

V.B.7 The Effect of Airborne Contaminants on Fuel Cell Performance and Durability

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Contract Number: DE-EE0000467

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Project Start Date: April 1, 2010

Project End Date: December 31, 2015

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 2020 technical targets for 80-kW_e (net) integrated transportation fuel cell power systems operating on direct hydrogen, are considered.

- Durability: 5,000 h in automotive drive cycle
- Cost: \$40/kW_{net}
- Performance: 65% peak energy efficiency

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's material, design, operation, or maintenance changes to recover performance losses derived from contamination mechanisms.

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) 2016 Objectives

- Demonstrate successful mitigation of the impact of the four most important airborne contaminants.

FY 2016 Accomplishments

- Developed mitigation strategies based on the contamination mechanism for bromomethane, the only organic contaminant that led to an incomplete recovery after contaminant injection was interrupted. The performance loss during constant cell voltage tests is recoverable (>90% current density recovery) by desorbing Br⁻ anions from the Pt catalyst surface at a low cathode potential and promoting the formation of liquid water for dissolution and entrainment of anions.
- Assessed the impact of a lower cathode catalyst loading (decrease from 0.4–0.1 mg Pt cm⁻²) and a dilute contaminant mixture (0.5 ppm acetonitrile CH₃CN, 1 ppm bromomethane CH₃Br and 2 ppm propene C₃H₆) on cell performance. The loss was ~200 mV after 100 h (the almost linear decay did not reach a steady state) and

an incomplete recovery of ~100 mV was observed after interruption of the contaminant mixture injection.

- Evaluated the tolerance of a commercial PtCo cathode catalyst to SO_2 . The performance loss after 20 h (134 ppb SO_2 , 1.5 A cm^{-2} , 0.4 mg Pt cm^{-2} cathode loading) and irrecoverable losses after the contaminant injection was interrupted were similar for PtCo and Pt catalysts (respectively ~150 mV and ~70 mV).
- Determined the impact of four additional cleansers diluted by a factor of 20 or more on fuel cell performance.



INTRODUCTION

The composition of atmospheric air cannot be controlled and typically includes other gases including many volatile organic compounds, as well as ions entrained in liquid water and encountered as droplets in the form of rain, mist, etc., especially near marine environments. Materials require cleansers to remove oils and dirt introduced by fuel cell manufacturing and assembly operations. Specific types of air contaminants and cleansers may cause deleterious effects which include decreased cell performance and durability [1,2] of proton exchange membrane fuel cells. Numerous air contaminants and cleansers 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). Subsequently, contamination mechanisms were investigated for downselected contaminants (acetonitrile, acetylene, bromomethane, iso-propanol, methyl methacrylate, naphthalene, propene, Ca^{2+}) using a variety of ex situ and in situ characterization techniques [6] to facilitate the development of performance recovery procedures.

Only bromomethane and Ca^{2+} led to irrecoverable losses by interrupting contaminant injection (isopropanol only leads to irrecoverable losses if used in the more concentrated form

of a cleanser). Ca^{2+} recovery procedures were reported [7]. Bromomethane recovery procedures were devised based on its contamination mechanism [8] and are summarized. Single contaminants were studied but do not readily occur in ambient air. Rather, air contains a mixture of contaminants. It was deemed important to obtain information about contaminant mixtures under realistic operating conditions, expose a commercially relevant low catalyst loading and reduce commercialization risks. This statement equally applies to the use of Pt alloys developed to minimize energy losses associated with the reduction of oxygen to water [9] because the overwhelming majority of contamination studies were devoted to Pt [2]. Finally, cleansers were selected for fuel cell screening tests because that contaminant class has not been previously explored. Screening results for four cleansers were reported [7]. Results for another four cleansers are summarized.

APPROACH

For bromomethane recovery tests, the performance loss was first established at a constant cell voltage of 0.63 V to facilitate data interpretation because catalyst surface processes are potential dependent. Subsequently, changes in operating conditions were used to desorb Br^- (N_2 or H_2 circulation in the cathode compartment). As a final step, the presence of liquid water was favored (high current density operation, liquid water injection in the cathode compartment, increase in air relative humidity from 50% to 100%, cell temperature decrease from 80°C to 55°C) to enable dissolution of the bromide ions and their entrainment toward the cell outlet port.

For the contaminant mixture test, only three species were used to minimize the injection system complexity. Acetonitrile, bromomethane and propene were selected because they were the only downselected organic species leading to ohmic losses, irrecoverable losses and small gains in performance after recovery, respectively. Contaminant concentrations were decreased from 20–0.5 ppm acetonitrile, 20–1 ppm bromomethane and 100–2 ppm propene. The larger concentrations were previously used for tests focusing on the determination of contamination mechanisms. The concentration decreases are insufficient to reach typical values in air for all mixture species (respectively 1.6 ppm, 0.0066 ppm, and 0.034 ppm annual maximum over a 24 h period for acetonitrile, bromomethane, and propene) but were deemed sufficiently large to anticipate a significant degradation within a reasonable amount of time. The cell was first operated with air to define a baseline. The contaminant mixture was subsequently introduced into the cell for a period of ~100 h. Contaminant injection was stopped after an ~100-h period because the cell voltage loss was already large and the decay was not slowing down. The cell was then operated until a steady state was reached and the recovery

was maximized. Diagnostics were regularly performed (impedance spectroscopy, polarization, cyclic voltammetry).

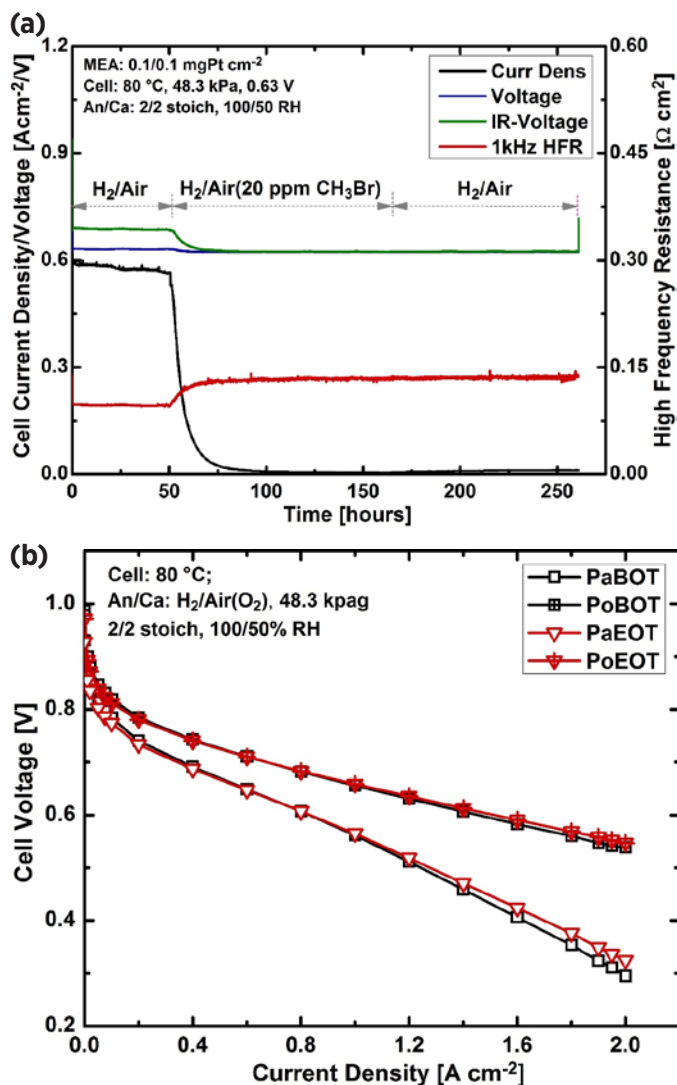
The impact of SO_2 was measured for both Pt and PtCo catalysts with a concentration of 134 ppb (near the 75 ppb daily maximum over a 1 h period). A temporary sulfur dioxide injection of 20 min was used and diagnostics were completed before and after the contaminant injection period (polarization, cyclic voltammetry).

Cleaners were selected on the basis of prior suggestions provided by industry. The fuel cell injection method is based on the cleanser boiling point. The cleanser is evaporated for a liquid with a boiling point below 20°C whereas it is injected as a mist above that temperature. The cleanser is diluted by a factor of 20 or more (a 5% cleanser–water mixture by volume) which is the leftover concentration estimated on the basis of two rinses (approximate high speed water entrainment or evaporation depending on vapor pressure). The cleanser is temporarily injected in the cathode compartment. Focus is given to the cell performance loss resulting from the cleanser injection for screening and selection purposes although diagnostics were completed (impedance spectroscopy, cyclic voltammetry).

RESULTS

Figure 1a illustrates the evolution of the current density at 0.63 V for a cell with a low cathode catalyst loading of 0.1 mg cm^{-2} contaminated by bromomethane. The cell current before the introduction of the contaminant is relatively stable (0–50 h). After the contaminant is introduced, the current density rapidly decreases to a value near 0 in approximately 50 h. A following period of operation in excess of 100 h without contaminant did not significantly recover the current density. A two-step recovery procedure was applied to the cell. First, the cathode potential was decreased by replacing air with N_2 (non-operating cell) to desorb the Br^- from the catalyst surface. These bromide ions are produced by hydrolysis of bromomethane [8]. This step was followed by successive cell operation periods at a progressively lower cell voltage (higher current density) to promote the presence of liquid water within the cell. Liquid water is necessary to dissolve the desorbed anions and entrain them along the flow field channel toward the cell outlet. Figure 1b shows polarization curves with air and oxygen obtained before contamination and after recovery which indicate that the two-step recovery procedure is effective and does not lead to any residual losses assigned to contamination for practical cell voltages above 0.6 V .

Figure 2 depicts cell voltage and high frequency resistance transients for a cell with a low cathode catalyst loading of 0.1 mg cm^{-2} contaminated with the ternary mixture. The cell voltage is constant before the contaminant mixture is injected. Upon injection, a short and rapid cell voltage drop is observed ($\sim 50\text{ mV}$) which is followed by



MEA – Membrane electrode assembly; RH – Relative humidity; IR – Current and resistance product; BOT – Beginning of test; EOT – End of test

FIGURE 1. (a) Cell voltage, ohmic loss compensated cell voltage, current density, and high frequency resistance at 1 kHz transients for a cell temporarily exposed to 20 ppm bromomethane. (b) Polarization curves obtained with air and oxygen before the cell was contaminated with bromomethane and after the cell was subjected to recovery procedures.

a large and approximately constant voltage decay rate ($\sim 1.5\text{ mV h}^{-1}$). The total cell voltage loss at the end of the contamination period is $\sim 200\text{ mV}$. After the injection of the contaminant mixture is interrupted, the cell voltage recovers but reaches a value at steady state which is significantly lower than the original value by $\sim 100\text{ mV}$. The high frequency resistance slightly increases especially toward the end of the contamination period. The change in high frequency resistance is reversed at the end of the recovery period. Bromomethane is the only mixture contaminant leading to irrecoverable losses. Thus, irrecoverable voltage losses

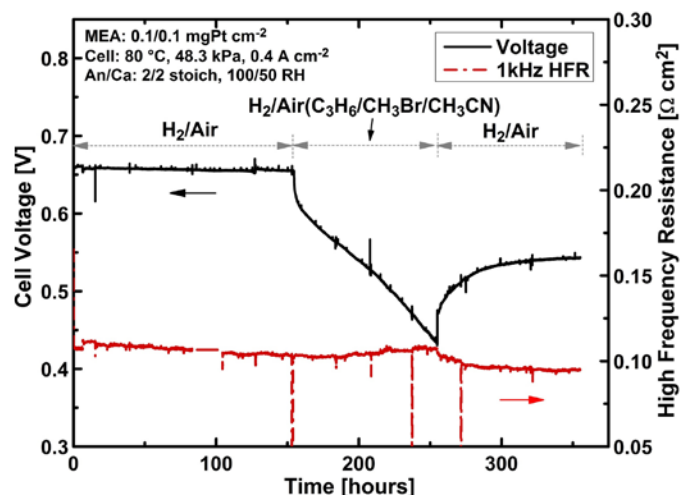


FIGURE 2. Cell voltage and high frequency resistance transients for a cell exposed to a temporary contaminant mixture of 0.5 ppm acetonitrile, 1 ppm bromomethane, and 2 ppm propene

are attributed to the formation of Br^- by bromomethane hydrolysis which cannot be desorbed from the catalyst surface at the operating cathode potential of ~ 0.49 V (~ 0.45 V + ~ 0.1 ohm $\text{cm}^2 \times 0.4$ A cm^{-2}) [8]. Acetonitrile is the only mixture contaminant leading to ohmic losses. Therefore, the increase in high frequency resistance is ascribed to the formation of NH_4^+ by acetonitrile hydrolysis which are exchanged with ionomer and membrane protons H^+ [10]. Although signatures from the single contaminants are noted in Figure 2, data are insufficient to evaluate the presence of interactions between the three mixture species. This situation is in part due to the dual decrease in catalyst loading and contaminant concentration. For a larger catalyst loading of 0.4 mg Pt cm^{-2} , the decrease in acetonitrile and propene concentration to respectively 0.5 – 2 ppm was not expected to modify the cell voltage [11]. However, the cell voltage loss due to bromomethane was expected to be still significant at 1 ppm as it is weakly dependent on concentration (a 49% to 38% loss in cell voltage for a decrease from 20 – 2 ppm) [11]. For the relatively large and fixed contaminant concentrations employed for the determination of mechanisms, a decrease in Pt loading from 0.4 – 0.1 mg cm^{-2} promoted an increase in cell voltage loss of respectively 58%, -10% , and 224% for acetonitrile, bromomethane, and propene [12]. Data were not obtained for changes in both contaminant concentration and catalyst loading. Even if interactions between the three contaminants cannot be evaluated, the dilute ternary contaminant mixture creates a large cell voltage loss for a commercially relevant catalyst loading. Additional work should be pursued in this area to revise and predict contaminant tolerance limits for mixtures and commercially relevant cathode catalyst loadings.

Figure 3 summarizes the impact of a temporary exposure to SO_2 on Pt and PtCo catalysts. The cell voltage

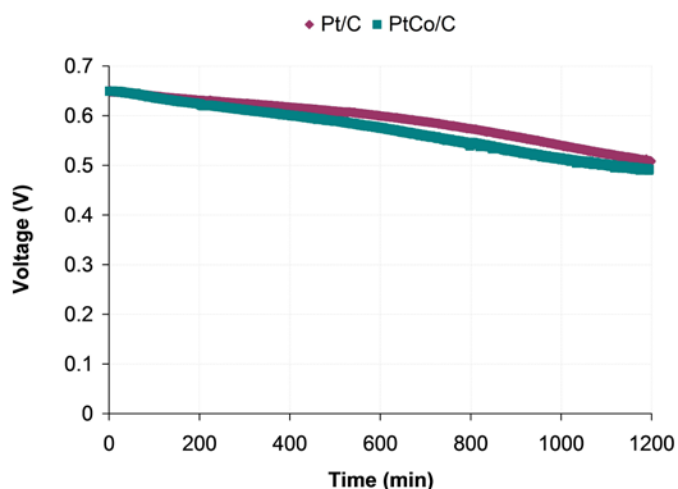


FIGURE 3. Cell voltage transients for cells temporarily exposed to 134 ppb sulfur dioxide. 0.4 mg Pt cm^{-2} / 0.1 mg Pt cm^{-2} for the cathode/anode, 1.5 A cm^{-2}

for both catalysts linearly decreases by ~ 150 mV without reaching a steady state. After the contaminant injection was interrupted, the cell voltage partly recovered leaving 70 mV in irrecoverable losses (not shown). Therefore, the alloy does not have an advantage in terms of contamination. This statement may not necessarily apply to other contaminants or PtCo alloys.

The results obtained by temporarily contaminating cells with four different cleansers were briefly reported [7]. Data for four additional cleansers were acquired during this reporting period. Data for all eight cleansers are summarized in Table 1. None of the cleansers are compatible with fuel cells either because the cell voltage was partially recoverable within a single vehicle fuel fill (~ 14 h), or the cell voltage fell below the power electronics low end operating point (0.45 V). Therefore, additional work is needed to identify a suitable cleanser, design an appropriate cleanser composition or develop cleaning alternatives for fuel cell components (such as cleanser removal).

CONCLUSIONS AND FUTURE DIRECTIONS

- An effective method was established to reverse irrecoverable cell voltage losses induced by bromomethane contamination.
- A dilute ternary contaminant mixture led to a large cell voltage loss and an irrecoverable loss for a commercially relevant 0.1 mg Pt cm^{-2} cathode catalyst loading, prompting additional work to revise and predict tolerance limits for such operating conditions.
- A commercial PtCo alloy cathode catalyst has a similar tolerance to SO_2 than a Pt catalyst.

TABLE 1. Summary of the Screened Fuel Cell Components' Cleansers, Experimental Parameters and Key Results

Sample	Class	Principal Component	Injection Method	Concentration (%)	Injection Rate ($\mu\text{L min}^{-1}$)	Decay Rate ^a (mV h^{-1})	Recovery (%) ^b
A	cationic	2-butoxyethanol	nebulizer	5	130	~1.4	~0
B	amine	triethanolamine	nebulizer	5	130	~22	~46
C	cationic	sodium dodecylbenzenesulfonate	nebulizer	5	130	<1.4	<0 ^c
D	citrate	citrus terpenes	nebulizer	5	130	~1,500	~96
				0.5	130	~2	~60
E	amine	sodium lauryl ether sulfate	nebulizer	5	130	<15	~25
F	amine	ethylenediaminetetraacetic acid	nebulizer	5	130	~3.3	<0 ^c
G	organic	naphtha	nebulizer followed by vaporization	0.2	10	5 ^d	~100
				1	50	100 ^d	~100
				3	250	150 ^d	~100
				3	250	240 ^{d,e}	~100
H	organic	isopropanol	nebulizer followed by vaporization	0.2	10	70 ^d	~90

^aBaseline decay rate is $\sim 0.2 \text{ mV h}^{-1}$. ^bAfter interruption of cleanser injection. ^cThe cell voltage continues to drop during the recovery period. ^dStep change in mV. ^e100% relative humidity at the cathode.

- All eight cleansers for fuel cell components, readily available and common name brands, were unsuitable suggesting additional work to identify a suitable cleanser, design an appropriate cleanser composition or develop cleaning alternatives.
- Bromomethane contamination tests with metallic bipolar plates will be completed to assess the existence of interactions (bromine promotes corrosion).
- We will continue to analyze, summarize, and disseminate the large fuel cell contamination database.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. J. St-Pierre, J. Ge, "Fuel Cell Catalyst Ink Active Surface Area Measurement," United States provisional patent 62/262,137, December 2, 2015 (inspired by the contamination mechanisms that were developed).

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