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Enhanced power generation using a novel polymer-coated nanoparticles dispersed-carbon micro-nanofibers-based air-cathode in a membrane-less single chamber microbial fuel cell

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ABSTRACT

A novel polymer-metal nanoparticle-carbon micro-nanofiber-based nanocomposite was developed as an efficient air-cathode of a membrane-less single chamber microbial fuel cell (SMFC) for bio-energy production using *Escherichia coli* as a microbial catalyst. The polymeric material was synthesized using suspension polymerization, with polyvinyl alcohol as a monomer and poly methyl vinyl ether-alt-maleic anhydride (PMVEMA) as a cross-linking agent. The synthesized polymer composite was coated over the alumina (AA) and nickel (Ni) nanoparticles (NPs)-dispersed multi-scale web of activated carbon fiber (ACF) and carbon nanofiber (CNF). The PMVEMA polymer facilitated proton exchange from anolyte to cathode in SMFCs. AA:Ni-ACF/CNF served as an electron acceptor as well as the catalyst for atmospheric oxygen reduction at the cathode. The polarization curves determined using linear sweep voltammetry demonstrated the prepared polymer-metal-carbon nanocomposite to be an efficient air-cathode of the SMFC with a maximum electrical potential of 980 ± 10 mV and a maximum power density of 1270 ± 30 mW/m^2.

Introduction

Conventionally, microbial fuel cells (MFCs) have been used for wastewater treatment and simultaneous production of bio-energy via bio-electrochemical reactions. Biodegradable organic compounds and wastewater serve as fuels for MFCs, which could otherwise be responsible for water pollution. Bacteria grown on anodes derive their food from organic wastes and act as a bio-electrocatalyst, releasing electrons and protons during the anaerobic respiration. The electrons are transported to cathode through an external circuit, completing the oxidation–reduction cycle and generating current [1–4].

The configuration of MFC is an important parameter that affects its performance. On the basis of configurations, there are two different types of the commonly used MFCs: double chamber (DCMFCs) and single chamber (SMFCs) [1,5–8]. The

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basic principles of working for both MFCs are the same. In DCMFCs, anode and cathode chambers are usually separated by a proton exchange membranes (PEM), though selective ion exchange membranes or non-ion separators are also used. In SMFCs, the readily available atmospheric oxygen is used as the terminal acceptor of electrons released by bacteria at cathode, instead of the potassium ferricyanide or potassium permanganate catholyte that is commonly used in DCMFCs. Such cathodes are called air-cathodes. SMFCs may have a PEM with air-cathode, where a sandwich electrode arrangement is considered: anode, PEM and air-cathode in sequence.

Recently, global research has shifted towards developing efficient air-cathodes for membrane-less SMFCs. The advantages of the air-cathode-based SMFCs over DCMFCs are less cost, reduced cell volume, operation without requiring oxygen-aeration and the regeneration of catholyte [6,9,10]. There are, however, a few drawbacks in using air-cathodes. In such devices, both electrodes are in direct contact with anolyte (wastewater). Therefore, the direct exposure of cathode to anolyte can facilitate the biofilm formation on the cathode surface, thereby increasing the proton transport resistance and decreasing the power generation efficiency [11]. Another drawback of a SMFC is the diffusion of oxygen to anode through porous cathode material, which can also lower the efficiency [12]. The biofilms developed on the solution side of the cathode may maintain an anaerobic atmosphere by consuming oxygen entering from the porous surface of the cathode [1].

From the above-overview of MFCs, it is clear that the cathode is a restrictive component of SMFCs. A slow oxygen reduction kinetics, large over-potential of oxygen, mass transport limitation due to the diffusion of oxygen through porous cathode, low solubility and diffusivity of oxygen in water, and the accumulation of inert gases in the pores of the cathode material may undermine the performance of SMFCs [13]. Different types of efficient and inexpensive cathode electrocatalysts such as iron phthalocyanine, cobalt naphthalocyanine, cobalt-tetra-methyl phenylporphyrin, manganese oxide, lead dioxide, and activated carbon have been used for oxygen reduction reaction (ORR), but they are unable to achieve high power and current density as compared to expensive noble metals such as platinum (Pt)-based catalysts [12,14–20]. Recently, transition metal/carbon composites, including Ni/carbon have been found to be promising cathode materials because of their high activity towards ORR. Such materials are also less expensive than noble Pt-based electrodes. A relative comparison of the costs has been provided in the supplementary file (S1). One more advantage of transition metal-based materials is that these are chemically inert in the electrolytes, besides providing a favorable environment to the bio-catalyst [4,21–24].

Conventionally, air-cathodes have been prepared by doping/brushing of cathode electrocatalysts with the Nafion/polytetrafluoroethylene (PTFE) binders on the anolyte-side of the carbon cloth/mesh, and a few layers of hydrophobic PTFE/poly(dimethylsiloxane) (PDMS) as diffusion layers on the air-side of the material. These diffusion layers are highly permeable to oxygen, and are capable of controlling water losses [13,25–29]. Ideally, the separator used on the anolyte-side of the cathode should have a superior hydrophilicity to facilitate cationic transport, and also, should suppress the diffusion of oxygen. They should also have a low internal resistance [30]. In this context, poly methyl vinyl ether-alt-maleic anhydride (PMVEMA) is an inexpensive copolymer which may be used as an alternative to Nafion as a proton exchanger in the MFCs. A water soluble copolymer, PMVEMA contains two main functional groups: (1) maleic anhydride unit with two carboxylic groups, which have proton-donor property and can form hydrogen bonds with hydroxyl and ether groups, and (2) methyl vinyl ether which is a proton-acceptor with respect to hydroxyl groups [31–33]. The PMVEMA cross-linked with PVA allows the transport of protons from anolyte to cathode, but it acts as a barrier to the oxygen transport [34] (supplementary file S2).

In this study, a novel polymer-coated, metal nanoparticles-dispersed carbon micro-nanofiber was developed as an air-cathode for a membrane-less SMFC with *Escherichia coli* (*E. coli*) as a microbial catalyst. The polymer was synthesized using suspension polymerization with PVA and PMVEMA used as a monomer and a cross-linking agent, respectively. The synthesized polymer composite was coated over the alumina (AA) and Ni nanoparticles (NPs)-dispersed multi-scale web of activated carbon fiber (ACF) and carbon nanofiber (CNF). The overall objective of the present study is to prepare a novel air-cathode material, which is inexpensive, chemically inert and active towards ORR.

Materials and methods

Materials

Aluminum nitrate nonahydrate GR ($Al(NO_3)_3 \cdot 9H_2O$, purity > 98.5%), nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, purity > 97%), sodium dodecyl sulfate (SDS, purity > 99%), benzene (C_6H_6, purity > 99%), sodium acetate (CH_3COONa, purity >98%), sucrose and other chemicals used for buffer preparation, including NaCl, KH_2PO_4, Na_2HPO_4 and KCl were procured from Merck (India). The hydrogen (H_2, purity > 99.999%) and nitrogen (N_2, purity > 99.999%) gases were purchased from Sigma Gases (India). The phenolic resin precursor-based ACFs were purchased from Gun Ei Chemical Industry Co. Ltd. (Japan). PMVEMA (molecular weight ~216,000) and partially hydrolyzed cold water soluble PVA (molecular weight ~100,000) were procured from Sigma–Aldrich (Germany). The culture of *E. coli* K-12 was procured from an indigenous source. The reagents used to prepare Luria Bertani (LB) medium, including tryptone and yeast extract were purchased from Thomas Baker Laboratory Reagent (India). All aqueous solutions were prepared in Milli-Q water. The MFC was fabricated from acrylic purchased from a local market.

Catalyst preparation

The as-received ACF samples were pretreated as per the procedure described in the previous study [35]. The ACFs were highly microporous, with the BET surface area (S_{BET}) of ~1200 m^2/g and total pore volume of ~0.6 cc/g of ACF, thereby serving as a good support to metal NPs [36,37]. The pretreated