

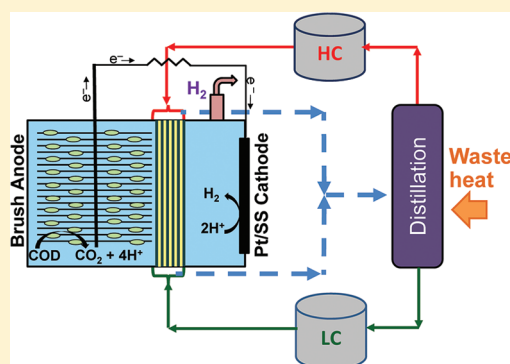
Hydrogen Generation in Microbial Reverse-Electrodialysis Electrolysis Cells Using a Heat-Regenerated Salt Solution

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Supporting Information

ABSTRACT: Hydrogen gas can be electrochemically produced in microbial reverse-electrodialysis electrolysis cells (MRECs) using current derived from organic matter and salinity-gradient energy such as river water and seawater solutions. Here, it is shown that ammonium bicarbonate salts, which can be regenerated using low-temperature waste heat, can also produce sufficient voltage for hydrogen gas generation in an MREC. The maximum hydrogen production rate was $1.6 \text{ m}^3 \text{ H}_2/\text{m}^3\cdot\text{d}$, with a hydrogen yield of $3.4 \text{ mol H}_2/\text{mol acetate}$ at a salinity ratio of infinite. Energy recovery was 10% based on total energy applied with an energy efficiency of 22% based on the consumed energy in the reactor. The cathode overpotential was dependent on the catholyte (sodium bicarbonate) concentration, but not the salinity ratio, indicating high catholyte conductivity was essential for maximizing hydrogen production rates. The direction of the HC and LC flows (co- or counter-current) did not affect performance in terms of hydrogen gas volume, production rates, or stack voltages. These results show that the MREC can be successfully operated using ammonium bicarbonate salts that can be regenerated using conventional distillation technologies and waste heat making the MREC a useful method for hydrogen gas production from wastes.



INTRODUCTION

Hydrogen gas can be electrochemically produced at the cathode in a microbial electrolysis cell (MEC) from current generated using microorganisms at the anode by adding a voltage ($>0.11 \text{ V}$ using acetate) that is theoretically much less than that needed to split water ($>1.2 \text{ V}$).¹ In practice, the applied voltages are much higher and typically 0.4 to 1 V , substantially lowering the possible overall energy recovery.² A renewable source of the electrical power is needed for applying this added voltage to make the MEC a green and sustainable method of hydrogen production.

It was recently shown that salinity-gradient energy could be harnessed as the source of voltage needed to enable hydrogen gas production.³ Reverse electrodialysis (RED) is a method for converting salinity differences between seawater and river water into electrical power. The RED stack consists of a series of alternating anion exchange membranes (AEMs) and cation exchange membranes (CEMs) that dictate the direction of the flow of positive or negative ions from the high salinity solution creating a method to convert an electrochemical potential into electrical current. In a RED system, seawater and river water are pumped between the membranes in a stack that can contain ~ 20 or more membrane pairs (~ 0.1 to 0.2 V per membrane pair) to generate sufficient potential to split water.^{4,5} However, by incorporating a RED stack of only ~ 5 membrane pairs between the electrodes in an MEC, it is possible to both avoid the need to split water and also to eliminate the need for an external power source for hydrogen gas production. This

combined MEC and RED process, called a microbial reverse-electrodialysis electrolysis cell (MREC), was recently shown to produce hydrogen gas from acetate using high (0.6 M) and lower concentrations (0.006 to 0.012 M) of NaCl solutions.³

One limitation of the MREC for hydrogen gas production is that this process requires sources of organic matter and seawater in close proximity making the process useful only in coastal and not inland regions. This is possible for many large cities in the USA that are located on the coast with wastewater treatment plants that discharge into the ocean, as the wastewater can first serve as a source of organic matter, and then as the low salinity solution in the RED stack. Another potential limitation of this process is the use of seawater, which can result in biofouling of the membranes unless water is treated as it is in reverse osmosis desalination systems.⁶

The need for close access to seawater and biofouling of the water in the stack could be avoided by using recycled sources of clean salt solutions. Different salts such as ammonium bicarbonate (NH_4HCO_3), magnesium sulfate, sodium sulfate, sodium chloride, potassium sulfate, potassium nitrate, potassium chloride have all been used in forward osmosis (FO) systems using osmosis pressure gradient for desalination.^{7–9} Ammonium bicarbonate is unique among these salts as it can

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easily be regenerated at temperatures ($\sim 60^\circ\text{C}$) below the boiling point of water.^{10,11} When ammonium bicarbonate is used in an FO process, concentrated ammonium bicarbonate and clean water can be produced by conventional distillation technologies using low-grade waste heat sources of around 60°C or higher.⁶ This allows the ammonium bicarbonate to be reused in a closed-loop system through regeneration of high salt solutions using low-grade waste heat sources, which are usually readily available in wastewater treatment plants. We reasoned that this solution could also be used effectively as the high salt solution in a RED stack to produce electricity or in an MREC for hydrogen gas production.

In this study, we investigated the effectiveness of an ammonium bicarbonate for providing a regenerable high salinity solution to produce hydrogen gas without any external power source in MRECs. To maximize performance of this system with NH_4HCO_3 , we examined different salinity ratios, salt concentrations, and flow directions (co- or counter-current) of solutions in the RED stack. Previous work has shown a saline solution can improve cathode performance in an MEC.¹² However, one concern with using an ammonium bicarbonate solution as the catholyte is that as the pH is increased during hydrogen production and consumption of protons, NH_3 gas ($\text{p}K_a = 9.3$) would be formed and released into the gas stream reducing hydrogen gas purity. Therefore, a sodium bicarbonate (NaHCO_3) solution was used as the catholyte to avoid NH_3 gas generation. The concentrations of the sodium bicarbonate solution were varied to determine conditions for optimum performance.

MATERIALS AND METHODS

Reactor set up. Two cubes of polycarbonate were drilled to produce cylindrical anode and cathode chambers 3 cm in diameter and 4 cm long (30 mL each). A cylindrical glass tube for gas collection was attached on the top of the cathode chamber and sealed with a butyl rubber stopper and an aluminum crimp cap.¹³ The RED stack, situated between the anode and cathode chambers, contained 5 CEMs and 6 AEMs (Selemon CMV and AMV, Asahi glass, Japan) forming 5 high concentration (HC) and 5 low concentration (LC) solution cells.¹⁴ Silicon gaskets having rectangular open sections ($4 \times 2\text{ cm}^2$) for flow were placed between adjacent membranes (empty bed volume of 1 mL) that contained a polyethylene mesh spacer to prevent membrane deformation (0.13 cm thick). The anodes were heat treated graphite fiber brushes (2.5 cm diameter \times 2.5 cm length; fiber type; PANEX 33 160 K, ZOLTEK). The cathodes were made from stainless steel mesh (Type 304, #60 mesh, wire diameter 0.019 cm, pore size 0.0023 cm; McMaster-Carr), a Pt catalyst (0.5 mg Pt/cm²), and carbon particles and a binder (Vulcan XC-71, 33.3 mL/cm² of 5 wt % Nafion; projected cross sectional area of 7 cm²). Each chamber was equipped with an Ag/AgCl reference electrode (RE-5B; BASi) to measure electrode potentials and stack voltage.

Experiments and Measurements. The anode was preacclimated with exoelectrogenic microorganisms in an MFC. The inoculum was effluent from a microbial fuel cell (MFC), which had originally been inoculated with wastewater and acetate. The acclimated anode was transferred to the MREC after the anode produced the same stable voltage for three consecutive batch cycles. The anode solution in the MREC contained 1.0 g/L CH_3COONa and a buffered nutrient medium consisting of 8.4 g/L NaHCO_3 , 0.31 g/L NH_4Cl , 0.13 g/L KCl, 0.05 g/L Na_2HPO_4 , 0.03 g/L $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, trace

vitamins, and minerals. The cathode chamber was filled with 1 M NaHCO_3 solution ($\sim 55\text{ mS/cm}$) unless otherwise noted. The HC solution was 1.4 M NH_4HCO_3 solution, with the concentration of NH_4HCO_3 in the LC solution adjusted to produce salinity ratios (SRs) of 100, 200, 400, and 800. In some tests, low conductivity deionized (DI) water was used as the LC solution, resulting in an SR defined as “infinite”, as the conductivity of the DI water was $<0.0004\text{ mS/cm}$. Each solution was supplied into the stack at a fixed flow rate of 0.8 mL/min. The HC solution was pumped into the HC cell from the cathode chamber and flowed serially through 5 HC cells in the RED stack.^{3,14} Similarly, the LC solution flowed through all the 5 LC cells, but in the opposite direction from the anode to cathode side, unless otherwise noted (Figure S1 of the Supporting Information). The anode and cathode chambers were operated in fed-batch mode at room temperature and were refilled when the current decreased to less than 0.5 mA forming one complete cycle of operation. The HC and LC solutions were continuously supplied to the stack from the beginning to the end of a fed-batch cycle.

Gas was collected for analysis in gas bags (0.1 L capacity; Cali-5-Bond, Calibrated Instruments Inc.) with gas volume measured using a respirometer (AER-200, Challenge Environmental). Gas chromatographs (GCs, SRI Instruments) were used to analyze the gas composition in the reactor headspace as well as in the gas bags for H_2 , N_2 , CO_2 , and CH_4 as previously described.¹⁵ Total chemical oxygen demand (COD) was measured at the beginning and end of each batch (COD Reagent, HACH Co.). Total ammonia concentration (nitrogen-ammonia reagent (salicylate), HACH Co.) was determined with a UV spectrophotometer (DR2010, HACH Co.). The pH and conductivity of samples were monitored with conductivity and pH meters (SevenMulti, Mettler-Toledo International Inc.). A $10\ \Omega$ resistor was connected between the anode and cathode to measure current using a multimeter (Model 2700, Keithley Instrument).

Calculations. The performance of the MREC was evaluated as previously described in terms of: Coulombic efficiency (η_{CE} , %) based on total coulombs recovered compared to the mass of substrate consumed; cathodic hydrogen recovery (r_{cat} , %), the moles of hydrogen actually recovered at the cathode compared to the moles that theoretically could have been produced from the current; volumetric hydrogen production rate (Q , $\text{m}^3\text{ H}_2/\text{m}^3/\text{d}$) normalized to the anolyte volume; and hydrogen yield (Y , mol H_2/mol acetate) based on the hydrogen produced and acetate consumed.³ The volumetric current density (I_{vol} , A/m^3) was an average of the maximum current production over a 1 h period divided by the anolyte volume. Cathode overpotential was calculated by subtracting the theoretical cathode potential calculated by the Nernst equation from the measured cathode potential.¹⁶

Energy recovery (r_E) was calculated relative to the total energy provided to the MREC as the ratio of energy content of hydrogen produced, or

$$r_E = \frac{\Delta H_{\text{H}_2} n_{\text{H}_2}}{\Delta H_s n_s^{\text{in}} + X^{\text{in}}} \times 100 \quad (1)$$

where ΔH is the heat of combustion (J/mol), n is the amount of hydrogen or substrate (moles), the superscript in and the subscript s denote the influent and the substrate, respectively, and X^{in} is the theoretical energy (J) estimated by the change in

the free energy involving complete mixing of HC and LC solutions as:

$$X^{\text{in}} = RT \sum_i \left(V_{\text{HC}} c_{i,\text{HC}}^{\text{in}} \ln \frac{a_{i,\text{HC}}^{\text{in}}}{a_{i,\text{M}}} + V_{\text{LC}} c_{i,\text{LC}}^{\text{in}} \ln \frac{a_{i,\text{LC}}^{\text{in}}}{a_{i,\text{M}}} \right) \quad (2)$$

where R the gas constant, T the absolute temperature, V the volume of solution, c the molar concentration of ionic species i in the solution, and a the activity of ionic species i in the solution. The subscripts HC, LC, and M denote high concentration, low concentration, and mixed solutions, respectively. The energy leaving the reactor is the same as eq 2 but based on the conditions for the water leaving the reactor (superscript out). The percent change in energy of the HC and LC solutions is therefore $X^{\text{util}} = (X^{\text{in}} - X^{\text{out}})/X^{\text{in}}$.

To calculate energy efficiency (η_E), energy leaving the MREC was subtracted from the added energy as:

$$\eta_E = \frac{\Delta H_{\text{H}_2} n_{\text{H}_2}}{\Delta H_{\text{S}}(n_{\text{S}}^{\text{in}} - n_{\text{S}}^{\text{out}}) + X^{\text{in}} - X^{\text{out}}} \times 100 \quad (3)$$

The concentration of free ammonia (NH_3) was calculated using

$$\frac{[\text{NH}_3]}{[\text{TAN}]} = \left(1 + \frac{10^{-\text{pH}}}{10^{-\text{p}K_a}} \right)^{-1} \quad (4)$$

where $[\text{NH}_3]$ is the NH_3 concentration (mg N/L), and $[\text{TAN}]$ is the total ammonia nitrogen concentration (mg N/L). The $\text{p}K_a$ was calculated using the empirical relationship $\text{p}K_a = 0.0918 + 2729.92/T$.¹⁷

RESULTS AND DISCUSSION

Performance with a Fixed HC and Variable LC. Current and hydrogen gas were successfully generated in the MREC using only the ammonium bicarbonate solution and no external power supply. The peak volumetric current densities ranged over a small range of $137 \pm 8 \text{ A/m}^3$ to $152 \pm 8 \text{ A/m}^3$ (Table 1)

Table 1. Electrode Potential (vs Ag/AgCl), Stack Voltage, Volumetric Current Density at Different Salinity Ratios and NH_4HCO_3 Concentration of the HC Solution

SR	HC (M)	anode potential (mV)	cathode potential (mV)	stack voltage (mV)	I_{vol} (A/m^3)
100	1.4	-427 ± 8	-734 ± 14	348 ± 15	143 ± 0
200	1.4	-460 ± 6	-736 ± 10	315 ± 3	152 ± 8
400	1.4	-468 ± 12	-740 ± 13	305 ± 10	137 ± 8
800	1.4	-474 ± 6	-738 ± 9	321 ± 21	146 ± 15
infinite	1.4	-466 ± 5	-740 ± 14	307 ± 3	148 ± 5
infinite	0.9	-487 ± 6	-753 ± 2	282 ± 6	119 ± 5
infinite	0.6	-491 ± 12	-751 ± 1	269 ± 20	95 ± 3
infinite	0.4	-494 ± 13	-748 ± 1	259 ± 17	83 ± 7
infinite	0.1	-528 ± 6	-752 ± 1	210 ± 5	43 ± 2

for the different SRs, with single fed-batch cycle times of $23 \pm 1 \text{ h}$ at all SRs (part A of Figure 1). Whereas the current density was relatively insensitive to the SRs examined here, eliminating the salinity gradient in the stack ($\text{SR} = 1, 1.4 \text{ M NH}_4\text{HCO}_3$) resulted in a loss of current, confirming that salinity gradient energy from the RED stack was essential for hydrogen production (data not shown). This result on the effect of the SR is different from previous studies using NaCl and

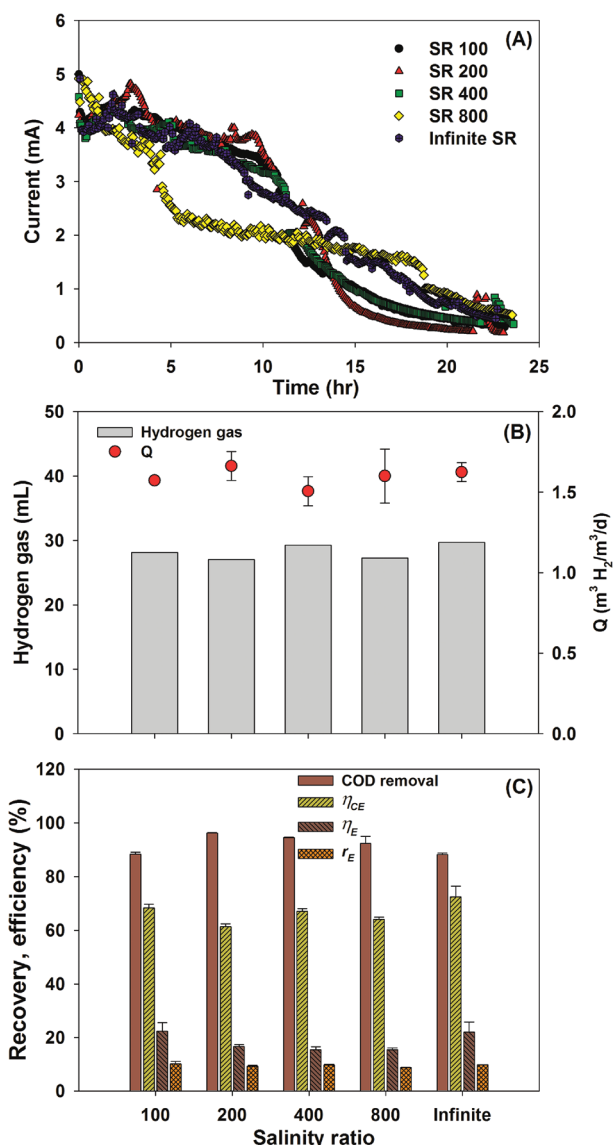


Figure 1. MREC performance with different salinity ratios (A) current generation (B) gas production (C) COD removal efficiency, Coulombic efficiency, energy recovery, and efficiency at different SRs.

NH_4HCO_3 solutions for power production in a microbial reverse-electrodialysis fuel cell (MRC) where varying the SR affected performance.^{14,18} Optimum SRs for MRCs were $\text{SR} = 50$ with NaCl and $\text{SR} = 100$ with NH_4HCO_3 , as raising the SR increases the resistance of LC cells, and lowering the SR decreases the electrochemical junction potential in the stack. The SRs examined here were mostly higher than those previously tested using NaCl solutions. We assume that the MREC performance at each SR was somewhat limited at higher current ranges by either the resistance of the LC cells or different junction potentials, or both.

The produced gas was consistently 92–94% H_2 and 6–8% CO_2 at the different SRs. The use of a RED stack prevented the consumption of hydrogen generated at the cathode by hydrogenotrophic methanogens, resulting in a methane-free, high hydrogen purity gas.^{15,19} Total hydrogen generation ranged from 27 mL H_2 ($Y = 2.8 \text{ mol H}_2/\text{mol acetate}$, $\text{SR} = 200$) to 30 mL H_2 ($Y = 3.4 \text{ mol H}_2/\text{mol acetate}$, $\text{SR} = \text{Infinite}$) over each fed-batch cycle (part B of Figure 1), which is similar to the

reported value with NaCl salts in MRECs.³ There was no significant linear relationship between gas volume and salinity difference between the HC and LC streams ($R^2 = 0.18$, $p = 0.57$). The Coulombic efficiencies ranged from 61 to 72% at different SRs (part C of Figure 1), with complete recovery of current as hydrogen gas ($r_{\text{cat}} = 100\%$).

The final anolyte pH was 7.2 ± 0.1 (initial pH 8.2) due to the high buffering capacity of the bicarbonate buffer (100 mM) used for the anolyte, and the transport of carbonate species (CO_3^{2-} and HCO_3^-) from the RED stack through the adjacent AEM. This result is much different than that obtained in tests using NaCl solution where the anolyte became more acidic (final pH ~ 5.5) inhibiting exoelectrogenic activity due to the low pH.²⁰ The lack of a pH change enabled nearly complete substrate removal based on COD (88% to 96%) (part C of Figure 1). The final catholyte pH increased (8.9 ± 0.1 , initial pH 7.9) due to the proton consumption at the cathode. This pH change is also smaller than that previously observed with NaCl solutions (pH up to 12) due to the high NaHCO_3 concentration (1 M) in the cathode chamber.¹⁴

The anolyte conductivity increased from 10 mS/cm to 13–14 mS/cm due to anion transfer from the RED stack. Because the anode chamber was separated from the HC stream in the RED stack by an AEM, it was expected that carbonate species would be transferred into the anode chamber. However, ammonia was also detected in the anolyte, with a total ammonia (NH_4^+ and NH_3) concentration ranging from 547 ± 41 mg-N/L to 685 ± 64 mg-N/L. Whereas little transport of the ammonium cation is expected through an AEM, negatively charged carbamate (NH_4CO_3^-) is able to pass through this membrane. Whereas high free ammonia concentrations can inhibit exoelectrogenic activity,²¹ calculated free ammonia concentrations here (5–6 mg N/L at all SRs) were below those needed to produce inhibition.²² Further evidence for a lack of adverse effects of ammonia on the exoelectrogenic activity of the anode biofilm was demonstrated by stable anode potentials over the fed batch cycle (-427 to -474 mV vs Ag/AgCl) (Table 1). The loss of ammonia in the anode solutions will need to be minimized or eliminated, perhaps through the use of a LC stream next to the anode or a high concentration sodium bicarbonate stream.

The highest energy efficiency of $\eta_E = 22\%$ was obtained at an SR = 100 and for the case of SR Infinite. This energy efficiency is lower than that obtained with NaCl ($\eta_E = 65\%$ at a flow rate of 0.8 mL/min)¹⁴ but it is comparable to those obtained in RED systems (14 to 35%).²³ The energy recovery remained low ($r_E = 9$ –10%) in all tests, due to the relatively large amount of salinity driven energy that was added to the stack (2860 J – 3250 J). The salinity driven energy accounted for 90% of the total energy provided, with the balance substrate energy (10%). The energy recovery could be enhanced by using a lower flow rate and by recycling the saline solution with reduced liquid volume as the concentration of the recycled HC concentration was still high (>90 mS/cm).

Performance with a Fixed LC and Variable HC. A reduction in the HC concentration (1.4 to 0.1 M) with a fixed LC solution (SR Infinite) reduced the range of working solution conductivities for the HC stream from 103 to 10 mS/cm, decreased current (Table 1), and increased the time needed to complete a fed-batch cycle (part A of Figure 2). The reduction in current decreased the recovery of hydrogen gas from 30 mL- H_2 to 17 mL- H_2 (93–94% H_2 , 6–7% CO_2) and decreased the gas production rate from 1.6 $\text{m}^3 \text{H}_2/\text{m}^3\text{d}$ to

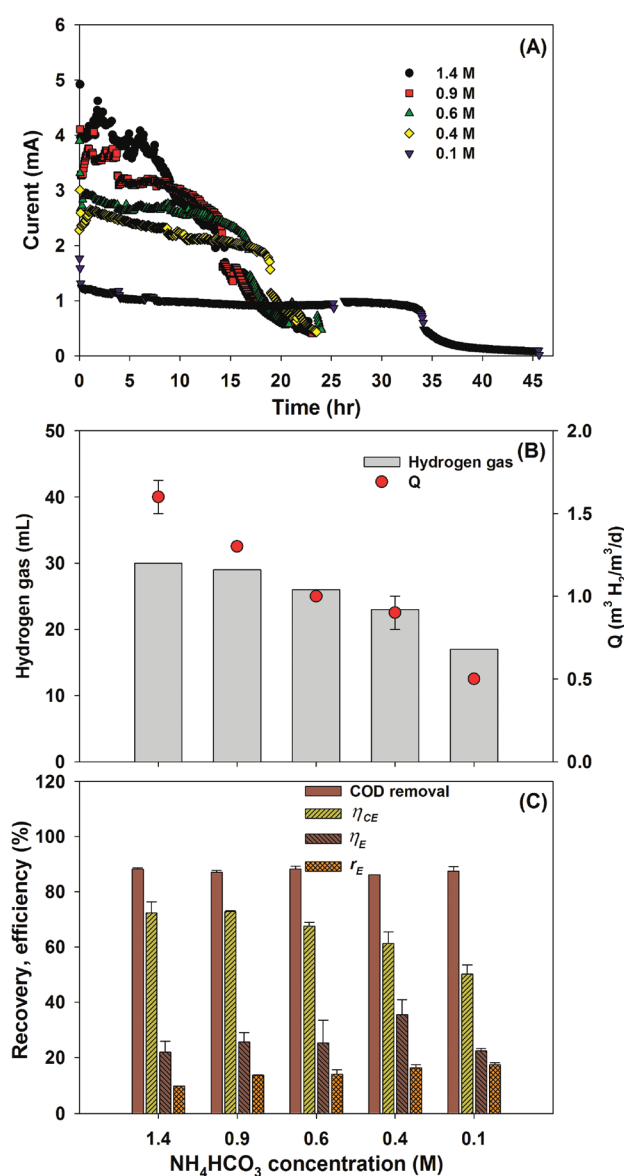


Figure 2. MREC performance with different HC concentration (A) current generation (B) gas production (C) COD removal efficiency, Coulombic efficiency, energy recovery, and efficiency.

0.5 $\text{m}^3 \text{H}_2/\text{m}^3\text{d}$ (part B of Figure 2). The lower performance with the lower HC concentration was due to decrease in the salinity driven energy (X^{in}) and the stack voltage during fed-batch operation decreased from 307 ± 3 mV at 1.4 M HC to 210 ± 5 mV at 0.1 M HC (Table 1). The X^{in} was reduced from 3090 J (1.4 M HC) to 790 J (0.1 M HC).

COD removal efficiency (86–88%) was not affected by the HC concentration. However, the coulombic efficiency substantially decreased with HC concentration from $\eta_{\text{CE}} = 72\%$ to 50% using the 0.1 M HC (part C of Figure 2). There was little change in the cathode potential (-740 to -752 mV), likely as a result of the high conductivity of the catholyte (~ 55 mS/cm) that produced a low ohmic resistance. Reducing the HC concentration decreased the voltage produced by the stack resulting in lower anode potentials (Table 1). This reduction in anode potential is consistent with tests using MECs where anode potential is also reduced with lowering applied voltage.¹⁵ The final anolyte conductivity decreased from 13 mS/cm to 10 mS/cm with HC concentration due to the reduction in the

concentration gradient between the anode chamber and the first HC compartment in the RED stack. This also reduced ammonia transfer into the anode chamber through the AEM (Figure 3) from 547 ± 41 mg N/L (1.4 M HC) to 195 ± 9 mg N/L (0.1 M HC).

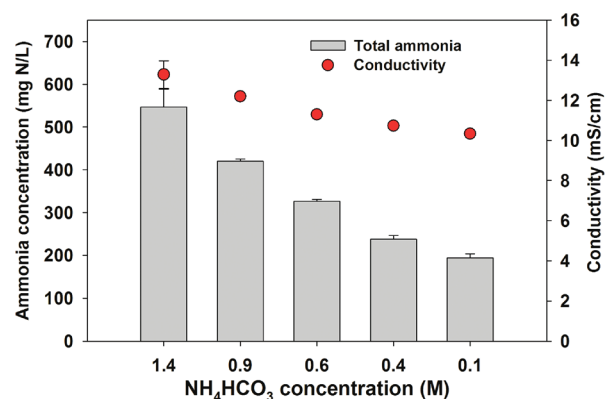


Figure 3. Total ammonia concentration and final anolyte conductivity at different HC concentration.

The energy recovery increased inversely with the HC concentration from $r_E = 10\%$ to 18% due to the reduction in energy applied to the system (part C of Figure 2). The reduced energy input resulted in an increase in the utilization of the applied salinity driven energy of up to $X^{\text{util}} = 75\%$ (0.1 M HC). The highest energy efficiency ($\eta_E = 35\%$) was achieved using an HC = 0.4 M. Thus, the decrease in performance in terms of current densities and hydrogen production rates was balanced by an overall increase in energy recovery and efficiency.

Effect of Catholyte Concentration on Performance. A decrease in the NaHCO_3 concentration used in the cathode chamber from 1 to 0.1 M decreased the solution conductivity from 55 to 8 mS/cm and did not affect anode potentials (Figure 4). The cathode overpotential with the 0.1 M solution

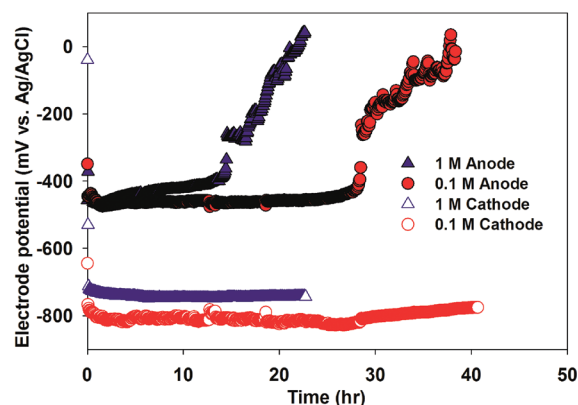


Figure 4. Variation of electrode potentials with different NaHCO_3 concentration in the cathode chamber.

(-540 mV at pH 8) was much higher (77 mV) than with the 1 M solution (-463 mV) resulting in a longer time for a fed-batch cycle (~ 41 h) (part A of Figure S2 of the Supporting Information). This reduction in the catholyte concentration to 0.1 M decreased the volumetric current density by $\sim 50\%$ ($I_{\text{vol}} = 76 \pm 6$ A/m³), gas production rate ($Q = 0.9$ m³ H₂/m³·d), and volume of hydrogen gas produced (22 mL H₂) (part B of

Figure S2 of the Supporting Information), but COD removal (88%) and CE (69%) remained high (part C of Figure S2 of the Supporting Information). The longer time needed for a fed-batch cycle using the 0.1 M NaHCO_3 solution resulted in more salinity driven energy added to the system (5510 J, versus 3090 J for the 1 M NaHCO_3 at the same SR) and as a result a lower energy recovery ($r_E = 5\%$) and efficiency ($\eta_E = 7\%$) (part C of Figure S2 of the Supporting Information).

Counter-Current versus Cocurrent Operation. To see if system performance could be improved by the RED stack, the solutions were switched from counter-current to cocurrent flow (entering on the cathode side). However, there was no appreciable change in current ($I_{\text{vol}} = 129$ A/m³ counter-current, $I_{\text{vol}} = 127$ A/m³ cocurrent) or gas generation (30 mL H₂ counter-current and 29 mL H₂ cocurrent) (part A of Figure 5).

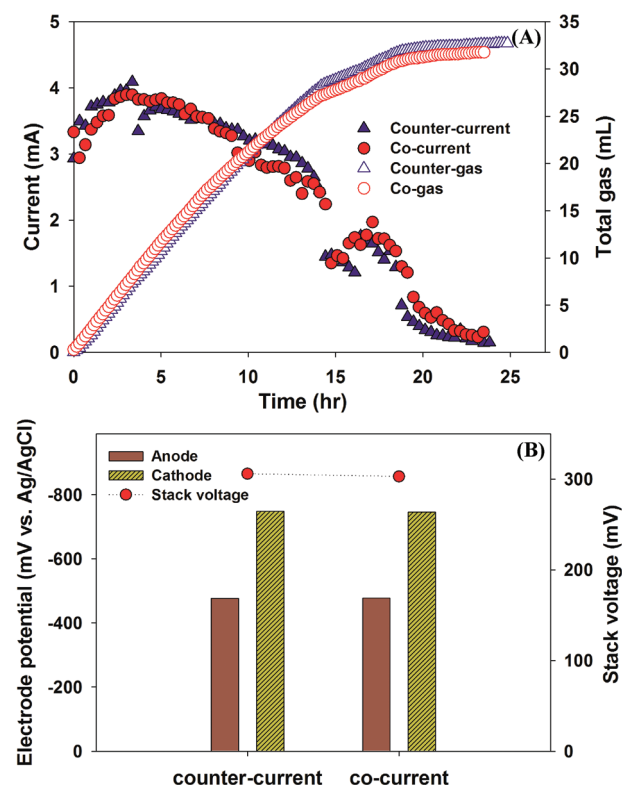


Figure 5. Co- and counter current operation of the MREC at infinite SR with 1.4 M HC solution (A) current and gas generation (H₂ 92% and CO₂ 8%) and (B) electrode potential and stack voltage at stable current generation.

This is a different result than that obtained with a 25-cell RED stack where cocurrent operation was more efficient due to less pressure differences between the compartments and relatively constant power generation in each cell.⁵ However, the 25-cell RED stack was larger (25×75 cm²) than our 5-cell stack (4×2 cm²). Previous research has shown that the effect of the flow direction is relatively unimportant when using a small stack.²⁴ However, the flow direction might need to be taken into consideration in a larger scale MREC.

There were some small changes in COD removal efficiency (92% counter-current, 87% cocurrent) and CE (73% counter-current, 78% cocurrent) but there are insufficient data to know if these differences were significant. The total coulombs were essentially the same (204 C counter-current, 206 C cocurrent) and there were no appreciable changes in electrode potentials

or stack voltages (part B of Figure 5). The relatively constant performance independent of the flow direction could be due to low local pressure differences between the cells due to the membrane stack having a small effective cross sectional area (8 cm²) and the use of low flow rates (0.8 mL/min).

Outlook. These results show that the use of ammonium bicarbonate solutions in an MREC for hydrogen gas production can achieve several goals for energy recovery and improvement in system performance. The MREC is effective in organic matter removal, which can lead to effective wastewater treatment. Hydrogen gas is produced, which could be used or sold as an energy carrier or for use in industrial processes. No electrical grid energy is needed, and therefore both hydrogen production and wastewater treatment would be carbon neutral as the organic matter is fixed and not derived from fossilized carbon. The ammonium bicarbonate solution chemistry can be carefully maintained avoiding biofouling using natural waters and the potential for changes in water quality.

The energy produced based only on the COD removals measured for acetate (30 mL-H₂, ΔCOD = 0.75 g/L, and 286 kJ/mol-H₂) achieved an overall energy recovery of 15 kJ/g-COD (4.2 kWh/kg-COD). This is slightly better than that possible with anaerobic digestion for the same conditions (dry gas basis, STP), which theoretically could produce 14 kJ/g-COD (assumes a methane conversion efficiency of 100% or 0.35 L-CH₄/g-COD and 889 kJ/mol-CH₄). The gas produced in the MREC is >90% H₂, which is a higher percentage than that produce from either dark fermentation of glucose to hydrogen production, or the relative percentage of methane in digester gas as both contain much higher concentrations of CO₂. This energy production, however, does not include the energy in the waste heat needed to produce the ammonium bicarbonate solutions. However, it is estimated that there is 54 GW that could be recovered from waste heat produced in industrial processes, and there are few methods available to capture energy from waste heat at low temperatures. Thus, the MREC using ammonium bicarbonate salts may have a high potential for use as a renewable method for energy production in the form of hydrogen gas.

■ ASSOCIATED CONTENT

Supporting Information

Schematic of MREC system, and figure of MREC performance. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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