

## V.B.2 The Effect of Airborne Contaminants on Fuel Cell Performance and Durability

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### Fiscal Year (FY) 2012 Objectives

- Quantify performance loss for at least four different contaminants under various operating conditions.
- Initiate and partly complete activities to identify principal poisoning mechanisms for the same four contaminants.

### 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 2017 transportation technical targets are considered:

- Durability: 5,000 h in automotive drive cycle
- Performance: 60% energy efficiency at 25% of rated power

Airborne contaminants are studied and the information will be used to impact both preventive measures and recovery procedures:

- Filtering system component specification input derived from contaminant tolerance limits leading to negligible performance losses.
- Fuel cell stack material, design, operation or maintenance changes to recover performance losses derived using contamination mechanisms.

### FY 2012 Accomplishments

- The 19 airborne contaminants derived from the overall validated list of more than 260 species using first tier qualitative down selection criteria (first tier airborne contaminants) were tested with both wet and dry reactant streams and ranked using two quantitative, empirical selection criteria.
- Seven second tier airborne contaminants are organic and representative of different functionalities: acetonitrile (nitrile), acetylene (alkyne), bromomethane (halocarbon), iso-propanol (alcohol), methyl methacrylate (ester), naphthalene (aromatic), propene (alkene).
- The effect of the operating conditions impacting contamination more severely, contaminant concentration, current density and temperature, was investigated using second tier contaminants:
  - Tests for six of the seven second tier contaminants were completed.
- Impedance spectroscopy data indicate that all seven second tier airborne contaminants lead to kinetic and mass transport losses whereas only acetonitrile leads to additional ohmic losses.
- Tests with first tier ionic contaminants ( $K^+$ ,  $Ca^{+2}$ ,  $Ba^{+2}$ ,  $Al^{+3}$ ,  $Cl^-$ ,  $OH^-$ ,  $ClO_4^-$ ) indicated that water management related operating conditions and membrane electrode assembly design significantly impact contamination, and suggested new avenues for mitigation strategy development.



## Introduction

The composition of atmospheric air cannot be controlled and typically includes contaminants, volatile compounds as well as ions entrained by liquid water drops in the form of rain, mist, etc. 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 down-selected to manageable yet representative groups (first tier and second tier). Screening tests were completed 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. Fuel cells are used under a wide range of operating conditions. It is therefore important to determine the contamination effect under many operating conditions including temperature and relative humidity (startup and shutdown periods), current density (power demand during drive cycle) and local atmosphere composition variations. The contaminant concentration effect is particularly important because it provides guidance on contaminant threshold concentrations and invaluable information to define air filtering system tolerances (prevention). Also, during the screening and operating condition tests (first and second tier contaminants), impedance spectroscopy diagnostic tests were also completed for mechanism determination clues. This information will also be invaluable to design more effective recovery procedures (maintenance).

## Approach

Two methods were considered for contaminant ranking and rely on four time/voltage pairs (denoted by subscripts  $a$  to  $d$  in equations 1 and 2) that define steady-state changes in cell performance during contamination and recovery periods and associated time scales. These four parameters are general and were observed with all tested contaminants. 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:

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

$$SC_2 = \int_a^b (V_a - V) dt / \int_c^d (V - V_c) dt \quad (2)$$

where  $SC$  represents a selection criteria ( $V^2 \text{ ppm}^{-1}$  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 (V). Larger  $SC_1$  and  $SC_2$  values generally mean more significant performance losses.

A partial factorial design was used to limit the number of tests. Even with this restriction the number of tests is equal to 49 (seven contaminants, three operating conditions and three levels with a central point) and each generally requires at least a week for completion. The contaminant concentration is the first operating condition to be investigated. Subsequent tests at other current densities and temperatures are generally completed using the contaminant concentration that led to a loss in cell performance equal to or near 20%. For acetylene, experiments are currently being repeated with higher concentrations to ensure a 20% performance loss. For bromomethane, a performance loss higher than 20% was tolerated because tests would otherwise take too long to complete. For iso-propanol, higher gas phase concentrations were not possible and would lead to condensation.

Mechanistic information was collected during screening and operating condition tests (first and second tier contaminants). This information was obtained using impedance spectroscopy allowing separation in the frequency domain of the different processes. An equivalent circuit model was used to fit experimental data and extract key parameters including the different processes' resistances.

## Results

Table 1 shows the resulting contaminant rankings for the 19 first tier airborne contaminants. The largest five selection criteria values in each column are highlighted in red. Generally, the selection criteria values are not too sensitive to relative humidity. Two contaminants, highlighted in green, led to a cell performance after the recovery period exceeding the initial value. The  $SC_2$  selection criterion is able to pinpoint such contaminants (propene). For this reason and also because  $SC_2$  is less sensitive to the change in operating conditions, it was used to create the second tier list. As a result, all contaminants with highlighted  $SC_2$  values were selected with the exception of acetone. Rather, acetonitrile was added to the list because it was the only contaminant that led to ohmic losses.

**TABLE 1.** Gaseous Airborne Contaminant Rankings (Red highlight indicates the highest values in any given column. Green highlight indicates contaminants that led to a cell performance after recovery exceeding the initial value.)

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

<sup>a</sup> 20 ppm contaminant concentration with the exception of bromomethane (50 ppm for wet conditions), bisphenol A (0.1 ppm) and ozone (95/83 ppm for wet/dry conditions).

<sup>b</sup> anode/cathode relative humidity (%).

<sup>c</sup> also referred to as HFC-152a.

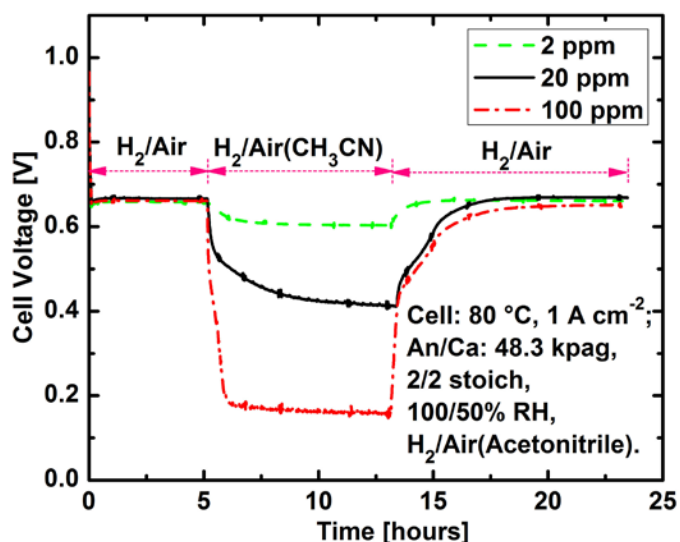
<sup>d</sup> also referred to as HFC-134a.

<sup>e</sup> also referred to as bisphenol A.

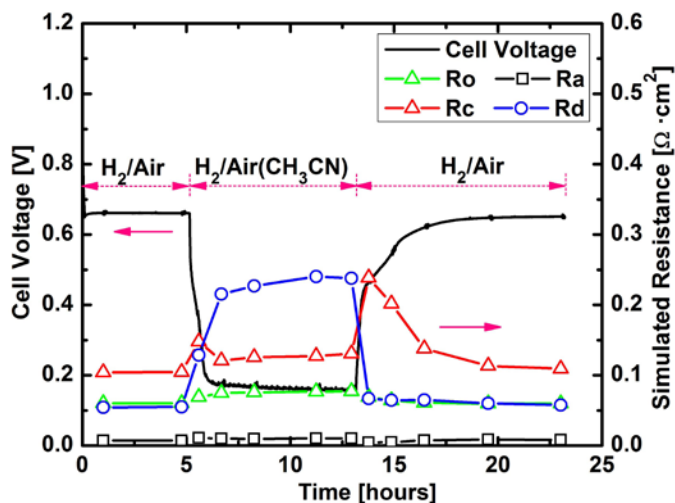
<sup>f</sup> also referred to as CFC-11.

Figure 1 illustrates the effect of acetonitrile concentration on cell performance for a temporary contaminant injection, which shows that the steady-state cell performance loss increases with acetonitrile concentration. Such a data set for all second tier airborne contaminants will be used to set tolerance limits which in turn will determine filtering system performance and design. Table 2 summarizes completed and planned operating condition tests for second tier airborne contaminants. Only a few bromomethane tests (highlighted in red) remain to be completed.

Figure 2 depicts the effect of 100 ppm of acetonitrile on cell performance. In addition, Figure 2 also shows several resistance values derived from the equivalent circuit model. Three resistances show increases in values during the temporary contaminant injection period. These increases are ascribed to kinetic, ohmic and mass transport losses. More specifically, acetonitrile impacts the cathode catalyst



**FIGURE 1.** Fuel cell response resulting from a temporary acetonitrile injection in the air stream. Gore M715 membrane electrode assembly, 25 BC SGL Technologies gas diffusion layer, 50 cm<sup>2</sup> active area, 80°C, 1 A cm<sup>-2</sup>, anode/cathode, H<sub>2</sub>/air, 48.3/48.3 kPag, 100/50% relative humidity, 2/2 stoichiometry.



**FIGURE 2.** Fuel cell response resulting from a temporary acetonitrile injection in the air stream and associated changes in ohmic ( $R_o$ ), anode ( $R_a$ ), cathode ( $R_c$ ) and diffusion ( $R_d$ ) resistances. Gore M715 membrane electrode assembly, 25 BC SGL Technologies gas diffusion layer, 50 cm<sup>2</sup> active area, 80°C, 1 A cm<sup>-2</sup>, anode/cathode, H<sub>2</sub>/air+100 ppm acetonitrile, 48.3/48.3 kPag, 100/50% relative humidity, 2/2 stoichiometry.

(surface coverage, change in oxygen reduction mechanism, etc), the membrane (absorption increases swelling, decreases the distance between ion exchange groups and reduces conductivity) and water transport (acetonitrile adsorption on the catalyst carbon support and gas diffusion layer carbon surface affects hydrophobicity). The presence of different cell performance losses likely requires multi-step recovery procedures, either sequential or in parallel.

**TABLE 2.** Summary of the contaminant concentrations and steady-state cell performance loss for the different contaminants and operating condition tests. Red highlight indicates tests that have not yet been completed.

Contaminant	Operating conditions <sup>a</sup>						
	80°C, 1 A cm <sup>-2</sup>	80°C, 1 A cm <sup>-2</sup>	80°C, 1 A cm <sup>-2</sup>	80°C, 0.6 A cm <sup>-2</sup>	80°C, 0.2 A cm <sup>-2</sup>	45°C, 1 A cm <sup>-2</sup>	10°C, 1 A cm <sup>-2</sup>
Acetonitrile	100 ppm (75%)	20 ppm (38%)	2 ppm (9%)	20 ppm (35%)	20 ppm (33%)	20 ppm (68%)	20 ppm (78%)
Acetylene	20 ppm (0%)	50 ppm (1%)	100/500 ppm (1/92%)	100 ppm (1%)	100 ppm (1%)	5/20/100 ppm (1/77/85%)	100 ppm (90%)
Bromomethane	<b>20</b> ppm	5 ppm (43%)	2 ppm (38%)	<b>5</b> ppm	<b>5</b> ppm	<b>5</b> /20/50 ppm (?/48%)	<b>5</b> ppm
Iso-propanol	250/700 ppm (2/2%)	5.2k ppm (7%)	8.6k ppm (9%)	8.6k ppm (8%)	8.6k ppm (6%)	8.6k ppm (23%)	8.6k ppm (>80%) <sup>c</sup>
Methyl methacrylate	100 ppm (34%)	20 ppm (11%)	2 ppm (3%)	20 ppm (8%)	20 ppm (5%)	20 ppm (73%)	20 ppm (>80%) <sup>c</sup>
Naphthalene	2.4 ppm (>80%) <sup>d</sup>	1.4 ppm (26%)	0.5 ppm (9%)	1.4 ppm (14%)	1.4 ppm (8%)	1.4/3.1/17 ppm (>80%) <sup>d</sup>	1.4 ppm (>80%) <sup>d</sup>
Propene	100 ppm (18%)	20 ppm (6%)	2 ppm (1%)	100 ppm (14%)	100 ppm (8%)	100/20 ppm (77/30%)	100 ppm (>80%) <sup>c</sup>

<sup>a</sup> Other operating conditions: H<sub>2</sub>/air+contaminant, 2/2 stoichiometry, 100/50% relative humidity, 48.3/48.3 (for 80°C), 10/10 (for 45°C) or 5/5 (for 10°C) kPag.

<sup>b</sup> Injection stopped before the steady state was reached. The time required to reach a steady state was greater than the planned test duration.

<sup>c</sup> Test stopped because the cell voltage was below the 0.1 V value triggering a contaminant injection interruption. At this particular time, the cell performance was still decreasing.

<sup>d</sup> Cell voltage oscillations appeared before a steady state was reached. These oscillations prevent a clear identification of the steady-state cell performance loss. Before these oscillations appeared, the cell performance loss was >80%.

## Conclusions and Future Directions

- Complete operating condition tests with second tier airborne contaminants and define tolerance limits that can be applied to filtering system component specifications.
- Collect other ex situ and in situ information to facilitate the determination of contamination mechanisms using methods such as rotating ring/disc electrode (catalyst effect), conductivity cell (membrane effect), residence time distribution (gas diffusion electrode and flow field channel liquid water content effect), gas chromatography (contaminant decomposition effect), segmented cell (current/voltage distribution effect) and fingerprinting using a mathematical model library (mechanism identification).
- Consider use of multi-step recovery procedures in view of the multiple and different contaminant effects observed with all second tier airborne contaminants.

## FY 2012 Publications/Presentations

1. J. St-Pierre, M.S. Angelo, Y. Zhai, 'Effect of Selected Airborne Contaminants on PEMFC Performance', *J. Electrochem. Soc.*, submitted.
2. J. St-Pierre, Y. Zhai, M. Angelo, 'Quantitative Ranking Criteria for PEMFC Contaminants', *Int. J. Hydrogen Energy*, **37** (2012) 6784-6789.
3. Y. Zhai, J. St-Pierre, M. Angelo, 'The Impact of Operating Conditions on the Performance Effect of Selected Airborne PEMFC Contaminants', *Electrochem. Soc. Trans.*, accepted.

4. B. Wetton, J. St-Pierre, 'Liquid Water Scavenging of PEMFC Contaminants', *Electrochem. Soc. Trans.*, accepted.
5. J. St-Pierre, 'PEMFC Contamination Model: Neutral Species Sorption by Ionomer', *Electrochem. Soc. Trans.*, **41** (1) (2011) 307-315.
6. J. St-Pierre, M.S. Angelo, Y. Zhai, 'Focusing Research by Developing Performance Related Selection Criteria for PEMFC Contaminants', *Electrochem. Soc. Trans.*, **41** (1) (2011) 279-286.
7. B. Wetton, J. St-Pierre, 'Liquid Water Scavenging of PEMFC Contaminants', in *Meeting Abstracts*, Electrochemical Society volume 2012-2, The Electrochemical Society, Pennington, NJ, 2012, abstract 1296 (forthcoming 222<sup>th</sup> Electrochemical Society meeting oral presentation).
8. Y. Zhai, M. Angelo, J. St-Pierre, 'The Impact of Operating Conditions on the Performance Effect of Selected Airborne PEMFC Contaminants', in *Meeting Abstracts*, Electrochemical Society volume 2012-2, The Electrochemical Society, Pennington, NJ, 2012, abstract 1294 (forthcoming 222<sup>th</sup> Electrochemical Society meeting oral presentation).
9. K.A. O'Leary, B. Lakshmanan, J. St-Pierre, 'Impact of Ethylene Glycol Contamination on Proton Exchange Membrane (PEM) Fuel Cells', in *Meeting Abstracts*, Electrochemical Society volume 2012-1, The Electrochemical Society, Pennington, NJ, 2012, abstract 1101 (221<sup>th</sup> Electrochemical Society meeting oral presentation).
10. J. St-Pierre, 'The Effect of Airborne Contaminants on Fuel Cell Performance and Durability', United States Department of Energy 2012 Annual Merit Review meeting, Washington, DC, May 16, 2012.
11. J. St-Pierre, 'The Effect of Airborne Contaminants on Fuel Cell Performance and Durability', US DRIVE Fuel Cell Tech Team meeting, Southfield, MI, December 14, 2011.

## 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.