



## Patterned ion exchange membranes for improved power production in microbial reverse-electrodialysis cells



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### HIGHLIGHTS

- Patterned membranes were designed for improved power production in MRCs.
- No spacers were needed due to the hemispherical surface on one membrane side.
- Internal resistance was reduced, increasing power in the MRC.
- Energy recovery and efficiency were also both increased in the MRC.

### ARTICLE INFO

#### Article history:

Received 10 July 2014

Received in revised form

5 August 2014

Accepted 7 August 2014

Available online 14 August 2014

#### Keywords:

Microbial reverse electro dialysis cell

Patterned membranes

Integrated spacer

Internal resistance

### ABSTRACT

Power production in microbial reverse-electrodialysis cells (MRCs) can be limited by the internal resistance of the reverse electro dialysis stack. Typical MRC stacks use non-conductive spacers that block ion transport by the so-called spacer shadow effect. These spacers can be relatively thick compared to the membrane, and thus they increase internal stack resistance due to high solution (ohmic) resistance associated with a thick spacer. New types of patterned anion and cation exchange membranes were developed by casting membranes to create hemispherical protrusions on the membranes, enabling fluid flow between the membranes without the need for a non-conductive spacer. The use of the patterned membrane decreased the MRC stack resistance by  $\sim 22 \Omega$ , resulting in a 38% increase in power density from  $2.50 \pm 0.04 \text{ W m}^{-2}$  (non-patterned membrane with a non-conductive spacer) to  $3.44 \pm 0.02 \text{ W m}^{-2}$  (patterned membrane). The COD removal rate, coulombic efficiency, and energy efficiency of the MRC also increased using the patterned membranes compared to the non-patterned membranes. These results demonstrate that these patterned ion exchange membranes can be used to improve performance of an MRC.

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### 1. Introduction

Salinity gradient energy is recognized as a large and sustainable source of energy. The amount of power that could be captured

globally from naturally occurring salinity gradients, such as river water and seawater, has been estimated to be 1.9–2.6 TW [1,2]. Reverse electro dialysis (RED) is one of several technologies being investigated to capture and convert salinity gradient energy into useful power. The RED process is based on a stack of alternating anion membranes (AEMs) and cation exchange membranes (CEMs) that separate high (HC) and low salt concentration (LC) solutions. When HC and LC solutions are fed into the RED stack, a potential difference is created across the membranes (e.g.,  $\sim 0.1$ – $0.2 \text{ V}$  per cell

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pair [3,4]), which can drive redox reactions at the electrodes and generate electricity. However, a large number of cell pairs are normally needed to overcome high electrode overpotentials and produce net power [5,6]. The use of many cell pairs not only increases the capital cost of the RED stack, but also increases energy consumption for pumping solutions through a large number of membrane channels due to high solution resistance [7].

A microbial reverse electrodialysis cell (MRC), which combines a microbial fuel cell (MFC) and a RED stack [8], recently emerged as a sustainable water treatment technology that can harvest chemical energy from organic matter and at the same time extract electrical energy from salinity gradients [9]. MFC electrodes can be used to spontaneously generate electrical current when exoelectrogenic bacteria metabolize organics in wastewater and release electrons, and oxygen in air is reduced at the cathode [10,11]. When MFC electrodes are used with a RED stack, providing favorable reactions at the electrodes, energy can be efficiently extracted by MRC stack using only a small number of membrane pairs. The inclusion of the MRC stack also improves the performance of the MFC electrodes, resulting in synergistically-enhanced power production compared to each individual process [8]. Further MRC performance improvement requires reducing the internal resistance of the MRC stack. For example, two membrane pairs of a small MRC stack accounted for nearly two-thirds (63%) of the total internal resistance of the MRC stack [12]. Reducing MRC stack resistance could substantially improve MRC performance and the efficiency of energy extraction from salinity gradients.

The internal resistance of the RED part of MRC reactor can be reduced by minimizing the space between the membranes [6,13]. In an MRC stack the inter-membrane distance is determined by the spacer thickness. Spacers are used to distribute the flow evenly across the membrane surface, and maintain separation between the membranes. The spacer thickness directly determines the ohmic resistances of HC and LC solutions [1], and therefore, decreasing the inter-membrane distance (by decreasing the spacer thickness) increases performance [14]. Commonly used spacers, made from nylon [5,14], polyethylene (PE) [8], and polyamide [15] polymers, are not ion-conductive materials. Non-conductive spacers mask a part of the ion exchange membrane area and block ion transport. This “shadow effect” of the spacer can increase internal stack resistance and lower power output [6,16]. The use of ion-conductive spacers in MRC can avoid this impact of surface coverage with a non-conductive material and improve MRC stack performance, but the spacers must be thin to avoid high solution resistances.

The use of patterned membranes has recently been proposed as a promising method to avoid the use of separate spacers in a RED stack and to minimize electrode spacing [17,18]. Patterned membranes examined so far had straight-ridge, wave or pillar structures that were integrated into the membrane design, allowing solution flow through these structures without the need for non-ionically conductive spacers [17,19]. Since the patterned structures are ion conductive, there is no shadow effect. The use of patterned membranes can therefore increase the area available for ion transport, and when properly designed, reduce the laminar boundary layer resistance to ion transport and increase the higher power density compared to that of flat membranes with spacers [17,19,20]. Although a variety of different structures of the patterned membranes have been used in RED [20,21] or electrodialysis (ED) [17], patterned structures membranes have so far not been examined for use in MRCs. Here we prepared patterned ion exchange membranes based on making hemispherical protrusions on one side of the membrane, and demonstrated that their use in MRCs increased the energy recovery and efficiency of the process by reducing inter-membrane distances and the membrane stack internal resistance.

## 2. Materials and methods

### 2.1. Patterned and smooth membrane fabrication

Poly(phenylsulfone) (Radel R-5500,  $M_w = 63 \text{ kg mol}^{-1}$ , dry density =  $1.29 \text{ g cm}^{-3}$ ) was kindly provided by Solvay Advanced Polymers, LLC. Poly(vinyl alcohol-co-ethylene) (PVA-co-PE), poly(vinylbenzyl chloride) (PVBC), *N,N*-dimethylacetamide (DMAc, anhydrous, 99.8%), and *N,N,N',N'*-tetramethyl-1,6-hexanediamine (99%) were purchased from Sigma–Aldrich, Inc. (USA) and were used without further purification. Polydimethylsiloxane (PDMS) (Sylgard 184) was obtained from Dow Corning, Inc. (MI, USA). A polytetrafluoroethylene (PTFE) plate was purchased from McMaster-Carr, (OH, USA).

Poly(phenylsulfone) was sulfonated [22] to prepare the cation exchange membrane polymer. The solution used to cast the cation exchange membrane (CEM) was prepared by first drying sulfonated poly(phenylsulfone) under vacuum for 24 h. Then, 1.50 g of this polymer was dissolved in DMAc (35 mL, anhydrous) at room temperature. The polymer solution used to make the anion exchange membrane (AEM) was prepared in four steps. First, 10.0 g PVA-co-PE was mixed with 90 mL DMAc. The solution was stirred at 80 °C for 2 h to allow the PVA-co-PE to completely dissolve. The solution was allowed to cool to room temperature and was filtered using a 5.0  $\mu\text{m}$  PTFE filter. Next, 10.0 g PVBC was dissolved in 90 mL DMAc at room temperature for 20 min. Then, 3.75 mL *N,N,N',N'*-tetramethyl-1,6-hexanediamine was added to 31.25 mL DMAc. Finally, aliquots the three solutions, PVA-co-PE (6.81 mL), *N,N,N',N'*-tetramethyl-1,6-hexanediamine (2 mL), and PVBC (1.7 mL) were mixed with DMAc (7.5 mL) and were stirred for 10 min.

The patterned membranes were made by casting the CEM and AEM polymer solutions using a micromachined PTFE mold (Fig. 1). The base of the mold was constructed from a block of PTFE (7 cm  $\times$  7 cm  $\times$  3 cm width) that was micro-machined to contain 200 hemispherical holes (diameter: 300  $\mu\text{m}$ , spacing: 2 mm). PDMS precursor solution (7 g, Sylgard 184) (10:1 ratio (v/v) with the curing agent of Sylgard 184 silicone elastomer curing agent) was dispensed on the base of the mold and then degassed using a vacuum oven to remove bubbles from the holes, and cured at 60 °C for 2 h. The polymerized PDMS was removed from the PTFE mold and reversed, creating an inversed replica of the PTFE mold with extruded hemisphere microstructures. The PDMS slab was then used as mold for membrane casting. The CEM or AEM polymer solution (10 mL) was poured into the PDMS mold and cured for 2 d at 35 °C (AEM) or at 50 °C (CEM) in an oven, producing the final patterned ion exchange membrane. The same process was used to prepare the smooth membrane (Fig. S1), except a smooth PTFE tray was used.

### 2.2. MRC construction and operation

The MRC reactor consisted of separate anode and cathode chambers separated by an MRC stack (Fig. 2). The anode chamber was made of a 4 cm long polycarbonate cubic block drilled to contain a cylindrical chamber (3 cm diameter). The cathode chamber was made the same way but it was only 2 cm long [8]. The anodes were heat-treated graphite fiber brushes (2.5 cm diameter  $\times$  2.5 cm length; PANEX 33 160 K, ZOLTEK), that were placed vertically in the middle of the anode chamber [23]. The air cathodes were made of carbon cloth (projected cross sectional area of 7 cm<sup>2</sup>) as previously described, with four diffusion layers made of PTFE on the air side, and a Pt/C catalyst layer (10% Pt on Vulcan XC-72, Fuel cell store) on the solution side [24]. Both anode and cathode chambers contained Ag/AgCl reference electrodes (Bio-analytical Systems, Inc., RE-5B; +0.209 V versus a standard

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