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

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Tetramer Technologies, L.L.C.
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Project ID # FC102

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Overview of Current Project

Timeline

- Start: Sept 17, 2012
- End: Sept 16, 2014
- Phase II Effort Complete: 80%

Budget

- Total Phase II project funding
  - DOE share: $999,815
  - Contractor share: $325,000
- Funding received in FY 13:
  - $524,131
- Total funding planned for FY14:
  - $305,855

Barriers

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

Partners

- Dana Holding Corporation
- General Motors
- Ballard
- Membrane Technology Research

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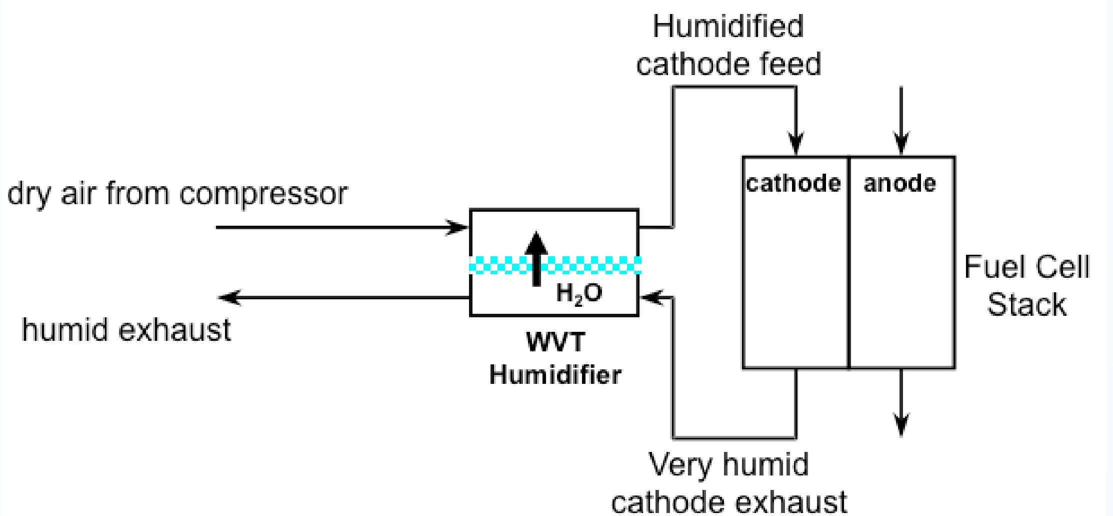
Relevance to DOE

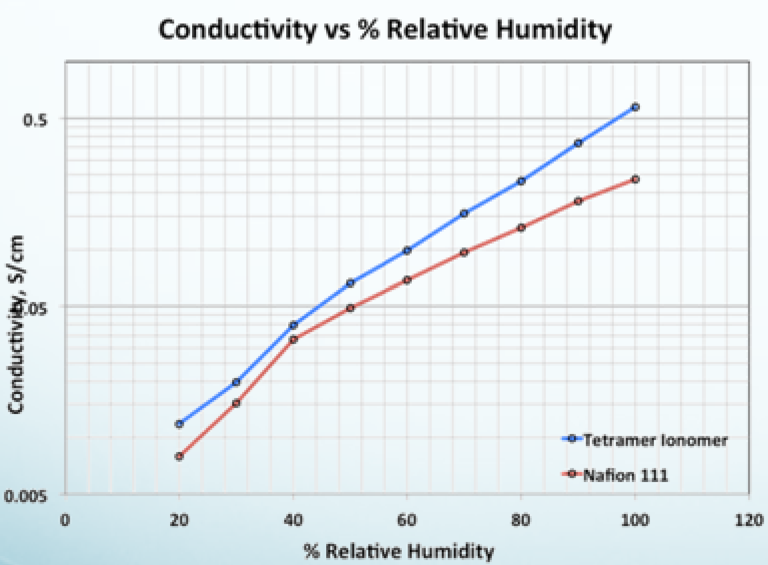
Design and develop high performance, low cost water vapor membranes for cathode humidification

DOE Barriers	2017 DOE Technical Targets Humidifier Membrane	Tetramer Targets Year 1	Tetramer Targets Year 2
Performance	• Maximum Operating Temperature >95 °C • Maximum Pressure differential 75 kPa • Water transfer flux =4.17 g sec^{-1} m^{-2}	Consistently produce 2.58 g sec^{-1} m^{-2} with no chemical degradation over 2000 hours	Produce 3.32 g sec^{-1} m^{-2} 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$ 500,000 systems per year	<$20/$m^2$ 500,000 systems per year	<$10/$m^2$ 500,000 systems per year

Relevance and Motivation

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





- **Water Vapor Transport (WVT) unit transfers moisture that is formed from fuel cell reactions within the stack from the cathode exhaust to the feed**
- **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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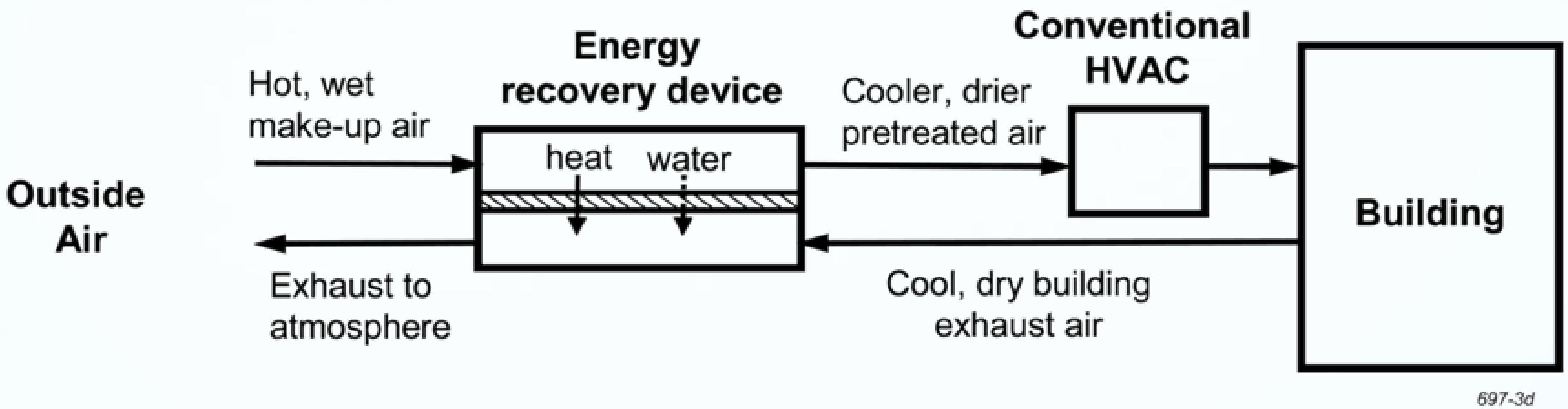
Relevance-HVAC Energy Savings



- On a summer day in the South Carolina midlands and coastal plains, 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.

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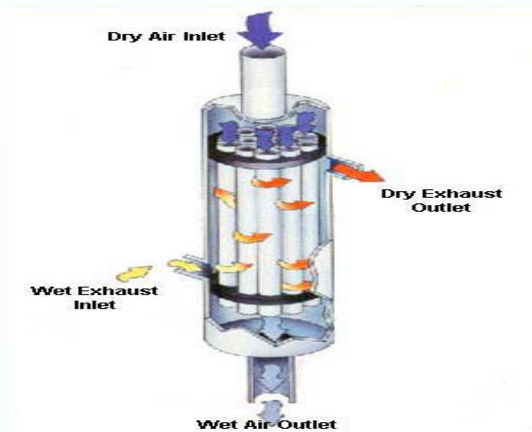
Approach: Current State of the Art

- Perma Pure™ units containing Nafion® have not yet met the desired cost, 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 <u>degradation was detrimental to permeation performance with a loss in permeance of up to 60% within 500 hours.</u>

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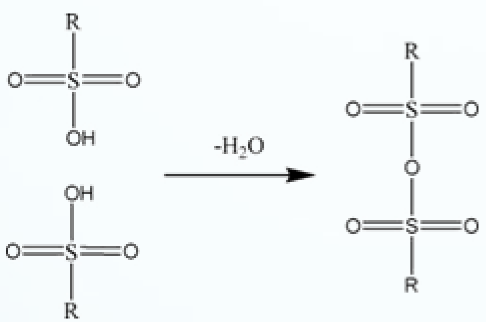
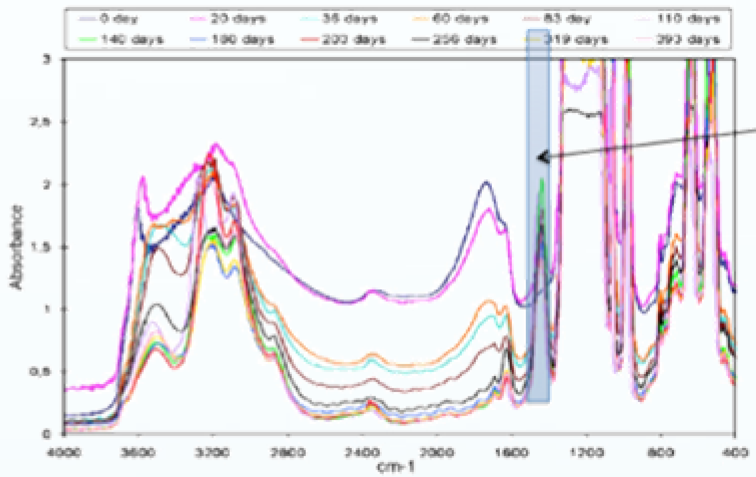
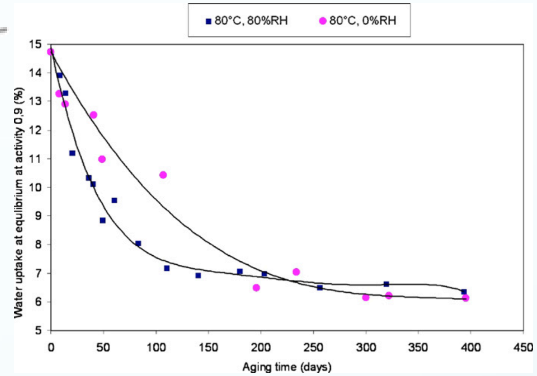
Approach: Current State Of The Art – WVT Commercialization Show Stoppers

- Anhydride Formation: Collette concluded that upon heating samples of PFSA at 80 °C, the formation of sulfonic anhydrides were seen.





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



- Ionic Contamination: In 2012 W.L. Gore (FC 067) demonstrated that salt contamination can contribute to >70 % reduction in water vapor permeance

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

Approach/Milestones
New Tetramer WVT Membranes

Year 2 Milestones	Completion Date	Status
Synthesis of new polymers with minimum target flux of 2.58 g sec^{-1} m^{-2} with an optimum performance of 3.32 g sec^{-1} m^{-2}	Feb. 2014	2.58 Achieved
Scale up to kg quantities	Sept. 2014	2 kg Achieved

Design proprietary polymer architectures which provide multiple water transport paths while mitigating or eliminating degradation pathways.

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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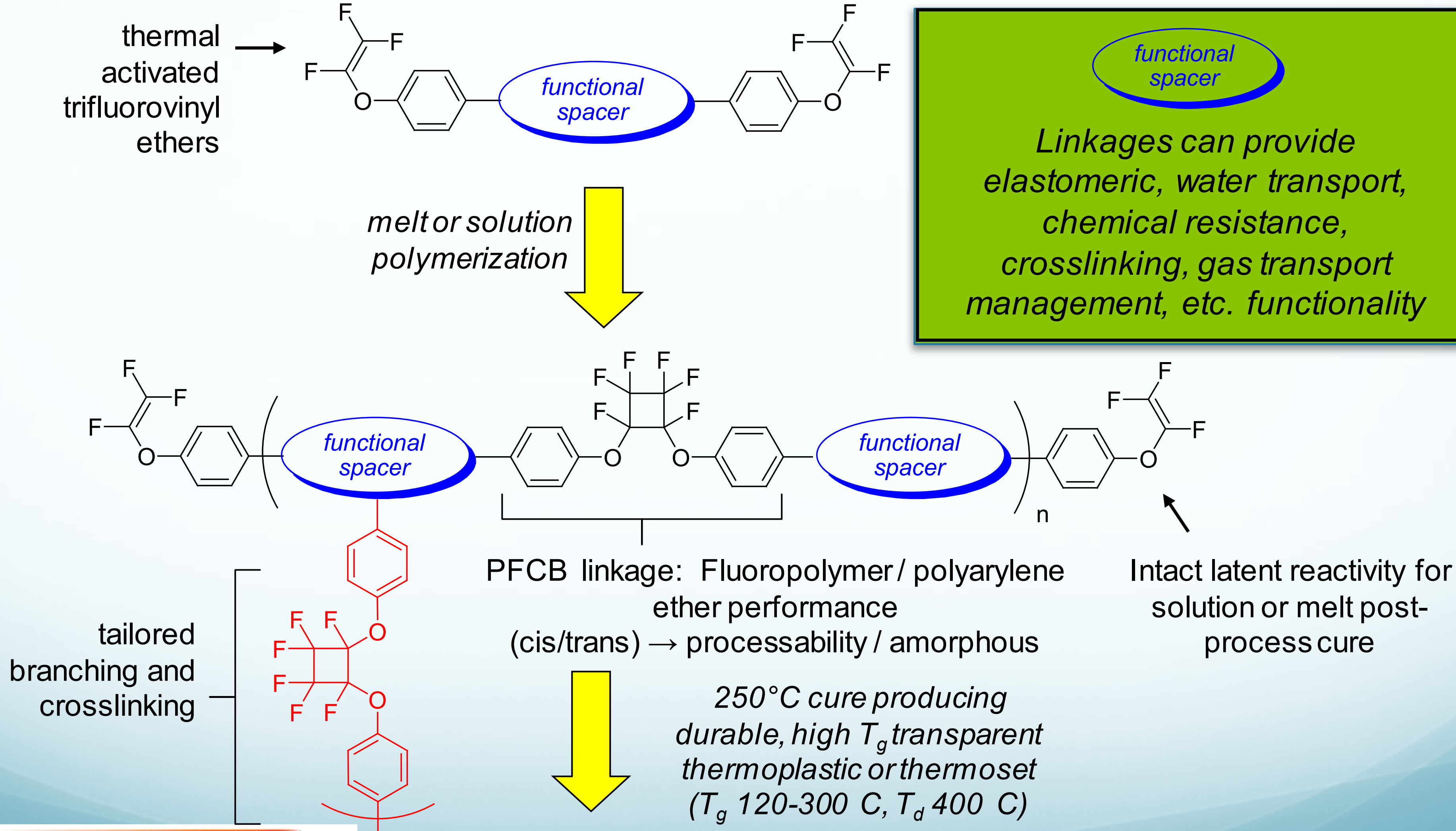
Approach: New PFCB Polymer Technology

versatility • processability • performance



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WVT Technical Accomplishments: New 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

- Synthesis of 15 new monomers and 26 new film forming polymer structures with these architectures have been achieved
- 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

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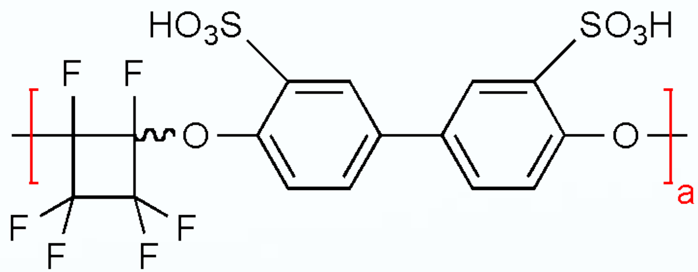
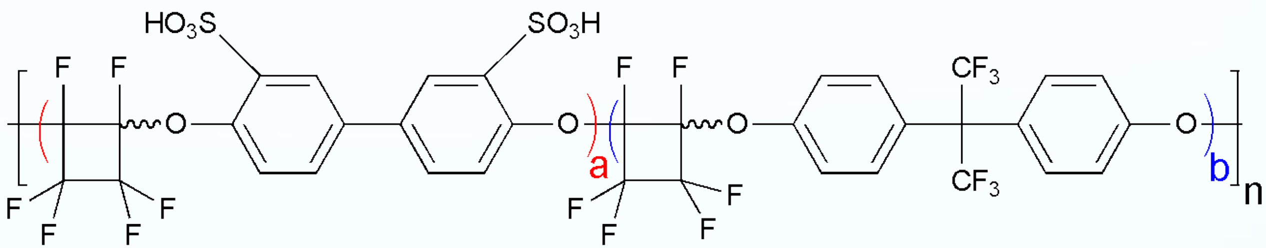
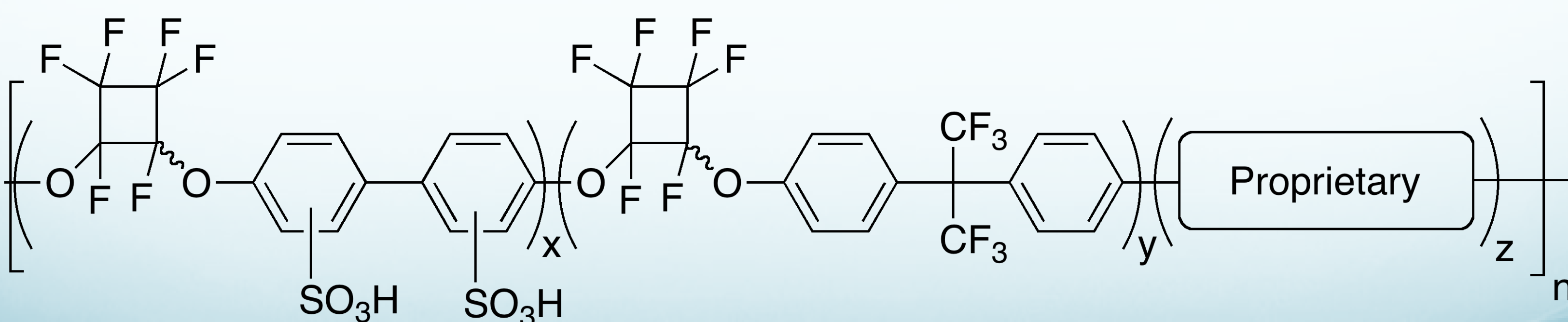
WVT Technical Accomplishments: New Polymer Molecular Architecture Design







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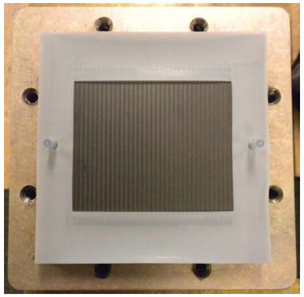
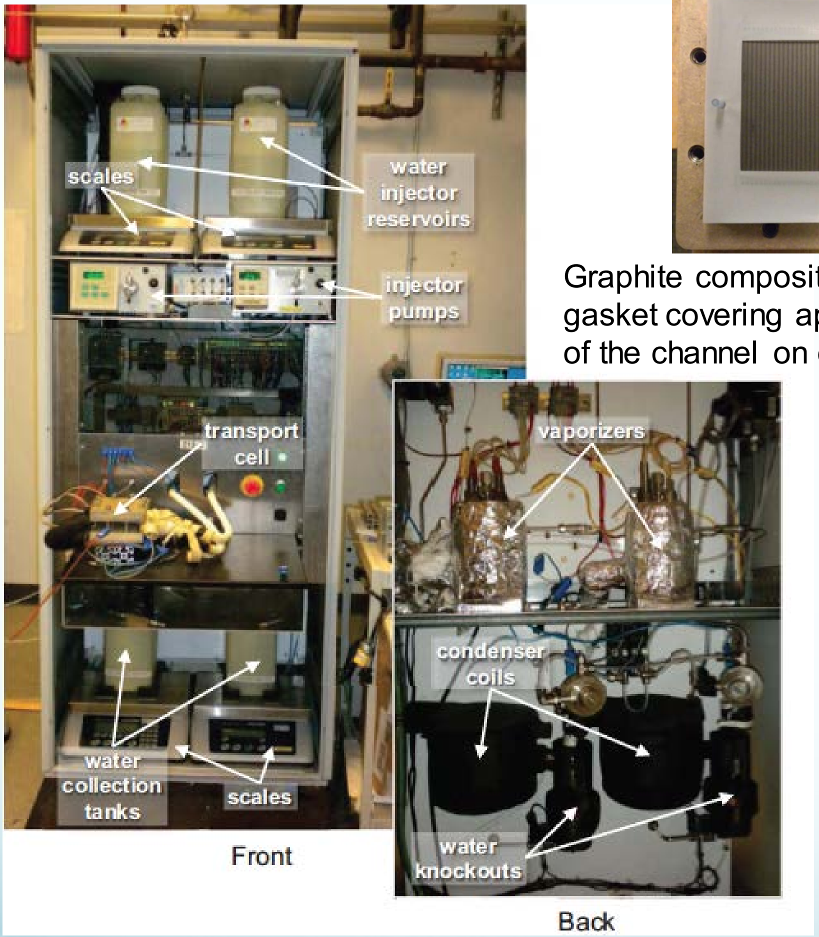
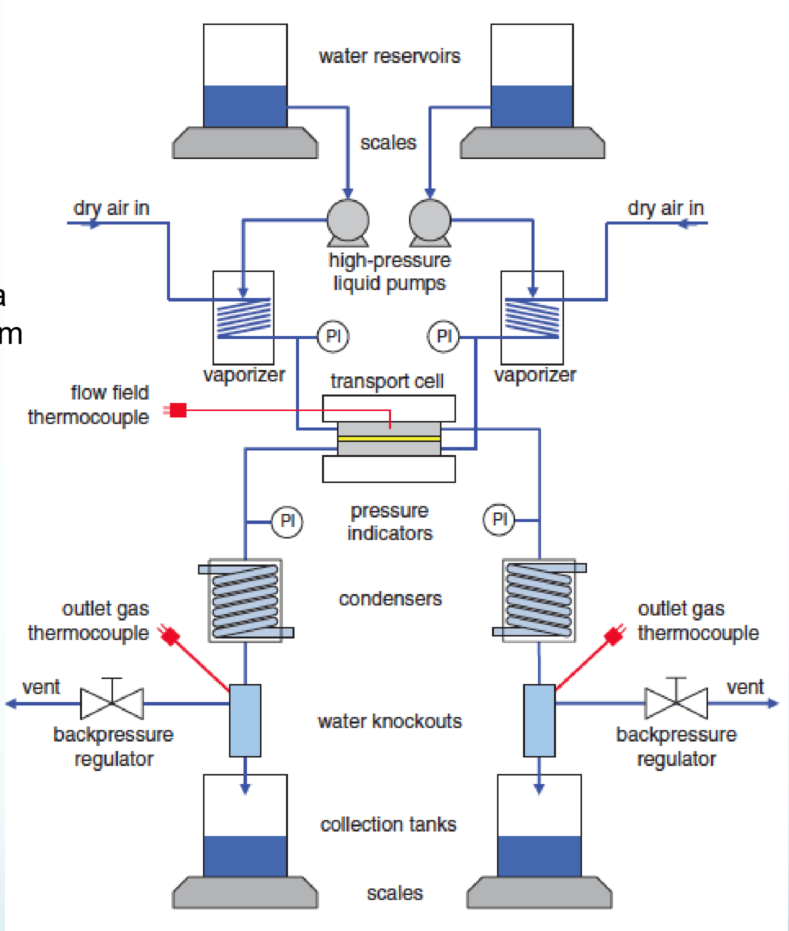
WVT Technical Accomplishments: MTR Provided Water Vapor Test Stand



Graphite composite flow field with a gasket covering approximately 5 mm of the channel on either end



Photographs of the test stand showing the location of various components



Schematic illustration of the test stand components

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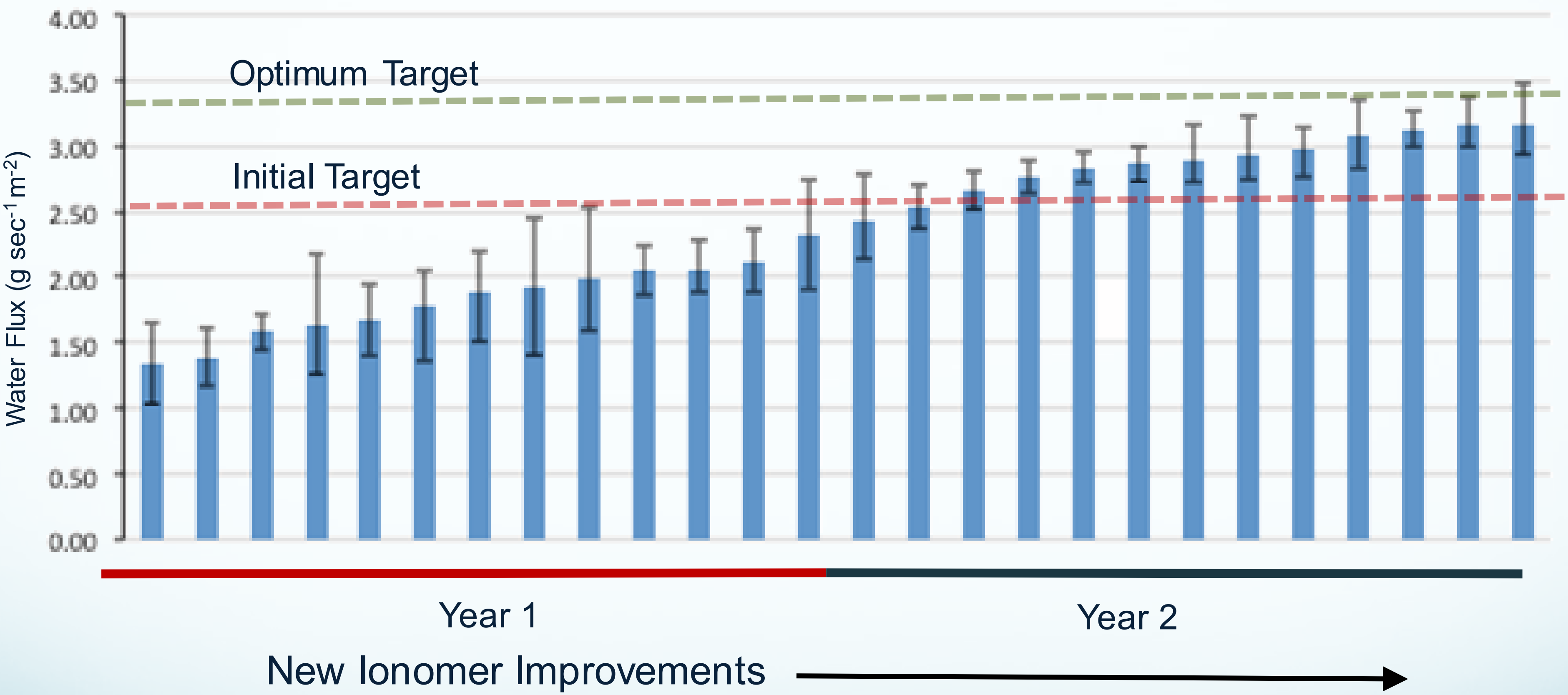
WVT Technical Accomplishments: Tetramer Membrane Improvements



- New Tetramer WVT membranes showed high water vapor gas permeation. These materials exceeded current commercial materials under DOE and commercial customer conditions

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WVT Technical Accomplishments: No Anhydride Formation

BLOCK A
Water Permeability
Hydrophilic groups, Ionic or Intermolecular attractions

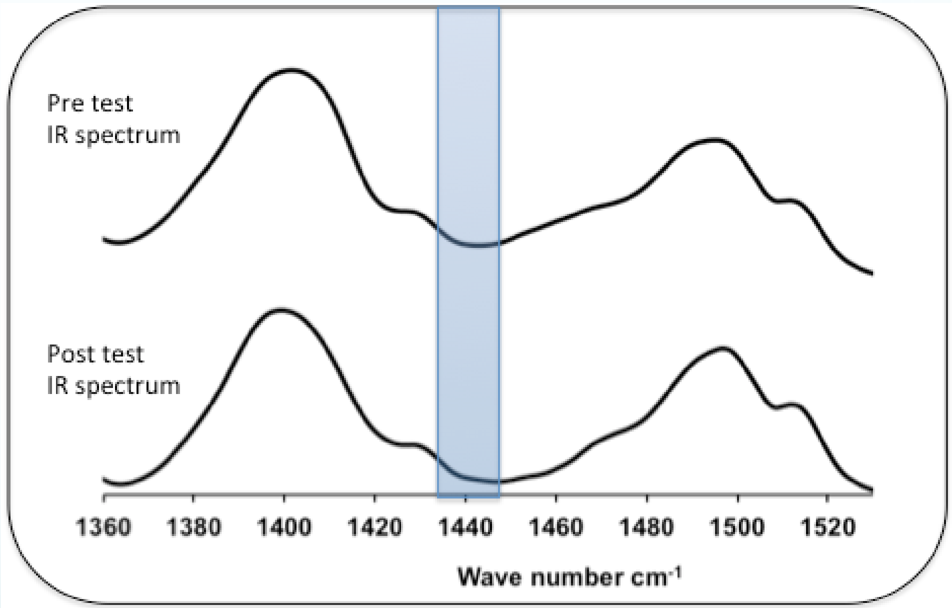
BLOCK B
Mechanical Strength
Rigid structures
Hydrophobic linkages

BLOCK C
Processability
Stereoisomeric structures,
Solubilizing groups

BLOCK D
Stability
Chemical resistance,
Crosslinking

- New synthetic polymers were tested under both Collette, et al. conditions at 80°C and 95°C for 240 hours and 4 hours at 140°C with <u>no indication of anhydride</u> formation at 1440 cm^{-1} in infrared!!

- Analysis of membranes after industrial partner testing up to >100°C has also shown no anhydride formation.



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WVT Technical Accomplishments

- RECENT TESTING OF TETRAMER WVT MEMBRANES BY INDUSTRIAL PARTNERS UNDER VARYING REAL WORLD COMMERCIAL CONDITIONS LOOK PROMISING vs. COMPETITOR MEMBRANES

- INDUSTRIAL PARTNER TESTING HAS EXPANDED TO INVOLVE SIGNIFICANTLY HIGHER TEMPERATURES THAN DOE TARGETS RANGING FROM 80 ^{o}C TO >100 ^{o}C.

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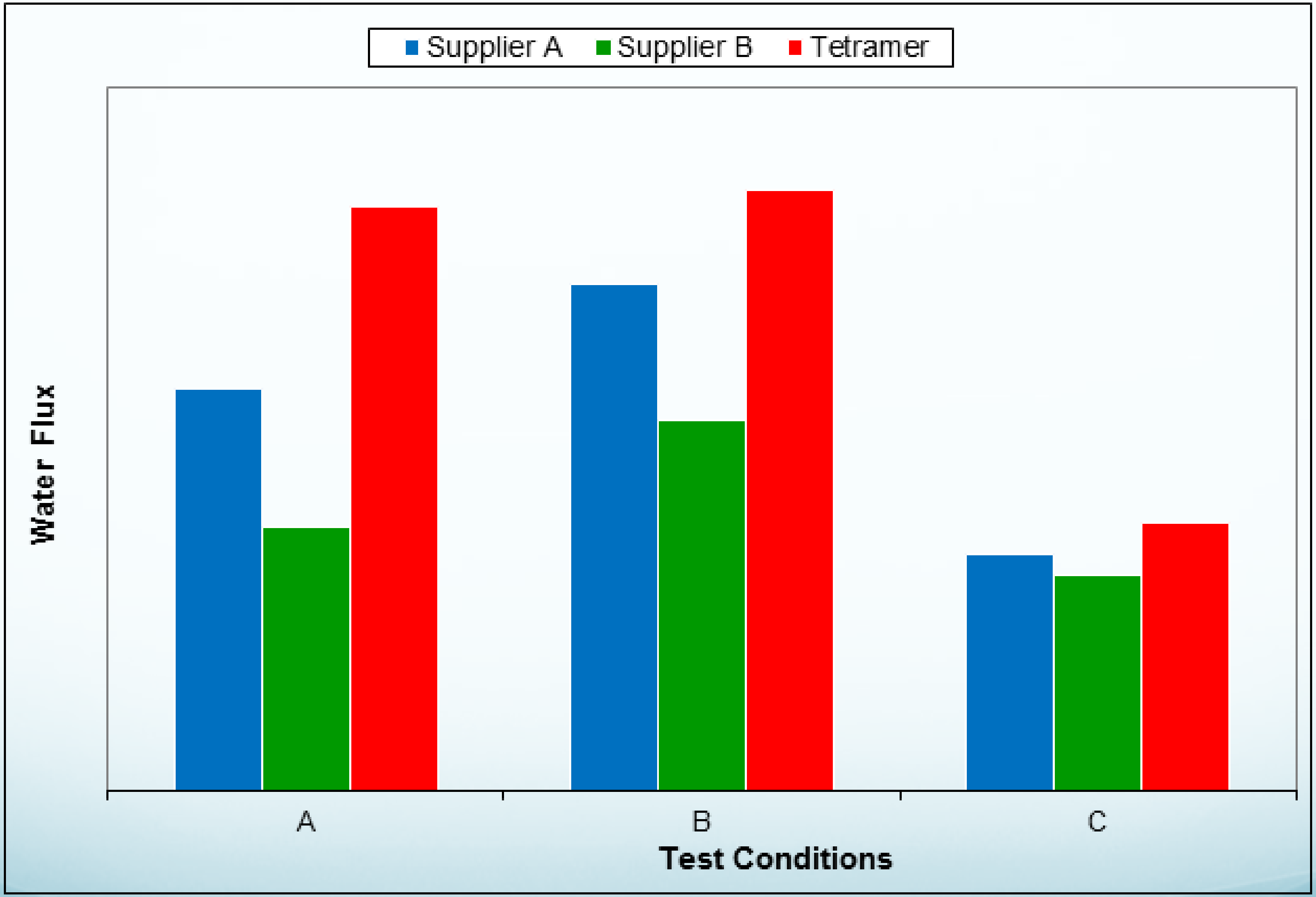
COMPARISON OF TETRAMER'S MEMBRANES VS COMMERCIAL COMPETITION



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Examples of Test Conditions

Condition	Dry air in				Wet air in			
	Dry gas flow (SLPM/cm^2)	Absolute pressure (kPa)	Temp (°C)	RH (%)	Dry gas flow (SLPM/cm^2)	Absolute pressure (kPa)	Temp (°C)	RH (%)
DOE Conditions	0.23	183	80	0	0.20	160	80	80
Example 1	0.13	178	80	0	0.13	146	80	69
Example 2	0.26	260	99	0	0.23	220	95	80
Example 3	0.29	246	>105	0	0.24	220	95	80

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Accomplishments: Scale-up and Development

1) Synthesis scale up from 50 g to 2 kg of the down selected material was successful

2) Cost target of $\$20/m^2$ for the ionomer achieved and $\$10/m^2$ is on target

3) 12 m^2 of membrane has been successfully coated through a commercial roll coater

1) These membranes tested fine at 80°C, but the conditions greater than 100°C caused the membrane to lose permeation and generate leaks.

2) Forensic analysis has indicated that the dimethylacetamide solvent used is causing problems

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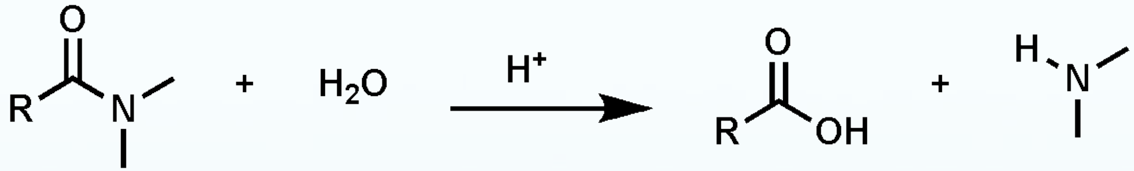
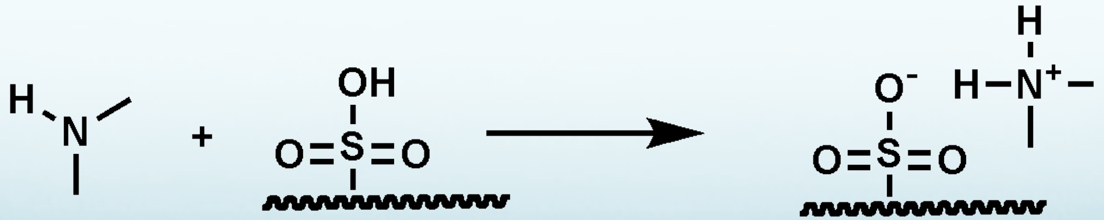
NEW WVT Potential Show Stopper Explored - Current Hypothesis: Solvent Association and Degradation

- Commonly used casting solvents for ionomers such as dimethylacetamide exhibit have shown strong interactions with sulfonic acid groups*

- The decomposition of dimethylacetamide through acid hydrolysis to form dimethylamine has been observed.

- 1) 

- 2) 

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* Kaliaguine, S. et al., "Casting solvent interactions with sulfonated poly(ether ether ketone) during proton exchange membrane fabrication", J. Memb. Sci. 330 (2009) 113-121.

NEW WVT Potential Show Stopper Explored – Current Hypothesis: Solvent Association and Degradation

- Tetramer ionomers were reacted with diethyl amine to demonstrate the formation the sulfonic acid amine salt

- A membrane with a flux of 2.61 g sec^{-1} m^{-2} after treatment with DEA decreased to 0.94 g sec (64% loss in flux) immediately

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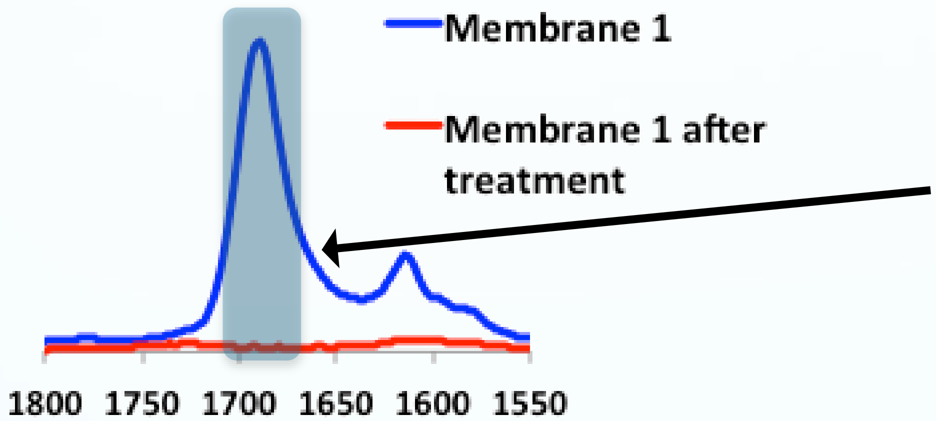
Solvent Problem Solutions Being Explored

1) Soaking membranes thoroughly to remove DMAC has shown positive results



Residual DMAC was removed after 24 h.

2) Develop new solvent system

Currently 6 new solvents are being explored

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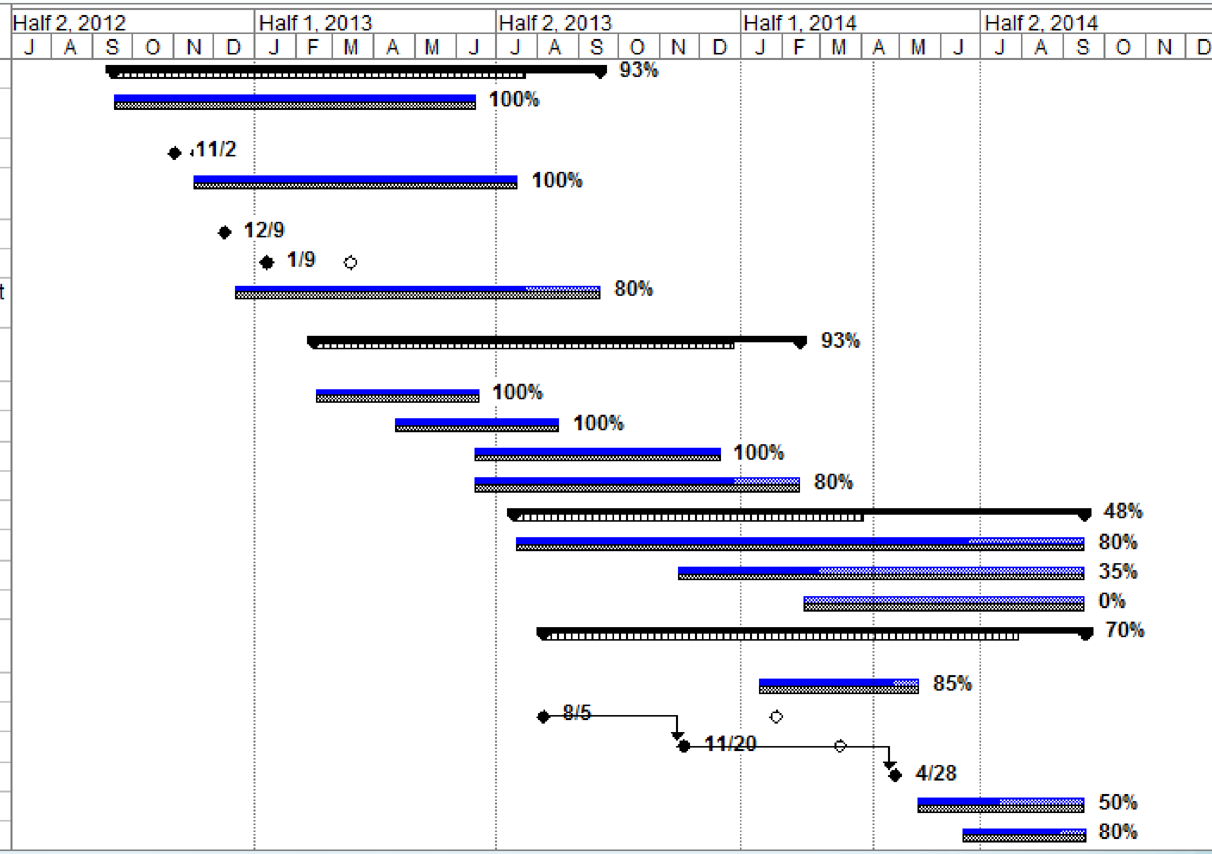
Accomplishments: 2 Year Task Schedule Overview and work progress

ID	Task Name
1	**Task 1: Performance Optimization for WVT Application**
2	Task 1.1: Synthesis of 8 New Monomers Resistant to Chemical Degradation
3	Synthesis of Stable Monomer
4	Task 1.2 Synthesis of 20 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



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Collaborations

Partners

- **Dana Holding Corporation (Industry)** has participated in testing and qualification of membrane materials according to automotive specifications.
- **General Motors (Industry)** has been a strong partner for over 5 years and has been very active in testing our materials
- **Ballard (Industry)** has received materials and done some very preliminary testing under non-automotive fuel cell conditions.
- **Membrane Technology Research (Industry)** has participated in membrane testing and will participate in module prototype production.

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Future Work for Phase II

- Resolve Solvent Degradation Issue
- Determine Optimum Support Composite Matrix
- Run Long Term Tests
- Manufacture 400 m^2 at commercial roll coater
- Construct Prototype WVT Module

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TASK SUMMARY TO DATE

- BOTH GM AND DANA TESTING SHOW ENCOURAGING WATER TRANSPORT RESULTS FOR NEW MOLECULAR ARCHITECTURES
- ANHYDRIDE FORMATION HAS NOT BEEN DETECTED
- 15 NEW MONOMERS, 26 NEW POLYMER STRUCTURES
- SCALE UP TO 2 KG. LEVEL HAS BEEN SUCCESSFUL

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TASK SUMMARY TO DATE

- PROTOTYPE COMMERCIAL ROLL COATING RUN WAS SUCCESSFUL- MORE PLANNED
- SOLVENT DEGRADATION ISSUES MUST BE RESOLVED BEFORE LONG TERM DATA ARE MEANINGFUL
- COST TARGET OF $\$20/m^2$ HAS BEEN ACHIEVED FOR THE IONOMER AND $\$10/m^2$ IS ON TARGET

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Water Vapor Membrane Development Summary

Relevance – Need still exists for improved low cost water vapor membranes for cathode humidification modules of fuel cells and HVAC applications.

Approach – Tetramer's new synthesis approach for new polymer molecular architectures has been validated as shown by increased water vapor transport with no degradation mechanisms at lower projected costs. Work is ongoing.

Technical Accomplishments – Detailed on previous slides. New monomers and polymers were successfully synthesized which have shown improved water vapor transport with no signs of chemical degradation.

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

Future Work – Resolve solvent degradation mechanisms and continue scale up for commercial roll manufacturing to evaluate durability and prototype construction.

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