

V.E.4 The Effect of Airborne Contaminants on Fuel Cell Performance and Durability

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Subcontractors

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- ² WPCSOL, East Windsor, CT
- ³ Ballard Power Systems, Burnaby, BC, Canada

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Project End Date: December 31, 2015

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) 2015 Objectives

- Demonstrate successful mitigation of the impact of the four most important airborne 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 2020 technical targets for automotive applications, 80 kW_e (net) integrated transportation fuel cell power systems operating on direct hydrogen, are considered:

- Durability: 5,000 hours in automotive drive cycle
- Cost: \$40/kW_e
- 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 2015 Accomplishments

- Assessed the impact of acetonitrile and Ca²⁺, which led to larger peroxide production rates in ex situ rotating ring disc electrode tests by up to 1,300%, on membrane degradation during long duration fuel cell tests and found a decrease in exhaust water fluoride concentration of 67% for acetonitrile
- Defined the partial effectiveness of two in situ recovery procedures to reverse the effects of Ca²⁺ contamination (cell performance loss, salt deposition): (1) operation at a low cell voltage and (2) acid solutions without or with isopropanol
- Determined the impact of four cleansers diluted by a factor of 20 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 using a variety of ex situ and in situ characterization techniques [6] to facilitate the development of performance recovery procedures. The series of ex situ tests aimed at isolating the kinetic contribution (rotating ring disc electrode) revealed much larger peroxide production rates, an oxygen reduction side reaction, in the presence of organic or cationic contaminants [7-10]. The membrane is more susceptible to degradation in the presence of peroxide [11,12]. It was deemed important to expose fuel cells to contaminants for a long period to confirm the peroxide impact on membrane degradation because the ex situ test is performed at a significantly lower temperature of 30°C in comparison to 80°C in an application and with a liquid electrolyte contacting the catalyst thin film. Although fuel cells contaminated with iron [13] and sulfur dioxide [14] have shown elevated levels of fluoride in the exhaust water, a product of membrane degradation, these indirect measurements were not corroborated with membrane/ electrode assembly material characterizations including membrane thickness and conductivity, and catalyst active surface. Although cation contamination data have revealed that the mechanism proceeds with an ion exchange step with the membrane proton [15-17], the evaluation of in situ recovery strategies that take advantage of that knowledge has not previously been attempted. The effectiveness of two cation contamination recovery methods was therefore investigated. Finally, cleansers were classified and selected

for fuel cell screening tests because that contaminant class has not been previously explored.

APPROACH

The contaminant pool was previously reduced to one cation (Ca^{2+}) and seven organic species (acetonitrile, acetylene, bromomethane, isopropanol, methyl methacrylate, naphthalene, propene) for detailed mechanistic studies [6]. For the long-term duration contamination tests, one contaminant was selected from each of these contaminant classes. The choice of the cation was straightforward whereas acetonitrile was chosen because it had a larger effect than five of the other six organic species according to one of the two quantitative down-selection criteria [3] and is the only organic species that impacted ohmic losses mostly associated with the membrane. As focus was given to membrane degradation, diagnostics included in situ membrane resistivity (impedance spectroscopy, milliohmeter), and fuel cell exhaust water analyses for fluoride (ion chromatography, ion selective electrode). Destructive tests were also considered at the end of the long duration test to measure the membrane and catalyst layer thicknesses by scanning electron microscopy.

Two in situ contamination recovery methods were investigated. A high current density, low cell voltage was used to assist foreign cation removal from the membrane by the high rate of water production at the cathode and the displacement of the foreign cations towards the cathode due to the predominant electric field effect [18,19]. Ion exchange was also used by circulating acid solutions in the cathode compartment. Only the acid solution approach was evaluated for the removal of salt deposits from the flow field channels and the gas diffusion layer after the cell was contaminated in situ. Both methods were assessed for their effectiveness on cell performance recovery after a controlled ex situ contamination step to avoid salt precipitation. The presence of salt was ascertained visually (photography, scanning electron microscopy) and spectroscopically (energy dispersive X-ray spectroscopy). Salt removal was also ascertained by measuring the membrane ion exchange capacity and the gas diffusion layer contact angle.

Cleansers 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 which is the leftover concentration estimated on the basis of two rinses. The cleanser is initially injected in the cathode compartment. If the cleanser has no effect on fuel cell performance, it is re-tested by injection on the anode side. Focus is given to the cell performance loss resulting from the cleanser injection for screening and selection purposes.

RESULTS

Figure 1 illustrates the ion chromatography results of outlet water samples collected during the 1,000-hour long-term test with 5 ppm acetonitrile. The presence of acetonitrile decreases the fluoride concentration in water samples. In particular, it is noted that after the contaminant is introduced, the fluoride concentration decreases whereas after the contaminant injection is interrupted, the fluoride concentration increases. The average fluoride concentration is respectively 0.15 mg L^{-1} and 0.05 mg L^{-1} during the recovery and contamination period corresponding to a 67% decrease during the contamination period. It is hypothesized that acetonitrile acts as a scavenger for the radicals and/or peroxide generated at the cathode. The present results contrast with iron [13] and sulfur dioxide [14] data which demonstrated an increase rather than a decrease in fluoride concentration. Therefore, the scavenging effect is contaminant specific and needs to be ascertained for each contaminant. Membrane resistances and catalyst layer and membrane thicknesses after the recovery period were not affected by the long term exposure to acetonitrile and support the acetonitrile as scavenger hypothesis.

The long duration test for Ca^{2+} was prematurely interrupted after more than 350 h of contamination due to salt deposits blocking the gas diffusion layer and the flow field channels. The membrane resistance obtained by impedance spectroscopy did not significantly change but the cathode catalyst layer became thinner (more than a 50% reduction in thickness). However, the ion selective electrode fluoride measurements were inconclusive as values were below the detection level. Samples will be re-analyzed by ion chromatography. Platinum dissolution which could negligibly

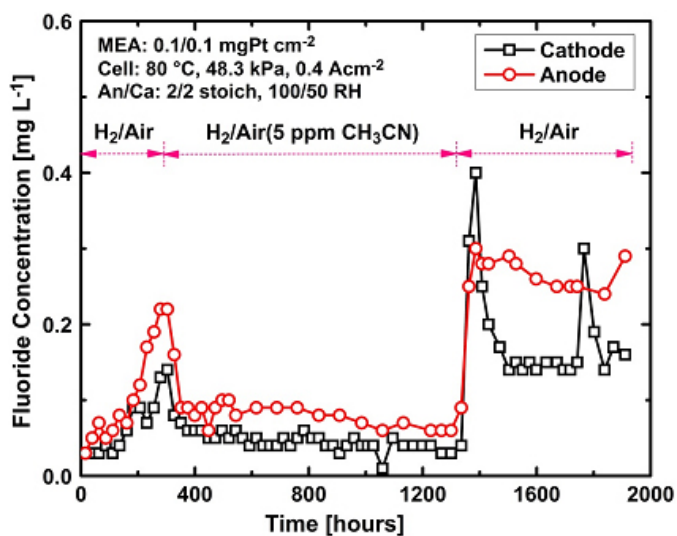


FIGURE 1. Fluoride concentration in liquid water samples extracted from fuel cell cathode and anode outlet streams as a function of time before, during and after an exposure to 5 ppm acetonitrile in air

contribute to a thinner catalyst layer (presumably, the carbon support network remains intact) was discounted because its concentration in water samples was not affected (inductively coupled plasma mass spectrometry) and the platinum signal although spread over a shorter distance was more intense (energy dispersive X-ray spectroscopy). The possibility remains that carbon corrosion might be partly responsible for the thinner cathode catalyst layer in addition to membrane degradation but a specific test is needed to discriminate between these two possibilities (for example, an increase in air outlet carbon dioxide concentration, a product of carbon corrosion).

The in situ circulation of an acid solution to recover performance losses sustained during Ca^{2+} contamination was only partly effective. The most direct evidence is depicted in Figure 2 with a catalyst coated membrane ion exchange capacity after recovery still lower than the value for a fresh sample by about 30%. The reason for this incomplete recovery which is significantly smaller than the extent that can be achieved by applying the method ex situ to a catalyst coated membrane, has not been clarified. It is likely related to the gas diffusion layer acting as a barrier. Ion exchange can only take place if there is a direct contact between the acid solution and the ionomer as revealed by ex situ contamination tests and immersing the catalyst coated membrane in the solution with and without a gas diffusion layer. The addition of isopropanol as surface active agent (a relatively benign contaminant [3]) did not improve the performance recovery. Sophisticated methods will be required to verify the contact between the acid solution and the ionomer, and improve the performance recovery. Cell operation at a high current density, low cell voltage was ineffective in recovering any cell performance losses due to calcium contamination even after ~40 h of operation under these conditions.

The in situ acid solution flush was largely effective in removing salt deposits on the cathode flow field channels and gas diffusion layer (Figure 3a). However, the cell

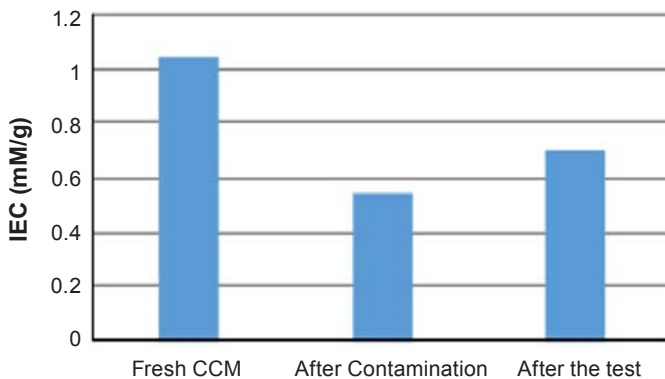


FIGURE 2. Catalyst coated membrane ion exchange capacity before, after contamination with Ca^{2+} and after recovery procedures

performance was only recovered in the mass transfer regime (Figure 3b). This observation is consistent with the extent of recovery achieved by contaminating the membrane electrode assembly ex situ (no salt deposits) and suggests that the presence of salt deposits has a smaller effect on cell performance than if the foreign cation penetrates the ionomer/membrane. A membrane electrode assembly cross section obtained after the test was completed confirms that the in situ acid solution flush is only partly effective as salt deposits of calcium sulfate are still present throughout the gas diffusion layer (Figure 3c, left image). This statement is confirmed by energy dispersive X-ray spectroscopy maps for sulfur (Figure 3c, center image) and calcium (Figure 3c, right image). The use of isopropanol did not improve the situation, concurring with the in situ observation that performance recovery is not improved with the addition of isopropanol. The impact of operating conditions on the salt dissolution rate may play a role and therefore they should be investigated.

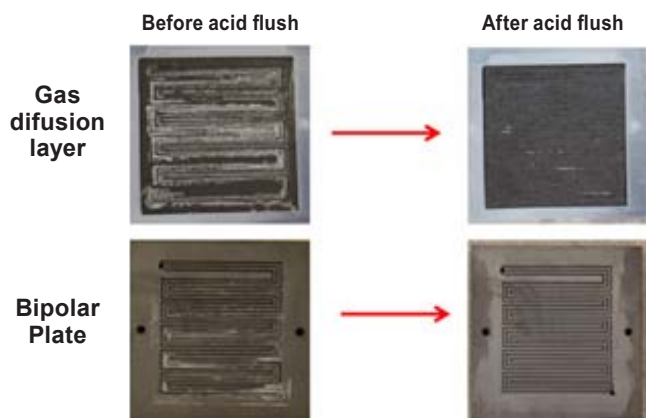


FIGURE 3A. Calcium salt deposit extent on the cathode gas diffusion layer and bipolar plate before and after in situ cleaning with an acid solution circulated in the cathode compartment

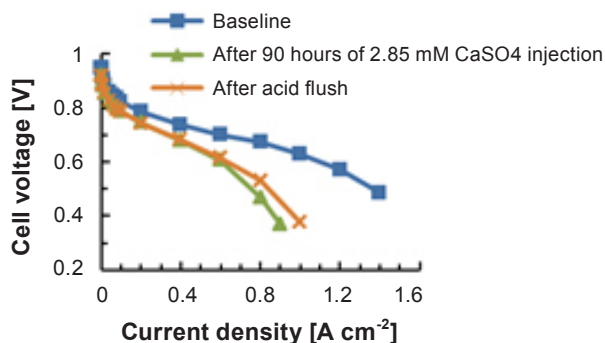


FIGURE 3B. Polarization curves obtained before and after in situ calcium contamination and after in situ recovery by circulating an acid solution in the cathode compartment

The project scope was expanded with the objective to screen a number of cleansers and determine their impact on fuel cell performance. The results related to four different cleansers were documented. The major components of Cleanser B include triethanolamine, ethoxylated alcohol and propylene glycol butyl ether. Figure 4 illustrates Cleanser B results. A large performance loss >0.2 V is observed over a period of approximately 10 h. This loss was partially recovered with a cell voltage gain >0.1 V. Results for all four cleansers already justify the need for this study. In each case, a significant loss in performance was noted.

CONCLUSIONS AND FUTURE DIRECTIONS

- Acetonitrile appears to scavenge the peroxide produced at the cathode or its decomposition products (radicals).
- The circulation of acid solutions in the cathode compartment was partly effective to recover both

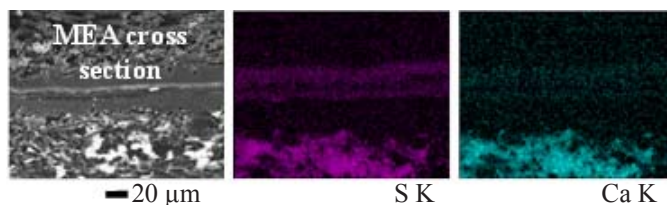


FIGURE 3C. Scanning electron microscopy image of the gas diffusion layer contaminated in situ with calcium after recovery with an acid solution (left) and corresponding sulfur S (center) and calcium Ca (right) maps obtained by energy dispersive X-ray spectroscopy; the cathode corresponds to the lower half of the image

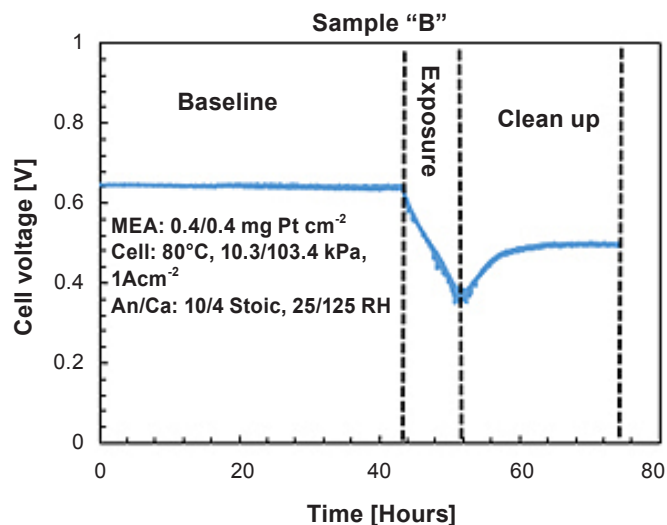


FIGURE 4. Voltage transient recorded during Cleanser B evaluation

- performance loss and removing salt deposits resulting from Ca^{2+} contamination.
- Cell operation at a high current density, low cell voltage was ineffective to recover performance losses resulting from Ca^{2+} contamination.
 - The four cleansers tested all lead to a loss in performance of at least 0.1 V when they were injected with a dilution factor of 20.
 - Water samples obtained during Ca^{2+} contamination will be re-analyzed to ascertain the impact on membrane degradation (fluoride concentration).
 - The long duration, low loading membrane electrode assembly contamination test ($0.1 \text{ mg Pt cm}^{-2}$) will be initiated with a mixture of organic contaminants using lower concentrations than those previously used during this program (moving towards practical operating conditions).
 - Recovery procedure tests for bromomethane, an organic contaminant characterized by a slow and incomplete recovery in comparison to the other six studied species from that group, will be initiated.
 - 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.

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