

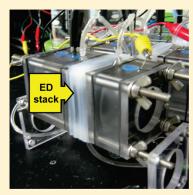
pubs.acs.org/est

Series Assembly of Microbial Desalination Cells Containing Stacked Electrodialysis Cells for Partial or Complete Seawater Desalination

Younggy Kim and Bruce E. Logan*

Department of Civil and Environmental Engineering, 212 Sackett Building, Penn State University, University Park, Pennsylvania 16802, United States

ABSTRACT: A microbial desalination cell (MDC) is a new approach for desalinating water based on using the electrical current generated by exoelectrogenic bacteria. Previously developed MDCs have used only one or two desalination chambers with substantial internal resistance, and used low salinity catholytes containing a buffered or acid solution. Here we show that substantially improved MDC performance can be obtained even with a nonbuffered, saline catholyte, by using an electrodialysis stack consisting of 5 pairs of desalting and concentrating cells. When 4 stacked MDCs were used in series (20 total pairs of desalination chambers), the salinity of 0.06 L of synthetic seawater (35 g/L NaCl) was reduced by 44% using 0.12 L of anode solution (2:1). The resistive loss in the electrodialysis stack was negligible due to minimization of the intermembrane distances, and therefore the power densities produced by the MDC were similar to those produced by single chamber microbial fuel cells (MFCs) lacking desalination chambers. The observed current efficiency was 86%, indicating separation of 4.3 pairs of sodium and chloride ions for every electron



transferred through the circuit. With two additional stages (total of 3.8 L of anolyte), desalination was increased to 98% salt removal, producing 0.3 L of fresh water (12.6:1). These results demonstrate that stacked MDCs can be used for efficient desalination of seawater while at the same time achieving power densities comparable to those obtained in MFCs.

■ INTRODUCTION

A microbial desalination cell (MDC) is a type of modified microbial fuel cell (MFC) that can be used to produce fresh water from salty water while simultaneously removing organic matter from an anode solution. In MDCs, exoelectrogenic bacteria oxidize substrates in water, such as organic matter in a wastewater, and release electrons to the anode, and these electrons flow to the cathode where oxygen is typically reduced to form water. The anode and cathode reactions create a potential gradient which drives the ionic transport between the electrodes, and removes salt in water held between ion-exchange membranes.

Previous MDCs have primarily been constructed from three chambers, with the desalination chamber separated from the anode and cathode chambers using appropriate ion-exchange membranes. 1-3 The amount of water used in the anode and cathode chambers to desalinate water has generally been large. For example, the electrical power producing MDCs examined by Cao et al. used 300 mL of anode and 100 mL of cathode solutions (phosphate buffer) to desalinate 3 mL of synthetic seawater (133:1), and the system of Jacobson et al.2 used 4 L of anolyte and 17.3 L of catholyte (sulfuric acid) to produce 0.35 L of water (61:1). One hydrogen producing system, where external power is needed, required 244 mL of anode and cathode solutions to desalinate 14 mL of 10 g/L NaCl⁴ (11:1). The system developed by Mehanna et al.^{3,5} required much less water for the analyte and catholyte (28 mL) but only removed 37-63% of the salt for a 20 g/L NaCl solution (2:1 to 2.6:1). Most importantly, all of these studies have used buffered solutions $^{1,3-6}$ or sulfuric acid² in the cathode chamber. Practical applications of MDC technologies will likely require the use of the same saline water in both the desalination and cathode chambers.

Water desalination using conventional electrodialysis relies on ionic transport in a stack of ion-exchange membranes containing pairs of desalting (diluate) and concentrating (concentrate) cells. A high voltage is typically applied to several to hundreds of stacked cell pairs. Because the ionic separation is repeated in every cell pair, the desalination rate is magnified by the number of cell pairs in the stack. For example, 100 pairs of sodium and chloride ions are separated for every electron transfer in a 100cell paired electrodialysis stack. This principle of an MDC stack was recently investigated by Chen et al. using 1-2 cell pair(s) between the anode and air cathode. However, the internal resistance was so large that the authors concluded that an MDC with more than 1.5 cell pairs (2 diluate and 1 concentrate chambers) would not be more efficient. Their system showed limited desalination of 20 g/L NaCl (~80% salt removal) using 500 mL of anolyte and 150 mL of buffered catholyte to produce 14 mL of desalinated water (46:1). This limited performance was likely due to the relatively thick desalination chamber (1 cm), which created a substantial Ohmic resistance. To improve the performance of MDCs, the internal resistance must be reduced in order to make the most efficient use of the maximum voltage that can be generated by this process (\sim 800 mV).

Received: February 20, 2011
Accepted: June 2, 2011
Revised: April 29, 2011
Published: June 15, 2011

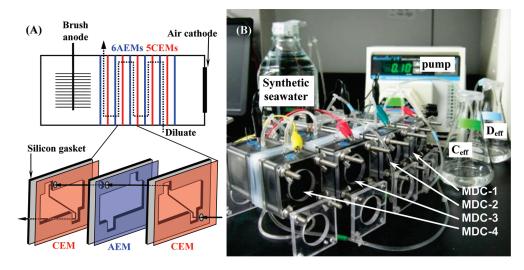


Figure 1. (A) Schematic design of an MDC containing an electrodialysis stack. The stack thickness of 10 cells is exaggerated. The shown flow lines indicate the diluate flow path, with the concentrate flow path countercurrent to the diluate. The 4×0.5 -cm² spacer is not shown. (B) Desalination system with 4 MDCs operated in series, with the concentrate effluent (C_{eff}) and diluant effluent (D_{eff}) reservoirs. The diluate solution is pumped from the seawater reservoir to flow successively through MDCs 1-4, with the concentrate solution flowing in the countercurrent direction.

The objective of this study was to show that development of an improved electrodialysis stack in MDCs can result in partial to complete desalination of seawater. Three separate innovations were used to substantially improve performance of the MDC: very thin stacks; the elimination of need for a buffered or chemical catholyte; and the incorporation of a novel water flow scheme through the stack. The use of very thin stacks makes it possible to substantially increase the extent and efficiency of desalination, and allow high power densities through the minimization of Ohmic resistances in the stacks. Synthetic seawater was fed to the cathode, avoiding the use of chemical buffer solutions, 1,3-6 sulfuric acid, 2 or a chemical catholyte (ferricyanide)¹ that have been previously used in MDCs. A novel flow design was also used here to maximize the extent of desalination, where the concentrate and diluate were directed serially into every desalination cell in the stack compared to the parallel flow in conventional electrodialyzers. The performance of this new type of stacked MDC design was evaluated in terms of the contributions of Ohmic resistances, junction potentials, and overpotentials to the total internal resistance. Because overpotentials are dependent on the current, the internal resistance in the MDC was analyzed as potential losses at a representative current. Another important issue in a stacked MDC is water transport through membranes, which reduces water recovery in the diluate and its quality due to electroosmosis and osmosis. In electroosmosis, water molecules associated with the charged ions are pulled through the nanoscale channels in ionexchange membranes. Whereas electroosmosis can not be eliminated in an MDC, the osmotic water loss can be minimized by reducing the hydraulic residence time or decreasing the crosssectional area of the membrane. The individual contributions of electroosmosis and osmosis were identified in order to understand how water loss might be minimized in the future.

■ MATERIALS AND METHODS

Solutions. Synthetic seawater (35 g/L NaCl) was continuously pumped into the diluate and concentrate cells except as noted. However, the anode and cathode chambers were operated

as fed-batch reactors over multiple cycles. When current decreased below 0.2–0.3 mA, synthetic seawater was placed in the cathode chamber, and fresh medium was provided in the anode chamber with 1 g/L sodium acetate in a phosphate buffer (9.16 g/L Na₂HPO₄; 4.9 g/L NaH₂PO₄–H₂O; 0.62 g/L NH₄Cl; 0.26 g/L KCl) with minerals and vitamins.⁸

MDC Construction. The cathode (18 mL) and anode (30 mL) chambers were cylindrical with a cross-sectional area of 7 cm² following a previously described design.³ The anode was a graphite fiber brush 2.7 cm in diameter and 2.3 cm long (Mill-Rose Lab Inc., USA).⁹ The air cathode contained platinum nanoparticle catalysts on the water side (3.5 mg Pt over 7 cm²) with a Nafion binder, and four polytetrafluoroethylene diffusion layers on the air side.¹⁰ The anode was inoculated with effluent from an existing MFC and enriched by operation in a conventional one-chamber MFC.^{3,5} During this start-up stage, the NaCl concentration was gradually raised to acclimate the anode bacteria in a high Cl⁻ environment, to avoid possible inhibition by Cl⁻ during MDC operation.

A five-cell pair electrodialysis stack (10 total cells) was built between the anode and cathode chambers (Figure 1A). The electrodialysis stack was constructed with 5 cation- and 6 anion-exchange membranes (Selemion CMV and AMV, Asahi glass, Japan). The membrane thickness was $\sim\!0.1$ mm, and swelling or shrinkage was not observed because the membrane was always exposed to NaCl solutions. Intermembrane distance (or cell width) was held constant by a piece of polyethylene mesh (4 \times 0.5 cm²) 1.3 mm thick, with each cell having a rectangular cross section (4 \times 2 cm²). The diluate solution was introduced from the cathode side and flowed serially through every diluate cell (Figure 1A). Similarly, the concentrate solution flowed through each of the concentrate cells.

MDC Operation. The continuous flow desalination system consisted of up to 4 MDCs operated in series (Figure 1B). From the seawater reservoir, the diluate flows from MDC-1 through MDC-4, while the concentrate is pumped in the opposite direction. The pumping rate was fixed at 0.1 mL/min (144 mL/d) for both flows, except as noted. The diluate flow was regulated at the outlet of the system, and the concentrate flow was controlled at the inlet of the system to quantify the water

transport by osmosis and electroosmosis. To find the contribution of electroosmosis, osmosis was minimized in a separate experiment with 4 MDCs by introducing the synthetic seawater (35 g/L NaCl) into the diluate stream but a lower concentration solution (14 g/L NaCl) into the concentrate stream. For these influent conditions, the concentration difference between the diluate and concentrate flows was minimized in each MDC, since the two flows were in opposite directions. This separate experiment was performed over three fed-batch cycles.

The 4-MDC system was also operated in three stages to increase desalination of the synthetic seawater. The diluate effluent from the first stage desalination was used as the diluate and concentrate influents in the second stage. The third stage was operated similarly with the diluate effluent collected during the second stage. All experiments were performed at 30 $^{\circ}$ C.

Analyses. The MDC was operated at a fixed external resistance $(10~\Omega)^6$ with the potential drop across the resistor recorded every 20 min using a multimeter (Keithley Instruments, USA). The desalination effluent, anolyte, and catholyte solutions were analyzed for conductivity and pH (SevenMulti, Mettler-Toledo International Inc., USA). COD (chemical oxygen demand) was measured for the anolyte using standard method (Hach Co., USA). The effect of chloride ions on the COD measurement was negligible due to 1:10 dilutions of samples.

The current efficiency (η_I) is the fractional contribution of the total charge transfer to the ionic separation in the MDC, ¹² and it is calculated as

$$\eta_I = \frac{F(c_{\rm in}^{\rm D}V_{\rm in}^{\rm D} - c_{\rm eff}^{\rm D}V_{\rm eff}^{\rm D})}{N_{\rm CP} \sum_{\rm reactor} \int idt}$$
(1)

where F is the Faraday constant, c is the molar concentration of NaCl, V is the solution volume, $N_{\rm CP}$ is the number of cell pairs in the electrodialysis stack, and i is the electric current. The superscript "D" indicates the diluate solution with the subscript "in" for the influent and "eff" for the effluent.

Resistive potential losses were determined by the Ohm's law. For a given resistivity of aqueous solution or membrane, the resistive loss was linearly proportional to the current density.

Overpotential was determined by the difference between two potential measurements. The equilibrium potential was found during a fed-batch cycle, instead of at the beginning of a cycle with fresh anolyte and catholyte, since the catholyte pH varied rapidly due to the absence of a pH buffer. Thus, when the current was stable at 4 mA, the electric circuit was disconnected for 2 h to measure the equilibrium potential for each electrode against the Ag/AgCl reference (Bioanalytical Systems, Inc., USA). After the measurement, the electric circuit was closed and the electrode potential was recorded.

The concentration difference between the diluate and concentrate cells creates a junction potential ($\Delta \phi_{\rm jct}$) across a single ion-exchange membrane, and its magnitude was quantified using

$$|\Delta \varphi_{\rm jct}| = \frac{RT}{F} \left[t_{\rm counter} \ln \left(\frac{a_{\rm counter}^{\rm C}}{a_{\rm counter}^{\rm D}} \right) - t_{\rm co} \ln \left(\frac{a_{\rm co}^{\rm C}}{a_{\rm co}^{\rm D}} \right) \right]$$
(2)

where R is the gas constant, T is the absolute temperature, a is the activity, and t is the transport number defined as the fractional contribution of the ionic flux to the current density in an ion-exchange membrane. The superscript "C" indicates the

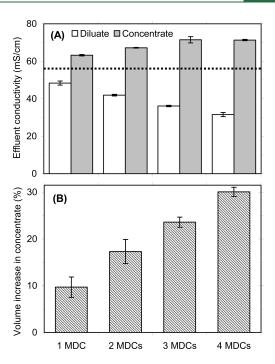


Figure 2. (A) Conductivity of the diluate and concentrate effluents. The dotted horizontal line indicates the conductivity of the influent synthetic seawater at 56 mS/cm. (B) Water transport from the diluate to concentrate. The effluents were collected during the first 12 h of a fedbatch cycle. The error bars indicate \pm SD based on 3-5 fed-batch cycles.

concentrate cell, while the subscripts "counter" and "co" indicate the counter- and co-ions for the ion-exchange membrane.

Chemical activities were calculated as the product of the chemical concentration and activity coefficient (f_i) . The NaCl concentration was calculated from the solution conductivity, while the activity coefficient was determined as

$$\log f_i = -\frac{A|z_i|^2 \sqrt{I_S}}{1 + Ba^0 \sqrt{I_S}} - \log(1 + 0.018m_i) + K_i I_S$$
 (3)

The Debye–Hückel constants were $A=0.5085~{\rm kg^{1/2}/mol^{1/2}}$ and $B=0.3282~{\rm \AA~kg^{1/2}/mol^{1/2}}$. The ion size parameter was $a^0=0.78~{\rm \AA~for~both~sodium}$ and chloride, while $K_{\rm Na}=0.105~{\rm and}$ $K_{\rm Cl}=-0.009~{\rm kg^2/mol^2}$. $I_{\rm S}$ is the ionic strength in molality, z is the ionic charge, and m is the molal concentration. ¹⁴ This equation is valid for a NaCl concentration of < 1 molality. ¹⁴

Power Generation. The power capacity of each MDC was examined independently from the desalination experiments, which had been performed over multiple cycles spanning \sim 50 days. The flow rate of the synthetic seawater was increased (1 mL/min) to maintain the theoretical hydraulic residence time (HRT) at 5 min in the electrodialysis stack. By reducing the HRT, there was essentially no salinity gradient, and therefore the energy loss by the junction potential was minimized. The MDC was under open-circuit condition for 1 h before the external resistance was increased every 20 min from 5 to 40 000 Ω .

■ RESULTS AND DISCUSSION

lonic Separation in the Stacked MDC. The extent of desalination was enhanced by increasing the number of stacked MDCs operated in series (Figure 2A). A single MDC removed 7.9 mS/cm from the diluate initially having a conductivity of

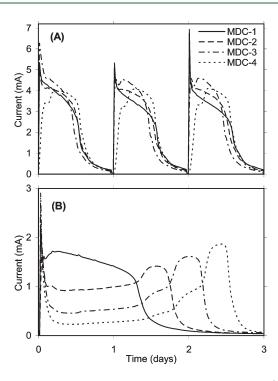


Figure 3. Current in the MDCs with the influent conductivity of (A) 56 and (B) 10 mS/cm. Note the different scales of ordinates. Typical fedbatch cycles are shown.

56 mS/cm. With 4 MDCs, the diluate conductivity decreased by 44% to 31 mS/cm, while the concentrate conductivity increased by 27% to 71 mS/cm. For each fed-batch cycle, active ionic separation lasted for \sim 12 h at stable currents of 3-5 mA in every MDC. Desalination effluent was collected during that time period (except for the first 2 h to eject the residual solutions from the previous cycle).

The diluate effluent remained neutral at pH 6.4 \pm 0.6 for an influent of pH of 6.3, while the concentrate effluent pH was 11.1 \pm 0.4. This increase in pH was due to the transport of hydroxyl ions from the cathode chamber into the concentrate stream. The catholyte pH increased over a cycle from 6.3 to 12.6 \pm 0.2 due to the consumption of protons for oxygen reduction. In a separate experiment, where the catholyte was replaced frequently during a cycle, it was found that there was relatively little improvement in current densities and thus control of catholyte pH was not needed (data not shown).

The anolyte pH decreased from 7.0 to 4.7 ± 0.5 over a fedbatch cycle due to proton production by bacteria from acetate degradation. The anolyte conductivity increased from 13.5 to 17.9 ± 1.1 mS/cm due to the transport of chloride ions into the anode chamber and the change in pH.³ The COD removal in the anode chamber over a fed-batch cycle averaged 91% (range of 77 to 99%, n=20). The low pH at the end of cycle was considered to inhibit complete acetate oxidation as a pH < 5 has been shown to deactivate exoelectrogens in MFCs.¹⁵ The Coulombic efficiency averaged 80% (range of 70 to 98%, n=20). This relatively high Coulombic efficiency indicates that there was little oxygen transfer through the anion-exchange membrane into the anode chamber. Otherwise, a greater portion of the acetate would have been oxidized by aerobic processes.

Water Transport from Diluate to Concentrate. The concentrate increased in volume due to water transport from the

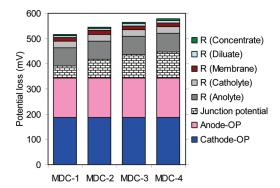


Figure 4. Individual potential loss at 4 mA during the 4-MDC operation with the synthetic seawater (35 g/L NaCl) as influents, where R indicates Ohmic resistances and OP indicates overpotentials. The resistive potential loss was determined based on conductivity measurements. Junction potential was determined by eq 2. The overpotential was measured with Ag/AgCl reference electrodes.

diluate. Because the partial volume of NaCl in seawater is about 1.1%, 16 the contribution of the salt to the volume increase was negligible. The volume increase was proportional to the number of the MDCs; with 1 MDC, the concentrate gained 10%, while with 4 MDCs the concentrate gained 30% of its influent volume (Figure 2B), resulting in the desalination recovery of 43% during the active desalination period ($\sim\!60$ mL of diluate effluent and $\sim\!80$ mL of concentrate effluent). This substantial water transport helps to explain the lack of a change in the concentrate conductivity between 3 and 4 MDCs in series (Figure 2A).

A separate experiment with 4 MDCs showed that electroosmosis was responsible for $19.4\pm1.6\%$ volume increase in the concentrate effluent (i.e., 65% of the increased volume). This value corresponds to the electroosmotic transport of 15.7 water molecules per separation of a sodium and chloride ion pair. By subtracting the electroosmotic volume increase, we conclude that about one-third of the water transport was driven by osmosis during the operation of 4 MDCs in series.

Current Efficiency. In each fed-batch cycle of operation, the current was relatively stable at 3-5 mA over 12 h, then it rapidly dropped to <1 mA mainly due to decreasing anolyte pH, and then it decreased slowly thereafter with further decrease in anolyte pH, depletion of substrate, and increase in the catholyte pH, until a new cycle was initiated (Figure 3A). During the active desalination period (first 12 h), the current efficiency was $86\pm5\%$. This indicates that 93% of the ionic flux through ion-exchange membranes was carried by counterions (i.e., selected ions by the membranes), while 7% was contributed by rejected co-ions due to nonideal performance of the ion-exchange membranes. Because the contribution of co-ions is $\sim\!10\%$ in typical ion-exchange membrane systems, 12 the perm-selectivity of the used ion-exchange membranes was well maintained during the slow ionic separation in the MDCs.

Potential Loss. The use of thin cells (1.3 mm) in the electrodialysis stack successfully minimized resistive potential losses to <16 mV in the diluate and concentrate cells (Figure 4). This resistive potential loss was estimated by assuming an average current of 4 mA in each MDC based on the observed current (Figure 3A), and a linear interpolation of the solution conductivity between the inlet and outlet to the electrodialysis stack. With the relatively low current density in the electrodialysis stack (0.5 mA/cm²), the potential loss by the concentration

polarization in the diffusion boundary layer would be negligible. 17 The potential loss associated with 11 pieces of the ion-exchange membranes was approximately 15.9 mV based the resistivity of $2.8-3.0\,\Omega$ cm 2 . 18 The junction potential calculated using eq 2 was added over 11 membrane junctions and found to increase substantially from 49 to 105 mV along the diluate flow. The increase in the junction potential was due to the decreasing concentration of the diluate solution, which flowed from MDC-1 through MDC-4. For the calculation, the effects of OH $^-$ were neglected due to its low concentration (0.001 M at pH 11.1), compared to the NaCl concentration ($\sim\!0.6\,\mathrm{M}$). Thus, the majority of the potential loss in the electrodialysis stack was contributed by the junction potential resistances, not by Ohmic resistances. The sum of all Ohmic resistances in the stack was $7\!-\!8\,\Omega$.

The resistive potential loss in the anode and cathode chambers was determined by averaging the initial and final conductivity. At a current of 4 mA, the resistive potential loss in these chambers was approximately 100 mV (Figure 4). This substantial potential drop implies that closer electrode placement relative to the electrodialysis stack can improve desalination performance. The overpotential was 154 \pm 11 mV for the anode, and 188 \pm 5 mV for the cathode, at 4.0 \pm 0.1 mA. The overpotentials were responsible for about 60% of the total potential loss in the MDC. This result implies that the MDC performance can be significantly improved by reducing the overpotential by improving catalyst performance or increasing the electrode surface areas.

The total potential loss in the MDCs was estimated between 515 and 577 mV at a given current of 4 mA (Figure 4), and the sum of the measured equilibrium potential for the two electrodes was 514 \pm 2 mV. The consistency between the consumed and created potential energy validates the estimation of the individual potential losses. In addition, there is a relatively constant potential loss among the 4 MDCs ($\pm 6\%$) indicating that the internal resistance was not appreciably changed as a result of the high conductivity of the influent solution (56 mS/cm). Consequently, there was little change in the measured current (Figure 3A).

Increasing the Extent of Desalination. The negligible resistive potential loss in the diluate and concentrate cells (11–16 mV) indicated that the MDC could be effective at desalination of less saline water. Therefore, the diluate effluent from the 4-MDC system (31 mS/cm) was used as the influent solution in the same system, with other experimental conditions remained unchanged. The current produced in the 4 MDCs ranged between 2 and 3 mA during the active desalination period, which lasted 16 h due to the decreased solution conductivity. The effluent conductivity was 10 ± 0.6 mS/cm for the diluate and 46 ± 0.9 mS/cm for the concentrate.

The diluate effluent of the second stage desalination (10 mS/cm) was then used in the third stage, but in this case the relatively low conductivity of this solution limited the performance of the individual MDCs. The low diluate conductivity from MDC-1 resulted in low current densities in the subsequent MDCs due to the high Ohmic resistance. When current production decreased in MDC-1 after ~36 h, there was less desalination of the diluate leaving this reactor, and thus MDC-2 had a diluate inflow of high conductivity and the current in MDC-2 started to rise (Figure 3B). Each downstream reactor produced current a little longer than the one before it (due to the lower current) and therefore each reactor in succession had an increase in current due to conductivity changes, before decreasing in current due to acidification of the anode. The total time for the effluent collection increased to 50 h for a single fed-batch cycle for all four

Table 1. Comparison of Desalination Performance with Reported MDC Systems

$V_{ m an}{:}V_{ m cat}{:}V_{ m desal}{}^a$	removal (%)	NaCl (g/L)	catholyte	ref.
100:33:1	93	35	phosphate buffer ^b	1
11:49:1	100	30	sulfuric acid	2
6:8:1	99 ^c	10	phosphate buffer	4
36:11:1	80	20	phosphate buffer	6
13:8:1	98	35	synthetic seawater	this study
1:2:1	63	20	phosphate buffer	3
1:1:1	37^d	20	phosphate buffer	5
2:1:1	44	35	synthetic seawater	this study

 a $V_{\rm an}$: anolyte volume, $V_{\rm cat}$: catholyte volume, $V_{\rm desal}$: desalinated water volume. b With ferriccyanide. c With additional voltage of 0.8 V. d With additional voltage of 0.55 V.

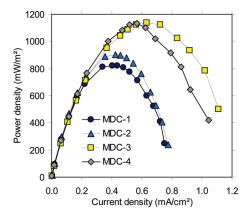


Figure 5. Power generation capacity of the MDC after \sim 50 days of operation with a 10- Ω external resistance. The influent (56 mS/cm) was pumped at 1.0 mL/min into both the diluate and concentrate to eliminate the effects of the junction potential.

MDCs. The final diluate conductivity was reduced to 1.4 ± 0.6 mS/cm while the concentrate conductivity was 17.3 ± 1.4 mS/cm. Thus, the three-stage operation of 4 MDCs in series achieved a total reduction in salinity of 97.6%. The desalination performance can be compared to that of other MDC studies as shown in Table 1. The required volume for anolyte and catholyte here was much less than that reported in other studies for an equivalent extent of desalination. Furthermore, only synthetic seawater was used as the catholyte, rather than buffer or acid solutions, or chemical catholytes.

Power Generation. The maximum power normalized by the cathode area (7 cm^2) ranged from 800 to 1140 mW/m^2 (Figure 5), which is much greater than that previously obtained in a three-chamber MDC $(424 \text{ mW/m}^2)^3$. The maximum power capacity of the stacked MDCs is similar to that of single-chamber MFCs with the same anode solution. These comparisons confirm that the Ohmic resistance of the electrodialysis stack was successfully minimized in our MDCs. By using a higher flow rate of 1 mL/min, the maximum change in NaCl concentration was theoretically $\sim 0.03 \text{ M}$ based on the observed highest current density (1.1 mA/cm^2) . This concentration change produced a corresponding sum of all the junction potentials of only $\sim 16 \text{ mV}$, indicating the power capacity test was not affected by junction potentials.

Outlook. These results show that stacked MDCs with 5 electrodialysis cell pairs can be used to partially or completely desalinate synthetic seawater (35 g/L NaCl). The performance of this system was substantially improved compared to previous MDC tests where only one desalination chamber was used between the electrodes, ^{1–5} and compared to a two cell-paired stack where it was concluded that an optimal stack would contain only 1.5 desalination cell pairs. The use of thin desalination chambers here minimized Ohmic resistances which resulted in efficient ion separation at current efficiencies about 86%. This high level of performance was even achieved using only synthetic seawater into the cathode chamber, compared to buffered solutions ^{1,3–6} or sulfuric acid 2 previously used in tests.

The performance of a stacked MDC is ultimately constrained by the limited voltage produced by the anode. Thus, there is a trade-off in the number of stacks that can be used in a single unit and optimization of power production. The addition of more stacks into a single unit will lower the current (or rate of ionic separation) and thus increase the hydraulic retention time needed to achieve a certain degree of desalination, resulting in increased water losses in the diluate due to osmosis. We have shown here that an effective approach to increase the extent of desalination is to link seawater flows to multiple MDCs in series. With this approach the ionic separation was maintained at currents above 3 mA so that the MDC performance was not dominated by the water loss in the diluate. Partial desalination of the synthetic seawater was obtained using four MDCs in series (using 20 total cell pairs), but to achieve 97.6% desalination three stages of desalination were needed through the series of 4 MDCs (3 sets of 4 MDCs, or 60 total cell pairs). This increased the total consumption of anode solution to 3.8 L for 0.3 L of desalinated water (ratio of 13:1) but it accomplished a very high level of desalination. The overpotentials at the anode and cathode were responsible for \sim 60% of the total potential loss in individual MDCs. This substantial contribution to the energy loss implies that the MDC performance can be dramatically improved by reducing the overpotentials. Thus, we suggest that future studies on MDCs focus on minimizing the overpotential by developing efficient electrodes. Continued improvements in stacked MDCs will be used to build integrated water systems simultaneously treating wastewater and producing fresh water. Development of such systems should be directed toward sustainable and energy independent operations by efficiently utilizing the energy extracted from wastewater for water desalination.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: blogan@psu.edu; phone: 814-863-7908.

ACKNOWLEDGMENT

This research was supported by funding through the King Abdullah University of Science and Technology (KAUST) (Award KUS-I1-003-13).

■ REFERENCES

- (1) Cao, X.; Huang, X.; Liang, P.; Xiao, K.; Zhou, Y.; Zhang, X.; Logan, B. E. A new method for water desalination using microbial desalination cells. *Environ. Sci. Technol.* **2009**, 43 (18), 7148–7152.
- (2) Jacobson, K. S.; Drew, D. M.; He, Z. Efficient salt removal in a continuously operated upflow microbial desalination cell with an air cathode. *Bioresour. Technol.* **2011**, *102* (1), 376–380.

- (3) Mehanna, M.; Saito, T.; Yan, J.; Hickner, M.; Cao, X.; Huang, X.; Logan, B. E. Using microbial desalination cells to reduce water salinity prior to reverse osmosis. *Energy Environ. Sci.* **2010**, *3*, 1114–1120.
- (4) Luo, H.; Jenkins, P. E.; Ren, Z. Concurrent desalination and hydrogen generation using microbial electrolysis and desalination cells. *Environ. Sci. Technol.* **2011**, *45* (1), 340–344.
- (5) Mehanna, M.; Kiely, P. D.; Call, D. F.; Logan, B. E. Microbial electrodialysis cell for simultaneous water desalination and hydrogen gas production. *Environ. Sci. Technol.* **2010**, *44* (24), 9578–9583.
- (6) Chen, X.; Xia, X.; Liang, P.; Cao, X.; Sun, H.; Huang, X. Stacked microbial desalination cells to enhance water desalination efficiency. *Environ. Sci. Technol.* **2011**, *45* (6), 2465–2470.
- (7) Logan, B. E. Microbial Fuel Cells; John Wiley & Sons, Inc.: Hoboken, NJ, 2008;
- (8) Lovley, D. R.; Phillips, E. J. P. Novel mode of microbial energy metabolism: Organic carbon oxidation coupled to dissimilatory reduction of iron or manganese. *Appl. Environ. Microbiol.* **1988**, 54 (6), 1472–1480.
- (9) Logan, B. E.; Cheng, S.; Watson, V.; Estadt, G. Graphite fiber brush anodes for increased power production in air-cathode microbial fuel cells. *Environ. Sci. Technol.* **2007**, *41* (9), 3341–3346.
- (10) Cheng, S.; Liu, H.; Logan, B. E. Increased performance of single-chamber microbial fuel cells using an improved cathode structure. *Electrochem. Commun.* **2006**, *8*, 489–494.
- (11) APHA. Standard Methods for the Examination of Water and Wastewater, 20th ed.; American Public Health Association, American Water Works Association, Water Environment Federation: Washington DC, 1998.
- (12) Strathmann, H. Ion-Exchange Membrane Separation Processes; Elsevier B. V.: Amsterdam, 2004.
- (13) Bard, A. J.; Faulkner, L. R. Electrochemical Methods: Fundamentals and Applications, 2nd ed.; John Wiley & Sons: New York, 2001.
- (14) Zhuo, K.; Dong, W.; Wang, W.; Wang, J. Activity coefficients of individual ions in aqueous solutions of sodium halides at 298.15 K. *Fluid Phase Equilib.* **2008**, *274*, 80–84.
- (15) He, Z.; Huang, Y.; Manohar, A. K.; Mansfeld, F. Effect of electrolyte pH on the rate of the anodic and cathodic reactions in an aircathode microbial fuel cell. *Bioelectrochemistry* **2008**, *74*, 78–82.
- (16) Poisson, A.; Chanu, J. Partial molal volumes of some major ions in seawater. *Limnol. Oceanogr.* **1976**, *21* (6), 853–861.
- (17) Kim, Y.; Walker, W. S.; Lawler, D. F. Electrodialysis with spacers: Effects of variation and correlation of boundary layer thickness. *Desalination* **2011**, 274, 54–63.
- (18) AGC Selemion specification/Selemion process. www.selemion.com/SEL3_4.pdf (accessed March 23, 2011).