Electrochimica Acta 199 (2016) 154–163

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Improvement of power generation of microbial fuel cell by integrating tungsten oxide electrocatalyst with pure or mixed culture biocatalysts

Jhansi L. Varanasi[a], Arpan K. Nayak[b], Youngku Sohn[c], Debabrata Pradhan[b], Debabrata Das[a,*]

[a] Department of Biotechnology, Indian Institute of Technology, Kharagpur 721302, India
[b] Material Science Centre, Indian Institute of Technology, Kharagpur 721302, India
[c] Department of Chemistry, Yeungnam University, Gyeongsan 712-749, Republic of Korea

ARTICLE INFO

Article history:
Received 16 January 2016
Received in revised form 9 March 2016
Accepted 25 March 2016
Available online 26 March 2016

Keywords:
tungsten oxide
electrocatalyst
biocatalyst
anode
microbial fuel cell

ABSTRACT

The anode of microbial fuel cell was impregnated with tungsten oxide (WO_3) and platinum-tungsten oxide (Pt/WO_3) nanocomposites to improve its power generation. The amended anodes were tested against pure and mixed culture type of biocatalysts. Improved performance was exhibited by the modified electrodes as compared to the uncatalyzed electrodes using both biocatalysts. However, pure culture showed higher power outputs as compared to the enriched mixed consortia. The maximum power density up to 0.15 mW cm^{-2} (1.46 W m^{-2}) was obtained using pure culture which was almost 45% higher as compared to uncatalyzed electrodes. The anode modification also helped in lowering the charge transfer resistance and improving the coulombic efficiencies of the MFCs. High capacitance with nanostructure catalysts implied their role in holding an electric charge while SEM and epifluorescent images revealed enhanced bacterial adhesion. The high electrode conductivity, stability, and biocompatibility of the modified anodes make them more attractive for practical microbial fuel cell applications.

1. Introduction

Microbial fuel cell (MFC) is a promising technology that converts chemical energy present in organic wastes directly into electricity. A major drawback of these systems is the low power generation which needs to be substantially improved for commercialization of this process [1]. Although several research work are focused towards the development of cathode materials for MFC considering its catalytic limitations [2–5], characteristics of bio-anode is also considered to be significant as it directly affects the bacterial interaction, electron transfer, and substrate oxidation [6]. Most of the electrogenic bacteria used in MFCs form electroactive biofilm over the electrode surface to perform direct electron transfer [7]. These biofilm structures increase the distance of electrons that need to travel from e^- donor to e^- acceptor [8]. At present, carbon-based anode materials (such as carbon paper, graphite, carbon felt, etc.) are used widely in MFCs to act as an exogenous solid electron acceptor. However, their low surface area fails to accommodate several microbial reactions occurring at the anode surface [9].

Electrode modification by using nanostructures with high surface area is an attractive strategy to improve the performance of MFCs [4,5]. The catalytic mechanism occurring in the anode involves a combination of biocatalysis and electrocatalysis [11]. The biocatalyst harvests electrons from the organic wastes and transfers these electrons to the anode (which acts as a terminal electron acceptor). These electrons are then traversed along the external circuit reaching cathode where they are utilized in the reduction of O_2 and H^+ ions producing an electric current in the process. Electrocatalysts on the other hand function at electrode surfaces which catalyze the undergoing electrochemical reactions and increase the rate of the reaction. The effective surface area of anode increases considerably with the help of nano-electrocatalysts and this improves the contact with the biocatalyst. Thus, it is essential that the nanostructure chosen should have high biocompatibility with the host bacteria and help in enhancing the electron transfer rate [12–15].

Tungsten oxide (WO_3) nanoparticles are known to have good biocompatibility and electric conductivity due to which they are extensively used in biosensors, bio-imaging and bioelectrochemical systems [16]. Recently, an anode electrocatalyst based on WO_3

* Corresponding author.
E-mail addresses: ddas.iitkgp@gmail.com, ddas52003@yahoo.com, ddas@hijli.iitkgp.ernet.in (D. Das).

http://dx.doi.org/10.1016/j.electacta.2016.03.152
0013-4686/

was developed for MFC applications [15]. It was suggested that due to the rough surface of the WO_3 particles, bacterial colonization was favored that enhanced biofilm formation [8,9]. So, in the present study, WO_3 nanoparticles were synthesized and fabricated as anode electrocatalysts due to their good electrocatalytic property, low cost, biocompatibility and non-toxicity while platinum-tungsten oxide (Pt/WO_3) composites were used to compare the performance of MFCs.

Most of the studies dealt with anode modification in MFCs used pure cultures such as *E.coli*, *Shewanella sp*. *Pseudomonas sp.* etc. as biocatalyst [8,10,11,12]. Use of pure cultures in MFCs require stringent sterile conditions and thus increases the overall cost of the process. Also, in a practical scenario of wastewater treatment, a diversity of the microbial population is expected to be present that can alter the performance of modified anode [20]. This suggests that anode modification studies with single species are not good enough to completely understand the biocatalyst-nanocatalyst interactions in MFCs that might help in enhancing electron transfer rates. Therefore, in the present study, an enriched mixed consortium was used in an unsterile environment and compared with a pure culture (*Shewanella* sp.) in sterile conditions to understand the effect of an electrocatalyst on different types of biocatalysts. The overall objectives of the present study were to investigate the electrocatalytic properties of WO_3 and Pt/WO_3 modified anodes in MFC and to compare the modified and unmodified anodes with respect to biocatalyst (pure and mixed cultures).

2. Materials and methods

2.1. Chemicals

Analytical grade of sodium tungstate dihydrate ($Na_2WO_4.2H_2O$) (SRL, India); hydrochloric acid (HCl) (Merck, India); oxalic acid ($C_2H_2O_4.2H_2O$) (Merck, India); ethanol (C_2H_5OH) (ChangshuYangyuan Chemical, China), chloroplatinic acid hexahydrate ($H_2PtCl_6.6H_2O$) (Sigma-Aldrich, India) were used in the present studies.

2.2. Synthesis of WO_3 nanoplates and Pt/WO_3 nanoplates

WO_3 flowers-like structures consisting of nanoplates were successfully synthesized by using a hydrothermal method. 1.6 g sodium tungstate hydrate (0.12 M) was added to 40 mL distilled water and stirred for few min. Then 4 mL of concentrated HCl (35% v/v) was added dropwise to the above solution. The resulting solution turns yellow. Then 1 g oxalic acid (0.2 M) was added to above solution. The solution became colorless. The final colorless solution was transferred to a 50 mL Teflon-lined stainless steel autoclave and sealed. The autoclave was heated at 200 °C in a muffle furnace for 12 h and then cooled naturally to room temperature. The precipitated product was collected by centrifuging. The powder was finally washed with ethanol and distilled water and dried at 60 °C for 4 h. For the synthesis of Pt nanoparticles decorated WO_3 nanoplates (Pt/WO_3), 1 mL of chloroplatinic acid hexahydrate (0.05 M) was added additionally keeping other reaction parameters constant.

2.3. Characterization

The surface morphology of synthesized power was examined using a Carl Zeiss SUPRA 40 field-emission scanning electron microscope (FE-SEM). The structural property of the samples was investigated with a PANalytical High-Resolution X-ray diffractometer (XRD) (PW 3040/60) operated at 40 kV and 30 mA with Cu Kα X-rays (1.54 Å) in the 2θ angle 20–80°. The detail microstructures of the samples were studied using an FEI TECNAI G2 transmission electron microscope (TEM).

2.4. NanostructuredWO_3 and Pt/WO_3 decorated anode preparation

Nanostructured WO_3 and Pt/WO_3 composites were used for the modification of anode in MFCs. A requisite amount of nanoparticle (0.5 mg cm^{-2}) was first dispersed in the acetone-isopropyl alcohol (1:1) solution. This solution was then mixed with 1% v/v polytetrafluoroethylene (PTFE; Sigma-Aldrich) which acts as a binder. The overall mixture was subsequently sprayed on a carbon felt (16 cm^2; projected surface area) by a gravity spray gun and dried at 70 °C in an oven for 6 h. The modified WO_3 (or) Pt/WO_3 composite loaded carbon felts were then used as anodes in MFCs.

2.5. Inoculum and anolyte

Shewanella putrefaciens (ATCC® BAA1097™) was used as inoculum for pure culture experiments while an enriched mixed consortium was developed from fly ash leachate in the laboratory [21]. This was used for mixed culture experiments. The anolyte comprised of synthetic wastewater with the composition of $NaHCO_3$–2.5 g L^{-1}; KCl – 0.1 g L^{-1}; NH_4Cl – 1.5 g L^{-1}; NaH_2PO_4–0.6 g L^{-1}; vitamins and trace elements; pH adjusted to 7. Sodium acetate was used as electron donor. Desirable chemical oxygen demand (COD) of 3 g L^{-1} was maintained by altering the electron donor concentration in the medium.

2.6. MFC assembly construction and operation

Twelve identical single chambered MFCs (sMFCs) made up of polyacrylic material (working volume 100 mL) were used for the experiments with an anode compartment and an air cathode placed on opposite side. The anode consisted of a carbon felt of working surface area 16 cm^2 with a stainless steel wire welded to form the terminal. The membrane cathode assembly was prepared by bonding the carbon ink coated anion exchange membranes (RALEX™ AM-PES, Mega Inc.) onto a flexible stainless steel (SS) mesh (32 cm^2). This SS mesh was then attached on the air-facing side of MFC with the help of a conducting paint (Siltech corp., India) serving as air cathode. Higher cathode surface area was maintained to minimize cathodic losses. Based on the type of modification on the carbon felt anode, the pure and mixed culture systems were divided as $MFC_{uncatalyzed}$ (unmodified), MFC_{WO3} ($WO_{3modified}$) and $MFC_{Pt/WO3}$ ($Pt/WO_{3compositemodified}$). All the experiments were carried out at room temperature (25 ± 5 °C).

2.7. Analytical measurements

Polarization and power density curves for MFCs were obtained by varying the external resistance using a variable resistance box (range 1000 KΩ – 10 Ω) in discrete steps and measuring the corresponding voltage drop. The current densities, power densities and coulombic efficiencies were calculated as described previously [21]. Cyclic voltammograms (CVs) of bioanode were recorded with a Potentiostat/Galvanostat system (Gamry Reference 600, United States of America) connected to personal computer at a scan rate of 1 mV s^{-1} and a potential window of +0.6 V to −0.6 V. A three electrode configuration consisting of bioanode (working), cathode (counter), and Ag/AgCl/3 M KCl (reference) was used for electrochemical measurements. Electron transfer behavior of bioanode was studied by electrochemical impedance spectroscopy (EIS). The EIS of bioanode was performed with a three electrode configuration consisting of bioanode, platinum wire, and Ag/AgCl as working, counter and reference electrode, respectively. EIS was