Minimal RED Cell Pairs Markedly Improve Electrode Kinetics and Power Production in Microbial Reverse Electrodialysis Cells

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Supporting Information

ABSTRACT: Power production from microbial reverse electrodialysis cell (MRC) electrodes is substantially improved compared to microbial fuel cells (MFCs) by using ammonium bicarbonate (AmB) solutions in multiple RED cell pair stacks and the cathode chamber. Reducing the number of RED membranes pairs while maintaining enhanced electrode performance could help to reduce capital costs. We show here that using only a single RED cell pair (CP), created by operating the cathode in concentrated AmB, dramatically increased power production normalized to cathode area from both acetate (Acetate: from 0.9 to 3.1 W/m²-cat) and wastewater (WW: 0.3 to 1.7 W/m²), by reducing solution and charge transfer resistances at the cathode. A second RED cell pair increased RED stack potential and reduced anode charge transfer resistance, further increasing power production (Acetate: 4.2 W/m²; WW: 1.9 W/m²). By maintaining near optimal electrode power production with fewer membranes, power densities normalized to total membrane area for the 1-CP (Acetate: 3.1 W/m²-mem; WW: 0.6 W/m²) reactors were much higher than previous MRCs (0.3−0.5 W/m²-mem with acetate). While operating at peak power, the rate of wastewater COD removal, normalized to reactor volume, was 30−50 times higher in 1-CP and 2-CP MRCs than that in a single chamber MFC. These findings show that even a single cell pair AmB RED stack can significantly enhance electrical power production and wastewater treatment.

INTRODUCTION

Microbial reverse electrodialysis cells (MRCs) are biotechnologies designed to generate renewable energy from unconventional sources of organic wastewater and salinity gradients. In the United States alone, ~155 GWh (1.23 kWh/m³) could be generated from organics in wastewater.1−3 Ammonium bicarbonate (AmB) is a thermolytic salt that decomposes to ammonia and carbon dioxide gas at low temperatures (40−60 °C).4 The low decomposition temperature of AmB could enable generation of salinity gradients from abundant sources of low grade thermal power such as waste heat (204 GW),5 geothermal (12 TW), and solar (120,000 TW).6 Within a MRC, the same electrodes used in a microbial fuel cell (MFC) are placed on each side of a reverse electrodialysis (RED) membrane stack.7 MFCs spontaneously generate electrical current by pairing a bioanode, on which exoelectrogenic microbes oxidize soluble wastewater organics and release electrons,8 and cathodes with oxygen reduction.9 The entropic energy released by mixing solutions of different ionic-strength is converted in a RED stack into electrical energy by separating chambers of high concentration (HC) and low concentration (LC) saline solutions with alternating anion (AEM) and cation (CEM) exchange membranes.10−12 The additive electrochemical junction potential (typically 0.1−0.2 V per cell pair)13 of the electrolytic-pile provides additional driving force for current generation at the MFC electrodes. Power generation in MRCs is synergistic because the RED stacks not only directly contribute voltage to power production but also enhance MFC electrode performance.7 When the electrodes were transferred from a single-chamber MFC to a MRC with a five cell pair RED stack fed AmB solutions, power production increased by >300% using acetate and by >700% with domestic wastewater.14

The improved performance of the MRC relative to a MFC was due to the use of multiple pairs of membranes in the RED stack, the use of AmB in the stack, and the improved electrode potentials. Power production with a 5-CP stack with acetate reached 5.6 W/m² based on projected cathode area (or equivalently cross sectional area between the electrodes), compared to 1.1 W/m² using only the MFC. While it is typical to normalize power density based on cathode area for MFCs, the total membrane area is typically reported in RED studies. When evaluated on the basis of total membrane area, MRC power densities have ranged from 0.3 to 0.5 W/m².7,14 The use of these membranes in the MRC adds substantial...
capital costs for reactor construction. Thus, reducing the number of membranes or further increasing power production could make MRCs a more commercially viable wastewater treatment biotechnology.

The use of AmB as the catholyte may have advantages compared to other chemical buffer electrolytes in which sodium is the cation. The presence of positively charged ammonium ions near the cathode surface could affect oxygen reduction kinetics as well as hydroxide ion gradients near the electrode. In comparison, HC solution with NaCl in the catholyte improves conductivity, but it does not buffer pH changes. As a result, the cathode pH increases due to the consumption of protons by the cathode and accumulation of OH⁻, leading to potential losses of >0.3 V.¹⁵⁻¹⁷ Phosphate or carbonate buffers can be used to mitigate pH changes, but comparisons to high conductivity NaCl solutions have shown that these negatively charged buffer species do not improve performance.¹⁷ Since concentrated AmB has only been used as a catholyte in the presence of an 11 membrane RED stack,¹⁴ the contribution of improved cathode kinetics to MRC electrode performance has not been separately examined from that of the stack performance.

The objectives of this study were to determine to what extent MRC performance could be improved using only a minimal number of RED cell pairs and distinguish between the benefits of AmB on catalytic oxygen reduction and the effects of RED stack potential on electrode performance. To study the effects of the AmB and RED cell pairs on MRC performance, power production and internal resistance were examined using three different reactor configurations: (1) a single chamber MFC with a bicarbonate buffer used as the single electrolyte in contact with both electrodes; (2) a one cell pair (1-CP) MRC where the anolyte formed an equivalent LC chamber with the bicarbonate buffer, and the catholyte was the HC solution (1 M AmB); and (3) a two cell pair (2-CP) MRC containing an additional membrane pair containing AmB LC and HC solutions (Figure 1, Table 1). To investigate the effect of anolyte composition on electrode and RED stack performance, sodium acetate (in 50 mM bicarbonate buffer) and domestic wastewater were used as fuels. The effect of anolyte conductivity was further examined in the 1-CP MRC configuration by amending the domestic wastewater with bicarbonate buffer (50 mM). To quantify the specific effects of AmB catholyte and RED stack potential on electrode activity, internal resistance was measured using linear polarization and galvanostatic electrochemical impedance spectroscopy (GEIS).

### MATERIALS AND METHODS

MFCs and MRCs were constructed as previously described with minor modifications. MFCs had a single 4-cm diameter chamber (Lexan, 28 mL empty bed volume) (Figure 1). To maintain the same electrode spacing in both MFC and MRC tests, the anode and cathode chambers of 1- and 2-CP MRCs were constructed using two 2-cm thick cubic chambers (14 mL empty bed volume). The anodes were graphite fiber brushes (2.7 cm in diameter, 2.3 cm in length; Mill-Rose Laboratories Inc., OH) that were heat treated prior to being inoculated with effluent from an existing MFC and enriched in single chamber MFC. The same anodes were used in all reactor configurations. The air-cathodes contained a Pt catalyst (0.5 mg Pt/cm²) on carbon-cloth and were constructed as previously described with a Nafion catalyst binder on the water side and four layers of polytetrafluoroethylene (PTFE) diffusion layers on the air side.

The 1-CP MRC contained a single anion exchange membrane (1-CP; Selemion AMV, Asahi Glass, Japan, 7 cm² active area) separating the anode and cathode chambers (Figure 1). The 2-CP MRC reactor contained an additional HC/LC cell pair between the anode and cathode chambers, requiring three membranes (1 cation- and 2 anion-exchange membranes) as well as the test reactor configurations and experiments performed.

### Table 1. Anode Substrate Characteristics Including Total (tCOD) and Soluble (sCOD) Chemical Oxygen Demand, Solution Conductivity (κ), and pH As Well As The Test Reactor Configurations and Experiments Performed

<table>
<thead>
<tr>
<th>anolyte</th>
<th>tCOD (g/L)</th>
<th>sCOD (g/L)</th>
<th>κ (mS/cm)</th>
<th>pH</th>
<th>reactor configurations</th>
<th>experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ac</td>
<td>1.8 ± 0.05</td>
<td>1.8 ± 0.05</td>
<td>5.5 ± 0.1</td>
<td>8.1 ± 0.1</td>
<td>MFC, 1-, 2-CP MRC</td>
<td>CP, EIS, BR</td>
</tr>
<tr>
<td>WW</td>
<td>0.38 ± 0.04</td>
<td>0.20 ± 0.02</td>
<td>1.5 ± 0.3</td>
<td>7.6 ± 0.2</td>
<td>MFC, 1-, 2-CP MRC</td>
<td>CP, EIS, BR</td>
</tr>
<tr>
<td>WW-HC</td>
<td>0.38 ± 0.04</td>
<td>0.20 ± 0.02</td>
<td>5.1 ± 0.1</td>
<td>8.1 ± 0.1</td>
<td>1-CP MRC</td>
<td>CP, EIS</td>
</tr>
</tbody>
</table>

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membranes, Selemion CMV and AMV, Asahi glass, Japan). Intermembrane chambers were sealed and separated by silicon gaskets (0.5 mm), each with an 8 cm² (2 cm × 4 cm) rectangular cross section cut out. The total ionic exchange membrane area in the 2-CP MRC was 24 cm². The HC solution entered the reactor at the cathode and exited from the HC cell next to the anode chamber. The LC AmB stream entered the RED stack near the anode and flowed upward through the LC cell in the stack. Both the HC and LC AmB solutions were continuously fed using a peristaltic pump (Cole Parmer, IL) at a flow rate of 1.0 mL/min. During power density curve experiments fresh saline solutions were pumped through the RED stack with the effluent collected in separate reservoirs. In batch recycle experiments 0.1 L of each solution was recycled through the stack in airtight flow paths. Before each batch the stack and tubing were flushed with matching solutions.

Anodes were fed either a buffered sodium acetate solution or raw domestic wastewater except as noted. The bicarbonate buffered acetate solution was designed to reduce solution and membrane resistances and provide a high concentration of electron donor for the anodic biofilm. The acetate solution contained 2 g/L of sodium acetate in the 50 mM bicarbonate buffer (4.2 g/L NaHCO₃) as well as 0.231 g/L NH₄H₂PO₄·0.16 g/L KCl, and trace vitamins and minerals.²⁰ The volume of acetate was 30 mL for each reactor configuration. In the 1-CP and 2-CP configurations, reduced anode volume required recirculation of 16 mL of sodium acetate. Domestic wastewater (WW) samples were collected from the Penn State University wastewater treatment plant primary clarifier effluent. High conductivity wastewater (WW-HC) was prepared by dissolving 4.2 g/L of NaHCO₃ in the wastewater. To avoid electron donor limitations that could occur due to low COD, experiments using wastewater were conducted by recycling 250 mL of substrate through the anode chamber of each reactor. The anolyte feed reservoirs were airtight glass vessels submerged in ice water to minimize external organics degradation.

The HC ammonium bicarbonate solution used in the one and two cell pair MRC reactors was prepared by dissolving chemical grade ammonium bicarbonate salt (Alfa Aesar, MA) into deionized water within an airtight vessel. The initial HC (1.0 M) and LC (0.01 M) concentrations tested were selected based on previous optimization experiments.¹⁴

Power densities and bulk internal resistances for each reactor configuration were determined using chronopotentiometry. Whole cell current intervals (20 min) were set with a galvanostat (Biologic VMP-3, USA). Prior to galvanostatic operation, reactors were held open circuit for 30 min. Power density was calculated by multiplying the electrical current (i) and total cell voltage and was normalized to either cathode or membrane projected area. Anode, cathode, and RED potentials were against Ag/AgCl (+0.210 V vs SHE) reference electrodes (BASI, IN) as previously described.¹⁴

Maximum power is obtained when the resistance of the external load matches the internal resistance of the electrochemical cell.²¹ RED stack power is often estimated from open circuit potentials and internal resistance as

\[ P_{\text{max}} = 0.95 \left( \frac{V^*}{4AR_{\text{RED}}} \right)^2 \]  

where \( P_{\text{max}} \) is maximum power density, \( V^* \) is the open circuit voltage, \( A \) is the normalization area, and \( R_{\text{RED}} \) is the measured internal resistance of the membrane stack. A similar method was used to estimate the effect optimized RED stacks would have on MRC power densities, except that a correction factor of 0.8 was used to account for electrode activation over-potentials.

\[ P_{\text{max,MRC}} = 0.8 \left( \frac{V_{\text{MRC}}^*}{4AR_{\text{MRC}}} \right)^2 \]  

MRC internal resistance (\( R_{\text{MRC}} \)) is the sum of potential dissipative forces at the anode (\( R_{\text{an}} \)), cathode (\( R_{\text{cat}} \)), and within the RED stack (\( R_{\text{RED}} \)), or \( R_{\text{MRC}} = R_{\text{an}} + R_{\text{RED}} + R_{\text{cat}} \). Internal resistance can be further separated into solution, membrane, kinetic, diffusion, and capacitive resistances. The solution and membrane resistance (\( R_{\text{solv}} \)) is dependent on electrode spacing, electrolyte, and membrane conductivity as well as diffusion area. Kinetic charge transfer occurs during current generation at the anode (\( R_{\text{an}} \)) and current consumption at the cathode (\( R_{\text{cat}} \)). Diffusion resistance can arise due to transport of substrate to the anode (\( R_{\text{an,dl}} \)) as well as protons and oxygen to the cathode (\( R_{\text{cat,dl}} \)). Diffusion boundary layer resistance (\( R_{\text{RED,dl}} \)), also known as concentration polarization, is caused by concentration and depletion of ions at the interface of ion-exchange membranes. The fixed charges of IEMs also create ionic double layer capacitance (\( R_{\text{RED,dl}} \)) that impede ion diffusion within the RED stack.²⁴–²⁶

Bulk internal resistances of the whole cell, anode, cathode, and RED membrane interfaces were determined from the slopes of linear polarization curves constructed for each reactor component.²⁵,²⁷ GEIS was used to characterize specific resistances at the electrode and RED interfaces. GEIS was conducted at a set current of 1.5 mA (2.1 A/m²) and amplitude of 0.21 mA (0.3 A/m²). GEIS spectra were simultaneously recorded for each reactor component by using three galvanostat channels operated in unison (one master channel that applied AC current and two reference channels that collected EIS spectra). Whole cell impedance was collected from the master channel terminals by setting the cathode as the working electrode and the anode as both the counter and reference electrode. Two reference galvanostat channels were used to obtain anode, RED, and cathode impedance spectra. Anode and cathode impedance was measured against an Ag/AgCl reference electrode. RED stack impedance was obtained with reference electrodes positioned at either side of the membrane stack. All EIS experiments were conducted within one hour of chronopotentiometry measurements to ensure similar working conditions. EIS data were analyzed using EC-Lab V10.32 to determine the specific resistances of each reactor component. Equivalent circuit model (ECM) software was used to determine specific resistances from the Nyquist plots of each reactor component. ECM diagrams and representative model fits are presented in the Supporting Information (Figure S5).

During batch-fed experiments, the voltage drop across an external resistor was recorded every 10 min by a digital multimeter (Keithley Instruments, OH). To maximize energy production, the fixed external resistance was set to match the internal resistance of the cell at each condition as determined from polarization data. All batch recycle experiments were conducted at 30 °C in a temperature controlled room.

Energy recovery in batch experiments with recycled anolyte was calculated as the energy produced (Wh) from the substrate
based on chemical oxygen demand removed (g-COD). Power production (W) was calculated for each measured voltage (V) divided by the sample interval (h), and summed over the entire fed-batch cycle. Volumetric COD removal rates were normalized by the duration of the fed-batch cycle and the reactor (r) volume (g-COD/Lr-d) to allow direct comparison among different reactor configurations. When fed wastewater in the anode was carbonated, the 2-CP RED stack potential reached 0 mV at a current density 56% higher than when the MRC was fed wastewater (Figure 2f). When fed carbonated buffered acetate, the 2-CP RED stack potential reached 0 mV at a current density 56% higher than when the MRC was fed wastewater (Figure 2f). The cathode in the single-chamber MFC had a linear dependence on the current density that was not appreciably affected by the RED stack potential. Since the magnitude of RED stack potentials in this study were much lower than electrode potentials, observed decreases in power density were primarily due to reductions in internal resistance. Quantifying the polarization resistance (Ω) of the electrodes and RED stacks from rates of electrochemical potential losses (mV/mA) observed in the linear polarization plots (Figure 2c–f) provides further insight into the relative effects RED stack potential, AmB catholyte, and anolyte composition had on MRC power production.

Anode potential loss in linear polarization experiments was influenced by the use of AmB catholyte as well as the magnitude of RED stack potential. In the single chamber MFCs, anode potential loss was highly dependent on the anolyte, with nearly a 90 Ω (or mV/mA) difference between bicarbonate buffered acetate (33 Ω) and domestic wastewater (120 Ω). In the 1-CP MRC, anode resistance decreased significantly for both substrates (Acetate: 21 Ω, WW: 28 Ω). In the 2-CP MRC configuration, additional RED stack voltage minimized anode resistance to the point at which potential loss was not appreciably affected by substrate composition (10 Ω in wastewater versus 8 Ω in buffered acetate, Figures 2c,d and S1). The similarity in 2-CP MRC anode performance implies that the magnitude of RED potential may influence bioanode activity.

During operation with the high concentrate AmB electrolyte, cathode potential loss was uniformly reduced in both the 1- and 2-CP reactor configurations relative to the MFC (Figure 2c,d). The cathode in the single-chamber MFC had a linear polarization resistance of 55 Ω (or 55 mV/mA) with buffered acetate and 220 Ω with domestic wastewater. When operated in

**RESULTS AND DISCUSSION**

**MRC Power Production.** The use of concentrated AmB solution as catholyte in the 1-CP MRC configuration resulted in a >300% increase compared to that obtained from the MFC containing only a bicarbonate buffer (MFC, 0.9 ± 0.05 W/m²-cath; 1-CP, 3.1 ± 0.1 W/m², Figure 2a). The 1-CP MRC also increased power production using domestic wastewater from 0.3 ± 0.02 W/m²-cath (MFC) to 1.8 ± 0.03 W/m² (1-CP). Previously, power production from two-chambered MFCs, with concentrated NaCl or phosphate buffer as catholyte, was lower than that obtained with a single chamber MFCs.15,17 The use of concentrated AmB catholyte in the two-chamber configuration (1-CP) reduced several limitations for bioelectricity production including ohmic solution resistance, transmembrane ionic transport resistance, and cathode potential loss from pH changes and diffusion resistance. Separating anode and cathode with an AEM and replacing 50% of the reactor electrolyte with concentrated AmB significantly reduced solution resistance within the reactor. The buffer capacity of 1 M AmB and presence of NH₄⁺ near the cathode prevented accumulation of OH⁻ and subsequent loss of cathode potential. The resulting concentration gradient also created a positive membrane potential and minimized power loss due to membrane transport resistance. Transport of HCO₃⁻ into the anode chamber instead of Cl⁻ also beneficially buffered anolyte pH.

The inclusion of a second RED cell pair between the electrodes (2-CP) further increased the peak power density to 4.1 ± 0.1 W/m²-cathode (1.3 ± 0.1 W/m²-mem). Power density from the 2-CP reactor fed wastewater was only slightly higher (1.9 ± 0.05 W/m²-cath, 0.6 ± 0.02 W/m²-mem, Figure 2b) than the 1-CP configuration. When fed the dilute and complex organic matter in wastewater, bioanodes could not sustain negative potentials at current densities above 6.5 A/m²-cath (Figure 2d), beyond which rapid anode polarization was observed. The low conductivity of wastewater also impeded ionic transport within the RED stack, causing rapid decay of stack potential. At peak MRC power, the 2-CP RED potential with wastewater in the anode was −100 mV (Figure 2f). When fed carbonated buffered acetate, the 2-CP RED stack potential reached 0 mV at a current density 56% higher than when the MRC was fed wastewater (Figure 2f) implying that anolyte composition can have a significant impact on RED stack performance.

**Electrode and RED Stack Polarization Resistance in MRCs.** Since the magnitude of RED stack potentials in this study were much lower than electrode potentials, observed increases in power density were primarily due to reductions in internal resistance. Quantifying the polarization resistance (Ω) of the electrodes and RED stacks from rates of electrochemical potential loss (mV/mA) observed in the linear polarization plots (Figure 2c–f) provides further insight into the relative effects RED stack potential, AmB catholyte, and anolyte composition had on MRC power production.

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HC AmB, the cathode polarization resistance dropped dramatically to 12–15 Ω in both the 1-CP and 2-CP MRC reactors. This implies that enhanced cathode performance in MRCs is attributed to the use of concentrated AmB catholyte and is not influenced by RED stack potential or anolyte composition. When the air cathode was operated in concentrated AmB, instead of 50 mM bicarbonate buffer, solution resistance decreased by over 90%, and oxygen reduction charge transfer resistance decreased by over 50% (Figure 4b).

**Figure 3.** Internal resistance of 1-CP reactors components fed raw domestic wastewater (WW), buffered wastewater (WW-HC), and buffered acetate (Ac), determined from (a) direct current (DC) polarization and (b) alternating current galvanostatic electrochemical impedance spectroscopy.

**Figure 4.** Internal resistance of MFC, 1-CP, and 2-CP MRC reactors components fed buffered acetate (Ac), determined from (a) direct current (DC) polarization and (b) alternating current (AC) galvanostatic electrochemical impedance spectroscopy.

Electrode potentials in the 1-CP and 2-CP MRCs were nearly identical with both organic fuel solutions, but power production from acetate remained significantly higher than from wastewater. This disparity can be linked to the effect that substrate composition had on RED stack potential loss. With buffered acetate in the anode chamber, RED resistance was 17 Ω in the 1-CP reactor, and it increased to 36 Ω with the inclusion of an additional cell pair (Figure 4b). When domestic wastewater filled the anode chamber, the RED stack resistance significantly increased in both the 1-CP (38 Ω) and 2-CP (97 Ω) MRCs. In order to increase power production from low conductivity wastewater, transport resistance at the terminal AEM/anolyte interface must be reduced. Minimizing anode chamber thickness would reduce solution resistance, and increasing solution flow rate at the membrane surface could reduce boundary layer resistance.23,26

**Effect of Anolyte Composition on Membrane Transport Resistance.** The two anode substrates evaluated in this study had different characteristics in terms of electron donor concentration and composition, buffer capacity, and specific conductance. In order to understand how buffer concentration influenced the specific resistances limiting MRC power production, experiments using GEIS were conducted on the individual reactor components (anode, RED interface, and cathode) with the same set current (2.1 A/m²) and amplitude (0.3 A/m²), using three different anode substrates: buffered acetate; raw domestic wastewater (WW); and wastewater amended with 4.2 g/L NaHCO₃ (WW-HC) that matched the conductivity of the buffered acetate.

The differences between membrane interface impedance values in the 1-CP MRC were primarily due to anolyte conductivity. Membrane resistance determined by alternating current (AC) impedance showed ohmic resistance (from anode and cathode solutions as well as the AEM, Rsol+m) and two overlapping semicircles representing double layer capacitance (Rdl) and diffusion boundary layer (Rdl) resistance (Figure S3c). All three types of membrane impedance were highest when the MRC was fed raw domestic wastewater (Rsol+m: 7.8 ± 0.1 Ω, Rdl: 0.9 ± 0.2 Ω, Rdl: 32 ± 0.8 Ω, Figure 3b). Raising the conductivity of the wastewater decreased both solution and diffusion boundary layer resistance (Rsol+m: 5.9 ± 0.1 Ω, Rdl: 0.4 ± 0.4 Ω, Rdl: 18 ± 0.8 Ω, Figure 3b). By raising anolyte conductivity and reducing membrane transport resistance, power density of the 1-CP MRC fed high conductivity wastewater (2.1 ± 0.05 W/m², Figure S2a) exceeded that of the 2-CP MRC with raw domestic wastewater. However, raising wastewater conductivity did not reduce membrane impedance to the levels of buffered acetate (Rsol+m: 5.0 ± 0.3 Ω, Rdl: 0.4 ± 0.2 Ω, Rdl: 8.8 ± 1.1 Ω). This implies that some other distinguishing characteristic of the wastewater, such as presence of particulate organic matter or other ions, may have adversely affected membrane transport properties. The summation of individual membrane resistances determined by GEIS closely corresponded with linear polarization resistance determined under direct current (DC) conditions (differences ranged from 0.5–2.9 Ω).

Electrode resistance values determined by GEIS were nearly identical for each substrate condition. Alternating current (AC) cathode impedance included 3.7 ± 0.4 Ω of solution resistance and 12 ± 0.5 Ω of charge transfer resistance for all three conditions (Figure 3b, S3c). The total cathode impedance values, based on the sum of individual resistances, were all quite similar (within 2 Ω) to cathode resistance values determined by the linear polarization slope method (DC resistance). Anode impedance spectra for all three conditions were comprised of a single charge transfer semicircle (Figure S3a). Anode charge transfer resistance values ranged from 13–15 Ω (Figure 3b, S3a) and were lower than DC resistances for all three substrates (Figure 3a,b). The discrepancy between DC (linear polarization) and AC (GEIS) anode resistance (WW: 15 Ω, WW-HC: 13 Ω, Acetate: 7 Ω) decreased with the magnitude of RED stack resistance (WW: 40 Ω, WW-HC: 24 Ω, Acetate: 16 Ω) implying that, under direct current conditions, negative membrane potential may adversely affect bioanode potential.

**Effect of RED Stack Potential on Bio-Anode Charge Transfer Resistance.** Anode resistances, determined from linear polarization experiments, sharply decreased as internal resistance decreased (1-CP) and RED stack potential increased (2-CP). GEIS was used to track anode biofilm catalytic activity, represented by charge transfer resistance, in the single chamber MFC, 1-CP, and 2-CP MRCs. In each configuration, the anode was fed buffered acetate, and GEIS was conducted as the same set current (2.1 A/m²) and amplitude (0.3 A/m²).

Nyquist plots of anode impedance in the single chamber MFC showed ohmic solution resistance (Rsol: 12 ± 0.1 Ω)
between anode and reference as well as charge transfer and diffusion resistance \( (R_{ct}: 16 \pm 0.01 \, \Omega, R_{diff}: 11 \pm 0.7 \, \Omega, \text{Figure 4b, S4a}) \). Anode impedance in the 1-CP configuration was represented by a single charge transfer semicircle that was similar, based on radius \( (R_{ct}: 14 \pm 0.2 \, \Omega, \text{Figure 4b, S4a}) \), to the anode kinetic resistance in the single chamber MFC. This similarity in charge transfer implies that eliminating solution and diffusion resistance in the 1-CP reactor led to the observed reduction in anode potential loss. In the 2-CP reactor, anode charge transfer resistance decreased to 4.2 \( \pm \) 0.8 \( \Omega \). At the GEIS set current, the 1-CP reactor RED potential was 0.01 mV and 2-CP RED potential was 150 mV, implying that positive RED potential not only adds to MRC power but also enhances the catalytic activity of anodic biofilms.

Wastewater Treatment Rates and Energy Recovery.
To investigate how increased MRC power would translate to COD removal and energy recovery, additional tests were conducted with buffered acetate or domestic wastewater recycled through the anode chamber. The rate of COD removal with the 1-CP system with acetate was 1.5 \( \pm \) 0.3 g-COD/Lr-d, nearly twice that of the MFC (Figure 5a). In the 2-CP MRC, COD removal further increased to 1.9 \( \pm \) 0.1 g-COD/Lr-d. Overall COD removal (77\%–91\%) was very high in both the 1-CP and 2-CP MRCs fed acetate. Energy recovery increased from 0.4 \( \pm \) 0.01 Wh/g-COD for the MFC to 0.7 \( \pm \) 0.01 Wh/g-COD for the 1-CP and 0.9 \( \pm \) 0.1 for the 2-CP MRCs (Figure 5b).

Volumetric COD removal rates and energy recoveries were also greatly increased with domestic wastewater. The COD removal rate of the 1-CP MRC (1.2 \( \pm \) 0.1 g-COD/Lr-d) was 20 times larger than that of the single chamber MFC (0.05 \( \pm \) 0.0007 g-COD/Lr-d, Figure 5a). Using the 2-CP MRC, the COD removal rate increased 2.3 \( \pm \) 0.2 g-COD/Lr-d, which is within the range reported for activated sludge systems.29 Increased wastewater treatment rates in the MRC configurations were caused by significant higher current density, which reduced the time required to treat 250 mL of wastewater from 5.0 \( \pm \) 0.5 d to 0.9 \( \pm \) 0.2 d in the 1-CP MRC and 0.7 \( \pm \) 0.2 d in the 2-CP reactor. The observed discrepancy between 1-CP and 2-CP treatment rates was likely caused by irregularity in the initial COD concentration of domestic wastewater. It should be noted that treatment rates with wastewater were amplified due to significant noncurrent based COD removal and large treatment volumes (250 mL vs 30 mL of the acetate solution). The overall COD removal with the MRCs (1-CP, 40 \( \pm \) 6\%, 2-CP, 49 \( \pm \) 1\%) was lower than that obtained with the single chamber MFC (68 \( \pm \) 2\%). It is possible that the difference in wastewater COD removal was caused by longer batch times in the single chamber, which would allow for enhanced fermentation of complex organics and aerobic respiration at the cathode interface. Energy recovery with wastewater followed the same trend as acetate, but values were lower (Figure 5b) due to organic degradation by nonanodic microorganisms. Coulombic efficiencies, which measure the percentage of COD removed by current generation, were significantly lower in all reactor configurations with wastewater (35–50\%) than with acetate (72–81\%).

Outlook.
By using AmB as catholyte and minimizing the number of RED cell pairs, it was shown that electrode kinetics could be dramatically enhanced with a single membrane. Although adding additional RED cell pairs could further increase power densities, calculated on the basis of projected cathode area, power did not proportionally increase on the basis of total membrane area. The inclusion of additional membranes lowered the membrane area normalized power density from 3.1 \( \pm \) 0.1 W/m² in the 1-CP configuration to 1.4 \( \pm \) 0.1 W/m². These values are significantly greater than membrane area normalized power densities of 5-CP MRCs (0.3–0.5 W/m²) and a 20-CP abiotic RED fed AmB (0.33 W/m²) and quite comparable to those reported for the optimized abiotic RED system.7,14,23,30,31

In order to increase the MRC performance on the basis of total membrane area, the resistance per RED cell pair must be decreased. The electrode chamber geometry, cross sectional membrane area, and RED flow channel thickness of the reactors used in this study promoted high solution and transport boundary layer resistance leading to 17 \( \Omega \) per CP with acetate and 48 \( \Omega \) per CP with wastewater. Previous studies
have shown that RED stack resistance can be reduced to less than 1 Ω per CP by increasing membrane area, reducing RED flow channel thickness and enhancing hydrodynamic turbulence at the membrane interfaces.2,3,10 If MRC stack resistance can attain similar optimization, 2-CP power densities would approach 10 W/m²-cathode (3 W/m²-membrane, Figure 6a, b). While reducing the number of RED cell pairs limits the potential to recover salinity gradient energy, these results show that increasing MFC electrode power with minimal RED stacks makes efficient use of membrane area while enabling high power densities and organic removal rates from domestic wastewater.

ASSOCIATED CONTENT
3 Supporting Information
Additional figures including: polarization resistance of all reactor conditions; linear polarization curves and of 1-CP MRC with acetate, unamended and high conductivity wastewater; representative Nyquist plots of GEIS spectra for all test conditions with equivalent circuit model fits. 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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