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Impact of Designated Contaminants in Hydrogen on the Performance of a Proton Exchange Membrane Fuel Cell

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Abstract

Platinum along with the Perfluorosulfonic acid membrane are at the heart of proton exchange membrane fuel cells. The REDOX reaction and the transport of proton across the membrane enables continuous electricity generation by the fuel cell. While these two elements enable electrochemical reaction and mass transport of ion, they are highly susceptibility to certain designated contaminants as identified by ISO 14687. The current work critically analyzes the impact of the designated contaminants on the fuel cell performance with specific focus on the contamination pathway. Emphasis is on sub-PPM level contaminants considering that ISO 14687 imposes some extremely stringent limitations on the quantity. On the PPM level contaminants, the impact analysis is broadly from the perspective of dilution, both thermochemically and electrochemically. One of the key outcome of the current work is the recognition that work on the impact of contamination levels in the vicinity of ISO specified numbers is extremely limited. Most of the analysis, is carried out for contaminant levels anywhere between 10 to 100 times larger than the prescribed limits. A consensus that seems to be evolving pertains to a call for raising the designated limits of contamination.

Introduction

Proton Exchange Membrane Fuel Cells (PEMFC) represent a class of electrochemical energy conversion systems characterized by high chemical to electrical energy conversion efficiencycompared to conventional thermochemical energy conversion systems [*Dimitrova, Z., & Nader, W. B. (2022)*]. The underlying shift in philosophy in the conversion of high enthalpy fuel to low enthalpy products in the form of transition from thermo-chemical to electrochemical conversion enables realization of high conversion efficiency. While the transition from thermo-chemical to electrochemical system enables realization of substantially high efficiencies, certain key challenges emerge, the influence of reactant quality being the most important [*Zhang, Q., Harms, C., Mitzel, J., Gazdzicki, P., & Friedrich, K. A. (2022)*]. It is important to note that in case of thermo-chemistry, once the ignition is initiated by external or auto mode, the initial fraction of fuel – air mixture is converted to products releasing sufficient energy for self-sustained combustion and release of heat. Once the initial ignition is successful, because of prevailing high temperatures, anything combustible (Carbon, Hydrogen, Sulfur compounds) will burn to respective oxides while some other compounds may get reduces or remain unreacted even at substantial fractions, up to percentage limits. The sensitivity of the ignition and combustion process

(only) is extremely low to the presence of range of non-fuel compounds [*Colliou, T., Giarracca, L., Lahaussois, D., Sasaki, T., Fukazawa, Y., Iida, Y., ... & Matrat, M. (2022)*]. On the other hand, in case of electrochemical systems like fuel cells, the role of catalyst in reducing the activation energy for the Oxidation / Reduction process becomes the key factor that dictates the entire conversion process [*Holze, R. (2019)*] [*Bagotsky, V. S. (Ed.). (2005)*]. Catalysts like Platinum, currently being used in PEM fuel cells, are extremely sensitive to a range of contaminants because,precisely by the virtue of their nature to reduce the activation energy for Oxidation / Reduction, they do so without being selectiveto fuel and oxidizer molecules alone. Any compound beyond the fuel and oxidizer, if present, is also prone to undergo Oxidation / Reduction reaction. In the best-case scenario, such compounds would not participate in any kind of reaction and act as a diluent or undergo regular Oxidation / Reduction reactions like the primary fuel and oxidizers. The impact of the presence of such compounds would not be felt beyond possibly the current and voltage. In the next level of impact intensity, such other compounds may potentially adsorb onto catalyst surface or undergo Oxidation / Reduction reactionsto produce compounds that may in turn adsorb onto the catalyst surface reducing the active sites. This may result in reduction of current density. However, most of such effects can be effectively reversed. In the worst-case scenario, the catalyst itself may actively participate in reaction with some of the compounds resulting in formation of highly stable compounds having no catalytic activity. Such reactions potentially represent a more permanent degradation of catalyst. Essentially, in case of reactions supported by catalytic activity, depending on the nature of the catalyst, specific compounds are identified as contaminants and limits are placed on the quantity of such compounds in the fuel and/or the oxidizer stream. The limits are also specific to end utility in the sense that they are different for use of Hydrogen in engines and PEM fuel cells. Again, within fuel cells, the limits differ for stationary and mobile applications.

The current work investigates the implication of the presence of compounds designated as contaminants for PEM fuel cells/stacks specifically when used for automotive purpose – ISO 14689[*International Organization for Standardization. (2019)*]on the performance of a PEM fuel cell/stack. In the current work, specific emphasis is on analysing the impact of sub-PPM (Parts Per Million) level contaminants considering that, as per literature, most of these sub PPM level contaminants have permanent poisoning effect. Efforts are directed at understanding thealteration introduced to the fundamental reaction pathway resulting in degraded performance. The impact of PPM level contaminants is broadly analyzed from the point of view of dilution effects, both from thermo-chemical and electro-chemical perspective.

1. ISO Specification for PEM fuel cells for automotive applications

The ISO 14687 – 2019 standard broadly specifies the minimum quality requirements for Hydrogen as a fuel forutilization in vehicular and stationary applications.The specification broadly covers three types of Hydrogen, Type I, Type II and Type III, segregatedby the physical state.Type I and Type II specify the standards for gas phase Hydrogen and liquid phase Hydrogen respectively while Type III addresses slush Hydrogen (cryogenic solid–liquid two-phase fluid). Each type has different grades and categories, grouped based on the end application. The specifications for PEM fuel cells, of interest for the current work, are covered under grade D and E under gas phase Hydrogen (Type I). Grade D covers the specifications forPEM fuel cells for road vehicles while grade E covers PEM fuel cells for stationary vehicles. Compared to grade E, the specifications for grade D are extremely stringent and are of interest in the current work. Table 1 specifies the threshold limit for contaminants for using Hydrogen in PEM fuel cells. In the table,

Table 2.1. Hydrogen quality specification - PEM fuel cells for road vehicles

Sr. No	Compounds	Specified Limit for Type 1 (Gaseous) Hydrogen (ppm)			
		Grade D	Grade E Cat 1	Grade E Cat 2	Grade E Cat 3
01	Hydrogen fuel index (minimum mole fraction)	99.97%	50%	50%	99.9%

02	Total non-Hydrogen gases (cumulative maximum)	0.03%	50%	50%	0.1%
Maximum concentration of individual components (on dry basis)					
01	Water (H_20)	5	Noncondensing (any condition)		
02	Non-methane hydrocarbons [a]	2	10	2	2
03	Methane (CH_4)	100	5%	1%	100
04	Oxygen (O_2)	5	200	200	50
05	Helium (He)	300	50%	50%	0.1%
06	Nitrogen (N_2)	300			
07	Argon (Ar)	300			
08	Carbon Dioxide (CO_2)	2	Part of non H2 gases		2
09	Carbon Monoxide (CO)	0.200	10	10	0.200 [b]
10	Total Sulphur Compounds [c]	0.004	0.004	0.004	0.004
11	Formaldehyde (HCHO) [b]	0.200	3.0	0.2	0.2
12	Formic Acid (HCOOH) [b]	0.200	10	0.2	0.2
13	Ammonia (NH_3)	0.100	0.1	0.1	0.1
14	Halogenated Compounds	0.050	0.050	0.050	0.050
15	Maximum particulate concentrations	1	1	1	1

a Include oxygenated organic species. Non methane Hydrocarbons are measured on C1 (Methane) equivalent basis.

b The sum total of CO, HCHO and HCOOH is limited to 0.2 ppm. As such, 0.2 ppm is not the individual limit

c Total sulfur compounds include H_2S, COS, CS_2 and mercaptans

Type 1 / Grade D corresponds to gaseous hydrogen, PEM fuel cells for road vehicles. Type 1, Grade E, Cat 1 corresponds to: Hydrogen-based fuel; high efficiency/low power applications; PEM fuel cells for stationary appliances
Type 1 / Grade E / Cat 2: Hydrogen-based fuel; high power applications; PEM fuel cells for stationary appliances
Type 1 / Grade E / Cat 3: Gaseous Hydrogen; high efficiency/high power applications; PEM fuel cells for stationary appliances
As is evident, the specifications are extremely stringent, particularly for compounds like Sulfur and Carbon monoxide. It is reported that the compounds designated as contaminants establish a pathway to the anode and cathode catalyst layers, occupy the catalyst sites and alter the electrochemical pathway ultimately resulting in reduced performance in the best case or irrecoverable degradation in the worst case [*Shabani, B., Hafttananian, M., Khamani, S., Ramiar, A., & Ranjbar, A. A. (2019)*].

2. Reduction – Oxidation pathway in presence of Platinum catalyst

Oxidation of Hydrogen on the anode and reduction of Oxygen at the cathode remains the principle mechanism creating the electron gradient within the fuel cell [*Oldham, K., & Myland, J. (2012)*]. In respect of the Hydrogen Oxidation Reaction (HOR) and Hydrogen Evolution Reaction (HER), pioneering work has been carried out by Tafel, Heyrovsky, and Volmer [*Kucernak, A. R., & Zalitis, C. (2016)*]. From HOR perspective, Tafel and Heyrovskyproposed independent pathways for surface adsorption of Hydrogen onto the catalyst while Volmer

proposed the pathway for the desorption and release of the proton and electron. The reaction pathways are consolidated in Table 3.1. In the table, $(H_2)_V$ represents Hydrogen molecule in the vicinity of the catalyst active site (S) while ($S\text{-}H_{ad}$) represents the adsorbed Hydrogen atom.

Table 3.1. Reaction pathway for Hydrogen Oxidation Reaction

Sr.No	Reaction	Number	Proposed By
01	$(H_2)_V + 2S \rightarrow 2(S\text{-}H_{ad})$	01	Tafel
02	$(H_2)_V + S \rightarrow (S\text{-}H_{ad}) + H^+ + e^-$	02	Heyrovsky
03	$(S\text{-}H_{ad}) \rightarrow S + H^+ + e^-$	03	Volmer

The pathway adopted in the Oxygen Reduction Reaction (ORR) is substantially more complex and the atomic understanding of the pathway issubject of intense debate.Each ORR basically involvesfour coupled Proton-Electron transfer (CPET) to the molecular Oxygen at the cathode [*Keith, J. A., & Jacob, T. (2010)*] as per the stoichiometric equation presented below.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \text{ ……. (04)}$$

In the course of global ORR, the first common process is the migration and adsorption of O_2 molecule to the catalyst active site. Subsequent to the adsorption, the formation of several short-lived intermediate compounds has been proposed. Some of the key intermediate groups are O_{ad} (adsorbed Oxygen), HO_{ad} (adsorbed hydroxyl) and HOO_{ad} (adsorbed superhydroxyl) [*Stephens, I. E., Bondarenko, A. S., Grønbjerg, U., Rossmeisl, J., & Chorkendorff, I. (2012)*].The potential process pathways are briefly described as below [*Jacob, T. (2006)*];

*The O_2 pathway:*The adsorbed Oxygen moleculesat the catalyst active site $(O_2)_{ad}$undergoes dissociation into $2(O)_{ad}$ and each of the adsorbed Oxygen atoms undergoes two CPETs to form water molecules.

The OOH pathway: The adsorbed Oxygen molecule at the active site $(O_2)_{ad}$ undergoesone CPET resulting in the formation of $(O)_{ad}$ and $(OH)_{ad}$. The $(O)_{ad}$ experiences two CPETs while the $(OH)_{ad}$experiences one CPETto ultimately form two water molecules.

*The HOOH pathway:*The adsorbed Oxygen molecule at the active site $(O_2)_{ad}$ undergoes two CPETs to form $(H_2O_2)_{ad}$. This $(H_2O_2)_{ad}$ then undergoes dissociation on the surface to form two $(OH)_{ad}$ species. These two species then experience two CPETs to ultimately form two water molecules.
The impact of contamination, wherever there are reactions with the catalyst, will be presented from the perspective of interference in the stated pathways.

3. Impact assessment from inert perspective

In the list of designates contaminants, there are some compounds that predominantly have dilution effect on the fuel side. Only under certain very specific conditions do they interfere with the catalytic activity of the electrodes or the ion transport ability of the membrane. Helium, Nitrogen, Argon, Carbon Dioxide and to a significant extent Moisture are the compounds that typically influence the PEM fuel cell from dilution perspective [Inbody, M. A., Vanderborgh, N. E., Hedstrom, J. C., & Tafoya, J. I. (1996)]. Addressing the impact of dilution from thermo-chemical perspective, the fundamental impact is on the lower heating value.The reduction in volume specific calorific value is a linear function of dilution fraction and remains independent of the diluting specie while the mass specific calorific value strongly depends on the diluting specie and its fraction. The mass specific calorific value depends on the specie owing to the molecular weight dependency. The variation of mass specific and mole specific calorific value is presented in Figure 4.1.Dilution to the extent of 50% (the upper limit of dilution as per ISO 14687 for Type I; Grade; Category 1 and 2 applications) is considered. It can be observed that the mole specific calorific value decreases monotonously with dilution fraction and remains independent of the diluent specie. On the other hand, the as can be observed, the mass specific calorific value reduces with different intensity for different species. The extent of reduction increases with molecular weight.

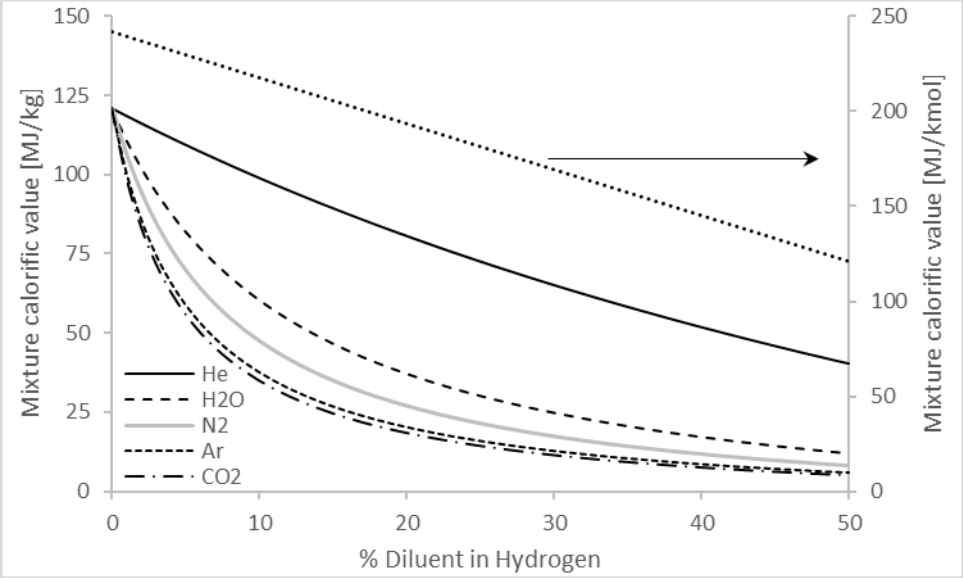

Figure 4.1. Variation of mole and mass specific calorific value with extent of dilution

While Figure 4.1 presents the reduction in the lower calorific value, from an electrochemical perspective, of greater significance is the open circuit cell voltage. The open circuit cell voltage is the maximum operating voltage when there is no current drawn from the system and is a function of chemical thermodynamics of the overall cell reaction [*O'hayre, R., Cha, S. W., Colella, W., & Prinz, F. B. (2016)*]. The Nernst equation establishes a relationship between the standard cell potential and the actual cell potential as a function of concentration of the products and reactants (in terms of partial pressure). The Nernst equation takes the form of equation (5) where E_{cell} is the cell potential, E^{o}_{cell} is the standard cell potentialP_{H2} and P_{O2} are the partial pressures of the reactants (Hydrogen and Oxygen) in the global reaction. The symbols R, T and F correspond to the universal gas constant, temperature and the Faraday's constant. The standard cell potential is estimated based on the change in Gibbs free energy.

$$E_{cell} = E^{o}_{cell} + \frac{RT}{2F}\ln\left[P_{O2}^{1/2}P_{H2}\right] \ldots\ldots\ldots (5)$$

Equation (5) provides a handle to estimate the change in cell potential as a function ofpartial pressure of the reactants and is used in the current case to assess the impact of introduction of diluents on the cell potential.

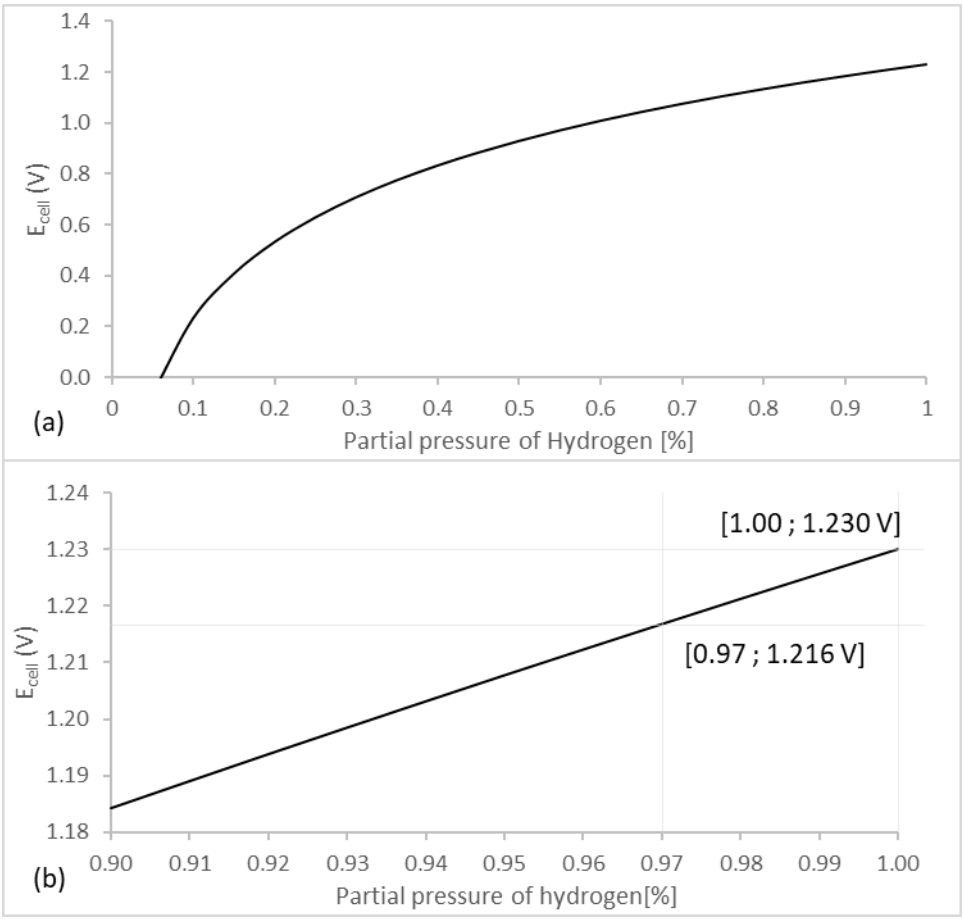

Figure 4.1. Variation of Nernst cell potential as a function of Hydrogen partial pressure

The variation of the cell potential estimated through Equation (5) is presented in Figure 4.1. While Figure 4.1 (a) presents the variation for the full range of partial pressure (1 to 0), Figure 4.1 (b)presents a narrower regime, relevant to ISO 14687 specification. It is evident from Figure 4.1 that as the dilution fraction increases, the open circuit voltage drops down. In the narrow regime of 100% pure Hydrogen to 99.97% pure Hydrogen, the drop in the open circuit voltage is near linear with the open circuit voltage dropping from 1.230 Volts to 1.216 Volts, a drop of little over a percent. While this is the case for open circuit voltage, when current is drawn from the fuel cell, any dilution will result in the onset of the concentration loss threshold at increasingly smaller values of current density.

4. Impact of substances with sub-PPM level tolerance

The ISO 14687 standard imposes sub-PPM level individual limitation on Carbon Monoxide, Sulfur compounds (total), Formaldehyde, Formic acid, Ammonia and Halogenated compounds. Among these, Carbon Monoxide and Sulfur compounds are known to have substantially adverse impact on the fuel cell apart from the fact that these are commonly found in the fuel stream.

5.1Impact of Sulfur compounds

Sulfur compounds potentially have the most adverse impact on the fuel cell at extremely low contamination levels. The effect is again primarily through the poisoning of the catalyst layer. The ISO 14687-2019 standard limits the total Sulfur compounds to 4 PPB which includes Hydrogen Sulfide (H2S), Carbonyl Sulfide (COS), Carbon Disulfide (CS2) and Mercaptans (compounds with -SH group, Methanethiol - CH3SH is the most common compound). If is important to note that if only one of the compounds is present, then that compound can be upto 4 PPB levels while if all the compounds are present in equal quantity,then the permissible limit drops to1 PPB each. The mechanism of platinum poisoning by Hydrogen Sulfide and Sulfur Dioxide has been reasonably well studied while only sparse information is available pertaining to the impact of Carbonyl Sulfide and Mercaptans. The underlying mechanism of catalyst poisoning remains broadly the same as in case of

Carbon Monoxide. Once compounds are in the vicinity of Platinum surface, they preferentially adsorb on to the active surface resulting in further non-availability of the active sites for Hydrogen oxidation. The key pathway resulting in the blocking of active sites by the Sulfur compounds are presented as below [*Sethuraman, V. A., & Weidner, J. W. (2010)*].

Platinum poisoning by Hydrogen Sulfide

$Pt + H_2S \rightarrow Pt\text{-}S_{ad} + H_2$ $\quad$ $Pt - H_2S_{ad} \rightarrow Pt\text{-}SH_{ad} + H^+ + e^-$

$Pt + H_2S \rightarrow Pt\text{-}H_2S_{ad}$ $\quad$ $Pt - SH_{ad} \rightarrow Pt\text{-}S + H^+ + e^-$

Platinum poisoning by Sulfur Dioxide

$Pt + SO_2 \rightarrow Pt\text{-}SO_{2\text{-}ad}$

$Pt + (SO_2)_{ad} + Pt \rightarrow Pt\text{-}SO + Pt\text{-}O$

Platinum poisoning by Carbonyl Sulfide

$Pt + COS \rightarrow Pt\text{-}COS$

$Pt\text{-}COS + Pt \rightarrow Pt\text{-}CO + Pt\text{-}S$

It is important to note that each compound of Sulfur Dioxide and Carbonyl Sulfide potentially blocks two active sites on the catalyst.In terms of the specific impact on the fuel cell response most of the information is concentrated to the impact assessment of Hydrogen Sulfide. This is primarily so because this contaminant is the most common in fuel streams. In a specific work addressing the impact of Hydrogen Sulfide, Cheng et al[*Cheng, X., Shi, Z., Glass, N., Zhang, L., Zhang, J., Song, D., ... & Shen, J. (2007)*] have reported on the temporal reduction in performance(operating voltage) with level of contamination in fuel stream for a particular current density. The results are consolidated in Table 5.1.1. It can be observed that while increasing the contaminant level does have an adverse impact, the extent of impact increases at higher current density levels.

Table 5.1.1. Performance degradation of the fuel cell on exposure to Sulfur Dioxide

Current density (mA/cm^2)	100			500			1000		
Contaminant level (PPM)	1.20	2.80	11.7	1.30	2.80	6.10	0.34	2.90	6.10
Pre seeding cell voltage (V)	0.85			0.7			0.5		
Time for 0.3 V drop voltage (h)	25	14	10	7.5	6	3.5	3	2	1.5

It must be noted that at higher current densities, since the exposure rate of active surfaceincreases, a commensurate increase in the contaminant deposition also increases resulting in enhanced degradation of active surface area. It has also been broadly reported that on elimination of the contaminants form the fuel stream, while recovery in the cell potential / current density is observed, complete recovery is not observed and when repeated contaminant loading-unloading is carried out cyclically the baseline continues to deteriorate.

5.2Impact of Halogenated compounds

Halogenated compounds are chemical compounds that contain one or more halogen atoms (Fluorine, Chlorine, Bromine, Iodine, or Astatine) bonded to carbon or other elements. Halogenated contaminants in Hydrogen, specifically Chlorine, Bromine, and Fluorine are reported to have significant adverse impact on the performance of proton exchange membrane fuel cells. The Halogenated compounds, similar to other sub-PPM level contaminants tend to poison the catalyst through selective adsorption onto the active surface resulting in reduced active sites. It is important to note that extremely limited literature is available in respect of anode side catalyst poisoning by Halogenated compounds with most of the analysis focusing on impact of air borne Halogenated contaminants on the cathode side. Park, S et.al., [Park, S., Shorova, D., & Kim, H. (2022)] conducted an experiment to evaluate the effect of cell voltage on the mechanism of NaCl poisoning in a proton exchange membrane fuel cell. In the investigation, investigations are initiated with pure Hydrogen and after about 10

minutes of baseline establishment, NaCl is seeded. The cell voltage is maintained at 0.6 V and the corresponding current density is continuously measured. It has been reported that the in about 60 minutes of operation from the start of injection of NaCl, the current dropped from 1.05 A/cm2 to 0.65 A/cm2. In a different experiment, Zhai, et.al, [Zhai, Y., Baturina, O., Ramaker, D. E., Farquhar, E., St-Pierre, J., & Swider-Lyons, K. E. (2016)] conducted Bromomethane contamination test to measure the cell volage responses to 20ppm Bromomethane contamination by holding the cell at a constant current of 1 A/cm2 at 45 ^{o}C. It has been reported that a near immediate drop in the fuel cell voltage was observed on the introduction of Bromomethane. However, gradually, the cell performance picked up close to the initial voltage level in about 4 hours.

5.3 Impact of Ammonia

Towards analyzing the influence of Ammonia on fuel cell, detailed control experiments have been carried out. One of the important features emerging from the investigations corresponds to the fact that the mechanism of Ammonia contamination is different from the other sub-PPM level contaminants. While most of the other contaminants degrade the fuel cell through preferential adsorption onto the catalyst surface and commensurate reduction in the cell active area (to a significant extent irreversibly), in case of Ammonia, the influence is largely through the change in conductivity of the membrane. Uribe et al [*Uribe, F. A., Gottesfeld, S., & Zawodzinski, T. A. (2002)*] have reported on the conductivity of N-105 Nafion membrane in presence of different cations. The conductivity value of H^+ at 0.133 S/cm is reported to drop to 0.106 when $NH4^+$ is introduced for a 1 hour exposure time while it drops to 0.032 S/cm for 66 hours of exposure time. The direct result of this is reflected in terms of the cell current. On a single cell, at a fixed voltage of 0.5 Volts, the current density drops from 1.25 A/cm^2 to 0.90 A/cm^2 at 30 PPM Ammonia which further drops to 0.45 A/cm^2 at 130 PPM Ammonia. They have also reported on cyclic voltammetry and state that no measurable adsorption of Ammonia was observed on the catalyst layer even after 60 minutes exposure of 30 PPM Ammonia. As such, the impact on conductivity because of replacement of H+ by NH4+ is being stated as the most likely cause of drop in cell performance. In a more recent work, Gomez et al [*Gomez, Y. A., Oyarce, A., Lindbergh, G., & Lagergren, C. (2018)*] have also reported on the impact of Ammonia on a fuel cell performance. A single cell under steady state was drawing 0.1 A/cm^2 current with the voltage at 0.82 with pure Hydrogen. After 45 minutes, when 200 PPM of Ammonia was injected into the fuel stream, over the next 75 minutes, the voltage is reported to have dropped to 0.55 Volts. What is particularly interesting is that during the same time, measurement of cell resistance indicated an increase from 60 micro-Ohms/cm^2 to 150 micro-Ohms/cm^2. It has been argued that Ammonia potentially gets bound to sulfonic acid sites (-SO3H), resulting in a reduced moisture uptake in turn resulting in decreased ionic conductivity [*Halseid, R., Vie, P. J., & Tunold, R. (2004)*][*Hongsirikarn, K., Mo, X., & Goodwin, J. G. (2010)*]. It has also been experimentally established that while short term exposure of Ammonia is reversible, long term exposure results in irreversible degradation in the performance.

5.4 Impact of Carbon monoxide

On the effect of Carbon Monoxide on the performance of a PEM fuel cell, the impact needs to be addressed with reference to Tafel equation as presented in Equation 1. It is reported that if Carbon Monoxide is present along with Hydrogen, Carbon Monoxide competes with Hydrogen for the active sites on the platinum catalyst under normal anode operating potentials [*Okonkwo, P. C., Ige, O. O., Uzoma, P. C., Emori, W., Benamor, A., & Abdullah, A. M. (2021)*].The heat of adsorption Carbon Monoxide on Platinum is 134 kJ per mol while it is 87.9 kJ per mol for Hydrogen, favouring CO adsorption. It is important to note that Carbon Monoxide not only blocks the available active sites, but it also proceeds to displace the adsorbed Hydrogen before the Oxidation reaction takes place. These two processes are described in Equations 6 and 7 respectively. Effectively Carbon Monoxide tends to adversely affect both the voltage and the current.

$(CO)_V + S \rightarrow S\text{-}CO_{ad}$……. (6)

$2(CO)_V + 2(S\text{-}H_{ad}) \rightarrow 2(S\text{-}CO_{ad}) + H_2$……. (7)

The reaction of Carbon Monoxide with Platinum can usually be detected by a reduction in the voltage. As such, measurement of voltage reduction at a particular current density is an important and scientific approach to identify the catalytic layer degradation. Gadducci et al [*Gadducci, E., Reboli, T., Rivarolo, M., & Magistri, L. (2022)*] have explored the drop in the voltage at three current densities by introducing Carbon Monoxide in the Hydrogen stream. Four Carbon Monoxide contamination levels in Hydrogen, two within the permissible

thresholds (100 PPB and 200 PPB) and two beyond the permissible thresholds (300 PPB and 400 PPB) are considered with exposure time of 4 hours at each level. The results are presented in Figure 5.4.1.

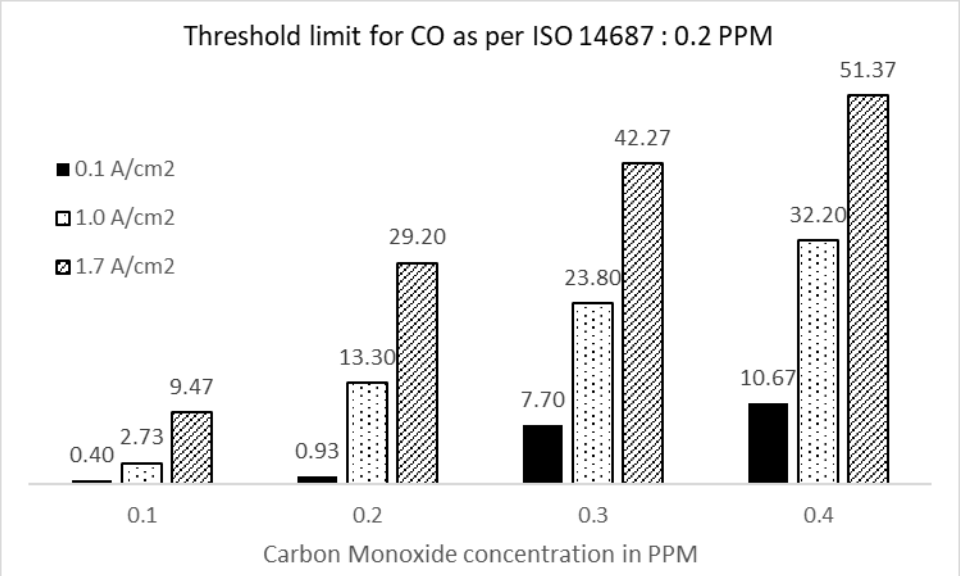

Figure 5.4.1 Effect of Carbon Monoxide contamination on cell voltage

At each level of contamination, it is observed that with increasing current density, the drop in voltage also increases. This is logical considering that increasing current density essentially means that the available fuel species are being used up making way for fresh charge to reach the catalyst surface. As this happens, over time, the extent of exposure of the catalyst surface to Carbon Monoxide continues to increase resulting in enhanced surface adsorption of Carbon Monoxide and hence reduction of active surfaces available for Hydrogen oxidation. It has been reported that at 1% of Carbon Monoxide in Hydrogen, close to 98% of the active sites remain blocked. At and beyond the permissible threshold of 200 PPB, it can be observed that the loss in voltage exceeds 50%. Limited long-term studies have also been conducted to examine the impact of Carbon Monoxide contamination of the catalyst layer. Angelo et al [*Angelo, M., Bender, G., Dorn, S., Bethune, K., Hossain, T., Posey, D., ... & Rocheleau, R. (2008)*] have reported on the irreversible loss of active area of both anode and cathode when exposed to 2 PPM of CO in Hydrogen for 1000 hours. They have established the loss of active area to the extent of 30% on both anode and cathode at by 800 hours of operation.

5.5 Bonding energy analysis – Carbon Monoxide and Ammonia

The general understanding has been that the compounds designated as contaminants under ISO 14687 – 2019 have high affinity to the catalyst surface. This aspect has been systematically investigated by Postole et al [*Postole, G., & Auroux, A. (2011)*] by comparing the adsorption capacities of Carbon Monoxide and Ammonia with Hydrogen on three different grades of Platinum designated as Pt/C-T; Pt/C-E and Pt/C-JM. The adsorption capacities have been quantified by using a heat-flow microcalorimeter. The adsorption capacities, heat of adsorption and total / irreversible uptake of compound as reported are presented in Table 5.5.1.

Table 5.5.1 Adsorption characteristics of Hydrogen, Ammonia and Carbon Monoxide

Catalyst	Compound	Heat of Adsorption kJ/mol	Molecule uptake µmoles per gram platinum	
			Total	Irreversible
Pt/C-T	Hydrogen	154	1110	945
	Ammonia	139	532	170
	Carbon Monoxide	96	470	132
Pt/C-E	Hydrogen	92	410	90

	Ammonia	126	657	195
	Carbon Monoxide	146	1062	918
Pt/C-JM	Hydrogen	94	460	67
	Ammonia	129	714	273
	Carbon Monoxide	168	1619	1371

Across the three Platinum types, it can be observed that the heat of adsorption is highest for Carbon Monoxide followed by Ammonia and Hydrogen. Effectively, any adsorbed Hydrogen molecule will be displaced easily by both Ammonia and Carbon Monoxide while Ammonia is displaced by Carbon Monoxide. This is evident by the very high total and irreversible molecule uptake for Carbon Monoxide as compared to Ammonia and Hydrogen.What is specifically interesting is the irreversible adsorption. Basically, once adsorption takes place, if fresh Hydrogen is passed over Platinum, it won't be able to displace either Ammonia or Carbon Monoxide. This is consistent with the difference in heat of adsorption and clearly answers the permanent degradation of catalyst.

5.6 Impact of Formic acid (CH_2O_2) and formaldehyde (CH_2O)

Formic acid and formaldehyde are two components dissolve in water, react and form other contaminants, and permeate the membrane to the cathode, making them a challenging contaminant.

Formaldehyde is known to decompose to a range of products in presence of platinum catalyst with Carbon Monoxide and Hydrogen being the primary products.Narusawa et al[Narusawa, K., Hayashida, M., Kamiya, Y., Roppongi, H., Kurashima, D., & Wakabayashi, K. (2003)] have reported on the influence of Formaldehyde and Formic acid on the performance of PEM fuel cell. In addressing the influence of Formaldehyde, 30, 100 and 500 PPM of the contaminant was introduced resulting in the current density at 0.4 volts dropping from 330 mA/cm^2 (baseline) to 290 mA/cm^2, 240 mA/cm^2 and 115 mA/cm^2 respectively. They have compared the performance drop due to formaldehyde contamination with Carbon Monoxide contamination where for the same contamination levels of 30, 100 and 500 PPM, the drop in current density from 330 mA/cm^2 has been 200 mA/cm^2, 75 mA/cm^2 and 20 mA/cm^2 respectively.It is argued based on these results that the impact of formaldehyde is substantially lower as compared to Carbon Monoxide, broadly about a tenth. It is also hypothesized that the contamination impact primarily emerges form the Carbon Monoxide formed by the decomposition of CH_2O rather than Formaldehyde itself. They have also experimentally established that once the Formaldehyde seeding in Hydrogen is stopped, an immediate spike in the current density is observed. In an extended work Viitakangas et al [*Viitakangas, J., Ihonen, J., Koski, P., Reinikainen, M., & Aarhaug, T. A. (2018)*] have carried out investigations using a 1 kWe fuel cell stack with 99.9999% pure Hydrogen being used for establishing the benchmark performance. They have compared the performance drop on injecting 2 PPM of CO and Formaldehyde independently. For the 2 PPM Carbon Monoxide injection while the drop in voltage was 45 mV within one hour of exposure, for Formaldehyde, the drop was about 3.5 mV after 4 hours of exposure. This again establishes the impact of Formaldehyde to be nominal.Further, the nominal voltage drop is completely recovered on removing the contaminant from the feed.

On repeating the experiments with Formic acid,Viitakangas et al [*Viitakangas, J., Ihonen, J., Koski, P., Reinikainen, M., & Aarhaug, T. A. (2018)*] observed that for 2 PPM of Formic acid, no measurable performance drop was noticed. To understand the implication of the contaminants, the contaminant concentration in the gas was increased to 20 PPM and for four hours of exposure time to 20 PPM of Formic acid, the drop in voltage was 1.0 mV against 45 mV for 2 PPM Carbon Monoxide exposure for one hour. However, after the removal of the contaminant from the feed, no recovery was observed.

One important aspect of the reported investigations, both from the perspective of Formaldehyde and Formic acid is the fact that for the kind of limits imposed by ISO 14687-2019 (200 PPB) no measurable performance degradation was noticed and as such, there are calls to relax the limit to more practical values.

6. Challenges in impact analysis in the vicinity of ISO specified limits

The discussions presented in respect of the sub-PPM gas phase contaminants have clearly brought out the fact that the investigations are mostly at PPM levels with extremely limited to no investigation being conducted around the limiting values of ISO 14687. It must be noted that generation of control mixtures of Hydrogen and designated contaminant in the limit specific by ISO 14687 has been a major challenge. The challenge arises due

to the extremely small quantity of contaminant that needs to be accurately quantified to create a running mixture or a premixed mixture. The largest of sub-PPM contaminant limit is at 0.2 PPM (Carbon Monoxide, Formaldehyde and Formic acid) while the smallest corresponds to 0.4 PPB for total Sulfur compounds. At 0.2 PPM, the contaminant will have to be weighed / flow rate controlled at the fraction of 0.0000002 while pure Hydrogen (devoid of any other contaminants) will have to have a flow rate of 0.9999998. When it comes to compounds of Sulfur, even if it is assumed that only one of the designated Sulfur compounds is present, the ratio of mixing would be 0.000000004 for the contaminant while it would be 0.999999996 for Hydrogen. Typically, if 1 SLPM is considered as the fuel flow rate for a single cell, if a 1 SLPM flow meter is considered then at least count of 1/200 of the full-scale range, control can be exercised only in the 1.005 to 0.995. As such, while generating contaminant free designate compounds is a challenge in itself, controlling the flow rate to the desired levels of accuracy and synthesis of a homogeneous mixture remain the principle challenge. As such, even while ISO 14687 specifies sub-PPM tolerance levels, impact testing is mostly carried out at much higher levels.

7. Impact of particulate matter

It is reported that presence of Particulate Matter in the Hydrogen fuel stream should not directly affect fuel cell performance from either electrochemistry perspective or its durability. However, particulate matter is reported to adversely affect the integrity of the balance of plant components such as seals, gaskets and valve seats resulting in fuel leaks and other such associated problems. The ISO and SAE standards specify a maximum particulate concentration (1 mg/kg H2) to ensure that filters are not clogged and/or particulates do not enter the fuel system and affect operation of valves and fuel cell stacks. It is also important to note that the limitation on quantity, 1 mg PM per kg of Hydrogen was primarily based on input from Hydrogen fuel suppliers that was agreed to by the automotive original equipment manufacturers. Exhaustive measurements on a number of fuel dispensing stations and based on available understanding of impact of particulate matter on balance of plant components has been used as the basis for arriving at the number of 1 mg PM per kg of Hydrogen. Measuring the particulate matter using polytetrafluorethylene (PTFE) filters for a typical Hydrogen flow rate of 5.5 +/- 2.0 grams per second, typical number of 0.05 +/- 0.003 mg PM per kg of Hydrogen have been measured and using this as the basis, the upper limit of 1 mg PM per kg of Hydrogen has been established. Having collected the samples, analysis of the samples indicated the elemental composition typical of dust or dirt and most of them were high in some combination of aluminium (Al) and silicon (Si). There were a large number of particles high in magnesium (Mg) that is not normally found in high concentrations in dust and dirt and may be from a specific source in the dispensing system. Steel and brass particles of varying composition were detected on many of the samples, and other metal particles, such as chromium (Cr), nickel (Ni), and zinc (Zn), were observed in some of the samples analyzed.

Towards analyzing the impact of particulate matter on the fuel cell, Betournay et al [*Betournay, M. C., Bonnell, G., Edwardson, E., Paktunc, D., Kaufman, A., & Lomma, A. T. (2004)*] have carried out testing of a 35 W proton exchange membrane fuel cell in mine like underground conditions. The tests involved stack operation for electricity generation when exposed to elevated levels of dust (mineral, and diesel particulate matter) and coal mine gases. They report that over the 50-hour period of testing, the fuel cell operated normally without any performance degradation using normal air filters. Dust level build up was observed on the filters which is typical for any filtration process.

8. Conclusions

The article has reported on the impact of designated contaminants on the performance of a proton exchange membrane fuel cell. The emphasis has been on sub-PPM contaminants with the impact of PPM level contaminants broadly described perceived from the point of view of dilution effect. Some of the key observations are;

a. Certain compounds having extremely high adsorption potential to platinum active surface and extremely low desorption potential from platinum active surface and those which further undergo Oxidation / Reduction to form intermediate compounds each of which has high adsorption potential are generally designated as contaminants for catalysts in general and fuel cells in particular.

b. Total Sulfur compounds, Halogenated compounds, Ammonia, Carbon Monoxide, Formaldehyde and Formic acid are the key ingredients designated as sub PPM level contaminants for proton exchange membrane fuel cells.

c. Formation of strongly adsorbed compounds on Platinum active surface is the most common route to catalyst poisoning except with Ammonia. The affinity of designated contaminants to adsorption and potential electron exchange is generally much higher than Hydrogen adsorption resulting in catalyst poisoning even at extremely low contaminant levels.

d. On the poisoning potential, while some compounds like Carbon Monoxide block one active site per molecule, some Sulfur based compounds with high affinity to reduction in presence of Platinum tend to block two active sites.

e. In analysing the impact of contaminants on the fuel cell performance, primarily in terms of drop in potential at fixed current densities, a key feature has been that very little work reports on the contamination levels in the vicinity of ISO specified numbers. Most of the analysis, is carried out for contaminant levels anywhere between 10 to 100 times larger than the prescribed limits.

f. In analyzing the sub-PPM level contaminants, creation of mixtures of binary species seems to be key challenge considering the extremely small flow rates of contaminants which need to be perfectly mixed with Hydrogen of very high purity.

g. Another hypothesis being proposed for testing at higher concentrations corresponds to the argument that restricting the contaminants at ISO 14687 levels results in substantially slow degradation levels requiring unreasonably large investigation times. Using higher levels of contaminants provides an immediate assessment of potential impact.

h. A consensus that seems to be evolving pertains to a call for raising the designated limits of contamination. If this happens based on scientific analysis, then the cost of Hydrogen can come down significantly.

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