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Understanding electricity generation in osmotic microbial fuel cells through integrated experimental investigation and mathematical modeling

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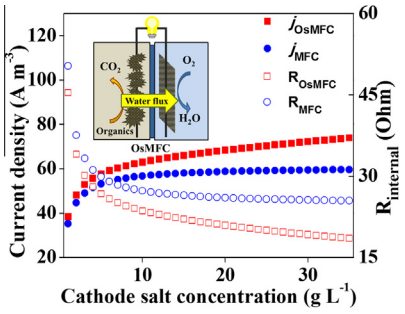
HIGHLIGHTS

- Osmotic microbial fuel cells produce more electricity than regular MFCs.
- The improvement is likely resulted from lower membrane resistance.
- The resistance of forward osmosis membrane is also affected by water flux.
- The first mathematical model for osmotic microbial fuel cells has been developed.
- The model confirms the experimental findings about membrane resistance.

GRAPHICAL ABSTRACT



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ABSTRACT

Osmotic microbial fuel cells (OsMFCs) are a new type of MFCs with integrating forward osmosis (FO). However, it is not well understood why electricity generation is improved in OsMFCs compared to regular MFCs. Herein, an approach integrating experimental investigation and mathematical model was adopted to address the question. Both an OsMFC and an MFC achieved similar organic removal efficiency, but the OsMFC generated higher current than the MFC with or without water flux, resulting from the lower resistance of FO membrane. Combining NaCl and glucose as a catholyte demonstrated that the catholyte conductivity affected the electricity generation in the OsMFC. A mathematical model of OsMFCs was developed and validated with the experimental data. The model predicated the variation of internal resistance with increasing water flux, and confirmed the importance of membrane resistance. Increasing water flux with higher catholyte conductivity could decrease the membrane resistance.

1. Introduction

Wastewater is considered as a valuable source of energy and other resources. Sustainable wastewater treatment aims to remove contaminants in a more energy-efficient way with resource recovery (McCarty et al., 2011). Microbial fuel cells (MFCs) emerge as a promising technology for sustainable wastewater treatment with direct electricity production from wastewater through microbial oxidation of organic contaminants (Li et al., 2014). Synergistic integration of forward osmosis (FO) into MFCs create osmotic microbial fuel cells (OsMFCs) (Zhang et al., 2011), which possess a new function of recovering high-quality water and thus benefit water reclamation towards reducing water footprint. In a FO process, water can move across a semipermeable membrane from a high water potential zone to a low water potential zone (Shaffer et al., 2015). The driving force is provided by a salt gradient that creates an osmotic pressure. Compared to other membrane-based

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processes, FO is less energy intensive and low membrane fouling (Lutchmiah et al., 2014).

An OsMFC inherits the advantages of both MFCs and FO systems, generating electricity from the organics by exoelectrogens and extracting clean water from wastewater by FO membrane (Zhang et al., 2011). This represents new synergy between bioelectrochemical systems and FO, and can be extended to microbial electrolysis cells (MECs) and microbial desalination cells (MDCs) for various purposes (Lu et al., 2014). Coupling the MFC (or MDC, MEC) with FO could achieve wastewater treatment, energy recovery, and resource recovery (such as clean water, nutrients) in one system (Qin and He, 2014; Yuan et al., 2015; Zhang and He, 2013). This promising combination encourages research to better understand the mechanism of the synergy. OsMFCs are the precursor of such synergy, and thus understanding of OsMFCs will help to understand other integrations towards further development. It has been demonstrated that OsMFC could produce more electricity than an MFC containing cation exchange membrane (CEM) in both batch mode and continuous mode (Ge et al., 2013; Zhang et al., 2011). Electricity can be generated by using either sodium chloride or artificial seawater as both catholyte and draw solution (Zhang et al., 2011), but sodium chloride resulted in the best performance of electricity generation and water flux among several tested draw solutes such as potassium phosphate buffer, $CaCl_2$ and glucose (Ge and He, 2012).

Although the use of FO membrane can lead to more electricity generation than that of CEM, it is not clear what factors contribute to this improvement. In general, the performance of an MFC is affected by its internal losses, including ohmic loss, activation loss, bacterial metabolic loss and concentration loss (Logan et al., 2006). Especially, replacing CEM with FO membrane could affect membrane resistance, variation of pH in catholyte and/or anolyte, and oxygen diffusion. It is also of strong interest to understand how water flux, a unique phenomenon for OsMFCs, can influence electricity generation. It was reported that an air–cathode OsMFC had a relatively lower internal resistance than the ones containing CEM or AEM according to the polarization curve, which might attribute to the acceleration of ion transport due to water flux (Werner et al., 2013). Proton movement could also be promoted by water flux, resulting in less increase in the catholyte pH and decrease in the anolyte pH (Zhang et al., 2011). In an air–cathode OsMFC, the decreased anolyte pH (0.86 pH unit) was 24% of the theoretical value, whilst the increased catholyte pH (4.06 pH unit) was only 63% of the theoretical value and 73% of that in a CEM-equipped MFC (Werner et al., 2013). Those findings indicate that the OsMFC may exert positive effect on pH stabilization and thus effectively reduce overpotential. In addition, the use of the high-conductivity catholyte can also help reduce the resistance of the catholyte, resulting in greater power production.

To better understand the OsMFC performance, experiments were conducted for comparing with a CEM-MFC and under different operating conditions, and a mathematical model has been developed. To our knowledge, this is the first mathematical model for OsMFCs. The objectives of this study are: (1) investigating the improvement of current generation with FO membrane; (2) validating the developed OsMFC model with experimental data; and (3) predicating the contribution of different factors of internal resistance to current generation with water flux.

2. Methods

2.1. The OsMFC/MFC setup and operation

The same reactor was used as either an OsMFC or an MFC, with FO membrane or CEM installed between the anode compartment and the cathode compartment. Each compartment had a liquid volume of 360 mL. Stainless steel mesh and carbon cloth was placed on both sides of the FO membrane as support materials. Two pretreated carbon brushes (Gordon BrushMfg. Co. Inc., Commerce, CA, USA) were inserted into the anode compartment as the anode electrodes. The cathode electrode was a piece of carbon cloth coated with Pt as the catalyst (0.3 mg cm^{-2}). The cathode compartment was aerated with air. The electrodes were connected by copper wires to an external resistor of 10 Ω. Before use, the FO membrane (Hydration Technology Innovations, LLC, Albany, OR, USA) was soaked in deionized (DI) water for 30 min according to the manufacturer's instructions. The surface area of the FO membrane was about 98 cm^2. The active layer of membrane was facing the anode (feeding solution).

The OsMFC/MFC was operated at room temperature of ~21 °C. The anode was inoculated with the anaerobic sludge from the Peppers Ferry Regional Wastewater Treatment Plant (Radford, VA, USA). The anode was fed with an acetate solution containing (per L of DI water): sodium acetate, 1 g; NH_4Cl, 0.15 g; NaCl, 0.5 g; $MgSO_4$, 0.015 g; $CaCl_2$, 0.02 g; $NaHCO_3$, 0.1 g; KH_2PO_4, 0.53 g; K_2HPO_4, 1.07 g; and trace element, 1 mL (Angenent and Sung, 2001). Two operation modes were applied in this study, batch mode and continuous mode. In the batch mode, a 500-mL glass bottle was connected to the anode compartment as an anolyte reservoir, while a 750-mL glass bottle was used as a catholyte reservoir. The cathode compartment of the OsMFC was filled with DI water to allow FO membrane to rest for 2 h every 22 h during the batch operation. In the continuous mode, the anolyte and the catholyte had the same feeding rate of 1.3 mL min^{-1}, resulting in a hydraulic retention time (HRT) of 4.5 h in each compartment, and were recirculated at 100 mL min^{-1}.

2.2. Measurement and analysis

The cell voltage was recorded every 5 min by a digital multimeter (2700, Keithley Instruments Inc., Cleveland, OH, USA). The pH was measured using a benchtop pH meter (Oakton Instruments, Vernon Hills, IL, USA). The conductivity was measured by a benchtop conductivity meter (Mettler-Toledo, Columbus, OH, USA). The polarization curve was performed by a potentiostat (Reference 600, Gamry Instruments, Warminster, PA, USA) at a scan rate of 0.2 mV s^{-1}. The volumetric densities of power and current were calculated based on the liquid volume of the anode compartment, according to a previous study (Zhang et al., 2010). Two Ag/AgCl reference electrodes (0.197 mV vs standard hydrogen electrode, SHE) were installed close to the anode electrode and cathode electrode, respectively. The anode potential and cathode potential were measured with the digital multimeter. The COD was measured using a DR/890 colorimeter (HACH Co., Ltd., USA) according to manufacturer's instruction. Water flux into the cathode (L m^{-2} h^{-1}, LMH) was calculated by the change of weight recorded on the balance (Scort Pro, Ohous, Columbia, MD, USA) (Wang et al., 2010a). The analysis of electrochemical impedance spectroscopy (EIS) of the membrane was conducted with different concentration of NaCl solution according to a previous research (Ge et al., 2013). Coulombic efficiency (CE) was calculated as previously described (Logan et al., 2006).

2.3. OsMFC model development

2.3.1. Mass balance of substrate in the anode

The OsMFC model was developed based on previously developed two-population MFC model, MDC model and FO model (Cath et al., 2006; Ping et al., 2014; Pinto et al., 2010) Anodophilic and methanogenic microbial populations are considered as the microbial community in the anode. The substrate