DEVELOPMENT OF CONDUCTING POLYMER BASED ENZYME CATALYZED GLUCOSE BIOFUEL CELL ANODES

SUMMARY
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SUMMARY

Research on biofuel cells is the interdisciplinary combination of fuel cells and biotechnology. Like conventional fuel cells, biofuel cells convert chemical energy into electrical energy by catalyzing redox reactions at the cathode and anode and manage the flow of electrons and charge-compensating positive ions to form a complete electric circuit. Unlike conventional fuel cells, biofuel cells utilize living organisms, organelles, enzymes or DNA as catalysts to facilitate the charge transfer. The applications of biofuel cells are many but the focused and intuitive applications of biofuel cells are in implanted medical devices such as pacemaker, biosensors, micro drug pumps, deep brain stimulators, cochlear devices and contact lenses. These devices displace the old conventional lithium ion batteries because of their massive size, toxicity issues and most importantly these devices get discharged after a certain period of time. But, on the opposite side the biofuel cells work indefinitely by utilizing body glucose and oxygen, if implanted in the body. Most of the current biofuel cell technology utilizes non-biocompatible mediated enzymatic systems. It is of interest to employ mediators that should be biocompatible and directly convert the chemical signal to an electrical one by transferring electron effectively from the deeply buried active site of enzyme to the electrode surface modified with conducting polymers to assist in electron transfer. The goal is to fabricate and design bioanode by utilizing biocompatible mediator to carry out mediated electron transfer and at the same time improving the current density, lifetime and the problems hindering the performance of biofuel cells. After considering the above parameters these biofuel cells can be properly implanted within the patient’s body without distressing the patient.
Some of the important characteristics of the present thesis are:

- Chemical or electrochemical synthesis of conducting polymers to promote electron transport by decreasing electron tunneling distance of the enzyme active sites to the conducting solid supports.
- Fabrication of bioanode by using biocompatible redox active mediator.
- Proper immobilization of the biocatalyst and mediator with the aim of increasing the lifetime and current density of resultant biofuel cell anode.
- Physicochemical and electrochemical characterization of bioanode in different concentrations of glucose.

The research work presented in this thesis has been divided into five chapters.

**Chapter 1**

It deals with the basic information regarding the deleterious effects of fossil fuels by explaining the hazards and pollution caused by them with the main emphasis lying on the fact that they soon become vanish. It then explains the emergence and importance of the present day miniaturized biofuel cells replacing the conventional fuel cells. The information about the types of biofuel cells, their working principle, chemical reactions involved and applications along with a piece of literature on the work carried out during the last decade is discussed in this chapter.

**Chapter 2**

In this chapter, a single wall carbon nanotubes (SWNTs)/graphene/ferritin/GOx layer on a glassy carbon electrode (GCE) acting as a biofuel cell anode was fabricated using a SWNTs/graphene/ferritin composite as an electron transfer mediator from the enzyme to the electrode. In the presence of glucose, the
SWNTs/graphene/ferritin/GOx composite showed a higher current response than SWNTs/graphene/GOx composite and the electrocatalytic oxidation of glucose on the anode increased linearly with increasing concentration of glucose. The highly distributed SWNTs/graphene/ferritin composite acts as a platform for enzyme immobilization resulted in an enhanced electrocatalytic activity towards glucose. The SWNTs/graphene/ferritin composite showed an enhanced electron transfer from enzyme to the electrode; therefore, SWNTs/graphene/ferritin/GOx composite can be used as an anode in biofuel cells.

Chapter 3

In this chapter, a glassy carbon electrode (GCE) was tailored with conducting polymer polythiophene and further immobilized by an enzyme glucose oxidase (GOx). A thin film of polymer was developed by electrochemical polymerization of thiophene monomer. During electrochemical polymerization of the monomer the enzyme GOx and the redox active mediator ferritin (Frt) were entrapped within this polymer matrix. In this novel approach, the entrapment of enzyme and mediators within a polymer matrix occurs without chemical reaction that could affect their activity. The entrapment of enzyme and mediator within the conducting polymer matrices increases the surface area of the electrode. The tailored GCE/Ptp/Frt/GOx electrode showed a high catalytic activity. The increased surface area causes a high rate of electron transfer between the electrode and Frt engaged as an electron transfer mediator. The electrochemical properties of the electrode were determined by cyclic voltammetry (CV) and linear sweep voltammetry (LSV). The fabricated bioanode showed a current density of 3.9 mA cm$^{-2}$ at 1.0 V vs. Ag/AgCl in a 45 mM glucose solution and suggests proficient chances in biofuel cells (BFCs) applications.
Chapter 4

In this chapter, the polyaniline/polyvinyl alcohol/multiwalled carbon-nanotubes (PANI/PVA/MWCNTs) composite nanofibres were synthesized using electrospinning technique. Their morphology has been characterized using scanning electron microscopy. The electrospun PANI/PVA/MWCNTs nanofibres with average diameter of about 60-100 nm exhibited smooth surface at higher magnifications. The PANI/PVA/MWCNTs nanofibres modified electrode showed good electron transfer behavior because of the excellent properties of carbon nanotubes and the three dimensional and porous structures of electrospun nanofibres. The enzyme glucose oxidase (GOx) covalently immobilized with the PANI/PVA/MWCNTs nanofibres exhibited good electro catalytic activity towards oxidation of glucose through redox active as well as biocompatible mediator ferritin (FRT). The maximum current density using this nanostructured bioanode was 7.5 mA cm$^{-2}$ at 100 mV s$^{-1}$ vs Ag/AgCl in a 20 mM glucose solution was attained. The heterogeneous electron transfer rate constant ($K_s$) was found to be 3.09 s$^{-1}$. The results indicated that these electrospun PANI/PVA/MWCNTs nanofibres have potential to be used in BFC device as anode.

Chapter 5

This chapter deals with the synthesis of novel composite of conducting polymer poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) and sulphonated graphene oxide (SGO). Where in SGO displays synergistic effect by acting as charge balancing dopant as well as conductive filler. The conducting polymer PEDOT:PSS along with SGO serve as a means to facilitate electron transfer and co-immobilize the enzymes at the same time. Large surface area possessed by SGO leads to high enzyme loading and enables to improve the
current density of the cells. Synthesized composite shows outstanding electrical properties. Ferritin further enhances the transportation of electrons by acting as a redox active mediator that effectively transfers electrons from enzyme to the conducting support. Investigation of electrochemical performance of modified bioanode in presence of glucose for biofuel cells (BFCs) applications was carried out by means of cyclic voltammetry (CV) and linear sweep voltammetry (LSV) at different scan rates (20–100 mV s\(^{-1}\)) in 35 mM of glucose solution prepared in 0.3 M potassium ferrocyanide \([K_4Fe(CN)_6]\). The findings revealed that current increases with increase in glucose concentration and electrode exhibited good electrocatalytic activity with saturation current density of 27±2 mA cm\(^{-2}\).