Journal of Power Sources 342 (2017) 579–588

Contents lists available at ScienceDirect

Journal of Power Sources

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

The performance of 3-D graphite doped anodes in microbial electrolysis cells

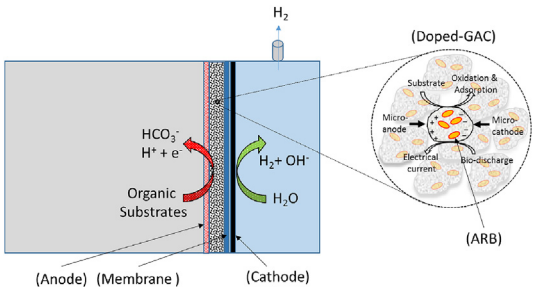
Nael G. Yasri*, George Nakhla*

Department of Chemical and Biochemical Engineering, University of Western Ontario, London, Ontario N6A 5B9, Canada

HIGHLIGHTS

- Conductivity in MEC is not the mean factor when dealing with common species of ARB.
- 3-D GAC doped with less conductive CaS outperformed the more conductive doping.
- GAC as 3-D MEC did not prove advantageous over the 2-D sandwich type MEC.
- CaS can be proposed as an anode doping material for MEC.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 May 2016
Received in revised form
5 December 2016
Accepted 21 December 2016

Keywords:
Microbial electrolysis cell
3-D anode
Anodic respiring bacteria
Granular activated carbon
Hydrogen production
Iron and sulfide doping

ABSTRACT

This study investigated the use of granular activated carbon (GAC) as high surface area 3-dimensional (3-D) anode in MECs systems. The interfacial anodes' charge transfer resistance of the doped GAC did not impact the overall performance of MECs. Based on our finding, the 3-D anode packed with GAC-doped with nonconductive calcium sulfide (CaS) outperformed the more conductive iron (II) sulfide (FeS), magnetite (Fe_3O_4), or GAC without doping. The results showed higher current densities for 3-D CaS (40.1 A/m^3), as compared with 3-D FeS (34.4 A/m^3), 3-D Fe_3O_4 (29.8 A/m^3), and 3-D GAC (23.1 A/m^3). The higher current density in the 3-D CaS translated to higher coulombic efficiency (96.7%), hydrogen yield (3.6 mol H_2/mol acetate), and attached biomass per anode mass (54.01 mg COD biomass/g GAC). Although the 3-D MEC achieved similar hydrogen yield, hydrogen recovery efficiency, and COD removal rate to a conventional sandwich type MEC, the current density, coulombic efficiency, and overall energy efficiency were higher.

1. Introduction

Biological hydrogen (H_2) production technologies include dark fermentation [1], photobiological processes [2], and microbial electrolysis cells (MECs) [3]. In dark fermentation the majority of organic matter is converted to volatile fatty acids, whereas, photobiological processes, require enzymes to catalyze H_2 production [2]. The utilization of anode-respiring bacteria (ARB) for H_2 productions in MEC is a green technology that combines pollution abatement with clean energy production [3].

In MECs, ARB oxidize biodegradable organic compounds and other forms of biomass into protons, electrons, and bicarbonate. Electrons flow from the ARB to the anode, reach the cathode and react with water to evolve H_2. Although MECs hold great promise, the production of economic hydrogen still faces technical

* Corresponding authors. Department of Chemical and Biochemical Engineering, Alexander Charles Spencer Engineering Building, Room SEB 3037, University of Western Ontario, London, Ontario N6A 5B9, Canada.
E-mail addresses: nyasri@uwo.ca (N.G. Yasri), gnakhla@uwo.ca (G. Nakhla).

http://dx.doi.org/10.1016/j.jpowsour.2016.12.081
0378-7753/

challenges e.g. slow H_2 conversion and low efficiencies [4].

Important factors affecting the performance of MECs are the type of anode materials and their configuration. Generally, conductive carbonaceous materials are favored for anodes [5], and the choice of these materials for ARB cultivation is always related to their conductivity, chemical stability, porosity, the high surface area [6], as well as their ability to be modified or functionalized with various groups that are attractive to biota [7,8]. Carbonaceous fabric anodes that are usually utilized in MEC are: carbon cloth, carbon fiber, carbon felt, carbon mesh, carbon paper, and granular carbon [6].

The possible uses of graphite material, especially granular activated carbon (GAC) as conductive and high-surface area electrode in electrochemical systems has widened their application in MEC [9–11]. GAC in electrochemical systems enhances conductivity and mass transfer of the substrate by creating bipolar fields on the granules as well as increasing the electrode surface area to form a 3-D electrochemical cell system [10,12,13]. Thus, GAC within an electric field, forms micro-anodes and micro-cathodes. This results in a large number of micro-electrolytic cells with an effective number of cells that may enhance ARB growth. Additionally, GAC can practically undergo pretreatment, i.e. thermal [8] and chemical [7] treatments to optimize its use in MEC.

Although GAC has been postulated as a suitable anode material for large-scale microbial electrolysis systems (MESs) [6,14], practical applications have rarely been reported [11]. The performance of some MESs using GAC as 3-D anodes for various applications is summarized based on the coulombic efficiency (CE, %) and COD removal efficiency in Table 1. It is apparent from Table 1 that generally the presence of GAC in 3-D electrode enhanced the performance of the system. For example, the cubiod-shaped reactor filled with GAC (CSGAC 3-D) outperformed the same reactor without GAC (i.e. CS 2-D) as reflected by the findings of Wang et al. [10], who observed an increase in CE from 33.7% for membrane-less MEC reactor without GAC to about 45% for the same reactor packed with GAC (Table 1). However, despite the innovative performance of GAC as 3-D electrode system, there is, to the best of our knowledge, very limited research on the comparative performance of 3-D anodes and the traditional sandwich type MEC has been reported.

Furthermore, research confirmed the advantages of introducing surface functional groups to anode in order to induce ARB cultivation and electron transfer efficacy [5,7,15]. Functional groups categorized upon their impacts on the growth and enhancement of biomass. For examples, Santoro et al. [7]. found that chemical modification of anode surface with ionized hydrophilic groups enhanced the surface attachment and growth of ARB more than those of hydrophobic groups. Other approaches to enhance ARB growth include, thermal or ammonia pretreatment [8,16], electrode spacing [17], anode potential [18], pH [19], and anode conductivity [5,7,15]. However, considering the fact that altering the conductivity of the electrode interface may require modification of the anode surface with conductive materials which may contain functional groups (e.g. sulfur, nitrogen, or other), that are attracting biota as well as their conductivity effect, the role of conductivity in enhancing anode biofilms performance is not clearly understood. For example, Kang et al. [15]. who used a conductive poly(3,4-ethylenedioxythiophene (PEDOT) film showed superior biocatalytic performance for acetic oxidation when coated on a carbon felt anode. However, the chemical structure of PEDOT contains thiophene (sulfur) group as well as other groups which may act as micronutrients rather than conductive particles to attract ARB. Many similar examples of cultivating ARB on conductive material such as polypyrrole doped carbon nanotubes [20], and polyaniline [21] compounds exist in the literature [5,20,21].

In view of the literature cited above and in light of the sparsity of research on 3-D MECs, the two main objectives of this study are: 1-) evaluation of the impact of conductivity on the performance of 3-D anode by various doping materials, and 2-) comparing 3-D anodes with conventional sandwich type MEC.

In this study, we evaluated MECs packed with GAC as 3-D electrode system and doped with conductive (Fe_3O_4), semi-conductive (FeS), nonconductive (CaS), or GAC without doping and compared the optimum performance with that we previously obtained using sandwich type anode-membrane-cathode MEC system with no GAC packed between the anode and the membrane.

2. Experimental

2.1. Reactor and electrochemical system

Four identical two-compartment MEC systems were used in these batch experiments. A schematic and pictures of the 3-D MEC are shown in Fig. 1.

The cells were fabricated from plexiglass with anodic chamber (a) and cathodic chamber (b) volumes of 350 mL and 180 mL respectively. The anode (c) was made of stainless steel frames with carbon fibres (type 2293-B, 24 K Carbon Tow, Fibre Glast

Table 1
Efficiency of various MECs contained GAC as 3-D electrode.

Reactor/operation mode/ membrane & area	Culture condition	Anode type	Substrate/applied voltage	Influent COD (MG/L)	CE (%)	COD removal efficiency (%)	Ref.
CS 2-D[a]/batch/25.2 cm^2	Activated sludge	Carbon cloth no GAC	Acetate/0.6 V	1000	20	11.6	[10]
CSGAC 3-D[b]/batch/25.2 cm^2	Activated sludge	Granular activated Carbon packed between anode and membrane	Acetate/0.6 V	1000	45	35.5	[10]
Fcb[c]/continuous/CEM 11 cm^2	Working MFC	GAC flow through 5.2 mL/min	Acetate/0.2 V vs NHE	600[g]	27	65–72	[22]
GACSC MFC[d]/batch/NA	Municipal wastewater	carbon cloth with GAC	Acetate/–	1000	15	90	[14]
MFEEC[e]/batch flow through/ NA	Geobacter sulfurreducens PCA	graphite block with fluidized GAC	Acetate/0.8 V	1500	90	59–64	[23]
TMFC[f]/flow-through/NA	Working MFC	GAC backed flow-through	Acetate/–	365 mg/day[h]	75	23 ± 22	[24]

[a] CS 2-d is cubiod-shaped 2-dimentioal electrode.
[b] CSGAC 3-D is cubiod-shaped filled with GAC 3-dimentioal electrode.
[c] FCB is fluidized capacitive bioanode.
[d] GACSC MFC is GAC single-chamber MFC.
[e] MFEEC is microbial fluidized electrode electrolysis cell.
[f] TMFC is tubular microbial fuel cells.
[g] At hydraulic retention time of 6.7 h.
[h] Data calculated from reference.