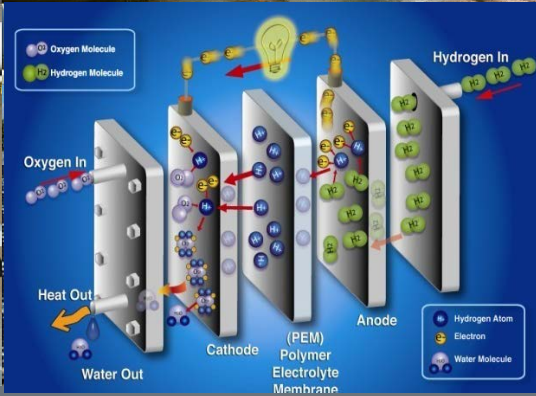
An Overview of NREL's Online Data Tool for Fuel Cell System-Derived Contaminants

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy



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An Overview of NREL's Online Data Tool for Fuel Cell System-Derived Contaminants

Venue: DOE EERE FCTO Webinar

Presenter: Huyen Dinh

National Renewable Energy Laboratory

Date: May 27, 2014

Outline

- Motivation
- Material Selection
- Methodology
- Screening Result Examples
- Website/Interactive Material Data Tool Demo

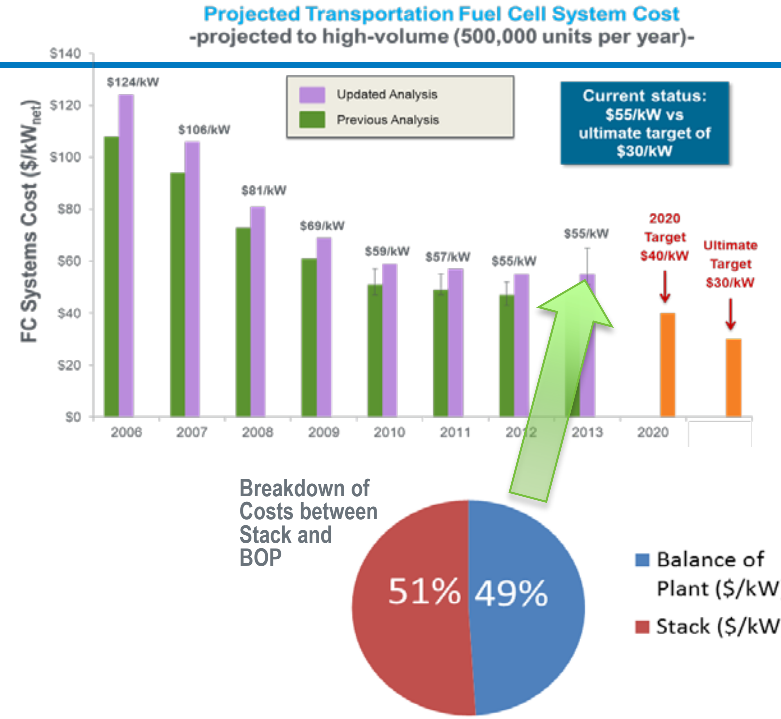
Fuel Cell Electric Vehicle is Almost Here!

Manufacturer	Launch
Ford	~2017
GM	~2020
Honda	~2015
Hyundai	2013-2015
Daimler	~2017
Nissan	~2017
Toyota	~2015

Motivation

- **Balance of plant (BOP) costs have risen in importance with decreasing stack costs.**
  - **Decrease overall fuel cell system costs by lowering BOP material costs.**

- **System contaminants have been shown to affect the performance/ durability of fuel cell systems.**
  - **Increase performance and durability by limiting contamination related losses**



Examples of common additives in automotive thermoplastics:

- Glass fiber
- Antioxidant
- UV Stabilizer
- Flame retardant
- Processing aids
- Biocides
- Catalysts
- Residual polymer
- Residual solvents

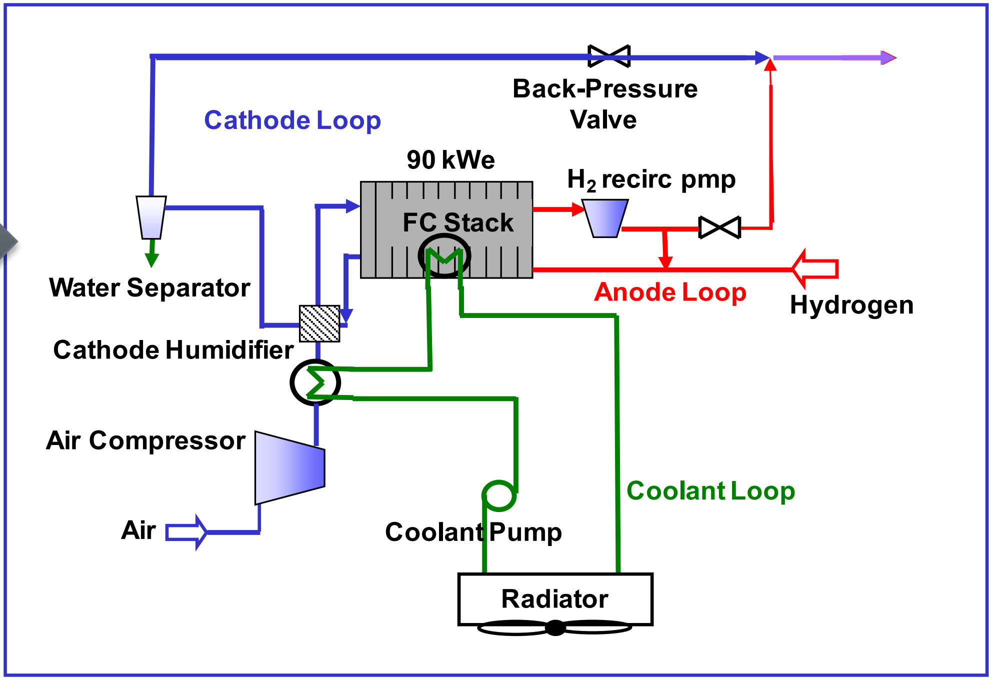
Record Source: http://www.hydrogen.energy.gov/pdfs/13012_fuel_cell_system_cost_2013.pdf

Fuel Cell Stack & Balance of Plant (BOP)

Fuel Cell Stack

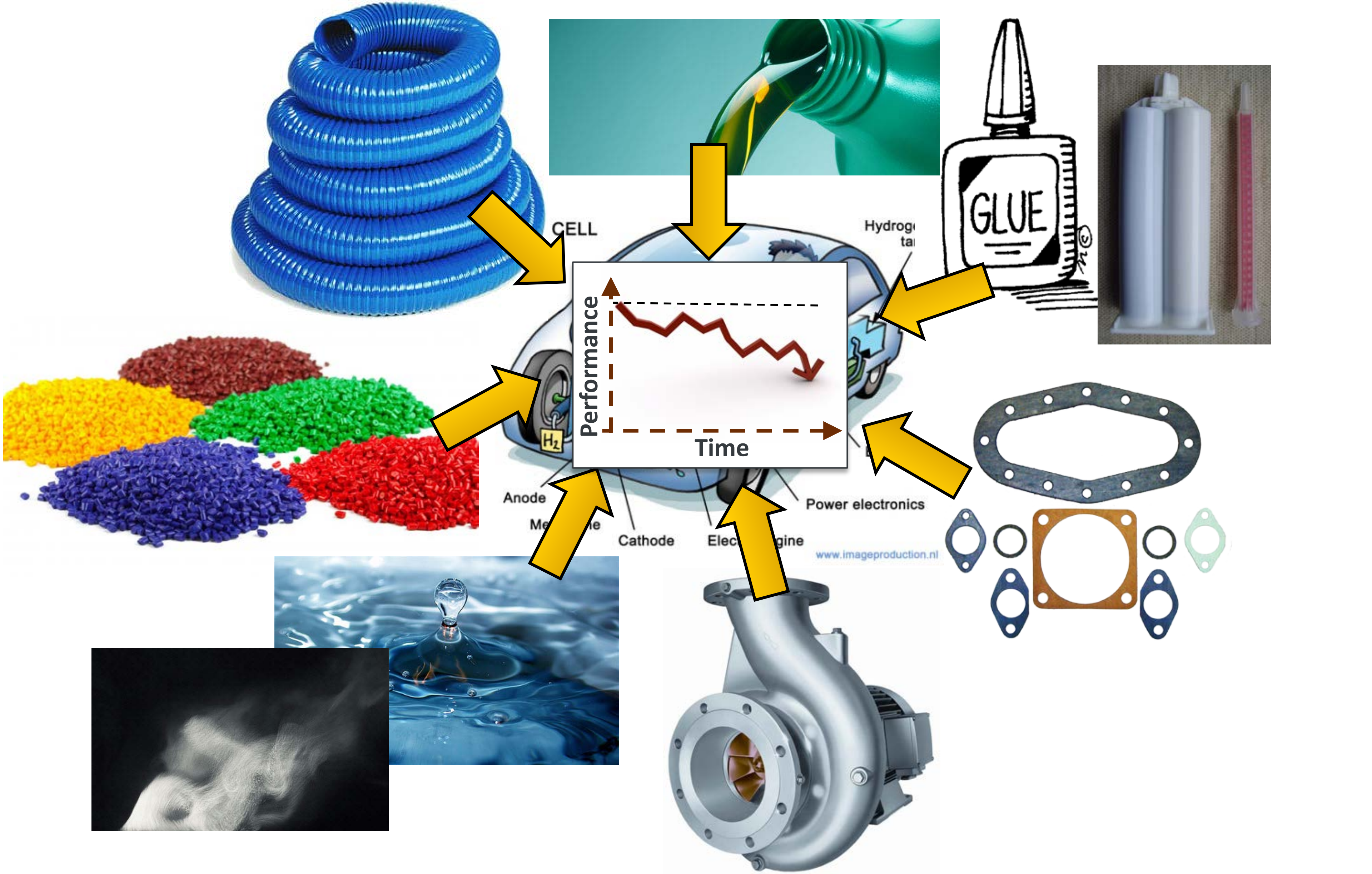
http://www.hydrogen-motors.com/chevrolet-equinox-fuel-cell.html

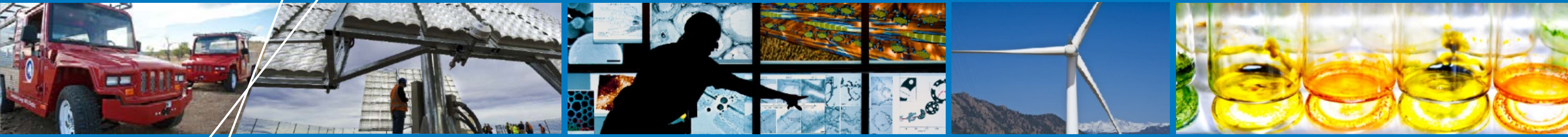
Fuel Cell System = Fuel Cell Stack + Balance of Plant



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

System Contaminants Originate From the System Itself





Material Selection

Material Selection

Materials chosen based on:

1. **Physical properties**
   - **Operating conditions (0-100% RH, -40-90˚C)**
2. **Commercial availability**
3. **Cost**
4. **Processability**
5. **Input from OEMs and fuel cell system manufacturers**
   - **GM (active project collaborator)**
   - **Ballard Power Systems**
   - **Nuvera**

Material Selection Prioritization:

based on wetted surface area, total mass/volume, proximity to MEAs, function, cost, and performance implications

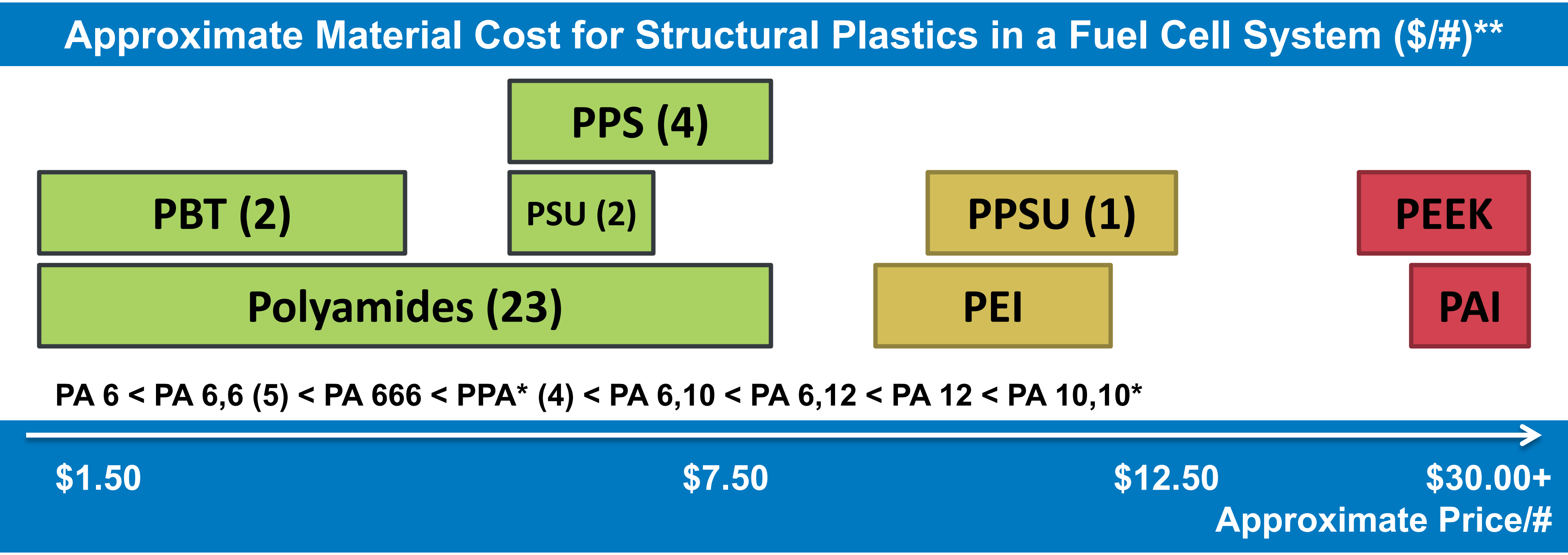
1. **Structural materials**
2. Coolants
3. **Elastomers for seals**
4. **Elastomers for (sub)gaskets**
5. **Assembly aids (adhesives, lubricants)**
6. **Hoses**
7. **Membrane degradation products**
8. Fuel Impurities
9. Ions from catalyst alloys

Note: materials highlighted in red were chosen for this study

The materials selected for the study were not made specifically for fuel cell application.

- Identify and quantify what contaminants leach out from BOP materials
- Understand where the contaminants come from (e.g., additives)
- Determine impact on fuel cell performance
- Help guide fuel cell developers & material suppliers select & design BOP materials for fuel cell applications

Example of BOP materials selected for the study based on physical property and cost



** Prices are approximations based on 5/2010 dollars, they are dependent on market and specific material. Figure should be used as a general guideline only. Scale is non-linear.

PA = polyamide (nylon); PPA = polyphthalamide; PSU = polysulfone; PPS = polyphenylene sulfide; PPSU = polyphenylsulfone; PEI = polyethylene imine; PEEK = polyether ether ketone; PAI = polyamide imide; PBT = polybutylene terephthalate

(Number of materials studied to-date)

Size of Component

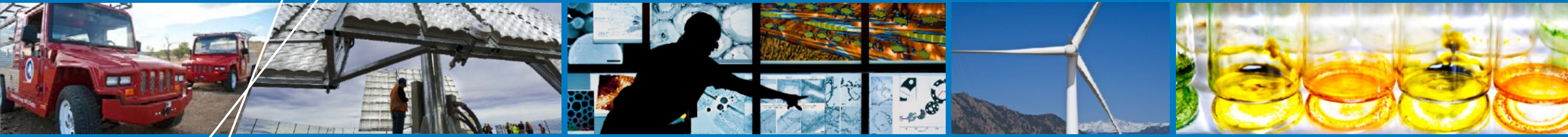
Information provided by GM

Screened 60 BOP materials

Function Description	Chemical Description	Manufacturer	Total Grades
Structural Plastic	Polyamide (PA), polyphthalamide (PPA) (Nylon)	DuPont, EMS, BASF, Solvay,	23
Structural Plastic	Polyphenylene sulfide (PPS)	Chevron Phillips	4
Structural Plastic	Polysulfone (PSU)	Solvay	2
Structural Plastic	Polyphenylsulfone (PPSU)	Solvay	1
Structural Plastic	Polybutylene terephthalate (PBT)	DuPont	2
Structural Plastic	Epoxy	Sumitomo	1
Structural Plastic	Phenolic	Sumitomo	1
Lubricant/Grease	Perfluoroalkylether/ polytetrafluoroethylene (PFAE/PTFE)	DuPont	4
Adhesive/Seal	Urethane	3M, Bostik, Henkel	6
Adhesive/Seal	Silicone	3M	2
Adhesive	Epoxy	3M, Reltek	3
Adhesive	Acrylic acrylate	LORD	1
Thread Lock/Seal	Polyglycol dimethacrylate (PGDMA),	Henkel	4
Thread Sealant	PTFE, Diacetone alcohol	LACO, Rectorseal	3
Hose	Silicone	VenAir	3
	Total		**60**

Structural Material

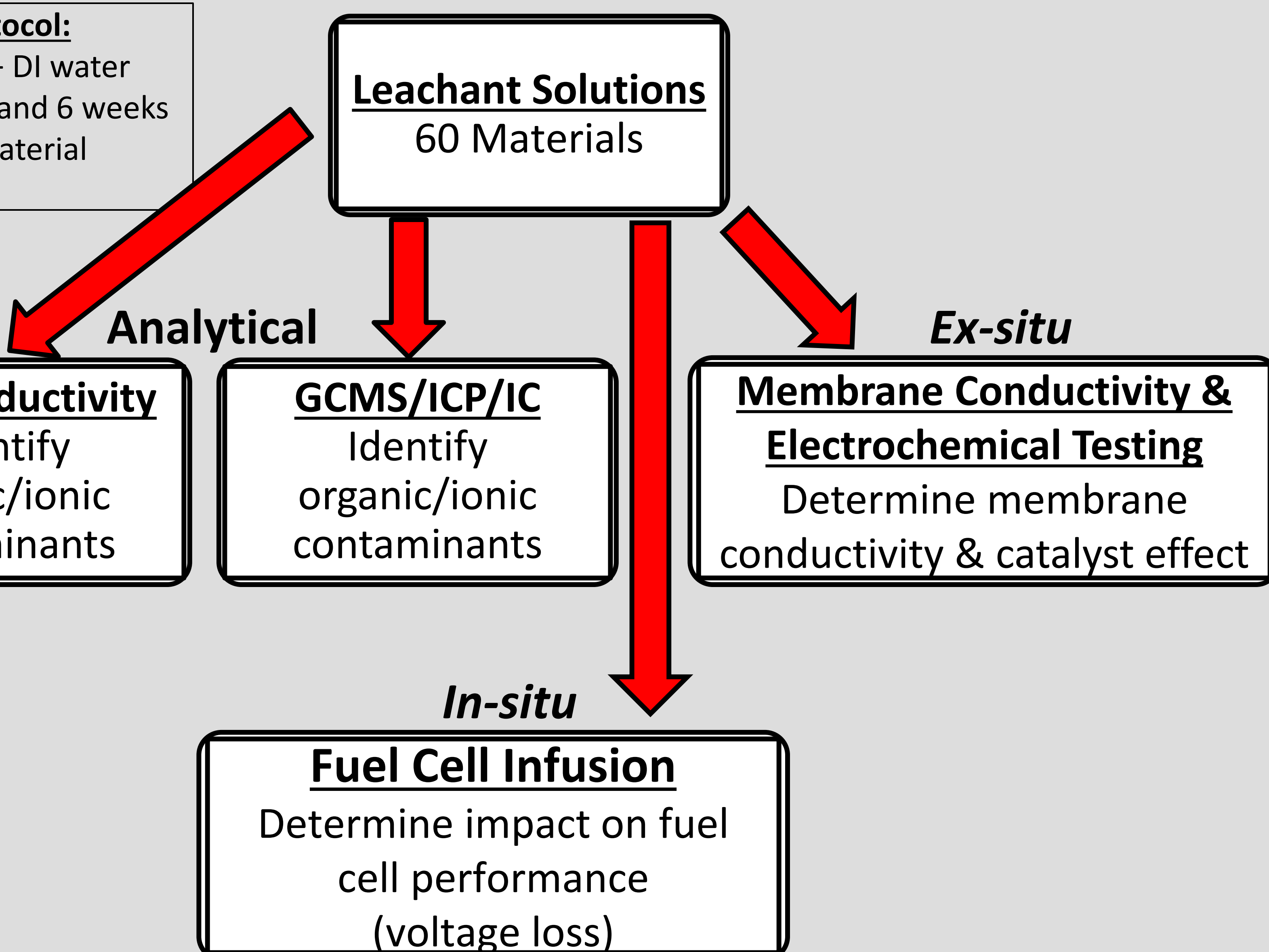
Assembly Aids



Methodology

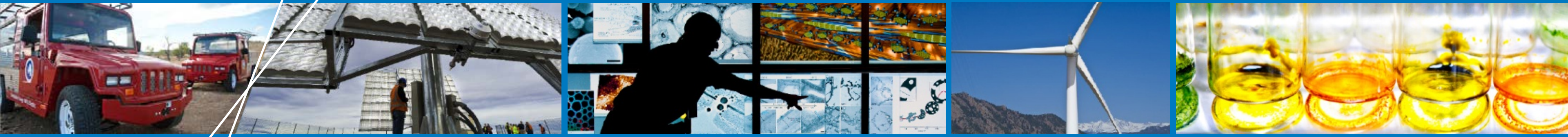
Approach/Experimental Methods

Leaching Protocol:
- Materials + DI water
- 90°C for 1 and 6 weeks
- Remove Material



Interactive Web Tool

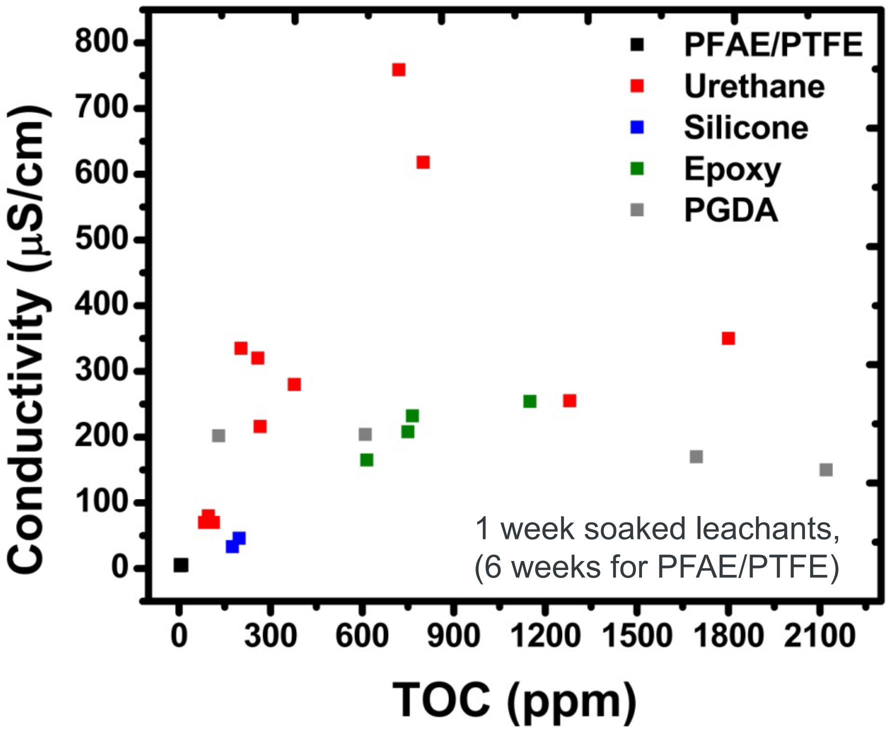
Input: Material Selection	Data Output
• Material type • Material class • Manufacturers • Trade name & Use • Material Grade	• Solution conductivity • Total organic carbon (TOC) • Ion Chromatography (IC) • Inductively Coupled Plasma (ICP) • Gas Chromatography Mass Spectrometry (GCMS) • Leaching Index • In situ fuel cell performance impact



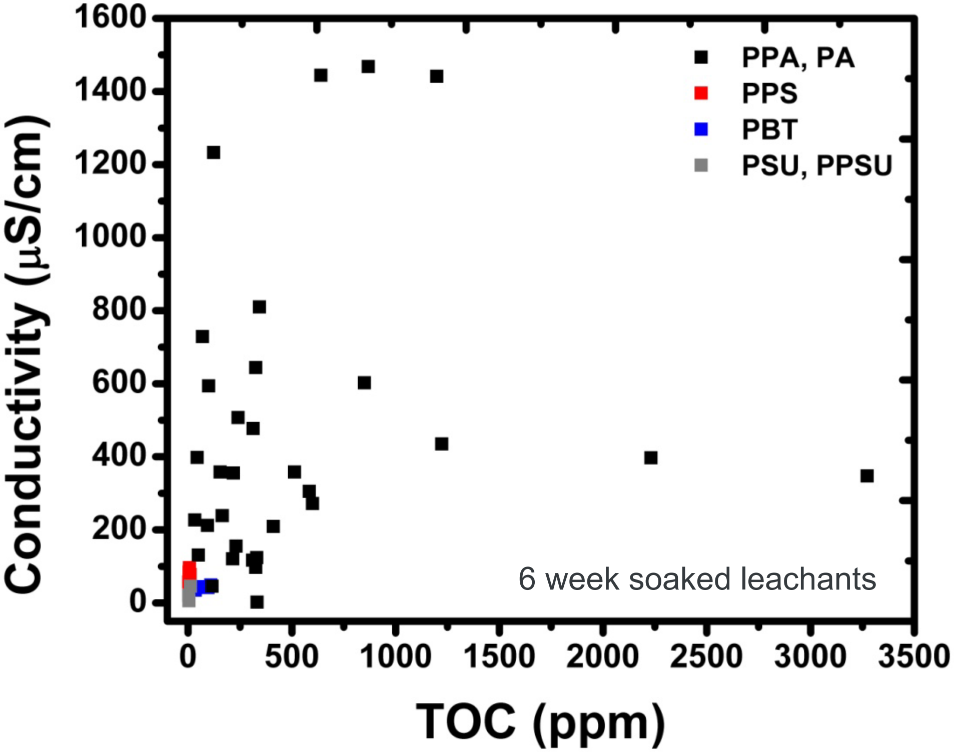
Screening Result Examples

TOC and Conductivity Screening of Extract Solutions

Assembly Aids Materials



Structural Materials



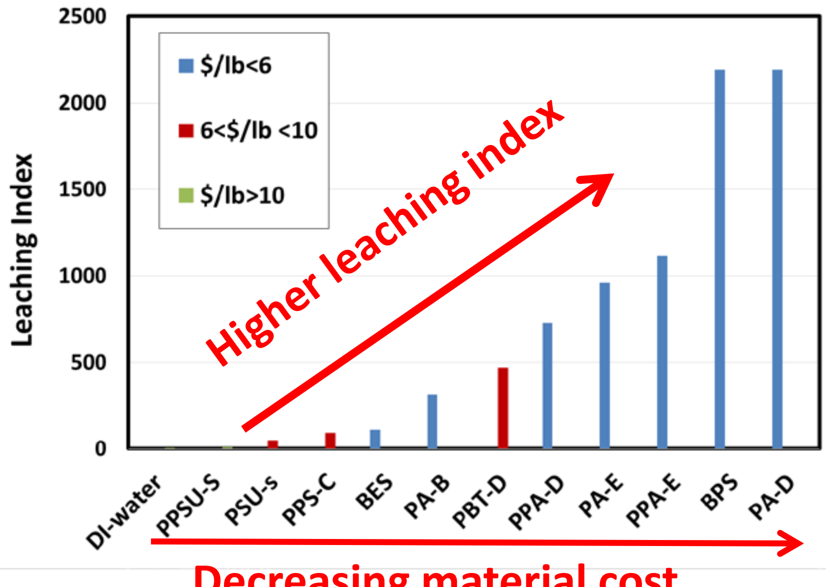
- Potential contaminants consist of a mixture of species: organics, inorganics and ions.
- Likely target BoP materials: low TOC and low solution conductivity
- Higher cost, non-commodity materials (PFAE/PTFE, PPS, PBT, PSU, PPSU) leached out less ionic and organic contaminants.

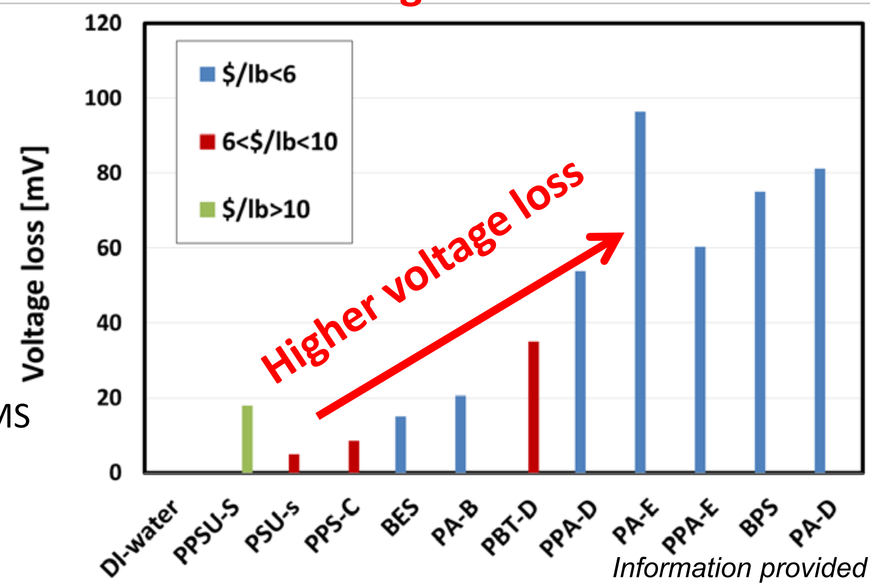
TOC = Total Organic Carbon

Leaching Index as a Quick Material Screening Method

GM screened and categorized 34 plastic materials into groups based on their basic polymer resin and brands

- Leaching index (conductivity + total organic carbon) is a quick way to screen plastic materials
- Leaching index shows trends with voltage loss and material cost; In general, the higher the leaching index,
  - Higher cell voltage loss
  - Lower material cost





BES = Bakelite epoxy-based material – Sumitomo;
BPS = Bakelite phenolic-based material – Sumitomo;
S = Solvay; C = Chevron Philips; B = BASF; D = Dupont; E = EMS

Dinh, H.N. "Effect of System Contaminants on PEMFC Performance and Durability." DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, Washington, DC, on June 18, 2014.

Information provided by GM

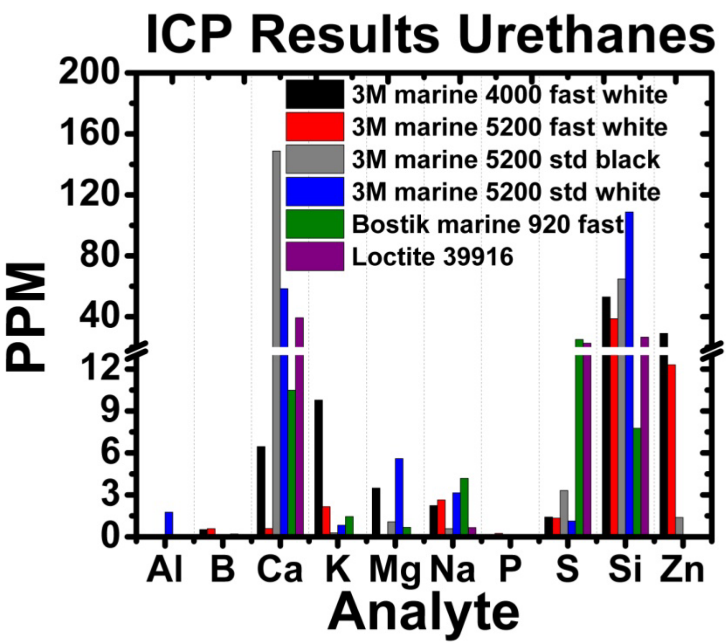
Elemental speciation by ICP

Elemental analysis identify leached species, which were linked to fillers and additives (base on knowledge of the type of plastic, common additives and information from datasheets).

Common additives in urethanes[1,2]:

- **Flame retardant**
  - **Alumina trihydrate (hydroxide) [Al], K**
- **Fillers and flame retardants**
  - **Limestone, dolomite, talc (Ca,Mg, Si)**
- **Catalysts**
  - **K, Zn**

Major Species Identified via ICP-OES Elemental Analysis



Ag	Be	Cu	Mg	Pb	Tl
Al	Ca	Fe	Mn	S	U
As	Cd	K	Na	Se	V
B	Co	Li	Ni	Si	Zn
Ba	Cr	Mg	P	Sr	

29 elements; ICP-OES elemental analysis

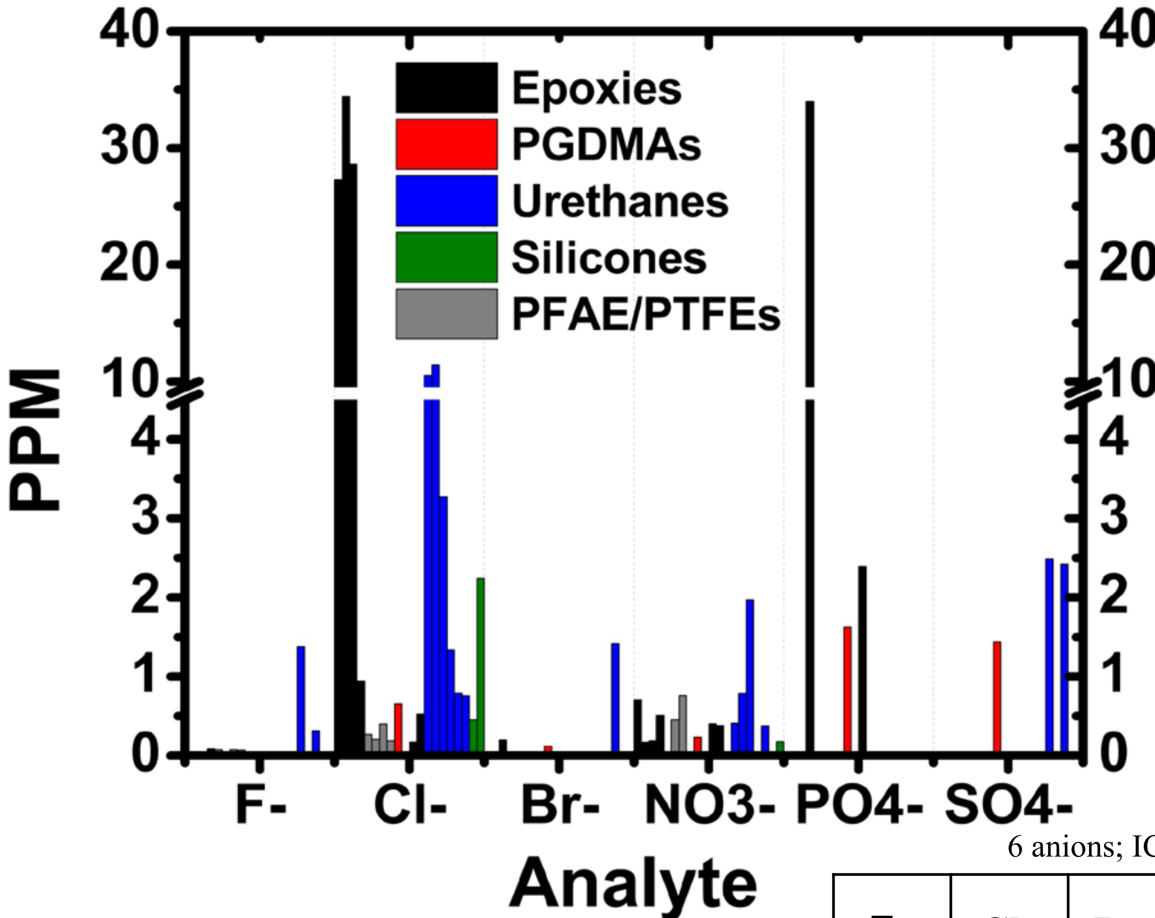
Macomber, C.S.; Christ, J.; Wang, H.; Pivovar, B.S.; Dinh, H.N. "Characterizing Leachant Contaminants from Fuel Cell Assembly Aids, a Prelude to Effects on Performance." *ECS Transactions* (50:2), 2013; pp. 603-618.

ICP = inductively coupled plasma
OES = optical emission spectroscopy

1. Manufacturer's MSDS; 2. Lindholm, J., et al., J. Appl. Polym. Sci. 123(3): p. 1793-1800 (2011).

Anions Quantified by Ion Chromatography [IC]

Observed species can be attributed to fillers and additives



6 anions; IC ionic analysis

F^-	Cl^-	Br^-	NO_3^-	PO_4^-	SO_4^-

Macomber, C.S.; Christ, J.; Wang, H.; Pivovar, B.S.; Dinh, H.N. "Characterizing Leachant Contaminants from Fuel Cell Assembly Aids, a Prelude to Effects on Performance." *ECS Transactions* (50:2), 2013; pp. 603-618.

Organic Compounds Identified via GCMS

Material function	Chemical description	Major organic compounds identified	Source of species
Lubricant/ Grease	**PFAE/PTFE**	None	
Adhesive/Seal	**Urethane**	methyl benzenediamine	hydrolysis product of residual monomer
		4- methyl benzenesulfoneamide	hydrolysis product of a cyano water scavenger
		2-(2-ethoxyethoxy)-ethanol acetate	Residual solvent (added for material flowability)
		2-(2-ethoxyethoxy)-ethanol	
Adhesive/Seal	**Silicone**	benzyl alcohol	
		2-(2-ethoxyethoxy)-ethanol acetate	
		2-(2-ethoxyethoxy)-ethanol	
Adhesive/Seal	**Epoxy**	benzyl alcohol	
		[p/o]-tert-butyl-phenol	
Adhesive/Seal	**Acrylic Acrylate**	2-methyl-2-hydroxyethyl ester, 2-propenoic acid	
Thread Lock/Seal	**PGDA**	polyethylene glycol dimethacrylate	Lower molecular weight molecule derived from original polymer

- **Organic compounds come from polymer resins, additives, residual solvents, and by-products of incomplete polymerization.**
- **The more expensive materials such as PFAE/PTFE are clean (no organics detected).**

Macomber, C.S.; Christ, J.; Wang, H.; Pivovar, B.S.; Dinh, H.N. "Characterizing Leachant Contaminants from Fuel Cell Assembly Aids, a Prelude to Effects on Performance." *ECS Transactions* (50:2), 2013; pp. 603-618.

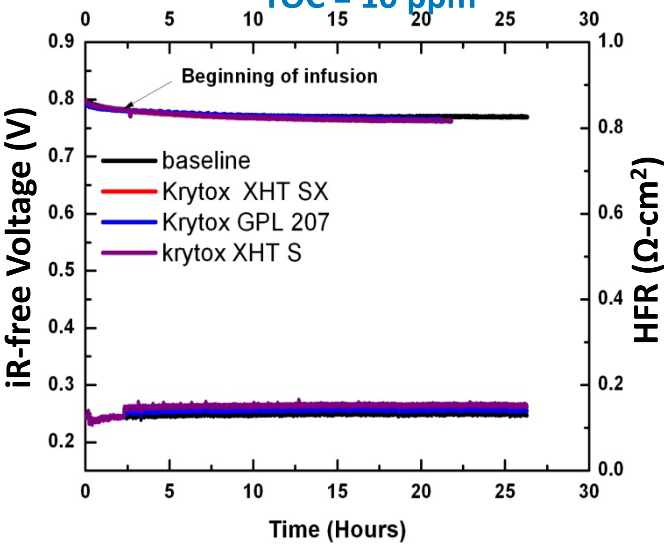
PFAE/PTFE = Perfluoroalkylether/ polytetrafluoroethylene;
PGDA = Polyglycol Dimethacrylate

GCMS = gas chromatography mass spectrometry

In-situ infusion screening for impact on fuel cell performance (at 0.2 A/cm^2)

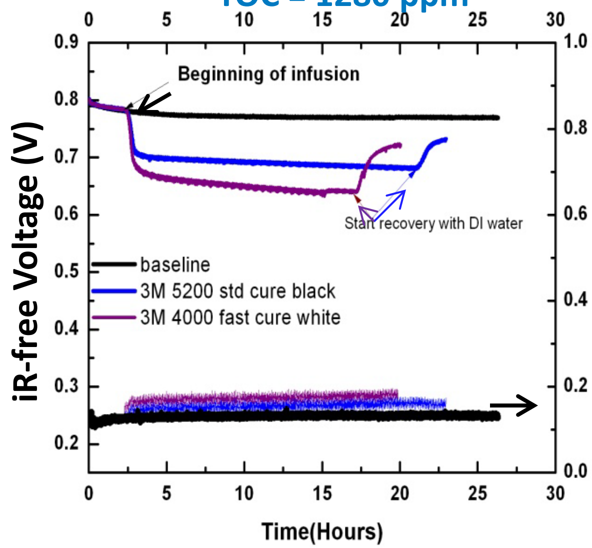
PFAE/PTFE example

TOC = 10 ppm



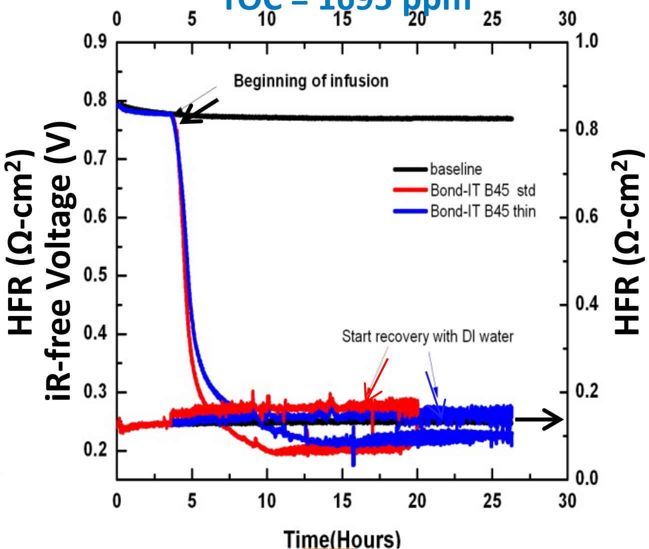
Urethane example

TOC = 1280 ppm

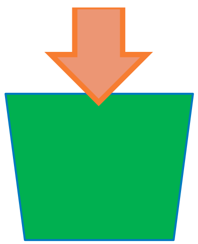


Epoxy example

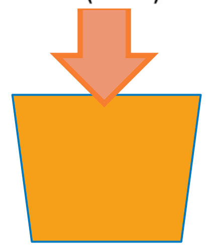
TOC = 1695 ppm



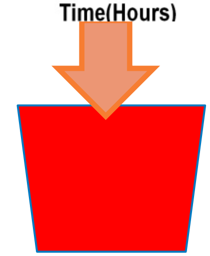
Material Classification by Result



clean



Contaminates, partially recovers



Contaminates, Does not recover

System contaminants can have an adverse effect on fuel cell performance, but the effect is complex. Some contamination are recoverable while others are not.

Opu, M.S.; Ohashi, M.; Cho, H.S.; Macomber, C.S.; Dinh, H.N.; Van Zee, J.W. "Understanding the Effects of Contaminants from Balance of Plant Assembly Aids Materials on PEMFCs-In Situ Studies." *ECS Transactions* (50:2), 2013; pp. 619-634.

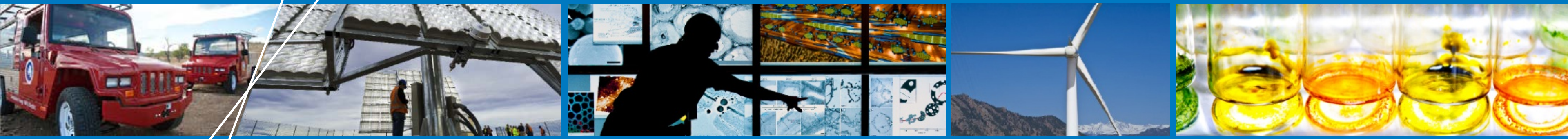
Performance Impact & Mitigation Strategy Remarks

Fuel Cell Performance Impact Considerations

- Contamination impact depends on operating conditions (current density, concentration, Pt loading, RH interaction with Pt loading & concentration, temperature).
- Operating conditions (e.g., time, temperature) that cause more liquid/plastic contact need to be considered in developing a fuel cell system
- **Cost, resin type & additives need to be considered when selecting BOP plastic materials**

Suggested mitigation strategies:

- Minimize extract solution concentration (low leaching index)
  - Minimize contact time of the plastic materials with water in the fuel cell system
  - Minimize exposure of plastic material to high temperature
  - Increase RH (water flush) or increase RH and potential cycling (ex-situ recovery)
  - Choose clean BOP materials (usually more expensive, resin type)
  - Modify commercial plastic materials to minimize contaminants (i.e., coating, less or alternative additives)
- Add filter and/or consider other mitigation methods



Website Live Demo

Summary

- A relatively large material data base is now publicly accessible & all of the information can be found in one place
- Intended to help fuel cell industry select appropriate BOP materials & in cost-benefit analyses.
- Help fuel cell developers and material suppliers develop clean materials for fuel cell application
- Designed the web tool to be interactive, informative & easy to use
- Will continue to improve the website, so feedback is welcome
- Look for our publications for more in depth analysis of the results

Acknowledgements

The Department of Energy EERE Fuel Cell Technology Office for project funding.

- Dave Peterson & Kathi Epping, Technology Development Manager

3M, Ballard Power Systems, Nuvera Fuel Cells, Proton Onsite, Sumitomo, BASF, Chevron Phillips, DuPont, Solvay, EMS, Bostik, Henkel, LORD, Reltek, LACO, Rectorseal, VenAir for providing materials for screening development.

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University of Hawaii: J. St-Pierre, K. Bethune
Colorado School of Mines: J. Christ, R. Richards
Los Alamos National Laboratory: T. Rockward
3M: S. Hamrock

NREL Contacts

Website

http://www.nrel.gov/hydrogen/contaminants.html

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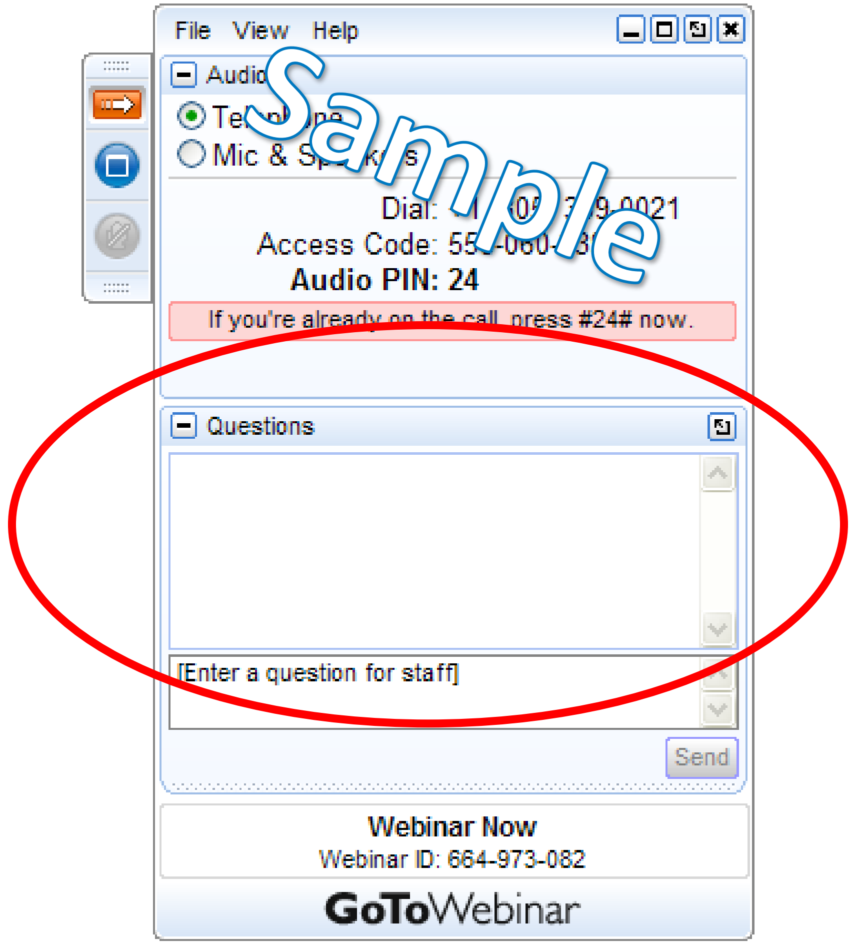
Question and Answer

- Please type your question into the question box



hydrogenandfuelcells.energy.gov

Thank You

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