Supplementary Information

CO_2 extraction from seawater using bipolar membrane electrodialysis

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S1. Membrane contactor efficiency

Experiments with varying seawater flow rates (2.5 to 6.25 lpm) were conducted in order to observe the effect of different flow rates on the efficiency of $CO_2(aq)$ extraction from acidified (pH 4) seawater using the membrane contactor. The membrane contactor efficiency is defined as the measured rate of $CO_2(g)$ extraction divided by the rate at which $CO_2(aq)$ is flowed through the contactors. Since we know the amount of bicarbonate and carbonate in the solution, and we know that 99% of the dissolved inorganic CO_2 is in the form $CO_2(aq)$ at pH 4, we know the concentration of $CO_2(aq)$ in the acidified solution. A Liqui-Cel® X50 fibre type 2.5x8 Membrane Contactor was used for the removal of CO_2 from the titrated seawater. The membrane contactor has an inlet and outlet for vacuum and an inlet and outlet for the liquid solution, and in this way allows the vacuum stripping of CO_2 from the acidified seawater solutions. As shown in Figure S1, the seawater flow starts from the acid tank, enters the membrane contactor through liquid inlet and exits from the liquid outlet back to the acid tank. The gas outlet is connected to the vacuum pump and then to CO_2 flow meter. The CO_2 coming out of the flow meter is released to open air. The gas inlet of the membrane contactor was kept plugged during the experiments for the optimal flow rate determination. All the experiments were performed under similar conditions using 0.5M NaCl/2.5mM $NaHCO_3$ solution. The following steps were followed for each experiment: (1) The tank was filled with 5 litres of 0.5M NaCl/2.5mM $NaHCO_3$ solution; (2) The solution was circulated through the system at the desired flow rates; (3) The vacuum pump was started (making sure the gas outlet from the pump is in bypass mode); (4) The gas outlet was connected to the CO_2 flow meter, providing a flow-meter offset measurement prior to acidification; (5) The amount of HCl required to bring the pH of the solution down to a value of 4 was added and stirred gently; (6) Stirring was stopped after the pH stopped changing; and (7) After the CO_2 flow rate dropped down to the previous level, the vacuum pump outlet was switched to bypass mode and the pump was turned off.

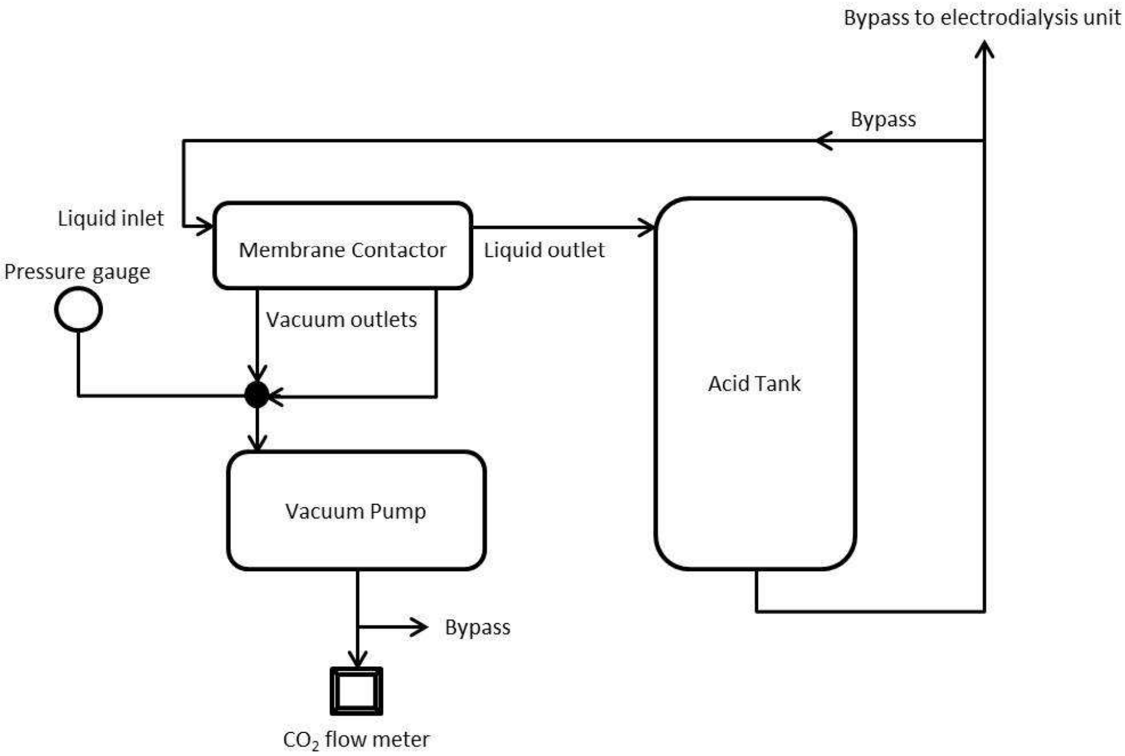

Figure S1: Schematic of experimental setup used to measure the membrane contactor efficiency.

The data for different flow conditions were analysed and the results are shown in Figure S2 in terms of the efficiency of the membrane contactor at different numbers of circulation through the contactor for varying flow rates.

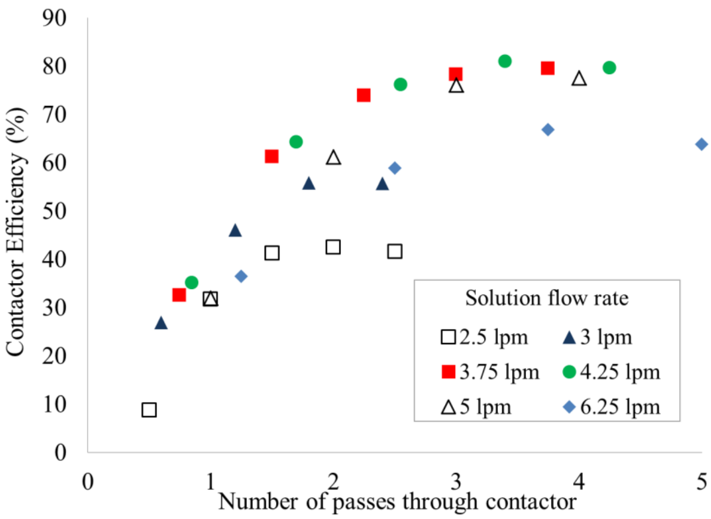

Figure S2: Membrane contactor efficiency for various solution flow rates of acidified (pH 4) 0.5M NaCl/2.5mM $NaHCO_3$ solution, versus the number of passes through the contactor.

S2. Prototype performance

Table S1 lists numerical values for the data plotted in Fig. 3.

Table S1: Numerical values for the data shown in Fig. 3.

Acid flow rate in lpm (solution type)	Acid solution pH	Normalized current density (mA cm^{-2} lpm^{-1})	Mean total voltage (V)	Efficiency (%)	CO_2 flow rate (slpm)	Energy (kJ mol^{-1}(CO_2))
3.1 (SW)	3.2	0.60	14.5	63	0.16	397
	3.3	0.56	13.8	67	0.17	332
	3.5	0.50	13.3	48	0.12	405
	5	0.40	12.4	59	0.15	242
	5.8	0.30	11.3	36	0.09	275
3.6 (SW)	4.0	0.43	13.4	65	0.19	258
	4.1	0.39	12.7	58	0.17	251
	5.5	0.34	12.3	48	0.14	256
4.1 (SW)	3.7	0.45	14.3	66	0.22	285
	5.4	0.38	13.1	51	0.17	281
	6	0.30	12.4	30	0.1	362
6 (SW)	3.7	0.52	14.3	68	0.33	285
	4.8	0.46	13.3	57	0.28	278
	5.4	0.41	12.9	47	0.23	287
	5.8	0.35	12.3	37	0.18	300
3.6 (RO)	2.9	0.94	17.6	67	0.38	371
	3.8	0.77	15.8	62	0.35	297
	5.0	0.69	15.4	51	0.29	310
	6.3	0.34	12.3	14	0.08	449

S3. Calculation of CO_2 extraction efficiency

In this section we outline the procedure used to calculate the CO_2 extraction efficiency listed in column 6 of Table S1 and plotted in Fig. 3b. We define this efficiency as the measured rate of CO_2 extraction (column 7 of Table S1 and Fig. 3c) divided by the rate of dissolved inorganic carbon (DIC = $[CO_2] + [HCO_3^-] + [CO_3^{2-}]$, where $[CO_2] = [CO_2(aq)] + [H_2CO_3]$) flowing through the BPMED unit. The rate of DIC flowing through the BPMED unit is calculated using the measured solution flow rate, the mass of Instant Ocean® sea salt used per litre of deionized (DI) water, and the reported concentration of HCO_3^- and CO_3^{2-} ions in Instant Ocean® sea salt.

The solutions labelled as "SW" in Table S1 consist of 35.95 g of Instant Ocean® sea salt per litre of DI water. Using the fact that the fraction of $HCO_3^- + CO_3^{2-}$ by weight in the salt is 0.0057,[1,2,3] a seawater density of 1.023 kg/litre,[1] a measured pH of 8.2, and the following equilibrium relations for seawater at 25C and salinity of 35 parts per thousand:[4]

$$[CO_3^{2-}]/[HCO_3^-] = 10^{-9.12}/10^{-pH} \quad (S1.1)$$

$$[CO_2]/[HCO_3^-] = 10^{-pH}/10^{-6}, \quad (S1.2)$$

we calculate a DIC concentration ($[CO_2] + [HCO_3^-] + [CO_3^{2-}]$) of 0.00334 moles/litre, and the separate concentrations of $[CO_2]$, $[HCO_3^-]$, and $[CO_3^{2-}]$ to be 0.02mM, 2.97mM, and 0.36mM, respectively. Using these same equilibrium relations and assuming the DIC stays constant, the concentrations can also be calculated as a function of pH, yielding the well-known fact that at a pH of 6, 5, and 4, the fraction of DIC contained in dissolved CO_2 is approximately 50%, 91%, and 99%, respectively. For the data in Table S1 and Fig. 3b, the efficiency is calculated by dividing the measured flow rate of extracted CO_2 gas (converted from the measured slpm to mol min^{-1} by dividing by 24.35 L mol^{-1}, the molar volume of CO_2 at 25C and 1 atm[5]) by the moles per minute of DIC flowing into the acid compartment of the BPMED unit (0.00334mol L^{-1} × solution flow rate in L min^{-1}). The solution labelled as "RO" in Table S1 and Fig. 3 consists of 71.9g of Instant Ocean® sea salt per litre of DI water, and to calculate the efficiency for this system, a DIC concentration of 0.00668 moles/litre was used.

References

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