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

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Overall Objectives

- Identify and mitigate the adverse effects of airborne contaminants on fuel cell system performance and durability
- Provide contaminants and tolerance limits for filter specifications (preventive measure)
- Identify fuel cell stack’s material, design, operation or maintenance changes to remove contaminant species and recover performance (recovery measure)

Fiscal Year (FY) 2014 Objectives

Quantify spatial variability of performance loss and identify principal poisoning mechanism for at least four different contaminants.

Technical Barriers

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

(A) Durability
(B) Cost
(C) Performance

Technical Targets

The following 2017 technical targets for automotive applications, 80-kWₑ (net) integrated transportation fuel cell power systems operating on direct hydrogen, are considered:

- Durability: 5,000 hours in automotive drive cycle
- Cost: $30/kWₑ
- Performance: 60% energy efficiency at 25% of rated power

The effects of specific airborne contaminants are studied including a commercially relevant low-cathode-catalyst loading and the resulting information will be used to impact both preventive measures and recovery procedures:

- Airborne contaminant tolerance limits to support the development of filtering system component specifications and ensure negligible fuel cell performance losses
- Fuel cell stack material, design, operation, or maintenance changes to recover performance losses derived from contamination mechanisms

FY 2014 Accomplishments

- Completed characterization database using ex situ and in situ diagnostic techniques for seven airborne contaminants and one foreign cation to support the development of contamination mechanisms and recovery procedures that diminish the contamination impact on system durability and performance
- Assessed the effect of a decrease in cathode catalyst loading from 0.4 to a commercially relevant 0.1 mg Pt cm⁻² on the steady-state cell voltage loss during contamination for seven airborne contaminants
• Developed a transient, one-dimensional, through
  the membrane/electrode assembly plane model for
  foreign cation contamination to isolate individual cell
  performance effects which are not experimentally
  accessible and advance the understanding of
  contamination mechanisms
• Evaluated and modeled the scavenging effect of product
  liquid water for two cases, contaminant dissolution
  and contaminant dissolution followed by dissociation
  reactions, to determine effective contaminant
  concentrations within the cell and increase the accuracy
  of cell performance loss correlations

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., especially near marine environments.
Proton exchange membrane fuel cells operated with ambient
air are therefore susceptible to deleterious effects which
include decreased cell performance and durability [1,2].
Numerous air contaminants have not yet been tested in
fuel cells and consequently their effects as well as recovery
methods are unknown [2,3]. Furthermore, prevention is
difficult to achieve because tolerance limits are also missing
in most cases [2]. This increases the risk of failure for fuel
cell systems and thus jeopardizes their introduction into
the market.

Airborne contaminants and foreign ions have previously
been selected using a cost-effective two-tiered approach
combining qualitative and quantitative criteria [3].
Automotive fuel cells are used under a wide range of
operating conditions resulting from changes in power
demands (drive cycle). Temperature and current density
impact fuel cell contamination the most [4]. The effect of
contaminant concentration is also particularly important.
Contaminant threshold concentrations for predetermined
fuel cell performance losses were determined [5] to facilitate
the definition of air filtering system tolerances (prevention).
The effect of inlet reactant relative humidity is linked to the
presence of liquid water within the cell which in turn may
affect the effective contaminant concentration by dissolution
and entrainment in water drops. This scavenging effect has
not previously been considered. Cell design parameters also
impact the severity of contamination. However, the effect
of catalyst loading, which is important for cost reduction,
has only been determined for a few species [2]. It is likely
that prevention will be insufficient to avert all contaminant
effects. Therefore, recovery procedures will also be needed,
and these are more easily devised by understanding the
origins of the contaminant effects (mechanisms). However

for the case of foreign cations, present experimental methods
are insufficient to separate the different contributions to cell
performance loss (thermodynamic, kinetic, ohmic, mass
transport) [2,6,7]. Mathematical modeling is a valuable
substitute approach. However, existing models either need
improvement [8] or are incomplete. A separation factor more
accurately represents ion exchange processes [9,10] and the
change in oxygen permeability in the ionomer due to the
presence of a foreign cation has not previously been tackled
[11,12].

APPROACH

Impedance spectroscopy was first used to classify
airborne contaminant effects into different resistance losses
to focus subsequent activities. As a second step, more
detailed information was obtained using other diagnostics
methods to unravel contamination mechanisms: rotating
ring/disc electrode, membrane conductivity cell, segmented
fuel cell for current/cell voltage distributions over the active
area, and gas chromatography/mass spectrometry. Because
many of these diagnostics methods are not applicable or are
irrelevant to foreign ions partly due to their different state
(in a liquid rather than a gaseous state) and behavior (salt
precipitation within the fuel cell), other diagnostic methods
were employed including photography, scanning electron
microscopy and energy dispersive X-ray spectroscopy.
Mathematical modeling was also exploited as experimental
data obtained with many in situ diagnostic methods are
subject to misinterpretations because the presence of foreign
ions in the membrane and ionomer affects fuel cell resistance
losses that invalidate assumptions needed to separate
individual performance loss contributions.

The cathode catalyst loading impact was investigated
under a single set of operating conditions. The scavenging
effect of liquid water was studied with an inactive fuel cell
to minimize the presence of side reactions. The contaminant
was carried inside the fuel cell with a saturated and inert
carrier gas whereas the water was transferred from the
anode compartment by thermo-osmosis [13]. Water transfer
was facilitated by avoiding the use of a gas diffusion layer
on the anode side. The amount of water transferred was
measured by collection at the fuel cell outlet. Methanol and
sulfur dioxide were used as model contaminants that either
only dissolve in water or hydrolizes and reacts to form
a bisulfite ion. For methanol, outlet water samples were
analyzed by cyclic voltammetry and total organic carbon.
For sulfur dioxide, outlet gas samples were analyzed by gas
chromatography.

RESULTS

Table 1 summarizes key metrics obtained from the in
situ and ex situ diagnostic tests. Electrochemical catalyst
areas and peroxide production currents indicate that the
### Table 1. Summary of Ex Situ And In Situ Diagnostic Methods’ Results for Seven Airborne Contaminants and One Foreign Cation To Resolve Contamination Mechanisms

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Kinetic Current (% loss in air at 30°C and 0.9 V vs RHE)</th>
<th>Electrochemical Catalyst Area (% loss in N2 at 30°C)</th>
<th>H2O Current (% gain in air at 30°C and 0.5 V vs RHE)</th>
<th>Membrane Conductivity (% loss at 80°C and 50% relative humidity)</th>
<th>Dimensionless Local Current (maximum % loss and gain in air at 80°C)</th>
<th>Contaminant Conversion (% in air at 80°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>79-84 (16.9 mM)</td>
<td>&gt;76 (16.9 mM)</td>
<td>850-1300 (16.9 mM)</td>
<td>0 (100 ppm), N product detected by ISE (IC tests planned)</td>
<td>Step change followed by a cell potential triggered evolution reaching −15 to 12 at steady state (20 ppm)</td>
<td>Traveling current wave reaching −28 to 22 to values approximately equal to initial values (20 ppm)</td>
</tr>
<tr>
<td>Acetylene</td>
<td>100 (4,030 ppm)</td>
<td>100 (4,040 ppm)</td>
<td>2,700-3,800 (4,030 ppm)</td>
<td>1-2 (500 ppm)</td>
<td>Traveling current wave of −99 to 100 synchronized with voltage transient followed by −17 to 18 at steady state (300 ppm)</td>
<td>Step change to values approximately equal to initial values (300 ppm)</td>
</tr>
<tr>
<td>Bromomethane</td>
<td>54 (400 ppm)</td>
<td>43 (400 ppm)</td>
<td>56 (400 ppm)</td>
<td>No ohmic loss in fuel cell</td>
<td>Gradual change starts after voltage steady state reaching −19 to 13 (5 ppm)</td>
<td>Trend continues reaching −21 to 21 (5 ppm)</td>
</tr>
<tr>
<td>Iso-propanol</td>
<td>7 (1 mm)</td>
<td>18 (1 mm)</td>
<td>No ohmic loss in fuel cell</td>
<td>Step change of −9 to 5 (3,500 ppm)</td>
<td>Reverse step change (5,300 ppm)</td>
<td>Reverse step change (20 ppm)</td>
</tr>
<tr>
<td>Methylmethacrylate</td>
<td>65 (1 mm)</td>
<td>43 (H₂O) and 82 (PiO reduction) (1 mm)</td>
<td>1,300 (1 mm)</td>
<td>No ohmic loss in fuel cell</td>
<td>Step change of −7 to 6 (20 ppm)</td>
<td>Reverse step change (20 ppm)</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>66 (sat soln)</td>
<td>90 (sat soln)</td>
<td>780 (sat soln)</td>
<td>No ohmic loss in fuel cell</td>
<td>Traveling current wave of −25 to 14 synchronized with voltage transient (2.3 ppm)</td>
<td>Traveling current wave of −39 to 40 synchronized with voltage transient (2.3 ppm)</td>
</tr>
<tr>
<td>Propene</td>
<td>53 (1,010 ppm)</td>
<td>26 (H₂O) and −50 (PiO reduction) (1,010 ppm)</td>
<td>620-960 (1,010 ppm)</td>
<td>No-ohmic loss in fuel cell</td>
<td>Step change of −8 to 6 (100 ppm)</td>
<td>Reverse step change (100 ppm)</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>37 (90 mM Ca(ClO₄)₂, 21 (5 ppm))</td>
<td>2 (90 mM Ca(ClO₄)₂, 16-46 (5 ppm))</td>
<td>660 (90 mM Ca(ClO₄)₂)</td>
<td>1.1-11 (5 ppm)</td>
<td>Gradual change up to −50 to 20 (5 ppm)</td>
<td>Gradual change up to −60 to 40 (5 ppm)</td>
</tr>
</tbody>
</table>

*The total current is still mostly due to oxygen reduction in spite of a large peroxide production rate increase. †Observed products include: for acetonitrile, ammonia/amine; for acetylene, CO and CO₂; for iso-propanol, CO₂; for methyl methacrylate, CO₂; for naphthalene, 1,2,3,4-tetramethyl-benzene, 1,3,5,7-tetramethyl-adamantane, pentamethyl-benzene, 1-penten-3-one, 1-(2,6,6-trimethyl-1-cyclohexen-1-yl); for propene, CO₂, 0.25 mM solubility at 25°C. ‡Derived from in situ polarization curve and cyclic voltammetry tests. §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. ‖Other than 1 A cm⁻² and before a steady state is reached at 100 h. Figures in parentheses represent the contaminant concentration either in the gas phase (ppm) or liquid phase (M). Both concentration units are used for the Ca²⁺ ion. RHE – reference hydrogen electrode; GDE – gas diffusion electrode; IC – ion chromatography; ISE – ion selective electrode; TBD – to be determined; UPD - under-potential deposition.

change in kinetic resistance associated with contamination is not only due to a decrease in surface area but also to a modification of the oxygen reduction mechanism in favor of a 2 rather than a 4 electrons path leading to increased amounts of hydrogen peroxide. Only Ca²⁺ did not significantly affect the electrochemical surface area. Generally, organic contaminants undergo chemical or electrochemical reactions within the fuel cell as detected by gas chromatography/mass spectrometry analysis of outlet gases. Only bromomethane was inactive. Iso-propanol could not be analyzed because the sample gas stream drying step, which is necessary to avoid equipment damage, entrains a significant portion of isopropanol. Ca²⁺ is not expected to be converted to Ca in the fuel cell because the electrode potentials are not sufficiently low. Acetonitrile and Ca²⁺ were the only contaminants that led to an ohmic resistance change. For acetonitrile, the change was ascribed to a decomposition product because the membrane conductivity measured ex situ was not affected by acetonitrile. Ammonium was detected in the fuel cell outlet water. It is possible that a nitrogen organic compound is also present because the ion selective electrode cannot discriminate between such species. For Ca²⁺, ion exchange with the ionomer proton modifies ionic conductivity as well as other physico-chemical parameters. The current distribution was not affected by iso-propanol, methyl methacrylate and propene. This observation is consistent with relatively slow catalyst surface kinetics, rapid transport processes and a relatively uniform contaminant concentration across the cell. However, the other contaminants revealed varied behaviors that may be useful to facilitate mechanism identification and generalize contamination mechanisms [14]. It is hypothesized that a change in rate determining step along the contaminant transport to the catalyst surface, catalyst surface kinetics, contaminant and products transport away from the catalyst surface sequence is responsible for the change in behavior. The gas diffusion electrode water content
has not yet been measured because the increase in mass transport loss in the presence of organic contaminants was largely attributed to contaminant adsorption on the catalyst [15].

The presence of elevated levels of peroxide is expected to affect cell durability. The presence of contaminant products and the uneven current distribution may complicate performance recovery strategies.

Table 2 illustrates that a 75% reduction in Pt catalyst loading from 0.4 to 0.1 mg cm$^{-2}$ leads to a decrease in cell voltage at steady state due to contamination (the difference between the cell voltage before contamination and during contamination) that generally exceeds 75% and reaches values of 92 to 6,325%. As a result, filter system specifications either need to be revised or should be determined for commercially relevant Pt catalyst loadings.

Figure 1A depicts a schematic representation of the one-dimensional (x direction) modeled membrane/electrode assembly portion. Figure 1B calculations show that the presence of a foreign cation in the catalyst layers’ ionomer and membrane significantly affects the oxygen concentration distribution due to a smaller ionomer water content [16] and oxygen permeability [17]. The oxygen concentration gradient is steeper and the average oxygen concentration is lower than values in absence of foreign cation contamination. The lower oxygen concentration affects thermodynamic (Nernst equation), kinetic (oxygen reduction is a first order reaction) and mass transport contributions. The foreign cation contamination model also demonstrates that the change in oxygen permeability of the ionomer accounts for a significant fraction of the decrease in cell performance. This new information is important to focus activities aimed at minimizing the effect of foreign cation contamination on cell performance.

Figure 2A illustrates the cell and method used to measure the impact of liquid water scavenging on contaminant concentration. Figure 2B shows that the CH$_3$OH concentration at the cell outlet measured by two different methods acceptably fits the liquid water scavenging model over a stoichiometry range exceeding the normal operating regime of approximately 1.5 to 2.5. The same conclusion is reached from Figure 2C for the case of SO$_2$. However, for this particular case of a species hydrolizing and reacting by forming a bisulfite ion, the amount of species scavenged is concentration dependent which is important for predictive purposes. Figure 2C depicts the amount of SO$_2$ scavenged, which is the difference between the full line and the dash line. The amount of SO$_2$ scavenged increases with a decrease in inlet SO$_2$ concentration. Therefore, cell performance extrapolations to lower contaminant concentrations using only high concentration data while disregarding the scavenging effect are conservative.

The scavenging model reduces to a simple expression because a time-scale analysis of all relevant phenomena

### Table 2. Summary of the Impact of a Cathode Catalyst Loading Reduction on Steady-State Cell Performance Loss for Seven Airborne Contaminants

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Acetonitrile</th>
<th>Acetylene</th>
<th>Bromomethane</th>
<th>Iso-propanol</th>
<th>Methyl methacrylate</th>
<th>Naphthalene</th>
<th>Propene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell voltage loss</td>
<td>58 (20 ppm)</td>
<td>6,325 (100 ppm)</td>
<td>-10 (5 ppm)</td>
<td>92 (~8,000 ppm)</td>
<td>104 (20 ppm)</td>
<td>187 (1.4 ppm)</td>
<td>224 (100 ppm)</td>
</tr>
</tbody>
</table>
revealed that liquid water accumulation within the cell is the slowest step. As a result, the liquid water is saturated by the contaminant, which simplified model derivation by eliminating the need to track individual water droplets. The model expression, which depends on two dimensionless parameters is simple which facilitates its use to calculate effective concentrations and improve correlations with cell performance losses:

\[ \frac{c(x)}{c(0)} = \left( \frac{W_x x}{1 + W_x x} + \frac{W_x^2 x^2}{(1 + W_x x)^2} + \frac{1}{1 + W_x x} \right)^2 . \]

where \( c \) is the molar concentration of contaminant X in the gas phase (mol m\(^{-3}\)), \( x \) the dimensionless flow field channel length, \( c_{\text{in}} \) the inlet contaminant X concentration in the ambient air on a dry basis (mol m\(^{-3}\)), \( c_r \) the molar concentration of non vapor gases at saturation conditions within the fuel cell (mol m\(^{-3}\)), \( W_1 \) represents the dimensionless number characterizing the severity of the liquid water scavenging effect on the contaminant X, and \( W_2 \) represents the dimensionless number characterizing the severity of the liquid water scavenging effect on the contaminant X in the presence of dissociation reactions.

**CONCLUSIONS AND FUTURE DIRECTIONS**

- Contamination mechanisms for seven airborne contaminants and one foreign cation were refined by building a database using a variety of ex situ and in situ diagnostic methods.
• The performance loss at steady state due to contamination is generally and proportionally larger than the decrease in cathode catalyst loading thus suggesting a revision of filter system specifications for commercially relevant low catalyst loadings.

• For foreign cation contamination, the performance loss associated with the decrease in oxygen permeability through the ionomer is significant and cannot be ignored to minimize its impact.

• Contaminant scavenging by liquid water was demonstrated and modeled to improve correlations between fuel cell performance losses and the effective contaminant concentration.

• Complete long-term tests to assess the impact of increased peroxide production in the presence of airborne contaminants on fuel cell durability.

• Develop mitigation strategies for the most important contaminants.

• Continue to disseminate the large fuel cell contamination database.

**FY 2014 PUBLICATIONS/PRESENTATIONS**


15. J. St-Pierre, J. Ge, Y. Zhai, T. Reshetenko, M. Angelo, 224th Electrochemical Society meeting oral presentation, abstract 1330.

16. Y. Zhai, J. St-Pierre, J. Ge, 224th Electrochemical Society meeting oral presentation, abstract 1329.


18. J. Ge, Y. Zhai, J. St-Pierre, 224th Electrochemical Society meeting oral presentation, abstract 1302.


**REFERENCES**


