Dimensionally Stable High Performance Membranes

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Overview

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

Barriers addressed
- A. Durability
- B. Cost
- C. Performance

Technical Targets (DOE 2017 Targets)
- 0.02 Ω.cm² at 1.5 kPa H₂O Air inlet
- <$20/m²
- > 5000 h lifetime, >20,000 RH Cycles

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

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 m² 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

80% Void

- Add ionomer solution (~ 25%)
- Dry

Film on top & bottom

Center:
20% support
20% ionomer
60% void

Center:
50% ionomer
50% support.
Conductivity penalty
= 2*tortuosity

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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

- **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” H₂ Pump with low ionomer conductivity
Relevance: Giner’s DSM™ Success

- Large Scale Electrolyzer For Energy Storage
  - 290 cm² Platform
  - World Best Efficiency @ 1500 mA/cm² (~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.

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

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
</table>
| 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**

![Diagram of Phase Inversion Process]

**Note the microporosity of the DSM™ support**
Achievements: UV Microreplication

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

[Diagram showing the process of UV microreplication with steps: Apply liquid monomer, apply the template, UV light, pressure, template release, DSM™ substrate on PFSA.]
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.
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

- 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.
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/m²)
  - Insufficient material properties

- Mechanical Deformation (Focus)
  - Best materials choices (thermoplastics)
  - Currently $50/m², <$5/m² 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/m² (late ‘14), <$5 /m² 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)