Phase III Xlerator Program: Dimensionally Stable High Performance Membranes

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FC 036

Overview

Timeline

- Begin 10/01/2010
- End 02/28/2014
- <75% Complete

Budget

- Total project funding
  - DOE Share: $1,552K
  - Cost Share: N/A
- Funding Received in FY11: $491K (Year 1)
- Funding Received in FY12: $409K (Year 2)
- Planned Funding for FY13-14: $652K (Year 3)

Barriers addressed

A. Durability
B. Cost
C. Performance

Technical Targets (DOE 2017 Targets)

- 0.02 $\Omega.cm^2$ at 1.5 kPa H_2O Air inlet
- <$20/$m^2$
- > 5000 h lifetime, >20,000 RH Cycles

Partners

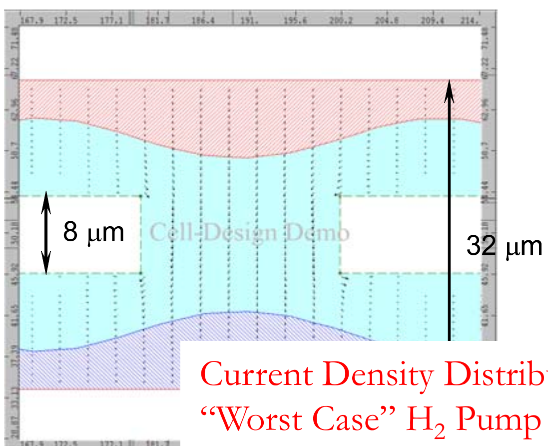
- UMass – Amherst
- Impattern Technologies

Overview

- Why Dimensionally Stable Membranes (DSM™)
- SBIR Phase III Xlerator Program and Year 2 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?

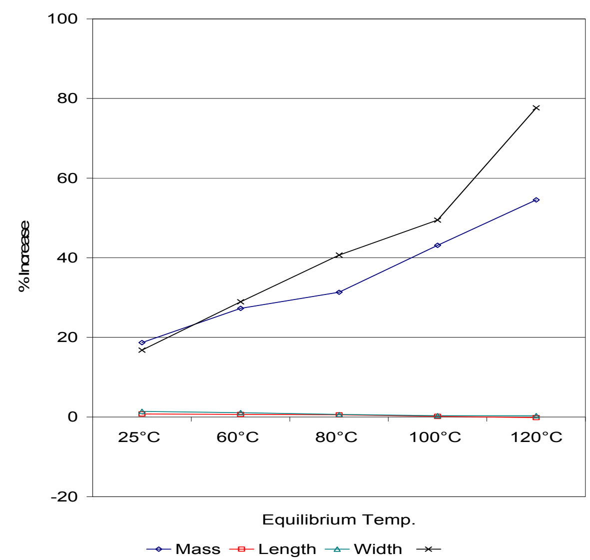
Overview: DSM™ - What We Know

- **DURABILITY**
  - Lack of Substrate Ionomer/Ionomer Interface does not lead to delamination
  - FCTT RH Cycling Metric 20k Cycles 80 C shown
- **PERFORMANCE**
  - Very Small "Blind Spot" Loss at Typical Aspect Ratios
- **CONDUCTIVITY**
  - 25-30% Penalty
  - (~50% for expanded PTFE)
- **DIMENSIONAL STABILITY**
  - Nearly Eliminates all x-y swelling



Current Density Distribution for "Worst Case" H_2 Pump with low ionomer conductivity

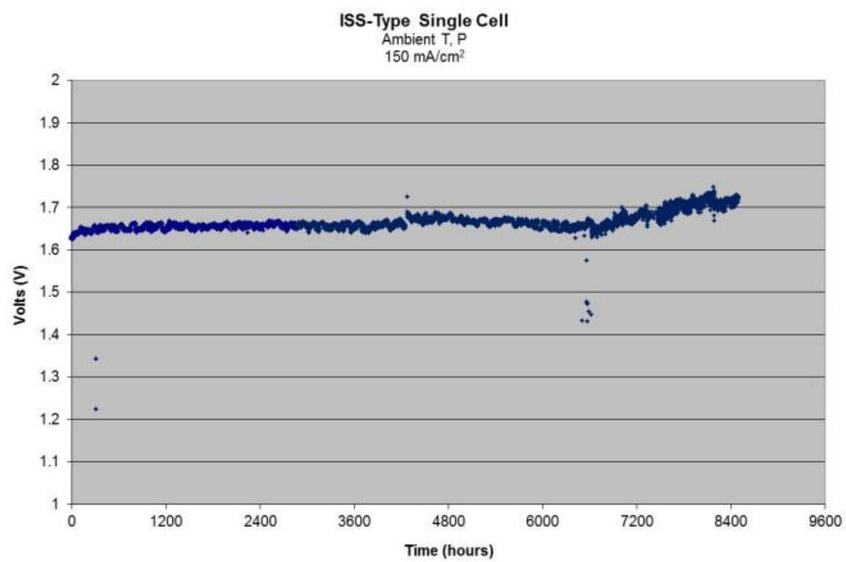
Focus of this Program is to Lower Cost of Substrate



Overview: DSM™ - What We've Done

- **Large Scale Electrolyzer for Energy Storage**
  - 290 cm² Platform
  - World Best Efficiency @ 1500 mA/cm²
  - Confirmed by NREL

- **NASA Life Support Electrolyzer**
  - Operates at low RH
  - Floods on Shut-Down
  - >8000 hours
  - >6000 on/off cycles



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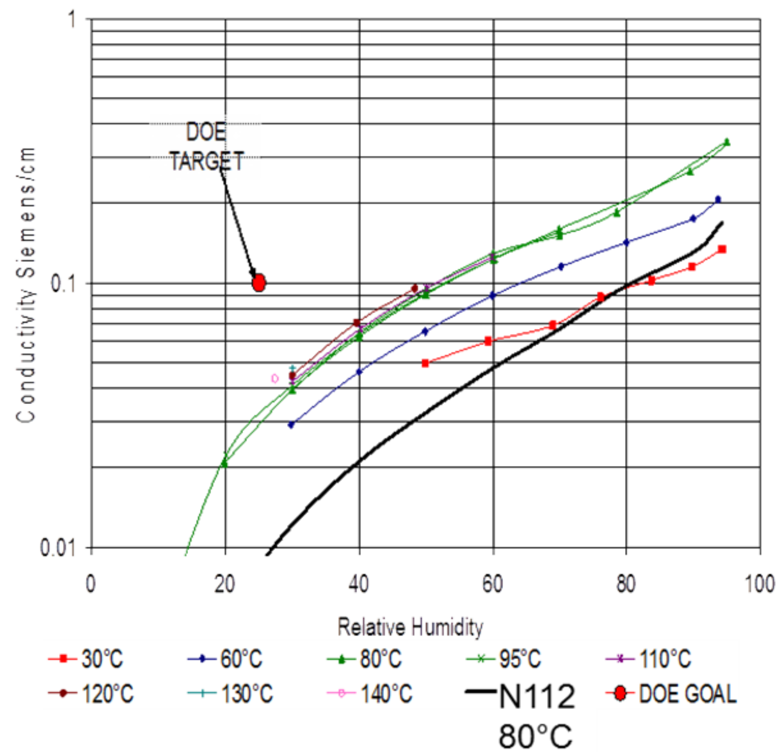
Approach: Giner Two-Dimensional Stable Membranes

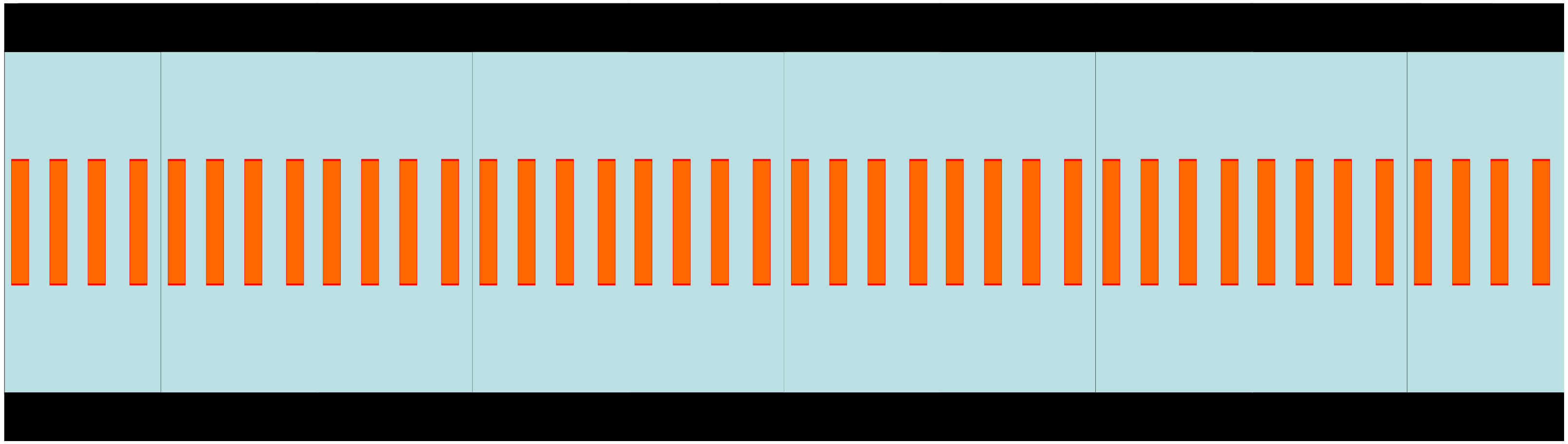
- Giner had the most *technical* success with two dimensional stable membranes
- Laser drilling approach is not practical due to cost
- Phase II program successfully showed pathway to obtaining these microporous supports in high-volume, low-cost processes
- Giner is already using DSMs™ with laser-drilled holes for manufacturing of large-scale electrolyzers.



Approach: Keys to 2D DSM™

Total membrane thickness 12-25 μm

Key aspect ratios:



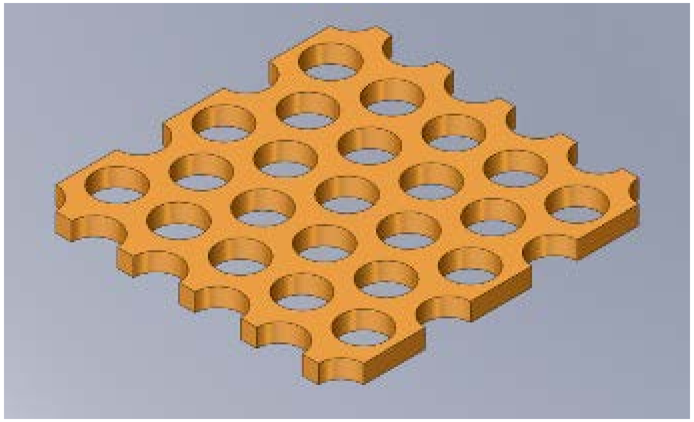
Very close is better, but very difficult to manufacture

Approach: Criteria for DSM™ Manufacturing

- **Design:** 4-8 μm thick support structures with 8-20 μm diameter holes and 50% porosity to accommodate low EW ionomers.
- **Process:** Flexible materials with 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

Optimal DSM™ support design:

- Close hexagonal packing
- 4-8 μm thickness
- 20 μm hole diameter
- 50% open area



Achievements: Identification of Cost-Effective Pathways for DSM™ Fabrication

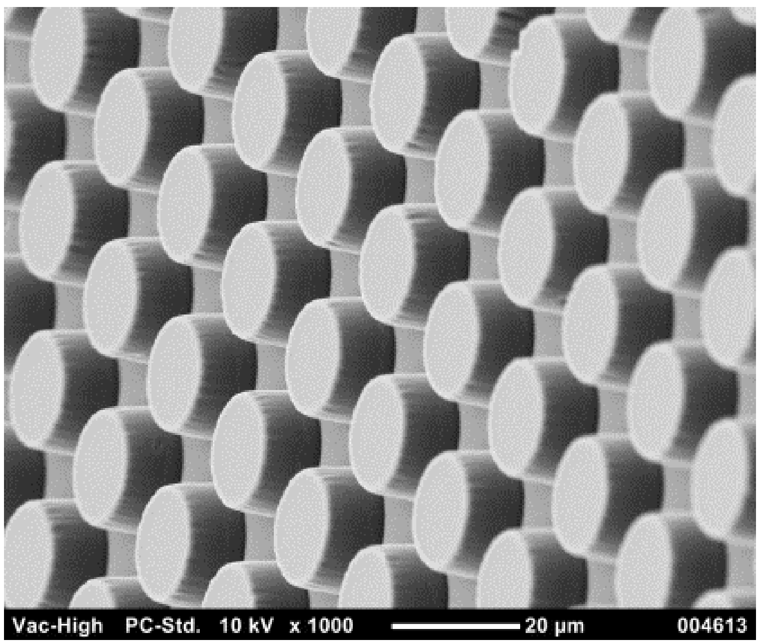
- Giner investigated various approaches in YEAR 1 and identified three scalable and cost-effective fabrication routes.
- DSM™ supports and composite DSM™ membranes were fabricated in YEAR 2 at 4" diameter pilot scale for validation of materials and refinement of processes.
- Giner actively pursued the following three fabrication routes:

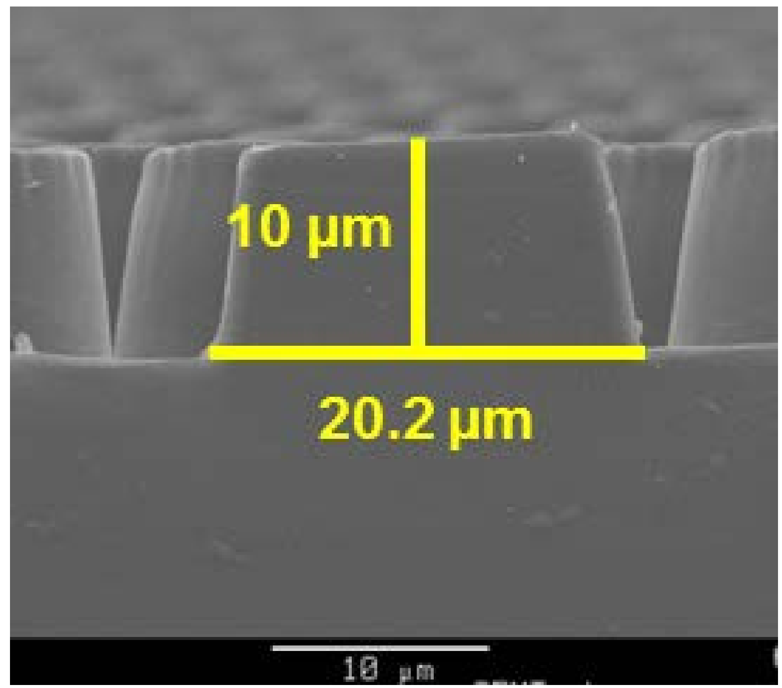
Technique	Description	Pros	Cons
I - UV Microreplication	UV curing of polymers between a mold and a backing substrate	• Rapid film formation • Easy roll integration	• High material risk • R&D cost
II - Mechanical Deformation	Mechanical deformation via mold pillars	• Proven materials	• Ragged features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

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

Achievements:
UV Microreplication - Polymer Molds

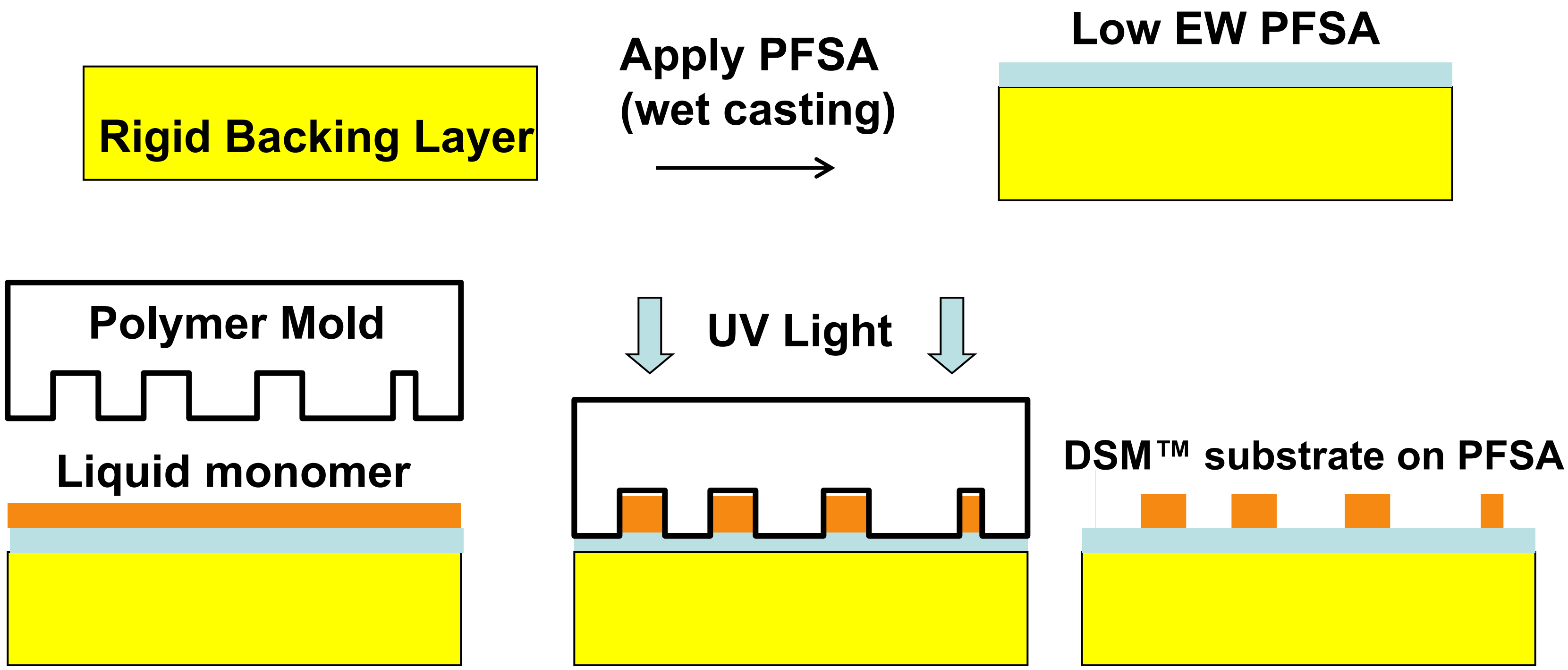
- High modulus polymer replica molds were fabricated at Umass-Amherst from nickel molds with hole patterns.
- Tilted and cross-sectional SEM views of mold pillars showing flawless replication.





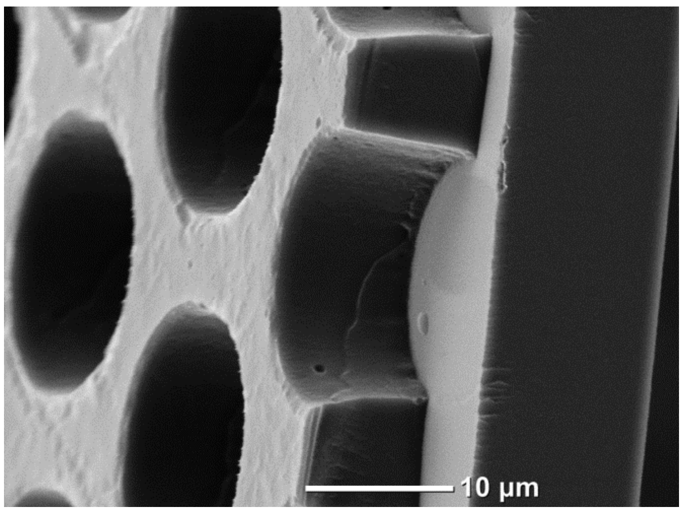
Achievements: UV Microreplication- Processing

- In collaboration with UMass-Amherst, a state-of-the-art Nanonex Imprintor has been utilized for processing.
- DSM™ supports have been successfully fabricated and released from molds with minimal residual layers.

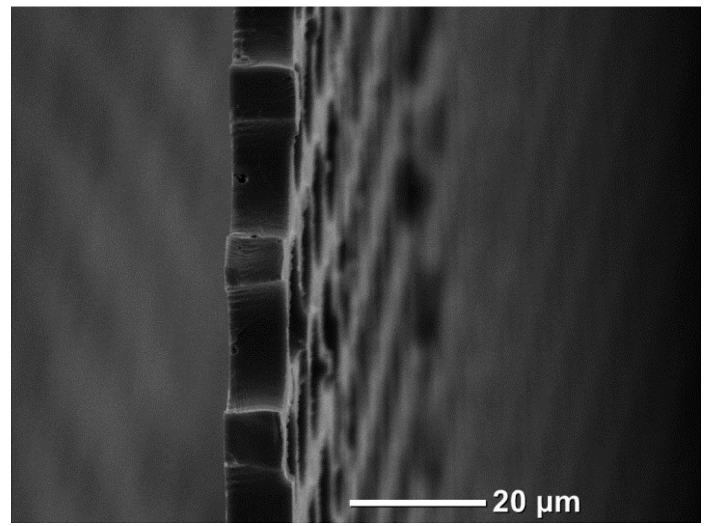


Achievements: UV Microreplication - Processing

- Upon optimization of the processing conditions such as wet monomer thickness, applied pressure, and imprint duration, it is possible to obtain 100% residual-layer free films



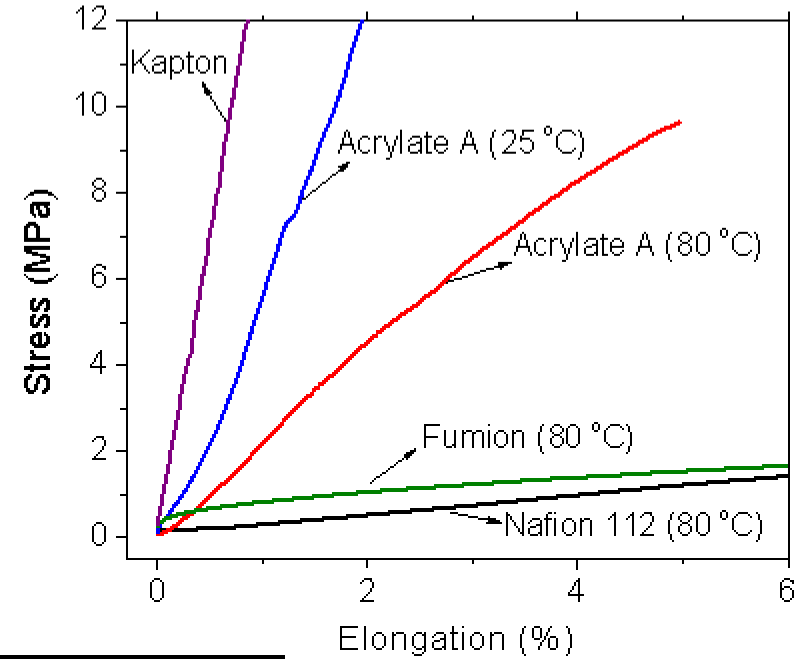
DSM™ support formed on a low EW ionomer film.



Free-standing DSM™ support

Achievements: UV Microreplication -Materials

- After testing various UV-curable materials, a high strength acrylate resin was used to develop formulations to obtain optimized mechanical properties.
- Results were compared to a low EW ionomer that is incorporated into the microporous support.
- Fuel cell compatibility needs to be demonstrated



Polymer Film	Temp (C)	Tensile Strength (MPa)	Modulus (MPa)	Elongation at Break (%)
Nafion® 112 (110 EW)	80	6.08	21.36	94
Fumion® (FumaTech, 830EW)	25	5.68	29.64	23.59
	80	**2.34**	**11.9**	**12.93**
Acrylate A	25	>12	741.45	>1.63
	80	**8.32**	**141.2**	**7.44**
Acrylate A + Elastomer 1 (Formulation 1)	25	14.67	772.4	1.97
	80	**13.6**	**91.66**	**19.03**
Acrylate A + Elastomer 2 (Formulation 2)	25	>13.23	785.4	>1.71
	80	**12.71**	**173**	**13.44**

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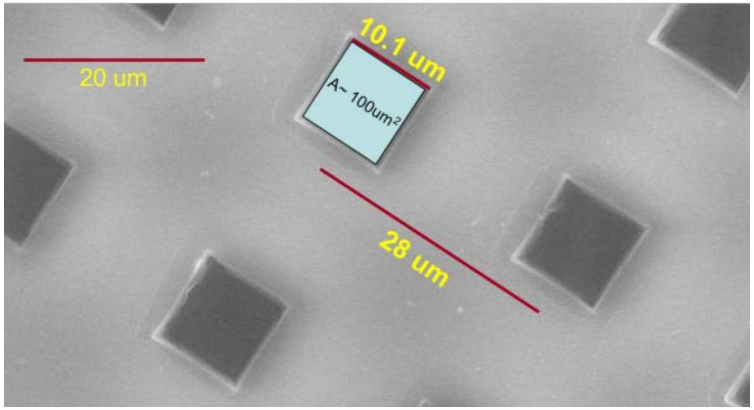
Achievements: Mechanical

- Best scalable route with proven materials; low projected cost in roll-to-roll
- Partnering with a micro fabrication "enabler" company to investigate fabrication of microporous DSM™ substrates
- Proven high volume continuous roll-to-roll manufacturing capability up to 1 m wide.

- Prior issues with severe (20°) tapering and low (13%) porosity.
- Close hexagonal packing of a micromold array will allow successful puncturing of thermoplastics with high porosity

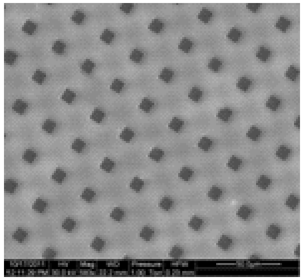


Achievements: Mechanical

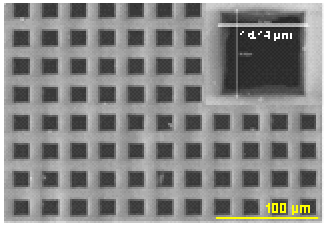
- Successfully opened holes on polysulfone films using the hot embossing method
- REACHED OUR 50% TARGET
  - Up from 15% 1 year ago and 35% 6 months ago
- Release from mold has also improved substantially
- The process favorably scales to roll-to-roll

A square-row arrangement was cheaper for a trial run. Can move to hexagonal or circular pattern if needed

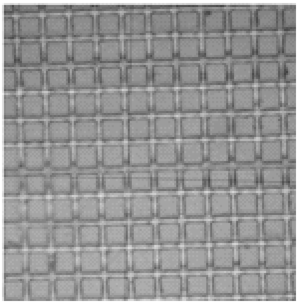
1/2012, ~15% porosity



8/2012, ~35% porosity

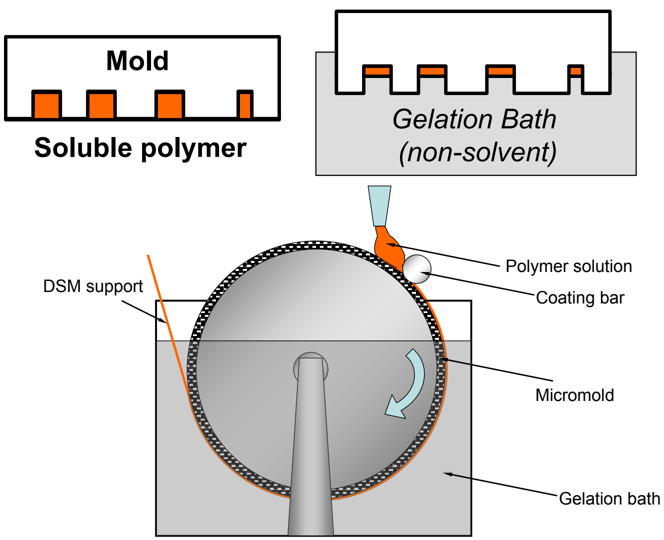


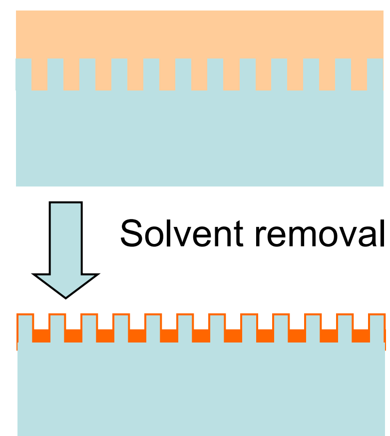
3/2013, ~50% porosity



Achievements: Phase Inversion Solvent Casting

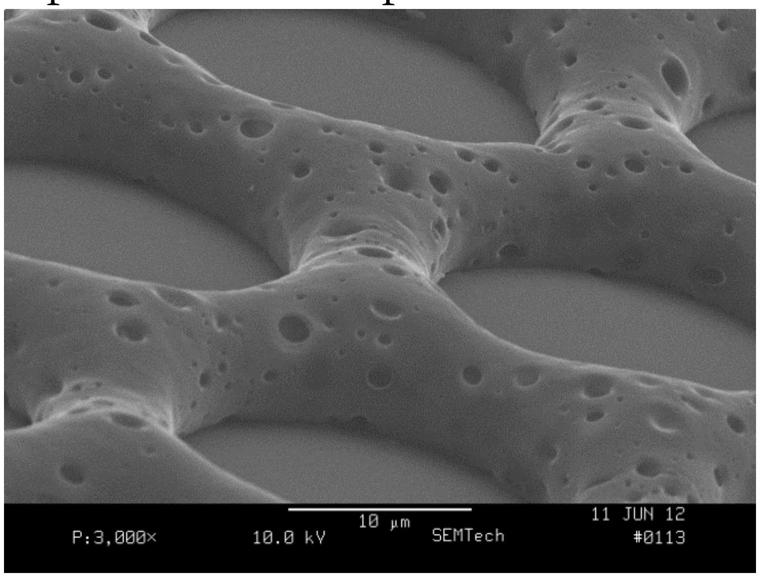
- Investigating improvements over the Phase II program
- A polyethersulfone (PES) film solution cast on a micromold followed by its precipitation using a non-solvent

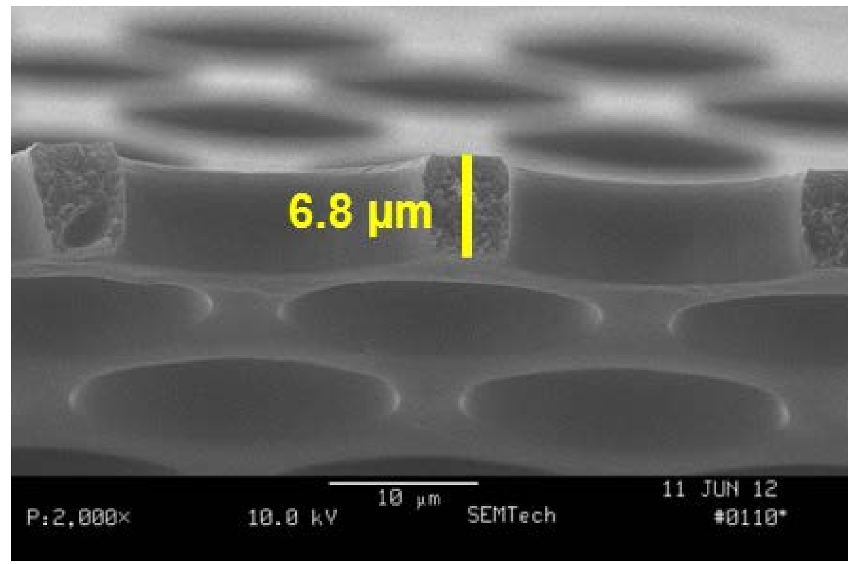




Achievements: Phase Inversion Solvent Casting

- 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.



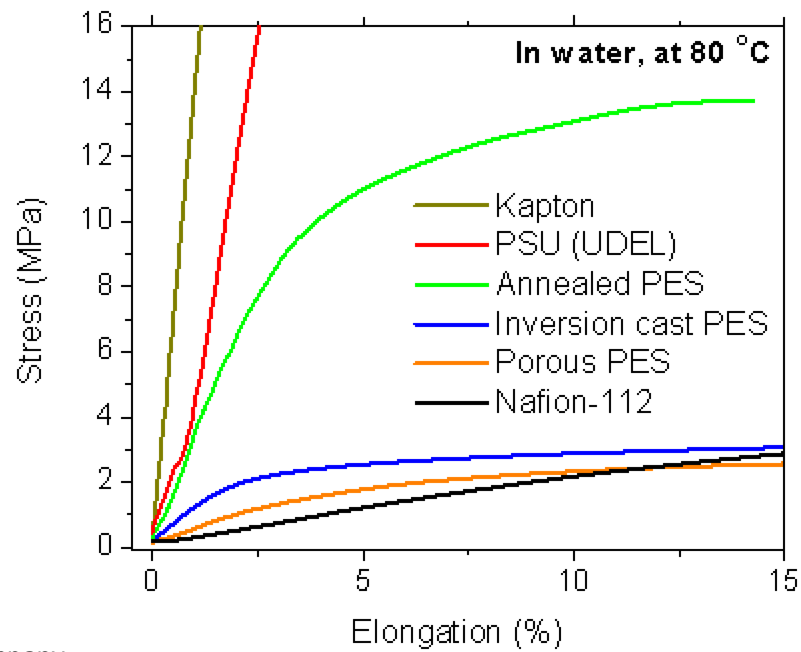


Cross-sectional view of a 7 µm thick polysulfone DSM™ support. Note the microporosity of the inverted film.

Achievements: Phase Inversion Solvent Casting

- Mechanical properties of inversion cast films are inferior to thermoformable counterparts due to microporosity. Annealing helps, but increased brittleness
- Due to the complications with solvent processing/removal, the need for post-fabrication treatment, and non-ideal mechanical properties, we are no longer pursuing this approach

Mechanical properties In water, at 80°C	Tensile Strength (MPa)	Elastic Modulus (MPa)	Elongation at Break (%)
Kapton	231	1377	72
Nafion 112	6.1	21.4	94.1
Polysulfone(UDEL)	36.8	710.9	19.1
PES (1.2 μm pores)	3.6	44.8	76.1
Inversion cast PES	3.5	94.4	35.8
Annealed PES	13.7	306.3	14.3



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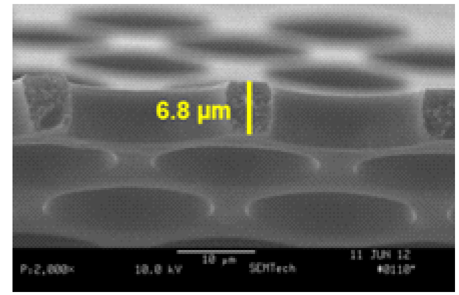
Collaborations

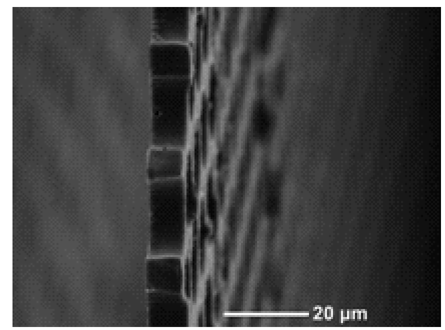
- The UMass- Amherst Nanoimprint Lithography Laboratory (Prof. Kenneth Carter)
- NIL Technology (Denmark)
- Impattern Technologies (Dr. Michael Watts)
- EV Group, Inc. (Garrett Oakes, North America Technology Director)
- Colorado Photopolymer Solutions (Dr. Neil Cramer) and the Bowman Research Group at CU Boulder

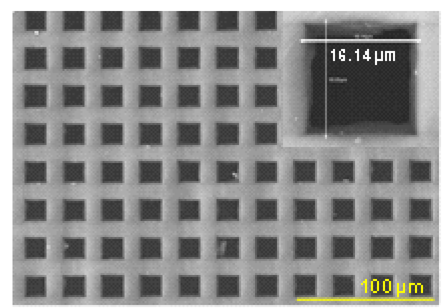
Summary

Three viable pathways were investigated in YEAR 2:

- Inversion Casting (Inactive)
  - Too many problems with process control
  - Intrinsic properties of inversion cast films are inferior
- UV Microreplication (Secondary Pursuit)
  - Lowest ultimate cost (< $20/m^2)
  - Achieved desired material properties
  - Straight-forward scaling for the process
- Mechanical (Focus)
  - Best materials choices (thermoplastics)
  - Currently $50/m^2, << for roll-to-roll
  - When high (50%) porosity is reached, this yields the best performing DSMs™







Future Work

In YEAR 3, Giner will focus on evaluating the performance of DSMs™ under relevant fuel cell conditions as well as scaling-up the manufacturing process. Goal will be to develop process as far as possible with suitable materials.

- We've completed the riskiest steps
  - Mold fabrication
  - Process demonstration to yield highly porous films
  - Material development
- Primary Focus is on Mechanical Method
- If this fails
  - Will pursue roll-to-roll UV-microfabrication at UMass Amherst
  - Will pursue batch scaling (12") with EV Group, Inc.

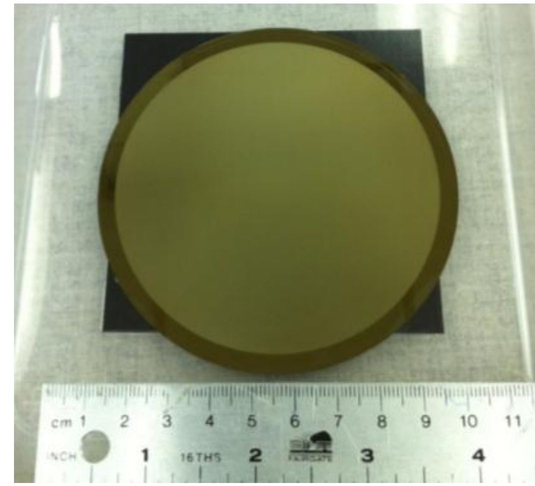
Technical Back-Up Slides

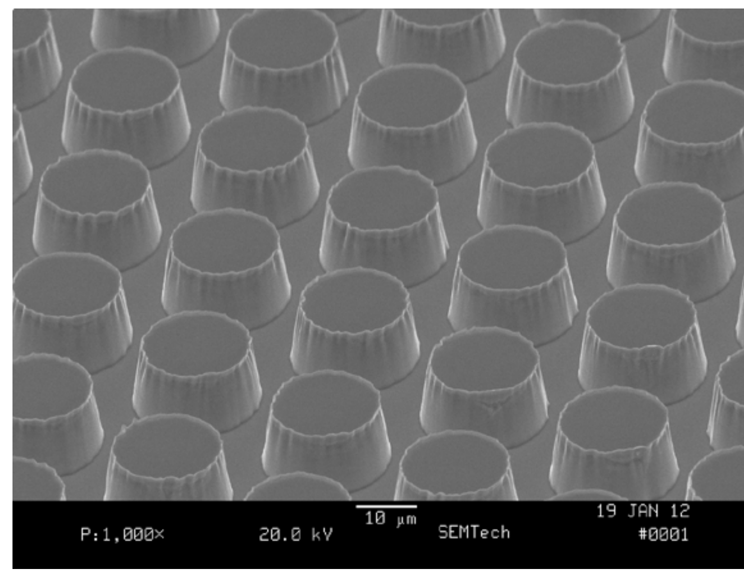
GINER

DOE Hydrogen Program

UV Microreplication: Nickel Shims

- NILT (Denmark) manufactured master and replica nickel molds
  - **4”** diameter round molds replicated
  - 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





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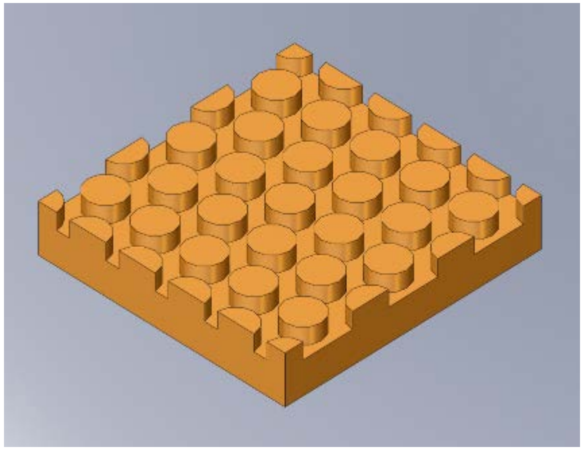
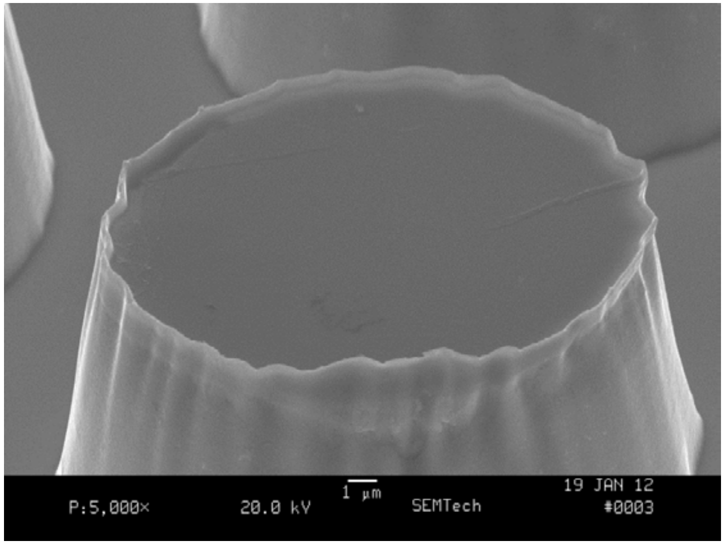
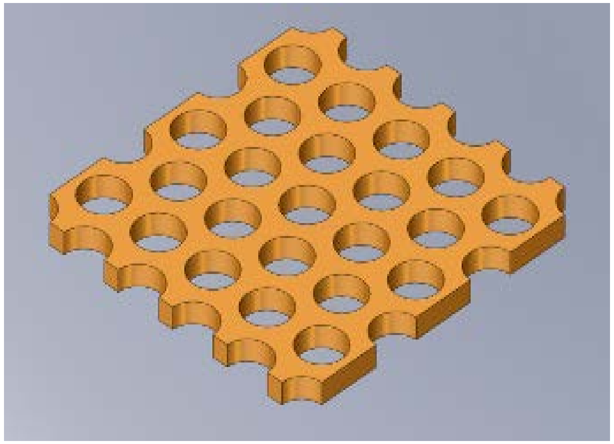
UV Microreplication: Nickel Shims

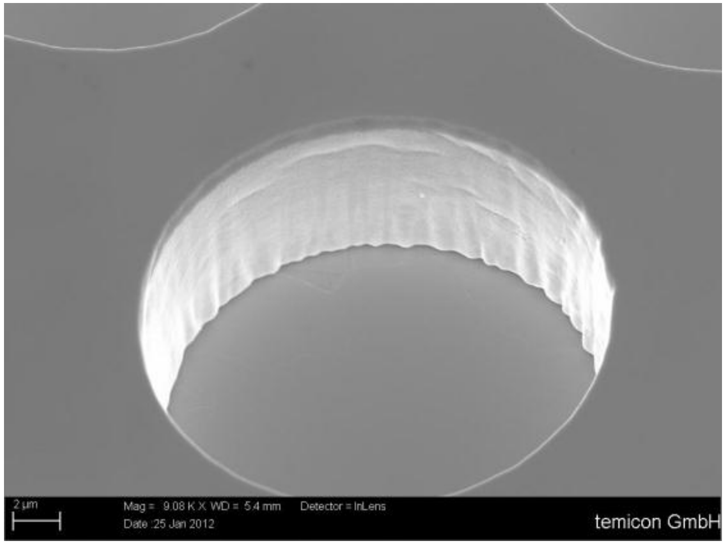
Nickel shims with 10 μm high pillars





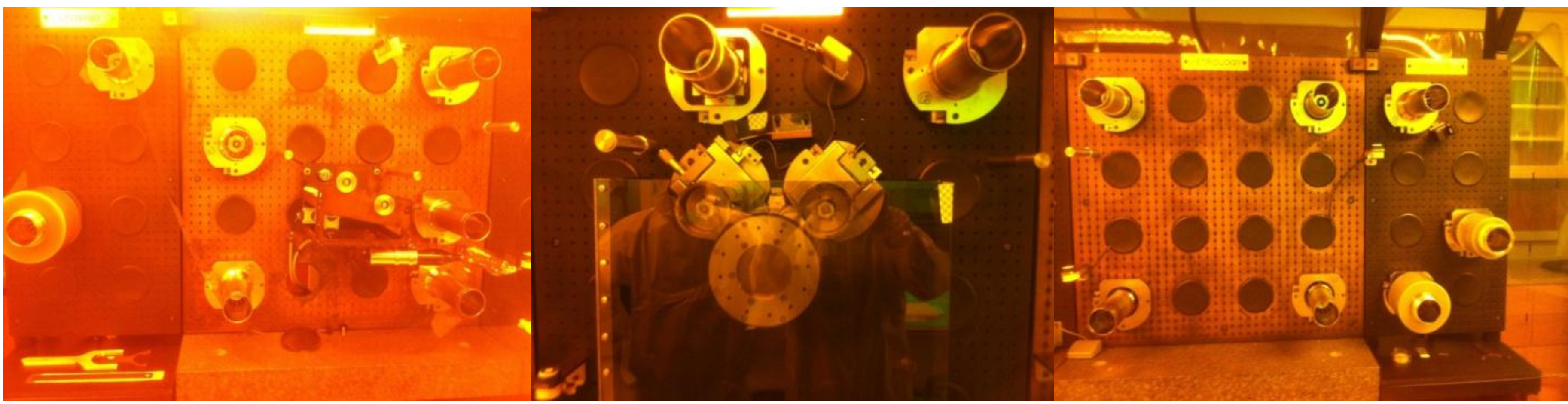
Nickel shim with 10 μm deep holes





UV Microreplication - Processing

- The use of roll-to-roll equipment at Umass-Amherst clean room facilities will allow for pilot demonstration.
- From left to right is shown the various sections of the setup used for coating, imprinting, and in-line analysis.



Unwind Coat Emboss Metrology Rewind

FUTURE WORK

Comprehensive Membrane and Fuel Cell Testing

- Dimensional Changes in Water
- Mechanical Properties (In water, 80°C)
- Membrane Conductivity (Through-plane)
- Wet/Dry Cycling
- Freeze-Thaw Stability
- Fuel Cell Performance