

The Effect of Airborne Contaminants on Fuel Cell Performance and Durability

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June 18, 2014

Project ID # FC065

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Overview

Timeline

- Project start date: April 1, 2010
- Project end date: March 31, 2015

Budget

- Total funding spent as of 3/31/14: \$2,616,797
- Total DOE project value: \$4,566,878
- Cost share percentage: 20.1

Barriers

- (A) Durability
 - 5000 h in automotive drive cycle by 2017 (automotive application)
- (C) Performance
 - Energy efficiency
 - 60 % at 25 % of rated power by 2017 (automotive application)

Partners

- Interactions/collaborations: University of Connecticut*, WPCSOL (new)*,**, Ballard Power Systems*

* subcontractor; **consultant, formerly from UTC Power

Relevance

Project objective: Identification and mitigation of the airborne contaminants adversely impacting system performance and durability

- Preventive: contaminants and tolerance limits for filter specifications
- Recovery: material, design or operation changes to remove contaminant species

2013-2014 objective: Establish degradation mechanisms for key contaminants

Project impact:

- Obtained detailed characterization information about the performance impact causes of 8 contaminants
- Information will support the development of mitigation strategies

**Table 3.4.3 Technical Targets for Automotive Applications:
80-kW_e (net) Integrated Transportation Fuel Cell Power Systems Operating on Direct Hydrogen^a**

Characteristic	Units	2011 Status	2017 Targets	2020 Targets
Energy efficiency ^b @ 25% of rated power	%	59	60	60
Power density	W / L	400 ^c	650	850
Specific power	W / kg	400 ^c	650	650
Cost ^d	\$ / kW _e	49 ^e	30	30
Cold start-up time to 50% of rated power				
@-20°C ambient temp	seconds	20 ^f	30	30
@+20°C ambient temp	seconds	<10	5	5
Start up and shut down energy ^g				
from -20°C ambient temp	MJ	7.5	5	5
from +20°C ambient temp	MJ	-	1	1
Durability in automotive drive cycle	hours	2,500 ^h	5,000 ⁱ	5,000 ⁱ
Assisted start from low temperatures ^j	°C	-	-40	-40
Unassisted start from low temperatures ^j	°C	-20 ^f	-30	-30

Project targets

Approach

- Systematic use of multiple in situ and ex situ characterization techniques to resolve kinetic, ohmic and mass transfer cell voltage losses
- Selected airborne contaminants expand other research
 - Limited scope of prior air contaminants studies, mostly SO_x, NO_x and NH₃
 - Activities complement former hydrogen and system contaminants projects

Task	Objectives
1.1 Impurity Identification and Screening	<ul style="list-style-type: none"> • Identify potential contaminants originating from air pollution and road side environments. • Screen and prioritize impurities based on degradation of cell performance or chemical interaction with the MEA.
1.2 Contaminant Impact	<ul style="list-style-type: none"> • Quantify impact of contaminant and contaminant mixtures on fuel cell performance and durability at different operating conditions. • Quantify all reaction products to aid identification of reaction and adsorption processes. • Quantify spatial variability of contaminant processes using segmented cell.
1.3 Cell Recovery	<ul style="list-style-type: none"> • Quantify cell recovery resulting from removal of contaminant and change of operating conditions.
1.4 Ex-situ Analysis	<ul style="list-style-type: none"> • Characterize changes in catalyst, MEA and GDL structure resulting from exposure to contaminant and contaminant mixtures.
2.1 Real World Operation	<ul style="list-style-type: none"> • Characterize effect of contaminant at 'real world' operating conditions.
2.2 Mitigation Strategies	<ul style="list-style-type: none"> • Explore operating strategies and novel techniques to mitigate contaminant effects.
3.0 Model Development and Application	<ul style="list-style-type: none"> • Validate and use empirical performance models to quantify and understand spatial variability of contaminant effects in PEMFCs. • Develop and validate mechanistic models that quantify material degradation. • Establish the relationship between those mechanisms and models, and the loss of PEMFC performance.
4.0 Outreach	<ul style="list-style-type: none"> • Conduct outreach activities to disseminate critical data, findings, models, and relationships that describe the effects of airborne contaminants on PEMFC performance and durability.

Focus of this reporting period



Approach

- Milestone M3 due in March 2013 was completed
 - Quantify spatial variability of performance loss for at least 4 different contaminants. Identify principal poisoning mechanism for same

Milestone	Status	Due Date
M4 (interim): Complete the identification of intermediate or reaction products Determine the effect of acetonitrile intermediate or reaction products on membrane conductivity Complete segmented fuel cell measurements Complete 4 outreach products	Only 2 species left (June 2014) Only NH ₃ /NH ₄ ⁺ tests with GCMS and ion selective electrode left (June 2014) Only 1 species left (June 2014) 4 journal papers	March 2014 ~95 % complete
M4 (interim): Characterize the long term effects of a contaminant mixture Characterize the effect of acidic and cleaning solutions circulation on performance recovery Complete 5 outreach products	In progress	June 2014
M4 (interim): Identify differences introduced by metallic bipolar plates Characterize the long term effects of an organic contaminant Characterize the long term effects of a foreign cation contaminant Complete 4 outreach products	In progress	September 2014
M4 (interim): Characterize the effect of sustained OCV periods on fuel cell performance recovery Complete 7 outreach products		December 2014
M4: Demonstrate successful mitigation of the impact of the most important 4 airborne contaminants Characterize the effect of sustained air starvation and point of zero charge periods on fuel cell performance recovery Complete 7 outreach products		March 2015

Highlighted text indicates new interim milestones and deliverables

Accomplishments and Progress - Metrics Summary

- ~95 % completion of ex situ and in situ diagnostic tests to determine the performance impact causes of 8 contaminants

- Measurements from this reporting period are highlighted in blue
- Contaminants sources are in the technical backup slides

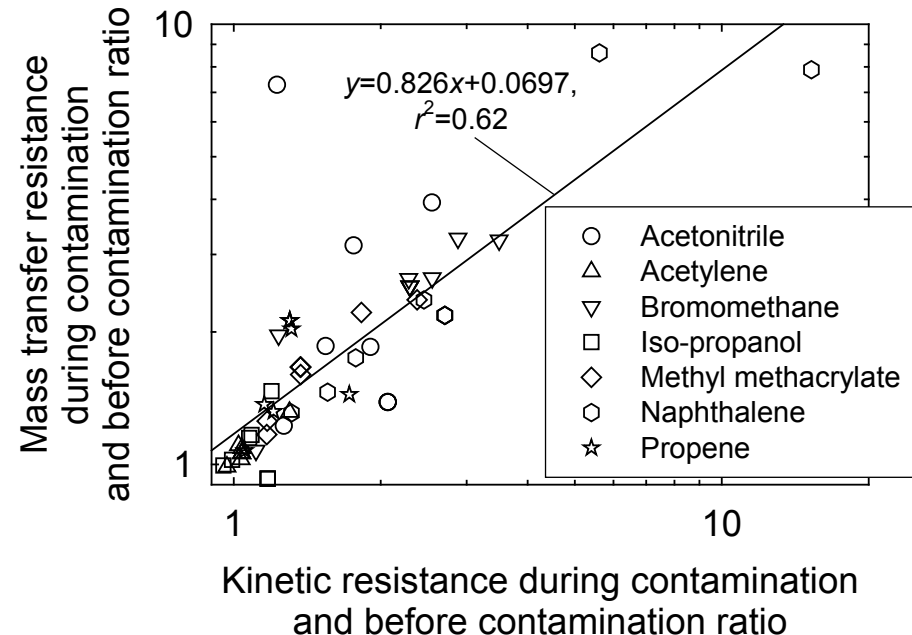
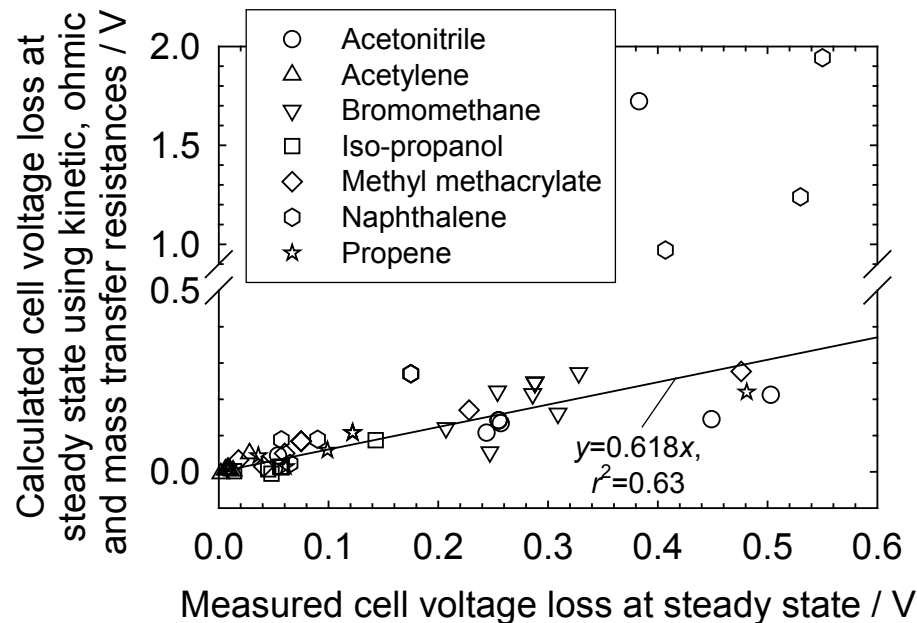
Metric discussed in the next slide

Contaminant	Kinetic current (% loss in air at 30 °C and 0.9 V vs RHE)	Electrochemical catalyst area (% loss in N ₂ at 30 °C)	H ₂ O ₂ current (% gain in air at 30 °C and 0.5 V vs RHE) ^a	Membrane conductivity (% loss at 80 °C and 50 % relative humidity)	GDE water content	Dimensionless local current (maximum % loss and gain in air at 80 °C)		Contaminant conversion (% in air at 80 °C) ^b
						Contamination phase	Recovery phase	
Acetonitrile	79-84 (16.9 mM)	>76 (16.9 mM)	850-1300 (16.9 mM)	0 (100 ppm), product effect? (in progress)	TBD	Step change followed by a cell potential triggered evolution reaching -15 to 12 at steady state (20 ppm)	Traveling current wave reaching -28 to 22 to values approximately equal to initial values (20 ppm)	20 to 45 for 0.55 to 0.65 V (20 ppm)
Acetylene	100 (4030 ppm)	100 (4040 ppm)	2700-3800 (4030 ppm)	1-2 (500 ppm)	TBD	Traveling current wave of -99 to 100 synchronized with voltage transient followed by -17 to 18 at steady state (300 ppm)	Step change to values approximately equal to initial values (300 ppm)	0.8 to 100 for 0.55 to 0.85 V (300 ppm)
Bromomethane	54 (400 ppm)	43 (400 ppm)	56 (400 ppm)	No ohmic loss in fuel cell	TBD	Gradual change starts after voltage steady state reaching -19 to 13 (5 ppm)	Trend continues reaching -21 to 21 (5 ppm)	In progress
Iso-propanol	12 (1 mM)	7 (1 mM)	18 (1 mM)	No ohmic loss in fuel cell	TBD	TBD	TBD	Not applicable
Methyl methacrylate	65 (1 mM)	43 (H _{UPD}) and 82 (PtO reduction) (1 mM)	1300 (1 mM)	No ohmic loss in fuel cell	TBD	Step change of -7 to 6 (20 ppm)	Reverse step change (20 ppm)	49 to 57 for 0.55 to 0.68 V (20 ppm)
Naphthalene	66 (sat soln) ^c	90 (sat soln) ^c	780 (sat soln) ^c	No ohmic loss in fuel cell	TBD	Traveling current wave of -25 to 14 synchronized with voltage transient (2.3 ppm)	Traveling current wave of -39 to 40 synchronized with voltage transient (2.3 ppm)	In progress
Propene	53 (1010 ppm)	26 (H _{UPD}) and ~50 (PtO reduction) (1010 ppm)	620-960 (1010 ppm)	No ohmic loss in fuel cell	TBD	Step change of -8 to 6 (100 ppm)	Reverse step change (100 ppm)	43 to 89 for 0.55 to 0.85 V (100 ppm)
Ca ²⁺	37 (90 mM Ca(ClO ₄) ₂) 21 (5 ppm) ^d	2 (90 mM Ca(ClO ₄) ₂) 16-46 (5 ppm) ^d	660 (90 mM Ca(ClO ₄) ₂)	1.1-11 (5 ppm) ^e	-	Gradual change up to -50 to 20 (5 ppm) ^f	Gradual change up to -60 to 40 (5 ppm) ^f	-

^a The total current is still mostly due to oxygen reduction in spite of a large peroxide production rate increase. ^b In all cases, observed products include the unaltered contaminant, CO and CO₂. ^c 0.25 mM solubility at 25 °C. ^d Derived from in situ polarization curve and cyclic voltammetry tests. ^e In situ result by current interrupt for 0.6-1 A cm⁻² and 125 % relative humidity before a steady state is reached at 100 h. ^f 0.6 rather than 1 A cm⁻² and before a steady state is reached at 100 h. Highlighted text indicates completion during this reporting period. Highlighted text indicates completion by June 2014.

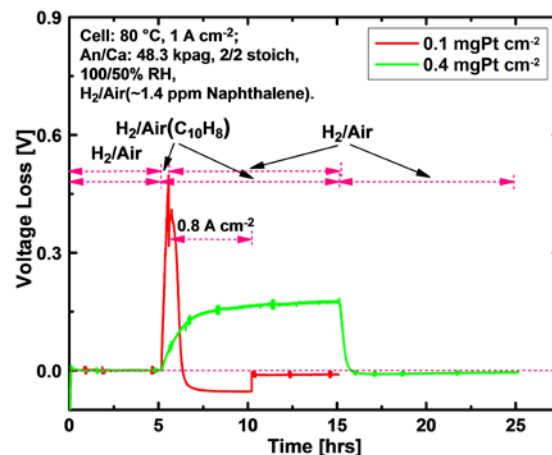
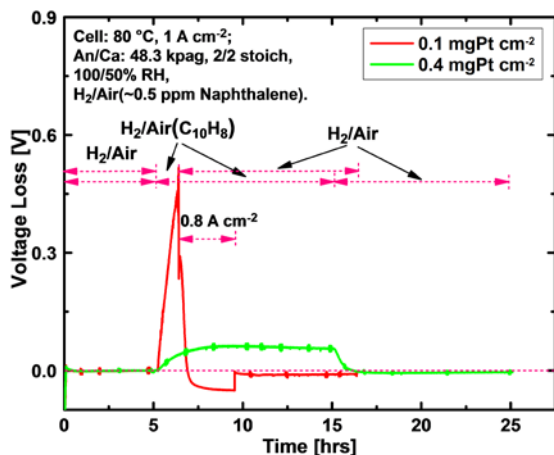
Accomplishments and Progress - Metrics Summary

- Strong correlations between cell voltage and impedance spectroscopy measurements indicated that the mass transport loss is largely due to contaminant adsorption on the catalyst
- The importance of GDE water content measurements was consequently reduced
 - Measurements will still be completed as part of another program (ONR) for confirmation



Accomplishments and Progress - Catalyst Loading Impact

- Generally, the cell voltage loss, percentage gain for a Pt loading reduction of 0.4 to 0.1 mg cm⁻², is proportionally larger (92 up to 6300 %) than the Pt loading decrease (75 %) and is dependent on operating conditions
 - Measurements from this reporting period are highlighted in blue
- Observation emphasizes the need to revise filter system specifications especially for low Pt catalyst loadings

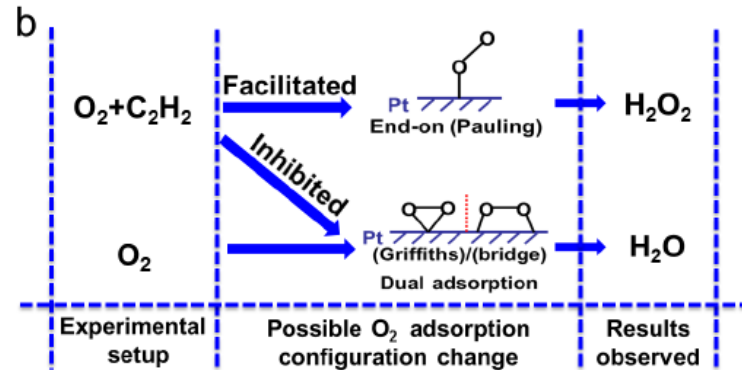
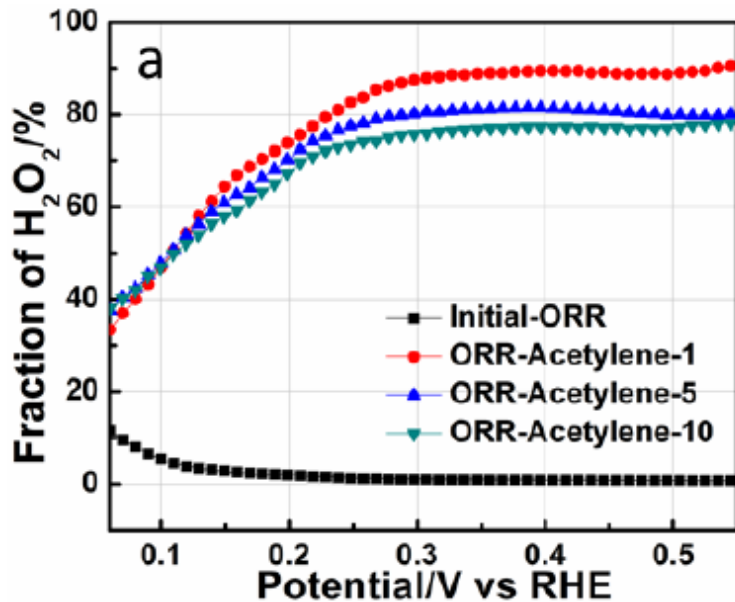


Contaminant	Acetonitrile	Acetylene	Bromomethane	Iso-propanol	Methyl methacrylate	Naphthalene	Propene	Ca ²⁺
Cell voltage loss (% gain for a Pt loading reduction of 0.4 to 0.1 mg cm ⁻² in air at 80 °C)	58 (20 ppm)	6325 (100 ppm)	-10 (5 ppm)	92 (~8000 ppm)	104 (20 ppm)	187 (1.4 ppm)	224 (100 ppm)	In progress

Highlighted text indicates completion during this reporting period. Highlighted text indicates completion by June 2014.

Accomplishments and Progress - ORR RRDE Tests

- Rotating ring/disc electrode data indicate that the fraction of peroxide created is much larger in the presence of an organic or cation species
 - Tests planned to establish the long term impact on the membrane degradation
 - Organic species adsorption on the catalyst surface sterically hinders the oxygen reduction path to water requiring a dual adsorption site
- Foreign cation contamination leads to a significant increase in hydrogen crossover especially with a higher concentration and current density
 - Tests planned to establish the long term impact on the membrane degradation
 - Effect ascribed to a localized electro-contraction and mechanical stresses

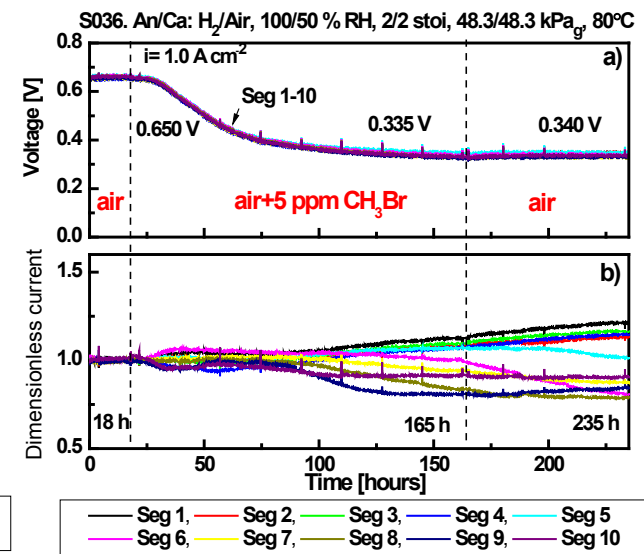
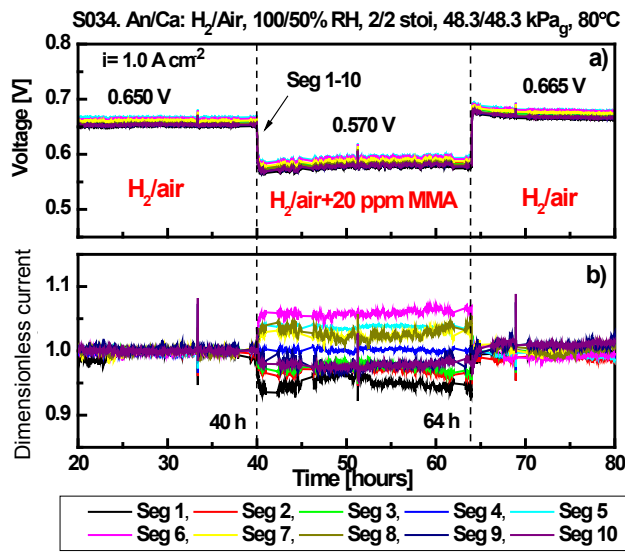
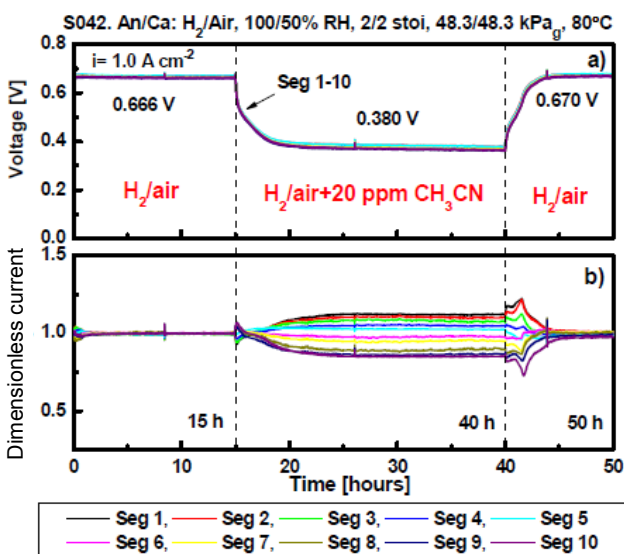
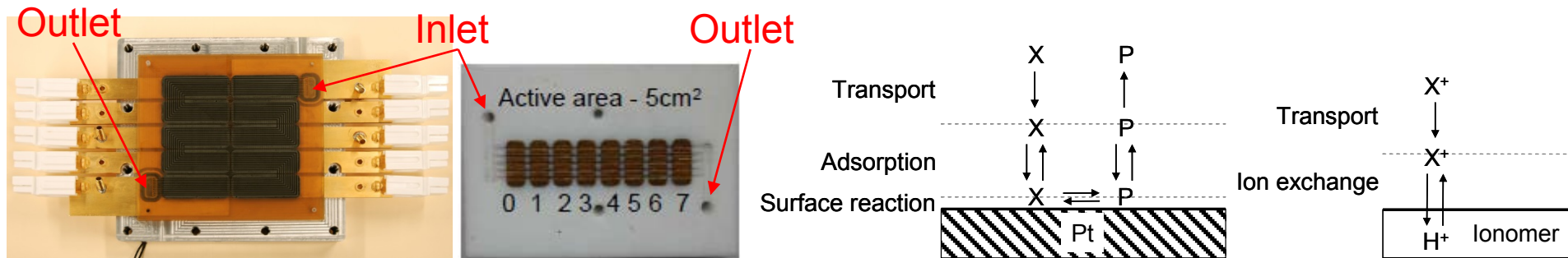


Cell No	H ₂ XO at BOT, mA/cm ²	H ₂ XO at EOT, mA/cm ²
1 A/cm ² with 2 ppm CaSO ₄	2.68	2.93
1 A/cm ² with 5 ppm CaSO ₄	2.75	90.7
1 A/cm ² with 10 ppm CaSO ₄	2.94	Too high to measure
0.6 A/cm ² with 5 ppm CaSO ₄	2.56	8.68
0.2 A/cm ² with 5 ppm CaSO ₄	2.89	3.55

H₂ XO:
hydrogen
crossover
rate

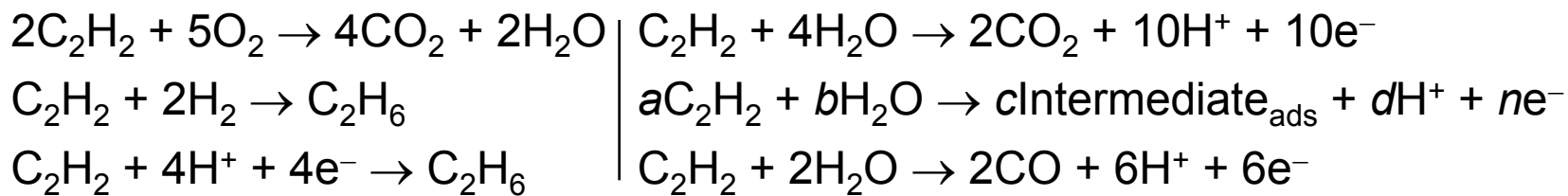
Accomplishments and Progress - Segmented Cell Tests

- Segmented cell data revealed varied organic and cation contaminant responses symptomatic of different mechanism's rate determining steps
 - The contamination effect is not always uniform across the active area and its local long term impact remains to be defined
 - Possible contamination mechanism diagnostic tool



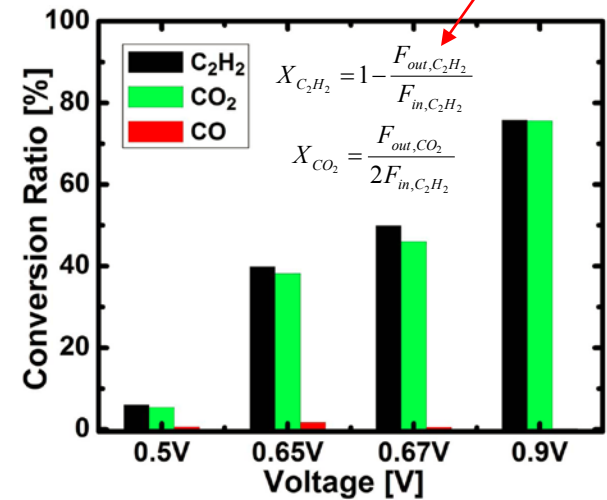
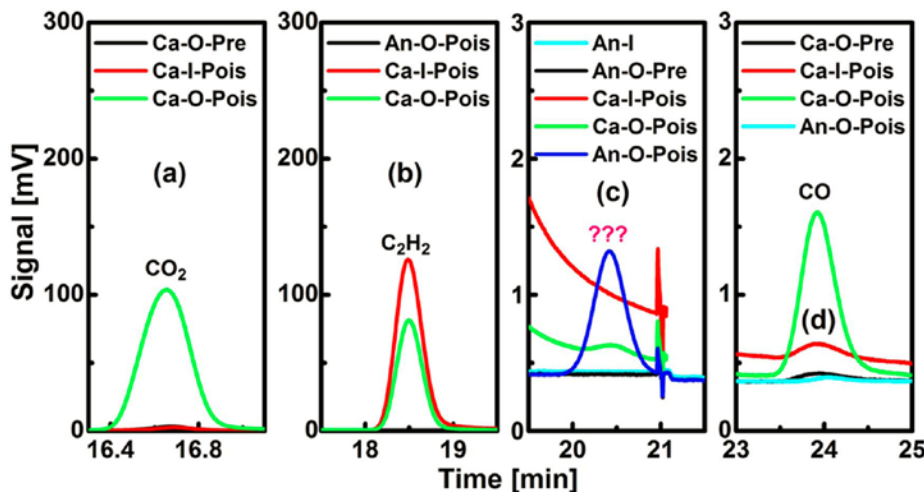
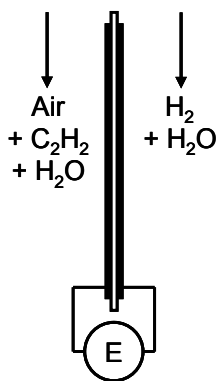
Accomplishments and Progress - Gas Chromatography Tests

- Data from a single cell equipped with a gas chromatograph indicate that organic species contamination mechanisms may be complex
 - Presence of both chemical and electrochemical reactions
 - Electrochemical reaction products are potential dependent
 - Situation may complicate performance recovery and suggest the use of several cell potentials to evaluate the effectiveness of recovery procedures



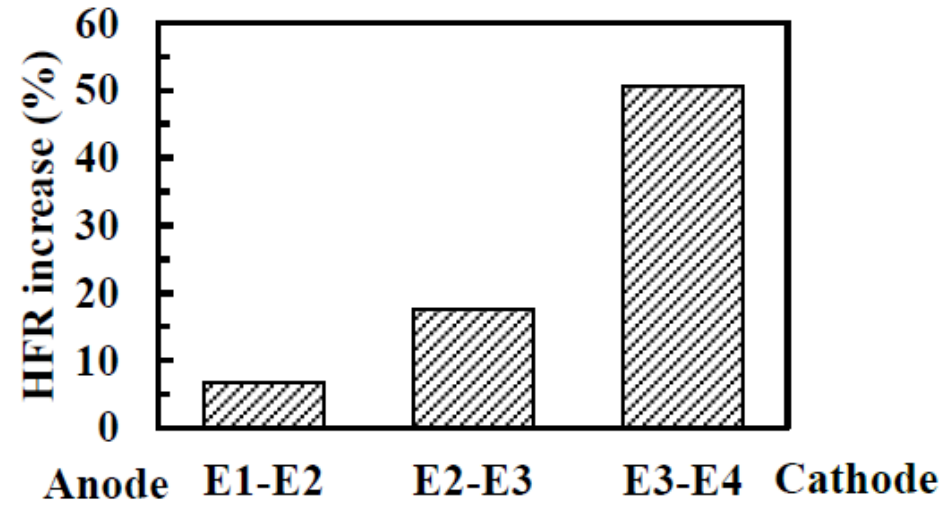
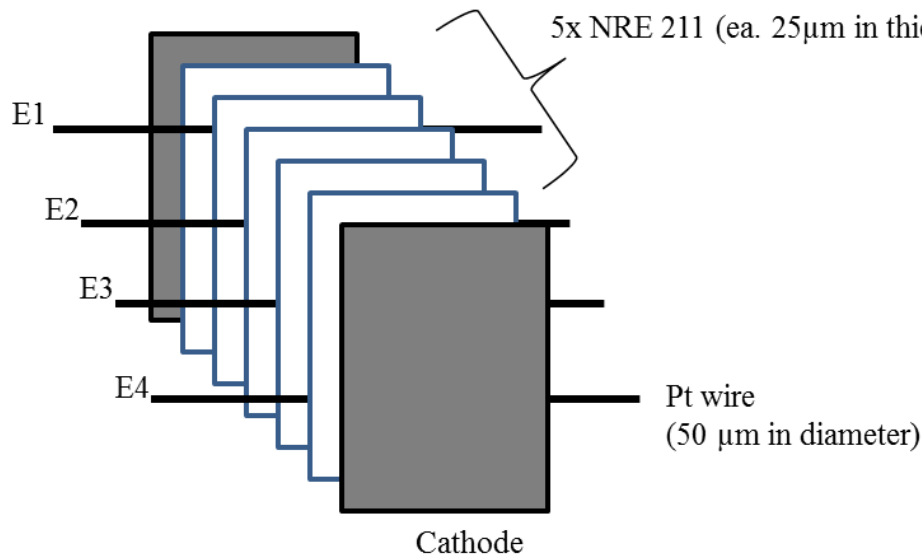
Conversions are differently defined to emphasize the observed mass balance

All reactions



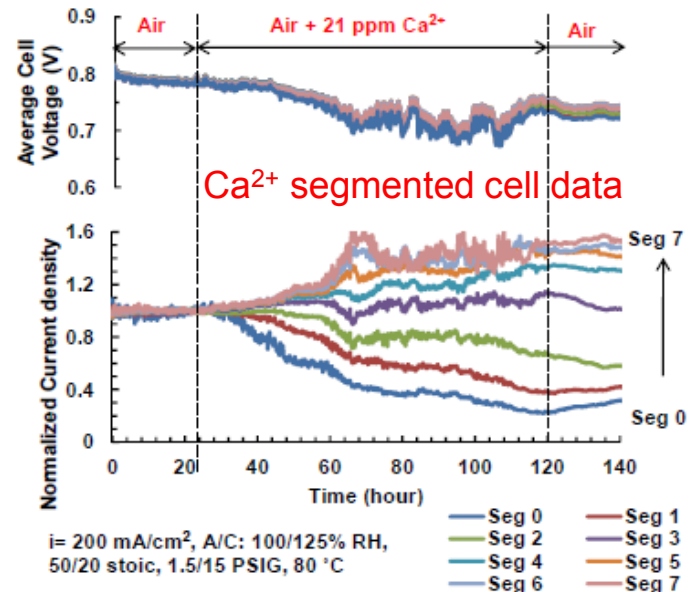
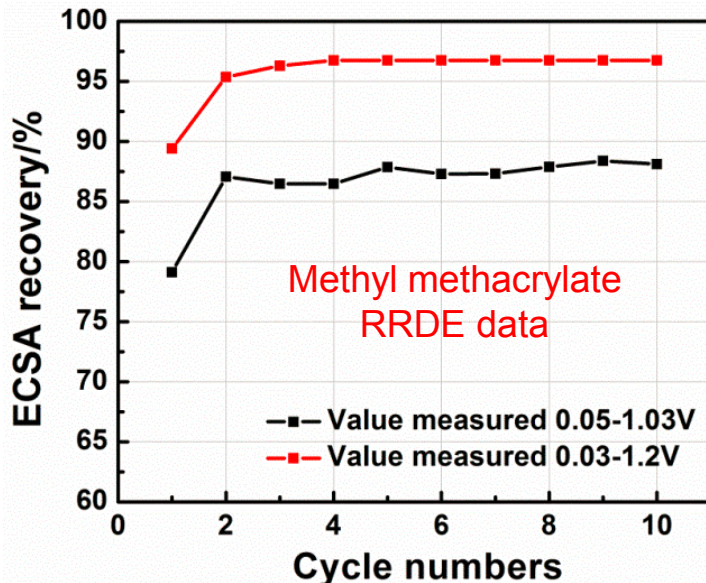
Accomplishments and Progress - Foreign Ion Contamination

- Foreign cation contamination is relatively more difficult to achieve and the performance effect is less severe than for organic species
 - The potential gradient pushes the foreign cations towards the cathode (higher resistance near the cathode) limiting ingress within the ionomer and membrane during operation
 - The presence of foreign cations at the cathode affects kinetic, ohmic and mass transfer overpotentials



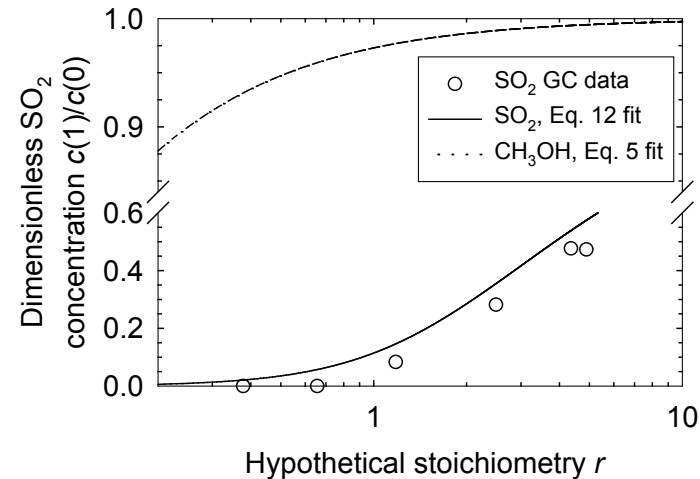
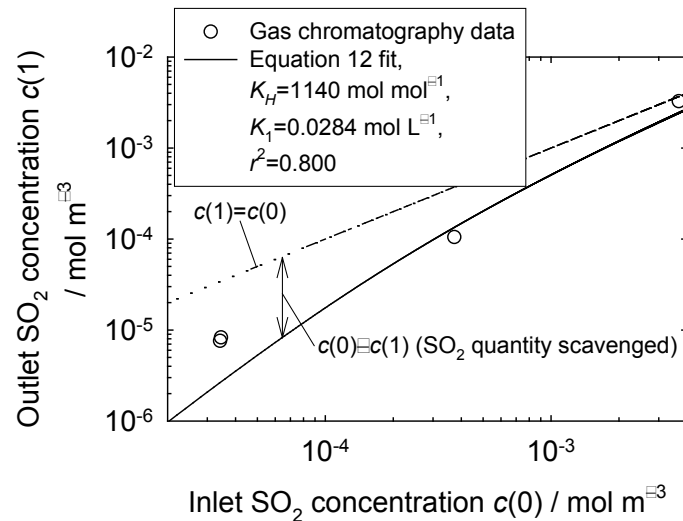
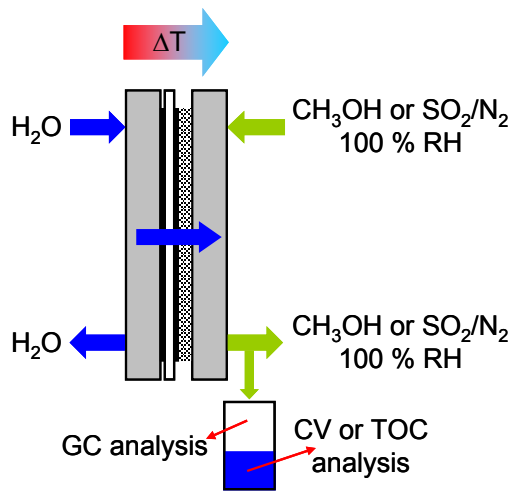
Accomplishments and Progress - Performance Recovery after Contamination

- Rotating ring/disc electrode data indicate that performance is largely recovered by stopping organic contaminant exposure
- However, organic residues remain on the catalyst surface that require cathode potentials up to 1.2 V for a near complete removal
 - Several lower potential recovery options will be explored (0-1 V cell, slide 5)
- Segmented cell data show that performance is not recovered by interrupting foreign cation exposure
 - Several aqueous solution based recovery options will be explored (slide 5)



Accomplishments and Progress - Modeling

- The liquid water scavenging model was validated for SO_2 , an important airborne contaminant that reacts with water to form sulfurous acid H_2SO_3 that subsequently dissociates to bisulfite HSO_3^- and proton H^+ ions
 - Methanol, which does not significantly dissociate, was used as a model contaminant for the 7 organic species in previous experiments
- Performance extrapolations to lower SO_2 concentrations that neglect the scavenging effect result in conservative air inlet tolerance limits
- The use of an effective contaminant concentration for soluble species to correlate performance data is also re-emphasized



Accomplishments and Progress - Responses to Previous Year Reviewers' Comments

- “UH needs to classify the hazard of the contaminants based on degradation mechanism and reasonable contaminant concentration.”
 - Foreign cations have already been classified as more benign (slide 12). As for the organic contaminants, their behavior is more variable (dimensionless local current, slide 6 for example) and an attempt will be made to classify them. A classification based on concentration is difficult to implement as contaminants (severity) and their concentrations (probability) vary according to location
- “While the project has a reasonable list of collaborators, more stack manufacturers are needed to update the project on the catalysts used in systems that are either in field trials or being readied for commercial release.”
 - The project team is open to consider adding new collaborators, stack manufacturers (sub-scale stacks), and materials as time and resources permit
- “The project may need to focus on publishing data in a format easily utilized by industry.”
 - The existing database is currently being published. However, the project team is open to recommendations giving a clear and detailed description of the format that would be most useful

Collaborations

- Project team members (all within the DOE fuel cells program)
 - Hawaii Natural Energy Institute (prime university organization, focus on airborne contaminants)
 - University of Connecticut Center for Clean Energy Engineering (university sub-contractor, focus on foreign cations)
 - WPCSOL and Ballard Power Systems (independent and industry sub-contractors, consulting role)
- Other collaborators (outside the DOE fuel cells program)
 - Air composition and filter specification definition support (Nuvera, ClearEdge Power)
 - Air filters for analysis (GM, Nuvera, UTC Power)
 - Nebulizer design and integration support (GM)
 - Heating tube for contaminant evaporation (GM)
 - Membrane contamination by a chemically and electrochemically inactive species model support and validation data (GM)
 - *Mutual support including activities overlap avoidance (project ID # FC048)*
 - Requested contaminants for validation (LANL, NREL, ANL, FCHEA, NRL, SAE, NIST, Praxair, Air Liquide, Air Products, Carrier, CaFCP, CaSFCC, EPA, NCAR, Nuvera, CARB, AFCC, NASA, NEDO/JARI)
 - *DOE durability working group*
 - Metallic bipolar plates to study interactions with contaminants (TreadStone Technologies)
 - *RRDE, membrane conductivity cell and residence time distribution apparatus use (ONR)*
 - *Halogenated compounds x-ray absorption spectroscopy measurements (NRL, George Washington University)*
 - *RDE method development for catalyst characterization, DOE RFI DE-FOA-0000926 (NRL)*

Italic and underlined items indicate activity during this reporting period

Remaining Challenges and Barriers

- How can contaminant effects be mitigated? How can mitigation strategies be implemented at a fuel cell system level?
 - Several existing options will be explored (slide 5) and additional ones are expected to be derived based on contamination mechanisms
 - For contaminants that lead to a performance recovery after the exposure is interrupted, the objective is a decrease in recovery time
 - The contamination time scale is also an important parameter

Proposed Future Work

- Fiscal year 2014
 - A. Analyze, summarize and disseminate the large database to industry to support the development of filter specifications and mitigation strategies
 - B. Develop mitigation strategies for catalysts, ionomers and gas diffusion layers based on fluid circulation including product water and established contamination mechanisms
 - C. Investigate long term operation with contaminants to determine the impact of increased peroxide generation (organic species) and membrane brittleness (foreign cation) with a 0.1 mg Pt cm⁻² loading
 - D. Determine the impact of a contaminant mixture with concentrations closer to atmospheric values with a 0.1 mg Pt cm⁻² loading
- Fiscal year 2015
 - Maintain 2014 activity A
 - Prolong 2014 activity B using potential changes
 - Milestone 4: Demonstrate successful mitigation of the impact of the most important 4 airborne contaminants (March 31, 2015)

Summary

Relevance

- Fuel cell performance and durability impacts are mitigated by providing input into air filter specifications and fuel cell material selection, design, operation or maintenance

Approach

- Systematic use of multiple in situ and ex situ fuel cell characterization techniques to resolve all cell voltage losses; kinetic, ohmic and mass transfer

Accomplishments and Progress

- Created an extensive database for 7 organic and 1 cation species to support the derivation of contamination mechanisms
- Established the significant impact of a lower cathode catalyst loading of 0.1 mg Pt cm⁻² on fuel cell contamination for 7 organic and 1 cation species
- Model activities extended and supported the identification and development of contamination mechanisms
 - Liquid water scavenging model, transient cation contamination model and simplified model library

Collaborations

- Interactions with team organizations, project ID # FC048, the DOE durability working group, ONR, NRL and George Washington University leveraged durability knowledge from the fuel cell community and made possible an increase in the contaminant database breath

Proposed future work

- Development of mitigation strategies for contaminated fuel cells based on potential changes (0-1 V cell voltage), fluid circulation in the cathode compartment and contamination mechanisms

Technical Backup Slides

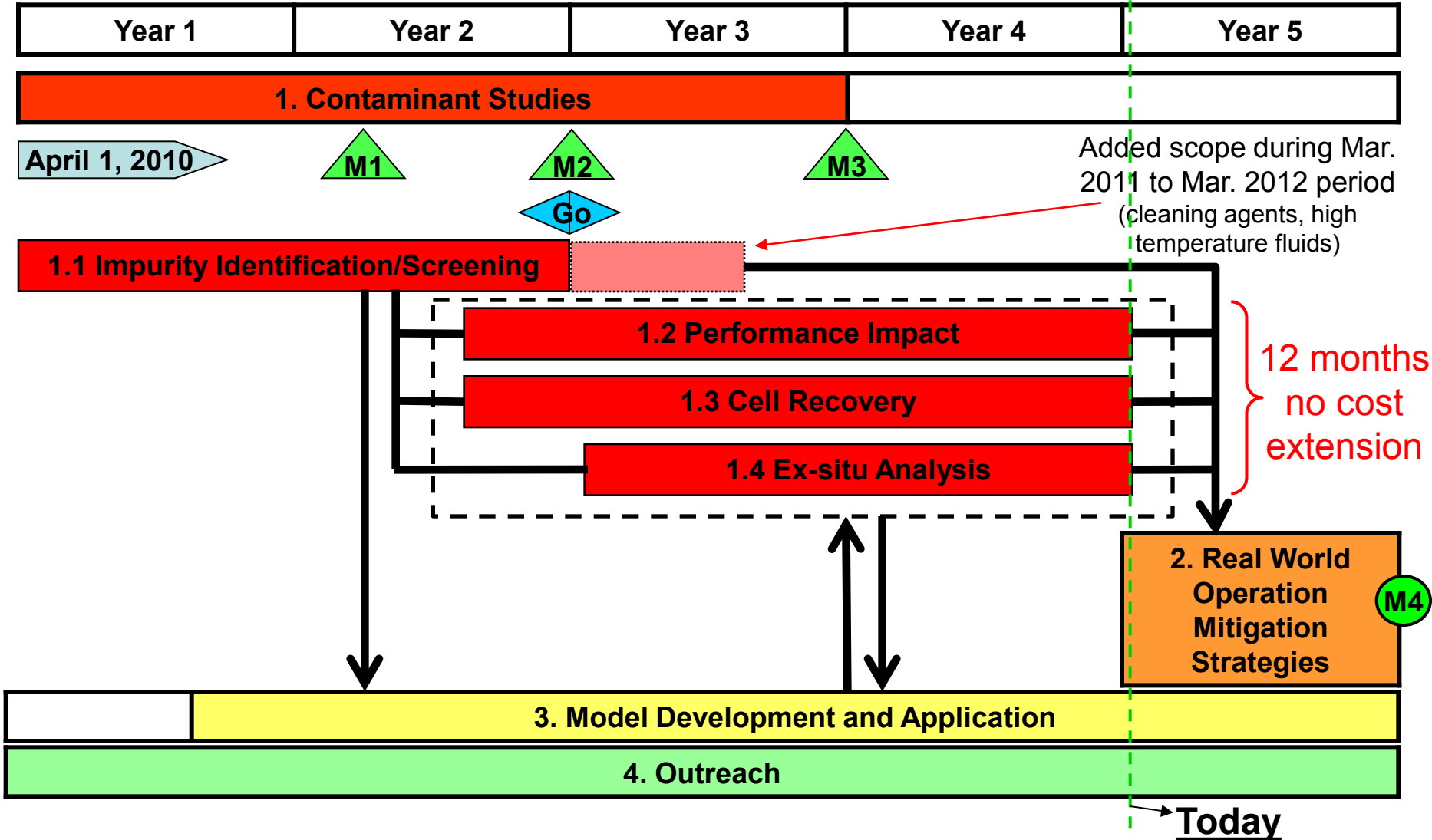


Contaminant Sources

- 8 contaminants were down selected for detailed studies to determine mechanisms

Contaminant	Acetonitrile (CH ₃ CN)	Acetylene (C ₂ H ₂)	Bromomethane (CH ₃ Br)	Iso-propanol (C ₃ H ₈ O)	Methyl methacrylate (CH ₂ C(CH ₃)COOCH ₃)	Naphthalene (C ₁₀ H ₈)	Propene (C ₃ H ₆)	Ca ⁺² (Ca-Cl ₂ or -SO ₄)
Source	Solvent and chemical intermediate	Welding fuel and chemical intermediate	Fumigant	Solvent, chemical intermediate, and windshield de-icer	Synthesis precursor for poly(methyl methacrylate), a shatter-resistant alternative to glass	Model aromatic, chemical intermediate and fumigant	Synthesis precursor for polypropylene used for films, packaging, etc	Road de-icer, desiccant, fertilizer and soil conditioner

High Level Plan Schedule



Other Model Activities

- A transient, 1 dimensional model was developed for foreign cation contamination to isolate individual effects which are not experimentally accessible
 - The presence of a foreign cation in the ionomer and membrane affects the H^+ , H_2O and O_2 transport and concentration
 - The previously unknown effect of a foreign cation on cell voltage loss due to O_2 permeability in the ionomer is not negligible

1) proton transport

$$\{N\} = -2c_{SO_3^-} [B]^{-1} \{\nabla y\} - \frac{2F c_{SO_3^-}}{RT} [B]^{-1} \{zy\} \nabla \phi$$

$$\nabla(-N_j) + R_j = \frac{\partial C_j}{\partial t}$$

2) Water transport in the ionomer

$$D_w^{m,eff} = y_{H^+} \times D_{w,H^+}^m + y_{Na^+} \times D_{w,Na^+}^m$$

$$\lambda^{eq}(a) = y_{H^+} \times \lambda_{H^+}^{eq} + y_{Na^+} \times \lambda_{Na^+}^{eq}$$

3) Oxygen diffusion in the ionomer phase

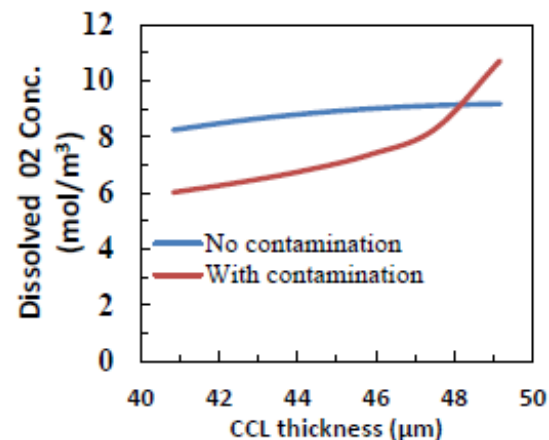
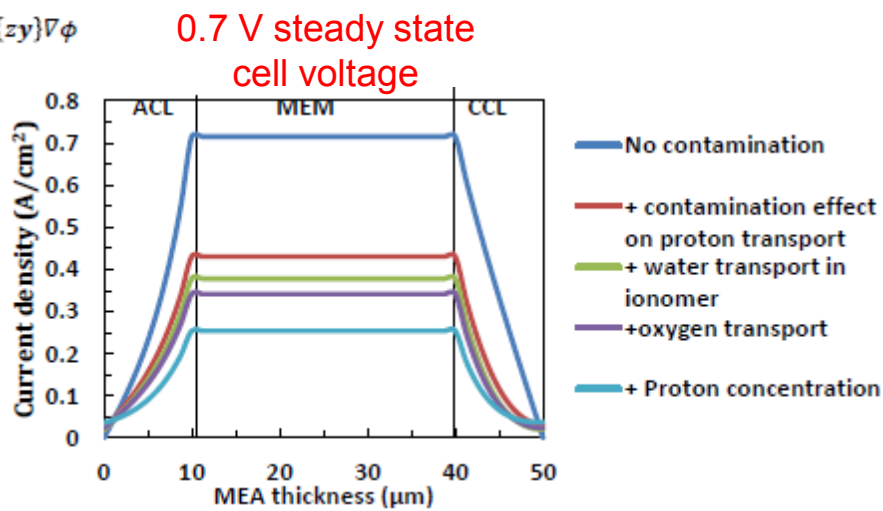
$$D_{O_2}^{m,eff} = y_{H^+} \times D_{O_2,H^+}^m + y_{Na^+} \times D_{O_2,Na^+}^m$$

4) Nernst potential

$$E_a = \frac{RT}{nF} \ln(y_{H^+}^2)$$

$$E_c = E_c^0 + \frac{RT}{nF} \ln(y_{H^+}^2)$$

$$E_c^0 = 1.23 - 9 \times 10^{-4}(T - 298.15)$$



Other Model Activities

- The airborne contaminant model database will be used to analyze constant cell voltage data to confirm or refine mechanisms

Measured variable for step changes in contaminant concentration			$i (c_R \neq 0)$	i_X or $i_{X^{+n}} (c_R = 0)$	
Catalyst contamination kinetics	X electroactive leading to a product P_2	X reaction rds			
		P_2 desorption rds			
		Irreversible P_2 adsorption			
	X electroinactive				
Membrane contamination kinetics	X^{+n} electroinactive				
	X electroinactive	X ionization			
		X chemically inactive			

