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Energy Capture from Thermolytic Solutions in Microbial Reverse-Electrodialysis Cells

Roland D. Cusick, Younggy Kim, Bruce E. Logan*

Department of Civil and Environmental Engineering, 131 Sackett Building, Pennsylvania State University, University Park, PA 16802, USA.

*To whom correspondence should be addressed. E-mail: blogan@psu.edu

Reverse electrodialysis allows for capture of energy from salinity gradients between salt and fresh waters, but potential applications are currently limited to coastal areas and the need for a large number of membrane pairs. Using salt solutions that could be continuously regenerated using waste heat (≥ 40 °C) and conventional technologies would allow much wider applications of salinity-gradient power production. We used reverse electrodialysis ion-exchange membrane stacks in microbial reverse-electrodialysis cells to efficiently capture salinity gradient energy from ammonium bicarbonate salt solutions. The maximum power density using acetate reached 5.6 W/m^2-cathode surface area, which was five times that produced without the dialysis stack, and 3.0 ± 0.05 W/m^2 with domestic wastewater. Maximum energy recovery with acetate reached 30 ± 0.5%.

Microbial fuel cell (MFC)-based technologies are promising methods for direct electrical power production from waste organic matter, wastewater treatment, and the capture of salinity gradients in salt- and fresh-water sources (*1*–*3*). Exoelectrogenic microorganisms can oxidize soluble organic matter, such as that present in wastewater (*4, 5*), and release electrons to an electrode. Power densities with air-cathode MFCs have reached 2.7 W/m^2 using optimized solutions with equally-sized electrodes (*6*), but are lower when using complex organics or solutions (0.26 – 0.45 W/m^2) with ionic conductivities typical of domestic wastewater (~1 mS/cm) (*7*–*9*).

Reverse electrodialysis (RED) is a process for direct electricity production from salinity gradient energy, obtained from seawater and freshwater sources, based on the use of many pairs of anion and cation exchange membranes situated between two electrodes. Many membrane pairs needed for effective harnessing of salinity gradients as electricity, resulting in high costs for standalone RED systems (*10*–*12*). The use of natural waters in RED can result in membrane fouling without extensive pre-treatment of fresh and salt water. In principal, salinity-gradient energy can be effectively captured with in a microbial reverse-electrodialysis cell (MRC) using only a small number of membrane pairs (Fig. 1). Bacterial oxidation of organic matter and oxygen reduction provide favorable electrode reactions, resulting in efficient capture of energy in the RED stack (*13*). However, RED and MRC applications are currently limited to estuarine or coastal areas due to the need for both fresh and salt water solutions (*13*).

Thermolytic solutions such as ammonium bicarbonate (NH_4HCO_3), which can be concentrated with low grade thermal energy, theoretically may be able to provide the salinity gradient energy source for a RED stack. When combined with a favorable reaction at the electrodes in an MFC, or used in a microbial electrolysis cell (MEC) for hydrogen gas production (*13, 14*), an MRC using ammonium bicarbonate could result in more efficient capture of energy from wastewaters and other sources of biomass than an MFC. The capture of waste heat (>40°C) energy with ammonium bicarbonate is possible with conventional and well proven technologies, such as vacuum distillation (*15*), that can produce high concentrate (HC) and low concentrate (LC) salt solutions. The resulting energy difference between 1M and 0.01M ammonium bicarbonate HC and LC solutions, is equivalent to 370 m of hydraulic head, even greater than that of typical ocean and river water (270 m) (*12*). Ammonium bicarbonate is relatively unique among many different chemicals that have been proposed for capturing energy by pressure differences, in a process called pressure retarded osmosis (PRO), due to the easily volatilized ionic species (*16*). PRO requires the flow of water through unique types of membranes, distillation of larger volumes of water than would be needed for a RED stack, and mechanical conversion of pressure into electrical power. This is different than the MRC process where electricity is directly generated by bacteria and voltages are increased by the salinity gradient, conventional ion exchange membranes are used, and there is no direct contact of the water and salt solutions.

To test the utility of ammonium bicarbonate solutions for energy production, we examined four different salinity ratios (SRs) with a single HC ammonium bicarbonate solution (0.95

M, conductivity of 65.5 mS/cm) in MRCs (58.4 mL) containing five membrane pairs (Fig. 1) at a fixed solution flow rate (1.6 mL/min). The maximum power (normalized to projected cathode area of 7 cm^2) was 5.4 W/m^2 (SR = 100) with 1 g/L of sodium acetate. For these conditions, the RED stack contributed 2.1 ± 0.01 W/m^2 (39%) of the produced power, compared to 3.3 ± 0.04 W/m^2 (61%) from the oxidation of the substrate (Fig. 2a). The cell obtained peak power at a total cell voltage of 0.75 V and current density of 0.72 mA/cm^2. Lowering the flow rate (fig. S2) from 1.6 to 0.85 mL/min (4.9 ± 0.1 W/m^2) reduced power by an amount equivalent to using an SR = 50 (4.7 ± 0.1 W/m^2). The use of the RED stack and a saline catholyte alone increased power, as shown by an MRC power density of 1.7 ± 0.05 W/m^2 with membranes all containing the same saline solution (SR = 1), relative to that of a single-chamber MFC (no membranes; 1.08 ± 0.03 W/m^2). This improved performance of the MRC could be due to a number of factors, including improved charge transfer at the cathode (65.5 mS/cm), a salinity gradient between the stack and the anode, and the flow of bicarbonate ions through the anion exchange membrane which helps to maintain anode pH at 6.9 ± 0.1, compared to a decrease in pH to 5.5 using NaCl salt solutions (*13*).

We further examined power production using different concentrations of HC and LC solutions at a fixed salinity ratio (SR = 100). MRC power density reached a maximum of 5.6 ± 0.04 W/m^2 for the 1.1 M HC solution (Fig. 2b). This was 20% higher than that produced with an artificial seawater (NaCl) and freshwater (*13*). Internal resistances, obtained from the slope of the polarization curves (fig. S6), ranged from 170 Ω (HC = 0.5 M) to 138 Ω (1.8 M).

The most substantial impact of the RED stack on MRC performance was that it increased maximum power production using organic matter. Electrode reactions in the MRC produced up to 3.2 ± 0.2 W/m^2, which is three times the power produced in the absence of the stack in a single-chamber MFC (1.08 ± 0.03 W/m^2, Fig. 2). The contribution of the electrodes to total power generation did not appreciably vary for HCs between 0.5 M and 1.1 M (SR = 100), although power was reduced at the highest HC (1.8 M, Fig. 2b). The use of the RED stack produced a very stable cell voltage with increasing current, with electrode potentials maintained very close to their open circuit values as current density increased (Fig. 3). In contrast, MFC electrode potentials substantially changed with increasing current. High salt concentrations (1.1 and 1.8 M) adversely affected the anode biofilm at the highest current densities, as shown by a rapid increase in the electrode potential (Fig. 3). This rapid change in electrode potential resulted in substantially reduced power densities in subsequent cycles, indicating damage to the anode biofilm. Several additional cycles were needed at low current densities (high resistances) to restore performance.

Energy recoveries (based on total energy entering) and energy efficiencies (energy-in minus that going out) were higher for the MRC than a MFC. Energy recoveries for the MRC, at a fixed salinity ratio (SR = 100), ranged from 30 ± 0.5% (HC = 0.5 M) to 20 ± 0.0% (HC = 1.8 M), with energy efficiencies of 34 ± 0.5% (HC = 0.5 M) to 25 ± 0.0% (HC = 1.8 M) (Fig. 4). Maximum energy recovery in the MFC was only 14 ± 2%, with a slightly larger energy efficiency of 16 ± 2%. Coulombic efficiencies, or the percentage recovery of electrons from the substrate, were higher in the MRC (66 ± 4%) than the MFC (35 ± 4%) due to the membrane stack reducing oxygen crossover from the cathode to the anode (*13, 17*).

The utilization of a salinity-gradient power source in the MRC also resulted in very high power production from domestic wastewater, with up to 2.9 ± 0.05 W/m^2 (fig. S6) produced at a HC concentration of 0.95 M (SR = 100, 1.6 mL/min flow rate). The power derived from the electrode reactions was 2.0 ± 0.05 W/m^2, which is a 740% increase in power production compared to that achieved with wastewater in a single chamber MFC (0.27 ± 0.05 W/m^2). This power production by the electrode reactions is 50% larger than that achieved with carbon nanotube coated electrodes in the absence of a RED stack (*18*). Power production from wastewater dropped off after only two hours, indicating rapid treatment of easily degraded organic matter (fig. S7). The percent of organic matter removal based on chemical oxygen demand (COD) was 35 ± 2%, with an energy production of 0.94 kWh/kg-COD. In contrast, conventional wastewater treatment using activated sludge processes can consume 1.2 kWh/kg-COD (*19*). The relatively low COD removal with wastewater, compared to essentially complete removal with acetic acid, is typical for biofilm processes used in wastewater treatment (*20*). Soluble COD (that passing a 0.45 µm-pore-diameter filter) can easily be removed by the biofilm in a trickling filter, for example, with particulate COD removed in a secondary solids contact process (*21*) that can be used to generate methane (*19*).

One limitation in a MRC stack arrangement with ammonium bicarbonate is nitrogen cross-over from the stack into the anode chamber. The predominant nitrogen forms in the ammonium carbonate solution are ammonium (NH_4^+), ammonia (NH_3), and carbamate ($NH_4CO_3^-$). Negatively charged carbamate ions crossed the anion exchange membrane and moved into the anode chamber to balance charge (protons released by the bioanode). Total ammonia nitrogen concentrations in the anode following a fed-batch cycle ranged from 263 ± 32 mg/L (HC = 0.5 M) to 590 ± 36 mg/L (HC = 1.8 M) (fig. S8). For the observed values of effluent anode pH (6.8 – 7.1), free ammonia nitrogen concentrations in the anode chamber ranged from 1.0 ± 0.2 mg/L to 2.6 ± 0.03 mg/L. Total ammonia nitrogen concentrations above 500 mg/L and free ammonia concentrations above 11 mg/L are known to inhibit power production in MFCs (*22*). However, the main concerns of nitrogen cross-over are contamination of the anode solution with ammonia, and loss of the salt solution. These losses can be minimized in future designs through the use of bipolar membranes or a low salt solution in the membrane stack nearest the anode.

The use of thermolytic solutions in RED stacks could substantially change the energy balance for wastewater treatment, enable sanitation in energy poor areas, and allow for energy capture from renewable energy sources such as solar thermal and waste heat. Three types of wastewaters (food processing, animal, and domestic) contain nearly as much energy (17 GW) as that used for the whole water infrastructure in the USA (*23*). There is ~9× more energy in domestic wastewater than that required to treat it using conventional methods (*24*). In energy poor areas, production of electrical power from wastewater creates incentive for a community to operate a treatment plant, and therefore accomplish water sanitation. Other biomass and heat sources could also be harvested in MRCs. For example, cellulose and end products from cellulose fermentation can be used in these bioelectrochemical systems (*25–27*), and as much as 1.34 billion tons of biomass could be produced annually in the USA without affecting food production (*28*). Industrial applications offer a good opportunity to recover the 7 – 17% of energy used in the USA that is lost as waste heat (*29*), but solar or geothermal heat sources could also be used. All of these renewable energy sources provide opportunities for producing electricity, or alternatively hydrogen gas (*14*), from salinity gradients and biomass sources.

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Supporting Online Material

www.sciencemag.org/cgi/content/full/science.1219330/DC1

Materials and Methods

Figs S1 to S7
References (*30*–*36*)

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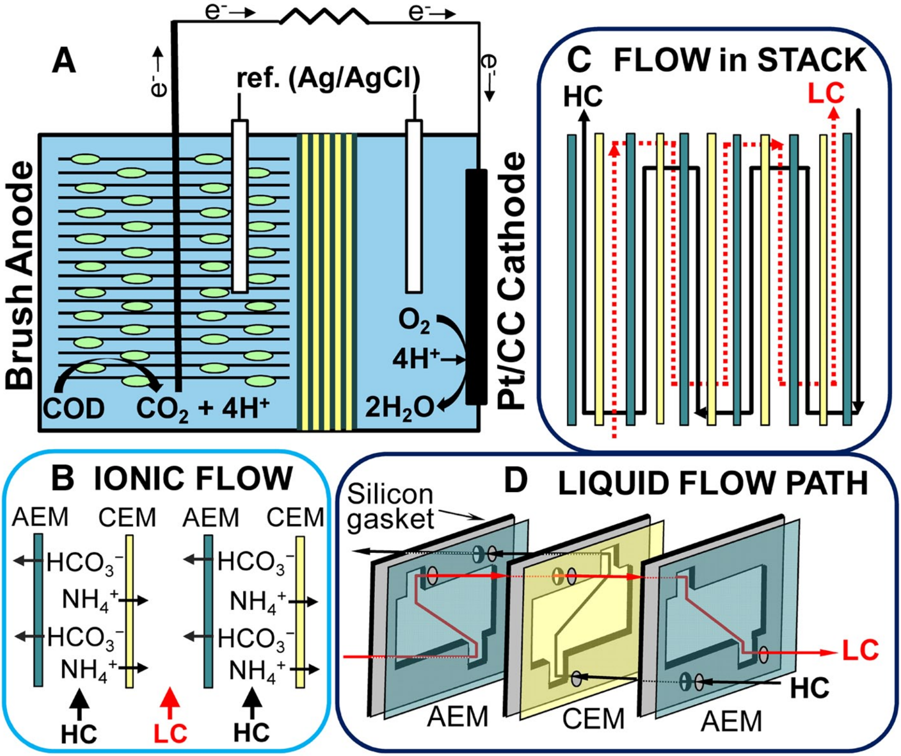
Fig. 1. (**A**) Main components of the microbial reverse electrodialysis cell (MRC), showing the membrane stack between the electrodes, the reference electrodes and the circuit containing a load (resistor). (**B**) Example of how the anion- (AEM) and cation- (CEM) exchange membranes are used to selectively drive the flow of positive ions to the right (towards the cathode) and the negatively-charged ions to the left (towards the anode). The flow of these charged ions adds potential to the current produced by the microbes on the anode and maintains electroneutrality at the electrodes. (**C**) Expanded view of the membrane stack showing flow path of the high (HC) and low (LC) concentrate solutions of ammonium bicarbonate. (**D**) Construction of the gaskets used to direct the flow from one LC chamber to the next LC chamber, avoiding the HC chamber through a short flow path through the membrane and gasket.

Fig. 2. Peak power densities obtained from polarization curves, apportioned to power from the RED (salinity gradient power) compared to the electrodes (organic matter power). (**A**) Effect of salinity ratio (SR) on peak power density with a fixed high concentrate (HC) solution (0.95 M). (**B**) Effects of HC concentrations on power. The dashed line represents peak power density of the same electrodes in a single chamber.

Fig. 3. (**A**) Reverse electrodialysis (RED) stack voltage and (**B**) anode (A) and cathode (C) potentials vs. current density for the MRC using different high concentrate (HC) solutions (0.95, 1.1, and 1.8 M). The stability of the anode potential at higher current densities was the primary reason for the increased power density.

Fig. 4. Energy recovery (rE) and energy efficiency (ηE) for the microbial reverse electrodialysis cell (MRC) in batch recycle experiments, using different high concentrate (HC) solutions. Energy recovery is defined by the ratio of energy produced by the MRC reactor and the energy input as substrate and salinity gradient. Energy efficiency was calculated as the ratio of energy produced to the energy consumed based on the substrate used and the salinity gradient. The dashed line indicates energy recovery and efficiency using the same electrodes in a single chamber MFC reactor (no membranes).


A
e⁻→
e⁻→
e⁻→
e⁻→
ref. (Ag/AgCl)
Brush Anode
COD
CO₂ + 4H⁺
O₂
4H⁺
2H₂O
Pt/CC Cathode
C FLOW in STACK
HC
LC
B IONIC FLOW
AEM
CEM
AEM
CEM
HCO₃⁻
NH₄⁺
HCO₃⁻
NH₄⁺
HCO₃⁻
NH₄⁺
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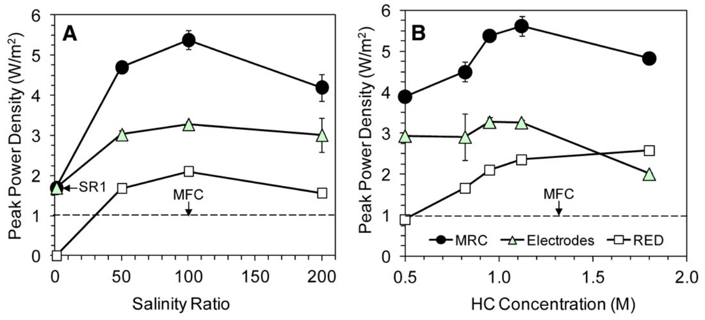
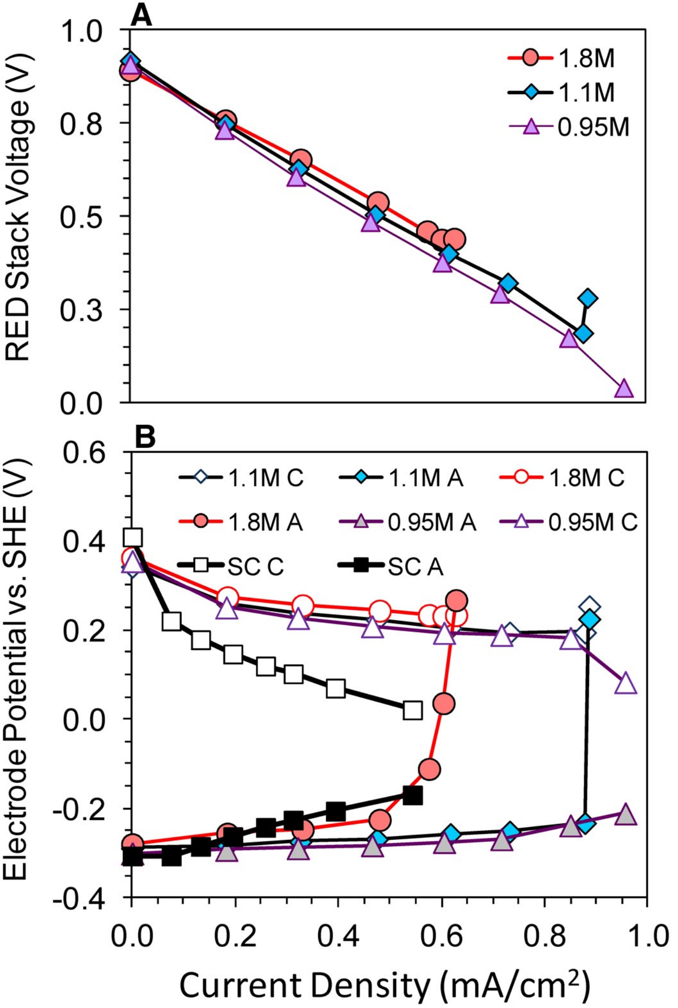
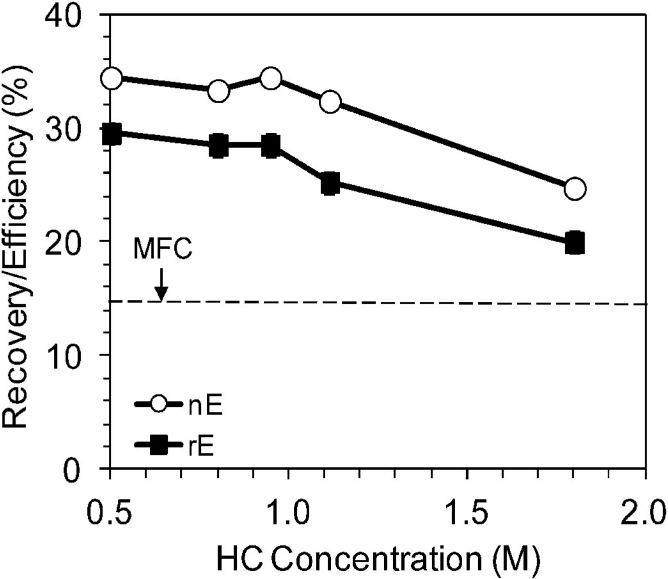
NH₄⁺
HC
LC
HC
D LIQUID FLOW PATH
Silicon gasket
LC
HC
AEM
CEM
AEM


A
Peak Power Density (W/m²)
0
1
2
3
4
5
6
SR1
MFC
0
50
100
150
200
Salinity Ratio
B
Peak Power Density (W/m²)
0
1
2
3
4
5
6
MFC
MRC
Electrodes
RED
0.5
1.0
1.5
2.0
HC Concentration (M)


A
RED Stack Voltage (V)
1.0
0.8
0.5
0.3
0.0
1.8M
1.1M
0.95M
B
Electrode Potential vs. SHE (V)
0.6
0.4
0.2
0.0
-0.2
-0.4
1.1M C
1.1M A
1.8M C
1.8M A
0.95M A
0.95M C
SC C
SC A
0.0
0.2
0.4
0.6
0.8
1.0
Current Density (mA/cm2)



Recovery/Efficiency (%)
40
30
20
10
0
MFC
nE
rE
0.5
1.0
1.5
2.0
HC Concentration (M)

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