Phase III Xlerator Program: Dimensionally Stable High Performance Membranes

Cortney Mittelsteadt (P.I.)
Avni Argun
Castro Lacier
Jason Willey
Pam Maxwell

Giner, Inc.

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FC036

Dimensionally Stable High Performance Membranes

Timeline

- Begin 10/01/2010
- Review 09/30/2012
- <75% Complete

Budget

- Total project funding
  - DOE Share: $800K
  - Cost Share: N/A
- Funding Received in FY11: $491K
- Planned Funding for FY12: $309K

Barriers addressed

A. Durability

B. Cost

Technical Targets (DOE 2017 Targets)

0.02 Ωcm^2 at 1.5 kPa H_2O Air inlet

- <$20/m^2$
- > 5000 h lifetime, 20k RH Cycles
- Stability in condensing conditions

Partners

- UMass - Amherst
- Impattern Technologies
- Colorado Photopolymer Solutions

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Overview

- Why Dimensionally Stable Membranes
- Phase III Program and Results
  I. UV Microreplication
  II. Mechanical Deformation
  III. Inversion Casting
- Go/No-Go after each year
  – YEAR 1 Go/No-Go decision: Has scalable micro-molding method been generated to produce the desired DSMs?
  – YEAR 2 Go/No-Go decision: Does selected method generate DSM based MEAs that meet DOE targets for cost, performance and durability? Is it feasible to scale up the bench manufacturing process?

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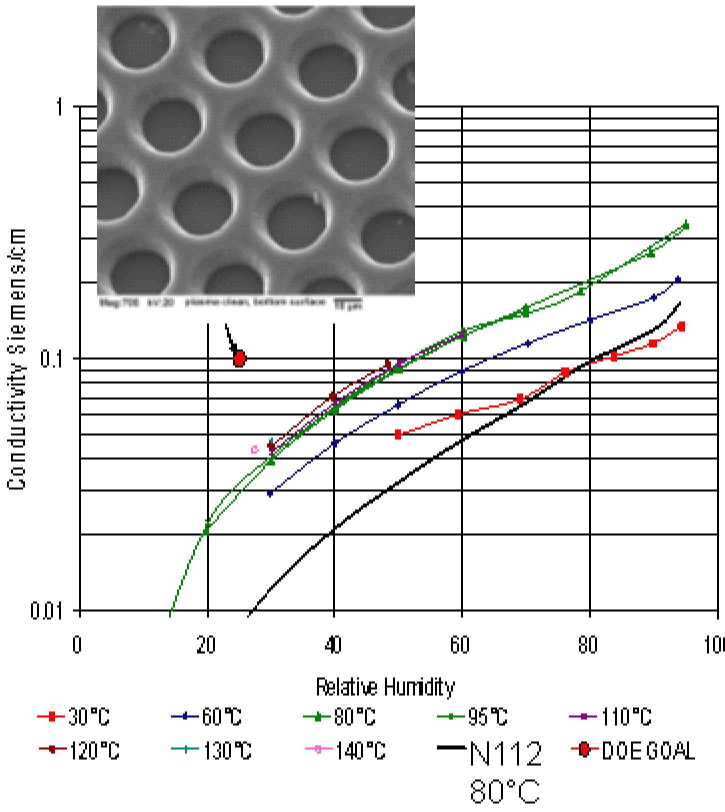
Approach: Giner Two-Dimensional Stable Membranes

- Giner had the most *technical* success with two dimensional stable membranes
- Laser drilling approach is not practical due to cost
- Phase II program showed pathway to obtaining these supports in high-volume, low-cost processes



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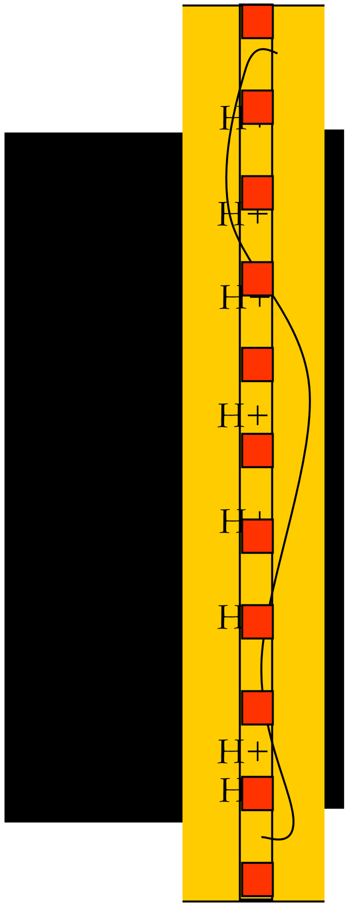
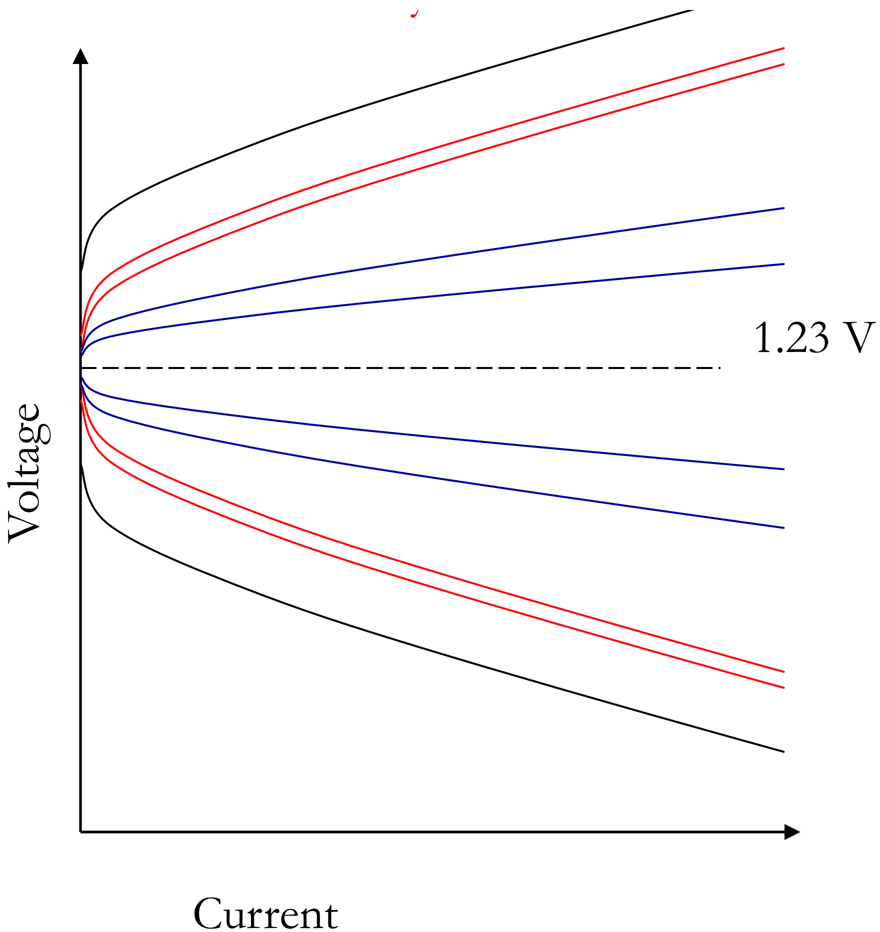
Relevance: WHY DSM?

Challenges to build a better MEA for Fuel Cells and Electrolyzers

ADD SUPPORT STRUCTURE

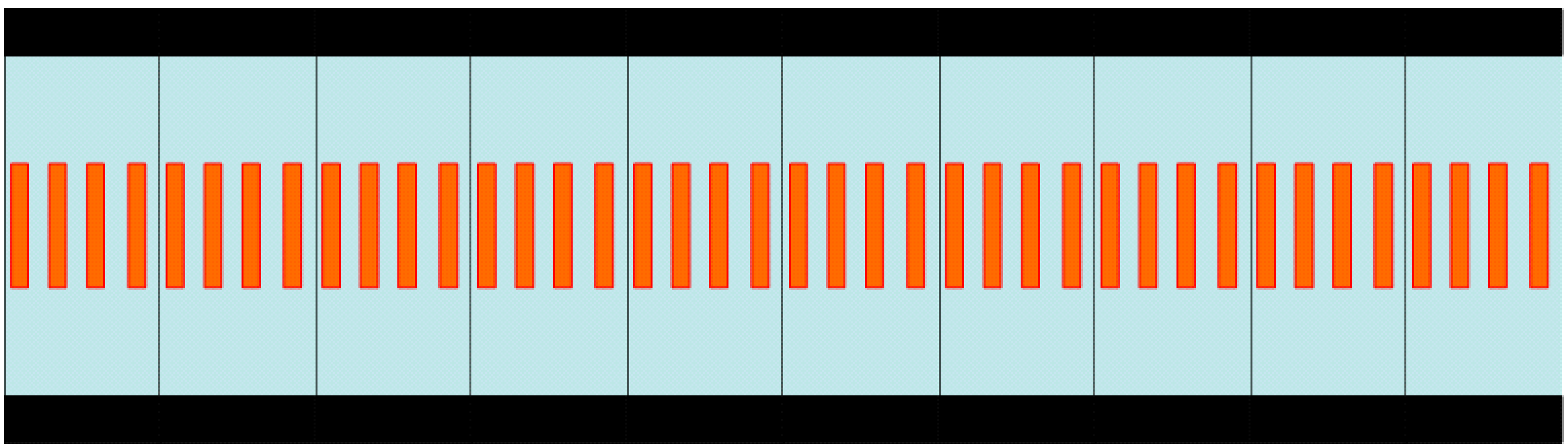




Approach: Keys to 2D DSM

Membrane thickness will likely be 12-25 μm

Key aspect ratios:

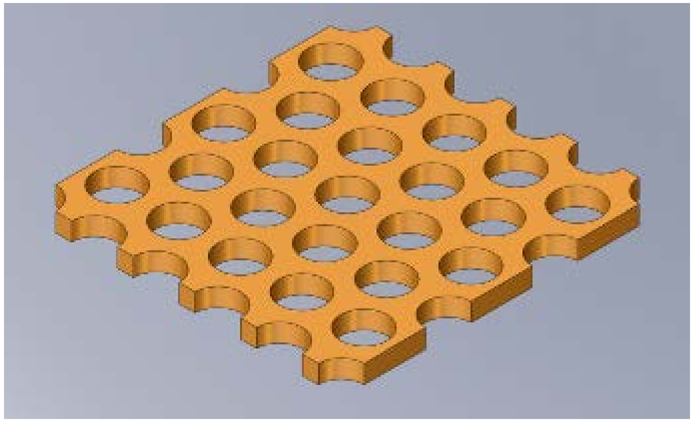


Very close is better, but very difficult to manufacture

Approach: Criteria for DSM Manufacturing

- **Design:** 6-8 μm thick support structures with 8-20 μm diameter holes and 50% porosity to accommodate ionomers.
- **Process:** High tensile strength to handle in a roll-to-roll system without tearing and breaking
- **Performance:** Negligible expansion in the XY plane and preserved modulus when exposed to wet/dry cycles.
- **Durability:** High durability to survive 20,000 wet/dry cycles without crack failure.
- **Stability:** High-temperature stability in the range of -30 to 120°C

DSM support design with 20 μm hole diameter and 50% open area



Achievements: Pathways Identified DSM Support Fabrication

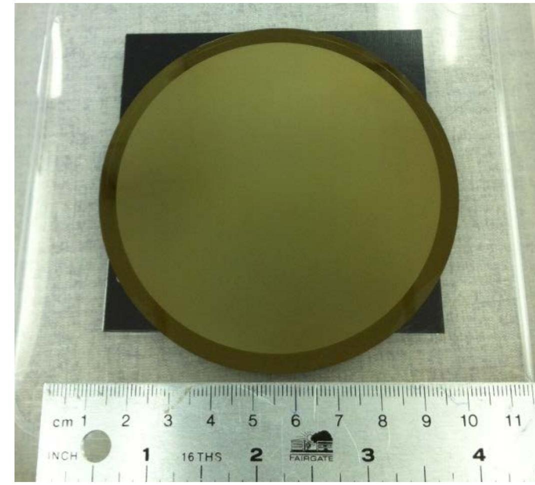
- In Year 1, Giner investigated various approaches to identify a scalable and cost-effective route.
- Currently Giner is actively pursuing the following three DSM fabrication routes:

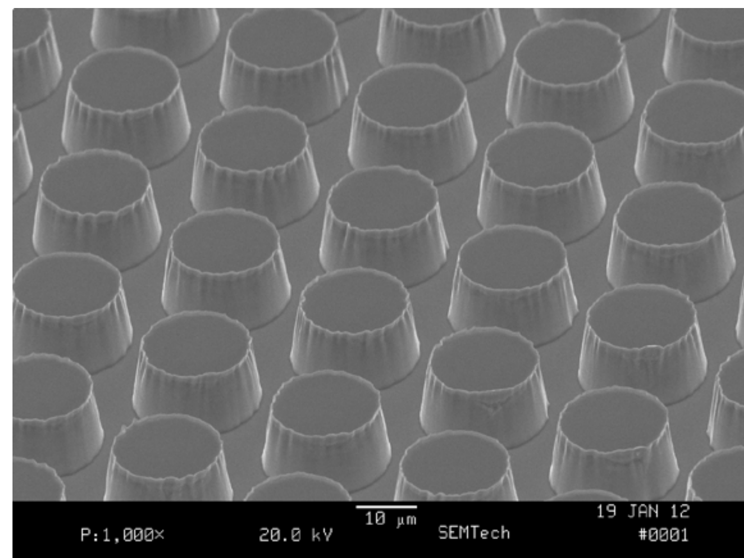
Technique	Description	Pros	Cons
I- UV Microreplication	UV curing of polymers between a mold and a backing substrate	•Rapid film formation •Easy roll integration	•High material risk •R&D cost
II- Mechanical Deformation	Mechanical deformation via mold pillars	Proven materials	•Resolution •Ragged features
III- Phase Inversion Solvent Casting	Precipitation of polymers on a mold using a non-solvent.	•Ease of processing •Well defined material	•Waste solvent •Film shrinkage

Each path starts with the same first step: Design of the mold

Achievements: I- UV Microreplication: Nickel Molds

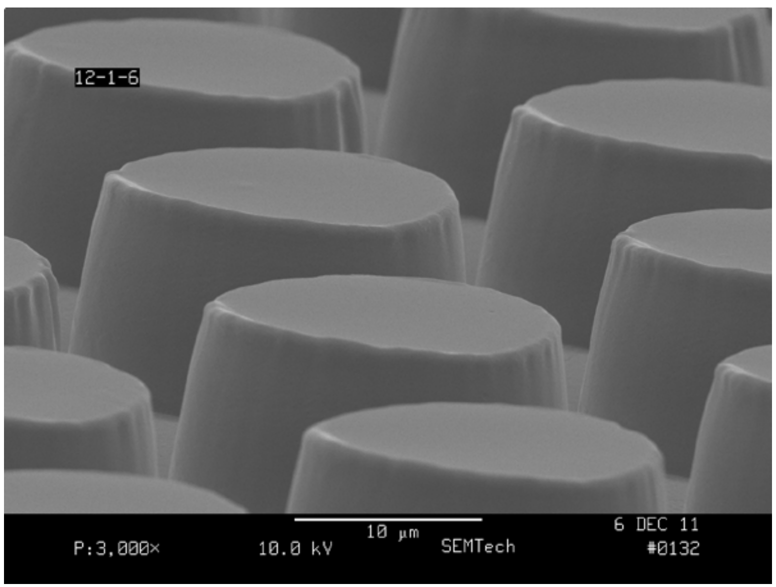
- NILT of Denmark manufactured master and replica molds
  - **4"** diameter round molds replicated from master
  - 20 μm diameter, 10 μm feature height, 50% density
  - Nickel shims (flat molds for prototypes)
- Easy to scale to 12" x 12"
- Easy to replicate using electroformed nickel shims

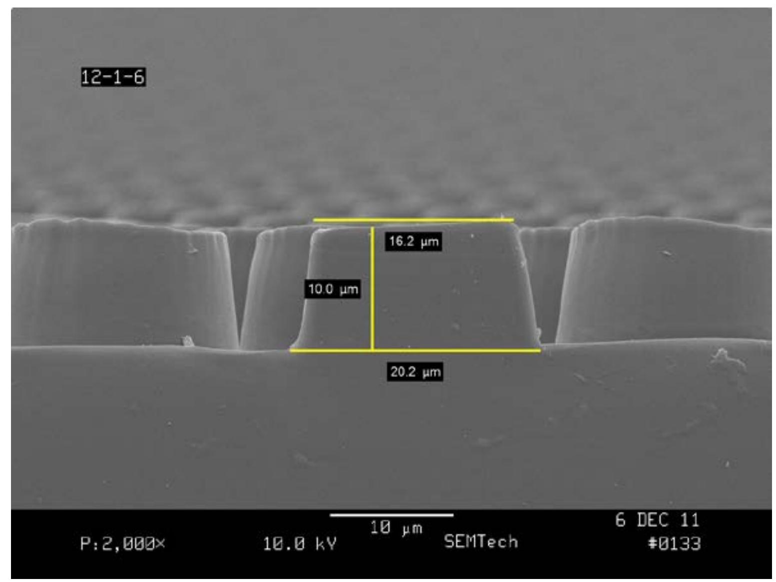




I- UV Microreplication: Molds

- Fabrication of high modulus polymer replica molds from nickel molds with hole patterns.
- Tilted and cross-sectional SEM views of mold pillars showing flawless replication.





Achievement: I- UV Microreplication: Materials

Various UV-curable materials have been evaluated as candidates for rapid and large scale DSM manufacturing

Material Group	Pros	Cons
Acrylate	• Highly established chemistry • Ease of processing • Rapid curing	• Often yields brittle materials • Inert atmosphere necessary • Not suitable at high temperature
Thiol-ene	• Great variety of thioles and -enes • Proven in high res patterning	• Not tested in fuel cell environments • Low hydrolytic stability
Epoxy	• Excellent water and chemical stability • Wide temperature range	• Strong adhesion on molds • Not tested for reel-to-reel
Polyimide	• Proven to work as DSMs • Tough, durable material with high chemical resistance	•High material cost •High temperature processing (375 °C)

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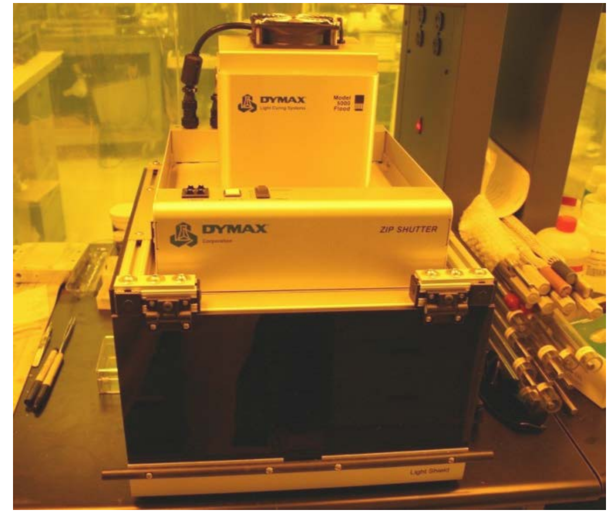
GINER

DOE Hydrogen Program

Achievement: I- UV Microreplication: Materials

- A high power UV curing flood lamp is situated in a UV-shielded cleanroom facility to screen photocurable DSM supports
- Of the 20+ formulations tested, only a few formulations have passed Giner's strict criteria on water uptake, dimensional stability, and mechanical stability



Formulation	Tensile Strength (MPa)	Elastic Modulus (MPa)	Elongation at Break (%)	Creep @2 MPa, 2 hours (%)	Water Uptake (%)	Dimensional (x, y) change (%)
Polyimide (Kapton)	>24	1319.5	N/A	0.3	0	0
Ionomer (Nafion)	6.08	21.36	94.1	16.3	33	22
Polysulfone	36.8	710.9	19.1	1.4	0.3	0.2
Thiol-ene (Norland)	>10	583	N/A	-	0.5	-
Thiol-ene (CPS)	1.61	35.34	4.3	1.4	0.5	0.3
Epoxy	0.3	1.64	13	-	1.8	2.7

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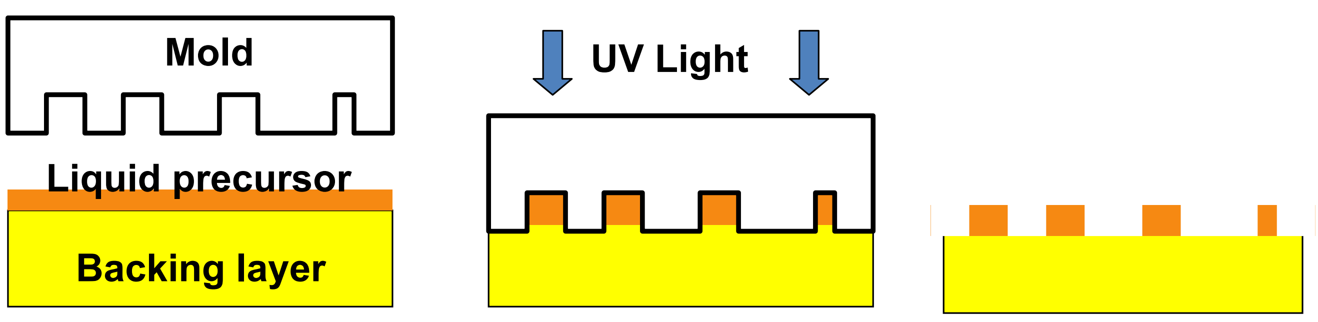
Achievement: I- UV Microreplication: Materials

- Colorado Photopolymer Solutions (CPS) is developing UV-curable thiol-ene formulations for Giner
  - Low-viscosity monomer, instantly polymerized to ensure fast fabrication
  - Acid resistive to ensure long-term durability in fuel cell environment
- Key challenge is to ensure high mechanical stability at high temperature and RH.

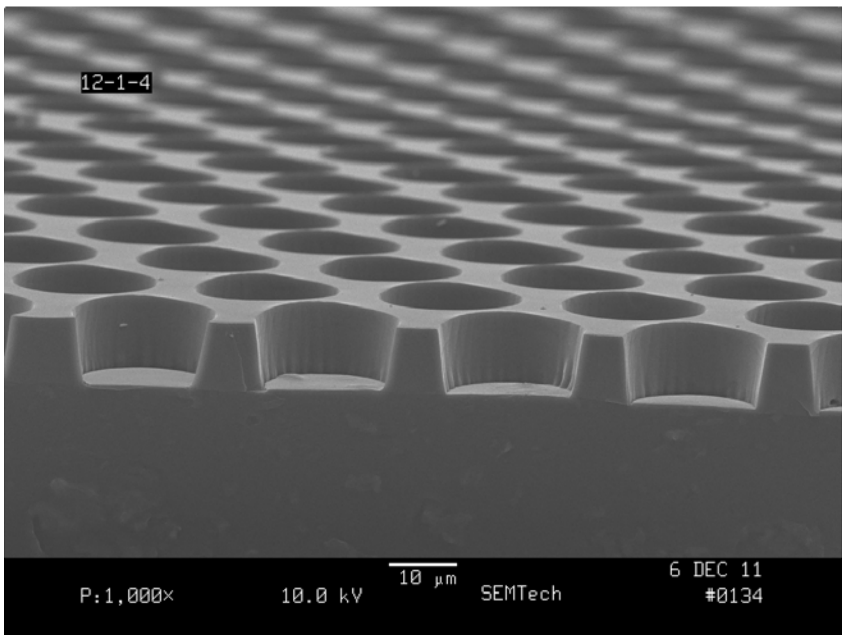
Achievement: I- UV Microreplication: Processing

- In collaboration with Ken Carter of UMass-Amherst, the first series of microfabrication has been conducted using NILT's molds and CPS's liquid formulations.
- A state-of-the-art Nanonex NX-200 Universal Imprintor has been utilized for processing.
- During the first round, DSM supports have been successfully fabricated and released from molds.

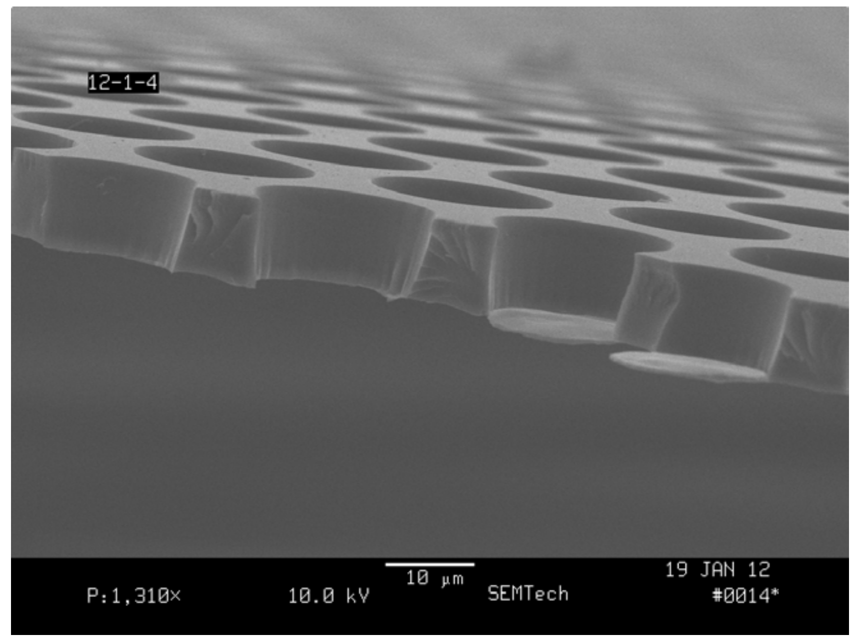


Achievement: I- UV Microreplication: Materials

- A thiol-ene film UV-cured in between a high modulus mold and a backing layer to form an 8-10 μm thick DSM support.



Thiol-ene DSM support formed on a sacrificial backing layer.



Free-standing DSM support

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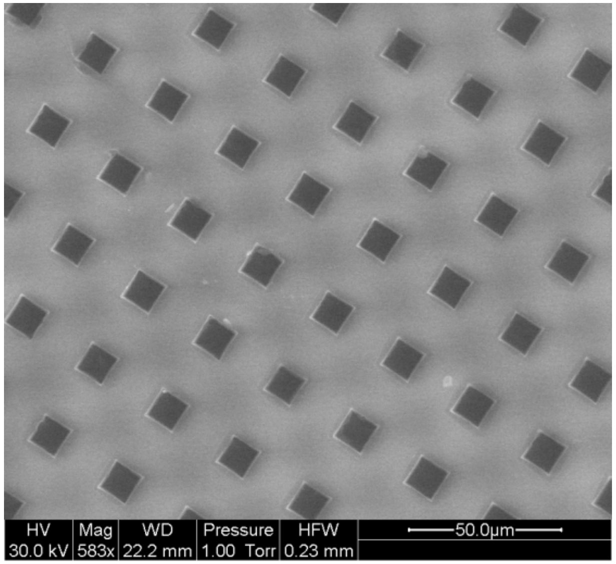
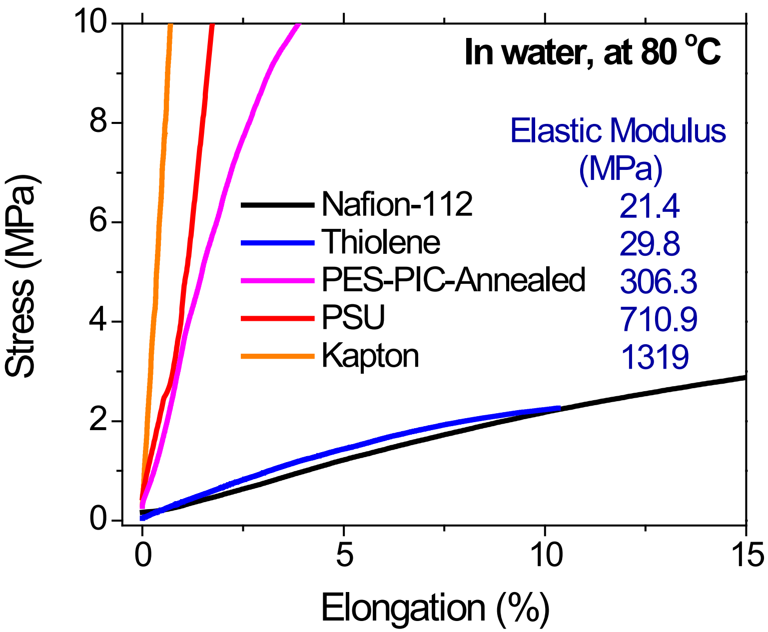
Achievement: Method II- Mechanical Deformation

- Best scalable route with proven materials ($50/m^2) batch process; lower in R2R



Porous polysulfone DSM support



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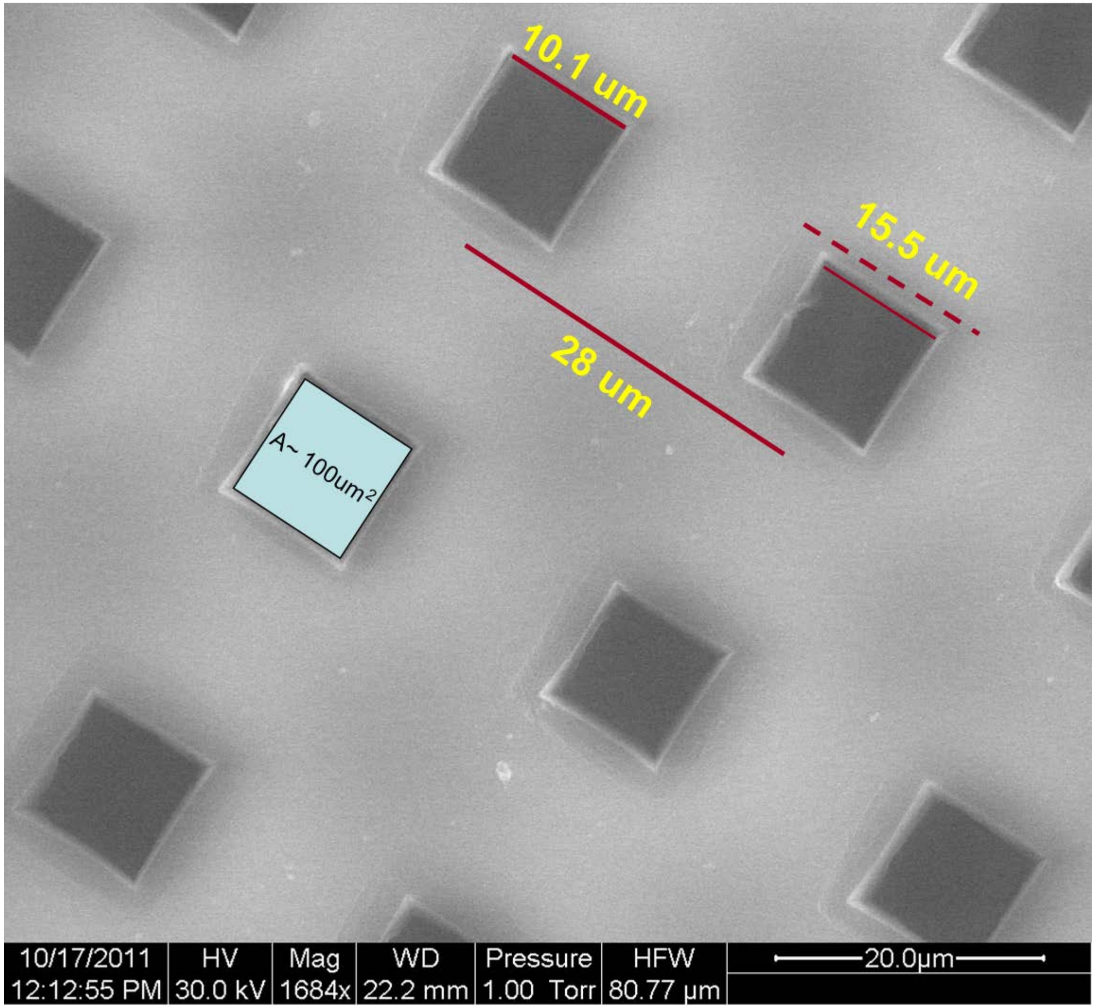
Achievement: Method II- Mechanical Deformation

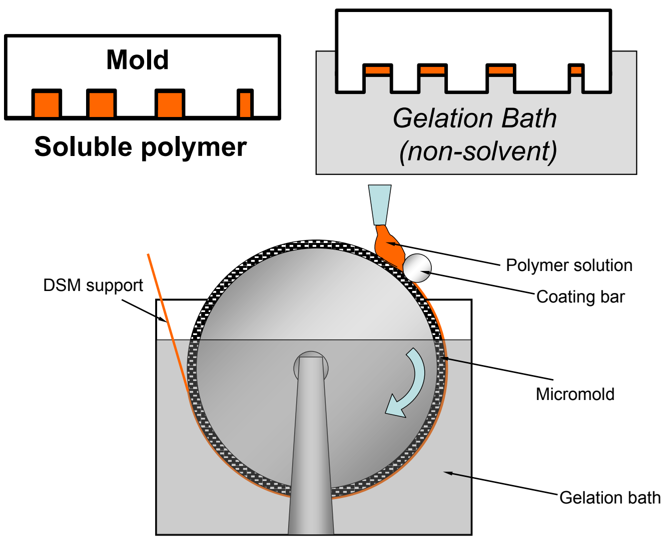
- Successfully opened holes
- Current porosity on an 8 μm thick film is 15-30% (target porosity: 50%)

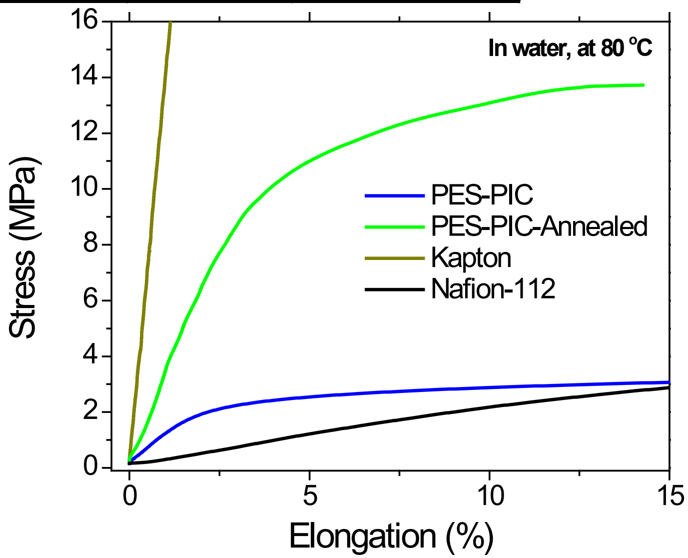


Achievement Method III- Phase Inversion Solvent Casting

- Investigating improvements over the Phase II program
- A polyethersulfone (PES) film has been cast on a PDMS micromold followed by annealing above T_g

	Thickness (mm)	Tensile Strength (MPa)	Elastic Modulus (MPa)	Elongation at Break (%)	Creep @2 MPa, 2 hours (%)
As cast	0.063	3.48	94.45	35.8	2.5
Annealed above Tg	0.035	13.73	306.3	14.26	0.6





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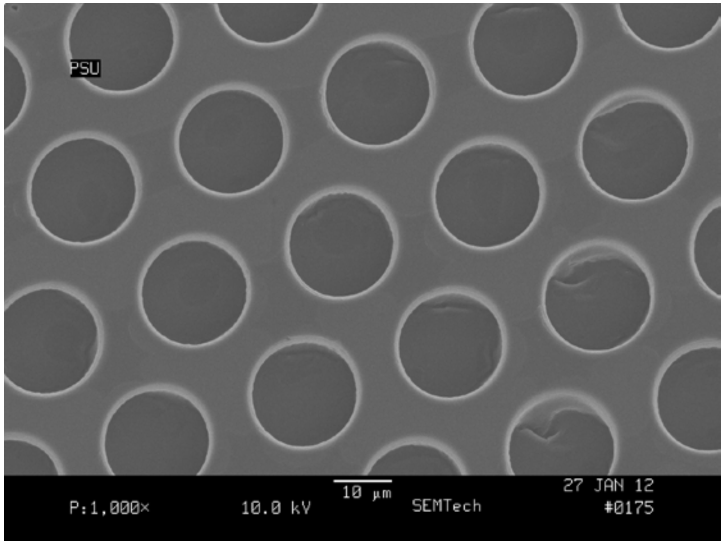
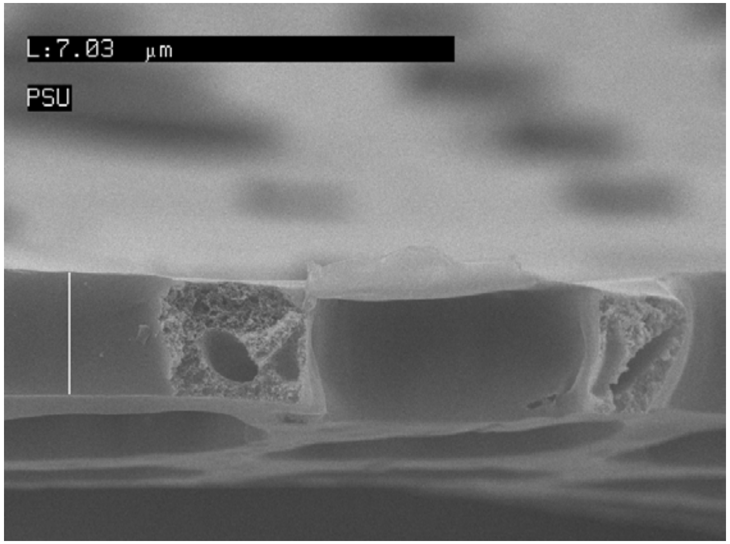
Achievement Method III- Phase Inversion Solvent Casting

- Using a new material for pillar molds, a polysulfone DSM support has been formed. High modulus of mold material provides better durability during the phase inversion process.



Top-down view of a polysulfone DSM support cast from a high modulus mold.



Cross-sectional view of a 7 μm thick polysulfone DSM support. Note the microporosity of the inverted film.

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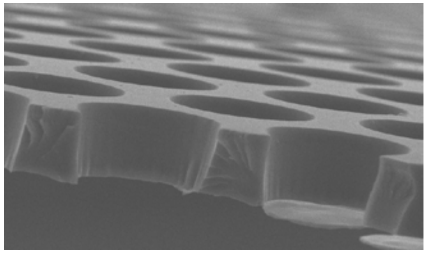
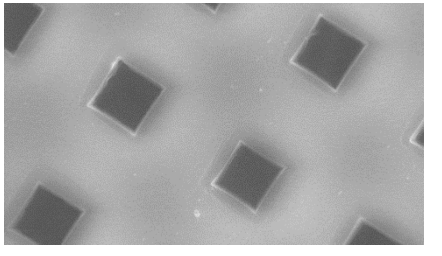
Summary

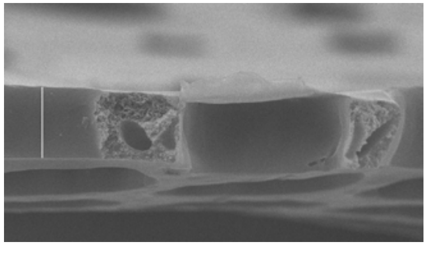
- **The goal at the end of YEAR 1 was to demonstrate a scalable and cost-effective process for DSM manufacturing.**

Three viable pathways have been shown:

- UV Microreplication
  - Lowest ultimate cost (< $20/m^2)
  - Narrow material selection
- Mechanical Deformation
  - Best materials choices
  - Currently $50/m^2, << for R2R
  - Technical hurdle remains to increase pore size
- Inversion Casting
  - Good material selection
  - Need to increase intrinsic properties
  - Projected cost ~$20/m^2







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FUTURE WORK

In YEAR 2, Giner is actively pursuing all three processes based on the criteria of scaling, performance optimization, and cost reduction.

- We've completed the most expensive/riskiest steps
  - Mold fabrication
  - Process demonstration
- Will pursue scaling UV microreplication at UMass Amherst
- Pursuing inversion casting route in house
- Fuel Cell Qualification for manufactured membranes
  - Chemical Durability
  - Mechanical Stability
  - Performance (through plane conductivity)

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Extra Slides

Giner Membranes Compared to DOE Targets

As tested by FSEC

Characteristic	Units	Target 2017	A1	A2	A3	A4	NRE211
Thickness µm			20	40	30	32	25
Area specific proton resistance[c] at:							
120°C, water partial pressures from 40 to 80 kPa	Ohm cm^2	≤ 0.02	0.35	0.33	0.41	0.23	0.18
80°C and water partial pressures from 25 - 45 kPa	Ohm cm^2	≤ 0.02	0.10	0.08	0.09	0.06	0.05
Maximum Hydrogen cross-over [a]	mA / cm^2	2	0.75	1.6	0.61	0.70	0.76
Minimum electrical resistance [b]	Ohm cm^2	1000	65	358	1073	813	2100
Performance @ 0.8V (¼ Power)	mA / cm^2 mW / cm^2	300 250	94 75	222 177	112 89	81 65	151 120
Performance @ rated power	mW / cm^2	1000	300	708	356	260	480

*Values are at 80°C unless otherwise noted
a.Measure in humidified H_2/N_2 at 25°C
b.Measure in humidified H_2/N_2 using LSV curve from 0.4 to 0.6 V at 80°C (taken from RFP)
c.Average cell resistance from current interrupt

Believe interface is adding some resistance;
However we have not been able to use lowest EW PFSA's that we would like to, nor have we been able to obtain supports as thin as we would like.
If we had 18 um membrane with our lowest EW ionomer resistance would be ~ 1/3

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