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CO₂ extraction from seawater using bipolar membrane electro dialysis†

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An efficient method for extracting the dissolved CO₂ in the oceans would effectively enable the separation of CO₂ from the atmosphere without the need to process large volumes of air, and could provide a key step in the synthesis of renewable, carbon-neutral liquid fuels. While the extraction of CO₂ from seawater has been previously demonstrated, many challenges remain, including slow extraction rates and poor CO₂ selectivity, among others. Here we describe a novel solution to these challenges – efficient CO₂ extraction from seawater using bipolar membrane electro dialysis (BPMED). We characterize the performance of a custom designed and built CO₂-from-seawater prototype, demonstrating the ability to extract 59% of the total dissolved inorganic carbon from seawater as CO₂ gas with an electrochemical energy consumption of 242 kJ mol⁻¹(CO₂).

Introduction

The separation of CO₂ from any mixed-gas source typically involves two steps: (1) the selective capture of CO₂, usually accomplished by contacting the CO₂-containing mixed-gas source with a solid or liquid adsorber/absorber; and (2) the desorption of pure CO₂ gas from the adsorber/absorber.^{1,2} In previous experiments, our lab investigated the use of bipolar membrane electro dialysis (BPMED) for CO₂ desorption from potassium carbonate and bicarbonate solutions at ambient

pressure³ and elevated pressures as high as 10 atm.⁴ The electro dialytic desorption of CO₂ gas from aqueous solutions has the potential to improve the efficiency of CO₂ separation from a wide array of mixed gas sources, including power-plant flue-gas^{5,6,7} and the atmosphere.^{3,4,8,9,10,11}

For such capture/desorption systems, the volume of gas that must be processed scales inversely with the concentration of CO₂ in the mixed-gas source, adding significant challenges to the separation of CO₂ from dilute sources such as the atmosphere.^{12,13} One way around this problem is to notice that the CO₂ in the atmosphere establishes equilibrium with the total dissolved inorganic carbon (DIC) in the oceans,[§] which is largely in the form of bicarbonate ions (HCO₃⁻) at the ocean pH of 8.1–8.3.^{14,15} This means that an efficient method for extracting CO₂ from the DIC of the oceans would effectively enable the separation of CO₂ from atmosphere without the need to process large volumes of air.

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† Electronic supplementary information (ESI) available: details of the membrane contactor efficiency measurement, numerical values for the data plotted in Fig. 3, and details of the calculation of CO₂ extraction efficiency. See DOI: 10.1039/c2ee03393c

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§ The total dissolved inorganic carbon (DIC) is given by DIC = [CO₂] + [HCO₃⁻] + [CO₃²⁻], where [CO₂] = [CO₂(aq)] + [H₂CO₃].^{14,15}

Broader context

The efficient separation of CO₂ from the atmosphere would be a transformational technology, enabling direct reduction of the atmospheric CO₂ concentration, the mitigation of CO₂ emissions from “mobile emitters” such as the transportation sector, and the synthesis of carbon-neutral liquid fuels. One of the primary challenges, however, is the large volume of air that must be processed. The equilibrium between atmospheric CO₂ and the dissolved inorganic carbon (DIC) of the oceans implies that an efficient method for extracting CO₂ from the DIC of the oceans would effectively enable the separation of CO₂ from atmosphere without the need to process large volumes of air. We describe a novel technique for extracting CO₂ gas from the DIC of seawater and reverse osmosis brine solutions using bipolar membrane electro dialysis (BPMED). Seawater is pumped through a BPMED system and results in two output streams: acidified and basified seawater. In the acidified stream, the HCO₃⁻ and CO₃²⁻ ions in the input seawater area converted into dissolved CO₂, which is subsequently vacuum stripped, producing a stream of pure CO₂ gas. The CO₂-depleted acidified solution can then be combined with the basified solution, creating a neutral-pH solution that can be returned to the ocean.

One of the most attractive uses for CO₂ extracted from the ocean is the synthesis of a renewable, carbon-neutral liquid fuel *via* reaction of the extracted CO₂ with H₂.^{16,17,18} If the entire process (CO₂ extraction, H₂ generation, and fuel synthesis) is powered using a carbon-neutral source such as wind, solar, or nuclear, then no net CO₂ is emitted into the atmosphere during the combustion of the synthesized fuel. While cost estimates suggest that fuel produced in this way could be cost-competitive in the commercial market in the near future,¹⁹ this process also represents a very attractive possibility for on-site, on-demand fuel synthesis at sea for military applications,^{19,20} and for remote communities or research stations.²¹ We note that CO₂ extracted from seawater can also be used as an enriched CO₂ source in the synthesis of renewable, carbon-neutral algal biofuels.²² It is important to note that for both the non-biological^{16,18} and biological²² routes to liquid fuel synthesis, CO₂ separation from the atmosphere (in this case indirectly through the extraction of CO₂ from seawater) allows a truly carbon-neutral fuel, in contrast to CO₂ separated from flue-gas, which could produce a fuel with reduced, but not zero, net CO₂ emissions.

Previous investigations have demonstrated the extraction of CO₂ from the DIC in seawater,^{23,24,25} but challenges remain, including slow extraction rates for membrane-based extraction without acidification,²³ poor selectivity of CO₂-containing ions for ion-exchange approaches without acidification,²⁴ and the need for water with low conductivity and hardness (such as deionized (DI) water) for ion-exchange approaches with acidification.²⁵

In this article, we describe a novel approach to these challenges – efficient CO₂ extraction from seawater using BPMED.²⁶ Seawater is pumped through a BPMED system, resulting in two output streams: acidified seawater and basified seawater. In the acidified stream, the HCO₃⁻ and CO₃²⁻ ions in the input seawater area converted into dissolved CO₂, which is subsequently vacuum stripped, producing a stream of pure CO₂ gas. The CO₂-depleted acidified solution can then be combined with the basified solution, creating a neutral-pH solution that can be returned to the ocean.

Experimental methodology

Setup and equipment

Fig. 1 shows a schematic and labelled photograph of the experimental setup. A BPMED unit consisting of a nine-cell

membrane stack that converts input seawater into two separate output streams: acidified seawater and basified seawater. CO₂ gas is vacuum stripped from the acid solution using commercial membrane contactors (two Liqui-Cel® X50 fibre type 2.5 × 8 membrane contactors from Membrana-Charlotte), and then the acid and base output solutions are recombined into a neutral-pH waste solution. The input seawater flow is divided so that some flows through the acid compartment of the BPMED unit and the remainder flows through the base compartment, while electrode solution is pumped through both the anode and cathode compartments. Any gases present in the anode and cathode output solutions are separately vented before recombining the solutions in the electrode solution tank. Variable pumps (IDNM 3534 motor and VSIMX Microdrive, Baldor Electric Company) and valves are used to control the flow rate and pressure of seawater and electrode solution. Balancing the pressure among all the compartments in the BPMED unit is crucial to avoiding mechanical damage to the BPMED membrane stack and the unwanted mixing of different solution streams within the membrane stack.

We measure and automatically record with control software the following experimental parameters every 5 s: current, voltage, solution flow rates, solution pH values, pressure in each compartment, and the CO₂ flow rate. A programmable DC power supply (XHR40-25, Xantrex Technology, Inc.) is used to supply constant current. The sensors include (all from Omega Engineering, Inc.): FP5603 for measuring liquid solution flow rates, FMA1620A for CO₂ gas flow rate, pressure sensor PX 309, and pH sensor PHE-4581.

Fig. 2 shows the custom-designed BPMED unit in more detail. The unit consists of nine cells in series, with each cell consisting of: a basified solution compartment, a bipolar membrane (BPM, Neosepta BP-1E, Ameridia Corp.) an acidified solution compartment, and an anion exchange membrane (AEM, Neosepta ACS, Ameridia Corp.). At each end of the membrane stack, a cation exchange membrane (CEM, Neosepta CMX-S, Ameridia Corp.) is used to separate the membrane stack from electrode compartment. Broadly speaking, under an applied voltage, water dissociation inside the BPM and the ion-selective membranes comprising a BPM will result in the transport of H⁺ ions from one side of a BPM, and OH⁻ ions from the opposite side. AEMs/CEMs, as their names suggest, only allow the transport of negatively/positively charged ions through the

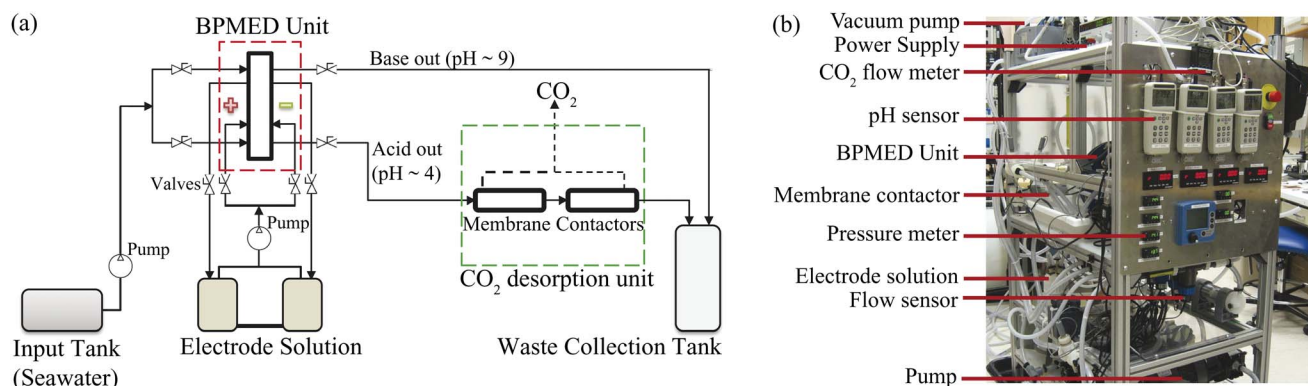


Fig. 1 (a) Schematic of the experimental setup. BPMED = bipolar membrane electro dialysis. (b) Photo of experimental setup.

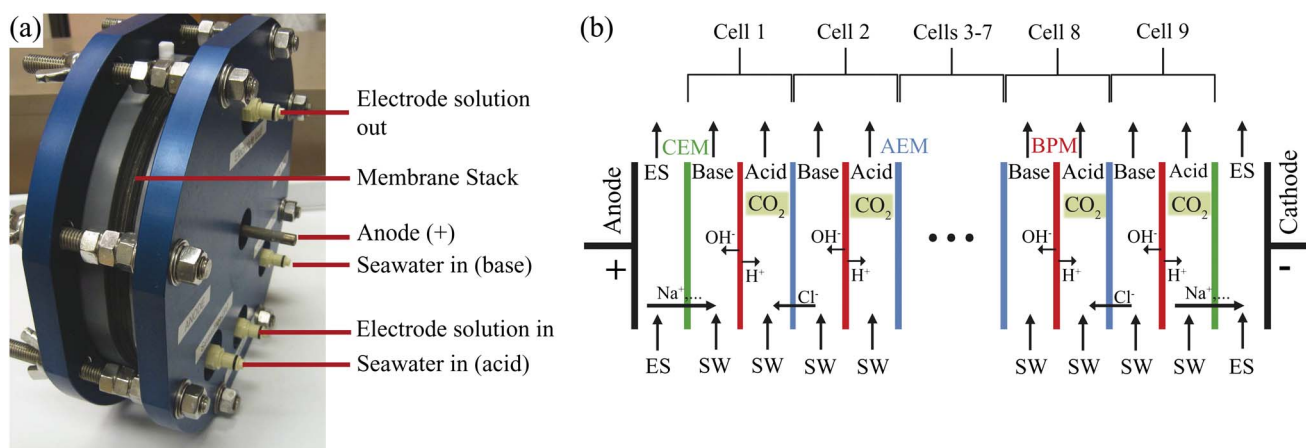


Fig. 2 (a) Picture and (b) schematic of the CO₂-from-seawater BPMED unit. ES = electrode solution, SW = seawater, CEM = cation exchange membrane, AEM = anion exchange membrane, BPM = bipolar membrane. In panel (a), the opposite side of the unit that is not visible contains the cathode (–), Electrode solution in and out for the cathode, Seawater out (acid), and Seawater out (base).

membrane.²⁷ The properties of these membranes, such as electrical resistance, burst strength, and thickness are provided by the manufacturer;²⁸ the Neosepta ACS and CMX-S are monovalent-anion and monovalent-cation permselective membranes, respectively. The electrodes are titanium with an iridium-ruthenium based coating (custom electrodes, De Nora Tech Inc.). The solution compartments between adjacent membranes are filled with 762 μm thick polyethylene mesh spacers, and these compartments are sealed against leaks using axial pressure and 794 μm thick EPDM rubber gaskets. Each membrane has an active area of 180 cm². The next section describes in detail how this system extracts CO₂ from seawater.

Procedure

The experiments described below are all continuous, “flow-through” experiments (in contrast to batch mode) in which each volume element of seawater passes through the system exactly once. For each experiment, constant flow rates are chosen for the acid, base, and electrode solutions. Depending on these flow rates and the Faradaic efficiency of the BPMED process, a constant current value is chosen that will result in the desired pH for the output acid solution. Acid and base flow rates of 3.1 lpm, 3.6 lpm, 4.1 lpm, and 6 lpm and acid output pH values in the range 3–6 were investigated in the experiments described below. A membrane stack consisting of nine cells (a shown in Fig. 2b) was used for all experiments described below, except for the 6 lpm seawater experiment, for which an eight-cell membrane stack was used.

The input seawater solutions are prepared by adding 35.95g of Instant Ocean® sea salt per litre of DI water. The electrode tanks are filled with a 0.1M H₂SO₄/0.25M Na₂SO₄ solution (solutes were ACS reagent grade, purchased from Sigma-Aldrich). For some experiments (labelled “RO” in Fig. 3, a solution with twice the ionic concentration of seawater – 71.9 g of Instant Ocean® sea salt per litre of DI water – was used in order to mimic a typical reverse osmosis (RO) brine solution).

Once the seawater and electrode solutions are prepared and loaded into the input solution tank and electrode solutions tanks,

respectively, the pumps and flow-control are adjusted to achieve the desired solution flow rates and pressures. The seawater and electrode solutions are started flowing together to prevent pressure drops between different compartments. The degassing vacuum pump is turned on, with its output initially venting to atmosphere. After the initial turn-on, the output of the degassing vacuum pump is directed through the CO₂ flow meter in order to measure the rate of CO₂ extraction. The rate measured by the CO₂ flow meter before current is applied to the BPMED unit is recorded to determine the flow-meter offset, and this value is subtracted from the recorded flow rate during operation to calculate the net CO₂ extraction. The power supply is then connected to the BPMED-unit electrodes and the software is used to set a constant-current value, at which point the pH of the acid solution begins to drop and the pH of the base solution begins to rise. As the acid solution pH drops, the rate of CO₂ gas extraction increases until the solution pH values and the CO₂ extraction rate reach steady-state values. The experiment is run and data is recorded until we observe a constant acid pH reading for 15 s (3 data points, with each data recorded every 5 s). These last three data points, for which the value of the acid output pH is constant, are averaged to obtain the measured value shown in Fig. 3. After each experiment, the acid and base compartments are rinsed with seawater to remove any residual acidic or basic solutions from the BPMED membrane stack that might influence the data for the next experiments.

The value of constant current for a given experiment is chosen to achieve a desired end-pH value for the output acid solution, given the other experimental parameters such as solution flow rate and Faradaic efficiency. For each of the solution flow rates studied in our experiments, several constant-current experiments were performed, with the current chosen to achieve output acid solution pH values in the range of 3–6.

When a voltage is applied across the BPMED stack, and the current density exceeds the limiting current density for the BPM (typically < 10 mA cm⁻²), water dissociation is induced in the BPM, producing H⁺ and OH⁻ ions which move in the applied field (H⁺ toward the negatively-charged cathode, and OH⁻ toward the positively-charged anode). A theoretical minimum

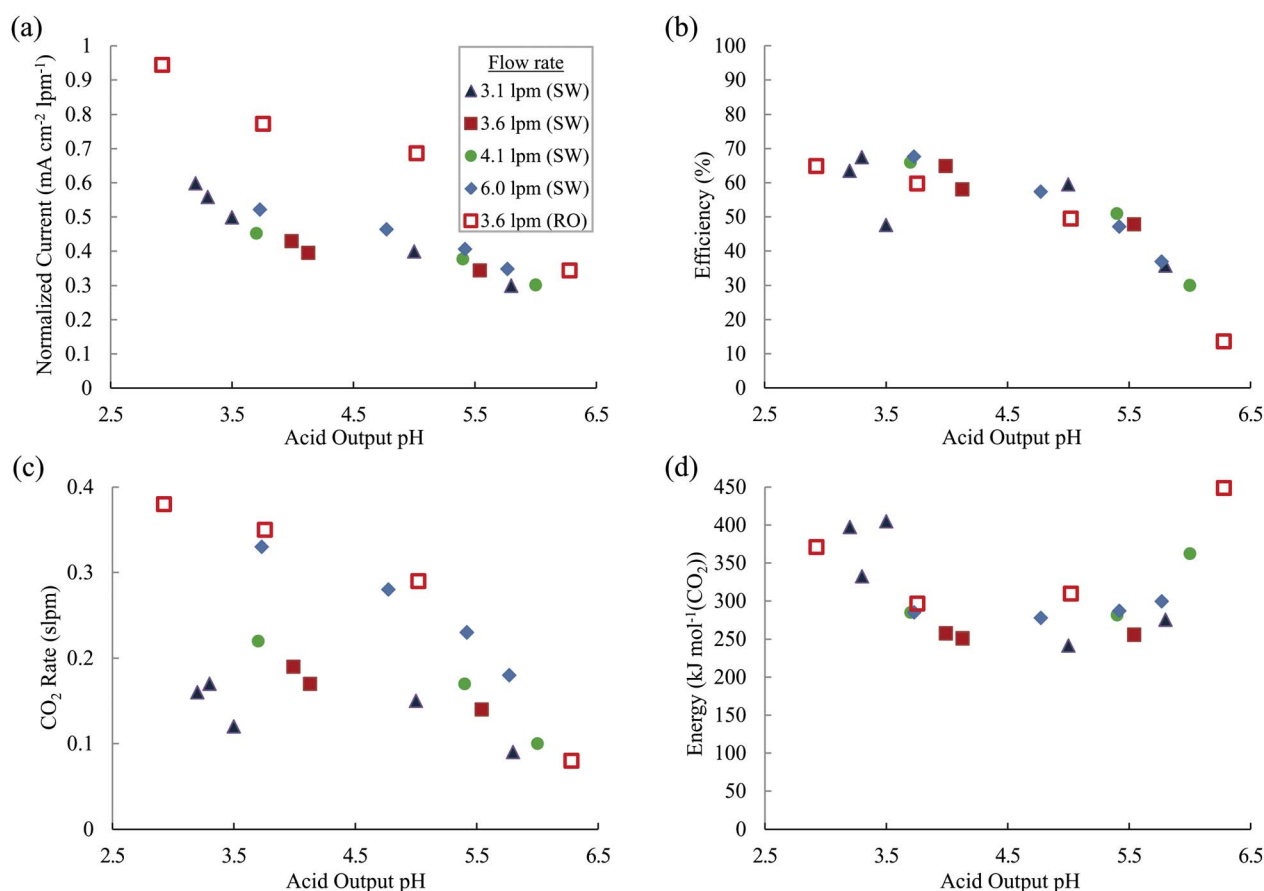


Fig. 3 CO_2 -from-seawater prototype performance. (a) Normalized current density (total current per total active membrane area per acid solution flow rate in units of $\text{mA cm}^{-2} \text{lpm}^{-1}$), (b) Efficiency of CO_2 extraction, (c) CO_2 flow rate (slpm), and (d) Energy ($\text{kJ mol}^{-1}(\text{CO}_2)$) as functions of the pH of the output acid solution for various solutions and flow rates.

polarization of 0.83 V per BPM is required to induce significant water dissociation at room temperature, with higher voltages required at higher current densities.²⁷ From Fig. 2b, we see that the dissociation of water in the BPMs results in acidification (from H^+ ions) and basification (from OH^- ions) of alternating compartments in the BPMED membrane stack. Adjacent to each BPM is an AEM that allows anions in the input seawater (primarily Cl^- ions) to be transported across the membrane towards the positively-charged anode. In this way, the combined action of the BPMs and AEMs under the applied voltage is to add H^+ ions and Cl^- ions to the acidified compartments, and to replace Cl^- ions with OH^- ions in the basified compartments. At each end of the membrane stack is a CEM that separates the alternating stack of BPMs and AEMs from the electrode compartments. As shown in Fig. 2b, this means that Na^+ and other cations from the anode compartment are transported across a CEM from the anode compartment into the adjacent base compartment, and that Na^+ and other cations are transported across a CEM from the acid compartment adjacent to the cathode compartment into the cathode compartment.

As is well known, increasing the H^+ ion concentration of seawater shifts the equilibrium of the carbonate buffer system (*via* the reactions $\text{CO}_3^{2-} + 2\text{H}^+ \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \rightleftharpoons \text{CO}_2 + \text{H}_2\text{O}$) such that most of the DIC is in the form of dissolved CO_2 for pH values less than 6 (compared to natural seawater with pH values

of 8.1–8.3, for which most of the DIC is in the form of HCO_3^- ions). Using standard equilibrium relations for seawater, one can show that at a pH of 6, 5, and 4, approximately 50%, 91% and 99% of the DIC is in the form of dissolved CO_2 .^{14,15} Given the concentration of DIC in seawater (typically 2.2–2.5 mM),¹⁴ the equilibrium between CO_2 gas dissolved in the acidified seawater and directly above the acidified solution means that the partial pressure of CO_2 gas above the solution must be less than 0.08 atm to allow continuous extraction of the dissolved CO_2 . For this reason (assuming pure CO_2 gas is desired as output, thus eliminating the possible use of a sweep gas to extract the CO_2 from solution), we use the membrane contactors and vacuum pump shown in Fig. 2 to vacuum strip the CO_2 from the acidified solution.

It is important to note that the extraction of CO_2 from seawater described in this manuscript works in a fundamentally different manner than the extraction of CO_2 from $\text{KHCO}_3/\text{K}_2\text{CO}_3$ solutions previously investigated in our lab.^{3,4} The previous work on the extraction of CO_2 from $\text{KHCO}_3/\text{K}_2\text{CO}_3$ solutions was performed for solutions with concentrations in the range of 0.125M–2M, for which HCO_3^- and CO_3^{2-} were the primary anions present in solution. In these experiments, CO_2 was extracted by transporting HCO_3^- ions and CO_3^{2-} ions across AEMs into adjacent solutions that were acidified *via* the operation of BPMs, with the HCO_3^- and CO_3^{2-} ions effectively acting

as “carrier molecules” for CO₂. The acidic solution converted the HCO₃⁻ and CO₃²⁻ into dissolved CO₂ which then bubbled out of solution.^{3,4} In contrast, the extraction of CO₂ from seawater described in this article does not involve the transport of HCO₃⁻ or CO₃²⁻ across the AEMs (see Fig. 2b). Natural seawater has a DIC concentration (typically 2.2mM–2.5mM) that is over 200 times smaller than the concentration of Cl⁻ ions (typically 546 mM),¹⁴ and therefore any process that relied on the transport of HCO₃⁻ ions across an AEM would be very inefficient since over 99.5% of the applied energy would be used to transport Cl⁻ ions, assuming similar transport properties for HCO₃⁻ and Cl⁻ ions through the membrane. Instead, the experiments described in this article acidify and basify incoming seawater in alternating compartments of the BPMED unit, using the H⁺ and OH⁻ ions that are produced on opposite sides of the BPMs. In the acidic compartments, the DIC in the input seawater is converted into dissolved CO₂ *via* the reactions CO₃²⁻ + 2H⁺ ⇌ HCO₃⁻ + H⁺ ⇌ CO₂ + H₂O, and this CO₂ is extracted by vacuum stripping. As shown in Fig. 2, as OH⁻ ions flow into the basic solution, anions are transported from the basic solution to acidic solution, and anions with the highest concentration (for example, Cl⁻) will carry a proportionally large fraction of this current across the AEM. Assuming that the fraction of current carried across the AEM by a given anion depends linearly on its concentration, one can show that for the normalized current densities used in our experiments (approximately 0.4 mA cm⁻² lpm⁻¹ as shown in Fig. 3a), only 0.07% of the DIC in the seawater input to the basified compartment is transported across the AEM into the acidic compartment. This demonstrates that the extraction of CO₂ from seawater described here does not rely on the transport of HCO₃⁻ or CO₃²⁻ across the ion-selective membranes, but rather results from the acidification of the seawater input to the acidified compartments.

Results and discussion

Experiments were performed under steady-state conditions to explore the effect of varying the acid solution output pH for different solution flow rates. Acid solution flow rates of 3.1 lpm, 3.6 lpm, 4.1 lpm, and 6 lpm were investigated in the experiments described below, with base solution flow rates equal to the acid solution rate in all cases. For a given flow rate, a constant current value was chosen to achieve a desired pH value for the output acid solution. Generally, three to five constant-current experiments were run for each acid flow rate value, yielding acid output pH values in the range 2.9–6.3. In addition to using seawater (35.95 g of Instant Ocean® sea salt per litre of DI water) as an input solution to the BPMED unit, we also tested a solution with a sea-salt concentration two times higher than the seawater solution (71.9 g of Instant Ocean® sea salt per litre of DI water, labelled as “RO” in Fig. 3). Although the concentrations of various ions in real-world RO brines vary depending on the feed solution and process conditions,^{29,30} the “RO” solution is meant to provide a representative solution to test the use of RO brine as an input to the BPMED unit.

Before starting the measurements on seawater and RO brine solutions, we first performed a series of control experiments. The first experiments compared the measured rate of CO₂ extraction for input solutions of 0.5M NaCl with: (1) a solution of 0.5M

NaCl/2.5mM NaHCO₃ (a solution with salt and bicarbonate ion concentrations very similar to that of seawater), and (2) an Instant Ocean® seawater solution (35.95 g of Instant Ocean® sea salt per litre of DI water). The CO₂ extraction rate for the 0.5M NaCl solutions was too small for our system to detect, while the extraction rates for the 0.5M NaCl/2.5mM NaHCO₃ and seawater solutions were very similar to the rates shown below in Fig. 3c for seawater solutions. In addition, for each of these input solutions, gas samples from the output ports of the membrane contactors were analysed using gas chromatography. The 0.5M NaCl/2.5mM NaHCO₃ and seawater solutions each produced a pronounced CO₂ peak that was absent in the 0.5M NaCl data, verifying that CO₂ is extracted from seawater solutions by our system. Finally, we performed a control experiment clearly demonstrating that the observed CO₂ extraction does not depend on the transport of HCO₃⁻ or CO₃²⁻ across the anion exchange membranes from the basic solution to the acidic solution. This experiment used 0.5M NaCl (with no HCO₃⁻ or CO₃²⁻ ions) as the basic solution and 0.5M NaCl/50mM NaHCO₃ as the acidic solution. Feeding these solutions into the BPMED system resulted in significant CO₂ extraction from the acid solution, demonstrating that this process does not rely on the transport of HCO₃⁻ or CO₃²⁻ ions from the basic solution to acidic solution.

We note that because no degassing of the input solution is performed prior to acidification and vacuum stripping, some N₂ and O₂ are extracted along with the CO₂. As described in the Procedure section above, the rates of N₂ and O₂ extraction would be included in the baseline offset determined for the flow meter by measuring the flow meter reading with the solution flow and vacuum pump on, but no current applied to the BPMED stack. This means that while the gas extracted by our system as described will include some O₂ and N₂ mixed in with the CO₂, the measured rate of extraction (shown in Fig. 3c) only considers the rate of CO₂ extraction. If desired, the N₂ and O₂ could be eliminated from the extracted gas mixture by adding a vacuum stripping stage prior to the BPMED unit.

Once confirming the principle of operation of our system *via* these control experiments, we moved on to characterize the performance of this system for CO₂ extraction from seawater and RO brine solutions. Fig. 3 shows measured values of normalized current density (total current per total active membrane area per acid solution flow rate in units of mA cm⁻² lpm⁻¹) (Fig. 3a), efficiency of CO₂ extraction (Fig. 3b), CO₂ flow rate (slpm) (Fig. 3c), and energy (kJ mol⁻¹ (CO₂)) (Fig. 3d) as functions of the pH of the output acid solution for constant-current, constant-flow-rate experiments for seawater input at flow rates of 3.1 lpm, 3.6 lpm, 4.1 lpm, and 6 lpm and RO brine input at a flow rate of 3.6 lpm.

From Fig. 3a we see that the normalized current density required to acidify seawater to a given pH value is the same for different flow rates in the range 3.1 lpm–6 lpm. This makes sense, since normalizing the total applied current by the total membrane area and volumetric flow rate means that the normalized current density (as defined here) required to achieve a given pH should only depend on the ionic composition of the input solution. The data from Fig. 3a support this assertion, both in the fact that the seawater data at all flow rates collapse onto a single curve, and the fact that the “RO” solution requires

a much higher normalized current density to achieve a given pH because the concentration is twice that of the seawater solution.

Fig. 3b shows the CO₂ extraction efficiency as a function of the pH of the acid solution. We define this efficiency as the measured rate of CO₂ extraction divided by the rate at which DIC§ flows through the acid compartment of the BPMED unit (see ESI,† Section S3).

We performed separate tests of the membrane contactors in order to optimize the membrane contactor efficiency (measured rate of CO₂(g) extracted divided by rate at which CO₂(aq) is flowed through the contactor *via* the input solution) as a function of the solution flow rate (see ESI,† Section S1). Our measurements indicated that the membrane contactors (Liqui-Cel® X50 fibre type 2.5 × 8 membrane contactors from Membrana-Charlotte) extracted dissolved CO₂ gas from solution most efficiently for flow rates in the range 3.75 lpm–5 lpm, with relatively decreased efficiency at lower (2.5 lpm and 3 lpm) and higher (6.25 lpm) flow rates. For the optimum flow-rate range of 3.75 lpm–5 lpm, we found that one, two, and three passes through a membrane contactor gave an extraction efficiency of about 33%, 60%, and 75%, respectively. Based on these results, and the need to minimize pressure imbalances in the system, we chose to use two membrane contactors connected in series for the prototype used for the experiments described in this paper (see Fig. 1).

Fig. 3c shows the rate of CO₂ extraction (in slpm) as a function of the pH of the acid solution. This rate depends on the DIC§ in the input solution, the flow rate of the input solution, the pH of the acid solution (which determines the fraction of HCO₃⁻ and CO₃⁽²⁻⁾ in the input solution that is converted into CO₂(aq), and depends on the applied current density and the Faradaic efficiency of the electrodialysis process), and the efficiency with which the membrane contactors extract CO₂(aq) from solution. From Fig. 3c we see that for a given input solution at a fixed acid pH value (and therefore a fixed concentration of CO₂(aq)), the rate of CO₂ extraction increases with increasing flow rate due to the increasing rate of CO₂(aq) flowing through the membrane contactors. It is important to note, however, that the CO₂ extraction rate shown in Fig. 3c doesn't simply scale linearly with solution flow rate for a fixed solution and pH value due to the dependence of membrane contactor extraction efficiency on flow rate (see ESI,† Section S1). We also note that the CO₂ extraction rate for our "RO" solution flowed at 3.6 lpm is approximately equal to that of the seawater solution flowed at 6 lpm because the DIC§ of the RO brine solution is twice that of the seawater solution.

Finally, Fig. 3d shows the energy of CO₂ extraction in kJ mol⁻¹(CO₂). The energy plotted in Fig. 3d is calculated by multiplying the current times the voltage to yield the applied power, dividing the result by the measured rate of CO₂ extraction shown in Fig. 3c, and converting the units to kJ mol⁻¹(CO₂). As such, this energy represents the electrochemical energy that must be applied to the BPMED unit to acidify the incoming solution to the desired pH, and does not include the energy required to pump the seawater solution through the system or the energy needed to vacuum strip CO₂ from the acidified seawater. Additionally, the energy shown in Fig. 3d was calculated using the total voltage measured over the entire nine-cell BPMED membrane stack, including the contribution from the end

electrodes. Previous measurements in our lab have shown that approximately 30% of the total voltage for a seven-cell BPMED unit is due to the electrodes.³ Since the fractional contribution of the electrode voltage to the total voltage scales as the inverse of the number of cells, then for a commercial-scale unit with over 100 cells, the contribution of the electrode voltage to the total voltage becomes negligible, and so we would expect a commercial-scale system to consume approximately 23% less electrochemical energy (30% × 7/9) than the data shown in Fig. 3d. The minimum energy shown in Fig. 3d (see ESI,† Table S1 for a table of numerical values) is 242 kJ mol⁻¹(CO₂) for seawater at a flow rate of 3.1 lpm acidified to pH 5 with 59% CO₂ extraction efficiency. A higher CO₂ extraction efficiency of 68% was observed for seawater at 6 lpm acidified to a pH of 3.7, with a small increase in the energy to 285 kJ mol⁻¹(CO₂).

Conclusions

We have described the design, construction, and characterization of a novel prototype for the efficient extraction of dissolved inorganic carbon from seawater as CO₂ gas using BPMED. We characterized the performance of the prototype and demonstrated the ability to extract 59% of the total dissolved inorganic carbon from seawater as CO₂ gas with an electrochemical energy consumption of 242 kJ mol⁻¹(CO₂). To put this number into context, simplistically considering the reaction of three moles of H₂ and one mole of CO₂ to form one mole of methanol (CH₃OH, LHV = 644 kJ mol⁻¹)³¹ with an overall energy storage efficiency of 20%, the CO₂ extraction energy of 242 kJ mol⁻¹(CO₂) represents only 7.5% of the required energy input.

This technology has the potential for significant impact in a wide range of fields, including CO₂ mitigation and carbon-neutral liquid fuels. Importantly, BPMED is a technology that is already deployed at commercial scale for many diverse applications, and the performance of a commercial-scale CO₂-from-seawater system is expected to be even better than the results demonstrated here due to various favourable effects with the scale-up of BPMED systems, such as the reduced fractional contribution of electrode voltage to the total voltage.

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