Bioresource Technology 169 (2014) 532–536

Contents lists available at ScienceDirect

Bioresource Technology

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

Highly durable anodes of microbial fuel cells using a reduced graphene oxide/carbon nanotube-coated scaffold

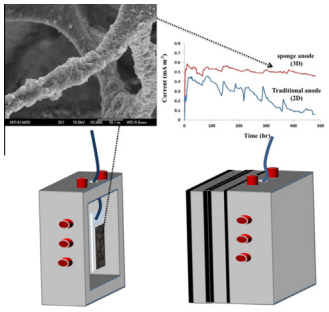
Hung-Tao Chou [a], Hui-Ju Lee [b], Chi-Young Lee [a], Nyan-Hwa Tai [a,*], Hwan-You Chang [b]

[a] Department of Materials Science and Engineering, Hsin Chu 300, Taiwan
[b] Department of Medical Science, National Tsing Hua University, Hsin Chu 300, Taiwan

HIGHLIGHTS

- A porous, conductive carbon coated sponge is used as anode.
- High specific area and biocompatibility anode promotes bacteria immobilisation.
- ONPG assay is used to analyse the activity of bacteria immobilised on anodes.
- Well transportation proliferate the bacteria, prolonging the MFC durability.
- Sponge anodes yield high durability and current density.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 April 2014
Received in revised form 28 June 2014
Accepted 4 July 2014
Available online 16 July 2014

Keywords:
Microbial fuel cell
Graphene
Macroporous anodes
Bioenergy
Biocatalyst

ABSTRACT

Melamine sponges coated with reduced graphene oxide/carbon nanotube (rGO–CNT sponges) through a dip-coating method were fabricated that provide a large electrical conductive surface for *Escherichia coli* growth and electron transfer in microbial fuel cell. Four rGO–CNT sponges with different thicknesses and arrangements were tested as an anode in this study. The thinnest one (with a thickness of 1.5 mm) exhibited the best performance, providing a maximum current density of 335 A m^{-3} and a remarkably durable life time of 20 days at 37 °C. Analyses of bacterial colonisation on the rGO–CNT sponges using FE-SEM and the bacterial metabolic activity using the β-galactosidase assay indicates that the rGO–CNT sponges provide excellent biocompatibility for *E. coli* proliferation and could help to maintain high bacterial metabolic activity, presumably due to the high mass transfer rate of the porous scaffold. In this regard, the rGO–CNT sponges showed higher durability and performed better electrochemical properties than traditional carbon-based and metal-based anodes.

1. Introduction

Fossil fuels are essential for our daily energy needs. However, the exhaustion of fossil fuel reserves and the negative impacts by fossil fuel consumption on our environment, including air pollution and global warming, have prompted scientists to develop renewable energy technologies. One promising low-cost alternative energy technology is microbial fuel cells (MFCs), which are devices that convert bacterial metabolic chemical energy into electrical energy (Mohan et al., 2008; Rabaey and Verstraete, 2005). In MFCs, electrons are generated at the anode when bacteria oxidising carbon sources to produce protons and carbon dioxide. The electrons travel through an external circuit while the protons move by diffusion to the cathode, where they react with electron acceptors, most frequently oxygen, to complete the electricity

* Corresponding author. Tel.: +886 3 5742568.
E-mail addresses: nhtai@mx.nthu.edu.tw (N.-H. Tai), hychang@mx.nthu.edu.tw (H.-Y. Chang).

http://dx.doi.org/10.1016/j.biortech.2014.07.027
0960-8524/

generation process. Numerous publications have demonstrated that microbial fuel cells show great potential for power generation, waste water treatment, and biosensor applications (Li and Sheng, 2012; Kalathil et al., 2012).

An MFC typically comprises two compartments: an aerobic chamber containing the cathode and an anoxic chamber that houses the anode and the bacteria which act as catalysts. Because of its advantageous properties including rapid growth rate and avirulence, *Escherichia coli* is one of the most frequently used bacterial model in laboratory for electrochemical oxidation of carbon sources in MFCs although several other bacteria species such as *Pseudomonas aeruginosa* and *Shewanella* spp. that are more suitable for the use in wastewater have also been tested (Herrero-Hernandez et al., 2013).

The desired properties of an anode in an MFC should include excellent electric conductivity, large surface area, and high biocompatibility for bacteria colonisation (Cheng and Logan, 2007; Qiao et al., 2007; Wang et al., 2009). Carbon materials, such as carbon cloth, carbon paper, and activated carbon meet these requirements. However, surface fouling of these carbon materials by microorganism secretions during MFC operation is common. The poor mass transfer of metabolic wastes and nutrients and decreases of surface area for bacterial colonisation can lead to lose of electrode functionality, exhibited by electric current decay and life-span reduction (Gutierrez et al., 2007; Katuri et al., 2011). To enhance the durability of MFC and reduced the cost, significant effort has been exerted on providing a large specific surface area of the anode (Gutierrez et al., 2007; Katuri et al., 2011; Vazquez-Larios et al., 2010).

Graphene is an atomic layer of carbons arranged in a hexagonal manner. Because of its high specific surface area and high electrical conductivity, graphene has been widely used in lithium ion batteries, solar cells, and super capacitors. Additionally, the material can support catalysts and is a promising material in biofuel applications (Xiao et al., 2012; Yuan et al., 2012; Liu et al., 2012; Zhang et al., 2011). Several published articles have demonstrated that graphene is capable of promoting microorganism to secrete signalling molecules, which could accelerate the growth of bacteria and act as an electrical mediator to enhance the power transfer efficiency (Liu et al., 2012; Zhang et al., 2011; Jain et al., 2012). Studies on the applications of graphene in MFCs have been focused on the promotion of the oxygen-reducing capability of the cathode. However, few articles have addressed utilising the biocompatibility and high specific surface area features of graphene to improve anode performance (Wen et al., 2012).

This work reports the fabrication of a conductive 3-dimensional structure for the purpose of improving anode performance of MFCs. The device is generated by coating reduced graphene oxide (rGO) and multi-walled carbon nanotubes (MWCNTs) on commercial melamine sponge through a simple dip-coating process. The fabricated structure exhibits high porosity and specific surface area, which are beneficial for bacteria immobilisation to provide higher current output. An enhancement in current generation stability and electrode durability are also reported herein.

2. Experimental

Suppliers of raw materials and chemicals are listed in Table S1.

2.1. Nanomaterial preparation and characterisation

Graphene oxide was prepared by a modified Hummer's method and was further treated with $NaBH_4$ at 120 °C for 7 days to form rGO (Hummers and Offeman, 1958). The resulting rGO was subjected to functionalisation to improve its dispersibility in solvent. In short, 1.0 g of rGO suspended in 50 mL 10% $KMnO_4$ (w/v) was acidified using 200 mL of 3 M H_2SO_4. After under sonication for 6 h, the rGO was mixed with 50 mL 10 M HCl solution and the mixture was stirring at 75 °C for 30 min. Finally, the rGO was washed to neutral pH with double distilled water. The product after each processing step was collected by filtration through a 0.22-μm cellulose filter (ADVANTEC) examined by X-ray diffraction using a Shimadzu XRD6000 instrument. The well-dispersed functionalised MWCNTs (f-MWCNTs) were obtained as described previously (Chou et al., 2013).

Both the f-MWCNTs and the functionalised rGO (f-rGO) were analysed by Fourier Transform InfraRed spectroscopy (Spectrum RX, Perkin-Elmer) to examine the presence of carboxyl function groups. The lateral size of f-rGO was determined using Zeta potential measurement by the Zeta-sizer (Malvern). The purity of the synthesized f-MWCNTs and the f-rGO were estimated based on residual weights obtained from thermogravimetric analysis (TGA, Pyris Diamond TG/DTA, Perkin-Elmer).

2.2. Anode preparation and characterisation

Functionalised rGO and f-MWCNTs were mixed with poly(3, 4-ethylenedioxyth-iophene) poly(styrenesulphonate) (PEDOT:PSS) ink, each at a final concentration of 0.5%. The ink was used to enhance conductivity and adherence of carbon materials on the sponge scaffold. The mixture is designated as rGO–CNT ink.

Two melamine sponges, each has a thickness of 1.5 mm and 3.0 mm, respectively and a cross sectional area of 2.5 cm × 2.5 cm were prepared and dipped into rGO–CNT ink for 10 min followed by a drying process. The dipping–drying process was repeated three times to increase the carbon load and to enhance the uniformity of the coating layer on the scaffold. The surface topology of the rGO–CNT-coated sponge was examined using a field-emission scanning microscope (JSM-6500F FE-SEM, JEOL, Japan).

The as-prepared rGO–CNT sponge was adhered to a 6 cm × 6 cm stainless steel slice (SSS) using carbon paste. The stainless steel surface was coated with polydimethylsiloxane (PDMS) to create an insulation layer and prevent microorganism from immobilisation. Graphite slice (GS), SSS, and SSS coated with rGO–CNT ink (C-SSS) were then tested under the same experimental condition using the rGO–CNT sponge as a comparison. The rGO–CNT coated on the C-SSS surface has the same composition as those coated on the sponge.

2.3. Microbial fuel cell construction and operation

The MFC, as schematically depicted in Fig. S1, was assembled according to the procedure described in published articles (Rabaey and Verstraete, 2005; Wen et al., 2012). The anolyte consists of sterilized Luria-Bertani (LB) broth, phosphate buffered saline (PBS), methylene blue (an electron transfer mediator, 0.03 mM), glucose, and bacteria solution (OD = 0.3). The catholyte contained 0.1 M $K_3[Fe(CN)_6]$ in PBS buffer. After the MFC was assembled, the electrolyte was pour into the chamber at an equal volume (400 mL), and the whole device was placed in an incubator set at 37 °C.

The current generation of the MFC was recorded when 10 mL *E. coli* JM109 (OD = 0.3) were injected into the anodic chamber and the electric potential was zero. Additional glucose was added every 60 h. The fuel cell was monitored using a digital multi-metre, and the circuit was operated under a fixed external resistance of 1000 Ω, which was determined according to the polarisation curve.