The Effect of Airborne Contaminants on Fuel Cell Performance and Durability

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Project ID # FC065

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Overview

Timeline

- Project start date: April 1, 2010
- Project end date: March 31, 2014
- Percent complete: 75 %

Budget

- Total project funding
  - DOE share: $3,649,116
  - Contractor share: $917,762
- Funding received in FY12: $ 400,000
- Funding for FY13: $ 997,742

Barriers

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

Partners (subcontractors)

- University of Connecticut, Center for Clean Energy Engineering, UTC Power, Ballard Power Systems
- Project lead: Jean St-Pierre

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Relevance

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

- Preventive: provide contaminants and tolerance limits for filter specifications
- Recovery: identification of fuel cell stack's material, design, operation or maintenance changes to remove contaminant species and recover performance

2012-2013 objective: Establish degradation mechanisms for key contaminants

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

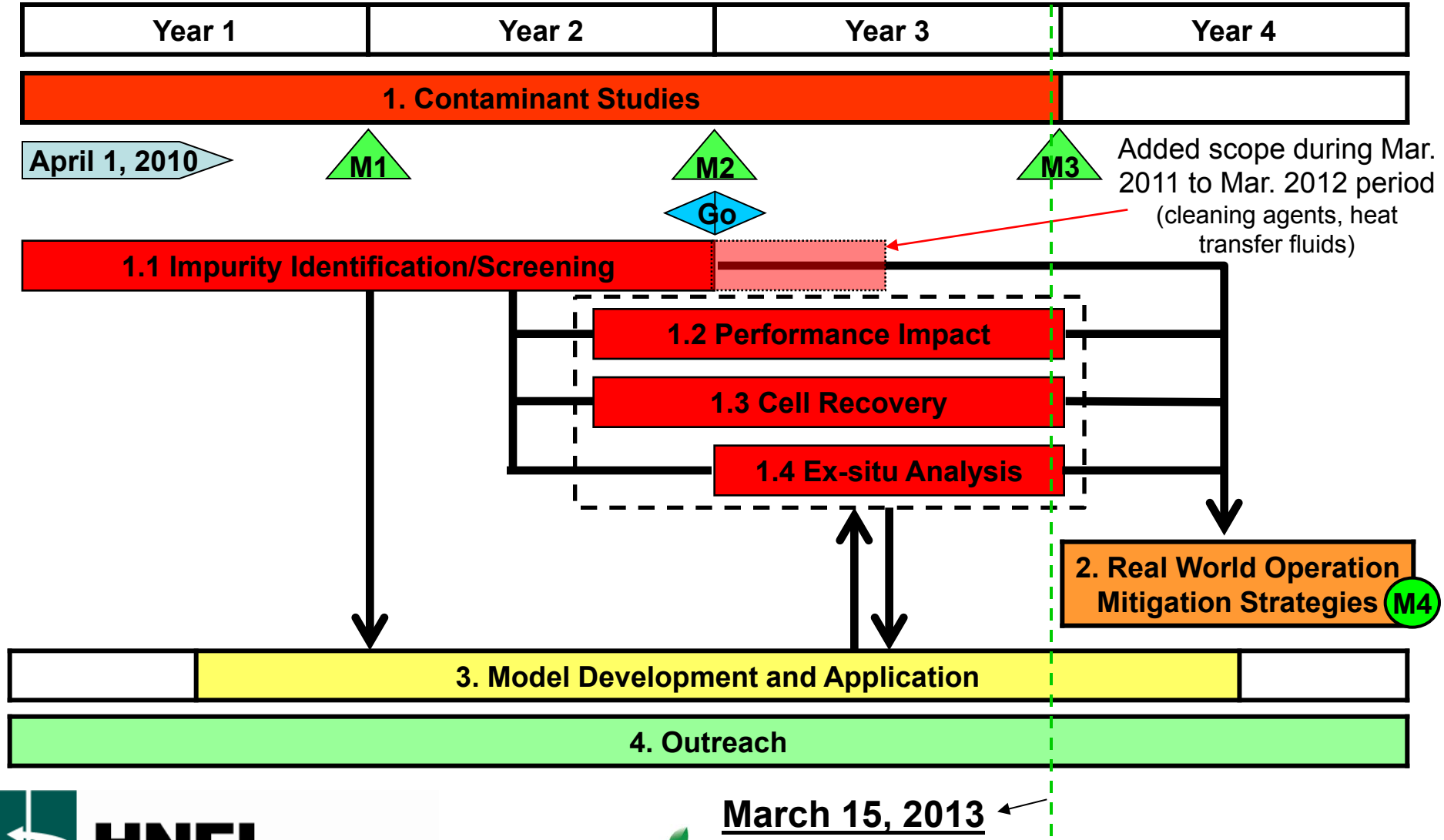
Characteristic	Units	2011 Status	2017 Targets	2020 Targets
Energy efficiency[b] @ 25% of rated power	%	59	60	60
Power density	W / L	400[c]	650	850
Specific power	W / kg	400[c]	650	650
Cost[d]	$ / kW_e	49[e]	30	30
Cold start-up time to 50% of rated power				
@–20°C ambient temp	seconds	20[f]	30	30
@+20°C 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

Milestone or Go/No-Go Decision	Status	Due Date
M1: Prioritize a group of ~10 airborne contaminants of relevance to stationary and automotive fuel cell applications	Completed with industry recommendations for contaminant selection and tests for 11 organic species	March 2011
M2: Quantify performance loss for at least 4 different contaminants under various operating conditions	Completed with 7 organic and 1 cation species for selected contaminant concentration, temperature and current density ranges	March 2012
G1: Identified contaminants (and concentrations) resulting in performance loss ≥ 20 % of initial performance loss G2: Effects of various conditions on cell poisoning quantified. Data reported to modelers G3: Mitigation strategies, restoring cell to 90 % of initial performance, identified for reversible contaminants	G1: Completed with 7 organic species tests by varying the contamination concentration to achieve < and > 20 % performance loss G2: Completed with tests performed under different temperatures, contaminant, concentrations and current densities G3: Completed with 7 organic species by varying operating conditions	March 2012
M3: Quantify spatial variability of performance loss for at least 4 different contaminants. Identify principal poisoning mechanism for same	Ongoing tests with 7 organic and 1 cation (slides 8, 9, 11-16, 26, 28)	March 2013
M4: Demonstrate successful mitigation of the impact of the most important 4 airborne contaminants		March 2014

Approach



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Approach

- Selected contaminants integrate with other research
  - The limited scope of previous airborne contaminants studies, mostly SO_x, NO_x and NH_3, is not duplicated
  - Extensive outreach was conducted by contacting, interfacing and following contaminant selection recommendations from the industry
  - This project fills the knowledge gap in airborne contaminants and complements former hydrogen contaminants and ongoing system contaminants projects
    - Project ID # FC048 focuses on fuel cell system materials sources
    - Fuel contaminants were studied in previous projects (ID # FC045, FC046, FC047)

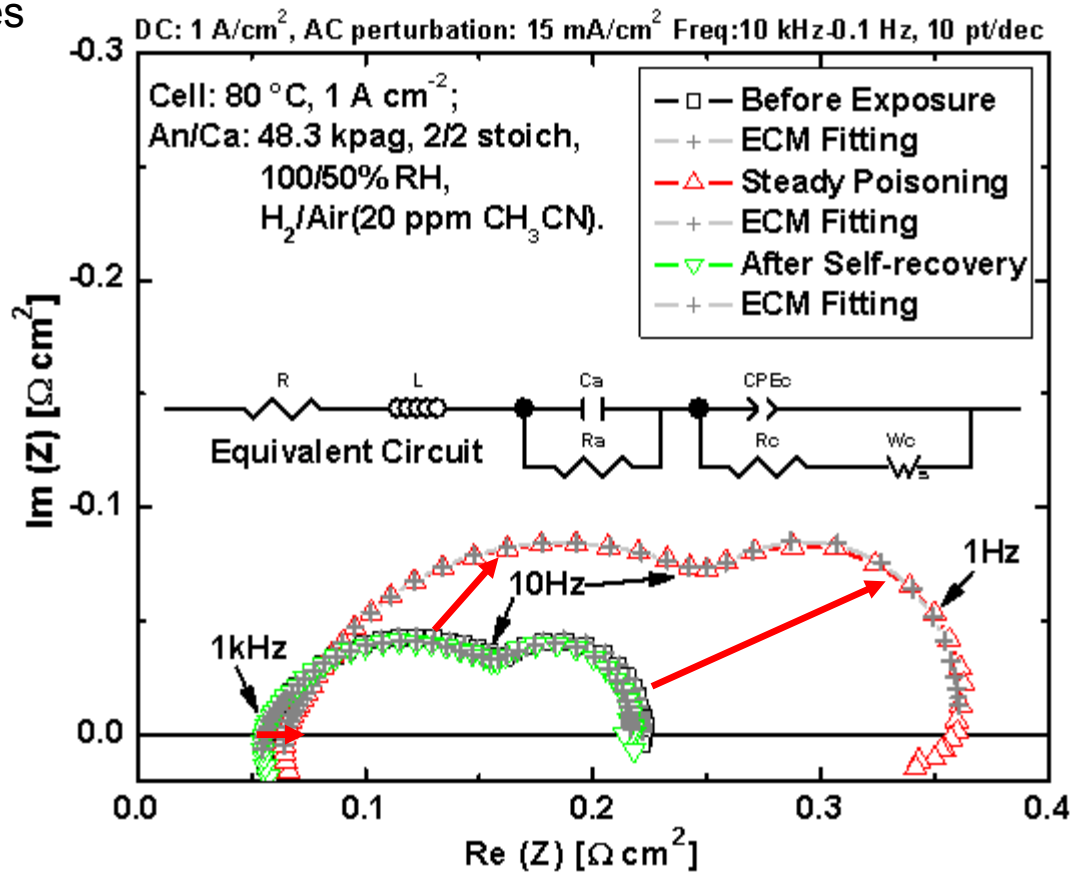
Accomplishments and Progress

- The performance loss due to organic species and a cation under different operating conditions was partially reported at the 2012 AMR with remaining results included in slides 22-24 (milestone 2)
- New PEMFC contamination mechanism results are reported in the following slides with a focus on acetylene, a common welding fuel (milestone 3)
- Other contamination mechanism results are summarized in slides 26 and 28
- Contamination mechanisms will provide the background necessary to facilitate the development of mitigation strategies (milestone 4)

Contaminant	Acetonitrile (CH_3CN)	Acetylene (C_2H_2)	Bromomethane (CH_3Br)	Iso-propanol (C_3H_8O)	Methyl methacrylate ($CH_2C(CH_3)COOCH_3$)	Naphthalene ($C_{10}H_8$)	Propene (C_3H_6)	Ca^{+2} ($Ca\text{-}Cl_2$ or $\text{-}SO_4$)
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

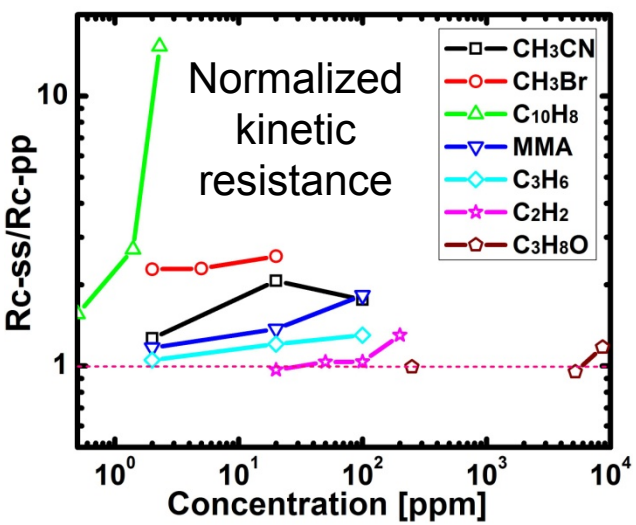
Accomplishments and Progress

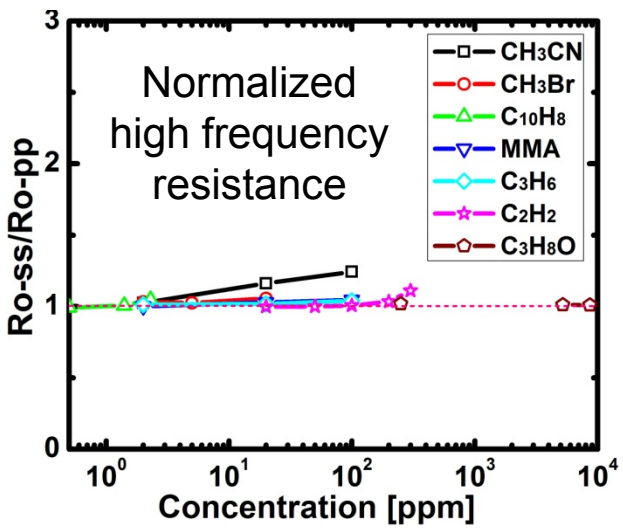
- Milestone 2 database includes data obtained with 7 contaminants, 7 operating condition cases and varying times (>490 impedance spectra)
  - Impedance data were fitted to a common electrical equivalent circuit to extract kinetic, ohmic and mass transfer resistances
  - Depicted acetonitrile example shows kinetic, ohmic and mass transfer resistance increases

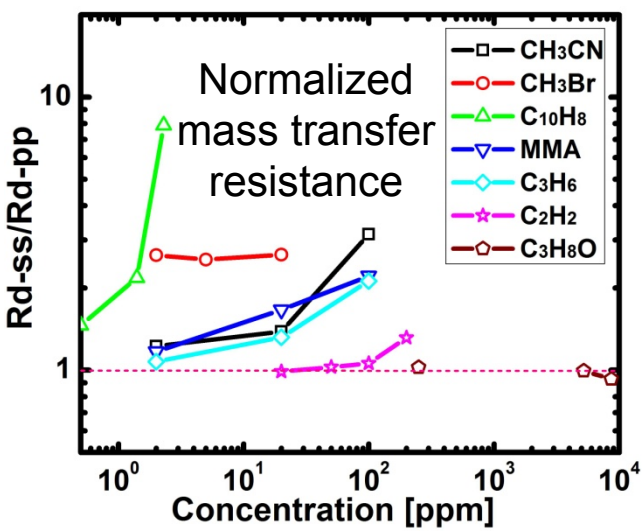


Accomplishments and Progress

- Contamination effects were separated (1st iteration) into different types
  - All 7 airborne contaminants increased charge and mass transfer resistances
    - Acetonitrile, acetylene, bromomethane, iso-propanol, methyl methacrylate (MMA), naphthalene, propene
  - Only acetonitrile increased the high frequency resistance
  - Multi-step recovery procedures may be needed
- Tests were completed or planned to understand in more detail the origin of these different losses (2nd iteration)

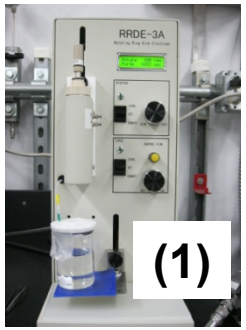


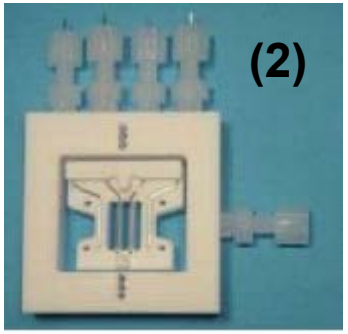


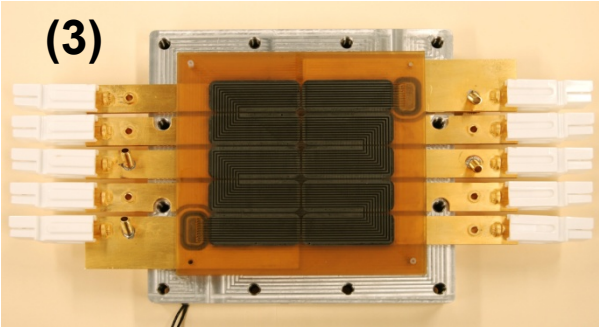


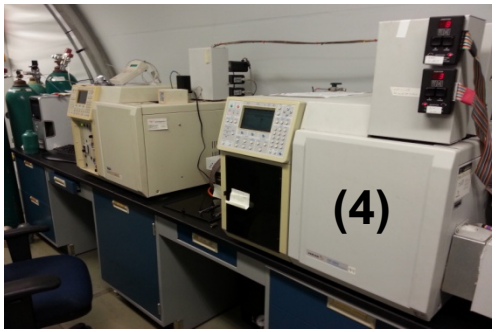
Accomplishments and Progress

- For the contamination mechanism 2nd iteration, measurement methods are used that probe all performance loss types
  - Kinetic: rotating ring/disc electrode or RRDE (1)
  - Ohmic: membrane conductivity cell (2)
  - Mass transfer: residence time distribution or RTD (liquid water volume change)
  - All types: segmented fuel cell (3) and single fuel cell with gas chromatography (4)
- A lower catalyst loading of 0.1 rather than 0.4 mg Pt/cm^2 was also investigated to assess commercially relevant materials
- Acetylene (a common welding fuel) results are shown as example (slides 11-16)



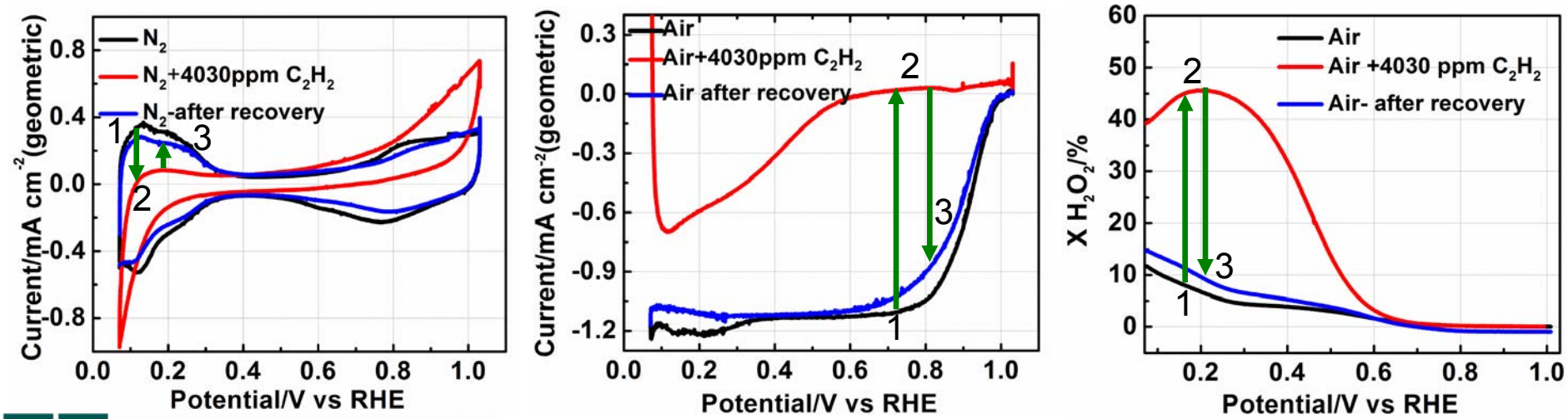






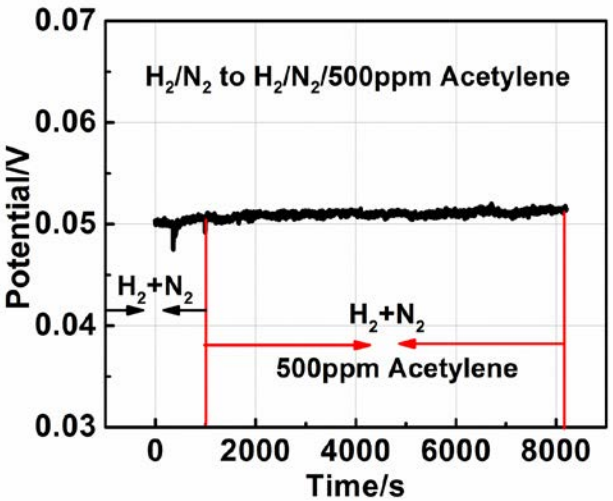
Accomplishments and Progress

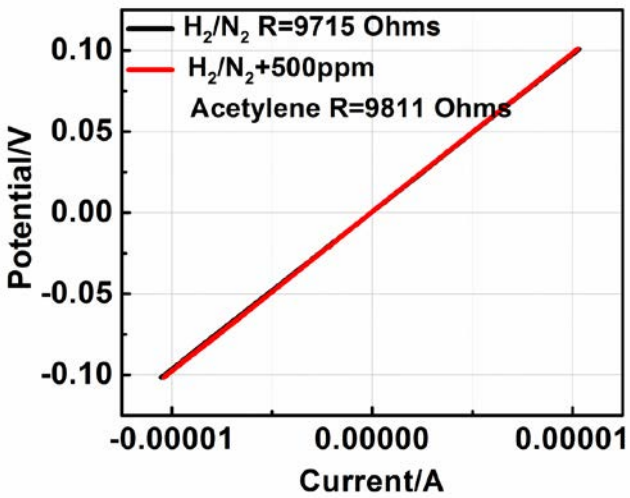
- Acetylene (a common welding fuel) impacts both catalyst active area and oxygen reduction mechanism reducing performance and durability
  - Reduced catalyst area and performance due to acetylene adsorption
  - Increased peroxide formation, an oxygen reduction side reaction, and faster membrane backbone attack
  - After recovery, the oxygen reduction current is largely regained but a significant catalyst surface area loss and peroxide formation rate gain remain

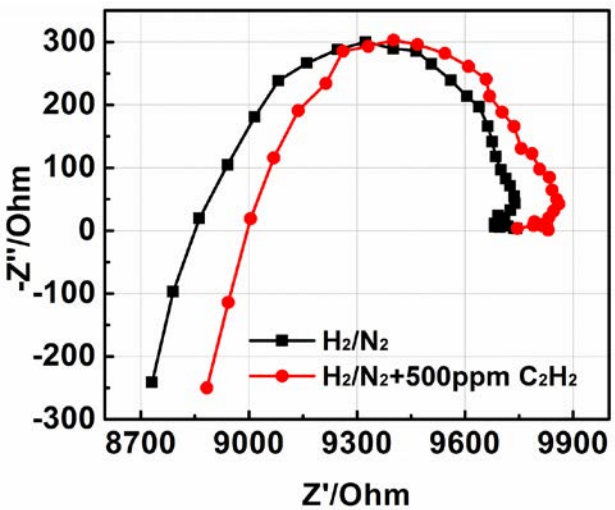


Accomplishments and Progress

- Acetylene (500 ppm, a common welding fuel) minimally impacts membrane conductivity with a 1-2 % change as measured by chronopotentiometry, cyclic voltammetry and impedance spectroscopy
- Results correlate well with fuel cell normalized high frequency resistance data (slide 9)







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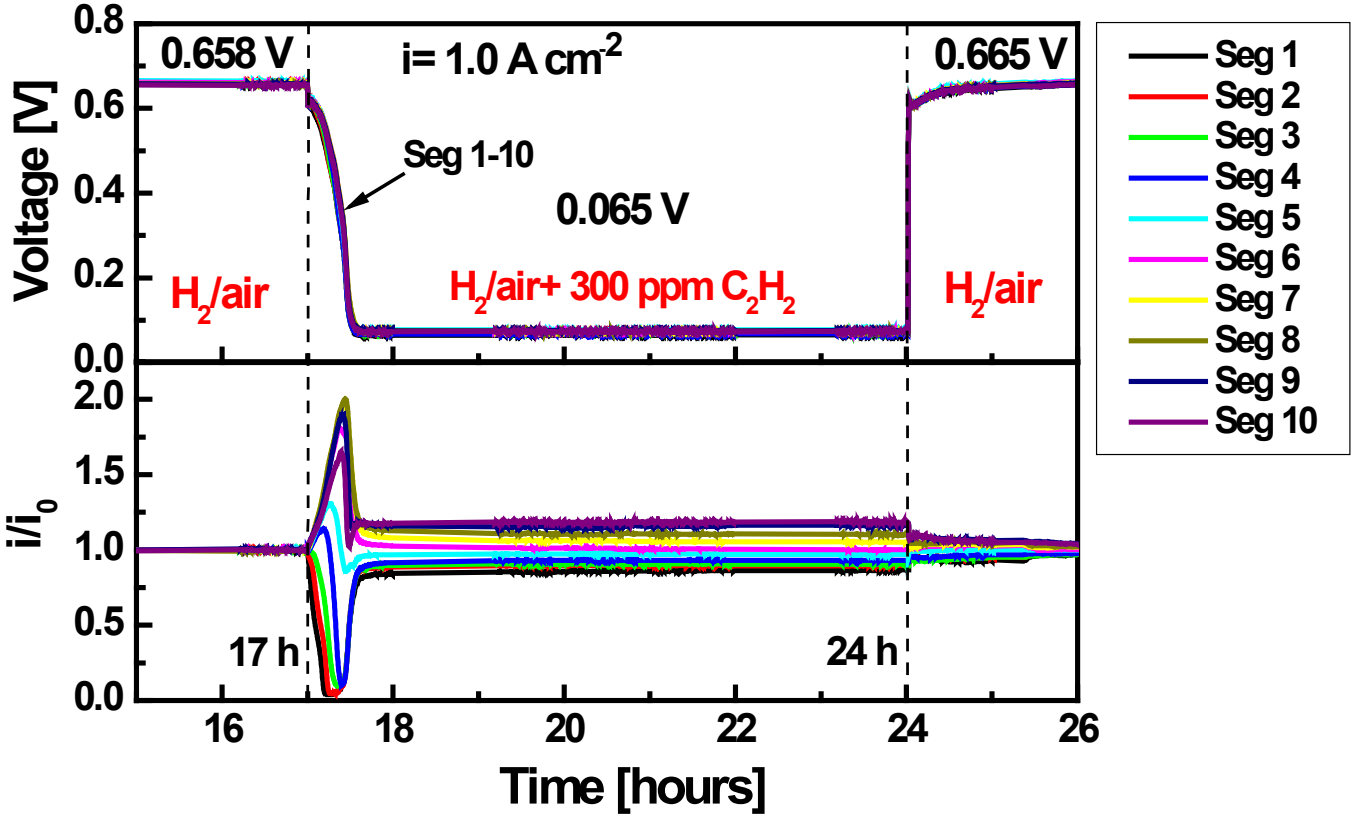
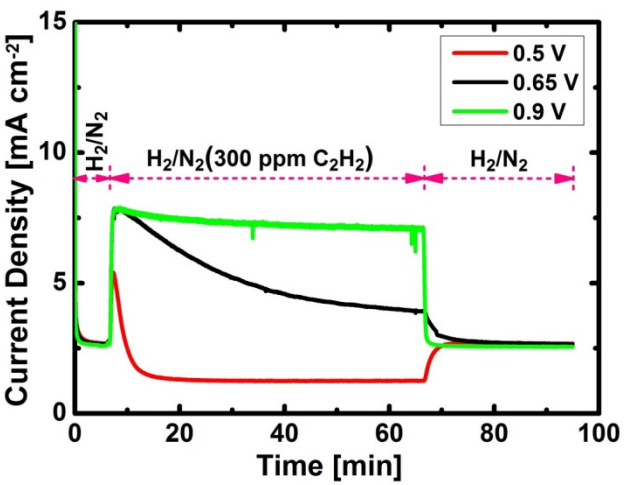
Accomplishments and Progress

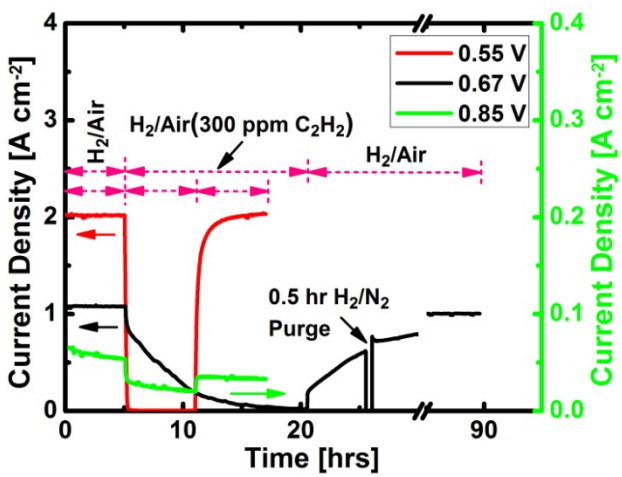
- Acetylene (a common welding fuel) causes a current redistribution due to the gradual adsorption on both catalyst surface and carbon (catalyst support, sub-layer, gas diffusion layer)
- Localized higher current densities (lower electrode potentials), temperatures and peroxide production rate may accelerate catalyst and ionomer degradation



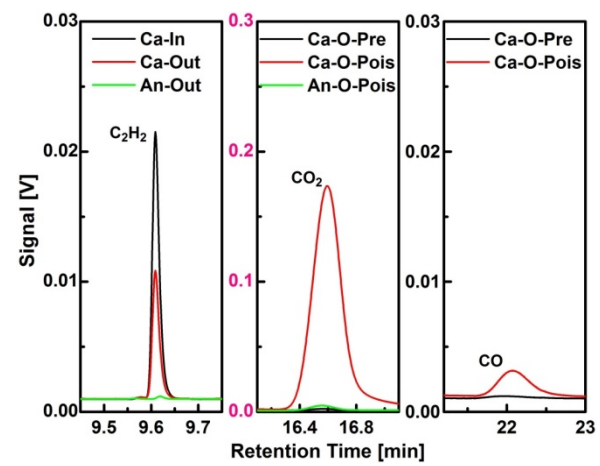
Accomplishments and Progress

- Acetylene (a common welding fuel) oxidizes yielding CO and CO_2 products
  - At 0.85 V vs H_2 electrode, ~100 % acetylene conversion
  - At 0.67 V vs H_2 electrode, ~50 % acetylene conversion
  - At 0.55 V vs H_2 electrode, <1 % acetylene conversion
- In spite of the presence of acetylene oxidation, the significant contaminant effect on fuel cell performance remains supporting the development of filtering system specifications



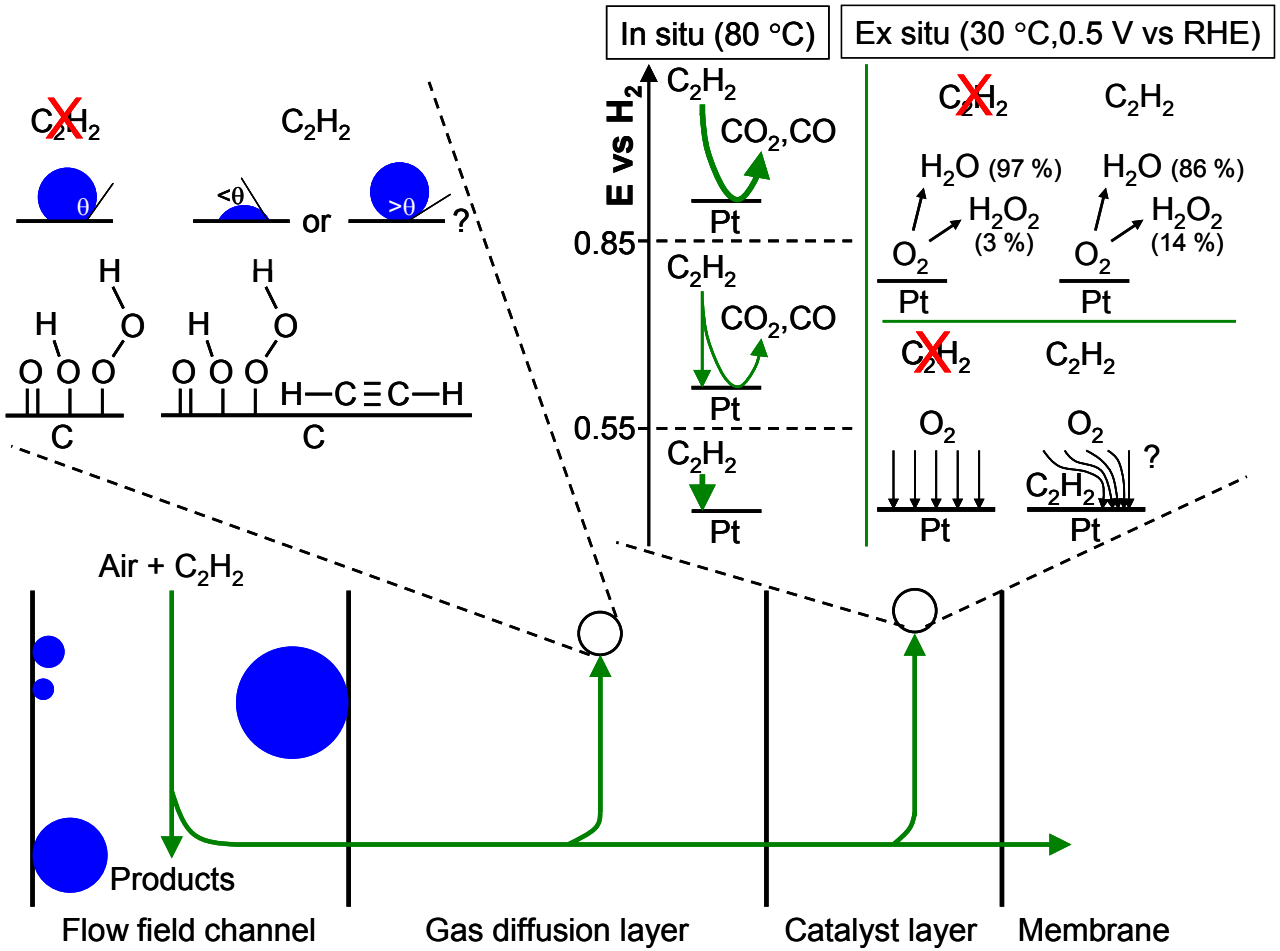


Air + 300 ppm C_2H_2, 0.67 V vs H_2



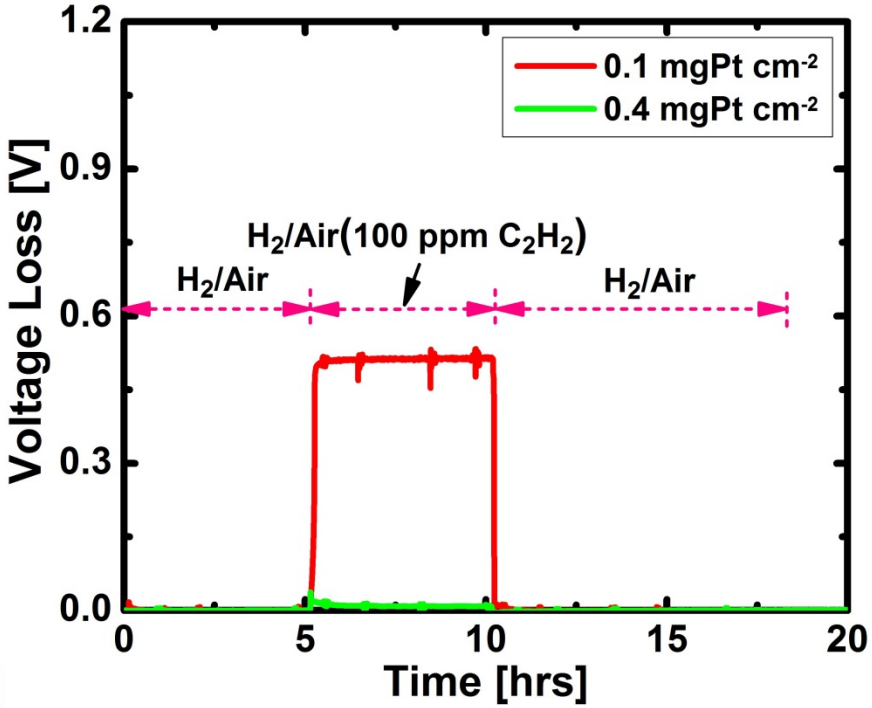
Accomplishments and Progress

- Acetylene (a common welding fuel) contamination mechanism proposed
- Mass transfer loss validation is planned with residence time distribution measurements of liquid water in the gas diffusion layer



Accomplishments and Progress

- A lower catalyst loading is substantially more affected (7000 % increase in voltage loss) by the presence of acetylene (a common welding fuel) supporting the development of filtering system specifications



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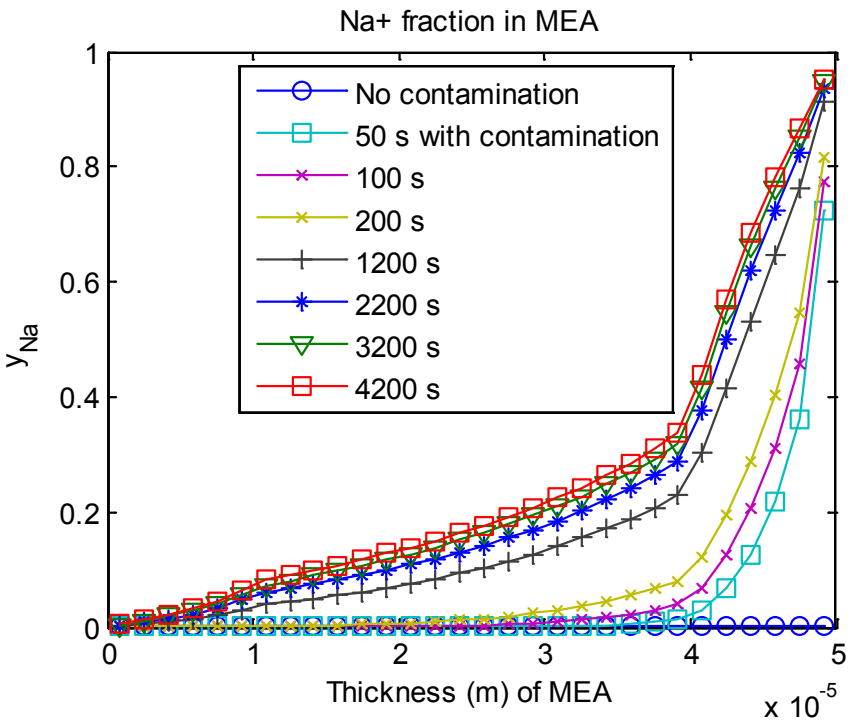
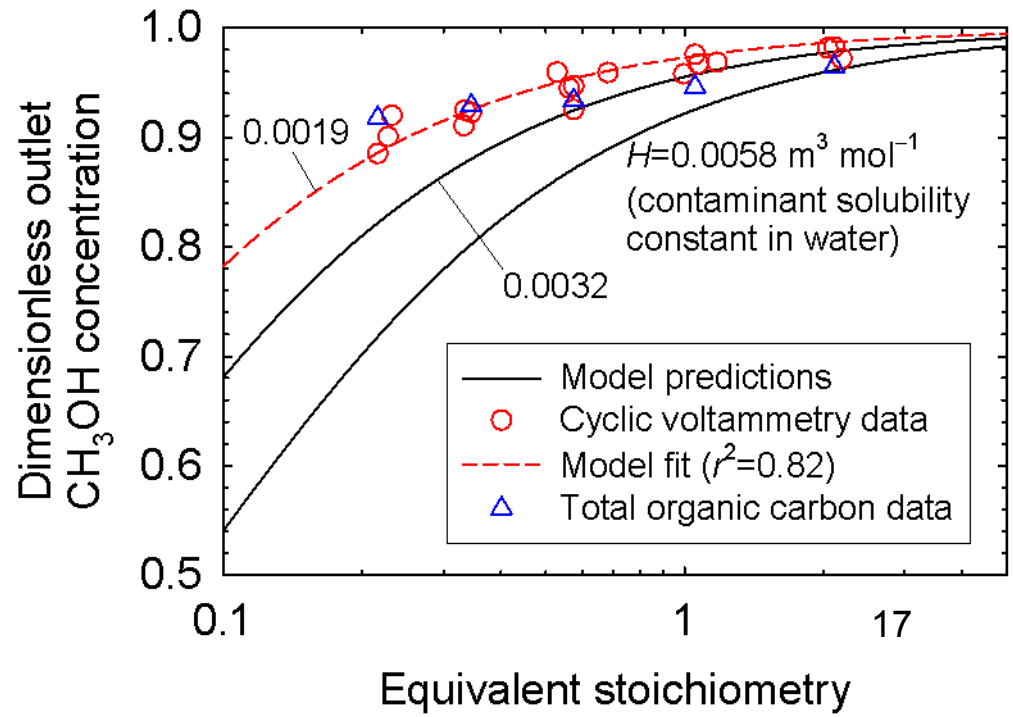
Accomplishments and Progress

- A transient cation transport model is being developed to support experimental data interpretation because kinetic and mass transfer as well as ohmic losses occur due to cation accumulation at the ionomer interface
- Mathematical models were also derived for contaminants dissolving in water without or with subsequent dissolution reactions
  - Contaminant entrainment in liquid water reduces the contaminant concentration suggesting the use of an effective value for performance data correlations





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)
  - UTC Power and Ballard Power Systems (industry sub-contractors, consulting role)
- Other collaborators
  - 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)

Proposed Future Work

- Fiscal year 2013
  - Milestone 3: Quantify spatial variability of performance loss for at least 4 different contaminants. Identify principal poisoning mechanism for same (March 31, 2013)
  - Complete experiments supporting the elucidation of contamination mechanisms for the 7 organic and 1 cation species
    - Rotating/ring disc electrode, conductivity cell, residence time distribution, segmented fuel cell, single fuel cell coupled with gas chromatography, etc
  - Analyze, summarize and disseminate the large database to industry to support the development of filter specifications
  - Initiate the development of mitigation strategies for catalysts, ionomers and gas diffusion layers based on potential changes, fluid circulation including product water and established contamination mechanisms
- Fiscal year 2014
  - Investigate long term operation with contaminants to determine the impact of increased peroxide generation and induced changes over active area (current distribution, etc)
  - Determine the impact of a contaminant mixture with concentrations closer to atmospheric values with a 0.1 mg Pt cm^{-2} loading
  - Milestone 4: Demonstrate successful mitigation of the impact of the most important 4 airborne contaminants (March 31, 2014)

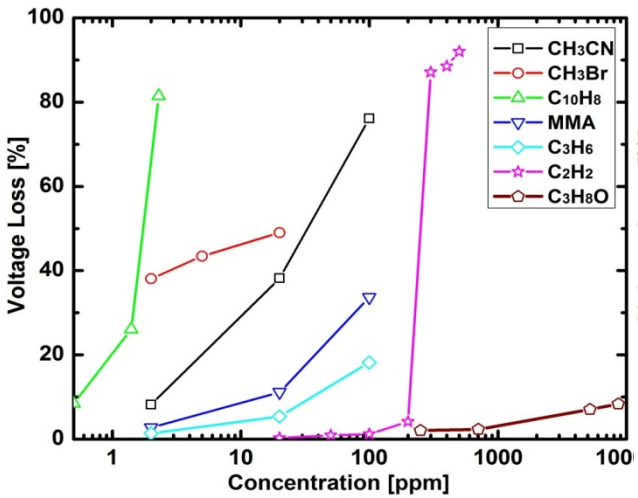
Summary

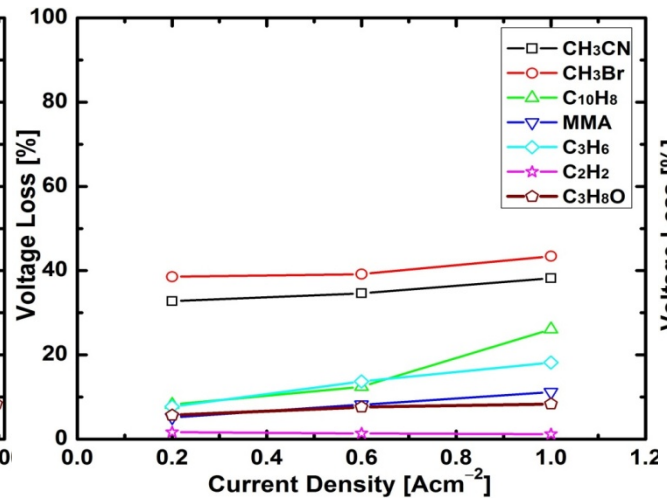
- Relevance
  - Performance and durability impacts are mitigated by providing input into filter specifications (slide 24) and, fuel cell material selection, design, operation or maintenance
- Approach
  - Document operating conditions effects on contamination with in situ tests
  - Determine contamination mechanisms with extensive in situ and ex situ measurements
  - Develop mitigation strategies based on potential changes, fluid circulation and mechanisms
- Technical accomplishments and progress
  - Contamination mechanisms for airborne contaminants and a cation
    - Airborne contaminants effects were separated into different resistance types
    - Acetylene contamination mechanism proposed and development for all other contaminants is ongoing
    - Catalyst loading sensitivity established for 4 airborne contaminants
  - Commissioning of custom residence time distribution apparatus (ONR award)
  - Cation transport and liquid water scavenging mathematical models for data interpretation and mechanism development
- Collaborations
  - Multi-faceted interactions with team organizations, project ID # FC048, consumers, suppliers, the DOE durability working group and an interest group including fuel cell industries add relevance to activities
- Proposed future work
  - Development of mitigation strategies for catalysts, ionomers and gas diffusion layers

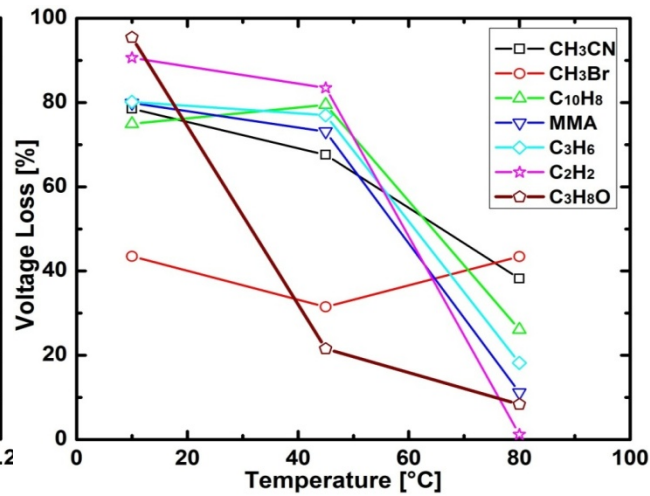
Technical Backup Slides

Milestone 2 Results

- The steady state effect of selected airborne contaminants as a function of operating conditions was summarized
  - Acetonitrile (CH_3CN), acetylene (C_2H_2), bromomethane (CH_3Br), iso-propanol (C_3H_8O), methyl methacrylate (MMA, $CH_2C(CH_3)COOCH_3$), naphthalene ($C_{10}H_8$), propene (C_3H_6)
- **<u>The effect of operating conditions is generally similar for all airborne contaminants with the bromomethane temperature effect as an exception</u>**







Milestone 2 Results

- **<u>The effect of calcium sulfate $CaSO_4$ (Ca^{+2} is the cation of $CaCl_2$ de-icing agent) as a function of operating conditions was summarized and does not reach a 20 % loss</u>**
  - Higher concentrations are worse
    - ~80 mV in 100 hours at 10 ppm (5.7 mM $CaSO_4$ and 130 μL/min)
    - ~7 mV in 100 hours at 2 ppm (1.14 mM $CaSO_4$ and 130 μL/min)
  - Lower current densities are worse
    - Salt precipitation near the cathode outlet due to increased water loss to anode
      - At 0.2A cm^{-2}, cells cannot reach 100 operating hours with $CaSO_4$ injection

Effect of operating conditions on ΔV (100 hours) and rate of resistance increase (current interrupt)

	Operating Conditions				
Contaminant	**1 Acm^{-2} 2 ppm**	**1 Acm^{-2} 5 ppm**	**1 Acm^{-2} 10 ppm**	**0.6 Acm^{-2} 5 ppm**	**0.2 Acm^{-2} 5 ppm**
$CaSO_4$	6.69 mV 17.8 μΩ cm^2/h	49.07 mV 102.1 μΩ cm^2/h	75.87 mV 98.7 μΩ cm^2/h	16.51 mV 51.9 μΩ cm^2/h	123.32-685.9 μV/h 0-1135.4 μΩ cm^2/h

For the 0.2 A cm^{-2} and 5 ppm case, 3 separate tests did not reach 100 h due to salt precipitation. As a result, the degradation rate was instead calculated. For other cases, the degradation rate in μV h^{-1} is obtained by multiplying the loss in mV by 10.

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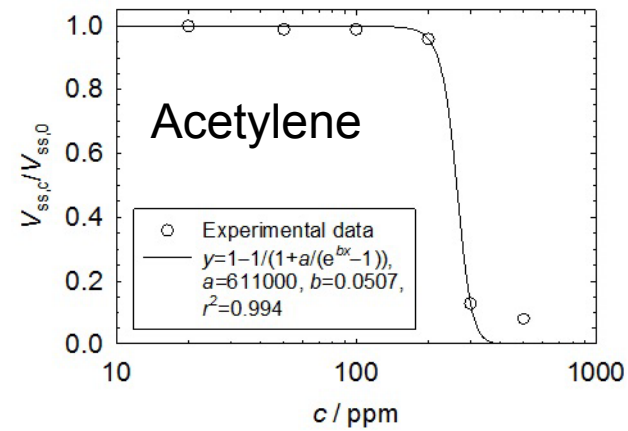
Milestone 2 Results

- **Tolerance limits were established for selected contaminants and filter specifications using semi-empirical relations**
  - For 0.4 mg Pt cm^{-2} and a steady state reached within 5000 h
  - Confidence level varies
    - High (green), medium (yellow) and low (red)
- **A similar analysis needs to be completed for the other operating conditions (*i*, *T*)**



$$\frac{V_{ss,c}}{V_{ss,0}} = 1 - \frac{1}{1 + \frac{a}{e^{bc} - 1}}$$

$$\frac{V_{ss,c}}{V_{ss,0}} = 1 - \frac{1}{1 + \frac{a}{c^{b}}}$$

Contaminant	Predicted contaminant tolerance *c* (ppm)			Experimental contaminant concentration range (ppm)	Empirical correlation parameters[a]		
	$V_{ss,c}/V_{ss,0}$=0.95	$V_{ss,c}/V_{ss,0}$=0.99	$V_{ss,c}/V_{ss,0}$=0.995		*a*	*b*	r^2
Acetonitrile	1.7	0.33	0.16	2-100	9.03×10^{-5}	2.80×10^{-6}	0.995
Acetylene	210	170	158	20-500	611000	0.0507	0.994
Bromomethane	5.7×10^{-6}	1.1×10^{-9}	3.0×10^{-11}	2-20	1.84	0.193	0.995
Iso-propanol	4200	800	400	250-8600	8.53×10^{-5}	1.07×10^{-9}	0.857
Methyl methacrylate	9.9	1.9	0.95	2-100	4.03×10^{-6}	2.13×10^{-8}	0.988
Naphthalene	0.63	0.21	0.12	0.5-2.4	59.2	2.26	0.987
Propene	23	4.5	2.2	2-100	6.86×10^{-6}	1.56×10^{-8}	0.978

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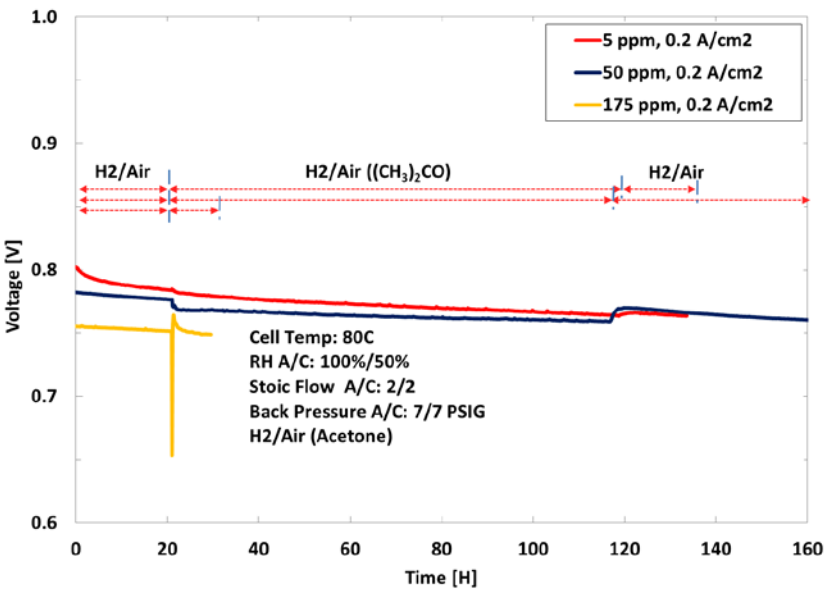
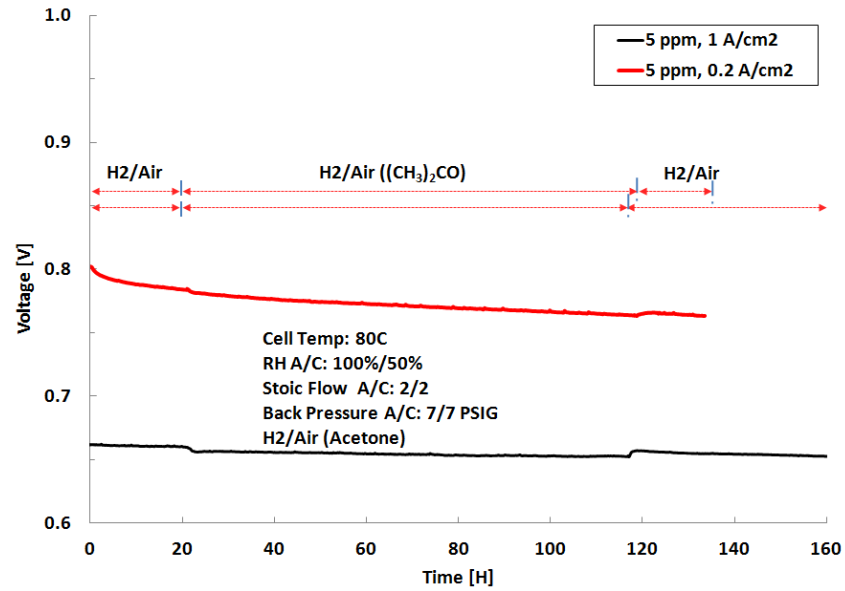
Milestone 2 Added Scope

- **<u>Two fuel cell system materials cleaning agents were identified</u>**
  - **<u>Acetone effect is small and <20 mV for 5-175 ppm and 0.2-1 A cm^{-2}</u>**
  - Citric acid effect has not been determined
- **<u>Application relevant heat transfer fluids have been included</u>**
  - HFC-152a and HFC-134a were included for airborne contaminants screening
  - Ethylene glycol was used for the ionomer contamination by an uncharged species model validation





Milestone 3 Results

- **<u>Measurements aimed at probing performance loss types for selected airborne contaminants so far indicate significant decreases in key fuel cell material parameters</u>**

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_2O_2 current (% gain in air at 30 °C and 0.5 V vs RHE)[1]	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)[2]	Cell voltage loss (% gain for a Pt loading reduction of 0.4 to 0.1 mg cm^{-2} in air at 80 °C)
Acetonitrile	85 (16.9 mM)	>60 (16.9 mM)	130 (16.9 mM)	0 (100 ppm)	TBD	TBD	TBD	77 (20 ppm)
Acetylene	100 (4030 ppm)	>90 (4040 ppm)	601 to 1027 (4030 ppm)	1-2 (500 ppm)	TBD	−17 to 18 (300 ppm)	0.8 to 100 for 0.55 to 0.85 V vs H_2 (300 ppm)	7004 (100 ppm)
Bromomethane	TBD	TBD	TBD	-	TBD	TBD	TBD	TBD
Iso-propanol	TBD	TBD	TBD	-	TBD	TBD	TBD	TBD
Methyl methacrylate	72 (1 mM)	65 (1 mM)	350 to 491 (1 mM)	-	TBD	TBD	49 to 57 for 0.55 to 0.68 V vs H_2 (20 ppm)	129 (20 ppm)
Naphthalene	TBD	TBD	TBD	-	TBD	TBD	TBD	TBD
Propene	52.6 (1010 ppm)	38 (1010 ppm)	604 (1010 ppm)	-	TBD	−8 to 6 (100 ppm)	43 to 62 for 0.55 to 0.73 V vs H_2 (100 ppm)	257 (100 ppm)

[1] In spite of a large peroxide production rate increase, the total current is still mostly due to oxygen reduction
[2] In all cases, observed products include the unaltered contaminant, CO and CO_2