An Experimental Overview of the Effects of Hydrogen Impurities on Polymer Electrolyte Membrane Fuel Cell Performance

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Abstract:

Hydrogen quality is critical for increasing the reliability, stability, and durability of polymer electrolyte (PEM) fuel cells. In this work, several hydrogen impurities have been studied to understand their effects on PEM fuel cell performance at various operating concentrations. Our studies have shown that the following impurities suggested by industry stakeholders do not result in substantial fuel cell degradation when they are the sole impurity in hydrogen: 5 ppm formaldehyde, 2 ppm formic acid, 19 ppm chloromethane, 30 ppm acetaldehyde, 5% ethylene, 20 ppm toluene, and 10 ppm benzene. In addition, a specific mixture of impurities called the “specification concentration level cocktail” consisting of 0.2 ppm carbon monoxide, 4 ppb hydrogen sulphide, 0.2 ppm formic acid, 2 ppm benzene, and 0.1 ppm

ammonia in hydrogen, also does not show significant effects on cell performance. In comparison, when a cocktail having five times the specification concentration is introduced into the cell, significant performance loss is evident.

Keywords: PEM fuel cells; hydrogen impurity; contaminant study; single impurity tests; cocktail impurity study

1. Introduction

Hydrocarbon fuels are not a renewable resource. As the economies of the world grow, the available stores of these fuels are being consumed at ever increasing rates. As a result, additional greenhouse gases are released as by-products of combustion leading to rapidly increased pollution. Therefore, sources of clean and sustainable energy are needed to make better use of available resources. The polymer electrolyte membrane (PEM) fuel cell is a promising energy conversion device which emits almost no pollutants and has high working efficiency. The PEM fuel cell is believed to be one of the best near term solutions for the energy problem [1].

Many challenging issues must be addressed and solved before large-scale commercial applications of PEM fuel cells would be feasible. Generally, the performance of two key PEM fuel cell components needs to be significantly improved. The first of these is the catalyst. Different types of catalyst have been tested to improve their tolerance for impurities which “poison” active sites. In addition, the platinum catalyst loading must be decreased to reduce cost [2-8]. The other key component is the membrane. According to the United States Department of Energy (DOE), PEM fuel cells are required to have more than 5,000 hours life for cars, 20,000 hours life for buses, and 60,000 hours life for stationary applications [9]. However, the current PEM fuel cells only have approximately 2,000 hours life for cars [10, 11], 10,000 hours life for buses [11], and 22,000 hours life for stationary applications [12]. To reach the required durability, membrane lifetimes must be improved by a factor of two to three. Many researchers are working on these issues and progress is being made [13-18].

Industry produced hydrogen is the most promising fuel for PEM fuel cells. Improving the fuel quality will extend the working life and facilitate the application of PEM fuel cells [19]. There is significant potential for modifying the current hydrogen manufacturing processes to make it better suited for fuel cell applications. In general, fewer impurities in hydrogen fuel are preferred because that reduces the contaminant effects on the catalyst and lowers the degradation rates of the membrane. Therefore, longer operating life is expected. However, fewer impurities also mean a higher price for hydrogen. Therefore, it is very important to understand the contaminant effects of each impurity and determine the concentration ranges which will not result in substantial PEM fuel cell degradation.

Multiple techniques have been employed for hydrogen production. Among them, steam methane reforming (SMR) is the dominant technique. In the United States, approximately 95% of hydrogen is made via SMR [20]. Besides SMR, coal/oil partial oxidation, coal destructive distillation, and electrolysis of water are also widely used to produce hydrogen. In these processes, nitrogen (N_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), ammonia (NH_3), sulfur compounds, benzene (C_6H_6), toluene (C_7H_8), and other organic chemicals can be produced as by-products. Some of these chemicals, such as hydrocarbons, contaminate PEM fuel cells either by direct adsorption, or by decomposing into carbon monoxide which adsorbs on the catalyst surface to reduce the electrochemically active surface area (ECSA) of the catalyst. Other impurities, such as ammonia which is widely used as tracer gas in natural gas distribution system, can replace protons in Nafion[®], reducing the proton conductivity and mechanical properties of the membrane [21-24]. Some chemicals, such as N_2 , only dilute the fuel and reduce performance. They will not cause performance degradation and are believed to be safe for PEM fuel cell operation.

Over past few years, many impurities that are produced during hydrogen production, transportation, and storage, have been studied [25-28] which include formaldehyde, formic acid, chloromethane, acetaldehyde, ethylene, toluene, benzene, carbon monoxide, hydrogen sulphide, and ammonia.

However, these studies are normally focused on one or two impurities at a time at various operating conditions. So far, no work has been done to evaluate the effects of mixed impurities.

In this work, research has been done to study the effects of both single impurities and mixed impurities in hydrogen on PEM fuel cell performance based on an identical test protocol. The goal is to determine the maximum impurity concentrations that PEM fuel cells can tolerate without inducing significant performance degradation. The significance of performance degradation is decided by comparing the performance differences between impurity tests and the baselines (without impurities).

The purpose of this research was to provide experimental data as well as a possible qualitative mechanism analysis for prioritizing the contaminant effects of impurities in hydrogen. In particular, this research addressed the degradation of the fuel cell power system performance that can be restored by means of practical changes to operating conditions and/or fuel composition. Because of the requirements and priorities assigned by DOE and the US Drive Fuel Cell Tech Team – which includes critically important stakeholders such as the automakers, fuel producers, and major fuel cell developers, our team was constrained to a series of very specific screening tests that were representative of certain operational scenarios. The tests were structured to investigate the contaminant effects of impurities in hydrogen and prioritized to highlight the possible contaminants that may be generated during hydrogen production. This work was focused on several screening tests as well as some recovery tests. The mitigation strategies employed to alleviate hydrogen impurity contamination and the corresponding mechanisms have been widely studied by researchers and are addressed in the literature [21, 29-37].

Many PEM researchers use the terms “recovery” and “mitigation” interchangeably in the literature, and for most research there is no ambiguity. However, for the DOE Hydrogen contaminant program that supported this research, these terms were given specific and distinct meanings. For this program, the term “recovery” was defined as “the degradation of the fuel cell power system performance that can be restored by practical changes of operational conditions and/or fuel composition” [38], and all other

mechanisms, both *in-situ* and *ex-situ*, for improving performance that was lost due to operating with contaminants in the fuel supply gas, were defined as “mitigation”. The reason for this distinction stems from the down selection process that was established to manage the very large number of potential fuel side contaminants. This process was used by a number of researchers, and then formalized by St. Pierre *et. al* [39].

The down selection of contaminant species was based on fixed criteria which included: 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 provided by industry and research institutions [39, 40]. However, these criteria do not consider the effects of contaminant species on fuel cell performance. Therefore, St-Pierre *et. al* proposed two quantitative down selection criteria based on empirical methods [39]. The first criterion analyzes the performance degradation/recovery rates, performance loss induced by contamination, recoverable/irrecoverable performance losses and contaminant concentration. The second criterion examines the combination of the energy loss in degradation and regained energy during self-recovery. The advantage of these two criteria is that the analysis is based on a series of recovery tests which have been widely employed by researchers [30-32, 39-47], and this data is available for analysis and interpretation.

In a typical recovery test, the process is divided into three stages which include the baseline, the contaminant test and the self-recovery if significant contamination is detected. Therefore, distinct parameters related to the fuel cell performance can be obtained. These include the time for cell performance to reach a steady state after introducing contaminants, the performance loss during this period, the performance loss rate at the steady state after introducing contaminants, the time for the cell to regain performance and reach a steady state after removing the contaminants, the performance recovered in this recovery stage, and the performance loss rate at the steady state after removing contaminants. By analyzing these parameters, the significance of these contaminants is identified.

In our research, the above test method is employed. We hope this experimental data and the qualitative analysis will help the DOE, automakers, fuel producers, major fuel cell developers and other researchers prioritize additional work concerning how these impurities affect the PEM fuel cell performance.

2. Experimental

The approach in this research is to down select candidate impurities based on previously published work and known impurity levels for the established hydrogen production processes. For each selected impurity, a relatively high concentration which is cost effective for hydrogen production is tested first. If the impurity at this concentration does not induce significant cell performance degradation, no further tests are needed. Otherwise, the impurity is further tested at a lower concentration. This process is repeated until a concentration at which the cells do not show significant performance degradation is reached.

Prior to testing, we understood that the cell performance using pure hydrogen would likely vary over a specific range. This is known to happen even though otherwise identical cells are constructed in accordance with detailed assembly procedures and tested with fixed protocols. Therefore, the tests are initiated with pure hydrogen to generate a baseline. Given this baseline, the cell performance degradation, which is usually caused by mechanical degradation, thermal degradation, and chemical degradation, can then be measured. After switching to the impurities, the performance degradation caused specifically by the impurities can be calculated by subtracting the cell performance degradation rates of the baselines from the total cell performance degradation rates. For each impurity and each test, the contaminant effects of the impurities can be determined based on the differences between the performance degradation rates before and after introducing the impurity.

As discussed above, most common impurities in hydrogen are hydrocarbons, sulfur compounds, ammonia, carbon monoxide, and carbon dioxide. Under ideal conditions, if all the impurities can be

adsorbed on the catalyst or be able to replace protons in the Nafion® membrane without time delay, it will take no more than a few hours for ppm level impurities with constant flow to cover all the active area of the catalyst or replace all the protons in the Nafion® membrane. However, impurities may need extra time to reach their functional sites because of resistance and flow characteristics in a real situation. As a tradeoff between testing hours and impurity transport capability, 100 hours are generally believed to be sufficient for impurities to show their initial effects. With this reasoning, the impurity test period in this research is set to 100 hours for the convenience of performance comparison.

The experimental setup is shown in Figure 1. Dry impurities are mixed with hydrogen to reach the desired concentrations. Since the target concentrations are very low (ppm or ppb level), the source impurity gases shown in Figure 1 are usually certified standard mixtures with the balance containing nitrogen or hydrogen to dilute impurities, which is necessary for controlling flow rates. After the mixing point, a gas chromatograph (HP 5890 II) is deployed to continuously verify the gas composition with a sampling rate of 10 standard cubic centimeters per minute (sccm) from the fully mixed gases.

Figure 1. Experiment schematics.

During the tests, UHP grade hydrogen (from AirGas®) and ultra zero grade air (from AirGas®) are used as fuel and oxidant. Cells are conditioned by running at constant voltage 0.6 V at 80°C with anode/cathode relative humidity (RH) of 100%/75%, without back pressure, gas stoichiometric flow 2/2, overnight. After conditioning, the initial test is started which normally continues operation for 100 hours to obtain a stable baseline. After that, the desired level of impurities is injected into the hydrogen stream to begin the impurity test. This process normally lasts for 100 hours. In order to ensure the data

reproducibility, each impurity at each concentration is tested at least twice. Performance loss rates with and without impurities are calculated and compared. The contaminant effects of impurities are then determined from the data.

The cell temperature is 80°C for all tests. Two sets of conditions are employed for the remaining test parameters. The first set is: current densities of 800 mA/cm², RH of 100%/75%, back pressure of 170/170 kPa gauge pressure (~25/25 psig, ambient pressure 1 atm), gas stoichiometric flow of 2/2, for anode/cathode, respectively. The other set is: current densities of 1000 mA/cm², RH of 75%/25%, back pressure of 50/50 kPa gauge pressure (~7/7 psig), gas stoichiometric flow of 1.2/2, for anode/cathode, respectively. The reason for employing test conditions with the higher current density is to accelerate performance loss due to the more stressful parameters (drier electrodes and higher current density).

In order to acquire uniform data, commercial fuel cell components are used in cell assemblies. All cells are assembled using hardware from Fuel Cell Technologies, catalyst coated membranes (CCMs) with the active area of 25 cm² from GORETM PRIMEA®, and gas diffusion layers (GDLs) 25BC from SIGRACET®. Cell compression is controlled by selecting appropriate thickness of Teflon® sealing gaskets to establish the load on the active area of the CCMs. The pinch is set to 20% of the total thickness of the CCM and two GDLs. Tests are conducted on fuel cell test stations with 890C/890CL electronic load from Scribner®.

The hydrogen crossover data and ECSA data are measured by linear sweep voltammetry and cyclic voltammetry to characterize the membrane status and electrocatalyst layers, respectively. In the tests, H₂ is fed into the counter electrode side at a flow rate of 250 sccm and nitrogen is fed into the working electrode side at a flow rate of 250 sccm. The voltage-scan range is from 0 V to 0.4 V and the voltage-scan rate is 2 mV/s for the linear sweep voltammetry tests. The voltage-scan range is from 0 V to 0.8 V and the voltage-scan rate is 20 mV/s for the cyclic voltammetry tests. Ambient conditions (room temperature and without back pressure) are employed.

In this paper, the voltage curves plotted in all the figures are internal resistance (IR) corrected. That is, IR loss has been added to the reported voltage. The IR value represents the ohmic resistance across the cell and is measured by the current interrupt technique. Therefore, it includes the bulk membrane proton resistance, the GDL electronic resistance, and contact resistance between the fuel cell components. In general, the majority of the IR comes from the membrane proton resistance since other resistances are small and stable compared with that of the membrane. The membrane proton resistance strongly depends on the membrane hydration level [29]. With this reasoning, the IR curves presented in the figures mostly indicate the resistance and hydration level of the membranes.

Since the goal of this research is to provide the first level view of the effects of impurities, ECSA data are not regularly measured. In future studies, electrochemical impedance spectroscopy and polarization curves [21, 22], as well as ECSA data would provide much more detailed information for understanding the contaminant effects of impurities.

3. Results and Discussion

3.1 Fuel cell performance analysis

PEM fuel cells have three types of performance losses. They are kinetic loss, ohmic loss, and mass transport loss. In the extended hour tests, cell performance loss can be increased due to the degradation of fuel cell components, *e.g.*, membrane degradation, catalyst degradation, and GDL degradation. Membrane degradation will change the proton conductivity and physical properties of the membrane. There are three types of membrane degradation, *i.e.*, thermal degradation, mechanical degradation, and chemical degradation [9, 48, 49]. Catalyst degradation is caused by changes in morphology and surface properties of the catalyst (especially the cathode catalyst) and the catalyst support materials (normally carbon particles) [50-52]. GDL degradation is caused by the gradual change of the hydrophobicity and gas permeability of GDLs during fuel cell operations [53-56].

In this research, since all cells are built using the same procedure, the performance loss should be similar for each test before impurities are introduced. The membranes are less likely to have thermal degradation since cells are operated with highly saturated reactants at 80°C. Because the test times are short (approximately 100 hours) and the test conditions are steady, GDL degradation is expected to be negligible. Membrane mechanical degradation is minimized by precisely controlling the assembling and operating processes. This is further verified by the consistent data obtained during the baseline tests. Membranes are more likely to have chemical degradation considering the corresponding degradation mechanisms. Catalyst degradation is another contributor to the performance loss considering the kinetic loss and ECSA loss in 100 hours.

After impurities are introduced, the performance degradation mechanisms become complicated. In addition to the performance degradation mechanisms mentioned above, extra cell performance loss can be induced by impurities through chemical attack on the membrane and adsorption on the catalyst surface. The extent of contaminant effects can be characterized by the difference in the degradation rates before and after introducing impurities.

3.2 Data report and analysis

3.2.1 Single impurity test, formaldehyde/formic acid/chloromethane/acetaldehyde/ethylene

In this section, formaldehyde, formic acid, chloromethane, acetaldehyde, and ethylene are tested as single impurities in hydrogen. The test condition for these impurities is, current density 800 mA/cm², cell temperature 80°C, RH of 100%/75%, back pressure of 170/170 kPa gauge pressure, gas flow stoichiometric of 2/2, for anode/cathode, respectively.

In the formaldehyde test, the source impurity is formaldehyde mixed with nitrogen. The baseline test uses hydrogen (from the test station) and nitrogen (from the impurity line) as the anode gas to simulate the dilution effects of nitrogen and obtain comparable data (the flow rate of nitrogen is the same as the flow rate used in the impurity test). From Figure 2, the voltage increases slightly and the internal

resistance decreases slightly while switching to the 1 ppm formaldehyde. This performance variation is believed to be caused by small changes in the gas supply (switching from N₂ to formaldehyde balance with N₂). After this performance variation, the cell voltage stabilizes and remains stable until the end of the test. During the baseline test, the voltage loss rate is 103.8 $\mu\text{V}/\text{hour}$. After introducing 1 ppm formaldehyde, the voltage loss rate changes to 132.6 $\mu\text{V}/\text{hour}$. The voltage loss rate increases approximately 29 $\mu\text{V}/\text{hour}$ after changing to the impurity, which is small compared with the voltage loss rate with hydrogen. Considering the normal performance variations in the test, the conclusion is that the voltage loss rate with 1 ppm formaldehyde is not significant. The internal resistance change rates are -34.7 $\mu\Omega\cdot\text{cm}^2/\text{hour}$ and 1.2 $\mu\Omega\cdot\text{cm}^2/\text{hour}$ before and after introducing formaldehyde, respectively. Though the change is at the level of one order of magnitude, the absolute value is still small, which means the internal resistance does not change much during the test process. The change is believed to be caused by the RH variation during replacing impurity gas supply (from N₂ to formaldehyde balance with N₂) as well. Since 1 ppm formaldehyde is not high enough to induce significant cell performance degradation, the formaldehyde concentration is increased to 5 ppm. Figure 3 shows the data of the 5 ppm formaldehyde test. The voltage loss rate at baseline is 30.5 $\mu\text{V}/\text{hour}$. After introducing 5 ppm formaldehyde, the voltage loss rate increases to 38.1 $\mu\text{V}/\text{hour}$. The IR change rate is changed from -11.2 $\mu\Omega\cdot\text{cm}^2/\text{hour}$ to -1.2 $\mu\Omega\cdot\text{cm}^2/\text{hour}$, respectively. These data do not show significant performance degradation either. Since 5 ppm formaldehyde in hydrogen does not induce significant cell performance degradation and can be easily achieved by hydrogen production, it is appropriate to stop testing formaldehyde at this concentration.

Figure 2. Impurity test with 1 ppm formaldehyde. Operating condition: current density 800 mA/cm^2 ; cell temperature 80°C ; RH A/C 100%/75%; back pressure A/C 170/170 kPa gauge pressure; gas flow stoichiometric A/C 2/2.

Figure 3. Impurity test with 5 ppm formaldehyde. Operating condition: current density 800 mA/cm^2 ; cell temperature 80°C ; RH A/C 100%/75%; back pressure A/C 170/170 kPa gauge pressure; gas flow stoichiometric A/C 2/2.

The impact of 2 ppm formic acid is shown in Figure 4. The cell voltage loss rate is $67 \mu\text{V}/\text{hour}$ at baseline compared with $34.6 \mu\text{V}/\text{hour}$ with 2 ppm formic acid in hydrogen, and the IR change rates are $11.7 \mu\Omega\cdot\text{cm}^2/\text{hour}$ at baseline and $14.7 \mu\Omega\cdot\text{cm}^2/\text{hour}$ with 2 ppm formic acid in hydrogen. During these tests, the voltage loss rates are comparable when working with and without 2 ppm formic acid. Therefore,

since this concentration (2 ppm formic acid in hydrogen) is high enough for hydrogen production, no further testing on formic acid is conducted.

Figure 4. Impurity test with 2 ppm formic acid. Operating condition: current density 800 mA/cm^2 ; cell temperature 80°C ; RH A/C 100%/75%; back pressure A/C 170/170 kPa gauge pressure; gas flow stoichiometric A/C 2/2.

The chloromethane impurity test is started at 1 ppm. From Figure 5, the cell voltage loss rate is $29.6 \text{ } \mu\text{V/hour}$ and the IR change rate is $6.8 \text{ } \mu\Omega\cdot\text{cm}^2/\text{hour}$ when working with 1 ppm chloromethane in hydrogen. Compared with the voltage loss rate of $27.3 \text{ } \mu\text{V/hour}$ and the IR change rate of $-24.5 \text{ } \mu\Omega\cdot\text{cm}^2/\text{hour}$ when working with pure hydrogen, the differences are very small. It is concluded that 1 ppm chloromethane in hydrogen does not induce significant cell performance degradation. Further tests have been conducted to study the effects of chloromethane at a higher concentration. Figure 6 shows the testing results of 19 ppm chloromethane in hydrogen. In this figure, the cell voltage loss rate is $30.9 \text{ } \mu\text{V/hour}$ and the IR change rate is $5.5 \text{ } \mu\Omega\cdot\text{cm}^2/\text{hour}$ at baseline. For comparison, the cell voltage loss rate is $43.4 \text{ } \mu\text{V/hour}$ and the IR change rate is $-9.3 \text{ } \mu\Omega\cdot\text{cm}^2/\text{hour}$ after switching to 19 ppm chloromethane in hydrogen. Cell performance does not change significantly. After that, a recovery test with pure hydrogen is conducted to further analyze the contaminant effects of 19 ppm chloromethane. In this stage, the cell voltage loss rate is $49.4 \text{ } \mu\text{V/hour}$ and the IR change rate is $10.3 \text{ } \mu\Omega\cdot\text{cm}^2/\text{hour}$.

These data confirm that 19 ppm chloromethane in hydrogen does not result in substantial fuel cell degradation. Since this concentration (19 ppm chloromethane in hydrogen) is high enough for hydrogen production, no further testing on chloromethane is conducted.

Figure 5. Impurity test with 1 ppm chloromethane. Operating condition: current density 800 mA/cm^2 ; cell temperature 80°C ; RH A/C 100%/75%; back pressure A/C 170/170 kPa gauge pressure; gas flow stoichiometric A/C 2/2.

Figure 6. Impurity Test with 19 ppm chloromethane. Operating condition: current density 800 mA/cm^2 ; cell temperature 80°C ; RH A/C 100%/75%; back pressure A/C 170/170 kPa gauge pressure; gas flow stoichiometric A/C 2/2.

The impurity concentration used for testing acetaldehyde is 30 ppm. From Figure 7, the voltage loss rate is 120.8 $\mu\text{V}/\text{hour}$ and the IR change rate is $-77.8 \mu\Omega\cdot\text{cm}^2/\text{hour}$ at baseline. After switching to 30 ppm acetaldehyde in hydrogen, the voltage loss rate is 115.0 $\mu\text{V}/\text{hour}$ and the IR change rate is $-20.5 \mu\Omega\cdot\text{cm}^2/\text{hour}$. These performance data are comparable. We conclude that 30 ppm acetaldehyde in hydrogen does not result in substantial fuel cell degradation. There is a voltage gap (approximately 22 mV) when switching from pure hydrogen to the impurity (acetaldehyde in hydrogen). Since the IR does not change simultaneously, this voltage gap should not be related to water re-distribution or RH fluctuation inside the cell [29]. Following the contaminant test, a recovery test is conducted. From Figure 7, the voltage loss is fully recovered by another voltage gap in the reverse direction after switching back to pure hydrogen. The reason for the voltage gap is not fully understood. It is presumably caused by the increased catalyst kinetic loss or mass transport loss (decrease of ECSA) since IR is stable in this period. After stopping acetaldehyde introduction, the adsorption of acetaldehyde on the catalyst surface is quickly flushed away due to the surplus of hydrogen. With the effective catalyst ECSA recovered, the performance improves. Additional work is needed to understand the mechanism in detail. In spite of that, it is safe to conclude that 30 ppm acetaldehyde in hydrogen has no permanent degradation effects on the cell performance. Since this concentration (30 ppm acetaldehyde in hydrogen) is high enough for cost effective hydrogen production, no further testing on acetaldehyde is required.

Figure 7. Impurity test with 30 ppm acetaldehyde. Operating condition: current density 800 mA/cm^2 ; cell temperature 80°C ; RH A/C 100%/75%; back pressure A/C 170/170 kPa gauge pressure; gas flow stoichiometric A/C 2/2.

Five percent ethylene in hydrogen is tested to determine the effects of ethylene. Figure 8 shows the results of the test. The voltage curves are stable though there is a small voltage drop after switching to the impurity. This voltage drop is approximately 5 mV and is believed to be mostly caused by the hydrogen dilution in the fuel cell anode [57]. Since the hydrogen supply is only 95% of the baseline flow rate, the hydrogen partial pressure is reduced which leads to the decrease of cell theoretical equilibrium voltage (which is approximately 0.8 mV) as defined by the Nernst equation. Additional performance drop is presumably caused by the increased hydrogen oxidation charge transfer resistance due to the hydrogen dilution [57]. In this test, the voltage loss rate is $54.9 \text{ } \mu\text{V}/\text{hour}$ and the IR change rate is $-97.4 \text{ } \mu\Omega\cdot\text{cm}^2/\text{hour}$ at baseline. After switching to the impurity, the voltage loss rate is $31.6 \text{ } \mu\text{V}/\text{hour}$ and the IR change rate is $-42.9 \text{ } \mu\Omega\cdot\text{cm}^2/\text{hour}$. These values are comparable and we conclude that five percent ethylene in hydrogen does not have significant contaminant effects on cell performance.

Figure 8. Impurity test with 5% ethylene. Operating condition: current density 800 mA/cm²; cell temperature 80°C; RH A/C 100%/75%; back pressure A/C 170/170 kPa gauge pressure; gas flow stoichiometric A/C 2/2.

Table 1 summarizes the results for this section.

Table 1. Single impurity tests with formaldehyde/formic acid/chloromethane/acetaldehyde/ethylene.

Operating condition: current density 800 mA/cm²; cell temperature 80°C; RH A/C 100%/75%; back pressure A/C 170/170 kPa gauge pressure; gas flow stoichiometric A/C 2/2.

Impurity	Concentration [ppm]	Voltage Loss Rate [μ V/hour], Baseline/Impurity	IR Change Rate [$\mu\Omega\cdot\text{cm}^2$ /hour], Baseline/Impurity
Formaldehyde, HCHO	1	103.8/132.6	-34.7/1.2
Formaldehyde, HCHO	5	30.5/38.1	-11.2/1.2
Formic Acid, HCOOH	2	67.0/34.6	11.7/14.7
Chloromethane, CH ₃ Cl	1	27.3/29.6	-24.5/6.8
Chloromethane, CH ₃ Cl	19	30.9/43.4	5.5/-9.3
Acetaldehyde, CH ₃ CHO	30	120.8/115.0	-77.8/-20.5
Ethylene, C ₂ H ₄	50000	54.9/31.6	-97.4/-42.9

3.2.2 Single impurity test, ethylene/toluene/benzene

For the remaining tests, the following conditions are employed (current density of 1000 mA/cm², cell temperature 80°C, RH 75%/25%, back pressure 50/50 kPa gauge pressure, and stoichiometric flow 1.2/2, for anode and cathode, respectively). The reason for changing testing conditions is that the cells only show very low performance loss under the previous working condition. In order to obtain significant

performance loss, more stressful conditions which includes drier anode and cathode and a higher current density, are employed. Before employing this new test condition, it is important to test it with an impurity known for not resulting in substantial fuel cell degradation.

One percent ethylene in hydrogen has been chosen to conduct the test. Figure 9 shows the details. The data indicates some small changes in the IR curve. This is believed to be caused by water management changes. Since the stoichiometric flow of anode is only 1.2, it is possible that liquid water accumulates and then periodically clears away to cause the IR fluctuations. In summary, the voltage loss rate is 184.4 $\mu\text{V}/\text{hour}$ and the IR change rate is 98.2 $\mu\Omega\cdot\text{cm}^2/\text{hour}$ at baseline. After switching to the impurity, the voltage loss rate is 217.6 $\mu\text{V}/\text{hour}$ and the IR change rate is 65.6 $\mu\Omega\cdot\text{cm}^2/\text{hour}$. These values are comparable so we can proceed with the testing.

Figure 9. Impurity test with 1% ethylene. Operating condition: current density 1000 mA/cm^2 ; cell temperature 80°C; RH A/C 75%/25%; back pressure A/C 50/50 kPa gauge pressure; gas flow stoichiometric A/C 1.2/2.

The toluene test is started with the concentration of 20 ppm. Figure 10 shows the test details. From this figure, the voltage loss rate is 40.8 $\mu\text{V}/\text{hour}$ and the IR change rate is 0.2 $\mu\Omega\cdot\text{cm}^2/\text{hour}$ when testing with hydrogen. After introducing toluene, the voltage loss rate is 63.7 $\mu\text{V}/\text{hour}$ and the IR change rate is 6.3 $\mu\Omega\cdot\text{cm}^2/\text{hour}$. Though the voltage loss rate has increased a little, this increase is very limited.

Therefore, we believe that 20 ppm toluene in hydrogen does not result in substantial fuel cell degradation. Since this concentration (20 ppm toluene in hydrogen) is high enough for hydrogen production, no further testing on toluene is required.

Figure 10. Impurity test with 20 ppm toluene. Operating condition: current density 1000 mA/cm²; cell temperature 80°C; RH A/C 75%/25%; back pressure A/C 50/50 kPa gauge pressure; gas flow stoichiometric A/C 1.2/2.

10 ppm benzene is added to hydrogen and tested to determine the effects of contamination. From Figure 11, the voltage loss rate is 62.3 μ V/hour and the IR change rate is 37.1 $\mu\Omega\cdot\text{cm}^2$ /hour at baseline. After benzene is introduced, the voltage loss rate is 89.8 μ V/hour and the IR change rate is 33.8 $\mu\Omega\cdot\text{cm}^2$ /hour. The voltage loss rates are at about the same level with and without the impurity. So we can conclude that no significant degradation is found. Since this concentration (10 ppm benzene in hydrogen) is high enough for hydrogen production, no further testing on benzene is required.

Figure 11. Impurity test with 10 ppm benzene. Operating condition: current density 1000 mA/cm²; cell temperature 80°C; RH A/C 75%/25%; back pressure A/C 50/50 kPa gauge pressure; gas flow stoichiometric A/C 1.2/2.

As a summary for all the tests in this section, the results are listed in Table 2.

Table 2. Single impurity tests with ethylene/toluene/benzene. Operating condition: current density 1000 mA/cm²; cell temperature 80°C; RH A/C 75%/25%; back pressure A/C 50/50 kPa gauge pressure; gas flow stoichiometric A/C 1.2/2.

Impurity	Concentration [ppm]	Voltage Loss Rate [μV/hour], Baseline/Impurity	IR Change Rate [μΩ·cm ² /hour], Baseline/Impurity
Ethylene, C ₂ H ₄	10000	184.4/217.6	98.2/65.6
Toluene, C ₇ H ₈	20	40.8/63.7	0.2/6.3
Benzene, C ₆ H ₆	10	62.3/89.8	37.1/33.8

3.2.3 Mixed contaminant test, carbon monoxide/benzene/toluene

In the previous tests, the impurities are tested separately. But in practice, impurities are likely mixed together in a typical hydrogen supply system. The effects of hydrogen impurities on PEM fuel cells may be additive, or the impurities may interact with each other causing the resulting contaminant effects to differ from the summation of the individual effects. In order to investigate the mixed effects of multiple impurities, “cocktail tests” with mixed impurities are devised and tested.

In this section, carbon monoxide, benzene, and toluene have been selected for the first mixed contaminant test. This test is initiated on pure hydrogen for a period of 108 hours to establish a baseline. Once the baseline is obtained, an impurity test with 10 ppm benzene and 1 ppm carbon monoxide in hydrogen is initiated. This step lasts for 100 hours. A recovery step with pure hydrogen lasting 51 hours is conducted to evaluate the possibility of recovery. The mixed contaminant test is then continued with another impurity (10 ppm toluene) added to the previous mixture. This test is conducted for a period of 114 hours, and then it is followed by the second recovery test which lasts for 49 hours. Afterwards, 1 ppm carbon monoxide in hydrogen is provided to the cell for 143 hours to measure the contaminant effects of carbon monoxide alone. The entire mixed contaminant test is completed after the third recovery test which lasts for 28 hours. The test data are shown in Figure 12. The corresponding voltage loss rates and IR change rates are listed in Table 3.

Figure 12. Mixed contaminant test with carbon monoxide, benzene, and toluene. Operating condition: current density 1000 mA/cm²; cell temperature 80°C; RH A/C 75%/25%; back pressure A/C 50/50 kPa gauge pressure; gas flow stoichiometric A/C 1.2/2.

Table 3. Mixed test with carbon monoxide, benzene, and toluene. Operating condition: current density 1000 mA/cm²; cell temperature 80°C; RH A/C 75%/25%; back pressure A/C 50/50 kPa gauge pressure; gas flow stoichiometric A/C 1.2/2.

Test Step	Test	Duration [hour]	Voltage Loss Rate [$\mu\text{V}/\text{hour}$]	IR Change Rate [$\mu\Omega\cdot\text{cm}^2/\text{hour}$]
1	H ₂ , baseline	108	38.6	27.4
2	10 ppm C ₆ H ₆ +1 ppm CO	100	72.5	58.2
3	H ₂ , recovery, the 1 st time	51	35.4	-58.5
4	10 ppm C ₆ H ₆ + 1 ppm CO+ 10 ppm C ₇ H ₈	114	111.7	42.8
5	H ₂ , recovery, the 2 nd time	49	20.6	24.7
6	1 ppm CO	143	78.7	30.3
7	H ₂ , recovery, the 3 rd time	28	3.2	26

The cell baseline exhibits a voltage loss of 38.6 $\mu\text{V}/\text{hour}$, and the first and second recovery tests show voltage losses of 35.4 $\mu\text{V}/\text{hour}$ and 20.6 $\mu\text{V}/\text{hour}$, respectively. These values are of similar magnitude. The voltage loss rate of the third recovery test is 3.2 $\mu\text{V}/\text{hour}$ and is far lower than those of the other two recovery tests. In general, all the performance loss is shown to be recoverable after changing back to pure hydrogen.

It is seen from Table 3 that the dominant contaminant effects are from carbon monoxide [58-60]. The voltage loss rate of 1 ppm carbon monoxide is approximately two times higher than that of the pure hydrogen. 1 ppm carbon monoxide plus 10 ppm benzene in hydrogen has a voltage loss rate of 72.5 $\mu\text{V}/\text{hour}$ which is similar to that of 1 ppm carbon monoxide alone (78.7 $\mu\text{V}/\text{hour}$). 1 ppm carbon monoxide, 10 ppm benzene, and 10 ppm toluene together have a voltage loss rate of 111.7 $\mu\text{V}/\text{hour}$ which provides a somewhat higher performance loss. It is suspected that 10 ppm benzene and 10 ppm toluene have some collective contaminant effects in the presence of carbon monoxide though their effects are not significant enough when tested alone.

There are two possible reasons for this. The first reason is that when the total concentration of impurities is high enough, the combined contaminant effects can be measurable though the effects of each impurity are very small or negligible. The second reason is that when different impurities are mixed together, there may be an additive effect that intensifies the degradation. The detailed mechanism is still not clear and needs to be studied further.

From Figure 12, voltage and IR gaps are found when switching from impurities to pure hydrogen. These gaps are presumably caused by RH fluctuation and carbon monoxide inside the cell. In the process of introducing or removing impurities, the flow rate and dew point of the anode gas from test stations are changed. Therefore, the voltage and internal resistance can have some variations. In addition to that, since CO-Pt bonds are stronger than H-Pt bonds, the adsorption of carbon monoxide on Pt sites can reduce the available ECSA for hydrogen oxidation reactions. This decrease of ECSA continuously increases cell performance loss. After removing the impurities, the occupied CO-Pt bonds can be consumed through the reaction

This is indicated in the figure as an increase in voltage.

3.2.4 Initial cocktail test, the specification concentration level

Five impurities are selected for evaluation of the initial cocktail test. These impurities are 0.2 ppm carbon monoxide, 4 ppb hydrogen sulphide, 0.2 ppm formic acid, 2 ppm benzene, and 0.1 ppm ammonia. The corresponding concentration is called the “specification concentration level”. Among them, carbon monoxide is a well known contaminant for PEM fuel cells and extensive research has been done on it [2, 26, 35, 61-65]. Hydrogen sulphide is also a well known contaminant for PEM fuel cells [26, 66-68]. In addition, ammonia can contaminate the membrane and the electrodes of PEM fuel cells [21-23], and formic acid easily decomposes into carbon monoxide which is expected to result in a performance loss though it does not show significant contaminant effects at 2 ppm in our tests [28, 69]. Finally, benzene has been identified in literatures as a Pt contaminant by several surface science techniques [60, 70].

Figure 13 shows the data of the specification concentration level cocktail test. No voltage loss is detected in the first 60 hours when the cell operates with hydrogen and the IR change rate is -29.5 $\mu\Omega\cdot\text{cm}^2/\text{hour}$. After switching to the impurities, the voltage loss rate is 27.3 $\mu\text{V}/\text{hour}$ and the IR change

rate is $5.7 \mu\Omega\cdot\text{cm}^2/\text{hour}$ for 440 hours. This voltage loss rate is very small and similar to that of pure hydrogen. Considering that the test term is long (440 hours) and performance variations are common in a long period, it is reasonable to conclude that no significant cell performance degradation is found in this test.

Figure 13. Specification concentration level cocktail test, with 0.2 ppm carbon monoxide, 4 ppb hydrogen sulphide, 0.2 ppm formic acid, 2 ppm formic acid, 2 ppm benzene, and 0.1 ppm ammonia. Operating condition: current density $1000 \text{ mA}/\text{cm}^2$; cell temperature 80°C ; RH A/C 75%/25%; back pressure A/C 50/50 kPa gauge pressure; gas flow stoichiometric A/C 1.2/2.

3.2.5 Intensified cocktail test, five times the specification concentration level

In the intensified cocktail test, impurities of five times the specification concentration level are tested to determine the contaminant effects of this higher concentration cocktail. The components include 1 ppm carbon monoxide, 20 ppb hydrogen sulphide, 1 ppm formic acid, 10 ppm benzene, and 0.5 ppm ammonia.

The intensified cocktail test is initiated with a pure hydrogen test for approximately 145 hours to establish a performance baseline. Once the baseline is obtained, the test with impurities of five times the specification concentration level in hydrogen is started. This phase lasts for 206 hours. The entire test is completed after finishing a short hydrogen recovery test which lasts for 29 hours.

Table 4 provides the test results of Figure 14. From the data, the baseline shows a voltage loss of 65.2 $\mu\text{V}/\text{hour}$ and an IR change rate of 19.1 $\mu\Omega\cdot\text{cm}^2/\text{hour}$. After switching to the five times the specification concentration level cocktail, the voltage and internal resistance curves indicate sharp performance changes. From Figure 14, the voltage decreases approximately 20 mV and the IR increases approximately 12.6 $\mu\Omega\cdot\text{cm}^2$ in 2 hours. Since the concentrations of the impurities in the cocktail are not high and their contaminant effects are not expected to become quickly evident, these changes are believed to be mostly related to the changes inside the cell. After switching to the cocktail, dry impurity gases are mixed with humidified hydrogen from the test station and introduced to the anode inlet. In order to keep the same RH and total flow rate as the baseline, the dew point of the wet hydrogen from the test station is increased from 73°C to 79°C and the flow rate is decreased from 210 sccm to 147 sccm. The large mixing ratio of dry impurities and wet hydrogen can change the water distribution inside the fuel cell and requires time to reach a new balance. This can lead to a resistance change and voltage variation of the whole cell.

Table 4. Cocktail test with impurities of five times the specification concentration level. Operating condition: current density 1000 mA/cm²; cell temperature 80°C; RH A/C 75%/25%; back pressure A/C 50/50 kPa gauge pressure; gas flow stoichiometric A/C 1.2/2.

Test	Duration [hour]	Voltage Loss rate [$\mu\text{V}/\text{hour}$]	IR Change Rate [$\mu\Omega\cdot\text{cm}^2/\text{hour}$]
H ₂ , baseline	145	65.2	-19.1
5 times the spec level cocktail	206	323.7	161.7
H ₂ , recovery, the 2 nd time	29	0	-89.3

Figure 14. Five times of the specification concentration level cocktail test, with 1 ppm carbon monoxide, 20 ppb hydrogen sulphide, 1 ppm formic acid, 10 ppm benzene, and 0.5 ppm ammonia. Operating condition: current density 1000 mA/cm^2 ; cell temperature 80°C ; RH A/C 75%/25%; back pressure A/C 50/50 kPa gauge pressure; gas flow stoichiometric A/C 1.2/2.

After the initial sharp shift, the cell performance starts to degrade steadily. The voltage loss rate is $323.7 \text{ } \mu\text{V/hour}$ which is approximately five times higher than that of pure hydrogen. The IR change rate is $161.7 \text{ } \mu\Omega\cdot\text{cm}^2/\text{hour}$ and the IR is increased $33.3 \text{ m}\Omega\cdot\text{cm}^2$ in 206 hours. These data indicate significant performance loss.

Since it is difficult to quantify the individual contaminant effects of each impurity in this cocktail test, qualitative analysis is necessary to understand the performance altering mechanisms. From Figure 14, catalyst contamination is one of the most important reasons for leading to the rapid performance loss because carbon monoxide and hydrogen sulphide are well known for causing kinetic loss and decrease of ECSA. In addition to kinetic loss and mass transport loss induced by the decrease of ECSA, ohmic loss is another important contributor to the rapid performance loss. From the figure, the internal resistance increases significantly in this period. The increase of the internal resistance is believed to be partially induced by ammonia reacting with protons to produce ammonium ions (ammonia cation). The ammonium ions may repel water from the membrane and electrodes to increase the internal resistance

[21] . The ammonium ions can replace protons in the Nafion® membrane and protons in the ionomer of the electrodes to decrease proton concentration as well, which leads to cell voltage drop [21, 22].

It is still unclear that if the other two components in the cocktail, 1 ppm formic acid and 10 ppm benzene, play any roles in the performance loss. From the results of sole impurity tests, these two impurities do not show significant contaminant effects when they are tested alone. It seems that these two chemicals do not result in substantial fuel cell degradation (the induced performance loss in the cocktail test is not very tremendous). However, further study still needs to be done to determine the exact roles of these impurities on cell performance when they are tested in the cocktail.

After completing the test with impurities and switching back to pure hydrogen, the performance is mostly recovered. The cell voltage and internal resistance are recovered to the values that would be expected for working continuously with pure hydrogen. The voltage loss rate and internal resistance change rate are recovered to the same level as the initial baseline as well. This means the performance loss induced by the catalyst and membrane contamination is mostly recoverable. This is presumably due to the low concentration of impurities. After stopping the cocktail impurities, it is fairly easy to remove the contaminants from both the electrodes and the electrolyte. The absorbed carbon monoxide on catalyst can be eliminated through reaction (1). Similarly, the remaining ammonium ions can be oxidized to nitrogen and/or nitric oxides or volatilized through the reaction (2) and (3) because of the equilibrium between the ammonium ions in the membrane and gas phase ammonia [21, 23]. Though some contaminants may be left (mainly Pt-S_{ads} induced by hydrogen sulphide) [33, 68], they are too diluted to show their effects.

The ECSA data is checked before the baseline and after the recovery test and is shown in Figure 15. The BoT ECSA of anode is 63.2 m² Pt/g Pt. At the end of the test (EoT), the ECSA of anode is 62.2 m² Pt/g Pt.

The anode ECSA does not change much. The BoT ECSA of cathode is 73.2 m² Pt/g Pt. At EoT, the ECSA is 60.0 m² Pt/g Pt. The decrease is approximately 18.1%. Considering the operating hours (around 380 hours) and the high oxygen reduction reaction rate at 1000 mA/cm², this ECSA loss is reasonable for normal fuel cell operations without impurities. This means the ECSA does not have much permanent change in the cocktail test.

Figure 15. ECSA change of the cell for five times of the specification concentration level cocktail test.

In order to determine the integrity of the cell, hydrogen crossover tests are conducted to evaluate the status of the membrane. It is found that the hydrogen crossover current density is increased from 1 mA/cm² to 37 mA/cm² during the entire test period. Considering the total test time is relatively short (around 380 hours), the membrane is expected to be in good condition if working without impurities. The increased hydrogen crossover rate indicates significant degradation of the membrane caused by the cocktail test. Since the hydrogen crossover rate (37 mA/cm²) is low compared with the operating current density of 1000 mA/cm², the membrane degradation would not contribute significantly to the performance drop at the operating current density (1000 mA/cm²). However, the impurities may cross the membrane resulting in effects on the cathode oxygen reduction reaction.

Figure 16. I-V curves of the intensified cocktail test. Operating condition: cell temperature 80°C; RH A/C 100%/75%; back pressure A/C 0/0 kPa gauge pressure; gas flow stoichiometric A/C 2/2.

Figure 16 shows the I-V curves. From the I-V curves, the voltage at open circuit decreases approximately 15 mV. The cell shows a reduction in performance as well. The calculated average voltage loss rate at 1 A/cm² is approximately 60 μ V/hour during the entire test period and is comparable with the voltage loss rate with pure hydrogen. Considering the open circuit voltage drop and the normal voltage decay at 1 A/cm², the cell voltage loss is believed to be due to degradation rather than contamination.

From the data, five times the specification concentration level cocktail shows significant contamination effects on cell performance in the 206 hours test period. Some of the impurities, such as hydrogen sulphide and carbon monoxide, can affect catalyst and cause kinetic loss and mass transport loss. Other impurities, such as ammonia, can affect the membrane and electrodes to cause ohmic loss. From the results of the cocktail test, the performance loss appears to be temporary (at least in the 206 hours test period). After switching back to pure hydrogen, the performance loss is mostly recovered. However, an increased hydrogen crossover current density is detected in this test.

4. Summary

In this research, several impurities are introduced into the anode of PEM fuel cells to test their effects as contaminants. It is found that 5 ppm formaldehyde, 2 ppm formic acid, 19 ppm chloromethane, 30 ppm acetaldehyde, 5% ethylene, 20 ppm toluene, and 10 ppm benzene in hydrogen do not result in substantial fuel cell degradation when they are tested alone. Beyond single impurity tests, cocktail tests are conducted to check the collective contaminant effects of impurities on cell performance. The specification concentration level cocktail, which includes 0.2 ppm carbon monoxide, 4 ppb hydrogen sulphide, 0.2 ppm formic acid, 2 ppm benzene, and 0.1 ppm ammonia, does not show significant contaminant effects on cell performance. On the other hand, the five times the specification concentration level cocktail, which includes 1 ppm carbon monoxide, 20 ppb hydrogen sulphide, 1 ppm formic acid, 10 ppm benzene, and 0.5 ppm ammonia, results in significant contaminant effects. After the five times the specification concentration cocktail is removed, the cell performance is mostly recovered though the membrane is permanently damaged.

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References

- [1] EG&G Technical Services I. Fuel Cell Handbook. 7th ed: U.S. Department of Energy; 2004.
- [2] Hubert A. Gasteiger NMM, Philip N. Ross, Jr. H₂ and CO Electrooxidation on Well-Characterized Pt, Ru and Pt-Ru. 1. Rotating Disk Electrode Studies of the Pure Gases Including Temperature Effects. *J Phys Chem.* 1995;99:8290-301.
- [3] Wilson MS, Valerio JA, Gottesfeld S. Low platinum loading electrodes for polymer electrolyte fuel cells fabricated using thermoplastic ionomers. *Electrochimica Acta.* 1995;40:355-63.
- [4] Wagner FT, Gasteiger HA, Makharia R, Neyerlin KC, Thompson EL, Yan SG. Catalyst Development Needs and Pathways for Automotive PEM Fuel Cells. *ECS Transactions.* 2006;3:19-29.
- [5] Lin R-B, Shih S-M. Kinetic analysis of the hydrogen oxidation reaction at Nafion film covered Pt-black rotating disk electrodes. *Journal of the Chinese Institute of Chemical Engineers.* 2008;39:475-81.
- [6] Martín AJ, Chaparro AM, Folgado MA, Rubio J, Daza L. Rotating disk electrode analysis of oxygen reduction at platinum particles under limiting diffusion conditions. *Electrochimica Acta.* 2009;54:2209-17.
- [7] Sethuraman VA, Weidner JW, Haug AT, Pemberton M, Protsailo LV. Importance of catalyst stability vis-à-vis hydrogen peroxide formation rates in PEM fuel cell electrodes. *Electrochimica Acta.* 2009;54:5571-82.
- [8] Maric R, Roller JM, Neagu R, Fatih K, Tuck A. Low Pt Thin Cathode Layer Catalyst Layer by Reactive Spray Deposition Technology. *ECS Transactions.* 2008;12:59-63.
- [9] Wu J, Yuan XZ, Martin JJ, Wang H, Zhang J, Shen J, et al. A review of PEM fuel cell durability: Degradation mechanisms and mitigation strategies. *Journal of Power Sources.* 2008;184:104-19.
- [10] Keith Wipke SS, Jennifer Kurtz, Todd Ramsden, Christ Ainscough, Genevieve Saur. Controlled Hydrogen Fleet and Infrastructure Analysis. 2011 DOE Annual Merit Review and Peer Evaluation Meeting: National Renewable Energy Laboratory (NREL); 2011.
- [11] Fuel Cell Technologies Office Multi-Year Research, Development and Demonstration Plan. <http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/>: U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE); 2012.
- [12] ClearEdge. HTAC Meeting2010.
- [13] Galperin D, Khalatur P, Khokhlov A. Morphology of Nafion Membranes: Microscopic and Mesoscopic Modeling. 2009. p. 453-83.
- [14] Mauritz KA, Moore RB. State of Understanding of Nafion. *Chemical Reviews.* 2004;104:4535-86.
- [15] Lee J-R, Kim N-Y, Lee M-S, Lee S-Y. SiO₂-coated polyimide nonwoven/Nafion composite membranes for proton exchange membrane fuel cells. *Journal of Membrane Science.* 2011;367:265-72.
- [16] Jao T-C, Jung G-B, Kuo S-C, Tzeng W-J, Su A. Degradation mechanism study of PTFE/Nafion membrane in MEA utilizing an accelerated degradation technique. *International Journal of Hydrogen Energy.* 2012.
- [17] Maldonado L, Perrin J-C, Dillet J, Lottin O. Characterization of polymer electrolyte Nafion membranes: Influence of temperature, heat treatment and drying protocol on sorption and transport properties. *Journal of Membrane Science.* 2012;389:43-56.
- [18] Liu F, Yi B, Xing D, Yu J, Zhang H. Nafion/PTFE composite membranes for fuel cell applications. *Journal of Membrane Science.* 2003;212:213-23.
- [19] Park SM, O'Brien TJ. Effects of several trace contaminants on fuel cell performance. 1979. p. Medium: X; Size: Pages: 27.
- [20] http://www1.eere.energy.gov/hydrogenandfuelcells/production/natural_gas.html. The Office of Energy Efficiency and Renewable Energy; 2012.

- [21] Zhang X, Serincan MF, Pasaogullari U, Molter T. Contamination of Membrane-Electrode Assemblies by Ammonia in Polymer Electrolyte Fuel Cells. *ECS Transactions*. 2009;25:1565-74.
- [22] Uribe FA, Gottesfeld S, Zawodzinski TA. Effect of Ammonia as Potential Fuel Impurity on Proton Exchange Membrane Fuel Cell Performance. *Journal of The Electrochemical Society*. 2002;149:A293-A6.
- [23] Halseid R, Vie PJS, Tunold R. Effect of ammonia on the performance of polymer electrolyte membrane fuel cells. *Journal of Power Sources*. 2006;154:343-50.
- [24] Soto HJ, Lee W-k, Van Zee JW, Murthy M. Effect of Transient Ammonia Concentrations on PEMFC Performance. *Electrochemical and Solid-State Letters*. 2003;6:A133-A5.
- [25] Institute JAR. Influence of Impurities in Hydrogen on Fuel Cell Performance. Influence of Impurities in Hydrogen on Fuel Cell Performance. United States Department of Energy Office of Energy Efficiency and Renewable Energy 2004.
- [26] Cheng X, Shi Z, Glass N, Zhang L, Zhang J, Song D, et al. A review of PEM hydrogen fuel cell contamination: Impacts, mechanisms, and mitigation. *Journal of Power Sources*. 2007;165:739-56.
- [27] Freni S, Mondello N, Cavallaro S, Cacciola G, Parmon VN, Sobyannin VA. Hydrogen Production by Steam Reforming of Ethanol: A Two Step Process. *Reaction Kinetics and Catalysis Letters*. 2000;71:143-52.
- [28] Narusawa K, Hayashida M, Kamiya Y, Roppongi H, Kurashima D, Wakabayashi K. Deterioration in fuel cell performance resulting from hydrogen fuel containing impurities: poisoning effects by CO, CH₄, HCHO and HCOOH. *JSAE Review*. 2003;24:41-6.
- [29] Wang X, Huang X, Bonville LJ, Russell Kunz H, Perry ML, Condit D. Impact of In-Cell Water Management on the Endurance of Polymer Electrolyte Membrane Fuel Cells. *Journal of The Electrochemical Society*. 2014;161:F761-F9.
- [30] Wang X, Qi J, Ozdemir O, Uddin A, Pasaogullari U, Bonville LJ, et al. Ca²⁺ as an Air Impurity in Polymer Electrolyte Membrane Fuel Cells. *Journal of The Electrochemical Society*. 2014;161:F1006-F14.
- [31] Zhang X, Galindo HM, Garces HF, Baker P, Wang X, Pasaogullari U, et al. Influence of Formic Acid Impurity on Proton Exchange Membrane Fuel Cell Performance. *Journal of The Electrochemical Society*. 2010;157:B409-B14.
- [32] Qi J, Wang X, Pasaogullari U, Bonville L, Molter T. Effect of Al³⁺ Contaminant on Polymer Electrolyte Fuel Cell Performance. *Journal of The Electrochemical Society*. 2013;160:F916-F22.
- [33] Mohtadi R, Lee W-k, Cowan S, Van Zee JW, Murthy M. Effects of Hydrogen Sulfide on the Performance of a PEMFC. *Electrochemical and Solid-State Letters*. 2003;6:A272-A4.
- [34] Qi Z, Kaufman A. Enhancement of PEM fuel cell performance by steaming or boiling the electrode. *Journal of Power Sources*. 2002;109:227-9.
- [35] Zamel N, Li X. Transient analysis of carbon monoxide poisoning and oxygen bleeding in a PEM fuel cell anode catalyst layer. *International Journal of Hydrogen Energy*. 2008;33:1335-44.
- [36] Lopes T, Paganin VA, Gonzalez ER. The effects of hydrogen sulfide on the polymer electrolyte membrane fuel cell anode catalyst: H₂S–Pt/C interaction products. *Journal of Power Sources*. 2011;196:6256-63.
- [37] de Bruijn FA, Dam VAT, Janssen GJM. Review: Durability and Degradation Issues of PEM Fuel Cell Components. *Fuel Cells*. 2008;8:3-22.
- [38] SAE International. Hydrogen Fuel Quality for Fuel Cell Vehicles. SAE International Surface Vehicle Standard, . http://standards.sae.org/j2719_201109/2011. p. 14.
- [39] St-Pierre J, Zhai Y, Angelo M. Quantitative ranking criteria for PEMFC contaminants. *International Journal of Hydrogen Energy*. 2012;37:6784-9.
- [40] St-Pierre J, Angelo M, Zhai Y. Focusing Research by Developing Performance Related Selection Criteria for PEMFC Contaminants. *ECS Transactions*. 2011;41:279-86.
- [41] St-Pierre J, Jia N, Rahmani R. PEMFC Contamination Model: Competitive Adsorption Demonstrated with NO₂. *Journal of The Electrochemical Society*. 2008;155:B315-B20.

- [42] St-Pierre J. PEMFC contaminant tolerance limit – Foreign cations in ionomers. *International Journal of Hydrogen Energy*. 2011;36:5527-35.
- [43] Zhai Y, St-Pierre J, Angelo MS. The Impact of Operating Conditions on the Performance effect of Selected Airborne PEMFC Contaminants. *ECS Transactions*. 2013;50:635-47.
- [44] Ge J, St-Pierre J, Zhai Y. PEMFC cathode catalyst contamination evaluation with a RRDE-Acetonitrile. *Electrochimica Acta*. 2014;134:272-80.
- [45] Uddin MA, Wang X, Qi J, Ozdemir MO, Bonville LJ, Pasaogullari U, et al. Effects of Chloride Contamination on PEFCs. *ECS Transactions*. 2013;58:543-53.
- [46] Li H, Wang H, Qian W, Zhang S, Wessel S, Cheng TTH, et al. Chloride contamination effects on proton exchange membrane fuel cell performance and durability. *Journal of Power Sources*. 2011;196:6249-55.
- [47] Lopes T, Paganin VA, Gonzalez ER. Hydrogen sulfide tolerance of palladium–copper catalysts for PEM fuel cell anode applications. *International Journal of Hydrogen Energy*. 2011;36:13703-7.
- [48] Rodgers MP, Bonville LJ, Kunz HR, Slattery DK, Fenton JM. Fuel Cell Perfluorinated Sulfonic Acid Membrane Degradation Correlating Accelerated Stress Testing and Lifetime. *Chemical Reviews*. 2012;112:6075-103.
- [49] Borup R, Meyers J, Pivovar B, Kim YS, Mukundan R, Garland N, et al. Scientific Aspects of Polymer Electrolyte Fuel Cell Durability and Degradation. *Chemical Reviews*. 2007;107:3904-51.
- [50] Antolini E. Formation, microstructural characteristics and stability of carbon supported platinum catalysts for low temperature fuel cells. *Journal of Materials Science*. 2003;38:2995-3005.
- [51] Xie J, Wood DL, More KL, Atanassov P, Borup RL. Microstructural Changes of Membrane Electrode Assemblies during PEFC Durability Testing at High Humidity Conditions. *Journal of The Electrochemical Society*. 2005;152:A1011-A20.
- [52] Ferreira PJ, la O' GJ, Shao-Horn Y, Morgan D, Makharia R, Kocha S, et al. Instability of Pt / C Electrocatalysts in Proton Exchange Membrane Fuel Cells: A Mechanistic Investigation. *Journal of The Electrochemical Society*. 2005;152:A2256-A71.
- [53] J. Frisk WB, M. Hicks, M. Kurkowski, R. Atanasoski, A. Schmoeckel. 2004 Fuel Cell Seminar, San Antonio, TX, USA. 2004.
- [54] Kangasniemi KH, Condit DA, Jarvi TD. Characterization of Vulcan Electrochemically Oxidized under Simulated PEM Fuel Cell Conditions. *Journal of The Electrochemical Society*. 2004;151:E125-E32.
- [55] Lee C, Mérida W. Gas diffusion layer durability under steady-state and freezing conditions. *Journal of Power Sources*. 2007;164:141-53.
- [56] Schulze M, Wagner N, Kaz T, Friedrich KA. Combined electrochemical and surface analysis investigation of degradation processes in polymer electrolyte membrane fuel cells. *Electrochimica Acta*. 2007;52:2328-36.
- [57] Boillot M, Bonnet C, Jatroutakis N, Carre P, Didierjean S, Lapique F. Effect of Gas Dilution on PEM Fuel Cell Performance and Impedance Response. *Fuel Cells*. 2006;6:31-7.
- [58] Baschuk JJ, Li X. Carbon monoxide poisoning of proton exchange membrane fuel cells. *International Journal of Energy Research*. 2001;25:695-713.
- [59] Lebedeva NP, Koper MTM, Feliu JM, van Santen RA. Mechanism and kinetics of the electrochemical CO adlayer oxidation on Pt(111). *Journal of Electroanalytical Chemistry*. 2002;524-525:242-51.
- [60] Jasen PV, Brizuela G, Padin Z, Gonzalez EA, Juan A. Benzene and carbon monoxide co-adsorption on Pt(111): a theoretical study. *Applied Surface Science*. 2004;236:394-405.
- [61] de Becdelièvre AM, de Becdelièvre J, Clavilier J. Electrochemical oxidation of adsorbed carbon monoxide on platinum spherical single crystals : Effect of anion adsorption. *Journal of Electroanalytical Chemistry*. 1990;294:97-110.
- [62] Baschuk JJ, Li X. Carbon monoxide poisoning of proton exchange membrane fuel cells. *Fuel and Energy Abstracts*. 2002;43:260-.

- [63] Chu HS, Wang CP, Liao WC, Yan WM. Transient behavior of CO poisoning of the anode catalyst layer of a PEM fuel cell. *Journal of Power Sources*. 2006;159:1071-7.
- [64] Selvaraj V, Grace AN, Alagar M. Electrocatalytic oxidation of formic acid and formaldehyde on nanoparticle decorated single walled carbon nanotubes. *Journal of Colloid and Interface Science*. 2009;333:254-62.
- [65] Yan W-M, Chu H-S, Lu M-X, Weng F-B, Jung G-B, Lee C-Y. Degradation of proton exchange membrane fuel cells due to CO and CO₂ poisoning. *Journal of Power Sources*. 2009;188:141-7.
- [66] Mohtadi R, Lee WK, Cowan S, Van Zee JW, Murthy M. Effects of Hydrogen Sulfide on the Performance of a PEMFc. *Electrochemical and Solid-State Letters*. 2003;6:A272-A4.
- [67] Mohtadi R, Lee WK, Van Zee JW. The effect of temperature on the adsorption rate of hydrogen sulfide on Pt anodes in a PEMFC. *Applied Catalysis B: Environmental*. 2005;56:37-42.
- [68] Sethuraman VA, Weidner JW. Analysis of sulfur poisoning on a PEM fuel cell electrode. *Electrochimica Acta*. 2010;55:5683-94.
- [69] Zhang X, Galindo H, Grace H, Baker P, Wang X, Pasaogullari U, et al. Influence of Formic Acid Impurity on Proton Exchange Membrane Fuel Cell Performance. *ECS Transactions*. 2009;25:1633-44.
- [70] Johnson AL, Muetterties EL. Orientation of complex molecules chemisorbed on metal surfaces: near-edge x-ray absorption. *Journal of the American Chemical Society*. 1983;105:7183-5.