National Renewable Energy Laboratory
Innovation for Our Energy Future

Effect of System and Air Contaminants on PEMFC Performance and Durability

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National Renewable Energy Laboratory

June 11, 2010

2010 Annual Merit Review and Peer Evaluation Meeting

FC048

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

Overview

Timeline

Start: July 2009
End: September 2013
% complete: ~5%

Budget

DOE Cost Share	Recipient Cost Share	TOTAL
$6,000,000	$788,850	$6,788,850*
88%	12%	100%

	DOE Budget ($K)
FY 2009	1035
FY 2010	700
FY 2011	1438
FY 2012	1476
FY 2013	1351

*Final award amounts are subject to appropriations and award negotiations.

Barriers

Barrier	2015 Target
A: Durability	5,000 h for Transportation 40,000 h for Stationary
B: Cost	$30/kW for transportation $750/kW for Stationary

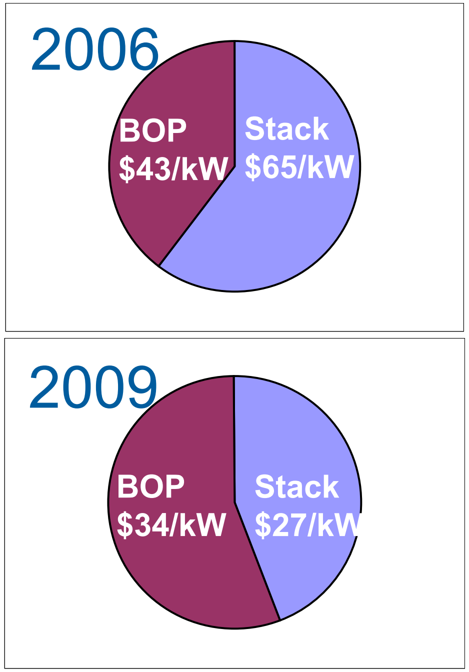
Partners (contract date)

General Motors* (3/10)
University of South Carolina* (1/10)
Los Alamos National Laboratory* (8/09)
University of Hawaii* (TBD)
3M (N/A)

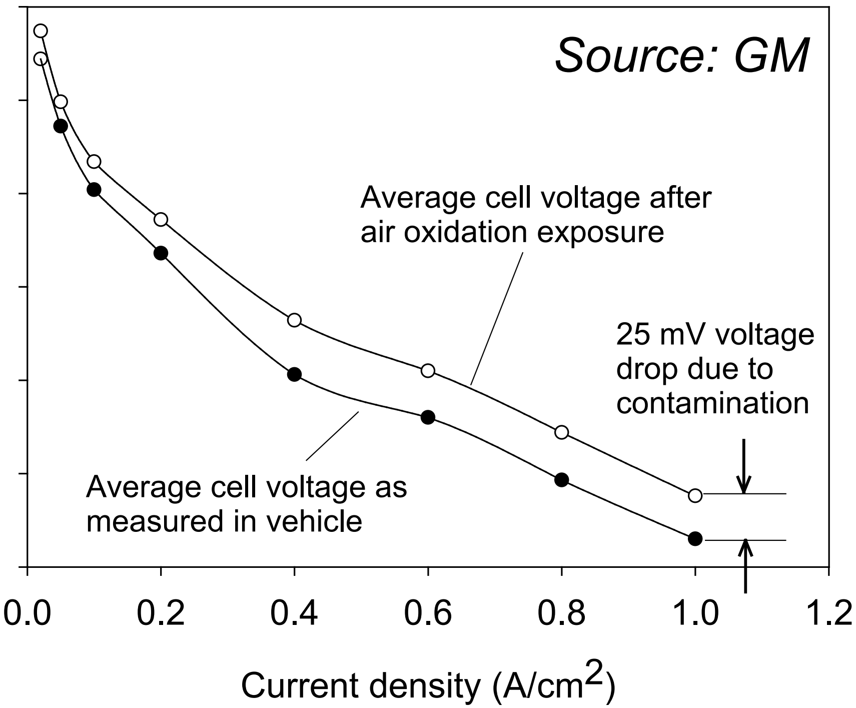
** denotes subcontractor*

Relevance

- Balance of plant (BOP) costs have risen in importance with decreasing stack costs.
- Contaminants from system components (GM) have been shown to affect the performance/durability of fuel cell systems.
- Durability requirements limit performance loss due to contaminants to at most a few mV over required lifetimes (1000s of hours). ~Zero impact for system contaminants.



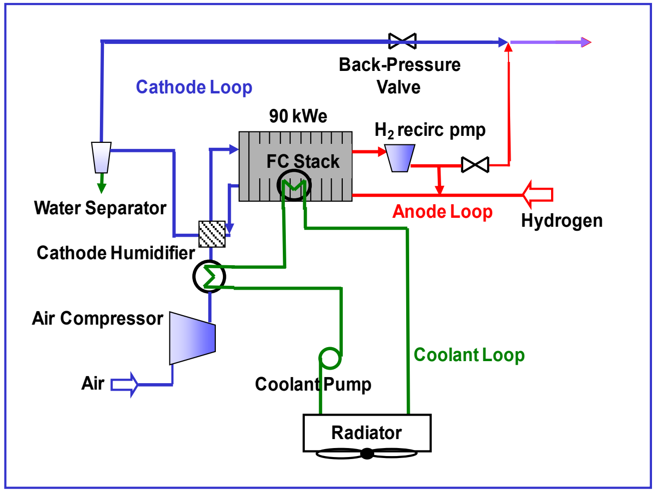
R. Farmer's presentation on Fuel Cell Technologies: FY2011 Budget Request Briefing, Feb. 12, 2010



Average cell performance of a 90kW fuel cell stack after 850+ hours of use in test vehicle. The cell performance improved after exposure to oxidation. The recoverable 25 mV voltage loss was attributed to system-based contaminants. (provided by GM)

Relevance

- **Unfortunately, commercially relevant, system-derived contaminants have many potential sources.**



Typical automotive fuel cell system.

Typical "gas wetted" components used in a PEMFC system.

Air management	Fuel management	Stack	Integration
Compressor	Gas metering	Bipolar plates	Stack manifolds
Humidifier	Recirculation pump	Seals/sealants	Seals/sealants
Heat exchanger	Valves	Subgaskets	Conduits/hoses
Valves	Sensors	Membrane	
Sensors	Seals/sealants	Electrodes	
Seals/sealants	Conduits/hoses	Insulators and ports	
Conduits/hoses		Seals/sealants	
		Conduits/hoses	

•D.A. Masten, A.B. Bosco Handbook of Fuel Cells (eds.: W. Vielstich, A. Lamm, H.A. Gasteiger), Wiley (2003): vol. 4, chapter 53, p. 714.

Examples of common additives in automotive thermoplastics

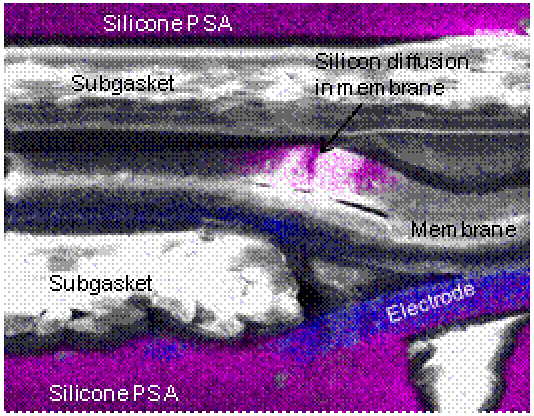
Glass fiber sizing	Primary antioxidant	Secondary antioxidant	UV stabilizer	Flame retardant	Processing aids	Biocides	Other
Vinyl silane	Hindered phenols	Organophosphates	Hindered amines	Antimony oxide	Calcium stearate	Triclosan	Residual monomer
Amino silane	Organotins	Thio esters	Benzophenones	Borates	Amide wax	Oxy-bisphenoxarsine	Catalysts
Mercapto silane	Mercapto-		Hydroxyphenyl	Bromates	Oligomeric wax		Residual solvents
Epoxy silane	benzoimidizoles		benzotriazoles	Phophates	Fatty acid amides		
					Glycerides		

Budinski, K. G.; Budinski, M. K. Engineering Materials: properties and selection. 8th ed. Upper Saddle River, NJ: Prentice Hall; 2005, p. 768.

Relevance – Background Data

- In-situ experiments have shown a clear negative impact from system-based contaminants.
- For the case shown, the impact is observed through membrane failure, voltage loss and HFR gain.
- While little has been done in the area of system contaminants, our team members have been leaders in the limited amount reported in this area.

Pink = Si
Blue = Pt

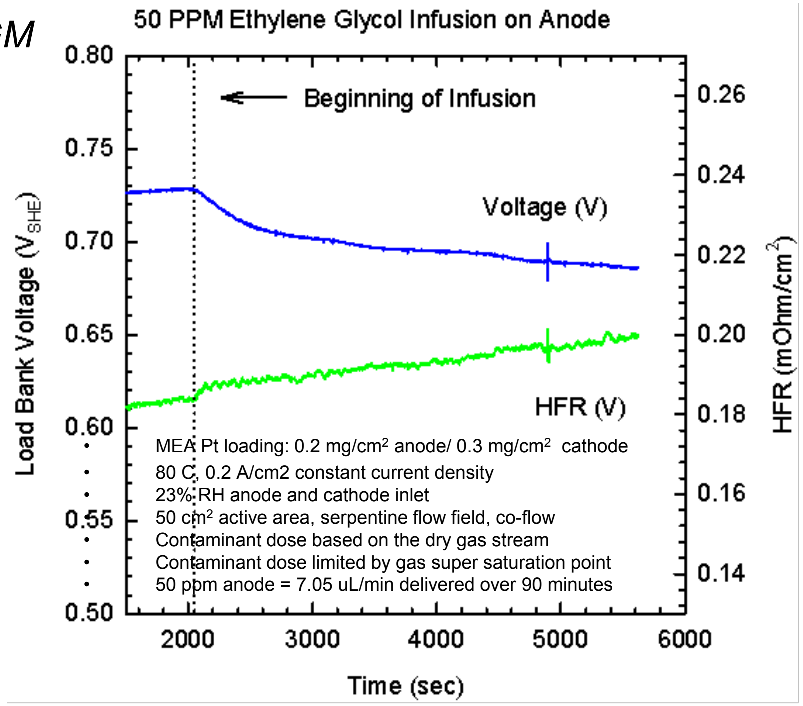


MEAs were assembled with a siloxane containing adhesive

- Siloxane degraded and migrated into the membrane, which became embrittled and mechanically failed.

A non-Si containing adhesive was selected

Source: GM

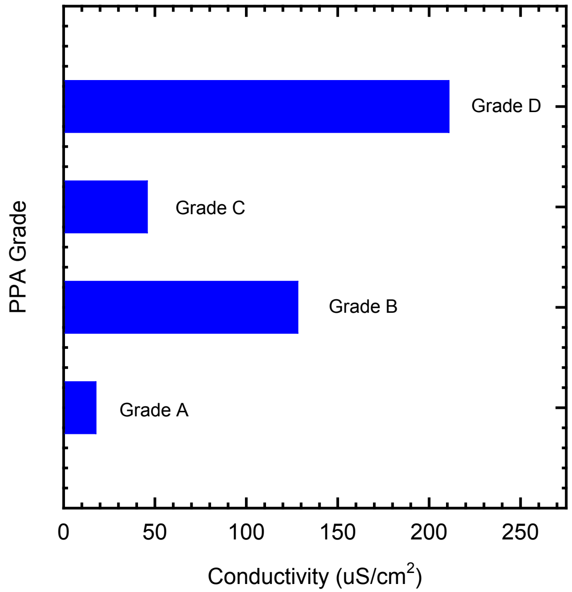


K. O'Leary, M. Budinski, B. Lakshmanan, "Methodologies for Evaluating Automotive PEM Fuel Cell System Contaminants.", NRC-CNRC Workshop, 2009

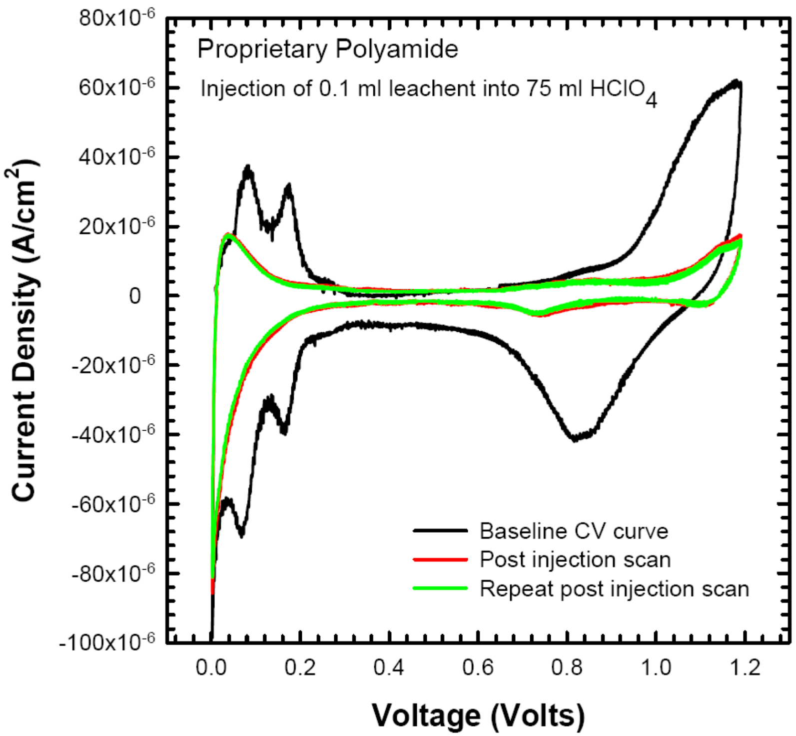
Relevance – Background Data

Ex-situ experiments are effective methods for quickly screening materials.

Leachants obtained from different grades of the same family of polymers results in very different conductivities (potentially reflecting quantity and type of contaminant).



Electrochemical data, including leachant solutions, shows that system contaminants impact catalysts.



Leaching Soak Test of Solid or Gel Materials:

- Soak in DI water for 250 hours at 90°C in PE bottles
  - Standard part surface area
  - Standard volume of water
- Extract leachant for experimentation

Testing Liquid Materials:

- Direct testing of liquids

K. O'Leary, M. Budinski, B. Lakshmanan, "Methodologies for Evaluating Automotive PEM Fuel Cell System Contaminants.", NRC-CNRC Workshop, 2009

Relevance/Approach

Objectives/2009-2010 Milestones

Objectives

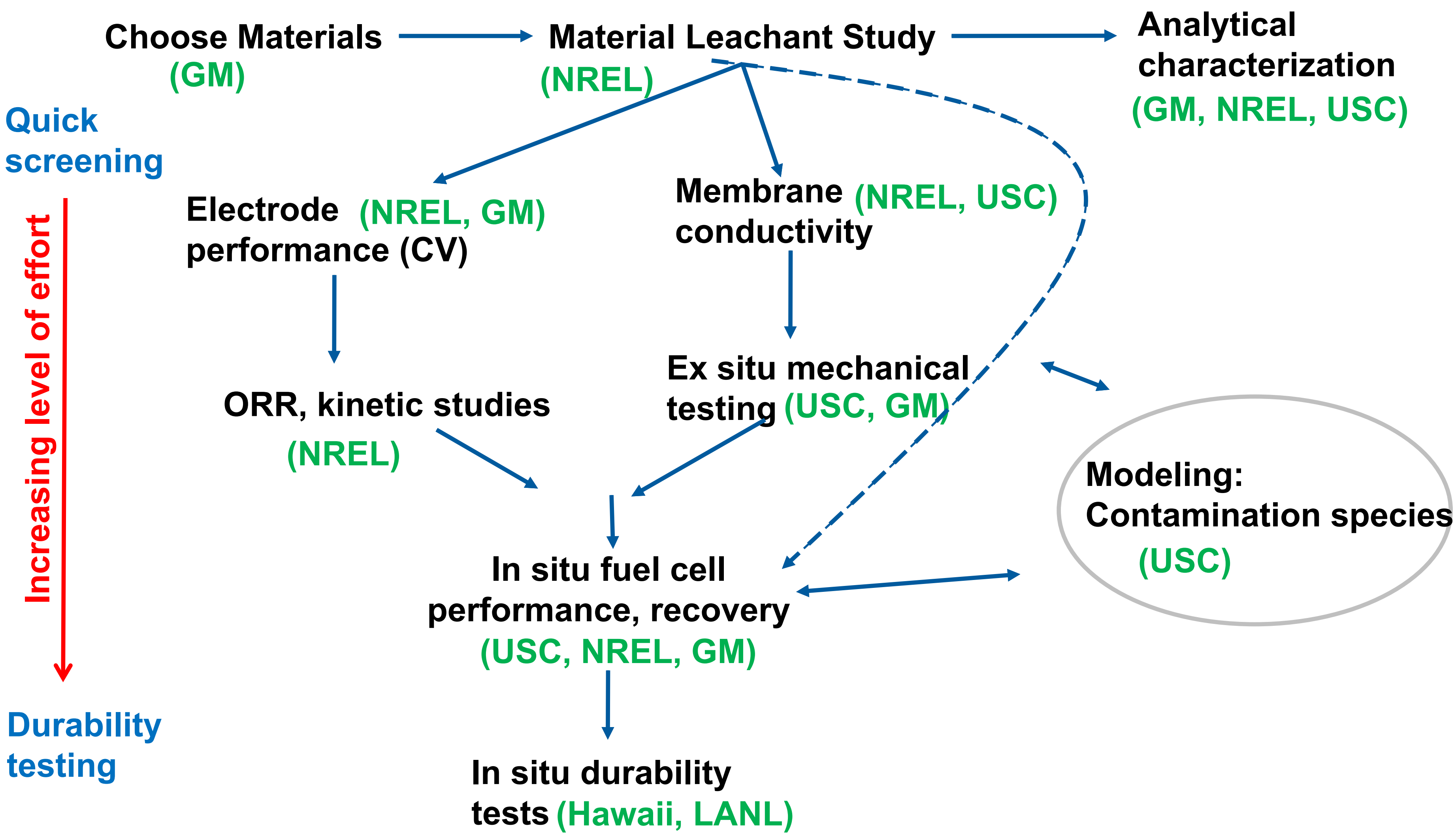
Decrease the cost associated with system components without compromising function, fuel cell performance, or durability

- Identify and quantify system derived contaminants
- Develop *ex-situ* and *in-situ* test methods to study system components
- Identify severity of system contaminants and impact of operating conditions
- Identify poisoning mechanisms and investigate mitigation strategies
- Develop models/predictive capability
- Develop material/component catalogues based on system contaminant potential to guide system developers on future material selection
- Disseminate knowledge gained to community

2009-2010 Milestones

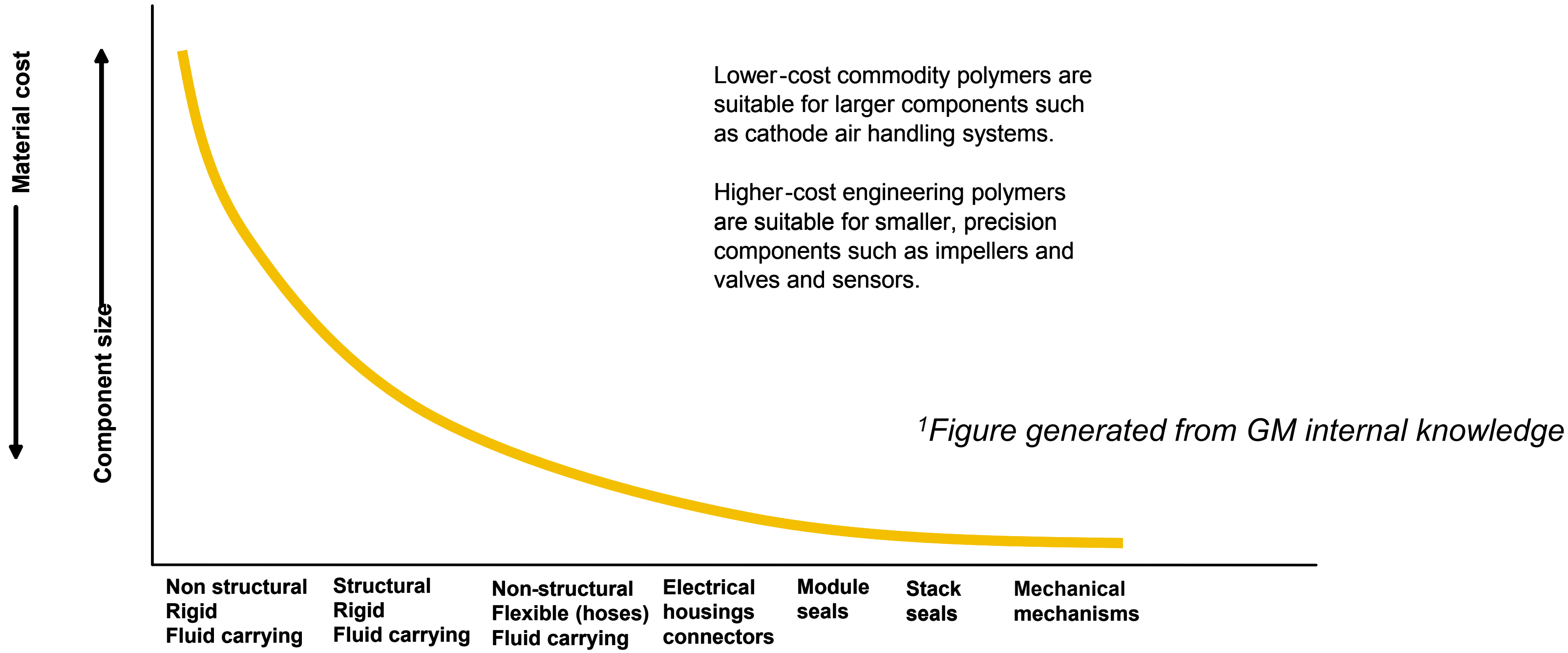
1	Quantify impact of (at least 3) leaching conditions on leachants obtained from (at least 3) polymer samples.	09/09 100% complete
2	Compile comprehensive list of identified, plausible polymer families for fuel cell systems.	07/10 50% complete
3	Quantify the impact of identified leachant mixtures (at least 4) on fuel cell performance and durability.	09/10
4	Isolate electrochemically inhibiting compounds from (at least 4) polymeric leachants.	09/10

Approach* – Project Overview



*Beyond what is presented here, our approach is driven by other input, in part, provided in supplemental slides. For example, hydrophillicity changes are not currently included in work plan.

Approach – General Terms



Stack and Module Materials[1]

Examples of polymer classes with generalized costs for the system[2]

PSU>PC>PBT>PPS>PPA>PA>PPO>POM>PET>PU>UP>Phenolic>Melamine>ABS>PS>PE>PP>PVC

Higher cost → Lower cost

[2]Budinski, K. G.; Budinski, M. K. Engineering Materials: properties and selection. 8th ed. Upper Saddle River, NJ: Prentice Hall; 2005, p. 768.

Our materials selection is based on issues such as exposed surface area, total mass/volume, fluid contact, function, cost, and performance implications.

Approach – Materials Prioritization

Current prioritization for perceived impact of potential system contaminants (based on GM internal knowledge)

1. Structural materials
2. Coolants*
3. Elastomers for seals
4. Elastomers for (sub)gaskets
5. Assembly aids (adhesives, lubricants)
6. Hoses
7. Membrane degradation products
8. Bipolar/end plates
9. Ions from catalyst alloys

* Limited efforts within this project, due to options and existing data.

- **Strong polymer focus, as much of the system is polymer based**
- **Component list contains commodity materials or materials developed for other applications where issues of fuel cell contamination would not be a concern.**
- **Try to leverage synergies between these materials (for example: small molecule, organic leachants or common additives/processing aids)**

Approach – Protocols/Testing

GM's established test protocols used on leachant from polyamide polymer

Measurement	Method*	Requirement	Polyamide
★ Leaching Test	FCA-T0008	N/A	N/A
Total organic content (TOC)	FCA-T0008	<TBD mg/l	124 mg/l
Total inorganic content (TIC)	FCA-T0008	<TBD mg/l	40 mg/l
Total surface tension	FCA-T0008	>TBD mN/m	Not measured
★ Color change	FCA-T0008	no color change via UV-Vis	No change
★ Olfactory test	FCA-T0008	no odor	Amine
★ pH	FCA-T0008	TBD	Not measured
★ Conductivity	FCA-T0008	<TBD uS/cm	210 uS/cm
Proton conductivity test	FCA-T0015	TBD	Not measured
GDL surface energy test	FCA-T0016	>140° water contact angle	Not measured
BPP wetting contamination test	FCA-T0017	TBD	Not measured
FC Cyclic voltammetry test	FCA-T0018	TBD	Not measured
★ Analytical Characterization	FCA-T0008	TBD	Not measured
★ Beaker CV test	FCA-T0019	TBD	Not measured

- **Standard test protocols are important in evaluating materials as this approach will allow for broader studies to be performed.**
- **GM has put significant work in establishing test protocols and these will be disseminated to the community as part of the project.**

★ Test methods NREL used to date in project

Technical Accomplishments and Progress

- 87% of subcontract funding now in place.
- Kickoff Meeting (3/24 – 3/25/2010).
- Obtained relevant materials sets.
- Initiated leachant experiments for polymeric samples.
- Applied and evaluated multiple techniques for analyzing leachants (e.g., GC-MS, FTIR-ATR, ICP-MS, pH, conductivity, TOC, contact angle).
- Established competencies for GM established test protocols.

Technical Accomplishments and Progress

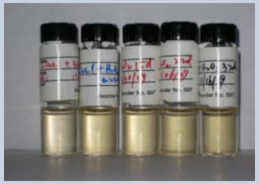
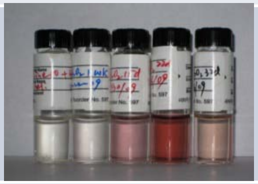
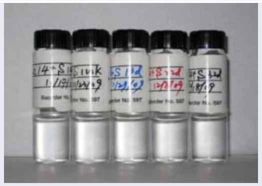
Investigated Leaching Test Procedures:

- 2 pieces of 1x4 inches^2 were prepared, giving a ratio of 103 cm^2 to 100 ml solution
- 100 ml total of solution was used for each sample
- Three different solutions (at 80°C)
  - DI water
  - 0.1M H_2SO_4
  - 3%H_2O_2+0.1M H_2SO_4
- 5 ml aliquots were collected at:
  1, 7, 15, 22, 32, 45, 60 day intervals
- pH, conductivity, FTIR and GCMS were performed on each sample

Relevant Polymeric Materials Tested:

- *Acrylic Buna-N Blended Rubber*
- *Aramid/Buna-N*
- Abrasion resistant *SBR Rubber (Red)*
- Weather resistant *EPDM Rubber (Plain black)*
- *FDA*-compliant *Silicone Rubber (Plain black)*
- Corrosion resistant *Viton® Fluoroelastomer*
- Amber *Polyurethane* Sheet
- M-strength *Neoprene Rubber (Plain black)*
- Silicone gasket
- Teflon coated fiberglass (Furon)

Technical Accomplishments and Progress
Leachant Experiments on Relevant Materials

	in DI water	0.1M H_2SO_4	3% H_2O_2 + 0.1M H_2SO_4
Control (no polymeric material)			
1. Acrylic Buna-N Blended Rubber (Gasket Sheet)			
2. Aramid/Buna-N Gasket			
3. Abrasion resistant ***SBR Rubber*** Red			
4. Weather resistance ***EPDM Rubber*** Plain black			

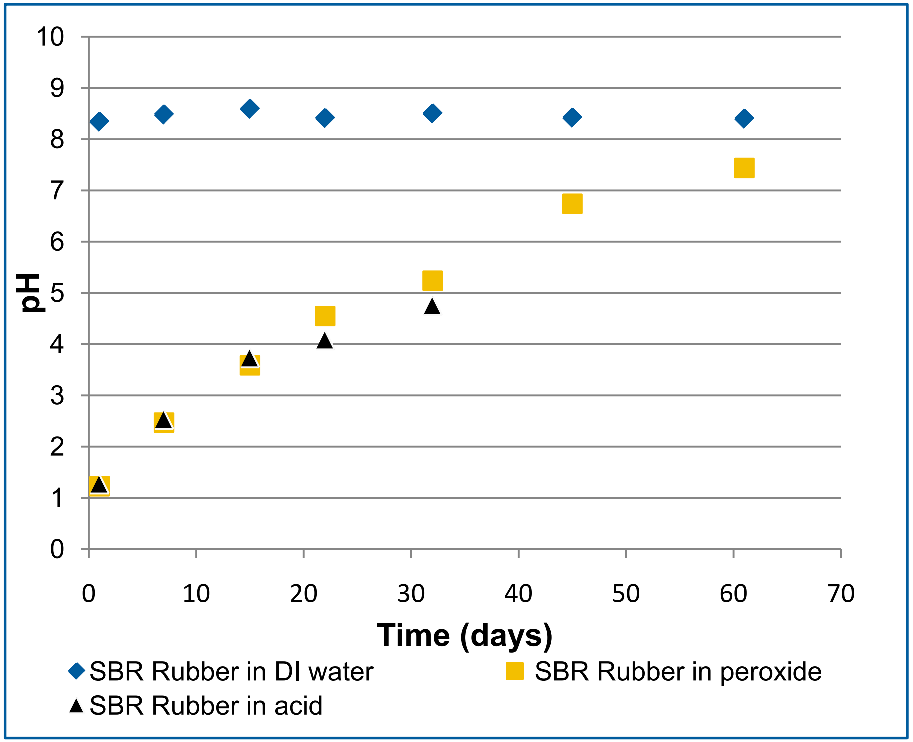
Some material resulted in obvious change in color, smell, and turbidity, as well as precipitation formation of leachant solutions.

We present SBR Rubber as a case study material for this presentation.

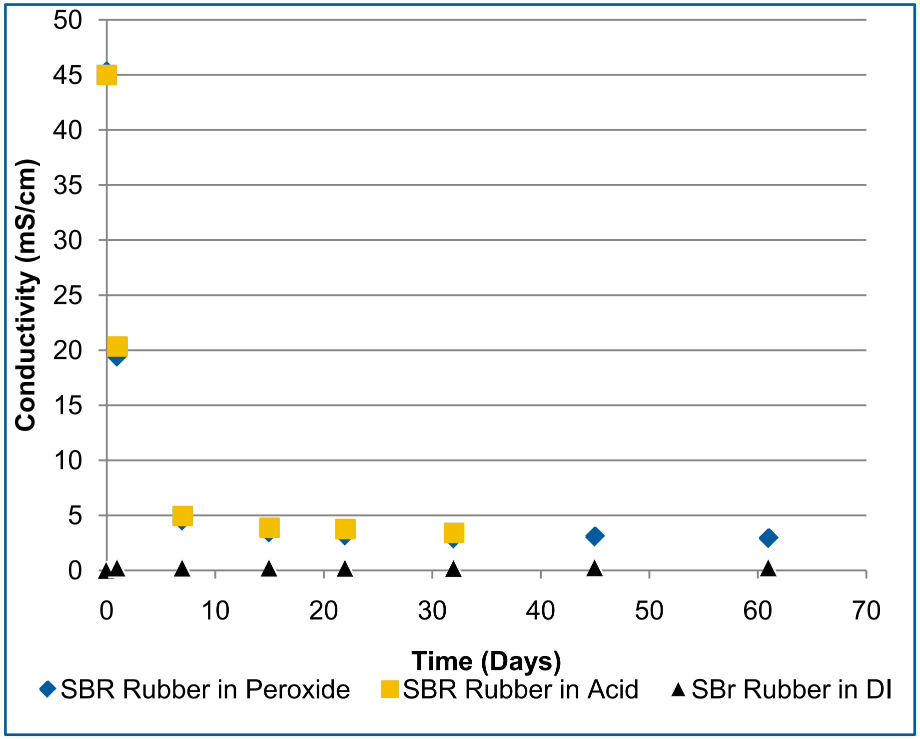
Technical Accomplishments and Progress
Develop Test Methods

SBR Rubber (Red)

pH



Conductivity

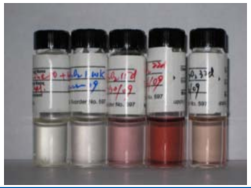


Acid solutions caused a large pH & conductivity change in material that broke down.

In DI water

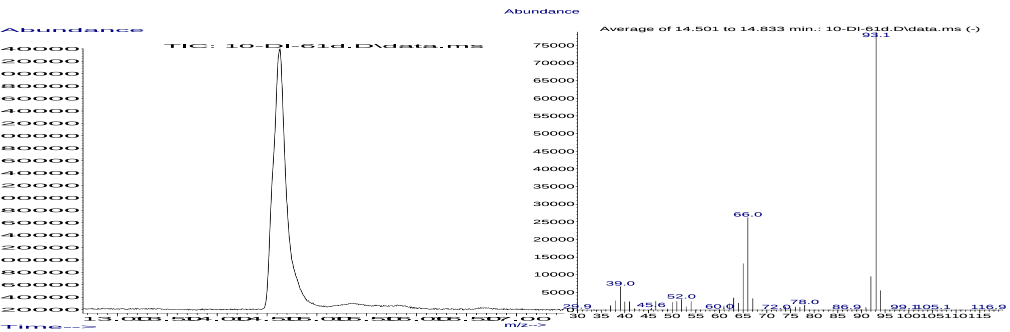
0.1M H_2SO_4

3%H_2O_2+0.1M H_2SO_4



Technical Accomplishments — Develop Test Methods

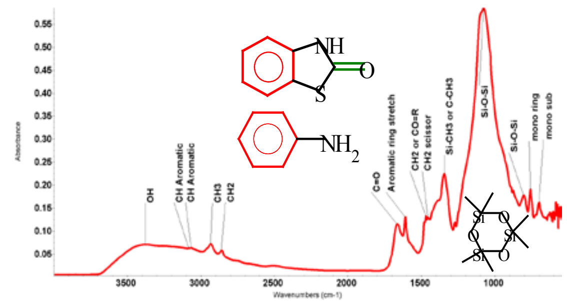
Gas Chromatography Mass Spectroscopy [GCMS]



Separates leachant components and identifies chemical compounds

- **Aniline is major leachant in SBR (quality = 91)**

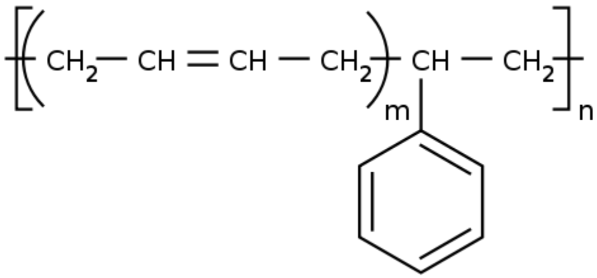
FTIR / ATR – Attenuated Total Reflection



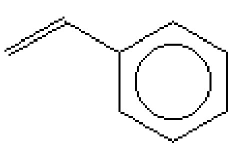
Confirms major functional groups of compounds identified by GCMS

- **Aromatic rings in SBR**

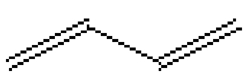
Chemical designation of abrasion-resistant styrene butadiene rubber (SBR)-Red



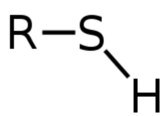
- Styrene



-
- Butadiene



Polymerization of monomer involves:
Chain transfer agent such as an alkyl mercaptan



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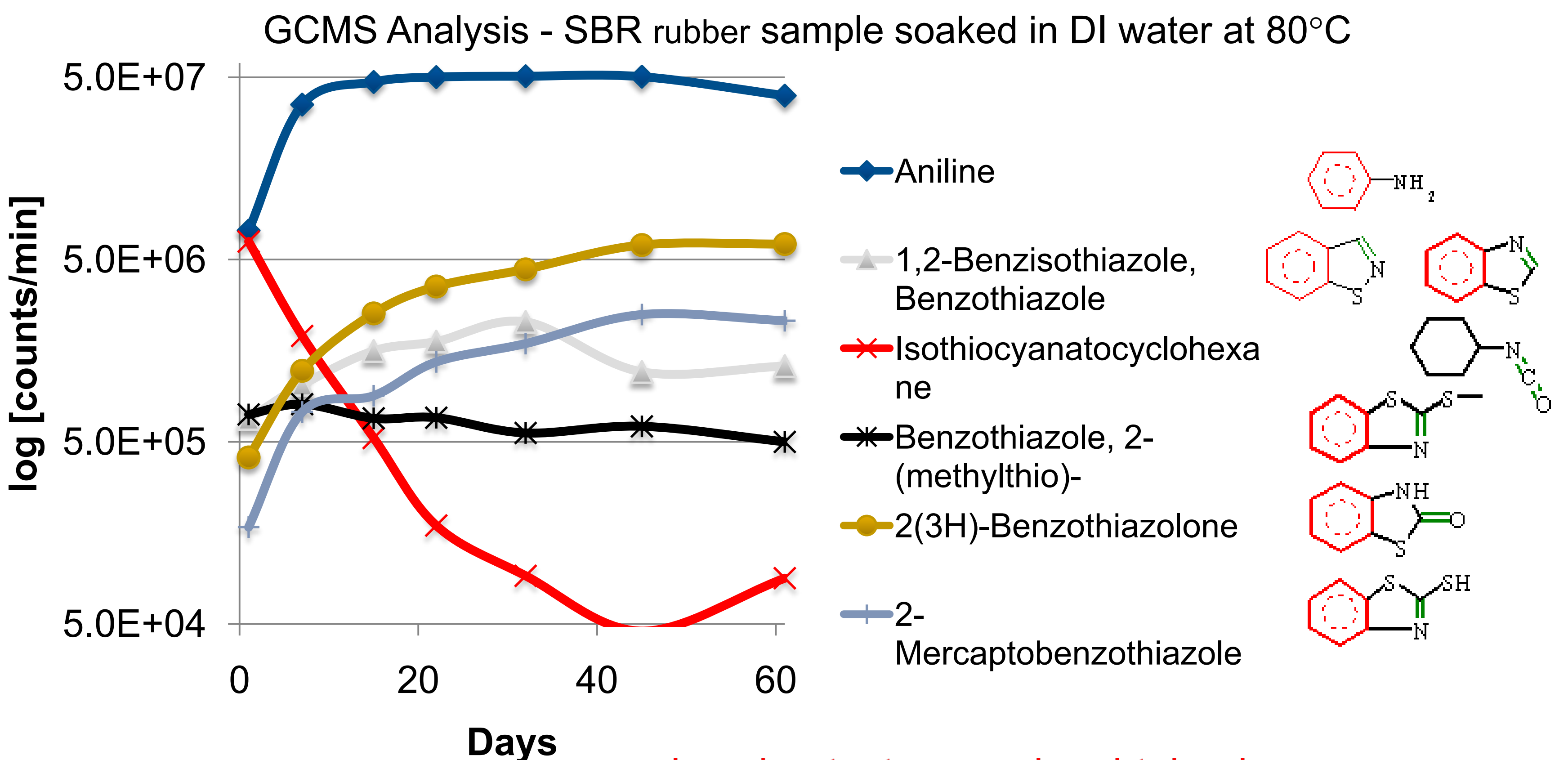
Technical Accomplishments — Develop Test Methods

Identified leachant components studied over time



Leachant rates may be obtained.

Identified components seem reasonable based on known polymer chemical structure and FTIR. GC-MS seems to be a good method to identify leachants.

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Collaborations

PRIME

National Renewable Energy Laboratory: Huyen Dinh (PI), Bryan Pivovar, Guido Bender, Heli Wang, Clay Macomber, Kevin O'Neill, and Shyam Kocha, Sidney Coombs

SUBCONTRACTS

General Motors (GM): Kelly O'Leary, Balsu Lakshmanan, and Rob Reid

University of South Carolina (USC): John Van Zee and Jean St. Pierre

Los Alamos National Laboratory (LANL): Tommy Rockward

University of Hawaii (UH): Rick Rocheleau

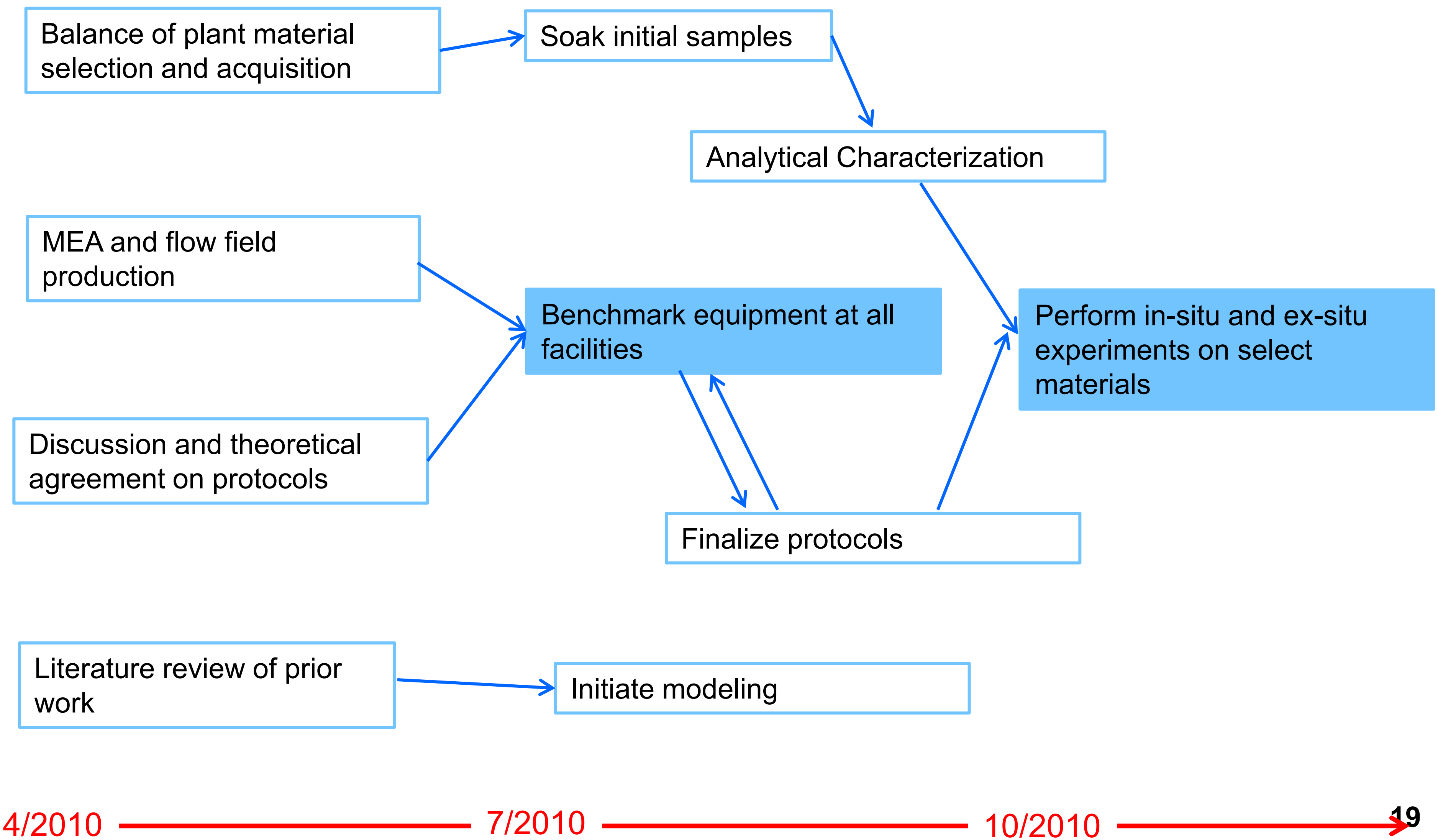
3M*: Steve Hammrock

- **Contaminant identification** (GM)
- **Test method development & validation** (NREL, GM, USC)
- **Contaminant characterization** (GM, NREL, USC, LANL, UH)
- **Poisoning mechanisms identification** (NREL, GM, USC)
- **Mitigation strategies investigation** (NREL, GM, USC)
- **Model development** (USC)
- **Model validation** (USC, GM, NREL)
- **Data compilation and public dissemination** (NREL, GM, USC, LANL, UH)

* Provide membrane degradation products

Proposed Future Work:

Work Plan From Kick Off Meeting (4/2010-12/2010):



Summary

Relevance: Focus on overcoming the cost and durability barriers for fuel cell systems.

Approach: Perform parametric studies of the effect of system contaminants on fuel cell performance and durability, identify poising mechanisms and recommend mitigation strategies, develop predictive modeling and disseminate material catalogues that benefit the fuel cell industry in making cost-benefit analyses of system components.

Technical Accomplishments and Progress: 85% of the subcontract and funding are in place. We obtained relevant materials set and initiated leachant experiments for over 10 polymeric samples. We initiated evaluation of various methods for analyzing leachants (e.g., GCMS, FTIR-ATR, ICP-MS, pH, conductivity, total organic content, contact angle), and established competencies mimicking GM established test protocols.

Collaborations: Our team has significant background data and relevant experience. It consists of a diverse team of researchers from several institutions including 2 national labs, 2 universities, and 2 industry partners.

Proposed Future Research: Select and study polymeric structural materials because they have the highest impact of potential system contaminants. Develop standard testing protocols and benchmarking equipment/methods.

Supplemental Slides

Approach – Fuel Cell Impact Prioritization

4 major components susceptible to contamination (in exposure order):

1. Plate hydrophilicity/ hydrophobicity
2. Diffusion Media hydrophilicity/ hydrophobicity
3. Electrode
4. Membrane

Consequences of contamination & prioritization of fuel cell performance impact: (in order of prioritization)

1. Electrode performance
2. Increased membrane resistance
3. Decreased membrane durability
4. GDL Water management issues

Learnings to Date:

1. Continuous soak in DI water for 1000 hours is current procedure of choice. Conductivity measured 1 x/week. Odor, appearance, bubbling recorded. Shake test, pH, and conductivity are most useful quick screening methods.
2. CV is extremely useful and we've developed a number of techniques depending on what we're studying. It is currently used for 2 types of experiments: a quick screen, and a recovery screen
3. Membrane resistance work has been limited, but needs further exploration
4. Plate hydrophilicity/ hydrophobicity is too sensitive to obtain useful data
5. Diffusion media hydrophilicity/ hydrophobicity has shown little to no effects on water management

Source: GM

Example Work Flow: Nylon 6,6

1. Order variety of Nylon 6,6 from 2 manufacturers: hydrolytically stabilized, 25% reinforced w/ glass, carbon, carbon rods, clay, etc

2. Soak samples in di water as soon as they arrive

3. Measure pH, H conductivity, odor, color, CV, and membrane conductivity, all in parallel. Start soaking membrane in extract for aging
   a. During steps 4 and 5, perform chemical analysis on extract and bulk material

4. If possible or beneficial, perform extended CV experiments on extracts

5. Perform in situ fuel cell experiments with and w/o current distribution, perform DOE on concentration, temperature, current, RH, and Pt loading (all on extract sln)
   a. Work on recovering with fluid circulation and potential ranges
   b. Understanding tolerances

6. Repeat 4 and 5 with select substrate chemicals

7. Measure membrane properties of aged materials

8. Decide if any durability tests should be run and which: RH cycling w/ or w/out load

9. Feed information into mechanistic understanding

10. Feed mechanisms into simple modeling

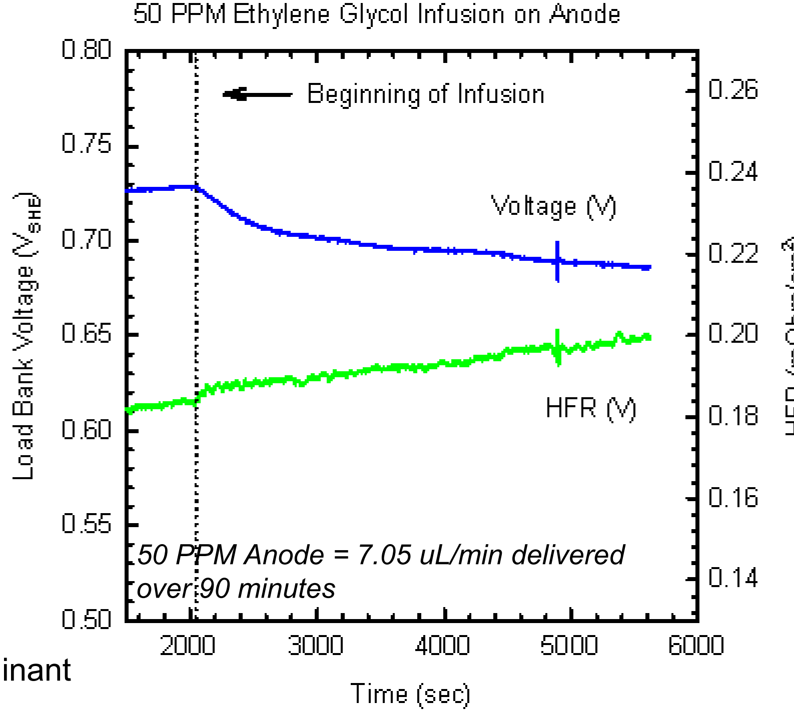
Source: GM

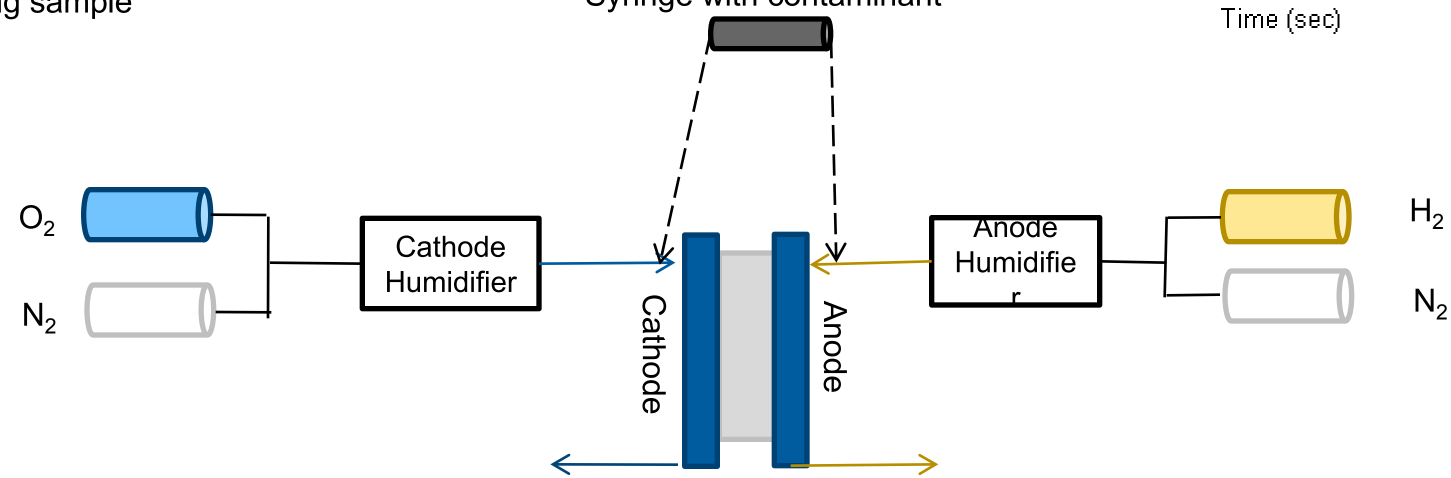
Approach – Background Data

In-situ fuel cell experiments are then performed to evaluate effects of operating conditions as well as dosage.

Test Conditions:
- 80°C, 0.2 A/cm^2 constant current density
- MEA Pt loading: 0.2 mg/cm^2 anode/ 0.3 mg/cm^2 cathode
- 23% RH anode and cathode inlet
- 50 cm^2 active area, serpentine flow field, co-flow
- Contaminant dose based on the dry gas stream
- Contaminant dose limited by gas super saturation point

Benefits of Infusion:
- Ability to treat leachant solutions as 'black box', allowing delivery of all constituent contaminants at once, ignoring partitioning coefficient if vaporizing sample





K. O'Leary, M. Budinski, B. Lakshmanan, "Methodologies for Evaluating Automotive PEM Fuel Cell System Contaminants.", NRC-CNRC Workshop, 2009

Source: GM

Technical Accomplishments
Predictive Modeling (USC)

Model development for air contaminants has been extensive and similar model can be applied to system contaminants.

Desorbing contaminant product

Contamination

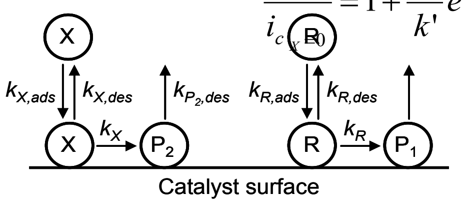
$$\frac{i}{i_{c_X=0}} = 1 - \frac{k''}{k'}\left(e^{\frac{k't}{\rho}} - 1\right)$$

Recovery

$$\frac{i}{i_{c_X=0}} = 1 + \frac{k''}{k'} e^{\frac{-(k_{X,des}+k_X)t}{\rho}}$$

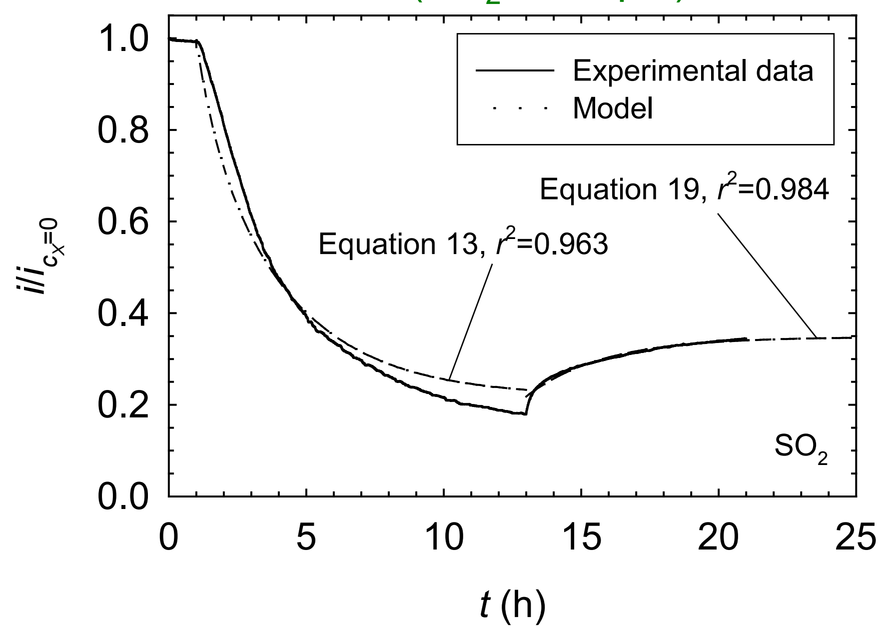
or

$$\frac{i}{i_{c_X=0}} = 1 + \frac{k''}{k'} e^{\frac{-k_{P_2,des}t}{\rho}}$$



J. St-Pierre, N. Jia, R. Rahmani, *J. Electrochem. Soc.*, **155** (2008) B315.
J. St-Pierre, *J. Electrochem. Soc.*, **156** (2009) B291.
J. St-Pierre, *Electrochim. Acta*, **55** (2010) 4208.

Irreversibly adsorbed contaminant product
(SO_2 example)

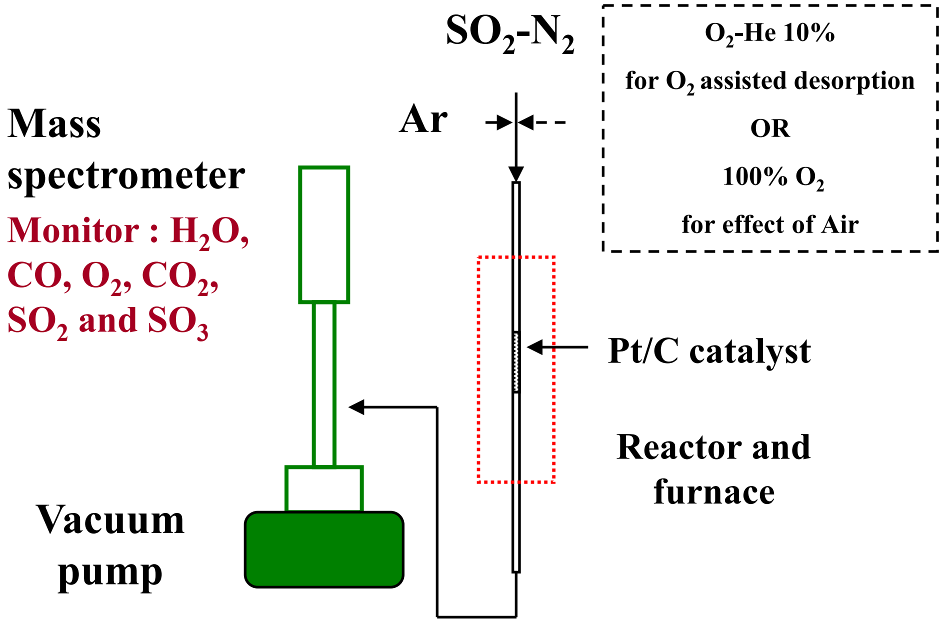


B. D. Gould, O. A. Baturina, K. E. Swider-Lyons, J. Power Sources, 188 (2009) 89.
J. St-Pierre, *J. Power Sources*, accepted.

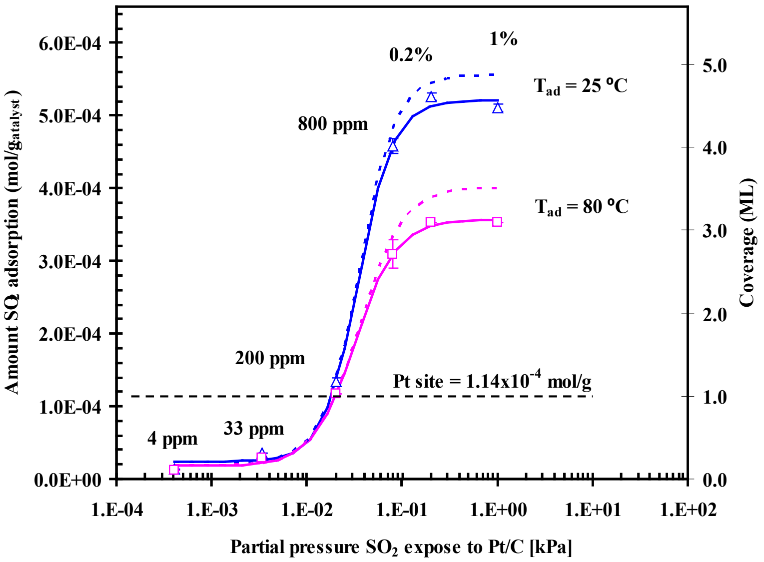
Methods for Studying Air Contaminants Can Be Applied to System Contaminants (USC)

Effect of O_2 on the adsorption SO_2 on Pt/C electrocatalyst

Schematic of Temperature Programmed Desorption (TPD) Apparatus

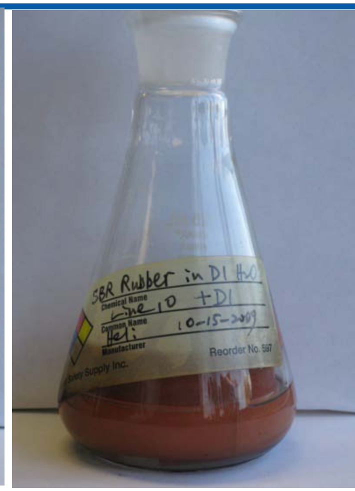


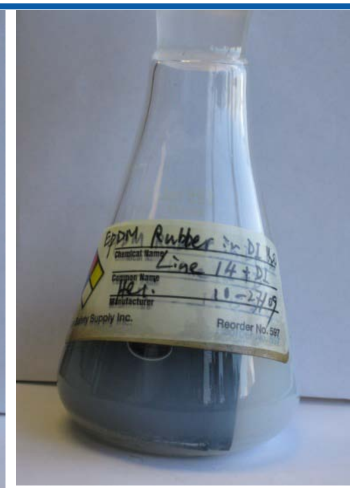
Isotherm of C-SO_2 compared to the SO_2 adsorption (Pt-SO_2 + C-SO_2)

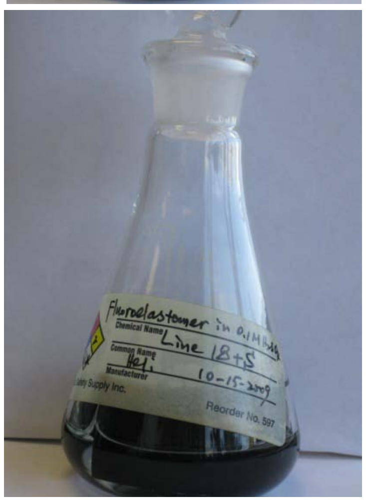


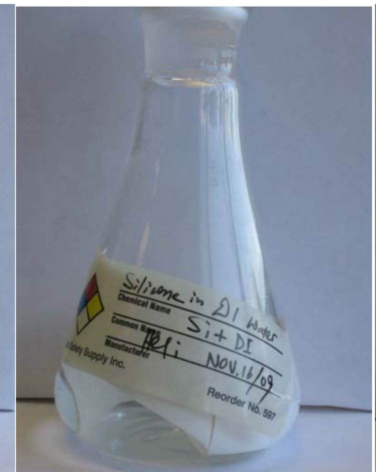
TPD can aid in understanding the mechanisms of contamination on catalyst (USC).

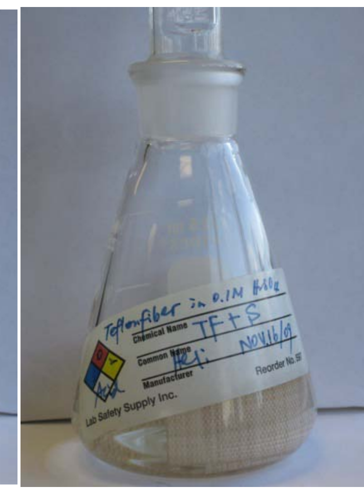
Sealing materials in different leachant conditions



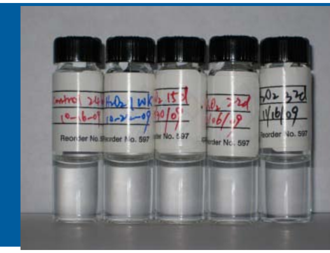
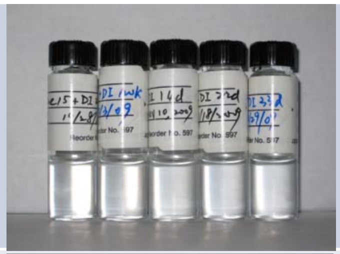
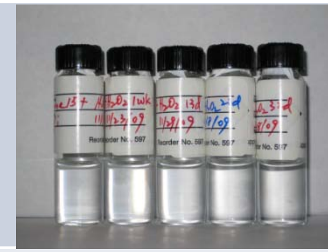
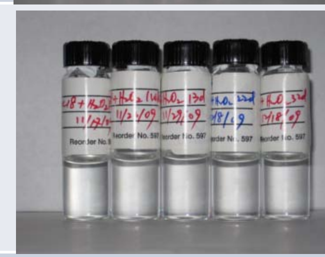


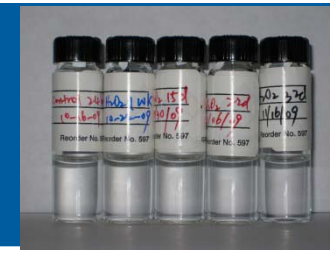
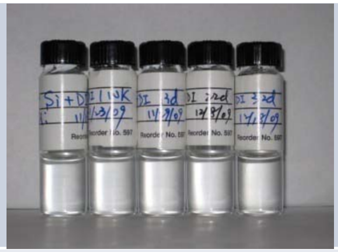
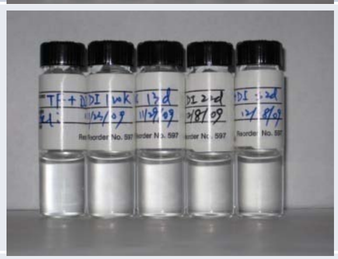
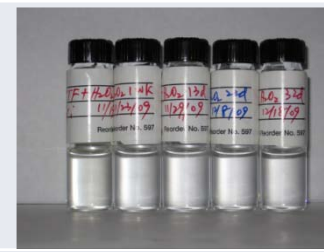






Sealing material has disintegrated in H_2SO_4+H_2O_2 solution (perhaps too aggressive).

	In DI water	0.1M H_2SO_4	$3\%H_2O_2$+0.1M H_2SO_4
Control (no polymeric material)			
5. FDA-compliant ***Silicone Rubber*** Plain black			
6. Corrosion resistant ***Viton®*** ***Fluoroelastomer***			
7. Amber ***Polyurethane*** Sheet			
8. M-strength ***Neoprene Rubber*** Plain black			

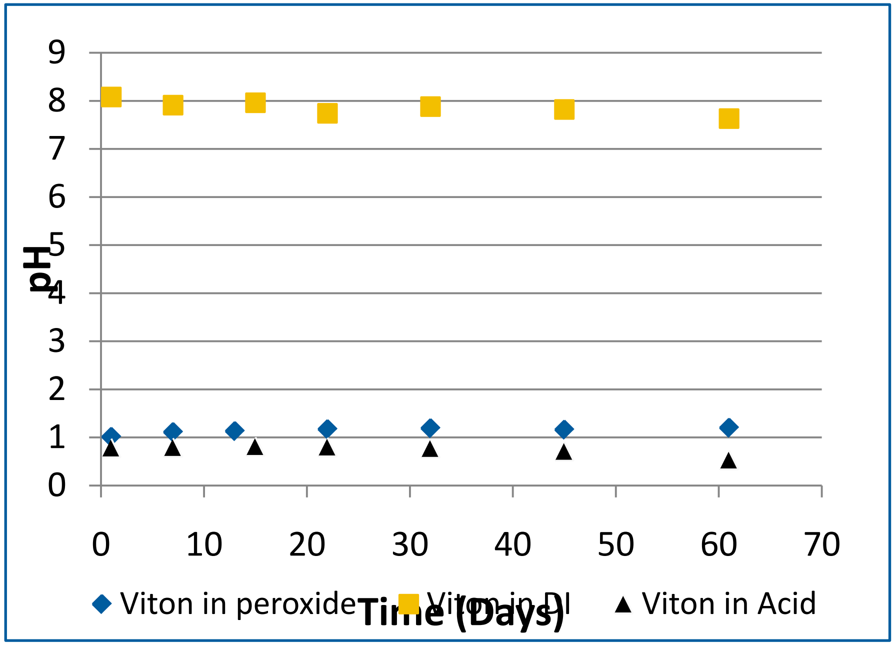
	In DI water	$0.1M\ H_2SO_4$	$3\%H_2O_2+0.1M\ H_2SO_4$
Control (no polymeric material)			
9. Silicone gasket			
10. Teflon coated fiberglass (***Furon***)			

Some material resulted in obvious change in color, smell, and turbidity, as well as precipitation formation.

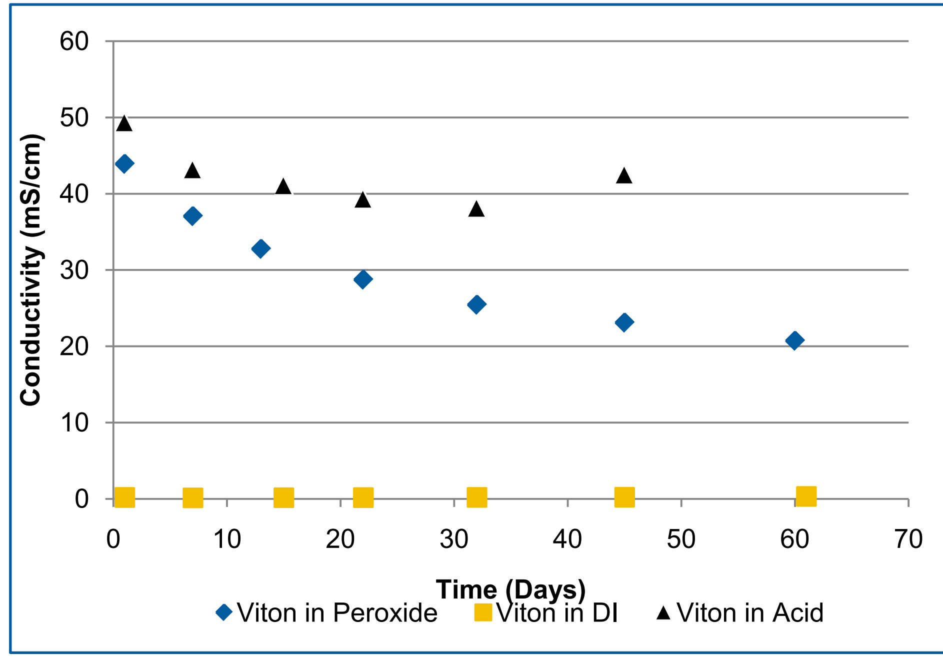
pH and Conductivity Measurements

Viton® Fluoroelastomer

pH



Conductivity



Minimal change in pH and conductivity for an expensive fluoroelastomer.

In DI water

0.1M H_2SO_4

3%H_2O_2+0.1M H_2SO_4

Gas Chromatography Mass Spectroscopy [GCMS]

Coupled Technique

Inert Purge, N_2

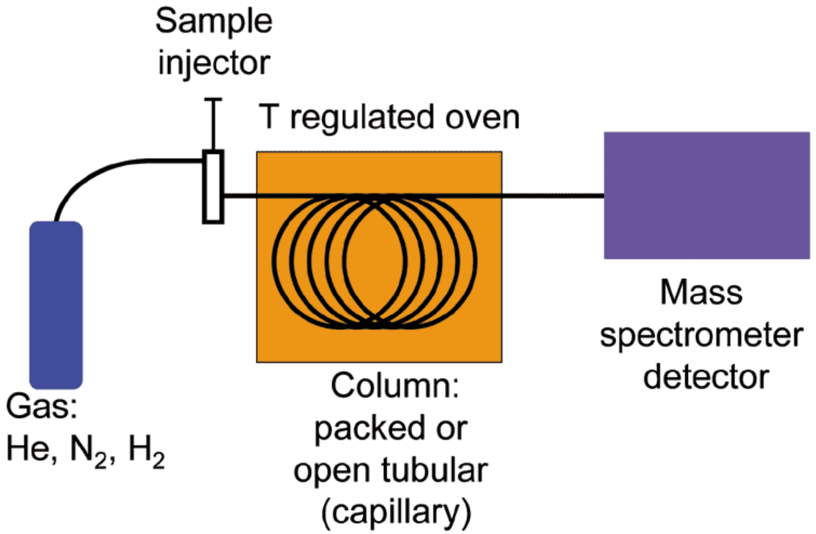
Liquid injection

Volatilized to gas

Separation along column

Components introduced into mass spectrometer

Ionized and separated in the quadrupole by m/z



Fourier Transform Infrared Spectroscopy [FTIR/ATR]

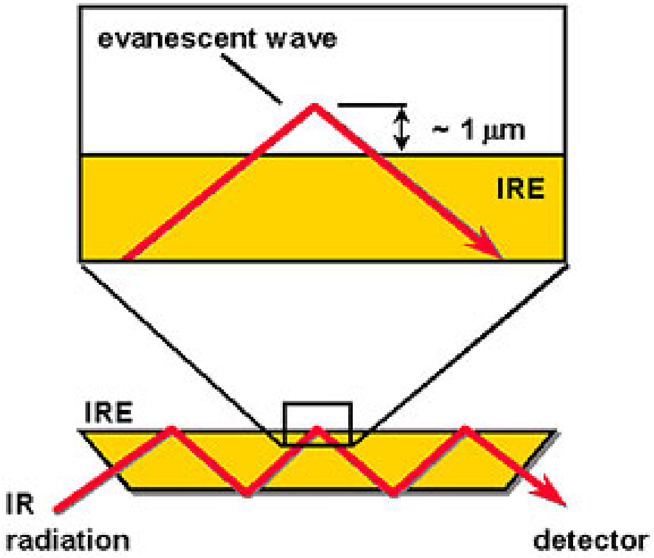
Vibrational spectroscopy
Identify functional groups
Spectral features shift with matrix

ATR – Attenuated Total Reflection

- Liquid and solid sampling accessory
- No sample preparation
- ZnSe cell is hydrophobic, no acids
- Ge cell is acid resistant

Evanescent standing wave

- Penetrates sample by a few microns
- Better contact = Better spectra



Blended Rubber Leachants via GCMS

Aged in DI water

Hexamethylcyclotrisiloxane

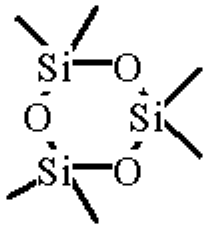
Octamethylcyclotetrasiloxane

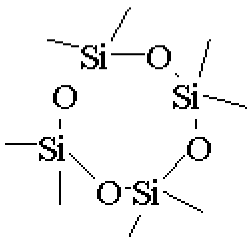
Decamethylcyclopentasiloxane

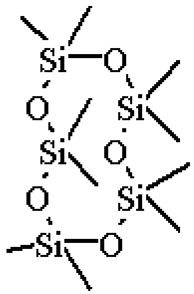
N,N dibutyl Formamide

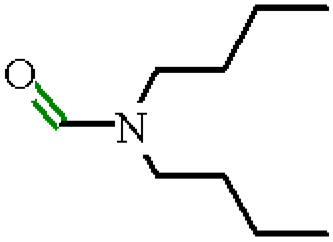
Dodecamethylcylohexasiloxane

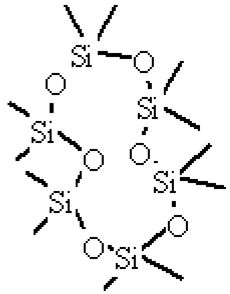
Tetradecamethylcycloheptasiloxane

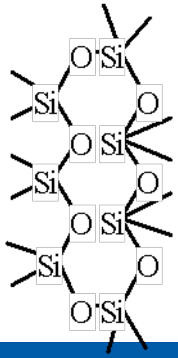












Main leachants identified for blended rubber are siloxanes & and formamide.

Blended Rubber Leachants over Time