Journal of Membrane Science 469 (2014) 364–370

Contents lists available at ScienceDirect

Journal of Membrane Science

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

# Enhanced water desalination efficiency in an air-cathode stacked microbial electrodeionization cell (SMEDIC)

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ARTICLE INFO

*Article history:*
Received 20 March 2014
Received in revised form
26 May 2014
Accepted 29 June 2014
Available online 8 July 2014

*Keywords:*
Microbial desalination cell
Ion exchange resin
Electrodeionization
Brackish water desalination
Seawater desalination

ABSTRACT

A microbial desalination cell was developed that contained a stack of membranes packed with ion exchange resins between the membranes to reduce ohmic resistances and improve performance. This new configuration, called a stacked microbial electro-deionization cell (SMEDIC), was compared to a control reactor (SMDC) lacking the resins. The SMEDIC+S reactors contained both a spacer and $1.4 \pm 0.2$ mL of ion exchange resin (IER) per membrane channel, while the spacer was omitted in the SMEDIC-S reactors and so a larger volume of resin ($2.4 \pm 0.2$ mL) was used. The overall extent of desalination using the SMEDIC with a moderate (brackish water) salt concentration (13 g/L) was 90–94%, compared to only 60% for the SMDC after 7 fed-batch cycles of the anode. At a higher (seawater) salt concentration of 35 g/L, the extent of desalination reached 61–72% (after 10 cycles) for the SMEDIC, compared to 43% for the SMDC. The improved performance was shown to be due to the reduction in ohmic resistances, which were 130 Ω (SMEDIC-S) and 180 Ω (SMEDIC+S) at the high salt concentration, compared to 210 Ω without resin (SMDC). These results show that IERs can improve performance of stacked membranes for both moderate and high initial salt concentrations.



## 1. Introduction

Water scarcity is a major global challenge, and it is predicted that by 2025 two-thirds of the world's population will be living in water-stressed countries [1]. Desalination of seawater and brackish water can be used to alleviate water stress, and it is estimated that the number of seawater desalination facilities will increase substantially over the next 10 years. Current commercial desalination technologies, including electrodialysis (ED), electrodeionization (EDI), thermal desalination, and reverse osmosis (RO) are energy intensive and therefore there is great interest in other technologies that use less electrical energy [2,3].

Microbial desalination cells (MDCs) have recently drawn attention as a low-energy method of water desalination. The simplest MDC is a microbial fuel cell (MFC) that is modified to contain a middle chamber for desalination, by using two ion exchange membranes between the anode and cathode chamber [4]. In the anode chamber organic matter is oxidized by exoelectrogenic bacteria [5], with the electrons released to the circuit and protons into solution. Electrons from the anode flow to the cathode where they combine with protons and oxygen to form water [4,5]. The production of protons at the anode and consumption of protons at the cathode drives desalination of saltwater in the middle chamber, as salt ions in the saline water in the middle chamber migrate through the cation and anion exchange membranes to balance charge [6]. The performance of MDC is limited by several factors including the microbial community composition on the anode, electrode materials, pH imbalances, and internal resistance [7,8,11,13]. The internal resistance has several different components including solution and membrane (ohmic), charge transfer, contact, and mass transfer resistances. The low ionic conductivity of less saline waters (1–10 g/L) can substantially increase ohmic resistances, particularly as the water becomes progressively desalinated [4–6,9,10].

Several methods have been proposed to reduce internal resistance and enhance desalination performance and rates of MDCs. Instead of using only a pair of ion exchange membranes, a stack of membranes can be placed between the electrodes [10] similar to stack configurations used for conventional ED. However, a large spacing between the electrodes can produce a high solution resistance. In one early study, only 1.5 cell pairs could be used in the stacked-MDC at the voltage generated, due to the wide spacing between the electrodes (1 cm) which produced a high ohmic resistance (18 Ω per membrane pair) [10]. Performance was improved by reducing the chamber width to that of the thin spacers used to separate the membranes (1.3 mm), enabling the

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http://dx.doi.org/10.1016/j.memsci.2014.06.058
0376-7388/

use of a five-cell pair membrane stack that substantially improved MDC performance with a high initial salt concentrations (35 g/L). However, the desalination performance of this 5-cell stack was reduced at a low salt concentration of 6 g/L due to high ohmic resistance of the lower conductivity solution [11]. Omitting spacers can improve performance [12], although this can result in the deformation of the membranes and adversely affect flow through the chamber. Another approach is to use ion-exchange resins (IERs) to increase the ion conductivity in the solution between the membranes [6,9]. This IER approach was shown to enhance the desalination of lower salinity solutions (0.7–10 g/L) in a single-desalination-chambered MDC due to the reduction in the ohmic resistance [6,9].

The objective of this study was to further improve the performance of the 5-cell stack MDC developed by Kim and Logan [11] by using IERs in the solution chambers in a stack of ion exchange membranes, for both high and moderate salt concentration solutions. This configuration is referred to as a stacked microbial electro-deionization cell (SMEDIC), due to the expected enhanced deionization effect of the IERs on performance. The desalination performance of the SMEDIC was examined for solutions with two different salt concentrations (13 g/L and 35 g/L) in order to demonstrate that improved performance with the IERs was not limited to using only lower conductivity solutions. The performance of the system was compared to a control reactor, lacking IERs, referred to as a stacked MDC (SMDC). The performance of the SMEDIC was evaluated in terms of the volumes of IERs used and the presence or absence of spacers, in terms of desalination efficiency (extent of desalination), electrical power production, and internal resistance.

## 2. Experimental

### 2.1. Construction and operation of SMEDIC and SMDC

The anode (30 mL; empty bed volume) and cathode (18 mL; empty bed volume) chambers were made from polycarbonate cylindrical chambers with a cross-sectional area of 7 $cm^2$ following a previous design [11,13]. The anode was a graphite fiber brush 2.7 cm in diameter and 2.3 cm long, and it was heat treated before use (Mill-Rose Lab Inc., USA) [14]. The air cathode contained platinum nanoparticle catalysts on the water side (3.5 mg Pt) with a Nafion binder, and four polytetrafluoroethylene diffusion layers on the air side [15]. The desalination chamber in both the SMEDIC and SMDC reactors contained a five-cell pair ED stack (10 total cells) built between the anode and cathode chambers (Fig. 1A). The ED stack was constructed with 5 cation-(CEM) and 6 anion-(AEM) exchange membranes (Selemion CMV and AMV, Asahi glass, Japan). The membranes (~0.1 mm thick) were pretreated by storage in a 0.6 M NaCl solution for 24 h, and then rinsed with deionized water. Silicon gaskets (~1.3 mm thickness) were used between the membranes to create a water tight seal and provide a flow path across the membranes [11]. Polyethylene mesh spacers (4 cm × 0.5 cm; 1 mm thickness) were used to maintain cell thickness in the SMDC. SMEDIC reactors were tested in two configurations (with and without spacers) which required the use of different amounts of resin. When spacers were used, the reactors were packed with 1.4 ± 0.2 mL of IERs (SMEDIC+S). When spacers were omitted (SMEDIC-S), additional resin was used (2.4 ± 0.2 mL) in order to completely fill the chamber and maintain a constant chamber size. The diluate or desalinated water volumes were 144 mL (SMDC), 85 mL (SMEDIC+S), and 82 mL (SMEDIC-S).

The anion IER used was a strong base resin type with a total exchange capacity of 1.1 eq/L (DOWEX MONOSPHERE 550A (OH), DOW Chemicals, USA). The cation IER used was a strong acid resin type with a total exchange capacity of 2.0 eq/L (DOWEX MONOSPHERE 650C (H), DOW Chemicals, USA). Cation- and anion-exchange resins were mixed at a ratio of 1:1.6 (v/v) based on their different exchange capacities, and these mixed-beds were employed between adjacent AEM and CEM pairs.

The anodes were initially acclimated in MFCs until the peak voltage was stable at around 550 mV for three reproducible cycles (external resistance of 1000 Ω) [10]. The MFCs were inoculated with primary clarifier effluent and operated in a fed-batch mode with acetate as the main carbon and energy source. After acclimation, the anodes were transferred to the different desalination reactors, and operated at a lower external resistance (10 Ω) to improve power production [10].

Two concentrations of synthetic salt solution were tested: 13 g/L, representing brackish water; and 35 g/L, representing seawater. The salt solution was continuously pumped (from the bottom to the top of the chamber) into the diluate and concentrate cells in the ED stack at a rate of 0.1 mL/min (144 mL/d). The anode and cathode chambers were operated in a fed-batch mode over multiple batch cycles. When current decreased below 0.20 mA, the catholyte solution was replaced with fresh synthetic salt solution (13 g/L or 35 g/L NaCl) and the anolyte solution was replaced with fresh medium consisting of 1 g/L sodium acetate in a phosphate buffer (9.16 g/L $Na_2HPO_4$; 4.9 g/L $NaH_2PO_4$–$H_2O$; 0.62 g/L $NH_4Cl$; 0.26 g/L KCl) with minerals and vitamins [11,16]. The desalinated effluent (diluate solution) was recycled through the ED stack over several fed-batch cycles of anode operation. The diluate solution was continuously recycled using a 200 mL salt water reservoir, while the concentrate solution was not recycled. The diluate solution flowed serially from the cathode side through every diluate cell, and the concentrate solution flowed co-currently through the concentrate cells (Fig. 1A). All reactors were operated in duplicate, at 27 ± 2 °C.

### 2.2. Analyses and calculations

Power density and polarization curves were generated using a potentiostat (VMP3 Multichannel Workstation, Biologic Science Instruments, USA) at 30 °C. Current was scanned from 0 mA to 3 mA, with each current step held for 15 min to reach steady conditions. Power densities ($mW/m^2$) were normalized by cathode projected working area (7 $cm^2$).

Influent and effluent conductivities and pH for the diluate, concentrate, anolyte and catholyte solutions were measured using a conductivity-pH meter (Seven Multi, Mettler-Toledo International Inc., USA). The salinity was estimated from conductivity measurements using an in situ conductivity conversion as previously outlined by Bennett [17], and assuming the conductivity measured was due only to NaCl. Salinity reduction was calculated based on the influent and effluent conductivities. Current efficiency was determined as the ratio of ionic separation of NaCl to the total number of electrons passed through the circuit, as

$$\eta = \frac{F(c^D_{in}v^D_{in} - c^D_{out}v^D_{out})}{N_{cp}\sum \int i dt} \quad (1)$$

where $F$ is Faraday's constant, $c$ the molar concentration of NaCl in the diluate, $v$ the volume of the diluate, $N_{cp}$ the number of cell pairs in the ED stack, and $i$ the current generated in the reactor. The subscript "*in*" indicates conditions at the beginning of the cycle, "*out*" the end of the cycle, and the superscript "*D*" indicates diluate [11].

At the end of each desalination cycle, the total desalination rate (TDR) was calculated to evaluate desalination performance