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Effect of composites based nickel foam anode in microbial fuel cell using *Acetobacter aceti* and *Gluconobacter roseus* as a biocatalysts

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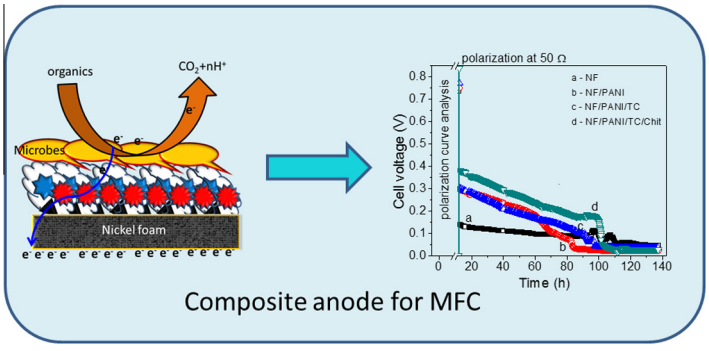
HIGHLIGHTS

- Bio-composite anode material was investigated in microbial fuel cells.
- Effects of conducting polymer, biopolymer and metal carbide were studied.
- The biocompatible composite anode material delivers the power density of 18.8 W m^{-3}.
- This power density is ≈2.3 times higher than the bare electrode (8.3 W m^{-3}).

GRAPHICAL ABSTRACT



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ABSTRACT

This study explores the use of materials such as chitosan (chit), polyaniline (PANI) and titanium carbide (TC) as anode materials for microbial fuel cells. Nickel foam (NF) was used as the base anode substrate. Four different types of anodes (NF, NF/PANI, NF/PANI/TC, NF/PANI/TC/Chit) are thus prepared and used in batch type microbial fuel cells operated with a mixed consortium of *Acetobacter aceti* and *Gluconobacter roseus* as the biocatalysts and bad wine as a feedstock. A maximum power density of 18.8 W m^{-3} (≈2.3 times higher than NF) was obtained in the case of the anode modified with a composite of PANI/TC/Chit. The MFCs running under a constant external resistance of (50 Ω) yielded 14.7% coulombic efficiency with a maximum chemical oxygen demand (COD) removal of 87–93%. The overall results suggest that the catalytic materials embedded in the chitosan matrix show the best performance and have potentials for further development.

1. Introduction

Microbial fuel cell (MFC) is a bioelectrochemical device which generates electrical energy from the metabolic activity of living organisms. Various parameters such as selection of substrates, the choice of biocatalysts and their direct electron transferring capability, the choice of mediators, the choice of terminal electron acceptors (cathode), pH, temperature, dissolved oxygen etc will

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limit the performance of MFCs. One of the major issues contributing to low performance is the inefficient anodic process responsible for transferring the electrons from the bacteria to the electrodes (Liu et al., 2015). Literature reports reveal that many attempts has been made to prepare efficient anode materials for MFC. Most of the MFC studies that utilize conventional carbon/-graphite materials for anodes (Liu et al., 2010). Further improvement in the performance has been achieved by modifying carbon/graphite with functional materials, which include polypyrrole-coated carbon, carbon felt doped with quinone derivatives, ammonia-treated carbon cloth and Iron, sulfur and phenyl group based modifications (Zhao et al., 2010). These modifications have led to only two to three fold improvements in the current density and the preparation of the modified electrodes requires complex preparation procedures (Hai et al., 2009).

Graphite anode modified with ammonia treatment showed 48% increased power output which could be due to the increased surface charges of the treated carbon electrodes (Cheng and Logan, 2007). Use of carbon nanotubes along with a coating of ferrocene on the anodes led to a foam like structure and resulted in high surface area and high catalytic activity (Morozan et al., 2007). Combination of carbon nanotube and polyaniline to form a novel composite anode exhibited an increased specific surface area and enhanced charge transfer capacity (Qiao et al., 2007). Compared to the use of carbon nanotubes as anode materials, the conductive polymers show significant improvement as MFC anode materials (Zhao et al., 2010). Among all the conductive polymers, polyaniline- and polypyrrole-based composite materials effectively improve the MFC performance. Recent studies on PANI and poly (aniline-co-o-aminophenol) (PAOA) modified carbon felt anodes resulted in about 35% and 18% improvement, respectively, when compare to unmodified carbon felt (Li et al., 2011). The electrochemically active polymers such as polypyrrole on vitreous carbon electrode could enhance the power output to a high level of 2400 W m^{-3} with an anolyte volume of 10 mL (Yuan and Kim, 2008). Moreover, graphite felt modified with quinone groups (C/HNO treatment) showed three fold improvement compared to unmodified graphite felt (Scott et al., 2007).

A conductive polyaniline nanowire network (PANI-NN) with three-dimensional nanosized porous structures was formed on anodes and it has been evaluated in MFCs with self-organized microbial communities (Zhao et al., 2010). Microsized pores in graphite felts would provide an increased area for microbial attachment, while nanoporous structures in PANI-NN would efficiently collect electrons from mediators excreted by microbes (Zhao et al., 2010). On the other hand, PANI finds applications in rechargeable batteries, corrosion protection of metals, molecular sensors and it is relatively easy to dope PANI. Another way of improving the efficiency of extra cellular electron transport is the immobilization of an electron redox mediator on the anode surface (Feng et al., 2010). The immobilization of AQDS (anthraquinone-2, 6-disulphonic disodium salt) on a carbon felt anode was accomplished by electro-polymerization of pyrrole with AQDS as the dopant and this anode produced 13 times higher power than the unmodified carbon felt (Feng et al., 2010). Ten times improvement in the power output has been achieved by coating electron mediators such as Mn^{4+} or neutral dyes on graphite (Park and Zeikus, 2002). A high surface area graphene was synthesized as an anode material in mediator MFC which delivered 18 times higher power output (2668 mW m^{-2}) than that of the unmodified anode (Zhang et al., 2011).

It has been observed that chitosan is a biopolymer having an *N*-deacetylated derivative of chitin, which could be obtained from exoskeletons of crustacean, mollusks and insects. Since chitosan has useful properties such as biocompatibility, nonirritant, good film forming nature, high mechanical strength and adhesion, it can be utilized for a wide range of applications such as sustained releasing systems, waste water treatments, packaging, separation membranes and biosensors (Marcasuzaa et al., 2010). The combination of PANI with chitosan has showed good electrical conductivity due to the H-bonding occurring between the chitosan backbone (H-acceptor amide group) and PANI backbone (H-donor imino group) (Marcasuzaa et al., 2010; Tiwari and Singh, 2007).

Reducing the activation barrier and to lower the cost of electrode, researchers were attempted to interface an electro catalyst to improve the performance of MFC. It was reported that interfacing the electrocatalyst (Tungsten carbide) could significantly improve the performance of microbial anode since it can oxidize the microbial fermentation products (eg. Formate) (Rosenbaum et al., 2006). Carbon electrode coated with tungsten carbide showed two fold increase in the power output in a glucose fed MFC (Rosenbaum et al., 2006). Carbide materials such as Nickel–tungsten carbide, Tungsten carbide, and Molybdenum carbide can be interfaced along with biocatalyst and they can also be increase the MFC performance not only due to the oxidation of fermentation product also it can improve the reaction kinetics by lowering the activation barrier of the electrode (Nagai et al., 2007; Rosenbaum et al., 2007; Zeng et al., 2010, 2012; Wang et al., 2014). As far as our knowledge goes, the synergistic effects of conducting polymer, biopolymer and metal carbide for the development of anode material in microbial fuel cells has not been investigated.

In the present study, the influence of incorporating titanium carbide along with the conducting polymer PANI is studied using nickel foam as a base substrate. The effect of chitosan matrix on the composite catalyst PANI + Titanium carbide is also investigated to increase power out from bad wine. Two compartments batch type MFCs were constructed with the aforesaid materials and the MFC performance was evaluated. *Acetobacter aceti* and *Gluconobacter roseus* were used as biocatalysts, bad wine was used as feedstock and ferricyanide was used as the catholyte.

2. Methods

2.1. Anode modification and electrode preparations

Nickel foam was chosen as a base material for MFC anode due to the porous structure can acts as a good support for the incorporation of the composite material. The nickel foam (5 × 5 × 0.2 cm, MarkeTech International, Inc.) was pretreated by sonication in acetone for 10 min followed by immersion in 5% HCl for 1 min to remove any surface impurities and finally rinsed thoroughly with distilled water and dried at room temperature (Dai et al., 2008). After that the electrode was modified by brush coating with the composite slurry obtained by the mixer of activated carbon – 5%, polyaniline-1% (PANI, Aldrich, emeraldine salt, grafted with lignin), polyvinylenedifluoride – 10% (PVDF, Aldrich) in N-methyl-2-pyrrolidone (NMP) (Alfa Aesar, HPLC grade, 99.5%). For further modification, titanium carbide (1%) and chitosan (2%) (from shrimp shells, Sigma Aldrich) were used. Then the coated anodes (coating thickness 0.5 mm) were dried at room temperature for about 48 h (see Supplementary information S1, S2). The total composite layer is around 100–180 mg/cm^2 of nickel foam. The nickel foam anode and the modified nickel foam of every modification was separately evaluated as anode material. Four different types of anodes viz., were evaluated for their performance in the MFCs (Fig. S2).

I. unmodified nickel foam (NF)
II. NF/PANI: *NMP = 50 mL, PANI = 0.5 g (1%/v), PVDF-5g (10%/v), Activated carbon: 2.5 g (5%/v)*