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Original article

Modification of carbon felt anode with graphene oxide-zeolite composite for enhancing the performance of microbial fuel cell

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ABSTRACT

The present investigation explores the potentiality of porous tetrahedral zeolite clay composited with graphene oxide (GO) to be used as superior biocompatible anode material for microbial fuel cell (MFC). Anode base material carbon felt was modified either with GO-zeolite (GZMA) or only GO (GMA) and used as anode in the MFCs. Cyclic voltammetry analysis demonstrated oxidation peaks at −0.29 mV and +0.179 mV with respective peak current of 2.4 mA and 0.22 mA using GZMA. These currents were found to be much higher than the other two tested anodes *viz*. GMA and bare carbon felt anode. Power density and coulombic efficiency of 280.56 mW/m^2 and 44 ± 2.8%, respectively, from MFC using GZMA were found to be 3.6 and 2.75-times higher as compared to MFC using bare carbon felt anode (77.82 mW/m^2 and 16.3 ± 1.4%, respectively). High specific surface area of graphene oxide facilitated extensive support for zeolite capping and superior bacterial cell adhesion property of zeolite enhanced the anode bio-compatibility of GZMA, which resulted in considerable improved performance of MFC.

Introduction

Microbial fuel cell (MFC) is a bio-electrochemical system that directly converts chemical energy into electricity and has potential application for simultaneous wastewater treatment and energy recovery [1,2]. However, performance of MFC has not reached up to the optimum level owing to the overpotential losses occurring during the bioconversion of organic matter, which leads to lower the power output. Additionally, unfavourable physicochemical conditions for microbial growth and system architecture also contribute in power loss from MFC [3,4]. Anode material is the most important factor that impacts energy conversion in MFCs by interlinking microbiology and electrochemistry. To reduce the overpotential losses, enhancement of conductivity and biocatalytic activity of anode are the vital factors. For example, graphite disk anode encompassed with Au and Pd nanoparticles in comparison with uncoated anode showed enhanced biocompatibility and enhanced the current generation in MFC [5]. Hence, modification in anode materials could be a promising approach to overcome the overpotential losses. Modification of anode changes its physical and chemical properties thereby providing better microbial attachment by increasing electrochemically active surface area and enhancing electron transfer due to enhanced conductivity of anode material.

Edifying research works have been triggered, till date to bring forth effective modifications in anodes of MFCs. For instance, anode material made of carbon cloth, modified with formic acid [6] increased the maximum power density of a single-chambered MFC by 38.1% (from 611.5 ± 6 mW/m^2 to 877.9 ± 5 mW/m^2). Also, electrolysis of carbon cloth anode in nitric acid followed by soaking in aqueous ammonia yielded high power density of 3.20 ± 0.05 W/m^2 for two-chambered MFC [7]. Rajesh et al. [8,9] reported maximum coulombic efficiency of 45.18% and 11.6%, respectively, in MFC inoculated with mixed anaerobic sludge in anodic chamber and using *Chaetoceros* algae and lauric acid as methanogenic inhibitor. Anthraquinone-2-sulfonic acid (AQS), an electron transfer mediator, was immobilized onto the surface of graphite felt anode via spontaneous reduction of *in situ* generated AQS diazonium cations [10]. Anode modified with AQS in MFC enhanced the maximum power density, from 967 ± 33 mW/m^2 to 1872 ± 42 mW/m^2. In addition, mediators like lignin [11] and neutral red [12] have also been used to enhance bio-catalytic activity of anode in MFCs. Anode properties of paramount importance are conductivity as well as the specific surface area available for bacterial attachment, which can be enhanced using graphene to facilitate improved electron shuttle.

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Zeolites are a family of natural minerals of hydrated alumina-silicates that belong to the family of tectosilicates, where the SiO_4 tetrahedral form three-dimensional super-cages [13]. Due to their three dimensional rigid network, they facilitate ion exchange without undergoing any significant structural change and are also not governed by any shrink-swell changes [14]. Zeolite-modified electrodes (ZMEs) have the added advantage of ion exchange voltammetry along with their unique molecular sieving properties [15]. ZMEs are easily affordable and are finding increased applications in fields of water purification and biosensor development [16,17]. In presence of Ferrocene (FcH), zeolite modified carbon paste anode has been found to be efficient for biochemical oxidation of NADH [18].

In the present endeavour, carbon felt anodes were modified with graphene oxide-zeolite composite (GZMA) and graphene oxide (GMA) and performance of MFCs using these anodes was compared with the MFC having bare carbon felt as anode. This study was aimed to evaluate the feasibility of using graphene oxide-zeolite modified anode to increase power density and coulombic efficiency of MFCs, so as to have an alternate composite anode material that can improve performance of MFCs at low fabrication cost.

Material and methods

Synthesis of graphene oxide

Graphene oxide (GO) was synthesized using modified Hummer's method as reported in literature [19,20]. In brief, 3 g of graphite flake was slowly added to the mixture of concentrated H_2SO_4 (320 ml) and H_3PO_4 (80 ml) and then 18 g of $KMnO_4$ was supplied for oxidation. The above one-pot reaction mixture was stirred at room temperature for 72 h for complete oxidation. Later, the oxidation process was stopped by drop-wise addition of 30% H_2O_2 and change in colour of the solution was observed, from deep brown to bright yellow, which indicates good oxidation of graphite flakes. The solids were recovered by high speed centrifugation at 5000 rpm angular speed and treated with 1 N HCl (3–4 times) followed by washing with ultra-purified distilled water until the pH of the solution was found to be neutral. The treatment and washing process turned the colour from bright yellow to gel-like deep brown, suggesting exfoliation of GO [21]. Recovered GO was dried in vacuum oven at 60 °C and then stored at vacuum desiccator for further use.

Preparation of electrodes

The GO and commercially available zeolite (NaY, Himedia, India) at a ratio of 2:1 (100 mg GO + 50 mg zeolite) were dispersed in 50 ml of deionised water using titanium horn probe sonicator (Piezo-U-Sonic, India). After 3 h of sonication, 0.5 ml of 5% polyvinyl alcohol (PVA) was added to the composite solution and further sonicated for 30 min. The concentration of GO and zeolite in the composite solution, was maintained at 2 mg/ml and 1 mg/ml, respectively. Pieces of carbon felts having actual surface area of 9 cm^2 (3.0 cm × 3.0 cm) were rinsed with 1 N HCl. These pieces were cleaned under sonication for 30 min in deionised water to remove attached dust particles and subsequently rinsed repeatedly with deionised water and ethanol (35%) followed by heat treatment in muffle furnace for 30 min at 400 °C. Treated carbon felt was soaked in the above solution of GO and zeolite in a clean petri dish for 24 h at a temperature of 60 °C so as to obtain GO-zeolite modified anode (GZMA). A GO modified carbon felt anode (GMA) was fabricated adopting same procedure as stated above without the presence of zeolite in the solution. Modified anodes were further dried in hot air-oven at 60 °C for 24 h. Dried anodes were then weighed to get actual surface mass deposition of GO-zeolite composite or GO.

The air-cathodes of the MFCs were fabricated on the support of stainless steel (SS) wire mesh (6 cm × 6 cm) used as current collector. SS wire mesh was coated with ink-based solution containing Pt-C catalyst (0.5 mg/cm^2, Sigma-Aldrich, USA) and PDMS (Polydimethyl siloxane) binder with loading of 33.33 µl/cm^2 dispersed in acetone. Fabricated air-cathodes were then dried in vacuum oven at 80 °C for 6 h and stored in desiccators for use in MFCs.

MFC fabrication and operation

Three identical single-chambered MFCs were fabricated using acrylic sheet (Plexiglas) having an anodic chamber volume of 30 ml. These MFCs were having different anodes e.g. GZMA, GMA and bare carbon felt anode (control) and rest of the components were alike. MFC using bare carbon felt, GMA and GZMA coated anodes were termed as MFC-1, MFC-2 and MFC-3, respectively. Cation exchange membrane (Ultrex, USA) with an area of 16 cm^2 was used to separate anodic chamber and cathode in MFCs and to allow migration of H^+ ions from anodic chamber to air-cathode reaction interface. Electrode membrane assembly (EMA) in MFCs were held together with nut-bolt joint. Anode and cathode were connected through high grade concealed copper wires across a 100 Ω external load.

Mixed anaerobic sludge collected from the bottom of a septic tank was used as inoculum in the anodic chamber. The anaerobic sludge of volume 100 mL was pre-treated for 10 min in oven at 100 °C in order to suppress the growth of methanogens before inoculating in the MFCs. Initially, the mix-anaerobic sludge was ultrasonicated at 40 kHz frequency in Ultrasonic Processor (Piezo-U-Sonic) having constant supplied power of 120 W and then heat pre-treatment of was carried out in hot air-oven for 10 min at 100 °C. The beaker containing ultrasonicated sludge was kept in the hot-air oven at ambient temperature and allowed to increase the temperature. After reaching 100 °C, the sludge was kept in the oven for 10 more min for proper suppression of methanogens as reported in literature [22]. From this pre-treated sludge, 20 mL of the sludge was used as inoculum in anodic chamber for each MFC. Synthetic wastewater having sodium acetate of 3 g/l with suitable nutrient medium was used as substrate in the MFCs [23]. The experiments were conducted in three different identical single-chambered MFCs having different modified anodes. However, the observations were taken for multiple number of feed cycles in duplicate, hence giving reliability to the performance results obtained. These MFCs were operated in batch mode with a fresh feeding interval of 3 days under ambient temperature varying from 33 to 37 °C.

Analysis and calculation

Daily current generation was monitored with a digital multi-meter (CIE 122, Taiwan). Polarisation study was performed under variable external resistance mode in which resistance was decreased from 20,000 Ω to 5 Ω and the corresponding voltage was recorded for at least 30 min interval using a data logger (Agilent 34970A, Malaysia). The power density with respect to the projected surface area of anode was calculated according to P_d (mW/m^2) = EI/A, where E and I are voltage and current, respectively, corresponding to a particular external resistance and A is the anode surface area. The internal resistance of MFC was calculated by taking slope of the linear part of voltage vs. current curve. Coulombic efficiency (CE) was calculated using Eq. (1) [1].

$$CE,\% = \frac{M\int_0^t Idt}{FbV\Delta COD}\text{x}100 \quad (1)$$

where M is the molecular weight of the oxygen, I is current over time t, F is Faraday's constant, b is the stoichiometric electron exchanged, V is the working volume of anodic chamber and ΔCOD is the change in COD concentration over time t. The COD concentration in the influent (feed) and effluent after each batch cycle was estimated using closed reflux protocol as suggested by APHA, 1998 [24].