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Functionalization of electrochemically deposited chitosan films with alginate and Prussian blue for enhanced performance of microbial fuel cells

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ABSTRACT

This work is aimed at finding new strategies for the modification of anode and cathode that can lead to improved performance of microbial fuel cells (MFCs). The electrochemical deposition of chitosan onto carbon felt followed by further modification with alginate led to the formation of a biocompatible platform for the prolific growth of microorganisms on the anode (Chit–Alg/carbon felt anode). The novel modification strategy for the formation of Prussian blue film, on the electrochemically deposited chitosan layer, has helped in circumventing the disadvantages of using ferricyanide in the cathode compartment and also for improving the electron transfer characteristics of the film in phosphate buffer. The anode was tested for its efficacy with four different substrates viz., glucose, ethanol, acetate and grape juice in a two compartment MFC. The synergistic effect of the mixed culture of *Acetobacter aceti* and *Gluconobacter roseus* was utilized for current generation. The electrocatalytic activity of the biofilm and its morphology were characterized by cyclic voltammetry and scanning electron microscopy, respectively. The power densities were found to be 1.55 W/m^3, 2.80 W/m^3, 1.73 W/m^3 and 3.87 W/m^3 for glucose, ethanol, acetate and grape juice, respectively. The performance improved by 20.75% when compared to the bare electrode.

1. Introduction

Microbial fuel cells are the bioelectrochemical systems that make use of the catalytic activity of the microorganisms in which the reduction equivalents are utilized for the generation of bioelectricity. As a future potential energy source, microbial fuel cells have to compete not only to increase the yield but also to decrease the cost of the bioprocess. Hence there is a strong need to increase the power yield of microbial fuel cells [1,2]. Scaling up of MFCs do not increase the power yield because on increasing the surface area of the anode the maximum power density generated by an MFC does not increase linearly, instead the power density increases proportional to the logarithm of the surface area of the anode [3–5]. The application of MFCs as capacitors was tried but they could not provide high power continuously [6,7]. Electrode materials and their spatial orientation play a key role in enhancing the MFC performance [8]. Though several materials like graphite, carbon felt, and carbon cloth are used in microbial fuel cells the electron transfer between the bacteria and the bare electrodes is often difficult due to the complex structure of its redox centers [9]. Recently several approaches are developed for modifying the electrodes for enhancing the power output in microbial fuel cells. They are mostly based on enhancing the conductivity of the electrode materials by using nanomaterials, carbon materials such as carbon nanotubes, graphene, conducting polymers and so on [10–14]. Electrode materials are mainly chosen based on the physical properties such as good conductivity and the concepts related to interaction of microorganism with the material, their growth, metabolism and physiology is given least significance. In this work, a study on the effect of biocompatible chitosan–alginate composite modified bioanode on the electrogenic activity of the coculture of *Acetobacter aceti* and *Gluconobacter roseus* is attempted. *A. aceti* and *G. roseus* are gram negative microorganisms with an excellent potential to oxidize a wide range of substrates and can be used as model organisms for electrochemical investigations. These organisms contain pyrroloquinoline quinone (PQQ) containing enzymes on the periplasmic membrane which aids in the oxidation of a wide variety of substrates [15,16]. This group of genera can also perform direct electron transfer with its membrane bound quinoheme

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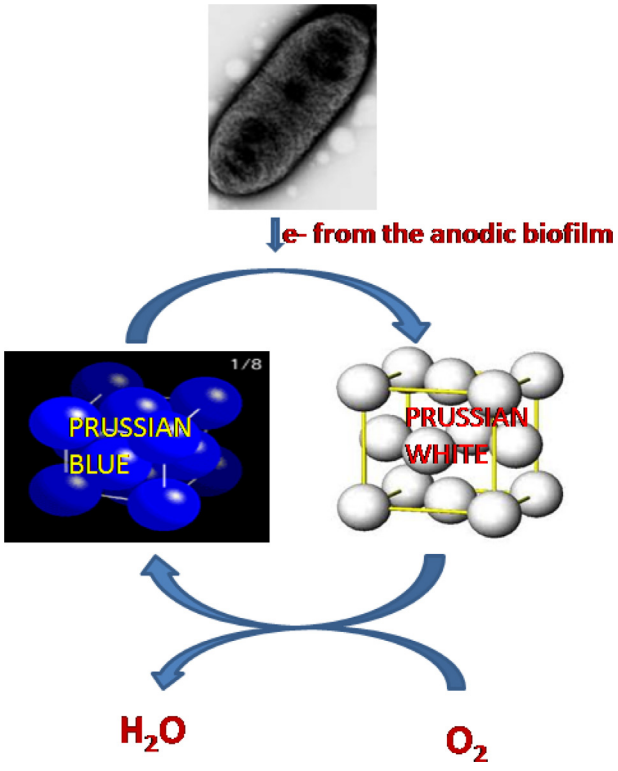
protein–cytochrome C complex. The bioelectrocatalytic activity of these two microorganisms and their synergistic effect are previously reported [17]. Bioaugumentation is a potential tool to enhance the power output of microbial fuel cells. Modification of electrodes with biopolymers is based on the bioaugumentation technique wherein a suitable environment supporting the adherence, survival and multiplication of the microorganisms on the electrode surface is developed leading to good anchorage of bacteria on the electrode surface and decrease in the interfacial electron transfer resistance [18]. These biopolymers may also aid in quorum sensing which in turn stimulate biofilm formation leading to enhanced power generation, however such mechanisms were not well understood. Chitosan possesses several interesting properties such as excellent membrane-forming ability, high permeability toward water, good adhesion, biocompatibility and nontoxicity. They have reactive amino and hydroxyl functional groups and the chemical modifications can be made easily [19–21]. Sodium alginate is a natural polysaccharide consisting of linked 1,4-*d*-mannuronic acid and L-guluronic acid residues [22]. Like chitosan, it has some special features such as non-toxicity, biocompatibility, biodegradability, chelating ability and hydrophilicity and so it is widely used in medical applications such as wound dressing, tissue engineering and in the immobilization of biocatalysts [23–25].

Ferricyanide solution is used as an electron acceptor conventionally in MFCs. We have addressed the disadvantages of ferricyanide solution and it can be overcome by modifying the cathode by chromium hexacyanoferrate. [26] It is known that the electrocatalytic film of Prussian blue (iron hexacyanoferrate) is stable only at low pH values [27,28], and therefore, its integrity and activity are badly affected by bulk and local changes in pH caused due to electron-transfer events in the interfacial region [29]. Gold bead electrode modified with Prussian blue containing starburst PAMAM dendrimer afforded mixed and stable electrocatalytic layers and also showed an enhanced stability at neutral pH values [29]. Fu et al. [30] reported an electrochemical glucose biosensor by immobilization of glucose oxidase (GOx) by one-pot chitosan (CS)-incorporated sol–gel process in the presence of Prussian blue deposited multi-walled carbon nanotubes hybrids. Prussian blue has excellent oxygen reducing abilities and Prussian blue/polyaniline-modified cathode was recently reported for its application in microbial fuel cells in an acidic catholyte [31,32].



Scheme 1. Schematic diagram illustrating the operational principle of the microbial fuel cell.

Herein, the Prussian blue film formed on the electrochemically deposited chitosan layer on carbon felt affords a novel platform for improving the electron transfer characteristics of the Prussian blue film in phosphate buffer. Prussian blue often gets desorbed from the electrode surface and use of chitosan for immobilization may aid to enhance the stability and longevity of the PB in the electrochemical system. Fernandes et al. [33] reported the mechanism for chitosan electrodeposition. The pH dependent solubility of chitosan allows the electrodeposition of chitosan on the conductive material from a bulk solution in response to cathodic signals. The rate of electrodeposition is proportional to the current density which can be adjusted by changing the applied voltage. Electrodeposition of chitosan yields a uniform film and it helps to assemble nanoscale particles into higher-order structures for further investigations [34]. Biopolymers are also widely used for the modification of bioanodes [35,36] and biocathodes [37,38] and we report herein the effect of chitosan modified cathode immobilized with Prussian blue for the microbial fuel cell applications. In this investigation we have studied the efficacy of the Chit–Alg carbon felt anode along with Chit–Prussian blue modified carbon felt cathode for current generation in a two compartment MFC (Scheme 1).

2. Materials and methods

2.1. MFC construction

The construction of the fuel cell has been described in detail by us in our earlier report [17]. Briefly two-compartment microbial fuel cells (MFCs) were constructed with proton exchange membrane (Nafion 115) as a separator. The volume of each compartment was 120 mL. Carbon felt was used as the base material for the modification of anode and cathode. *A. aceti* (NCIM No. 2116) and *G. roseus* (NCIM No. 2049) were procured from NCL, Pune, India and after sub culturing in suitable media, a mixture of these two microorganisms were used for the formation of biofilm on the anode. The microorganisms were subcultured in the medium whose composition is as follows: tryptone (1 g), yeast extract (1 g), glucose (1 g), and CaCO3 (1 g) in 100 mL of distilled water.

2.2. Modification of anode

Carbon felt ($5 \times 5 \times 0.5$ cm) was used as the base for fabricating the modified anode. 1% chitosan in 0.1 M acetic acid was prepared and was electrodeposited on the carbon felt at −10 V. The chitosan deposited electrode was left undisturbed till it becomes dry. Then 8% sodium alginate was dip coated on the chitosan deposited felt and is allowed to dry. This chitosan–sodium alginate coated felt was kept in 2% $CaCl_2$ overnight for the formation of calcium alginate and then was used as anode in MFC experiments.

2.3. Modification of cathode

The carbon felt (of dimension $5 \times 5 \times 0.5$ cm) was used for Prussian blue modification. Initially 3% chitosan in 0.1 M acetic acid was electrodeposited on the carbon felt by applying a constant potential difference of −10 V using a power supply. Then it was treated with 7 mM of $FeSO_4 \cdot 7H_20$ for 1 h. Then it was treated with a mixture of 0.15 M KCl, 0.1 M acetic acid and 5 mM of Ferricyanide overnight for Prussian blue formation and it is dried at room temperature. Similar films were also formed on carbon felt of smaller dimensions