Biosensors and Bioelectronics 50 (2013) 373–381

Contents lists available at SciVerse ScienceDirect

Biosensors and Bioelectronics

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

Biotic and abiotic characterization of bioanodes formed on oxidized carbon electrodes as a basis to predict their performance

Bibiana Cercado [a], Luis Felipe Cházaro-Ruiz [a], Vianey Ruiz [b], Israel de Jesús López-Prieto [b], Germán Buitrón [b], Elías Razo-Flores [a,*]

[a] Instituto Potosino de Investigación Científica y Tecnológica, A.C. División de Ciencias Ambientales, Camino a la Presa San José No. 2055, Lomas 4a Sección, 78216 San Luis Potosí, San Luis Potosí, México

[b] Laboratorio de Investigación en Procesos Avanzados de Tratamiento de Aguas, Unidad Académica Juriquilla, Instituto de Ingeniería, Universidad Nacional Autónoma de México, Campus Juriquilla, UNAM. Blvd. Juriquilla No. 3001, 76230 Querétaro, México

ARTICLE INFO

Article history:
Received 26 March 2013
Received in revised form
14 June 2013
Accepted 24 June 2013
Available online 4 July 2013

Keywords:
Bioanode
Carbon based electrodes
Oxidation treatments
Electroactive biofilm
Electrode characterization

ABSTRACT

Bioelectrochemical systems (BESs) are based on the catalytic activity of biofilm on electrodes, or the so-called bioelectrodes, to produce electricity and other valuable products. In order to increase bioanode performance, diverse electrode materials and modification methods have been implemented; however, the factors directly affecting performance are yet unclear. In this work carbon cloth electrodes were modified by thermal, chemical, and electrochemical oxidation to enhance oxygenated surface groups, to modify the electrode texture, and consequently the electron transfer rate and biofilm adhesion. The oxidized electrodes were physically, chemically, and electrochemically characterized, then bioanodes were formed at +0.1 V vs. Ag/AgCl using domestic wastewater amended with acetate. The bioanode performance was evaluated according to the current and charge generated. The efficacy of the treatments were in the order Thermal > Electrochemical > Untreated > Chemical oxidation. The maximum current observed with untreated electrode was 0.152 ± 0.026 mA (380 ± 92 mA m^{-2}), and it was increased by 78% and 28% with thermal and electrochemical oxidized electrodes, respectively. Moreover, the volatile solids correlated significantly with the maximum current obtained, and the electrode texture was revealed as a critical factor for increasing the bioanode performance.

1. Introduction

In the last decade interest in BESs has increased. BESs are based on the catalytic activity of biofilm adhered to electrodes to convert the chemical energy present in organic matter into electrical energy. The applications of BESs comprise microbial fuel cells (MFCs), microbial electrolysis cells (MECs), and more recently, MFC-based biosensors (Su et al., 2011). BESs are dependent on multiple factors, one of which is the biofilm formation on different electrode surfaces. Electrode materials and their modifications have been broadly studied (Zhou et al., 2011), as well as the electron transfer mechanisms between the microbial cells and the electrodes (Torres et al., 2010). Carbon materials are the most widely used electrodes due to their chemical stability, conductivity, biocompatibility, and relatively low cost; they traditionally include carbon, graphite, activated carbon, glassy carbon, and nanotubes, in different structures such as plate, foil, rod, brush, paper, felt, cloth, mesh, or particles. To increase BESs performance, different modifications focus on changing the pore texture, increasing the surface area, and modifying the surface chemistry. Some modifications of carbon electrodes are summarized in Table 1. Among the methods that have been explored are covering with metals or polymers, heat treatments under specific atmospheres and electrochemical and chemical oxidation using acid soaks.

Recently carbon electrodes have been modified with electrochemically active species like RuO_2 and graphene (Liu et al., 2012;

Abbreviations: ANCOVA, Analysis of covariance; ANOVA, Analysis of variance; BES, Bioelectrochemical system(s); C, Capacitance; %CE, Coulombic efficiency; CO, Chemically oxidized electrode; CODs, Soluble chemical oxygen demand; CPE, Constant phase element; CV, Cyclic voltammetry; %CV, Coefficient of variation; EAA, Electrochemically active area; EO, Electrochemically oxidized electrode; ΔEp, Potential peak separation; I, Current; *Ip*, Current peak; M, Diffusion element; MEC, Microbial electrolysis cell(s); MFC, Microbial fuel cell(s); OCP, Open circuit potential; PEIS, Potentiostatic electrochemical impedance spectroscopy; PZC, Point of zero charge; Q, Constant phase element; *R*, Resistance; R_{CT}, Charge transfer resistance; Ro, Ohmic resistance; SSA, Specific surface area; TO, Thermal oxidized electrode; UE, Untreated electrode; VS, Volatile solids; W, Warburg's diffusion element

* Corresponding author. Tel.:+52 444 8342026; fax:+52 444 8342010.
E-mail addresses: bibiana.cercado@ipicyt.edu.mx, bbcercado@gmail.com, bbcercado@yahoo.com.mx (B. Cercado), luis.Chazaro@ipicyt.edu.mx (L.F. Cházaro-Ruiz), VRuizL@iingen.unam.mx (V. Ruiz), ilopezp@iingen.unam.mx (I.de J. López-Prieto), gbuitronm@ii.unam.mx (G. Buitrón), erazo@ipicyt.edu.mx (E. Razo-Flores).

0956-5663/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.bios.2013.06.051

Table 1
Overview of studies on carbon-based electrodes, their modifications and performance.

Inoculum	Substrate	Device	Carbon electrode	Modification method	Performance increase[b]	Reference
Compost leachate	Dairy wastewater	Electrochemical cell[a]	Graphite felt	Electrochemical oxidation and organic matter adsorption	Current from 450 to 1600 mA m^{-2} (256%)	Cercado-Quezada et al.,, (2011)
Domestic wastewater	Acetate	One-chamber MFC	Cloth	Heating in ammonia gas atmosphere	Surface charge from 0.38 to 3.99 meq m^{-2}; reduce starting time by 50%	Cheng and Logan (2007)
Effluent of MFC	Acetate	Two-chamber MFC	Graphite	Al_2O_3 blasted graphite	Current from 3 to 4.7 A m^{-2} (57%)	Heijne et al., (2008)
Marine sediment	Marine sediment	Electrochemical cell[a]	Randomly oriented graphite (ROG) Glassy carbon (GC)	Electrochemical oxidation	Changes in microbial community. ROG, 45 mA cm^{-2} GC, Jo=29 mA m^{-2} (79%)	Liu et al., (2007)
Pseudomona aeruginosa	Glucose	Two-chamber MFC	Carbon cloth	Graphene deposited onto the electrode	Promotes bacteria growth. Power density 52.5 mW m^{-2} (169%)	Liu et al., (2012).
Marine sediment	Marine sediment	Marine MFC	Graphite plates Glassy carbon Graphite rods	Electrochemical oxidation Treatment with AQDS. Treatment with Sb (IV) complex. Oxidation-AQDS.	Kinetic activities 57.8, 1.7, 1.9, 218 times	Lowy and Tender (2008)
Shewanella decolorationis S12 Mixed consortia with activated sludge	Lactate	Two-chamber MFC	Carbon felt	RuO_2 coated electrode	Increase electrical conductivity. Pure culture: 3080 mW m^{-2} (1611%) Mixed: 1060 mW m^{-2} (1004%)	Lv et al., (2012)
Shewanella oneidensis MR-1	Lactate	Electrochemical cell[a]	Polyacrilonitrile (PAN) composites	PAN-Activated carbon (AC) PAN-Graphite (G)	PAN, 1150 mA m^{-2} PAN-AC, 1390 mA m^{-2} (21%) PAN-G, 1550 mA m^{-2} (35%)	Patil et al., (2013)
Domestic wastewater	Acetate	One-chamber MFC	Cloth	Heating in air atmosphere Heating in ammonia gas atmosphere at various concentrations	Power 910 mW m^{-2} (20%), 938 mW m^{-2} (24%), best performance with low concentration	Saito et al., (2011)
Brewery and domestic wastewater	Domestic wastewater	One-chamber MFC	Graphite felt Ketjen black Carbon nanofiber Carbon	Depositing/binding carbon or polymers on graphite felt. PANI nanofiber Carbon-PANI nanofibers PANI carbon composite Carbon activation with HNO_3	Highest power with HNO_3, 28.4 mW m^{-2} (199%).	Scott et al., (2007)
From previous MFC	Acetate	Two-chamber MFC	Graphite felt	Electrochemical oxidation	Current up to 1.13 mA (35%) and power to 930 mW m^{-2}	Tang et al., (2011).
Wastewater	Acetate	One-chamber MFC	Cloth	Covering with carbon nanotubes	Power from 26 to 65 mW m^{-2} (150%)	Tsai et al., (2009)
Pre-acclimated inoculum	Acetate	One-chamber MFC	Mesh Cloth	Heating in air or ammonia atmosphere	Heating in air: 922 mW m^{-2} Heating in gas ammonia: 1015 mW m^{-2}	Wang et al., (2009)
Anaerobic sludge	Glucose	One-chamber MFC	Mesh	Electrochemical oxidation in HNO_3, NH_4NO_3, ammonium persulfate	Reduce internal resistance. Power (W m^{-2}): 792 (43%) 736 (33%) 567 (3%)	Zhou et al., (2012)
Lagoon sediment	Glucose	One-chamber MFC	Activated carbon fiber	Oxidation in HNO_3 and etylendiamine (EDA) treatments.	Reduce starting up time. Power (mW m^{-2}): EDA. 1641 (59%), HNO_3, 2066 (100%).	Zhu et al., (2011)

[a] Three-electrode electrochemical cell under potentiostatic control.
[b] Percent increase in parenthesis.

Lv et al., 2012). These modifications resulted in the creation of nanostructures and activation centers on the carbon electrodes to increase both the specific surface area and electron transfer kinetics.

The increases in BES performance reported are clearly dependent on their operational parameters, but the characteristics of the electrodes that contribute to the reported performance are yet unclear. It has been signaled that enlarging the specific surface of the electrode and/or improving its electrocatalytic activity could increase bioanode performance (Lowy and Tender, 2008). However, Heijne et al. (2008) did not find a direct correlation of power generation with the increase of electrode surface area. It has been reported that chemical surface groups promote electron transfer, notably the surface oxygenated groups (Leon y Leon and Radovick, 1994), although a reduction of O/C ratio after oxidation electrode treatment and disagreement of N/C ratio with the power density was reported by Zhu et al. (2011). Moreover, the power increase by introducing either nitrogen or oxygenated groups has resulted very similar (Saito et al., 2011). In order to deepen the knowledge of BESs and to study how bioanodes performance can be improved, an exhaustive and systematic electrode and bioanode characterization should be performed, which includes physical–chemical, electrochemical, and microbiological investigations.

The aims of the present work were to select an oxidation method to modify carbon cloth electrodes in order to increase bioanode performance through a simple and effective treatment, and to identify the biotic and abiotic factors with the highest impact on bioanode performance, which could be consequently useful as predictive parameters.