

Supporting Information

Carbon Dioxide Splitting using an Electro-Thermochemical Hybrid Looping Strategy

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Experimental Details

Fabrication of nanoporous Ag electrode

Nanoporous Ag cathodes were fabricated using a modified dealloying technique. In brief, a $40 \times 5 \times 5 \text{ cm}^3$ Ag-Al ingot that was synthesized using a vacuum induction process was purchased from Sophisticated Alloys, Ltd (USA). The ingot was then cut in to 25 cm^2 Ag-Al precursor sheets with thickness of $500 \mu\text{m}$ using electrical discharge machining. The precursor sheets were then annealed at $546 \text{ }^\circ\text{C}$ for 24 hours and then quenched in an ice water bath to achieve the desired phase. Subsequently, the precursor sheets were leached in dilute hydrochloric acid, rinsed several times in de-ionized water, and then immediately placed into the CO_2 electrolyzer.

Ir-catalyst coated Nafion membrane

Ir-catalyst coated membrane (Ir-CCM) anode was constructed via a hand-airbrush technique. A catalyst ink was prepared by sonicating a slurry containing commercial iridium black nanoparticles (surface area $55\text{-}65 \text{ m}^2$ per gram, Premetek Co.), Nafion solution (5 wt%, DuPont), DI water, and isopropanol. The weight ratio of catalyst to dry Nafion ionomer was 4:1. The iridium containing slurry was then sprayed on to Nafion XL that has been sandwiched between two self-adhesive Mylar laminate (DuPont) with a 25 cm^2 window. The resulting Ir-CCM anode was dried at $40 \text{ }^\circ\text{C}$ for one hour. The procedure was repeated until a catalyst loading of 1 mg cm^{-2} was achieved. After, the desired weight was obtained, the as-sprayed Ir-CCM was then hot pressed at $135 \text{ }^\circ\text{C}$ and 2 MPa for 1 min.

Operation of CO_2 electrolysis cell

The CO_2 electrolyzer was a two-compartment electrochemical flow cell which was constructed out of stainless steel and then plated with a $2 \mu\text{m}$ gold layer as shown in Figure S1. The np-Ag catalyst was used as the cathode, while the Ir-CCM was used to separate the two compartments as well as the catalyst for the anode. A CO_2 -saturated 0.5 M NaHCO_3 (99.9999%, Sigma Aldrich) aqueous electrolyte solution was fed and recirculated at a flowrate of 150 mL min^{-1} through the cathode compartment. Prior to experiments, the sodium bicarbonate solution was purified of trace metal by stirring the as-made solution with Chelex® 100 Resin (50-100 mesh, Sigma Aldrich) overnight. A gear pump (EW-74013-40, Cole-Parmer) was used to drive the electrolyte from a reservoir, through a flow meter (1XLX3, Brooks), then through an in-line CO_2 contactor, and then finally to the cathode compartment. For activity testing, CO_2 gas (Grade 5, Keen) was fed at 20 mL min^{-1} through a porous ceramic (Refractron) in a custom built in-line CO_2 contactor. To optimize single pass CO_2 conversion at 3.0 V , CO_2 gas was fed at 7.25 mL min^{-1} . The outlet stream from the electrolyzer was then fed to a gas/liquid separator. The separator was a homemade stainless steel knockout drum with a bore through union tee on the inlet and back pressure regulator on the outlet. Low solubility gases such as CO and H_2 were separated for quantification while the electrolyte was recycled back to the reservoir for continuous operation. No electrolyte was used for the anode compartment and this prevented water from crossing over from the anode to cathode that could dilute the catholyte and degrade performance. Gas products from the gas/liquid separator were fed into a 1 mL sample loop of a gas chromatograph (Shimadzu, GC- 2010) equipped with PLOT Mol Sieve 5A and Q-bond PLOT columns to confirm and separate the CO

and H₂ products. Argon (99.999%) was used as the carrier gas and a thermal conductivity detector was used for product quantification. Though in trace amounts, the production of formate was quantified using a Bruker AVIII 600 MHz NMR spectrometer. Typically, 500 μL of electrolyte was sampled at the conclusion of the electrolysis was mixed with 100 μL D₂O, and 1.67 ppm (m/m) dimethyl sulphoxide (≥99.9%, Alfa Aesar) was added as the internal standard. The one-dimensional ¹H spectrum was measured with water suppression using a pre-saturation method. An Autolab PGSTAT128N potentiostat with a 10-amp booster was used for constant potential experiments.

To regenerate the Ir-CMM, the used membrane was soaked in 0.05 M sulfuric acid for 3 hours and subsequently washed with DI water. The membrane was then placed back into the CO₂ electrolyzer for further testing.

Structural Characterization

A Zeiss Auriga-60 scanning electron microscopy (SEM) setup was used to image the surface morphology of the np-Ag catalyst and Ir-CCM. A Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer (XPS) System was used to analyze the surface composition of the np-Ag catalyst before and after CO₂ electrolysis.

Operation of CO catalytic bed reactor

The reactor assembly (Figure S4) consisted of 5 parts: the reactor chamber which was fabricated from Aluminum Bronze 614, tee sections on either side of the reactor, ball valves at each end, servicing assembly, and a carbon/catalyst receiving assembly. A “clamp shell” type furnace was used to heat up the reactor chamber to 500 °C. During operation, CO was fed to the reactor chamber through a tee valve at one end. CO decomposed into elemental C and CO₂ within the reactor chamber. Carbon was retained, while CO₂ exited the other tee valve on the other end. The ball valves at either end of the tee valves sealed the whole reactor assembly during operation. After reaction, the servicing assembly consisted of a ram was attached. The ball valves were opened, and the ram was used to push the carbon/catalyst material out of the reactor into the receiving assembly. New catalyst materials were loaded in a similar manner. GMT grade 0 steel wool was dipped in 10 vol% acetic acid solution for 3 min followed by rinsing with DI water and air drying prior to being loaded into the reactor chamber for testing. In addition, a recuperative heat exchanger was connected to the reactor chamber to heat the inlet gaseous stream with the hot outlet gaseous stream. The power of the furnace and the temperature were controlled by a furnace controller (Mellen). A custom-built data acquisition system recorded the temperatures and pressures within the reactor assembly. The CO₂ concentration of the outlet stream was continuously monitored with an infrared carbon dioxide analyzer (GD-888, CEA Instruments, Inc.) with a reading resolution of 0.1% and accuracy of ±5%.

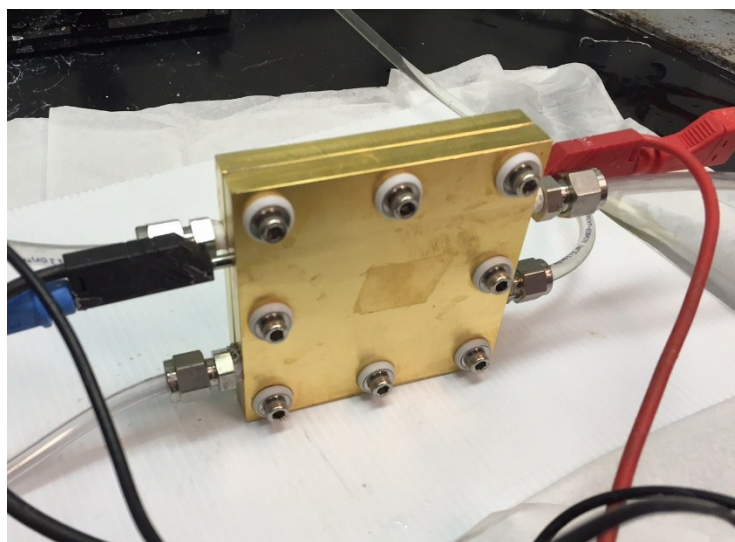


Figure S1. Photograph of CO₂ electrolysis cell.

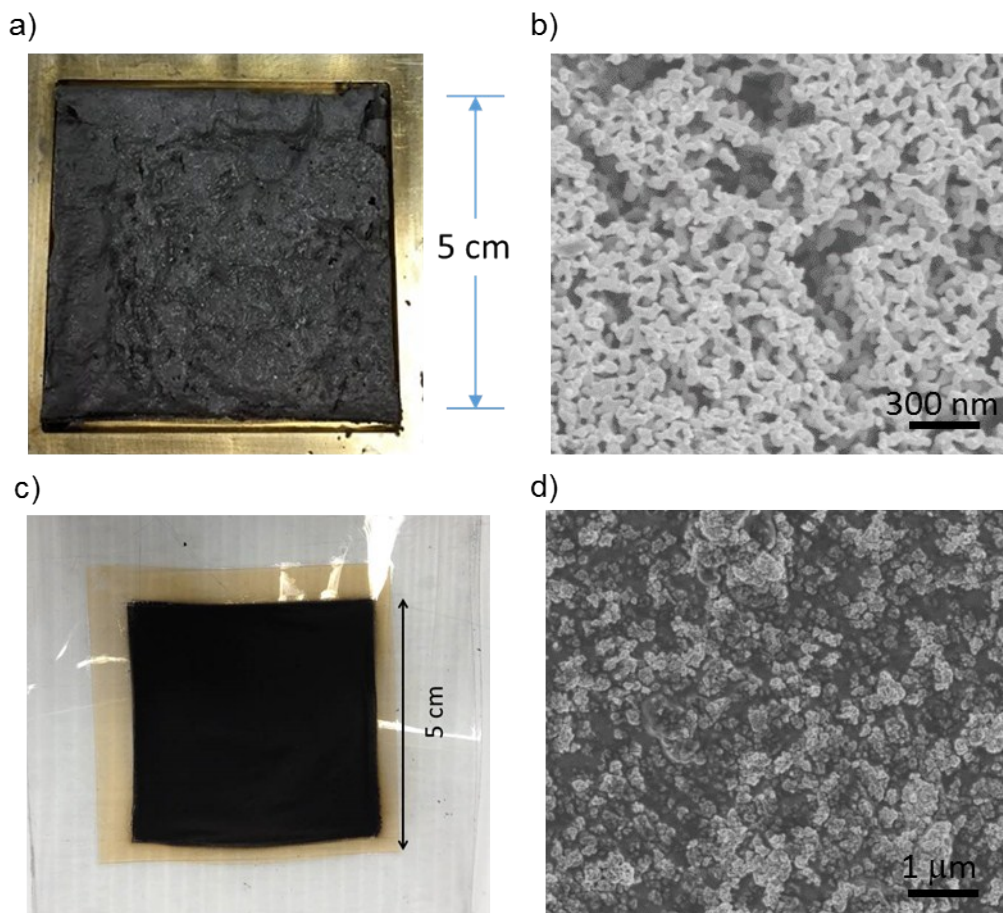


Figure S2. CO₂ electrolyzer electrodes. a) Photograph and b) SEM images of the as-synthesized np-Ag catalyst. c) Photograph and d) SEM images of the iridium catalyst coated membrane.

a)



b)

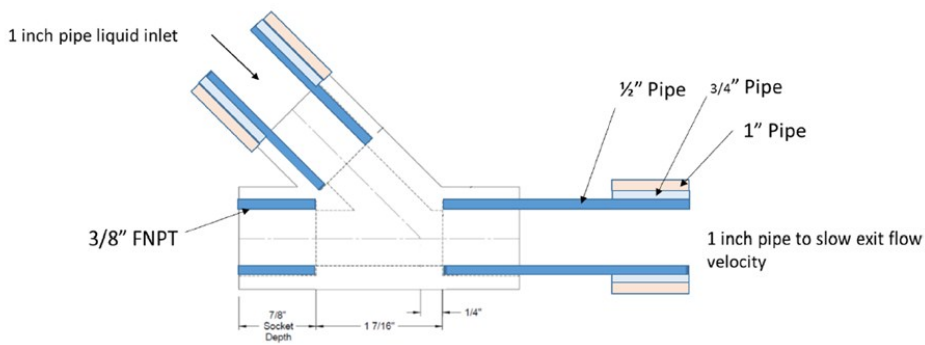


Figure S3. a) Photograph and b) schematic of the in-line CO₂ contactor.

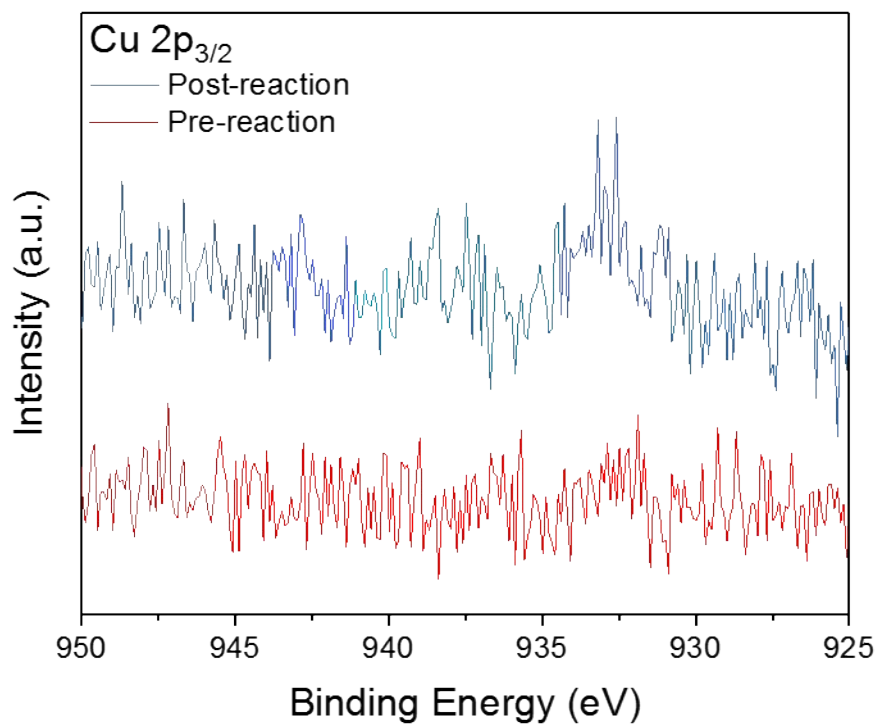
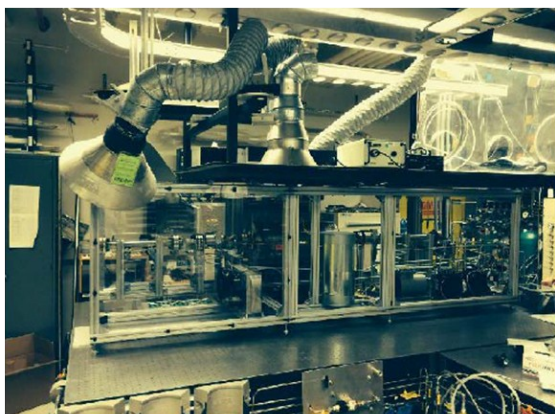
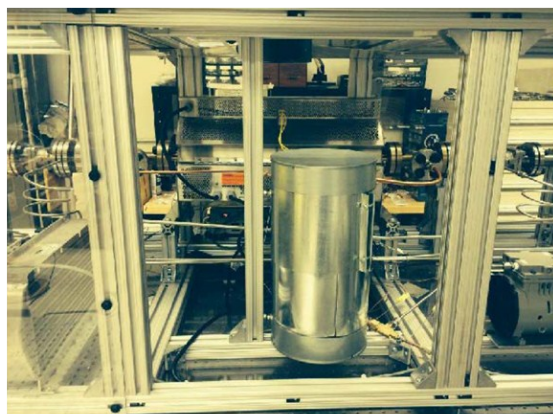


Figure S4) Pre and post reaction XPS analysis of np-Ag catalyst.

a)



b)



c)



d)



Figure S5. CO catalytic bed reactor: Photographs of the a) rear view of the reactor assembly, b) recuperative heat exchanger, c) furnace and data acquisition system, and d) furnace opened with the view of the reactor chamber.

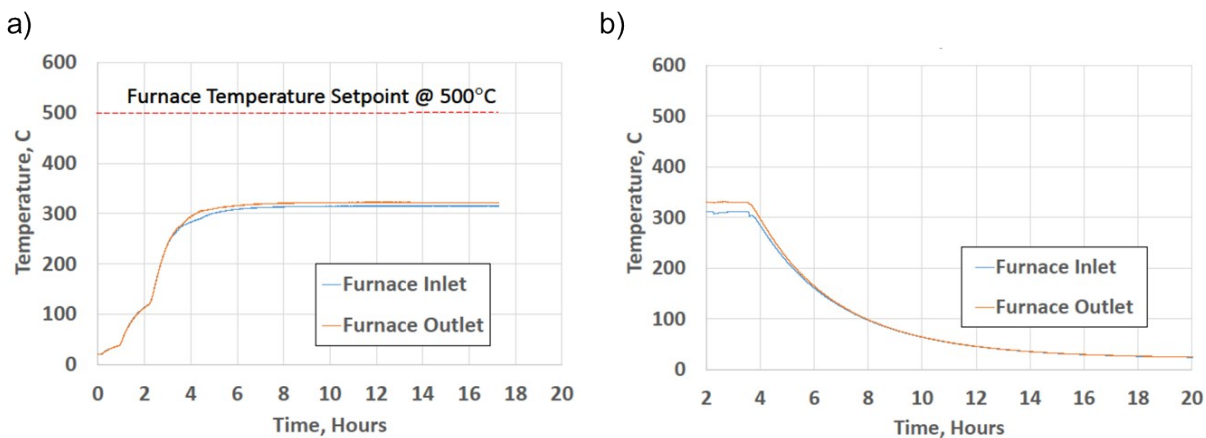


Figure S6. Reactor heat-up and cool-down performance. The furnace inlet and outlet temperatures were measured just outside the reactor chamber enclosure. The furnace took ~4 hours to stabilize upon heating up and took ~10 hours to cool-down to ambient temperature. Again, the reactor was design such that the loading and unloading of the catalyst could be completed without cooling and reheating; and thus, more experiments could be run.

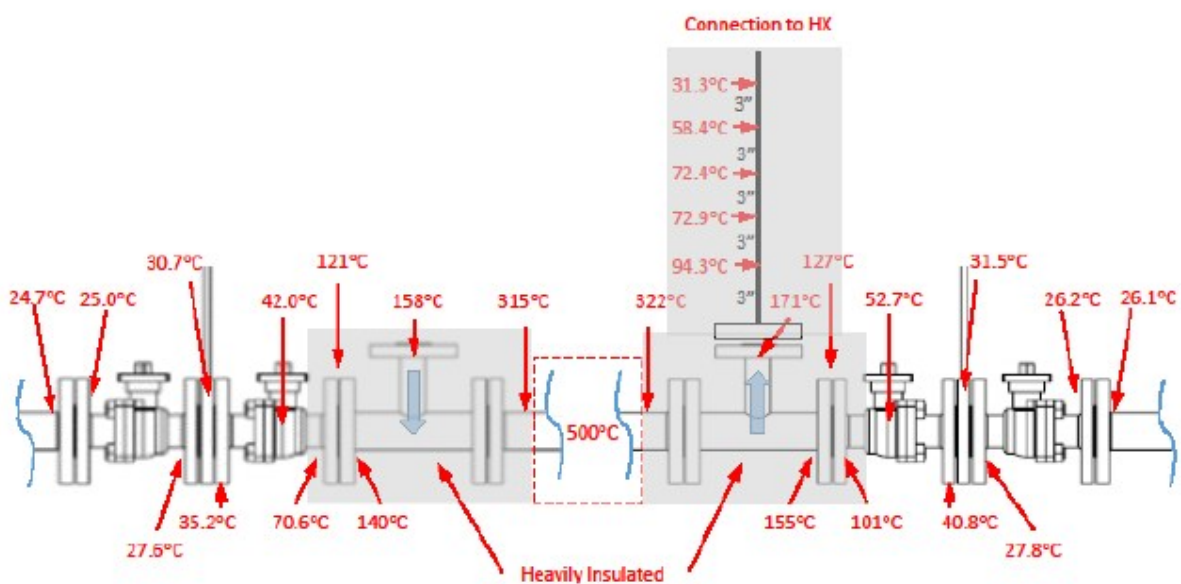


Figure S7. Temperature profile of the entire reactor assembly. The reactor chamber was maintained at 500 °C for experiment studies.

Table S1. Long-duration test results (tests of two hours or longer).

Trial	Duration (min)	Catalyst mass (g)	Unloaded mass (g)	Inlet gas composition	Carbon mass (g)	Carbon to Catalyst (g/g)
1	121	5.0114	17.9931	95% CO ₂ , 5% H ₂ , 0% CO ₂	12.9817	2.59
2	180	5.6282	22.1732	95% CO ₂ , 5% H ₂ , 0% CO ₂	16.545	2.94
3	240	5.6575	31.2667	95% CO ₂ , 5% H ₂ , 0% CO ₂	25.6092	4.53
4	180	3.9954	22.794	95% CO ₂ , 5% H ₂ , 0% CO ₂	18.7986	4.71
5	155	4.8308	21.0664	95% CO ₂ , 5% H ₂ , 0% CO ₂	16.2356	3.36
6	128	5.0968	15.7039	80% CO ₂ , 20% H ₂ , 0% CO ₂	10.6071	2.08
7	157	4.922	18.2912	60% CO ₂ , 20% H ₂ , 20% CO ₂	13.3692	2.72

Oxygen Recovery Calculations:

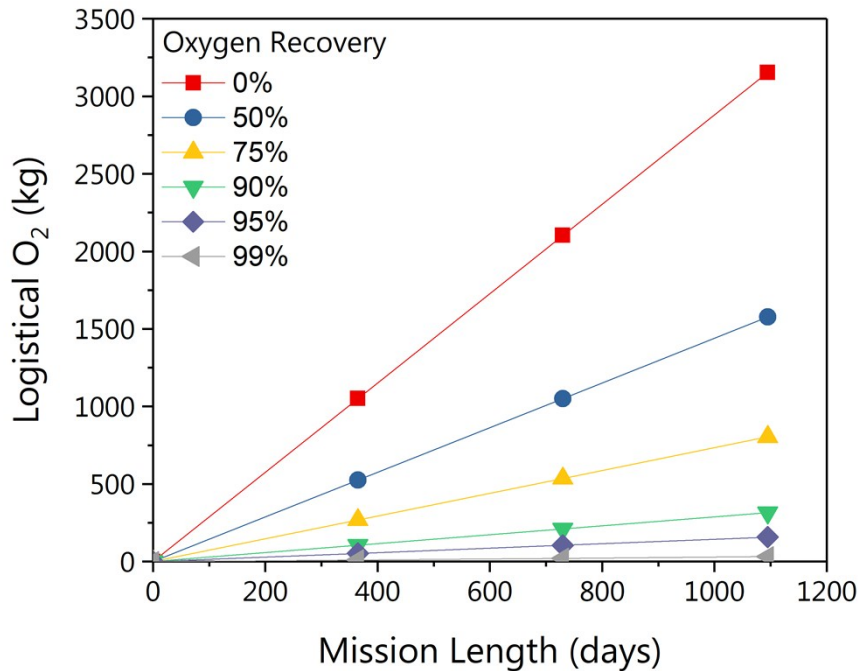


Figure S8: Calculation of required oxygen needed to support a space crew of 4 individuals for 3 years based on 720 g of consumed O₂ per individual per day.

If 90% O₂ recovery can be achieved, ~315 kg of logistical O₂ is needed to be brought on the spacecraft which is a significant reduction compared to the scenario if no oxygen recovery was implemented, ~3154 kg of O₂. If 99% O₂ recovery can be achieved, further reduction of logistical O₂ can be achieved.

Active area needed for CO₂ electrolyzer for one individual:

CO₂ metabolic production rate, ~990 g of CO₂ per day (1 individual)

CO₂ recycle rate from CO reactor, ~990 g of CO₂ per day

Total CO₂ processing rate for CO₂ electrolyzer, ~1980 g of CO₂ per day

CO₂ electrolyzer performance at 3.0V, 44 mA cm⁻², 92% CO Faradaic efficiency

Active area needed, ~2483 cm²

If 25 cm² cell is used, ~100 cells are needed

Total weight of catalyst needed for CO catalytic bed reactor to process ~3154 kg of O₂:

The stoichiometric molar ratio of C to O₂, 1

Deposited carbon to catalyst weight ratio, 4

Catalyst needed, ~300 kg of catalyst

The total weight of catalyst needed is less than 10% of the total weight of O₂ needed to support the space crew if no oxygen recovery system was implemented.

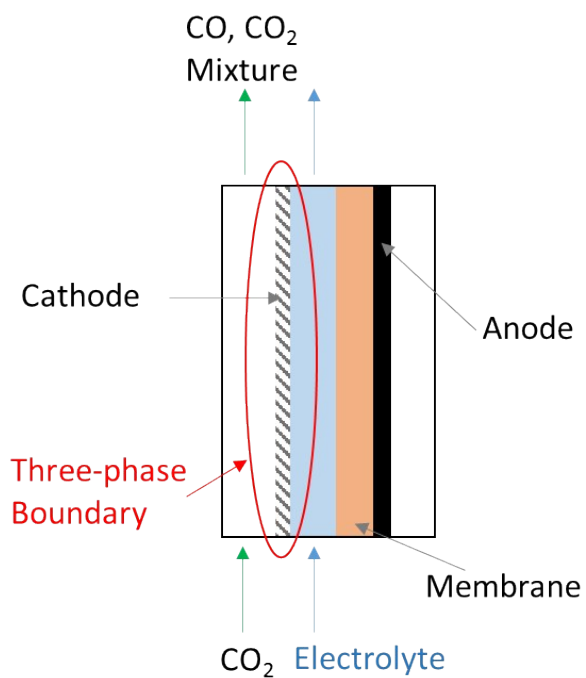


Figure S9. An alternative cell configuration to overcome the solubility limitation of CO₂ in aqueous solution. However, CO₂/CO gas separation may be required if the CO₂ single pass conversion is low.¹

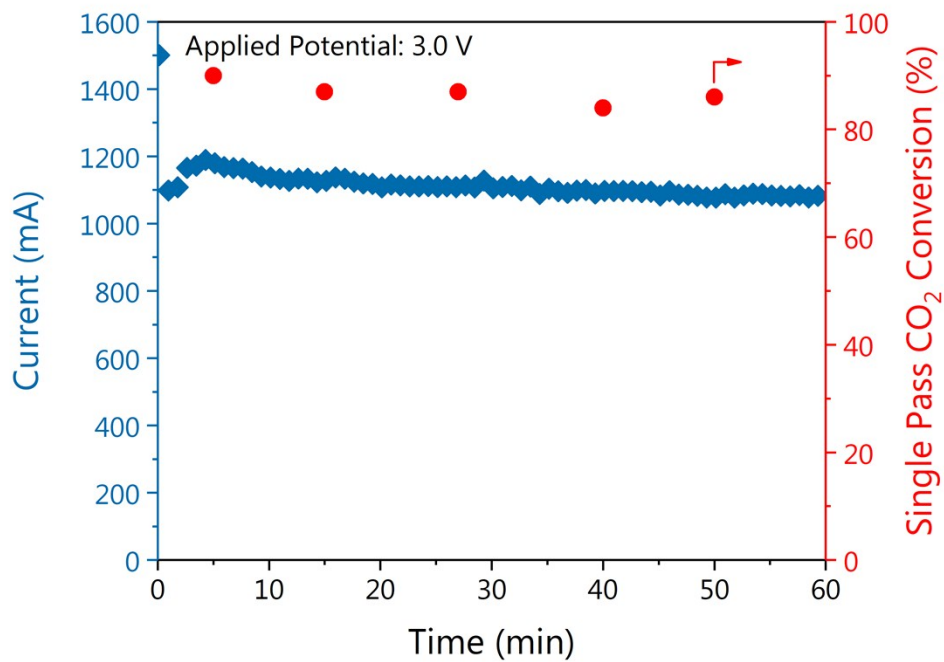
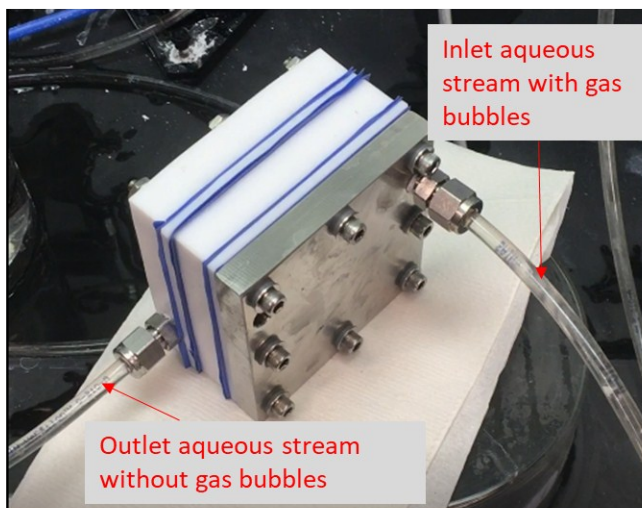


Figure S10. Single pass conversion of CO₂ electrolyzer. The CO₂ gas feed rate was set to 7.25 mL min⁻¹. The CO Faradaic efficiency ranged from 81 to 86%.

a)



b)

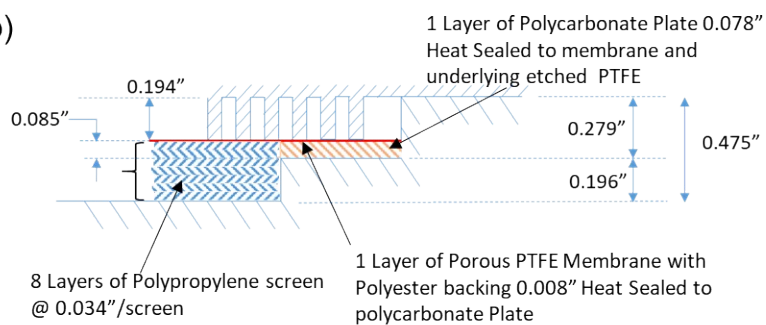


Figure S11. a) Photograph and b) schematic of a porous membrane gas/liquid separator.

References

1. Whipple, D. T.; Finke, E. C.; Kenis, P. J. A., Microfluidic Reactor for the Electrochemical Reduction of Carbon Dioxide: The Effect of pH. *Electrochemical and Solid-State Letters* **2010**, *13* (9), B109-B111.