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Enhanced response of microbial fuel cell using sulfonated poly ether ether ketone membrane as a biochemical oxygen demand sensor

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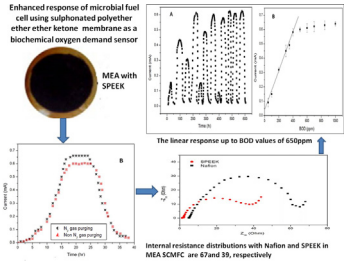
HIGHLIGHTS

- Sulfonated poly ether ether ketone (SPEEK) membrane in SCMFC used to determine the BOD.
- The biosensor produces a good linear relationship with the BOD concentration up to 650 ppm.
- This sensing range was 62.5% higher than that of Nafion®.
- SPEEK exhibited one order lesser oxygen permeability than Nafion®.
- Nafion® shows high anodic internal resistance (67 Ω) than the SPEEK (39 Ω).

GRAPHICAL ABSTRACT



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ABSTRACT

The present study is focused on the development of single chamber microbial fuel cell (SCMFC) using sulfonated poly ether ether ketone (SPEEK) membrane to determine the biochemical oxygen demand (BOD) matter present in artificial wastewater (AW). The biosensor produces a good linear relationship with the BOD concentration up to 650 ppm when using artificial wastewater. This sensing range was 62.5% higher than that of Nafion®. The most serious problem in using MFC as a BOD sensor is the oxygen diffusion into the anode compartment, which consumes electrons in the anode compartment, thereby reducing the coulomb yield and reducing the electrical signal from the MFC. SPEEK exhibited one order lesser oxygen permeability than Nafion®, resulting in low internal resistance and substrate loss, thus improving the sensing range of BOD. The system was further improved by making a double membrane electrode assembly (MEA) with an increased electrode surface area which provide high surface area for electrically active bacteria.

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1. Introduction

The BOD is an indicator for biodegradable organic load present in wastewater, widely used for the evaluation of wastewater quality [1]. However, the conventional method for determining the BOD is time-consuming (5 days of incubation) and usually requires expertise to achieve reproducible results. Development of alternative methods based on the dissolved oxygen consumption or photometric methods such as luminescence and fluorescence have been undertaken [2–5].

All these biosensors demonstrated a very good relationship with the BOD concentration but presented the limitation of having a very short operational stability and very low substrate versatility and also the measuring range is also very low, generally on the order of 0–110 ppm [4,6].

MFCs have been proposed in the past as biosensors for measuring environmental parameters such as BOD and water toxicity [3,4,7–11]. Varieties of MFC BOD sensors have been developed with the use of an electron-mediator, where the mediators are used to facilitate electron transfer from the microbial cells to

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the electrode. Even though the addition of mediators in these biosensors can enhance the electron transfer, toxicity of mediators results in poor stability of these biosensors. Mediator-less MFCs have been exploited to fabricate novel BOD sensors for continuous and real-time monitoring and showing an operational stability of over 5 years with minimum maintenance [3,4]. In addition, Kim et al. reported that the performance of an MFC as BOD sensor was improved using respiratory inhibitors. The signal from MFCs decreased in the presence of electron acceptors of higher redox potential such as nitrate and oxygen. The addition of azide and cyanide did not change the signal in the absence of the electron acceptors. A huge amount of oxygen diffuses into the anode compartment through the ion-exchange membrane, which separates the anode compartment from the cathode compartment [12]. A novel biomonitoring system using microbial fuel cells has been developed for the purpose of on-line monitoring of the inflow toxic substances into water systems [8]. MFC based sensing was explored to provide for the development of an in situ bioremediation monitoring approach for substrate concentrations and microbial respiration rates [10].

Mirella et al. tested a SCMFC, with an air cathode, as a BOD biosensor for the first time. The aim was to make a more compact and simple system with reduced cost of operation. An air-cathode MFC does not require aeration, recycling chemical regeneration of catholyte. Moreover the range of BOD concentrations detected by the biosensor increased because of a better oxygen supply to the cathode [6]. Upon review of the literature published in the area of fuel cells, it was noted that most of the biosensor related works, both previously as well as currently, utilized Nafion® despite the several problems associated with it.

In previous studies, a linear relationship between substrate concentration and current generated was observed only up to 150 ppm [4]. The SCMFC biosensor output had a linear relationship with the BOD concentration up to 350 mg BOD ppm [6]. The limitation was attributed to system design parameters, like electrode surface area, microbial efficiency, mass transfer, or cathode design [10]. The power production in the MFC among many factors mainly depends on the reactor configuration and the electrode material, performance of proton exchange membrane (PEM), the specific source of substrate and operating conditions such as temperature and pH. Many more improvements in the materials used for MFC construction will be necessary before its practical implementation to make it economically viable with the currently available treatment systems [13].

It is known that PEM influences the power output of the MFC. Nafion® is the most widely used PEM in the MFCs because of its high selective permeability to protons. However, Nafion® 117 being expensive, results in inflation in the production cost of the MFCs. Additionally Nafion® 117 shows a number of problems associated with it such as high cost ($1500 m^{-2}), oxygen leakage from cathode to anode, substrate loss and cation transport and accumulation rather than protons in the long run, Among these, leakage of oxygen into the anode chamber can lower the energy recovery and leads inaccurate measurement of BOD due to the substrate loss from aerobic respiration by facultative bacteria, and they can inhibit the growth of obligate anaerobes. Therefore, it is of great interest to develop a new membrane which can reduce the oxygen diffusion without greatly affecting the internal resistance or power density [14–17]. Among the various polymers, poly ether ether ketone (PEEK) is a promising polymer which is actively being researched by the fuel cell community to replace the Nafion®. PEEK is a low-cost polymer having good thermal stability and mechanical properties. Proton conductivity for this polymer can be achieved by sulfonation (sulfonated PEEK, i.e., SPEEK), and the degree of sulfonation (DS) can be easily controlled by varying the parameters of the sulfonation reaction [18,19]. In our earlier reports, we have described that SPEEK and its performance in MFC was doubled when compared with commercially available Nafion®, which was due to its one order lesser oxygen cross over than that of Nafion®. Further the SPEEK based MFC was used for waste water treatment [16]. Yusof et al. also reported the same that the SPEEK exhibited excellent power generation compared to the Nafion® 117 [20]. In this work we intended to use the SPEEK membrane for biosensor application in SCMFCs and using the electrochemical studies the system efficiency was studied in the aspects of oxygen cross over.

Table 1
Comparison of membrane properties.

Membrane specifications	SPEEK	Nafion®
Proton conductivity (S cm^{-1})	0.5×10^{-2}	1.2×10^{-2}
IEC (meq g^{-1})	1.23	0.952
Water swelling (%)	27	22
Thickness (μm)	170	175
K_0 (cm s^{-1})	2.6×10^{-6}	2.8×10^{-5}
BOD sensing range (ppm)	650	400
Internal resistances (Ω) (anode)	39	65

In the present study, the SPEEK membrane and the Nafion® membrane were evaluated in SCMFC as a biosensor in terms of its BOD detecting range and response time. The effect of the double MEA-MFC was also investigated.

2. Material and methodology

2.1. Electrolyte

Synthesis and characterization of PEM, i.e., SPEEK have been described in earlier reports and its performance in MFC was doubled when compared with a commercially available Nafion® and also its oxygen cross over was one order lesser than that of Nafion® [16]. In this work we plan to increase the degree of sulfonation (DS) to attain equal proton conductivity to Nafion®. In a typical experiment, 10 g of dry PEEK powder (Victrex, England) was dissolved in 150 mL of sulfuric acid under nitrogen atmosphere. To increase DS the reaction mixture was allowed to proceed for 8 h with constant stirring at 50 °C. The reaction was terminated with ice. The synthesized PEM showed good water uptake (27%), ion exchange capacity (1.23 meq g^{-1}) and proton conductivity (0.58×10^{-2} S cm^{-1}) (Table 1). Degree of sulfonation was determined as 70% from FTIR spectrum, based on the method of Khanh Ngan et al. (supplementary data 1) [21]. The only problem with the usage of SPEEK was that at higher degrees of sulfonation it was susceptible to dissolution in water at temperatures (above 60 °C). However, in the case of MFC this problem is not encountered as the MFC operation temperature is usually performed at room temperature which is about 30 °C.

2.2. MFC construction

The fabricated MFC consisted of an acrylic cylindrical chamber 4 cm long and 4 cm in diameter (empty bed volume of 50 mL) separated by a SPEEK or Nafion® proton exchange membrane. The anode electrode used was a carbon cloth which was 30% wet proofed. The cathode was prepared using a carbon cloth having 0.5 mg cm^{-2} platinum coating as a catalyst. The experiment was carried out with a MEA prepared using SPEEK and Nafion® membranes. The MEA was prepared according to the below mentioned brief procedure. The proton conducting membrane was sandwiched between the prepared anode and cathode electrodes and hot pressed at 70 °C under 1 tonne pressures for 2 min. The MEA was further assembled into the cylindrical single-chambered MFC with the cathode-side of the MEA facing the air (single MEA-SCMFC) as our previous designs

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