New High Performance Water Vapor Membranes To Improve Fuel Cell Balance of Plant Efficiency and Lower Costs

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Tetramer Technologies

May 14, 2013

Project ID # FC102

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Overview

Timeline

- Start: Sept 17, 2012
- End: Sept 16, 2014
- Phase II Effort Complete: 25%

Budget

- Total Phase II project funding
  - DOE share: $999,815
  - Contractor share: $325,000

Barriers

- Overcome Chemical Degradation
- Mechanical Durability
- Performance – stack water management
- Cost

Partners

- General Motors (Automotive Prototype Membrane Performance Testing)
- Ballard (Non-automotive Prototype Membrane Performance Testing)
- Membrane Technology Research (Module Prototype Production)
- Dana Corporation (New Partner)

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Relevance to DOE

Design and develop high performance, low cost water vapor membranes for cathode humidification

DOE Barriers	2017 DOE Technical Targets for Cathode Humidifier Membrane	Tetramer Targets Sept 2013	Tetramer Targets Sept 2014
Performance	• Maximum Operating Temperature >95 °C • Pressure differential <75 kPa • Water transfer flux =0.025 g min^{-1} cm^{-2}	Consistently produce 18,000 GPU at 85 C with no chemical degradation over 2000 hours	Consistently produce 30,000 GPU at 90 C max. with no chemical degradation over 5000 hours
Durability	5000 hours with < 10% drop in performance	2000 hours with < 20% drop in performance	5000 hours with < 10% drop in performance
Cost	<$10/$m^2$	~$20/$m^2$	~ $10/$m^2$

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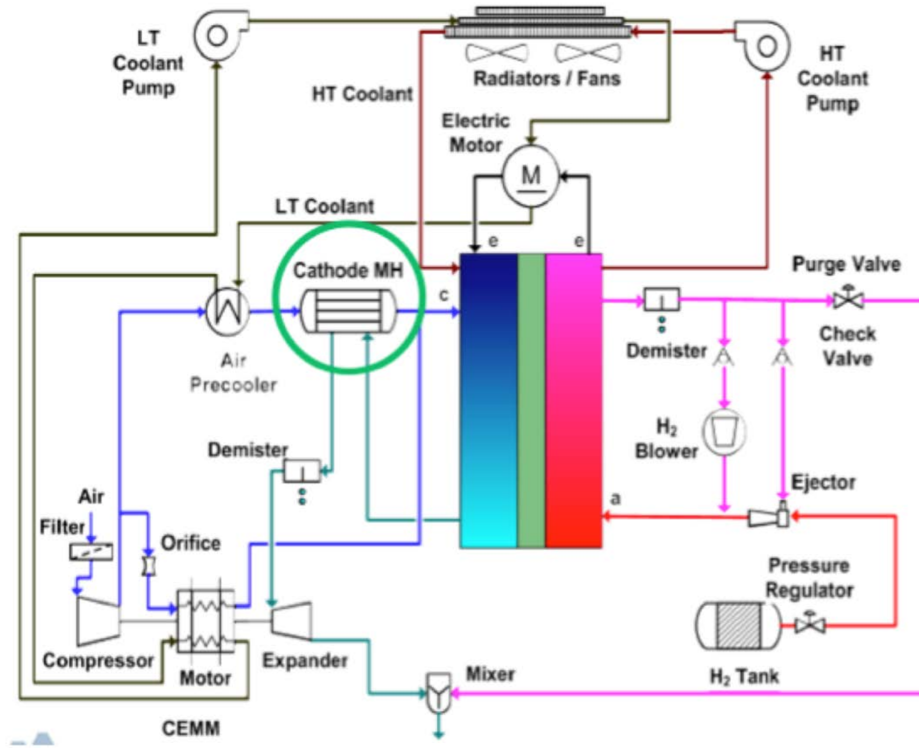
Relevance and Background

- PEMs in fuel cells are more durable and perform more efficiently at higher hydration levels.



- More efficient, low-cost humidifiers that recycle the water generated from cathode effluent both increase performance and lower balance of plant costs.
- Size of fuel cell stack can be decreased by running under wetter conditions.

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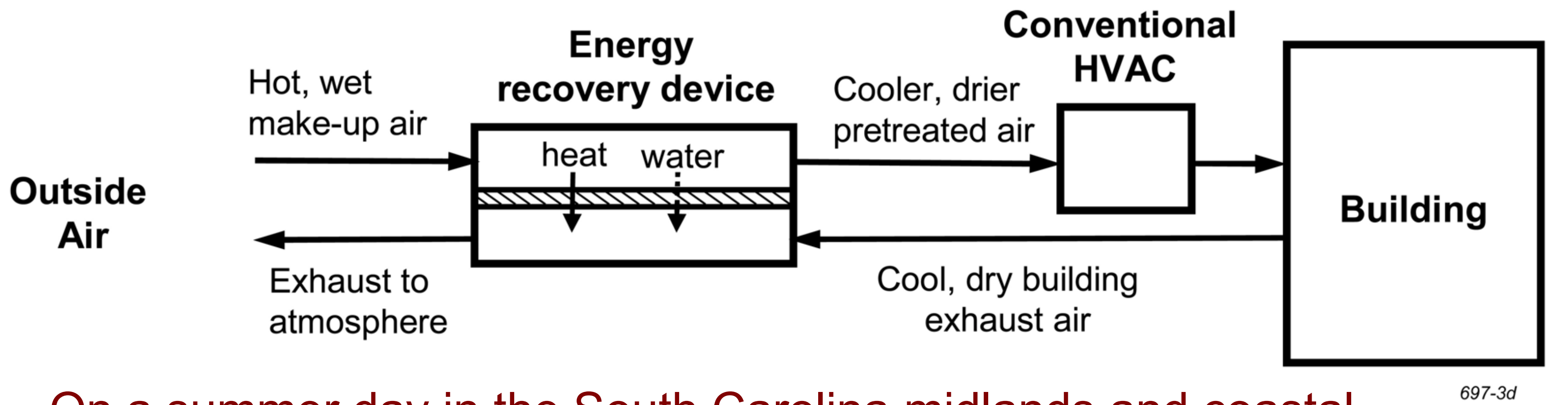
Relevance-HVAC Energy Savings



- On a summer day in the South Carolina midlands and coastal plains, <u>two thirds of the total energy costs for air conditioning are attributable to moisture removal.</u>
- A membrane dehumidifier decreases the compressor load on a conventional air conditioning system, resulting in energy savings of up to 40%.
- Large, shorter term accessible market will increase volume and lower the cost of the membrane for fuel cell applications.

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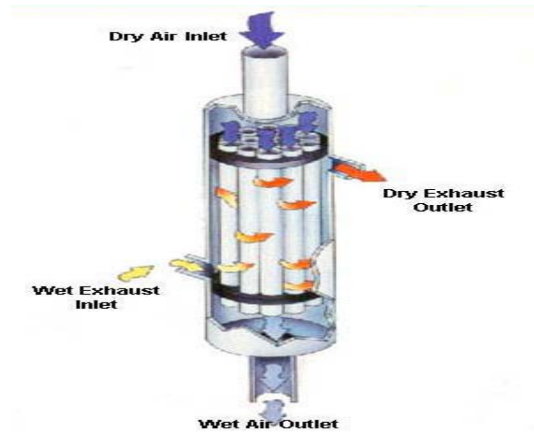
Tetramer Approach: Current State of the Art

- Perma Pure™ units containing Nafion® have not yet met the desired size, weight and pressure drop requirements.

dPoint / WL Gore Module



Perma Pure™ Unit

- W.L. Gore reported at the 2012 AMR on both new PFSA and hydrocarbon membranes in flat plate configuration. However severe chemical degradation was detrimental to permeation performance with a loss in permeance of up to 60% within 500 hours.

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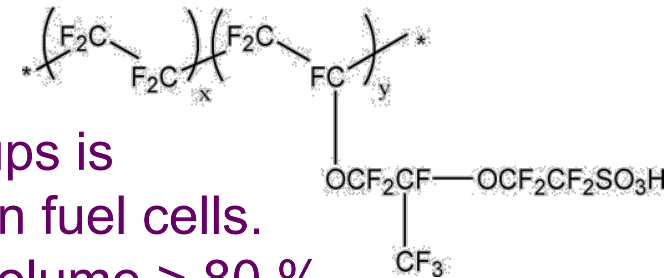
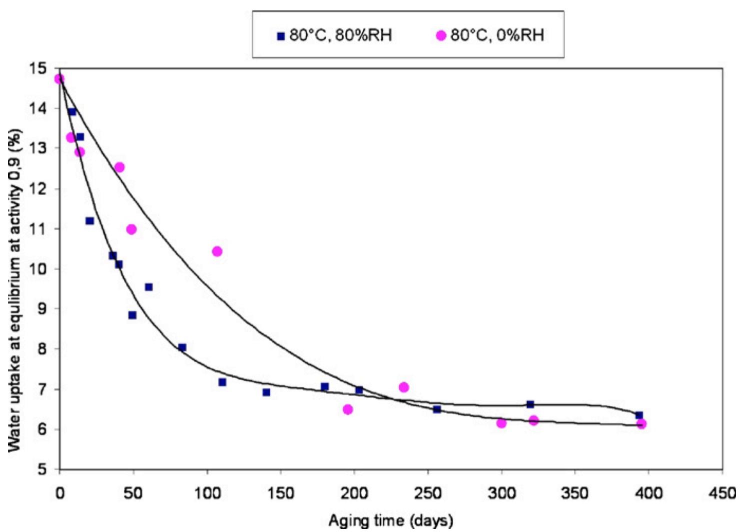
Approach Strategies
Current WVT Show Stoppers: Anhydride and Salt Formation

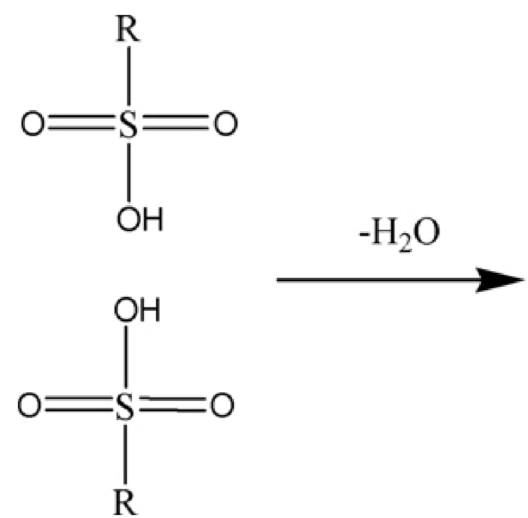
- In 2009, Collette et al. concluded that upon heating samples of PFSA at 80 °C at both 0 % and 80% RH, the formation of sulfonic anhydrides were seen.



Chemical Structure of Nafion®

- This reduction in accessible sulfonic acid groups is detrimental to performance parameters used in fuel cells. Reduction in water uptake > 50%, Langmuir volume > 80 % and ionic conductivity of > 80 % within 200 days at 80 °C.





Ref: Collette, R. M. et al., “Hygrothermal Aging of NAFION®”, J. Memb. Sci. 330 (2009) 21-29.

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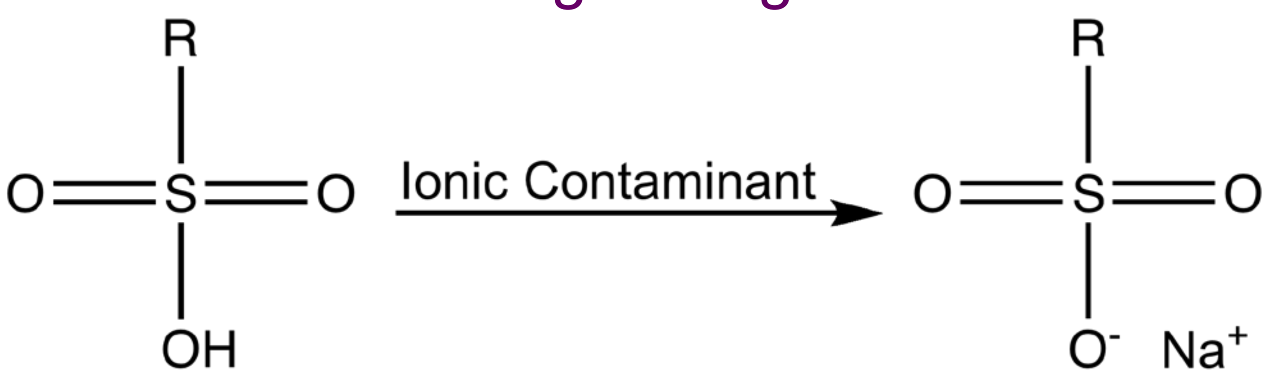
Approach Strategies
WVT Show Stopper: Contamination via Salt Formation

- During the 2012 annual merit review, W.L. Gore (FC 067) demonstrated that salt contamination can contribute to water permeance reduction where >70 % reduction in permeance was observed for an ionomer that was fully converted to its salt form.

- They also mentioned that customers had observed this contamination issue during testing.



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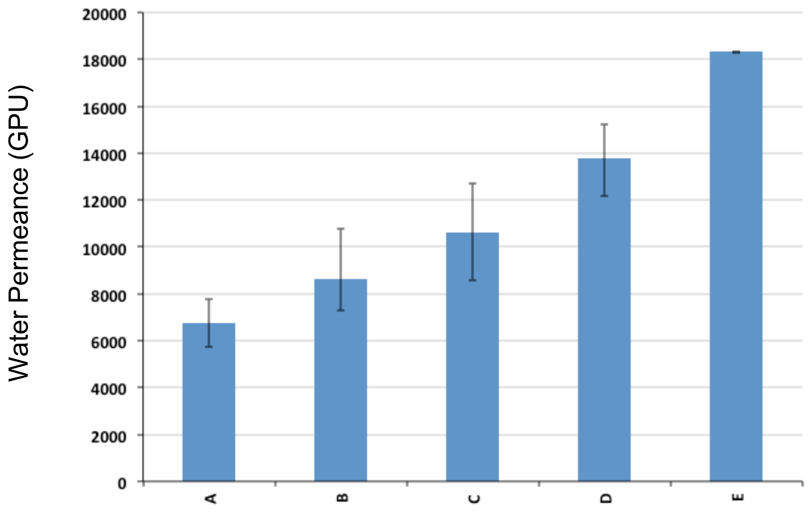
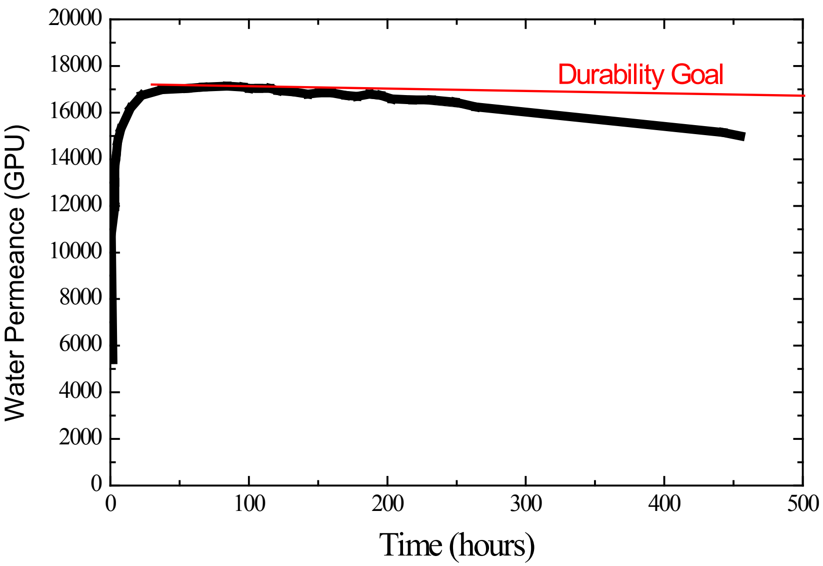
Tetramer Approach: Phase I Positive Permeation Results of Different Molecular Architectures





Phase I Tetramer Membrane Development

Over 150% improvement (left figure) of water vapor permeation achieved through Tetramer's proprietary membranes. However, degradation rate of 11% decline over 500 hours (right figure) was unacceptable. Some anhydride formation was possible.

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Tetramer Approach for Phase II

Proprietary polymer architectures which provide multiple water transport paths while mitigating or eliminating anhydride formation and salt blocking structures were proposed and accepted by DOE for Phase II.

Polymer Design Elements

BLOCK A
Water Permeability
Hydrophilic groups, Ionic or Intermolecular attractions

BLOCK B
Mechanical Strength
Rigid structures
Hydrophobic linkages

BLOCK C
Processability
Stereoisomeric structures, Solubilizing groups

BLOCK D
Stability
Chemical resistance, Crosslinking

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Phase II Approach
2 Year Technical DOE Targets

Sept. 2014 Objectives
(1) Demonstrate a water vapor transport membrane with >30,000 gas permeation units at 90°C max with little chemical degradation over 5000 hours
(2) Develop a water vapor membrane with durability of less than 10% projected loss water permeation over 5000 hours
(3) Limit the crossover leak rate to less than 150 GPU
(4) Design temperature durability of 90°C with excursions to 100°C
(5) Limit the cost to less than $\$10/m^2$ at medium volumes.

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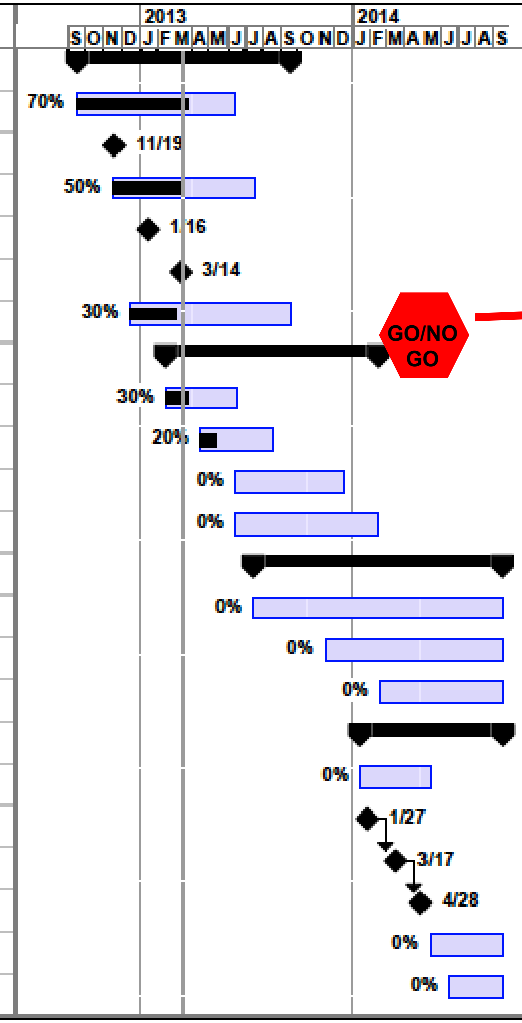
Approach/ Accomplishments: 2 Year Task Schedule Overview and 6 month progess

ID	Task Name
1	Task 1: Performance Optimization for WVT Application
2	Task 1.1: Synthesis of New Monomers Resistant to Chemical Degradation
3	Synthesis of Stable Monomer
4	Task 1.2 Synthesis of New Polymers Resistant to Chemical Degradation
5	Synthesis of Homopolymers
6	Synthesis of Copolymers
7	Task 1.3 Evaluation of Chemical, Mechanical and Water Transport Stability
8	Task 2: Performance and Durability Optimization of New Polymers from Task 1
9	Task 2.1 Purification of Monomers and Polymers
10	Task 2.2 Stabilitization of Degradation Mechanisms Route 1
11	Task 2.3 Stabilization of Degradation Mechanisms Route 2
12	Task 2.4 Stabilization of Degradation Mechanisms Route 3
13	Task 3 Down Selected Prototype Preparation and Testing
14	Task 3.1 Automotive Testing
15	Task 3.2 Non-Automotive Testing
16	Task 3.3 HVAC Testing
17	Task 4 Scale-up of Down Selected Polymers and Cost Confirmation Estimates
18	Task 4.1 Scaleup
19	Scaleup of First Batch
20	Scaleup of Second Batch
21	Scaleup of Third Batch
22	Task 4.2 Technology Tranfer Package Preparation
23	Task 4.3 Cost Analysis



Permeance Decline Mechanism Identified and Solved

Synthesis Process 80% Defined

30,000 GPU Achieved

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Six Month Accomplishments:
Task 1: Polymer Molecular Architecture Design

BLOCK A
Water Permeability
Hydrophilic groups, Ionic or Intermolecular attractions

BLOCK B
Mechanical Strength
Rigid structures
Hydrophobic linkages

BLOCK C
Processability
Stereoisomeric structures,
Solubilizing groups

BLOCK D
Stability
Chemical resistance,
Crosslinking

- Synthesis of 6 new monomer and 12 new film forming polymer structures with these architectures has been achieved in the past 6 months
- Extensive reaction condition optimization has been necessary to get purity and film forming polymers
- Purification and characterization (NMR, MS, EA, FTIR and GPC) of these materials has been defined
- Yield and better processing conditions identified for Task 2

Six Month Accomplishments:
Task 1: Polymer Molecular Architecture Design

BLOCK A
Water Permeability
Hydrophilic groups, Ionic or Intermolecular attractions

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Mechanical Strength
Rigid structures
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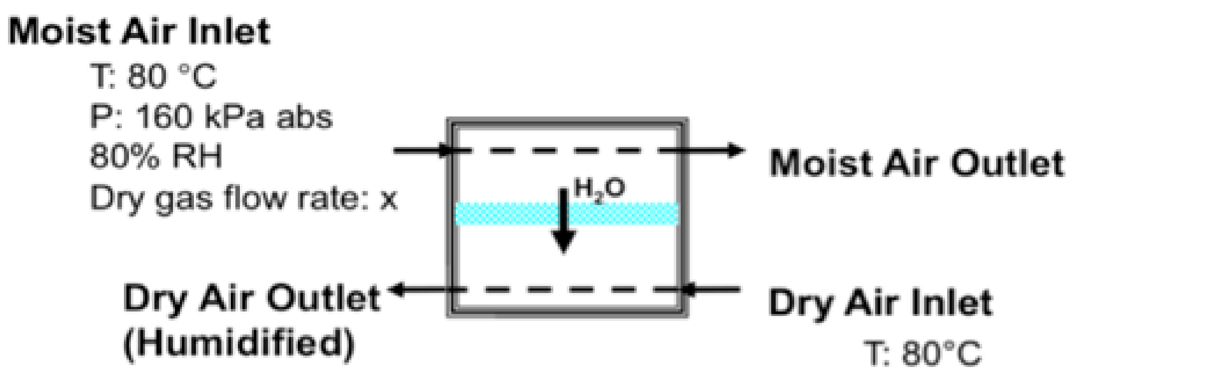
Stability
Chemical resistance, Crosslinking



GM Testing Conditions

Membanes are cast on an Erichsen casting table in a class 1000 clean room then 50 cm^2 square stamps tested

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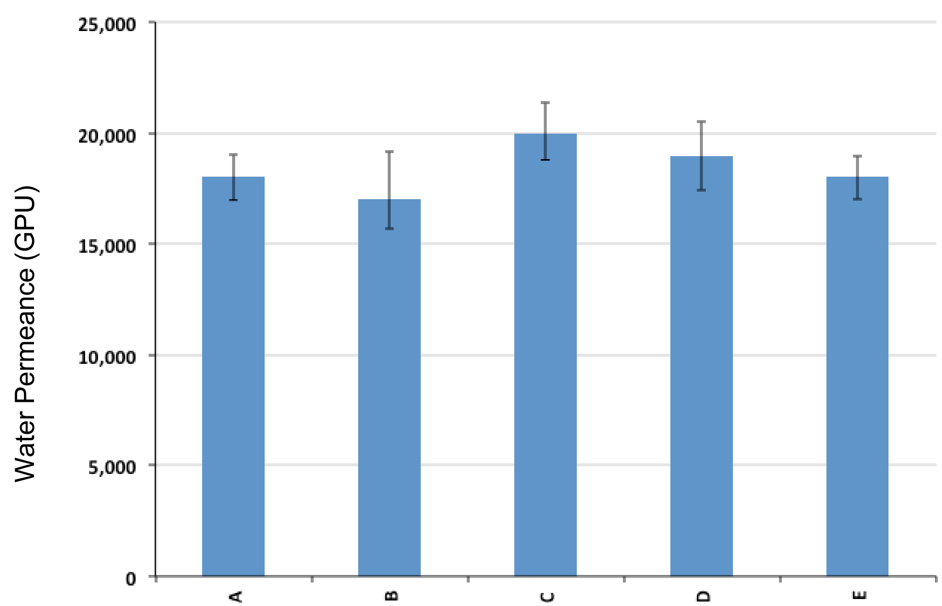
Six Month Accomplishments: Task 1: Polymer Molecular Architecture Design

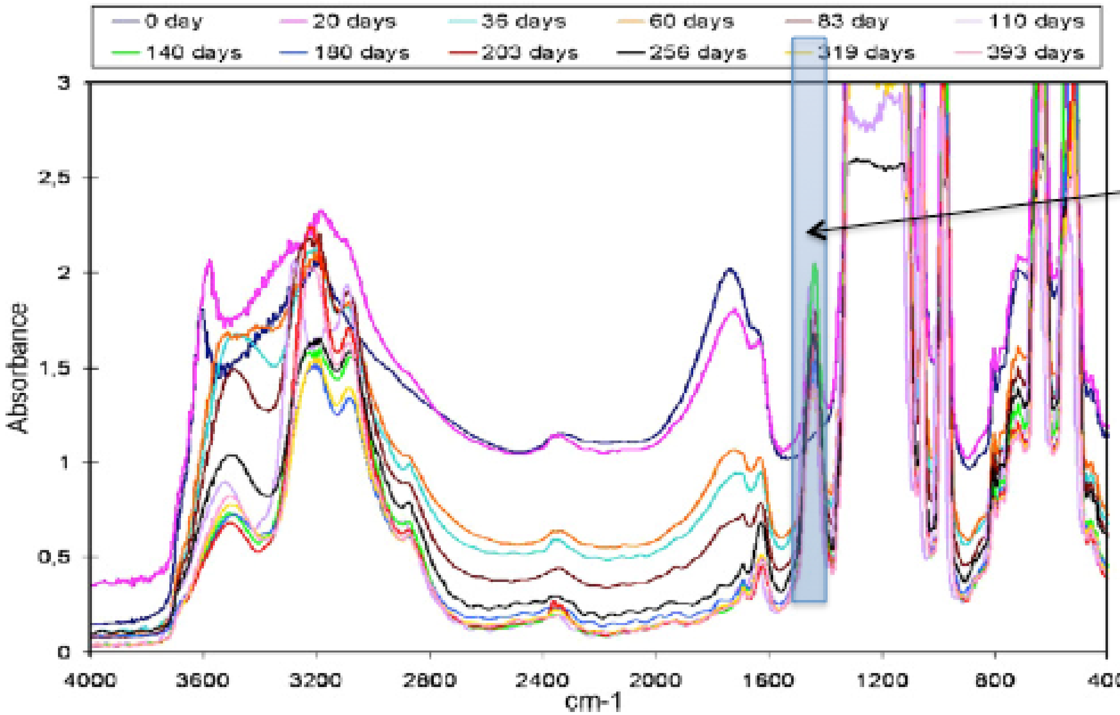
BLOCK A	BLOCK B	BLOCK C	BLOCK D
Water Permeability	***Mechanical Strength***	***Processability***	**Stability**
Hydrophilic groups, Ionic or Intermolecular attractions	Rigid structures Hydrophobic linkages	Stereoisomeric structures, Solubilizing groups	Chemical resistance, Crosslinking

Results: Testing by GM under conditions has indicated that we have achieved between 17,000 and 20,000 GPU for 5 of the new polymer structures!



Six Month Accomplishments:
Task 1: Polymer Molecular Architecture Design

- FTIR analysis shows evidence of anhydride formation in NAFION® after heating at 80 °C, 80% RH (*F.M. Collette et al., Journal of Membrane Science 330 (2009) 21–29*)



Signal characteristic of anhydride formation in NAFION® (1440 cm^{-1})

- Evidence of significant anhydride formation in NAFION® membranes was reported after within 20 days of heating at 80°C.

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Six Month Accomplishments:
Task 1: Polymer Molecular Architecture Design

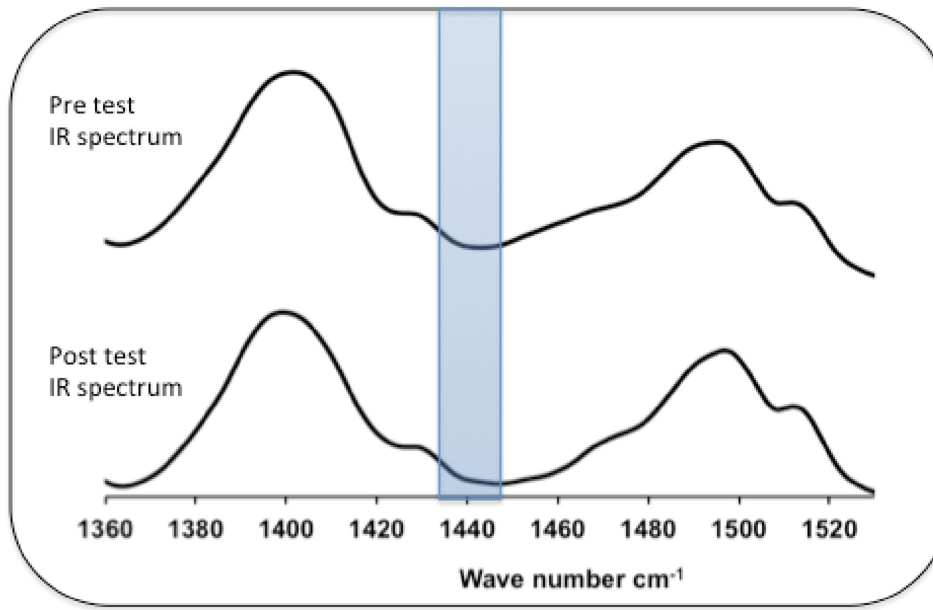
BLOCK A
Water Permeability
Hydrophilic groups, Ionic or Intermolecular attractions

BLOCK B
Mechanical Strength
Rigid structures
Hydrophobic linkages

BLOCK C
Processability
Stereoisomeric structures, Solubilizing groups

BLOCK D
Stability
Chemical resistance, Crosslinking

- Five new polymers were tested under Collette, et al. conditions for both 240 hours at 80 °C and 4 hours at 140 °C and no indication of anhydride formation at 1440 cm^{-1} in infrared was detected!!
- More time and higher temperature (95 °C) testing is underway



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Key Phase II Accomplishments After 6 Months

Tasks	Status	Completion Date %Complete
Task 1: Synthesize Polymer Membranes With Resistance To Chemical Degradation at 80^{o}C and 95^{o}C for 2000 hours	Tetramer has synthesized 6 new monomers and 12 viable new polymer structures that have not shown any anhydride formation at 80 ^{o}C after 250 hours.	Sept. 2013 50%
Task 2: Improve water transport to 30,000 GPU with chemical stability as defined In Task 1	The new membranes are consistently achieving the initial ~18,000 GPU target for durability testing.	Feb. 2014 25%

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Collaborations

Partners

- **General Motors (Industry)** has been a strong partner for over 5 years and is very active in testing our materials under automotive fuel cell conditions
- **Ballard (Industry)** has received samples and done some very preliminary testing under non-automotive fuel cell conditions. They will do Prototype Membrane Performance Testing in year 2
- **Membrane Technology Research (Industry)** has participated in water vapor transport testing and will participate in module prototype production in year 2
- **New Collaborator- Dana Corporation (Industry)** has participated in water vapor testing and will contribute both prototype testing and fuel cell system design

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Future Work for Phase II

FY 2013

- Continue durability tests at higher temperatures (95 °C) and longer times to assure chemical resistance. In parallel, continue synthesis of new polymer architectures to increase water vapor transport from 20,000 GPU to 30,000 GPU
- Utilize initial results to optimize membrane durability to less than 20 % loss in performance after 2000 hours.
- Use these new molecular architectures to increase temperature durability from 80 °C to 90 °C with excursions of 100 °C
- Automotive prototype membrane performance testing

FY 2014

- Down selected membranes will be then tested for non-automotive prototype membrane performance using module prototype production

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Phase II Six Month Summary

Relevance – Develop improved low cost water vapor membranes to cathode humidification modules for fuel cells and HVAC applications

Approach – Synthesize new polymer molecular architectures which avoid chemical degradation, increase water vapor transport, mechanical durability at lower cost.

Technical Accomplishments – New monomers and polymers successfully synthesized which have indicated chemical resistance with acceptable water vapor transport.

Collaborations – Partners in place to build and evaluate prototype modules with down selected materials.

Future Work – Continue chemical resistance tests to determine longer term stability. In parallel, continue synthesis of higher permeability polymer architectures. Down select best candidates for scaleup and provide prototypes to collaborators.

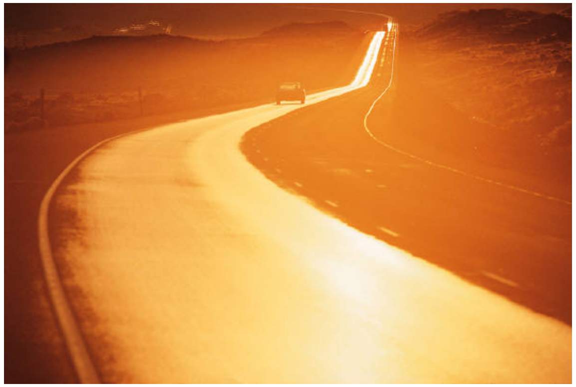
Phase II Six Month Summary

Overall:

Good Start

Slightly Ahead of Schedule

Still a Long Winding Road Ahead



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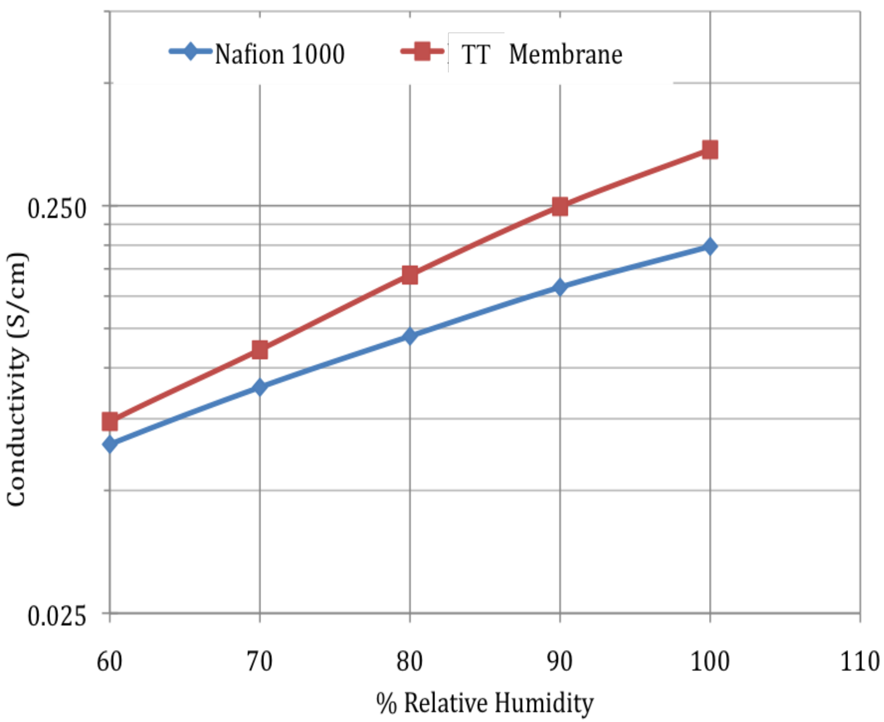
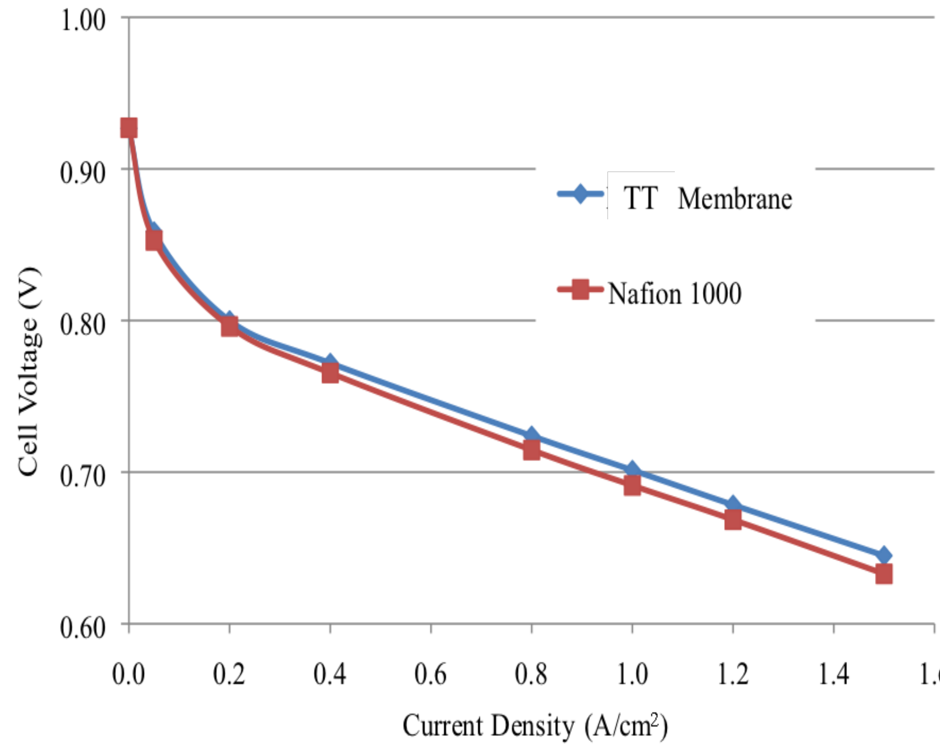
Technical Back-Up Slides

Improved PEM Performance vs. Nafion® 1000





- Membrane conductivity as a function of relative humidity (RH) for proprietary Generation 1 TT PEM ionomer and Nafion® 1000.
- Fuel cell polarization curve at 150 % RH_{out} for proprietary TT ionomer membrane and Nafion® 1000.

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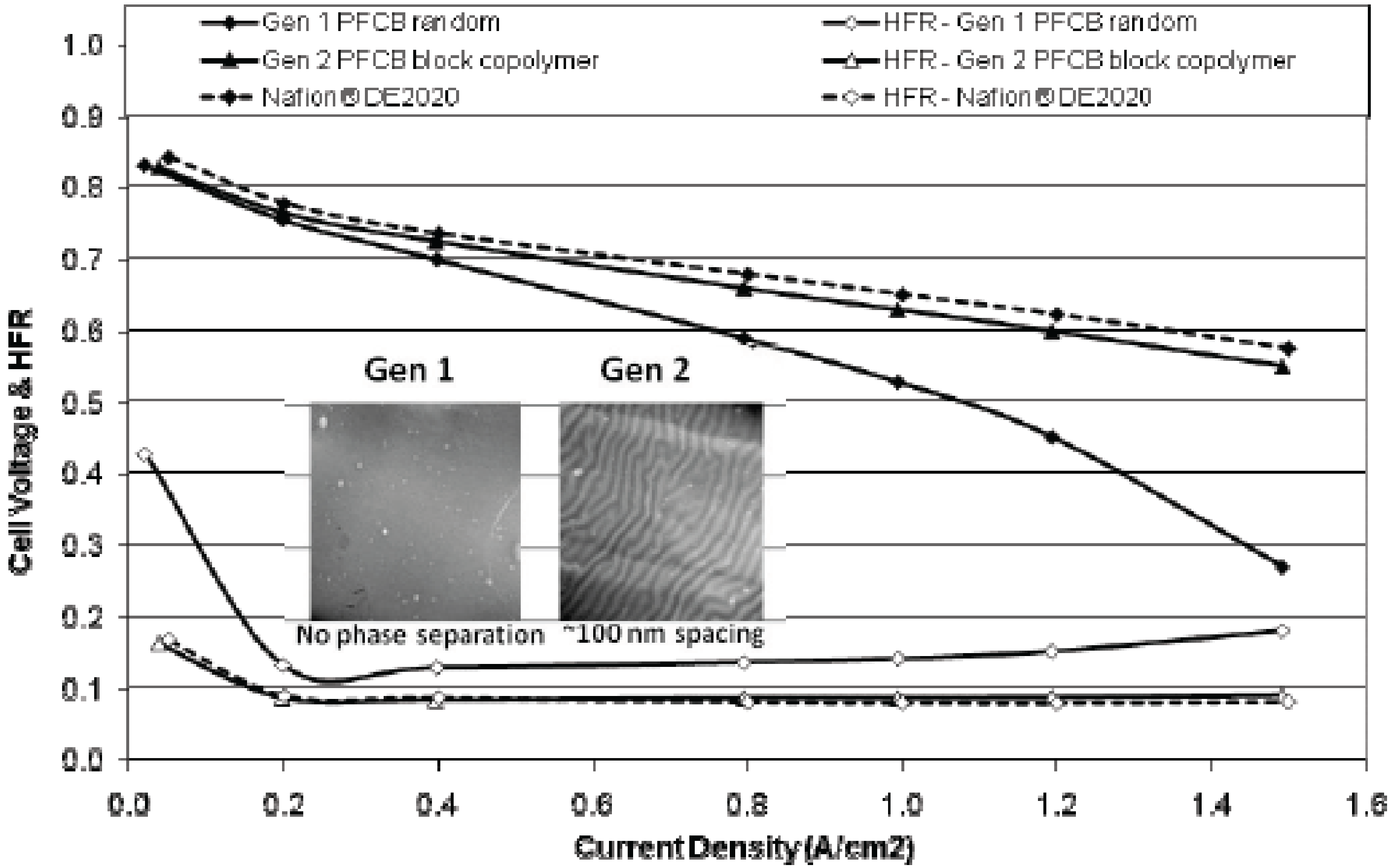
Improved Performance through Microstructured Materials



- 50 cm^2 single cell, serpentine flow field
- 80°C, 3/3 A/C stoich, 175kPa, 0.4/0.4 $mgPt/cm^2$

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26

Table 3.4.9 Technical Targets: Cathode Humidification System for 80-kW$_e$ Transportation Fuel Cell Systems Operating on Direct Hydrogen		
Characteristic	**Units**	**2017 Targets**
Maximum operating temperature	°C	>95
Maximum pressure differential between wet and dry sides	kPa	75
Maximum pressure drop at full flow (each side)	kPa	3.5
Water transfer at full flow[a]	$g\ s^{-1}$	5
Durability[b]	h	5,000
Maximum air leakage at full flow	%	0.5
Volume	L	5
Weight	kg	5
Cost[c]	$	100

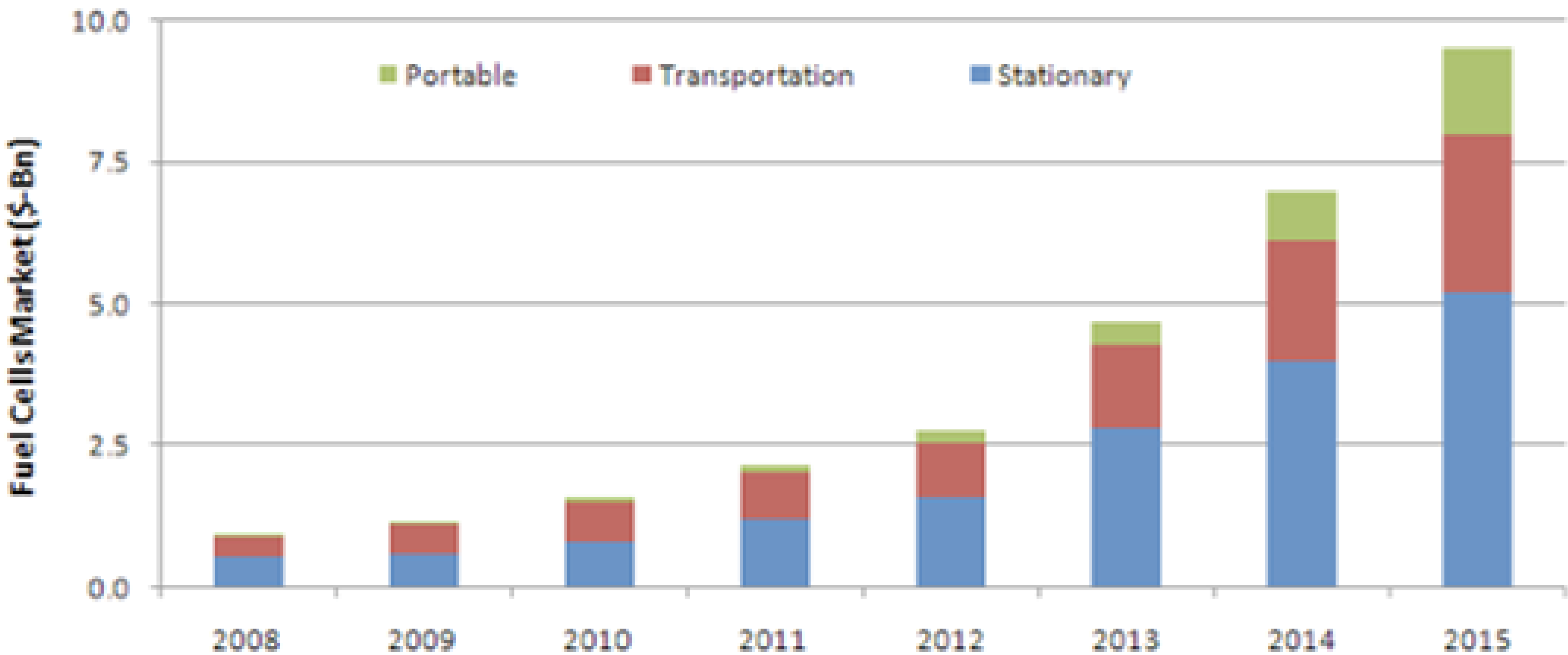
Table 3.4.10 Technical Targets: Cathode Humidifier Membrane for 80-kW$_e$ Transportation Fuel Cell Systems Operating on Direct Hydrogen		
Characteristic	**Units**	**2017 Targets**
Maximum operating temperature	°C	>95
Maximum pressure differential between wet and dry sides	kPa	75
Water transfer flux at full flow[a]	$g\ min^{-1}cm^{-2}$	0.025
Durability[b]	h	5,000
Cost[c]	$\$/m^2$	10

a Dry air in: 0.23 SLPM/cm^2 dry gas flow, 183 kPa (absolute), 80°C, 0% RH. Wet air in: 0.20 SLPM/cm^2 dry gas flow, 160 kPa (absolute), 80°C, 85% RH.

b Based on U.S. DRIVE Fuel Cell Tech Team Cell Component Accelerated Stress Test and Polarization Curve Protocols (http://www.uscar.org/guest/view_team.php?teams_id=17), <10% drop in water transfer at full flow.

c Cost projected to high-volume production (500,000 systems per year).

Market Size for Fuel Cells



Source: Tradition Equities and Innovative Research and Products

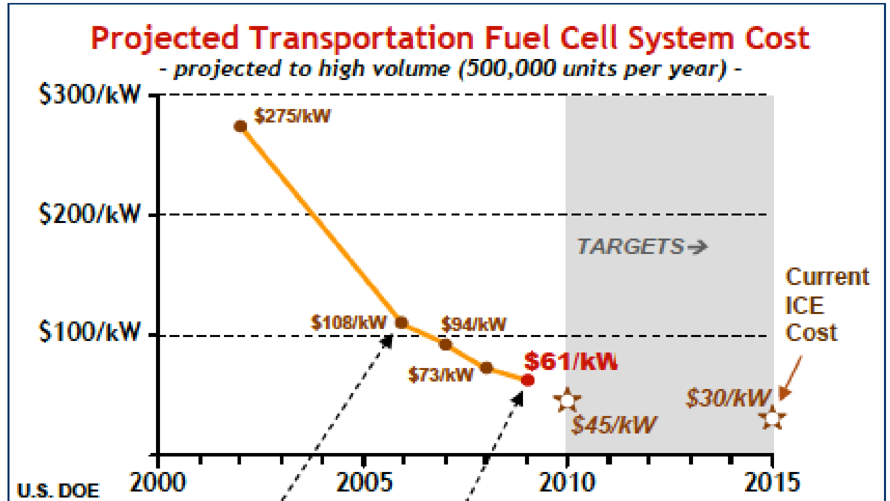
Fuel Cell R&D — *Progress*

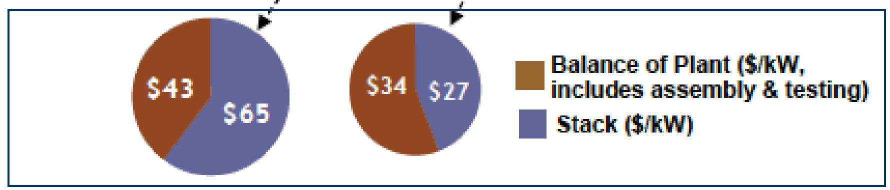
We've reduced the projected high-volume cost of fuel cells to $61/kW*

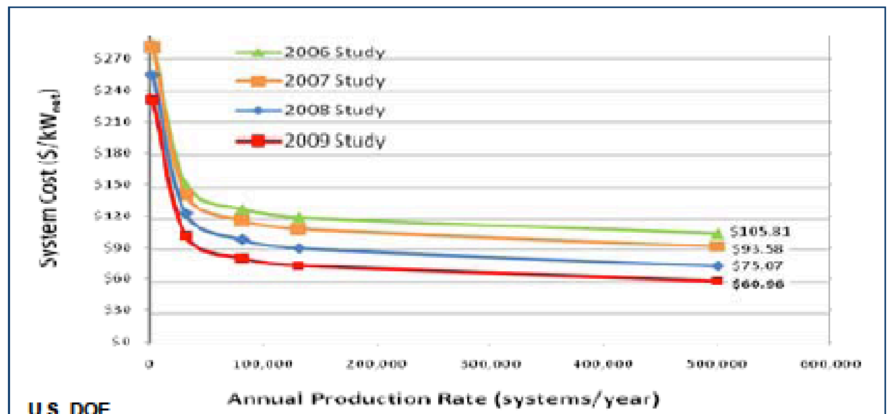
- ***More than 35% reduction in the last two years***
- ***More than 75% reduction since 2002***
- ***2008 cost projection was validated by independent panel*****

We've more than doubled durability in the last few years

- ***More than 7,300 hrs with single cell, exceeding 5,000 hr target***







*Based on projection to high-volume manufacturing (500,000 units/year).

**Panel found $60 – $80/kW to be a "valid estimate": http://hydrogendoedev.nrel.gov/peer_reviews.html

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29