The Effect of Airborne Contaminants on Fuel Cell Performance and Durability

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Project ID # FC065

Overview

Timeline

- Project start date: April 1, 2010
- Project end date: March 31, 2014
- Percent complete: 10-15 %

Budget

- Total project funding
  - DOE share: $3,649,116
  - Contractor share: $917,762
- Funding received in FY10: $250,021
- Funding for FY11: $950,000

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

- Mitigation of the unknown effects of many airborne contaminants on membrane/electrode assembly materials, adversely impacting system performance and durability, represents the main project objective

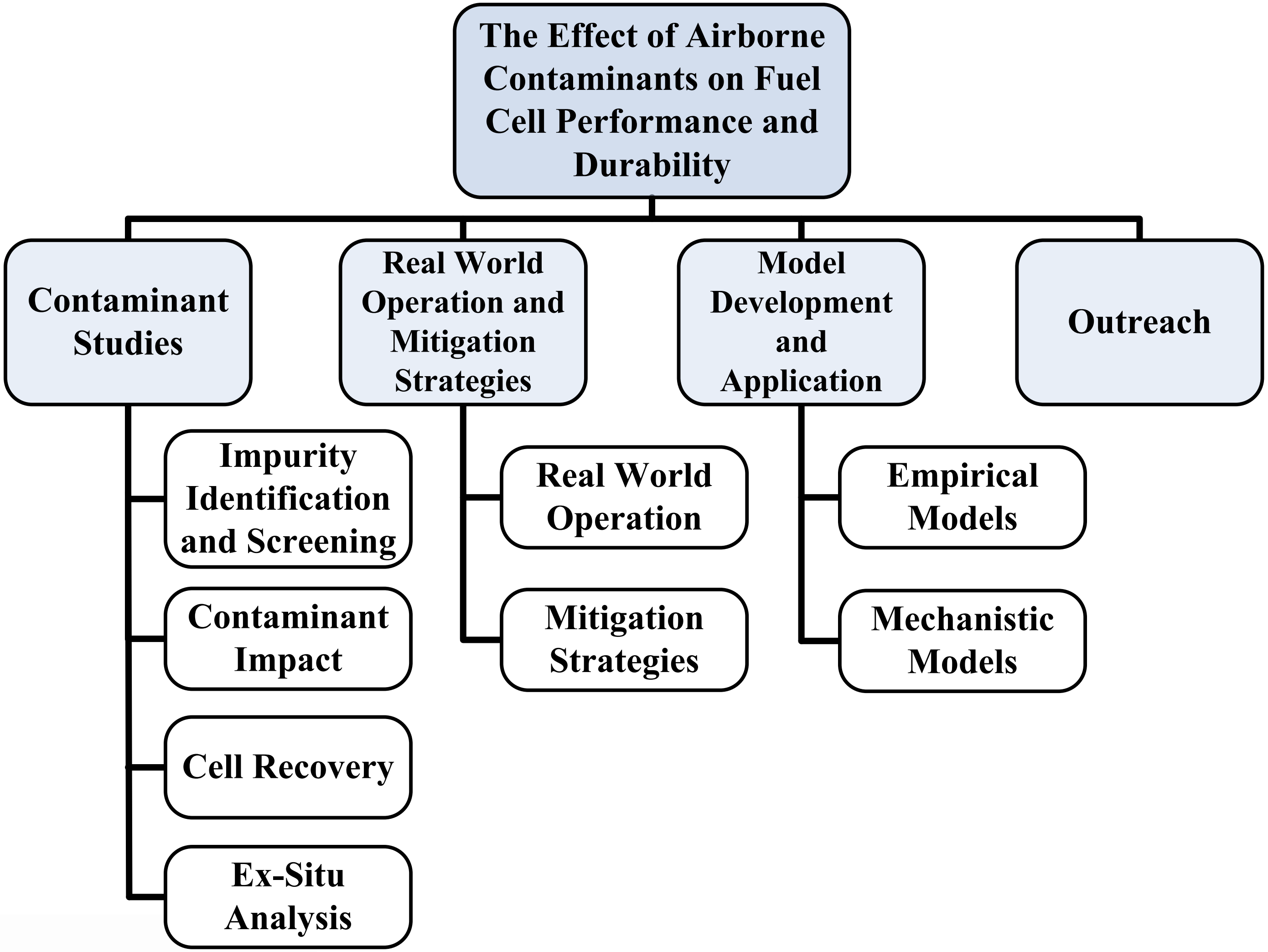
Technical Targets for Automotive Applications: 80-kW_e (net) Integrated Transportation Fuel Cell Power Systems Operating on Direct Hydrogen					
Characteristic	**Units**	**2003 Status**	**2005 Status**	**2010**	**2015**
Energy efficiency @ 25% of rated power	%	59	59	60	60
Energy efficiency @ rated power	%	50	50	50	50
Power density	W / L	440	500	650	650
Specific power	W / kg	420	470	650	650
Cost	$\$ / kW_e$	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

Relevance - Objectives

- Detailed project objectives include:
  - Characterize, analyze, understand and prevent the effects of airborne contaminants
  - Disseminate this information in a useful form to industry and other end users

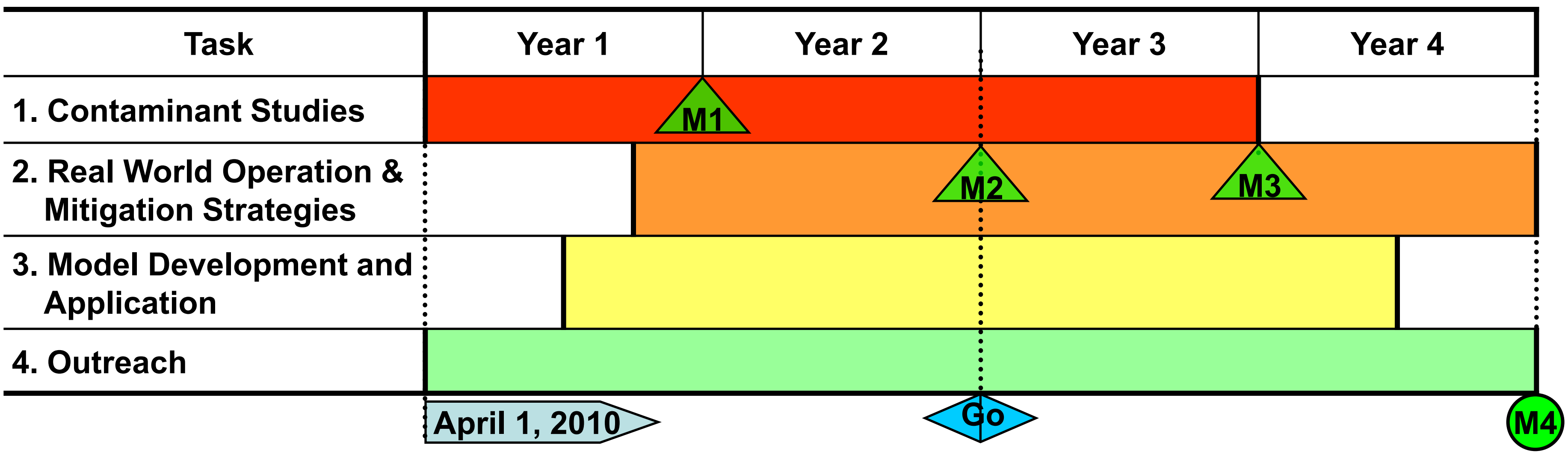
Task	Objectives
1.1 Impurity Identification and Screening	• Identify potential contaminants originating from air pollution and road side environments. • Screen and prioritize impurities based on degradation of cell performance or chemical interaction with the MEA.
1.2 Contaminant Impact	• Quantify impact 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.

Approach - High Level Plan



Approach - High Level Plan

- Milestones and go/no go decisions are described in a subsequent slide



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: 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: 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

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)
- 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 that all contaminant sources are studied
  - "Effect of System and Air Contaminants on PEMFC Performance and Durability" project (project ID # FC048) focuses on system sources
  - Fuel cell contaminants were studied in previous DOE projects (project ID # FC045, FC046, FC047)

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Technical Accomplishments and Progress - Contaminant Identification

- 187 airborne contaminants, 68 indoor pollutants and 12 roadside species were identified using multiple information sources
- A down selected list was created from the airborne contaminants and indoor pollutants on the basis of the following criteria:
  - Presence at a significant level
  - Expectation of reactivity within the fuel cell
  - Absence of recorded data
  - Largest range in chemical functionalities
  - Compound toxicity
    - Represents a safety concern due to the use of concentrated mixtures
- Future selections will be reviewed by an interest group
  - DOE laboratories, FCHEA (formerly NHA and USFCC), OEM Fuel Cell Tech Team, Carrier, durability working group, DOD, SAE, NIST, Praxair, Linde, Air Liquide, CaFCP, CaSFCC

Technical Accomplishments and Progress - Contaminant Identification

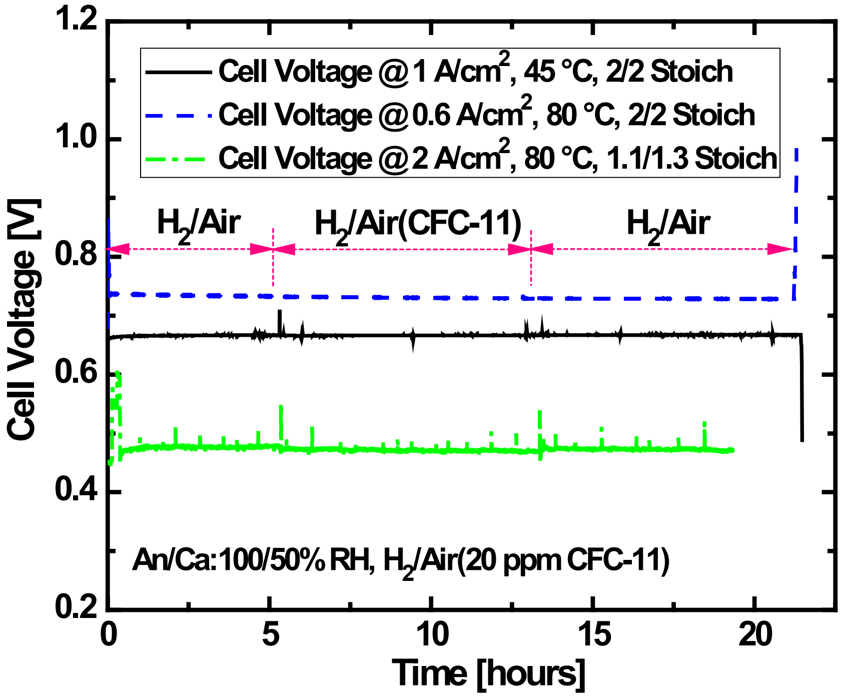
- Selected and tested (highlighted in green) contaminants

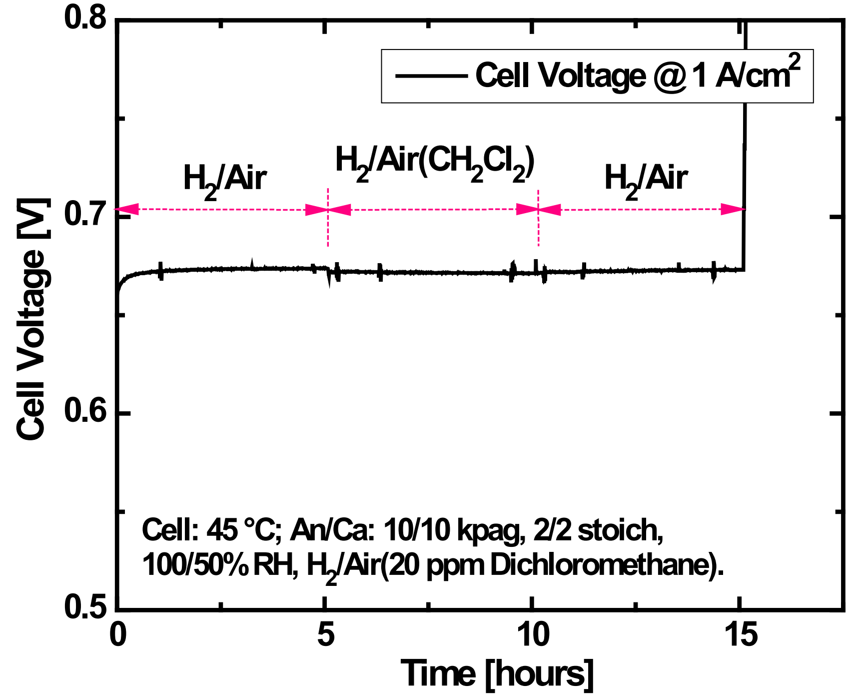
Contaminants			Annual maximum concentration (ppm C)*			Source	OSHA PEL (ppm)**
Hydrocarbon functionality	Common name	Formula	1 h average	3 h average	24 h average		
N/A	Ozone	O_3	0.197			Chemical manufacture reagent, bleaching agent,	400
Alcohol	2-Propanol	$CH_3CH(OH)CH_3$	0.65 μg/m³ (indoor max) 0.08 μg/m³ (indoor mean)			Cleaning fluid and solvent	No limit
Aldehyde	Acetaldehyde	CH_3CHO	0.022 μg/m³ (indoor max) 0.007 μg/m³ (indoor mean)			Chemical manufacture precursor	200
Alkene	Propene	C_3H_6	0.625	0.0819	0.102	PP synthesis precursor and petrochemical feedstock	No limit
Alkyne	Acetylene	C_2H_2	0.117	0.0376	0.0386	Welding fuel and chemical manufacture precursor	No limit
Benzene	Toluene	$C_6H_5CH_3$	0.296	0.0545	1.17	Solvent and industrial feedstock	200
Phenol	Bisphenol A	$(HOC_6H_4)_2(CH_3)_2C$			17 pg/l	Epoxy resin and plastic precursor	0.5
Ketone	Acetone	CH_3COCH_3		0.190	0.2022	Solvent and polymer synthesis precursor	750
Ether	Methyl tert-butyl ether	$(CH_3)_3COCH_3$		0.0017	0.0192	Gasoline additive and solvent	N/A
Ester	Vinyl acetate	$CH_2CHOOCCH_3$			0.102	PVA synthesis precursor	10
	Methyl methacrylate	$CH_2CCH_3COOCH_3$			0.00267	PMMA synthesis precursor	100
Nitrogen compound	Acetonitrile	CH_3CN			3.1	Butadiene production solvent	40
Polycyclic aromatic	Naphthalene	$C_{10}H_8$			0.05	Mothball primary ingredient	No limit
Halogen compounds	Dichloromethane	CH_2Cl_2		8.7×10^{-4}	0.124	Paint and degreaser solvent	25
	Chlorobenzene	C_6H_5Cl			0.0026	Commodity production intermediate	75
	Bromomethane	CH_3Br			0.0066	Solvent and chemical manufacture precursor	N/A
	CFC-11	CCl_3F			2.7×10^{-4}	Former refrigerant	1000

* unless otherwise noted. ** PEL: permissible exposure limit.

Technical Accomplishments and Progress - Contaminant Screening

- Several cell performance contamination and recovery behaviors were observed
  - Absence of a significant effect (CFC-11, dichloromethane)





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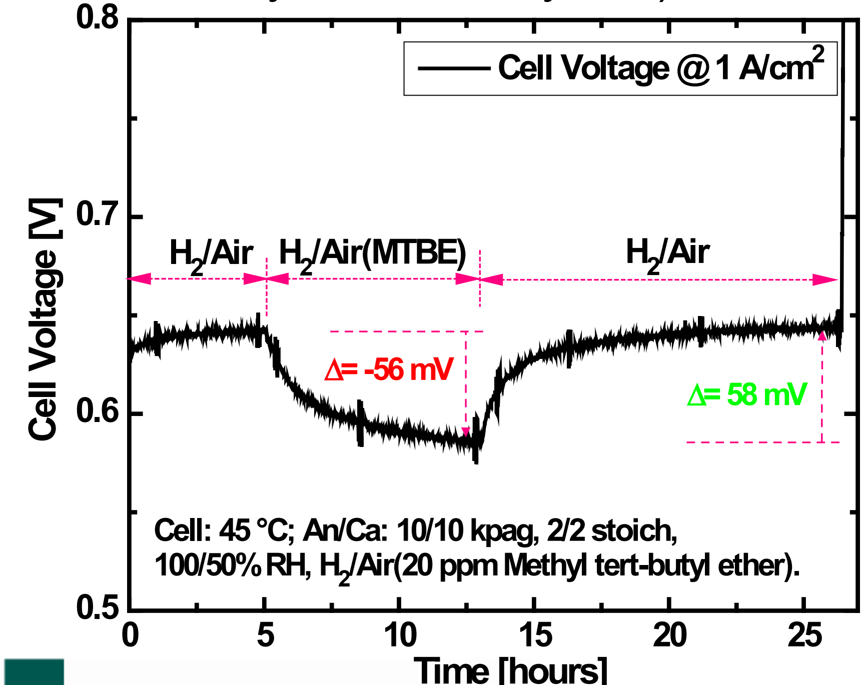
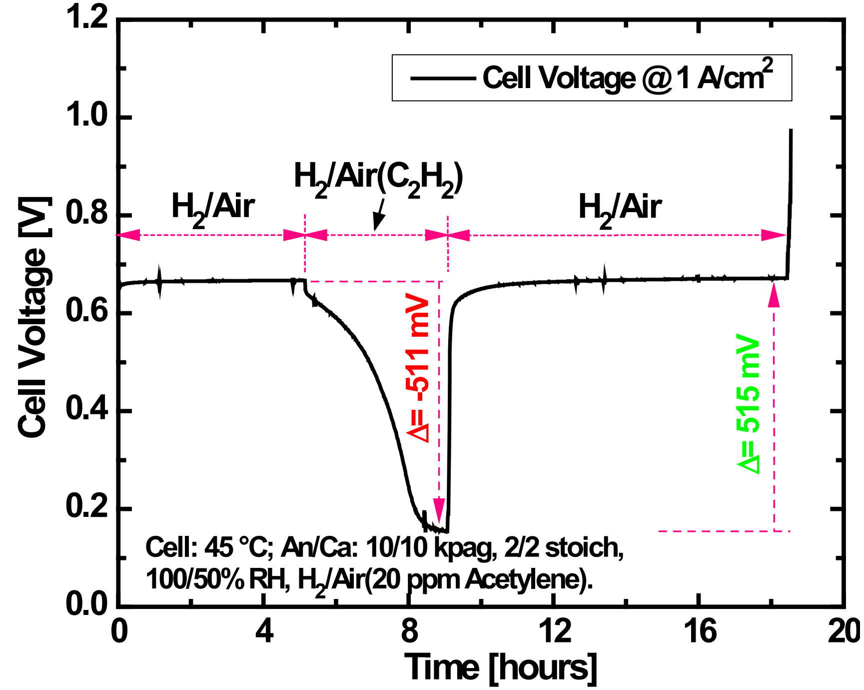
Technical Accomplishments and Progress - Contaminant Screening

- Several cell performance contamination and recovery behaviors were observed
  - A significant contamination effect but complete recovery (methyl tert-butyl ether, acetylene)





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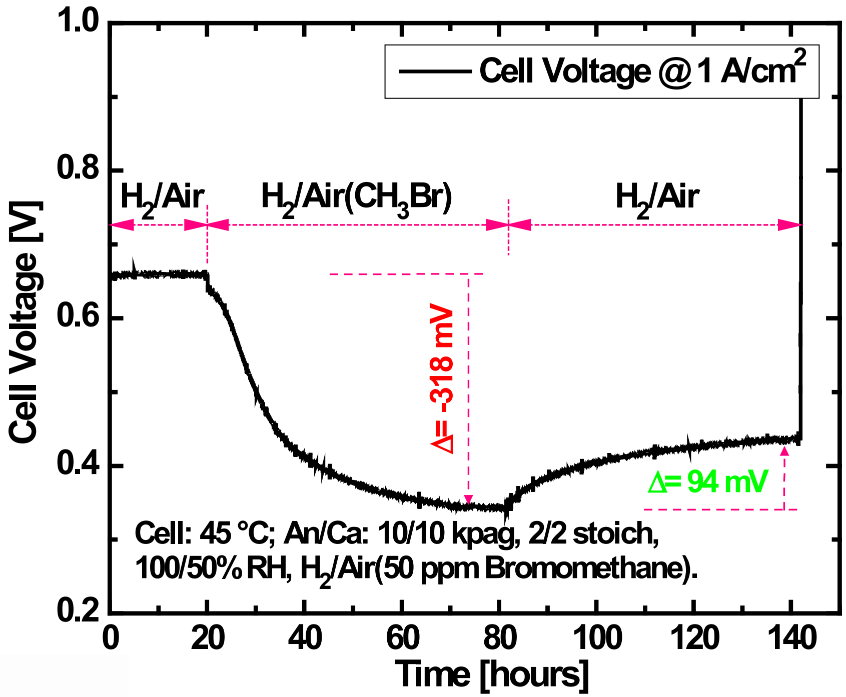
Technical Accomplishments and Progress - Contaminant Screening

- Several cell performance contamination and recovery behaviors were observed
  - A significant contamination effect and incomplete recovery (bromomethane)



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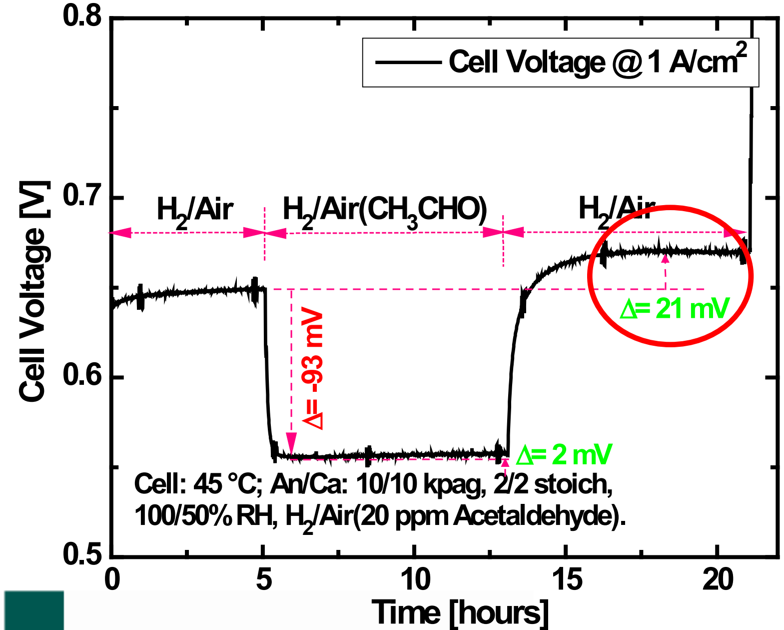
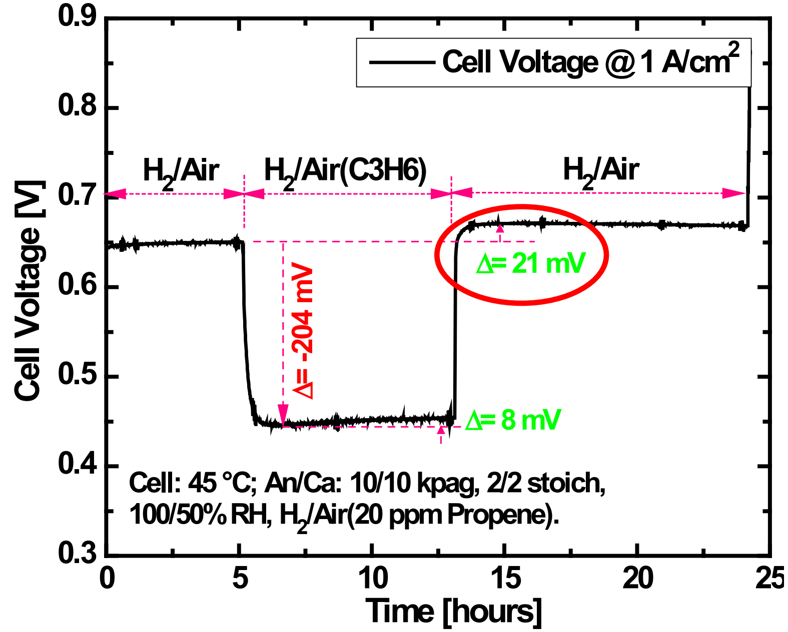
Technical Accomplishments and Progress - Contaminant Screening

- Several cell performance contamination and recovery behaviors were observed
  - A significant contamination effect and a recovery exceeding the initial loss (acetaldehyde, propene)
    - Behavior is new and undocumented suggesting an investigation of its cause





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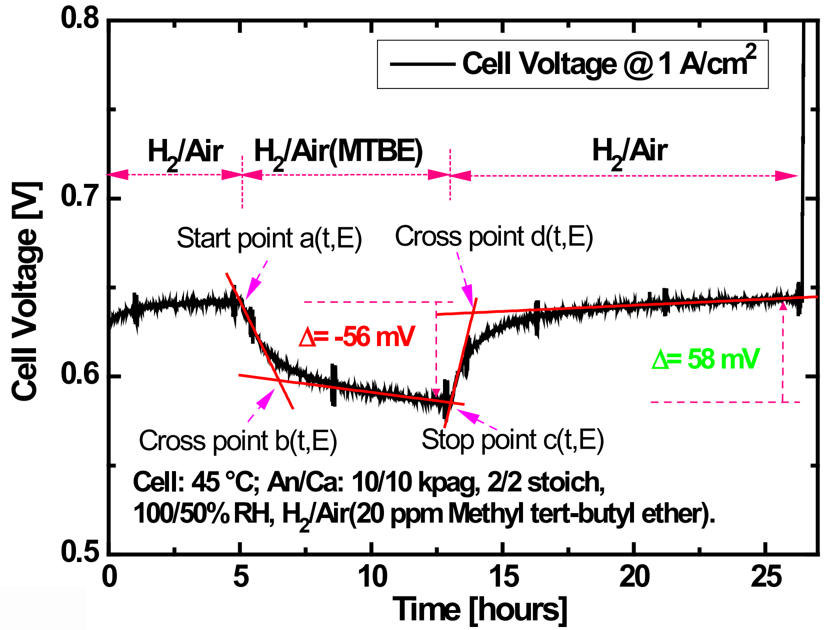
Technical Accomplishments and Progress - Contaminant Ranking

- Two methods were considered for contaminant ranking
  - Method 1 relies on the combination of steady state contamination and irrecoverable performance losses and corresponding time scales
    - The selection criterion SC_1 is:

$$(a(E)-b(E))^2(a(E)-d(E))(d(t)-c(t))/c_{contaminant}(d(E)-c(E))(b(t)-a(t))$$



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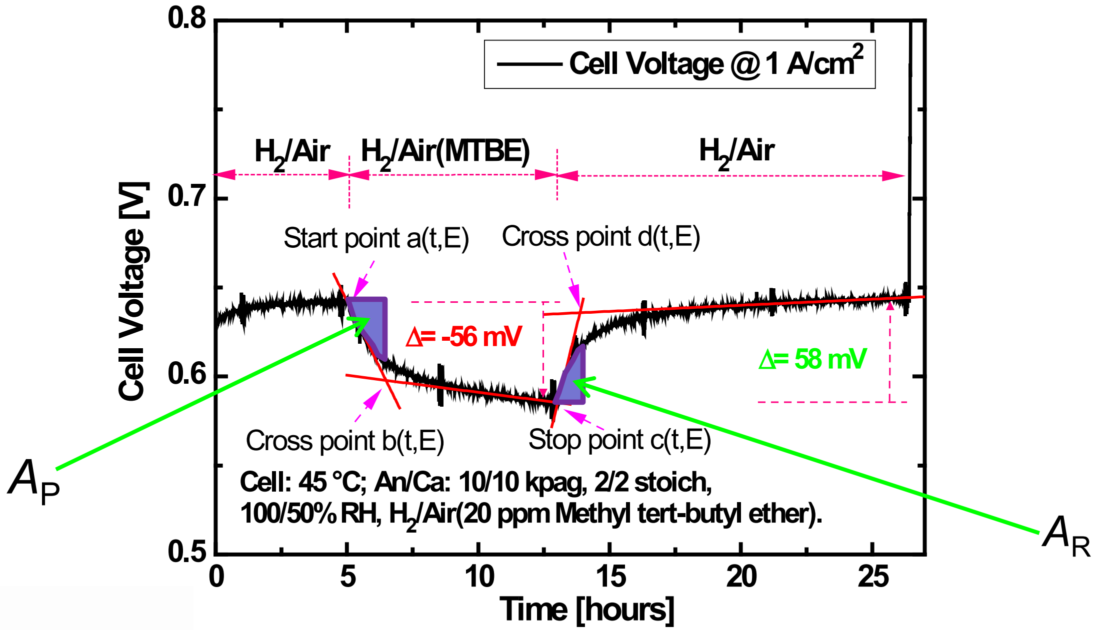
Technical Accomplishments and Progress - Contaminant Ranking

- Two methods were considered for contaminant ranking
  - Method 2 relies on the combination of the energy lost to contamination and regained during self-recovery
    - The selection criterion SC_2 is:

A_P/A_R



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Technical Accomplishments and Progress - Contaminant Ranking

- Larger SC_1 and SC_2 values mean more significant performance losses
- Only 9 contaminants appear on the table because 2 did not lead to significant performance losses (ranked at the lowest interest level)
- The range in values is larger for SC_1 (more sensitive parameter)
- The top 4 contaminants are almost the same for SC_1 and SC_2
  - A more detailed analysis will be completed to assess SC_1 and SC_2 differences

Contaminant	SC_1 (V^2 ppm^{-1})	SC_2
Acetaldehyde	-2.40×10^{-4}	-0.231
Acetone	-2.90×10^{-7}	0.040
Acetylene	3.13×10^{-6}	30.623
Bromomethane	4.04×10^{-3}	7.434
Iso-propanol	-2.55×10^{-7}	17.796
Methyl Tert-Butyl Ether	2.38×10^{-5}	2.054
Propene	-3.08×10^{-5}	0.920
Toluene	5.38×10^{-4}	0.349
Vinyl Acetate	-4.42×10^{-5}	1.1940

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

Proposed Future Work

- Fiscal year 2011
  - Complete contaminant screening tests and repeat with lower humidification reactant streams (liquid water scavenging effect?)
    - Concentrated streams are used to accelerate tests and therefore precautions need to be implemented to properly contain toxic species and avoid damage to personnel and equipment
  - Investigate the cause of the recovery exceeding the contamination performance loss (acetaldehyde, propene)
  - Determine which contaminant selection criterion will be used for down selection
  - Initiate modeling activities
- Fiscal year 2012
  - M2: Quantify performance loss for at least 4 different contaminants under various operating conditions

Summary

- Relevance
  - The project fills a knowledge gap and minimizes commercialization uncertainties; the impact of unknown airborne species on fuel cell system performance
- Approach
  - Mitigation strategies will be based on a fundamental understanding of contamination effects
  - The development of validated predictive models will accelerate the future study of other species considered relevant
- Technical accomplishments and progress
  - A list of airborne contaminants originating from large industrial operations was created by minimizing effort duplication and maximizing its applicability range
  - 11 contaminants were tested revealing a wide range in behavior (negative but also positive)
  - Two quantitative contaminant ranking criteria were proposed
- Collaborations
  - Fuel cell industry representatives involvement adds relevance to project activities
- Proposed future work
  - The screening of selected contaminants will be completed and a selection criterion will be used to down select 4 contaminants for detailed studies