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Multi-variable mathematical models for the air-cathode microbial fuel cell system

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HIGHLIGHTS

- Applied the version control system into the microbial fuel cell modeling.
- Systematically applied the electrochemical equations into the cathode & anode.
- The model method helped the simulation results fit the experimental curves well.
- Validated the oxygen transport in the MFC cathodic materials with new assumptions.
- Model gave quantitative power output comparison for biocatalyst and metal catalyst.

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ABSTRACT

This research adopted the version control system into the model construction for the single chamber air-cathode microbial fuel cell (MFC) system, to understand the interrelation of biological, chemical, and electrochemical reactions. The anodic steady state model was used to consider the chemical species diffusion and electric migration influence to the MFC performance. In the cathodic steady state model, the mass transport and reactions in a multi-layer, abiotic cathode and multi-bacteria cathode biofilm were simulated. Transport of hydroxide was assumed for cathodic pH change. This assumption is an alternative to the typical notion of proton consumption during oxygen reduction to explain elevated cathode pH. The cathodic steady state model provided the power density and polarization curve performance results that can be compared to an experimental MFC system. Another aspect considered was the relative contributions of platinum catalyst and microbes on the cathode to the oxygen reduction reaction (ORR). Simulation results showed that the biocatalyst in a cathode that includes a Pt/C catalyst likely plays a minor role in ORR, contributing up to 8% of the total power calculated by the models.

1. Introduction

The microbial fuel cell (MFC) is a bioelectrochemical system that is able to generate electrical current via *exoelectrogens*, biomass capable of transporting electrons outside their cell walls [1]. Responses of the bioelectrochemical mechanisms in MFCs must be understood to design MFCs with increased current and power output via optimized materials, transport, kinetics, and architecture. The single chamber air-cathode MFC is a simple structure conducive to scale-up and can generate relatively high power because of its lower internal resistance compared with other MFC designs such as the two chamber MFC reactor [1]. An added benefit to this design is reduced cost since no ion exchange membrane is necessary. These benefits prompted selection of the single chamber air-cathode MFC as the subject for the experiments and modeling in this work.

Computational modeling has been utilized for MFC analysis in specific regions, such as the biofilm growth on the anode [2] or the electrochemical reactions in MFC [3]. Initial MFC models included the simulations of steady-state biofilm growth, multi-factor transient mixed-culture states of electrochemical reactions, and

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bacterial growth processes [4,5]. Wanner [5] highlights the complex, transient, 1-D microbial biofilm growth process dependent on nutrient consumption, multispecies competition, and materials. Biofilm simulation becomes more complex when considering the biofilm liquid phase volume fraction, detachment and attachment of cells and particles, and the mass transport of dissolved components in bulk liquid and biofilm [6]. In addition, the local electrical potential and the proton/hydroxide transport are important to MFC system behavior. Bacterial growth in MFC systems does not only depend on nutrient concentration but also the local electrical potential and pH environment. Models become increasingly complex when the anode and cathode are comprehensively considered in the case of regional or half-cell simulation (Steady state or transient MFC models focused on the anode local mass transport or electrochemical performance, the intricate cathodic reactions were usually simplified to an ORR, and mass transport in cathodic materials was neglected in the full cell system simulations.), resulting in few published full cell models [2,3].

Cathode performance is rarely simulated in MFC models, though the cathode reactions have experimentally been shown to limit the overall power generation in many MFC systems [7–10]. In the air-cathode systems, oxygen functions as the electron acceptor and is reduced at the cathode, often with a Pt/C catalyst. The cathodic biofilm has also been found to play a role in catalyzing the cathodic reduction reactions, though its significance in catalyzing the ORRs is still unclear from the experiments [11]. Recent results [8,9] suggest that the ORR in an MFC cathode is not the same as found in a polymer electrolyte fuel cell [12]. The ORR in the polymer electrolyte fuel cell is shown in Eqn. (1):

$$0.25O_2 + e^- + H^+ \rightarrow 0.5H_2O \quad (1)$$

However, MFC cathodes have been found to follow the ORR described in the Eqn. (2) [8,9], which was adopted that hydroxide ions govern potential losses in the cathode catalyst layer.

$$0.25O_2 + e^- + 0.5H_2O \rightarrow OH^- \quad E^0 = +0.40\ V \quad (2)$$

Biofilm growth at the cathodic surface is also an influential factor affecting the distribution of hydroxide and other ions [9], and the resultant pH strongly influences the Pt-catalyzed oxygen reduction, microbial growth, and overall power generation [13]. A complicating feature of the cathode is that the abiotic regions of the air-cathode structure are made of multiple layers and materials instead of a homogeneous layer. The material and structure in the cathode affect the gas phase and liquid phase mass transport through the cathode, impacting the whole system performance [10]. Thus, hydroxide and oxygen transport in the cathode are important considerations in MFC cathode models.

In this paper, a series of MFC models was developed for the anode and cathode in the MFC reactor. The simulation procedures, electrochemical reactions, and numerical methods that couple the multiple parameters in the anode and cathode were established separately. The anode half-cell model is presented to discuss MFC performance as influenced by electric migration in the mass transport governing equation. Primary considerations for the cathode half-cell model include cathodic mass transport via simulating the hydroxide effects on the ORR, the contribution of the Pt/C catalyst layer (designated “metal catalyst” [11] to distinguish from the biocatalyst in the cathode biomass) on the ORR, and the cathode biofilm effects on pH distribution, oxygen utilization, and potential cathode oxidation. This work will provide a foundation for future model development of a full-cell MFC system.

2. Model formulation

The control version system GIT was used to develop subroutines and sub-models in the following research into the model system. The GIT tracks model development, allowing versions over time to be compared, which aided both steady state and transient models. The general procedure for the mode development in MFC system was: a) adopt reasonable assumptions based on physical structure and materials; b) analyze electron transfer, dependent on mass transport; c) derive the mathematical electrochemical/biological equations and build the mass transport governing equations; d) adopt appropriate numerical methods for simulations. The electrochemical equations and the transport expressions were initially developed for the anodic model; GIT then allowed these relationships to readily be adapted for application to the cathode model.

2.1. Anode assumptions

The microorganisms were batch-fed a pH-buffered medium containing 1.0 g/L sodium acetate as the sole electron donor. Suspended bacteria growth in the bulk liquid was neglected in the model. The system coulombic efficiency changes with time as the biofilm grows and develops, and has been reported over a large range from 0.04% to 97% [14]; a constant anodic coulombic efficiency of 80% was assumed here to simplify the stoichiometric relations for anode biofilm growth. Therefore, 20% of acetate-derived electrons were consumed by the anode-respiring bacteria (ARB) for endogenous respiration and new biomass growth, while the remaining 80% were conducted directly to the anode through the extracellular polymeric substances (EPS) and *exoelectrogens*. The overall microbial fuel cell was a 4 × 4 × 4 cm cubic reactor. The anodic biofilm was assumed to be fully grown with a constant thickness of 0.025 mm in the steady state model. The initial acetate concentration in the half-cell model and the acetate concentration on the liquid side boundary were 1.0 g/L. In this anode half-cell model, the cathodic potential was fixed so the influence from the cathodic electrochemical changes was neglected in the calculations.

2.2. Anode steady state model

The anode structure was divided into three domains that include: anode metal (as current collector), the anode electrode (biofilm support and electron conductor), and biofilm. While graphite fiber brushes and carbon paper are two commonly used anode materials in MFCs [1], the anode was approximated as a planar surface. Fig. 1 is a schematic of the anode region.

The comprehensive equation for the anodic biological acetate oxidation reaction is shown in the Eqn. (3). New biomass and protons are produced by this reaction. Electrons are conducted through the anodic biofilm into the anode [2,15].

$$CH_3COO^- + Y_N NH_4^+ + Y_W H_2O \rightarrow Y_X C_5H_7O_2N + Y_{Car} HCO_3^- + Y_e e^- + Y_H H^+ \quad (3)$$

where Y_X was assumed to be 0.02 (g ARB/g acetate) [16], and Y_H was 4.17×10^{-5} (mol H^+/g acetate). In the steady state model, the electrode current was known and the electron distribution was able to be calculated based on the electron balance [3]. The electronic conduction is described in the Eqn. (4) where i_A is the anode current density (A/m^2) distributed in every control volume, F is the Faraday constant (C/mol), M_{Ac} and M_{ARB} are the molar mass (g/mol) for acetate and ARB respectively, Y_{Ac} (mol e^-/mol Acetate) and Y_{ARB} (mol e^-/g ARB) are the electron equivalences [3,11].