Energy-efficient electrochemical CO_2 capture from the atmosphere

M. D. Eisaman[*], D. E. Schwartz, S. Amic, D. Larner, J. Zesch, F. Torres, and K. Littau

Palo Alto Research Center (PARC), 3333 Coyote Hill Rd., Palo Alto, CA 94304 USA,
[*]Matt.Eisaman@parc.com

ABSTRACT

We discuss our experimental progress toward energy-efficient electrochemical CO_2 capture from the atmosphere. First we discuss the latest results from an ongoing project that uses a modified-fuel-cell-based approach for CO_2 concentration [1]. Using this approach, we have demonstrated CO_2 capture from atmospheric concentrations with an energy consumption of less than 400 kJ/mol(CO_2). We also discuss progress on a second approach to electrochemical CO_2 concentration: a novel pH-controlled, high pressure electrodialysis system that allows energy-efficient, high-rate CO_2 separation from the atmosphere [2].

Keywords: carbon capture, fuel cell, electrodialysis

1 INTRODUCTION

As atmospheric CO_2 concentrations continue to increase and the effects of global warming become more obvious, developing technologies capable of decreasing the atmospheric CO_2 concentration becomes increasingly important. To achieve this goal, technologies are being pursued that produce CO_2-free power. A complementary approach is to capture the CO_2 emitted by existing power sources. The captured CO_2 can then be sequestered underground, used for industrial processes, or used as a component of synthetic fuel.

While CO_2 capture is more efficient and less costly at high concentrations, such as in the flue gas emitted by coal plants, emissions from the transportation sector account for about 28% of all CO_2 emissions in the United States [3]. The cost of carrying the captured CO_2 emitted by a vehicle prohibits the obvious solution of onboard capture. Consequently, capturing emissions from these mobile sources requires CO_2 capture directly from the atmosphere, a task made difficult by the low concentration of CO_2 in the atmosphere (0.039%).

To address this challenge, we have developed a fuel-cell concentrator capable of capturing CO_2 at atmospheric concentrations. The fuel cell, which uses hydrogen gas (H_2) as an energy source, intakes CO_2 from a low-concentration source, such as the atmosphere, and outputs it at high concentration. This concentrated CO_2 can then be combined with the already-present hydrogen to form the liquid fuel methanol, or it can be sequestered. We show that the concentrator can capture CO_2 from a source with atmospheric concentrations (400 ppm) with an energy consumption of only 350 kJ/mol(CO_2).

In addition, PARC is developing a novel electrodialysis-based CO_2 concentrator that promises to be at least as energy efficient as the fuel-cell system, but with much higher current densities. This will allow the electrodialysis concentrator to capture the CO_2 emitted by a given source using much less membrane area than the fuel cell.

This paper is organized as follows. In Section 2, we describe the structure and operation of the fuel cell and present experimental results demonstrating its performance. We also discuss the effects of the membrane and electrolyte on efficiency. In Section 3, we discuss our progress on the electrodialysis concentrator. In Section 4, we conclude with a brief evaluation of our systems in the context of real-world requirements.

2 FUEL-CELL CONCENTRATOR

2.1 Experimental Setup and Procedure

A schematic of the fuel-cell concentrator is shown in Figure 1. At its heart is a 50-cm^2 membrane sandwiched between two gas diffusion electrodes (GDEs). The membrane is wetted with an electrolyte solution and serves as a support for the transfer of ions between the electrodes. The stainless steel current collector plates of the anode and cathode also serve as gridded gas flow fields that deliver gases at known flow rates to the electrodes: H_2 at the anode and a combination of N_2, O_2 and CO_2 at the cathode. The proportion of O_2 to N_2 is maintained at the atmospheric ratio (26.8%), while the concentration of CO_2 is varied. The electrodes are electrically connected through a variable resistive load, operated in fixed-voltage mode, completing the circuit. A water cooling system maintains the cell at a

Anode		Cathode	
$H_2 \rightarrow 2H^+ + 2e^-$	A1	$1/2\,O_2 + H_2O + 2e^- \rightarrow 2OH^-$	C1
$HCO_3^- + H^+ \rightarrow H_2O + CO_2$	A2	$CO_2 + OH^- \rightarrow HCO_3^-$	C2
$CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2$	A3	$HCO_3^- + OH^- \rightarrow H_2O + CO_3^{2-}$	C3

Table 1: Electrode reactions.

constant temperature of 25° C. The CO_2 concentration of the output gas is continuously measured with a gas analyzer. The GDEs consist of 325-µm-thick carbon paper loaded with 5% (wt) polytetrafluoroethylene (PTFE). The

membrane side of each GDE is coated with carbon-particle-supported platinum catalyst. CO_2 transport in the fuel-cell concentrator is achieved by an electrochemically pumped concentration gradient. The reactions that occur at the electrodes when the cell is in operation are listed in Table 1. The creation of H^+ at the anode (A1) and OH^- at the cathode (C1) generate a pH gradient across the membrane. The CO_2 supplied at the cathode dissolves in the solution and reacts with hydroxide ions to form bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions (C2 and C3). The total solubility of dissolved CO_2 (CO_2, HCO_3^-, and CO_3^{2-}) is greater at the more basic cathode than at the more acidic anode. Thus after the HCO_3^-, and CO_3^{2-} ions diffuse to the anode, they recombine with H^+ ions to form concentrated CO_2 gas and water (A2 and A3).
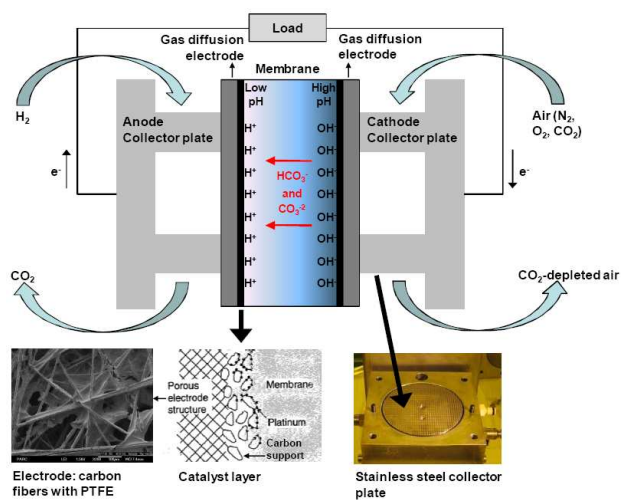

Figure 1: Schematic of a fuel-cell concentrator.

2.2 Results

Faradaic efficiency (η) is measured as the ratio of the number of CO_2 molecules transferred across the membrane to the total number of electrons transported from the cathode to the anode. The ideal efficiency of η=100% corresponds to pure HCO_3^- transport. With pure CO_3^{2-} transport, the maximum efficiency is η=50%. Efficiency is also degraded by ionic current carried by H^+ and OH^-.

In these experiments, two different membranes are used. The first is 390-μm-thick cellulose filter paper saturated with aqueous cesium carbonate (Cs_2CO_3) solution (61.5% wt/wt), which has the advantage of low cost, but no ionic selectivity. To improve efficiency by preventing H^+ transport, a 500-to-600-μm-thick fumasep® FTAM anion exchange membrane (AEM) is employed. The AEM is soaked in a 0.1-M aqueous K_2CO_3 solution for 48h.

For the filter-paper membrane, Figure 2 shows η as a function of the fraction CO_2 available to the cathode that is transported across the membrane, for several CO_2 concentrations and cell voltages. The highest efficiencies are achieved at the highest initial CO_2 concentration

(1745 ppm). However, for lower concentrations, a much higher fraction of the input CO_2 is captured.

With 3000-standard-cm^3/minute (sccm) input air containing 400 ppm CO_2 (atmospheric concentration) at the cathode, 0.16 sccm CO_2 per 50 cm^2 are transported through the fuel cell with an efficiency of 5% and energy consumption of 2170 kJ/mol. With the concentration roughly doubled to 845 ppm, 0.41 sccm CO_2 per 50 cm^2 are transported at 6% efficiency. For comparison, a NASA system for purifying cabin air using a Cs_2CO_3 solution in an asbestos matrix was able to transfer 1.52 sccm CO_2 per 50 cm^2 at 20% efficiency for 3000-sccm air containing 800 ppm CO_2 [4].
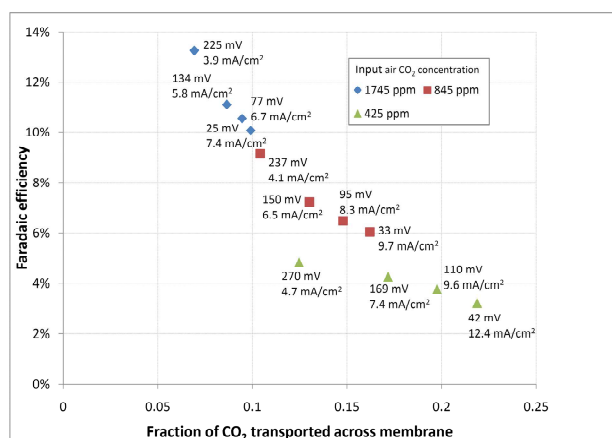

Figure 2: Results using cellulose filter paper and Cs_2CO_3.

To increase efficiency by eliminating H^+-ion transport, the filter paper is replaced with the AEM. As can be seen in Figure 3, a maximum efficiency of 50% is achieved for 3000-sccm input air with 4215 ppm CO_2, an energy consumption of 232 kJ/mol, and a CO_2 transfer rate of 0.56 sccm per 50 cm^2. This limiting efficiency likely represents pure CO_3^{2-} transport. With input air containing 400 ppm CO_2 (atmospheric concentration), 0.05 sccm of CO_2 per 50 cm^2 are transported, consuming 350 kJ/mol at 23% efficiency.

As the membranes tend to dry out when the relative humidity of the input gas is below that of the electrolyte solution, the experiments shown in Figs. 2 and 3 were performed using fully humidified gases. However, over time, this causes the gas flow fields to flood. Because of their low relative humidity, room-temperature ionic liquid (RTIL) electrolyte solutions have the potential to mitigate these limitations. In preliminary RTIL experiments, we prepare a filter-paper membrane with a 1-M cesium bicarbonate ($CsHCO_3$) electrolyte solution dissolved in 75% 1-Butyl-1-methylpyrrolidinium dicyanamide, and 25% 18-MΩ deionized water.

The negligible vapor pressure of the RTIL gives the aqueous RTIL solution a measured relative humidity of only 63% at 25° C. Furthermore, because the RTIL is a liquid phase, even if the membrane were to dry out,

remixing with water is easily accomplished. Preliminary measurements using this membrane with 400-ppm-CO_2 input air give 0.05 to 0.15 sccm per 50 cm^2 CO_2 transport, and efficiencies of 15% to 20%.
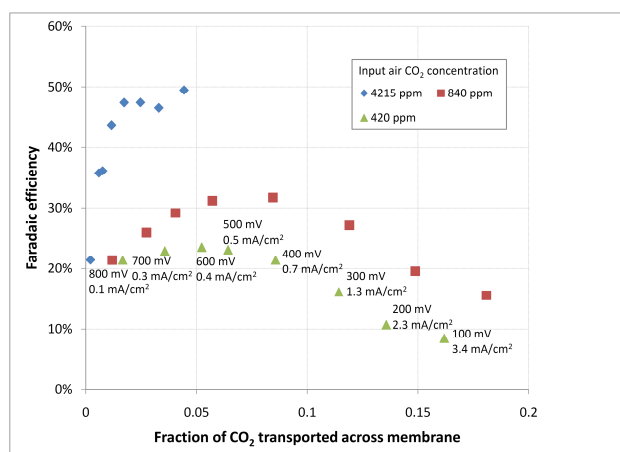

Figure 3: Results using fumasep® FTAM anion exchange membrane.

3 ELECTRODIALYSIS CONCENTRATOR

3.1 Experimental Setup and Procedure

A schematic of the proposed electrodialysis-based CO_2-capture system [2] as well as a detailed view of the bipolar membrane electrodialysis stack are shown in Figs. 4(a) and 4(b), respectively. Using well-established techniques, air is first passed through a spray tower consisting of a counter flow of a 10% to 50% aqueous K_2CO_3 solution at ambient conditions. The capture solution, loaded with CO_2, is then pressurized (10 to 100 atm, depending on conditions) and introduced into the bipolar membrane electrodialysis unit, depicted in Fig. 4(b). The bicarbonate is transferred across the anion exchange membrane to the CO_2-rich acid stream that is held at a constant pH of 3 to 4 by a combination of acidic buffers and flow-rate control. The capture solution is buffered against excessive pH increases and held at a constant pH of 8 to 10 by the presence of significant concentrations of HCO_3^- and CO_3^{2-} ions. The capture solution is regenerated by the OH^--ion flux from the bipolar membrane and by partially depleting it of HCO_3^- and CO_3^{2-} ions via electrodialysis.

The high-pressure acid stream is transferred to a gas evolution/separation tank where the pressure is reduced with concomitant release of pure CO_2. The now CO_2-depleted acid stream is returned to the electrodialysis unit via a repressurization pump while the regenerated capture solution is returned to the spray tower.

Constant monitoring of the pH of the acid and base streams ensures that the minimum possible electrical potential is used for electrodialysis, thereby optimizing the energy efficiency. We ultimately envision utilizing 100-cell electrodialysis stacks to decrease the fractional energy used for H_2/O_2 gas formation at the electrodes to 1% to 2%.
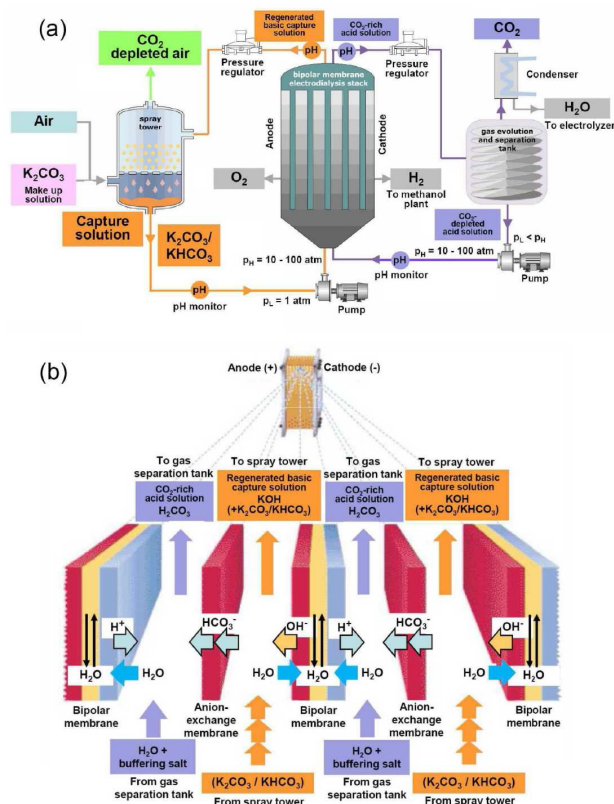

Figure 4: Schematic of the electrodialysis concentrator. (a) Atmospheric CO_2 separation using a continuous-flow electrodialysis system. (b) Detailed view of the bipolar membrane electrodialysis stack. Portions of this figure courtesy of Ameridia Corp.

Existing electrodialysis systems involving gas evolution must operate at very low concentrations to prevent in-stack gas evolution that is ultimately fatal to the system. These low concentrations lead to reduced current densities of 10 mA/cm^2 or less [5]. PARC's compact system should achieve current densities at least ten times this high (≥ 100 mA/cm^2) by operating at very high pressures (10 - 100 atm, depending on conditions), allowing increased ionic concentration without in-stack gas evolution. The ten-fold increase in current density compared to previous demonstrations means that PARC's proposed system requires ten-times less membrane area and is ten-times more compact than using existing technology to separate the same amount of CO_2. In addition, due to active control of the acid-base pH difference to ≤ 7, the PARC CO_2 capture system will consume less than half the energy of commercial electrodialysis systems.

The three key innovations in PARC's proposed solution [2] to this problem, (1) active pH control for energy efficient CO_2 concentration, (2) very high-pressure

operation for suppression of in-stack gas evolution, and (3) very high current densities in a gas-evolving system, are also the three main challenges that must be overcome. While not demonstrated in commercial electrodialysis units, active control of the acid-base pH difference to achieve energy-efficient operation is an engineering task that should be easily met via flow rate control and the use of buffers. In contrast, the demonstration of high-pressure, high-current-density operation for a gas-evolving solution has never been demonstrated.

To overcome these challenges, PARC is designing and implementing completely new electrodialysis stack architectures and membrane materials to survive high-pressure, high-current-density operation. We are concurrently investigating novel membrane designs and materials that allow higher current densities at high pressures.

3.2 Current Status and Preliminary Results

Initial experiments have investigated CO_2 concentration using a bipolar-membrane electrodialysis stack, as shown in Fig. 4(b). Implementation of the entire system shown in Fig. 4(a) will follow successful development and testing of a prototype electrodialysis stack capable of high-pressure, pH-controlled, electrodialysis-based CO_2 concentration.

CO_2 concentration tests have been performed on a bipolar membrane electrodialysis stack used in the same configuration as shown in Fig. 4(b). The stack was purchased from Ameridia Corp. and consists of 7 cells, with each membrane having an area of 200 cm^2. Since the stack is not designed for high-pressure operation, all tests using this unit must be performed at ambient pressure.

Experiments were performed using K_2CO_3 (10g/L to 100g/L) as input to the base compartment, K_3PO_4 (to provide an initial conductivity of 10 mS/cm) as input to the acid compartment, and KOH (2M) as an electrode solution. Flow rates of 140 L/hr (300 L/hr) were used for the acid and base (electrode) compartments, and the current was tuned between 15 A and 19 A. After a few minutes of operation, gas was visibly bubbling out of solution at the output of the acid compartment. This gas was collected and tested using a gas chromatograph. As soon as the gas was collected from the electrodialysis unit, the unit was shut down to prevent bubble formation inside the stack that could lead to membrane damage due to localized regions of very high current density.

The chromatograph results for the gas sample from the electrodialysis unit were compared to chromatograph analysis of bottled N_2 and CO_2, as well a sample of air. This comparison confirmed that the gas bubbling out of solution at the acid compartment output is CO_2.

Future work will involve optimizing the pH control at ambient pressure and construction and testing of a prototype electrodialysis stack capable of high-pressure operation.

4 CONCLUSIONS

Using a fuel-cell concentrator, CO_2 was concentrated from air at 400 ppm CO_2 using 350 kJ/mol(CO_2) at 23% current efficiency and a current density of 0.5 mA/cm^2. This is the most energy efficient atmospheric CO_2 capture yet demonstrated to our knowledge. However, to allow practical application of the technology, the current density must be increased. For example, combusting a gallon of gasoline produces 19.4 lbs. of CO_2 [6] and a 30-mpg car travelling at 60 mph emits 38.8 lbs. of CO_2 per hour. Capturing this CO_2 with a fuel-cell concentrator operating at 0.5 mA/cm^2 would require 2141 m^2 of membrane area.

Electrodialysis-based CO_2 concentrators may offer a solution to this problem. Preliminary analysis indicates that under realistic operating conditions, a high-pressure, pH-controlled electrodialysis concentrator [2] should be able to concentrate CO_2 from atmospheric concentrations to pure CO_2 at 1 atm using 62 kJ/mol(CO_2) at 85% current efficiency and 100 mA/cm^2. Such a system could capture the CO_2 emitted by a 30-mpg car travelling at 60 mph with only 11 m^2 of membrane. This efficient membrane utilization would allow the technology to be scaled to industrial applications. Preliminary results indicate that this technology works in principle. Research and development are continuing on a high-pressure, pH-controlled prototype optimized for CO_2 concentration that will allow application of this technology to industrial scales.

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