

V.B.3 The Effect of Airborne Contaminants on Fuel Cell Performance and Durability

Jean St-Pierre (Primary Contact), Yunfeng Zhai, Michael Angelo, Trent Molter, Leonard Bonville, Ugur Pasaogullari, Mark Aindow, William Collins, Silvia Wessel

Hawaii Natural Energy Institute
1680 East-West Road
Honolulu, HI 96822
Phone: (808) 956-3909
E-mail: jsp7@hawaii.edu

DOE Managers

HQ: Nancy Garland
Phone: (202) 586-5673
E-mail: Nancy.Garland@ee.doe.gov
GO: Reginald Tyler
Phone: (720) 356-1805
E-mail: Reginald.Tyler@go.doe.gov

Contract Number: DE-EE0000467

Subcontractors:

- University of Connecticut, Storrs, CT
- UTC Power, South Windsor, CT
- Ballard Power Systems, Burnaby, BC, Canada

Project Start Date: April 1, 2010

Project End Date: March 31, 2014

tests conducted under high concentrations and using derived mechanistic understanding to increase these tolerance limits with fuel cell mitigation strategies applicable during operation or maintenance cycles.

- Durability: 5,000 h under cycling conditions
- Performance: 60/50 energy efficiency under 25/100% rated power

FY 2011 Accomplishments

- Identified more than 260 airborne contaminants and completed first tier down selection using six qualitative selection criteria including absence of prior data.
- Two quantitative cell performance ranking criteria were devised and the first tier list is currently being prioritized for detailed tests with varied operating conditions.



Introduction

The composition of atmospheric air cannot be controlled and typically includes contaminants. Proton exchange membrane fuel cells operated with ambient air are therefore susceptible to deleterious effects which include decreased cell performance and durability [1]. Numerous air contaminants have not yet been tested in fuel cells and consequently their effects are unknown. This increases the risk of failure for fuel cell systems and thus jeopardizes their introduction into the market. A significant amount of resources is required to characterize the effect of each species on fuel cell performance. Therefore, a method for species down selection is essential to keep the research scope within feasible limits. In this project, airborne contaminants were identified from a variety of sources and down-selected to a manageable yet representative group (first tier). Screening tests were conducted on the first tier contaminants to determine their effects on performance and the ability of the fuel cell to self recover after contaminant exposure. These factors were accounted for with two quantitative cell performance ranking criteria which were used for a second tier down selection. The results of these tests will facilitate the design of mitigation methods.

Approach

Contaminants are separated into three classes (gaseous species, foreign cations and solids) because testing requires different injection strategies and hardware. Key project team organizations are focusing on specific contaminant classes to minimize time consuming benchmarking activities and capabilities duplication. Gaseous species have already been identified and down selected (first tier, Table 1). All

Fiscal Year (FY) 2011 Objectives

Mitigation of the unknown effects of many airborne contaminants on membrane/electrode assembly materials, adversely impacting system performance and durability:

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

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (C) Performance

Technical Targets

The following 2015 transportation technical targets will be addressed by determining contaminant tolerance limits leading to negligible performance losses by extrapolation of

TABLE 1. Down-Selected Gaseous Airborne Contaminants and Some of their Characteristics

Contaminants			Annual maximum concentration (ppm carbon)*			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, disinfectant	400
Alcohol	2-Propanol	CH ₃ CH(OH)CH ₃	0.65 µg m ⁻³ (indoor max) 0.08 µg m ⁻³ (indoor mean)			Cleaning fluid and solvent	No limit
Aldehyde	Acetaldehyde	CH ₃ CHO	0.022 µg m ⁻³ (indoor max) 0.007 µg m ⁻³ (indoor mean)			Chemical manufacture precursor	200
Alkene	Propene	C ₃ H ₆	0.625	0.0819	0.102	Polypropylene synthesis precursor and petrochemical feedstock	No limit
Alkyne	Acetylene	C ₂ H ₂	0.117	0.0376	0.0386	Welding fuel and chemical manufacture precursor	No limit
Benzene	Toluene	C ₆ H ₅ CH ₃	0.296	0.0545	1.17	Solvent and industrial feedstock	200
Phenol	2,2-bis(4-hydroxyphenyl) propane	(HOC ₆ H ₄) ₂ (CH ₃) ₂ C			17 pg l ⁻¹	Epoxy resin and plastic precursor	0.5
Ketone	Acetone	CH ₃ COCH ₃		0.190	0.2022	Solvent and polymer synthesis precursor	750
Ether	Methyl tert-butyl ether	(CH ₃) ₃ COCH ₃		0.0017	0.0192	Gasoline additive and solvent	N/A
Ester	Vinyl acetate	CH ₂ CHOOCC ₃ H ₇			0.102	Polyvinyl alcohol synthesis precursor	10
	Methyl methacrylate	CH ₂ CCH ₃ COOCC ₃ H ₇			0.00267	Poly(methyl methacrylate) synthesis precursor	100
Nitrogen compound	Acetonitrile	CH ₃ CN			3.1	Butadiene production solvent	40
Polycyclic aromatic	Naphthalene	C ₁₀ H ₈			0.05	Mothball primary ingredient	No limit
Halogen compounds	Dichloromethane	CH ₂ Cl ₂		8.7x10 ⁻⁴	0.124	Paint and degreaser solvent	25
	Chlorobenzene	C ₆ H ₅ Cl			0.0026	Commodity production intermediate	75
	Bromomethane	CH ₃ Br			0.0066	Solvent and chemical manufacture precursor	N/A
	Trichlorofluoromethane	CCl ₃ F			2.7x10 ⁻⁴ ***	Former refrigerant	1,000
	1,1-difluoroethane	CH ₃ CHF ₂			1x10 ⁻⁵ ***	Refrigerant	N/A
	1,1,1,2-tetrafluoroethane	CH ₂ FCF ₃			6x10 ⁻⁵ ***	Refrigerant	N/A

* unless otherwise noted

** OSHA - Occupational Safety and Health Administration

PEL - permissible exposure limit

*** yearly average in atm

N/A - not applicable

selected contaminants will be confirmed by a representative interest group including industry, government and advocacy organizations. Fuel cell performance screening tests will be used to down select contaminants for more detailed studies (second tier) that include variations in key operating conditions (contaminant concentration, current density, temperature, relative humidity). Pressure and stoichiometry are not considered. Pressure represents an alternative to a

gaseous concentration change and is not relevant for ionic or solid contaminants. Stoichiometry is irrelevant because the contaminant concentration is approximately constant within the fuel cell based on transport and contamination processes time scales arguments. The project ensures that all contaminant sources are studied. Fuel contaminants were previously studied whereas system contaminants released by

fuel cell materials are currently being investigated in another DOE-funded project.

Results

Species down selection was initially completed on the basis of six criteria (first tier): i) atmospheric presence at a significant level, ii) expectation of reactivity within the fuel cell, iii) absence of recorded data, iv) largest range in chemical functionalities, v) compound toxicity, and vi) suggestions given by project monitors or the fuel cell community. These criteria were sufficient to create a shorter list of 19 contaminants (Table 1) from the larger list of 260+ candidates.

Table 1 shows that most contaminants are organic and are grouped within 12 different chemical functionality classes. Inorganic contaminants are only represented by ozone. All contaminants also originate from large scale industries with production levels exceeding in many cases a million ton per year.

Figures 1 and 2 results show a wide variety of contaminant behaviors. Acetonitrile demonstrates a significant effect but the performance is completely restored after exposure. Other behaviors include: absence of an effect (trichlorofluoromethane), significant effect with an incomplete recovery after exposure (bromomethane), significant effect with a recovery exceeding the initial loss (acetaldehyde). Contamination and recovery time scales also significantly vary within a <1 h to ~20 h range. Such a variety of parameters (performance lost and recovered, time scales) complicates contaminant down selection suggesting the need to develop quantitative criteria consistently applied for selection and minimize qualitatively based decisions.

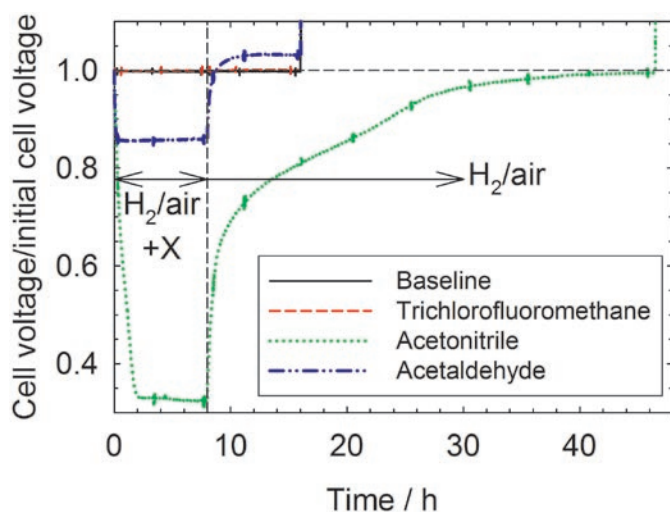


FIGURE 1. Fuel cell response resulting from a temporary contaminant X injection (20 ppm). Gore M715 membrane/electrode assembly, 25 BC SGL Technologies gas diffusion layer, 50 cm² active area, 45°C, anode/cathode, H₂/air, 10/10 kPag, 100/50% relative humidity, 2/2 stoichiometry.

Contaminants predominantly behave as illustrated in Figure 3. Upon injection of the contaminant, the cell performance drops until a steady-state is reached after a variable amount of time dependent on operating conditions. After the contamination injection is interrupted, the initial cell performance is partially, fully or supra-recovered. Points a and c correspond to the measured voltage at the time the contaminant is injected and injection is terminated. Points b and d are defined by the intersection of two asymptotes at the beginning and end of the contamination and recovery periods. Two methods were considered for contaminant ranking and rely on these four time/voltage pairs (points a to d). Method 1 relies on the combination of steady-state contamination and irrecoverable performance losses, corresponding time scales and contaminant concentration. Method 2 relies on the combination of the energy lost to contamination and regained during self-recovery:

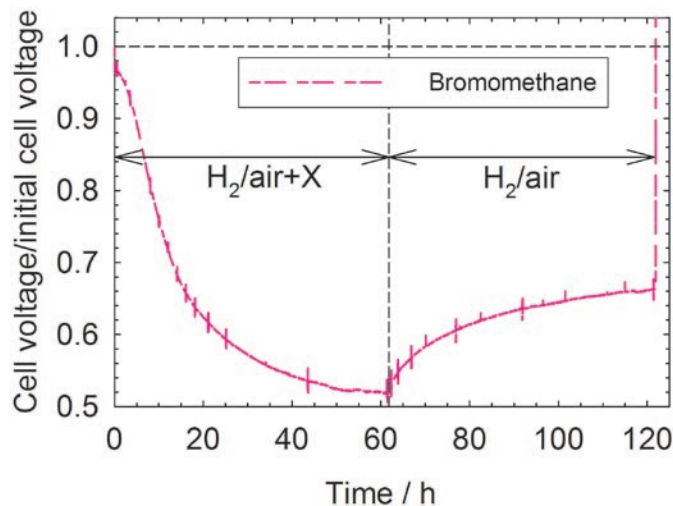


FIGURE 2. Fuel cell response resulting from a temporary contaminant X injection (50 ppm). Gore M715 membrane/electrode assembly, 25 BC SGL Technologies gas diffusion layer, 50 cm² active area, 45°C, anode/cathode, H₂/air, 10/10 kPag, 100/50% relative humidity, 2/2 stoichiometry.

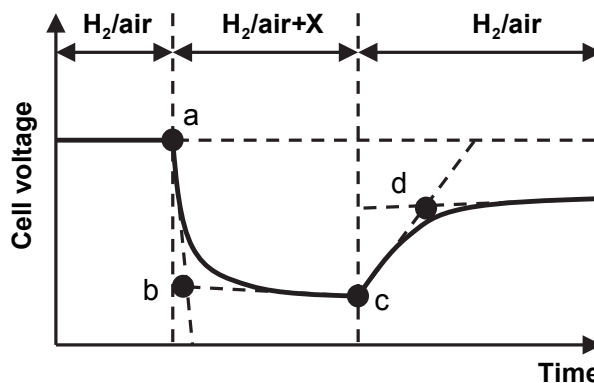


FIGURE 3. Graphical representation of the two methods parameters (points a, b, c and d) used to prioritize tested contaminants. X represents a contaminant.

$$SC_1 = \frac{(V_a - V_b)^2 (V_a - V_d)(t_d - t_c)}{c_{\text{contaminant}} (V_d - V_c)(t_b - t_a)} \quad [1]$$

$$SC_2 = \int_{t_a}^{t_b} (V_a - V) dt / \int_{t_c}^{t_d} (V - V_c) dt \quad [2]$$

where SC represents a selection criterion ($V^2 \text{ ppm}^{-1}$ or dimensionless), V_i the cell voltage at point i (V), t_i the time at point i (h), $c_{\text{contaminant}}$ the contaminant concentration in the dry reactant stream (ppm), and V the cell voltage.

Larger SC_1 and SC_2 values generally mean more significant performance losses. Table 2 shows the resulting contaminant rankings. Under wet conditions (100/50% relative humidity), the range in values is larger for SC_1 (more sensitive parameter). Only one of the top four contaminants is the same for SC_1 and SC_2 (bromomethane, italic font). For contaminants that led to a recovery exceeding the initial loss (acetaldehyde, propene), rankings (underlined font) either correspond to low SC_1 values or are scattered over the SC_2 range. Interestingly, SC_2 is not only useful to pinpoint contaminants that have a large negative effect on performance but also others that lead to a recovery exceeding the initial loss (propene). These seemingly beneficial contaminants are a good example of the envisaged use of both

selection criteria as a quantitative measure to guide decisions. A strict application of SC_1 would preclude any further interest. However, acetaldehyde and propene unusual behavior may hide some permanent performance benefit.

Conclusions and Future Directions

- Expand tier 1 airborne contaminant list with foreign cations and solids.
- Complete fuel cell contaminant screening tests (tier 1).
- Investigate the cause of the recovery exceeding the contamination performance loss (acetaldehyde, propene).
- Determine which contaminant selection criterion will be used for down selection (tier 2).
- Quantify performance loss for at least four different contaminants under various operating conditions.

FY 2011 Publications/Presentations

1. J. St-Pierre, M. S. Angelo, Y. Zhai, Focusing research by developing performance related selection criteria for PEMFC contaminants, in *Meeting Abstracts*, Electrochemical Society volume 2011-2, The Electrochemical Society, Pennington, NJ,

TABLE 2. Gaseous Airborne Contaminant Rankings

Contaminant *	SC_1 ($V^2 \text{ ppm}^{-1}$)		SC_2	
	100/50 **	0/0 **	100/50 **	0/0 **
1,1-difluoroethane	7.23×10^{-4}		0.0259	
1,1,1,2-tetrafluoroethane	2.16×10^{-4}		0.0414	
2,2-bis(4-hydroxyphenyl)propane				
Acetaldehyde	-2.35×10^{-4}		<u>0.214</u>	
Acetone	-2.86×10^{-7}		6.747	
Acetonitrile	5.78×10^{-3}	9.51×10^{-3}	0.0575	0.0410
Acetylene	3.13×10^{-6}		<i>30.623</i>	
Bromomethane	4.04×10^{-3}		<i>7.567</i>	
Trichlorofluoromethane	No effect		No effect	
Chlorobenzene	1.57×10^{-2}		0.165	
Dichloromethane	No effect	No effect	No effect	No effect
Iso-propanol	-2.55×10^{-7}		<i>17.796</i>	
Methyl methacrylate	1.44×10^{-5}	1.32×10^{-4}	4.863	3.936
Methyl tert-butyl ether	6.69×10^{-6}		2.054	
Naphthalene				
Ozone				
Propene	-3.08×10^{-5}		<u>32.063</u>	
Toluene	5.38×10^{-4}		0.349	
Vinyl acetate	-4.42×10^{-5}		1.194	

* 20 ppm contaminant concentration with the exception of bromomethane (50 ppm); ** anode/cathode relative humidity (%).

2011, abstract 1035 (forthcoming oral presentation during the 220th Electrochemical Society meeting).

2. J. St-Pierre, K. O'Leary, PEMFC contamination model: Neutral species sorption by ionomer, in *Meeting Abstracts*, Electrochemical Society volume 2011-2, The Electrochemical Society, Pennington, NJ, 2011, abstract 1132 (forthcoming oral presentation during the 220th Electrochemical Society meeting).

3. J. St-Pierre, PEMFC contamination model validation: Foreign cations in ionomers, *Electrochem. Solid-State Lett.*, submitted.

References

1. J. St-Pierre, Air impurities, in *Polymer Electrolyte Fuel Cell Durability*, Edited by F.N. Büchi, M. Inaba, T.J. Schmidt, Springer, 2009, pp. 289-321.