# Microbial Reverse-Electrodialysis Electrolysis and Chemical-Production Cell for H_2 Production and CO_2 Sequestration

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ABSTRACT: Natural mineral carbonation can be accelerated using acid and alkali solutions to enhance atmospheric CO_2 sequestration, but the production of these solutions needs to be carbon-neutral. A microbial reverse-electrodialysis electrolysis and chemical-production cell (MRECC) was developed to produce these solutions and H_2 gas using only renewable energy sources (organic matter and salinity gradient). Using acetate (0.82 g/L) as a fuel for microorganisms to generate electricity in the anode chamber (liquid volume of 28 mL), 0.45 mmol of acid and 1.09 mmol of alkali were produced at production efficiencies of 35% and 86%, respectively, along with 10 mL of H_2 gas. Serpentine dissolution was enhanced 17−87-fold using the acid solution, with approximately 9 mL of CO_2 absorbed and 4 mg of CO_2 fixed as magnesium or calcium carbonates. The operational costs, based on mineral digging and grinding, and water pumping, were estimated to be only \$25/metric ton of CO_2 fixed as insoluble carbonates. Considering the additional economic benefits of H_2 generation and possible wastewater treatment, this method may be a cost-effective and environmentally friendly method for CO_2 sequestration.
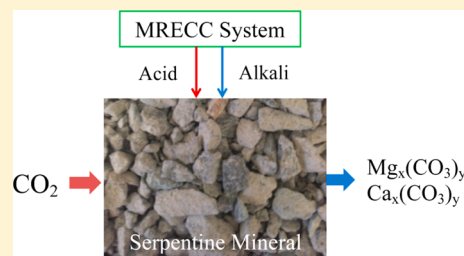
INTRODUCTION

Carbon dioxide concentrations in the atmosphere continue to increase primarily due to the combustion of fossil fuels.[1−3] CO_2 sequestration is therefore essential to reduce the contribution of CO_2 emissions to climate change. Atmospheric carbon is naturally captured into solid carbonates such as calcite ($CaCO_3$) and magnesite ($MgCO_3$)[4−6] from the weathering of calcium and magnesium silicate minerals, respectively.[7−9] For example, the capture of carbon by serpentine can occur via

$$Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O \tag{1}$$
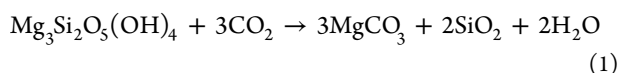
Silicate minerals are sufficiently abundant to allow the capture of an estimated 1400−5550 gigatons of CO_2, but natural rates are extremely slow.[5,10] These rates can be accelerated using acid solutions to dissolve minerals and alkaline solutions for carbonate precipitation as insoluble carbonates.[11−13]

Electrical power can be used to produce acid and alkali solutions, but the energy source needs to be carbon-neutral to accomplish green and sustainable CO_2 sequestration. Microbial fuel cells (MFCs) can be modified to produce acid and base solutions, by creating a multichamber device containing a bipolar membrane (BPM).[14−16] MFCs produce electricity by using microorganisms to break down organic matter at the anode and typically an inorganic catalyst for oxygen reduction at the cathode. To recover acid, an additional chamber is created using the BPM to separate the anode and cathode chambers. The BPM results in water dissociation, maintaining an almost neutral pH in the anode chamber and producing a low-pH solution in the acid chamber. A highly basic solution is produced in the cathode chamber because of the consumption of protons for oxygen reduction. The use of the BPM requires a voltage higher than that generated only by the bioanode and cathode, and therefore, additional energy must be added for chemical production. The first devices, called microbial desalination and chemical-production cells (MDCCs), were modified MFCs designed to desalinate water while producing acidic and basic solutions.[14,15] Subsequently, it was shown that these acid and base solutions could be used for CO_2 sequestration.[16] Serpentine dissolution rates were increased 20−145-fold using acid produced by the MDCC, and 13 mg of CO_2 was fixed as calcium and magnesium carbonates using the base solution.[16] However, this process needed to use an additional ∼1 V that was added from a separate power source to drive desalination and overcome the energy losses of the BPM. An internal reverse-electrodialysis (RED) stack of membranes was shown to function as the power source using renewable salinity gradient energy, avoiding the need for electrical grid energy.[17] This system, termed a microbial reverse-electrodialysis chemical-production cell (MRCC), used a RED stack with five membrane pairs primarily to overcome the energy losses associated with the BPM. The main disadvantage of the MRCC was inefficient base production compared to acid production (1:2.3 base:acid ratio), and therefore, the solutions produced by this cell were not suitable for CO_2 sequestration.

To avoid the need for electrical grid power sources for making acid and base solutions, and to increase the efficiency of base solution production, we developed a system based on a microbial electrolysis cell (MEC) rather than an MFC. This reactor, which used a RED stack as the power source, is called a microbial reverse-electrodialysis electrolysis and chemical-production cell (MRECC) (Figure 1). One primary advantage
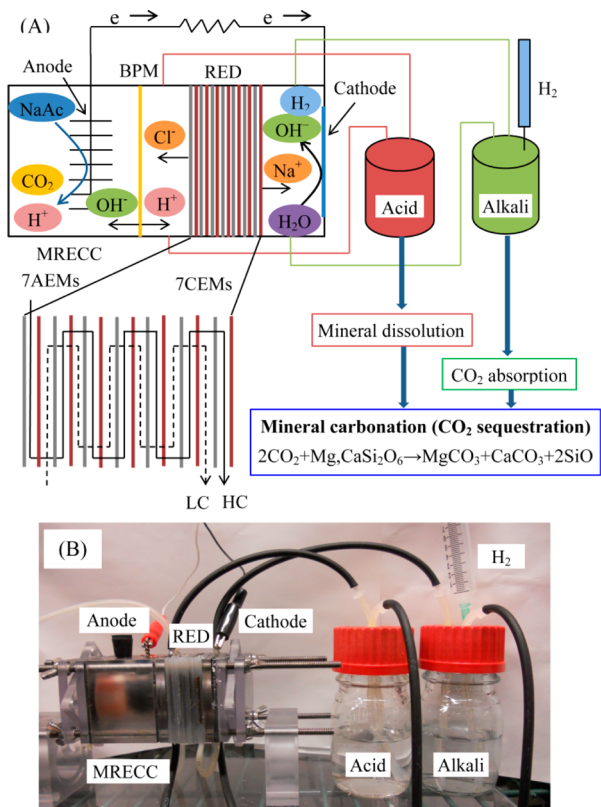

Figure 1. Schematic design (A) and photograph (B) of the MRECC system.

of this system compared to the previous MRCC[17] is the carbon-neutral production of H_2 gas at the cathode, as this gas could be collected and used as a method to store energy produced by the process. Additional changes were also made in the reactor design to improve performance. The widths of the acid- and alkali-production chambers were reduced, and the anode was moved closer to the BPM to decrease internal resistances. A membrane stack of seven cell pairs was used to generate the higher potentials needed to drive H_2 evolution and overcome ohmic losses of the BPM. These changes resulted in a highly sustainable and effective system for achieving both CO_2 sequestration (using serpentine) and fuel production (H_2 gas).

■ MATERIALS AND METHODS

MRECC Construction and Operation. The MRECC reactor made from polycarbonate cubes with 3 cm diameter cylindrical holes consisted of an anode chamber (4 cm long), an acid-production chamber (5 mm long), a reverse-electrodialysis (RED) stack, and a cathode (i.e., alkali-production) chamber (5 mm long) (Figure 1). The anode was a heat-treated graphite fiber brush [2.5 cm (diameter) × 2.5 cm (length)][18] placed vertically in the anode chamber close to the BPM (Fumasep-FBM) used to separate the anode and the acid-production chambers. The RED stack placed between the acid-production

and alkali-production chambers consisted of seven high-concentration (HC) and six low-concentration (LC) cells constructed using seven AEMs and seven CEMs (Selemion AMV and CMV membranes). Silicon gaskets placed between adjacent membranes had rectangular open sections [4 cm (width) × 2 cm (height) × 0.13 cm], and polyethylene mesh spacers were used to allow water flow with minimal membrane deformation.[19] The cathode (projected surface area of 7 cm^2) was made of stainless steel mesh [50 × 50 (McMaster-Carr)] and contained 0.86 mg/cm^2 of Pt catalyst on the membrane-facing side and a 8.6 mg/cm^2 carbon black layer on the other side.[20]

The anode was preacclimated with exoelectrogenic microorganisms in a MFC originally inoculated with wastewater for ~1 month. After current generation became stable over 20 fed-batch cycles (external resistance of 10 Ω), the anode was transferred to the MRECC reactor. The anolyte (28 mL) contained 0.82 g/L sodium acetate in a 50 mM phosphate-buffered nutrient medium [4.28 g/L Na_2HPO_4, 2.45 g/L $NaH_2PO_4 \cdot H_2O$, 0.31 g/L NH_4Cl, 0.13 g/L KCl, trace minerals, and vitamins (pH 7); conductivity of 6.74 mS/cm].[21] The HC solution was 35 g/L NaCl (54 mS/cm), and the LC solution was 0.35 g/L NaCl (0.72 mS/cm), producing a salinity ratio of 100. HC and LC solutions were continuously supplied to the RED stack (1.6 mL/min). Separate LC solutions (15 mL each) were recycled (2 mL/min) between the acid-production chamber and an external reservoir (2 mL/min) and between the alkali-production chamber and its external reservoir. Hydrogen produced at the cathode was collected in the headspace of the alkali reservoir. The acid and alkali solutions and headspaces were sparged with nitrogen gas at the beginning of each cycle.

Analytics. A 10 Ω resistor was connected between the anode and cathode to measure current using a multimeter (model 2700, Keitheley Instrument). Polarization data were obtained using a potentiostat (Uniscan PG580RM) under galvanostatic conditions (0−1.2 mA in 0.2 mA increments). The solution pH was measured using a meter (VWR SB70P) with a pH probe (SymphHony), and the conductivity was measured using a separate meter (VWR SB90M5) and probe (SymphHony). The H_2 concentration was detected by gas chromatography (GCs, SRI Instrument) with a 6 ft molsieve column at 80 °C.[22]

H^+ and OH^- concentrations were calculated from changes in pH in the acid-production and alkali-production chambers.[23] The acid-production (or alkali-production) efficiencies were calculated on the basis of H^+ (or OH^-) concentrations compared to the total recovered coulombs.[14]

CO_2 Sequestration. Serpentine from the Cedar Hills quarry in southeastern Pennsylvania, donated by the Department of Energy and Geo-Environmental Engineering of The Pennsylvania State University, was ground in a ball mill and sieved to <38 μm. The mineral (0.625 g, 50 g/L) was dissolved in the acid produced by the MRECC in a stirred bottle at 50 °C for 24 h.[16] The solution was filtered through a 0.45 μm pore diameter cellulose acetate membrane and analyzed for Mg^{2+} and Ca^{2+} concentrations by ion-exchange chromatography (Dionex ICS-1100). Part of the MRECC-generated alkali was used to increase the leachate pH to 9.8 to absorb CO_2 (130 mL sealed bottle, 99.99% CO_2 headspace gas). The CO_2 concentration was measured after 24 h by gas chromatography (GCs, SRI Instrument) with a 3 ft silica gel column at 60 °C to determine the mass of CO_2 absorbed. Then, the remaining

alkali solution was added to the leachate for carbonate precipitation, with the produced solids determined after filtration (0.45 μm) and drying at room temperature (24 h), with gravimetric analysis and crystalline composition analysis by X-ray diffraction (XRD). XRD was performed with a PANalytical MPD XRD system using Cu Kα radiation, with an operating voltage of 45 kV and a current of 40 mA.

■ RESULTS AND DISCUSSION

The maximal current produced by the MRECC was 1.58 ± 0.03 mA (Figure 2A). The current gradually decreased over a
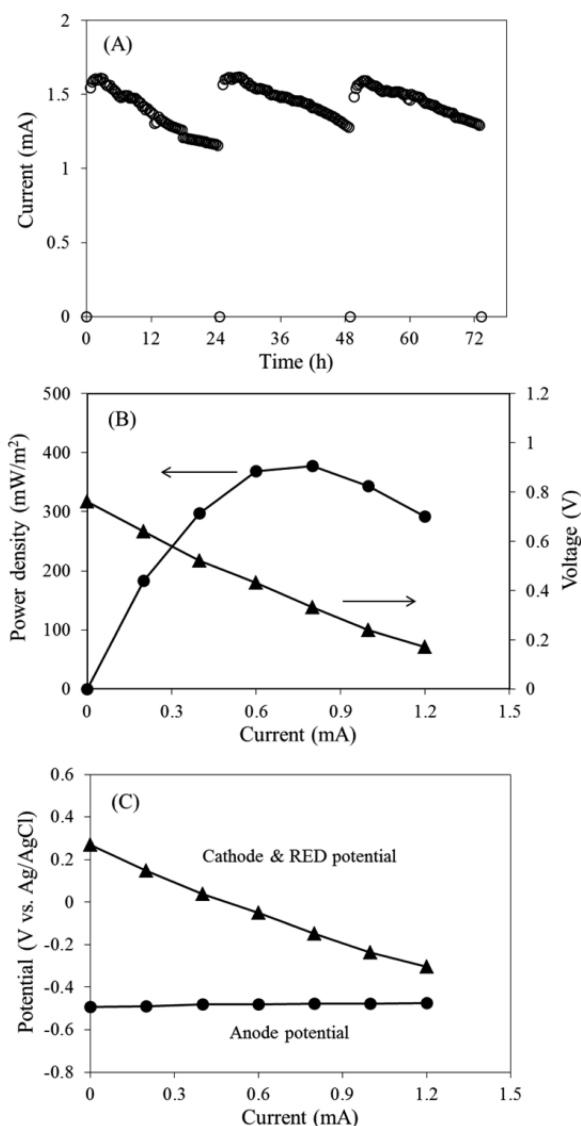

Figure 2. Current generation (A), polarization curves (B), and the anode, cathode, and RED potentials vs current (C) for the MRECC system at a salinity ratio of 100.

fed-batch cycle (24 h), likely because of an increase in internal resistance resulting from the increase in the pH of the catholyte (alkali-production chamber). The maximal power density based on polarization data was 377 ± 23 mW/m^2 (Figure 2B). The total internal resistance, derived from the slope of the polarization data, was 493 ± 16 Ω. The anode potential was very stable at −0.48 ± 0.01 V versus Ag/AgCl. The overall performance of this system was therefore limited by the

cathode and RED stack, as indicated by the decrease of the cathode and RED stack potentials from 0.27 to −0.30 V versus Ag/AgCl over a measured current range of 0−1.2 mA (Figure 2C). To produce more chemicals (acid, alkali, and H$_2$), the system was operated under peak current mode. Over a single fed-batch cycle, the pH of the solution in the acid-production chamber decreased to 1.53 ± 0.01, while the pH of the alkali-production chamber increased to 12.86 ± 0.05. The final chemical concentrations were therefore 29.7 ± 0.8 mM acid and 72.7 ± 7.9 mM base, or 0.45 ± 0.01 mmol of acid and 1.09 ± 0.02 mmol of base, respectively. H$_2$ gas production was 10.3 ± 0.7 mL over a fed-batch cycle, with a production efficiency of 73 ± 2%. These results demonstrated that the MRECC system could generate acid, base, and hydrogen gas, using only renewable energy supplied by organic matter and the salinity gradient energy, preventing the need for electrical grid power.

The current of 1.6 mA produced here was slightly lower than those previously obtained with the MRCC (3.5 mA).[17] This lower current resulted in a level of acid production for the MRECC (0.45 ± 0.01 mmol) that was lower than that obtained with the MRCC (1.35 ± 0.13 mmol).[17] This reduction in current was primarily due to the potential needed for H$_2$ evolution (E^θ = −0.828 V vs NHE, for the reaction 2H$_2$O + 2e ⇌ H$_2$ + 2OH$^-$) being larger than that needed for oxygen reduction (E^θ = 0.401 V vs NHE, for the reaction O$_2$ + 2H$_2$O + 4e ⇌ 4OH$^-$).[24] Adding additional membranes to the RED stack would increase this current density.[25−27]

The main advantage of the new MRECC design for chemical production, relative to CO$_2$ sequestration, was substantially improved alkali production. The overall efficiency of current conversion to base production increased to 86 ± 13%, compared to 25 ± 3% in the earlier MRCC reactors.[17] This improvement could result from the change in the cathode reaction from oxygen reduction to hydrogen gas production. Therefore, the amount of base produced in the MRECC (1.09 ± 0.02 mmol) was much higher than that produced in the previous MRCC (0.59 ± 0.14 mmol) even though less current was generated. The recovery of an amount of alkali greater than that obtained using the MRCC[17] avoids the need for purchasing additional alkali that would be needed for the final CO$_2$ sequestration process.

Serpentine particles dissolved in the acid solution obtained from a single MRECC cycle produced a leachate containing 863 ± 38 mg/L of Mg^{2+} and 347 ± 56 mg/L of Ca^{2+}. These concentrations were 17 times (Mg^{2+}) and 87 times (Ca^{2+}) higher than those of the controls (51 ± 4 mg/L Mg^{2+} and 4 ± 1 mg/L Ca^{2+}, respectively, with 0.35 g/L NaCl, pH 6.8 ± 0.1). The leachate was filtered, and the pH was adjusted to 9.8 ± 0.3 using part of the alkali solution produced by the MRECC in a sealed bottle filled with a headspace of 99.99% CO$_2$. The pH decreased to ∼6 due to the absorption of 9.3 ± 1.6 mL of CO$_2$, resulting in the formation of Mg and Ca carbonates. Although essentially pure CO$_2$ was used here, more dilute CO$_2$ sources such as combustion gases could also be used. The rest of the alkali solution was then added to increase the solution pH to ∼11 and precipitate the carbonates, producing 12.5 ± 1.1 mg of solids.

Crystals of the solids analyzed by XRD (Figure 3) were shown to contain ∼78% magnesium and calcium carbonates (such as calcite, hydromagnesite, and nesquehonite) and ∼22% brucite. If the CO$_2$ gas released in the anode chamber (measured by a headspace syringe to be approximately 0.8−1 mL) is included in the carbon balance, the net absorbed CO$_2$ of
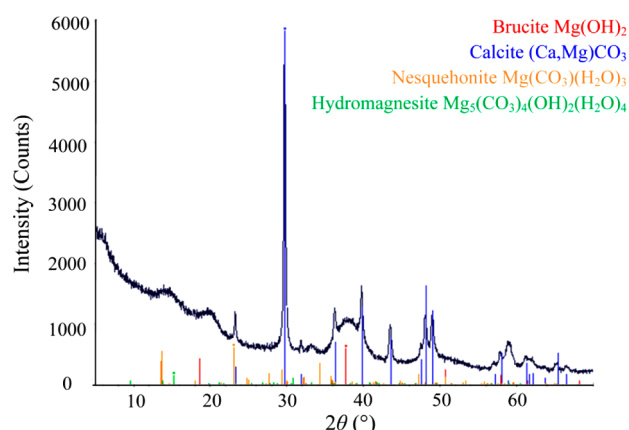
Figure 3. XRD graph for produced magnesium and calcium carbonates.

this system was nearly 8 mL (i.e., almost 16 mg of CO_2 based on a molar volume of an ideal gas of 22.4 L) and the net CO_2 fixed as carbonates was approximately 4 mg over a fed-batch cycle.

A comparison of these CO_2 sequestration results with those previously obtained using a MEDCC[16] shows that the overall performance was slightly reduced due to lower levels of acid and alkali production, resulting in 15−40% decreases in mineral dissolution rates, ∼33% less CO_2 absorbed, and ∼70% less solids produced. However, the external power at 1 V needed for the MEDCC would require 5.72×10^{-5} kWh of electric grid energy over a fed-batch cycle, resulting in an estimated cost of $286 just for the electricity needed to fix 1 metric ton of CO_2.[16] In contrast, the MRECC operated using renewable energy derived from organic matter and a salinity gradient. There are abundant organics in wastewaters (food processing, animal, and domestic) containing nearly 17 GW of energy.[28] Worldwide, there is ∼1.7 TW of energy available from salinity gradients derived from seawater and river water.[29] Substantial energy is also available from salinity gradients generated using waste heat and thermolytic solutions.[22,30] Thus, it should be possible to tap into these available energy sources for MRECC operation.

The operating costs of the MRECC system mainly include mineral mining and grinding costs, and water pumping costs. The digging and grinding cost for typical ores (e.g., copper) was estimated to be approximately $4/ton.[5] Because theoretically 2.3 tons of serpentine is required to bind 1 ton of CO_2,[5] these costs are estimated to be $9.2/ton of CO_2. Energy losses for pumping through the membrane stack are estimated to be 4×10^{-5} W based on a head loss of ∼15 cm.[19] For a 24 h fed-batch cycle, this energy consumption for pumping would be 9.6×10^{-7} kWh. If this power was produced by electrical grid energy ($0.065 kWh^{-1}), it would cost $15.6/ton of CO_2, although the H_2 gas produced by the MRECC could be used to produce this power. On the basis of only the ore and pumping costs, the operational cost would be approximately $25 to fix 1 metric ton of CO_2 as solid carbonates. This cost is lower than the cost of other more developed technologies for CO_2 sequestration (more than $65/metric ton of CO_2).[31−33] However, our estimate does not include capital and other operating costs (e.g., reactor maintenance) for the MRECC, and these estimates are based on a small laboratory-scale reactor. If the H_2 generated was not used for power generation, its value as a product gas of approximately $550/ton of CO_2 (assuming 2.5×10^3 m^3 of H_2 produced/ton of CO_2, and a

value of $2.5/kg of H_2) would well offset these operational costs for CO_2 sequestration. In addition, there would be added economic benefits using wastewater as the source of the organics.

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Notes

The authors declare no competing financial interest.

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234

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