

The Effect of Airborne Contaminants on Fuel Cell Performance and Durability

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Project ID # FC065

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

Overview

Timeline

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

Budget

- Total recipient share: \$930,262
- Total federal share: \$3,699,116
- Total DOE funds spent*: \$3,650,000

* as of 3/31/15

Barriers

- (A) Durability
 - 5000 h in automotive drive cycle by 2020 (automotive application)
- (C) Performance
 - Energy efficiency
 - 60 % at 25 % of rated power by 2020 (automotive application)

Partners

- Interactions/collaborations: University of Connecticut*, WPCSOL^{*,**}, 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

2014-2015 objective: Demonstrate mitigation for species that do not lead to a performance recovery by ceasing contaminant exposure

Project impact:

- The gas diffusion layer acts as a barrier to cation contamination
- Acid solutions partially recover the performance lost by cation contamination

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

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

Project targets

Approach

- Focused, contaminant dependent approaches to recover performance and improve durability
 - Flushing solutions for foreign cations (ion exchange) including product water
 - Potential excursions for organic species (oxidation, reduction, or desorption)
- 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

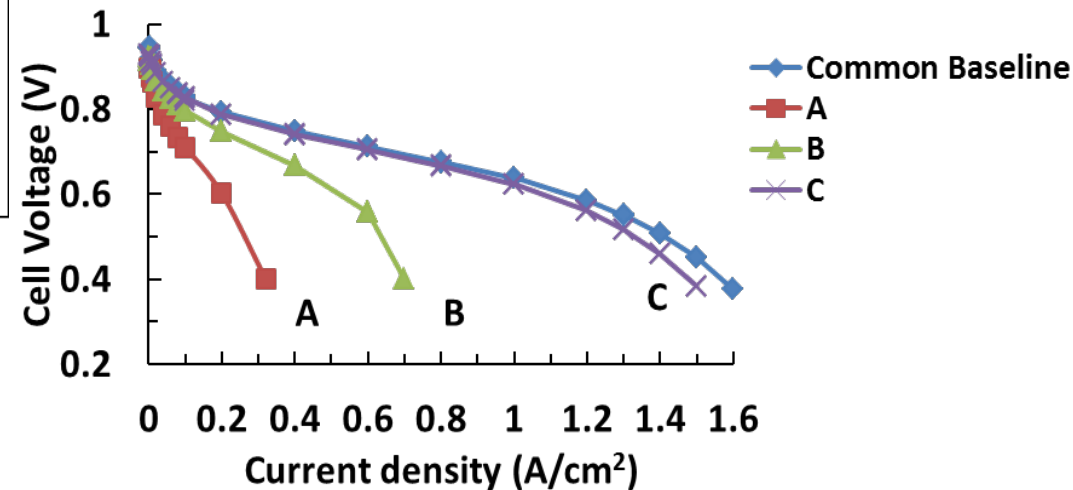
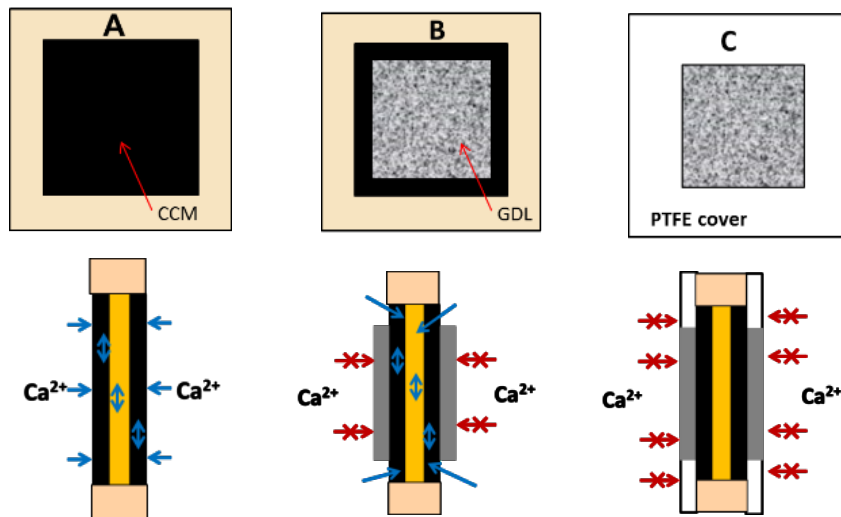
- Milestone M3 due in March 2013 was completed
 - Quantify spatial variability of performance loss for at least 4 different contaminants. Identify principal poisoning mechanism for same

Milestone	Status	Due Date
<p><u>M4 (interim)</u>: Complete the identification of intermediate or reaction products</p> <p>Determine the effect of acetonitrile intermediate or reaction products on membrane conductivity</p> <p>Complete segmented fuel cell measurements</p> <p>Complete 4 outreach products</p>	<p>Completed</p> <p>Completed</p> <p>Completed</p> <p>4 journal papers</p>	<p>March 2014</p>
<p><u>M4 (interim)</u>: Characterize the long term effects of a contaminant mixture</p> <p>Characterize the effect of acidic and cleaning solutions circulation on performance recovery</p> <p>Complete 5 outreach products</p>	<p>Delayed (November 2015)</p> <p>Completed</p> <p>3 journal papers, 4 proceedings, 5 conference, GM and SAE presentations</p>	<p>June 2014</p>
<p><u>M4 (interim)</u>: Identify differences introduced by metallic bipolar plates</p> <p>Characterize the long term effects of an organic contaminant</p> <p>Characterize the long term effects of a foreign cation contaminant</p> <p>Complete 4 outreach products</p>	<p>Delayed (November 2015)</p> <p>Completed</p> <p>Completed</p> <p>2 journal papers, 2 proceedings, 4 conference presentations</p>	<p>September 2014</p>
<p><u>M4 (interim)</u>: Characterize the effect of sustained OCV periods on fuel cell performance recovery</p> <p>Complete 7 outreach products</p>	<p>Delayed (August 2015)</p> <p>1 journal paper, 1 conference presentation</p>	<p>December 2014</p>
<p><u>M4</u>: Demonstrate successful mitigation of the impact of the most important 4 airborne contaminants</p> <p>Characterize the effect of sustained air starvation and point of zero charge periods on fuel cell performance recovery</p> <p>Complete 7 outreach products</p>	<p>Delayed (November 2015)</p> <p>Delayed (August 2015)</p> <p>6 journal papers, 1 SAE presentation</p>	<p>March 2015</p>

Accomplishments and Progress - Mitigation with Ex Situ Ca^{2+} Contamination Procedure

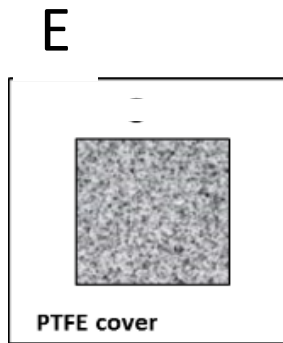
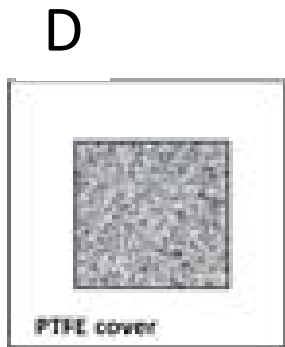
- In-situ recovery techniques were investigated using three different ex situ contamination procedures
- The contamination effect becomes less severe as the access to the ionomer and membrane is more constricted by the gas diffusion layer and gasket

Cell	Soaking description
A	The CCM is in direct contact with the Ca^{2+} solution
B	Portion of the CCM is in direct contact with the Ca^{2+} solution.
C	The CCM is not in direct contact with the Ca^{2+} solution

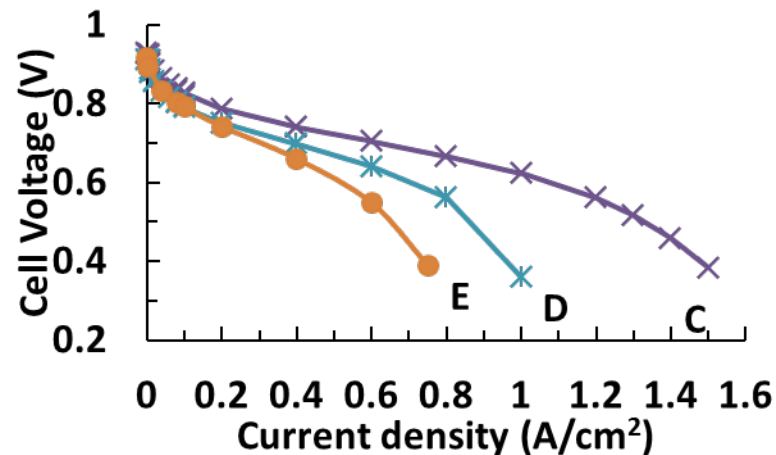
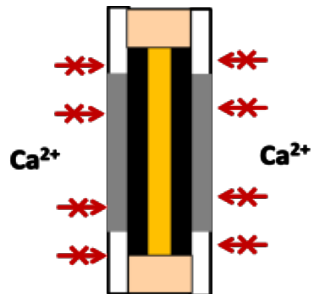
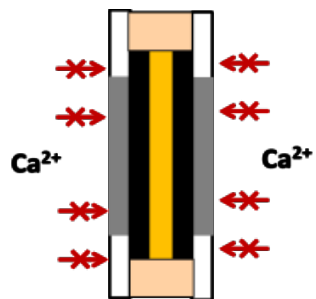


Accomplishments and Progress - Mitigation with Ex Situ Ca^{2+} Contamination Procedure

- Additional ex situ contamination procedures were also investigated by modifying the solution composition for procedure C
- Procedures D and E, which is the same as procedure C with the addition of a surfactant (respectively 1 and 15 % iso-propanol), further demonstrates the important role of the gas diffusion layer
 - Iso-propanol (IPA) was selected over methanol, ethanol and Triton® X as its contaminant effect is relatively small and reversible

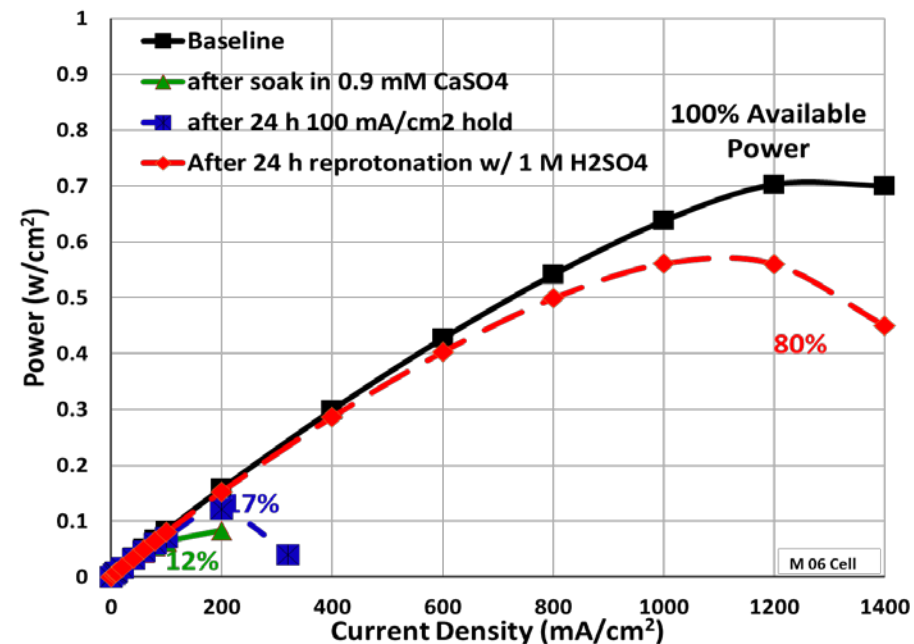
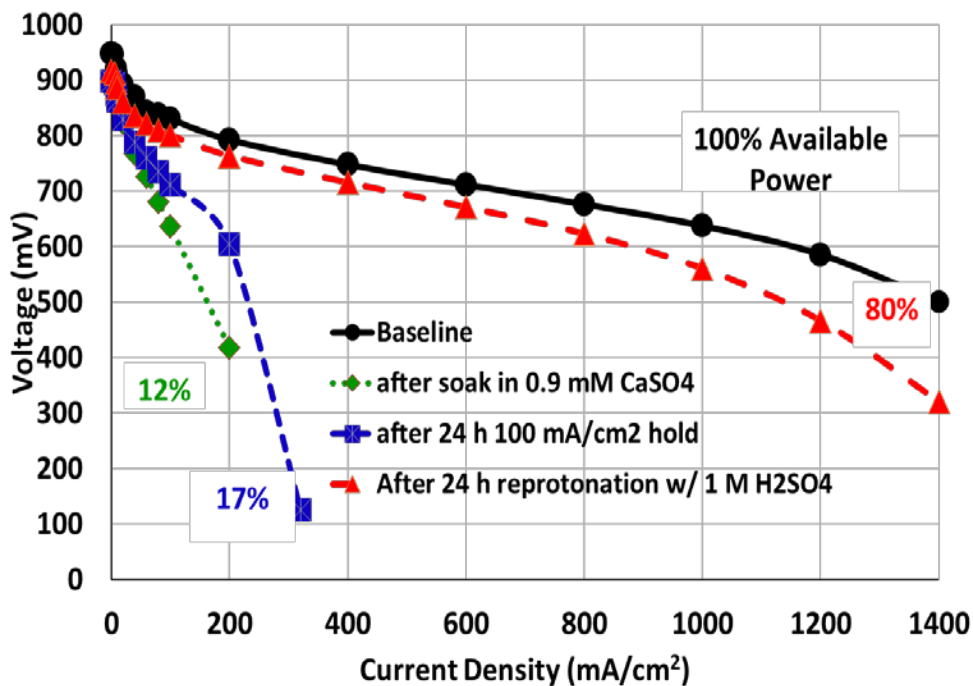


Cell	Soaking description	Wetting agent
C	Method C	No IPA
D	Method C	1% IPA
E	Method C	15% IPA



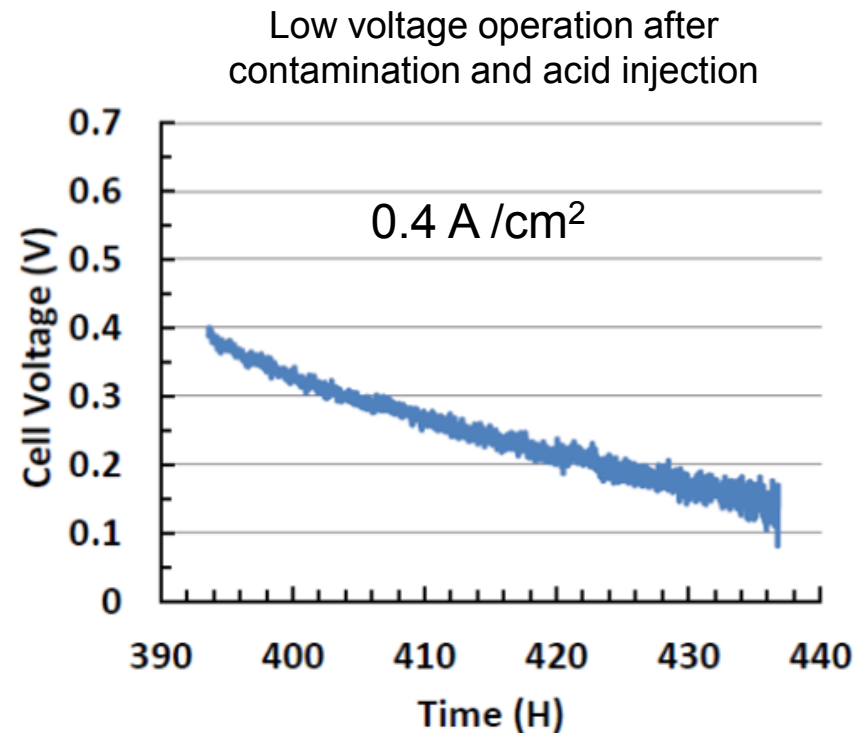
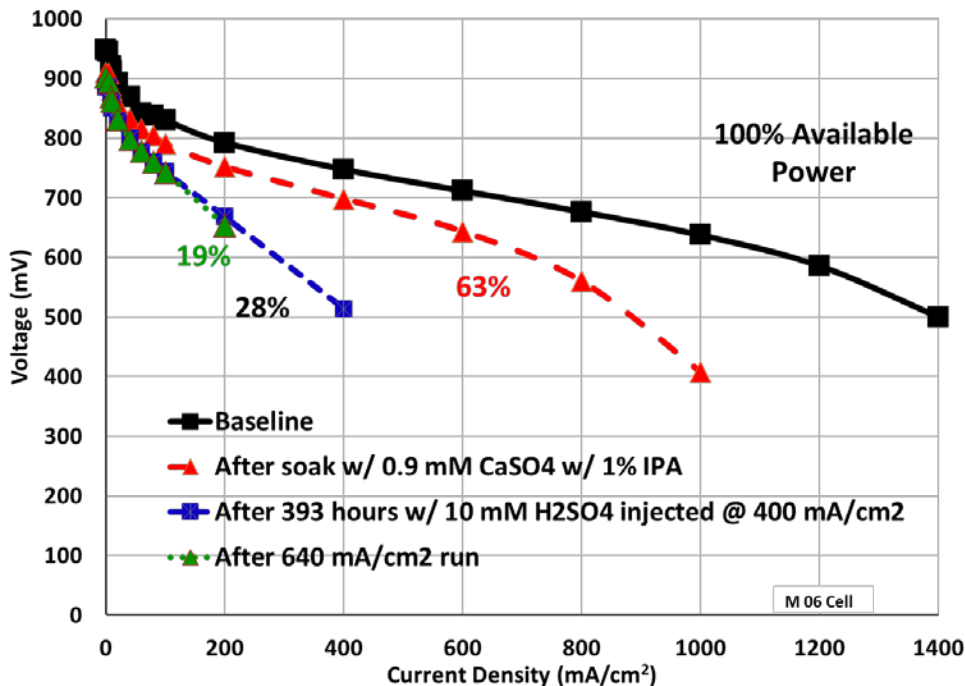
Accomplishments and Progress - Recovery from Ca^{2+} Contamination Using Ex Situ Procedure

- An ex situ recovery with an acid solution soak of the catalyst coated membrane contaminated ex situ with the cell A configuration was partly effective



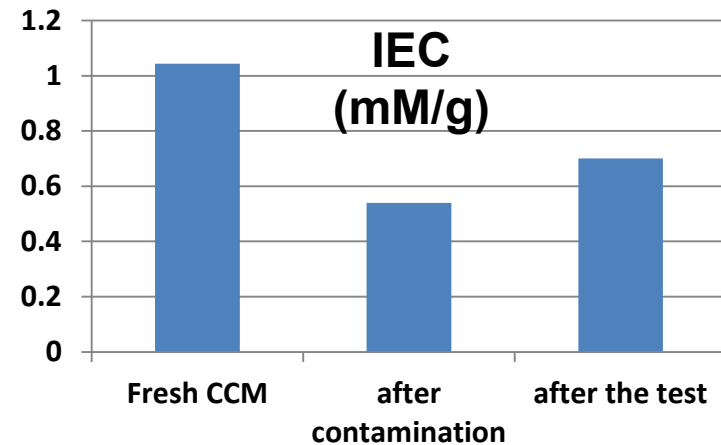
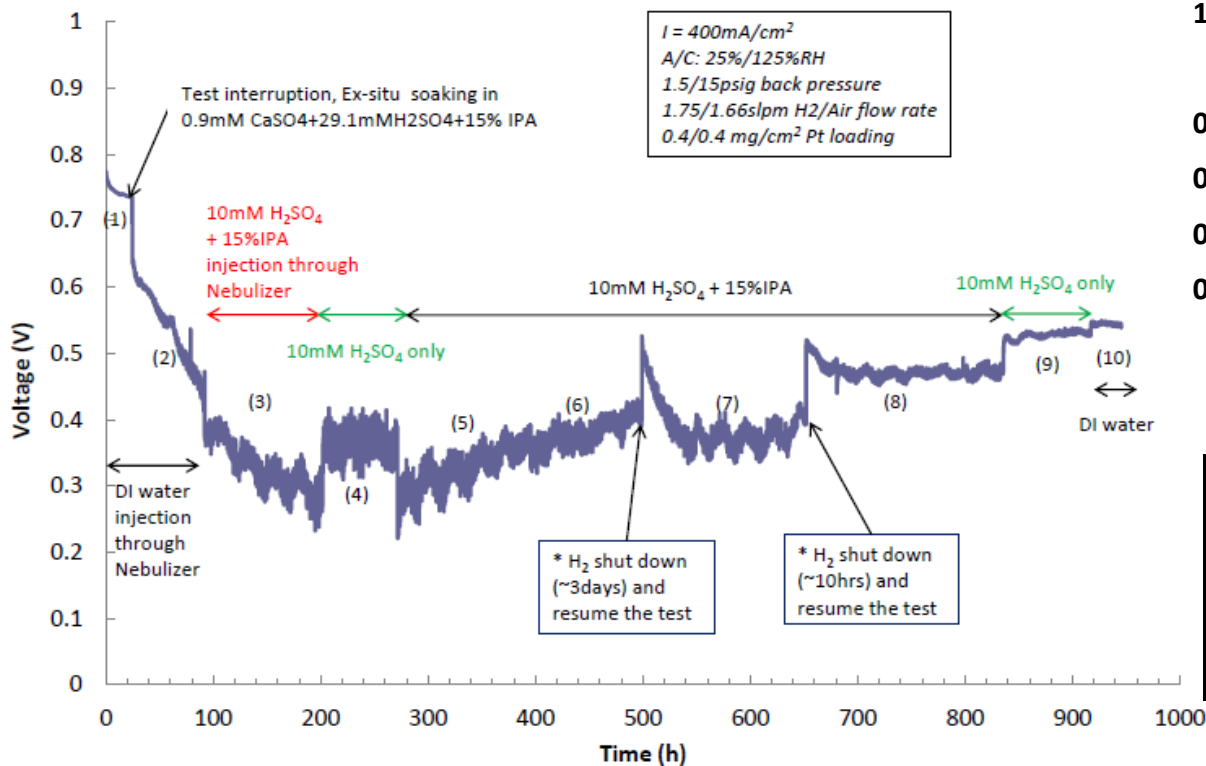
Accomplishments and Progress - Recovery from Ca^{2+} Contamination Using In Situ Acid Injection and Low Voltage Operation

- In situ recovery by acid solutions after contamination with the cell D configuration was not entirely effective
- Cell operation at a low voltage was also not effective in recovering performance even with a supersaturated cathode stream



Accomplishments and Progress - Recovery from Ca^{2+} Contamination Using In Situ Acid + Iso-Propanol Injection

- In situ recovery by acid or acid + iso-propanol solutions after contamination with the cell E configuration was not entirely effective
- The ion exchange capacity of the membrane and the gas diffusion layer contact angle after the test support the partial recovery observation



Cathode sample treatment	Advancing angle ($^\circ$)*	Receding angle ($^\circ$)*
As received	164.9	62.6
After in situ testing**	98.7	-
After water cleaning**	132.1	9.5
After acid cleaning**	156.5	12.8

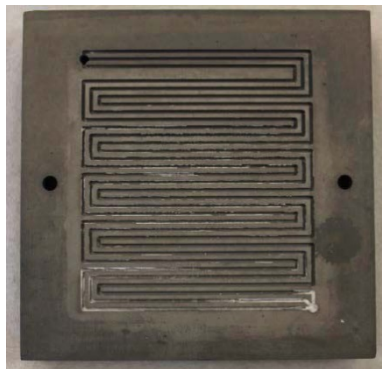
* Derived from tensiometer values.

** Near the air outlet.

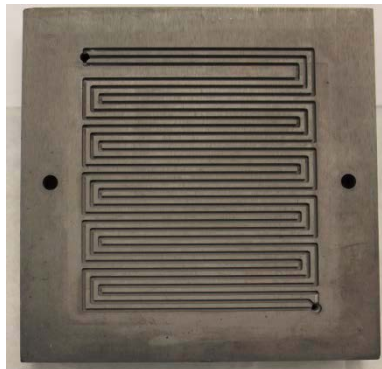
Accomplishments and Progress - In situ Ca^{2+} Contamination and Recovery Using an Acid Bath

- Water management significantly affects contamination by Ca^{2+} which may result in salt precipitation (mass transfer loss)
- An ex situ wash with a dilute acidic solution was effective in removing salt deposits from the bipolar plate and gas diffusion layer

Before cleaning

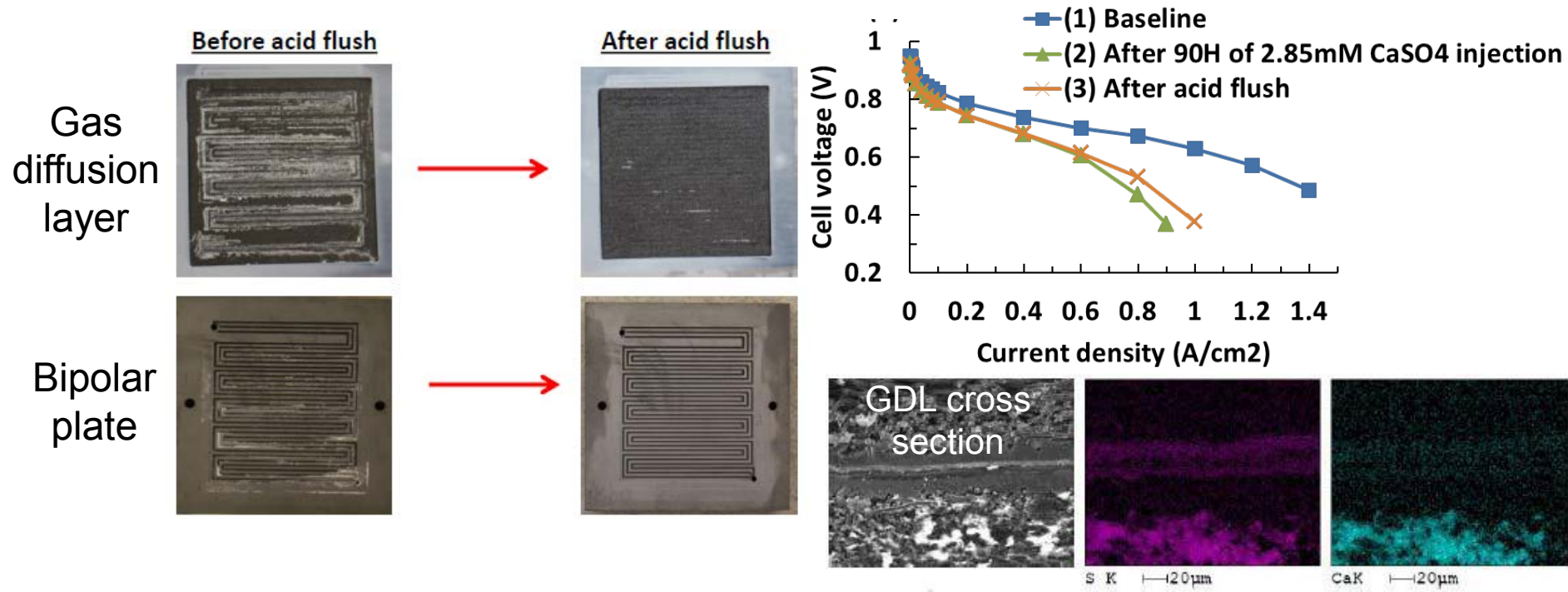


After cleaning



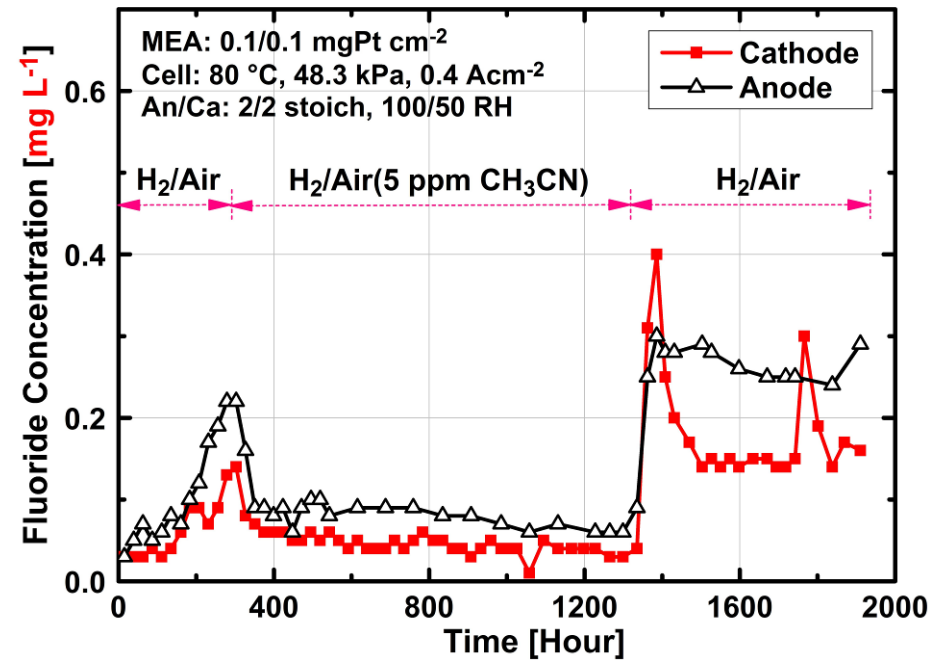
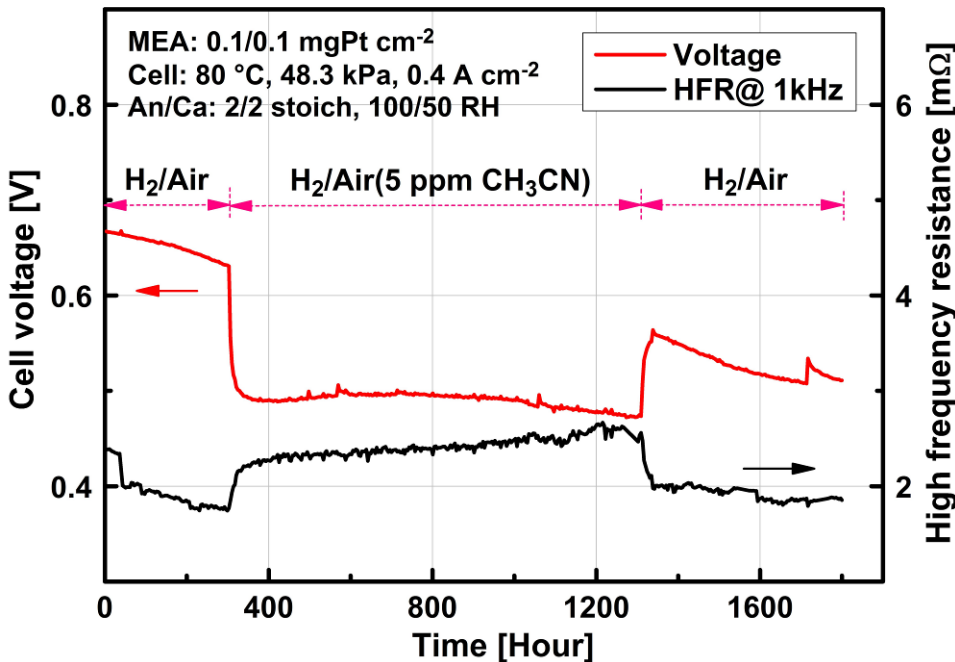
Accomplishments and Progress - In situ Ca^{2+} Contamination and Recovery Using an Acid Flush

- An acid solution circulation was largely effective in removing salt deposits from the bipolar plate and gas diffusion layer
- However, the cell performance was only improved in the mass transfer regime and Ca^{2+} was still detected in the gas diffusion electrode



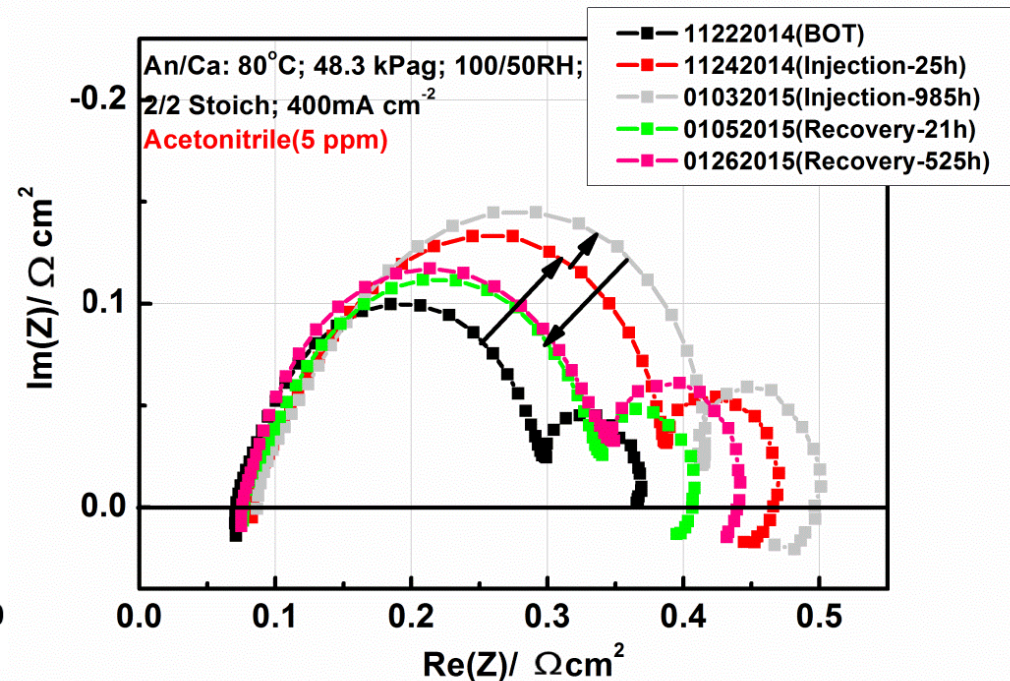
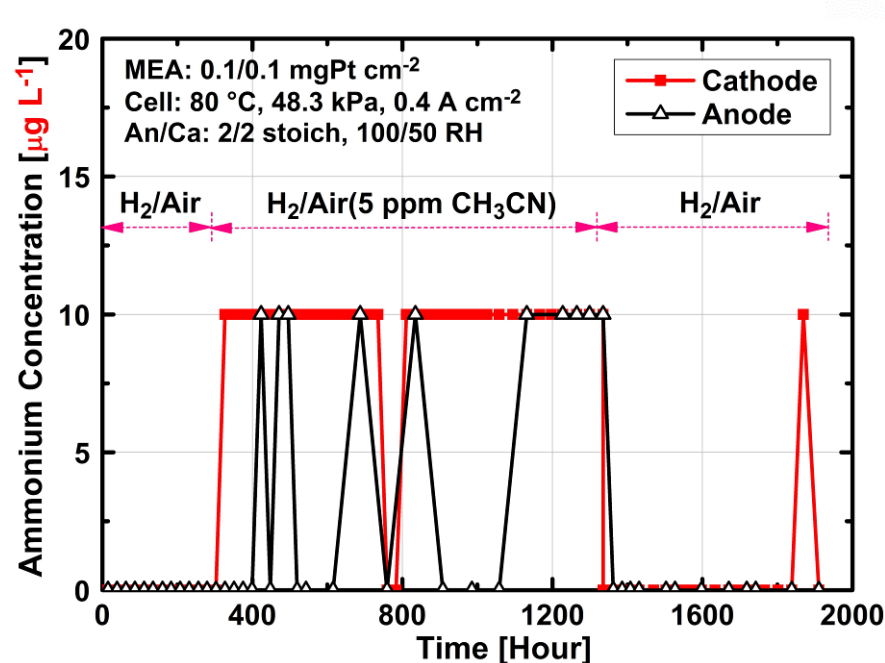
Accomplishments and Progress - Long Term Contamination Tests

- A long term test was completed (0.1 mg Pt/cm²) to assess the impact of larger peroxide production rates in the presence of acetonitrile on membrane degradation
- Analysis of outlet water samples show that the presence of acetonitrile decreases the fluoride emission rate
- Acetonitrile possibly acts as a scavenger for the radicals and/or peroxide



Accomplishments and Progress - Long Term Contamination Tests

- Analysis of outlet water samples also show the presence of ammonium ions which are responsible for the high frequency resistance increase
 - Acetonitrile hydrolysis is a likely reaction leading to ammonium ions
- Impedance spectroscopy data indicate that the performance recovery is incomplete in contrast to shorter duration tests with 0.4 mg Pt/cm²



Accomplishments and Progress - Responses to Previous Year Reviewers' Comments

- Comment (9 other similar comments): “The project has focused on Pt catalysts at relatively high loadings...the focus should have shifted to lower loadings and current state-of-the-art alloy catalysts...(comparable to DOE targets).”
 - Response: Low Pt loading membrane/electrode assemblies are not commercially available and their performance variability is larger. Commercially available low Pt loading cells degrade faster and their life is more limited...The value of testing alternate catalysts is acknowledged but their use would have significantly increased the project scope...selections also allowed comparisons with prior work...characterization of the effects of low Pt loadings would be interesting and significant...all of these are sound suggestions...they require additional resources beyond what is available in the current program...
- Comment (3 other similar comments): “The focus has been on collecting test data with relatively little in depth interpretation of the mechanism of performance loss and recovery or development of viable mitigation strategies...”
 - Response: ...in depth interpretations...have already been published but are only presented as a summary...due to a limited presentation time. Recovery strategies that are system compatible were explored for foreign cations and will be explored for organic species...
- Comment (3 other similar comments): “...it should be possible to construct a data table that consists of the contaminant, the reaction pathway, the rate of reaction or adsorption, and the method of cleaning with the associated rate. This table would provide the capability to cast the data into other performance models...to establish the design/cost effects on the fuel cell system.”
 - Response: The proposed data table is a good suggestion and it will be considered...results have routinely been reported to the US Drive Fuel Cell Tech Team, the AMR, the Electrochemical Society via meeting presentations...the fuel cell community via publications...the SAE Fuel Cell Standards Committee, Interface Task Force, the ultimate customers

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, *GC-MS 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)
 - *X-ray scattering and RRDE measurements with Pt single crystals and cations (ANL, TBD)*
- 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 were and will be explored (slides 6-12) and additional ones are expected to be derived based on experimental results and contamination mechanisms

Proposed Future Work

- Fiscal year 2015
 - Complete milestone 4: Demonstrate successful mitigation of the impact of the most important 4 airborne contaminants (March 31, 2015)
 - Establish the effectiveness of mitigation strategies based on sustained OCV and, point of zero charge and low (air starvation) cathode potentials
 - Determine the impact of a contaminant mixture with concentrations closer to atmospheric values with a 0.1 mg or lower if available Pt cm⁻² loading
 - Continue the analysis, synthesis and dissemination of the database to industry to support the development of filter specifications and mitigation strategies
- Fiscal year 2016
 - See next slide

Technology Transfer Activities

- Technology transfer activities are not envisaged
 - Developed processes and methods are public domain
 - Technical support will be made available as agreed between parties
- Present and future funding
 - Investigate contamination areas that are poorly documented (ONR)
 - Low Pt loading and catalysts other than Pt
 - Effects of contaminants on other components such as catalyst supports and seals
 - Other contaminant classes such as cleansers
 - System contaminant effects on hydrogen oxidation reaction
 - Contaminant mixtures
 - Contaminant impact on fuel cell stack behavior including recovery
 - Fuel cell system aspects such as fuel recirculation and contaminant accumulation
 - Study fundamentals of foreign cation impacts on the oxygen reduction reaction (ANL, UConn, funding TBD)
- Patenting or licensing activities are not envisaged
 - Developed processes and methods are public domain

Summary

Relevance

- Fuel cell performance and durability impacts of contaminants are mitigated by fuel cell material selection, design, operation or maintenance recommendations

Approach

- Focused, contaminant dependent performance recovery approaches
 - Cleaning solutions for foreign cations (ion exchange) including product water
 - Potential excursions for organic species (oxidation, reduction, or desorption)

Accomplishments and Progress

- Flushing solutions were partially effective to recover performance losses due to Ca^{2+} ingress
- Acetonitrile decreased the fluoride emission rate during a long term exposure

Collaborations

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

Proposed future work

- Establish the effectiveness of mitigation strategies for fuel cells contaminated with reactive species based on sustained potentials (~0-1 V cathode potentials)
- Determine the impact of a contaminant mixture with concentrations closer to atmospheric values with a $0.1 \text{ mg Pt cm}^{-2}$ cathode loading

Technical Back-Up 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

Performance Decay Rates for Reactive Contaminants

Common name	Formula	Conc. (ppm _v)	Current Density (mA/cm ²)	Stoichiometry	Decay (mV)	Elapsed Time (hr)	Decay Rate (mV/hr)
Iso-propanol	CH ₃ CH(OH)CH ₃	5200	1000	2	58	0.15	386.7
Propene	C ₃ H ₆	100	1000	2	134	0.23	595.6
Acetylene	C ₂ H ₂	300	1000	2	587	0.57	1020.9
Methyl methacrylate	CH ₂ CCH ₃ COOCH ₃	20	1000	2	82	0.32	252.3
Bromomethane	CH ₃ Br	5	1000	2	254	47.49	5.3
Acetonitrile	CH ₃ CN	20	1000	2	147	0.60	245.0
Naphthalene	C ₁₀ H ₈	1.4	1000	2	131	1.70	77.1

Contaminant Tolerance Limits

- Contaminant tolerance limits for 5, 1 and 0.5 % fuel cell performance losses at 80 °C and 1 A cm⁻² were derived with the assumption that a steady state is reached within the 5000 h automotive system life
- With a 200-400 ppm permissible exposure limit, the driver would be impacted by iso-propanol before the fuel cell (tolerance limit ≥400 ppm)

Contaminant ¹	Predicted contaminant tolerance (ppm)			Experimental contaminant concentration range (ppm)	8 h total weight average permissible exposure limit (ppm) ²	Empirical correlation parameters ³		
	$V_{ss,c}/V_{ss,0}=0.95$	$V_{ss,c}/V_{ss,0}=0.99$	$V_{ss,c}/V_{ss,0}=0.995$			a	b	r^2
Acetonitrile	1.7	0.33	0.16	2-100	40	9.03×10^{-5}	2.80×10^{-6}	0.995
Acetylene	210	170	158	20-500	Simple asphyxiant	611000	0.0507	0.994
Bromomethane	5.7×10^{-6}	1.1×10^{-9}	3.0×10^{-11}	2-20	5	1.84	0.193	0.995
Iso-propanol	4200	800	400	250-8600	200-400 ⁴	8.53×10^{-5}	1.07×10^{-9}	0.857
Methyl methacrylate	9.9	1.9	0.95	2-100	50-100	4.03×10^{-6}	2.13×10^{-8}	0.988
Naphthalene	0.63	0.21	0.12	0.5-2.4	10	59.2	2.26	0.987
Propene	23	4.5	2.2	2-100	500	6.86×10^{-6}	1.56×10^{-8}	0.978
Ca ²⁺	3.7	0.71	0.35	2-10		2.13×10^{-7}	3.05×10^{-9}	0.925

¹ confidence level in contaminant tolerance limits: high in green (located within the experimental contaminant concentration range), medium in yellow (smaller than the lower end of the experimental contaminant concentration range by a factor approximately less than 10) and low in red (much smaller than the lower end of the experimental contaminant concentration range).

² from OSHA and/or ACGIH.

³ contaminant tolerance limits were estimated based on 2 empirical equations. $V_{ss,c}/V_{ss,0}=1-1/[1+(a/c^b)]$ for acetonitrile, acetylene, iso-propanol, methyl methacrylate, naphthalene, propene and Ca²⁺, and $V_{ss,c}/V_{ss,0}=1-1/[1+(a/(e^{bc}-1))]$ for bromomethane where $V_{ss,c}$ is the steady state cell voltage during contamination (100 h value for Ca²⁺), $V_{ss,0}$ is the steady state cell voltage before contamination, c is the contaminant concentration and, a and b are fitted parameters.

⁴ for iso-propanol, the driver would be affected before the fuel cell.

Milestone 3 Metrics Summary - Quantify Spatial Variability and Identify Principal Poisoning Mechanisms

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), N product detected by ISE (IC confirmed NH ₄ ⁺ product)	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)	0 for 0.1 to -1 V (10 ppm)
Iso-propanol	12 (1 mM)	7 (1 mM)	18 (1 mM)	No ohmic loss in fuel cell	TBD	Step change of -9 to 5 (5300 ppm)	Reverse step change (5300 ppm)	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)	Detectable but not quantifiable for 0.5 to 0.85 V (1.4 ppm)
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	TBD	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. ISE: ion selective electrode, IC: ion chromatography.

Milestone 3 - Principal Poisoning Mechanisms Summary

Cathode contaminant type		<ul style="list-style-type: none"> • Organic <ul style="list-style-type: none"> -Acetonitrile: an -Acetylene: ae -Bromomethane: b -Iso-propanol: i -Methyl methacrylate: m -Naphthalene: n -Propene: p 	<ul style="list-style-type: none"> • Foreign cation -Ca²⁺
Performance losses	Kinetic	<ul style="list-style-type: none"> • Catalyst surface area loss due to contaminant adsorption (all) • Interactions between catalyst adsorbates lead to ORR mechanism changes <ul style="list-style-type: none"> -More peroxide (all) -Tafel slope increase (an, ae, m, n, p) 	<ul style="list-style-type: none"> • Catalyst surface area loss due to contaminant adsorption • Interactions between catalyst adsorbates and cation lead to ORR mechanism changes <ul style="list-style-type: none"> -More peroxide
	Ohmic	<ul style="list-style-type: none"> • Acetonitrile intermediate displaces protons in the ionomer (NH₄⁺) 	<ul style="list-style-type: none"> • Ca²⁺ displaces protons in the ionomer which is also leading to kinetic and mass transfer losses during operation
	Mass transfer	<ul style="list-style-type: none"> • Observed increase in impedance loop at low frequencies (all) requires assignment confirmation <ul style="list-style-type: none"> -Initial explanation: decrease in active surface area increases oxygen path to reaction sites -Recent re-interpretation based on additional impedance data: contaminant intermediates artifact <ul style="list-style-type: none"> - TBD (contaminant adsorption on C modifying water management) • Distributed effects along the channel length (scale up) (an, ae, b, n) 	<ul style="list-style-type: none"> • Salt precipitation causes flow field and gas diffusion layer blockages • Ca²⁺ reduces the gas diffusion layer hydrophobicity (water management) • Distributed effects along the channel length (scale up)
Recovery		<ul style="list-style-type: none"> • 90 % of initial cell performance restored after contaminant injection stopped at 80 °C (an, ae, i, m, n, p) • For bromomethane, supersaturated operation and potential excursions recovers performance above 90 % of initial cell performance 	<ul style="list-style-type: none"> • Both in situ and ex situ methods (acid, surfactant) did not fully recover performance
Other losses		<ul style="list-style-type: none"> • Fluoride emission rate decrease possibly due to contaminant scavenging of peroxide/radicals (an) 	<ul style="list-style-type: none"> • TBD (long duration test in progress to assess peroxide and electrostriction impact) • TBD (cell components corrosion namely end plates, bus plates and metal connector fittings)