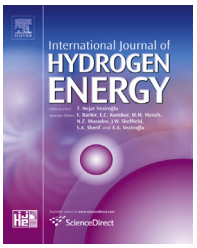
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2014) 1–9

Available online at www.sciencedirect.com

ScienceDirect

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



Performance of a microbial electrolysis cell (MEC) for hydrogen production with a new process for the biofilm formation

L. Verea [a], *Oumarou Savadogo* [b], *A. Verde* [a], *J. Campos* [a], *F. Ginez* [a], *P.J. Sebastian* [a,*]

[a] *Departamento de materiales solares, Instituto de Energías Renovables, Universidad Nacional Autónoma de México, Temixco 62580, Morelos, Mexico*

[b] *Laboratoire de Nouveaux Materiaux pour l'electrochimie et l'energie, Ecole Polytechnique de Montreal, C. P. 6079, Succ. Centre-Ville, Montreal, QC H3C 3A7, Canada*

ARTICLE INFO

Article history:
Received 23 December 2013
Received in revised form
23 March 2014
Accepted 26 March 2014
Available online xxx

Keywords:
Electrolysis
Hydrogen
MEC
Biofilm
Bacteria

ABSTRACT

The microbial electrolysis process allows producing hydrogen (H_2) as a result of the cathodic reaction of the protons coming from the oxidation of the organic matter contained in waste water. For the application of this technology it is necessary to study the optimal operating conditions that allow to scale-up a microbial electrolysis cell to produce hydrogen efficiently at low cost. This study used a new approach to get high hydrogen production rate in a MEC by achieving in a very short time the process for making the anode's bacteria enrichment for the biofilm formation. The hydrogen production efficiency was optimized through the change of the electrolyte conductivity and the electrode surface area/electrolyte volume ratio. It was found that the hydrogen production rate increased with the increase of the electrolyte conductivity. Its rate (Q_{H_2}) increased from 0.13 to 0.82 m^3H_2/m^3 per day when the electrolyte conductivity increased from 7.5 mS/cm to 15 mS/cm. From the optimization of the electrolyte conductivity and the electrode surface area/electrolyte volume ratio, the highest cathodic reaction efficiency of 97% and coulombic efficiency of 21% were obtained. These results show for the first time that the improvement of the electrodes bacteria enrichment process at the anode is an important approach to enhance the hydrogen production rate in a MEC. The results in this study were verified by repeating the experiments more than once and comparing our results with similar studies already published in the literature.

Introduction

The microbial electrochemical cell technology to produce H_2 is emerging as a promising renewable energy alternative to fossil fuels because in this device the hydrogen can be produced from the organic matter contained in waste water [1]. A microbial electrolysis cell (MEC) takes advantage of some bacteria ability to transfer electrons as part of their respirative process. These bacteria are known as exoelectrogens [2].

* *Corresponding author*. Tel.: +52 55 56229752; fax: +52 55 56229742.
E-mail addresses: sjp@ier.unam.mx, sjp@mazatl.cie.unam.mx (P.J. Sebastian).

http://dx.doi.org/10.1016/j.ijhydene.2014.03.203

To date, exoelectrogens include members from diverse genera of bacteria like *Geobacter*, *Shewanella*, *Pseudomonas*, *Clostridium*, *Desulforomonas*, *Escherichia,* and *Klebsiella* [3] and phyla, such as *Alpha-*, *Beta-*, *Gamma-*, and *Deltaproteobacteria*, *Firmicutes*, *Acidobacteria*, and yeast [4]. These microorganisms can be present in marine sediment, soil, waste water, fresh water sediment and activated sludge [5]. Many researchers utilize them as inoculum to get a mixed culture of bacteria for anodic biofilm formation.

Some researchers have reported that mixed cultures of bacteria have a better performance in a MEC because the biofilms formed with pure single species present adaptiveness, and the need for sterile operation. The mixed cultures of bacteria are characterized by a broad ecological niche, i.e. they are flexible to the environmental variables and offer the access to wide range of substrates, and thus, are considered to be robust in bioelectrochemical systems [6]. However, one major disadvantage of using mixed culture of bacteria microbial is the undesired selection for methanogenic bacteria [7]. Methanogens combine the CO_2 produced by exoelectrogens with the H_2 generated via electrohydrogenesis to produce methane (CH_4), ultimately lowering H_2 yields [8].

Up to now the reported process for the anodic biofilm growth is the anode enrichment in a microbial fuel cell [9] and some times the anode is pretreated with ammonia [10] that requires temperatures of 700 °C and several days to ensure the biofilm formation [11]. Then there is a need to develop a selective bacteria method to enrich the anode with exoelectrogens to form a biofilm in a shorter time than that has been done until now and to be more factible to scale up.

In a MEC the exoelectrogens carry out an anaerobical respiration process in which the oxidation of organic matter occurs and the electrons are transferred to a solid electrode (anode) [3]. This process requires the utilization of energy since the organic matter (substrate) decomposition is not spontaneous under standard conditions (STP: 25 °C, 1 bar) [8,12]. Then, the anaerobic respiration of the exoelectrogens can serve as an electron source to produce H_2 gas from water and the process can be stimulated by applying a small voltage in a MEC [13].

The theoretical applied voltage (E_{app}) in a MEC for H_2 production is 0.11 V vs standard hydrogen electrode (SHE), because at pH 7 the cathode potential (E_c) is −0.41 V and exoelectrogens generate an anode potential (E_a) of approximately −0.3 V [12]. However, there are energy losses occurring in a MEC and consequently the applied voltage must be greater than 0.13 V and typically is in the range of 0.6–1.2 V [14].

On the other hand, the energy loss of the anode occurs by the effect of concentration gradients of the reactants and the products in the biofilm, the intracellular gradient of the electron potential due to the exoelectrogen metabolism and owing to the extracellular electron transfer (EET) towards the anode [3]. In a membrane-less MEC energy losses are caused by electrical resistance to current in conducting components (e.g. in the electrodes and connecting wire) and due to the counter ion transfers in the liquid medium for charge neutrality. These energy losses depend on the distance between the electrodes, resistivity of the electrolytes (liquid medium), and current density [15]. To reduce the energy losses, buffers like carbonate buffer can be used to increase the solution conductivity [16].

The challenge of making the MEC viable is the requirement for an external energy supply to increase the energy of the generated electrons as well as achieving a high H_2 production rate which is important for keeping capital costs low. The volumetric production rate (e.g. m^3 H_2/m^3d) depends on the current density at the anode (A/m^2) and anode specific surface area (m^2/m^3), since the H_2 production rate and substrate utilization rate of exoelectrogens is proportional to the current [15]. Acetate is an ideal electron-donor substrate for exoelectrogens, since it is not fermentable and has relatively rapid oxidation kinetics in MFC/MEC [17]. The anode potential determines the exoelectrogens respiration rate and compounds such as O_2, H_2O and H^+ can be reduced (terminal electron acceptor) in the cathode [18]. Besides these results in the literature, there is no specific approach related to the improvement of the MEC performance based on the optimization of the electrolyte conductivity and/or the ratio between the electrode surface area and the cell volume (m^2/m^3). These conditions of the MEC operation were employed simultaneously in a MEC with an anode containing a biofilm formed with a method not reported before. It may be highlighted the following from this study:

It was proved the feasibility for hydrogen production in a membrane-less MEC with this anode.

The hydrogen production in this MEC with carbonate buffer was compared with the hydrogen production reported with similar devices and phosphate buffers.

The conductivity of the electrolyte was increased with the buffer concentration and three different ratios between the electrode surface area and the cell volume were tested in order to improve the hydrogen production.

The performance of the MEC was also studied for continuous batch cycles to investigate the stability of the hydrogen production and the performance of the cathode and the anode at different operating conditions.

Materials and methods

Anode bacteria enrichment

The anode was made with carbon cloth without wet proofing (3 × 3 cm^2 E-Tek) and previous to the bacteria enrichment it was treated as an anode in a conventional electrolysis process during 24 h. Then the anode was enriched with exoelectrogens in a 100 mL working volume sealed electrochemical cell with three electrodes. The process consisted of setting a constant anode potential of −0.42 vs 3 M Ag/AgCl–KCl reference electrode (0.195 V vs standard hydrogen electrode, SHE) for 8 h as reported earlier [19]. The medium consisted of 70 mL of synthetic wastewater (SWW) composed of 1 g/L NH_4Cl, 1 g/L $NaHCO_3$, 1 g/L Na_2CO_3, 0.2 g/L K_2HPO_4 and 10 μL of vitamin and 10 μL mineral solutions [20]. It was seeded with a mixed culture of bacteria from anaerobic sludge stabilized by the American Type Culture Collection (ATCC) reports for *Geobacter Sulfurreducens* growth and 34 mM of sodium acetate as substrate or carbon source. The medium was pH 9, purged with N_2 gas for 10 min and maintained on anaerobic conditions at

Please cite this article in press as: Verea L, et al., Performance of a microbial electrolysis cell (MEC) for hydrogen production with a new process for the biofilm formation, International Journal of Hydrogen Energy (2014), http://dx.doi.org/10.1016/j.ijhydene.2014.03.203