The Effect of Airborne Contaminants on Fuel Cell Performance and Durability

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University of Hawaii – Manoa, Hawaii Natural Energy Institute

May 16, 2012

Project ID # FC065

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Center for Clean Energy Engineering, University of Connecticut

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Overview

Timeline

- Project start date: April 1, 2010
- Project end date: March 31, 2014
- Percent complete: 50 %

Budget

- Total project funding
  - DOE share: $3,649,116
  - Cost share: $917,762
- Funding received in FY11: $436,408
- Planned funding for FY12: $400,000

Barriers

- Durability
  - 5000 cycling h by 2015 (automotive system)
- Performance
  - 50 % energy efficiency at rated power (automotive system)

Partners

- Interactions/collaborations: University of Connecticut, Center for Clean Energy Engineering (subcontractor), UTC Power (subcontractor), Ballard Power Systems (subcontractor)
- Project lead: Jean St-Pierre

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Relevance - Objectives

- Identification and mitigation of the airborne contaminants adversely impacting system performance and durability
  - Filtering system component specification input
  - Fuel cell stack material, design, operation or maintenance changes to recover performance losses

Technical Targets for Automotive Applications: 80-kWe (net) Integrated Transportation Fuel Cell Power Systems Operating on Direct Hydrogen

Characteristic	Units	2003 Status	2005 Status	2010	2015
Energy efficiency @ 25% of rated power	%	59	59	60	60
Energy efficiency @ rated power	%	50	50	50	50
Power density	W / L	440	500	650	650
Specific power	W / kg	420	470	650	650
Cost	\$ / kWe	200	110	45	30
Transient response (time from 10% to 90% of rated power)	seconds	3	1.5	1	1
Cold start-up time to 50% of rated power @–20°C ambient temp @+20°C ambient temp	 seconds seconds	 120 60	 20 <10	 30 5	 30 5
Start up and shut down energy from –20°C ambient temp from +20°C ambient temp	 MJ MJ	 N/A N/A	 7.5 N/A	 5 1	 5 1
Durability with cycling	hours	N/A	~1,000	5,000	5,000
Unassisted start from low temperatures	°C	N/A	–20	–40	–40

Project targets

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Relevance - Objectives

- Task I Contaminant studies
  - Identification of the worst contaminants leading to a significant loss with fuel cell tests
  - Mechanism determination by in situ tests and ex situ tests
    - A segmented cell, product stream and water analyses, residence time distribution measurements, and fingerprinting with a generic model library were either seldom or not previously used
- Task 2 Real world operation and mitigation strategies
  - Potential changes, fluid circulation and other strategies derived from contamination mechanisms
  - Compatibility with fuel cell system constraints and effectiveness over long operation periods
- Task 3 Model development and application
  - Generic model library expansion with identified gaps in contamination mechanisms
- Task 4 Outreach
  - Patents, publications, presentations

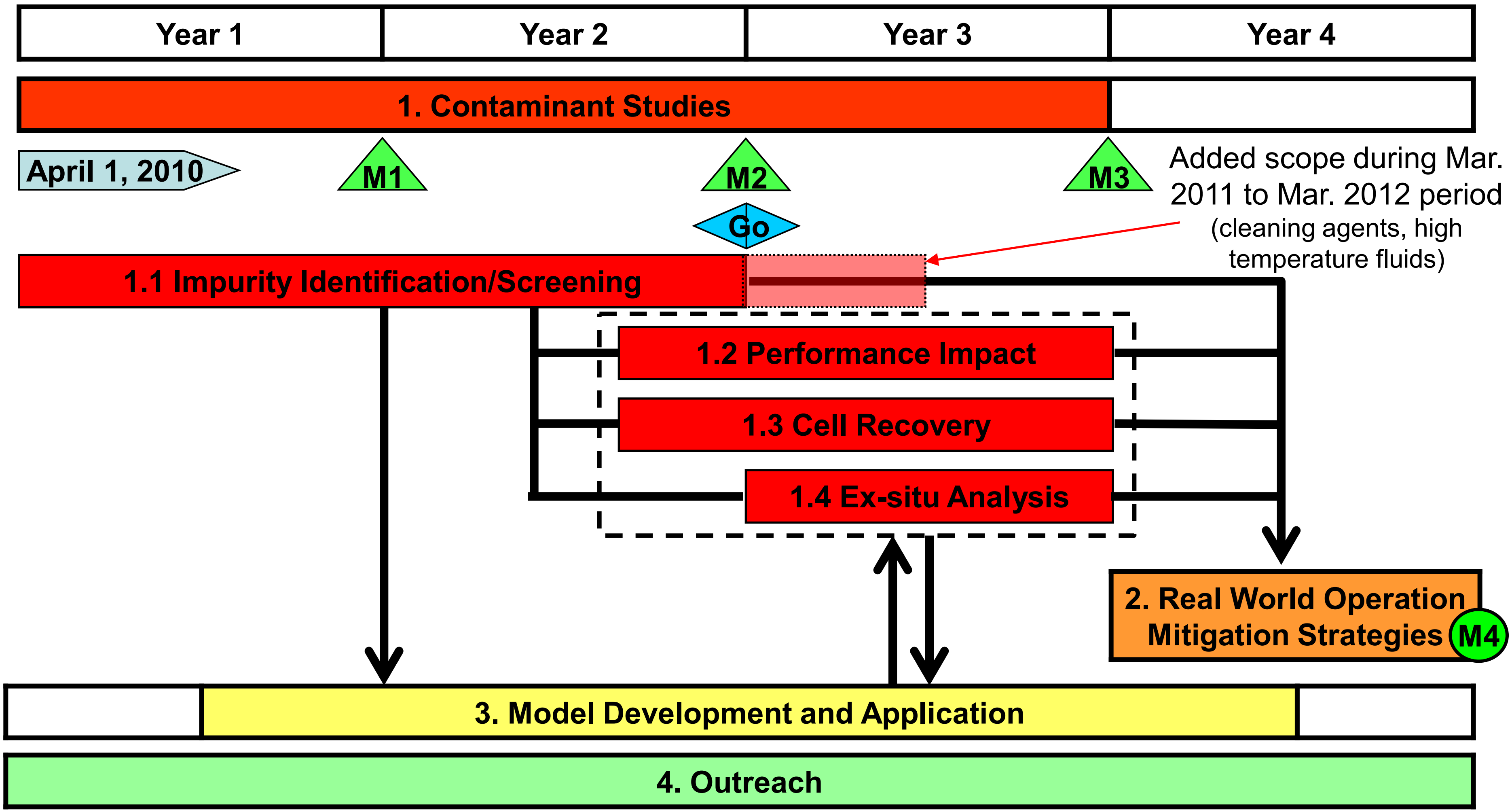
Relevance - Objectives

- Detailed project objectives for the relevant reporting period include:

Task	Objectives
1.1 Impurity Identification and Screening	• 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	• 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	• Quantify cell recovery resulting from removal of contaminant and change of operating conditions.
1.4 Ex-situ Analysis	• Characterize changes in catalyst, MEA and GDL structure resulting from exposure to contaminant and contaminant mixtures.
2.1 Real World Operation	• Characterize effect of contaminant at 'real world' operating conditions.
2.2 Mitigation Strategies	• Explore operating strategies and novel techniques to mitigate contaminant effects.
3.0 Model Development and Application	• 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	• Conduct outreach activities to disseminate critical data, findings, models, and relationships that describe the effects of airborne contaminants on PEMFC performance and durability.

March 2011 to March 2012 objectives

Approach - High Level Plan



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Approach - Significant Decisions Points

- Milestones at the end of each project year
  - M1 (**completed**): Prioritize a group of ~10 airborne contaminants of relevance to stationary and automotive fuel cell applications based on
    - Their performance impact (screening results)
    - Occurrence (literature results, industry exchange)
  - M2 (**March 31, 2012**): Quantify performance loss for at least 4 different contaminants under various operating conditions
  - M3: Quantify spatial variability of performance loss for at least 4 different contaminants. Identify principal poisoning mechanism for same
  - M4: Demonstrate successful mitigation of the impact of the most important 4 airborne contaminants
- Go/No go decision criteria at the end of the second project year
  - G1 (**March 31, 2012**): Identified contaminants (and concentrations) resulting in performance loss $\geq$ 20 % of initial performance loss
  - G2 (**March 31, 2012**): Effects of various conditions on cell poisoning quantified. Data reported to modelers
  - G3 (**March 31, 2012**): Mitigation strategies, restoring cell to 90 % of initial performance, identified for reversible contaminants

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Approach – High Level Plan

- Institution dependent contaminant focus
  - Foreign cations (originating from salts in marine environments, for example) and road side contaminants (C2E2)
  - Airborne contaminants (HNEI)
- Approach minimizes need for time consuming benchmarking activities
  - Benchmarking already completed (USFCC and a DOE project activities)
  - Different setup designs are needed for each group
    - Foreign cations and road side contaminants require liquid or solid injection
    - Airborne contaminants require gas injection
- The project ensures the widest range in contaminant sources is studied
  - "Effect of System and Air Contaminants on PEMFC Performance and Durability" project (ID # FC048) focuses on system sources
    - Duplication is avoided because the PI is a team member
  - Fuel cell contaminants were studied in previous DOE projects (ID # FC045, FC046, FC047)
    - Contaminants are not duplicated or are studied at the cathode rather than the anode

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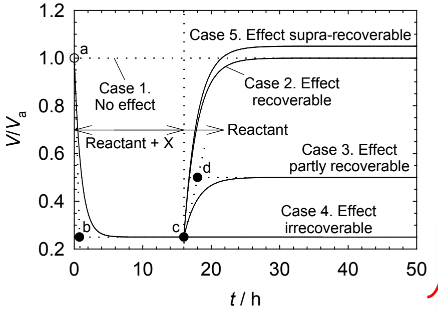
Accomplishments and Progress – Task 1 Contaminant Studies

- 4 deleterious contaminants and corresponding concentrations leading to a 20 % fuel cell performance loss identified (M2, G1-3)
  - Input for filter system component specifications definition

Existing data duplication, organic functionalities representation, cation charge, etc (foreign cation criteria completed during this period)

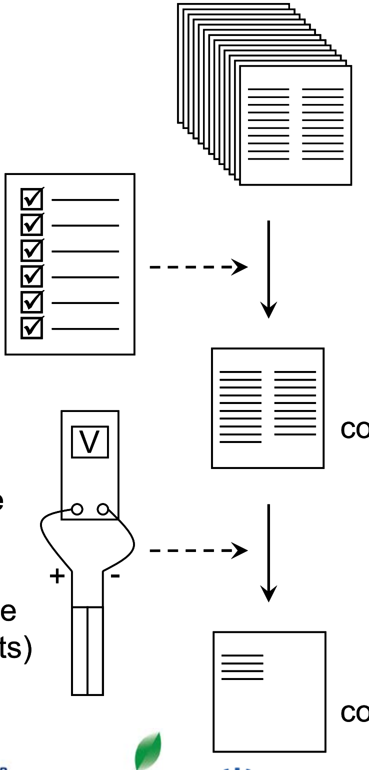
$$SC_1 = \frac{(V_a - V_b)^2 (V_a - V_d)(t_d - t_c)}{c_{contaminant} (V_d - V_c)(t_b - t_a)}$$

$$SC_2 = \int_{t_a}^{t_b} (V_a - V) dt \Big/ \int_{t_c}^{t_d} (V - V_c) dt$$



1st tier qualitative selection criteria (check list)

2nd tier quantitative selection criteria (performance measurements)



Identified airborne contaminants (EPA, samples analysis, interest group suggestions)

1st tier contaminants

- 11 contaminants tested in previous period (wet conditions)
- 19 contaminants tests (wet and dry conditions) and exploratory foreign cation tests completed during this period

2nd tier contaminants

- 4 contaminants tested under different operating conditions during this period

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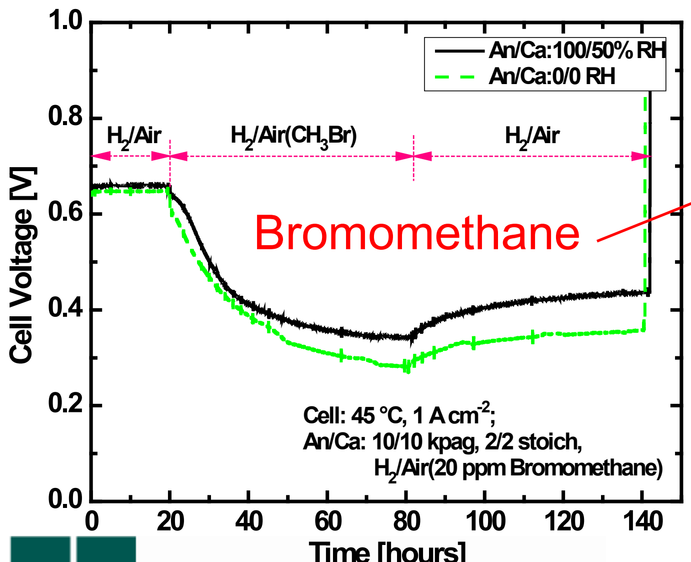
Accomplishments and Progress – Task 1 Contaminant Studies (Inorganic and Organic)

- 1st tier contaminants tests completed during this period (March 2011 to March 2012)
- SC_2 identified as preferable during this period ($SC_2 = \int_{t_a}^{t_b}(V_a - V)dt / \int_{t_c}^{t_d}(V - V_c)dt$)
  - Sensitive to contaminants, "beneficial" species but much less to operating conditions
- 2nd tier contaminants selected during this period
  - Acetylene, bromomethane, iso-propanol, methyl methacrylate, naphthalene, propene
    - Representative of alkenes, alkynes, alcohols, esters, halogenated hydrocarbons and aromatics

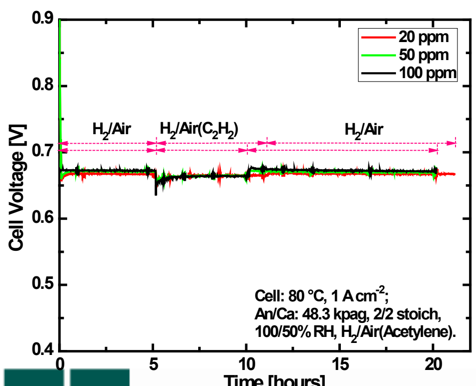


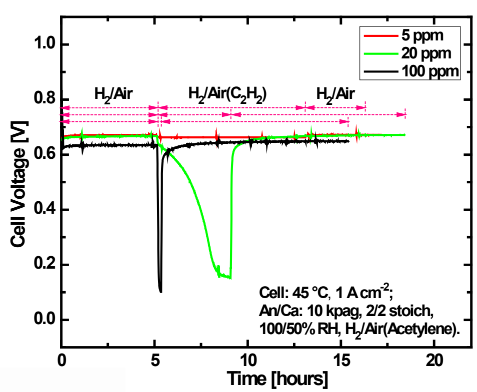
Solvent and chemical manufacture precursor

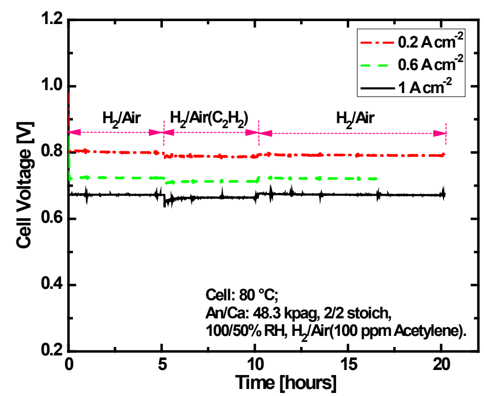
Contaminant	SC_1 (V^2 ppm^{-1})		SC_2	
	100/50 RH	0/0 RH	100/50 RH	0/0 RH
1,1-difluoroethane	7.23 x 10^{-4}	3.74 x 10^{-4}	0.0259	0.0682
1,1,1,2-tetrafluoroethane	2.16 x 10^{-4}	1.88 x 10^{-4}	0.0414	0.00532
2,2-bis(4-hydroxyphenyl)propane	No effect	No effect	No effect	No effect
Acetaldehyde	–2.35 x 10^{-4}	–1.03 x 10^{-4}	0.214	0.409
Acetone	–2.86 x 10^{-7}	1.24 x 10^{-6}	6.75	6.59
Acetonitrile	5.78 x 10^{-3}	9.51 x 10^{-3}	0.0575	0.0410
Acetylene	3.13 x 10^{-6}	3.86 x 10^{-6}	30.6	16.5
Bromomethane	4.04 x 10^{-3}	7.37 x 10^{-3}	7.57	8.03
Chlorobenzene	1.57 x 10^{-2}	4.09 x 10^{-2}	0.165	0.0978
Dichloromethane	No effect	No effect	No effect	No effect
Iso-propanol	–2.55 x 10^{-7}	1.54 x 10^{-4}	17.8	0.100
Methyl methacrylate	1.44 x 10^{-5}	1.32 x 10^{-4}	4.86	3.94
Methyl tert-butyl ether	6.69 x 10^{-6}	4.62 x 10^{-4}	2.05	0.260
Naphthalene	∞	∞	∞	∞
Ozone	5.38 x 10^{-4}	4.68 x 10^{-4}	0.149	0.188
Propene	–3.08 x 10^{-5}	–6.55 x 10^{-5}	32.1	1.05
Toluene	5.38 x 10^{-4}	1.34 x 10^{-3}	0.349	0.247
Trichlorofluoromethane	No effect	8.76 x 10^{-4}	No effect	0.277
Vinyl acetate	–4.42 x 10^{-5}	–1.16 x 10^{-4}	1.19	0.879

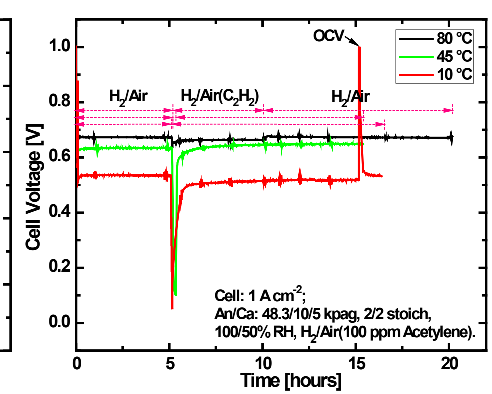
Accomplishments and Progress – Task 1 Contaminant Studies (Operating Condition Effects)

- 4 2nd tier contaminants tested under different operating conditions during this period (March 2011 to March 2012)
  - Acetylene data appear below (others are in the technical backup slides section)
- Effect of operating conditions on acetylene contamination determined
  - Higher concentrations are worse
    - >100 ppm for a 20 % performance loss at 80 °C
    - ~16 ppm for a 20 % performance loss at 45 °C
  - Higher current densities are worse
  - Lower temperatures are worse









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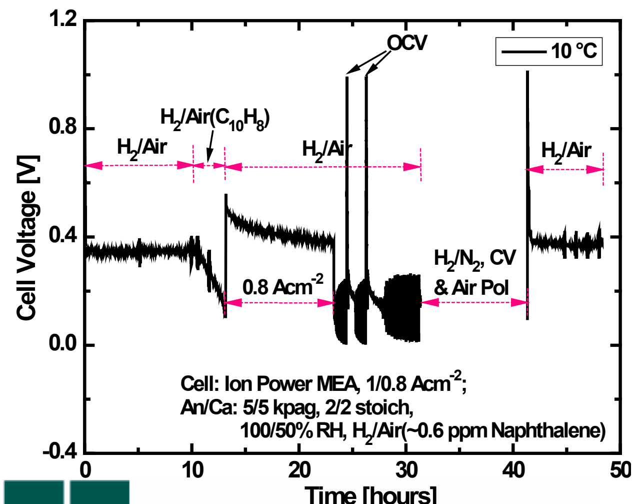
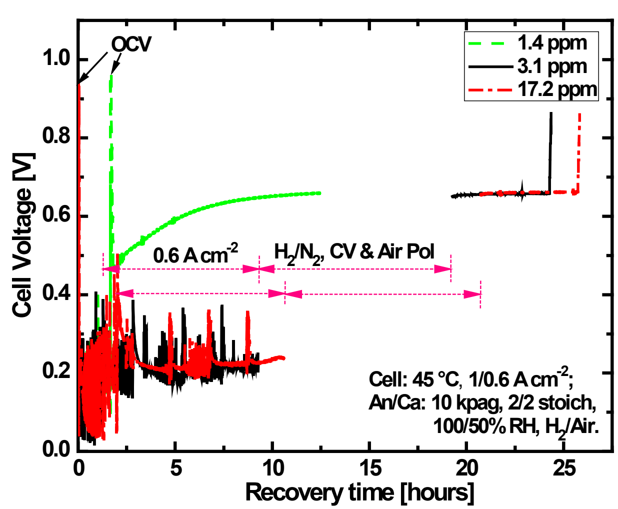
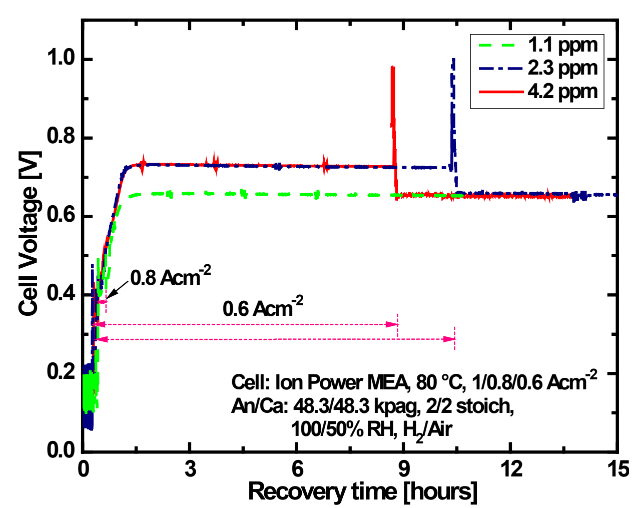
Accomplishments and Progress – Task 1 Contaminant Studies (Recovery)

- For all 4 2nd tier contaminants tested
  - More than 90 % of the voltage loss at steady state is recovered after contaminant injection interruption with the exception of naphthalene for some operating conditions
  - Operation condition changes were sufficient to recover performance after naphthalene exposure
    - Recovery is more difficult at low temperatures and higher concentrations







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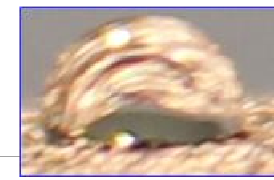
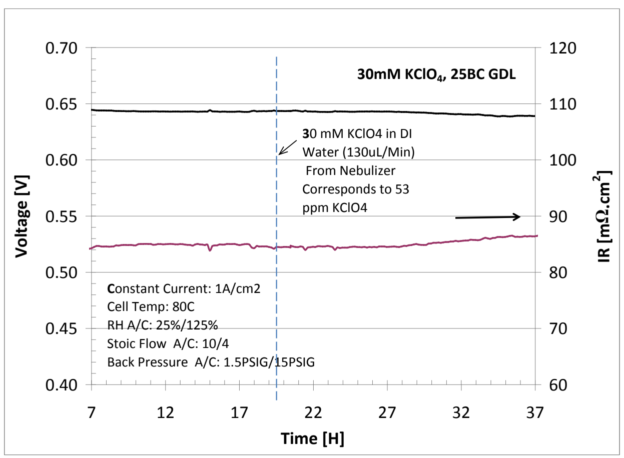
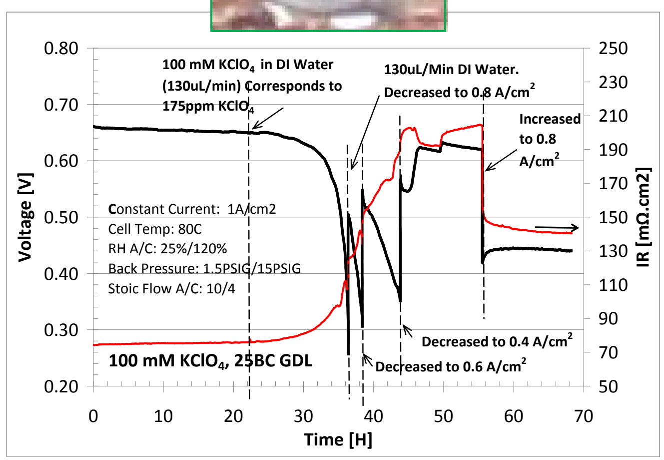
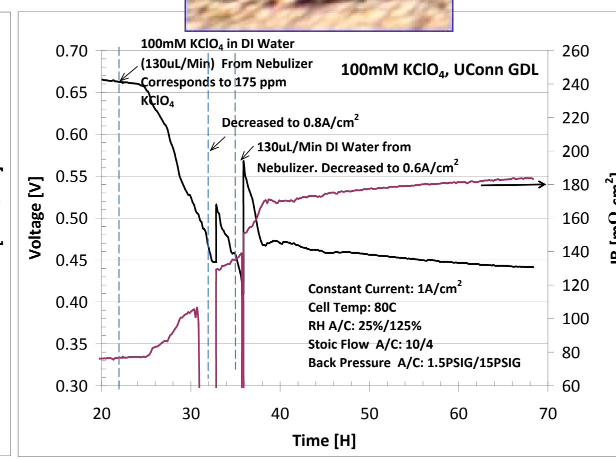
Accomplishments and Progress – Task 1 Contaminant Studies (Foreign Cations)

- 1st tier foreign cation contaminants identified during this period
  - K^{+}, Ba^{+2}, Ca^{+2}, Al^{+3}
- Exploratory foreign cation tests completed during this period
  - A higher contaminant concentration and a more hydrophilic gas diffusion layer increase the degradation rate









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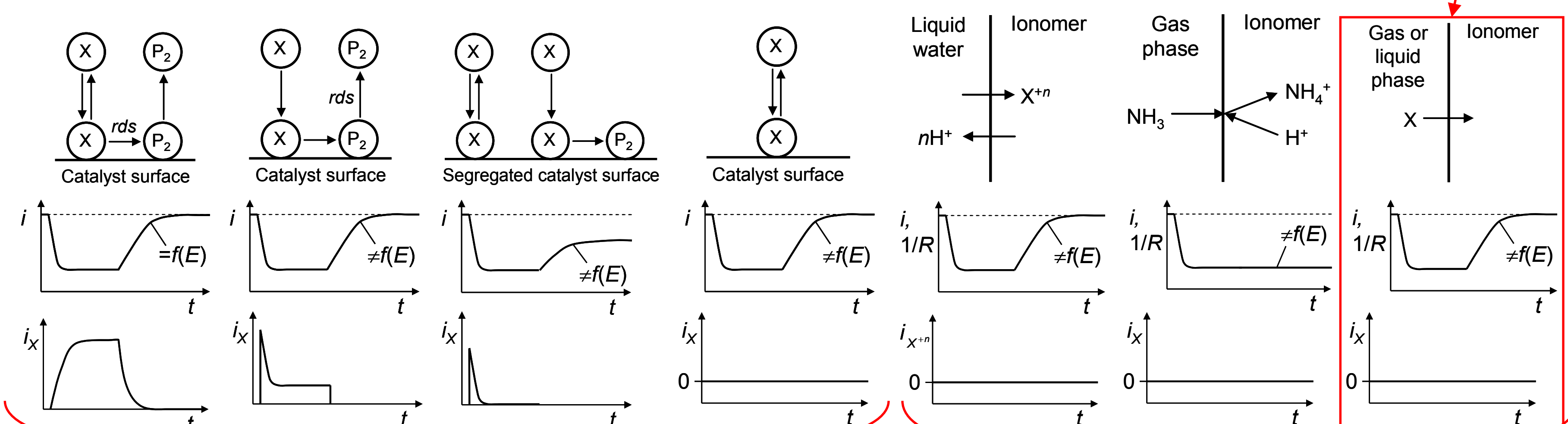
Accomplishments and Progress – Task 3 Model Development and Application

- A library of widely applicable generic models is planned to
  - Ease identification of mechanisms (fingerprint characteristics)
    - Practical approach because few mechanisms were identified
  - Facilitate cell performance predictions and the definition of tolerance limits
    - Explicit expressions for concentration dependent steady state and time constants
- The model library will be expanded
  - 4 cases initially planned with 3 incomplete cases related to mass transport losses

Completed this period



Kinetic losses

Ohmic losses

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Collaborations

- HNEI (prime university organization)
  - All tasks with a focus on airborne contaminants
    - Contaminant studies, real world operation and mitigation strategies, model development and application, outreach
- C2E2 (university sub-contractor)
  - All tasks with a focus on foreign cations and roadside contaminants
    - Contaminant studies, real world operation and mitigation strategies, model development and application, outreach
- UTC Power (industry sub-contractor)
  - Contaminant identification and test protocols development support, experimental data and analysis review, SEM/TEM analysis
- Ballard Power Systems (industry sub-contractor)
  - Contaminant identification and test protocols development support, experimental data and analysis review

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Collaborations

- Provided to Nuvera
  - Air filter specification definition support
- GM provided
  - Nebulizer design and integration support
  - Heating tube for contaminant evaporation (for example, naphthalene)
  - Membrane contamination by a chemically and electrochemically inactive species model support and validation data
- GM, Nuvera and UTC Power provided
  - Air filters
- Frequent interactions with the "Effect of system and air contaminants on PEMFC performance and durability" project team (ID # FC048)
  - Mutual support including activities overlap avoidance
- DOE durability working group
- Requested 1st tier contaminants validation by an interest group that includes
  - LANL, NREL, ANL, FCHEA, NRL, SAE, NIST, Praxair, Air Liquide, Air Products, CaFCP, CaSFCC, EPA, NCAR, Nuvera, CaARB, AFCC, NASA, JARI
    - Information received does not require any project plan change
- Treadstone Technologies will supply
  - Metallic bipolar plates to investigate interactions with contaminants

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Proposed Future Work

- Fiscal year 2012
  - Milestone 2 and go/no go decisions 1 to 3 (March 31, 2012)
  - Complete 1st tier foreign cation screening tests (task 1.1) and 2nd tier foreign cation impact (task 1.2) and cell recovery (task 1.3) tests
  - Complete added contaminant identification and screening (task 1.1) scope
    - Cleaning agents and high temperature fluids
  - Initiate activities supporting mechanism determination for 2nd tier contaminants using in situ (task 1.2) and ex situ data (task 1.4), and generic model library
  - Develop models for the impact of liquid water on contaminant scavenging and for a contaminant supply limitation (task 3)
- Fiscal year 2013
  - Investigate interactions between contaminants and metallic bipolar plates (task 1.2)
  - Develop a model for the uneven ionomer proton distribution in the presence of a foreign cation (task 3)
  - M3: Quantify spatial variability of performance loss for at least 4 different contaminants. Identify principal poisoning mechanism for same

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Summary

- Relevance
  - Performance and durability impacts are mitigated by providing input into filtering system component specification and fuel cell material selection, design, operation or maintenance
- Approach
  - Document in situ contaminant-concentration-dependent effects
  - Determine contamination mechanisms with extensive in situ and ex situ measurements, and generic model library
  - Develop mitigation strategies based on potential changes, fluid circulation and mechanisms
- Technical accomplishments and progress
  - Two-tiered contaminant down-selection approach
  - Performance losses for 4 2^{nd} tier contaminants with varying operating conditions
  - Membrane contamination by an inactive contaminant model
- Collaborations
  - Multi-faceted interactions with team organizations, project team ID # FC048, consumers, suppliers, the DOE durability working group and an interest group including fuel cell industries add relevance to activities
- Proposed future work
  - Complete in situ and ex situ characterization tests, and several generic models to support the identification of mechanisms for 2^{nd} tier contaminants

Technical Backup Slides

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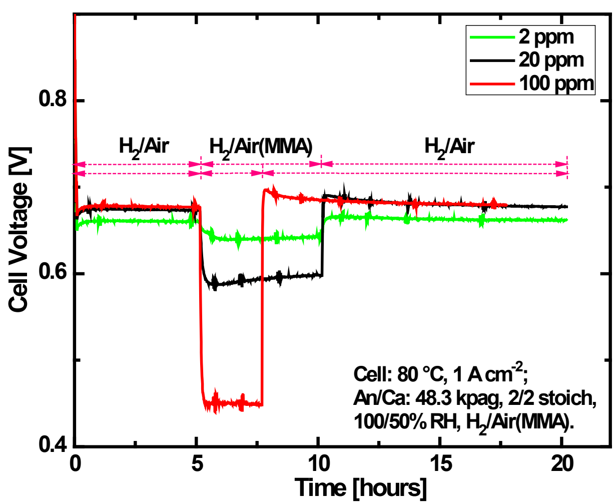
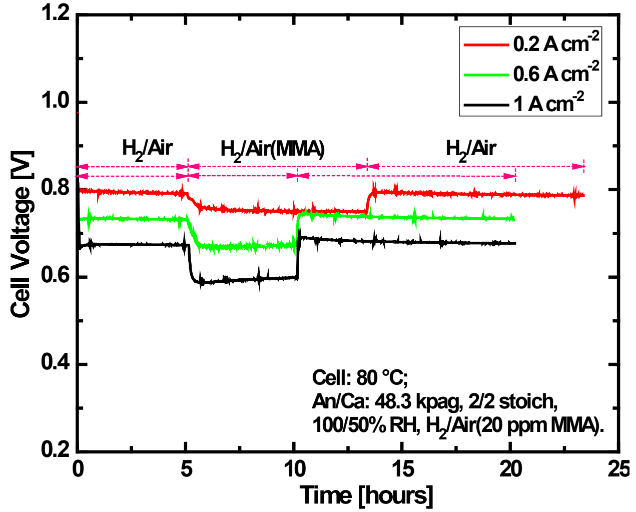
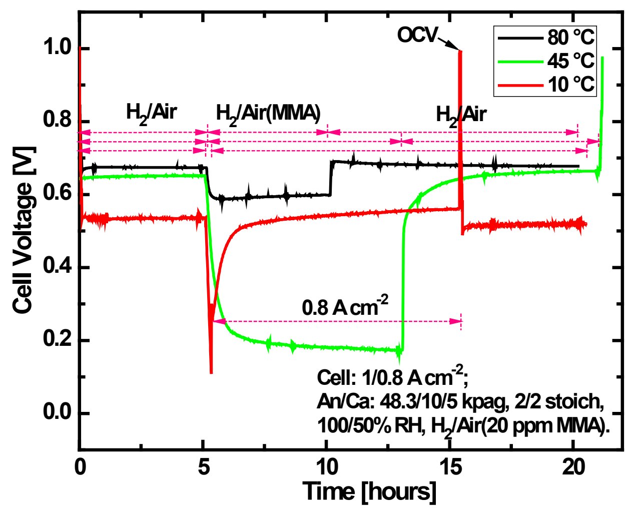
Accomplishments and Progress – Task 1 Contaminant Studies

- Effect of operating conditions on methyl methacrylate contamination determined
  - Higher concentrations are worse
    - ~20 ppm for a 20 % performance loss
  - Higher current densities are worse
  - Lower temperatures are worse







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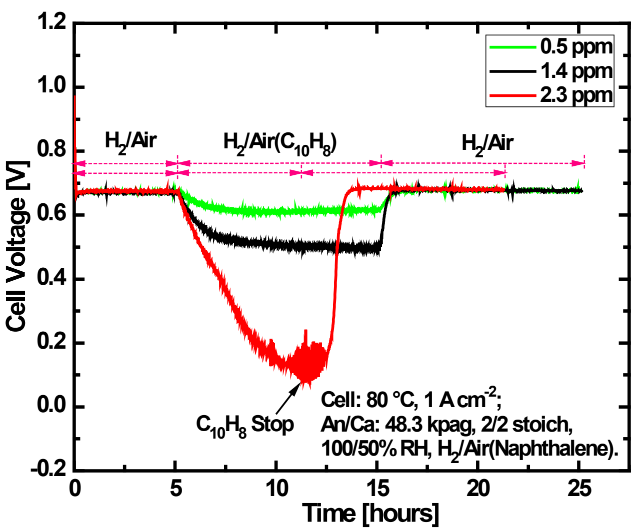
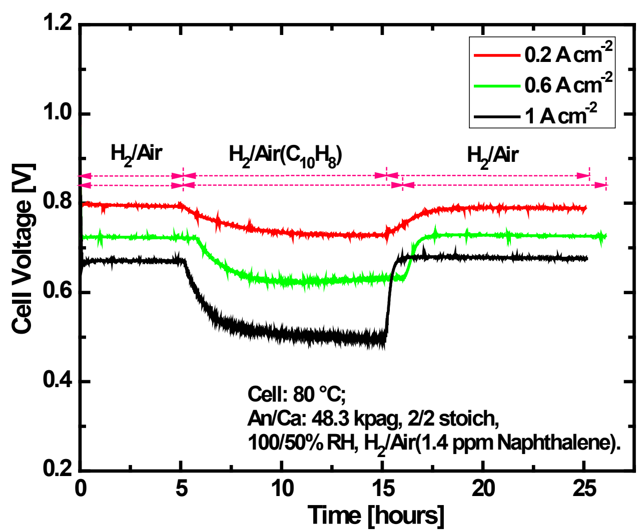
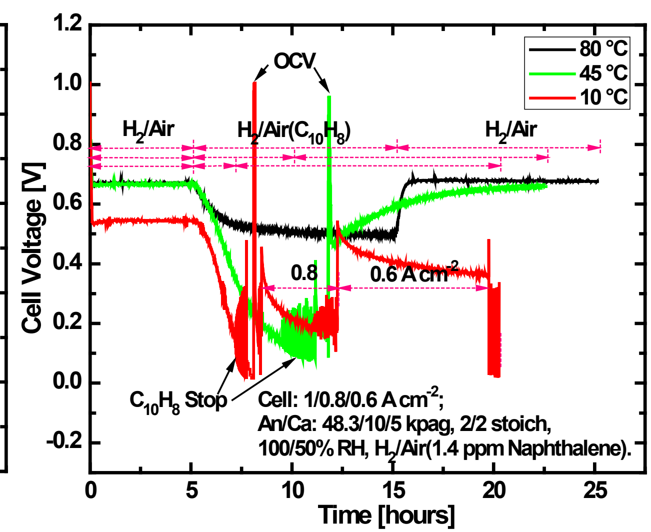
Accomplishments and Progress – Task 1 Contaminant Studies

- Effect of operating conditions on naphthalene contamination determined
  - Higher concentrations are worse
    - ~1.4 ppm for a 20 % performance loss
  - Higher current densities are worse
  - Lower temperatures are worse







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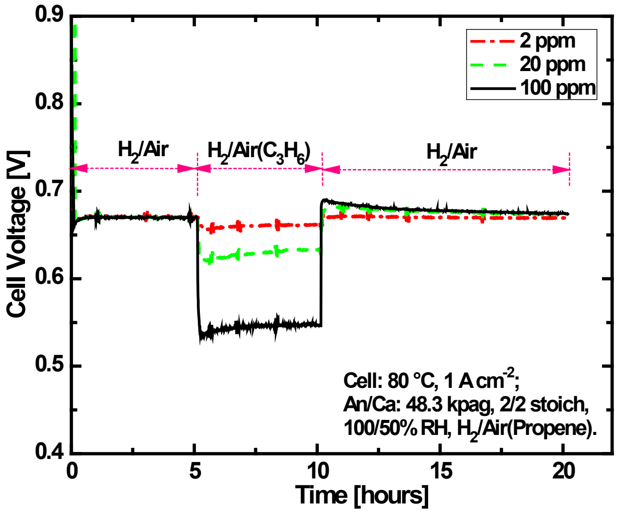
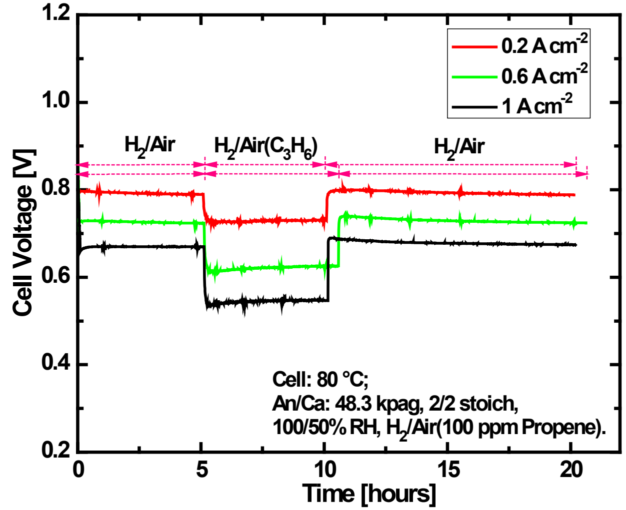
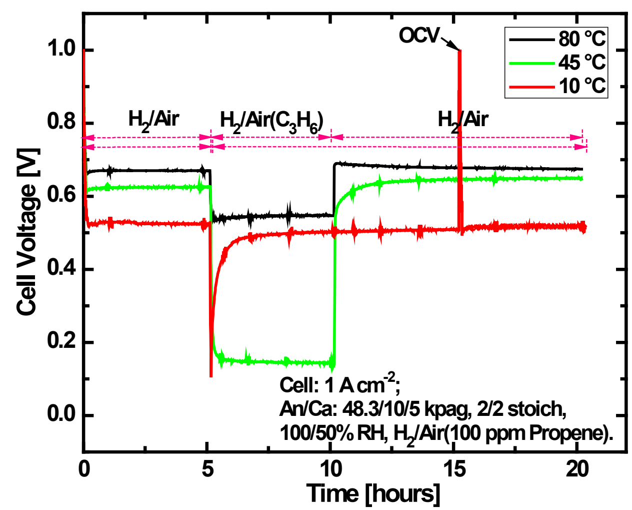
Accomplishments and Progress – Task 1 Contaminant Studies

- Effect of operating conditions on propene contamination determined
  - Higher concentrations are worse
    - ~100 ppm for a 20 % performance loss
  - Higher current densities are worse
  - Lower temperatures are worse







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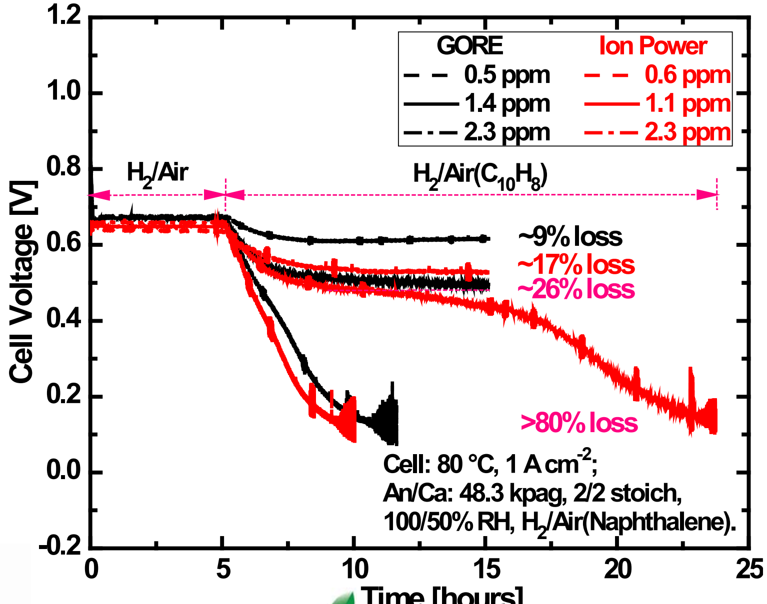
Accomplishments and Progress – Task 1 Contaminant Studies

- Initially planned to use Ion Power membrane/electrode assemblies
  - Only supplier willing to supply materials for ex situ studies (catalyst, ionomer, etc)
- Later shift to Gore® membrane/electrode assemblies provided an opportunity to compare the effect of different designs on naphthalene contamination
  - Ion Power membrane/electrode assemblies performance too variable
  - Similarities include catalyst (supported Pt), cathode catalyst loading (~0.4 mg/cm²), ionomer (Nafion®) and gas diffusion layer (SGL 25 BC)
  - An effect was observed but the cause remains to be determined



Draft Milestone 3 Plan

	2012									2013		
	Apr	May	June	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar
Task 1.1. Impurity identification and screening												
Impurity identification												
Cleaning agents						x						
High temperature fluids						x						
Impurity screening												
Cleaning agents						x						
High temperature fluids						x						
Task 1.2. Contaminant impact and Task 1.3. Cell recovery												
Cleaning agents TBD												
High temperature fluids TBD												
Task 1.2. Contaminant impact (milestone 2, 2nd tier contaminants)												
Segmented cell tests (spatial performance variability)								x				
Mass balance and product species GC analyses*							x					
Constant cell potential tests with and without contaminant (data feed into model library task 3 for mechanism identification)					x							
Exhaust water collection collection and analysis**							x					
Metallic bipolar plates effect									x			
Task 1.4. Ex situ analysis (milestone 2, 2nd tier contaminants)												
RRDE for catalyst evaluation				x								
Conductivity cell for membrane conductivity						x						
Other tests as needed such as GDL contact angle, etc TBD												
Mechanism identification (milestone 2, 2nd tier contaminants)												
Review M2 characterization data for mechanistic clues			x									
Synthesize task 1 results											x	
Task 3. Model development and application (model library to be used to identify mechanisms in task 1.2, predict losses and define tolerance limits)												
Liquid water drops contaminant scavenging	x											
Foreign cation in ionomer (uneven cation distribution)											x	
Contaminant supply limitation						x						

* Gas and liquid phases? Local measurements?

** Several contaminants characterized by different water solubilities are planned but may not correspond to milestone 2 2nd tier contaminants.