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UNIVERSITY OF CALIFORNIA,
IRVINE

Countercurrent Concentration of Gases and Development of Dynamic Surface Remodeling

DISSERTATION

submitted in partial satisfaction of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

in Chemistry

by

Kyle S. Brubaker

Dissertation Committee:
Associate Professor Aaron Palmer Esser-Kahn, Chair, Chair
Assistant Professor Shane Ardo
Distinguished Professor Kenneth J. Shea

2017

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DEDICATION

To my wife Dr. Jessalyn Bolkema and my parents, Nancy and Russel Brubaker for their
ever present encouragement and support.

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CURRICULUM VITAE

Kyle S. Brubaker

EDUCATION

Ph.D., Organic Chemistry

University of California, Irvine

2017

Irvine, California

B.S., Chemistry (ACS Certified)

Hope College

2012

Holland, Michigan

RESEARCH EXPERIENCE

Graduate Research Assistant

University of California, Irvine

2012–2017

Irvine, California

REFEREED JOURNAL PUBLICATIONS

Countercurrent Amplification of Oxygen and Carbon Dioxide.

N/A

Submitted

Diffusion controlled surface remodeling mediates dynamic structural changes via chemical non-equilibrium.

N/A

Submitted

Bio-Inspired Morphogenesis Using Microvascular Networks and Reaction Diffusion.

Chem. Mater.

2015

Three-Dimensional Confomal Coatings through the Entrapment of Polymer Membrane Precursors.

ACS Applied Materials and Interfaces

2014

PRESENTATIONS

Diffusion controlled surface remodeling enables dynamic structural changes via chemical non-equilibrium

International Conference on Self Healing Materials - Friedrichshafen

2017

POSTERS

Structural Equilibrium through Chemical Non-equilibrium 2016

Multifunctional Materials Gordon Conference

Concentration of oxygen through countercurrent multiplication 2014

ACS - San Francisco

New Applications for High Performance Dyes 2011

NOS - Princeton

TEACHING EXPERIENCE

Teaching Assistant 2012–2017

Guest Lecturer, Chemistry 225 - Graduate Polymers, Winter 2017

TA, Chemistry 1B - General Chemistry, Winter 2017

Instructor, Chemistry 51LC - Organic Lab, Spring 2016

TA, Chemistry 1P - General Chemistry, Fall 2013

Instructor, Chemistry 51LC - Organic Lab, Spring 2013

Instructor, Chemistry 51LB - Organic Lab, Winter 2013

TA, Chemistry 51A - Organic Lecture, Fall 2012

ABSTRACT OF THE DISSERTATION

Countercurrent Concentration of Gases and Development of Dynamic Surface Remodeling

By

Kyle S. Brubaker

Doctor of Philosophy in Chemistry

University of California, Irvine, 2017

Associate Professor Aaron Palmer Esser-Kahn, Chair, Chair

Assistant Professor Shane Ardo

Distinguished Professor Kenneth J. Shea

Nature, while slow to change, has had the benefit of billions of years competitive pressure to hone approaches to interesting problems. In this work, we take advantage of this preexisting work, and make progress towards replicating the benefits found in nature in artificial systems. Taking inspiration from dynamic, living structures such as bone, and muscle, we demonstrate partial synthetic recreations of the conceptual pieces required to mimic such materials. Diffusion controlled etching is used to demonstrate functional optimization of preexisting structures. Incorporating growth into the system allows dynamic, reversible changes in structure to take place. We show the migration of a channel through a solid matrix.

We also took inspiration from deep sea fish to develop a device that concentrates gas more efficiently than a simple countercurrent flow separator. Existing methods including hollow-fiber membrane contactors, vacuum swing adsorption, and cryogenic distillation represent a significant portion of the worlds energy needs.⁵ Countercurrent amplifiers found in the swimbladders of teleost fish, can efficiently concentrate gases at least 15,000 times above the ambient concentrations. Incorporating the architecture found in the swim bladders of deep sea fish with modern CO₂ and O₂ capture fluids enables a feedback loop of concentration within our artificial device to drive an increase in the release rates of both gases.

Chapter 1

Introduction

1.1 Introduction: Synthetic analogue to biological structure growth and modification

Modern materials science has a broad selection of options to choose from when trying to pick the optimum choice for any given application. Progress in the field over the last 50 years has focused on expanding the combinations of properties available in any given material. Higher and higher molecular weight polyethylenes, polyaramides and composite materials have all pushed to increase the capability, and durability of the objects made with them by reducing the likelihood of an initial damage event. Recent work in the field has focused on increasing the longevity of materials by incorporating mechanisms of repair directly in the material. White and coworkers have pioneered using releasable healing agents as part of a Grubb's metathesis system to heal scratches and cuts.⁶ Other systems use reversible Diels-Alder reactions to facilitate healing through dynamic bond rearrangement at high temperature.⁷ Applications of these materials take advantage of the dynamic bonds, or encapsulated repair media to reduce the aesthetic and structural effect of surface scratches

and structural failures. These materials are reactionary - only responding once a failure has occurred and usually restoring less than 80 % of the original strength. Contrast this to living systems where structural changes are made before failure in a preventative fashion to yield a stronger more resilient system than was started with. Bone is a classic example of a material undergoing preventative structural maintenance. Both the shape and density of bone can change in response to changing environmental stresses. Increases in bone mass and changes in geometry that lead to increased strength and toughness result from applications of increased stress. Situations with decreased stress lead to decreased bone mass, and a subsequent reduction in the energy cost of the bone to the organism. The competition of bone growth and removal leads to a continuous process of structural optimization currently not possible with today's synthetic materials. Bone functions in this way primarily due to two groups of cells - the osteoblasts, responsible for bone growth and the osteoclasts responsible for bone removal (Figure 1.1). Lack of stress leads to accelerated removal by the osteoclasts, something that plays out dramatically in space where an astronaut can lose up to 1.5 % of areal bone mineral density per month.⁸ Conversely, continuous cycles of applied stress lead to an increase in the rate of bone growth mediated by the osteoblasts.

This process of dynamic structural remodeling underlies the complexity of biological materials and has inspired a growing area of research for micro-patterning.⁹ Previous studies have demonstrated that reaction and diffusion mechanisms can generate elegant, scalable structures in micro to millimeter length scale.^{10,11,12,13,14,15,16,17} However, most structures remain static and two dimensional. Here we demonstrate an increase in mass transfer between pre-existing microfluidic channels using diffusion controlled surface removal. We also demonstrate the movement of channels within a solid matrix using diffusion controlled surface growth and removal.

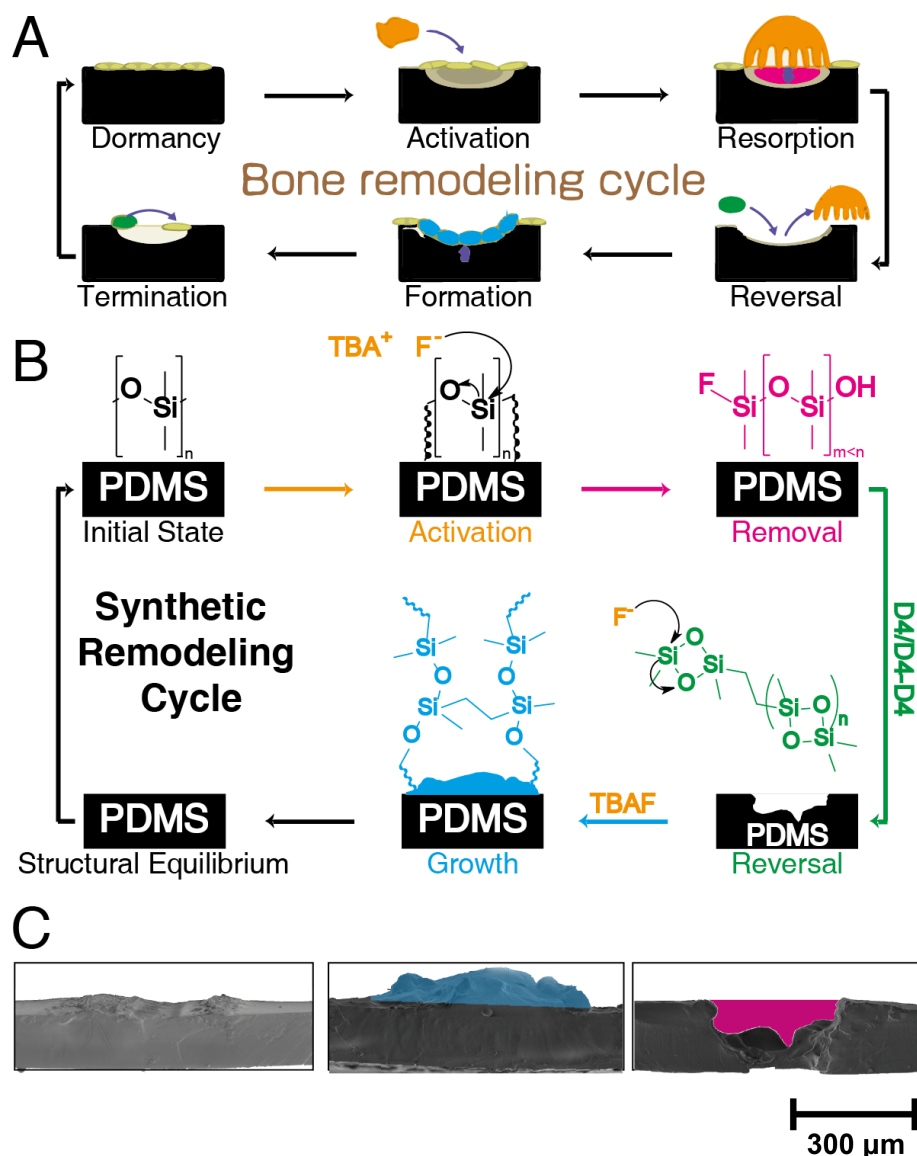


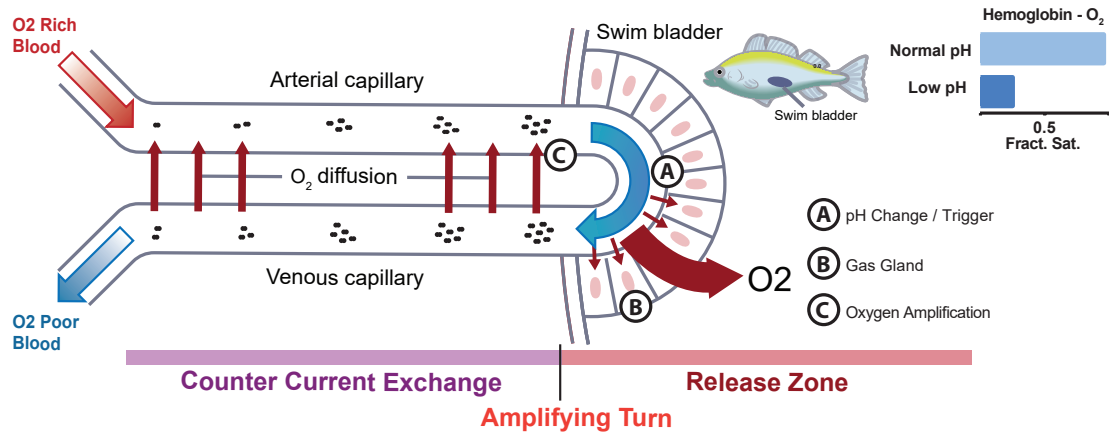
Figure 1.1: Synthetic remodeling cycle. (A) The bone remodeling cycle (based on²) - the biological inspiration for synthetic remodeling cycle. In the bone, osteoclast cells (orange) sense damage and are activated to remove the damaged area. This process is then reversed and osteoblast cells (green) form new bone tissue. This process ends with a similar, though not identical, bone structure. (B) Our synthetic remodeling cycle. A PDMS membrane is remodeled using TBAF (orange) as the activating agent. The naked fluoride depolymerizes the PDMS (magenta) removing material from the surface. This process is reversed by the introduction of D4/D4-D4 (green), which forms new material (cyan) via ring opening polymerization initiated by fluoride (orange). The two processes when balanced result in a structural equilibrium of the system. (C) Representative SEM micrographs of a PDMS membrane after removal of material (right, removal is false colored in magenta), growth of new material (center, growth is false colored in cyan) or at structural equilibrium (left).

1.2 Introduction: Countercurrent amplification of gases

The swimbladder found in physoclist fish is a fascinating example of nature's many elegant solutions to complex problems. In deep sea fish, the swim bladder is able to concentrate oxygen from a surrounding concentration of 0.0003 M to at least 3.9 M - a 15,000 fold increase in concentration. Fish use this method of concentration to reduce the energy costs of depth-holding, by adjusting the overall density of their bodies to ensure neutral buoyancy at a given depth. Unlike shallow water fish that can swim to the surface and fill the swim bladder by ingesting air through the mouth, physoclist fish do not have a direct connection between the mouth and the swim bladder. Living at depths greater than 50 meters, daily trips to the surface would be very energy intensive. Instead, the physoclists utilize a system of adjacent blood vessels looped back on themselves and a pH dependent hemoglobin to drive the concentration through the bloodstream. Blood flowing into the swim bladder passes by a loop adjacent to a gas storage bladder where the release of oxygen from hemoglobin is triggered due to the interaction of released lactic acid and a pH sensitive hemoglobin. Now rich in free oxygen, the blood flows back alongside the incoming channel where free oxygen can diffuse into the incoming channel, increasing the concentration of hemoglobin bound oxygen. The cycle repeats, successively increasing the oxygen concentration in the loop until an equilibrium is reached. (Figure 1.2) The countercurrent amplification process produces a higher output concentration for a given release trigger than could be obtained in bulk solution.

A method to reach similar levels of concentration could be useful in a number of fields. Concentration of dilute solutions is a central problem in separations ranging from protein isolation, to concentration of commodity gases.^{18,19,20,21} Current methods for gas concentration, including cryogenic distillation, vacuum swing adsorption, and chemo-selective permeable membranes have each advanced modern industry to where they now account for 10-15% of the world's energy consumption. Lively and Scholl recently published a perspective on this

a) Inspiration - Fish Gas Bladder



b) Concept - Counter Current Amplifier

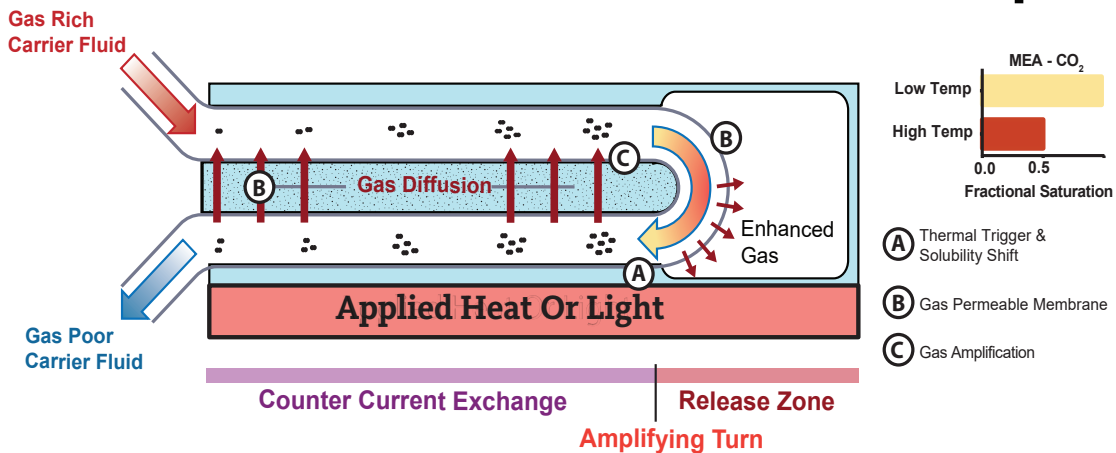


Figure 1.2: (a) Diagram of the fish O₂ concentration mechanism. a - location of the lactic acid gland used to trigger the release of O₂ from hemoglobin as a result of a shift in pH. b - gas gland composed of a semipermeable layer of cells at the interface of the blood vessels and the swimbladder. c - Back diffusion of O₂ into the inlet channel leading to a concentration amplification. (b) Conceptual diagram of the artificial concentration mechanism. a - Location of the thermal or light based trigger for gas release from the carrier solution. b - Location of the gas permeable membranes allowing the diffusion of gas between fluid channels and between fluid and gas channels. c - Back diffusion of gas into the inlet channel, leading to concentration amplification.

challenge stating that new methods that are more energy efficient could save 100 million tonnes of carbon dioxide emissions and US\$4 billion in energy costs annually.⁵ Here we show a synthetic swim bladder, that employs counter-current amplification to extract CO₂ or O₂ from capture solutions. We fabricated a model counter-current amplifier consisting of a single, looped channel, separated by a gas permeable membrane. On the release face of the loop, photo/thermal energy is applied triggering a change in solubility. We demonstrate that an increase in the rate of gas release from the system for a discrete energy input can be tied to the counter-current amplification architecture controlling for both heat and gas diffusion. In designing an artificial gas-bladder, we sought a general test platform that could be applied to a wide range of target solutes and solutions. In a fish’s swim-bladder, the amplification of solute concentration is a result of a vascular geometry where a single vessel is looped back on itself and separated by a thin semipermeable membrane. Triggered release of the solute from a carrier fluid in the looped section creates a concentration gradient between the incoming and outgoing vessels, that sets off a feedback loop where the solute concentration entering the looped section increases leading to a larger subsequent triggered release of solute in the looped section.²² To build an artificial system, our design requires a looped geometry fabricated using micro-machining, a compatible carrier fluid that can be easily triggered to release the solute of interest, and a triggering mechanism - the change in solubility with increasing temperature. In picking example solutes, we selected CO₂ and O₂ both for their importance as separations processes and fulfillment of these 3 criteria making them compatible with counter-current amplifiers. To test the potential of counter-current multiplication to enhance gas concentrations, we built a model system consisting of a single looped channel, separated by a gas permeable membrane. To facilitate design of control experiments, the model system is modular, allowing different membranes and channel configurations, which we used to validate counter current amplification. At its highest performance, this synthetic swim bladder can increase gas release by 250%. The experimental findings were duplicated using a COMSOL model and the effect of changing channel sizes was investigated.

Chapter 2

Structural remodeling through diffusion controlled surface removal¹

2.1 Introduction

Material microstructure is a key design element in advanced materials. Microstructure improves a material's performance for compression, mass and heat transfer, and solar energy conversion efficiency.^{23,24,25,26,27,28,29,30} Shaping microstructures is also important in biological composites. Natural composites gain unmatched performance by continuously adapting their microstructure to their environment via Reaction-Diffusion (RD) sequences a process termed morphogenesis.^{31,32,33,34,35,36} RD is the formation of spatial micro-patterns by two reactive molecules diffusing at distinct, controlled rates.³⁷ During lung development, for example, microstructures are morphed via RD. This action increases the efficiency of gas exchange by changing a micron-scale bud to a half-meter long, hierarchical composite composed of thousands of identical micron-scale alveoli.^{38,39,4,40,41,3,42} (Figure 2.1A and B) Current RD-based synthesis of microstructures create elegant patterns^{16,14,11,12,15} from mi-

crons to millimeters^{13,43,17,11}, but are not a continuous process, are incapable of adaptation, and are limited to two dimensions. Still lacking in synthetic systems, is the dynamic, continuous restructuring of 3D patterns that are the key principle that biological systems use to improve performance. Here we show a synthetic system that improves microstructure performance through RD based microstructure change. Inspired by lung morphogenesis, we developed a synthetic depolymerization/inhibition (push/pull) method that remodels microstructures dynamically. Our method selectively improved the mass transfer performance of an experimental micro-contactor and allowed us to fabricate asymmetric structures from symmetric precursors. We developed a finite element model using COMSOL to describe the function and results of the process. Microstructures dictate the properties of bulk materials as diverse as composites and batteries and optimization of these structures is an active area of research.^{44,45,46} Adaptive RD based micro fabrication could be used for dynamically altering such structures to adapt a material to a given function. In our previous work, we fabricated 3D micro-structured materials using VaSC (Vaporization of a Sacrificial Component) and formed patterns of 3-dimensional circular channels.^{47,48} (Method Section and Appendix A) In the current work, we use diffusion between the channels, formed by VaSC, as the basis for our RD-based restructuring method. (Figure 2.1) To continuously change the shape of our template micro-vascular structure, we sought a reaction scheme that enabled dynamic, continuous remodeling. We developed a synthetic RD push/pull mechanism inspired by lung restructuring. (Figure 2.1B and C) In the system, a circular channel is changed by a depolymerizing agent as the first, push, component (arrows). To counter depolymerization, a sacrificial, reactive agent, in an adjacent channel diffuses through the material. This reactive agent inhibits depolymerization; creating the second, pull, component (T-junction). The rate of structural change is a function of the local concentration of depolymerizing/push reagent, which is dependent on diffusion of the sacrificial/pull reagent.

For the depolymerization agent, we used a reactive fluoride, tetrabutyl ammonium fluoride (TBAF), as it depolymerizes PDMS membranes with micron precision.^{49,50} The current

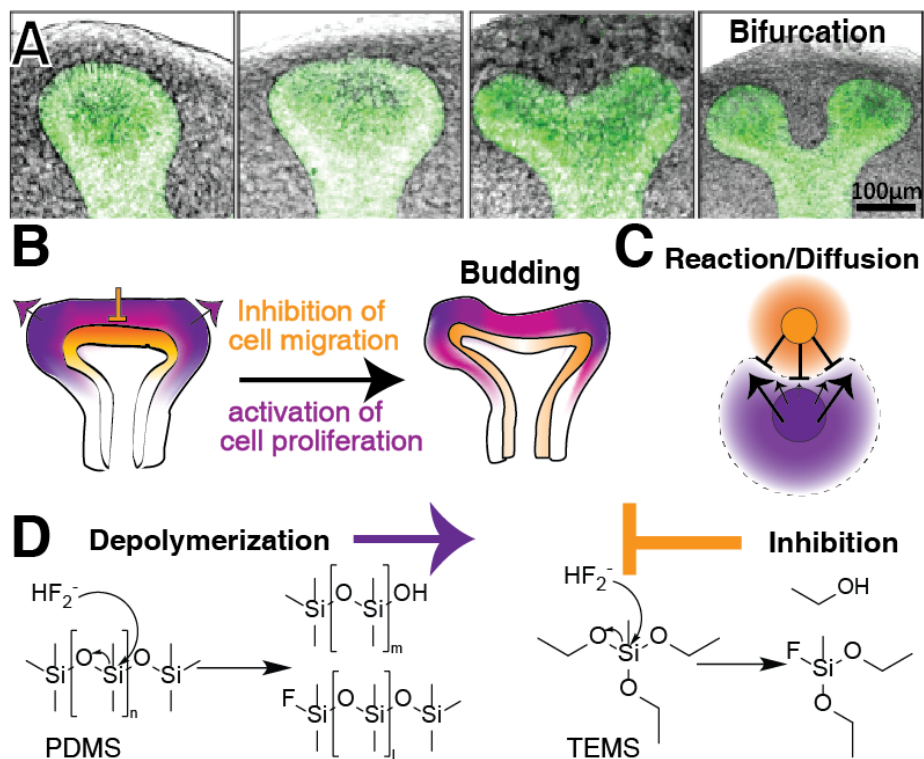


Figure 2.1: Natural and synthetic microstructure patterning. (A) Images of lung bud morphogenesis. Reproduced with permission.³ 2013, Wiley Periodicals Inc. (B) A schematic mechanism for lung bud morphogenesis. The push element (purple) is the driving force for cell proliferation (arrows). The pull element (orange) prevents cell proliferation (T-junction). Cell proliferation occurs only where the inhibitor concentration is low enough.⁴ (C) A synthetic morphing system: depolymerization and inhibition of depolymerization. Different concentrations of depolymerizing agent (purple gradient) are the driving force/push of different rates of depolymerization (arrows). A gradient is formed from the radial diffusion of the inhibitor (orange) which inhibits/pulls the depolymerization of PDMS (T-junctions). (D) Chemical reactions of the system. A nucleophilic attack of a depolymerizing agent (HF_2^-) results in material lost from depolymerization/push (purple arrow), or inhibition of that depolymerization/pull by reaction with a sacrificial inhibitor - TEMS (orange T-junction).

hypothesis of the active nucleophile of TBAF supports HF_2^- and so we refer herein to the nucleophilic/push species as HF_2^- .⁵¹ For the inhibitor, we used triethoxymethylsilane (TEMS) as it diffuses through PDMS, reacts with HF_2^- in a competitive manner, and prevents depolymerization of the siloxane backbone of PDMS. (Figure 2.1D) High rates of structural change occur in locations with a high concentration of HF_2^- , while a low rate of change occurs where reaction with TEMS lowers the concentration of HF_2^- . Thus reaction and diffusion of TEMS and HF_2^- dictate the final microstructure.

2.2 Experimental

Sample Fabrication: We fabricated 3D micro-structured materials using VaSC (Vaporization of a Sacrificial Component). This method has been reported previously.⁵² Briefly, we used sacrificial fibers as a positive mold of 3-dimensional microvascular structures in PDMS. The fibers were then vaporized, leaving a designed pattern of channels. **Reaction Rate Measurements:** We determined the rate constant for reaction between TEMS and TBAF using NMR analysis by measuring the loss of siloxane and formation of free ethanol. (Figure A.8) The reaction formed 2 or 3 molecules of Ethanol per loss of one TEMS molecule, depending on the solvent. We assumed a second order reaction and estimated the rate constant as $2\text{ M}^{-1}\text{ s}^{-1}$. To estimate the reaction rate of PDMS with TBAF, we examined the change in radii of circular channels exposed to increasing concentrations of TBAF, using optical microscopy. (Figure A.7) We averaged the channel radii along the channel at different time points and then averaged the change in width with time. We produced a graph describing the etch rate as a function of TBAF concentration. (Figure A.8) **Diffusion Rate Measurements:** To measure the diffusion coefficient of TEMS within the PDMS, we quantified the visual disappearance of TEMS into a PDMS membrane. We compared this to the visual disappearance of Ethanol into PDMS. Based on the measured diffusion coefficient of Ethanol

in PDMS and the diffusion equation for a cylinder, we estimated the diffusion coefficient to be $7.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. (Figure A.5) We measured the diffusion coefficient of the fluoride species within the TBAF solution using ^{19}F DOSY and found it to be $4.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. (Figure A.6) All other relevant diffusion coefficients were estimated using the Stokes-Einstein equation.

2.3 Results and Discussion

To fine-tune our process and to develop a computational model, we investigated the kinetic parameters of our system. This includes the reaction and diffusion of TEMS, TBAF and PDMS. We measured via NMR: (1) the reaction rate constant between TEMS and TBAF as $2 \text{ M}^{-1} \text{ s}^{-1}$, (2) the diffusion coefficient of active fluoride in TBAF as $4.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. We used optical analysis to measure (1) the diffusion coefficient of TEMS in PDMS as $7.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and (2) the depolymerization rate of PDMS by TBAF. (Method Section and Appendix A). To provide us with a theoretical test-bed, we developed a finite element model of the system using COMSOL multiphysics, and inputting the measured parameters. We built two different geometries for the model; (1) a linear geometry composed of a central channel flanked by two smaller channels (Figure 2.2A), and (2) a triangular geometry with one central channel and three surrounding, outer channels arranged in a triangle. (Figure 2.2B) All channels were parallel. In each geometry, a parameterized TBAF was placed in the central channel at a concentration of 683 mM flowing at 0.5 ml/min, while, TEMS was simulated diffusing from the outer channel with concentrations between 750-1,000 mM flowing at 0.08 ml/min. All flows were laminar. (Table A.1) The change in HF_2^- concentration over time was controlled by the diffusion rate of TEMS across the membrane. (Figure 2.2) The model adjusted the microstructure as a function of local HF_2^- concentration and predicted accurate geometries derived from the initial geometry. (Figure 2.2) To test the concept

of diffusion based micro-structural change, we examined micro-structures analogous to the model. (Figure 2.2) In the linear structure, the central channel, 500 μm in diameter and the side channels, 200 μm in diameter, were separated at a distance of 100 μm . The push agent, HF_2^- , TBAF (75% in water) in DMF (1:3 v/v) flowed through the central channel at 0.5 ml/min. The pull agent, TEMS in EtOH (20% v/v) flowed through the side channels at 0.08 ml/min in the same direction as the TBAF solution. To examine the result, cross-sections were taken from the edge of the sample every hour and visualized by Scanning Electron Microscopy (SEM). According to our model, the concentration of free HF_2^- on the surface of the channel varies between 35 mM and 150 mM. As a result, the channel changed shape, favoring growth in the direction of lower TEMS concentration. As our model predicted, the central channel diameter grew 3 times more along the low TEMS axis (Figure 2.2A) than along the high TEMS axis. We then performed the same experiment in a triangular geometry. In this structure, the central channel was 300 μm in diameter and the membrane thickness between channels was 50 μm . As thinner membranes permit faster diffusion, we lowered the TEMS concentration to 18% (900 mM). The central channel changed its structure only where the TEMS concentration fell below 50 mM in the model. The initial circular structure bifurcated branching to avoid the higher concentration of TEMS. (Figure 2.2B)

To verify this on a larger scale, we fabricated a sample with the triangular structure periodically repeating seven times. Owing to increased concentration of TEMS in the repeated structure, we decreased the TEMS concentration, further, to 15% (750 mM). We kept one channel (upper left) free of TEMS as an internal control to observe a non-RD structure. (Figure 2.2C) Again, cross sections were taken over 2 h and the pattern repeated itself 6 times with minor variations in each channel. The 7th, control, section differed with complete removal of the membrane adjacent to the channel lacking any pull/TEMS. (Figure 2.2C) A hallmark of biological structural change is improvement of function a critical component in micro-scale adaptation. Using this approach, the human lung achieves a specific surface area above $50.000\text{ m}^2\text{ m}^{-3}$, drastically improving mass transfer capabilities. To test if our new method

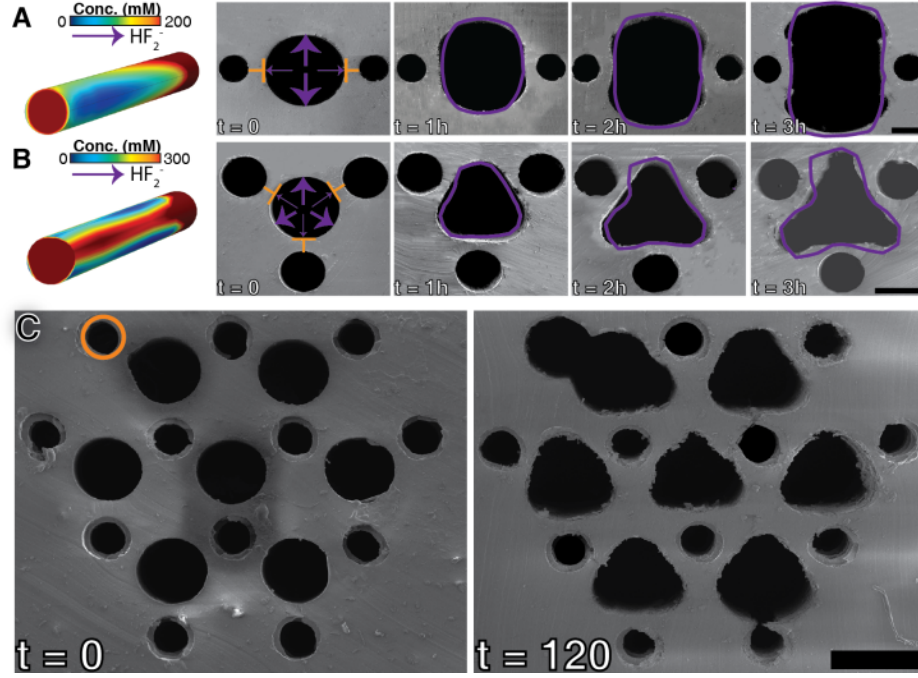


Figure 2.2: Modeling and fabrication of RD based dynamic structural change in microstructures. TBAF (push) is flowed through the central channel flanked by channels filled with TEMS (pull). A and B left side A colored gradient indicating the modeled change in TBAF concentration at the surface of the central channel. (A) Overlay of modeling results with micrographs of cross sections of a 2-dimensional sample undergoing RD for 3 h. Scale bar = $100\ \mu\text{m}$. (B) Overlay of model results with micrographs of cross-sections of a 3-dimensional sample undergoing RD for 3 h. Scale bar = $100\ \mu\text{m}$. (C) Generalization of seven repeats of a 3-dimensional structure. The upper left channel (orange circle) lacks a pull/TEMS agent. Scale bar = $200\ \mu\text{m}$.

could improve the mass transfer rate of our microstructures, we tested mass transfer on both the initial and adapted triangular structures. Using COMSOL, we modeled mass transfer efficiency (Table A.2) - predicting a 23% improvement in mass transfer efficiency of the adapted channel. (Figure 2.3C) To experimentally measure mass transfer, we used 10% CO₂ (balanced N₂) as a diffusing gas and its reaction with mono-ethanolamine (MEA) to measure the mass transfer rate.⁴⁷ (Figure 2.3A, A.13, A.14). We measured CO₂ mass transfer in the central channel using a pH sensitive fluorescent dye (5-(and-6)-Carboxynaphthofluorescein, 1 mg/mL).⁵³ When CO₂ flowed through the gas channels (3 ml/min), it diffused through the PDMS and reacted with the MEA in the surrounding channels. The reaction between CO₂ and MEA forms carbamic acid reducing the pH of the solution (Figure A.13); decreasing the fluorescence intensity. (Figure 2.3B) We calculated mass transfer efficiency for both initial and post RD process structures. (Figure A.14) The RD process had a positive effect on mass transfer efficiency, increasing the mass transfer rate from $7.4 \times 10^3 \text{ mol h}^{-1} \text{ m}^{-3}$ for the circular structure to $14.4 \times 10^3 \text{ mol h}^{-1} \text{ m}^{-3}$ for the newly formed structure, representing an increase of almost 100% percent, exceeding our prediction. (Figure 2.3C) We flowed TEMS and TBAF through the initial structure for 10 min prior to mass transfer experiments, to eliminate any nonstructural effects on mass transfer improvement. In order to confirm that our increased mass transfer efficiency is due to our RD process and is not simply a result of increased surface area, we modeled two geometries of a central channel. Both geometries were circular, though one of them had features increasing its surface area. (Figure A.11) The featured channel had a surface area 17% higher than the circular channel, yet the mass transfer only improved by 0.2%. This is in comparison to the RD system in which surface area increased by 50% and mass transfer efficiency increased by 23%. This shows that while the RD method increases surface area, it does so in a unique way that causes an increase in mass transfer efficiency.

Finally, we wanted to determine if a RD-based fabrication system could create unique and potentially beneficial structures that are inaccessible to microfabrication. Asymmetric struc-

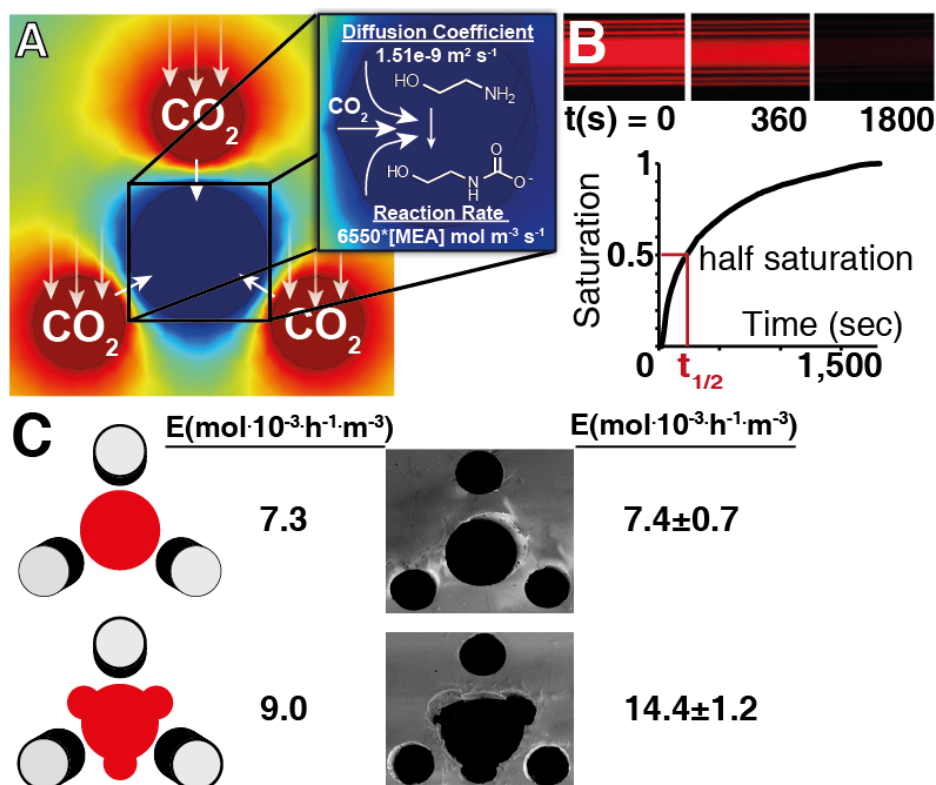


Figure 2.3: Reaction diffusion structural change induces improved performance. (A) Schematic of the mass transfer experiment. (B) A representative run of a mass transfer experiment. The fluorescence changes as a function of time (top panel, scale bar = $200 \mu\text{m}$). This change was normalized for degree of saturation of the MEA channel. The channel saturation as a function of time is graphed. (C) Comparison of mass transfer efficiency between the different structures. Results for both experiment and model are shown. Scale bar = $100 \mu\text{m}$.

tures are important for many organs and potentially beneficial to materials development,^{54,55} but are difficult to fabricate using lithographic techniques. By independently controlling the concentrations in our micro-vascular structure, we hypothesized we might control the resulting pattern to generate asymmetry from symmetry. To test this idea, in a linear geometry, we placed 20% TEMS on one side and 5% TEMS on the opposing side (Figure 2.4A). The reaction proceeded for 4 h. Cross sections were collected every hour and visualized using SEM. Due to a concentration gradient of TEMS across the central channel; the depolymerization process resulted in an asymmetric structure following the pattern of the gradient. (Figure 2.4A) We then tested these dynamics in our triangular geometry using a gradient formed by 3 concentrations of TEMS. One channel contained 3% TEMS, the second contained 8% TEMS and the third 20% TEMS (Figure 2.4B). The structure was then altered as a function of the TEMS concentration. After 4 h, the resulting sample was visualized using X-ray computed tomography (μ CT), at a 4x resolution and power of 80 kV, to test the uniformity and elucidate the overall structure. (Figure 2.4C) The thickness of the membrane was consistent along the channel length.

Structuring materials via RD could successfully change the shape and pattern of the channels, but we sought to test the generality of the technique in patterning 3-dimensional microstructures. Using VaSC, we created two structures with 3-dimensional elements. The first structure was a cork-screw channel traversed by a straight channel. The second was a 3 ringed structure a central u-shaped channel, with two parallel u-shaped channels wrapped around different sections. In the cork-screw pattern, TBAF was flowed through the straight channel at a lower concentration of 90 mM, as the unique shape and different distances from the TEMS channel might have caused breakage in the membrane at a higher depolymerization rate. We chose concentration to be 10% v/v (0.5 M), as the diffusion pattern in the curved straight channel was different than the one in the straight channel and distances between the TEMS and TBAF channels varied along the structure. TEMS was flowed through the cork-screw channel for 8 h. The final result was visualized using μ CT in wide field, 4X

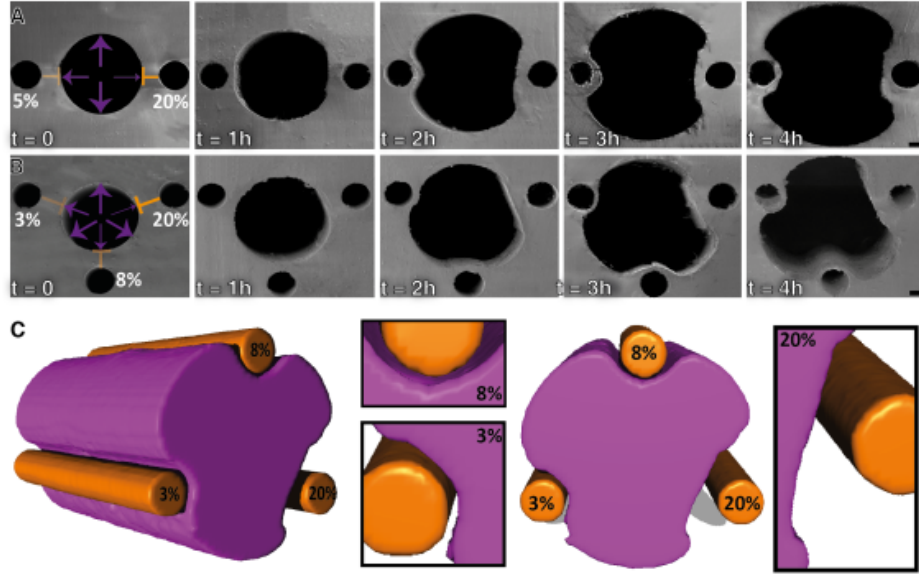


Figure 2.4: Formation of asymmetrical patterns starting from symmetrical patterns. (A) A 2-dimensional asymmetric experiment. Side channels contained either 20% TEMS (right channel) or 5% TEMS (left channel). Cross-sections were visualized by SEM at the noted time points. (B) A 3-dimensional asymmetric experiment. We used 3% TEMS (10 o'clock), 8% TEMS (6 o'clock) and 20% TEMS (2 o'clock). Cross-sections were taken and visualized by SEM at the indicated time points. (C) The final time point of the 3-dimensional asymmetric experiment was visualized via μ CT, showing the full 3-dimensional structure of the asymmetrically morphed channel.

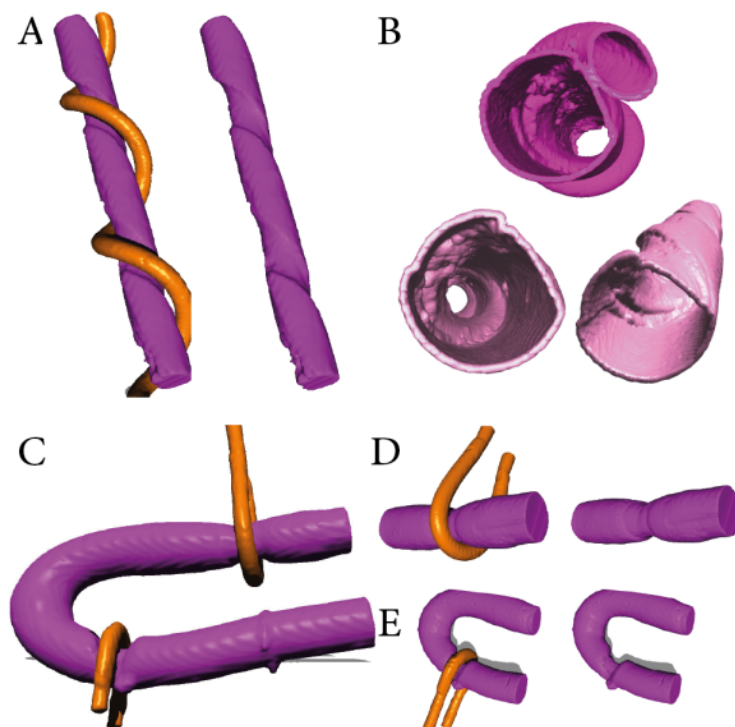


Figure 2.5: Formation of asymmetrical patterns starting from symmetrical patterns. (A) A 2-dimensional asymmetric experiment. Side channels contained either 20% TEMS (right channel) or 5% TEMS (left channel). Cross-sections were visualized by SEM at the noted time points. (B) A 3-dimensional asymmetric experiment. We used 3% TEMS (10 o'clock), 8% TEMS (6 o'clock) and 20% TEMS (2 o'clock). Cross-sections were taken and visualized by SEM at the indicated time points. (C) The final time point of the 3-dimensional asymmetric experiment was visualized via μ CT, showing the full 3-dimensional structure of the asymmetrically morphed channel.

resolution, and a power of 40kV. (Figure 2.5A and B) We observed that the central channel shape changed corresponding to the diffusion gradient of the corkscrew shape. We observed a unique structure of the PDMS surface (Figure 2.5B) which will be difficult to generate with current fabrication methods.

The u-shaped structure underwent similar local changes in its structure. Here, the central channel contained 683 mM TBAF and the external, wrapped channels had 20% v/v TEMS, to emphasize local effects, flowing for 8 h. The final result was visualized using a μ CT in

wide field, 4X resolution and a power of 40kV. (Figure 2.5B) Again, the structural change of the central channel is localized to the area surrounding the TEMS channels. The structural change due to the inhibition differs between the two locations. This difference in size change is the result of decreasing TBAF due to the directional flow of TBAF through the central, u-shaped channel.

2.4 Conclusions

In summation, we present a new approach for the dynamic, continuous reconfiguration of microstructures. This method aims to create a synthetic material that employs one of nature’s greatest strengths to adapt to a specific function. In an initial demonstration, we adapted a microstructure using a RD based mass transfer system to improve its mass transfer rate. Using RD in 3-dimensions enabled us to fabricate asymmetric patterns from a symmetrical micro-channel array, as well as unique 3-dimensional patterns, not accessible in other current methods of fabrication. Our method complements many previous types of PDMS micro-fabrication including soft-lithography.^{56,57,58} While this chapter shows improvement in mass transfer, applying this concept more broadly in micro-fabrication could yield improvements in surface area or structural application. Our mechanism is a first step in mimicking natural systems’ ability to adapt structures at a microscopic level. The key component of this method is its dynamic and continuous reconfiguration of microstructures to improve function. In this chapter we demonstrated the balance between depolymerization and inhibition, allowing for the modification of existing structures by the removal of existing material. Natural morphogenesis processes include surface removal, in addition to material growth. This allows for reversible modifications to structures to take place in response to external stimuli. The balance between growth and removal of material is necessary for structures to change in response to an ever changing environment. In the next chapter we discuss

a system where growth and removal take place simultaneously within a microfluidic system.

Chapter 3

Structural remodeling through diffusion controlled surface growth and removal

3.1 Introduction

Here we show a synthetic system that uses reaction and diffusion to both grow new material via polymerization and remove material through breaking polymer backbones - mimicking the process of natural systems, rather than the structure. Researchers have explored using reaction/diffusion to pattern microstructures with much success^{11,10,12,13,14,15,16,17}, but very little work focuses on using these processes to shape microstructures in a dynamic manner. This report provides an example of a dynamic system that can reshape itself using diffusion gradients. Mimicking this dynamic process for other structures, new materials might be designed to undergo chemically-driven adaptation to external stresses.

Microstructures underlie many modern materials and research areas from microchips to syn-

thetic organs.^{59,60,61,62,63,64,28,27} In each case, the microstructures' pattern is "pre"-determined via a top-down or bottom up fabrication approach.⁶⁵ In contrast, biological systems constantly adapt their microstructure in response to their environment using non-equilibrium, diffusion-based patterning that requires polymerization and depolymerization.⁶⁶ In homeostatic materials, these chemical non-equilibria result in the material's overall structural equilibrium. By relying on a chemically enforced structural equilibrium, the material adapts in response to changing environmental stimuli. Well-studied examples include bone which optimizes its structure for strength⁶⁷ and heart valve tissue which adapt their microstructures to increase blood flow.⁶⁸ Many great advances have been made by mimicking the structure of biological systems including work mimicking mussels, plants, tissue, lungs, mollusks.^{53,69,70,71,72,20,73} However, few methods exist to mimic the process that nature employs to build these structures.

Biological structures are dynamic and change in response to environmental conditions. They repattern their structural scaffolds through cellular mediated remodeling of polymeric matrices.⁶⁶ An example for such remodeling process is observed in trabecular bone. In bone, osteoclast cells sense damage and remove damaged areas.^{74,75,76,77,78} This removal of material is followed by a growth of new material, mediated by osteoblast cells.^{79,80} (Figure 3.1A) This dynamic remodeling of structure is crucial for adaptation to environmental conditions.⁶⁷

This process of dynamic structural remodeling underlies the complexity of biological materials and has inspired a growing area of research for micro-patterning.⁹ Most previous studies demonstrated that reaction and diffusion can generate elegant, scalable structures in micro to millimeter length scale.^{10,11,12,13,14,15,16,17} However, most structures remain static and two dimensional. A few examples of dynamic and three dimensional micro patterning have been presented,⁸¹ but to our knowledge, none of those incorporated two opposing, dynamically controlled, processes - material growth and destruction - that are together responsible for the reconfiguration of a microstructure, as is often seen in the biological system.

In our previous work we showed a reaction-diffusion based remodeling of material involving the irreversible removal of material and the inhibition of that removal.¹ We used a siloxane backbone and fluoride ions from Tetrabutylammonium fluoride (TBAF) to break the siloxane bonds and dissolve the material in areas of high fluoride concentration allowing an irreversible modification of the original structure. Work from the McCarthy lab, and Dow-Corning demonstrated an anion initiated ring-opening polymerization of cyclic siloxane monomers that once polymerized, can undergo dynamic remodeling of the polymer networks as a result of nucleophilic attack by persistent siloxanate anions.^{82,36}

Initiating the D4 polymerization with TBAF, a competition between polymer growth and F⁻ mediated chain scission is established. Controlling this competition allows a dynamic structural equilibrium to be established where the polymer growth rate (addition of material) is balanced with the polymer scission rate (removal of material) on the initial structure (Figure 3.1B and 3.1C). The resulting material is chemically dynamic and capable of reshaping its structure in response to diffusion gradients, facilitating both structural changes and structural homeostasis, reminiscent of the mechanism of bone remodeling. Adjusting the conditions of the reactions taking place, features can be added to and removed from a surface dynamically using the same reagents. To quantify the relation between the balanced chemical reactions and the structure, we measured the growth and removal rates of these opposing reactions using a model system. Then we employed the reaction-diffusion process to remodel a material via the reconfiguration of micro-vascular elements within a material. Notably, the microvasculature retained its feature sizes while shifting its position dynamically within the material. Finally, to determine that this process was amenable to both different length scales and repeating patterns, we modified a repeating array of micro-pillars used in many advanced bio-mimetic applications.^{83,84,85,86}

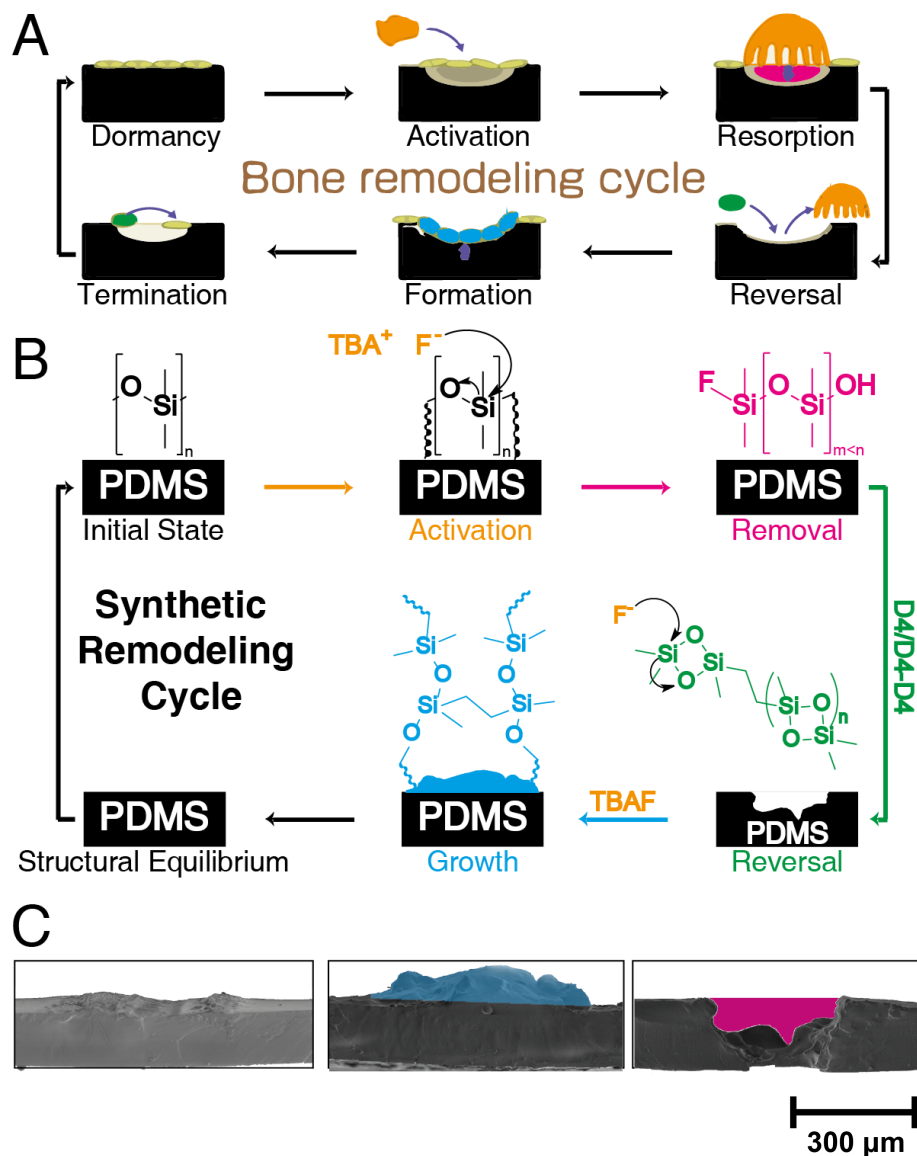


Figure 3.1: Synthetic remodeling cycle. (A) The bone remodeling cycle (based on²) the biological inspiration for synthetic remodeling cycle. In the bone, osteoclast cells (orange) sense damage and are activated to remove the damaged area. This process is then reversed and osteoblast cells (green) form new bone tissue. This process ends with a similar, though not identical, bone structure. (B) Our synthetic remodeling cycle. A PDMS membrane is remodeled using TBAF (orange) as the activating agent. The naked fluoride depolymerizes the PDMS (magenta) removing material from the surface. This process is reversed by the introduction of D4/D4-D4 (green), which forms new material (cyan) via ring opening polymerization initiated by fluoride (orange). The two processes when balanced result in a structural equilibrium of the system. (C) Representative SEM micrographs of a PDMS membrane after removal of material (right, removal is false colored in magenta), growth of new material (center, growth is false colored in cyan) or at structural equilibrium (left).

3.2 Materials:

Unless otherwise noted, all solvents were purchased from Fisher Scientific and used as received. Polydimethylsiloxane (Sylgard 184 silicone elastomer kit) was purchased from Dow Corning and used at 10:1 w/w Base to curing agent. 75% (w/w) Tetra n-butylammonium fluoride (TBAF) in water was purchased from Aldrich and was used in all experiments. Hydride terminated linear PDMS (24kD), Trimethylsilyl chloride (TMSCl), tetraethylsilane (TES) and Benzoyl Peroxide (BPO) were purchased from Sigma-Aldrich and used as received. Octamethylcyclotetrasiloxane (D4) was purchased from Gelest and used as received. Gel permeation chromatography (GPC) was conducted on an Agilent 1260 Infinity system equipped with a refractive index detector RID-10A and two Polymer Laboratories PLgel 5 μ m mixed D columns (with guard column). Tetrahydrofuran (THF) (HPLC grade) at 40 °C was used as solvent (flow rate: 1 mL/min). Microscope images were taken on a Zeiss Axio Observer.A1 microscope. SEM images were taken on a FEI Magellan 400 XHR SEM and a Philips XL-30 FEG SEM. Sputter coating was performed using South Bay Technology Ion Beam Sputtering/Etching System with an Iridium target.

3.2.1 Preparation of D4-D4:

200 mL of D4 were heated to 120 °C in a dry 3-necked round bottom flask under argon atmosphere. BPO, 5 g, was slowly added to the flask. The mixture was stirred at 120 °C for 1 hr. The solution was passed through a basic alumina column to remove the BPO byproducts. The final solution contained $\approx$ 1% w/w D4-D4/D4 as determined by ^1H -NMR (see appendix B).

3.2.2 Solution phase polymerization and depolymerisation:

20 μ L of a linear 24 kD PDMS (0.81 μ mol of polymer chains or 262 μ mol of Si-O groups) or 20.4 μ L of D4 (65.75 μ mol or 263 μ mol of Si-O groups) were mixed with different concentrations of TBAF (0.05M, 0.1M, 0.2M) in 1 mL of Dimethyl Sulfoxide (DMSO). The reaction was stirred at 65 °C in a glycerol bath for 30 min followed by addition of 3 mM TMSCl to quench excess fluoride. The reaction mixture was then frozen in liquid nitrogen. The solid reaction mixture was lyophilized under low pressure (0.018 mbar) using a LabConco FreeZone plus 4.5 L Freeze Dry System for 24 hr. The remaining polymers were resuspended using 1 mL of THF. 50 μ L of the resulting mixture was injected into a GPC instrument.

3.2.3 Membrane Preparation:

Seven grams of 10:1 w/w base to curing agent of PDMS (Sylgard 184) was poured on a 5" x 5" heat resistant borosilicate glass plate, purchased from McMaster-Carr. A Laurell spin coater was used at 1500 rpm for 10 sec (acceleration of 500 rpm/sec), forming a membrane of 100-150 μ m wide. The membrane was cured for 30 min at 85 °C.

3.2.4 Membrane growth/removal experiments:

Microfluidic open-faced, glass flow cells were purchased from Translume with 300 μ m wide by 250 μ m deep by 38 mm long channels. A 5cm x 1cm PDMS membrane was preswelled by a mixture of D4/D4-D4 and tetraethylsilane at 90% v/v or 75% v/v for 30 min. The membrane was then sandwiched between the glass flow cell and a standard microscope glass slide. The apparatus was submerged in a 65 °C glycerol bath. The ports on the flow cell were connected to crack resistant polyethylene tubing purchased from McMaster-Carr. TBAF in DMSO was flowed through the channel for 30 min at various concentrations (0.05M, 0.1M

and 0.2M) and flow rates (0.05, 0.1 and 0.4 mL/min). The membrane was then removed and washed with acetone. The membranes were then placed in a Fisher Scientific Isotemp Model 282A vacuum oven at 115 °C and 170 mbar for 2 hr. The membrane was cut, perpendicular to the channel length, 7 mm from the exit port and the cross section was imaged using light microscopy.

3.2.5 Estimation of membrane growth:

Membrane cross section images were processed using ImageJ software to maximize contrast. The images were converted into black and white images. The images representing the channel were compared to a rectangle with width and height matching the channel width and membrane thickness respectively, which was determined based on a reference image of the membrane cross section, taken at the same conditions as the channel cross section. The image was then analyzed in Mathematica with code that counted the white pixels at higher height than the rectangle height as etching and the black pixels lower than the rectangles height as growth. The number of etched pixels was then subtracted from the number of growth pixels for the final outcome of change in area. See Figure B.4 in appendix B for additional information.

3.2.6 Demonstration of lateral microstructure movement:

Two circular channels, 300 μm in diameter, embedded in PDMS, separated by 60 μm were prepared using the VaSC technique previously described (see Figures B.6-B.9 in appendix B for details). The sample was submerged into a 65 °C glycerol bath. The D4/D4-D4 (99%/1% w/w) mixture was flowed through one channel using a needle inserted into the channel and connected to a syringe at a constant rate of 0.05 mL/min. The rate was held constant using a syringe pump (syringepump.com). After 5 min of the D4/D4-D4 flow, 0.1M of TBAF

in DMSO was flowed through the second channel, in the same direction as the D4/D4-D4 solution, at a constant rate of 0.1 mL/min. Both solutions flowed through both channels for a total of 30 min, after which the sample was placed at a Fisher Scientific Isotemp Model 282A vacuum oven at 115 °C and 170 mbar over-night. A top down view of the sample was visualized using light microscopy. A cross section was taken from near to the exit side and visualized via Scanning Electron Microscopy (SEM), using Philips XL-30 FEG SEM at 1 kV.

3.2.7 Structural change of three dimensional pillars:

3-dimensional pillar structure was made by adding 3 g of 10:1 w/w base to curing agent of PDMS (Sylgard 184) to a PDMS mold (for mold preparation details see appendix B), applying vacuum for 2 hr and curing at 65 °C for 1 hr with a glass cover on top. For the stationary structural change, the pillar structures were swelled in TES or a D4/D4-D4 (99%/1% w/w) mixture for 30 min. The swollen structures were submerged in a 0.1M TBAF in DMSO solution for different times (between 30 s and 5 min). For the flowing structural change, the pillar structure was swollen in 2.9M D4/D4-D4 in TES for 30 min. The swollen structures were then incorporated in the experimental settings of the membrane growth/removal experiments. 0.1M TBAF in DMSO was flowed at 0.1 mL/min for 30 min. The structures were washed with acetone and placed in a Fisher Scientific Isotemp Model 282A vacuum oven at 115 °C and 170 mbar for 2 hr. The structures were then sputter coated with 2 nm thick Iridium coating using South Bay Technology Ion Beam Sputtering/Etching System followed by imaging using FEI Magellan 400 XHR SEM with EDT detector and free field lens at 2 kV and 0.2 nA.

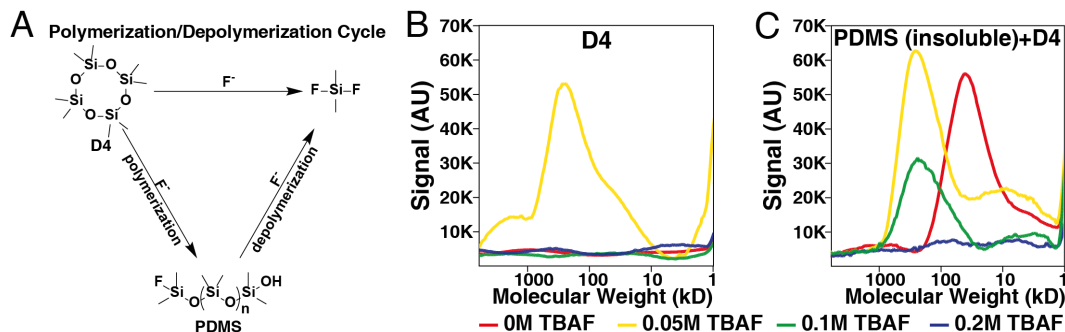


Figure 3.2: The effect of activator concentration on the polymerization/depolymerization process. (A) Two competing reactions with the same initiator. The fluoride nucleophile, when interacting with a D4 monomer, can either polymerize it (down arrow) or make it unreactive (right arrow). The polymer that is formed can then also react with the fluoride nucleophile to depolymerize and form a none reactive species (upwards arrow) (B) D4 polymerization shows strong dependence on TBAF concentration. Low concentration of TBAF (0.05M, yellow curve) forms high molecular weight polymers (170kD). Higher concentration of TBAF (0.1M green curve and 0.2M blue curve) give no detectable high molecular weight polymers. (C) Competition between TBAF reaction with either PDMS or D4. Low TBAF concentration (0.05M, yellow curve) shows high molecular weight polymer (190kD). Intermediate TBAF concentration (0.1M, green curve) gives slightly lower molecular weight polymer (140kD) at a lower intensity. This polymer appears due to PDMS presence at the beginning of the reaction, despite the D4 presence. At the highest TBAF concentration (0.2M, blue curve) there is no visible high molecular weight polymer due to D4 presence, despite PDMS initial presence.

3.3 Results and Discussion

Initially, we sought to determine if the fluoride in TBAF could both polymerize and depolymerize Octamethylcyclotetrasiloxane (D4) simply by varying its concentration. As a first step, we compared TBAF, our initiators', ability to depolymerize Polydimethylsiloxane (PDMS) and polymerize D4 monomers under identical conditions. A reaction between D4 monomers or a PDMS linear polymer with different concentrations of TBAF (0.05M, 0.1M and 0.2M) in DMSO was performed. The two competing reactions (polymerization and depolymerization) should occur in a vial where both polymers and monomers were present. (Figure 3.2A) The molecular weights of the resulting polymeric species were quantified via GPC. (see experimental section and appendix B for details)

We examined a range of fluoride concentrations to determine the conditions that enable subsequent polymerization of D4 and depolymerization. The D4 polymerized only at the lowest TBAF concentration (0.05M) (Figure 3.2B, yellow curve). The polymerization reaction at this concentration resulted in a high molecular weight polymer ($\approx 170\text{kD}$). However, increasing TBAF concentration to either 0.1M or 0.2M resulted in the complete loss of the polymeric species. (Figure 3.2B, green and blue curves) This suggests there could be an ideal concentration for the nucleophilic species, to initiate the polymerization reaction. As the TBAF concentration increases above this ideal point, there are presumably a large number of initiation events resulting in shorter polymer chains that are not detectable by GPC.

When we treated a mixture of both linear PDMS chains ($\text{MW} = 24\text{kD}$) and D4 in the same vial with TBAF, the molecular weight of the resulting polymeric species depended on the TBAF concentration, with a different concentration needed for breaking the chain. (Figure 3.2C) At the lowest TBAF concentration (0.05M), we observed a higher molecular weight polymeric species of $\approx 190\text{kD}$ (Figure 3.2C, yellow curve). At the intermediate TBAF concentration (0.1M) we found a lower molecular weight polymer of $\approx 140\text{kD}$ at a lower intensity. (Figure 3.2C, green curve) At the highest TBAF concentration (0.2M), we could not detect any high molecular weight polymers. (Figure 3.2C, blue curve) The presence of linear PDMS at the intermediate TBAF concentration encouraged the formation of a high molecular weight polymer that could not be formed with D4 alone (compare green curves in Figure 3.2B and 2C). In contrast, at the highest TBAF concentration, the larger molecular weight polymers disappeared and the D4 only formed low molecular weight species (blue curves in Figure 3.2B and 2C, compare with blue curve in Figure B.2). This data suggests a strong correlation between the TBAF concentration and the formation of high molecular weight polymers of PDMS. The length of the new polymeric chain depends on the initial state, with pre-formed polymers giving much higher molecular weight polymers.

With the understanding that D4 and PDMS polymerization and depolymerization could be

controlled within a range of TBAF concentrations, we examined if a similar concentration range would restructure cross-linked siloxanes. We sought to determine whether the balance between removal and growth of material would restructure the material. To test restructuring, we used a flow system as previous work showed that removal of material required flow.^{52,49,87,88} We cast a 100-150 μm wide PDMS membrane and preswelled it with varying concentrations of a D4/D4-D4 mixture (2.4M and 2.9M as measured by NMR, see Figure B.3). We used a D4/D4-D4 mixture to maintain chemical homogeneity and to provide crosslinking. We prepared D4-D4 in D4 at 1% w/w as described in the experimental section and appendix B. We then diluted the mixture with inert tetra-ethyl-silane (TES) to achieve the desired concentration. We sandwiched the preswelled PDMS membrane between a glass plate and a microfluidic open-faced glass flow cell and submerged the entire structure within a 65 °C glycerol bath. (Figure 3.3A) We then flowed TBAF, at increasing concentration (0.05M, 0.1M and 0.2M) and increasing flow rates (0.05, 0.1 and 0.4 mL/min) through the flow cell. After 30 min, we removed, cleaned and cut the membrane for visualization. (see experimental section and Appendix B) The cross section was visualized with light microscopy (Figure 3.3B, first row) and the changes in the membrane width due to growth or removal of material were analyzed with ImageJ software. (Figure 3.3B and appendix B) To quantify the extent of growth or removal, we compared images with a threshold showing the edge of the reacted membrane to an unreacted membrane. (Figure 3.3B, growth - cyan, removal - magenta). The total growth area of the membrane was measured in four replicates for each set of conditions. (Figure 3.3C and B.5) Generally, we observed that at lower D4/D4-D4 concentrations, material is more likely to be removed from the membrane. This reduction in monomer concentration lowers the polymerization rate relative to the depolymerization rate – resulting in more removal than growth. In addition, there was a minimum flow rate threshold necessary for removal of material. Conversely, under low flow rates we only observed growth of material. These observations suggest there is a balance between flow rate, concentration of initiator and concentration of monomer that will either initiate growth or

removal of material. For example, at 0.1 mL/min, 2.4M D4/D4-D4 the maximum growth occurred at 0.05M TBAF while at 2.9M D4/D4-D4 the maximum growth occurred at 0.1M TBAF. (Figure 3.3C)

With this information, we sought to relate the membrane growth/removal results with those observed in solution. Since all components of the system participate in the reshuffling of the chemical bonds, the chain length will be determined by all of these parameters. The concentration of TBAF changes the size of the resulting polymer, as was shown in solution. (Figure 3.2) In our flowing system, both the small chains of depolymerized PDMS and the polymerized D4 oligomers are constantly either being polymerized or depolymerized in a process initiated by TBAF, while at the same time, these siloxane chains are flowing into and out of specific locations in the system. This complex interplay enables a dynamic structural equilibrium (Figure 3.3B) where a material can be reshaped just by shifting between the two states of polymerization and depolymerization.

Interest in observing growth and removal of material simultaneously in the same system, led to the development of a method that allows a channel to migrate within a solid matrix. This behavior occurs commonly in nature, where tissue microvasculature re-patterns the underlying structure by shifting vascular pathways.⁸⁹ We used our system to mimic a microvascular re-patterning event by altering the structure of a single micro channel, shifting it in space. The VaSC technique^{52,48} was used to fabricate two parallel micro channels, 300 μm in diameter and separated by a 60 μm wide PDMS membrane. To induce polymerization, we submerged the sample in a 65 °C glycerol bath and applied the conditions for maximal growth, with a high monomer concentration. (Figure 3.3C) We flowed D4/D4-D4 at 0.05 mL/min through the left channel (Figure 3.4). The D4/D4-D4 diffused through the PDMS membrane. Through the adjacent channel, we flowed 0.1M TBAF in DMSO at 0.1 mL/min in the same direction. We let the solutions flow for 30 min followed by the removal of D4/D4-D4 for visualization by heating the sample under vacuum (115 °C, 170 mbar) over night.

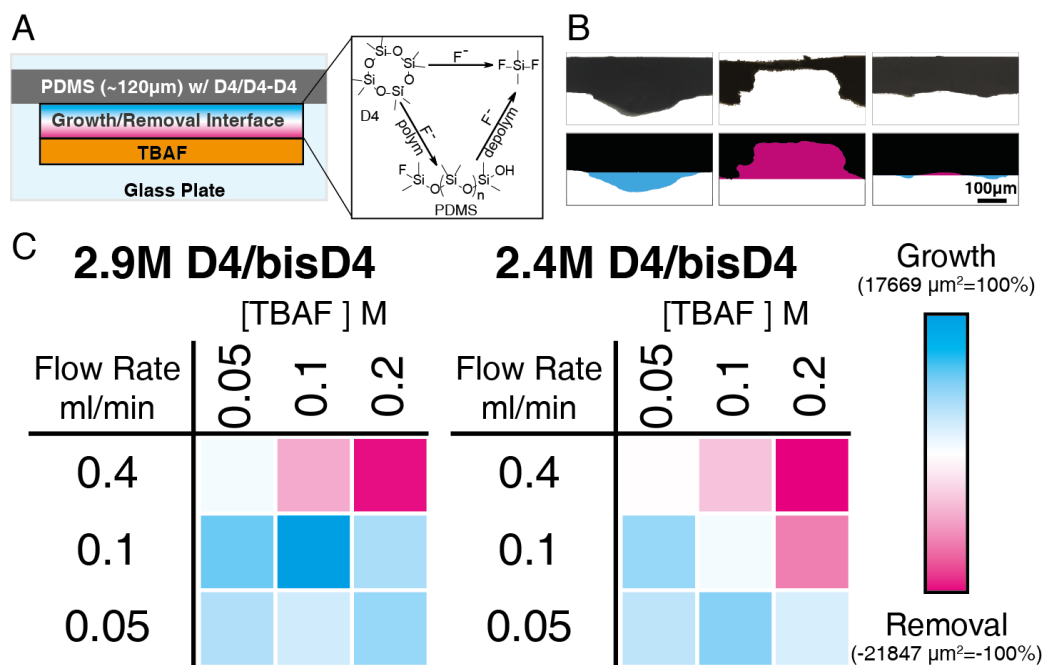


Figure 3.3: Material remodeling in a flowing system. (A) Channel cross-section demonstrating the experiment: A 100-150 μm wide PDMS membrane (black) was pre-swelled with D4/D4-D4 at concentrations ranging from 2.4M to 2.9M then sandwiched between a microscope glass plate and a microfluidic open-faced glass flow cell (light blue). TBAF at concentrations ranging from 0.05M to 0.2M (orange) was flowed through the channel at flow rates ranging between 0.05 and 0.4 mL/min. Removal or growth of material (magenta/cyan gradient) was observed at the interface of the PDMS membrane and the flowing TBAF. (B) Top: representative light microscopy images of the membrane cross section. Bottom: the resulting image processing images false colored with magenta to represent removal of material and cyan to represent growth of material. (C) Quantitative results of the removal or growth of material were observed in 4 repeats under different monomer (D4/D4-D4) and activator (TBAF) concentrations as well as different flow rates. The removal parameter space is represented in magenta, while the growth parameter space is represented by cyan.

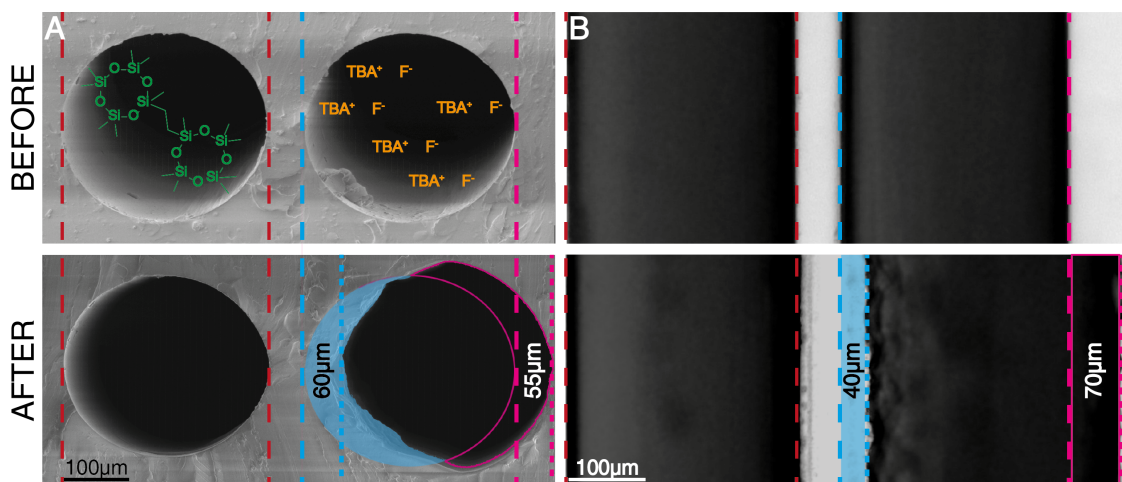


Figure 3.4: Concurrent growth and removal. Cross section (A) and top down (B) view of a shifting channel. Before: Two parallel circular channels embedded in PDMS were separated by a 60 μm wide PDMS membrane. After: D4/D4-D4 was flowed through the left channel at 0.05 mL/min, diffusing across the membrane. TBAF (0.1 M) was flowed through the right channel at 0.1 mL/min for 30 min, depolymerizing the PDMS where D4/D4-D4 concentration was low (away from the D4/D4-D4 channel, shown in magenta) and polymerizing D4/D4-D4 into PDMS where D4 concentration was high (near the D4/D4-D4 channel, shown in cyan). This concurrent growth and removal caused a shift of the channel through space, with almost no change in channel size.

We then compared both the cross section (Figure 3.4A, visualized by Philips XL-30 FEG SEM at 1 kV) and the top down view (Figure 3.4B, visualized by Zeiss Axio Observer.A1 microscope) of the sample before and after micro-vascular re-patterning. Since TBAF initiates both removal and growth of material, the dominant process in this case was determined by the relative local concentrations of the substrates. The TBAF channel polymerized new material on the edge adjacent to the D4 channel, while concurrently etching on the opposite face, following the concentration gradient of D4 diffusing away from the D4 channel. This combination of growth and etching resulted in the channel migrating through the solid PDMS matrix while maintaining the approximate dimensions of the original channel. The matrix of the material remodeled and adapted to the concentration while the microstructure features remained the same. This shifting of vascular channel through solid polymeric matrix is, in principle, identical to how vascular networks in biological systems undergo remodeling.

With this understanding of how polymerization and depolymerization could be balanced within a material to achieve microscale feature adaptation, we applied this process to periodic microstructures at lower length scales for concurrent structural adaptation. We prepared a PDMS pillar array. The pillars were 1 μm wide, 900 nm tall and arranged in a hexagonal pattern, with a distance of 3.4 μm between two neighboring pillars. (Figure 3.5A left column) The pillar structure was pre-swollen with either D4/D4-D4 for growth or TES as a control for 30 min and then submerged in 0.1M TBAF in DMSO at 65 $^{\circ}\text{C}$ for different periods of time (30 sec, 1, 2 and 5 min). (Figure 3.5A) In the samples that were not exposed to D4/D4-D4 and were only swollen with TES, the patterned structure disappeared upon longer TBAF exposure. In fact, after 1 min of TBAF exposure, only traces of the structure were visible and after 2 min of TBAF exposure, the structured side of the sample was indistinguishable from the opposing, non-structured side of the sample. (Figure 3.5A top row and Figure B.10) In contrast, the samples preswelled in D4/D4-D4 retained the full pattern after 5 min of TBAF exposure. Moreover, the characteristic features of the pattern grew after a 5 min exposure to TBAF to $\approx 2 \mu\text{m}$ wide, $\approx 1.5 \mu\text{m}$ tall pillars, reducing the distance between two neighboring pillars to $\approx 2 \mu\text{m}$ – a 100 % change in the overall width. (Figure 3.5A bottom row) The presence of D4/D4-D4 was essential for the preservation of the micro pattern. Additionally, the growth of material through D4 polymerization compensated for the removal of material initiated with TBAF and restored some of the damage imposed on the microstructure by the TBAF. As a result, the polymerization process enlarged the characteristic features of the structure.

In order to combine our understanding of the structural change across the two length scales (10^2 and $10^{-1} \mu\text{m}$) we examined, we applied our flowing experiment to the periodic microstructure. We made a 2 mm thick membrane with the periodic microstructure, preswelled it in 2.9M D4/D4-D4 in TES and flowed 0.1M TBAF in DMSO at 0.1 mL/min for 30 min using the setup shown in Figure 3.3A. The membrane grew greater than the pillar height (over 10 μm compared to less than 1 μm of pillar height); however, the patterned microstruc-

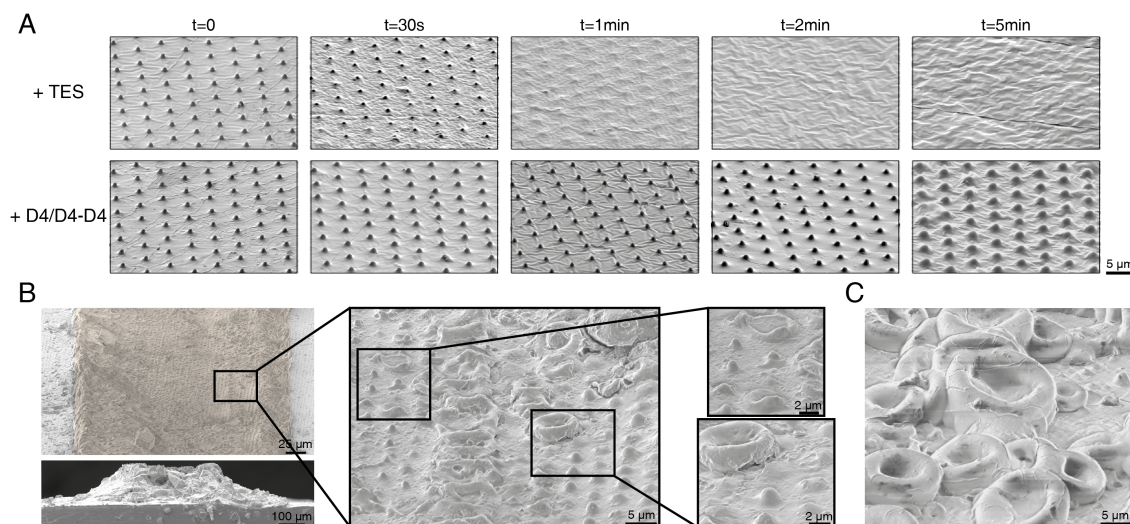


Figure 3.5: Dynamic restructuring of micro-features using polymerization and depolymerization. (A) A hexagonal micro pillar structure was made from PDMS. The structure was preswelled with either TES (top row) or D4/D4-D4 (bottom row) and then submerged in 0.1M of TBAF in DMSO at 65 C for 30 s, 1 min, 2 min and 5 min. The resulting structure was imaged using SEM. The pillars disappeared completely within 2 min when no D4/D4-D4 was present, however features were retained in the presence of D4/D4-D4 for up to 5 min. B. and C. Micro pillar structure was preswelled with 2.9M D4/D4-D4 in TES and exposed to flow of 0.1M TBAF in DMSO at 0.1 mL/min for 30 min. The resulting structure was imaged using SEM. The membrane grew (B, bottom left image). At the entry of the TBAF channel (B) upper left image, channel is false colored in orange) there were several different microstructures including pillars at the original size ((B) upper right image), pillar up to 2.5 times wider than original size ((B) lower right image) and donut like structures ((B) middle image). At the exit of the TBAF channel (C) the main microstructure that was found was the donut like structure. This restructure was separated from the larger scale structural change of the membrane as a whole.

ture was not erased but rather altered. (Figure 3.5B and C). Closer to the entrance point of the channel (Figure 3.5B) there were visible pillars. Some pillars retained their original size while some grew up to 2.5 times their original width. Additionally, some pillars grew together, forming toroidal (i.e., donut-like) structures. Moving towards the fluid exit of the channel, the pillars were subsumed by the toroids of varying size (i.e., packed donuts) until no pillars remained. (Figure 3.5C) These structures did not form when the micro pattern was not present. (Figure B.11) The unique structures most likely appeared due to the different flow in each location. TBAF flow has a large effect on the growth and etching of our system (as seen in Figure 3.3). In this experiment, the TBAF was flowing along a bumpy surface, causing localized turbulence in the flow, which might explain the appearance of these unique structures resulting from directional growth. This experiment shows that our system can independently alter microstructures in two length scale. Additionally, it demonstrates the system’s ability to form new and unusual structures starting from well-defined periodic patterns.

3.4 Conclusions

In conclusion, we present a synthetic system that mimics biological materials’ ability to reshape and restructure the matrix of a material. We use diffusion gradients to balance two opposing processes – the removal of material and the growth of new material. Using the same nucleophile for both reactions, both processes occur concurrently within the material – making our structures dynamic and responsive to concentration gradients. We show that either growth or removal can be controlled by slightly varying conditions such as flow rate, initiator concentration and local concentrations of monomer, controlled by diffusion and surface area. These materials can achieve structural equilibrium by maintaining a system that is chemically dynamic - enabling adaptive re-patterning and response to the micro-environment. In

future work, we will seek to apply different stimuli that trigger material reshaping and adaptation with the goal of creating bio-inspired materials capable of mechanical and electronic adaptation.

Chapter 4

Countercurrent amplification of gases

4.1 Introduction

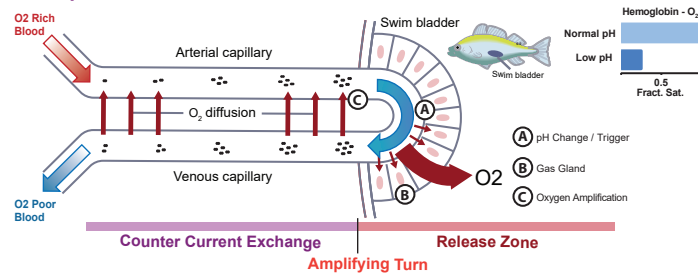
Concentration of dilute solutions is a central problem in separations ranging from protein isolation, to concentration of commodity gases.^{18,19,20,21} Current methods for gas concentration, including cryogenic distillation, vacuum swing adsorption, and chemo-selective permeable membranes have each advanced modern industry. Now, they account for 10-15% of the world's energy consumption. Lively and Scholl recently noted that more efficient methods of separation, “could save 100 million tonnes of carbon dioxide emissions and US \$4 billion in energy costs annually.”⁵

There are several methods of gas separation including, metal and persistent organic frameworks, perm-selective membranes, and electro-chemical methods.^{90,91,92,93} These methods include both the separation at the molecular level and processing of gas at the micro-level. For all of these, the best method remains countercurrent and cross-current exchange using hollow-fiber membrane contactors or micro-channels.^{19,94} Here, a solution high in solute concentration is separated by a semipermeable membrane from a fluid with low solute con-

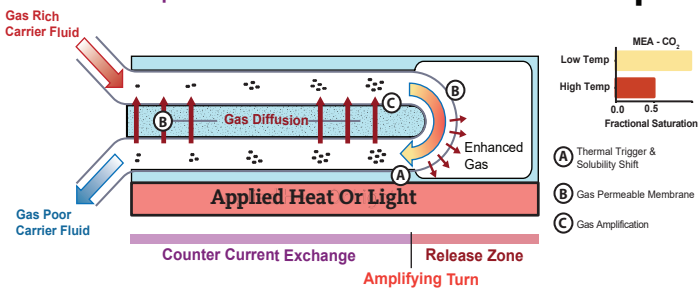
centration flowing in the opposite direction. For traditional countercurrent extraction, the output concentration is limited to the partial pressure of the gas above a bulk phase of the carrier fluid at the release conditions used. In contrast, countercurrent amplification allows the output concentration to reach many times that of bulk phase partial pressures. Used by many deep-sea fish to maintain neutral buoyancy even at great depths, countercurrent amplification can drive oxygen from ambient concentrations of 0.0003 M to 3.9 M.^{95,96,22,97,98} The key to attaining these concentrations is a series of looped blood vessels between which gas can diffuse combined with a gas release trigger. Blood flowing into the swim bladder passes by a loop adjacent to a gas storage bladder where the release of oxygen from hemoglobin is triggered due to the interaction of released lactic acid and a pH sensitive hemoglobin. Now rich in free oxygen, the blood flows back alongside the incoming channel where free oxygen can diffuse into the incoming channel, increasing the concentration of hemoglobin bound oxygen. The cycle repeats, successively increasing the oxygen concentration in the loop until an equilibrium is reached. (Fig 4.1a) The countercurrent amplification process produces a higher output concentration for a given release trigger than could be obtained in bulk solution. Here we show an engineered swim bladder, that employs a general mechanism of countercurrent amplification to extract CO₂ and O₂. We fabricated a model countercurrent amplifier consisting of a single, looped channel, separated by a gas permeable membrane. (Figure 4.1b,c) To trigger a change in solubility, we applied photothermal or thermal energy to one face of the amplifier (Figure 4.1a).

Countercurrent amplification offers a new process to supplement current separation methods, with two unique features that build on countercurrent exchangers. First, a countercurrent amplification system merges the gas release or “stripping” step from a solute with countercurrent exchange. In biological systems, this coupled exchange/release minimizes input energy and foot-print. Second, the amplification can achieve very high purity through selective binding and release. In our proof-of-concept methodology, we demonstrate that counter-current amplification can be performed in a single device with gas purities reaching

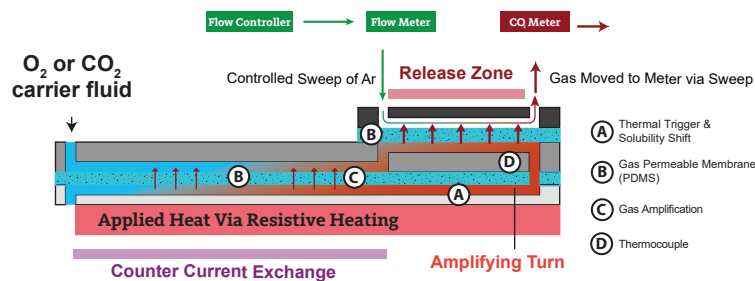
a) Inspiration - Fish Gas Bladder



b) Concept - Counter Current Amplifier



c) Design - Trigger & Gas Measurement



d) Fabrication - Acrylic Amplifier

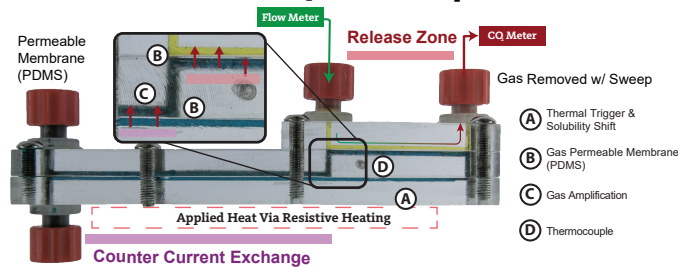


Figure 4.1: (a) Diagram of the fish O₂ concentration mechanism. a - location of the lactic acid gland used to trigger the release of O₂ from hemoglobin as a result of a shift in pH. b - gas gland composed of a semipermeable layer of cells at the interface of the blood vessels and the swimbladder. c - Back diffusion of O₂ into the inlet channel leading to a concentration amplification. (b) Conceptual diagram of the artificial concentration mechanism. a - Location of the thermal or light based trigger for gas release from the carrier solution. b - Location of the gas permeable membranes allowing the diffusion of gas between fluid channels and between fluid and gas channels. c - Back diffusion of gas into the inlet channel, leading to concentration amplification. (c) Design of the countercurrent amplification device used in this paper. (d) Photo of the fabricated device consisting of 3 layers of acrylic with machined channels and PDMS membranes between the layers.

up to 100 % purity from a continuously running counter current amplifier with an internal measured temperature of 40 °C. At an internal temperature of 35 °C, the system leveled off at 68 % CO₂. Our initial device results in a 242 % increase in the rate of gas release from the countercurrent amplification architecture compared to a channel that is heated, but does not experience countercurrent exchange. Due to the photo/thermal trigger, our system, unlike that of the fish, transfers both heat and gas across the membrane separating the incoming and outgoing channels of the device. (Figure 4.1) As such, to understand how our synthetic countercurrent amplification results in a higher rate of released gas, we determine the contributions of both heat and gas to our observed amplification.

In designing the countercurrent amplifier, we pursued a general test platform to address a wide range of target solutes and solutions. In the swim bladders of teleost fish, the amplification of solute concentration is the result of a counter-current vascular exchanger, the rete mirabile, where vessels are looped back onto themselves – separated by a thin semipermeable membrane. Triggered release of the solute from a carrier fluid in the loop creates a concentration gradient between the incoming and outgoing vessels. This looped gradient drives a positive feedback where the solute concentration entering the looped (release) section increases, resulting in a larger release of solute in the looped section (release section, Figure 4.1).⁹⁷ To build an artificial system, our design requires (1) a compatible carrier fluid, (2) a release trigger that changes solubility, and (3) easy fabrication for modularity. For solutes, we selected CO₂ and O₂ for their industrial and health importance, and well-studied capture solutions.

We broke the construction of the counter-current amplifier up into four main components, the countercurrent exchange zone, where diffusion takes place between the incoming and outgoing fluid channels, the release zone, where the solute of interest can escape from the system, the capture fluid, and the release trigger mechanism. (Figure 4.1c) Combined, these features replicate the mechanism of amplification described above. These components were

recreated in the design seen in Figure 4.1d. Acrylic (5 mm thick) was chosen as the structural material due to the low permeability of both CO_2 and O_2 through it, and the ease of machining small channels in the material.⁹⁹ Polydimethyl siloxane (PDMS, 140 μm thick) was chosen as the membrane material due to the ease of fabrication of varying thicknesses and the relatively high permeability of both CO_2 and O_2 (3800 and 800 Barrer respectively) through the material.¹⁰⁰ Gas selectivity in our test system was driven by the carrier fluid and the source gas, and the effect of this system on contaminant gas concentration was not investigated. The behavior of contaminants in our system likely depends on the change in solubility relative to the gas of interest. Most critically, this design allowed multiple iterations to be quickly fabricated and tested. Channels were all 1 mm x 1 mm with an overall path length of 192 mm (see SI Sec. 1 all dimensions). To measure flux rates, an argon sweep gas was used to decrease the temporal delay in gas release and gas measurement due to diffusion limits. Absolute concentration measurements were made in the absence of the sweep gas (SI Sec. 1.3). The release trigger consisted of an electric heating pad set to 65 °C. To deliver localized heating and increase efficiency, we employed a photothermal release mechanism which uses carbon black nanoparticles suspended in the dilute gas solution to selectively heat the solution only where a 300 W solar simulating lamp was shining. Characterization of the photo-thermal release behavior, characteristics of carbon black and efficiency were all previously reported.^{101,102,103} Incorporating the directed, photo-thermal release into the countercurrent architecture enabled a higher release rate of CO_2 from the system. Since each gas requires different carrier solutions, release conditions and measurements, each will be discussed separately. To determine the effects of counter-current amplification and the difference between the transfer of heat and the transfer of gas, we validated the countercurrent amplification mechanism using the MEA/ CO_2 system as well as explore O_2 as a potential application. (Figure 4.2a-d).^{104,101}

For many industrial processes, gas separations make up a large fraction of overall costs.⁵ Carbon dioxide is an important precursor chemical to many synthetic feedstocks and plays

an increasingly important role in the global climate.^{105,106,107,108} The industry standard for CO₂ capture uses aqueous amines to chemically bind the CO₂ combined with a pressure or thermally driven stripping process to transfer it to storage. The most predominant of these amines is monethanolamine (MEA) which has been extensively studied in the past.^{19,109,110,111} Within the temperature range of this study (25 – 65 °C, see SI Sec. 4.2), the standard MEA:H₂O 30:70 (w/w) solution has a temperature dependent change in bound CO₂ of -0.0048 M·K⁻¹.¹¹⁰ Improving this process of CO₂ capture and reducing costs, could enable more widespread use of this technology, reducing overall emissions. However, to establish the basic response and critical parameters of an engineered countercurrent amplifier, we have not focused on one specific application.

Beyond CO₂, O₂ has a great need for low-footprint, low-energy purification. Rapid access to concentrated O₂ in trauma scenarios plays a key role in reducing patient mortality and is necessary for many industrial processes including welding and production of steel.^{112,113} Expanding the breadth of available methods for oxygen concentration beyond existing cryogenic distillation and vacuum swing adsorption could expand the situations and applications where access to oxygen is available. As the gas bladder of fish already purifies oxygen, we engineered our synthetic gas bladder for O₂ enhancement. To keep the same photo/thermal triggering mechanism and apparatus, but test O₂ enhancement, we employed perfluorooctane as the carrier fluid which has a temperature dependent change in oxygen solubility of -0.00013 M·K⁻¹ within the temperature range of this study (25 - 65 °C).

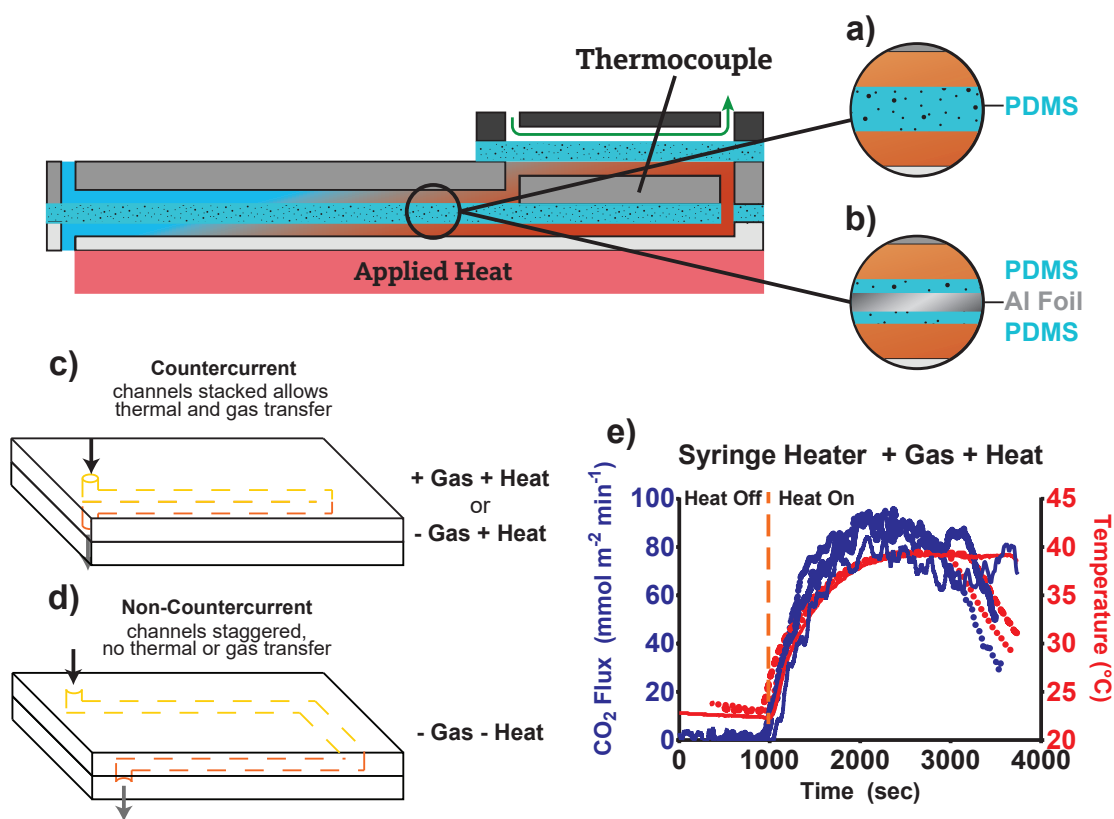


Figure 4.2: (a) Single 140 μ m PDMS membrane - allows the transfer of gas and heat between channels. (b) Aluminum foil sandwiched between two 70 μ m PDMS membranes - allows the transfer of heat, but not gas. (c) Channel setup for (+ Gas + Heat) and (- Gas + Heat) - the incoming (yellow) and outgoing (orange) channels are adjacent, allowing diffusion to take place. (d) Channel setup for (- Gas - Heat) - the incoming (yellow) and outgoing (orange) channels are shifted 5 mm laterally, preventing mass or thermal transfer between them. Note: the dimensions are not to scale and certain components are not shown for clarity. (e) Representative data output from the countercurrent amplifier showing three separate trials. (Blue: CO₂ flux, Red: temperature)

4.2 Results

4.2.1 Device Design and Validation of the Mechanism of Countercurrent amplification

For all initial experiments, the CO₂/MEA flow rate was 1 ml/min. Carbon dioxide was collected with argon as a sweep gas with a flow rate of 5 ml/min, and an applied surface temperature of 65 °C. Under these conditions, CO₂ was released at a rate of 6.4 $\mu\text{L}/\text{min}$ (80.2 $\text{mmol}\cdot\text{m}^{-2}\cdot\text{min}^{-1}$) with an internal temperature of ≈ 40 °C (Figure 4.3a). See Figure 4.2e for an example of the experimental output. This rate represents the contributions from countercurrent diffusion of gas and heat in the countercurrent exchange zone of the swim bladder in addition to the rate expected in the absence of the countercurrent exchange zone. The steady-state release rate was measured to increase the temporal resolution of the measurement.

To isolate the contributions of the heat and gas, we fabricated multiple control devices to separate counter-current heat and gas amplification. We altered the countercurrent exchange zone by blocking (a) gas and heat – achieved by diverting the returning channel, eliminating the gas and heat exchange (- Gas - Heat), or (b) eliminating the gas exchange between the fluid channels, but allowing heat (- Gas + Heat) – achieved by placing a small layer of aluminum foil within the membrane. (Figure 4.2a-d)

To test how much of the contribution came from the countercurrent amplification rather than simply from the applied heat, we built a gas bladder where the incoming and outgoing channels were laterally shifted – removing both heat and gas diffusion between the channels (- Gas - Heat) (Figure 4.2d). Under identical heating conditions, the laterally shifted, (- Gas - Heat), channels released 2.6 $\mu\text{L}/\text{min}$ (33.2 $\text{mmol}\cdot\text{m}^{-2}\cdot\text{min}^{-1}$) of CO₂ with an internal temperature within the countercurrent loop of ≈ 40 °C. Comparing these data with the full

countercurrent system (+ Gas + Heat) shows a 3.8 $\mu\text{L}/\text{min}$ (59 %) reduction in CO_2 release (Figure 4.3a). This percentage decrease can be directly contributed to the retention of heat and diffusion of gas due to the countercurrent architecture of the countercurrent exchange zone.

To isolate the contribution from countercurrent gas transfer between the fluid channels from the combined heat and gas transfer, we isolated the countercurrent heat transfer via a second control device. We fabricated a device with a membrane modified to prevent gas diffusion between the fluid channels, but allow heat transfer between incoming and outgoing channels (- Gas + Heat). The membrane between the fluid channel and the sweep gas channel was unchanged. The membrane consisted of two 70 μm PDMS membranes on either side of a 20 μm sheet of aluminum foil. Keeping the overall PDMS thickness the same results in a membrane with only a calculated 0.02 % increase in thermal resistivity compared to the original 140 μm thick PDMS membrane (SI Sec. 1.4). This keeps the countercurrent heat exchange in the countercurrent exchange zone essentially identical, isolating the elimination of gas diffusion in that zone as the only variable changed to an appreciable degree (- Gas + Heat). Under otherwise identical conditions, CO_2 was released at a rate of 4.3 $\mu\text{L}/\text{min}$ (53.9 $\text{mmol}\cdot\text{m}^{-2}\cdot\text{min}^{-1}$) with an internal temperature of $\approx 40^\circ\text{C}$. (- Gas + Heat) Compared to the full countercurrent system (+ Gas + Heat), the (- Gas + Heat) system showed a 33 % reduction in CO_2 release. The difference between the (+ Gas + Heat) and the (- Gas + Heat) system can be attributed to the elimination of gas diffusion in the countercurrent exchange zone. (Figure 4.3a).

To achieve precise measurement for our controls, we swept the channel with a slow, continuous flow of Argon. An argon sweep is commonly used in the Wicke-Kallenbach method of measuring permeation to enhance diffusion across the membrane and achieve higher rates of gas transfer. As such, argon may influence the measured release rate by providing a larger gradient during CO_2 release. The maximum output concentration of the system is of in-

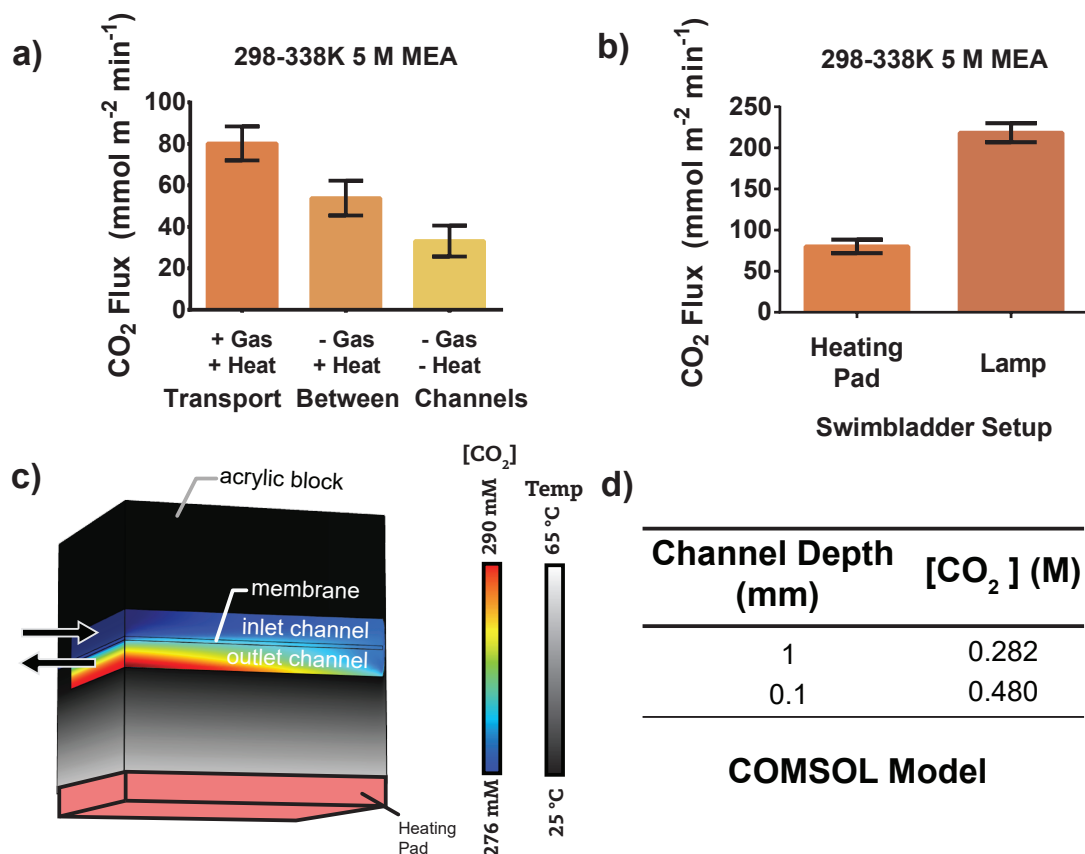


Figure 4.3: (a) Comparison of CO₂ release rates for the full countercurrent (+ Gas + Heat), partial countercurrent (- Gas + Heat) and no countercurrent (- Gas - Heat) systems. (b) Comparison of CO₂ release rates with a heating pad vs. a 300 W lamp. (c) Simplified COMSOL model of the countercurrent amplifier, scaled down along the length of the channel for clarity. Grey scale portion indicates the temperature in the acrylic section, and the rainbow scale portion indicates [CO₂] in the channel and membrane. (d) Comparison of the maximum CO₂ concentration (Initial concentration 0.276 M) in the looped section of the COMSOL model for channel depths of 1 mm and 0.1 mm.

terest, since it represents a more direct measure of the concentration of CO_2 in the release zone. A sealed adapter for the CO_2 meter used in previous experiments was designed and fabricated that allowed the sensor to be directly attached to the countercurrent amplifier. Fluid flow rates remained at 1 ml/min, while the sweep gas was eliminated. Gas diffusion is driven by the concentration gradient between the fluid side of the membrane and gas side until an equilibrium is reached. The head space of the sensor unit is initially filled with ambient air which accounts for the remainder of the gas composition at the experiment end. Without the sweep gas, the gas release rate was not directly measured, and a derived initial flow rate was not considered accurate enough to be reported. The device was preheated to desired the experimental temperature in the absence of the carrier fluid. When the measured CO_2 concentration was below 5 %, the carrier fluid was introduced to the system and flow was initiated. The experiment was run until no significant change in CO_2 concentration was observed for 5 minutes. With a measured internal temperature of $\approx 35\text{ }^\circ\text{C}$, a maximum concentration of 68 % CO_2 was observed. With a measured internal temperature of $\approx 23\text{ }^\circ\text{C}$ (no heating), a maximum concentration of 30 % was observed (SI sec. 2.1). At an internal temperature of $40\text{ }^\circ\text{C}$, a maximum concentration of at least 100 % CO_2 was observed.

4.3 Improving Countercurrent amplification using localized photo-thermal triggered release

While applying thermal heating demonstrated the principles of the countercurrent amplification, we sought to increase the efficiency of the device by maximizing the localization of triggering and diffusion. By localizing a heating source to within only the exchange section, we hypothesized we would see a much larger increase in countercurrent amplification and gas production. In previous work, we have implemented photo-thermal heating of nano-particles to trigger gas release at the nano-scale. This unique effect has been shown by others to

produce steam and vapor from water while only heating the solution to $\approx 70\text{ }^{\circ}\text{C}$.¹⁰³ This effect works by predominately heating the solution in direct contact with the nano-particles in solution. By limiting bulk heating, more of the absorbed energy goes into gas release versus heating the solution. In our own work, we showed that the photo-thermal heating of carbon black nano-particles was sufficient to strip CO_2 from MEA/ H_2O at a solution thickness of $100\text{ }\mu\text{m}$ or in bulk solution while only increasing the temperature to $65\text{ }^{\circ}\text{C}$ rather than the normal $120\text{ }^{\circ}\text{C}$. This localized heating and high release rate fit the criteria for our local triggering mechanism¹⁰², so we implemented photo-thermal release of CO_2 mediated by carbon black within only the releasing, outgoing channel replacing the applied heat pad. (Figure 4.1d) To stimulate the photo-thermal release of CO_2 , a 300 W halogen light source was applied at the face of the device with an intensity of 1500 W/m^2 . In this device, the transparent acrylic top allowed transmission of the light into the nanoparticle rich solution. The H_2O /MEA capture fluid now contained carbon black nanoparticles at 0.2 % (w/w) (see SI sec. 3) which did not significantly change the amount of CO_2 being moved, but provided a photo-thermal release source. This particle loading also blocks the transmission of light to the incoming channel – meaning no light penetrated the back/incoming channel preventing premature release of gas in the countercurrent exchange zone. (Figure 4.1d) By adding only light to the system, a release rate of $17.35\text{ }\mu\text{L/min}$ ($218.5\text{ mmol}\cdot\text{m}^{-2}\cdot\text{min}^{-1}$) was observed with an internal temperature of $\approx 40\text{ }^{\circ}\text{C}$, an increase of 170 % over the heat-pad triggered system (Figure 4.3b). We cannot directly compare the efficiency of these processes as though the temperature of the solution was only $40\text{ }^{\circ}\text{C}$, the amount of light entering the channel certainly increased the overall energy required to achieve this higher release rate. However, localizing the triggering mechanism can be used to increase the countercurrent amplification effect.

4.4 Countercurrent amplification applied to other dilute gases – purifying O₂

With the countercurrent amplification mechanism validated using the CO₂/MEA system, we tested the viability of O₂ release using PFO as the carrier solution. Our interest in oxygen stems from its applications both in industry and as an important piece of modern medical facilities. Oxygen amplification presents an additional challenge over CO₂ as the change in dissolved gas for a given temperature change of O₂/PFO is just 2.7 % of the CO₂ system^{114,115,116,100} while the permeability of O₂ through PDMS is only 21 % respectively of the CO₂/MEA system.^{114,115,116,100} The countercurrent amplifier configuration was adjusted to accommodate the flow and detection of the lower gas release rate. PFO was saturated with O₂ (0.02 M) prior to the start of the run and the flow rate of argon sweep was decreased from 5 ml/min to 1 ml/min to accommodate the expected decrease in gas release rate. The percent of O₂ was measured using a PreSens Microx 4 fiber optic sensor. All other conditions were kept the same, save for the modification of the carbon black nanoparticles with 1H,1H,2H,2H-Perfluorodecyltrimethoxysilane to improve the suspension within the PFO (See SI Figure 4.12,13).¹¹⁷ The rate of O₂ production was 0.8 $\mu\text{L}/\text{min}$ ($10.2 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{min}^{-1}$) for the PFO/O₂ system – 8 times less than the comparable experiment with the MEA/CO₂ system (Figure 4.4). See Figure 4.4b for an example of the experimental output. This result showed that the counter current amplification system can be extended to other gases where the thermal change in solubility can be induced within a carrier liquid. However, it also shows the importance of overall solubility of the desired purifying gas and the change in solubility upon triggering a change in solubility.

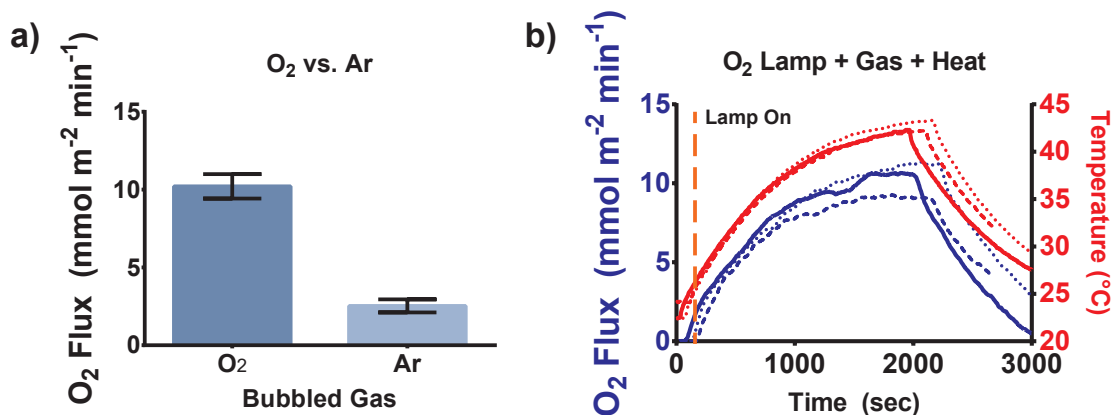


Figure 4.4: (a) Comparison of oxygen flow with oxygen or argon bubbled into the capture fluid reservoir. (b) Example of the oxygen flow rate data over time. (Blue: O₂ flux, Red: temperature)

4.5 Model to determine key parameters in countercurrent amplification

With the encouraging initial results of a counter current amplifier working for many gases, we sought to examine which parameters would lead to higher yields of gas. We developed a simplified COMSOL model to test how solubility changes, channel geometry and gas solubility could be used to improve performance of a counter current amplifier (Fig 4.3c, d). A major difference between the countercurrent amplification found in fish and our bio-mimetic system is the diameter of the channels. In the biological system, the channel diameter ranges from 0.001 – 0.01 mm compared to the 1 mm channel depths in our test system. The importance of channel size has been noted in various theoretical treatments of the swim-bladder system.^{22,97,118} Using a simplified COMSOL model, we saw that decreasing the channel depth to 0.1 mm from 1 mm resulted in a 34-fold increase in the difference between the initial concentration and the concentration under active heating (See SI Sec. 4 for additional details). The shorter average diffusive path between inlet and outlet channels allows for a greater proportion of released gas to be recycled into the inlet channel before exiting the system.⁹⁷ Our current design allows the device to be easily scaled using common fabrication tech-

niques including laser etching, or CNC machining in addition to pursuing the use of hollow fiber membrane contactors.¹¹⁹ In future work, we plan to tackle the engineering challenges required to create countercurrent amplifiers more closely matching those seen in nature.

4.6 Discussion

Our work is the first general application of a countercurrent amplification device outside of a biological system. Here, we fabricated a counter current amplifier using micro-machined acrylic components for the inlet and outlet channels and PDMS membranes for a semi-permeable membrane. (Fig 4.1d) The change in solubility was triggered using a thermal and photo-thermal effect that enabled changes in solubility along the axis of countercurrent exchange. We generalized the countercurrent system to release both CO₂ and O₂ by swapping the carrier fluid and matching each carrier fluid with a thermal switch of solubility. Using control devices we observed a 242 % improvement with our countercurrent amplification system (+ Gas + Heat) versus the sweep gas only system (- Heat - Gas) and were able to isolate the contributions of thermal and gas diffusion to the enhancement. Considering the countercurrent transfer of heat between channels, the total improvement due to the countercurrent diffusion of CO₂ was 150 %. Notably, in our best performing systems, the release mechanism was provided by simulated sunlight at ≈ 3 times a typical solar irradiance. The photo-thermal release mechanism might make solar amplification of gases a potential future application. Beyond broad light, narrow spectrum light of LEDs might be a highly efficiency way to implement a spatially controlled release.

Our results suggest that countercurrent amplification is a general principle that can be applied to many different heat driven gas separation challenges. In CO₂, a countercurrent amplifier could be used to lower the energy cost associated with stripping CO₂ during and capture and release process. The 242 % improvement in CO₂ released for an equivalent

amount of heat might lower the energy costs associated with stripping CO₂. For O₂, both the improved release rate and smaller footprint might improve oxygen delivery for combat and point of care treatment. In these applications, the lower power and smaller volume will be critical to making a more portable oxygen amplifier which could increase O₂ levels to near medical grade from atmospheric oxygen.

These exciting applications will require overcoming challenges and making improvements to countercurrent amplifiers. In this work, we constructed a model to examine how improvements in countercurrent amplification could be implemented. Notably, the rate of release and rate of permeation of the membrane should yield increases in countercurrent amplification. In particular, the membrane permeability can be rapidly adjusted by using semi-porous membranes that should allow direct CO₂ diffusion through liquid channels. The largest gain in performance can be achieved in size of individual channels, which currently exists at 1 mm, if lowered to 0.1 mm, could yield improvements of 35-fold in concentration increase due to the release trigger. Our intention is to develop countercurrent amplifiers with smaller channels that are interdigitated – analogous to our work on biomimetic exchangers.^{47,52} These smaller channels should yield the desired improvements in total gas released and gas purity as hinted at by the COMSOL work.

A major challenge of our current methodology is determining the purity of gas released. With small sample sizes, the measurement of released gas is challenging. In future systems, with improved release and a larger number of channels, it should be possible to measure the concentration and purity of the gas released from countercurrent amplification. In addition, larger changes in solubility are needed to achieve higher efficiencies and lower footprints. Photo-thermal heating mediates phase separation as well as gas release and we believe that a combination of solvents with different solubilities can be used to enhance the change in solubility for our photo-thermal triggering system.¹²⁰

Beyond these challenges and improvements, the potential of these systems to create large

concentration gradients opens the door to a variety of fields where a solute is concentrated from a dilute initial solution. We plan to apply this work to additional solutes and release triggers and are currently investigating the use of this technique for heavy metal cleanup, concentration of proteins, and isolation of other dilute gases.

4.7 Methods

4.7.1 Fabrication of countercurrent amplifier

All countercurrent devices were machined from 5 mm thick acrylic sheets purchased from McMaster Carr. Fluid channels are all 1 mm wide by 1 mm deep square cross sections for ease of fabrication. Technical drawings of the channel layouts can be found in appendix Figure 4.1 and 4.2.

4.7.2 Fabrication of hybrid membrane

A hybrid membrane was designed and fabricated as illustrated in Figure C.5 consisting of three layers. The two outer layers of PDMS maintain a consistent thermal resistivity compared to the original PDMS membrane as well as preventing corrosion of the aluminum layer by the MEA solution. The aluminum foil serves as a gas impermeable layer. Calculations detailing the thermal conductivity of the hybrid membrane compared to the PDMS membrane can be found in appendix section C.2.

4.7.3 Experimental setup

The gas detection system was designed to pick up gas flow rates in the 0.1 – 50 μL range. A photo of the experimental setup can be seen in appendix Figure C.6. A Smart-Trak 50 mass flow controller was used to ensure a consistent flow of argon. A Cole-Parmer mass flow logger (60 data points/second) and CO2Meters.com CO_2 sensor or PreSens O_2 sensor (1/3 Hz sampling frequency) enabled the release rate of the gas of interest to be measured. The flow meter was located upstream of the point of gas release due to the sensor's sensitivity to changes in gas composition. The additional volume of gas released by the countercurrent amplification system was considered negligible compared to the flow rate of the sweep gas. Flow rate data and percent gas data were combined in Mathematica by interpolating the data with a moving average of 20 points for the concentration data and 1000 points for flow rate data.

4.7.4 Oxidation of carbon black

Carbon black was oxidized using a modified procedure from Rouxhet et al.¹²¹ Two grams of carbon black (Cabot, N115) and 60 ml of 30 % H_2O_2 (VWR, 30%) were added to a 125 ml round bottom. The round bottom was fitted with a condenser and stir bar and brought to reflux for 24 hrs. The carbon black was separated from the H_2O_2 peroxide by filtration, washed with water and dried in a 120 $^\circ\text{C}$ oven. Oxidized carbon black was dried in a 110 $^\circ\text{C}$ vacuum oven for 1 hour.

4.7.5 Perfluorosilane modification of carbon black

Carbon black (500 mg) was weighed out into a 20 ml scintillation flask with stir bar charged with 5 ml of 1H,2H,2H,-perfluorodecyltrimethoxysilane. The flask was purged with argon

and sealed. The solution was stirred for 24 hours after which the solution was filtered and the carbon black nanoparticles were rinsed twice with hexanes and water then dried in the vacuum oven overnight. Characterization data can be found in appendix C.

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Appendix A

Structural remodeling through diffusion controlled surface removal

A.1 Sample Preparation

For a more detailed description please see our previous methods papers describing the fabrication procedure in great detail.⁵²

A.1.1 Catalyzation of the fibers:

To incorporate the SnOx Catalyst necessary for depolymerization in VaSC, a solution was prepared. 10 mL in total, the solution contained TFE, HCl and water at 50:12.5:37.5 vol/vol/vol respectively. The solution also contained a SnOx catalyst at loading of 13 mg/ml. The solution was placed in a 15 ml centrifuge tube, pierced to accommodate the fibers. The fibers were pulled up through the solution, using rotation, at a rate such that fibers had a residence time of 30 s within the solution. All experiments were performed at room temperature

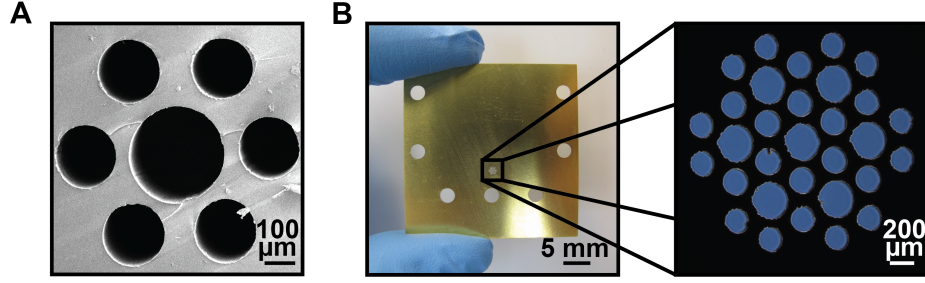


Figure A.1: Laser-etched micro-machined brass plates. Fibers are strung through the holes in the end caps, providing the desired pattern.

(21.5 °C).

A.1.2 Building the pattern:

Polydimethylsiloxane (PDMS) was created using mixtures of the Slygard 184 silicone elastomer base and curing agent (Dow Corning) with a 10:1 w/w ratio between base and curing agent via mixing in a paper cup. The mixture was degassed for 15 min to remove all trapped gas using a vacuum pump and glass bell jar. Treated fibers were patterned using laser micro-machined brass plates manufactured by Hodge Harland at the University of Illinois at Urbana-Champaign. (Fig. A.1) Fibers were strung through a pair of plates which were then screwed onto a Delrin mold box with dimensions of 25x25x25 mm. Fibers were tensioned until taut on a custom board with pairs of guitar tuning pegs on either side. (Fig. A.2, A.3) The degassed PDMS mixtures were poured into the mold and heated at 85 °C for 30 minutes to cure the mixtures.

A.1.3 Spreading the fibers:

Each fabricated unit of PDMS embedded with fibers was removed from the first mold and placed into a second mold box with dimensions of 25x25x50 mm. The fibers were separated and threaded through rubber end-caps made of polyurethane which were screwed onto the

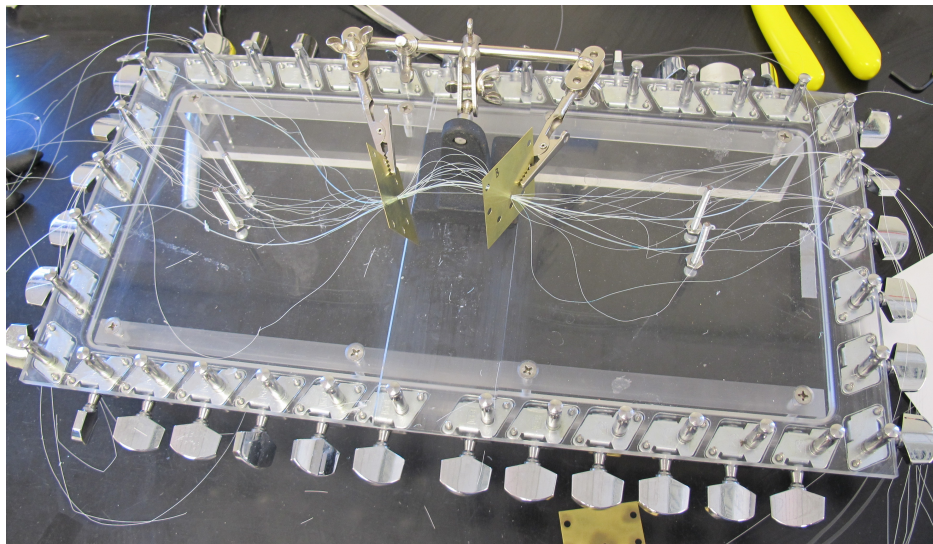


Figure A.2: Example custom molding board. Guitar tuners on either side provide tensioning for fibers.

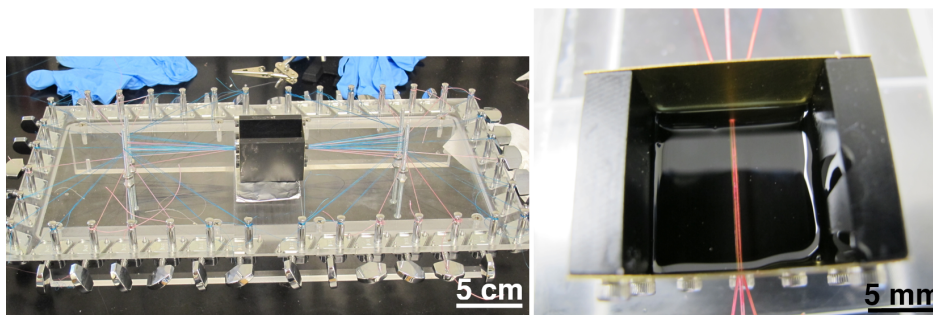


Figure A.3: Assembled molding setup. Fibers are tensioned through the brass end caps using the tuning board. Metal rods in the board act as pulleys allow the tuning pegs along the side of the board to tension the fibers.

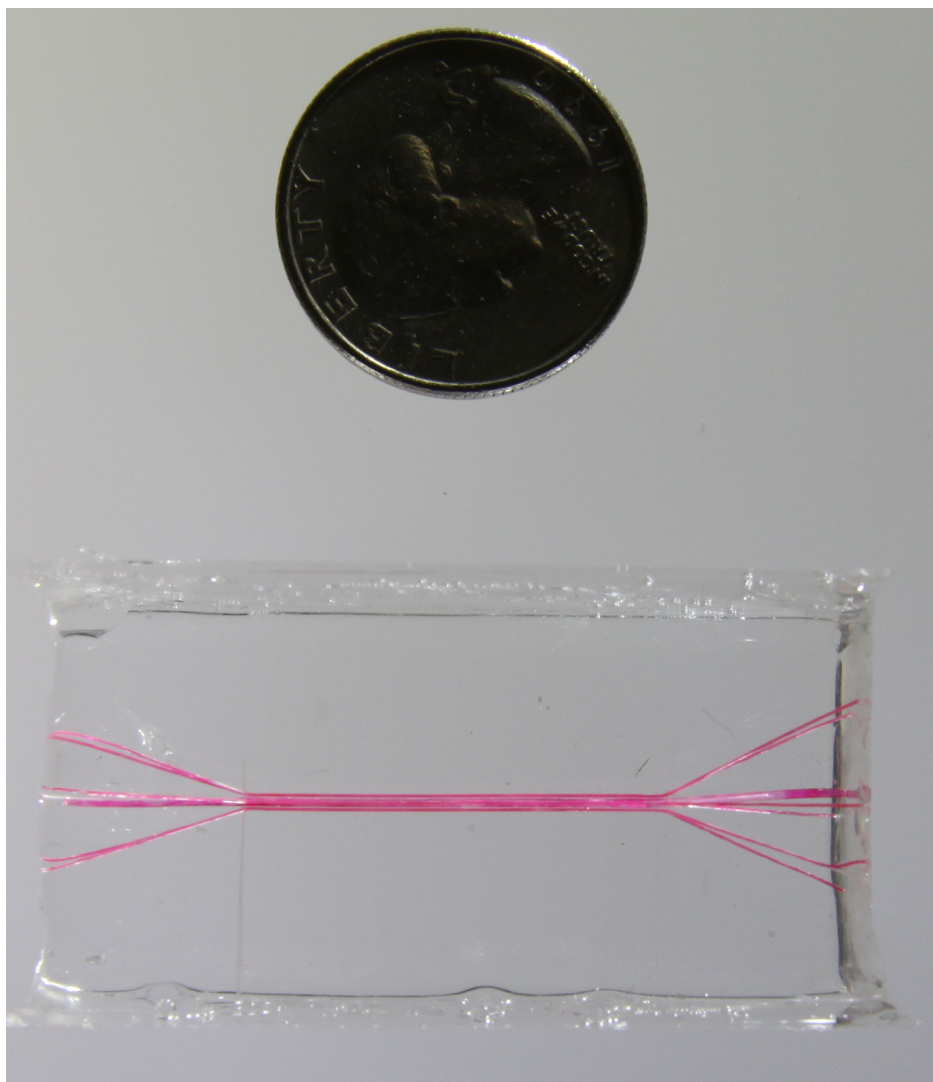


Figure A.4: Exchange unit after second molding. Fibers are separated into a larger pattern for easier loading of channels.

mold box. Syringe needles (B-D PrecisionGlide 18G1 Needle) were inserted through the PDMS end caps and fibers were threaded through the needles. The needles were removed leaving the fibers trapped in the end caps. The end caps were screwed onto the larger mold box and fibers were pulled taut by hand. A second mold of PDMS was cast again at 85 °C for 30 minutes (Fig. A.4). Longer samples were created using a 25x25x50 mm box as the first mold and 25x25x75 mm box as the second mold.

A.1.4 Vaporization of the fibers:

The vascular preforms were removed from the second mold. The vascular preforms were placed into a sealed vacuum oven (JEIO Tech Vacuum Oven Model OV-11/12) and subjected to a vacuum of 10 torr while heating at 210 °C for 48 h.

A.2 Diffusion Coefficient Measurements

TEMS Diffusion Coefficient in PDMS Using our generalized technique, two parallel channels, with 150 μm radius each were patterned in PDMS. One channel was filled with Ethanol and the other with Triethoxymethylsilane (TEMS) purchased from Sigma-Aldrich. Both channels were blocked to prevent evaporation with a PLA fiber. Over time, the TEMS and ethanol were absorbed into the material, resulting the volume of TEMS or Ethanol contained with the channel slowly decreasing. This change in volume resulted in a change of the solution length filling the channel, giving us a measure of their diffusion within the material. The change in height for both Ethanol and TEMS channels were tracked over time (Supplementary video 1). The distance of the fluid from the bottom of the channel was measured at 10 s intervals. The flux of material through the PDMS at those time points was calculated and plotted. (Fig. A.5) The diffusion coefficients were estimated based on the diffusion equation in a cylinder. The ethanol published diffusion coefficient of $1.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ¹²² in PDMS was used as a reference to determine the validity of the method.

A.3 HF_2^- Diffusion Coefficient in TBAF

The diffusion coefficient of HF_2^- was measured using 19F DOSY. 75% TBAF in water %vol, purchased from Sigma-Aldrich was diluted in deuterated DMF (Sigma-Aldrich) to

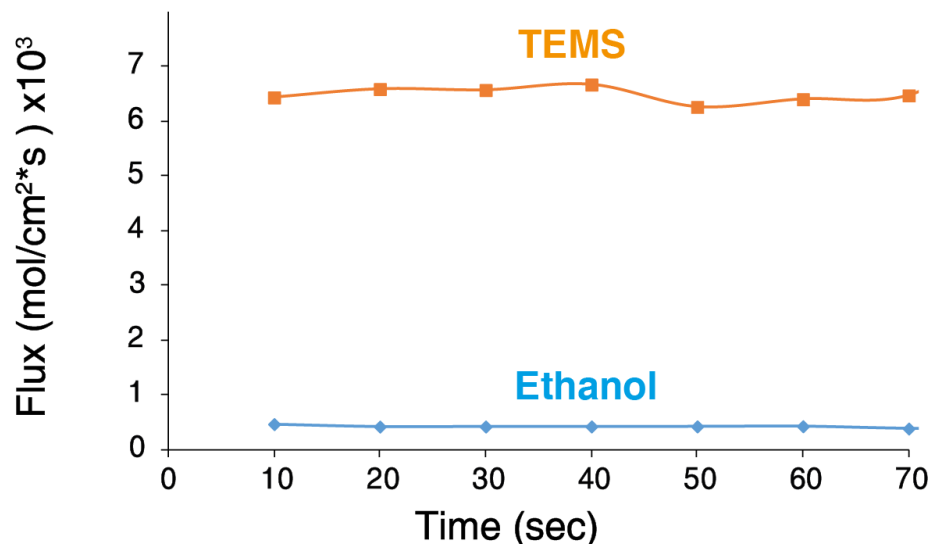


Figure A.5: Flux of TEMS and Ethanol through PDMS as was calculated from liquid volume change in a channel.

a final concentration of 683 mM of fluoride. The DOSY experiment was conducted via a stimulated echo sequence with self-compensating gradient schemes (convection corrected) at spectral widths of 16025.6 Hz. The relaxation delay, d1, was 5 s. The diffusion time, d20, was 75 ms. The gradient pulse length, p30, was 1.8 ms. The baselines of all of the spectra were corrected prior to data processing. The data were processed after the Fourier transformation of each FID with VNMRJ to obtain the chemical shift as the x-axis along with the calculated diffusion coefficient as the y-axis. (Fig. A.6) We found the diffusion coefficient to be $4.5 \text{ m}^2 \text{ s}^{-1}$ with about 90% accuracy.

A.4 Reaction Rates Measurements

A.4.1 PDMS etching rate

Six different concentrations between 2.73 mM and 683 mM of TBAF in DMF were flowed through a circular channel with diameter of $300 \mu\text{m}$. Using 40 X objective in Zeiss Axio

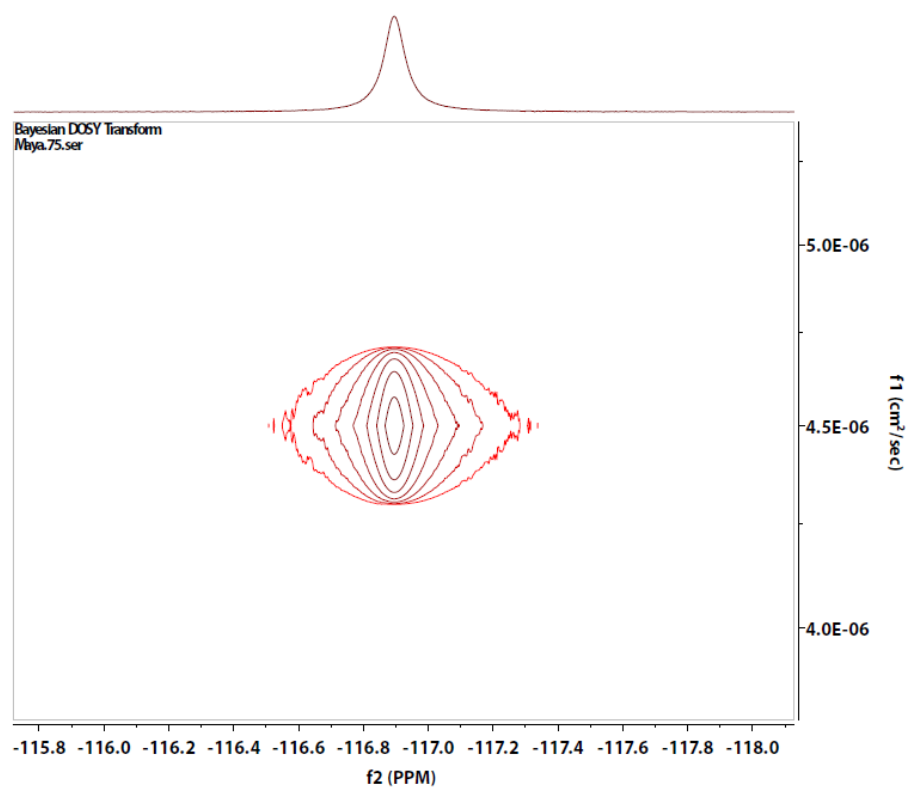


Figure A.6: Results for ^{19}F DOSY experiment. The x-axis corresponds to ppm, the chemical shift of the fluoride species is shown. The y axis is a logarithm of the diffusion coefficient.

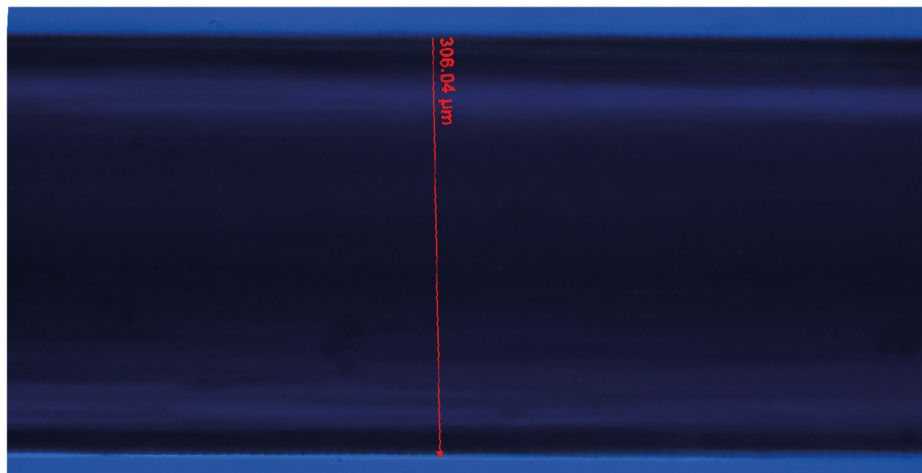


Figure A.7: A representative microscope image of channel width measurements.

Observer.A1 Microscope, the channel diameter was measured in ten different locations along the channel at three different time points (0, 24 and 48 min). The resulting average was used to calculate the width of the channel. (Fig. A.7) The difference in channel width between the time points was then calculated. The averaged rate of etching was then plotted as a function of TBAF concentration (Fig. A.8).

A.4.2 TBAF and TEMS reaction rate

The kinetics of the tetrabutylammonium fluoride (TBAF), triethoxymethyl silane (TEMS) reaction, were studied via NMR in deuterated chloroform and dimethylformamide (DMF). The reagents were obtained from Sigma-Aldrich with no further purification. The reagents were diluted to a final concentration of 90 mM (TBAF) and 10 mM (TEMS). Spectra were acquired on Bruker DRX500, and Bruker AVANCE600 spectrometers. Series of 8 scans (5.1 seconds each) were collected at intervals of 60 s (112 s total). The reaction proceeded slowly when run in chloroform with both the parent TEMS methylene peak and the ethanol methylene peak clearly visible throughout the reaction (Figure A.9). The observed ratio of ethanol production to TEMS depletion was 3:1. When run under the same conditions in

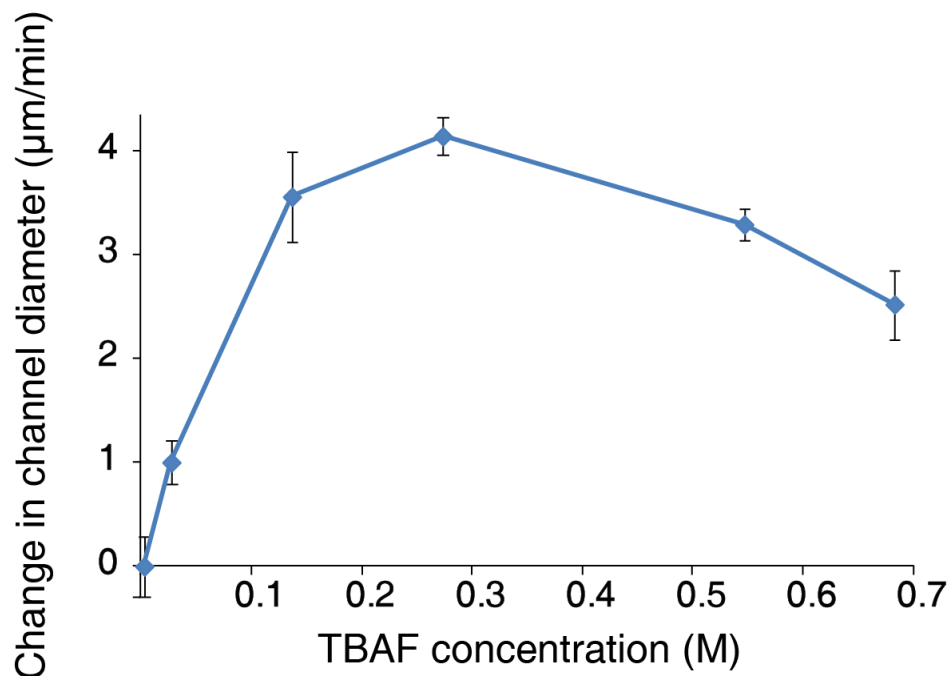


Figure A.8: Etching rate as a function of TBAF concentration. The change in channel diameter in $\mu\text{m}/\text{min}$ as it was measured when different concentrations of TBAF were flowed through a channel of $300\ \mu\text{m}$ initial diameter.

DMF, the reaction proceeded too quickly for observation via NMR. The initial starting conditions were diluted 30 times which allowed observation of reaction progress (Figure A.10). The diagnostic ethanol methylene peak was partially obscured by the ethanol hydroxyl peak. The line fitting function of Mnova was used to deconvolute the area of each peak. Assuming a second order reaction, we estimate the rate constant as $2\ \text{M}^{-1}\ \text{s}^{-1}$. Literature suggests that the TEMS/TBAF reaction is catalytic in the fluoride ion and results in the formation of silsesquioxane cages in the presence of water¹²³, therefore the data obtained provide an order of magnitude representation of the rate of the reaction, but further investigations is needed to obtain reaction orders and rate constants.

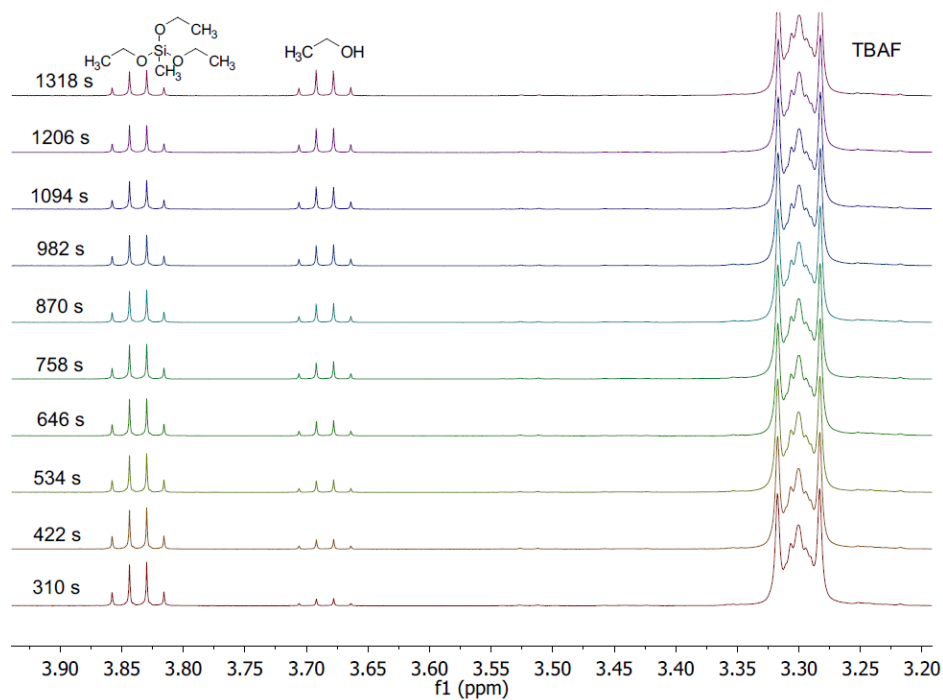


Figure A.9: Reaction run in deuterated chloroform with the following concentrations: TBAF $C_i = 90$ mM, TEMS = 10 mM.

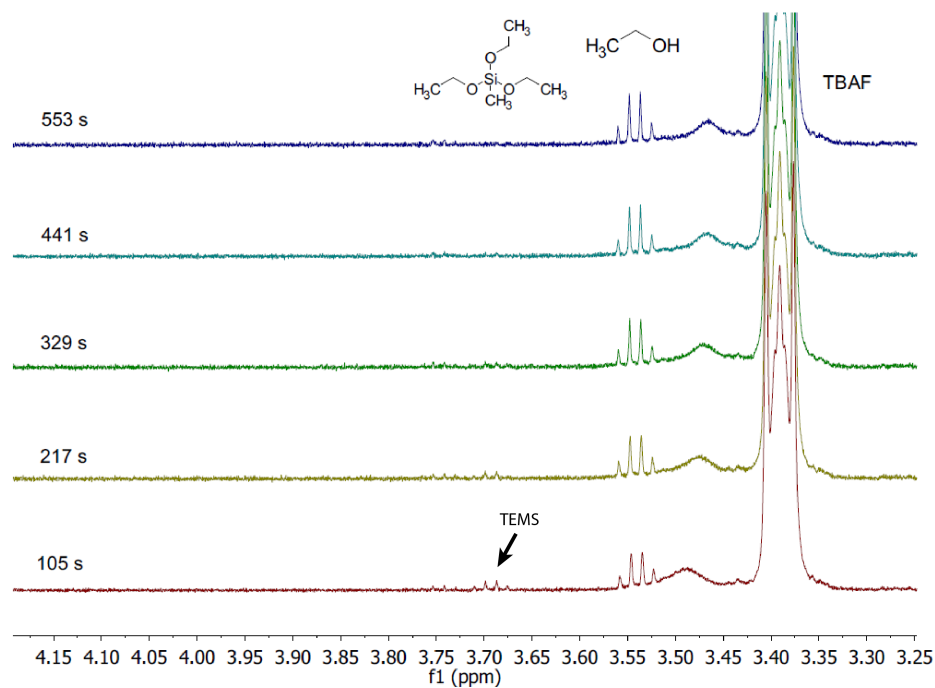


Figure A.10: Reaction run in deuterated DMF with the following concentrations: TBAF $C_i = 3$ mM, TEMS $C_i = 0.33$ mM.

A.5 COMSOL Model Details

A.5.1 Morphogenesis Model

The COMSOL Multiphysics program was used to create models of the morphogenesis process. The physical geometries of the units were generated using circular channels with length of 2.5 cm. Meshes composed of tetrahedrons were formed to approximate the physical geometries of the systems and allowed for numerical calculations within the model. Three sets of physics simulations modules were used (Laminar Flow, Transport of Diluted Species and Deformed Geometry) and the parameter definitions are as follows:

The program initially solved for the steady state velocities, pressures and concentrations in the fluid channels and PDMS membrane, assuming laminar flow followed by diffusion of TEMS and reaction with HF_2^- . The solution parameters from the HF_2^- concentrations were then used to determine the time-dependent solution to the deformed geometry within the model HF_2^- channel. The interpolation function found in the channel etching experiment (Figure A.8) was adjusted in the model to fit experimental results (though the general trend remained the same). It is likely that the presence of TEMS changes TBAF properties of etching due to consumption of water. The decrease in water concentration changes the equilibrium of HF_2^- formation.

A.5.2 Mass Transport Model

The COMSOL Multiphysics program was used to create models of the mass transfer process in both initial and morphed structures. The physical geometries of the units were generated using circular channels and direct observation for the morphed channel. The length of the channels was 2.5 cm. Meshes composed of tetrahedrons were formed to approximate the

Physics Module	Location	Parameter	Value
Laminar Flow	HF ₂ ⁻ Channel	Laminar inflow flow rate	0.5 cm ³ min ⁻¹ per channel
⋮	⋮	Entrance length	1 μm
⋮	TEMS Channels	Laminar inflow flow rate	0.08 cm ³ min ⁻¹ per channel
⋮	⋮	Entrance length	1 μm
N/A Transport of Dilute Species (TEMS)	All TEMS Channels	Velocity Field	spf/fp1
⋮	⋮	Diffusion coefficient (Stokes-Einstein equation)	5.8 × 10 ⁻¹⁰ m ² s ⁻¹
⋮	⋮	Inflow	1000 mol m ⁻³ (750 mol m ⁻³ in 3D geometry)
⋮	HF ₂ ⁻ Channel	Diffusion coefficient (Stokes-Einstein equation)	2.16 × 10 ⁻¹⁰ m ² s ⁻¹
⋮	⋮	Inflow	0 mol/m ³
⋮	⋮	Reaction equation (Figure A.9, A.10)	-2·[HF ₂ ⁻]·[TEMS]
⋮	PDMS	Diffusion coefficient (Figure A.5)	7.5 × 10 ⁻⁹ m ² s ⁻¹
Transport of Diluted Species (HF ₂ ⁻)	HF ₂ ⁻ Channel	Diffusion coefficient (Figure A.6)	4.5 × 10 ⁻¹⁰ m ² s ⁻¹
⋮	⋮	inflow	683 mol m ⁻³
⋮	⋮	Reaction equation (Figure A.9, A.10)	-2·[HF ₂ ⁻]·[TEMS]
Deformed Geometry	HF ₂ ⁻ Channel boundaries	Radial velocity (Figure A.8)	Interpolation function based on experimental data.

Table A.1: Coefficients and parameters used in the morphogenesis model.

Physics Module	Location	Parameter	Value
Laminar Flow	CO ₂ Channel	Laminar inflow flow rate	1 cm ³ min ⁻¹
⋮	⋮	Entrance length	1 μm
Transport of Diluted Species (CO ₂)	CO ₂ Channels	Velocity field	(spf/fp1)
⋮	⋮	Diffusion coefficient ¹²⁴	16 mm ² s ⁻¹
⋮	⋮	Inflow	4.5 mol m ⁻³
⋮	MEA Channels	Diffusion coefficient ¹²⁴	1.51 × 10 ⁻⁹ m ² s ⁻¹
⋮	⋮	Reaction equation ^{125,126}	-6550·[CO ₂]
⋮	PDMS	Diffusion coefficient (estimation based on this work)	1.5 × 10 ⁻⁹ m ² s ⁻¹
Transport of Dilute Species (MEA)	Outer Channels	Diffusion coefficient ¹²⁷	9.32 × 10 ⁻¹⁰ m ² s ⁻¹
⋮	⋮	Initial concentration	4900 mol m ⁻³
⋮	⋮	Reaction equation ^{125,126}	-6.550·2·[CO ₂][MEA]

Table A.2: Coefficients and parameters used in the mass transfer model.

physical geometries of the systems and allowed for numerical calculations within the model. Two sets of physics simulations modules were used (Laminar Flow and Transport of Diluted Species) and the parameter definitions are as follows:

The program initially solved for the steady state velocities and pressures in the gas channels, assuming laminar flow. The solution parameters from the gas flows were then used to determine the time-dependent solution for the transportation of species within the model gas exchange unit.

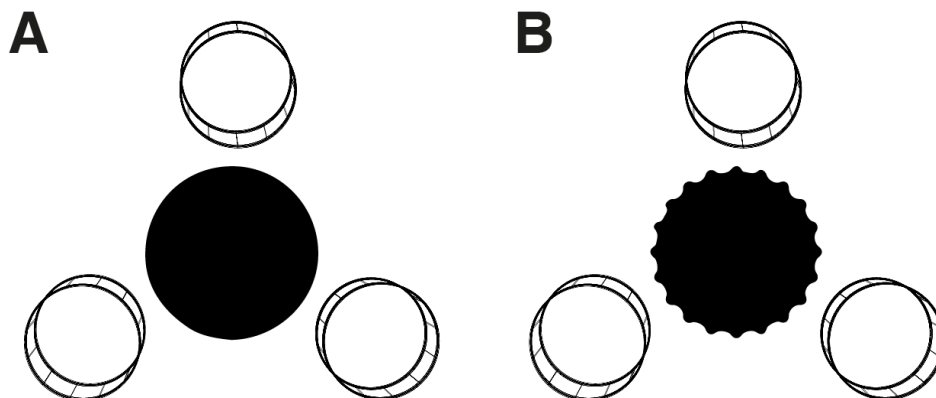


Figure A.11: The two geometries with different surface area that were compared for mass transfer. A. Central channel is circular. B. Central channel has a higher surface area yet location and general shape resemble a circular channel.

A.5.3 Increased Surface Area in Mass Transfer Model

We modeled two geometries of the central channel which differ in surface area. The modeling process was identical to the one described above. The two different channel geometries are shown in Fig. A.11.

A.6 Mass Transfer Experiment

A.6.1 CO₂ MEA Reaction Mechanism

The reaction between CO₂ and MEA is a two-step reaction mechanism which occurs through a zwitterionic intermediate (Fig. A.12)^{128,126,124}. MEA and CO₂ react to form a zwitterionic intermediate as the rate-determining step. Following this zwitterion formation, an acid-base reaction occurs between the zwitterion and another MEA to form a carbamate.

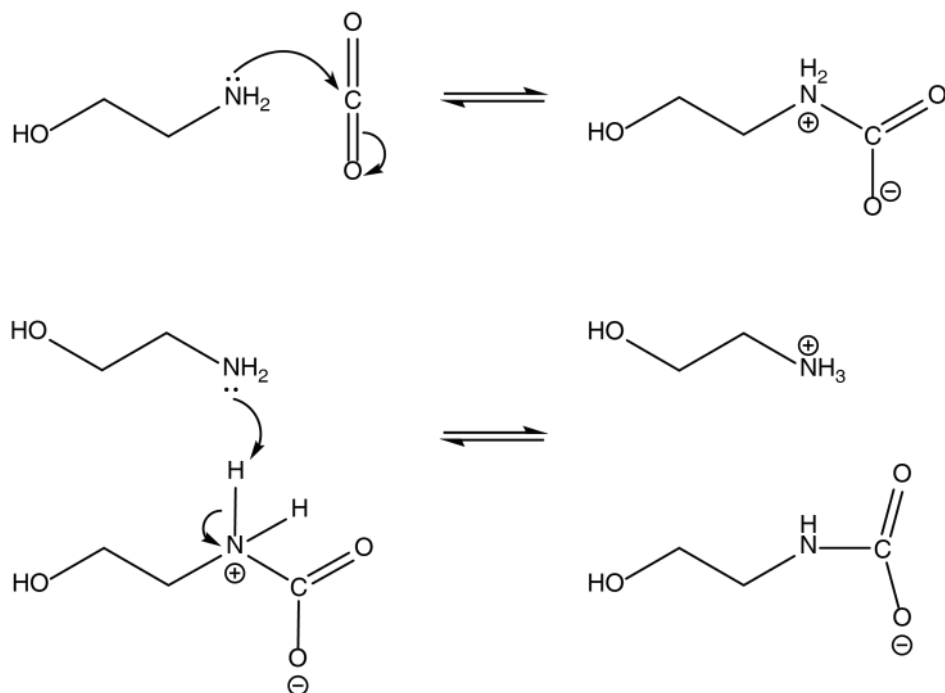


Figure A.12: CO₂-MEA reaction mechanism. Heating the solution drives the reverse reaction, releasing CO₂.

A.6.2 Experiment Settings

1 mg of 5-(and-6)-carboxynaphthofluorescein diacetate dye was added to 1 mL of 30% monoethanolamine (MEA) w/w in water to create a dyed solution. Each structure was separated into liquid and gas channels, with the larger channel corresponding to the liquid and the smaller channels corresponding to the gas channels. (See Figure 2.3A in main text) Dyed MEA was loaded into the liquid channel which was flanked by gas channels. CO₂ was flowed through the gas channels at a flow rate of 10 mL/min using a mass flow controller (SmartTrak 50 Mass Flow Controller). Time lapsed images were taken with a Zeiss Axio Observer.A1 Microscope using a 5 X objective at intervals of 20 s for 30 min (Fig. A.13, supplementary video 2). The power settings were those of a 120W Mercury Vapor Short Arc. The fluorescence intensity was set to 25% total illumination. The exposure time was 500 ms. The microscope shutter was manually closed between data points to prevent photobleaching of the dye. As 5-(and-6)-carboxynaphthofluorescein diacetate dye is pH sensitive,

it changed fluorescence as the CO_2 was absorbed. The intensity of red color was measured in the central channel using the microscope Axio-Vision program. The intensity was normalized to produce a value between 0 and 1. This value was converted to the weight percent of CO_2 inside the central channel, based on a calibration curve (Fig. A.14), and normalized again. The normalized parameter was plotted as a function of time and polynomial function of the 6th order was fitted to the data. The $t_{1/2}$ value was determined based on a linear extrapolation of the two points surrounding 0.5. The efficiency was calculated based on the volume of the channel (calculated for the circular channel and measured using ImageJ for the morphed channel) and the density of the water/MEA solution (1 g/ml). At $t_{1/2}$ there was 5 wt% of CO_2 in the solution (based on the calibration graph), and hence the number of moles of CO_2 per unit time per unit volume were calculated.

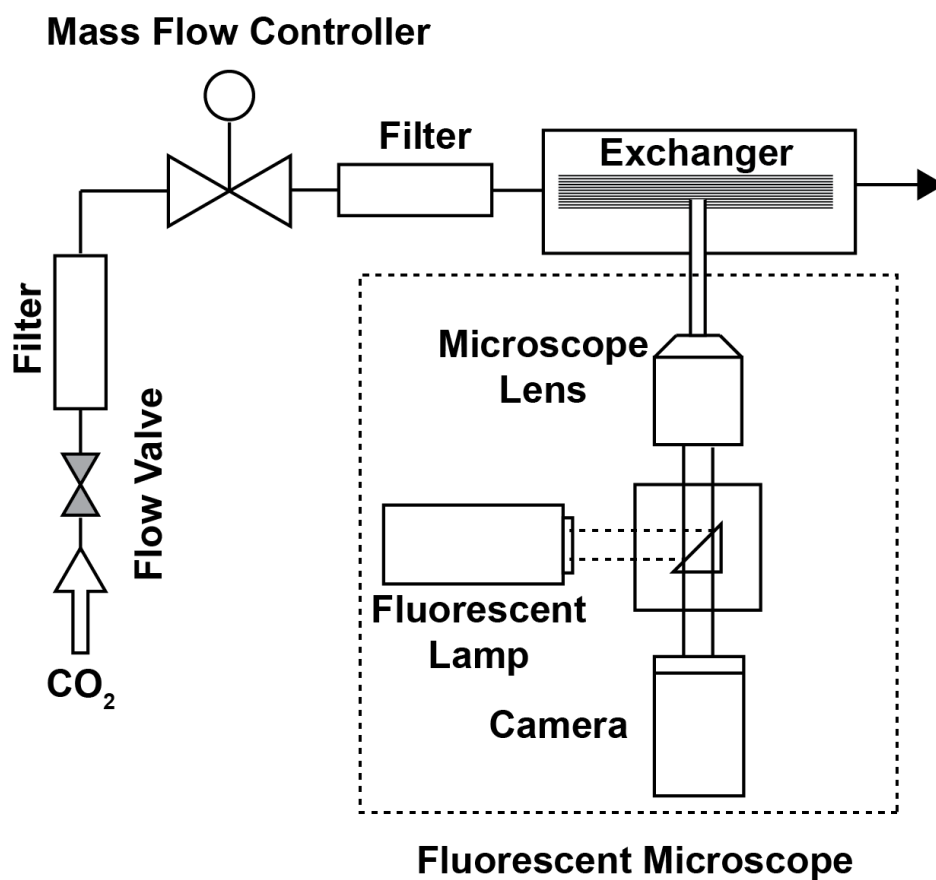
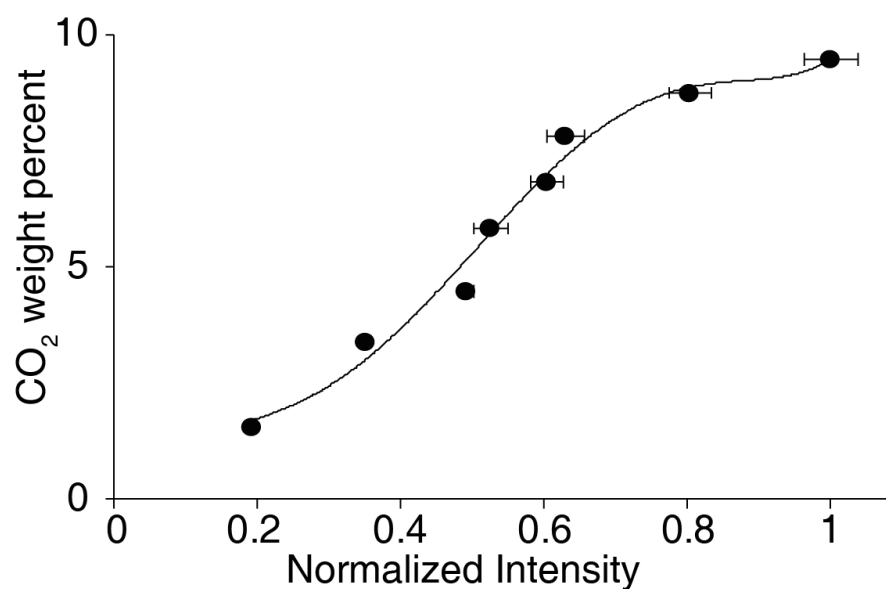


Figure A.13: Mass transfer experimental schematic. The flow of CO₂ is controlled by a mass flow controller to maintain a constant flow rate. A pH sensitive fluorescent dye monitors the transfer of CO₂ from one set of channels to another under the observation of a fluorescent microscope.



$$y = 171.38x^5 - 442.68x^4 + 383.75x^3 - 124.48x^2 + 21.505x$$

$$R^2 = 0.9833$$

Figure A.14: Calibration curve for the weight percentage of CO₂ in MEA as a function of normalized intensity.

Appendix B

Structural remodeling through diffusion controlled surface growth and removal

B.1 D4/D4-D4 quantification

D4/D4-D4 was prepared as explained in the Materials and Methods section of the text. ^1H -NMR spectra of the resulting mixture was taken on a GN500 (500 MHz) spectrometer and analyzed using MestreNova software. (Figure B.1) The D4/D4-D4 ratio was then calculated based on the ratio between the up field peak (Figure B.1, red) representing 24 of the D4 hydrogen and 42 of the D4-D4 hydrogen and the down field peak (Figure B.1, green) representing 4 of the D4-D4 hydrogen. With the different molecular weights of D4 and D4-D4, the final ratio was calculated to be 0.92% w/w of D4-D4 in D4.

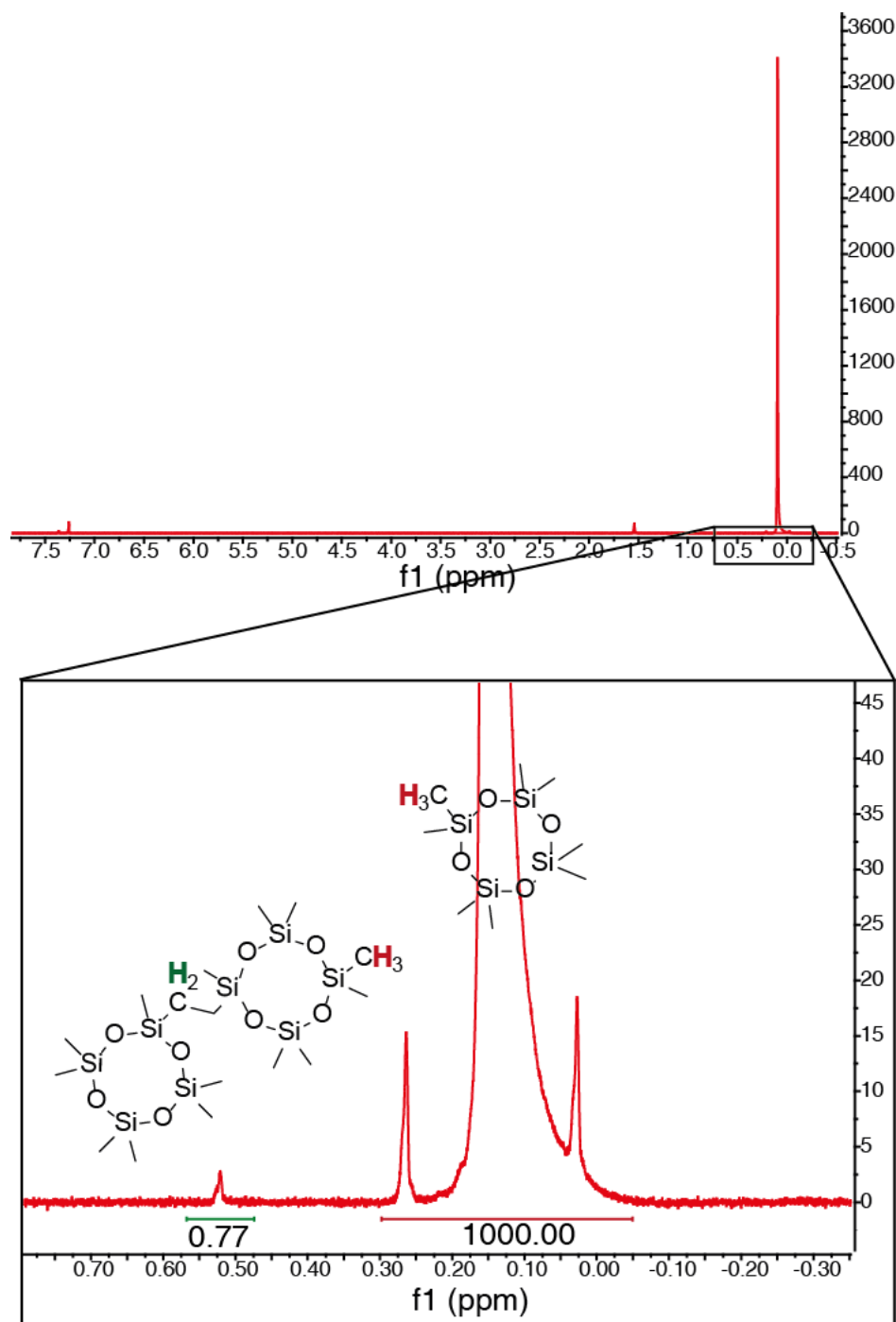


Figure B.1: D4/D4-D4 ^1H NMR spectra. NMR spectra of the mixture containing D4 and D4-D4. The bottom image presents a close up look enabling to see the D4-D4 hydrogen at low field (0.52 ppm) separated from the D4 hydrogen up field (0.11 ppm). The ratio between the two integrated peaks was used to calculate the w/w % of D4-D4 in D4.

B.1.1 Solution phase polymerization/depolymerization

We tested different concentrations of TBAF mixed with either PDMS polymer (24kD linear chain) or D4 monomer or both and tracked the average chain length of the resulting polymers. Different concentrations of TBAF in DMSO (0.05M, 0.1M or 0.2M) were mixed with either D4 monomers or linear 24kD PDMS or both. The solution was stirred for 30 min in a 65 °C glycerol bath. The reaction was stopped after 30 min by adding TMSCl to quench the fluoride. The vials were then submerged in liquid nitrogen followed by removal of any excess solvent by freeze drying the reaction mixture. The pellet was re-suspended with 1 mL of THF. (Figure B.2A)

We saw that linear PDMS forms longer PDMS chains that are shortened with increasing TBAF concentration. (Figure B.2B) The original PDMS chain resolved as ~34kD in our GPC chromatograph. (Figure B.2B, red curve) With 0.05M of TBAF we found a higher molecular weight chain, ~170kD. (Figure B.2B, yellow curve) The 0.1M TBAF gave rise to a shorter polymer, ~70kD (Figure B.2B, green curve). And finally, the reaction with 0.2M TBAF resulted in even shorter polymer chains of ~53kD. (Figure B.2B, blue curve) This strange growth is likely due to PDMS' insolubility in DMSO. The reaction of the PDMS with TBAF forms R_3SiO^- nucleophiles. These nucleophile can initiate the scrambling of the existing PDMS chains leading to the formation of longer chains. With increasing TBAF concentration, more nucleophiles are forming, which result in shorter chains.

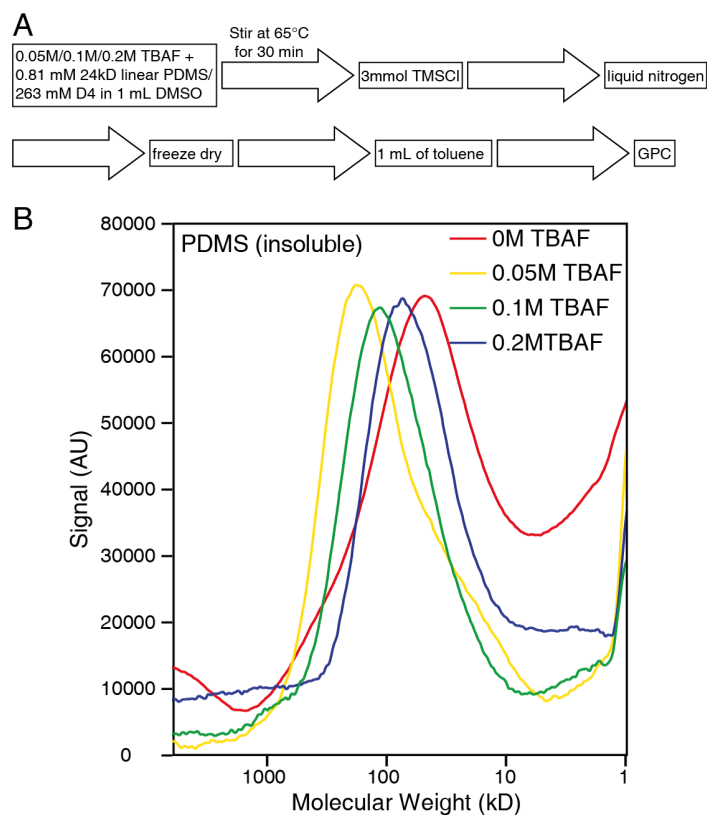


Figure B.2: Solution phase polymerization/depolymerization. A. Set up for measuring the effect of initiator concentration. Different concentrations of TBAF (0.05M, 0.1M and 0.2M) were stirred for 30 min at 65°C with either linear PDMS (24kD) or D4 monomers in DMSO. The reaction was arrested by adding TMSCl to quench the fluoride. The reaction was then frozen in liquid nitrogen and solvent was removed by freeze drying. The pellet was re-suspended with 1 ml of toluene. 50 μ L of the resulting solution was analyzed by GPC. B. PDMS TBAF reaction shows strong dependence on TBAF concentration. The original PDMS (red curve) is analyzed as a 34kD polymer chain. TBAF addition causes a higher molecular weight polymer chain that decreases in size as more TBAF is added to the solution.

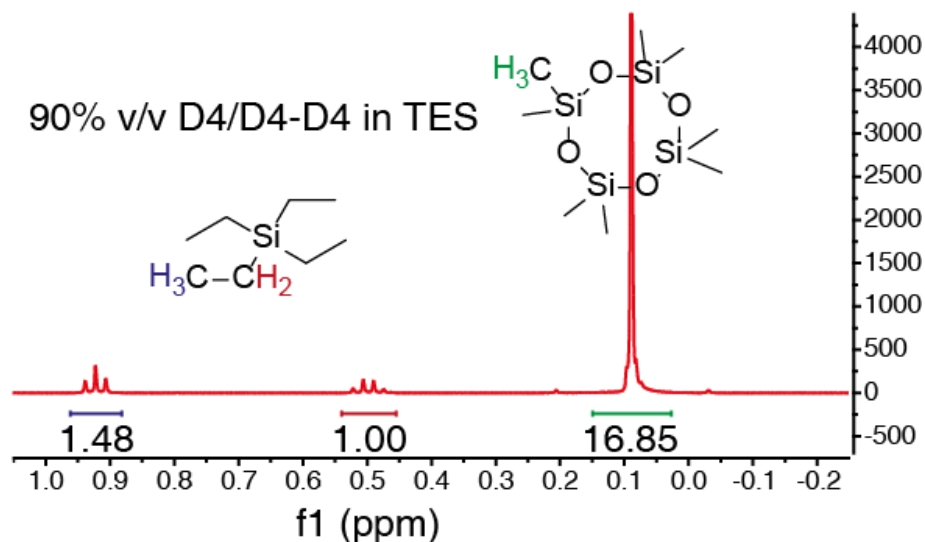


Figure B.3: D4/D4-D4 in TES ^1H NMR spectra. NMR spectra of the mixture containing 90% v/v D4/D4-D4 in TES. The integration of the peaks were used to evaluate the D4 concentration in the mixture as 2.9M.

B.2 Etching and Growth of Membrane

B.2.1 Measurement of D4/D4-D4 concentration

The membranes that were tested for etching/growth process were preswelled with a mixture of D4/D4-D4 and triethylsilane (TES). Two swelling mixtures were prepared – the first, was 75% v/v of D4/D4-D4 in TES and the second, 90% v/v of D4/D4-D4 in TES. 20 l of the solution were subjected to ^1H -NMR using GN500 (500MHz). The resulting peaks were integrated to find the exact molar ratio between the D4 and the TES. The 90% solution was calculated to be 2.9M of D4 in TES and the 75% solution was determined as 2.4M of D4 in TES. The relevant peaks are shown in Figure B.3.

B.2.2 Visualization of the membrane:

After running TBAF in a flowing cell to initiate growth or removal from the PDMS membrane, as described in Figure 3.3 of the main text, the membranes were visualized using light microscopy to measure the change in width. Membranes were placed on a microscope glass slide with the cross section perpendicular to the channel length slightly sticking out of the slide. The microscope slide was placed in a vertical position on the microscope stage. The cross section was visualized using Zeiss Axio Observer.A1 at 20X using a DIC filter. The cross section was visualized with the channel section roughly at the middle of the image. An image was taken under condition enabling maximum contrast between the membrane and the surrounding. The membrane stage was then moved on the x-direction to capture a channel free membrane cross section. An image of a channel free cross section was taken under the exact same parameters as the channel cross section image, only the focus was adjusted.

B.2.3 Calculation of membrane growth/etching:

The channel free cross section image of the membrane was matched, using ImageJ software, to the best rectangle in order to determine the exact membrane width. The channel cross section image was then processed using ImageJ into a black and white image with distinct boundaries between the membrane and the surroundings. The channel width was determined as 268 μm , based on the original channel width in the flow cell (300 μm) and the amount of shrinkage of the membrane due to the original swelling by D4/D4-D4 and TES. The amount of shrinkage was determined based on the change in channel length measured as 3.8 mm at the flow cell in comparison to 2.8 mm on the membrane after removal of D4/D4-D4 and TES using heat and vacuum. The channel length on the membrane was measured by the visible mark of the channel along the membrane and was consistent in length between samples. For

ease of calculations we assumed isotropic swelling and shrinkage, assuming that the shrinkage that was measured in the length of the channel was proportional to the width of the channel. The 268 μm width in the image was taken by having the biggest change in size in the middle of the 268 μm long line.

The black and white image of the channel was input into Mathematica and transferred into a matrix containing 1 or 0 in every pixel location, depending on their color. The rows in the matrix were then examined. White pixels above the membrane width row (determined by the reference rectangle) were added to the etching counting. Black pixels below the membrane width row were added to the counting for growth. The total number of pixels added (or removed) was translated to the area in μm^2 based on the image resolution. (Figure B.4) This area was measured by four repeats in each set of conditions. (Figure B.5 and Figure 3.3 in the main text)

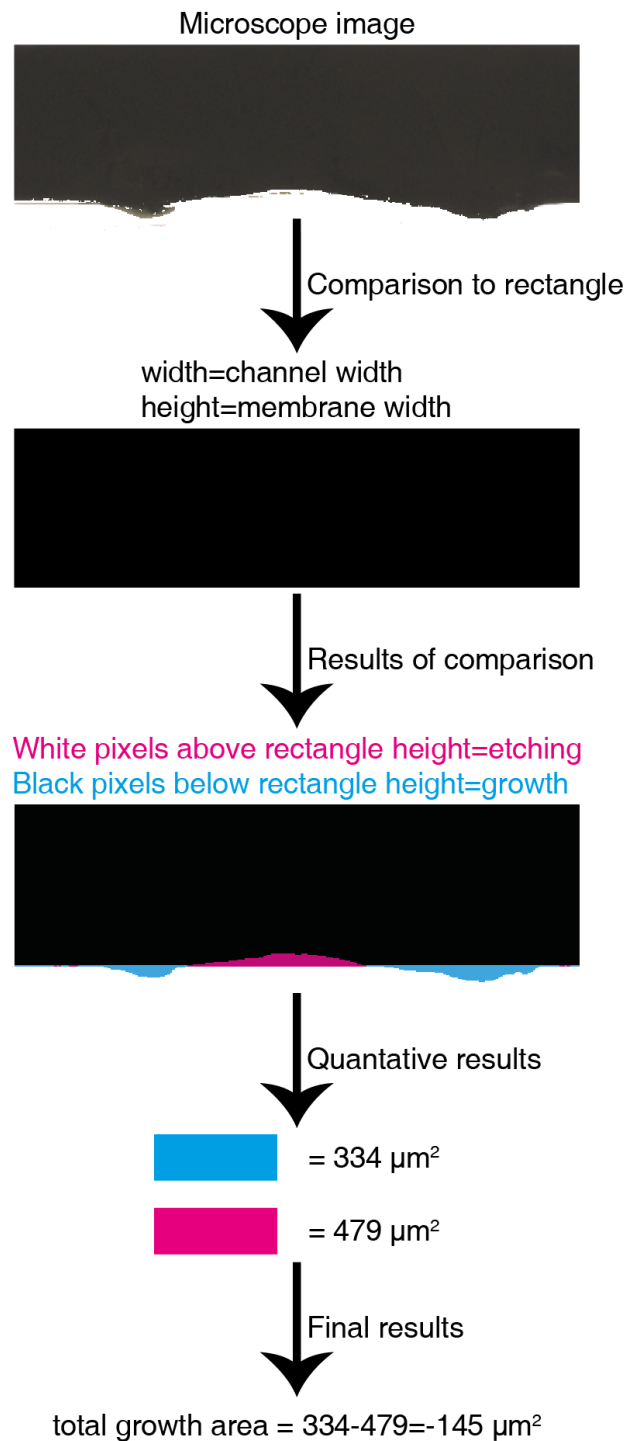


Figure B.4: Flow chart describing the quantification process for membrane growth. Step I: A well contrasted microscope image is taken, with the largest change in membrane width at the center of the image. Step II: This image is compared to a rectangle that has the width of the channel (268 μm) and the height of the unchanged membrane width. Step III: White pixels higher than the rectangle height are marked as etching (colored in magenta). Black pixels lower than the rectangle height are marked as growth (colored in cyan). Step IV: The number of etching and growth pixels is converted to area based on image resolution. Step V: The etching area is subtracted from the growth area for a final result of growth area (negative area indicates total etching, positive area indicates total growth).

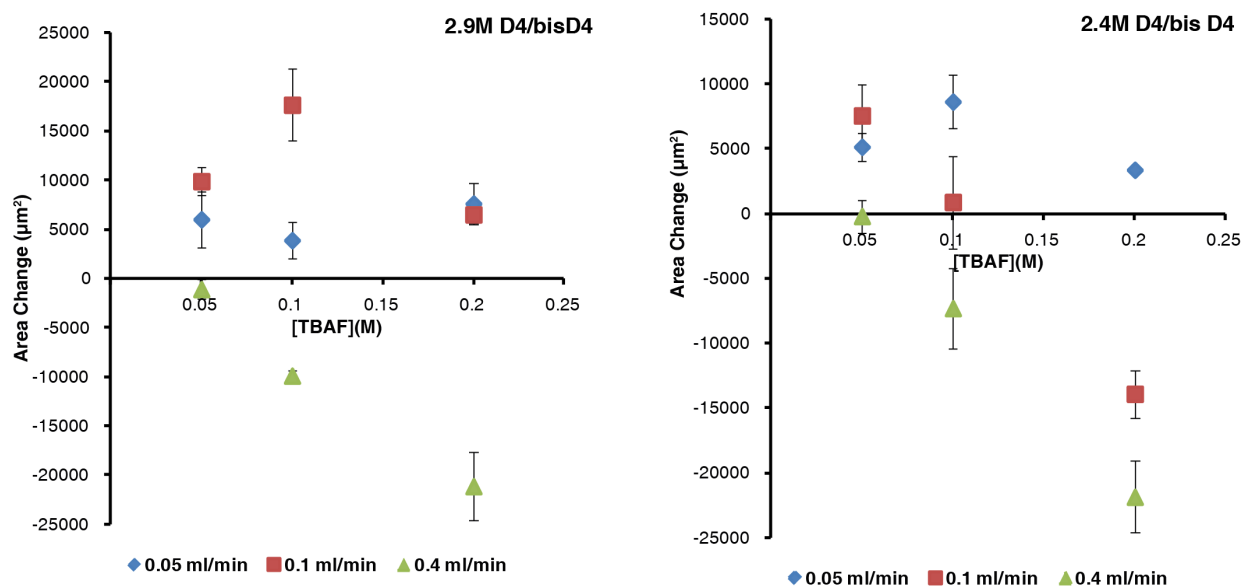


Figure B.5: Quantification of membrane growth/etching. Quantitative results of the removal or growth of material were observed in 4 repeats under different monomer (D4/D4-D4) and activator (TBAF) concentrations as well as different flow rates.

The Mathematica code used to calculate the growth area can be seen below.

```
scalefactor = 1 (* input pixel to micrometer conversion here *)
edges=Import["Put\\File\\Path\\Here"] (* expects an 8-bit image with the
    edges of the material displayed as black lines 1 pixel wide with the
    area to the left of the growth/etching section visble with a 1 pixel
    wide column of only white pixels separating the "control" area from
    the growth/etching area. The image should end at the right side of the
    growth/etching region *)
edgedata=ImageData[edges];
Length[edgedata]
Length[edgedata[[1]]]
(* edgedata is a table of pixel values. Length[edgedata] is the number of
    vertical pixels, and Length[[1]] is the number of vertical pixels *)
control=0;
baseline={};
dist={};
row = 1;
```

```

column=1;
blah=0;
endgrowth=0;
(* sets the variable values and defines the tables baseline and dist used
   below *)

(* records the distances for the control portion of the image *)
While[column<Length[edgedata[[1]]]&&control==0,
(* while the variable column is less than the number of horizontal pixels
   and control (defining what section is being analyzed) is 0 *)
If[row<Length[edgedata],
(* if the row variable is less than the number of vertical pixels *)
If[edgedata[[row,column]]==0&&blah==0,
(* if the value in the edgedata table at coordinates (row, column), (y, x
   ) is \[Equal] 0 (black pixel) and blah (how many black pixels have
   been found) \[Equal] 0 *)
blah=blah+1;
back=row;
row=row+1,
row=row+1];
If[edgedata[[row,column]]==0&&blah==1,
AppendTo[baseline,(row-back)*scalefactor]; (* record the distance between
   black pixels to the table baseline *)
row=1;
column=column+1;
blah=0],
row=1;
begingrowth=(column +1)*scalefactor;
column=column+1;
control=1 (* if no black pixels are found in a column, move to next while
   loop *)
]
];

```

```

begingrowth (* horizontal coordinate for the beginning of the growth/etch
            section *)

```

```

(* records the distances for the growth/etch section *)

```

```

While[column<Length[edgedata[[1]]]&&control==1,

```

```

If[row<Length[edgedata],

```

```

If[edgedata[[row,column]]==0&&blah==0,

```

```

blah=blah+1;

```

```

back=row;

```

```

row=row+1,

```

```

row=row+1];

```

```

If[edgedata[[row,column]]==0&&blah==1,

```

```

AppendTo[dist,(row-back)*scalefactor];

```

```

row=1;

```

```

endgrowth=(column+1)*scalefactor;

```

```

column=column+1;

```

```

blah=0],

```

```

row=1;

```

```

column=column+1;

```

```

control=0

```

```

]

```

```

];

```

```

endgrowth (* horizontal coordinate for the end of the growth/etch section
          *)

```

```

(* baseline distances *)

```

```

Histogram[baseline]

```

```

baseave=Mean[baseline] //N

```

```

StandardDeviation[baseline] //N

```

```

(* growth/etching distances + area *)

```

```

Histogram[dist- baseave]

```

```

average=Mean[dist- baseave] //N

```



```
StandardDeviation[dist-baseave] //N
area = average*(endgrowth-begingrowth)  (* area of just the grown/etched
region *)
```

B.2.4 Channel Sample Preparation

All of the methods described here were used to prepare the channel sample but were not developed during this work. This method is previously described in⁵².

B.2.5 Catalyzation of the fibers:

To incorporate the SnOx Catalyst necessary for depolymerization in VaSC, a solution was prepared. 10 mL in total, the solution contained TFE, HCl and water at 50:12.5:37.5 vol/vol/vol respectively. The solution also contained a SnOx catalyst at loading of 13 mg/mL. The solution was placed in a 15 mL centrifuge tube, pierced to accommodate the fibers. The fibers were pulled up through the solution, using rotation, at a rate such that fibers had a residence time of 30 s within the solution. All experiments were performed at room temperature (~ 21.5 °C).

B.2.6 Building the pattern:

Polydimethylsiloxane (PDMS) was created using mixtures of the Sylgard 184 silicone elastomer

base and curing agent (Dow Corning) with a 10:1 w/w ratio between base and curing agent via mixing in a paper cup. The mixture was degassed for 15 min to remove all trapped gas using a vacuum pump and glass bell jar. Treated fibers were patterned using laser

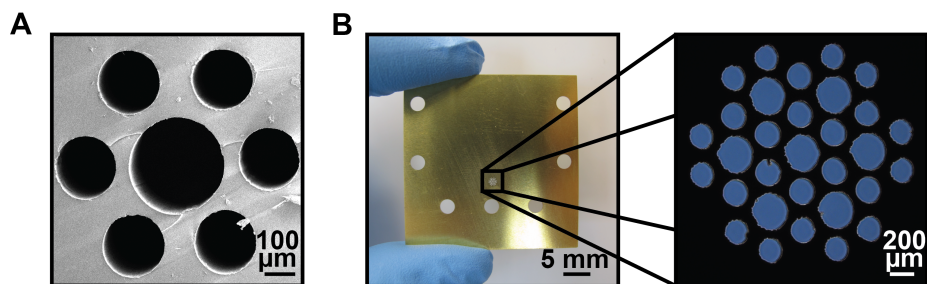


Figure B.6: Laser-etched micro-machined brass plates. Fibers are strung through the holes in the end caps, providing the desired pattern.

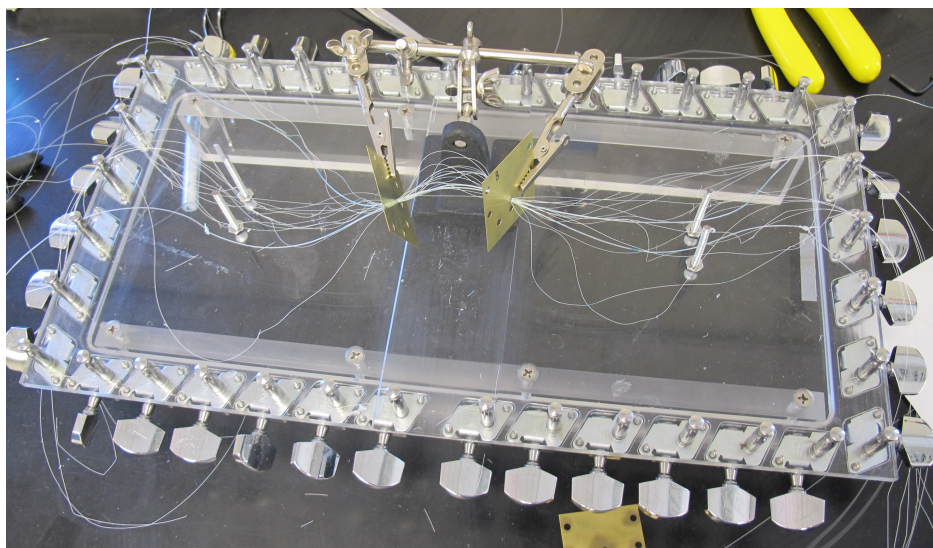


Figure B.7: Example custom molding board. Guitar tuners on either side provide tensioning for fibers.

micromachined brass plates manufactured by Hodge Harland at the University of Illinois at Urbana-Champaign. (Fig. B.6) Fibers were strung through a pair of plates which were then screwed onto a Delrin mold box with dimensions of $25 \times 25 \times 25$ mm. Fibers were tensioned until taut on a custom board with pairs of guitar tuning pegs on either side. (Fig. B.7, B.8) The degassed PDMS mixtures were poured into the mold and heated at 85°C for 30 minutes to cure the mixtures.

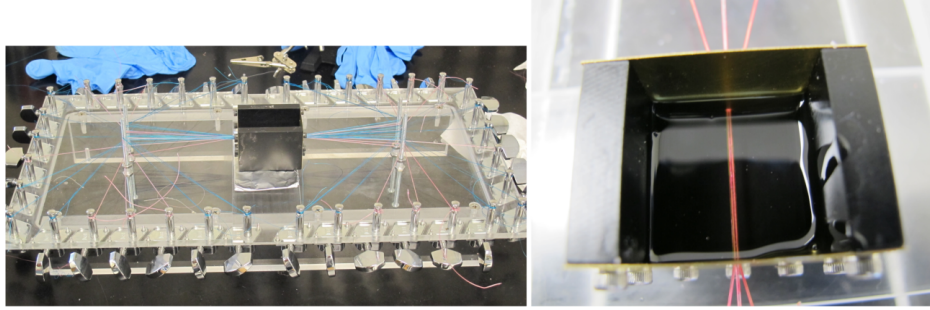


Figure B.8: Assembled molding setup. Fibers are tensioned through the brass end caps using the tuning board. Metal rods in the board act as pulleys allow the tuning pegs along the side of the board to tension the fibers.

B.2.7 Spreading the fibers:

Each fabricated unit of PDMS embedded with fibers was removed from the first mold and placed into a second mold box with dimensions of $25 \times 25 \times 50$ mm. The fibers were separated and threaded through a rubbery end-caps made of polyurethane which were screwed onto the mold box. Syringe needles (B-D PrecisionGlide 18G1 Needle) were inserted through the PDMS end caps and fibers were threaded through the needles. The needles were removed leaving the fibers trapped in the end caps. The end caps were screwed onto the larger mold box and fibers were pulled taut by hand. A second mold of PDMS was cast again at 85°C for 30 minutes (Fig. B.9). Longer samples were created using a $25 \times 25 \times 50$ mm box as the first mold and $25 \times 25 \times 75$ mm box as the second mold.

B.2.8 Vaporization of the fibers:

The vascular preforms were removed from the second mold. The vascular preforms were placed into a sealed vacuum oven (JEIO Tech Vacuum Oven Model OV-11/12) and subjected to a vacuum of 10 torr while heating at 210°C for 48 h.

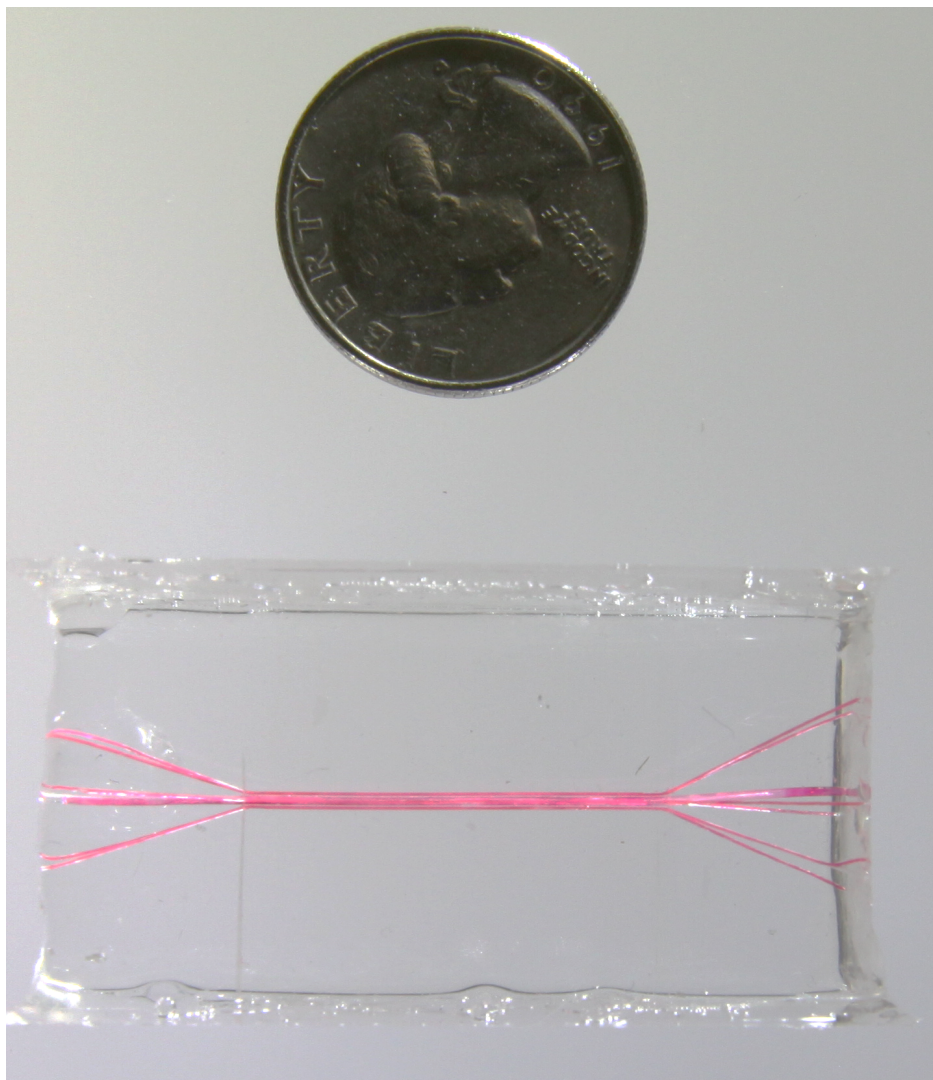


Figure B.9: Exchange unit after second molding. Fibers are separated into a larger pattern for easier loading of channels.

B.3 Pillar Sample Preparation

B.3.1 Silicon master fabrication

The silicon master molds were fabricated in $\langle 100 \rangle$ Si wafers. A quartz plate was utilized to develop a projection lithography mask. Details of methods and subsequent processes used have been described previously.¹²⁹ The Si wafers were vapor primed with hexamethyldisilazane (HMDS) to improve photo resist adhesion. SPR700 was used as an i-line resist and a Nikon 5x stepper was used to expose the coated wafers followed by post exposure bake and resist development using Microposit MF CD26. Descumming was performed prior to Bosch advanced silicon etch¹³⁰ in an STS deep reactive ion-etching (DRIE) tool. C₄F₈ and SF₆ chemistry was used for Si etching. Veeco profilometers and cross sectional (Zeiss) SEM was used to characterize and optimize exposure conditions, etch rates and etch profiles. The Si wafers were given a final overcoat of C₄F₈ to aid in any subsequent replication process.

B.3.2 Substrate fabrication

The substrates were fabricated using a commercial Dow Corning PDMS kit from silicon masters. PDMS prepolymer and crosslinking agent were poured onto microfabricated silicon substrates (masters) and cured. The PDMS mold was peeled off the silicon master and functionalized with (Heptadecafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane (purchased from Gelest) in order to prevent PDMS adherence to the surface. PDMS prepolymer and cross linking agent were poured into the mold, vacuumed for 2 h and cured at 65°C for 60 mins covered by a glass slide prefunctionalized with (Tridecafluoro-1,1,2,2-tetrahydrooctyl)trimethoxysilane (purchased from Gelest) in order to prevent PDMS adherence. The PDMS replicas were then peeled out of the PDMS mold and used in stationary and flowing TBAF systems. For the flowing systems, the PDMS replicas were elongated with additional PDMS in between 2

microscope glass plates to form 2 mm wide membranes with pillar structures at the center. The molds were reused for further replica fabrication.

B.3.3 Stationary and flowing TBAF experiments

The structured PDMS was subjected to TBAF in both stationary and flowing systems as described in the main text. (Figure 3.5) In the stationary system we found that the structures that were exposed to TBAF alone, without the presence of D4/D4-D4 were removed within 2 min. (Figure 3.5A in the main text) The patterned side was indistinguishable from the non-patterned side. (Figure B.10) In the flowing system, the formation of new micro features including wider pillars and donut shaped structures. (Figure 3.5B in the main text) Those structures were absent when the flow was applied on a PDMS membrane without the pillar structure under the same conditions. (Figure B.11)

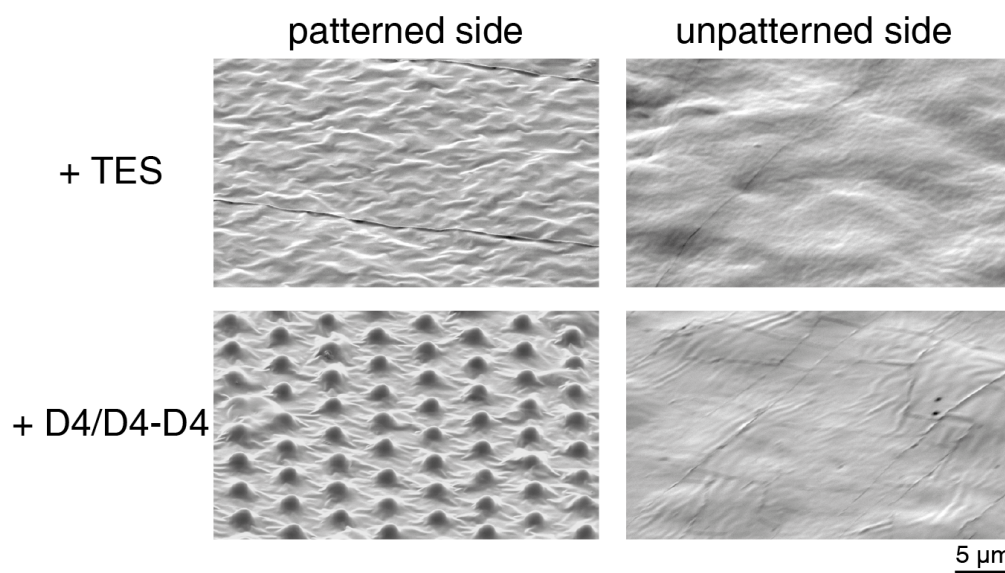


Figure B.10: Effect of TBAF on patterned and non patterned PDMS. A hexagonal micro pillar structure was made from PDMS. The structure was preswelled with either TES (top row) or D4/D4-D4 (bottom row) and then submerged in 0.1M of TBAF in DMSO at 65°C for 5 min. Both the result structure and the opposite, non structured side, were imaged using SEM. Without the presence of D4/D4-D4 the structure was completely removed and the patterned side was almost indistinguishable from the non patterned side. With the presence of D4/D4-D4 there was a clear difference between the two sides as the pattern was clearly visible.

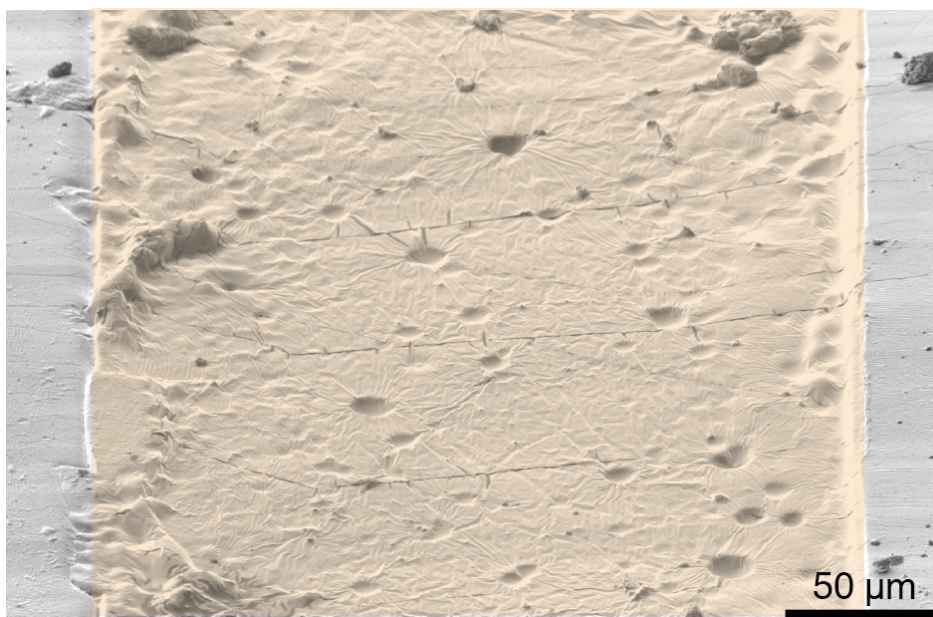


Figure B.11: Effect of flowing TBAF on unstructured PDMS. A 2 mm thick PDMS membrane was made and subjected to TBAF flow through the system described in Figure 3.3 of the main text. 0.1 M of TBAF in DMSO was flowing on the membrane for 30 min at 0.1 mL/min. The membrane surface was then imaged via SEM. No pillar like or donut like features were found on the membrane surface that was exposed to the TBAF channel (false colored in orange). The only irregularities were dimples in the surface which were also observed in the pillared structures under the same conditions.

Appendix C

Countercurrent Amplification

C.1 Design of countercurrent device

All countercurrent devices were machined from 5 mm thick acrylic sheets purchased from McMaster Carr. Fluid channels are all 1 mm wide by 1 mm deep square cross sections for ease of fabrication. Technical drawings of the channel layouts can be found in Figures C.1-C.3.

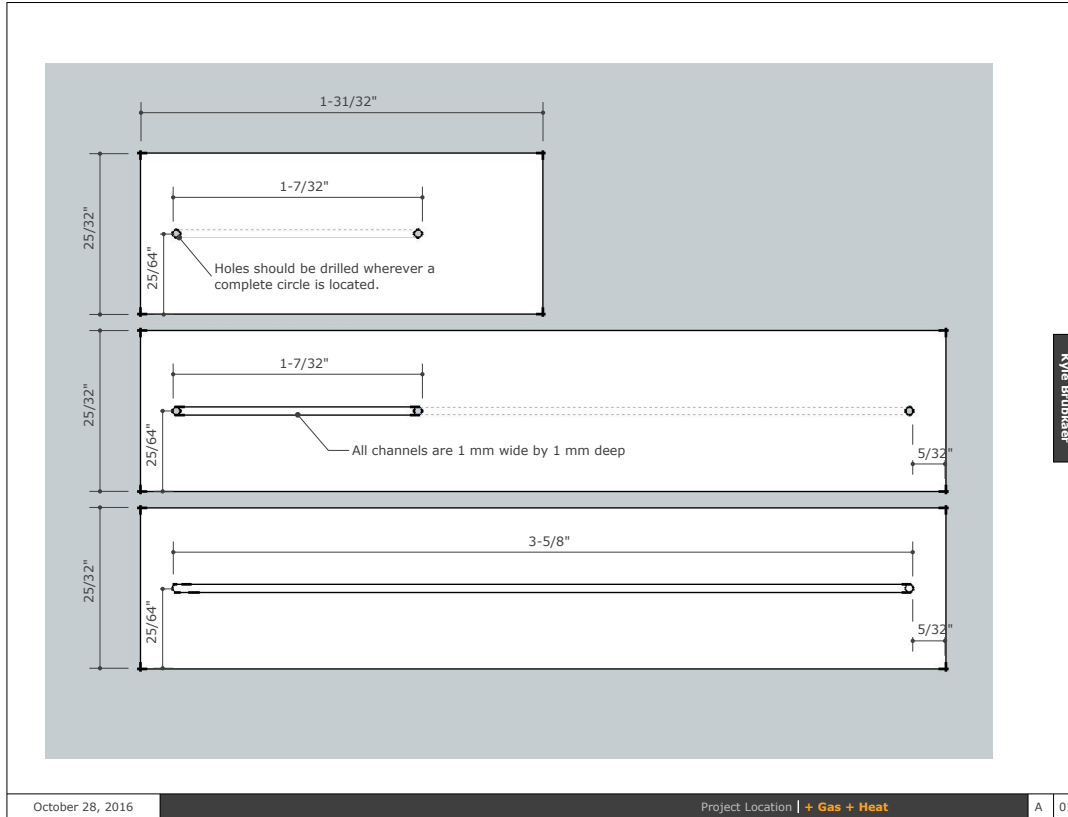


Figure C.1: Layout of the + gas + Heat or - Gas + Heat variant of the countercurrent amplifier. All dimensions in inches unless noted otherwise.

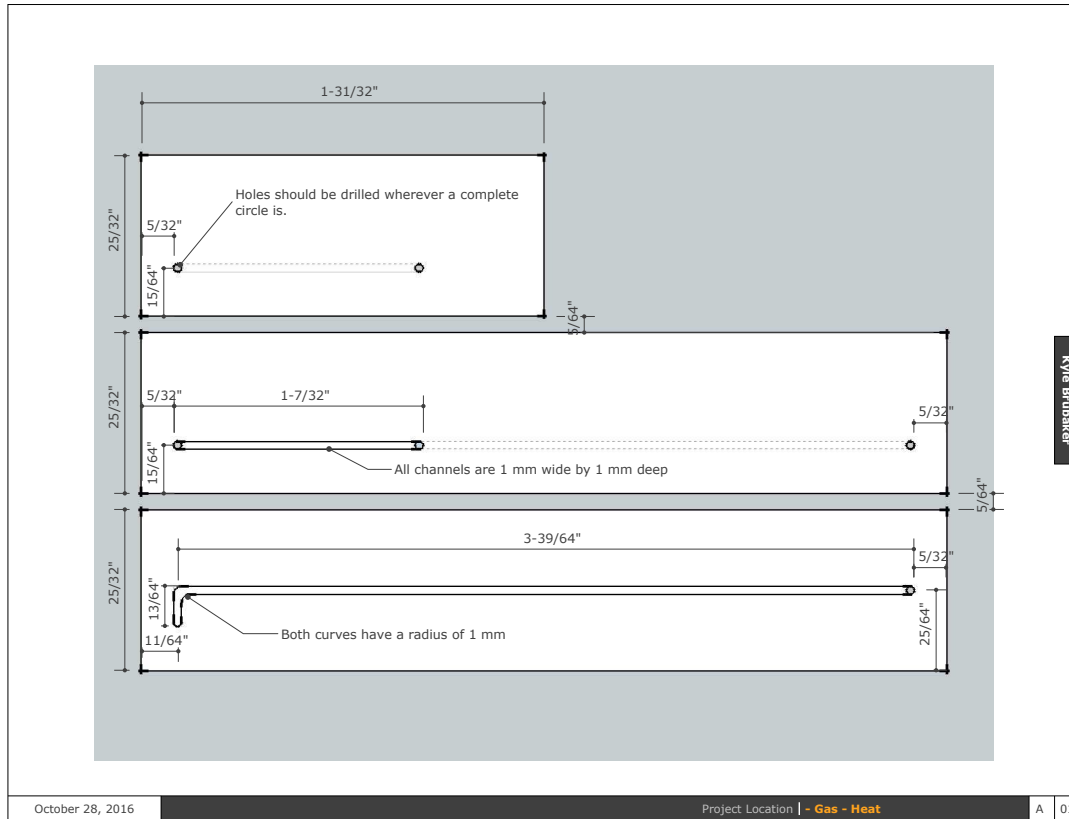


Figure C.2: Layout of the - gas - heat variant of the countercurrent amplifier. All dimensions in inches unless noted otherwise.

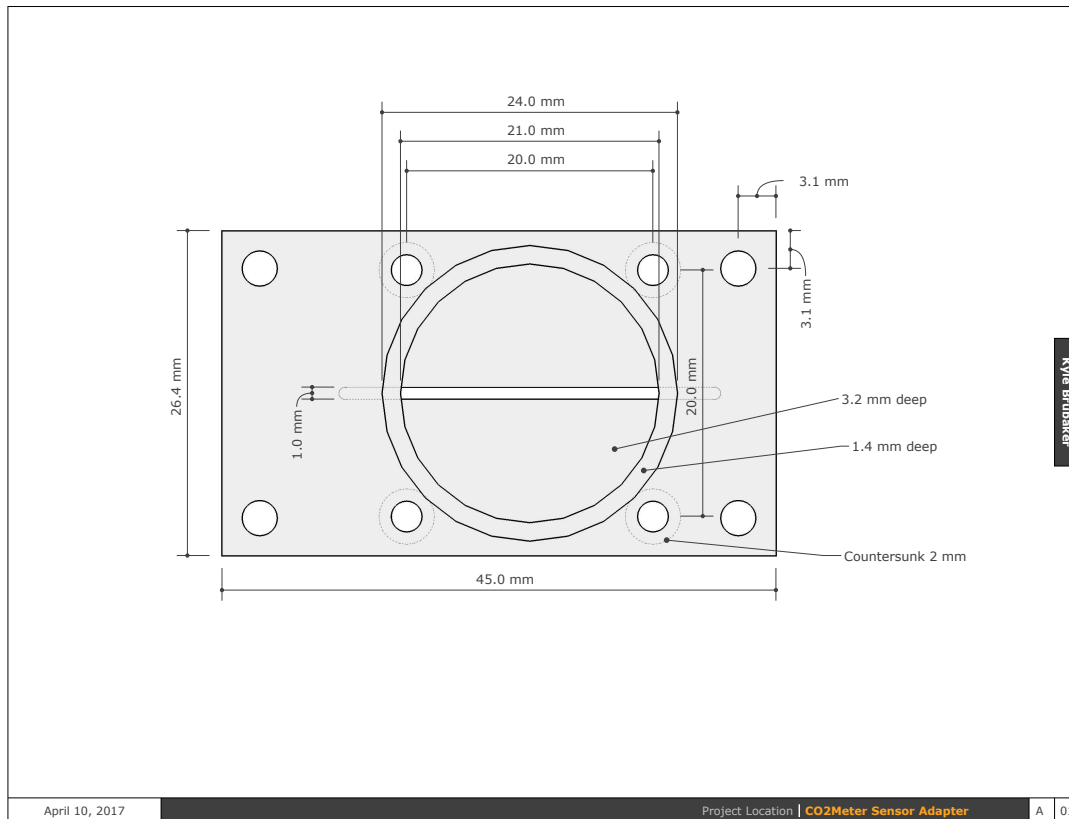


Figure C.3: Adapter to mount CO2Meter.com sensor directly on the release zone.

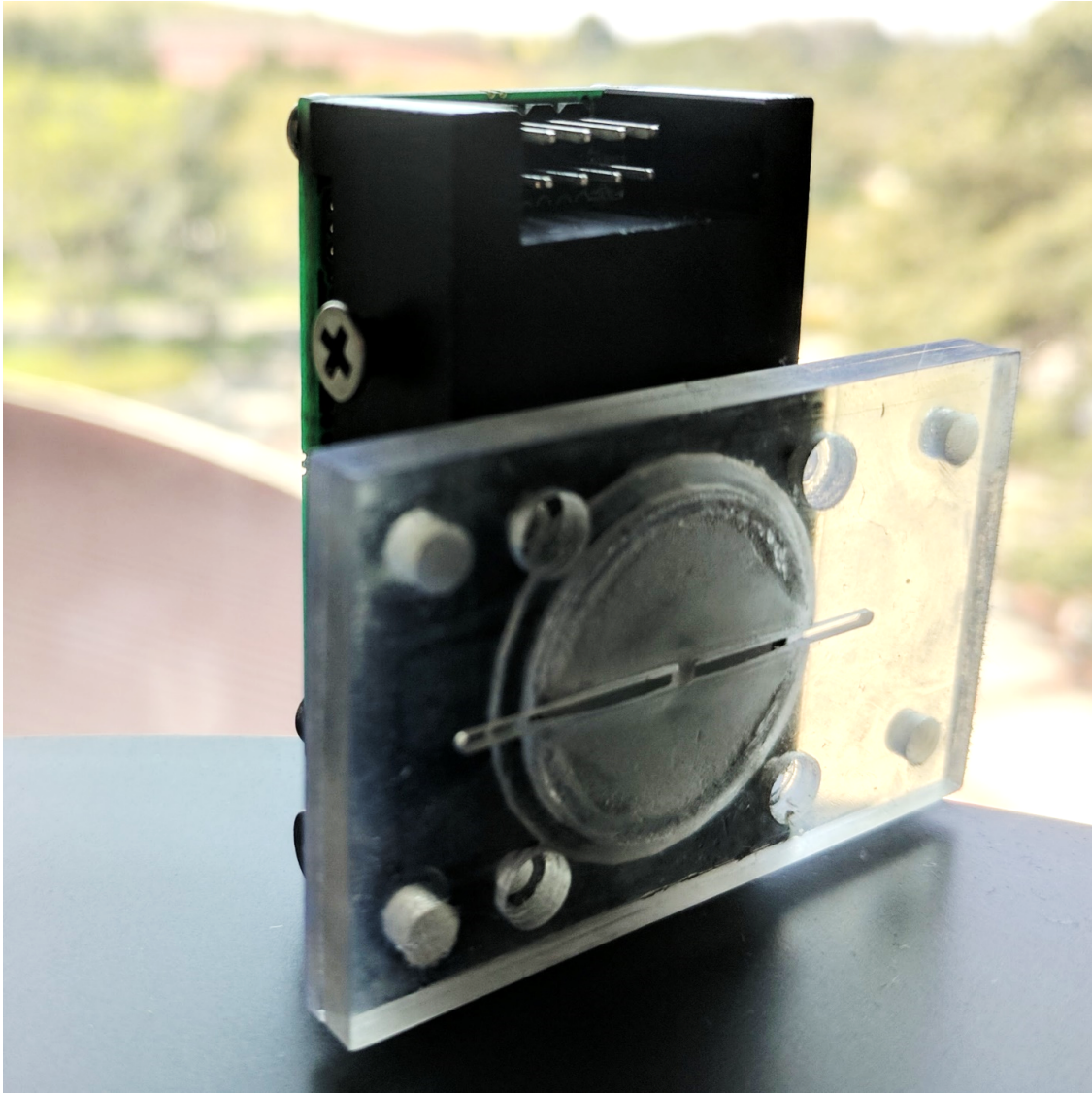


Figure C.4: Adapter to mount CO2Meter.com sensor directly on the release zone.

C.2 PDMS/aluminum foil hybrid membrane



Figure C.5: Illustration of the PDMS/Al hybrid membrane sandwich.

A hybrid membrane was designed and fabricated as illustrated in Figure C.5 consisting of three layers. The two outer layers of PDMS maintain a consistent thermal resistivity compared to the original PDMS membrane as well as preventing corrosion of the aluminum layer by the MEA solution. The aluminum foil serves as a gas impermeable layer. Calculations detailing the thermal conductivity of the hybrid membrane compared to the PDMS membrane can be found below.

The thermal resistivities of the the hybrid and the original membrane were compared as follows

$$R_h = R_{PDMS} + R_{Al} \quad (C.1)$$

where R_h , R_{PDMS} , and R_{Al} are the thermal conductivities of the hybrid membrane, the two PDMS layers, and the aluminum foil layer respectively. R_{PDMS} and R_{Al} can be described

by

$$R_{PDMS} = \frac{x_{PDMS}}{k_{PDMS}} \quad (C.2)$$

and

$$R_{Al} = \frac{x_{Al}}{k_{Al}} \quad (C.3)$$

Where k_{PDMS} ($0.15 \text{ Wm}^{-1}\text{K}^{-1}$), k_{Al} ($237 \text{ Wm}^{-1}\text{K}^{-1}$), and x_{PDMS} , x_{Al} are the thermal conductivities and total layer thicknesses for PDMS and aluminum respectively.^{131,132} Plugging the above values into equation 3.1 results in

$$R_h = \frac{0.000140m}{0.15\text{Wm}^{-1}\text{K}^{-1}} + \frac{0.000020m}{237\text{Wm}^{-1}\text{K}^{-1}} = 0.0009335 \frac{W}{K} \quad (C.4)$$

This results in a 0.02 % difference in thermal resistance between value of $0.0009333 \frac{W}{K}$ for the 140 m PDMS only membrane.

C.3 Experimental Setup

The gas detection system was designed to pick up gas flow rates in the 0.1 - 50 m range. A photo of the experimental setup can be seen in Figure C.6. A Smart-Trak 50 mass flow

controller was used to ensure a consistent flow of argon. A Cole-Parmer mass flow logger (60 data points/second) and CO2Meters.com CO₂ sensor or PreSens O2 sensor (1/3 Hz sampling frequency) enabled the release rate of the gas of interest to be measured. The flow meter was located upstream of the point of gas release due to the sensor's sensitivity to changes in gas composition. The additional volume of gas released by the countercurrent amplification system was considered negligible compared to the flow rate of the sweep gas. Flow rate data and percent gas data were combined in Mathematica by interpolating the data with a moving average of 20 points (60 sec) for the concentration data and 1000 points (16 sec) for flow rate data.

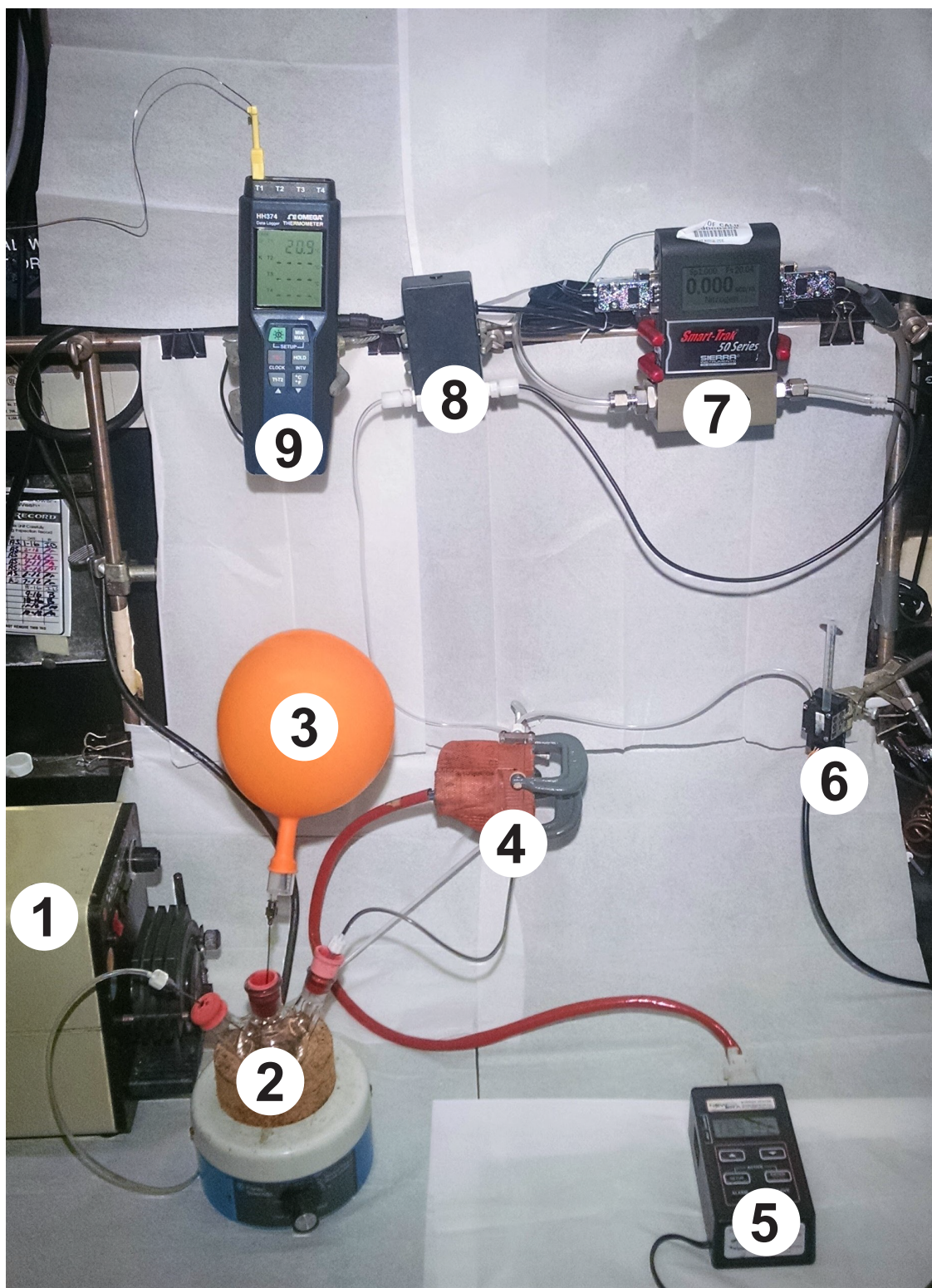


Figure C.6: Experimental setup of the countercurrent multiplier. (1) Buchler peristaltic pump (2) Capture fluid reservoir (3) Gas balloon (4) Countercurrent amplifier + heating pad (5) New Era syringe heater controller (6) CO₂Meter.com GC-0015 CO₂ meter (7) Smart-Trak 50 series mass flow controller (8) Cole-Parmer 0-20 ml/min mass flow logger (9) Omega HH374 Thermometer Data Logger.

C.4 CO₂ and O₂ flux and absolute concentration data

C.4.1 CO₂ Data

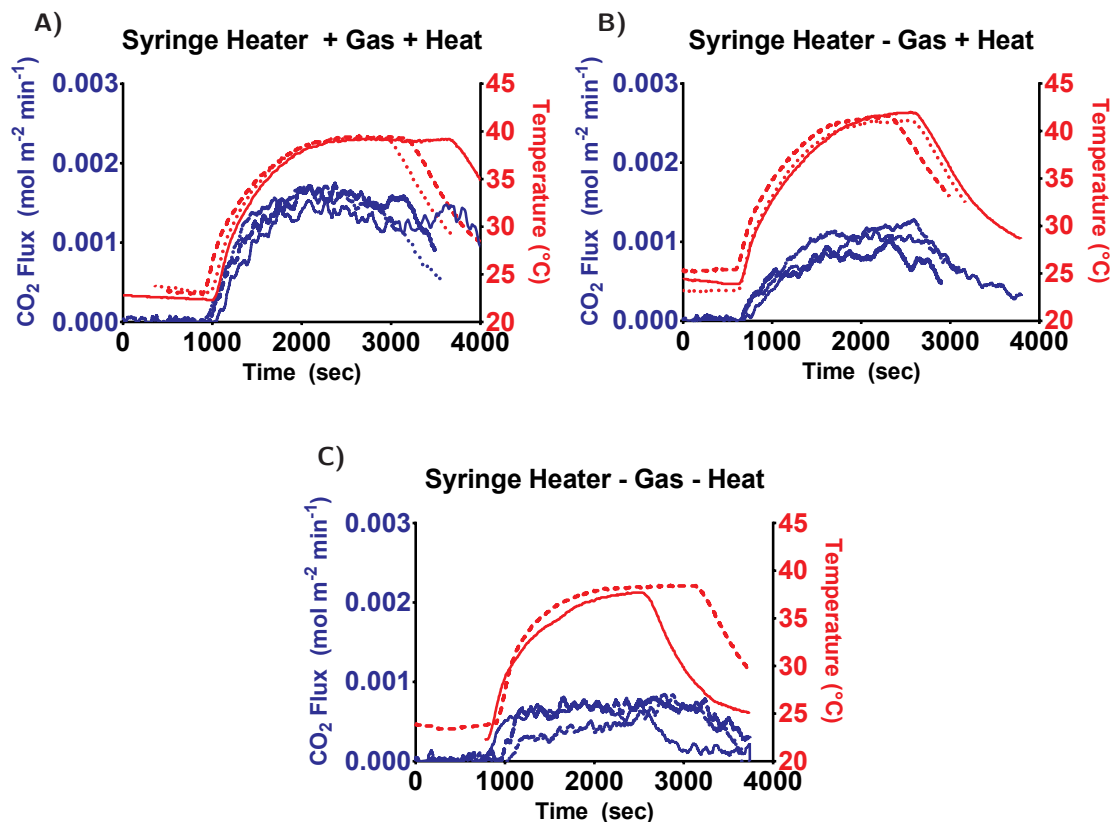


Figure C.7: Flux data for the CO₂/MEA system. Blue curves correspond to the gas flux rates. Red curves correspond to the temperature of the system. A) + Gas + Heat, full countercurrent. B) - Gas + Heat, only countercurrent heat. C) - Gas - Heat, no countercurrent flow.

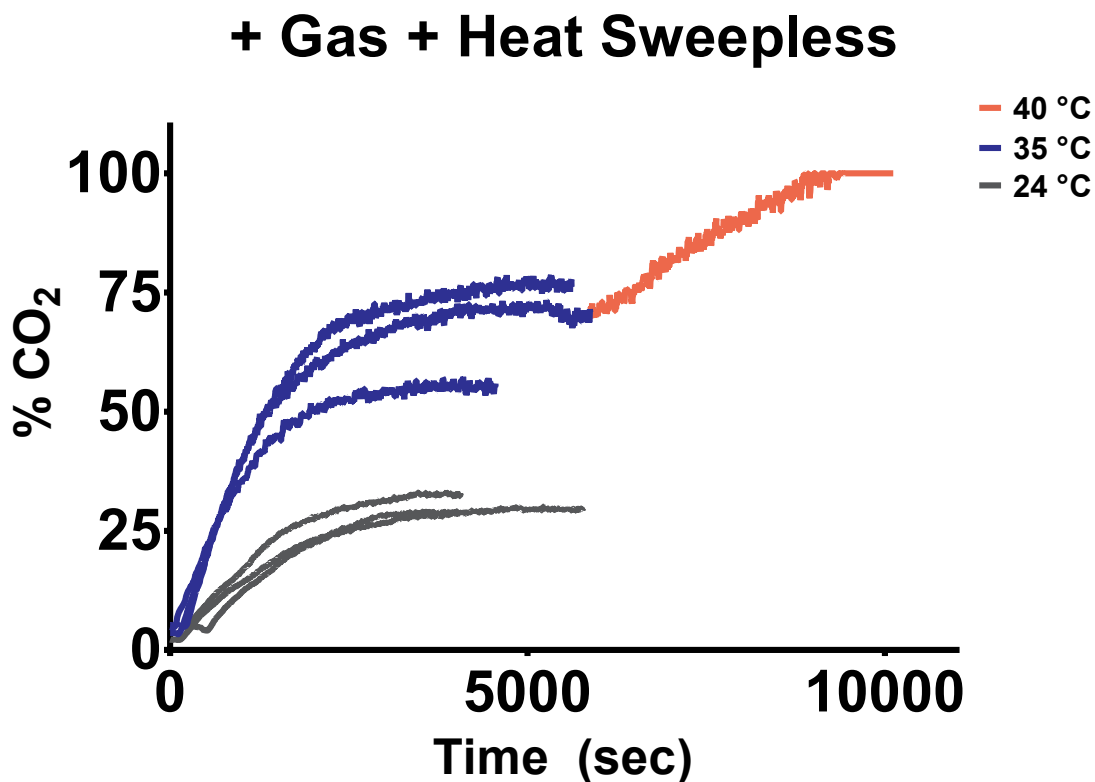


Figure C.8: Absolute concentration data for measured internal temperatures of 24 C, 35 C, and 40 C. The lower 24 C trace is composed of two experimental runs. The red 40 C trace is a continuation of the middle 35 C trace. Data was obtained using the sensor setup pictured in C.4.

C.4.2 O₂ Data

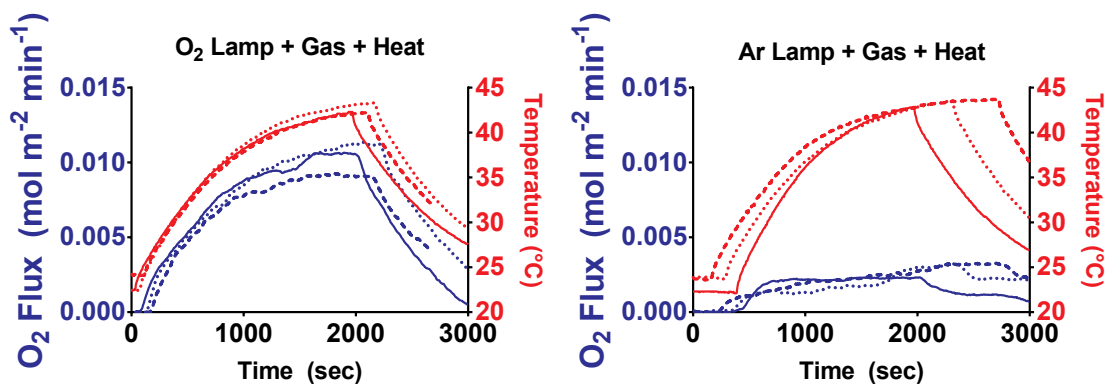


Figure C.9: Flow data for the PFO system. Blue curves correspond to the gas flow rates. Red curves correspond to the temperature of the system. A) PFO saturated with O₂. B) PFO saturated with Ar.

C.5 Carbon black surface modification

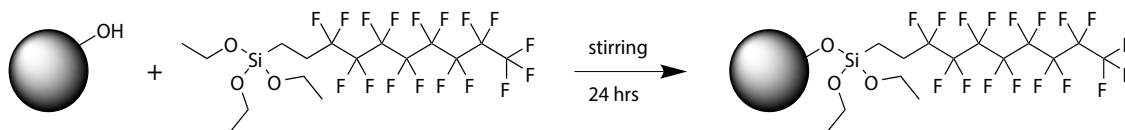


Figure C.10: Reaction scheme for the silanol coupling of carbon black and 1H,2H,2H,-pefluorodecyltrimethoxysilane.

C.5.1 Surface Oxidation

Carbon black was oxidized using a modified procedure from Rouxhet et al.¹²¹ Two grams of carbon black (Cabot, N115) and 60 ml of 30 % H₂O₂ (VWR, 30%) were added to a 125 ml round bottom. The round bottom was fitted with a condenser and stir bar and brought to reflux for 24 hrs. The carbon black was separated from the H₂O₂ peroxide by filtration, washed with water and dried in a 120 C oven. Oxidized carbon black was dried in a 110 C vacuum oven for 1 hour.

C.5.2 Perfluorosilane Modification

Carbon black (500 mg) was weighed out into a 20 ml scintillation flask with stir bar charged with 5 ml of 1H,2H,2H,-pefluorodecyltrimethoxysilane. The flask was purged with argon and sealed. The solution was stirred for 24 hours after which the solution was filtered and the carbon black nanoparticles were rinsed twice with hexanes and water then dried in the vacuum oven overnight. Characterization data can be seen below.

C.5.3 EDS Characterization

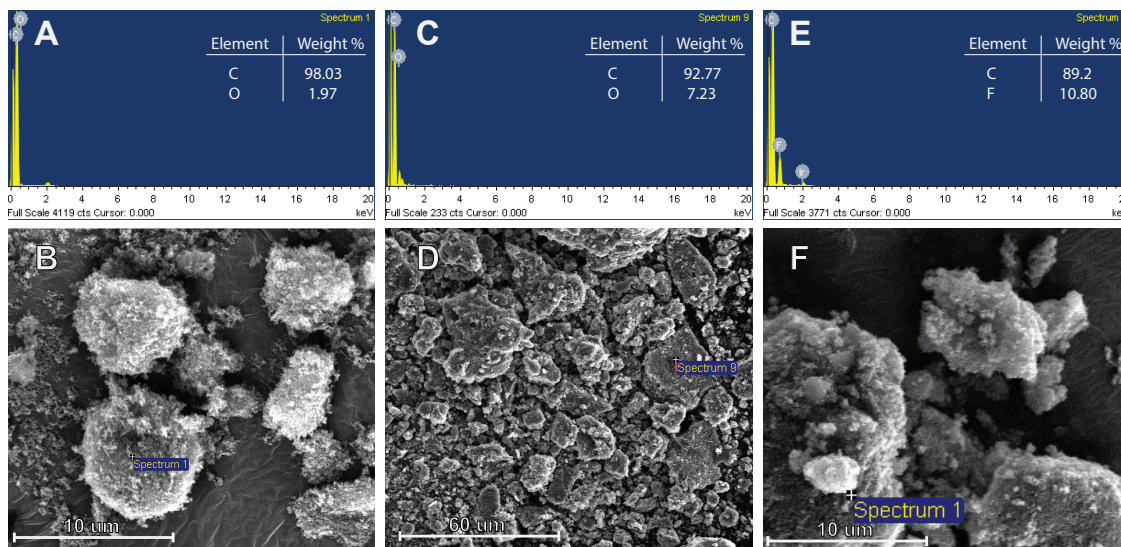


Figure C.11: EDS characterization data for unmodified carbon black, oxidized carbon black, and perfluorocarbon modified carbon black. All samples sputter coated with iridium. A) EDS spectra for unmodified carbon black. B) SEM image of unmodified carbon black. C) EDS spectra for oxidized carbon black. D) SEM image of oxidized carbon black. E) EDS spectra for 1H,2H,2H,-perfluorodecyltrimethoxysilane modified carbon black. F) SEM image of 1H,2H,2H,-perfluorodecyltrimethoxysilane modified carbon black.

C.5.4 Carbon Black in Perfluorooctane Suspension

The dispersion of the carbon black nanoparticles was measured relative to raw carbon black using optical microscopy. Carbon black was added to 1 ml of PFO at a concentration of 0.13 % w/w and then sonicated for 180 seconds after all additives were added. A drop of the resulting solution was placed on a microscope slide and viewed using a 5x objective.

Images were processed using ImageJ following a modified version of a tutorial from microscopy.ethz.ch.¹³³ The images were converted to binary, black and white images by thresholding. The resulting images were processed with the "Analyze Particles" tool resulting the mean, max, min and standard deviation of the particle area.

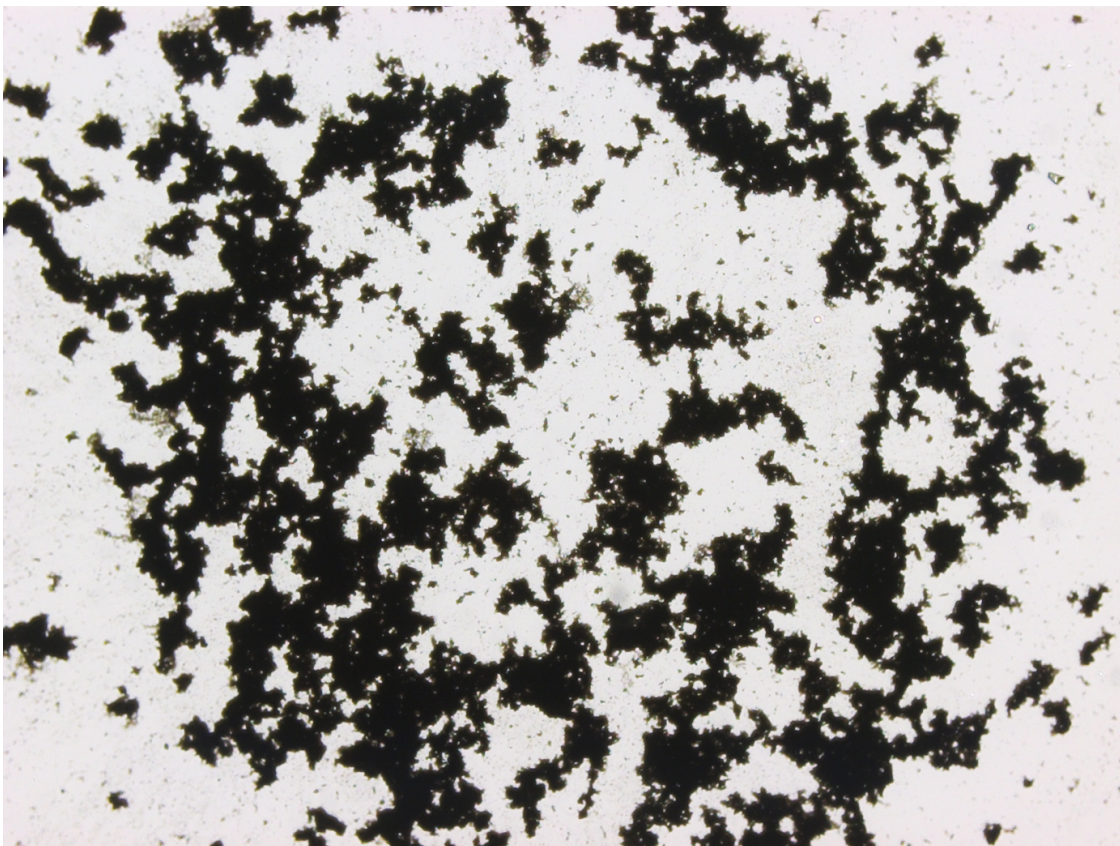


Figure C.12: Raw carbon black (0.113 % w/w) in PFO after 180 sec. of sonication.

	Area (μm^2)
Mean	812
Stdv	9785
Min	4
Max	265563

Table C.1: Distribution of raw CB particle sizes from ImageJ in PFO

	Area (μm^2)
Mean	21
Stdv	57
Min	4
Max	1501

Table C.2: Distribution of perfluorinated CB particle sizes from ImageJ in PFO

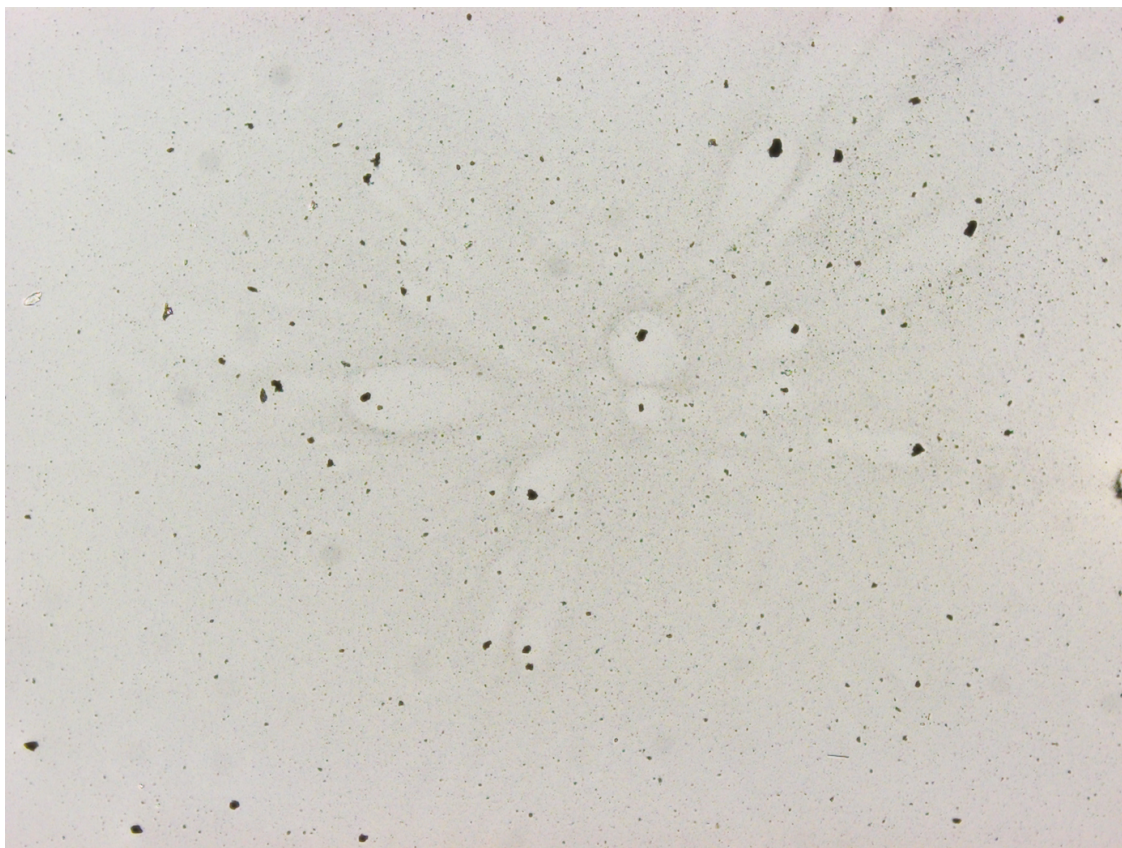


Figure C.13: Perfluorinated carbon black (0.113 % w/w) in PFO after 180 sec. of sonication.

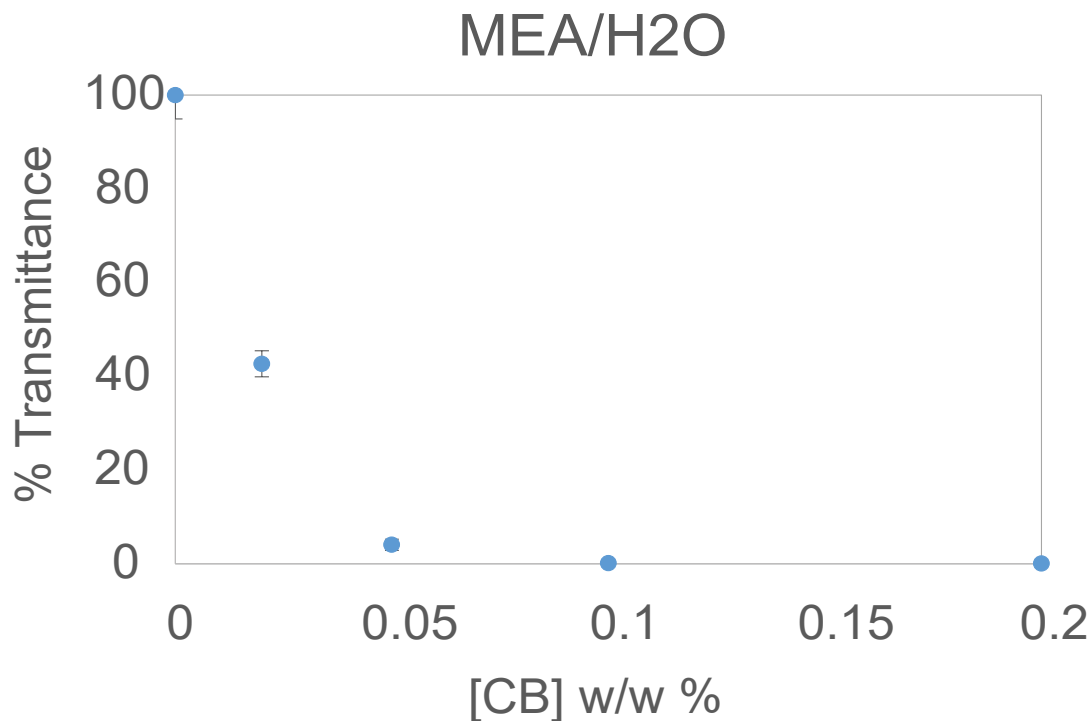


Figure C.14: Percent transmittance of carbon black nanoparticles in MEA/H₂O with 1 w/w % gum Arabic. A path length of 2 mm was used.

C.5.5 Carbon Black in Monoethanolamine Light Transmittance

Percent transmittances were measured using a Zeiss AXIO Observer.A1 microscope. Carbon black suspensions were placed in a 2 mm deep acrylic channel sealed with layer of PDMS. The microscope camera was set to an exposure time of 400 s and the lamp was set to the highest intensity possible without overexposing the RGB color channels.

C.6 COMSOL Model

C.6.1 Model Parameters

A simplified geometry was used in the model to reduce the computational load, enabling quicker iteration in model development.

Part	Dimension (mm)
Acrylic Layer Thickness	5.0
Channel Depth	1.0 -or- 0.1
Channel Length	100.0
Membrane Thickness	0.140

Table C.3: Distribution of perfluorinated CB particle sizes from ImageJ in PFO

Component	Diffusion Coefficient (10^{-5} cm ² /sec)
CO ₂ in MEA/H ₂ O ¹³⁴	$6.955 \cdot 10^{-8} \cdot e^{-\frac{1113(K)}{T}}$
CO ₂ in PDMS ¹⁰⁰	2.2
MEA in MEA/H ₂ O ¹²⁷	$2.487 \cdot 10^{-6} \cdot e^{-\frac{2436(K)}{T}}$
MEA–CO ₂ in MEA/H ₂ O [†]	$2.487 \cdot 10^{-6} \cdot e^{-\frac{2436(K)}{T}}$

Table C.4: Notable diffusion coefficients in MEA/H₂O system [†] Diffusion data could not be found for the MEA–CO₂ species, so the value was assumed to be the same as for MEA

C.6.2 Reaction Kinetics

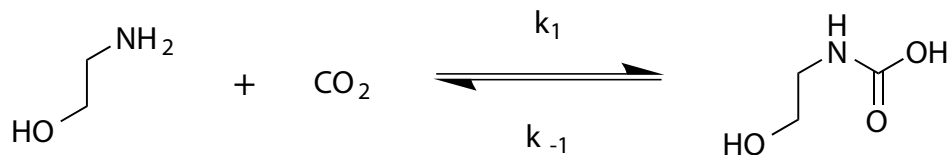


Figure C.15: Reaction of MEA with CO_2 . Forward reaction rate is denoted by k_1 and the reverse reaction rate is denoted by k_{-1} .

The reaction kinetics were obtained from work by Maeder et. al.¹¹⁰ The forward and reverse rates are given by:

$$k_1 = 5.8 \cdot 10^{10} \left(\frac{1}{\text{mol} \cdot \text{s}} \right) \cdot e^{\frac{-4872(K)}{R \cdot T}} \quad (\text{C.5})$$

and

$$k_{-1} = 1.0 \cdot 10^{13} \left(\frac{1}{\text{mol} \cdot \text{s}} \right) \cdot e^{\frac{-7583(K)}{R \cdot T}} \quad (\text{C.6})$$

where T is the temperature in Kelvin and R is the gas constant ($8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}$).

The overall rate is then given by:

$$\text{Rate} = k_{-1}[\text{MEA}-\text{CO}_2] - k_1[\text{CO}_2][\text{MEA}] \quad (\text{C.7})$$

or

$$Rate = 1.0 \cdot 10^{13} \left(\frac{1}{mol \cdot s} \right) \cdot e^{\frac{-7583(K)}{R \cdot T}} [MEA-CO_2] - 5.8 \cdot 10^{10} \left(\frac{1}{mol \cdot s} \right) \cdot e^{\frac{-4872(K)}{R \cdot T}} [CO_2][MEA] \quad (C.8)$$

The final rate is entered as shown for the formation rate of MEA and CO₂ and the reverse rate is entered for the formation of MEA—CO₂.

C.6.3 Initial Concentrations

Given

$$K_e = \frac{k_1}{k_{-1}} \quad (C.9)$$

and

$$K_e = \frac{[CO_2][MEA]}{[MEA-CO_2]} \quad (C.10)$$

[CO₂] can be solved for.

Assuming that [CO₂] = [MEA] at equilibrium and given an initial MEA concentration

([MEA_{tot}]) of 5 M, the equilibrium can be written as

$$K_e = \frac{[\text{CO}_2][MEA]}{[MEA_{tot}] - [\text{CO}_2]} \quad (\text{C.11})$$

Solving for [CO₂] gives

$$[\text{CO}_2] = \frac{-1 + \sqrt{1 + 4 \cdot [MEA_{tot}] \cdot K_e}}{2 \cdot K_e} \quad (\text{C.12})$$

This can be approximated within the temperature range of interest by

$$[\text{CO}_2] \approx 0.0051\left(\frac{M}{K}\right) \cdot T - 1.2(M) \quad (\text{C.13})$$

the two previous expressions can be seen plotted below

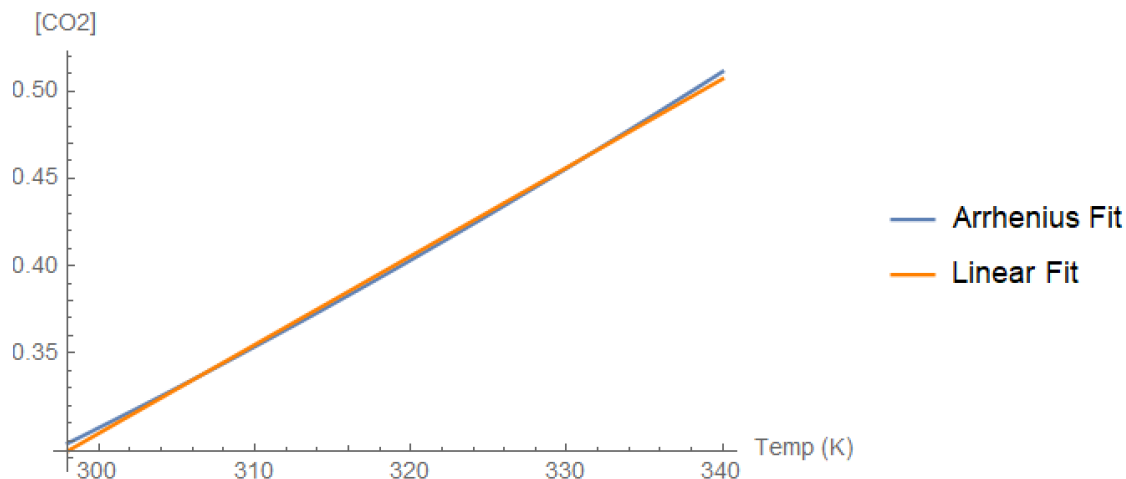


Figure C.16: Comparison of calculated $[\text{CO}_2]$ derived from the Arrhenius fit given by Conway et. al and a linear fit from 298 K to 340 K.

Solving the for $[\text{CO}_2]$ at the initial temperature of our system gives $[\text{CO}_2] = 0.298 \text{ M}$ The above value was used as a starting point, but a concentration of 0.2762 M was found to be the optimal concentration for the COMSOL model to reduce concentration oscillations.

C.6.4 Model Results

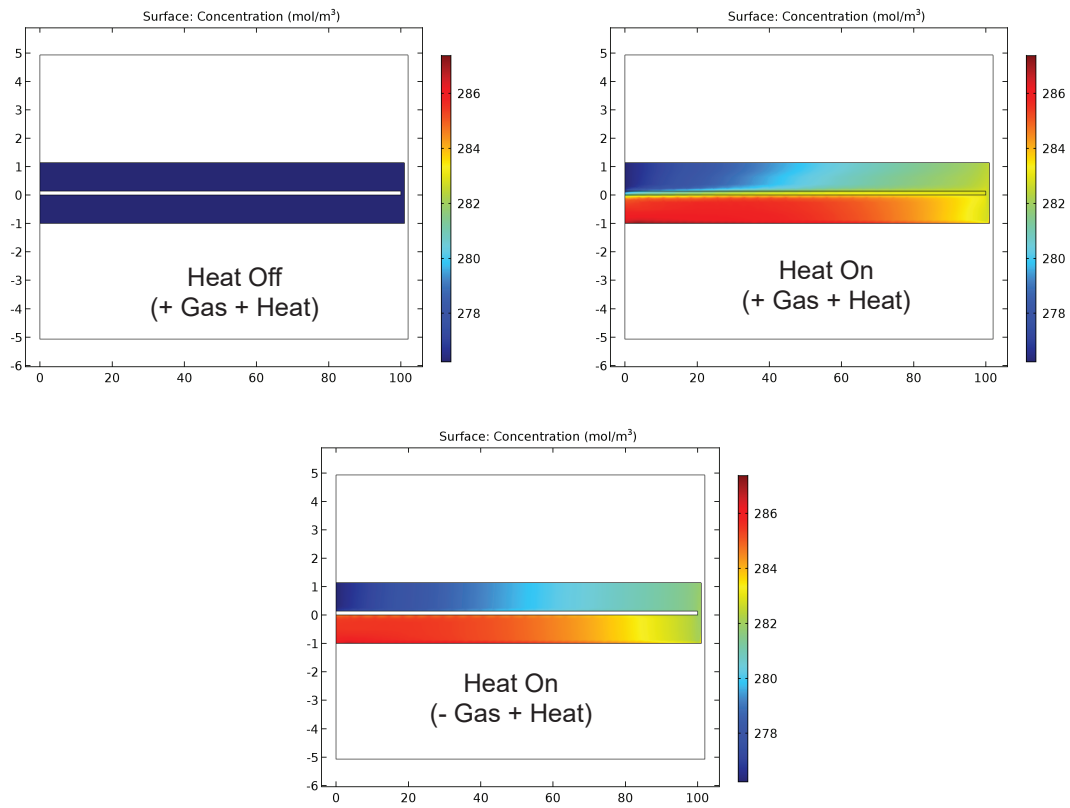


Figure C.17: Concentration of CO₂ in the middle of the inlet and outlet channels with different configurations. Heat is applied from the bottom face of each graphic. Capture fluid flows into the top channel and out through the bottom channel.

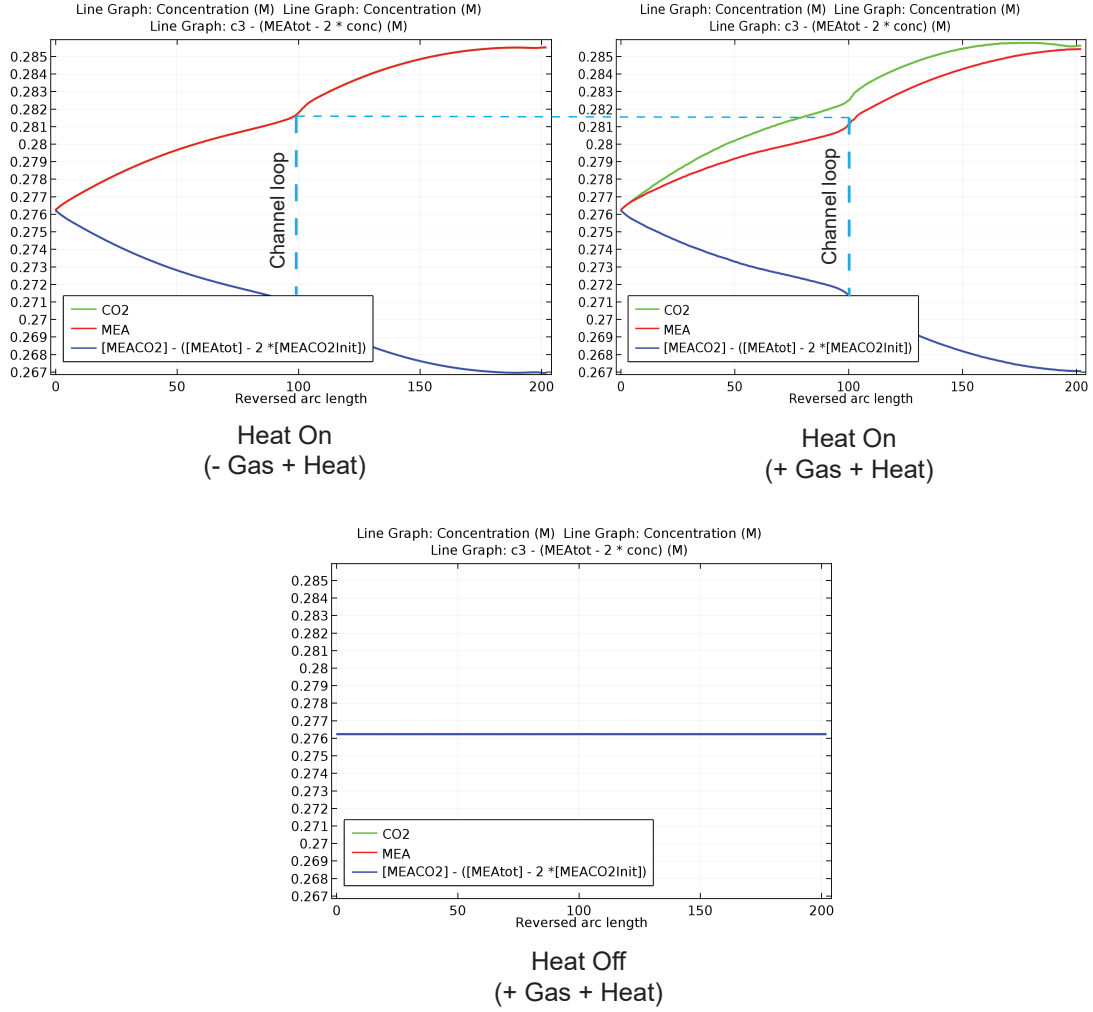


Figure C.18: Component concentrations in the middle of the inlet and outlet channels. Trigger off (bottom) and trigger on (top). Gas diffusion between channels disabled (left), gas diffusion enabled (right). The concentration of MEACO_2 was graphed as $([\text{MEACO}_2] [\text{MEA}]_t - 2 [\text{MEA}]_e)$ where $[\text{MEA}]_t$ is the total concentration of MEA species in solution and $[\text{MEA}]_e$ is the equilibrium MEA concentration without applied heat.

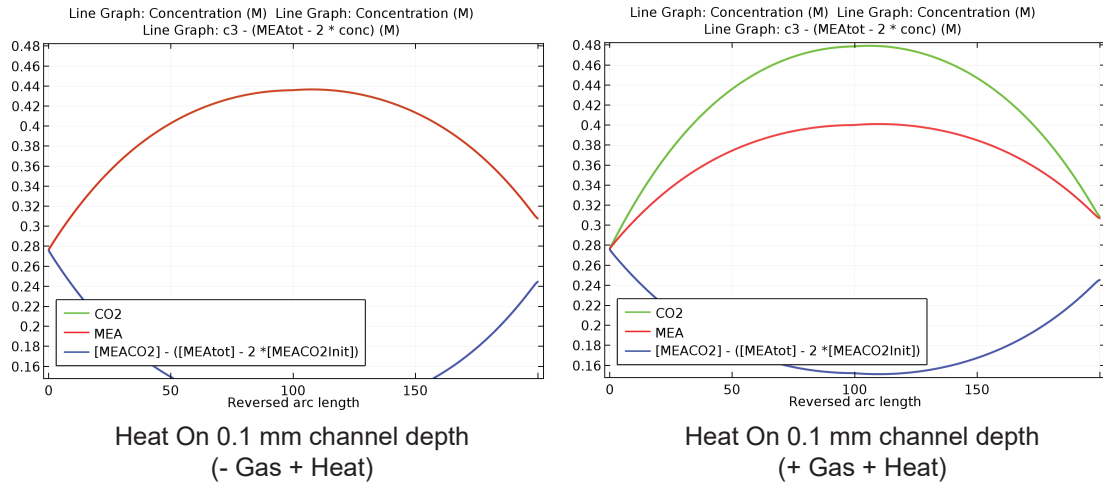


Figure C.19: Component concentrations along the PDMS adjacent face of the inlet and outlet channels (0.1 mm channel depth). Gas diffusion between channels disabled (left) and gas diffusion enabled (right). The concentration of MEACO₂ was graphed as $([\text{MEACO}_2] [\text{MEA}]_t - 2 [\text{MEA}]_e)$ where $[\text{MEA}]_t$ is the total concentration of MEA species in solution and $[\text{MEA}]_e$ is the equilibrium MEA concentration without applied heat.