH + 0.5 M H₂SO₄ for 10 consecutive sweeps at 10 mV s⁻¹ between 0 to 1.05 V, the potential range was reduced to 0 and 0.85 V and cycled at several sweep rates ranging from
2 to 100 mV s\(^{-1}\). In the reduced potential range, oxidation of phenol was absent and the effect of sweep rate was studied only on the H\(_2\)Q/Q redox couple. With increasing sweep rate, the anodic and cathodic peak currents were found to increase (Fig. 4.6), where the data for sweep rates from 2 to 20 mV s\(^{-1}\) are shown. At sweep rates higher than 20 mV s\(^{-1}\), the peaks were broad and therefore these voltammograms are not presented in Fig. 4.6. As the

![Cyclic voltammograms](image)

**Fig. 4.6.** Cyclic voltammograms of PEDOT/SS electrode in 0.01 M C\(_6\)H\(_5\)OH + 0.5 M H\(_2\)SO\(_4\) in the range of 0 - 0.85 V vs. SCE at different scan rates after 10 potentiodynamic sweeps in the range of 0 – 1.05 V vs. SCE. Shown in the inset is cyclic voltammogram in 0.5 M H\(_2\)SO\(_4\) at 5 mV s\(^{-1}\) after stirring the electrolyte for 30 minutes (charge passed for PEDOT deposition = 0.7 C cm\(^{-2}\)).
separation of anodic and cathodic peak potentials ($\Delta E_p$) is 117 mV at a low sweep rate (e.g. 2 mV s$^{-1}$) and $\Delta E_p$ increases with the sweep rate, the process is considered to be quasi-reversible [37]. Furthermore, the electrolyte was stirred for 30 min and voltammograms were recorded in the potential range of 0 to 0.85 V. The present voltammograms recorded were exactly identical to those obtained before stirring the electrolyte. Then, the electrode was taken out from the solution, washed thoroughly with the supporting electrolyte (0.5 M H$_2$SO$_4$) and cyclic voltammograms were recorded in the supporting electrolyte in the absence of phenol. Cyclic voltammograms were again reproduced (Fig. 4.6 inset). These experiments reveal that H$_2$Q and Q are strongly adsorbed on the porous PEDOT film on SS substrate, within the porous matrix. It is also possible that benzoquinone moiety could be attached to polyoxyphenylene and therefore free benzoquinone is not present in the electrolyte.

![Fig. 4.7. Scanning electron micrographs of PEDOT/SS electrode (A) before and (B) after subjecting the electrode for phenol oxidation for ten repetitive potential sweeps (charge passed for PEDOT deposition = 0.7 C cm$^{-2}$).](image-url)
Morphology of PEDOT was examined under scanning electron microscope. SEM images before and after subjecting a PEDOT/SS electrode for phenol oxidation for ten successive potential sweeps are shown in Fig. 4.7. It is seen that both micrographs comprise of globules and the morphology remains almost the same. It is thus inferred that the morphology of PEDOT is not affected by the phenol oxidation and also by adsorption of polyoxyphenylene.

4.3.2. The effect of phenol concentration: Figure 4.8 shows the first cycle of voltammogram of PEDOT/SS electrodes in 0.5 M H₂SO₄ containing phenol at various concentrations. A fresh PEDOT/SS electrode was used for recording each voltammogram. The increase in peak current at 0.9 - 1.0 V range is attributed to an increase in phenol oxidation rate due to increase in concentration. An increase in cathodic peak current at around 0.4 V - 0.6 V is also observed with concentration. This is due to an increased quantity of benzoquinone produced with an increase in phenol concentration. A linear increase in peak current density (I_{pa1}) with an increase in phenol concentration ranging from 0.005-0.5 M is observed (Fig. 4.9). These results further support that PEDOT/SS electrodes facilitate electrooxidation of phenol. Analytical application of PEDOT coated Pt for analysis of phenol was studied by Heras et al. [31] Square wave voltammetry was employed for high sensitivity and low analysis times. There was a good linear dependence of current on phenol concentration in the range 1 – 50 ppm.
4.3.3. The effect of sweep rate: Cyclic voltammograms were recorded for PEDOT/SS electrodes in 0.01 M C₆H₅OH + 0.5 M H₂SO₄ at different sweep rates (Fig. 4.10). During these experiments also, a fresh PEDOT/SS electrode was used for recording each voltammogram. There is an increase in peak current density with an increase in sweep rate.
Fig. 4.9. Voltammetric peak current density ($I_{pa1}$) of PEDOT/SS electrode at 10 mV s$^{-1}$ as a function of concentration of phenol. Standard deviation of the linear plot is 0.29 mA cm$^{-2}$ (charge passed for PEDOT deposition = 0.7 C cm$^{-2}$).

Furthermore, the peak potential ($E_p$) increases and merges with the current corresponding to oxidation of H$_2$O with increasing sweep rates. At sweep rates higher than 40 mV s$^{-1}$, the peak $P_{a1}$ was not clearly observed and the results presented in Fig. 4.10 are only for the sweep rates between 2 and 40 mV s$^{-1}$. 

\[ y = 2.76 + 64.52x \]
\[ R^2 = 0.99976 \]
Fig. 4.10. Cyclic voltammograms of PEDOT/SS electrode in 0.01 M C₆H₅OH + 0.5 M H₂SO₄ at a sweep rate of 2 (i), 5 (ii), 10 (iii), 20 (iv) and 40 (v) mV s⁻¹. Charge passed for PEDOT deposition = 0.7 C cm⁻².

From the shift of \( E_p \) in positive direction with increasing sweep rate, it is further concluded that the electron-transfer step corresponding to the formation of phenoxy radical from phenol is an irreversible process. The relationship between \( E_p \) and sweep rate \( \nu \) for an irreversible reaction is given by Eq. (4.7) [36,37].

\[
E_p = k + \left( \frac{2.3 \, R \, T}{2 \, n_a \, \alpha_a \, F} \right) \log \nu
\]  

(4.7)
where \( k \) is a constant, \( \alpha_a \) is transfer coefficient, \( n_a \) is number of electrons transferred up to the rate determining step of the oxidation and the other symbols have their usual meanings.

The product \( (2.3 \, R \, T / (n_a \, \alpha_a \, F)) \) is equivalent to the Tafel slope, which can be evaluate from Eq. (4.7). A plot of \( E_p \) versus \( \log \nu \) is shown in Fig. 4.11. The value of slope of this plot obtained for 0.01 M phenol is 0.085 V. Thus the Tafel slope is 0.170 V for oxidation of phenol to phenoxide radical. This value of Tafel slope is greater than 0.120 V, which is
generally expected for a reversible single electron transfer reaction (assuming $\alpha = 0.5$). The higher value of Tafel slope is due to irreversible nature of the reaction and also due to adsorption of phenoxide radical on PEDOT.

4.3.4. The effect of mass of PEDOT: From the above experiments, it is clear that bare SS electrode is not suitable for the electrooxidation of phenol, but it is useful if the surface is modified with PEDOT.

Fig. 4.12. Mass of PEDOT versus charge passed for deposition at 0.90 V vs. SCE in 0.1 M $H_2SO_4 + 0.01 M$ EDOT + 0.01 M SDS.
The electronic conductivity of PEDOT is due to the transport of polarons and bipolarons along the polymer chain. Since the PEDOT deposits are porous and the roughness factor can increase with mass of the polymer, the true surface available for the heterogeneous reaction is expected to increase with an increase in polymer specific mass (mass per unit area). Several PEDOT/SS electrodes were prepared with various values of charge passed during potentiostatic deposition at 0.90 V, and mass of each electrode was measures. Specific mass as a function of charge density is shown in Fig. 4.12. It is seen that there is a linear increase in mass with increase in charge. It was possible to coat thick PEDOT films with good adhesion on SS surface due to sandblasting. We failed to deposit adherent PEDOT films on smooth SS and Pt surfaces. The average coulombic efficiency of PEDOT deposition was 82 ± 2 %. PEDOT/SS electrodes of various specific mass values were used for studying the oxidation of 0.01 M C₆H₅OH in 0.5 M H₂SO₄. Cyclic voltammograms recorded in this solution for several values of mass of PEDOT are shown in Fig. 4.13.

From the data of Fig. 4.13, a plot of peak current density (Iₚᵃ¹) versus cycle number is presented in Fig. 4.14(A) for electrodes of different specific mass values of PEDOT. For all cycles, the peak current density is lower for thinner PEDOT/SS electrodes, and it increases with an increase in mass of PEDOT. This result confirms that the PEDOT deposited on SS is porous and the oxidation of phenol takes place not only on the surface but also inside the porous polymer matrix. As the real surface available for the oxidation of phenol increases with an increase of PEDOT mass, there is an increase in peak current as shown in Fig. 4.14(B) for the first voltammogram. The linearity of peak current density versus mass (Fig. 4.14(B)) is due to a linear increase of true surface with an increase in mass of PEDOT.
Fig. 4.13. Cyclic voltammograms of PEDOT/SS electrode in 0.01 M C₆H₅OH + 0.5 M H₂SO₄ at 10 mV s⁻¹ with charges of PEDOT preparation (A) 0.2, (B) 0.4, (C) 0.7 and (D) 2 C cm⁻².
However, there is a decrease in current density with an increase in cycle number for each electrode (Fig. 4.14(A)). Nevertheless, the relative decrease in current density is less in the case of thicker PEDOT electrode (Fig. 4.14(A) inset).

4.3.5. Impedance spectroscopy: A PEDOT/SS electrode was subjected to cyclic voltammetry in 0.01 M C₆H₅OH + 0.5 M H₂SO₄ for ten sweeps to obtain the data shown in Fig. 4.2(B).

In between any two consecutive sweeps, the electrode was removed from the electrolyte, washed in 0.5 M H₂SO₄, and impedance of the electrode was measured in 0.5 M H₂SO₄ at
Fig. 4.15. (A) Nyquist impedance spectra of PEDOT/SS electrode in 0.5 M H₂SO₄ at 0.46 V vs. SCE before phenol oxidation (i), after 1 (ii), 3 (iii), 5 (iv), 7 (v), 9 (vi) and 10 (vii) potential cycles in 0.01 M C₆H₅OH + 0.5 M H₂SO₄; and (B) same as (A) but for PEDOT/SS electrode cycled in 0.5 M H₂SO₄ in the absence of C₆H₅OH (charge passed for PEDOT deposition = 0.7 C cm⁻²). Frequency values (in Hz) are given for some data points. Experimental data are presented with various symbols and simulated spectra as smooth curves.
its open-circuit potential, which was about 0.46 V. For comparison, impedance data measured in 0.5 M H₂SO₄ during cycling of PEDOT/SS electrode in 0.5 M H₂SO₄ in the absence of C₆H₅OH are also shown in Fig. 4.15(B). Spectrum (i) in Fig. 4.15 recorded before subjecting the electrode for phenol oxidation by cyclic voltammetry consists of a high frequency intercept on real axis and a semicircle in high frequency region followed by a linear segment at low frequency range.

![Graph showing variation of polymer resistance (Rp) with cycle number of PEDOT/SS electrode cycled in 0.5 M H₂SO₄ (i) and 0.01 M C₆H₅OH + 0.5 M H₂SO₄ (ii). The equivalent circuit used for fitting the impedance data of Fig. 4.15 is shown in inset. R₀ is ohmic resistance, Q₁ is constant phase element (CPE) corresponding to the double-layer capacitance and Q₂ is CPE corresponding to capacitance of PEDOT (charge passed for PEDOT deposition = 0.7 C cm⁻²).](image)

Fig. 4.16. Variation of polymer resistance (Rp) with cycle number of PEDOT/SS electrode cycled in 0.5 M H₂SO₄ (i) and 0.01 M C₆H₅OH + 0.5 M H₂SO₄ (ii). The equivalent circuit used for fitting the impedance data of Fig. 4.15 is shown in inset. R₀ is ohmic resistance, Q₁ is constant phase element (CPE) corresponding to the double-layer capacitance and Q₂ is CPE corresponding to capacitance of PEDOT (charge passed for PEDOT deposition = 0.7 C cm⁻²).
Electrochemical impedance studies of electronically conducting polymers are reported widely [38]. For instance, Nyquist impedance spectrum of PANI in aqueous electrolytes is reported to consist of a semicircle at high frequency range and a linear spike at low frequency range [39] similar to the data shown for PEDOT/SS electrode in Fig. 4.15. Analysis of impedance data of porous conducting polymers is reported by Albery et al. [40], and Pickup [41]. Their equivalent circuits are proposed on transmission line models. Accordingly, the semicircle (Fig. 4.15(A)) is due to a parallel combination of a rail of resistance ($R_p$) of the conducting polymer and a capacitance ($C$). The low frequency data points of PEDOT/SS electrode before cycling (Fig. 4.15, spectrum (i)) fall on a straight line, which is nearly parallel to the imaginary axis. This indicates capacitive behavior of the electrode at low frequency regime.

The impedance data presented in Fig. 4.15(A) and (B) were subjected to non-linear least square (NLLS) fitting with the help of Scribner Associates program and a simple electrical equivalent circuit shown in inset of Fig. 4.16. In the equivalent circuit, capacitances are replaced by constant phase elements (CPEs) because the semicircle is depressed and the low frequency linear segment is not exactly parallel to the imaginary axis. There is a good agreement between the measured impedance data and the simulated curves from the fit results (Fig. 4.15). Furthermore, $\chi^2$ value of NLLS fitting was less than $1 \times 10^{-2}$, which is an indication for a good quality of curve fitting. These observations suggest that the curve fitting procedure is satisfactory. The variation of polymer resistance ($R_p$) with cycle number obtained both in 0.01 M C$_6$H$_5$OH + 0.5 M H$_2$SO$_4$ (Fig. 4.15(A)) and also in 0.5 M H$_2$SO$_4$ in the absence of C$_6$H$_5$OH (Fig. 4.15(B)) is presented in Fig. 4.16. It is seen that the value of $R_p$ is about 1.0 $\Omega$ before subjecting the PEDOT/SS electrodes for
cycling. In the absence of C₆H₅OH, there is a gradual increase in Rₚ to about 10 Ω after four cycles and it remains nearly invariant thereafter. This indicates electrochemical stabilization of Rₚ of PEDOT requires a few potential cycles. But in the presence of C₆H₅OH, there is a substantial increase in Rₚ from beginning to the end of ten cycles and it reaches 42 Ω after tenth cycle. The greater increase in Rₚ is due to increased coverage of polyoxyphenylene, which is formed on PEDOT during each cyclic voltammetric cycle.

4.4. CONCLUSIONS

The electrochemical oxidation of phenol on SS electrode modified by PEDOT was investigated. A significant improvement in repeatability cyclic voltammetry for phenol oxidation is seen on the PEDOT/SS compared to the bare Pt electrode. A pair of additional peaks for H₂Q/Q are also characterized and confirmed by externally added H₂Q. A significant effect of specific mass of PEDOT on electrooxidation of phenol is present. There is a decrease in fouling of PEDOT with an increase in its specific mass.

4.5. REFERENCES

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Supercapacitor studies of PEDOT deposited stainless steel substrate

ABSTRACT

In the present study, PEDOT is electrochemically deposited on SS substrates for supercapacitor studies. PEDOT/SS electrodes prepared in 0.1 M H₂SO₄ in presence of a surfactant, sodium dodecylsulphate (SDS), are found to yield higher specific capacitance (SC) than the electrodes prepared from neutral aqueous electrolyte. The effects of concentration of H₂SO₄, concentration of SDS, potential of deposition and nature of supporting electrolytes used for capacitor studies on SC of the PEDOT/SS electrodes are studied. Specific capacitance values as high as 250 F g⁻¹ in 1 M oxalic acid are obtained during the initial stages of cycling. However, there is a rapid decrease in SC on repeated charge-discharge cycling. Spectroscopic data reflect structural changes in PEDOT on extended cycling.

5.1. INTRODUCTION

Electrical double-layer formed at the interface between a metallic electrode and an electrolyte has been a topic of innumerable studies in the past [2]. The electrical interface plays a crucial role in kinetics, mechanisms and applications of a variety of electrochemical reactions. The importance of the interface lays in the fact that the mode of charge-transportation changes from ionic transport in the electrolyte to electronic transport in the metallic electrode at the instance of Faradaic reactions. The electron-transfer reactions lead to many important applications of electrochemistry, which include energy storage/conversion devices such as batteries and fuel cells. Nevertheless, the electrical charges separated across the interface even in the absence of electron-transfer reactions, can also be utilized for energy through reversible non-Faradaic charge/discharge processes [3].

The double-layer capacitance ($C_{dl}$) is defined by Eq. (5.1).

$$C_{dl} = \frac{dq}{dE}$$

(5.1)

where $q$ refers to charge on the metal and $E$ the electrode potential. The energy ($G$) associated with the $C_{dl}$ is according to Eq. (5.2):

$$G = C_{dl} \frac{E^2}{2}$$

(5.2)

Studies on double-layer capacitance, which is due to accumulated excess charges at the interface, for energy storage and conversion process have been investigated in recent years [4]. Double-layer charging and discharging processes occur at faster rates than the electron transfer reaction rates. This fact led to the discovery of electrical double-layer (EDL) capacitors or electrochemical supercapacitors, whose properties differ with those of batteries, for energy-storage and conversion. Batteries are high-energy and low-power devices, where as supercapacitors are low-energy and high-power devices. The faster rate
of double-layer charging-discharging processes than the Faradaic reactions reflects in realization of higher power in supercapacitor than in batteries. Supercapacitors employing high surface area carbon powders attracted interest in the early stages of the discovery. Subsequently, various other electrode materials such as transition metal oxides, electronically conducting polymers, etc. have been studied [5]. In these materials, in addition to the double-layer capacitance, pseudocapacitance involved in Faradaic reactions also contribute to capacitance.

For supercapacitor studies, conducting polymers are more interesting than carbons and transition metal oxides due to the following merits [6]: (i) conducting polymers have higher electronic conductivity than the metal oxides, (ii) they are cheaper than some oxides, e.g., RuO$_2$.xH$_2$O, (iii) they can be prepared by using electrochemical methods in a well controlled manners, (iv) electrochemical deposition ensures coherence and adherence to the current collecting substrates, and (v) electrochemical deposition avoids the procedures of electrode-fabrication with suitable binders. Among the conducting polymers, PEDOT is interesting as it is insoluble in most of the solvents, exhibits a high conductivity, changes in color due to applied potential, is stable in the doped state and exhibits reduced band-gap. Studies on supercapacitor properties of PEDOT are rarely reported [7-11]. Ghosh and Inganas [7] have reported electrochemical characterization of PEDOT, doped with excess polystyrene-sulphonate (PSS) in the form of a hydrogen conducting network. Due to high ionic mobility in the material, the electrochemical processes were reportedly not limited by ionic diffusion into the polymer, but by the resistance in the conducting network. As the hydrogel showed large capacitance and it was subjected to rapid charge-discharge processes, application of the polymer coated gold electrodes for supercapacitors was
envisaged. However, no studies related to supercapacitors were reported in this publication. In another study [8], PEDOT-PSS films (thickness: 1 μm) were electrochemically grown on gold electrodes, electrochemical quartz crystal microbalance (EQCM) and electrochemical impedance spectroscopic studies were carried out. From impedance studies in a non-aqueous electrolyte, a capacitance value of 25 F cm⁻³ is reported. Assuming the density [12] of the film equal to 1.45 g cm⁻³, this value leads to a specific capacitance (SC) value of about 17 F g⁻¹. This is not an attractive value for supercapacitor applications. Several thiophene derivatives were polymerized by oxidation of the respective monomers using a Fe³⁺ salt, the corresponding polymers were studied for capacitor characteristics [9]. In a non-aqueous electrolyte, a SC value of 103 F g⁻¹ were reported. Electrochemical properties of composites prepared from PEDOT and multiwalled carbon nanotubes were investigated for supercapacitor application [10]. Aqueous as well as non-aqueous electrolytes were employed for capacitor studies. Both chemical oxidation and electrochemical oxidation of EDOT in non-aqueous solutions were carried out for preparation of PEDOT. The values of SC ranged from 60 to 160 F g⁻¹. Ryu et al. [11] reported capacitance studies of PEDOT and carbon composites in a non-aqueous electrolyte. A maximum SC value of 56 F g⁻¹ is reported. Polymerization of EDOT with a Fe³⁺ salt in an aqueous medium was performed by subjecting the reaction mixture to ultrasonic irradiation. Pressed pellets of PEDOT with a binder were used as electrodes and capacitance values up to about 100 F g⁻¹ in a 1 M H₂SO₄ were reported.

From the above review of literature on supercapacitor studies of PEDOT, the following observations are made: (i) PEDOT is commonly prepared in non-aqueous media, (ii) it is generally prepared in a chemical oxidation route and then electrodes are fabricated
using a binder or as pellets, (iii) electrochemical preparation is carried out on noble-metal substrates, (iv) capacitance studies are also commonly made in non-aqueous electrolytes and (v) specific capacitance values are low. It is clear that there exists a scope for various investigations to employ aqueous electrolytes for both preparations of PEDOT and capacitor characterization studies, to use non-platinum metals as current collecting substrates for electrochemical preparation of PEDOT and also to obtain higher specific capacitance.

In the present study, PEDOT was deposited on stainless steel (SS) substrate from an aqueous solution of the monomer consisting of a surfactant. Several experimental conditions during the electrodeposition of PEDOT films and also during the studies concerning supercapacitor properties were varied with an aim to arrive at the appropriate experimental conditions to obtain high specific capacitance. A value of specific capacitance of 250 F g$^{-1}$ was obtained during the initial stages of an extended charge-discharge cycle-life test.

5.2. EXPERIMENTAL

PEDOT was electrochemically deposited on sand-blasted SS (geometric area = 1.4 cm$^2$) as described in Section 2.2.

A Sartorius balance of model CP225D-OCE with 0.01 mg sensitivity was used for weighing the electrodes. The scanning electron microscope (SEM) images were recorded using FEI scanning electron microscope model Quanta 200 or Sirion. Cyclic voltammetry and galvanostatic charge-discharge cycling were carried out using a potentiostat/galvanostat EG&G PARC model Versastat II or Solartron model 1286. For measuring SC, an electrode was subjected to 10 galvanostatic charge-discharge cycles, and the SC was calculated from
the second charge-discharge cycle, unless otherwise stated. UV-Visible and FTIR spectra were recorded by Perkin Elmer model Lambda 35-UV/VIS spectrometer and Bruker FT-IR model 66V spectrometer, respectively. For UV-Visible spectra, PEDOT was electrochemically deposited on indium tin oxide (ITO) coated glass plate. For recording IR spectra, PEDOT was scrapped carefully from the SS substrate, the powder was mixed with KBr and pressed into pellets. All experiments were conducted in an air-conditioned room at 22 ± 1 °C.

5.3. RESULTS AND DISCUSSION

5.3.1. Electrochemical oxidation: As described in Chapter 2, electrochemical oxidation of the monomer could be accomplished by galvanostatic, potentiostatic and potentiodynamic methods. Preliminary experiments were carried out by depositing galvanostatically (c.d: 2-5 mA cm⁻²), potentiostatically (E = 0.8-1.2 V) and potentiodynamically in the potential range of 0-1.2 V (sweep rate = 2-50 mV s⁻¹) and measuring capacitance. It was found that the potentiostatically prepared PEDOT/SS electrodes yielded higher SC. This may be because of difference in morphology of PEDOT films obtained methods. Therefore, the experiments were carried out with potentiostatically prepared PEDOT/SS electrodes.

5.3.2. The influence of concentration of surfactant and potential range: The influence of concentration of SDS on the rate of electrodeposition was studied. PEDOT/SS and PEDOT/Pt electrodes were prepared in 0.01 M EDOT + 0.1 M H₂SO₄ with varying concentration of SDS in 0-0.50 M range at 0.9 V for 300 s. The quantity of charge passed in each solution was taken as a measure of the rate of polymerization. A plot of charge density (q) against the concentration of SDS is shown in Fig. 5.1. In the absence of the surfactant, the values of q obtained for Pt and SS are about 60 and 105 mC cm⁻², respectively. Higher
Fig. 5.1. Amount of charge passed in 300 s after stepping the electrode potential to 0.9 V vs. SCE as a function of SDS concentration for the electropolymerization of EDOT on SS (●) and Pt (○) in electrolyte of 0.1 M H₂SO₄ + 0.01 M EDOT + 0.01 M SDS. The horizontal lines represent the polymerization charges for Pt and SS in the absence of SDS.

value of q for SS is due to greater surface area, which resulted from the sand blasting. The values of q for both Pt and SS increase with an increase in concentration of SDS from 0.002 M to 0.01 M. Further increase in SDS concentration results in a decrease in q. Thus maximum q values are obtained at 0.01 M of SDS. The increase in charge of SS electrode is from 105 to 320 mC cm⁻² when concentration of SDS is increased from 0 to 0.01 M in the electrolyte. The corresponding values of q for Pt are 60 to 250 mC cm⁻². At all concentrations of SDS, the rate of deposition of PEDOT on SS is greater than that of Pt,
due to greater surface area. The rates of deposition on both SS and Pt increase by about 3-4 times due to the presence of 0.01 M SDS. The influence of concentration of SDS on polymerization rate of EDOT may be explained on the basis of formation of complex between micells of SDS and EDOT $^+$ cation free radicals [12]. The critical micellar concentration (CMC) of SDS in water is 0.008 M [13]. There is a substantial decrease in CMC if the medium is changed to dilute H$_2$SO$_4$. The CMC of SDS in 0.5 M H$_2$SO$_4$ is 0.07 mM, which is about 100 times less than the CMC in water. Thus at all concentration of SDS used in the present work, micelle formation exists, and the micelles tend to accumulate on the electrode/electrolyte interface. As the concentration of SDS increases from 0.001 M to 0.01 M, the surface concentrations of micelle-EDOT $^+$ cation radical concentration increases, which facilitates increased rate of PEDOT film formation. By further increasing the concentration of SDS, which exceeds the concentration of the monomer, it is likely that the surface concentration of uncomplexed micells increases. As a result, the rate of PEDOT formation decreases.

The data in Fig. 5. 2 show that there is a marginal decrease in SC by increasing the potential from 0.8 V to 1.0 V. However, there is a drastic decrease of SC from about 160 F g$^{-1}$ for PEDOT/SS electrode prepared at 1.0 V to about 90 F g$^{-1}$ for the electrode prepared at 1.1 V. This is probably due to powdery PEDOT deposits formed at potentials $> 1.0$ V. In view of obtaining a high capacitance and also preparing the PEDOT at a reasonably fast rate, 0.9 V was chosen as the suitable potential for further studies.
5.3.3. Capacitance studies in HClO$_4$+ NaClO$_4$ solutions: Capacitance properties of PEDOT are studied and reported either in an organic medium or a dilute H$_2$SO$_4$ aqueous medium. The specific capacitance values varied from study to study, and a maximum value of $\sim$ 103 F g$^{-1}$ is reported [14]. The charges involved in doping/un-doping processes with in the conducting polymers strongly depend on the nature of the electrolyte, and accordingly SC values also differ from electrolyte to electrolyte. For instance, a mixed electrolyte of HClO$_4$ + NaClO$_4$ was reported to be a better electrolyte than a few other electrolytes for obtaining stable capacitance values of polyaniline [15]. Accordingly, in the present studies also, 0.1 M HClO$_4$ + 0.3 M NaClO$_4$ mixed electrolyte was employed for electrochemical characterization of PEDOT/SS electrodes. Capacitance behavior of PEDOT/SS electrodes
was studied by subjecting them to cyclic voltammetry and galvanostatic charge-discharge cycling. As a result of several preliminary studies, a potential window of 1.4 V from -0.5 to 0.9 V was found to be appropriate for capacitance studies. In this region of potential, the cyclic voltammograms recorded in 0.1 M HClO$_4$ + 0.3 M NaClO$_4$ mixed electrolyte is broad as shown in Fig. 5.3. A broad and rectangular shape of the voltammogram is an indication for capacitive behavior of an electrochemically active material. Galvanostatic

![Cyclic voltammogram recorded at a scan rate of 10 mV s$^{-1}$ of PEDOT/SS SS in 0.1 M HClO$_4$ + 0.3 M NaClO$_4$ mixed electrolyte. Mass of the PEDOT was 0.6 mg cm$^{-2}$.](image-url)
Fig. 5.4. galvanostatic charge-discharge curve at 0.7 mA cm$^{-2}$ (1.17 A g$^{-1}$ of PEDOT/SS in 0.1 M HClO$_4$ + 0.3 M NaClO$_4$ mixed electrolyte. Mass of the PEDOT was 0.6 mg cm$^{-2}$.

charge-discharge curves of PEDOT/SS electrode are presented in Fig. 5.4. The potential of the electrode increases linearly during the charging process and it decreases linearly during the discharge process. A linear variation of the electrode potential during charge-discharge cycling is another indication of capacitive behavior. The value of SC was calculated from the discharge data using Eq. (5.3).

$$SC = \frac{I \ t}{(1.4 \ m)} \quad (5.3)$$

where I is the discharge current, t is discharge time and m is mass of PEDOT. The value of SC obtained from the data of second cycle in Fig. 5.4 is 176 F g$^{-1}$. This value is greater than 103 F g$^{-1}$ generally reported for PEDOT in the literature [8]. The experimental
conditions in the present work are conducive for obtaining higher values of SC. The variation of SC during the initial 10 charge-discharge cycles is shown in Fig. 5.5. There is a substantial decrease in SC from 175 F g\(^{-1}\) obtained in the second cycle to 120 F g\(^{-1}\) in the tenth cycle. A considerable decrease in SC of PEDOT based polymer is reported in the literature on repeated charge-discharge cycling [8].

5.3.4. Influence of concentrations during preparation of PEDOT: It was intended to examine the influence of concentration of H\(_2\)SO\(_4\) and SDS used for preparation of PEDOT on SC. Several electrodes were prepared by varying the
concentration of H₂SO₄ from 0.1 to 2 M and keeping the concentration of SDS at 0.01 M. For each electrode, the mass of the PEDOT was 0.6 mg cm⁻². The electrodes were subjected to charge-discharge cycling in 0.1 M HClO₄ + 0.3 M NaClO₄ electrolyte, and the variation of SC with H₂SO₄ concentration is shown in Fig. 5.6. There is a steady decrease in SC from 175 F g⁻¹ for the PEDOT/SS electrode prepared in 0.1 M H₂SO₄ to about 120 F g⁻¹ for the electrode prepared in 2 M H₂SO₄. Thus 0.1 M H₂SO₄ was used for preparing PEDOT/SS electrodes for rest of the studies. In a similar way, PEDOT/SS electrodes were prepared in 0.1 M H₂SO₄ by varying the concentration of SDS from 0.001 M to 0.05 M, and SC values were measured in 0.1 M HClO₄ + 0.3 M NaClO₄ mixed electrolyte. The variation of SC

Fig. 5.6. Variation of specific capacitance of PEDOT with concentration of H₂SO₄ used as the supporting electrolyte for PEDOT deposition (mass of PEDOT = 0.6 mg cm⁻²).
with concentration of SDS is shown in Fig. 5.7. A maximum SC of 176 F g$^{-1}$ is obtained when SDS concentration is 0.01 M. There is a decrease in SC either by decreasing or increasing the concentration of SDS from 0.01 M.

From SEM micrographs (Fig. 5.7), it is seen that there is a considerable change in morphology by increasing the concentration of SDS. The PEDOT/SS electrode prepared in 0.1 M H$_2$SO$_4$ + 0.05 M SDS has smooth surface (Fig. 5.8) and the electrode prepared in 0.1
M H$_2$SO$_4$ + 0.01 M SDS has globules indicating higher surface area (Fig. 5.8). Thus a decrease in porosity and surface area by increasing the concentration of SDS accounts for a decrease in SC of PEDOT/SS electrodes (Fig. 5.7).

![SEM images of PEDOT/SS electrodes deposited in presence of (A) 0.01 M and (B) 0.05 M SDS at 0.9 V vs. SCE.]

Fig. 5.8. SEM images of PEDOT/SS electrodes deposited in presence of (A) 0.01 M and (B) 0.05 M SDS at 0.9 V vs. SCE.

5.3.5. Influence of pH during capacitance studies: The influence of pH of HClO$_4$ + NaClO$_4$ on SC was also examined. For this purpose 0.1 M HClO$_4$ + 0.3 M NaClO$_4$ was prepared
and pH was adjusted to the required value by adding dilute NaOH. The variation of SC of a PEDOT/SS electrode with pH of the electrolyte is shown in Fig. 5.9. There is a linear decrease in SC with pH of the electrolyte. This is due to the decrease in electronic conductivity of the polymer with increase in the supporting electrolyte.

Fig. 5.9. Dependence of specific capacitance of PEDOT/SS electrode on pH of NaClO₄ electrolyte. The mass of the material was 0.6 mg cm⁻². Charge-discharge current: 0.7 mA cm⁻² (1.17 A g⁻¹).

5.3.6. Capacitance studies in oxalic acid electrolytes: Subsequent to the above studies, it was intended to examine the effect of nature of the electrolyte on SC of PEDOT with an intention to obtain a maximum SC. Results of preliminary experiments on various
supporting electrolytes suggested that an aqueous solution of oxalic acid produced higher capacitance values than the 0.1 M HClO₄+0.3 NaClO₄ mixed electrolyte.

Fig. 5.10. Galvanostatic charge-discharge curve at 0.7 mA cm⁻² of PEDOT/SS in 1 M oxalic acid. Mass of the PEDOT was 0.6 mg cm⁻².

A broad voltammogram with a wide gap between the cathode and anodic parts, similar to the voltammogram recorded in 0.1 M HClO₄+0.3 NaClO₄ (Fig. 5.3) suggested that PEDOT exhibits capacitance behaviour in 1 M oxalic acid solution also. The linearity of charge-discharge curves (Fig. 5.10) without noticeable IR drop between -0.5 to 0.75 V indicates suitability of 1 M oxalic acid medium for capacitor studies of PEDOT. However, the upper limit of potential in 1 M oxalic acid was only 0.75 V against 0.9 V in 0.1 M
HClO$_4$ + 0.3 NaClO$_4$ electrolytes. The charge-discharge curves deviated from the linearity at potentials greater than 0.75 V in 1 M oxalic acid, and therefore the upper potential limit was fixed at 0.75 V. It is likely that oxidation of oxalic acid occurs at $>0.75$ V thus causing deviation from linearity of potential-time data. From the second cycle of the data shown in Fig. 5.10, a value of 180 F g$^{-1}$ is obtained for SC of PEDOT/SS electrode. This value is nearly the same as the value of SC obtained in 0.1 M HClO$_4$ + 0.3 NaClO$_4$ electrolyte in spite of the fact that the potential range is 1.25 V in 1 M oxalic acid against 1.4 V in 0.1 M

Fig. 5.11. variation of SC during 10 charge-discharge cycles of PEDOT/SS in 1 M oxalic acid. Mass of the PEDOT was 0.6 mg cm$^{-2}$. 
HClO$_4$+ 0.3 NaClO$_4$ electrolyte. Nevertheless, the stability of SC on repeated charge-discharge cycling is slightly better in oxalic acid (Fig. 5.11) than in 0.1 M HClO$_4$+ 0.3 NaClO$_4$ (Fig. 5.5). Therefore, the rest of the studies were conducted in oxalic acid electrolytes.

In an attempt to optimize the concentration of oxalic acid for obtaining the highest possible SC, experiments were conducted in the concentration range from 0.1 to 1.0 M. The value of SC increased with an increase in concentration of oxalic acid as shown in Fig. 5.12.

![Graph showing the effect of concentration of oxalic acid on the specific capacitance of PEDOT/SS electrode. The mass of the PEDOT was 0.6 mg cm$^{-2}$.](image)

*Fig. 5.12. The effect of concentration of oxalic acid on the specific capacitance of PEDOT/SS electrode. The mass of the PEDOT was 0.6 mg cm$^{-2}$.***
A maximum capacitance was obtained in 1.0 M oxalic acid. As the solubility of oxalic acid in water is limited close to about 1.0 M, experiments could not be carried out in oxalic acid solutions of higher concentrations.

5.3.7. Influence of thickness of PEDOT: Although the electrodeposited PEDOT films are found to have globular morphology (Fig. 5.8(A)) the porosity does not exist throughout the thickness of the film. Consequently, the electrolyte cannot penetrate into the interior of the film.

![Graph showing dependence of specific capacitance of PEDOT on specific mass of PEDOT](image)

**Fig. 5.13.** Dependence of specific capacitance of PEDOT in 1 M oxalic acid on its specific mass.

In order to arrive at the appropriate thickness for obtaining a maximum possible capacitance, PEDOT/SS electrodes with varying mass of PEDOT were prepared and SC
was measured in 1.0 M oxalic acid solution (Fig. 5.13). The SC increases from about 180 F g\(^{-1}\) at 0.6 mg cm\(^{-2}\) of PEDOT to about 250 F g\(^{-1}\) at 1.5 mg cm\(^{-2}\). On further increasing of specific mass, there is a decrease in SC to about 110 F g\(^{-1}\) at 5 mg cm\(^{-2}\), due to decreased in efficiency of utilization of the active material. Thus, the appropriate specific mass of PEDOT is 1.5 mg cm\(^{-2}\) to obtain a maximum value of SC under the present experimental conditions.

5.3.8. Extended cycling and impedance measurements: PEDOT/SS electrodes were subjected to an extended charge-discharge cycling and the cycle-life data are shown in Fig. 5.14.

![Graph showing cycle-life data](image)

*Fig. 5.14. Cycle-life data at 0.7 mA/cm\(^2\) of PEDOT/SS electrode prepared in presence (i) and in absence (ii) of the surfactant. In both cases, the specific mass of the material was 1.43 mg cm\(^{-2}\).*
For the purpose of comparison, data obtained with a PEDOT/SS electrode prepared without SDS are also shown in Fig. 5.14. Although the initial value of SC is as high as 250 F g$^{-1}$ (curve (i) in Fig. 5.14), there is a steep fall in SC within about 50 charge-discharge cycles. Thereafter, the SC remains nearly constant at about 100 F g$^{-1}$. The SC of the electrode prepared without SDS (curve (ii) in Fig. 5.14) is lower throughout the test. During the extended cycle-life test (Fig. 5.14 curve (i)) electrochemical impedance of the PEDOT/SS electrode was measured at a few intervals of cycling.

The Nyquist data of impedance recorded at 0, 200, 500, and 1000 cycles are shown in Fig. 5.15. All plots contain semicircles at high frequency region. The semicircle represents the resistance of the polymer and the linear spike corresponds to diffusion-limited Warburg or pseudocapacitance of the polymer [16]. The diameter of the semicircle, which is equal to the resistance of the polymer, increase from 0.75 Ω before cycling to 11 Ω after 200 cycles, 25 Ω after 500 cycles and 46 Ω after 1000 cycles. Thus there is a rapid increase in resistance of PEDOT (nearly 60 times) on subjecting to 1000 charge-discharge cycles.

In a separate experiment, surface morphology of a PEDOT/SS electrode was examined after it was subjected to 500 charge-discharge cycles. The morphology of cycled electrode remained the same as an un-cycled electrode, and it was similar to the SEM shown in Fig. 5.8. Thus changes occurring in electrochemical properties of PEDOT film due to charge-discharge cycling are not related to its morphological changes.

5.3.9. Spectroscopy: The FT-IR spectra of PEDOT is shown in Fig. 5.16 (curve (i)). The bands around 1348 and 1514 cm$^{-1}$ are due to stretching of C-C and C=C in thiophene ring and stretching of thiophene ring, respectively [17]. Bands at around 1186, 1140 and 1053
Fig. 5.15. Nyquist impedance spectra of PEDOT/SS electrode in 1 M oxalic acid at 0.5 V (open circuit potential) after (A) 0, (B) 200, (C) 500 and (D) 1000 charge-discharge cycles (Fig. 5.14 curve (i)). Frequency (Hz) values for some data points are indicated.

Vibrations cm\(^{-1}\) are originated from stretching of C-O-C bond in the ethylene dioxy group. Vibrations of C-S bond in the thiophene ring are also seen 977, 833 and 682 cm\(^{-1}\). In Fig. 5.16, the FT-
IR spectra after 100 cycles (curve (ii)) and 1000 cycle (curve (iii)) are also shown. With the increased cycling, there is shift of the 1186 cm\(^{-1}\) to higher wave numbers, while there is no change in the rest of the main bands.

![FT-IR spectrum of PEDOT](image)

*Fig. 5.16. FT-IR spectrum of PEDOT before cycling (i), after 100 cycle (ii) and after 1000 cycle (iii).*

For the purpose of recording UV-Vis spectra, a thin layer of PEDOT was deposited on an ITO coated glass plate and the electrode was subjected to charge-discharge cycling. The electrode was removed from the oxalic acid electrolyte, washed, dried and spectra were recorded at periodic intervals of cycling. The spectra are shown in Fig. 5.17(A). The band
Fig. 5.17. (A) The effect of cycling on UV-Vis spectra of PEDOT / ITO glass of before cycling (i), after 100 (ii), after 200 (iii), after 300 (iv), after 400 (v), after 500 (vi), after 700 (vii), after 900 (viii) and after 1000 cycles (ix), and (B) shift of $\lambda_{\text{max}}$ with cycle number.
at 840 nm (curve (i) in Fig. 5.17(A)) corresponds to charge-carriers and the 300 nm peak to \(\pi-\pi^*\) transition [18]. With an increase in cycling (curve (ii) - curve (ix) in Fig. 5.17(A)), there is a decrease in intensity of these two bands. Additionally, a new band at 500 nm appears and increases in intensity. Furthermore, there is a blue shift in the 840 nm band. Variation in wave number (\(\lambda_{\text{max}}\)) of charge-carrier bands are shown in Fig. 5.17(B).

The spectroscopic studies reflect the structural changes that occur in PEDOT as a result of electrochemical charge-discharge cycling. The shift in charge-carrier band suggests an increase in electronic resistance of the polymer on cycling, thus supporting the impedance data.

5.4. CONCLUSIONS

The PEDOT/SS electrodes prepared in 0.1 M H\(_2\)SO\(_4\) in presence of a surfactant, sodium dodecylsulphate (SDS), are found to yield higher specific capacitance (SC) than the electrodes prepared from neutral aqueous electrolyte. The influence of various experimental variables such as concentration of H\(_2\)SO\(_4\), concentration of SDS, potential of deposition and nature of supporting electrolytes used for capacitor studies are studied. Specific capacitance values as high as 250 F g\(^{-1}\) in 1 M oxalic acid are obtained during initial stages of cycling. However, there is a rapid decrease in SC on repeated charge-discharge cycling. Spectroscopic data reflect structural changes in PEDOT on an extended cycling, and also as increase in its electronic resistance.

5.5. REFERENCES


Insoluble poly(anthranilic acid) confined in Nafion membrane by chemical and electrochemical polymerization of anthranilic acid

ABSTRACT
Self-doped polyaniline (PANI) possesses superior electrochemical properties and processability in relation to the PANI due to an acid group substituted on the polymer backbone. However, the polar acid group causes the self-doped PANI to undergo dissolution in aqueous, in particular, acidic solutions. To prevent the solubility, poly(anthranilic acid), PANA, is confined in the cavities of the Nafion membrane by a novel electrochemical as well as a conventional chemical polymerization of anthranilic acid. The PANA is characterized by electrochemical, optical, spectroscopic and scanning electron microscopic studies.

6.1. INTRODUCTION

PANI is insoluble in most of the aqueous and non-aqueous solvents, thus restricting its use only as the solid. For the purpose of polymer processing, PANI solutions are essential and one of the approaches reported in the literature to dissolve is introducing an acid group in its structure [1]. For instance, sulfonic acid group has been substituted to hydrogen on the benzene ring of PANI, resulting in a self-doped PANI [2]. A post sulfonation of PANI makes the resulting polymer soluble. Also, polymerization of 2-amino benzene sulfonic acid (metanilic acid) in acidic aqueous solutions produces soluble poly(metanilic acid) [3]. Thus, preparation of a solid polymer of this type is not possible in aqueous acidic solutions, but it may be possible in a neutral solution of aqueous-organic mixed medium [4]. However, in order to exhibit the electrical and electrochemical properties, protonation of the imine nitrogen of PANI backbone in poly(metanilic acid) is essential, which requires an acidic solution [5]. Thus, the insolubility of PANI on one hand and the solubility of acid-group substituted PANI on the other, make the polymer system complex. An acid group substituted, self-doped PANI is expected to possess better electrical and electrochemical properties over wider pH range if it is available in solid form than the unsubstituted PANI. Thus the synthesis of an acid group substituted solid PANI from the corresponding monomer in acidic solutions is a challenging problem.

Anthranilic acid (2-amino benzoic acid) is an important monomer for the synthesis of carboxylic acid group substituted PANI. Similar to the poly(metanillic acid) [6], it is expected that poly(anthranilic acid), PANA, possesses electrochemical activity over a wide pH range in aqueous solutions owing to the substitution of carboxylic acid group. Studies on the synthesis of PANA from acidic aqueous solutions are scarcely reported in the
literature, probably due to the problem of its high solubility. Copolymer of aniline and anthranilic acid have been prepared by chemical polymerization to improve the solubility of PANI, study the self-doping mechanism and evaluate thermal properties [7]. Also, this study involves chemical polymerization of anthranilic acid in an alkaline solution [7]. However, the soluble PANA homopolymers (with or without external dopant HCl) exhibit very low conductivity compared to PANI. For the copolymers, the solubility increases while the conductivity decreases with the amount of anthranilic acid in the monomers. Also, chemical polymerization of anthranilic acid in dil. HCl results in the formation of PANA with very low yield due to its high solubility [7]. In another study [8], films of copolymers of aniline and anthranilic acid have been grown on gold electrodes by applying cyclic potential sweeps. A combined diffused reflectance spectro-electrochemistry with quartz crystal microbalance has been shown to be a useful technique to acquire multidimensional information during the growth of the copolymer films. These studies clearly suggest that preparation of PANA homopolymer in solid state is difficult because of its solubility.

In the present study, solid PANA is synthesized in an acidic medium from a chemical route and also a novel electrochemical route. The solid polymer thus formed is confined in the porous matrix of the Nafion membrane and it does not dissolve in acidic solutions. The PANI backbone of the PANA exhibits enhanced electrochemical activity due to self-doping of carboxylic acid group in electrolytes of a wide pH range, in relation to PANI.
6.2. EXPERIMENTAL

Analytical grade chemicals - anthranilic acid, H$_2$SO$_4$, Na$_2$SO$_4$, NaOH and NH$_4$S$_2$O$_8$ were used as received. Double distilled water was used for the preparation of all solutions. Nafion 112 membrane (thickness ~ 50 μm) was treated in boiling H$_2$O$_2$, H$_2$SO$_4$ and double distilled water before using for the experiments. A solution of PANA was prepared by dissolving 0.1 M anthranilic acid in 0.5 M H$_2$SO$_4$ and drop-wise addition of 0.1 M NH$_4$S$_2$O$_8$ solution. For the purpose of encapsulation of PANA in the Nafion, a strip (35 mm x 5 mm) of the Nafion membrane was soaked in 0.1 M anthranilic acid + 0.5 M H$_2$SO$_4$ for about 2 h. During this period, anthranilic acid entered the cavities of the Nafion membrane. Then the film was taken out, rinsed with double distilled water and soaked in 0.1 M NH$_4$S$_2$O$_8$ + 0.5 M H$_2$SO$_4$ for about 6 h. The anthranilic acid present in the Nafion membrane underwent oxidation producing PANA, which was noticed due to the change in colour of the membrane. For electrochemical polymerization, the anthranilic acid loaded Nafion membrane was rinsed with distilled water, wiped with filter paper to make the surface dry and the electrode assembly was made by sandwiching the Nafion membrane between two Pt foils (25 mm x 5 mm each) as shown in Fig. 6.1(A) and (B). A small portion (5 – 10 mm length marked (i) in Fig. 6.1(B)) was left un-sandwiched and a major portion of the film (20 – 25 mm length marked (ii) in Fig. 6.1(B)) was held in between the Pt foils. The Pt foils were electrically shorted by means of a copper wire and they were held tightly with the membrane by means of thick insulating supports made of Teflon and a clamp (Fig. 6.1(A)). This Nafion-Pt working electrode (WE) assembly was introduced into an electrochemical cell in such a way that the un-sandwiched part of the Nafion membrane alone made contact with the liquid electrolyte. Care was taken to avoid the contact of the Pt
foils with the solution. The electrochemical cell was made of glass, which had provision to introduce the Nafion-Pt WE assembly, Pt foil counter electrode and a saturated calomel reference electrode (SCE). Potential values are reported against SCE. An electrolyte of 0.5 M H$_2$SO$_4$ was taken in the cell.

A computer controlled potentiostat / galvanostat EG&G PARC model Versastat was used for electrochemical experiments. UV-visible and FTIR spectra were recorded by Perkin Elmer model Lambda 35-UV/VIS spectrometer and Bruker FT-IR model 66V spectrometers, respectively. Scanning electron micrographs (SEM) were recorded by JOEL microscope model JSM-840A.

6.3. RESULTS AND DISCUSSIONS

6.3.1. Oxidation of anthranilic acid: Similar to the oxidation of aniline, the oxidation of anthranilic acid to PANA occurs according to the reaction,

$$n \text{C}_6\text{H}_4(\text{COOH})\text{NH}_2 \rightarrow \text{--(-- C}_6\text{H}_3(\text{COOH})\text{NH--)}_n\text{--} + 2n \text{H}^+ + 2n \text{e}^- \quad (6.1)$$

The oxidation can occur by a suitable oxidizing agent in a chemical route, and also in electrochemical routes employing galvanostatic, potentiostatic and potentiodynamic methods. It is believed that the potentiodynamic method produces PANI films of better quality than those obtained by galvanostatic and potentiostatic methods [9]. It was attempted to examine the electrochemical preparation of a film of PANA on a Pt electrode in 0.5 M H$_2$SO$_4$ consisting of 0.1 M anthranilic acid. It was found that there was no solid film produced on the Pt anode even after a continuous electrolysis for extended periods using different electrochemical techniques. During the potentiodynamic cycling of the Pt electrode in the monomer solution, the cyclic voltammograms consisted of current peaks
corresponding to the oxidation of anthranilic acid (Fig. 6.2). However, there was no increase in the cyclic voltammetric charge in contrast to an increasing charge during the growth of PANI in aniline containing acidic solutions [10]. Additionally, the surface of the Pt electrode remained bright suggesting that there was no polymer film formed on it. But the electrolyte slowly changed to brown colour with continuation of electrolysis. It was also
attempted to oxidize the monomer in the above electrolyte by adding NH₄S₂O₈ as the oxidizing agent. While there was the formation of a soluble polymer formed as noted from the change in colour of the solution and also from UV-visible spectroscopy as described below, there was no solid polymer precipitated. It was therefore inferred that the PANA has high solubility in 0.5 M H₂SO₄ and it cannot be made in the solid form either as a powder or as a film on the anode. In contrast to these observations, a brownish-black powder has reportedly been obtained in a HCl solution of pH 0.2-0.5 after a prolonged reaction time, apparently with very low yield [8]. This powder was soluble in several organic solvents and aqueous NaOH to give reddish-brown solutions. It is inferred that a saturated solution of PANA would have exhibited a slow precipitation resulting in the formation of some powder. Nevertheless, it is understood that PANA is highly soluble in aqueous solutions.

6.3.2. PANA in Nafion membrane: chemical method: There has been interest on Nafion-conducting polymer composites in which the ionomer, besides behaving as a host network for the conducting polymer, provides doping anions and protons, which are essential for electronic conductivity [11]. Several methods have been reported for the preparation of Nafion-conducting polymer composites [12-14]. Electrochemical synthesis has been carried out by electro-polymerization of the appropriate monomer on Nafion-modified electrode [12-14]. Alternately, electrolysis of solutions containing both Nafion and the monomer has also been reported [15]. Chemical syntheses of conducting polymers in Nafion are expected to provide membranes with better mechanical properties, since it employs well-defined commercial Nafion membranes [14, 16]. The loading of the conducting polymer has been achieved either (i) by soaking the
Fig. 6.2. Cyclic voltammetry of Pt electrode in 0.1 M anthranilic acid + 0.5 M H₂SO₄.

Nafion membrane successively in solutions of the monomer and an oxidant, or (ii) by exposing one face of the membrane to the monomer solution and the other to an oxidant solution. While these studies involve loading of insoluble conducting polymer such as PANI, encapsulation of soluble conducting polymer such as PANA in Nafion membranes has not been reported to the knowledge of authors. For loading of solid PANA by chemical polymerization, a piece of Nafion 115 membrane was soaked in 0.5 M H₂SO₄ consisting of 0.1 M anthranilic acid for about 2 h followed by oxidation as detailed in the 6.2.
Experimental section. During the course of this polymerization process, the Nafion membrane gradually darkened to brown colour. A PANA-Nafion membrane was soaked in 0.5 M H$_2$SO$_4$ for a few days and it was found that the intensity of brown colour continued to be the same throughout. It was inferred that the PANA was tightly held with in the pores of the Nafion membrane probably by chemical interaction between –COOH group of PANA and the Nafion structure. This could have prevented dissolution of PANA in 0.5 M H$_2$SO$_4$ solution.

6.3.3. **PANA in Nafion membrane: Electrochemical method:** For electrochemical polymerization, an anthranilic acid loaded Nafion membrane was sandwiched between two Pt foils (Fig. 6.1(A) and (B)) as detailed in 6.2. Experimental section. The polymerization was carried out by fixing the WE potential at 1.2 V or by passing a constant current of 5 mA cm$^{-2}$. Alternatively the electrode was cycled between –0.2 and 1.2 V repeatedly at a sweep rate of 20 mV s$^{-1}$. After several sweeps, the WE was removed from the electrochemical cell, the Nafion membrane was separated from the Pt foils and washed with 0.5 M H$_2$SO$_4$. It was found that anthranilic acid present in the portion of the Nafion film between the Pt foil alone was polymerized and the monomer present in the part of the Nafion immersed in the electrolyte did not polymerize (Fig. 6.1(C)). Electrochemical polymerization of conducting polymers in Nafion has been carried out by coating an inert electrode with Nafion [12-14]. The inert metallic substrate acts as a current collector when dipped in a liquid electrolyte. It has also been reported [14] that a composite of Nafion-conducting polymer is deposited electrochemically on Pt electrode in a liquid electrolyte consisting of the Nafion suspension and the monomer. These studies involve polymerization in a liquid medium and the Nafion is present as a coating on an electrode.
Thus free standing films of conducting polymer-Nafion cannot be prepared by these methods. In the present study, contrarily, polymerization of anthranilic acid took place in the portion of the Nafion membrane that was not in direct contact with 0.5 M H₂SO₄. As the Nafion is proton conducting electrolyte membrane, the un-sandwiched part (Fig. 6.1(B) and (C) marked (i)) acts as a junction between the liquid electrolyte and the solid electrolyte, that is, the portion of the Nafion membrane sandwiched between the Pt foils (Fig. 6.1 (B) and (C) marked (ii)). Interestingly, while anthranilic acid in un-sandwiched part does not undergo oxidation, there is formation of PANA only in the portion of the membrane between the Pt electrodes. It was found O₂ evolution occurs instead of polymerization of anthranilic acid if the Pt foils of the WE assembly (Fig. 6.1(A)) were in contact with the H₂SO₄ electrolyte. By this novel electrochemical polymerization technique, it became possible to prepare free-standing PANA-Nafion membranes. In general, this procedure is expected to be useful for preparation of other conducting polymers in free-standing ionomeric membranes.

6.3.4. Spectroscopic studies of PANA-Nafion: UV-visible spectra of a chemically polymerized PANA-Nafion and an electrochemically polymerized PANA-Nafion are shown in Fig. 6.3. Spectrum of PANA solution in 0.5 M H₂SO₄ is also shown for comparison. The peak observed at 270-300 nm is attributed to π-π* transition in benzenoid units [17] and the peak at 550-580 nm to exiton-like transition in quinoid diimino units [18]. Another absorbance band at 420-430 nm is also due to exiton-like transition in emeraldine salt form. The less intensity of the bands observed for PANA in comparison with the spectra of PANI is due to steric effect of carboxylic group [19], smaller chain length and confinement in Nafion membrane. The
Fig. 6.3. UV-visible spectra of PANA solution (I), chemical PANA-Nafion membrane (II) and electrochemical PANA-Nafion membrane (III). The region between 800 and 400 nm is expanded and shown as the inset.

spectra of both chemical and electrochemical PANA-Nafion membranes resemble to the spectrum of PANA in solution thus providing evidence for the presence of PANA confined as a solid in the Nafion membranes. Furthermore, the spectra of PANA prepared by chemical and electrochemical routes are almost identical. The exact band positions depend on several parameters such as chain length, the overall oxidation state of the polymer, interchain or intrachain charge-transfer, the extent of conjugation between adjacent phenyl rings, the steric effect of the carboxylate groups in the polymer chain, etc [19]. The variations in band position of the spectra (Fig. 6.3) are likely to be due to variations in these parameters. The PANA-Nafion membranes were soaked in 0.5 M H2SO4 solution for a few
Fig. 6.4. FTIR spectra of (I) bare Nafion membrane and (II) PANA-Nafion membrane.

days, and UV-visible spectra were recorded again. The spectra were reproducible and the visual observation did not indicate any decrease in colour intensity due to soaking in the acidic solution. These observations suggest that PANA confined in the Nafion membrane does not undergo dissolution.

The confinement of PANA in Nafion membrane was further supported by recording FTIR spectra (Fig. 6.4). The bands at 1200, 1147, 1056, 981 and 969 cm\(^{-1}\) are due to the characteristic functional groups in Nafion [16]. The additional bands at 1710, 1561, 1500,
834 and 688 cm\(^{-1}\) observed in the spectrum of PANA-Nafion are attributed to PANA [13]. The absorption band at 1710 cm\(^{-1}\) (1693 cm\(^{-1}\) in [13]) is due to C=O stretching 1561 cm\(^{-1}\) (1575-1567 cm\(^{-1}\) [20]) is to benzenoid ring C=C stretching and 834-688 cm\(^{-1}\) (838-685 cm\(^{-1}\) [20]) is to C-H out of plane bending modes.

6.3.5. *Cyclic Voltammetry of PANA-Nafion*: The electrochemical behaviour of PANI films on Pt substrate have been widely reported by recording cyclic voltammograms in acidic electrolytes [21]. The voltammograms are characterized by several current peaks corresponding to intrinsic redox processes of PANI. Among them, a pair of current peaks at about 0.2 V corresponding to the reversible transformation of leucomeraldine/emeraldine and another pair at about 0.7 V corresponding to emeraldine/pernigraniline reversible transition are prominent. A PANA-Nafion film was sandwiched between two Pt foils (Fig. 6.1(A) and (B)), dipped the un-polymerized part of the Nafion in an electrochemical cell consisting of 0.5 M H\(_2\)SO\(_4\), and cyclic voltammograms were recorded at a sweep rate of 0.5 mV s\(^{-1}\). The voltammogram (Fig. 6.5) is characterized by a pair of broad current peaks in 0.5-0.6 V range, suggesting the electrochemical activity of PANA present inside the Nafion membrane. The nature of this voltammogram differs from the voltammogram of PANI films [21] because of the presence of –COOH group on PANI backbone, due to confinement in the Nafion pores and also due to the resistance of the membrane.

6.3.6. *Effect of pH on PANA-Nafion properties*: A PANA-Nafion membrane was examined for its optical properties in acidic (0.5 M H\(_2\)SO\(_4\)), neutral (0.5 M Na\(_2\)SO\(_4\)) and alkaline (0.5 M NaOH) media. The membrane was soaked in the respective solutions for about 2 h before recording UV-visible spectra (Fig. 6.6) and optical photographs (Fig. 6.7).
The photographs recorded for these membranes showed different colours, and the changes in colour were found reversible (Fig. 6.7 (i)). That is, the membrane soaked in acidic medium was transferred to alkaline medium, and then back to the acidic solution. The original colour was restored in acidic medium. The UV-visible spectra (Fig. 6.6) suggested that the absorbance bands at 270-300 nm, 390-420 nm and 560-570 nm were present for the membranes treated in solutions of a wide pH range. It is interesting to note that the 390-420 band of PANI is found only for pH < 7 and it disappears in alkaline solutions [22], whereas this absorbance band is clearly observed for PANA-Nafion in the present study.

Fig. 6.5. Cyclic Voltammogram of PANA-Nafion membrane. Area of each Pt foil used for Pt / Nafion / Pt sandwich is 1.25 cm².

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Fig. 6.6. **UV-visible spectra of PANA-Nafion after treating in 0.5 M H₂SO₄ (I), 1 M Na₂SO₄ (II) and 1 M NaOH (III). The region between 800 and 400 nm is expanded and shown as the inset.**

This is due to the presence of –(COOH) group present on PANA chain. It is also due to the likely fact that pH inside the Nafion membrane could be lower than the surrounding solution. Electrochemically prepared PANA-Nafion membranes were examined by recording SEM micrographs (Fig. 6.7 (i) and (ii)). The PANA crystallites are found in the shape of short, thick rods of about 2 μm length and 0.75 μm diameter occupying the voids present in the Nafion membrane. Similar SEM micrographs have been reported for a conducting polymer confined in polycarbonate membranes [23]. In this study,
electrochemical polymerization of o-methoxyaniline has produced 100-400 nm size crystallites of poly(o-methoxyaniline) in polycarbonate membranes.

Fig. 6.7. (i) Optical photographs of Nafion membranes. (A) Before polymerization, soaked in 0.5 M anthranilic acid + 0.5 M H₂SO₄. (B) After electrochemical polymerization (a) the portion of Nafion dipped in the electrolyte, (b) the portion sandwiched between Pt foils. (C) After chemical polymerization in 0.5 M H₂SO₄. (D) Chemical polymerization in neutral solution (E) chemical polymerization in basic solution. (ii) The SEM micrograph of electrochemically polymerized membrane (iii) the same membrane in higher magnification.
6.4. CONCLUSION

To prevent the solubility, poly(anthranilic acid) is confined in the cavities of the Nafion membrane by polymerizing anthranilic acid using novel electrochemical as well chemical methods. The PANA is characterized by electrochemical, optical, spectroscopic and scanning electron microscopic studies. It is anticipated that the solid form of poly(anthranilic acid) would be useful as a self-doped polymer for several applications.

6.5. REFERENCES


Electrochemical reduction of hydrogen peroxide on stainless steel electrodes

ABSTRACT

Electrochemical reduction of hydrogen peroxide is studied on a sand-blasted stainless steel (SSS) electrode in an aqueous solution of NaClO$_4$. The cyclic voltammetric reduction of H$_2$O$_2$ at low concentrations is characterized by a cathodic peak at -0.40 V versus standard calomel electrode (SCE). Cyclic voltammetry is studied by varying the concentration of H$_2$O$_2$ in the range from 0.2 mM to 20 mM and the sweep rate in the range from 2 to 100 mV s$^{-1}$. Cyclic voltammograms at concentrations of H$_2$O$_2$ higher than 2 mM or at high sweep rates consist of an additional current peak, which may be due to the reduction of adsorbed species formed during the reduction of H$_2$O$_2$. Amperometric determination of H$_2$O$_2$ at -0.50 V vs. SCE provides the detection limit of 5 μM H$_2$O$_2$. A plot of current density versus concentration has two segments suggesting a change in the mechanism of H$_2$O$_2$ reduction at concentrations of H$_2$O$_2$ $\geq$ 2 mM. From the rotating disc electrode study, diffusion co-efficient of H$_2$O$_2$ and rate constant for reduction of H$_2$O$_2$ are evaluated. Thus, stainless steel, which is inexpensive and a common alloy, is useful for studying electrochemical reduction of H$_2$O$_2$ and also for analytical application.

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7.1. INTRODUCTION

Hydrogen peroxide is an important ingredient in a wide range of industrial processes such as food processing (e.g., in the cold pasteurization of milk, wine aging, etc), textile bleaching, cosmetics preparation, pharmaceutical manufacturing, etc [1]. H₂O₂ is also an intermediate during the reduction of oxygen in fuel cells [2]. In fact, a challenging problem in fuel cell is the premature failure of the cell due to attack of the electrodes by H₂O₂ [3]. The presence of stable dioxygen intermediates is an indication of intrinsic cell inefficiency in the reduction of oxygen at the cathode. In biological aerobic organisms, energy is derived from oxygen, which is susceptible to form O₂•, OH• and H₂O₂, during its reduction by the electron transfer effect of mitochondria [4]. These radicals (reactive oxygen species) cause different kinds of disorder in the body such as Alzheimer’s, myocardial infarction, atherosclerosis, Parkinson’s, etc [5]. Hence, studies on H₂O₂ reduction are important in both chemistry and biology.

Electrochemical reduction of H₂O₂ at different electrodes has been studied by various groups [6-12]. On Pt electrodes, pH and over-potential play important roles on kinetics of H₂O₂ reduction [6]. Ag electrodes exhibit autocatalytic mechanism towards the reduction of H₂O₂ in acidic electrolyte [7]. Somasundrum et al. [8], studied H₂O₂ reduction on Cu metal in 0.1 M phosphate buffer solution (pH = 6.7). They reported the mechanism of H₂O₂ reduction at ambient temperature and also the effect of dissolved oxygen on H₂O₂ reduction. H₂O₂ reduction was also studied on polycrystalline copper in borax buffer in the light of surface oxidation in the presence of chloride ions in the electrolyte [9].

There are also a few reports on reduction of H₂O₂ on modified electrodes [10-12]. PdO₂ and IrO₂ modified glassy carbon electrodes (GCE) were used as the electrodes for
Electrochemical reduction of H₂O₂ in basic solution [10]. The electrocatalytic activity of a graphite electrode modified by micro quantities of platinum metals (Pd or Pt+Pd) towards the H₂O₂ reduction were characterized by Dodevska et al., and the electrode was used as a glucose biosensor [11]. A conducting polymer modified by Rh micro-particles on GCE was also used to detect H₂O₂, which was produced from the oxidation of glucose [12]. Generally noble metallic electrodes are used for studying electrochemical reactions because of their stability in the electrolytes. Non-noble metals are not preferred because they corrode in aqueous solutions. In the case of H₂O₂ reduction, copper was employed and mechanistic studies were reported [8,9]. There are no reports on electrochemical reduction of H₂O₂ on stainless steel (SS), to the best of authors’ knowledge. In the present work, SS, which is a very common alloy, is used as the electrode material for electrochemical reduction of H₂O₂ in neutral NaClO₄ electrolyte. Cyclic voltammetry, amperometry and rotating disc electrode (RDE) studies suggest that SS can be used for electrochemical determination of H₂O₂ at a concentration level as low as 5 μM.

7.2. EXPERIMENTAL

Analytical grade H₂SO₄, NaClO₄, NaOH and HCl were purchased from Merck, Purified H₂O₂ (30%) was purchased also from Merck. A high purity commercial 304 grade SS foil (thickness: 0.2 mm) was used as the substrate for H₂O₂ reduction. A solution of 0.5 M NaClO₄ (pH = 5.8) was usually used as the supporting electrolyte for H₂O₂. Some experiments were also conducted by varying pH of the electrolyte. All solutions were prepared in doubly distilled water. The electrolyte solutions were de-aerated by bubbling N₂ for at least 30 min prior to electrochemical measurements. A glass cell of about 70 ml capacity with suitable ground–glass joints to introduce a working electrode, Pt foil auxiliary
electrodes, and a SCE was used for electrochemical experiments. All potential values are reported against SCE.

A SS sheet was subjected to sand-blasting to generate a noticeable rough surface and washed copiously using a detergent followed by a mild etching in dilute H₂SO₄. A foil of 7 mm width and 6 cm length was sectioned out of a sand-blasted SS sheet, 1.4 cm² areas at one of the ends was exposed to the electrolyte and the rest of its length was used as a tag for taking electrical contacts. Hereafter, sand-blasted SS electrode is hereafter referred to as SSS. The SSS substrate was again washed thoroughly, rinsed with acetone and dried in vacuum at ambient temperature for about 30 min for further studies. Geometric area of the electrode was used for calculation of current density (mA cm⁻²).

Cyclic voltammetry and amperometry experiments were carried out using an EG&G PARC potentiostat/galvanostat Versastat II or Eco Chemie potentiostat/galvanostat model Autolab 30. RDE experiments were carried using Eco Chemie RDE model Rotator 188. The electrode tip was made of SS. Experiments were carried out with rotation speed in the range from 100 to 5000 rpm.

7.3. RESULTS AND DISCUSSIONS

7.3.1. Cyclic voltammetry: Cyclic voltammogram of a SSS electrode recorded in 0.5 M NaClO₄ + 7 mM H₂O₂ at 5 mV s⁻¹ in the potential range from -0.10 to -0.70 V is shown in Fig. 7.1. For comparison purpose, cyclic voltammogram recorded in 0.5 M NaClO₄ in the absence of H₂O₂ is also presented. In the absence of H₂O₂, cyclic voltammogram (Fig. 7.1 curve (i))
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Fig. 7.1. Cyclic voltammograms of SSS electrode in 0.5 M NaClO₄ in absence of H₂O₂ (i) and presence of 5 mM H₂O₂ (ii); and voltammogram of SS electrode in 0.5 M NaClO₄+ 7 mM H₂O₂ (iii) does not exhibit any current peak suggesting that SSS is stable in the potential range studied. In the presence of H₂O₂ in the electrolyte, however, current starts increasing at -0.10 V (Fig. 7.1 curve (ii)) in the forward sweep. On further extending the sweep in the negative direction, a reduction current peak (P₁) appears at -0.40 V. On reversing the direction of sweep at -0.70 V, no oxidation current peak is observed. The appearance of an irreversible reduction peak in the presence of H₂O₂ (Fig. 7.1 curve (ii)) and absence of peak in the absence of H₂O₂ (Fig. 7.1 curve (i)) suggest that the current peak P₁ is due to
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reduction of H₂O₂. In order to examine the effect of roughness of SSS surface due to sand blasting on the reduction of H₂O₂, a cyclic voltammograms recorded using a plain SS is shown in Fig. 7.1 (curve (iii)). It is observed that the voltammograms of SSS and SS are similar in shape and the peak current density on SSS is 68 % greater than on SS (Fig. 7.1). This indicates a 68 % increase in surface area of SSS due to sand-blasting. These results further suggest that basically the SS surface facilitates the electrochemical reduction of H₂O₂. For further studies, SSS was used. A SSS electrode was repeatedly cycled in 0.5 M NaClO₄ + 4 mM H₂O₂ at 5 mV s⁻¹, to examine its stability and activity towards reduction of H₂O₂. Cyclic voltammograms (not shown), similar to Fig. 7.1 curve (ii), were reproducible with very marginal decrease in peak current during ten cycles. Thus SSS is considered to retain its electrochemical activity for reduction of H₂O₂ without undergoing fouling or poisoning due to any intermediate species adsorbed during the reduction process.

Cyclic voltammograms of SSS electrode in 0.5 M NaClO₄ + 3 mM H₂O₂ were recorded at different sweep rates (ν) and the data are shown in Fig. 7.2. At low sweep rates (Fig. 7.2 curve (i)), there is single reduction current peak (P₁) appearing at about -0.38 V. As the sweep rate increases, however, another reduction peak (P₂) starts appearing and it becomes a clear, sharp peak at high sweep rates. At 100 mV s⁻¹, for instance, the peak P₂ is clearly seen at -0.66 V. The appearance of P₂ is likely to be due to reduction of intermediate species adsorbed on the SSS surface during H₂O₂ reduction, as discussed below. The variation of peak current density (Iₚ₁) of P₁ with ν⁵/₂ is shown in Fig. 7.3(A). There is a linear increase of Iₚ₁ with ν⁵/₂, suggesting that the reduction of H₂O₂ on
Fig. 7.2. Cyclic voltammograms of SSS electrode in 0.5 M NaClO₄ + 3 mM H₂O₂ at the sweep rate of 2 (i), 5 (ii), 10 (iii), 20 (iv), 50 (v) and 100 (vi) mV s⁻¹.
SSS is diffusion controlled. The relationship between $E_p$ and sweep rate ($\nu$) for an irreversible reaction is given by Eq. (7.1) [13]:

$$E_p = k + (2.3 \frac{RT}{(2n\alpha F)}) \log \nu$$  \hspace{1cm} (7.1)

where $k$ is a constant, $\alpha$ is transfer co-efficient, $n$ is number of electrons transferred up to the rate determining step of the reaction and the other symbols have their usual meanings.

The product $(2.3 \frac{RT}{(n\alpha F)})$ is equivalent to the Tafel slope, which can be evaluate from Eq. (7.1). A plot of $E_p$ versus $\log \nu$ is shown in Fig. 7.3(B). The value of slope $(= 2.3 \frac{RT}{(2n\alpha F)})$ of this plot obtained is 0.12 V. Thus the Tafel slope becomes 0.24 V. For a simple two electron transfer reaction, one can expect a value of 0.06 V for the Tafel slope.

Fig. 7.3. (A) the peak current density of $P_1$ versus $(sweep\ rate)^{1/2}$ of data presented in Fig. 7.2; and (B) potential of peak $P_1$ versus log(sweep rate) of SSS in 0.5 M NaClO$_4$ + 3 mM H$_2$O$_2$. 

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assuming $\alpha = 0.5$. As the experimental value (0.24 V) is about 4 times greater than the expected value, the reduction of $\text{H}_2\text{O}_2$ involves a complex mechanism as discussed below.

Cyclic voltammograms of a SSS electrode were recorded in 0.5 M NaClO$_4$ solution containing $\text{H}_2\text{O}_2$ at various concentrations. Some of the voltammograms are presented in Fig. 7.4. There is an increase in current with increasing concentration of $\text{H}_2\text{O}_2$. At low concentrations of $\text{H}_2\text{O}_2$, single reduction peak $P_1$ appears at about -0.5 V (Fig. 7.4, curve (ii)). However, the second peak $P_2$ is observed at high concentration of $\text{H}_2\text{O}_2$ (Fig. 7.4, curve (iv)). A plot of $I_{p1}$ versus concentration is shown in Fig. 7.5. There is a linear increase of $I_{p1}$ with an increase in concentration of $\text{H}_2\text{O}_2$. These results suggested that SSS is an appropriate electrode material for studying electrochemical reduction of $\text{H}_2\text{O}_2$.

Studies on mechanism of electrochemical reduction of $\text{H}_2\text{O}_2$ on different metallic electrodes occupied interest in the literature. Mechanistic studies were conducted on polycrystalline copper in a borax buffer electrolyte [9]. Copper electrode was shown to consist of CuO and Cu$_2$O layers. The oxides of Cu are considered to catalyze the reduction of $\text{H}_2\text{O}_2$. The proposed mechanism involves the chemical oxidation of Cu$_2$O by $\text{H}_2\text{O}_2$:

$$\text{Cu}_2\text{O} + \text{H}_2\text{O}_2 \rightarrow \text{CuO} + \text{H}_2\text{O} \quad (7.2)$$

which is followed by electrochemical reduction of CuO to Cu$_2$O as

$$\text{CuO} + \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{Cu}_2\text{O} + 2 \text{OH}^- \quad (7.3)$$

Thus the $\text{H}_2\text{O}_2$ reduction occurs indirectly with Cu$_2$O acting as a redox carrier. Furthermore, it was considered that CuO surface inhibits direct electron transfer to $\text{H}_2\text{O}_2$.  

Fig. 7.4. Cyclic voltammograms of SSS electrode at a sweep rate of 5 mV s\(^{-1}\) in 0.5 M NaClO\(_4\) with 0.8 (i), 1 (ii), 2 (iii), 3 (iv) mM of H\(_2\)O\(_2\).

for reducing the latter. Rate of the reaction was considered to be determined by the surface coverage of CuO.

Similar to the above mechanism of reduction of H\(_2\)O\(_2\) mediated by CuO, a mechanism mediated by IrO\(_2\) on glassy carbon electrode was also proposed [10]. An autocatalytic mechanism on Ag electrode was proposed [7]. The autocatalytic mechanism involving adsorbed OH\(_{ads}\) species was shown operative at potentials of about -0.30 V versus MSE (Hg/HgSO\(_4\), K\(_2\)SO\(_4\) (sat)) reference electrode, whereas the normal mechanism is operative at -0.40 V versus MSE.
In the present study of H$_2$O$_2$ reduction on SSS, the mechanism of the reaction is different from the above discussion, because the surface of SSS is free from oxide or a catalyst layer. The absence of any oxide layer is evident from the cyclic voltammograms of SSS in H$_2$O$_2$-free NaClO$_4$ electrolyte (Fig. 7.1 curve (i)), where no reduction peaks are observed. A mechanism involving decomposition (or disproportionation) of H$_2$O$_2$ leading to the formation of O$_2$ followed by the electrochemical reduction of O$_2$ is also reported in the literature [14, 15].

\[
2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2 \tag{7.4}
\]

\[
\text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- = 2 \text{H}_2\text{O} \tag{7.5}
\]
In order to examine the possibility of the above reaction, cyclic voltammograms of the SSS electrode were recorded in NaClO₄ saturated with O₂ gas. A peak corresponding to the reduction of O₂ appeared at about -0.20 V, which is more positive to -0.40 V observed for H₂O₂ reduction (Fig. 7.1 curve (ii)). Therefore disproportionation pathway for H₂O₂ reduction is ruled out. The possible mechanism, therefore, is as follows:

The direct reduction of H₂O₂ in a slightly acidic medium (pH = 5.8):

\[
H₂O₂ + 2 \ H^+ + 2e^- \rightarrow 2 \ H₂O \tag{7.6}
\]

can be considered to occur through the formation of adsorbed OHₐds species.

\[
H₂O₂ \text{ (bulk)} \rightarrow H₂O₂ \text{ (surface)} \tag{7.7}
\]

\[
H₂O₂ \text{ (surface)} + e^- \rightarrow OHₐds + OH^- \tag{7.8}
\]

\[
OH^- + H^+ \rightarrow H₂O \tag{7.9}
\]

\[
OHₐds + e^- \rightarrow OH^- \tag{7.10}
\]

\[
OHₐds + H^+ + e^- \rightarrow H₂O \tag{7.11}
\]

Diffusion of H₂O₂ from bulk to the electrode surface (step 7.7) followed by electron-transfer steps (reactions 7.8 and 7.10) is expected to result in the cyclic voltammetric peak current. OHₐds formed in reaction 7.8 can accept an electron to generate OH⁻ [16]. OH⁻ ion thus formed combine with H⁺ ion (reaction 7.9) at the electrode to produce the reaction product, namely, H₂O. Alternately, OHₐds can simultaneously accept an electron and combine with H⁺ ion producing H₂O in reaction 7.11. It is likely that at low sweep rates and low concentrations, where a single voltammetric peak is observed, steps 7.8-7.10 are appropriate to complete the overall reduction of H₂O₂. At high sweep rates and high concentrations of H₂O₂, step 7.11 also occurs together with steps 7.8-7.10, due to high
surface coverage of OH\textsubscript{ads}. The step 7.11 is likely to be responsible for the presence of second voltammetric peak (P\textsubscript{2}) at -0.66 V.

7.3.2. Amperometry: In an amperometry experiment, current flowing through a SSS electrode at -0.50 V was measured as a function of concentration of H\textsubscript{2}O\textsubscript{2} in 0.5 M NaClO\textsubscript{4} (Fig. 7.6).

---

**Fig. 7.6 Amperometry of SSS electrode in 0.5 M NaClO\textsubscript{4} with addition of different amounts of H\textsubscript{2}O\textsubscript{2}. The data corresponding to low concentration range are shown as the inset in an expanded scale**

The electrolyte was stirred uniformly by a PTFE covered magnetic bar during the experiment. A wide concentration range from 5 µM to 20 mM was studied. Subsequent to each addition of H\textsubscript{2}O\textsubscript{2}, the SSS electrode shows a rapid response in the increase of current. However, current tends to decrease with time at a given concentration of H\textsubscript{2}O\textsubscript{2} in the
Electrochemical reduction of the electrolyte due to adsorption of the reaction intermediate as discussed in cyclic voltammetric studies.

**Fig. 7.7.** current density versus concentration of $\text{H}_2\text{O}_2$ added (from Fig. 7.6). The low concentration data are magnified and shown in the inset.

Current was measured 5 min after each addition of $\text{H}_2\text{O}_2$ (Fig. 7.6), and the amperometric current density measured from Fig. 7.6 is shown in Fig. 7.7 as a function of concentration of $\text{H}_2\text{O}_2$. There are two linear segments of the data. The first segment between 5 $\mu$M and 2.5 mM is steeper than the second segment between 2.5 mM and 20 mM. Appearance of two segments is attributed to differences in surface coverage of $\text{OH}_{\text{ads}}$ (reaction 7.8) at low and high concentration ranges of $\text{H}_2\text{O}_2$. Thus, the rate of $\text{H}_2\text{O}_2$ reduction in lower
concentration range is higher than the rate in higher concentration range. The rate of the reaction is given by
\[ i = n F k \theta C^0 \]  
(7.12)
where \( i \) is the current density, \( k \) the rate constant, \( \theta \) the surface coverage by adsorbed species and \( C^0 \) the concentration of \( \text{H}_2\text{O}_2 \) in the electrolyte. The values of \( k\theta \) obtained at -0.50 V are \( 1.15 \times 10^{-2} \) and \( 1.02 \times 10^{-3} \) cm s\(^{-1}\), respectively, for low and high concentration regions. This study supports the cyclic voltammetric study, where two different processes depending on the concentration range and the sweep rate range are possible. The linear segment in Fig. 7.7 in lower concentration range is likely to be due to the direct addition of electron to \( \text{H}_2\text{O}_2 \) (reaction 7.8) or to \( \text{OH}_{\text{ads}} \) (reaction 7.10) because of low surface coverage. However at high concentrations of \( \text{H}_2\text{O}_2 \), the surface coverage is large and therefore the electron transfer and also the addition of \( \text{H}^+ \) to \( \text{OH}_{\text{ads}} \) can take place simultaneously (reaction 7.11).

Development of \( \text{H}_2\text{O}_2 \) sensors is an important activity in the area of chemical sensor as well as biosensors. It is interesting to note that the concentration dependence of current density of SSS electrode is linear in low concentration range of \( \text{H}_2\text{O}_2 \). The detection limit is close to 5 \( \mu \)M with sensitivity of 2.24 mA cm\(^{-2}\) mM\(^{-1}\). The detection limit reported by Somasundrum on copper electrode is about 1.2 \( \mu \)M [8]. Other studies on analysis of \( \text{H}_2\text{O}_2 \) suggest a range of detection limits from 20 to 0.3 \( \mu \)M [8, 17,18] and a range of sensitivities from 0.006 to 2.76 mA cm\(^{-2}\) mM\(^{-1}\) [8]. The detection limit obtained in the present study on SSS electrode is within the above range. Furthermore, the sensitivity of SSS electrode is at the upper level of the above sensitivity range. Thus, stainless steel is a useful electrode material for sensing and analysis of \( \text{H}_2\text{O}_2 \).
7.3.3. *Effect of electrolyte pH*: The influence of pH of NaClO$_4$ on the reduction of H$_2$O$_2$ was examined. For this purpose 0.5 M NaClO$_4$ (pH = 5.8) was prepared and pH was adjusted to the required value by adding dilute NaOH or dilute HClO$_4$. Cyclic voltammogram of a SSS in electrolytes consisting of 3 mM of H$_2$O$_2$ are shown in Fig. 7.8. At low pH value (pH = 1.5), no peak was observed due to the decomposition of H$_2$O$_2$ (Fig. 7.8(A)). At pH = 2.5, there are two reduction peaks (P$_1$ and P$_2$) with peak potentials at -0.17 and -0.50 V, respectively (Fig. 7.8(B)). When pH is increased to 5.8, there is a shift in peak potentials to -0.40 and -0.66 V, respectively, for P$_1$ and P$_2$ (Fig. 7.8(C)). The potential variation of H$^+$ ion dependent process (reaction 7.6) is 0.059 V per unit pH according to the Nernst equation. For the increase of pH from 2.5 to 5.8, a shift of potential in the negative direction by 0.195 V is expected. Accordingly, there is a large shift in potentials of peaks P$_1$ and P$_2$ by changing the pH from 2.5 to 5.8. Single cyclic voltammetric peaks are observed in electrolytes of pH values 10 and 11 (Fig. 7.8(D) and (E)). A plot of I$_{p1}$ versus pH (Fig. 7.8(F)) shows that the rate of H$_2$O$_2$ reduction is maximum at pH = 5.8, and it decreases by either decreasing or increasing pH from 5.8.

7.3.4. *Rotating disc electrode studies*: Experiments were carried out by subjecting a RDE made of SS to a linear sweep voltammetry at a sweep rate of 5 mV s$^{-1}$ in 0.5 M NaClO$_4$ consisting of H$_2$O$_2$ at varying concentrations. The speed of RDE was varied from 100 to 3000 rpm. A typical set of data obtained in 0.5 M NaClO$_4$ + 1 mM H$_2$O$_2$ with several rotation speeds are shown in Fig. 7.9. Current starts increasing at about -0.40 V and reaches a plateau in the potential range between -0.65 and -0.85 V. The plateau region commences at less negative
Fig. 7.8. Cyclic voltammograms of SSS in 3 mM H₂O₂ and 0.5 M NaClO₄ of pH (A) 1.5, (B) 2.5, (C) 5.8, (D) 10.0 and (E) 11.0; and (F) current density of peak P₁ versus pH of the solution.
Fig. 7.9. Linear sweep voltammograms of SS rotating disk electrode in 0.5 M NaClO₄ + 1 mM of H₂O₂ with speed of rotation of 100 (i), 200 (ii), 300 (iii), 500 (iv), 700 (v), 1000 (vi), 1500 (vii), 2000 (viii), 2500 (ix), 3000 (x) rpm.

potentials if the speed is low, whereas it commences at more negative potentials if the RDE speed is high. There is an increase in plateau current with increasing speed of rotation. The plateau current, which is generally known as limiting current density (iₐ) is related to rotation rate by Levich equation [19]:

\[ i_L = 0.62 n F A D^{\frac{1}{2}} v^{-\frac{1}{6}} C^0 \omega^{\frac{1}{2}} \]  

(7.13)
where \( \nu \) is the kinematic viscosity of the medium, \( \omega = 2 \pi f \) the angular velocity, \( f \) the frequency in rotation per second and the other symbols have their usual significance. Plots of \( i_L \) versus \( f^{1/2} \) were constructed from the data measured in electrolytes of different concentrations of \( \text{H}_2\text{O}_2 \) and presented in Fig. 7.10. All plots are linear suggesting that the RDE data follow Levich relationship for all concentrations studied. Adsorption effects are considered to be absent due to high rotation speeds of RDE and therefore \( \theta \) is not included.

Fig. 7.10. Levich plot for \( \text{H}_2\text{O}_2 \) concentration of 0.8 (i), 1 (ii), 2 (iii), 3 (iv), 5 (v), 10 (vi) mM.
in Eq. (7.13). From the slopes of the plots and Eq. (7.13), the values of apparent diffusion coefficient (D) of H$_2$O$_2$ are calculated and the average value is about 1.53×10$^{-6}$ cm$^2$ s$^{-1}$. These studies further confirm that SS substrate is quite suitable for studying the electrochemical reduction of H$_2$O$_2$.

The RDE data were further analyzed using Eq. (7.14) for irreversible reactions [20].

$$\frac{1}{i} = \frac{1}{(n F k C^0)} + \frac{1.61 \nu^{1/2}}{(n F C^0 D^{2/3} \omega^{1/2})}$$  \hspace{1cm} (7.14)

For the RDE data measured in 10 mM H$_2$O$_2$ + 0.5 M NaClO$_4$ electrolyte, current density measured at -0.50 V (Fig. 7.9) were used to plot $i^{-1}$ versus $f^{-1/2}$ as shown in Fig. 7.11. By extrapolation of the linear plot to the origin ($\omega \to$ infinity), the value of rate constant (k) is calculated to be 3.01×10$^{-3}$ cm s$^{-1}$. The values of kθ calculated from amperometry at -0.50 V is comparable to this value.

7.4. CONCLUSIONS

Electrochemical reduction of H$_2$O$_2$ was studied on a common alloy, namely, stainless steel in 0.5 M NaClO$_4$ aqueous solution of pH 5.8. Cyclic voltammograms consisted of single reduction peak at low concentrations of H$_2$O$_2$ and low sweep rates, whereas they consisted of two peaks at high concentrations of H$_2$O$_2$ and high sweep rates. This was attributed to a change in mechanism of reduction. This was supported by amperometric data, wherein a plot of current versus concentration consisted of two linear segments. The detection limit obtained was 5 μM H$_2$O$_2$ with sensitivity as high as 2.24 mA cm$^{-2}$ mM$^{-1}$. The RDE studies suggested that H$_2$O$_2$ reduction was diffusion controlled and the value of diffusion coefficient was calculated. These studies provide an insight for the usefulness of stainless steel substrate without involving any surface modification or employing any noble metal based catalyst for electrochemical reduction of H$_2$O$_2$. As the
applications of this reaction are wide such as sensors, it is expected that stainless steel has potentiality for developing sensitive, economical and reliable devices.

Fig. 7.11. Koutecky-Levich plot of the $\text{H}_2\text{O}_2$ reduction current at -0.50 V in 0.5 M NaClO$_4$ + 10 mM $\text{H}_2\text{O}_2$.

7.5. REFERENCES


Conclusions and Future directions

Among various conducting polymers, PEDOT is interesting because of its superior conductivity, transparency, thermal as well as electrochemical stability. To synthesize this polymer, one has to adopt either a chemical route or an electrochemical method. But for applications such as optoelectronics, sensors, energy storage devices wherein a film of the polymer on electrode surface is essential, electrochemical synthesis is an obvious choice. Generally, an inert substrate (Pt, Au, Ag, Pd, C, etc.,) is employed to deposit a film of conducting polymer. Common inexpensive metals such as SS, Al, Mg, Ni, etc., are interesting as substrates in view of applications. Hence, most of the studies reported in the thesis involve SS as the substrate for depositing PEDOT. Carbon paper is also used for some studies.

PEDOT is synthesized from an aqueous electrolyte of 0.01 M EDOT + 0.01 M SDS + 0.1 M H$_2$SO$_4$ on SS electrode by galvanostatic, potentiostatic and potentiodynamic methods. Thin film of PEDOT was characterized by SEM, AFM and impedance spectroscopy. The morphology of PEDOT prepared at low current densities, low potential and low potential range during cycling was essentially globular. The globules developed porosity at higher current densities and higher potentials in the case of galvanostatic and potentiostatic routes, respectively. In case of higher potential range of potentiodynamic deposition, however, the morphology became rod-like and fibrous. For AFM studies, PEDOT was coated potentiostatically on ITO coated glass. AFM studies indicate that a globular topography. PEDOT coated SS electrodes were further characterized by impedance spectroscopy. The Nyquist plots of impedance consist of depressed semicircle
which arises due to parallel combination of the polymer resistance and double layer capacitance. Impedance data suggested that the polymer resistance increased with potential of deposition. The increase in resistance was attributed to the irreversible oxidation of the polymer.

Oxidations of small organic molecules are important due to their implications in the fuel cells. Generally, noble metal particles are used as catalyst for oxidation of these molecules. Nanometric dimensions of noble metal particles are important to enhance the surface area and subsequently to increase oxidation rate. Electrodeposition of Pt and Pt-Ru catalyst particles is carried out on a PEDOT coated carbon paper from an acidic solution consisting of chloroplatinic acid and ruthenium chloride solutions. Studies suggest that a thin layer of PEDOT on the carbon paper facilitates the formation of uniform, well-dispersed, small clusters of nanosized particles. The cyclic voltammetry data suggest that peak currents of oxidation of methanol, formic acid, formaldehyde and ethanol are several times greater for electrodes with PEDOT than electrodes without PEDOT. Chronoamperometry data shows a good stability of the electrodes for oxidation of methanol, formic acid, formaldehyde and ethanol.

Studies on phenol oxidation are carried out on PEDOT coated on SS electrode. A significant improvement in repeatability cyclic voltammetry for phenol oxidation is seen on the PEDOT/SS compared to the bare Pt electrode. A pair of additional peaks for H₂Q/Q are also characterized and confirmed by externally added H₂Q. A significant effect of specific mass of PEDOT on electrooxidation of phenol is present. There is a decrease in fouling of PEDOT with an increase in its specific mass.
The PEDOT/SS electrodes prepared in 0.1 M H₂SO₄ are found to yield higher specific capacitance (SC) than the electrodes prepared from neutral aqueous electrolyte. The influence of various experimental variables such as concentration of H₂SO₄, concentration of SDS, potential of deposition and nature of supporting electrolytes used for capacitor studies are studied. Specific capacitance values as high as 250 F g⁻¹ in 1 M oxalic acid are obtained during initial stages of cycling. However, there is a rapid decrease in SC on repeated charge-discharge cycling. Spectroscopic data reflect structural changes in PEDOT on an extended cycling, and also as increase in its electronic resistance.

To prevent the solubility, poly(anthranilic acid) is confined in the cavities of the Nafion membrane by polymerizing anthranilic acid using novel electrochemical as well chemical methods. The PANA is characterized by electrochemical, optical, spectroscopic and scanning electron microscopic studies. It is anticipated that the solid form of poly(anthranilic acid) would be useful as a self-doped polymer for several applications.

Electrochemical reduction of H₂O₂ was studied on SS in 0.5 M NaClO₄ aqueous solution of pH 5.8. Cyclic voltammograms in low concentration of H₂O₂ and low sweep rates consisted of single reduction peak, whereas they consisted of two peaks at high concentrations of H₂O₂ and high sweep rates. This was attributed to a change in mechanism of reduction. This was supported by amperometric data, wherein a plot of current versus concentration consisted of two linear segments. The detection limit obtained was 5 μM H₂O₂ with sensitivity as high as 2.24 mA cm⁻² mM⁻¹. The RDE studies suggested that H₂O₂ reduction was diffusion controlled and the value of diffusion coefficient was calculated. These studies provide an insight for the usefulness of SS substrate without involving any
surface modification or employing any noble metal based catalyst for electrochemical reduction of \( \text{H}_2\text{O}_2 \).

The thesis work involves various electrochemical investigations employing PEDOT. The conducting polymer can be useful for various applications such as electrocatalysis, sensors, electrochromic windows etc. It can be predicated that sensing of bio-molecules is a thrust area in near future on new generation conducting polymer electrodes. PEDOT coated electrodes are expected to be useful in this application. Electrochromic windows or smart windows are expected to gain interest in future. PEDOT coated electrodes are likely to play a key role in this application also. Noble metal based catalyst nanoparticles dispersed on conducting polymers open a new area of catalysis. Catalyzing bio-molecules and fabrication of suitable nano-biosensor employing PEDOT is another aspect of future directions. In the thesis data are shown in Chapter 3 on nanoparticles deposited on PEDOT for electrocatalysis of small organic molecules. These studies can be extended to assembly of fuel cells (DMFC, DFAFC, DFFC and DEFC,) and their characterizations.
Appendix

On the basis of the comments of thesis examiners, the following additions are to be read in the appropriate pages as indicated for improving the clarity.

(1) Page 6, the following paragraph is added after the first paragraph:

Bredas and Street discussed the formation of polarons, bipolarons and solitons in detail (J. L. Bredas and G. B. Street, Acc. Chem. Res. 18 (1985) 309). In conducting polymers, the high electronic conductivity is due to doping by oxidizing or reducing agents. An insulating neutral polymer is converted into an ionic complex consisting of a polymeric cation (or anion) and a counter ion which is the reduced form of oxidizing agent (or oxidized form of the reducing agent). In a polymer, ionization process results in creating a hole on top of the valence band (VB). The charge on the chain is delocalized over the whole polymer chain. It is energetically favorable to localize the charge, which leads to local distortion of the polymer lattice. This localized charge is called a polaron. It is just a radical ion associated with a lattice distortion and the presence of localized electronic states in the gap referred to as polaron states. The binding energy of polarons is generally in the range 0.03 – 0.12 eV for conducting polymers. If a second charge is formed in the polaron by either oxidation or reduction, a bipolaron is formed. A bipolaron is considered as a pair of like charges (a dication or dianion) associated with a strong local lattice distortion. Some polymers such as trans-polyacetylene possess a degenerate ground state. In such polymers, an isolated charge can constitute a boundary between segments of the chain constituting two energetically equivalent states. This charge associated with the boundary is called soliton. A soliton can be viewed as an excitation of the system that leads from one potential well to another potential well of the same energy. On application of an electric field, the spinless bipolarons (which carry two charges) could become mobile at high dopant concentration.
In view of various electrocrystallization and growth models, equations are derived for kinetic controlled or diffusion controlled, two dimensional, three dimensional, etc., reactions and also for instantaneous or progressive nucleations (for a brief review please see Lefebvre and Conway, J. Electroanal. Chem. 480 (2000) 46). In all these equations, current is proportional to \(t^n\). If \(n = 1\), the electrocrystallization is kinetic controlled instantaneous nucleation; if \(n = 2\) it is kinetic controlled progressive nucleation; if \(n = 3\), it is three dimensional progressive nucleation, if \(n = -0.5\) diffusion controlled three dimensional instantaneous nucleation; if \(n = 0.75\), it is diffusion controlled three dimensional progressive nucleation. On the basis of this theory, Eq. (2.2) is considered as the relevant equation for the present results.

As expected from the Eq. 2.2, the ideal value for 3-D instantaneous diffusion control growth is -0.5. For 2-D disc instantaneous kinetic control growth, the slope value will be 1 (M. C. Lefebvre and B. E. Conway, J. Electroanal. Chem. 480 (2000) 46). As the slope of log current density versus log time curve (Fig. 2.2) is -0.3, which is close to -0.5, the predicted mechanism is diffusion controlled 3-D instantaneous nucleation.

Cyclic voltammetry was recorded for SS electrodes in 0.1 M H\(_2\)SO\(_4\) in the absence of EDOT and SDS. Current peaks indicating oxidation of SS in the supporting electrolyte were absent and current between 0.0 and 1.0 V was negligibly small in relation to the current measured in the presence of EDOT and SDS. Stability of SS in the mild acidic environment was ensured similar to the reports published previously (K. Rajendra Prasad and N. Munichandraiah, J. Electrochem. Soc. 149 (2002) A1393)"
(5) Page 61, lines 2-3, the sentence “These measurements were carried out in 0.1 M H₂SO₄” is replaced by following sentence:
“These measurements were carried out in 0.1 M H₂SO₄ at 0.30 V, which is the open circuit potential of PEDOT/SS electrodes.”

(6) Page 63, the following sentence is added at the end of the page:
“There is no significant change in the values of Rₜ, Q₁, n₁, Q₂ and n₂.”

(7) Page 75, last line, the following sentence is added:
“As the deposition required several minutes, it is likely that the double-layer charging has negligibly minor influence on the calculated charge. Additionally, the polymer does not exhibit redox behavior at 0.1 V. Furthermore, the potential of deposition is away from hydrogen evolution region, it is likely that the charge measured is consumed for the deposition of Pt.

(8) Page 80, the following sentence is added to the caption of Fig. 3.4 (A):
“TEM image with greater magnification is shown as inset in (A)”

(9) Page 87, at the end of 2nd line the following sentence is added:
“No additional current peaks pertaining to the conducting polymer PEDOT are present on the cyclic voltammogram. This is because PEDOT does not exhibit redox behavior in this potential range, unlike PANI which exhibits multiple redox peaks.”

(10) Page 75, at the end of 3rd line, the following sentence is added:
“Experiments were conducted using more than one electrode. Reproducibility of the data was ensured. The results of a representative electrode are only presented for discussions.”

(11) Page 107, the following sentence is added at the end of the page:
“The data of current density versus time (Fig. 3.22) indicate current oscillations. Current oscillations occur due to reported adsorption/desorption of reaction intermediates.”

(12) Page 114, the following sentence is added at the end of page:
“The data of current density versus time (Fig. 3.22) indicate current oscillations. Current oscillations occur due to adsorption/desorption of reaction intermediates as reported in detail in the literature.”

(13) Page 122, the following sentence is added at the end of 2nd paragraph:
“The data of current density versus time (Fig. 3.22) indicate current oscillations. Current oscillations occur due to reported adsorption/desorption of reaction intermediates”

(14) Page 129, the following sentence is added at the end of 1st paragraph:
“The data of current density versus time (Fig. 3.22) indicate current oscillations. Current oscillations occur due to reported adsorption/desorption of reaction intermediates”

(15) Page 143, the following sentence is added at the end of 1st paragraph:
“As PEDOT does not exhibit redox behavior in this potential range (unlike PANI, which exhibits multiple redox current peaks on cyclic voltammograms), there are no current peaks pertaining to PEDOT redox reaction present in Fig. 4.2.

(16) Page 172, the following sentence is added at the end of 1st paragraph:
“Experiments were conducted using more than one electrode. Reproducibility of the data was ensured. The results of a representative electrode are only presented for discussions.”
List of Publications


9) “Nanocatalyst impregnated conductive PEDOT electrodes for the electrooxidation of formic acid, formaldehyde and ethanol” S. Patra, M. Ganapathi, N. Munichandraiah, (Manuscript is under preparation).

10)“Atomic force microscopy and impedance spectroscopic study of PEDOT thin film” S. Patra and N. Munichandraiah. (Manuscript is under preparation).