

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

Earl H. Wagener (PI)

Brad P. Morgan

Tetramer Technologies

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Project ID # FC102



This presentation does not contain any proprietary, confidential, or otherwise restricted information

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)

Relevance to DOE

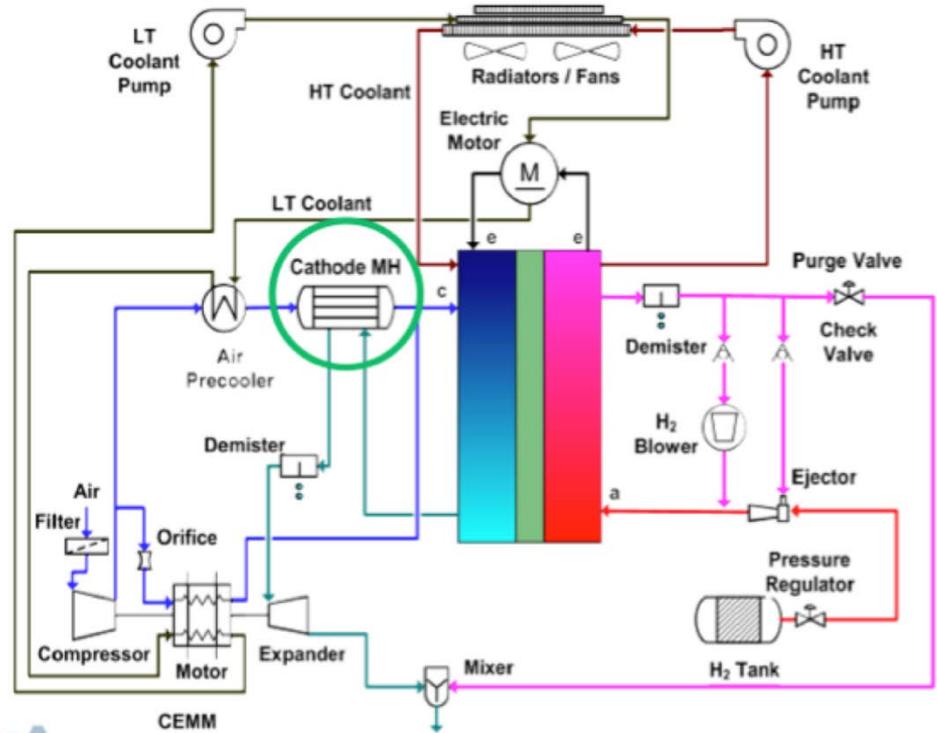
Design and develop high performance, low cost water vapor membranes for cathode humidification

DOE Barriers	2017 DOE Technical Targets for Cathode Humidifier Membrane	Tetramer Targets Sept 2013	Tetramer Targets Sept 2014
Performance	<ul style="list-style-type: none"> 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

Relevance and Background



Chevy Equinox Fuel Cell

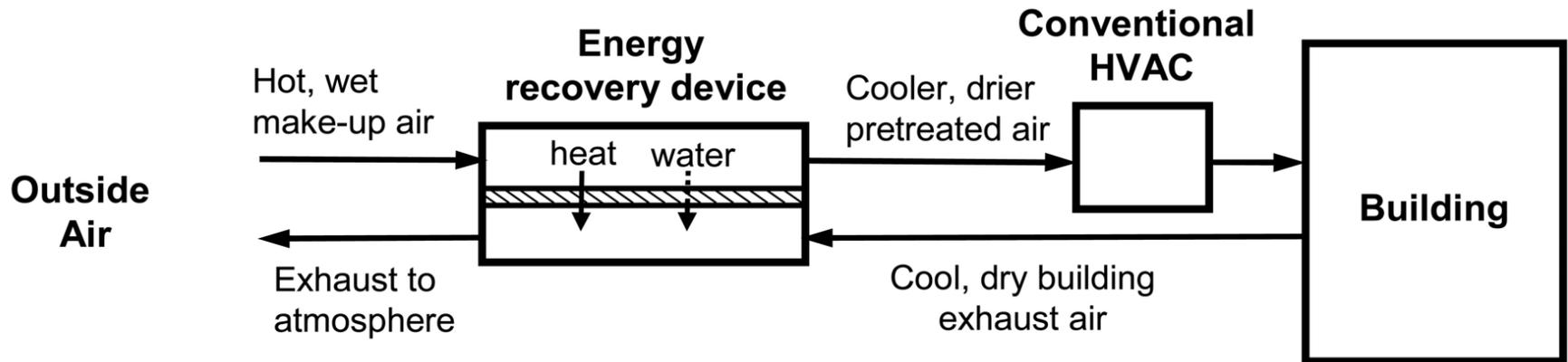


- PEMs in fuel cells are more durable and perform more efficiently at higher hydration levels.



- 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.

Relevance-HVAC Energy Savings



697-3d

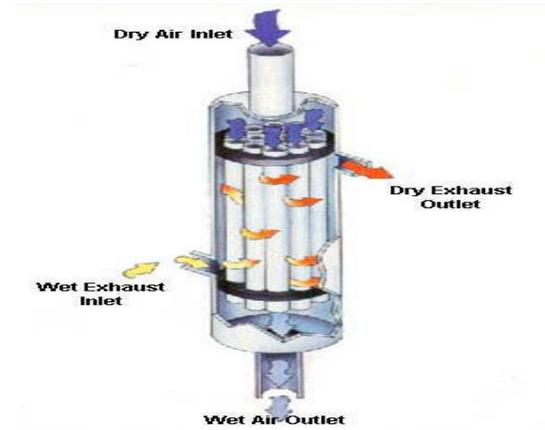
- On a summer day in the South Carolina midlands and coastal plains, two thirds of the total energy costs for air conditioning are attributable to moisture removal.
- A membrane dehumidifier decreases the compressor load on a conventional air conditioning system, resulting in energy savings of up to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

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

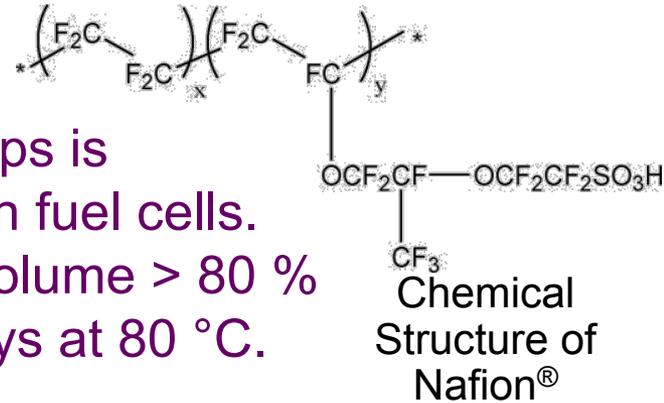


- W.L. Gore reported at the 2012 AMR on both new PFSA and hydrocarbon membranes in flat plate configuration. However severe chemical degradation was detrimental to permeation performance with a loss in permeance of up to 60% within 500 hours.

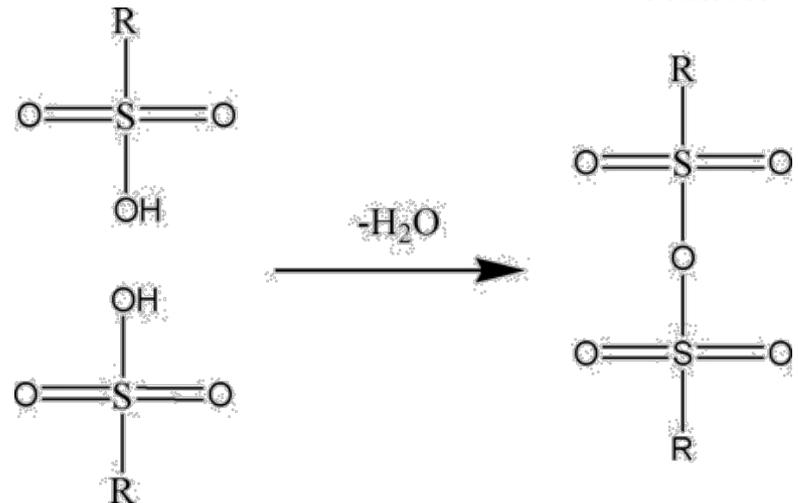
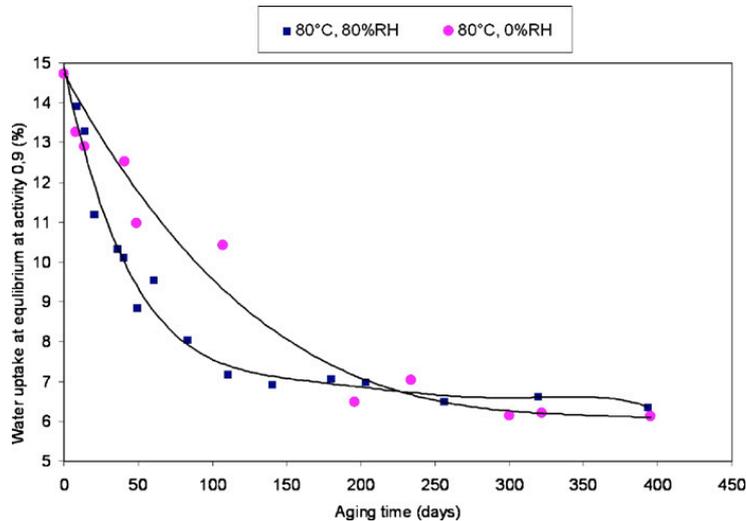
Approach Strategies

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.



- 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.

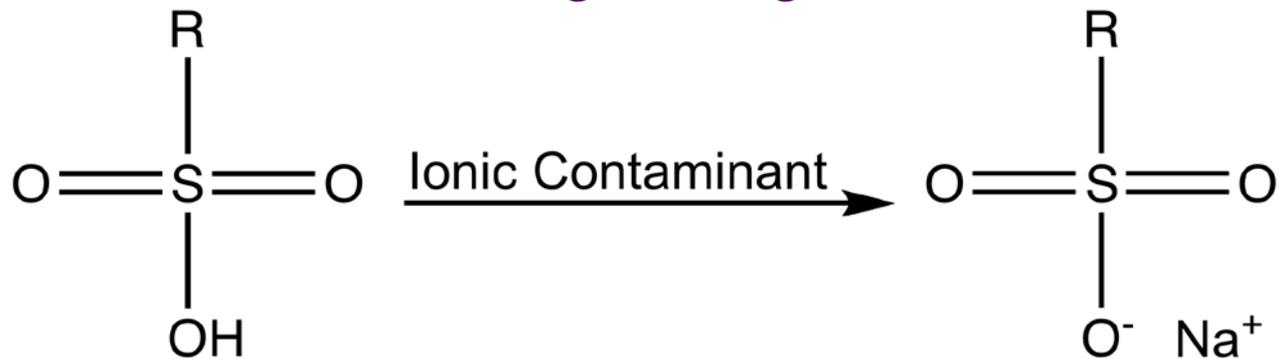


Ref: Collette, R. M. et al., "Hygrothermal Aging of NAFION®", J. Memb. Sci. 330 (2009) 21-29.

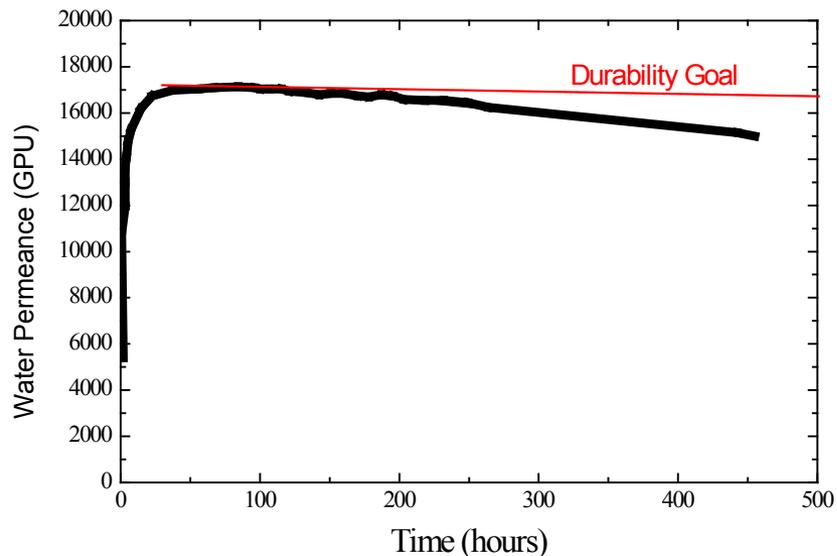
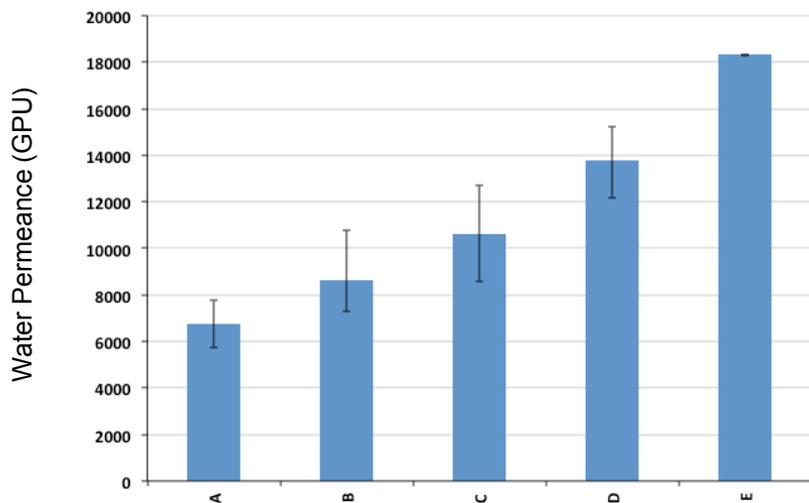
Approach Strategies

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.



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



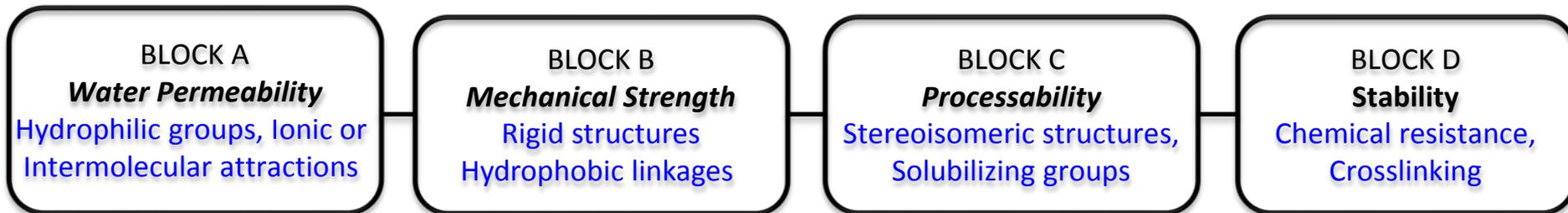
Phase I Tetramer Membrane Development

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.

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



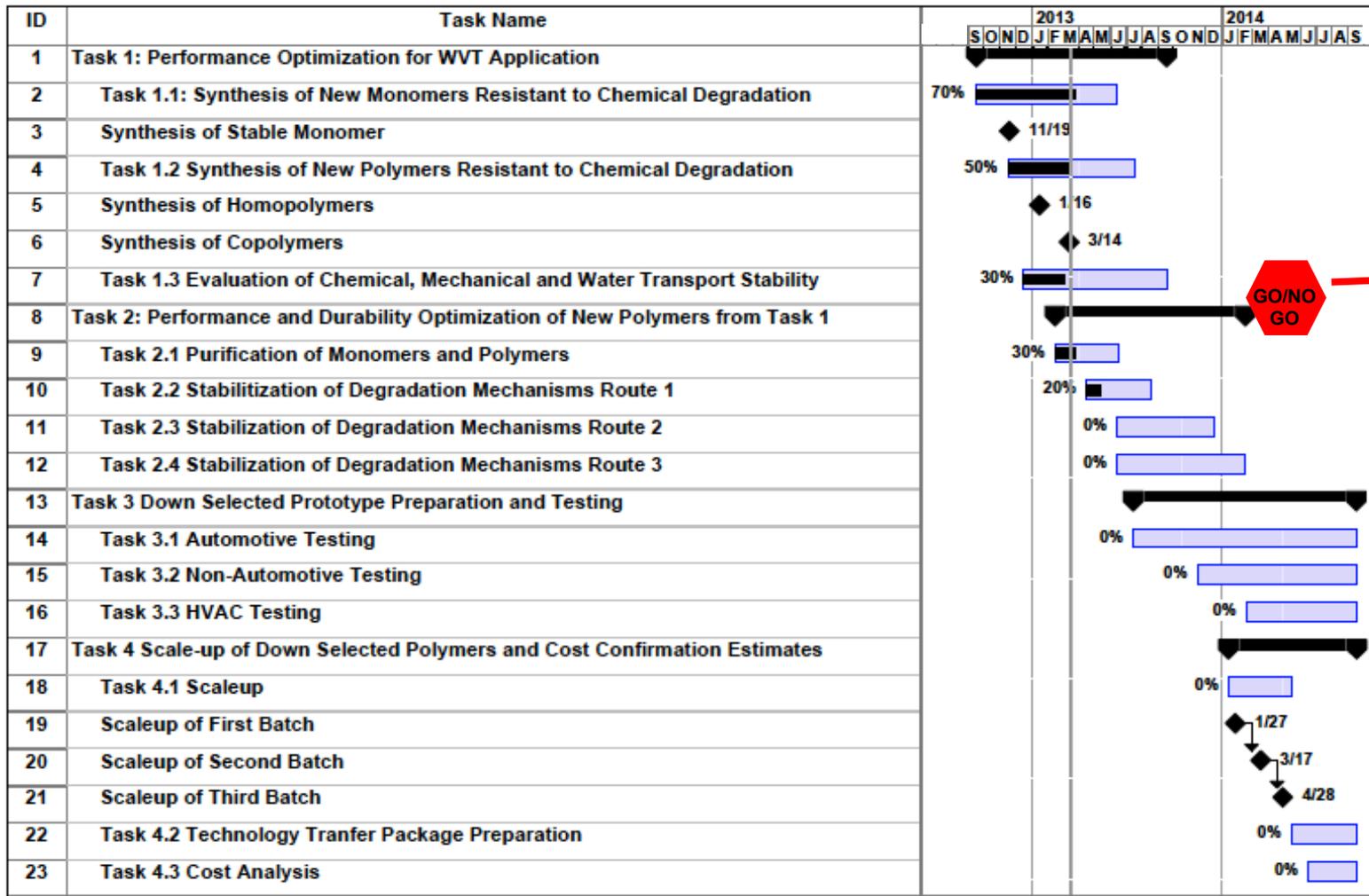
Phase II Approach

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/m² at medium volumes.

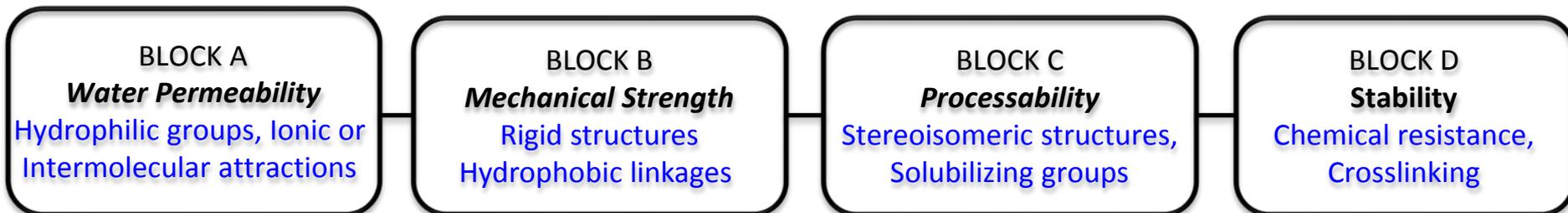
Approach/ Accomplishments: 2 Year Task Schedule Overview and 6 month progress



Permeance Decline Mechanism Identified and Solved
 Synthesis Process 80% Defined
 30,000 GPU Achieved

Six Month Accomplishments:

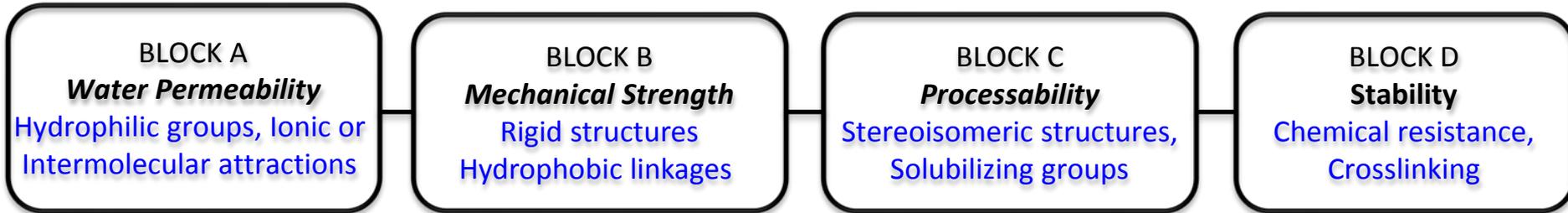
Task 1: Polymer Molecular Architecture Design



- 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

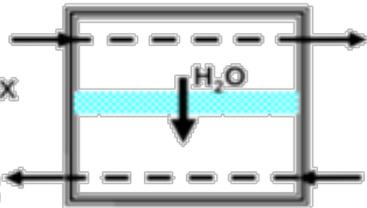
Six Month Accomplishments:

Task 1: Polymer Molecular Architecture Design



Moist Air Inlet

T: 80 °C
P: 160 kPa abs
80% RH
Dry gas flow rate: x



Moist Air Outlet

Dry Air Outlet
(Humidified)

Dry Air Inlet

T: 80°C
P: 183 kPa abs
0% RH
Dry gas flow rate: 1.2 x

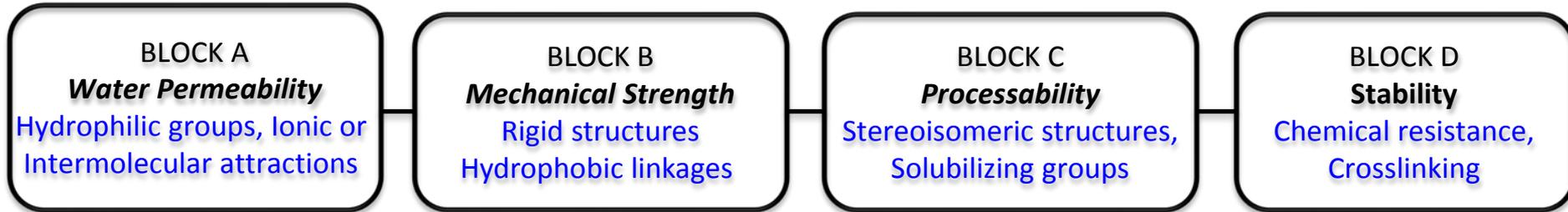
GM Testing Conditions



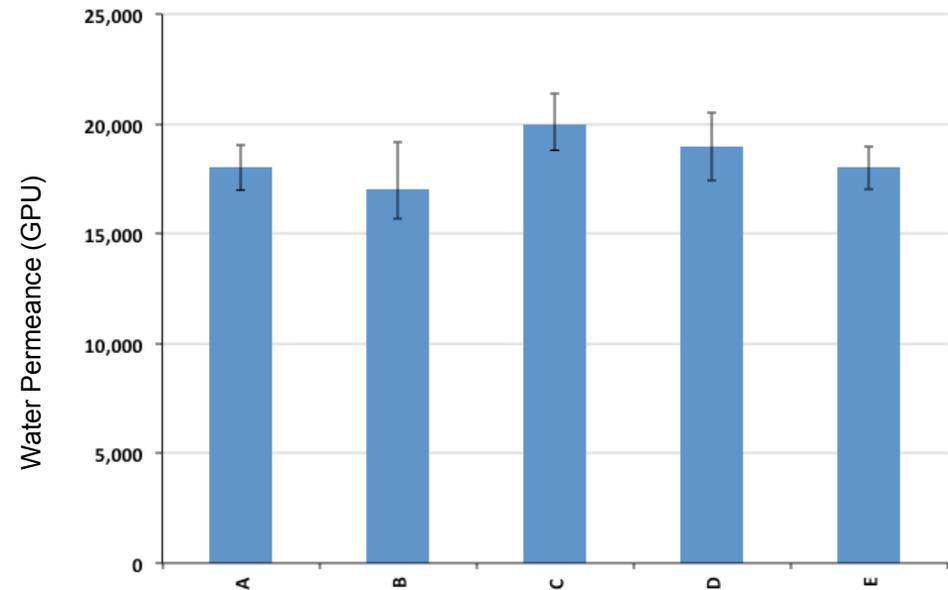
Membranes are cast on an Erichsen casting table in a class 1000 clean room then 50 cm² square stamps tested

Six Month Accomplishments:

Task 1: Polymer Molecular Architecture Design



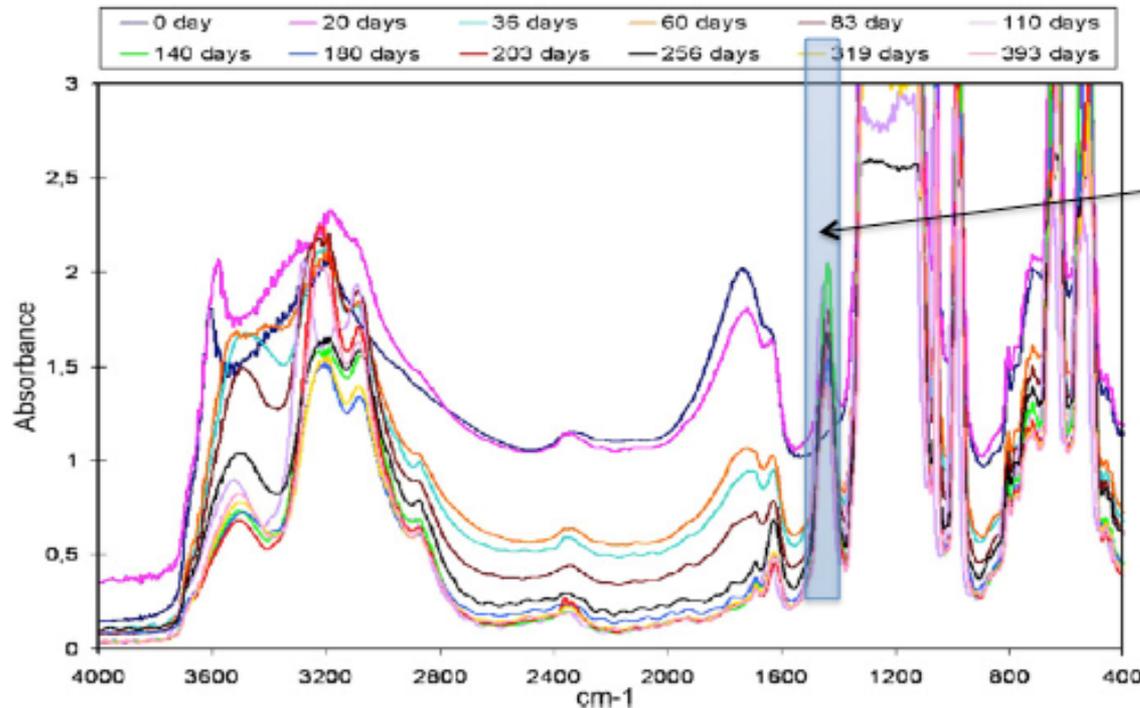
Results: Testing by GM under conditions has indicated that we have achieved between 17,000 and 20,000 GPU for 5 of the new polymer structures!



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.

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

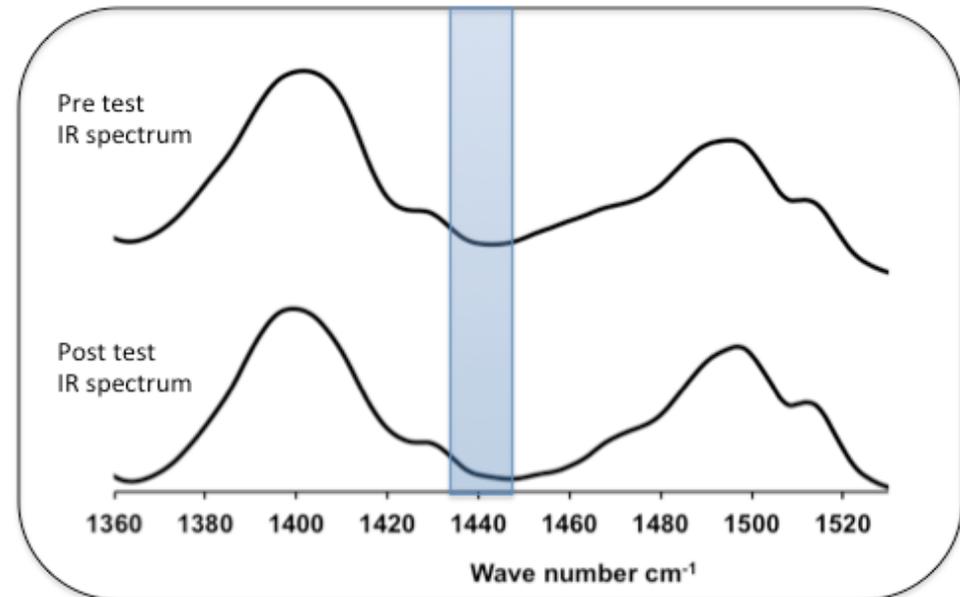
Stereoisomeric structures,
Solubilizing groups

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



Key Phase II Accomplishments After 6 Months

Tasks	Status	Completion Date %Complete
Task 1: Synthesize Polymer Membranes With Resistance To Chemical Degradation at 80°C and 95°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 °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%

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

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

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



Contact Information

Earl Wagener, CEO

earl.wagener@tetramertechologies.com

864.650.0430

Jeffrey DiMaio, Technology Manager

dimaio@tetramertechologies.com

864.903.9009

Brad Morgan, Senior Research Scientist

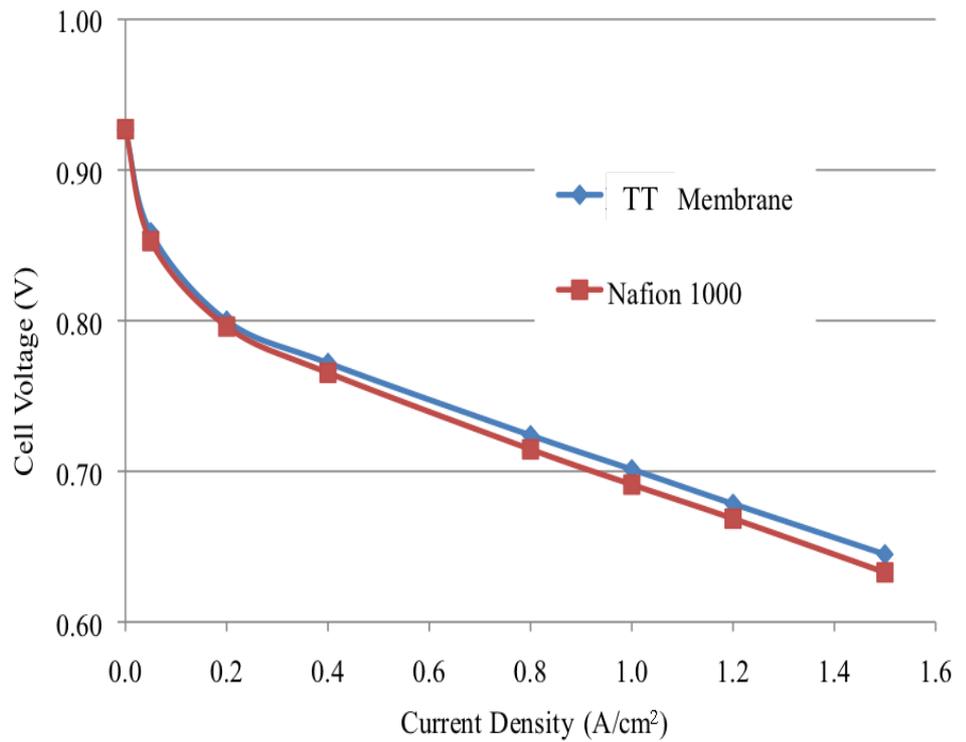
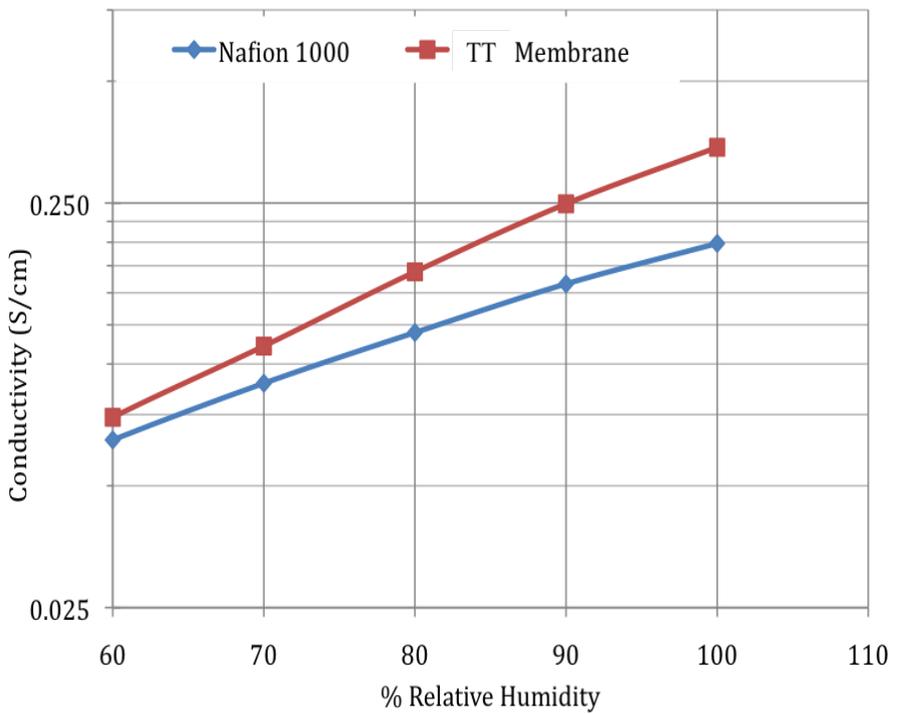
brad.morgan@tetramertechnooiges.com

864.506.1263

Technical Back-Up Slides

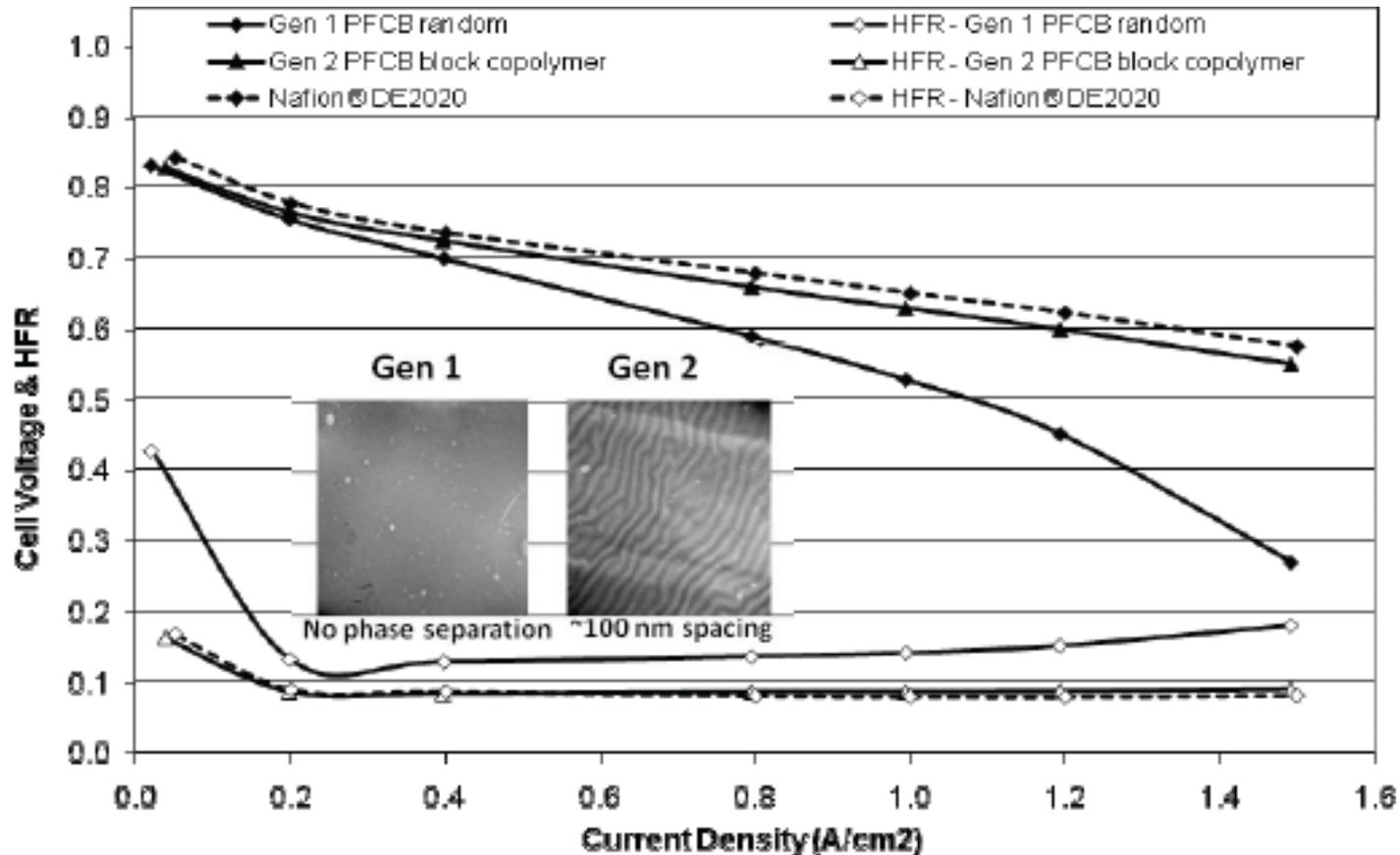
Previous Accomplishments -

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.

Improved Performance through Microstructured Materials



- 50 cm² single cell, serpentine flow field
- 80°C, 3/3 A/C stoich, 175kPa, 0.4/0.4 mgPt/cm²

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

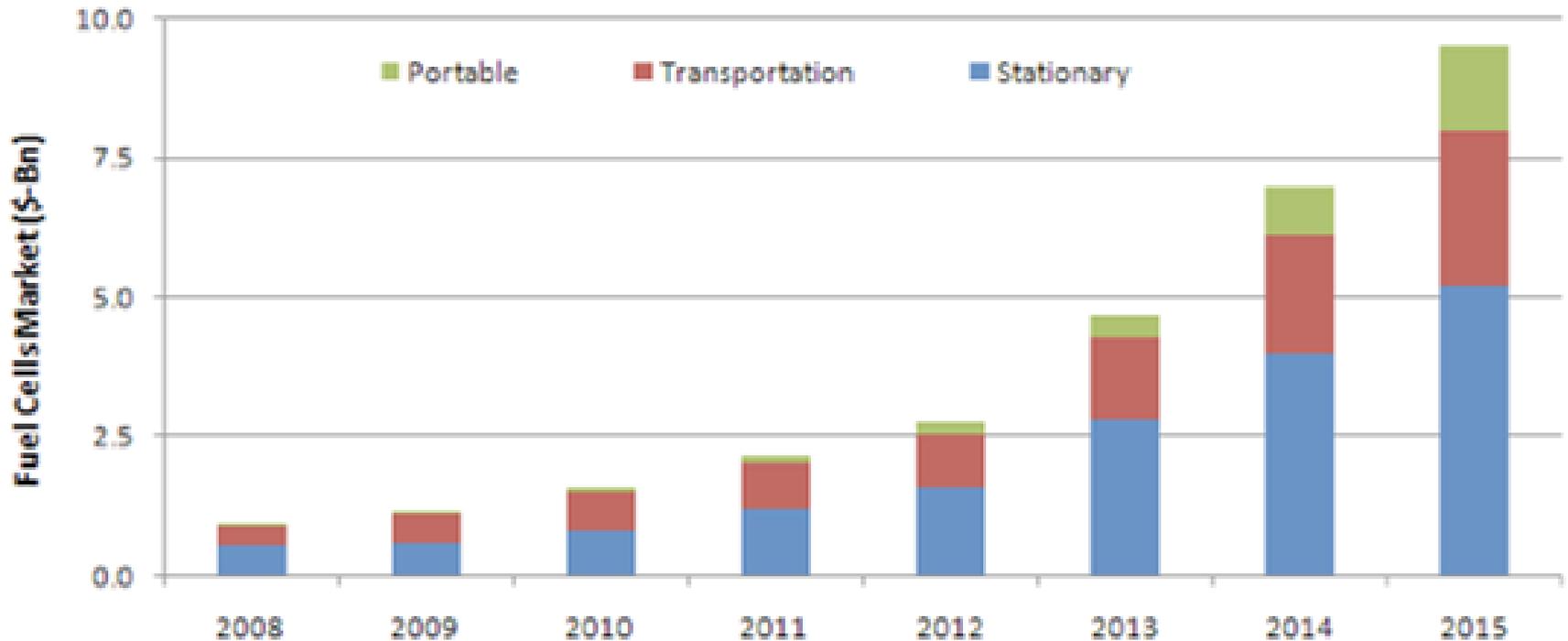
Characteristic	Units	2017 Targets
Maximum operating temperature	°C	>95
Maximum pressure differential between wet and dry sides	kPa	75
Water transfer flux at full flow ^a	g min ⁻¹ cm ⁻²	0.025
Durability ^b	h	5,000
Cost ^c	\$/m ²	10

^a Dry air in: 0.23 SLPM/cm² dry gas flow, 183 kPa (absolute), 80°C, 0% RH. Wet air in: 0.20 SLPM/cm² 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

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://hydrogen.doe.gov/peer_reviews.html

