Desalination 372 (2015) 26–31

Contents lists available at ScienceDirect

Desalination

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

Forward osmosis membrane favors an improved proton flux and electricity generation in microbial fuel cells

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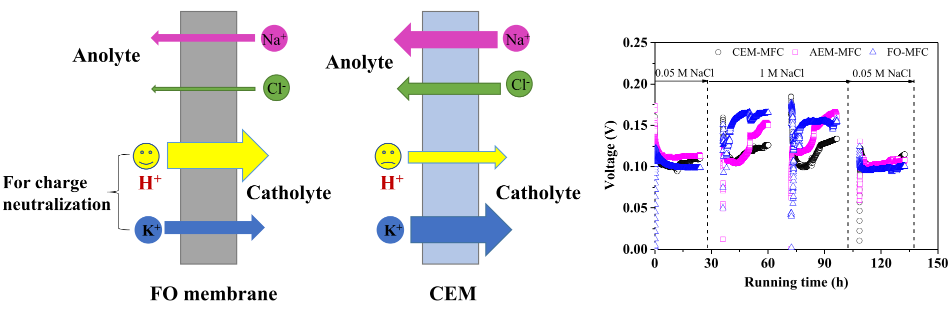
HIGHLIGHTS

- FO membrane favored higher electricity generation of MFC than CEM and AEM.
- FO-MFC exhibited lower internal resistance than MFC with other membranes.
- FO membrane favored improved flux of protons in relative to other cations.
- Size-selectivity and water flux of FO membrane favor the proton transport.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 4 February 2015
Received in revised form 13 June 2015
Accepted 16 June 2015
Available online 24 June 2015

Keywords:
Forward osmosis (FO) membrane
Microbial fuel cell (MFC)
Water flux
Cationic exchange membrane (CEM)
Anionic exchange membrane (AEM)
Internal resistance

ABSTRACT

Forward osmosis (FO)-microbial fuel cell (MFC) has been recently reported as an efficient system to treat wastewater and meanwhile recover energy, with better performance than conventional MFCs with cationic-exchange membranes (CEMs). However, the mechanism of FO membrane's superior performance remains unclear. This study compared the electrochemical performances of MFCs with FO membrane, CEM and anionic exchange membrane (AEM) as separators, and explored into the correlations between electricity generation and ion fluxes. The FO-MFC showed significantly lower internal resistance, due to higher salt accumulation and improved proton flux than other membrane systems. This led to an almost two-fold higher voltage in the FO-MFC than the CEM control. Unlike the CEM that encountered severe pH splitting due to suppressed proton diffusion by other competitive cations, the FO membrane favored an improved transport of protons in relative to other larger-sized cations attributed to its unique size-selectivity and the water flux as further driven force. The present work may have implications for the development and application of more efficient bioelectrochemical processes.

1. Introduction

Microbial fuel cells (MFCs), as an emerging technology for wastewater treatment and energy recovery, has undergone substantial development in the past few years [1,2]. However, a practical implementation of this technology still faces tremendous challenges, among which unsatisfactory performance of separators is frequently encountered. Although a success operation of separator-free MFCs has been demonstrated, separators are usually necessary to avoid oxygen and substrate crossflow, which would otherwise lower the power density [3–6]. However, one major constraint of traditional separators, currently dominated by cationic exchange membrane (CEM), is the low proton transfer efficiency due to competition of other cations. This usually leads to pH

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http://dx.doi.org/10.1016/j.desal.2015.06.011
0011-9164/

splitting and severe voltage losses [7–9]. In addition, the relatively high cost of CEM also makes their large-scale application prohibitory. In comparison, some low-cost, larger-porous separators such as ultrafiltration membrane and cloth generally allow a better proton transfer, but cross-flow become severe [5,6,8]. Therefore, suitable separators for MFC application are still to be developed.

Recently, forward osmosis (FO) membrane was proposed as a possible alternative for MFC application [10–14]. Previous studies show that FO membranes contributed to less pH accumulation in MFCs than CEM [12,13]. The substantially lower cost and the possibility to produce higher-quality effluent further add up to its attractiveness for wastewater treatment application [12,15–17]. The enhanced electricity generation of MFC by adoption of an FO membrane as the separator over CEM was considered mainly due to accelerated proton transfer driven by the water flux [12], lower membrane resistance, or raised anolyte conductivity resulting from reverse salt flux [13,18,19]. However, solid evidences for these mechanisms are still lacking and no unanimous conclusions have been reached so far.

This study aims to provide insights into the ion transport and electricity generation processes in an FO-MFC and reveal the underlying mechanisms of its superior performance. To understand the possible contribution of salinity gradients in power generation, an anion exchange membrane was also adopted as a control. Comparative studies are performed to examine the water flux, ion transport, internal resistance and electricity generation performance in MFCs with different membranes (i.e., FO membrane, CEM and AEM).

2. Materials and methods

2.1. Membranes

A commercial flat-sheet thin-film composite FO membrane (Hydration Technology Innovations, Albany, USA) was used in this study. The FO membrane material consists of a polyamide active layer and a polysulfone support layer. The membrane coupon was soaked in 18.2 Ω deionized (DI) water (Millipore Inc, USA) at 4 °C before use. CEM (Nafion-117, Dupont Co, DE) was pretreated by boiling in 3% H_2O_2 (30% v/v) and DI water, followed by soaking in 5% H_2SO_4 and DI water for 1 h each. AEM (AMI-7001, Membrane Inc. USA) was pretreated by emersion in 5% NaCl solution at 40 °C for 24 h to allow membrane hydration and expansion.

2.2. MFC setup and operation

Cubic-shaped two-chamber MFCs, assembled with different membranes, was adopted in this study. The system configuration of the FO-MFC is illustrated in Fig. 1. The effective volumes of feed solution (used as anolyte) and draw solution (used as catholyte) were 250 and 150 mL, respectively. The membrane area was 12.5 cm^2. A carbon felt (Beijing Sanye Carbon Co., China) with a projected area of 7.5 cm^2 was used as the anode, while a Pt-coated carbon paper (2 × 2 cm^2, 2 mg-Pt cm^{-2}; GEFC Co., China) was used as the cathode. The electrodes were connected across a 100-Ω external resistance for voltage recording. The active layer of the FO membrane faced the feed solution in order to decrease membrane fouling and ensure relatively stable water flux [20–22]. The same reactor configuration was adopted for the CEM-MFC and AEM-MFC.

The bioanodes were directly collected from another air-cathode MFC that had been continuously run for over 6 months. For each MFC, the anode chamber was filled with synthetic wastewater (feed solution), which contained (per liter): sodium acetate, 2 g; NH_4Cl, 0.15 g; NaCl, 0.5 g; $CaCl_2$, 0.02 g; $MgSO_4$, 0.015 g; $NaHCO_3$, 0.1 g; KH_2PO_4, 0.53 g; K_2HPO_4, 1.07 g, and trace element, 1 mL [12]. The cathode chamber was filled with 0.05 M or 1.00 M NaCl as the catholyte (draw solution) (Table 1). Here, 0.05 M NaCl was selected in order to create a non-osmotic pressure difference condition, because this concentration rendered the catholyte the same solution conductivity as the anolyte. The initial catholyte pH, with either 0.05 M and 1 M NaCl, was adjusted to 7.0 using 0.1 M NaOH.

Both the anodic and cathodic chambers were connected to independent external solution reservoirs and the solution was continuously recirculated using peristaltic pumps. The recirculation flow rate was

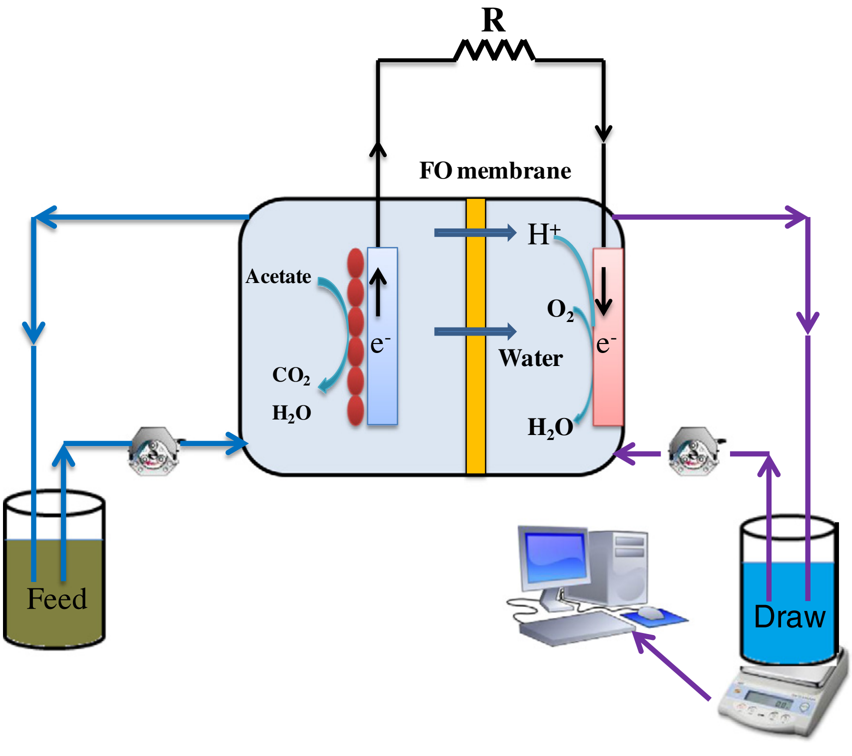

Fig. 1. Schematic diagram of the FO-MFC setup.