Dimensionally Stable High Performance Membranes

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FC 036

Overview

Timeline

- Project Start Date 10/01/2010
- Project End Date 06/30/2014

Budget

- Total Project Funding to Date: $1.41M
- Total Project Value: $1.52
- Cost Share %: N/A

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

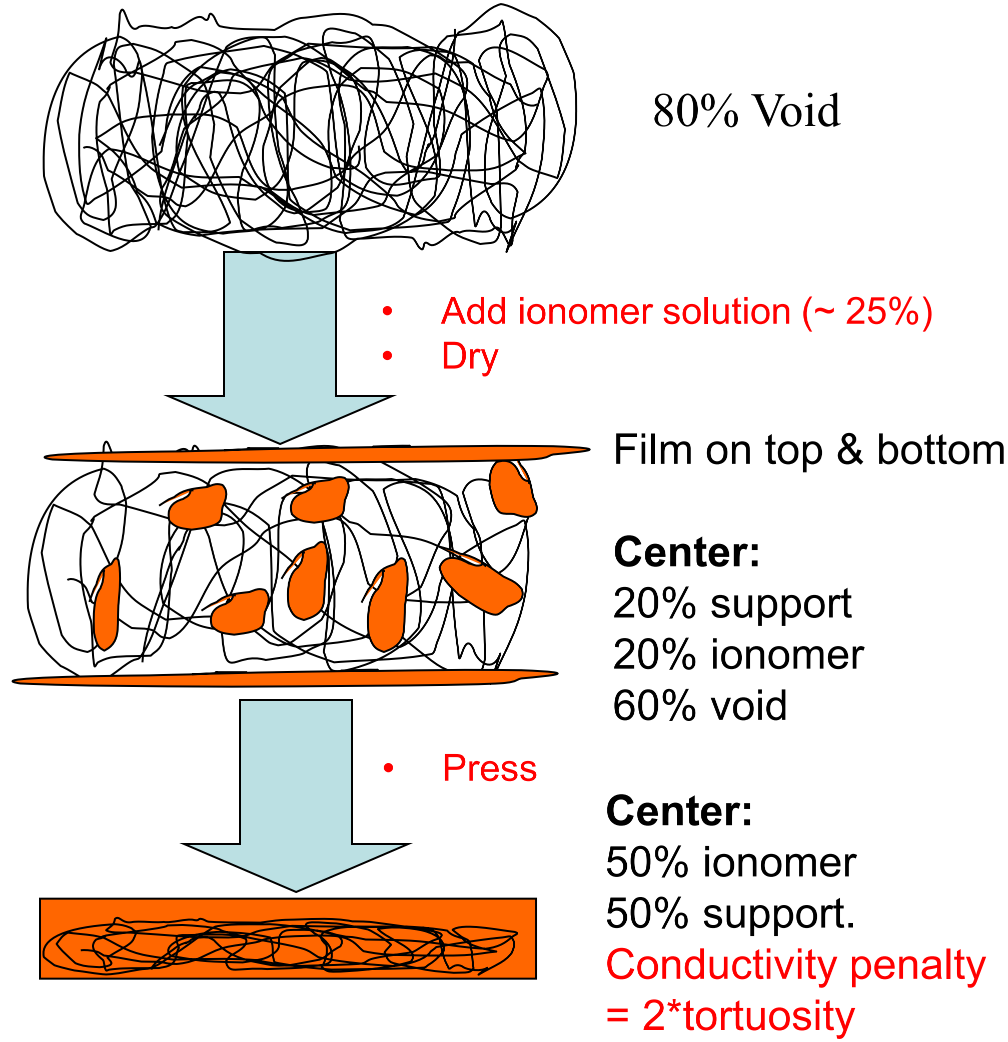
- Impattern Technologies
- NIL Technology

Overview

- Why Dimensionally Stable Membranes (DSM™)
- Phase III Results
- 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?
- Milestones
  - 4" diameter batch-produced DSMs™ (achieved)
  - 11" x 11" roll-produced DSM™ (pending)

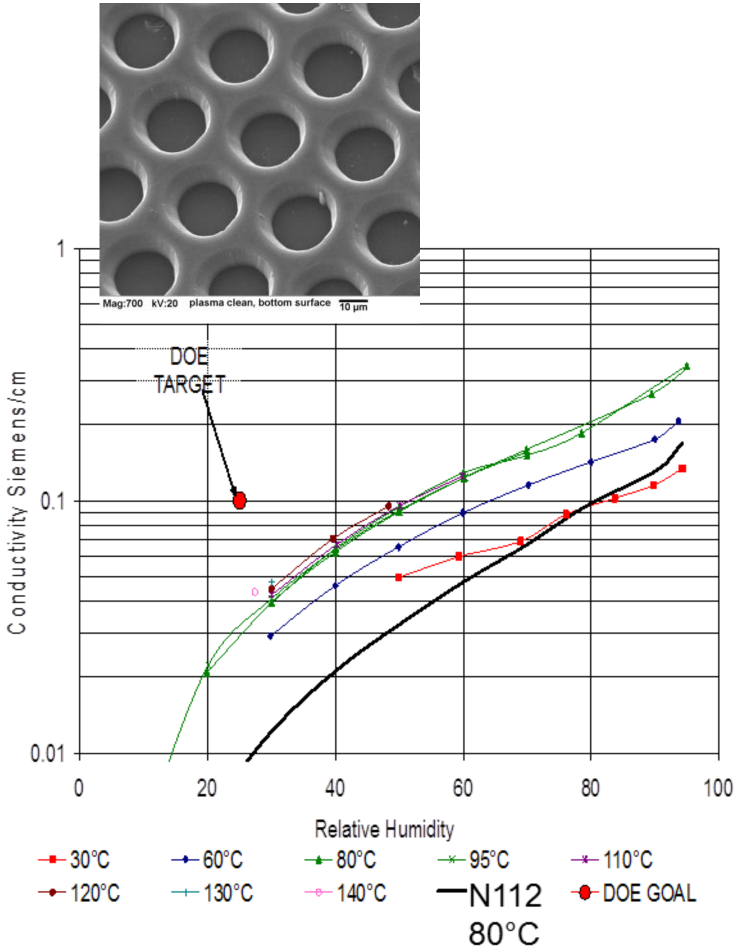
Relevance: Three Dimensional Supports

- **Advantages:**
  - Many commercially available
    - ePTFE
    - Made in 10k m^2 in a batch
  - Ionomer is added by solution
  - Roll to Roll processing
- **Disadvantages:**
  - Making thin supports for some materials
  - Support/Solution compatibility
  - **Getting high ionomer content**
    - **High wt% dispersion**
    - **High void volume**



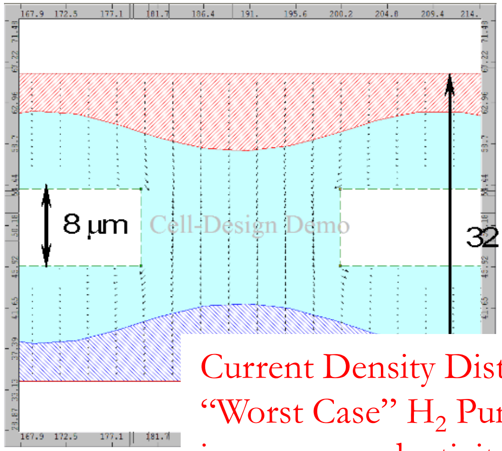
Relevance: Giner's 2D DSM™ Solution

- Giner had the most *technical* success with two dimensional stable membranes
- Laser drilling is not practical due to high cost
- Giner is already using DSMs for manufacturing of large scale electrolyzers.



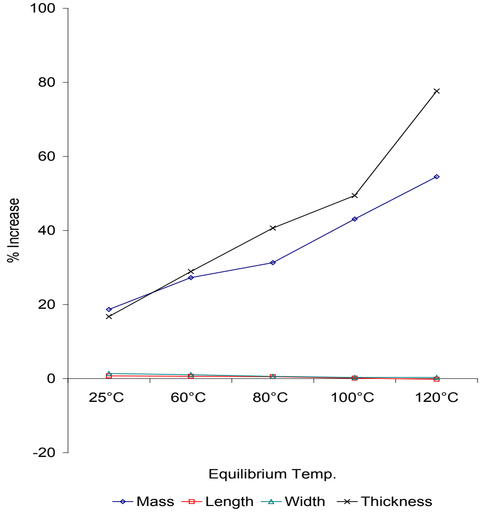
Relevance: DSM™ Background

- **DURABILTY**
  - 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



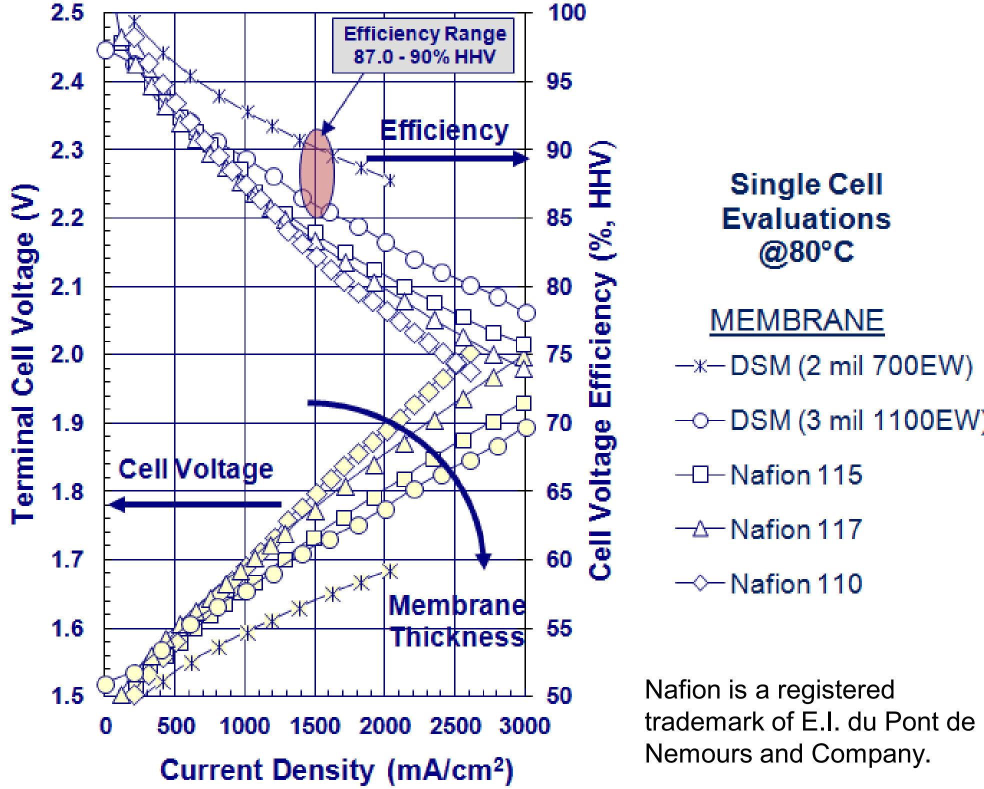
Current Density Distribution for "Worst Case" H_2 Pump with low ionomer conductivity

- **CONDUCTIVITY**
  - 25-30% Penalty
  - (~50% for expanded PTFE)
- **DIMENSIONAL STABILITY**
  - Nearly Eliminates all x-y swelling



Relevance: Giner's DSM™ Success

- **Large Scale Electrolyzer For Energy Storage**
  - 290 cm^2 Platform
  - World Best Efficiency @ 1500 mA/cm^2 (~90%)
  - Confirmed by NREL



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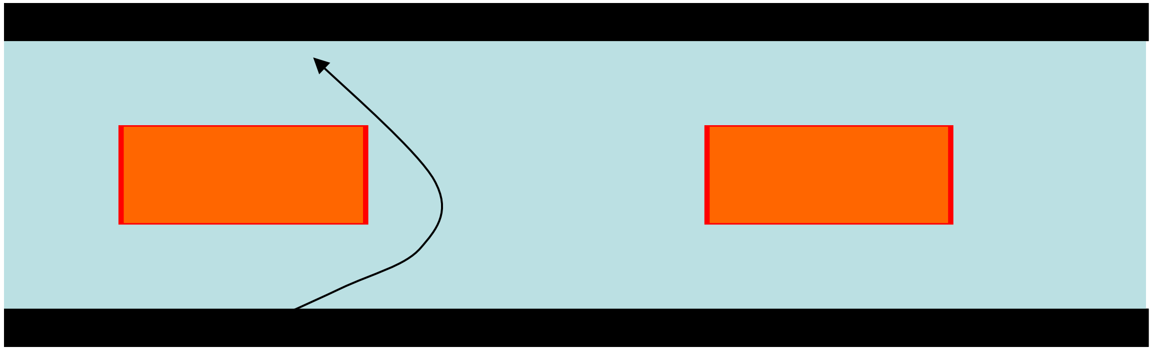
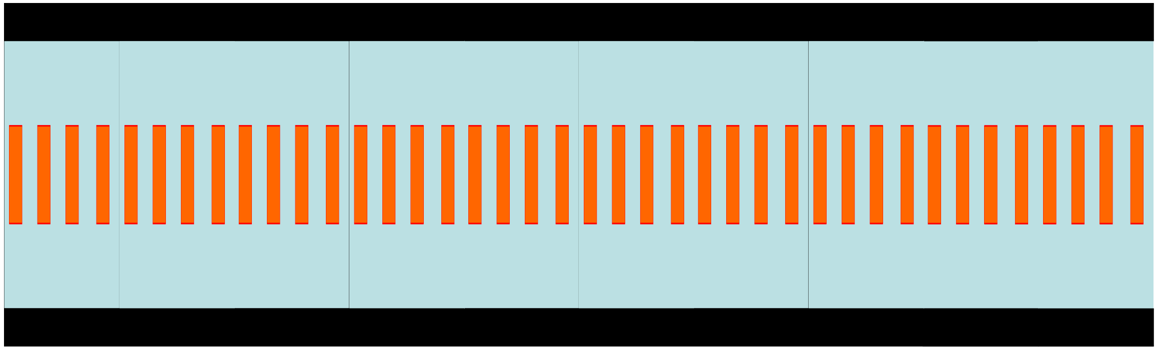
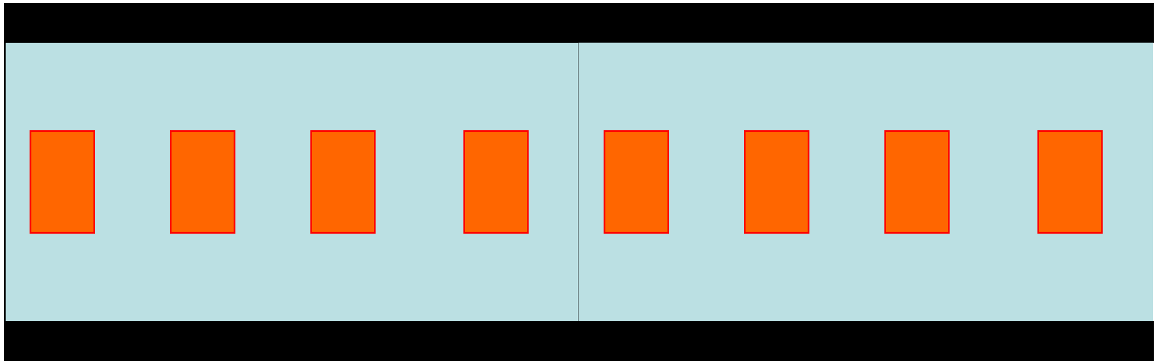
Approach: 2D DSM Aspect Ratios



Sub-par: Holes are too large, proton has high tortuosity



Ideal: Difficult to manufacture

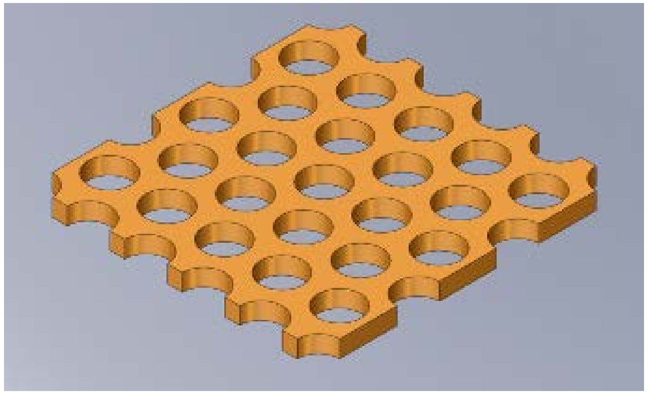


Optimal: Hole size must be close to membrane thickness

Approach: Criteria for DSM™ Manufacturing

- **Design:** 8-10 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

Optimized DSM™ support design:
- Close hexagonal packing
- 8-10 μm thickness
- 20 μm hole diameter
- 50% open area



Approach: Choice of Materials

- Mechanical properties of ionomers compared to the support materials.
- PTFE not optimal, Kapton® (polyimides) ideal, other engineering plastics would also work nearly as good.

Mechanical properties In water, at 80°C	Tensile Strength (MPa)	Elastic Modulus (MPa)	Elongation at Break (%)
PTFE / ePTFE	10-20	~500	200-300
Nafion® 112	6.1	21.4	94.1
Fumion® 830EW	2.3	11.9	12.9
Kapton®	231	1377	72
Polysulfone (UDEL)	70.3	2480	50-100

Approach: Program Objectives

- **Develop a high-throughput and cost-effective process for fabrication of DSM™**
- **Reduce membrane thickness by incorporating a microporous support layer.**
- **Address key durability, cost, performance barriers related to fuel cell systems.**

Achievements: Identification of DSM™ Fabrication Methods

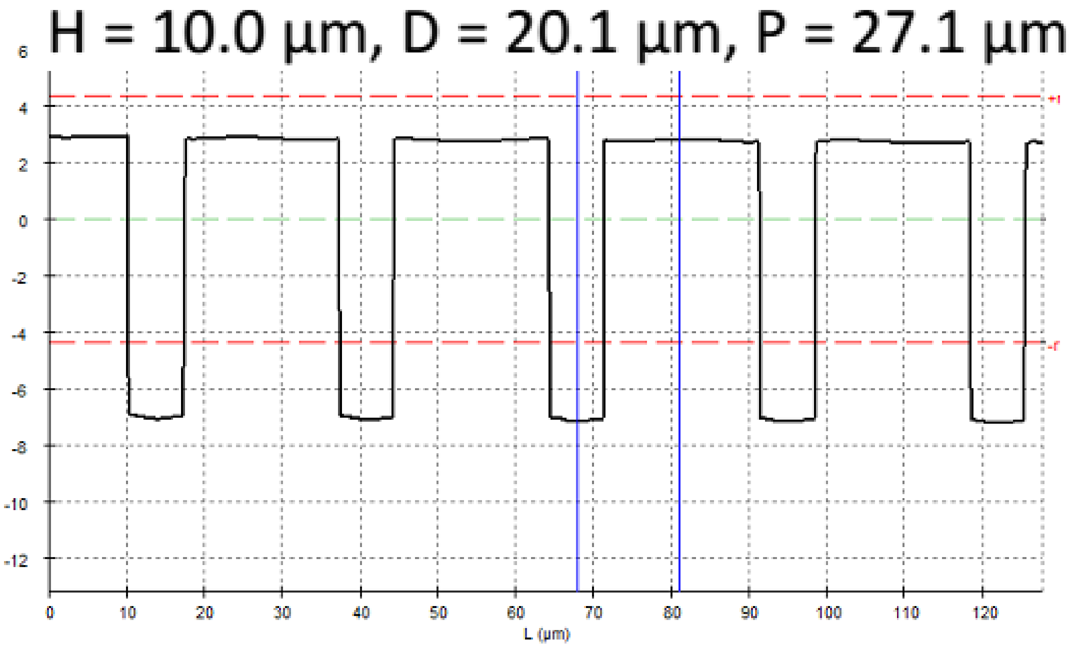
- Giner investigated various approaches and identified scalable and cost-effective fabrication routes.
- DSM™ supports and composite DSM™ membranes were fabricated at 4" diameter pilot scale
- Giner pursued the following three fabrication routes:

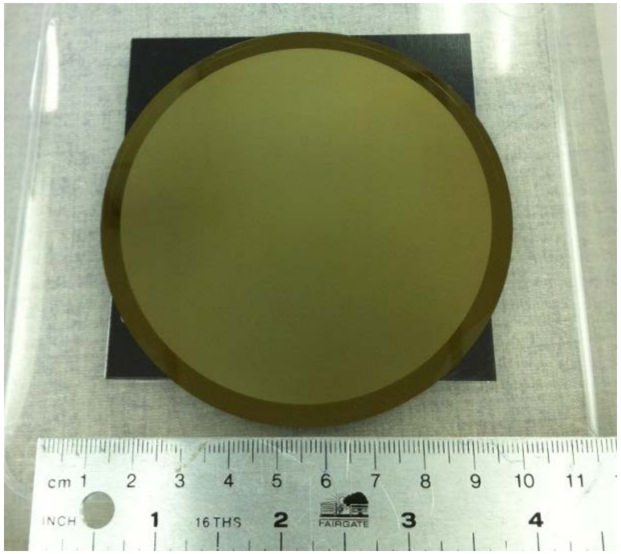
Technique	Description	Pros	Cons
Phase Inversion Solvent Casting	Precipitation of polymers on a mold using a non-solvent.	•Well defined material •Phase II results	•Waste solvent •Film shrinkage
UV Microreplication	UV curing of polymers between mold and substrate	•Rapid film formation •Easy roll integration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

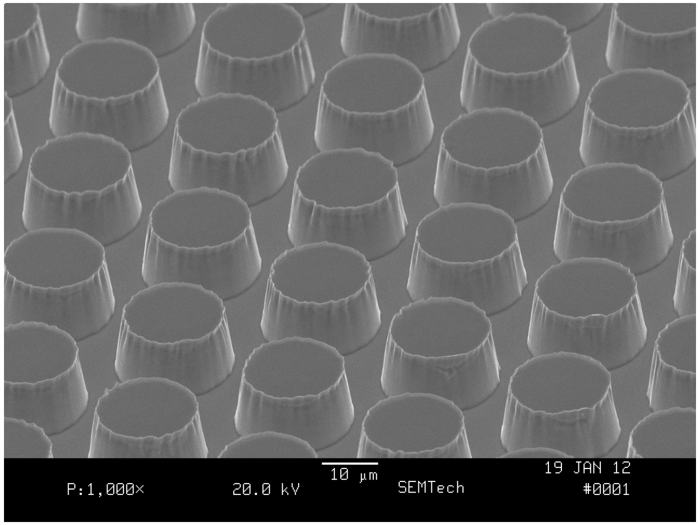
Each path starts with the same first step: Design of the mold

Achievements: Mold Fabrication

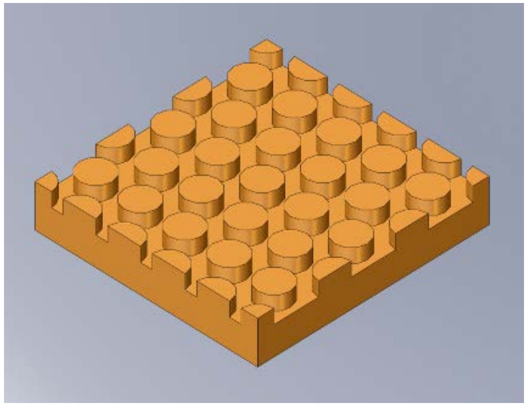
- Master and replica nickel molds
  - **4”** diameter round molds replicated
  - 20 μm diameter, 10 μm feature height, 50% density
  - Nickel shims
- Easy to scale up to 24” x 36”

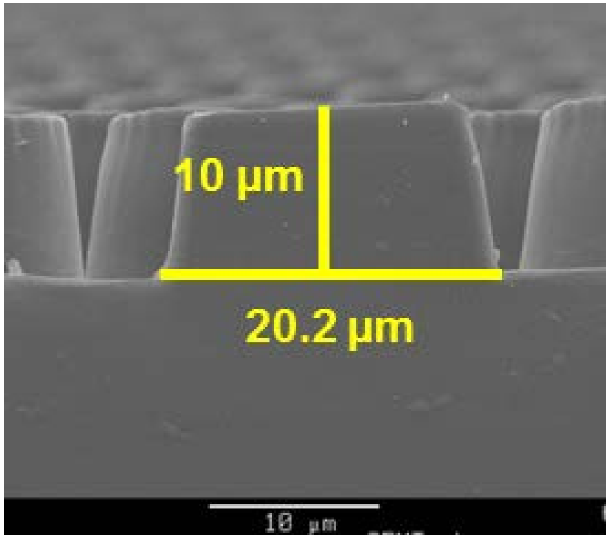






Achievements: Nickel Shim Molds

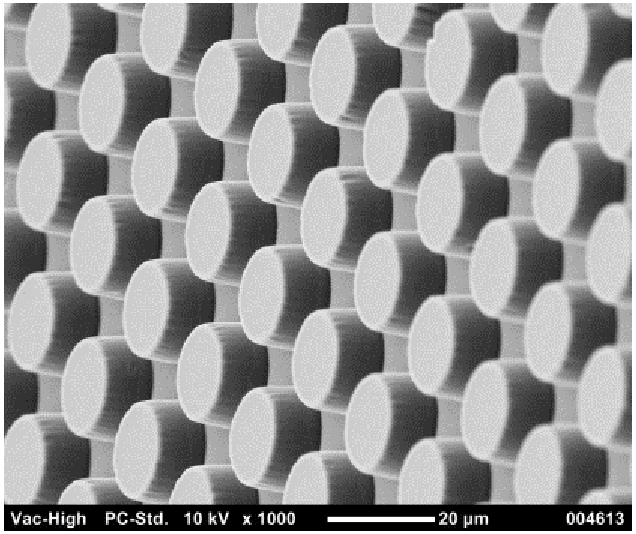




- **Mold properties** (nickel pillars)

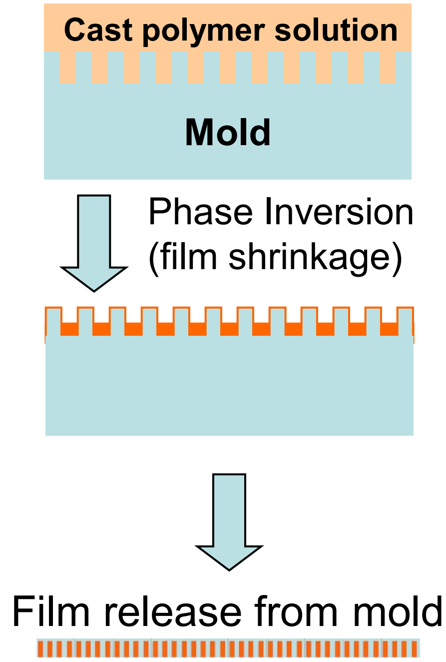
20 µm pillar diameter, 10 µm pillar height, 50% density

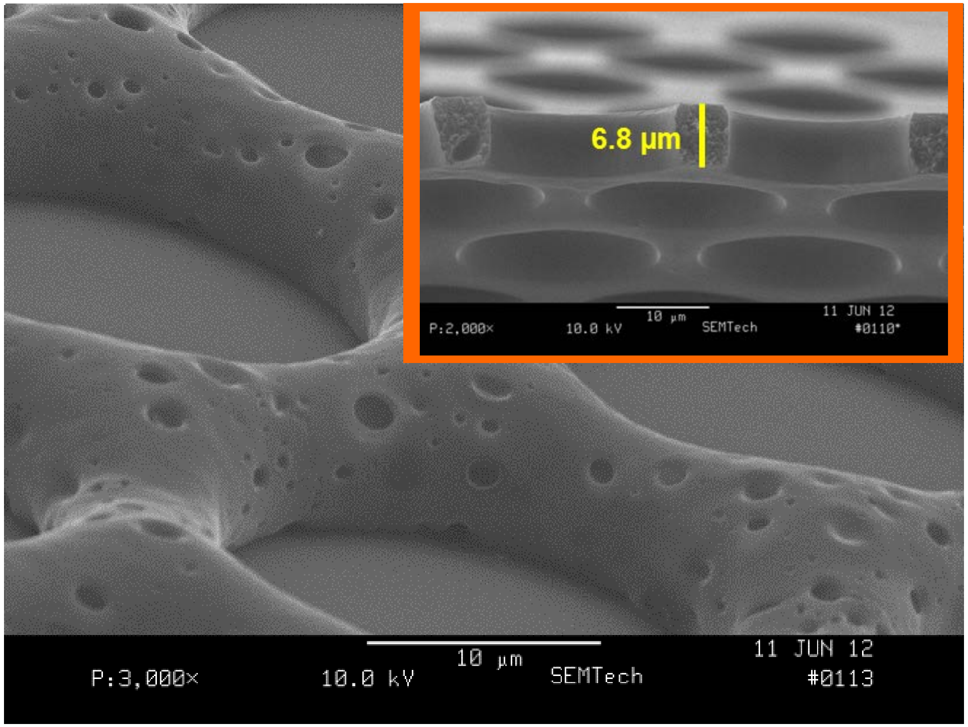
- **SEM images:** Cross-sectional and tilted of micromold pillars



Achievements: Phase Inversion Process

- A polymer solution cast on a mold and precipitation using a non-solvent
- Mechanical properties are inferior due to microporosity.
- Due to the complications with solvent removal, the need for post-treatment, and non-ideal mechanical properties, **Giner stopped pursuing this approach**

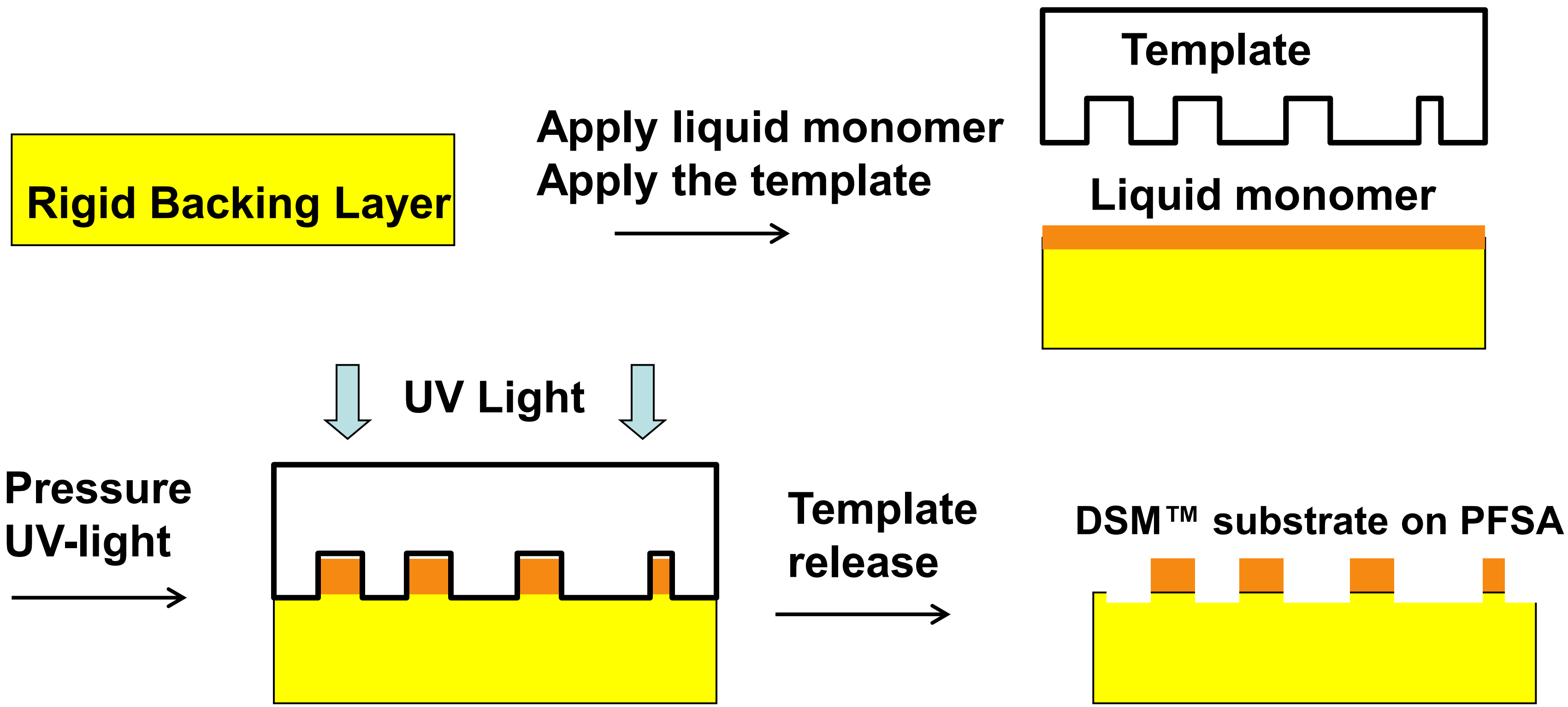




Note the microporosity of the DSM™ support

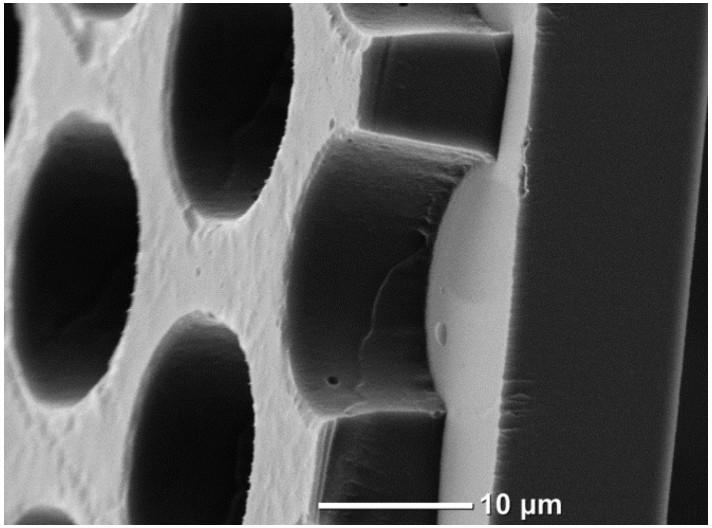
Achievements: UV Microreplication

- DSM supports have been successfully fabricated and released from molds with minimal residual layers.

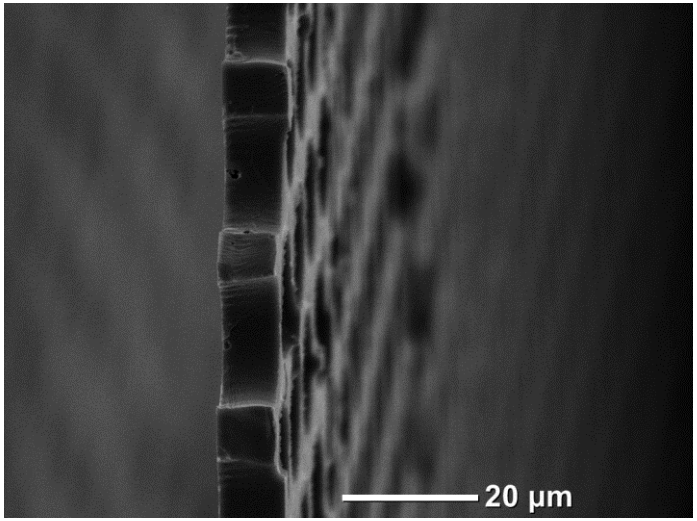


Achievements: UV Microreplication

- Upon optimization of the processing conditions it is possible to obtain robust DSM supports
- Despite the success of this method, **the base UV curable polymers are still not adequate mechanically.**



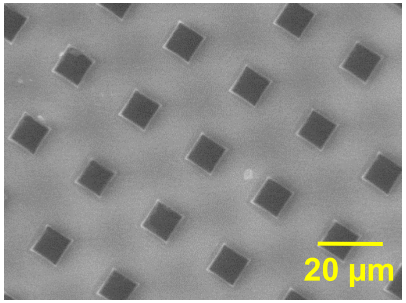
DSM support on an ionomer film.



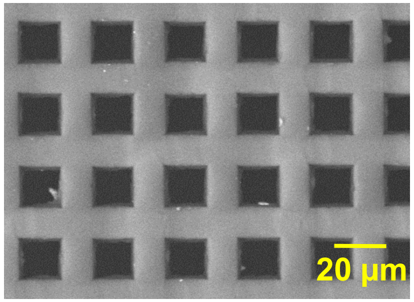
Free-standing DSM support

Achievements: Mechanical Deformation

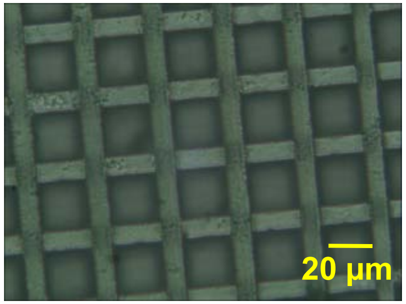
- The best scalable route with proven materials; low project cost in R2R
- Initial investigation with a square-row arrangement (pilot scale).
- Improved process with high porosity, issues of severe tapering
- Other problems with selection of suitable carrier, poor release, etc.
- The process also caused extremely rugged features



2011



2012



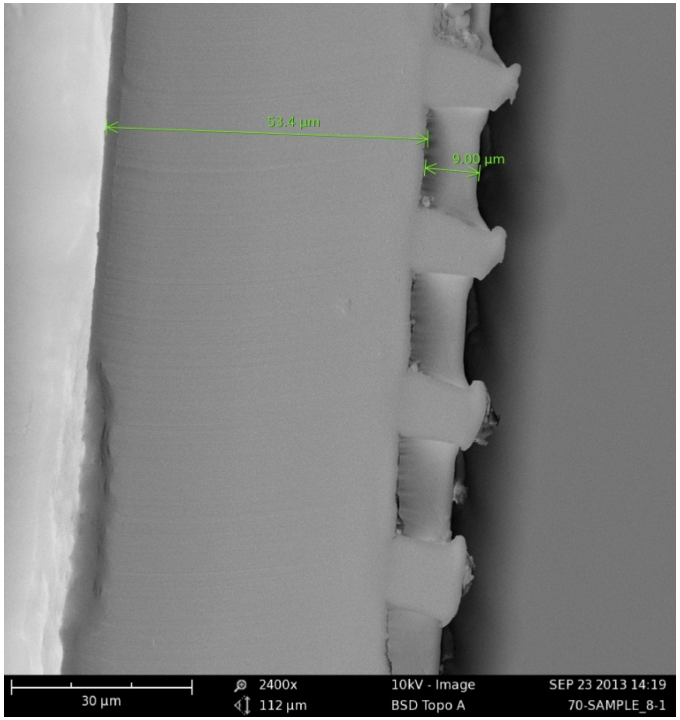
2013

- **Giner has substantially improved this approach and is currently pursuing it "in-house"**
- Transitioned to hexagonal geometry for better mechanicals

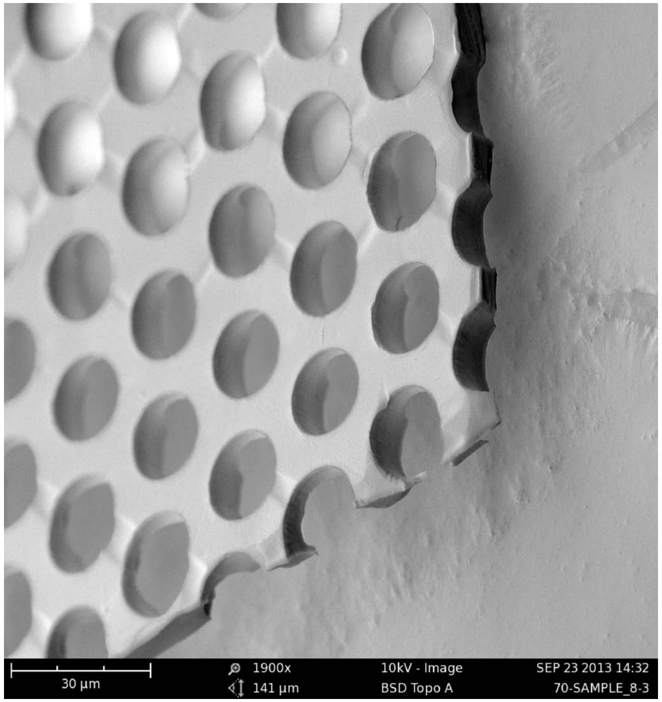
Achievements: Mechanical Deformation

- Giner has successfully fabricated DSM™ supports both on carriers and as free-standing films.

DSM support on Carrier

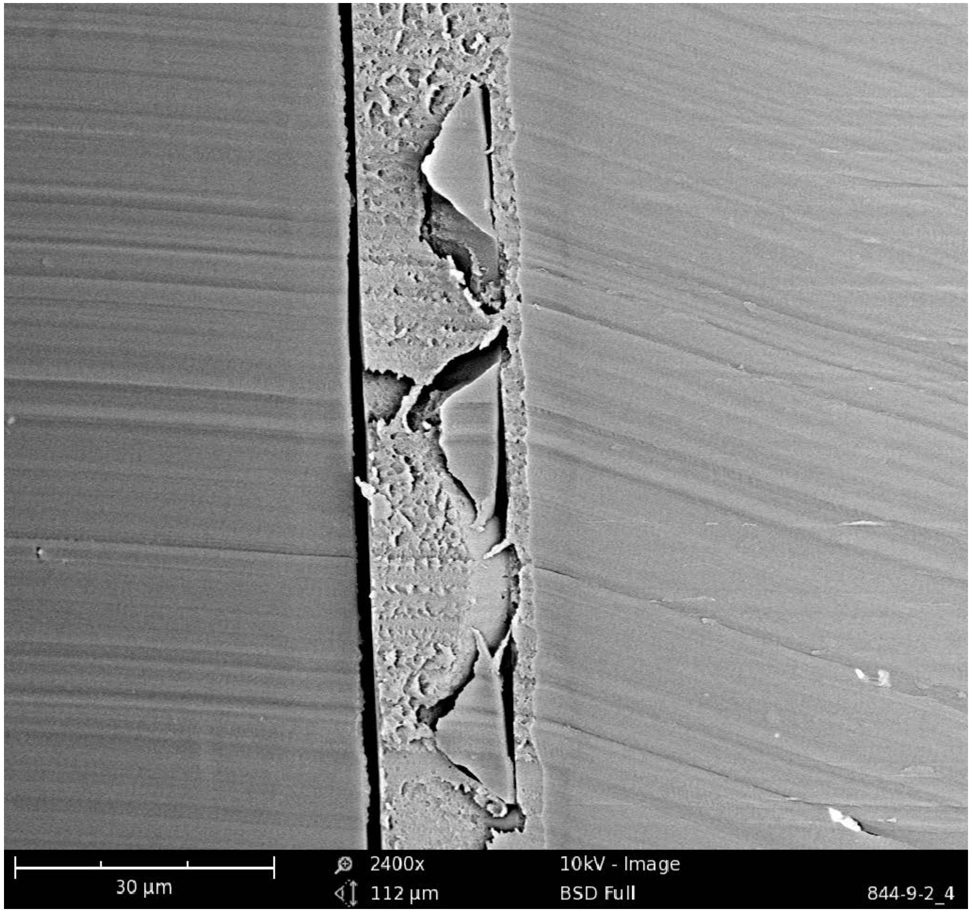


Free standing DSM support



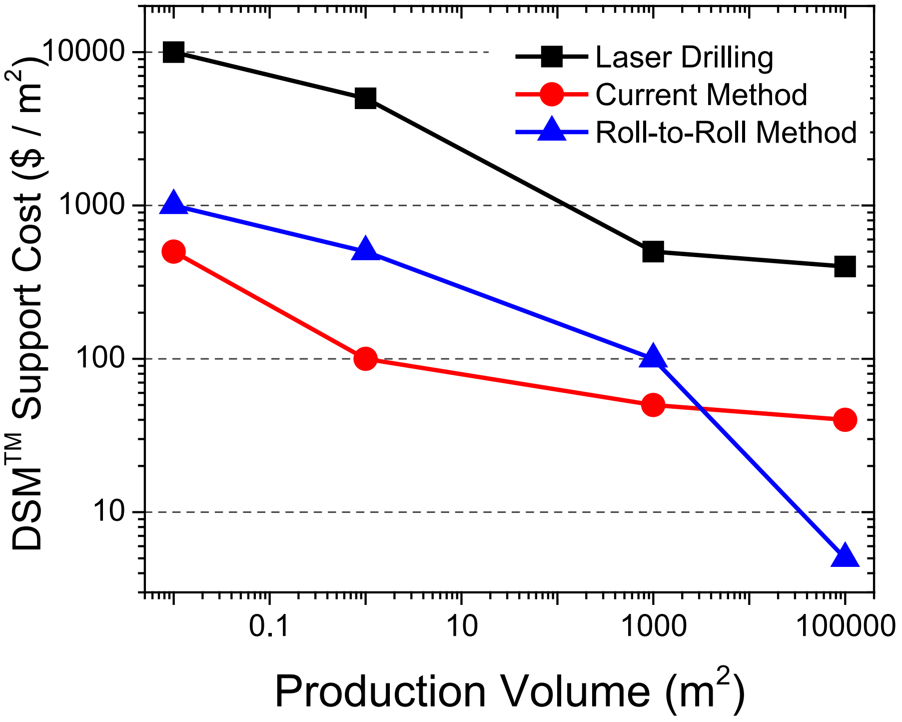
Achievements: Mechanical Deformation

- Using the route, it is possible to form the mechanical support followed by application of the ionomer.
- A close-up SEM image of a 20 μm thick DSM™ with its constituents:
  - the support
  - the ionomer



Achievements: High-volume Cost Projection for DSM™ Fabrication

- Giner investigated various scalable and cost-effective routes.
- Cost comparison of
  - Laser drilling
  - Giner's current method
  - Research "Roll-to-roll" method (late '14)



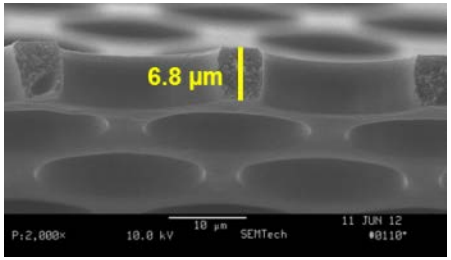
Projected DSM™ support cost : $5/m²

(Ionomer incorporation included; the cost of the ionomer material extra)

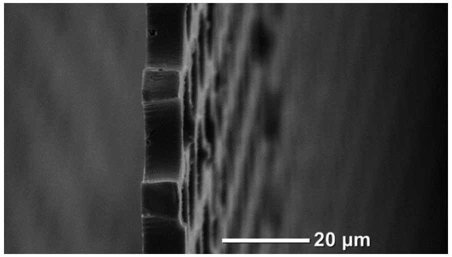
Achievements: Summary

Three viable pathways were investigated in this Phase III Program

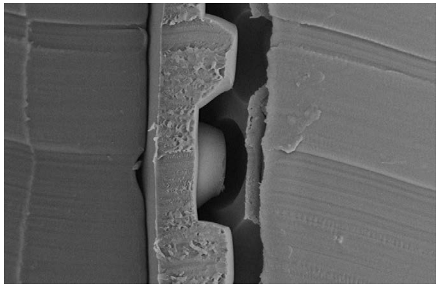
- Inversion Casting (Inactive)
  - Too many problems with process control
  - Intrinsic properties of inversion cast films are inferior



- UV Microreplication (Inactive)
  - Low ultimate cost (< \$20/m^2)
  - Insufficient material properties



- Mechanical Deformation (Focus)
  - Best materials choices (thermoplastics)
  - Currently \$50/m^2, <\$5/m^2 for R2R
  - Yields the best performing DSM™



Future Work

- DSM™ provides real benefits for both fuel cells and electrolyzers
- Giner is in the process of forming Roll-to-Roll Films
  - Working with toll-coating partners.
- Giner's method provides:
  - Best materials choices for fuel cell and electrolyzer operation
  - Proven integration to roll-to-roll operation
  - Current target is $20/m^2 (late '14), <$5 /m^2 for high volume R2R production

The current focus is on scaling-up the process. Goal is to develop the process as far as possible with suitable materials.

Collaborations

- The UMass- Amherst Nanoimprint Lithography Laboratory (Prof. Kenneth Carter)
- NIL Technology (Denmark)
- Impattern Technologies (Dr. Michael Watts)
- General Motors (Initial DSM™ funding)