2008 DOE Hydrogen Program

The Effects of Impurities on Fuel Cell Performance and Durability

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The University of Connecticut
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Project ID #FC31

Overview

Timeline

- Start March 2007
- End February 2011
- ~20% Complete

Barriers

- Establish Tolerance to Air, Fuel and System Derived Impurities

Budget

Total Project Funding $2,335,725
- DOE Share $1,868,580
- Contractor Share $467,145

Funding for FY07 - $350K
Funding for FY08 - $400K Received, $150K Anticipated

Partners

United Technologies Hamilton Sundstrand – Historical Contaminant Data
FuelCell Energy, Inc. - Contaminant Test Support
UConn CGFCC – Project Management, Testing, Modeling

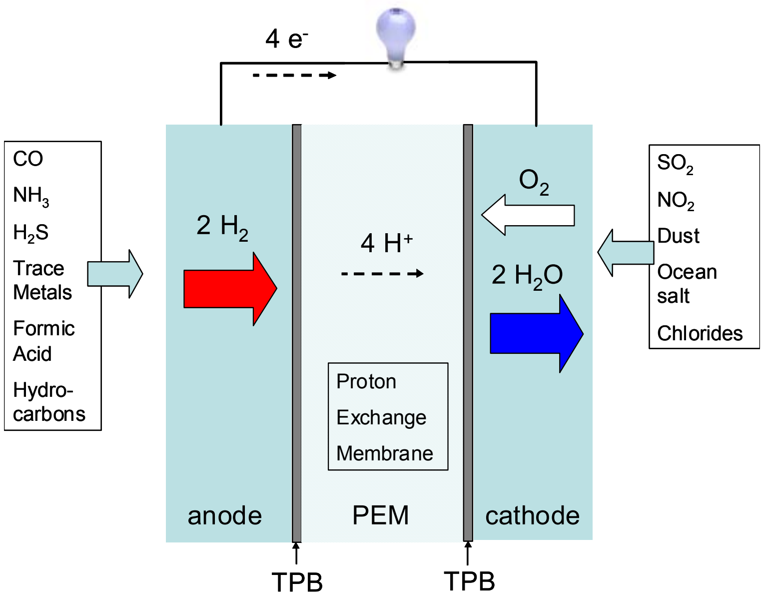
Objectives

- **Overall Objective – Develop an Understanding of the Effects of Various Contaminants on Fuel Cell Performance and Durability**
- **Specific Task Objectives Shown Below**

Task	Objectives
1.0 Contaminant Identification	• Identify specific contaminants and contaminant families present in both fuel and oxidant streams.
2.0 Analytical Method Development	• Development of analytical methods to study contaminants. • Experimental design of analytical studies. • Novel *in situ* detection methods.
3.0 Contaminant Studies	• Develop contaminant analytical models that explain these effects. • Establish an understanding of the major contamination-controlled mechanisms that cause material degradation in PEM cells and stacks under equilibrium and especially dynamic loading conditions
4.0 Contaminant Model Development	• Construct material state change models that quantify that material degradation as a foundation for multiphysics modeling • Establish the relationship between those mechanisms and models and the loss of PEM performance, especially voltage decay
5.0 Contaminant Model Validation	• Validate contaminant models through single cell experimentation using standardized test protocols.
6.0 Novel Mitigation Technologies	• Develop and validate novel technologies for mitigating the effects of contamination on fuel cell performance.
7.0 Outreach	• Conduct outreach activities to disseminate critical data, findings, models, and relationships etc. that describe the effects of certain contaminants on PEM fuel cell performance.

Approach

- Initiate Studies by Leveraging Existing Database From Prior Work
  - DOE Sponsored Activity
  - USFCC Data
  - Prior Electrolysis Product Experience
- Focus on Specific Contaminants/Concentrations Identified by DOE/Others
- Use Standardized Test Protocols Where Appropriate to Investigate Contaminant Effects
- Develop Empirical Models Based on Our Findings



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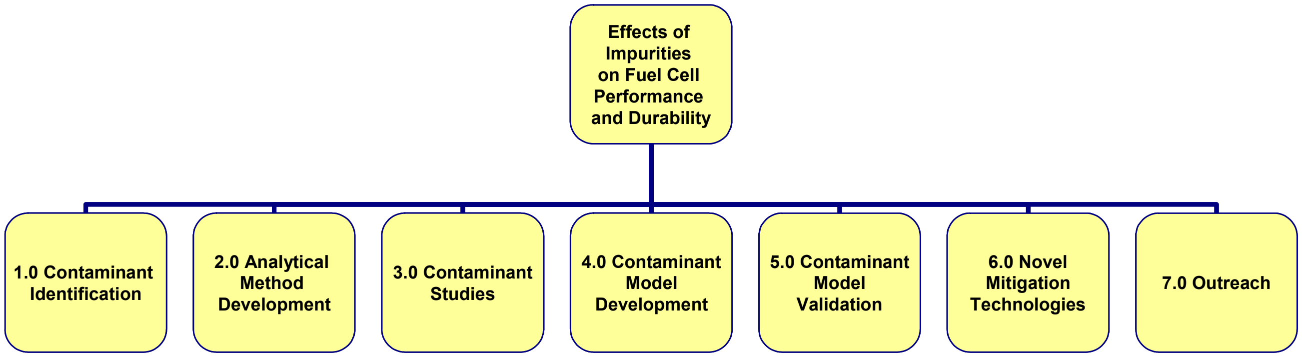
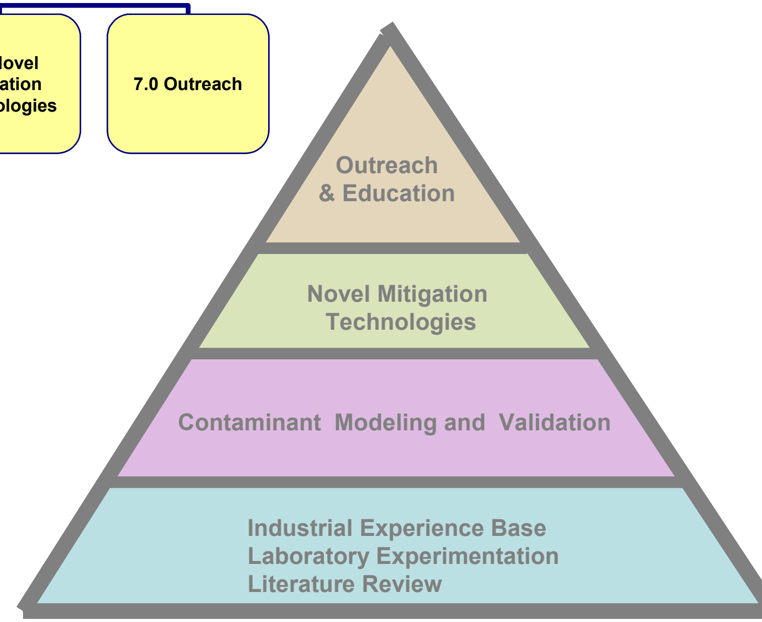
Project Work Plan/Deliverables





Deliverables

- Validated Contaminant Models
- New Mitigation Technologies

Outreach

Papers, Workshops, Technical Interchange, Etc.

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Roles of Participants

CGFCC
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The Universtiy of Connecticut
Connecticut Global Fuel Cell Center
Program Lead

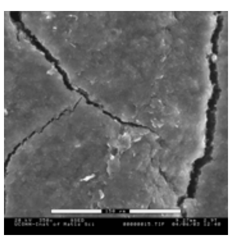
- **United Technologies Hamilton Sundstrand**
  Advise on Fate of Contaminants
- **The University of Connecticut Institute for Materials Science**
  Gas Analyses/Surface Studies
- **The University of Connecticut School of Engineering**
  Contaminant Testing
  Modeling & Mitigation Strategies
- **FuelCell Energy Inc.**
  Contaminant Identification
  Fuel Cell Testing

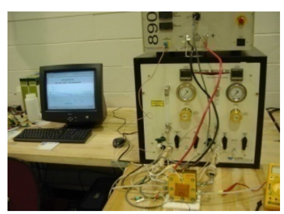
Electrolysis Contaminant Experience
Prior Contaminant Studies

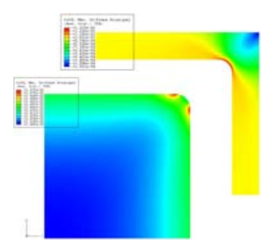
Surface Studies/Equipment
Gas Purity Analyses

Fuel Cell Testing
Modeling/Transport Expertise
Industry Relationships

Gas Contaminant Experience
Fuel Cell Test Experience







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In-Situ Contaminant Testing

Hydrocarbons and Halogenated Compounds

- Initiate Testing With Methane
- Establish Analytical Techniques, Test Protocols, Basic Performance Models
- Export Data in Common Format to Working Groups for Further Modeling
- Contaminant Strategy
  - Near Term Focus – Hydrocarbons and Halogenated Compounds
  - Choice Based on Industry Input
  - Start With High Level – Dilute if Effects are Noted
  - Empirical Models – Near Term
  - Multi-Physics Models – Long Term

In-Situ Contaminant Testing
Hydrocarbons and Halogenated Compounds

- Status (Contaminant Choices Based on Industry Input)
  - Methane - √
  - Ethane – √
  - Ethylene – In Process
  - Aldehydes – Formaldehyde, Acetaldehyde (In Process)
  - Organic Acids – Formic Acid
  - Glycols – Propylene Glycol, Ethylene Glycol

In-Situ Contaminant Testing
Hydrocarbons and Halogenated Compounds

MEA Definition

Parameter	Value
Membrane	Nafion 112
Anode Loading	0.4 mg/cm2
Anode Type	50% Pt on C
Cathode Loading	0.2 mg/cm2
Cathode Type	50% Pt on C
Cell Area	25 cm2
OEM	Fuel Cell Technologies

Operating Conditions

Parameter	Value
Anode Temperature	80C
Cathode Temperature	80C
Cell Temperature	80C
Anode Humidity	100%
Cathode Humidity	100%
Anode Stoich	1.3
Cathode Stoich	2.0
Anode Flow	Commensurate With Current Density
Cathode Flow	Commensurate With Current Density
Anode Pressure	25 psig
Cathode Pressure	25 psig

Cell Conditioning and Tests Performed in Accordance With Standardized Protocols

- Cell Conditioning and Verification per section 4.2 Appendix B Round Robin Test Results Document.
- ECA Measurement Per Appendix 8.
- H2 Crossover Per Appendix 7.
- Polarization Under Standard Hardware Conditions 0 – 1.3 A/cm2 per table next page, with a data sample rate of 25 sec. Repeat 3 times.

In-Situ Contaminant Testing

Hydrocarbons and Halogenated Compounds

Current	Time
20 Amp	1 Min.
25 Amp	1 Min.
30 Amp	1 Min.
25 Amp	15 Min.
20 Amp	15 Min.
15 Amp	15 Min.
10 Amp	15 Min.
5 Amp	15 Min.
Open Circuit	1 Min.
5 Amp.	10 Sec.
10 Amp	10 Sec.
15 Amp	10 Sec.
20 Amp	10 Min.

- Durability Test at 800 mA/cm2 for 100 Hours Under Standard Conditions.
- Durability Test at 800 mA/cm2 for 100 Hours Under Standard Conditions – except with TBD Conc.[1] contaminant in hydrogen.
- Repeat at 600 mA/cm2
- Repeat at 200 mA/cm2

1) 5% - 100 PPM – 50 PPM

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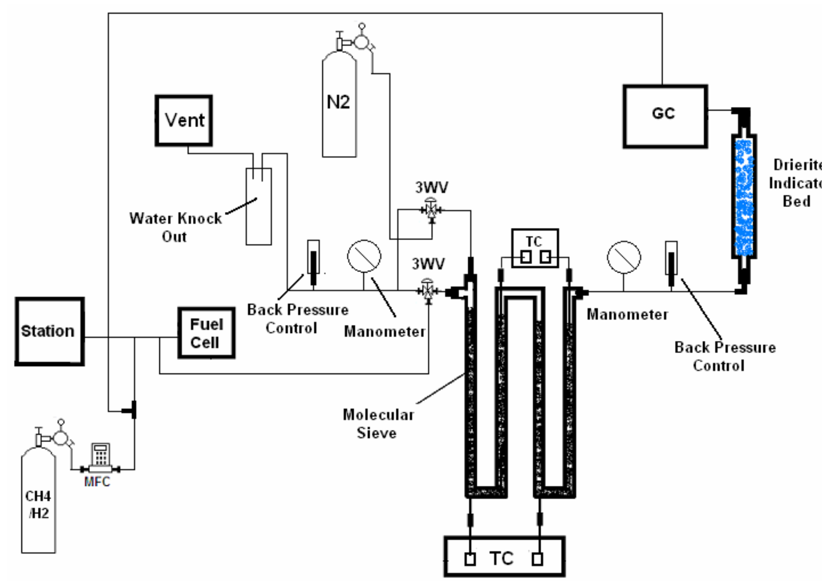
In-Situ Contaminant Testing
Hydrocarbons and Halogenated Compounds

- Lab Test Stand Configured for Initial Testing
- GC & Mass. Spec. Set Up for Contaminant Analysis
- Second Lab Test Stand Just Came Online
- Expect Additional Test Capability This Summer



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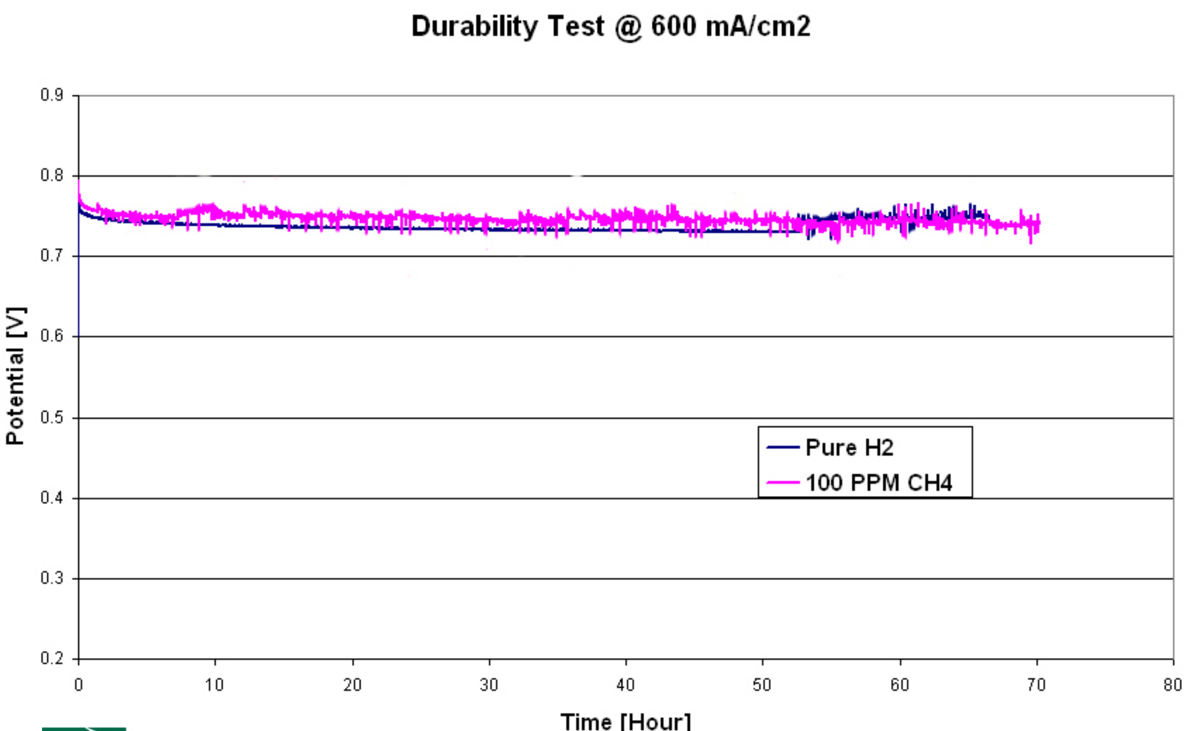
Durability Test (100 hours with/without CH4)

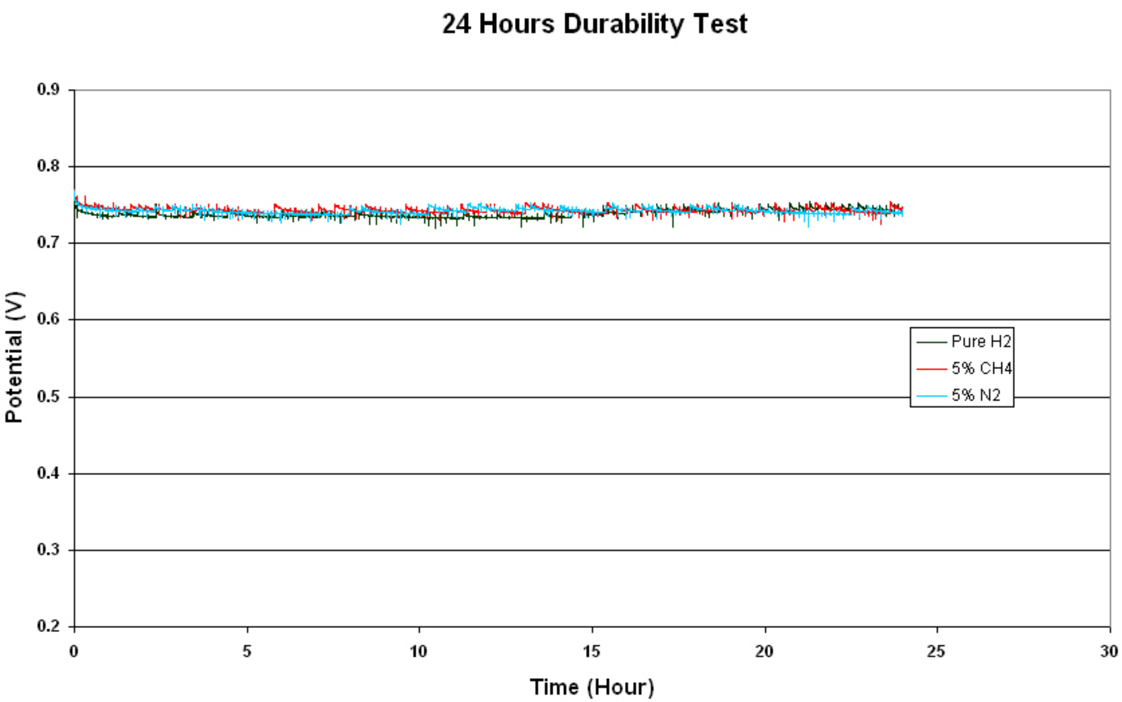
Anode / Cathode Pressure: 25 psig / 25 psig **Control Current @ 600 mA/cm^2**
Cell Temp: 80 ° C **Humudifier: 80 ° C**
Anode / Cathode Flow Rate: 175 sccm / 642 sccm



- Data Track Well for All Current Densities, Concentrations

Durability Test (24 hours with/without CH4, N2)

Anode / Cathode Pressure: 25 psig / 25 psig **Control Current @ 600 mA/cm^2**
Cell Temp: 80 ° C **Humudifier: 80 ° C**
Anode / Cathode Flow Rate: 175 sccm / 643 sccm

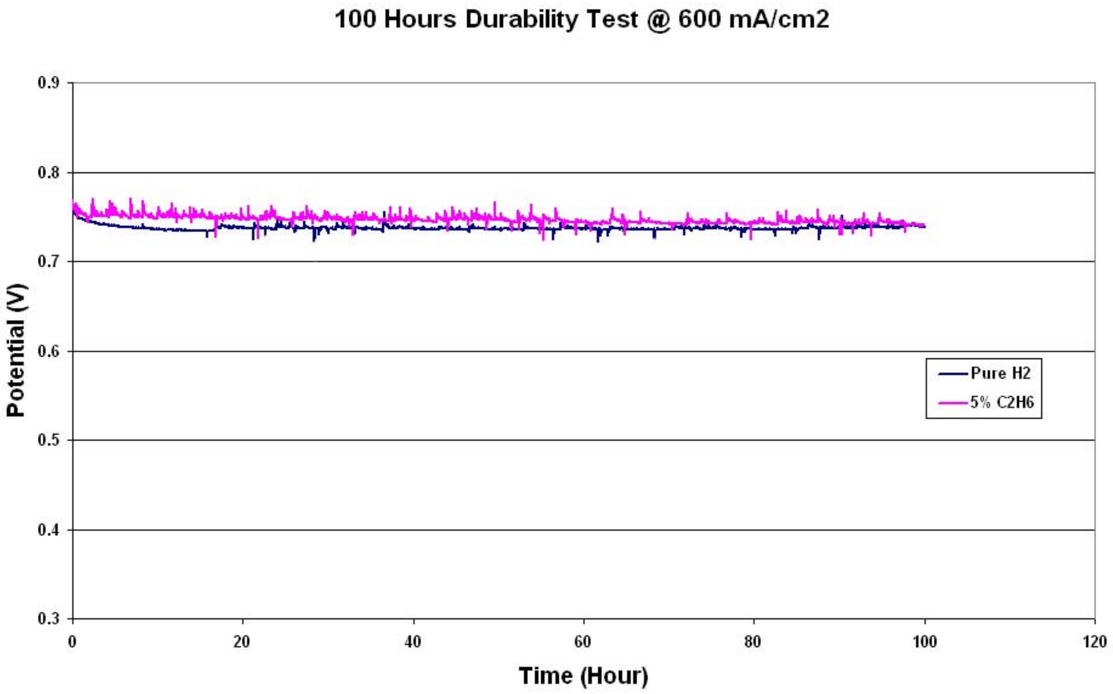


Data Show No Dilution Effect With Either N_2 or CH_4

Durability Test (100 hours with/without C_2H_6)

Anode / Cathode Pressure: 25 psig / 25 psig
Cell Temp: 80 ° C
Anode / Cathode Flow Rate: 172 sccm / 643 sccm

Control Current @ 600 mA/cm^2
Humudifier: 81 ° C / 80 ° C
Mixing Flow Rate: 9 sccm



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Membrane Studies
Cationic Contaminants

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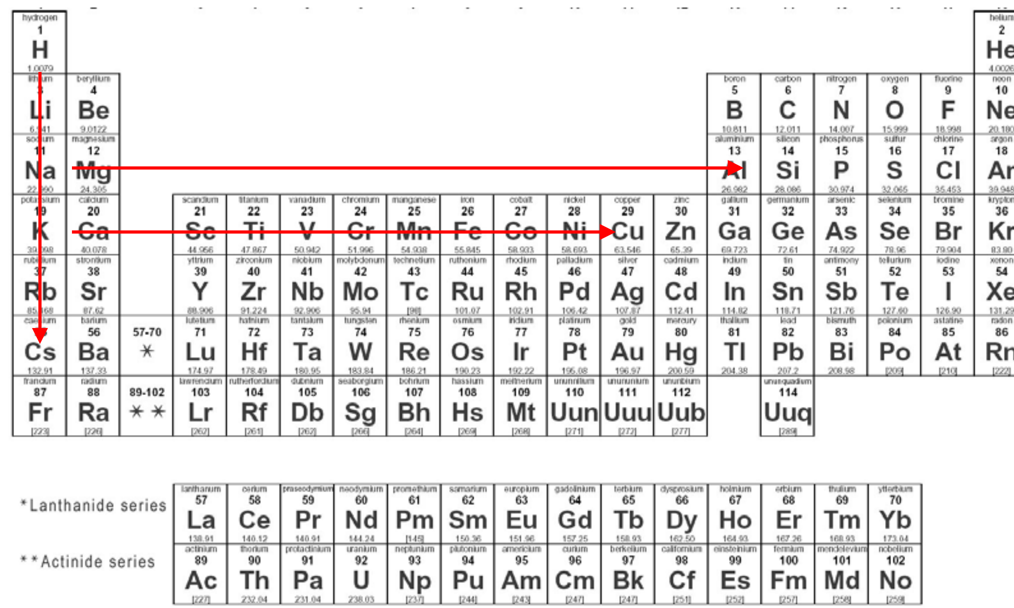
- Focus is on Membrane Properties Rather Than Fuel Cell Operational Tests
  - Fluids Permeability
  - Water Content
  - Ion Exchange Capacity
  - Conductivity/Ionic Resistance
  - Mechanical Properties
  - Contaminant Characterization Using SEM/EDX
- Move Down and Across Periodic Table to Examine Mass and Valence Effects of Common Ions



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Cation Evaluation - Test Matrix

Molarity	Ion	Sample Preparation	Water Content	IEC	N2 Permeability	H2 Permeability	O2 Permeability	Hydrodynamic Permeability	AC Resistance - Through Plane	Compressive Strength & Modulus	UTS & Elongation @ Break	Ionic Uptake	Ionic Dispersion and Transport
0	H+												
0.01	Na+												
0.1	Na+												
1	Na+												
0.01	Li+												
0.1	Li+												
1	Li+												
0.01	K+												
0.1	K+												
1	K+												
0.01	Cs+												
0.1	Cs+												
1	Cs+												
0.01	Mg+2												
0.1	Mg+2												
1	Mg+2												
0.01	Al+3												
0.1	Al+3												
1	Al+3												
0.01	Ca+2												
0.1	Ca+2												
1	Ca+2												
0.01	Cr+3												
0.1	Cr+3												
1	Cr+3												
0.01	Fe+2												
0.1	Fe+2												
1	Fe+2												
0.01	Ni+2												
0.1	Ni+2												
1	Ni+2												

Membrane Preparation & Contaminant Choices

Membrane Preparation

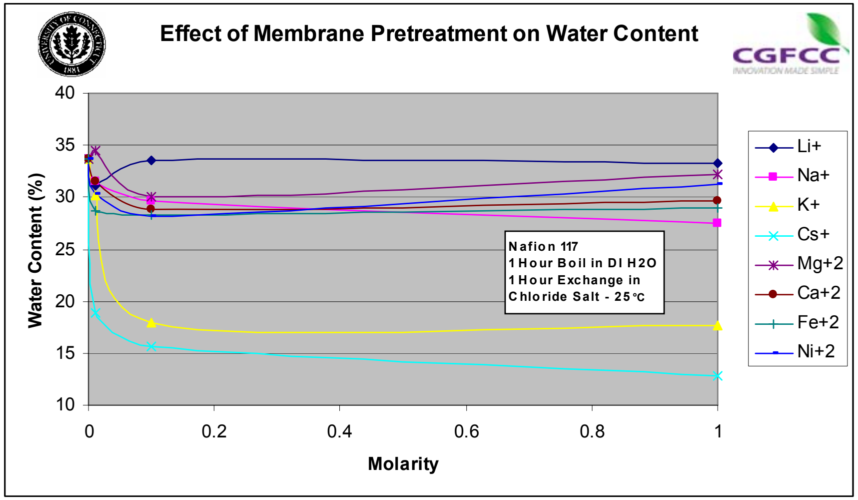
- Nafion 117 Membrane
- 1 Hour Boil in DI H_2O
- 1 Hour Soak in Cation Salts
  - 1 M
  - 0.1 M
  - 0.01 M

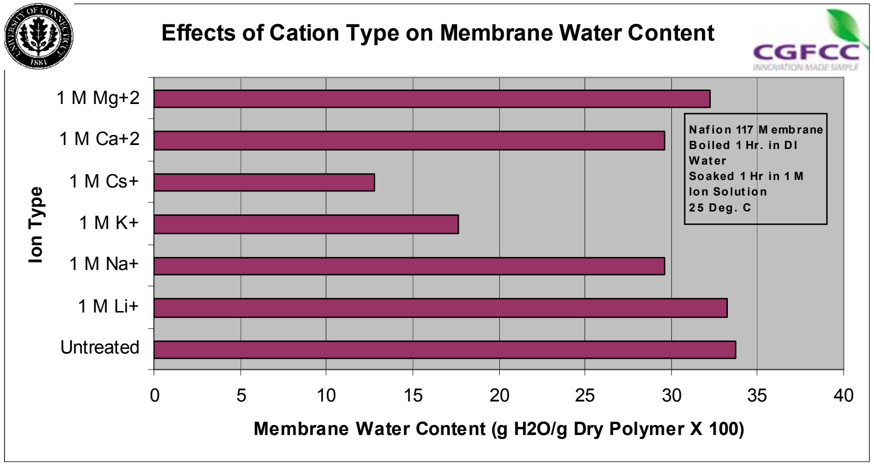
Contaminants Chosen From Constituents of Common Automotive Alloys Per Industry Recommendation, Plus Related Families of Constituents to Establish Scientific Trends

- Carbon Steels
- Low and Intermediate Alloy Steels
- Stainless Steels
- Copper and Copper Alloys
- Nickel and Nickel Alloys
- Aluminum Alloys

Water Content Assessment

- Membrane Water Content Drops Significantly With Cation Exposure
- Membrane Water Content Decreases Significantly as We Move Down Periodic Table – Largely Due to the Change in Hydration Shell for Each Ion





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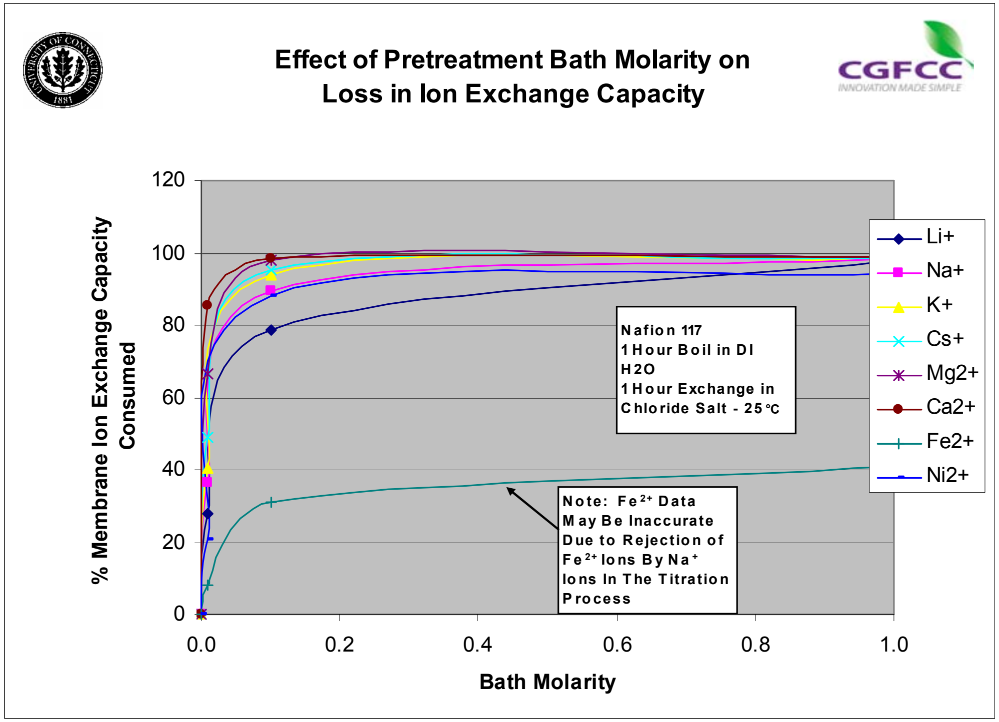
Ion Exchange Capacity

- Nearly 100% of Ion Exchange Sites Consumed for Most Cation Contaminants
- Sites Consumed at Low Concentration



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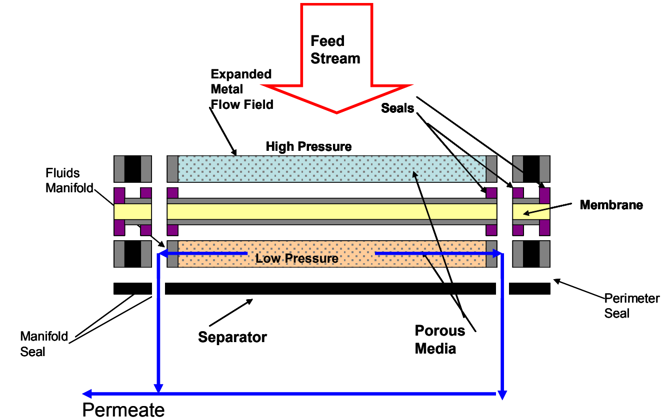
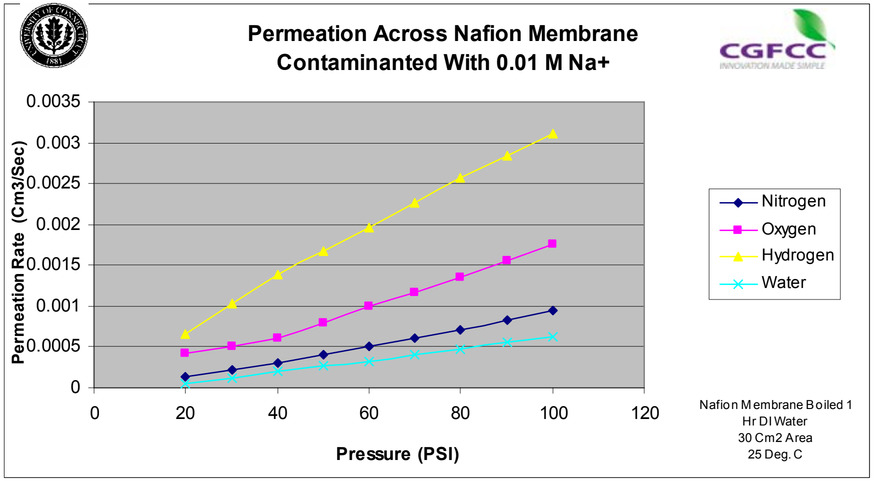
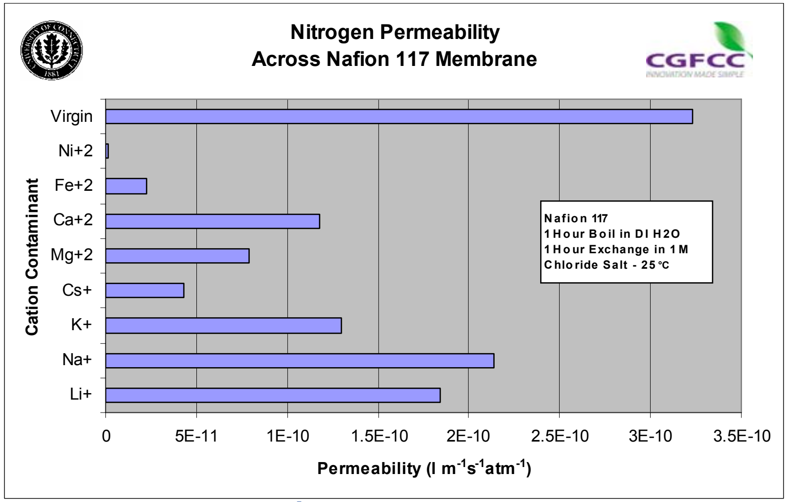
Fluids Permeability

- Permeability of Various Fluids Characterized
- Permeation Rate Appears to be Linear With Pressure (Fick's Law)
- Cationic Contaminants Affect Permeability in Different Ways
  - H_2, O_2, N_2 and H_2O Reduced







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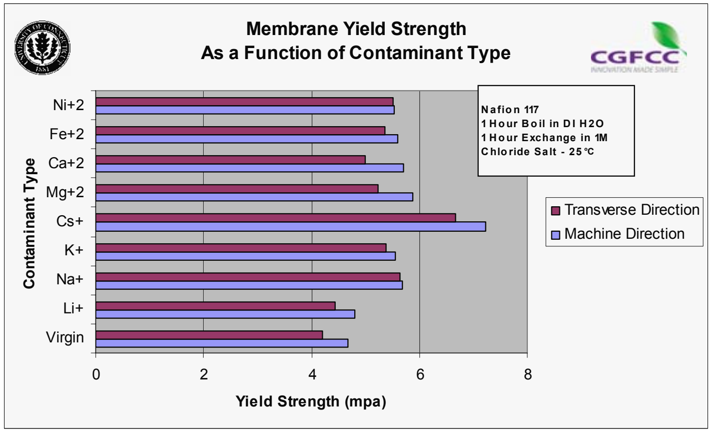
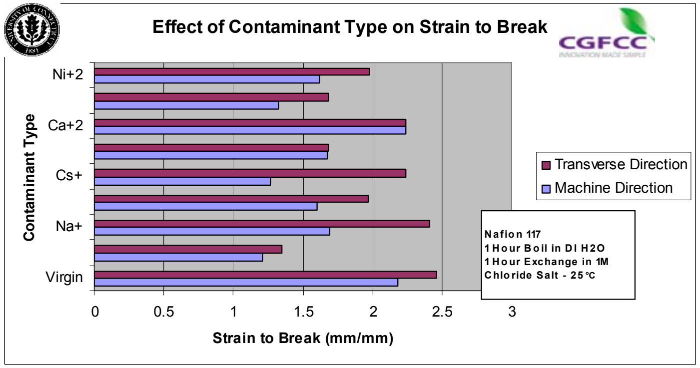
Mechanical Properties

- Yield Strength and Modulus Found to Increase With Contamination
- Tensile Strength and Elongation at Break Found to Decrease With Contamination





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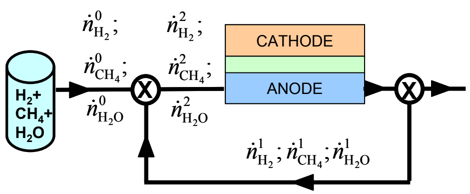
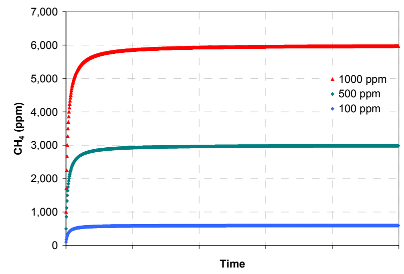
Impurities Modeling





- 6 Faculty Members Involved in Impurities Modeling
  - 4 Multi-Physics Based Modeling
  - 2 Models Based on Numerical Techniques
- Two Objectives
  - Interpret Existing Experimental Data
  - Develop a Predictive Tool to Analyze Effects of a Given Fuel Mixture
- Modeling at Different Levels
  - Systems Level
  - Macroscopic Fuel Cell Modeling
    - Kinetics
    - Transport
    - Durability
  - Microscale Modeling
- Validation

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Future Work

Task	Yr 1				Yr 2				Yr 3				Yr 4			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
1.0 Contaminant Identification	■	■														
2.0 Analytical Method Devt.		■	■	■												
3.0 Contaminant Studies				■	■	■	■	■								
4.0 Contaminant Model Devt.							■	■	■	■	■	■				
5.0 Contaminant Model Validation									■	■	■	■	■			
6.0 Novel Mitigation Tech.													■	■	■	■
7.0 Outreach	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
8.0 Project Management and Reporting	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■

Task	Milestone	Date Year/Quarter
1.0 Contaminant Identification	• Contaminant Identification Review With DOE Sponsor & Industry Focus Group	Y1/Q2
2.0 Analytical Method Development	• Validate Analytical Methods For Studying Contaminants With Ersatz Gases	Y1/Q4
3.0 Contaminant Studies	• Establish an Understanding of the Major Contamination-Controlled Mechanisms that Cause Material Degradation	Y2/Q4
4.0 Contaminant Model Development	• Determine the Relationship Between Contaminant Mechanisms and the Loss of PEM Performance, Especially Voltage Decay.	Y3/Q4
5.0 Contaminant Model Validation	• Validate Contamination Models Through Single Cell Experimentation Using Standardized Test Protocols and a DOE Approved Test Matrix	Y4/Q1
6.0 Novel Mitigation Technologies	• Demonstrate Novel Technologies for Mitigating the Effects of Contamination on Fuel Cell Performance	Y4/Q4
7.0 Outreach	• Dissemination of Results Through Reports (DOE Approved), Papers and Workshops	Continuous
8.0 Project Management and Reporting	• Program Written Reports and Program Reviews	Continuous

FY08:

- Complete Key Organic Species
- Complete Cations
- Characterize Membrane for Ammonia and H_2S Effects Including Crossover
- Initiate Modeling Efforts

FY09:

- Continue Organics
- Initiate Halogenated Hydrocarbons
- Complete Initial Empirical Models
- Begin Model Validation

4 Year Project

Time Phased Milestones

Activities and Expertise

Project Summary

Relevance - A Deeper Understanding of the Effects of Specific Contaminants on Fuel Cell Performance is Necessary for Successful Commercialization

Approach - Our Experienced Team Will:

- Leverage Existing Knowledge and Will Systematically Investigate Certain Fuel Contaminants of Interest
- Create Empirical and Detailed Analytical Models to Predict the Fate of Specific Contaminants and Their Effect on Fuel Cell Performance

Technical Accomplishments and Progress – Established Test Capability and Ability to Work With Common Protocols, Completed Evaluation of Methane and Ethane, Evaluated Cationic Effects on Membrane

Proposed Future Research – Continue Organics Per Industry Recommendation, Move on to Halogenated Compounds, Finish Cations, Initiate Modeling Efforts

Technology Transfer - Data Will Be Shared Through Papers, Workshops, Working Groups, Etc.

Collaboration – Active Partnership with UTC-HS and FCE, Coordination With Other Labs, Working Groups