CHAPTER II

STATE OF THE ART AND SCOPE OF THE INVESTIGATION

2.1. SELECTION OF 9,10-ANTHRAQUINONES AS ELECTROCATALYSTS

The importance of current research in the field of electrocatalytic studies lies in the utilization of modified electrodes [15-17], which catalyze the reduction of molecular $O_2$ to $H_2O_2$ or $H_2O$. Modifications of the electrodes have been carried out by immobilizing the electrocatalysts at the electrode surface and facilitating the electron transfer rate in slow electrochemical reactions. Perusal of literature reveals that many mediators such as titanium silicates [178], Au nanoparticle [179], copper [180], ruthenium-iron cluster [181], metal phthalocyanine [182], manganese oxide [183], metal macrocyclic complexes [5,184], pyrimidine bases [185], cobalt-iron oxide nanoparticles [96], cobalt porphyrin [120], palladium alloy [186], naphthoquinone [13,14] and anthraquinone [34,39,60,143] derivatives were employed as electrocatalysts for the reduction of oxygen to water or $H_2O_2$. Many studies were carried out using quinone mediators due to their facile reversible redox behavior [113-115]. 9,10-Anthraquinones are interesting compounds for the investigations in analytical and electroanalytical chemistry due to the fact that they contain the reducible $p$-quinone system and are electroactive.

Shamsipur et al reported the electrochemical behaviour of carbon paste electrodes spiked with amino derivatives of 9,10-anthraquinones at various pH [187]. Cyclic voltammograms of these amino derivatives exhibited quasi-reversible reduction processes. Mirkhalaf et al. [145] investigated the influence of substituents
on the electrochemical properties of quinone-modified GC electrodes and their
electrocatalytic activities for reduction of oxygen. They compared the kinetics of
oxygen reduction on GC electrodes modified with Bis-1,5-(thiophenyl)-9,10-
anthraquinone (AQ1), Bis-1,5-(benzenesulfonyl)-9,10-anthraquinone (AQ2), Bis-
1,5-(thiophenyl-4,4’diazo)-9,10-anthraquinone tetrafluoroborate (AQ3) and Bis-1,5-
(benzenesulfonyl-4,4’diazo)-9,10-anthraquinone tetrafluoroborate (AQ4). The
number of electrons transferred per oxygen molecule for all cases was close to two
indicating that the reduction of oxygen stops at the peroxide stage, but some
significant differences were noted. The redox potentials of substituted anthraquinone
in DMF solution were shifted positively compared to that modified with
anthraquinone. The change is in particular remarkable for AQ2-modified GC
surface, due to the stronger electron withdrawing properties of benzenesulfonyl
group, which results in the stabilisation of the radical intermediate. The rate constant
of one-electron reduction of substituted anthraquinone to the corresponding
semiquinone radical, was found to be 16 times faster for AQ2 than AQ1 in DMF
solution. This was explained by delocalisation of electrons caused by the sulfone
groups, which stabilises the radical formed. A positive shift of redox potential was
also observed for the AQ4-modified GC electrode in alkaline solution compared to
the AQ-grafted one. This is expected from inductive effects of the benzensulfonyl
group on radical formation as also observed in DMF. Hence, the semiquinone radical
is thermodynamically more probable when electron-withdrawing functional groups
are incorporated in the anthraquinone molecule. On the other hand, the chemical rate
parameter, \( k_I \), of oxygen reduction reaction is lower for AQ3 and AQ4 covalently
modified GC electrodes than for AQ-modified GC surface.
Salimi et al. [39] investigated the electrochemical behaviour, and the
electrocatalytic activity towards the oxygen reduction, of different 1-hydroxy-9,10-
anthraquinone substituted ‘podands’. GC electrodes modified with adsorptive films
of compounds were prepared by the electrochemical oxidation of glassy carbon
electrodes followed by immersing the electrodes in AQ solutions in acetonitrile. It
was shown that the resulting modified electrodes are stable in acidic solution as after
immersing in sulphuric acid for 16 hours; only a slight decrease of less than 5% of
the corresponding voltammetric peaks was observed in the time. The modified
electrodes are less stable in basic solutions with the greater loss of adsorbed species
manifested by the decrease of the voltammetric peaks. Species were found to
continuously desorb from the GC surface. However, it was demonstrated that the
very last few monolayers of the adsorbed species were remained tightly attached to
the preanodised GC electrodes. These adsorptive species stayed on the electrode
even after brief polishing with alumina. Residual adsorbed AQ derivatives could be
removed by extensive polishing with ‘sand-paper’ for a longer period. This is
probably because the AQ derivatives used were not only simply adsorbed but also
possibly trapped inside pores or crevices of the GC electrodes.

The cyclic voltammograms of the GC electrodes modified with the adsorbed
anthraquinone podands evidenced the presence of a single couple, two-electron, two-
proton redox reaction, with a formal potential around -200 mV vs. Ag/AgCl
(saturated KCl) electrode. Glassy carbon electrodes modified with each
anthraquinone derivative exhibited the expected Nernstian pH dependence of the
peak potentials for two-proton two-electron reduction in aqueous solutions for pH
values under 7.5. The corresponding plots of formal potential against pH resulted in a straight line with a slope between 61 and 64 mV/pH unit. However, in basic solutions of pH greater than 7.5, slope of the E-pH plots is about 31-32 mV per pH unit which is indicative of a two electron one-proton process resulting in the formation of the corresponding semi hydroquinone derivatives. The modified electrodes exhibited potential electrocatalytic activity towards oxygen reduction at pH 4.5, with an overpotential of about 380 - 470 mV lower than at a plain GC electrode.

Yan Jiao have investigated the electrocatalytic oxygen reduction activity of Graphene-Based Catalysts [188]. Also, the Electrocatalytic oxygen reduction on nitrogen-doped graphene in alkaline media was reported by Merlin Vikkisk et al [189]. Efficient Oxygen Reduction Electrocatalysts based on Winged Carbon Nanotubes was reported by Yingwen Cheng et al [190]. Mannan Boopathi et al have investigated the electrocatalytic reduction of Molecular Oxygen Using a Poly(terthiophene carboxylic acid) Appended by 1,5-Diaminonaphthalene Copper Complex [191].

Salimi et al also reported that the adsorbed 1,4-dihydroxy 9,10-anthraquinone derivatives [143] on glassy carbon electrodes showed excellent electrocatalytic ability for the reduction of oxygen to H2O2 with overpotentials from 560 to 650 mV at pH 6.0 – 7.0 lower than that of a plain glassy carbon electrode. Thus 9,10-anthraquinone and its derivatives are proved to be effective catalysts for the reduction of oxygen electrochemically. Hence any attempt to employ new derivatives of 9,10-anthraquinone or combination with various other electrocatalysts
or newer electrode modifications which may catalyse the reduction of oxygen and reduces considerably the reduction potential assumes importance. Thus the present investigation is aimed to study in detail the electrocatalytic behaviour of 9,10-anthraquinone and its derivatives at unmodified and various modified glassy carbon electrodes.

2.2. SCOPE OF THE PRESENT INVESTIGATION

Nowadays, mediators assume greater significance not only in day-to-day affairs of human beings but also in chemistry where enhancement of reactivity is needed. Electrocatalytic mediated redox reactions are preferable due to the better yield of products from the utilization of lesser quantity of energy. In recent years, there has been considerable interest in the electrocatalytic mediated reduction of oxygen under different experimental conditions [13, 32-36, 57, 145] mainly due to its involvement in energy conversion and storage. This catalytic reaction also resembles the oxygen reduction in biosystems. All these significances and relevance to the need of the society have led the present investigation towards the electrocatalytic mediated oxygen reduction. Various mediators [13, 14, 34, 60, 178-186] have been employed as catalysts and among these, 9,10-anthraquinone and its derivatives [39, 143, 145] showed promising results in mediating the oxygen reduction. The electrocatalytic ability of a glassy carbon electrode modified with riboflavin and polypyrrole in anthraquinone solutions were investigated by Manisankar et al. [156, 157]. Electrocatalytic properties of glassy carbon electrodes modified with hydroxy derivatives of 9,10-anthraquinone for oxygen reduction reaction was also reported by Manisankar et al. [192].
Modified electrodes proved their prominent utility in the catalytic reduction of oxygen over the past two decades and the search for the modifiers is still continuing. The electrode surface has been modified by the formation of polymeric films. As the field of conducting polymers is flourishing and become popular day by day, scientist are in search of newer materials to bring more advances in recent technologies. From this point of view, polymers such as polyaniline, polypyrrole and polythiophene have been used for modification. Conducting polymers hold significant promise as electrode coatings since the electrically conducting polymers are known to possess numerous features, which allow them to act as excellent materials for immobilization of molecules and rapid electron transfer for the fabrication of efficient sensors and electrodes. Recently, conducting polymers have attracted much interest in the development of sensors and fuel cells. Polymer and copolymer modified electrodes were in current interest towards the researchers for choosing the better electrocatalyst. Hence it has been proposed to utilize the polymer modified, copolymer modified with anthraquinone derivatives for the present investigation.

A newly modified electrode containing polymer and organic compound thus helps our environment to get electricity using fuel cells. Fuel cells are the pollution free technique which is advancing nowadays with greater hope. Also, they play important role in sensors which ensures a greater importance in industries. The oxygen reduction reaction involving two electrons or four electrons shows a notable attention in batteries, corrosion, electrocatalysis and industrial process.
The electrocatalytic reduction of oxygen on redox polymer coated electrodes has been the object of active investigation over the past two decades [9,176,193,194]. Various researches was carried out on oxygen reduction reaction [195-207]. As the catalytic properties depend on propagation of charge through the coating, redox polymer coated electrodes, due to immobilization of conducting solid polymer at the electrode surface, appear as particularly attractive modified electrodes for the electrocatalytic reductions.

Voltammetry is one of the few instrumental methods, which fulfill in a comprehensive manner the requirements of electrocatalytic studies. Cyclic voltammetry is often used as a first electroanalytical technique to study the electrochemical reactions. It is an important technique because of its ability to generate potentially reactive species, which enable us to examine them immediately by reversal. Its experimental simplicity leads to its ready usage and to study a variety of systems extensively. It can quickly provide qualitative information about catalysts and electrochemical reactions, such as the electrochemical response of catalysts and the catalytic activity of the catalysts with respect to some electrochemical reactions. Electrochemists have used this technique for the following purposes.

- To characterize the surface and interfacial structures.
- To evaluate the electron transfer reactions.
- To determine reaction mechanisms and substituent effects.
- To study the biosynthetic reaction pathways.
- To compare electrochemical reaction systems with bio-systems.
To evaluate the effects on the redox potential of the central metal ion in complexes and multi nuclear clusters and

To study the electrocatalytic mediated reactions.

The usefulness and importance of this technique has led to the selection of cyclic voltammetry for this investigation. Besides, chronoamperometry and chronocoulometry techniques are employed to determine kinetic parameters.

The major objectives of the present voltammetric studies in oxygen reduction are as follows:

- To study the electrocatalytic behaviour of selected 9,10-anthraquinone derivatives.
- To study the effect of pH on the electrocatalytic oxygen reduction.
- To study the electrocatalytic behaviour in polymer and copolymer modified electrode systems.
- To determine the number of electrons involved in anthraquinone reduction.
- To determine the diffusion coefficient of anthraquinones.
- To determine the number of electrons involved in oxygen reduction.
- To investigate possible mechanism for the oxygen reduction

Hence, in the present investigation, the electrocatalytic reduction of oxygen at various modified electrodes with 9,10-anthraquinones as catalysts in different pH region 1.0 to 13.0, has been examined by employing cyclic voltammetry, chronoamperometry and chronocoulometry techniques.
Chapter 3 presents the experimental setup and procedure adopted for the present study.

Chapter 4 deals with the electrocatalytic behaviour of four 9,10-anthraquinones at plain GCE in oxygen reduction.

Chapter 5 presents the electrocatalysis of oxygen by the same anthraquinone derivatives at poly (3,4 ethylenedioxythiophene) modified electrode (PEDOT/GCE).

Chapter 6 highlights the influence of the anthraquinone derivatives at poly(3-methylthiophene-co-3,4-ethylenedioxythiophene) (METH/EDOT/GCE) copolymer modified electrodes in the reduction of oxygen.

Chapter 7 reports the oxygen reduction reaction catalysed by the same anthraquinones at the copolymer poly(2-hexylthiophene-co-3,4- ethylenedioxythiophene) (HEX/EDOT/GCE) modified electrodes.

Chapter 8 includes the electrocatalytic effect of poly(2-octylthiophene-co-3,4-ethylenedioxythiophene) (OCT/EDOT/GCE) modified electrode combined with 9,10-anthraquinones in oxygen reduction.

Chapter 9 highlights the influence of the anthraquinone derivatives at poly(aniline) (PANI/GCE) modified electrodes towards oxygen reduction.

Chapter 10 includes the oxygen reduction in the presence of anthraquinones used at copolymer poly(aniline-co-3,4 ethylenedioxythiophene) (ANI/EDOT/GCE) modified electrodes.

Chapter 11 reports the summary of the investigations carried out in the present study.
Figure 2.1 Structure of anthraquinone derivatives used.

Figure 2.2 Structure of the monomers used.