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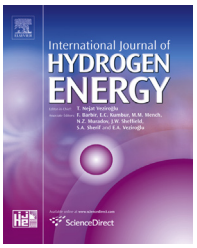

Control of dual-chambered microbial fuel cell by anodic potential: Implications with sulfate reducing bacteria

Tzu Yang Chou [a], *Chris G. Whiteley* [b], *Duu-Jong Lee* [a,c,*], *Qiang Liao* [d,e]

[a] *Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan*
[b] *Graduate Institute of Applied Science & Technology, National Taiwan University of Science and Technology, Taipei, Taiwan*
[c] *Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan*
[d] *Key Laboratory of Low-Grade Energy Utilization Technologies and Systems, Chongqing University, Chongqing 400030, China*
[e] *Institute of Engineering Thermophysics, Chongqing University, Chongqing 400030, China*

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ABSTRACT

Five dual chamber microbial fuel cell reactors were inoculated with a mixed culture of sulfate-reducing bacteria and fed with artificial wastewater containing lactate and sulfate. A negative poised anode potential enhanced the performance of this fuel cell while a positive poised anode potential or no anode potential had no effect on performance. The effect of this anode potential promoted microbial colonization on the anode surface (biofilm) thereby presenting an effective and successful way for the start-up of a sulfate reducing bacterial microbial fuel cell.

1. Introduction

Microbial Fuel Cell (MFC) technology can convert chemical energy, stored in organic and inorganic compounds, into electrical energy via the catalytic reaction of electrochemically active microorganisms (exoelectrogens) under anaerobic conditions. A dual-chambered MFC contains three parts: an anode, a cathode and a proton exchange membrane. At the anode the microbes oxidize organic substrates such as lactate and produce positively charged protons and negatively charged electrons. These electrons travel through an external circuit to the cathode. The protons generated in the anode will also diffuse to the cathode across the proton exchange membrane (PEM). Finally, the electrons and protons will combine with oxygen in the cathode to form water [Eqs. (1) and (2)]

$$\text{Anode}: CH_3CHOHCOO^- + 4H_2O \rightarrow 2CO_2 + HCO_3^- + 12H^+ + 12e^- \quad (1)$$

$$\text{Cathode}: O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (2)$$

Serious disadvantages of this dual MFC system design are that it generally generates low power density [1] which is often affected by surface area of cathode relative to that of anode and membrane. The power density is also hampered by the high internal resistance and electrode based losses. Many other MFC designs such as sediment MFC [2], stacked MFC system [3] and up-flow mode MFC system [4] have been used to either enhance organic substrates removal or increase voltage and current output.

There are many different technologies to remove sulfate from the environment. These include membrane

* *Corresponding author*. Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan. Tel.: +886 33663028; fax: +886 2 23625632.
E-mail addresses: djlee@ntu.edu.tw, djleetw@yahoo.com.tw (D.-J. Lee).

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biotechnology with seeded reverse osmosis (SRO) [5] and slurry precipitation and recycle reverse osmosis (SPARRO) [6]; electrical dialysis [7] and filtration [8]; removal of sulfate by salt precipitation and ion exchange [9] and the GYPCIX process [10,11] and through the precipitation of Ettringite [12] in the SAVMIN process. Perhaps the most environmentally friendly process in the biotechnology for sulfate removal would be via biological reduction to sulfide by anaerobic *Desulfovibrio* and *Desulfotomaculum* that both use sulfates and/or sulfites as final electron acceptors [13]. The organic substrates for these bacteria are usually lactic and pyruvic acid.

The presence of sulfate in the anode media has negligible effects on current generation in MFCs. On the other hand, sulfate can be reduced to sulfide by sulfate-reducing bacteria. The subsequent sulfide oxidation via electrochemical and biological processes would then result in current generation [3]. Although the presence of sulfate and sulfate-reducing bacteria is not predicted to negatively impact current production, these organisms can use some of the electron donor for growth, thereby reducing power density in MFCs. In addition, the sulfide generated from the reduction of sulfate is both toxic and odorous. Therefore, it is desirable to remove sulfide and inhibit sulfide generation in the MFC system.

The anode potential was proposed as an important operating parameter that can affect the diversity of the microbial community, the output current density, and the initial start-up time of MFCs [3,13–21]. There is still no agreement, however, on what is the optimal anode potential for the electroactive consortia. This present study, therefore, investigates the cell performances, electrode characteristics, microbial communities and anodic biofilms from different effects of positive and negative anode potentials on the dual chamber MFC system with SRB mixed culture to improve the performance of SRB–MFC.

2. Materials and methods

2.1. Inoculation, media preparation, and MFC

Activated sludge was collected from a bakery factory in Taoyuan County, Taiwan and used as the inoculums after sedimentation. The MFC was fed with medium containing (g l^{-1}): $MgSO_4 \cdot 7H_2O$, 2.0; sodium citrate, 5.0; NH_4Cl, 1.0; K_2HPO_4, 0.5; sodium lactate, 5.0 ml; $Fe(NH_4)_2(SO_4)_2$, 1.0; yeast extract, 1.0; Wolfes vitamin solution, 1.0 ml; Wolfes mineral solution, 1.0 ml with the pH adjusted to 7.5.

A dual chamber MFC design, consisted of two plastic cylindrical chambers each with an inner diameter of 4 cm, an outer diameter of 5.0 cm and a total working volume of 100 ml. Anodic and cathodic electrodes, prepared from 1.0 cm × 1.0 cm × 1.0 cm carbon felt [22] (CeTech Co, Taichung, Taiwan) and 3.0 cm × 3.0 cm carbon cloth (CeTech Co, Taichung, Taiwan) respectively were placed in their respective chamber 4.5 cm apart. The cathodic electrodes were coated with a platinum catalyst (C2-20 20%HP Pt on Vulcan XC-72R, BASF, USA) to enhance reduction reactions in the cathode chamber. Prior to use all the electrodes were first immersed in 1 M NaOH then in 1 M HCl for one-hour each to remove any residues on the electrodes surface. The two chambers were separated by a Cation Exchange Membrane (CEM) made from Ultrex CMI-7000 (Membrane International, Inc., Glen Rock, NJ, USA), cut into a circular shape according to the size of reactor and immersed in NaCl (30 min) solution (1% w/w).

The cathodic solution used to facilitate the reduction reaction at the cathode contained (g l^{-1}): $NaH_2PO_4 \cdot H_2O$, 17.77; Na_2HPO_4, 32.33; $K_3Fe(CN)_6$, 16.46 with the pH adjusted to 6.9.

2.2. Chemical analysis

Chemical Oxygen Demand (mg l^{-1}) was determined by a kit according to supplier's instructions (CHEMetrics, Inc., Calverton, VA, USA). Sulfide was determined according to the Hach Chemical Company [method: 8131; doc: 316.53.01136]. Biofilm samples (3.0 ml) containing sulfide ions (S^{2-}) were treated with $Zn(NH_3)_6(OH)_2$ solution (2.97 ml) followed by N,N-dimethyl-1-1,4-phenylene diammonium dichloride, DPDA solution (0.3 ml) and $FeCl_3$ (1%, 0.15 ml) were added to form a methylene blue solution which, after 15 min, was quantitatively analyzed using a sulfide standard curve at 665 nm. $Zn(NH_3)_6(OH)_2$ solution was prepared in distilled water by dissolving $ZnSO_4$ (5.0 g, 500 ml) and NaOH (6.0 g, 300 ml). The two solutions were mixed together followed by the addition of NH_4SO_4 (70 g) and the final volume was made up to 1000 ml. DPDA solution was prepared in dilute sulfuric acid (4×) by dissolving N,N-dimethyl-1-1,4-phenylene diammonium dichloride (0.2 g, 100 ml). $FeCl_3$ (1%) was prepared in dilute sulfuric acid (100×) by dissolving Fe (III) chloride (1.0 g, 100 ml).

2.3. SEM and CLSM

Biofilm samples (1.0 ml) from the anodic chambers of the MFC–SRB-A; MFC–SRB-B and MFC–SRB-C were first immersed in glutaraldehyde (2.5%, 60 min) then washed with phosphate buffer (0.1 M, pH 7.0, 3 times) and immersed, successively, in ethanol (30%, 50%, 70% and 90%, 10 min). Finally, the samples were treated with critical point drying to dehydrate the biological tissues and coated with gold [23].

For CLSM analysis the samples were stained using a staining protocol consisting of six dyes in the order of SYTO6320, FITC, ConA, CW, NileRed, and SYTOXBlue (Table 1) prior to being mechanically cut into 30–50 μm cross sections embedded in resin [Shandon Cryomatrix (Thermo scientific)] [24]. A Leica TCS SP5 confocal laser scanning microscope was used.

2.4. Microbial community analysis

The total 16S rRNA of the microbial community was amplified by PCR using specific primer sets 9F (5′-GCGGGCGGCGCGGGGCGC-GGGCAGGGCGGCGGGGGCGGGCG-3′), 9F GC(5′GCGGGCGGCGCGGGGCGCGGGCAGGGCGGCGGGGGCGGGCGAGTTTGATCC TGGCTCA-3′) and 524R (5′-ATTACCG CGGCTGCTGG-3′). Amplication was conducted in an Eppendorf mastercycler (Eppendorf AG, Hamburg, Germany) via denaturation at 95 °C, 10 min for 1 cycle, 35 cycles at 55 °C (annealing), 1 min, 35 cycles at 72 °C (extending), 1 min, 1 cycle at 4 °C (holding). After PCR procedure, each PCR product was electrophoresed on 1% agarose gel to confirm the results.

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