

# Using microbial desalination cells to reduce water salinity prior to reverse osmosis†

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A microbial desalination cell (MDC) is a new method to reduce the salinity of one solution while generating electrical power from organic matter and bacteria in another (anode) solution. Substantial reductions in the salinity can require much larger volumes of the anode solution than the saline water, but any reduction of salinity will benefit the energy efficiency of a downstream reverse osmosis (RO) desalination system. We investigated here the use of an MDC as an RO pre-treatment method using a new type of air-cathode MDC containing three equally sized chambers. A single cycle of operation using a 1 g L<sup>-1</sup> acetate solution reduced the conductivity of salt water (5 g L<sup>-1</sup> NaCl) by 43 ± 6%, and produced a maximum power density of 480 mW m<sup>-2</sup> with a coulombic efficiency of 68 ± 11%. A higher concentration of acetate (2 g L<sup>-1</sup>) reduced solution conductivity by 60 ± 7%, and a higher salt concentration (20 g L<sup>-1</sup> NaCl) reduced solution conductivity by 50 ± 7%. The use of membranes with increased ion exchange capacities further decreased the solution conductivity by 63 ± 2% (20 g L<sup>-1</sup> NaCl). These results demonstrate substantial (43–67%) desalination of water is possible using equal volumes of anode solution and salt water. These results show that MDC treatment could be used to substantially reduce salt concentrations and thus energy demands for downstream RO processing, while at the same time producing electrical power.

## Introduction

By the year 2025, two out of every three persons in the world could be living in water-stressed regions.<sup>1</sup> One of the solutions to increase potable water availability is desalination of brackish water and seawater. It is estimated that worldwide desalination capacity will increase 140% by 2015 to 97.5 million cubic metres of water per day,<sup>2</sup> with energy accounting for 40% of the total

water cost.<sup>3</sup> Energy demands for water desalination range from 650 kW h m<sup>-3</sup> for energy intensive single-stage evaporation of seawater to 68 kW h m<sup>-3</sup> for multistage flash evaporation and 3.7 kW h m<sup>-3</sup> for reverse osmosis (RO).<sup>4</sup>

A new concept for water desalination was recently demonstrated based on using electrical power generated by bacteria in devices called microbial desalination cells (MDCs).<sup>5</sup> The concept is similar to water electrodialysis in the fact that there is a voltage applied between the chambers in order to drive the ions out of the desalination compartment, but instead of using an external source of electrical energy desalination is achieved with the current and potential generated by bacteria in the MDC. When a lower salinity wastewater stream is used in the anode chamber to desalinate the water in the middle chamber, the MDC also has characteristics of a reverse electrodialysis (RED) process as the salinity gradient between the two chambers can contribute to current generation. In contrast, in electrodialysis all water

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## Broader context

Current desalination technologies such as reverse osmosis (RO) or distillation require a large amount of energy, ranging from 3.7 to 650 kW h per cubic metre of water treated. The amount of energy needed for RO increases in proportion to the initial salinity of the water. Recently a new device, called a microbial desalination cell (MDC), was shown to desalinate water without the use of any external electrical power. Electrical energy produced directly by the degradation of organic matter in water by bacteria was used to achieve desalination. However, large volumes of water were used in the anode chamber containing the bacteria, relative to volume of water desalinated. It is shown here that using equal volumes of water in the anode and desalination chamber it is possible to remove up to 60% of the salt in the water. No external power source was needed, and up to 480 mW was produced per square metre of electrode surface area. Removing over half the salt can substantially reduce energy requirements needed for subsequent treatment using RO.

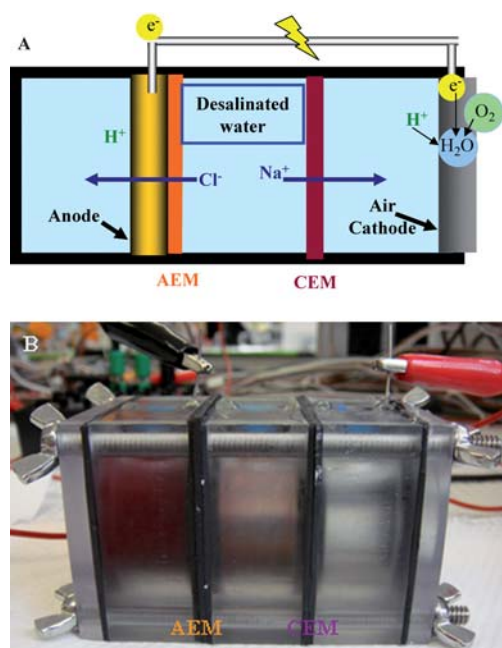
streams fed into the system are usually of equal salinity.<sup>6,7</sup> The MDC is constructed by modifying a microbial fuel cell (MFC) to contain three chambers, with the central desalination chamber separated from the anode by an anion exchange membrane (AEM), and the cathode by a cation exchange membrane (CEM). Bacteria metabolize organic matter on the anode and release electrons to the anode electrode and protons into the water. The AEM prevents protons and other positively charged ions from leaving the anode chamber, so charge is balanced by anions ( $\text{Cl}^-$ ) moving from the central desalination chamber into the anode chamber. Protons are depleted in the cathode chamber when they combine with electrons and oxygen to form water, with charge balanced by cations ( $\text{Na}^+$ ) passing from the desalination chamber through the CEM into the cathode chamber. As a consequence of these two charge-transfer processes,  $\text{NaCl}$  in the middle desalination chamber is removed and the water is desalinated.

The MDC concept was successfully demonstrated by Cao *et al.*<sup>5</sup> using a ferricyanide catholyte. As the conductivity of the saline water was reduced to low levels in their tests, the internal resistance of the cell increased and the voltage produced by the cell decreased. To reduce the solution conductivity in the middle chamber to very low levels, the anode solution was replaced many times over the cycle, requiring for example 200 mL of anolyte to desalinate 3 mL of saline water. Rather than using an MDC to completely desalinate the water, it may be more useful to use the process to partially desalinate water. We therefore determined here the extent that salt water could be desalinated in a single fed-batch cycle in an MDC under conditions of equal volumes of solution in the three chambers. In addition, we wanted to examine a process where desalination was sustained using oxygen at the cathode rather than ferricyanide. Chemical catholytes such as ferricyanide are not sustainable, but they generally produce higher cathode potentials than oxygen which may have aided the overall extent of desalination. We therefore examined the performance of an MDC using air cathode, so as to more practically assess the performance of the process. Previous studies have investigated the influence of different types of membranes on the performance of biocatalyzed electrolysis systems<sup>8</sup> and studied charge balance issues associated with separation of anode and cathode in bioelectrochemical systems (BES).<sup>9</sup> In an effort to improve upon the possible extent of desalination, we also examined the performance of two experimental ion exchange membranes having higher ion exchange capacities than commercially available membranes typically used in MFCs. Performance of the MDC was evaluated in terms of changes in water conductivity, maximum power densities, and coulombic efficiency, for two different initial substrates and  $\text{NaCl}$  concentrations.

## Methods

### Air-cathode MDC construction

The MDC consisted of three blocks of Lexan, each 2 cm long, machined to contain a cylindrical chamber 3 cm in diameter (14 mL each) (Fig. 1). Except when stated otherwise, the AEM (AMI-7001) and CEM (CMI-7000) were commercially manufactured membranes made from divinylbenzene cross-linked



**Fig. 1** (A) Schematic and (B) picture of the three-chamber air-cathode MDC.

poly(styrene) (Membranes International Inc., NJ). In some tests we used experimental membranes made in our laboratory based on ion-functionalized poly(phenylsulfone). Poly(phenylsulfone) (Radel R-5500,  $M_w$  63 000  $\text{g mol}^{-1}$ ) was kindly donated from Solvay Advanced Polymers, LLC. Sulfonated Radel R-5500 (experimental CEM) was prepared through post-sulfonation of Radel R-5500 with trimethylsilyl chlorosulfonate (Aldrich) in tetrachloroethane (Aldrich) solution.<sup>10</sup> The membranes of the synthesized sulfonated Radel R-5500 were obtained *via* casting polymer solution on glass plates from dimethylformamide (Mallinckrodt Analytical) and drying at 60 °C for 2 h, then heated at 80 °C for 2 h in an atmospheric environment, followed by drying in a vacuum oven at 80 °C for 5 h. Aminated Radel R-5500 (experimental AEM) was prepared by two step synthesis:<sup>11,12</sup> (1) chloromethylation of Radel R-5500 using dimethoxymethane (Aldrich), thionyl chloride (Aldrich) and zinc chloride (Aldrich) in tetrachloroethane; and (2) amination with trimethylamine (45% solution in water, Alfa Aesar) on a membrane form. Membranes of chloromethylated Radel R-5500 were cast from a chloroform (Mallinckrodt Analytical) solution onto glass plates, dried at room temperature in an atmospheric environment for 12 h, and then further dried at 70 °C for 5 h under vacuum. The membranes were converted to quaternary ammonium form by immersion in 45% aqueous trimethylamine for 48 h followed by complete rinsing in water. The ion exchange capacities (IECs) were determined using  $^1\text{H}$  NMR and IECs of the experimental CEM and AEM resulted in 1.76  $\text{meq g}^{-1}$  (CEM) and 2.05  $\text{meq g}^{-1}$  (AEM).

The charge-bearing functional groups were the same for both commercial and experimental membranes: sodium sulfonate for the CEMs and quaternary ammonium chloride for the AEMs. The experimental membranes were much thinner (AEM 0.041 mm and CEM 0.066 mm) than the commercial membranes (AEM and CEM, 0.46 mm) to decrease the ohmic resistance.

They also had higher ion exchange capacity (AEM, 2.05 meq g<sup>-1</sup> and CEM, 1.76 meq g<sup>-1</sup>) than the commercial membranes (AEM, 1.0 meq g<sup>-1</sup> and CEM, 1.3 meq g<sup>-1</sup>). Water uptake by the membranes was measured by the procedure of Kim *et al.*<sup>13</sup> All membranes were preconditioned by immersion in a 0.5 M NaCl solution overnight, then rinsed in distilled water.

The anodes were ammonia-treated<sup>14</sup> carbon cloth (BASF, NJ). Cathodes were made by applying platinum (0.5 mg cm<sup>-2</sup> Pt) and four PTFE diffusion layers on a 30% wet-proofed carbon cloth (type B-1B, E-TEK) as previously described.<sup>15</sup> Both electrodes had the same projected surface area of 7 cm<sup>2</sup>.

### Microorganisms and medium

MDCs were inoculated (50%, v/v) with a pre-acclimated suspension of bacteria from an existing MFC. The medium used for the anode chamber contained sodium acetate (1 or 2 g L<sup>-1</sup>) in a nutrient medium containing a 50 mM PBS buffer solution (PBS: 4.58 g Na<sub>2</sub>HPO<sub>4</sub>, 2.45 g NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O, 0.31 g NH<sub>4</sub>Cl and 0.13 g KCl), 12.5 mL mineral and 5 mL vitamin solutions.<sup>16,17</sup> The desalination chamber water contained 5 g L<sup>-1</sup> or 20 g L<sup>-1</sup> NaCl in distilled water. The cathode contained 50 mM PBS buffer. All solutions were replaced when the voltage decreased to <40 mV, forming a complete cycle of operation. MDCs were operated at ambient temperatures (23 ± 3 °C). Experiments were repeated four times over a period of 40 days.

### Analyses

The voltage (*E*) across an external resistor (1000 Ω, except as noted) in the MDC was monitored at 20 minute intervals using a multimeter (Keithley Instruments, OH) connected to a personal computer. Current (*I*), power (*P* = *IE*), and coulombic efficiency (CE) were calculated as previously described,<sup>18</sup> with the power density normalized by the projected area of the anode. Polarization curves were obtained by measuring the stable voltage generated at various external resistances ranging between 1000 Ω and 50 Ω (>15 minutes per resistor).

Phosphate was measured using the total phosphate method (HACH Company, Loveland, CO). Sodium and chloride ion concentrations were measured at the beginning and at the end of the experiments (ESI<sup>+</sup>) using combination electrodes and a meter (SympHony SB90M5, VWR International). Combination electrodes include both an ion-selective electrode and a reference electrode in a single unit.<sup>19</sup> Solution pH was monitored using a pH probe and meter (SympHony SB70P, VWR International). Electrolyte solution conductivities per cm were measured using a conductivity electrode (2 Cell Epoxy; SympHony SB90M5 meter; VWR International). All measurements were performed at the beginning and end of each fed-batch cycle. COD was measured according to standard methods.<sup>20</sup> Acetone, fatty acids (acetate, propionate and butyrate) and alcohols (methanol, ethanol, *n*-propanol and *n*-butanol) were analyzed using a gas chromatograph (Agilent, 6890) equipped with a flame ionization detector and a fused silica capillary column (Agilent, DB-FFAP) with helium as carrier gas.<sup>21</sup>

### Electromotive force

The electromotive force (*E*<sub>EMF</sub>), generated by the diffusion of sodium and chloride ions across the membranes, is the sum of the potentials generated by the diffusion of Na<sup>+</sup> across the AEM (*E*<sub>AEM</sub>) and Cl<sup>-</sup> across the CEM (*E*<sub>CEM</sub>), or *E*<sub>EMF</sub> = *E*<sub>AEM</sub> + *E*<sub>CEM</sub>. *E*<sub>AEM</sub> produced by the diffusion of Cl<sup>-</sup> ions from the desalination chamber to the anodic compartment is given by:

$$E_{\text{AEM}} = \alpha_{\text{AEM}} \frac{RT}{zF} \ln \frac{a_{\text{c}}^+}{a_{\text{d}}^+} \quad (1)$$

*E*<sub>CEM</sub> engendered by the diffusion of Na<sup>+</sup> ions from the desalination chamber to the cathodic compartment is given by:

$$E_{\text{CEM}} = \alpha_{\text{CEM}} \frac{RT}{zF} \ln \frac{a_{\text{c}}^+}{a_{\text{d}}^+} \quad (2)$$

where α<sub>AEM</sub> and α<sub>CEM</sub> are the permselectivities of the AEM and CEM respectively, *z* the ion valence, *R* the gas constant, *F* Faraday's constant, and *a*<sub>c</sub><sup>+</sup> and *a*<sub>d</sub><sup>+</sup> the activities of the ions (Na<sup>+</sup> or Cl<sup>-</sup>) in the concentrate and dilute compartments<sup>22</sup> computed from their respective concentrations since the activity coefficients were close to 1 [range of 0.97 (dilute) to 0.92 (concentrate)<sup>23</sup>]. The membrane's electromotive force was determined at the beginning and at the end of each cycle.

The permselectivity of a membrane reflects its ability to selectively allow the passage of one species while restricting the passage of other species. When an ion exchange membrane is in contact with an electrolyte (salt solution), ions with the same charge (co-ions) as the fixed ions cannot enter the membrane by Donnan exclusion and should not pass through the membrane, while the oppositely charged free ions (counter ions) can pass freely through the membrane.<sup>24</sup> The membrane permselectivity can be calculated as the ratio of the measured (Δ*V*<sub>m</sub>) to theoretical membrane potential (Δ*V*<sub>th</sub>) in a concentration cell as:

$$\alpha (\%) = \frac{\Delta V_{\text{m}}}{\Delta V_{\text{th}}} \times 100 \quad (3)$$

The Δ*V*<sub>m</sub> across a membrane (7 cm<sup>2</sup>) separating two 4 cm cubic reactor chambers (photograph in ESI<sup>+</sup>) was measured using the static membrane potential measurements method of Dlugolecki *et al.*<sup>25</sup> One cell was filled with 0.1 M NaCl, and the other with 0.5 M NaCl. The potential difference was measured using Ag/AgCl reference electrodes placed on either side of the membrane after steady conditions (30 minutes) at 25 °C. The Ag/AgCl electrodes (MF 2052, BASi Electrochemistry) were calibrated before (and after) each experiment using Zobell's solution, and were +206 mV vs. a standard hydrogen electrode (SHE) (precision of ±2 mV).

The theoretical potential was calculated using the Nernst equation as:

$$\Delta V_{\text{th}} = \frac{RT}{zF} \ln \frac{a_{\text{c}}}{a_{\text{d}}} \quad (4)$$

## Results and discussion

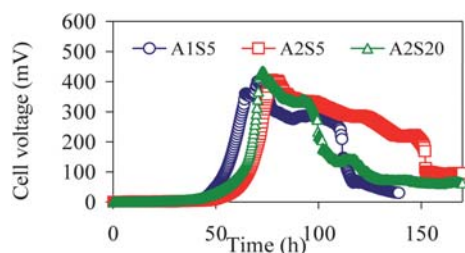
### MDC performance with different substrate concentrations

The MDCs acclimated to different substrate concentrations (1 or 2 g L<sup>-1</sup> acetate) produced stable and equivalent maximum

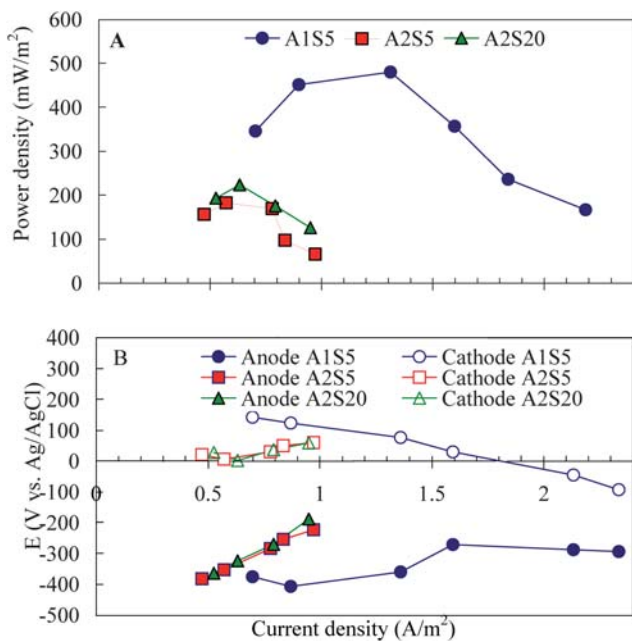
**Table 1** Summary of the conditions, extend of desalination in the desalination chamber (DC) and CE over multiple cycles, and maximum power and current densities from polarization curves

Acetate/g L <sup>-1</sup> (in mM)	NaCl/g L <sup>-1</sup> (in mM)	Membrane	Control (dialysis) NaCl (% decrease)	CE (%)	Desalination chamber (% decrease)				
					Conductivity	Na <sup>+</sup>	Cl <sup>-</sup>	<i>P</i> <sub>max</sub> /mW m <sup>-2</sup>	<i>I</i> <sub>max</sub> /A m <sup>-2</sup>
1 (12)	5 (85)	Commercial	18 ± 2	68 ± 11	43 ± 6	50 ± 1	61 ± 12	424 ± 57	2.80 ± 0.1
2 (24)	5 (85)	Commercial	31 ± 5	66 ± 11	60 ± 7	57 ± 8	67 ± 0	159 ± 34	0.84 ± 0.2
2 (24)	20 (342)	Commercial	15 ± 1	57 ± 22	50 ± 7	57 ± 9	43 ± 10	198 ± 36	0.90 ± 0.1
2 (24)	20 (342)	Experimental	43 ± 6	53 ± 5	63 ± 2	60 ± 6	53 ± 8	295 ± 27	0.81 ± 0.1

voltages of three fed-batch cycles after inoculation with a fixed resistance (1000 Ω), and 5 g L<sup>-1</sup> of NaCl in the desalination chamber. With 1 g L<sup>-1</sup> of acetate and 77 ± 3% COD removal, the conductivity of NaCl water decreased by 43 ± 6% and the CE over the cycle was 68 ± 11% (Table 1). Increasing the acetate concentration to 2 g L<sup>-1</sup> acetate increased the time of the cycle and the COD removal to 82 ± 6% and improved the reduction in



**Fig. 2** MDC performance as a function of initial substrate concentration and NaCl concentration. (A = Acetate concentration in the anode chamber; S = NaCl concentration in the desalination chamber; numbers indicate concentrations in g L<sup>-1</sup>).



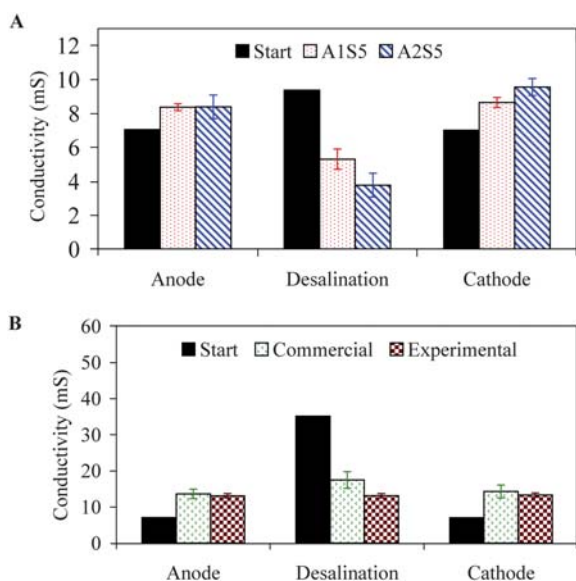
**Fig. 3** (A) Polarization curves, and (B) electrode potentials. (A = Acetate concentration in the anode chamber; S = NaCl concentration in the desalination chamber; numbers indicate concentrations in g L<sup>-1</sup>).

conductivity of the middle chamber to 60 ± 7%, but it did not substantially alter the CE (66 ± 11%) (Table 1).

The use of a higher substrate concentration reduced maximum power densities, although the cycle time was increased (Fig. 2). Based on polarization data, 424 ± 57 mW m<sup>-2</sup> was produced with 1 g L<sup>-1</sup> of acetate compared to 159 ± 34 mW m<sup>-2</sup> with 2 g L<sup>-1</sup> of acetate (Fig. 3A). The current densities with 1 g L<sup>-1</sup> acetate reached 2.80 ± 0.1 A m<sup>-2</sup>, compared to <1 A m<sup>-2</sup> with 2 g L<sup>-1</sup> of acetate (Table 1). Measurement of the electrode potentials showed the largest change for the anode potential, suggesting that the higher acetate concentration inhibited the anode performance (Fig. 3B). However, separate tests with single-chamber MFCs (2 cm cube reactor) did not show significant differences in power for reactors with 1 or 2 g L<sup>-1</sup> of acetate. This result suggests that the reduced performance of the anode was due to other factors, such as poorer microbial growth or biofilm inhibition due to the higher chloride concentrations with a greater extent of desalination, or low pH within the anode biofilm.<sup>26,27</sup> The cathode performance was also slightly altered, although much of the difference is likely due to the reduced current density at the higher acetate concentration. The internal resistance<sup>28</sup> with 1 g L<sup>-1</sup> acetate (449 ± 0.7% Ω), calculated from the slope of the polarization data, was about half that obtained with 2 g L<sup>-1</sup> acetate (809 ± 0.6% Ω) and was not affected by initial NaCl concentration.

Control experiments were performed under the same conditions without bacteria (dialysis experiments) to determine changes that would result from differences in osmotic pressure across the membranes during the same period of time as the biotic experiments. When the commercial membranes were used, conductivities of the abiotic controls decreased by 18 ± 2% (5 g L<sup>-1</sup> NaCl) using 1 g L<sup>-1</sup> of acetate over the same period of time required for a complete cycle with the biotic reactor (Table 1). With 2 g L<sup>-1</sup> of acetate there was a 31 ± 5% decrease in conductivity at the lower NaCl concentration (5 g L<sup>-1</sup>), and 15 ± 1% decrease at the higher NaCl concentration (20 g L<sup>-1</sup>). Thus, the higher acetate concentration (2 g L<sup>-1</sup>) reduced the initial difference in osmotic pressure, resulting in less desalination by dialysis (15% compared to 18%). With the experimental membranes, there was a 43 ± 6% decrease in conductivity just due to dialysis (2 g L<sup>-1</sup> acetate and 20 g L<sup>-1</sup> NaCl) (Table 1). These changes show that the difference in osmotic pressure contributed to the desalination of the water in addition to that produced by the electrical current generated by the bacteria.

The three compartments were tested for acetate and phosphate at the end of every cycle. All acetate was completely consumed and did not accumulate in any other chambers. Phosphate ions



**Fig. 4** Conductivities in MDC chambers for (A) commercial membranes with different anode and desalination chamber concentrations of acetate and NaCl (see Fig. 3 for key to legend); (B) performance of different membranes with 2 g L<sup>-1</sup> acetate (anode) and 20 g L<sup>-1</sup> NaCl (desalination chamber).

were not found to have migrated into the middle desalination chamber.

#### Changes in conductivity and pH in the electrode chambers

Conductivity changes in the anode and cathode chambers were much less than those in the desalination chamber (Fig. 4). For example, the anode chamber conductivity increased by only 16% when the conductivity of the middle chamber decreased by 60% (5 g L<sup>-1</sup> NaCl middle chamber and 2 g L<sup>-1</sup> acetate anode chamber). The reason for this smaller conductivity change is primarily due to changes in the predominant chemical species of the buffer. In a single cycle with 2 g L<sup>-1</sup> acetate and 5 g L<sup>-1</sup> NaCl in the desalination chamber, chloride ions increased from 0.4 g L<sup>-1</sup> to 2 g L<sup>-1</sup> in the anode chamber. Over the same cycle, the anode chamber pH decreased from 7.2 to 6.2 ± 0.2. At neutral pH, the buffer is primarily an equal mixture of HPO<sub>4</sub><sup>2-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>. However, as the bacteria release protons into solution the pH decreases, resulting in protonation of the buffer and reduced solution conductivity. When 1 g L<sup>-1</sup> of acetate was used, the final anode chamber pH was 6.2 ± 0.2. Under these conditions, the concentration of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> was 46 mM, compared to only 4.2 mM of HPO<sub>4</sub><sup>2-</sup>. Larger changes in pH occurred with 2 g L<sup>-1</sup> of acetate, with a final pH in the anode chamber of 4.5 ± 0.8, shifting the predominant phosphate species further to the protonated form (H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, 50 mM; H<sub>3</sub>PO<sub>4</sub>, 0.20 mM; and HPO<sub>4</sub><sup>2-</sup>, 0.11 mM). The resulting impact of both chloride addition to the anode chamber and the decrease in pH was therefore only a modest increase in anode chamber conductivity.

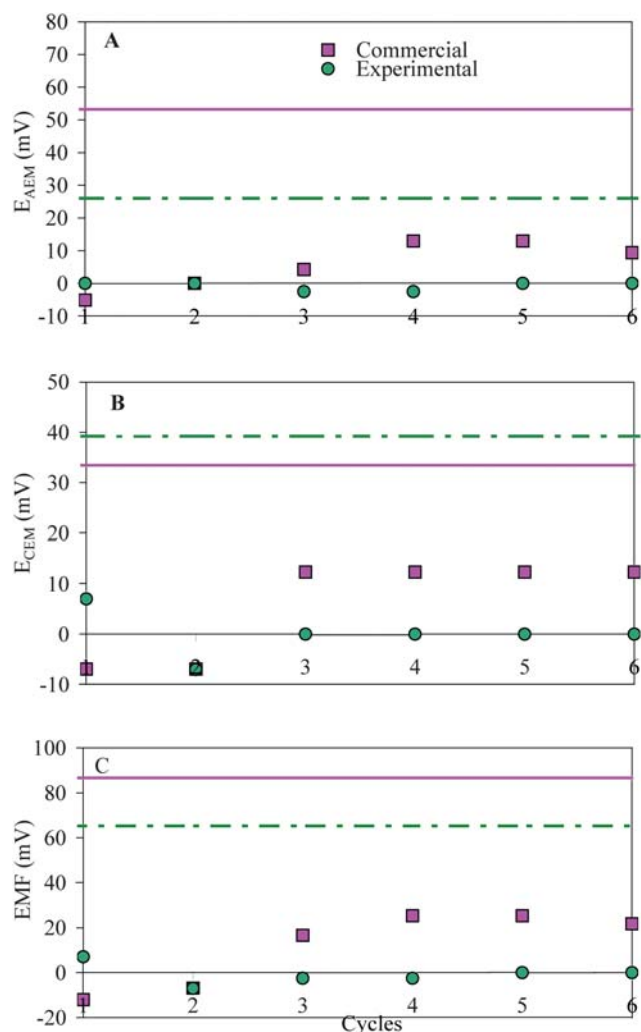
#### Effect of higher NaCl concentration

When 20 g L<sup>-1</sup> of NaCl were placed in the desalination chamber (2 g L<sup>-1</sup> acetate in the anode chamber), the initial maximum

voltage was similar to that achieved with 5 g L<sup>-1</sup> of NaCl, but the voltage dropped off more rapidly likely as a result of the greater influx of chloride into the anode chamber (Fig. 2). Even though the initial NaCl concentration was larger by a factor of four, the total desalination was reduced by only 17% to an overall 50% decrease in solution conductivity over the cycle (Table 1). Maximum power, electrode potentials (Fig. 3), and CE (Table 1) were similar to that obtained with 5 g L<sup>-1</sup> of NaCl at this initial acetate concentration.

#### Effect of the membranes on desalination and system performance

Water desalination and power densities were both improved through the use of the experimental membranes that were thinner and had higher IECs than the commercial membranes (Fig. 4). The conductivity of the NaCl solution in the middle chamber decreased by 63%, which is a 26% increase in desalination



**Fig. 5** Membrane potentials generated by ion concentration gradients: (A) across the AEM, from the desalination chamber towards the anode chamber; (B) across the CEM, from the desalination chamber to the cathode chamber; (C) the generated electromotive force (EMF). The lines indicate potentials at the beginning of each cycle for commercial (solid lines) and experimental (dashed) membranes.

compared to tests under the same conditions with commercial membranes (2 g L<sup>-1</sup> acetate and 20 g L<sup>-1</sup> NaCl) (Table 1). Power increased to 295 ± 27 mW m<sup>-2</sup> and the CE of 53 ± 5% was similar to that obtained with the commercial membranes.

### Membrane electromotive force

The membranes' electromotive force was determined at the beginning and at the end of each cycle. The magnitude of the membrane electromotive force over successive cycles with the two different membranes provides insight into the extent of charge transfer relative to equilibrium. The potentials at the beginning of each cycle relative to movement of ions from the middle chamber into the electrode chambers were both highly positive, resulting in an overall positive  $E_{EMF}$  (Fig. 5). The commercial AEM initially (time 0) had a higher  $E_{AEM}$  than the experimental AEM because the permselectivity coefficient of the commercial AEM was twice as large. The experimental CEM initially had a higher  $E_{CEM}$  than the commercial CEM since its permselectivity coefficient was 5% greater. The average permselectivities of the commercial membranes were  $\alpha_{AEM} = 94\%$  and  $\alpha_{CEM} = 90\%$ . For the experimental membranes, they were  $\alpha_{AEM} = 44\%$  and  $\alpha_{CEM} = 95\%$ . The  $\alpha_{AEM}$  of the experimental membrane was low because it had a high water uptake (70%) compared to the commercial AEM (21%) or CEM (26% commercial and 29% experimental).

The best desalination performances are usually obtained when the  $E_{EMF}$  is negative (ESI<sup>+</sup>) indicating that the ionic concentration in the center chamber was driven past equilibrium by the current and potential generated by the MDC and that the desalination chamber has lower ionic concentrations than the anode or cathode compartments. The lowest EMF values were obtained at the end of the first two cycles. The good performance of the first two cycles was due to the fact that the first cycles were longer so that the MDC remained at its maximum cell voltage for a longer period of time with greater desalination. After the third cycle, the MDC cell voltage decreased more rapidly and thus less current was available to drive the ions from the desalination chamber to the side compartments. At the end of each cycle, the AEM and CEM potentials for the experimental membranes were always close to zero while the potentials of the commercial membranes remained positive. The  $E_{EMF}$  values at the end of each cycle remained higher for the commercial membrane as expected, because fewer ions were transported through these membranes as compared to the experimental membranes.

### Outlook

While a previous study showed that very large amounts of water were needed for water desalination using an MDC, results here show that an MDC can be used to substantially reduce the salinity of water with equal volumes of anolyte and desalination chamber solutions. Using an anolyte containing 2 g L<sup>-1</sup> acetate, we were able to achieve up to a 63% reduction in the water salinity over a single cycle. This extent of desalination was accomplished using an air cathode system and not ferricyanide as in previous experiments. Although a Pt cathode was used here, cobalt tetramethoxyphenylporphyrin (CoTMPP) and activated carbon can also be used in air-cathode systems.<sup>29,30</sup> Recent tests

show that these cathode materials can perform as well as or better than Pt in saline solutions.<sup>31</sup>

While acetate was used as the substrate for bioelectricity generation, it is hoped that other sources of organic matter such as domestic and industrial wastewaters could be used for this purpose. The conductivity, concentration of organic matter, and the alkalinity (*i.e.* the buffering capacity) will be important wastewater characteristics. Power is increased by using wastewaters with higher conductivities. Although conductivity of the anolyte increased here over time due to chloride movement into the anode chamber, the increase in conductivity was small relative to the larger decrease in conductivity of the solution in the desalination chamber due to the decrease in pH in the anode chamber. A higher initial concentration of organic matter in the anode solution could theoretically increase the extent of desalination, but this can only occur if there is sufficient buffering capacity of the anolyte to prevent large decreases in pH. Thus, methods to balance charge, such as recirculation of the catholyte to the anode chamber, need to be further explored.

While the extent of desalination accomplished here is relatively large, and no external source of electrical was needed, the extent of desalination was insufficient to treat the water to levels needed for drinking water. This suggests that the most useful application for an MDC may be as a method to pre-treat saline water for downstream RO processing. The energy needed for RO decreases with a reduction in the salinity of the treated water, and thus reducing the conductivity of the saline water by 50% or more would greatly benefit energy consumption in the RO process. Passive ion transfer from the saline water to wastewater alone helps to partially desalinate the water, and it was observed here that even in the absence of bacteria there was a 15–31% decrease in salinity. The use of the MDC provided an added benefit of wastewater treatment and power generation, and substantially increased the extent of desalination. The combination of all these factors provides support for the use of MDCs as a pre-treatment method for subsequent RO desalination.

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### Notes and references

- 1 WHO, *Water, Health and Ecosystems*, <http://www.who.int/heli/risks/water/water/en/index.html>, paragraphs 6 and 7.
- 2 K. Christen, *Environ. Sci. Technol.*, 2007, **41**, 5579–5579.
- 3 K. Betts, *Environ. Sci. Technol.*, 2004, **38**, 246A–247A.
- 4 R. Semiat, *Environ. Sci. Technol.*, 2008, **42**, 8193–8201.
- 5 X. X. Cao, X. Huang, P. Liang, K. Xiao, Y. J. Zhou, X. Y. Zhang and B. E. Logan, *Environ. Sci. Technol.*, 2009, **43**, 7148–7152.
- 6 B. Pilat, *Desalination*, 2001, **139**, 385–392.
- 7 R. E. Lacey, *Ocean Eng.*, 1980, **7**, 1–47.
- 8 R. A. Rozendal, H. V. M. Hamelers, R. J. Molenkamp and C. J. N. Buisman, *Water Res.*, 2007, **41**, 1984–1994.
- 9 F. Harnisch and U. Schröder, *ChemSusChem*, 2009, **2**, 921–926.
- 10 T. Saito, M. D. Merrill, V. J. Watson, B. E. Logan and M. A. Hickner, *Electrochim. Acta*, 2010, **55**, 3398–3403.
- 11 A. Dyck, D. Fritsch and S. P. Nunes, *J. Appl. Polym. Sci.*, 2002, **86**, 2820–2827.

- 
- 12 M. R. Hibbs, M. A. Hickner, T. M. Alam, S. K. McIntyre, C. H. Fujimoto and C. J. Cornelius, *Chem. Mater.*, 2008, **20**, 2566–2573.
  - 13 Y. S. Kim, B. Einsla, M. Sankir, W. Harrison and B. S. Pivovar, *Polymer*, 2006, **47**, 4026–4035.
  - 14 S. Cheng and B. E. Logan, *Electrochem. Commun.*, 2007, **9**, 492–496.
  - 15 S. Cheng, H. Liu and B. E. Logan, *Electrochem. Commun.*, 2006, **8**, 489–494.
  - 16 D. R. Lovley and E. J. P. Phillips, *Appl. Environ. Microbiol.*, 1988, **54**, 1472–1480.
  - 17 S. A. Cheng, D. F. Xing, D. F. Call and B. E. Logan, *Environ. Sci. Technol.*, 2009, **43**, 3953–3958.
  - 18 B. E. Logan, B. Hamelers, R. A. Rozendal, U. Schroder, J. Keller, S. Freguia, P. Aelterman, W. Verstraete and K. Rabaey, *Environ. Sci. Technol.*, 2006, **40**, 5181–5192.
  - 19 A. D. McNaught and A. Wilkinson, *IUPAC, Compendium of Chemical Terminology, The Gold Book*, IUPAC, 1997.
  - 20 APHPA, *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington, DC, 1992.
  - 21 H. Liu and B. E. Logan, *Environ. Sci. Technol.*, 2004, **38**, 4040–4046.
  - 22 J. Veerman, J. W. Post, M. Saakes, S. J. Metz and G. J. Harmsen, *J. Membr. Sci.*, 2008, **310**, 418–430.
  - 23 G. Prentice, *Electrochemical Engineering Principles*, Prentice Hall, Englewood Cliffs, New Jersey 07632, 1991.
  - 24 F. Helfferich, *Ion Exchange*, McGraw-Hill Book Company, New York, 1962.
  - 25 P. Dlugolecki, K. Nymeijer, S. Metz and M. Wessling, *J. Membr. Sci.*, 2008, **319**, 214–222.
  - 26 H. S. Lee, C. I. Torres and B. E. Rittmann, *Environ. Sci. Technol.*, 2009, **43**, 7571–7577.
  - 27 A. E. Franks, K. P. Nevin, H. F. Jia, M. Izallalen, T. L. Woodard and D. R. Lovley, *Energy Environ. Sci.*, 2009, **2**, 113–119.
  - 28 B. E. Logan, *Microbial fuel cells*, J. Wiley & Sons, Inc., 2008.
  - 29 S. Cheng and B. E. Logan, *Water Sci. Technol.*, 2008, **58**, 853–857.
  - 30 F. Zhang, S. Cheng, D. Pant, G. V. Bogaert and B. E. Logan, *Electrochem. Commun.*, 2009, **11**, 2177–2179.
  - 31 S. C. X. Wang, X. Zhang, X. Y. Li and B. E. Logan, submitted.