



**HyCoRA – Hydrogen
Contaminant Risk Assessment
Grant agreement no: 621223**

**Review on the impact of
impurities on PEMFC and
analytical methods for hydrogen
QA.**

Authors: Pierre-André Jacques, Jari Ihonen, Pauli Koski

Confidentiality: Public

Submission date 11.7.2014

Revision 1.1 (proofreading by 29.10.2014)

Revision 1.2 (Table in Chapter 4 corrected after project midterm review)

Report's title Deliverable 1.1 Review on the impact of impurities on PEMFC and analytical methods for hydrogen QA.	
Customer, contact person, address Vasco Ferreira, FCH JU	Order reference Grant agreement no: 621223
Project name Hydrogen Contaminant Risk Assessment	Project number/Short name HyCoRA
Author(s) Pierre-André Jacques, pierre-andre.jacques@cea.fr Jari Ihonen, jari.ihonen@vtt.fi Pauli Koski, pauli.koski@vtt.fi	Pages 34
<p>Summary</p> <p>In this task, the extensive literature work achieved in HyQ project (GA 256773) is updated with the latest information from years 2012-2014. In the review, the focus is on critical assessment of the experimental results from the literature for determining limits in ISO 14687-2:2012 (Hydrogen fuel — Product specification — Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles).</p> <p>This report will also perform a short review of the methods currently available for hydrogen purity analysis. This review will focus on the components in the ISO 14687-2:2012 specification and cover laboratory-based methods, on-line methods and methods for measuring multiple impurities.</p> <p>As a conclusion, a strategy for the experimental fuel cell work in the HyCoRA project is presented.</p>	
Confidentiality	Public

Table of Contents

1.	A review of experimental methods and results for determining hydrogen fuel quality for automotive use	4
1.1	Scientific summary.....	4
1.2	Introduction.....	4
1.3	Experimental research for determining limits in ISO 14687-2:2012.....	4
1.4	The needs for the development of experimental methods and gaps in the knowledge of contaminants .9	
1.4.1	The effect of recirculation (anode operation mode).....	9
1.4.2	The effect of fuel utilisation.....	10
1.4.3	The acceptable level of performance drop	10
1.4.4	The duration of the measurements	10
1.4.5	The importance of average load (current)	11
1.4.6	The effect of start and stop (S/S)	11
1.4.7	The importance of concentration levels.....	11
1.4.8	The load (current) profile on the measurements	12
1.4.9	The importance of cell operating conditions (temperature, humidity, pressure).....	12
1.4.10	The analysis of recirculated or exit gas	13
1.4.11	The importance of anode catalyst loading (catalyst aging).....	13
1.4.12	The importance of gas permeation through the membrane (membrane thickness, aging)	14
1.4.13	The importance of inert gas accumulation.....	14
1.4.14	The importance of cross-contamination from cathode.....	15
1.4.15	The effect of carbon dioxide and RWGS	15
1.4.16	The effect of multiple contaminants.....	16
1.4.17	The effect of flow field geometry in the cells.....	16
1.4.18	The effect of GDL material through cathode mass transfer (flooding).....	17
1.4.19	The effect of system contaminants and cell degradation products.....	17
1.4.20	The effect of internal air bleed and risk of unintentional external air bleed	17
1.4.21	The effect of long conditioning before the experiment.....	18
1.4.22	The effect of contaminant dissolution in product water (wash-out).....	18
1.4.23	The spatial distribution of the contaminant effect.....	19
1.5	The recommendations for the future hydrogen contamination research.....	19
1.5.1	The development of single cell measurements for contaminant studies.....	19
1.5.2	The development of recirculation set-up with small gas volume	19
1.5.3	The development of gas analysis from anode recirculation loop or anode exit	20
1.5.4	The measurement of contaminant reactivity and reaction products	20
1.5.5	The development of methodology to study recovery from poisoning due to desorption	20
1.6	References for Chapters 1.4 and 1.5	21
2.	A review of supplementary results of hydrogen fuel contamination studies	24
2.1	Sulphur contamination	24
2.1.1	Mechanism of the sulphur contamination.....	24
2.1.2	Effect of the temperature on the sulphur pollution	25
2.1.3	Effect of the concentration on the sulphur pollution.....	25
2.1.3	Mitigation strategies for the sulphur pollution	26
2.2	Multiple contaminants	28
2.3	Contamination by carbon monoxide.....	29
2.4	Cross-contamination issue	30
3.	A review of analytical methods for measuring impurity levels in automotive grade (ISO 14687-2:2012) hydrogen	31
4.	Strategy for experimental fuel cell research in HyCoRA project	32

1. A review of experimental methods and results for determining hydrogen fuel quality for automotive use

1.1 Scientific summary

Hydrogen fuel quality is a major issue for commercialization of hydrogen fuel cell vehicles. The presence of contaminants in hydrogen fuel may become a major issue for both stationary as well as traction applications. Even trace impurities can have either reversible, partially reversible or irreversible effects on fuel cell vehicle performance.

In this paper, hydrogen contamination studies for determining hydrogen fuel quality for automotive use ISO 14687-2:2012 are comprehensively and critically reviewed. The focus of this study is on both effects of impurities as well as experimental methodology used in the studies. Recommendations for further research efforts are given as conclusions.

1.2 Introduction

Hydrogen fuel quality is one of the main issues for the large scale commercialization of fuel cell electric vehicles (FCEV). If levels for the contaminants in hydrogen fuel quality are not defined optimally, this will have negative impact on the FCEV commercialization. Too-high levels of contaminants would have a negative impact on the efficiency and lifetime of FCEV. On the other hand, too-low levels of contaminants would increase the cost of purification and even more importantly, the cost of quality assurance (QA).

Currently, there is an accepted standard for hydrogen fuel quality for automotive applications (ISO 14687-2:2012), which defines both the acceptable limits for impurities and the methods for hydrogen quality assurance (QA). Hydrogen fuel quality issues have been discussed in the papers of Aprea (2014).

The effect of hydrogen fuel contaminants have been studied extensively, and these works have been published in review papers (Zamel and Li, 2011; Cheng et al., 2007; Du, Pollard, Elter and Ramani, 2009). However, these review papers do not focus on the hydrogen fuel quality for automotive applications. In addition, critical and comparative analysis of the literature data and applied experimental methods has not been done.

Based on the analysis, recommendations are made for filling knowledge gaps both in developing suitable experimental research methods and determining the contaminant levels.

1.3 Experimental research for determining limits in ISO 14687-2:2012

The current standard (ISO 14687-2:2012) for hydrogen fuel for road vehicles was accepted in 2012. The following table lists some of the studies, which were used for the determination of the contaminant limits in the standard. Some earlier research studies have also been included. What is striking is the wide variability in catalyst loading, condition and operating mode.

Type of pollutant	concentration	Catalyst loading	Current conditions			Conditions			Performances	References	
			Potentiostatic	Galvanostatic	Dynamic profile		temperature	humidity			mode
					cycle	On/off					
CO	100ppm	Pt 1 mg cm ⁻²		0.5Acm-2			80°C	100%	Open end	60% loss after 125 min	Oetjen, ECS, 1996, 3838
CO	0.52 ppm	Pt A : 0.4 mg.cm ⁻² C : 0.4 mg.cm ⁻²		Yes, current unknown			60°C	100%	Dead end (purge 2s/45s)	4.3 % loss after 75 h	Benesch R, Salman S, Jacksier T, The effect of fuel and oxidant contaminants on the performance of PEM fuel cells. In: WHEC 16, Lyon, France; 2006.
CO	0.2 ppm	Pt A: 0.05 mg.cm ⁻² C: 0.4 mg cm ⁻²		1 Acm-2			80°C		Open end	3.6 % loss after 100h (2% loss with pure H2)	Hashimasa, International Work Shop on the Effect of Fuel & Air Quality to the Performance of Fuel Cells, September 10,2009
CO	0.2 ppm	Pt A: 0.1 mg.cm ⁻² C: 0.3 mg.cm ⁻²	0.6 V				60°C	A: 100% C: 50%	Open end	8% loss in 30 h	J.G. Goodwin, Jr. 2011 U.S. DOE Hydrogen Program Annual Merit Review and Peer Evaluation
CO	1 ppm	Pt A: 0.3 mgcm ⁻² C: 0.3 mg.cm ⁻²		1 A cm-2		80 °C	A: 77°C C: 70°C	Open end IV curve: Uf: 70% 10 hrs test Uf: 17%	0 % (IV curve) 3.5% loss after 10 h	Japan Automobile Research Institute 20. April 2004	
	5 ppm								0.9 % (IV curve); 3.5% loss after 10 h		
	10 ppm								Break down (IV curve)		

				0.5 A cm ⁻²					-1.1% (IV curve)	
CO	2 ppm	Pt : 0.4 mg.cm ⁻² (A/C not specified)		1 A cm ⁻² (regeneration cycle every 12 hrs by A.B)		60 °C	A: 100% C: 50%	Open-end, Pressure: A:7psig, C: 7psig. St: A: 2, C: 2	25 mV(3%) loss after 1000 hrs at 0.8 A.cm ⁻²	Angelo et al, ECS transactions, 16(2) 669 (2008)
CO	1 ppm	Pt A: 0.4 mg.cm ⁻² C: 0.4 mg.cm ⁻²		1 A cm ⁻²		60°C	A: 100% C: 50%	Open end, Pressure A and C: 48.3 kPag	175 mV loss after 55hrs	Bender et al, J. Power Sources, 193 (2009) 713-722.
CO	1ppm	Pt A: 0.4 mg.cm ⁻² C: 0.4 mg.cm ⁻²		1 A cm ⁻²		60°C	A: 100% C: 50%	Open-end, Pressure: A:7psig, C: 7psig. St: A: 2, C: 2	185 mV loss after 100 hrs	Thampan et al Mater. Res. Soc. Symp. Proc. 885 Warrendale, PA, 2006
						70°C			32 mV loss after 100 hrs	
	7 ppm				80°C	15 mV loss after 100 hrs				
	20 ppm					197 mV loss after 100 hrs				
								393 mV loss after 100 hrs		
H2S	2 ppm			1 Acm-2		80 °C	A: 77°C C: 50°C	Uf: 17%	Start of decrease after 3hrs, 60% loss after 4hrs)	Imamura, Hashimasa ECS transactions, 11, 1, 853 (2007)
SO2	Dealing with pollution in the air and the cathode side									Zhai et al, J. electrochem Soc. 157 (2010) B20 Zhai et al, ECS Transactions 16 (2) 873 (2008)
HCOOH	100 ppm	Pt A: 0.4 mg.cm ⁻² C: 0.4 mg.cm ⁻²		0.8 Acm ⁻²		80 °C	A:100 % C: 75 %	Open end , stoichio: 2 (A and C)	-30 mV (100 hrs)	Molter, 2010 DOE Hydrogen Program, May 9 2011
	2 ppm	Pt							0 % loss in	

		A: 0.1 mg.cm ⁻² C: 0.4 mg.cm ⁻²							100 hrs	
HCOH	5 ppm	Pt A: 0.1 mg.cm ⁻² C: 0.4 mg.cm ⁻²		0.8 Acm ⁻²		80 °C	A:100 % C: 75 %	Open end , stoichio: 2 (A and C)	0 %loss in 100 hrs	
CH ₃ COH	30 ppm	Pt A: 0.1 mg.cm ⁻² C: 0.4 mg.cm ⁻²		0.8 Acm ⁻²		80 °C	A:100 % C: 75 %	Open end , stoichio: 2 (A and C)	-30 mV (100 hrs)	
C ₇ H ₈								Open-end, Pressure:		
C ₆ H ₆	60 ppm	Pt A: 0.4 mg.cm ⁻² C: 0.4 mg.cm ⁻²		1 A.cm ⁻²		80 °C	A: 100% C: 50%	A:7psig, C: 7psig. St: A: 2, C: 2	No observable degradation	Thampan et al Mater. Res. Soc. Symp. Proc. 885 Warrendale, PA, 2006
CH ₃ Cl	19 ppm	Pt A: 0.1 mg.cm ⁻² C: 0.4 mg.cm ⁻²		0.8 Acm ⁻²		80 °C	A:100 % C: 75 %	Open end , stoichio: 2 (A and C)	0 % in 50 hrs	
mixture	0.2ppm CO 4 ppb H ₂ S 1 ppm NH ₃ 0.2 ppm HCOOH	Not specified		Yes, current not specified.		80 °C	A:75 % C: 25 %	Open end , stoichio: A:1.2;C:2.0	0 % in 150 hrs	Molter, 2010 DOE Hydrogen Program, May 9 2011
	1 ppm CO 20 ppb H ₂ S 5 ppm NH ₃ 1 ppm HCOOH 10 ppm C ₆ H ₆								-60 mV in 100 hrs	
Mixture	2ppm CO 20 ppm C ₇ H ₈	Pt : 0.4 mg.cm ⁻² (A/C not specified)		1 A cm ⁻²		60 °C	A: 100% C: 50%	Open-end, Pressure: A:7psig, C: 7psig. St: A: 2, C: 2	340 mV loss after 50 hrs (steady state)	Dorn et al, ECS transactions, 16 (2), 659 (2008)

	<p>Mechanistical study on the loss of proton diffusion with a PFSA membrane (Nafion211) polluted with NH₃ → no numerical on the loss of performance while utilization in a fuel cell</p>	<p>Hongsirikarn et al, Journal of Power sources 195 (2010)30-38</p>
<p>NH₃</p>	<p>Deal with a new method (based on esterification) to evaluate the proton conductivity loss of a nafion membrane polluted with ammonia</p>	<p>Hongsirikarn, Mo, Goodwin J. Power Sources 195 (2010) 3416 Hongsirikarn, Mo, Goodwin J. Power Sources 195 (2010) 5493</p>

1.4 The needs for the development of experimental methods and gaps in the knowledge of contaminants

When the current standard (ISO 14687-2:2012) was accepted, it was clear that there were still knowledge gaps in the development of experimental methods and more data was needed on a number of important topics. The research issues identified by Ohi (2007) are still objects of interest in the field. In addition, there are number of other additional issues, discussed in the following Chapters.

1.4.1 The effect of recirculation (anode operation mode)

The anode side can be operated in different ways in laboratory fuel cell systems and commercial applications. Therefore, the contaminants can be enriched in different ways. The problem of anode side operation mode is illustrated in Figure 1.

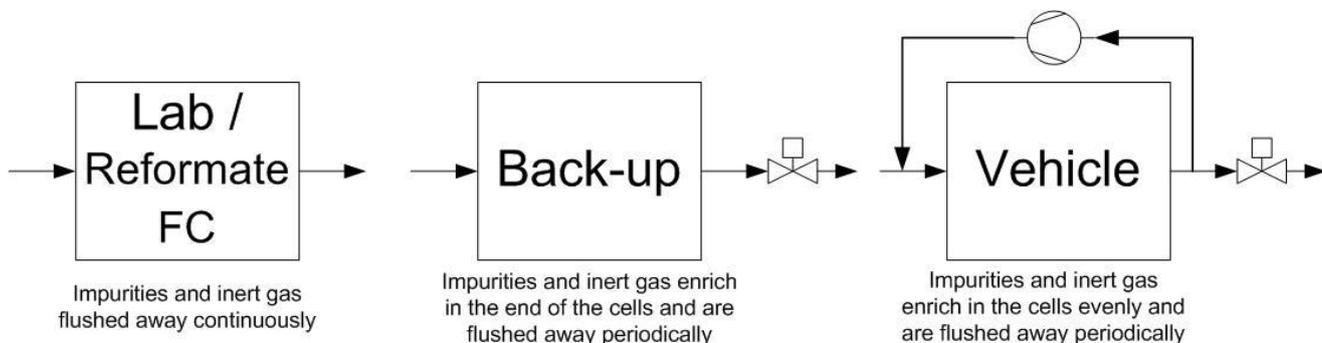


Figure 1: Anode side operation in different applications using pure hydrogen as fuel. a) Open anode mode with single pass b) Dead-end with purge c) Recirculation with purge.

Due to the problem of water accumulation in the channels, sufficient linear flow velocity must be maintained in the gas channels (Anderson, et al., 2010) or water should be removed by anode gas purge (Yu, et al., 2009; Dehn, Woehr and Heinzl, 2011).

The requirement of sufficient linear flow velocity for removing the water cannot be reached in open anode mode with high fuel utilisation, because hydrogen is consumed along the channels and flow velocity is reduced in the end of the cell.

When linear flow velocity is too low in the anode, there will be water accumulation, which causes uneven flow between the channels, and uneven current distribution at the end of the cell (Pérez, Ihonen, Sousa and Mendes, 2013) and fuel starvation (Kim, et al., 2014).

When hydrogen purge is applied in dead-end or recirculation mode, there is loss of hydrogen. Therefore, there will be different hydrogen utilisation rates and correspondingly different enrichment ratios of inert gases and contaminants. The amount of purged hydrogen and the enrichment ratio depend on operation conditions and purge (Nikiforow, Karimäki, Keränen and Ihonen, 2013).

When different impurities are studied, the choice of operation mode may have different levels of importance. If impurity is strongly adsorbing and is passing the cell, then the open anode mode could possibly be used.

However, it should be noted that an increase in flow velocity may change the adsorption and increase the slip of the contaminant, so that a large percentage of the contaminant passes the cell without adsorption (Pérez, et al., 2014). In addition, the change of single pass to recirculation operation mode has been shown to have a significant effect on the contamination process of strongly adsorbing hydrogen sulphide (Matsuda, et al., 2009).

1.4.2 The effect of fuel utilisation

The total fuel utilisation will determine the contaminant enrichment ratio. For different gases the enrichment may be different due to adsorption, reactivity, permeability through the membrane and dissolution in the anode water (Matsuda, et al., 2009).

The fuel utilisation per pass in a recirculation system can affect the contamination dynamics, because the flow velocity will affect the contaminant concentration in the beginning of the contamination process (Pérez, et al., 2014).

1.4.3 The acceptable level of performance drop

When contaminant measurements have been performed, there have not been unified criteria for the acceptable voltage or current drop. In a number of studies in the literature, the voltage drop has been several hundred millivolts (Zamel and Li, 2011; Cheng, et al., 2007).

When inert gas accumulation has been considered, the voltage drop has been between 3 mV and 24 mV in modelling studies and experimental work (Ahluwalia and Wang, 2007; Nikiforow, Karimäki, Keränen and Ihonen, 2013).

When the optimum CO level was modelled, the acceptable steady state cell voltage drop has been considered to be few tens of mV (Ahluwalia and Wang, 2008). In the experimental work of Pérez et al. (2014), 50 mV was the criteria to stop the measurement.

The acceptable voltage drop should be such that FCEV can operate safely and maintaining acceptable efficiency and durability. With the knowledge of the authors, a suitable criterion for the average voltage drop is 20-50 mV, while the weakest cell could experience a voltage drop of up to 100 mV.

1.4.4 The duration of the measurements

Almost all measurements in the literature have been performed with the time scale of or tens of hours or more. Typically, the measurements have been performed until steady-state has been reached or there was a very large voltage drop (Benesch, Salman and Jacksier, 2006; Barrio, Hasanov, de Souza and Starr, 2007; Besancon, et al., 2009; Colon-Mercado, 2010).

The use of continuous steady-state measurements for the FCEV is questionable, as there are processes during start and stop (S/S) that will affect the contamination dynamics. In addition, as FCEVs use different hydrogen refuelling stations, the hydrogen quality will be different almost each time.

The maximum duration of the measurement should correspond to the time needed to use up a full hydrogen tank in an FCEV. Currently, the hydrogen storage in passenger FCEVs is expected to be 4-6 kg for a vehicle with 100 kW PEMFC system.

If full power (e.g. 1.5 Acm^{-2}) is applied, then the hydrogen in the tanks of FCEV is consumed within one hour. If the FCEV is used at constant low partial load (20 %, 0.2 Acm^{-2}), then maximum continuous operation is 5-8 hours.

If full power is applied, then the operating conditions of the stack (temperature, humidity) will also be different from regular use. The expected operating temperature will be higher due to the heat rejection requirement, while the relative humidity of both anode and cathode would be decreased. For the estimation of the real operation condition, field data from FCEVs is urgently needed.

The duration of measurement period can be different for reversible and irreversible (strongly adsorbing) contaminants. For strongly adsorbing contaminants (e.g., sulphur) the quantification of desorption during S/S is very important, and therefore long steady-state measurements may not be useful for the determination of ISO 14687-2:2012 limits.

1.4.5 The importance of average load (current)

The average current during the measurement defines the hydrogen consumption. Therefore, the molar rate of contaminants entering the cell/stack will depend on the current level. The larger amount of contaminants can be adsorbed (and enriched) in the same time when current and hydrogen consumption are higher.

On the other hand, it has been shown by Bender, Angelo, Bethune and Rocheleau (2013) that high CO levels (2 ppm) cause relatively small voltage drops at low (0.2 Acm^{-2}) current densities. On a practical level, this means that a PEMFC system could possibly be operated with low (<20 % nominal) power even when highly CO-contaminated fuel is used.

1.4.6 The effect of start and stop (S/S)

The effect of S/S is of crucial importance, especially for CO oxidation by oxygen permeating from the cathode through the membrane. This process is generally referred to as internal air bleed.

During a longer shut-down, there the remaining hydrogen on the anode side will be consumed and a slow diffusion of oxygen from the atmosphere to the anode will occur via the cathode and through the membrane. This oxygen will eventually oxidise CO from the surface. The time needed for this process is strongly dependent on PEMFC system design and operation.

The effect of a shorter S/S is unclear. During a short S/S there will be a consumption of hydrogen in anode GDL and channels. Therefore, hydrogen concentration on the anode catalyst surface as well as temperature, will be reduced. Whether these changes can improve the poor selectivity of internal air bleed for CO oxidation is still an open question.

1.4.7 The importance of concentration levels

In the literature, most studies have been performed with concentration levels that were one or two orders of magnitude larger than in the ISO 14687-2:2012 standard.

For reversible contaminants, the contaminant levels of ISO 14687-2:2012 standard could be used, as the effect is measurable in a few tens of hours even with high anode catalyst loadings.

For reversible contaminants (most importantly, CO), some have been performed with concentration levels (sub-ppm for CO) that are close to the ones in the ISO 14687-2:2012 standard (Angelo, Bethune

and Rocheleau, 2010; Bender, et al., 2009; Bender, Angelo, Bethune and Rocheleau; Benesch, Salman and Jacksier, 2006; Besancon, et al., 2009; Colon-Mercado, 2010; Imamura, et al., 2007; Knights, et al., 2011; Pérez et al., 2014). However, these studies have been done in single-pass conditions (open anode) and without S/S effects.

For irreversible contaminants, (most importantly, H₂S), only a few studies have been performed with concentration levels close to or the same as the ones in the ISO 14687-2:2012 standard (Rockward, Davey, Fernandez and Garzon, 2010).

This is an understandable approach, as measurements with very low levels of, for example, H₂S are very expensive, and in these measurements the other factors affecting the performance degradation can be in the same order of magnitude as performance degradation due to H₂S contamination.

The poisoning and performance recovery processes depend on a number of factors. The impact of concentration may not be linear. The use of large concentrations of pollutants may be relevant to study the pollution mechanism. However, using concentration of impurities close to the one proposed in the standard is also useful to validate the pollution mechanism.

1.4.8 The load (current) profile on the measurements

As discussed earlier, the average load determines the molar flow rate of contaminants to the anode side. The effect of the load profile is more complex.

Most of the experiments presented in literature are made under steady state conditions. However, it is known that the voltage of the electrode (induced by the current profile) has a strong effect on the adsorption and the desorption rate of the impurities, especially sulphur (Imamura and Matsuda, 2011).

The effect of the current profile may have importance for both reversible (e.g., CO) and irreversible impurities. There have been no comparative studies with the same fuel utilisation and average load, but different load profiles. These measurements would be needed to estimate the need for using a load profile in the contamination studies.

When different load profiles are applied, they also affect water management, which further complicates the interpretation of data even when contaminants are not studied (Bloom, et al., 2013)

When discussing the use of a load profile, it is important to mimic the real hybridised PEMFC system. When a PEMFC system is hybridised, there is practically no operation with idle conditions, as auxiliary components of both PEMFC system and car always consume a minimum amount of power. Therefore, the minimum power of the PEMFC system is a low percentage of nominal power. Consequently, this should be taken into account when defining load profiles.

1.4.9 The importance of cell operating conditions (temperature, humidity, pressure)

The measurement conditions have a strong effect on the contamination process. This applies especially to CO (Murthy, Esayian, Lee and Van Zee, 2003).

The beneficial effect of temperature is clear for CO (Murthy, Esayian, Lee and Van Zee, 2003). The reasons for this effect are increased desorption of CO and increased electrochemical oxidation. The increase in temperature also increases oxygen permeability of the membrane (Kocha, Yang and Jung,

2006) and therefore internal air bleed is increased. On the other hand, the selectivity for CO oxidation may be decreased, similarly to external air bleed (Rajala, 2014).

The effect of humidity is less clear. Humidity affects the gas permeability and internal air bleed. The beneficial effect of the pressure is mostly due to increased internal air bleed (Murthy, Esayian, Lee and Van Zee, 2003).

1.4.10 The analysis of recirculated or exit gas

Exhaust gas analysis has only been applied in less than 15 studies, even if it has been shown that some of the most important contaminants can pass through the cell (CO, H₂S) and desorb during cell operation, as shown by Imamura, et al. (2007).

Exhaust gas analysis has not been applied systemically during operation and start-up/shut-down to identify desorption of contaminants during different operation modes.

The most studied components have been CO/CO₂ and H₂S/SO₂. However, the detection levels of contaminants have been too large in most of the studies for the identification of early pass-through. The relevant levels for CO/CO₂ and H₂S/SO₂ are in the levels of tens of ppb, which have not been measured.

Measurement of impurities or inert gas accumulation in the recirculation loop has been applied in only a few studies (Karimäki, et al., 2011; Nikiforow, Karimäki, Keränen and Ihonen, 2013; Matsuda et al., 2009).

If recirculated gas is analysed, then this may work as purge/bleed if the analysed gas is consumed (Matsuda et al., 2009) or replaced by inert gas (Koski, Pérez and Ihonen, 2014). The smaller the cell size, the larger the effect on fuel utilisation will be. When sensors can be used, as for humidity and hydrogen, then measurement does not change the gas composition.

The recirculated or exit gas analysis is also important when studying the reactivity of the contaminants. In the study of Imamura and Matsuda (2007), mostly H₂S was detected at the anode exit, even if SO₂ was used as contaminant. In the study of Martinez-Rodriguez et al. (2011) tetrachloroethylene was efficiently converted to other (unknown) products.

1.4.11 The importance of anode catalyst loading (catalyst aging)

Most of the CO research has been done with catalysts used in PEMFC, which use reformat fuel. These catalyst are alloys based on Pt (e.g. PtRu) and used with too-high loadings ($\geq 0.4 \text{ mg cm}^{-2}$) which is different from automotive applications. For automotive applications, anode catalysts are composed of pure Pt and the preferred anode loading is between 0.05 mg cm^{-2} and 0.1 mg cm^{-2} .

Catalyst loading has a strong effect on voltage degradation and operation dynamics when there is CO in the hydrogen. This is clearly illustrated in the study of Hashimasa, Matsuda and Akai (2010) for Pt/C catalyst and by Knights et al. (2011) for PtRu/C catalyst. Theoretically, the effect of catalyst (Pt/C) loading has been modelled by Ahluwalia and Wang (2008).

The results of Hashimasa, Matsuda and Akai (2010) show a much greater effect on cell voltage than the modelling of Ahluwalia and Wang (2008) when Pt level is decreased from 0.4 mg cm^{-2} to 0.05 mg cm^{-2} . However, in the study of Hashimasa, Matsuda and Akai (2010) no recirculation was applied. Therefore, the results are not directly comparable.

The effect of catalyst loading has also been studied with H₂S as a contaminant (Hashimasa, Matsuda, Imamura and Akai, 2011). When a constant current measurement was applied, the amount of H₂S fed in to the cell for the same voltage drop was linearly proportional to the catalyst loading.

When high quality hydrogen is used, the Pt loading of the anode can be reduced to 0.05 mgcm⁻² without a significant drop in the cell performance. This was shown first by Gasteiger, Panels and Yan (2004) and later quantified more accurately by Neyerlin, Gu, Jorne and Gasteiger, (2007). It seems that the reduction of Pt loading is limited by the hydrogen quality and possibly also by CO₂ permeation from the cathode.

The anode catalyst loading does not always have a discernible effect on the contamination process. In the case of ammonium, Hashimasa, Matsuda, Imamura and Akai (2011) did not find a relationship between anode catalyst loading and ammonium contamination. However, they found that cathode loading has importance, indicating that ammonium in hydrogen also has contamination effect on the cathode (cross-contamination).

The effect of catalyst aging on CO tolerance has been discussed by Tabata, Yamazaki, Shintaku and Oomori (2009). They noticed that it can be problematic to distinguish between catalyst degradation and gas diffusion layer degradation (increased flooding).

1.4.12 The importance of gas permeation through the membrane (membrane thickness, aging)

In PEMFC the membrane is permeable for gases (Kocha, Yang and Jung, 2006). The permeability data is available for at least hydrogen (Kocha, Yang and Jung, 2006; Matsuda, et al., 2009), oxygen (Baik, Hong and Kim, 2013), nitrogen (Baik and Kim, 2011), carbon dioxide (Ma, Odgaard and Skou, 2007), sulphur dioxide (Brosha, Rockward, Uribe and Garzon, 2010) and helium (Matsuda, et al., 2009).

Membrane permeability for hydrogen is greater than for oxygen or nitrogen (Kocha, Yang and Jung, 2006). However, if water solubility of the component is high, then permeability is also high, as shown for carbon dioxide and sulphur dioxide (Ma, Odgaard and Skou, 2007; Brosha, Rockward, Uribe and Garzon, 2010).

1.4.13 The importance of inert gas accumulation

Almost all of the studies in the literature have been performed using stoichiometric mode, in which there is no significant inert gas accumulation in the channels and cells. When a commercial fuel cell system is operated, there will be inert gas enrichment to the levels of several percent or even tens of percent, depending on the fuel quality, membrane permeability and hydrogen purge rate (Ahluwalia and Wang, 2007; Nikiforow, et al., 2013).

When there is a significant amount of inert gases in the recirculation loop, contaminants can have different effects, as shown by Bhatia and Wang (2004), who showed that the effect of CO is multiplied when there is significant dilution of hydrogen by nitrogen.

There is no consensus which level of inert gas accumulation is best for optimum efficiency, even when the effect of CO is not discussed. Nikiforow, Karimäki, Keränen and Ihonen (2013) have shown that the effect of inert gas accumulation on cell voltage is about twice as large as the value calculated using Nernst equation, which indicates clear mass transfer losses on the anode side.

1.4.14 The importance of cross-contamination from cathode

When the effect of fuel quality is studied, the air quality should be controlled and it should be comparable to the air quality in real PEMFC systems. The issue of air quality has also been reviewed by Zamel and Li (2011) as well as Cheng, et al. (2007).

PSFI membrane permeability for sulphur dioxide is very high, probably due to high solubility of SO₂ in water (Brosha, Rockward, Uribe and Garzon, 2010).

One of the main issues on the air side is sulphur. If there is any sulphur in the cathode air, some of it can be diffused on the anode. Cross-contamination by sulphur and sulphur permeability has been studied in a few papers (Brosha, Rockward, Uribe and Garzon, 2010; Zhai, et al., 2011). On the other hand, a part of the sulphur from the contaminated anode may exit via the membrane and cathode. This adds additional challenges for sulphur balance measurements in contamination studies.

Due to the possibility of anode sulphur contamination via cathode, the low limit (4 ppb) for sulphur compounds in ISO 14687-2:2012 seems unreasonable. However, the relative importance of membrane permeability for anode catalyst sulphur contamination and recovery requires more effort. This is not only for defining the limits of ISO 14687-2:2012, but also for defining the correct air quality requirements.

St-Pierre, Zhai and Angelo (2014) have recently studied systemically many potential airborne contaminants and have discussed the probability of cross-contamination.

It has not been discussed if anode side fuel utilisation has importance for cross-contamination from the cathode. The higher the fuel utilisation, the higher will be the concentration of any contaminant in the anode loop, including contaminants permeating from the cathode.

1.4.15 The effect of carbon dioxide and RWGS

The carbon dioxide limit of the ISO 14687-2:2012 is 2 ppm. At maximum fuel utilisation level (about 99.8%) this would lead to the level of 1000 ppm in the anode recirculation gas. However, the high permeability of CO₂ in wet conditions (Ma, Odgaard and Skou, 2005) can limit the level of CO₂ enrichment because there will be permeation to the cathode.

On the other hand, CO₂ from the cathode permeates to the anode as long as the CO₂ level on the anode side is lower than on the cathode. Therefore, there will always be some CO₂ on the anode even if the hydrogen fuel is completely CO₂-free.

The unavoidable existence of CO₂ on the anode side means that there can always be formation of CO via a reverse water gas shift (RWGS) reaction. The effect of CO₂ and the importance of CO formation via RWGS have been discussed in a number of studies, most of which are reviewed by Du, Pollard, Elter and Ramani, (2009). According to modelling work of Ahluwalia and Wang (2008), the acceptable level of CO₂ would be two orders of magnitude higher than the limit in ISO 14687-2:2012.

However, the effect of CO₂ has not been studied experimentally in the levels relevant to ISO 14687-2:2012 and not in combination with sub-ppm level of CO. This type of research would require very high fuel utilisation in order to quantify the accumulated CO₂ and CO.

The high permeability of CO₂ via membrane means that contamination studies should not be performed with CO₂-free air, as there can be formation of CO via RWGS.

1.4.16 The effect of multiple contaminants

The combinations of different contaminants have been studied only a few times (e.g. Molter, 2011; Rockward, et al., 2007). In most of these studies, no motivation was given for selecting the combinations and levels. In some cases, the maximum levels of ISO 14687-2:2012 have been selected.

However, when hydrogen is mostly produced from methane using steam reforming (SMR) and purified by pressure swing adsorption (PSA), the probability of contamination combinations is severely limited if no contamination event occurs in the transport and distribution of hydrogen. It seems that risk assessment is needed for the determination of the relevant combinations of contaminants.

In the early phase of FCEV commercialisation, a significant part of the hydrogen can be by-product hydrogen from the chemical industry. For this hydrogen the combinations of contaminants may be completely different from SMR-PSA.

Due to high permeability of CO₂, there will always be some CO₂ transfer from the cathode and consequently all the measurements are multiple contaminant measurements (CO₂ and other contaminants). For the quantification of the CO₂ influence on the contamination process, the measurement of CO₂ on the anode side could be applied.

1.4.17 The effect of flow field geometry in the cells

When the effects of contaminants have been studied, different cells have been used. However, the used cell structures used may have significant effect on the results.

There are recommendations for the single cell in standard IEC/TS 62282-7-1. In addition, in the work of Hashimasa et al. (2006), different issues related to fuel cell test cell hardware were comprehensively discussed.

If there are multiple channels in the research cell, then flooding of the channel may take place either on the anode or on the cathode if linear flow velocity is not sufficiently high all the time (Anderson, et al., 2010).

Flooding of the channel (formation of slug) or even uneven accumulation of the droplets may create significant differences between the stoichiometry in different channels. This will make it difficult to interpret the results as there will be different amounts of contaminants in different channels and channel flooding will also change the current distribution (Pérez, Ihonen, Sousa and Mendes, 2013). Flooding of the channel may also cause MEA degradation (Kim, et al., 2014).

For the abovementioned reasons a single channel structure may be recommended for the contamination studies. This, however, will limit the cell size to about 25 cm². Even with this relatively small cell size, the cathode channels must be large, at least 1 mm deep and wide, to avoid unrealistically high pressure drops.

The large channel size on the cathode will affect cell performance at high current densities, as shown by Hashimasa et al. (2006) and Goebel (2011). Hashimasa et al. (2006) showed that the channel depth also has a significant effect on the cell performance, in addition to channel and land widths.

Therefore, the combination of high cell performance in the mass transfer region and low turndown ratio is difficult, if not impossible, to reach in hydrogen fuel contamination studies.

If the focus of the research is in the high current region only, then multiple channel cells could be used, because linear flow velocity is high all the time. However, if current profiles with low current densities are used, then the use of a single channel flow field is necessary.

The orientation of the cell (co- or counter-flow) will affect the water balance and all the parameters that are dependent on that. In practical automotive PEMFC systems, the geometry is most probably always counter-flow as the anode recirculation will be used for the distribution of the water. Therefore, this could also be recommended in hydrogen fuel contamination studies.

1.4.18 The effect of GDL material through cathode mass transfer (flooding)

The GDL material has a crucial effect on the water management in automotive PEMFC systems. By choosing the right type of GDL material, water transfer to the anode can be enhanced. The drawback is that the system becomes more susceptible to flooding of the GDL.

When contamination studies are done, automotive MEAs and GDLs should be used to achieve the most representative results. However, the high performance operating range of these materials is quite narrow and optimised for automotive PEMFC systems. In practice, temperature and relative humidity should be within relative narrow limits to enable stable operation. This seriously limits the possibility of studying the effect of temperature and humidity on the contamination process.

When automotive type MEAs and GDLs are used, then the changes in current distribution due to contamination may trigger the problem of cathode flooding due to increased water production and change of humidity distribution.

1.4.19 The effect of system contaminants and cell degradation products

The effect of system contaminants on catalyst surface area and cell performance can be significant (Wang, et al., 2014; Opu, et al., 2012). The problem of system contaminants can be significant when the effects of both reversible and irreversible contaminants are measured, because the effect of system contaminants can also be either reversible or irreversible.

The longer the duration of the measurements, the more significant the effect of system contaminants, especially if high fuel utilisation is applied.

1.4.20 The effect of internal air bleed and risk of unintentional external air bleed

Oxygen diffusion from the cathode, known as internal air bleed, has a significant effect on the contamination process, especially for CO oxidation. The effect of internal air bleed is dependent on temperature, pressure and humidity because the oxygen permeability is dependent on these parameters (Wang, 2009).

One of the main questions is how much of the CO is oxidised by electrochemical oxidation and how much by chemical oxidation due to internal air bleed. Electrochemical oxidation is dependent on the temperature, anode potential and catalyst type (Zhang and Datta, 2003).

Selectivity of internal air bleed for CO oxidation is very low, as most of the oxygen is consumed by hydrogen oxidation (Alvarez, 2006; Ahluwalia and Wang, 2008). When external air bleed was applied, an oxygen to carbon monoxide concentration ratio in the range of one hundred was needed to mitigate the effect of CO when Pt was used as anode catalyst. Slightly less was needed for PtRu as a catalyst (Rajala, 2013).

One of the open issues is the effect of temperature on the selectivity. In one external air bleed study it was noted that more air was needed for the same recovery of performance when the temperature was increased (Rajala, 2013). This indicates that selectivity for CO oxidation is reduced when the temperature is increased. However, the result is valid only for PtRu as a catalyst and for external air bleed.

Unintentional external air bleed can occur due to oxygen dissolved in anode humidifier water. For example, in Helsinki municipal water the amount of oxygen is 15 mg/dm³. This would lead oxygen content of up to 10 ppm in hydrogen fuel, which is sufficient to affect sub-ppm CO contamination measurements. If a test station applies a periodic drain of humidifier water, the resulting oxygen concentration in hydrogen fuel can be hundreds of ppm.

1.4.21 The effect of long conditioning before the experiment

In some of the literature studies the cell is operated a long time, even tens of hours, before the measurements are performed (Molter, 2011; Reshетенko, Bethune and Rochelau, 2012). During this conditioning period there can be either clean-up of the catalyst surfaces or pre-contamination of the electrodes by CO, if there is any CO in the hydrogen. If long conditioning is used, then the control of hydrogen quality becomes more important.

The effect of CO is not visible in the relatively high surface coverage levels if CO is evenly distributed. However, the adsorbed CO reduces the available surface area for the adsorption of the studied contaminant and therefore influences the contamination process.

In longer experiments with high fuel utilisation, CO₂ enrichment and the formation of CO via RWGS should also be estimated. Otherwise, the experiments are started with pre-contaminated surfaces.

It would be beneficial to start the experiments from reproducible clean surfaces. It has been observed that nitrogen purging with some load remaining helps to clean the surface from CO (Pérez, et al., 2014). However, such S/S procedures may increase catalyst degradation on the anode or on the cathode.

1.4.22 The effect of contaminant dissolution in product water (wash-out)

The dissolution in the anode exhaust water is negligible for most of the contaminants, as shown by Bender et al. (2009). However, in wet conditions, a significant amount of water can be exhausted by the purge (Nikiforow, et al., 2013) and therefore the solubility in water cannot be neglected for the contaminants that have high Henry's constant. The relevant contaminants in ISO 14687-2:2012 standard include ammonia, formic acid, formaldehyde and to a certain extent sulphur dioxide (total sulphur).

The dissolution to the product water (purged water) may have a significant impact on the contamination mitigation for those impurities, which are assumed to accumulate in the anode recirculation loop. The fraction of the water leaving from the anode side as liquid water can be in the range of 5% of all exit water (Nikiforow, Karimäki, Keränen and Ihonen, 2013).

In practice, the wash-out of the impurity will limit the maximum concentration of the impurity in the recirculation loop. Most importantly, formic acid has a Henry's law constant for solubility in water (at 298.15 K) of about 5000, and for formaldehyde the Henry's law constant is about 5. In the case of formic acid it seems obvious that enrichment in the recirculation loop will be limited due to removal by purged

water. For formaldehyde removal by purged water may also have some significance, especially during S/S, when FC system is cooled down.

In their recent paper, St-Pierre, Zhai and Angelo (2014) have discussed the importance of wash-out for the selected airborne contaminants using Henry's law constants. A similar analysis for the contaminants on the anode side would be useful. In their model system approach, St-Pierre, Wetton, Zhai and Ge (2014) further studied the wash-out and found out that dissociation reactions (e.g., SO_2) further pronounce the effect of contaminant washout.

1.4.23 The spatial distribution of the contaminant effect

The effect of contaminants has been studied only a few times using equipment for measuring current distribution. Until 2011 these studies were reviewed by Pérez, Brandão, Sousa, and Mendes (2011). In 2012 Reshetenko, Bethune and Rocheleau published a study with a CO level of 2 ppm, which is such that the data is usable for determining research needed to revise ISO 14687-2:2012. The work of Reshetenko, Bethune and Rocheleau (2012) showed that there can be significant loss of the electrochemical area during the measurements and this loss was inhomogeneous in the cell, being larger at the exit of the cell (co-flow configuration).

1.5 The recommendations for the future hydrogen contamination research

1.5.1 The development of single cell measurements for contaminant studies

There is an urgent need for developing more a harmonised methodology for hydrogen and air impurity studies. The most important issue is defining when measurements can be done with a single pass (open anode) and when they must be done with fuel recirculation allowing similar fuel utilisation as in automotive PEMFC systems (>99%).

Since the catalyst area on the anode has a tremendous importance on the contamination process, the measurement of the anode catalyst area should be part of the standardised measurements protocols.

1.5.2 The development of recirculation set-up with small gas volume

The dynamics of impurity enrichment in the anode recirculation loop is dependent on the gas volume of the recirculation loop. Since automotive PEMFC systems are volume optimised, the gas volume in the anode recirculation loop is in the order of 0.1 dm^3 per kW of FC stack power. This corresponds to $0.1\text{-}0.2 \text{ cm}^3$ volume per cm^2 membrane area.

In small research cells this value is very difficult to reach. For example in the study of Matsuda et al. (2009), the volume of the recirculation loop for a 25 cm^2 cell was 4.2 dm^3 , and in the study of Koski, Pérez and Ihonen (2014) the volume was 0.3 dm^3 for the same size (25 cm^2) of cell.

However, the volume of the anode recirculation loop should be reduced to the level of $0.5\text{-}1 \text{ cm}^3$ volume per cm^2 membrane area. With this volume the dynamics of enrichment are visible in the range of typical user times (tens of minutes to 1-2 hours) of PEMFC automotive systems.

If recirculated gas is dried and humidity is added in the anode gas, then purity of the anode humidifier water has very high requirements. In practice, well-performed degassing of the used humidifier water used in the experiment is needed.

1.5.3 The development of gas analysis from anode recirculation loop or anode exit

Measuring the enrichment of contaminants in the anode recirculation loop or anode exit is crucial because it provides information about adsorption and reaction of impurities as well as information about diffusion through the membrane (especially CO₂).

Since the gas sampling is very difficult to perform without affecting the gas composition, it should be done so that it disturbs the system operation as little as possible, while still providing useful information.

One of the critical issues is the drying of the gas before the analysis. If only contaminants with low water solubility are analysed, then condensing of the water is sufficient. However, any remaining humidity must be measured or gas should be dried further using a membrane drier.

If contaminants with very high water solubility, such as formic acid, are studied, then careful condensing of the water and analysis of the product water can give valuable information about contaminant accumulation.

If water soluble gases are analysed, then analysis should be performed from both gas and condensed water. Alternatively, a membrane drier can be applied as done by Pérez et al. (2014).

1.5.4 The measurement of contaminant reactivity and reaction products

The reactivity of some of the most problematic contaminants (in terms of gas analysis) has not been measured. These include formic acid and formaldehyde in particular. These both have a very weak, but discernible poisoning effect (Zhang, et al., 2010; Narusawa, et al., 2003; Molter, 2011). However, the limits for these contaminants are 0.2 ppm and 0.01 ppm in ISO 14687-2:2012, respectively. These low limits are most probably due to the assumption of high enrichment in the anode recirculation loop, as the poisoning coefficients have been determined to be 0.1 times and 0.004 times that of CO for formic acid and formaldehyde, respectively (Narusawa, et al., 2003). If it is shown that these contaminants are converted to CO₂ or dissolved in water and removed during purge, then these limits could be changed.

1.5.5 The development of methodology to study recovery from poisoning due to desorption

Anode poisoning by sulphur is a difficult process to study. When the level of 4 ppb in the standard ISO 14687-2:2012 has been decided, it has probably been assumed that there will be a monolayer of sulphur on the anode catalyst and the electrode loading is 0.05 mgcm⁻², because the poisoning process is not dependent on the concentration level but the total moles of contaminant fed in to the cell (Hashimasa, Matsuda, Imamura and Akai, 2011).

However, numerous studies have shown that a large amount of sulphur can be desorbed from the anode or cathode catalyst surface (Gould, et al., 2010; Imamura, et al., 2007; Imamura and Hashimasa, 2007).

The adsorption of sulphur is decreasing the electrochemically active area for hydrogen oxidation reaction (HOR). However, it is also decreasing the available adsorption surface for carbon monoxide.

In one plausible scenario a significant part of the anode catalyst area is lost due to sulphur adsorption, but this will not disturb the performance if CO-free hydrogen is used. However, as soon as there is carbon monoxide in the fuel, then there will be a serious drop in the performance. In other words, the CO tolerance of the anodes pre-contaminated by sulphur should be studied.

The sulphur on the anode can originate from the fuel or from the air through cross-contamination (Brosha, Rockward, Uribe and Garzon, 2010). When it originates from the hydrogen fuel it may or may not be entering with high levels of carbon monoxide. The probability of simultaneous carbon monoxide and sulphur poisoning is dependent on hydrogen the production and purification method. The same is true for all other combinations of contaminants.

1.6 References for Chapters 1.4 and 1.5

Ahluwalia, R. K. and X. Wang. 2008. Effect of CO and CO₂ Impurities on Performance of Direct Hydrogen Polymer-Electrolyte Fuel Cells. *Journal of Power Sources* 180:122-31.

Ahluwalia, R. K. and X. Wang. 2007. Buildup of Nitrogen in Direct Hydrogen Polymer-Electrolyte Fuel Cell Stacks. *Journal of Power Sources* 171:63-71.

Alvarez, Marco V. S. 2006. Investigations of Current Density Inhomogeneities in Polymer Electrolyte Fuel Cells Zürich: ETH/PSI.

Anderson, Ryan, Lifeng Zhang, Yulong Ding, Mauricio Blanco, Xiaotao Bi and David P. Wilkinson. 2010. A Critical Review of Two-Phase Flow in Gas Flow Channels of Proton Exchange Membrane Fuel Cells. *Journal of Power Sources* 195:4531-53.

Angelo, Michael, Keith Bethune and Richard Rocheleau. 2010. The Impact of Sub Ppm Carbon Monoxide and Ppm Level CO/Toluene and Methylcyclohexane/CO Mixtures on PEMFC Performance and Durability. *ECS Transactions* 28:169-81.

Aprea, José L. "Quality Specification and Safety in Hydrogen Production, Commercialization and Utilization". *International Journal of Hydrogen Energy* .

Baik, K. D., B. K. Hong and M. S. Kim. 2013. Novel Technique for Measuring Oxygen Crossover through the Membrane in Polymer Electrolyte Membrane Fuel Cells. *International Journal of Hydrogen Energy* 38:8927-33.

Baik, K. D. and M. S. Kim. 2011. Characterization of Nitrogen Gas Crossover through the Membrane in Proton-Exchange Membrane Fuel Cells. *International Journal of Hydrogen Energy* 36:732-9.

Barrio, M., V. Hasanov, G. de Souza and F. Starr. 2007. D 3.2.2 DYNAMIS H₂ Quality Recommendations. .

Bender, G., M. Angelo, K. Bethune, S. Dorn, T. Thampan and R. Rocheleau. 2009. Method using Gas Chromatography to Determine the Molar Flow Balance for Proton Exchange Membrane Fuel Cells Exposed to Impurities. *Journal of Power Sources* 193:713-22.

Bender, G., M. Angelo, K. Bethune and R. Rocheleau. 2013. Quantitative Analysis of the Performance Impact of Low-Level Carbon Monoxide Exposure in Proton Exchange Membrane Fuel Cells. *Journal of Power Sources* 228:159-69.

Benesch, R., Salman, S. and Jacksier, T. 2006. The Effect of Fuel and Oxidant Contaminants on the Performance of PEM Fuel Cells. WHEC 16, Lyon, France. .

Besancon, B. M., V. Hasanov, R. Imbault-Lastapis, R. Benesch, M. Barrio and M. J. MølInvik. 2009. Hydrogen Quality from Decarbonized Fossil Fuels to Fuel Cells. *International Journal of Hydrogen Energy* 34:2350-60.

Bhatia, K. K. and C. -. Wang. 2004. Transient Carbon Monoxide Poisoning of a Polymer Electrolyte Fuel Cell Operating on Diluted Hydrogen Feed. *Electrochimica Acta* 49:2333-41.

Bloom, I., L. K. Walker, J. K. Basco, et al. 2013. A Comparison of Fuel Cell Testing Protocols - A Case Study: Protocols used by the U.S. Department of Energy, European Union, International Electrotechnical Commission/Fuel Cell Testing and Standardization Network, and Fuel Cell Technical Team. *Journal of Power Sources* 243:451-7.

Brosha, E. L., T. Rockward, F. A. Uribe and F. H. Garzon. 2010. Measurement of H₂S Crossover Rates in Polymer Fuel Cell Membranes using an Ion-Probe Technique. *Journal of the Electrochemical Society* 157:B180-6.

Cheng, X., Z. Shi, N. Glass, et al. 2007. A Review of PEM Hydrogen Fuel Cell Contamination: Impacts, Mechanisms, and Mitigation. *Journal of Power Sources* 165:739-56.

Colon-Mercado, H. 2010. Effect of Fuel Impurities on Fuel Cell Performance and Durability. Vol. SRNL-STI-2010-00596 United States: Savannah River National Laboratory.

Dehn, S., Woehr, M. and Heinzl, A. 2011. Development of a Near-Dead-Ended Fuel Cell Stack Operation in an Automotive Drive System. Paper presented at 2011 IEEE Vehicle Power and Propulsion Conference, VPPC 2011. .

Du, Bin, Richard Pollard, John F. Elter and Manikandan Ramani. 2009. Performance and Durability of a Polymer Electrolyte Fuel Cell Operating with Reformate: Effects of CO, CO₂, and Other Trace Impurities. Polymer Electrolyte Fuel Cell Durability. Edited by Felix N. Büchi, Minoru Inaba and Thomas J. Schmidt. Springer New York.

Gasteiger, H. A., J. E. Panels and S. G. Yan. 2004. Dependence of PEM Fuel Cell Performance on Catalyst Loading. Journal of Power Sources 127:162-71.

Goebel, S. G. 2011. Impact of Land Width and Channel Span on Fuel Cell Performance. Journal of Power Sources 196:7550-4.

Gould, B. D., G. Bender, K. Bethune, et al. 2010. Operational Performance Recovery of SO₂-Contaminated Proton Exchange Membrane Fuel Cells. Journal of the Electrochemical Society 157:B1569-77.

Hashimasa, Y., Matsuda, Y. and Akai, M. 2010. Effects of Platinum Loading on PEFC Power Generation Performance Deterioration by Carbon Monoxide in Hydrogen Fuel. Paper presented at ECS Transactions. .

Hashimasa, Y., Y. Matsuda, D. Imamura and M. Akai. 2011. PEFC Power Generation Performance Degradation by Hydrogen Sulfide and Ammonia - Effects of Lowering Platinum Loading -. Electrochemistry 79:343-5.

Hashimasa, Y., T. Numata, K. Moriya and S. Watanabe. 2006. Study of Fuel Cell Structure and Heating Method. Development of JARI's Standard Single Cell. Journal of Power Sources 155:182-9.

Imamura, D., D. Ebata, Y. Hashimasa, M. Akai and S. Watanabe. 2007. Impact of Hydrogen Fuel Impurities on PEMFC Performance. SAE Paper 2007-01-2010 .

Imamura, D. and Hashimasa, Y. 2007. Effect of Sulfur-Containing Compounds on Fuel Cell Performance. Paper presented at ECS Transactions. .

Karimäki, H., L. C. Pérez, K. Nikiforow, T. M. Keränen, J. Viitakangas and J. Ihonen. 2011. The use of on-Line Hydrogen Sensor for Studying Inert Gas Effects and Nitrogen Crossover in PEMFC System. International Journal of Hydrogen Energy 36:10179-87.

Kim, Mansu, Namgee Jung, KwangSup Eom, et al. 2014. Effects of Anode Flooding on the Performance Degradation of Polymer Electrolyte Membrane Fuel Cells. Journal of Power Sources 266:332-40.

Knights, S., Bashyam, R., He, P., et al. 2011. PEMFC MEA and System Design Considerations. Paper presented at ECS Transactions. .

Kocha, S. S., J. D. Yang and J. S. Yi. 2006. Characterization of Gas Crossover and its Implications in PEM Fuel Cells. AIChE Journal 52:1916-25.

Koski, P., L. C. Perez and J. Ihonen. 2014. Comparison of Anode Gas Recirculation with Hydrogen Purge and Bleed in New Type of PEMFC Laboratory Test Cell Configuration. Fuel Cells Manuscript submitted for publication:.

Ma, S., M. Odgaard and E. Skou. 2005. Carbon Dioxide Permeability of Proton Exchange Membranes for Fuel Cells. Solid State Ionics 176:2923-7. .

Ma, S. and E. Skou. 2007. CO₂ Permeability in Nafion® EW1100 at Elevated Temperature. Solid State Ionics 178:615-9.

Martinez-Rodriguez, Michael J., Elise B. Fox, William D. Rhodes, Christopher S. McWhorter, Scott Greenway and Hector R. Colon-Mercado. 2011. The Effect of Low Concentrations of Tetrachloroethylene on the Performance of PEM Fuel Cells. Journal of the Electrochemical Society 158:B698-702.

Matsuda, Y., Y. Hashimasa, D. Imamura, M. Akai and S. Watanabe. 2009. Accumulation Behavior of Impurities in Fuel Cell Hydrogen Circulation System. Review of Automotive Engineering 30:167-72.

Molter, T. 2012. Final Report - Effects of Impurities on Fuel Cell Performance and Durability. United States: The University of Connecticut.

Murthy, M., M. Esayan, W. -. Lee and J. W. Van Zee. 2003. The Effect of Temperature and Pressure on the Performance of a PEMFC Exposed to Transient CO Concentrations. Journal of the Electrochemical Society 150:A29-34.

- Narusawa, K., M. Hayashida, Y. Kamiya, H. Roppongi, D. Kurashima and K. Wakabayashi. 2003. Deterioration in Fuel Cell Performance Resulting from Hydrogen Fuel Containing Impurities: Poisoning Effects by CO, CH₄, HCHO and HCOOH. *JSAE Review* 24:41-6.
- Neyerlin, K. C., W. Gu, J. Jorne and H. A. Gasteiger. 2007. Study of the Exchange Current Density for the Hydrogen Oxidation and Evolution Reactions. *Journal of the Electrochemical Society* 154:B631-5.
- Nikiforow, K., H. Karimäki, T. M. Keränen and J. Itonen. 2013. Optimization Study of Purge Cycle in Proton Exchange Membrane Fuel Cell System. *Journal of Power Sources* 238:336-44.
- Opu, Md, Ohashi, M., Cho, H. S., Macomber, C. S., Dinh, H. N. and Van Zee, J. W. 2012. Understanding the Effects of Contaminants from Balance of Plant Assembly Aids Materials on PEMFCs - IN-SITU Studies. Paper presented at ECS Transactions. .
- Pérez, L. C., L. Brandão, J. M. Sousa and A. Mendes. 2011. Segmented Polymer Electrolyte Membrane Fuel Cells-A Review. *Renewable and Sustainable Energy Reviews* 15:169-85.
- Pérez, L. C., J. Itonen, J. M. Sousa and A. Mendes. 2013. Use of Segmented Cell Operated in Hydrogen Recirculation Mode to Detect Water Accumulation in PEMFC. *Fuel Cells* 13:203-16.
- Pérez, L. C., P. Koski, J. Itonen, J. M. Sousa and A. Mendes. 2014. Effect of Fuel Utilization on the Carbon Monoxide Poisoning Dynamics of Polymer Electrolyte Membrane Fuel Cells. *Journal of Power Sources* 258:122-8.
- Pérez, L. C., T. Rajala, J. Itonen, P. Koski, J. M. Sousa and A. Mendes. 2013. Development of a Methodology to Optimize the Air Bleed in PEMFC Systems Operating with Low Quality Hydrogen. *International Journal of Hydrogen Energy* 38:16286-99.
- Rajala, Taneli. 2014. Enhancement of Polymer Electrolyte Fuel Cell Tolerance to CO by Combination of Different Mitigation Methods (MSc. Thesis Work). Helsinki: Helsinki University.
- Reshetenko, Tatyana V., Keith Bethune and Richard Rocheleau. 2012. Spatial Proton Exchange Membrane Fuel Cell Performance Under Carbon Monoxide Poisoning at a Low Concentration using a Segmented Cell System. *Journal of Power Sources* 218:412-23.
- Rockward, T., Urdampilleta, I. G., Uribe, F. A., Brosha, E. L., Pivovar, B. S. and Garzon, F. H. 2007. The Effects of Multiple Contaminants on Polymer Electrolyte Fuel Cells. Paper presented at ECS Transactions. .
- St-Pierre, J., Y. Zhai and M. S. Angelo. 2014. Effect of Selected Airborne Contaminants on PEMFC Performance. *Journal of the Electrochemical Society* 161:F280-90.
- St-Pierre, Wetton, B., Y. Zhai and J. Ge. 2014. Liquid Water Scavenging of PEMFC Contaminants. *Journal of the Electrochemical Society* 161:E3357-64.
- Tabata, Takeshi, Osamu Yamazaki, Hideki Shintaku and Yasuharu Oomori. 2009. Degradation Factors of Polymer Electrolyte Fuel Cells in Residential Cogeneration Systems. *Polymer Electrolyte Fuel Cell Durability*. Edited by Felix N. Büchi, Minoru Inaba and Thomas J. Schmidt. Springer New York.
- Wang, H., C. Macomber, J. Christ, G. Bender, B. Pivovar and H. N. Dinh. 2014. Evaluating the Influence of PEMFC System Contaminants on the Performance of Pt Catalyst Via Cyclic Voltammetry. *Electrocatalysis* 5:62-7.
- Wang, W. 2009. The Effect of Internal Air Bleed on CO Poisoning in a Proton Exchange Membrane Fuel Cell. *Journal of Power Sources* 191:400-6.
- Yu, X., M. Pingwen, H. Ming, Y. Baolian and Z. -. Shao. 2009. The Critical Pressure Drop for the Purge Process in the Anode of a Fuel Cell. *Journal of Power Sources* 188:163-9.
- Zamel, N. and X. Li. 2011. Effect of Contaminants on Polymer Electrolyte Membrane Fuel Cells. *Progress in Energy and Combustion Science* 37:292-329.
- Zhai, J., M. Hou, H. Zhang, et al. 2011. Study of Sulfur Dioxide Crossover in Proton Exchange Membrane Fuel Cells. *Journal of Power Sources* 196:3172-7.
- Zhang, J. and R. Datta. 2003. Online Monitoring of Anode Outlet CO Concentration in PEM Fuel Cells. *Electrochemical and Solid-State Letters* 6:A5-8.

2. A review of supplementary results of hydrogen fuel contamination studies

In this Chapter some of the research studies are analysed in further detail in order to create strategy for the contamination measurement studies in the HyCoRA project.

2.1 Sulphur contamination

Studying the impact of H₂S is extremely challenging since a few ppb of H₂S in hydrogen is sufficient to severely poison the cell if the duration is long enough. The lowest reported concentrations are 20 ppb (Knights, et al., 2005) and 10 ppb (Garzon et al., 2006). In these tests the duration of the measurement is in the order of thousand hours or more. Since there are other sources of degradation, the use of a parallel reference cell would be necessary in order to distinguish the effect of H₂S from base level degradation.

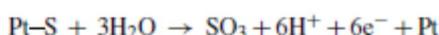
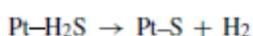
Rockward, Davey, Fernandez, and Garzon (2010) have measured 200-300 μV/h degradation with 4 ppb sulphur level. The degradation rate is 2-3 higher than in the measurements of Knights et al. (2005) with concentration of 20 ppb. This illustrated the difficulty of measurements with these low concentrations.

Clearly, measuring very low levels of sulphur poisoning is very challenging. In these measurements a parallel cell working with pure H₂ and otherwise similar conditions and cell components could be recommended.

The detection of very low level H₂S may also be difficult in the measurements. Wang et al have developed a method for the detection of SO₂ using the adsorption–desorption method (Wang, et al., 2010).

2.1.1 Mechanism of the sulphur contamination

The pollution is due to the dissociation of H₂S to 2H⁺, S and 2e⁻ whose standard potential is 0.144 V/NHE in acidic solution. On Pt, it occurs at about 0.5 V/DHE to form a Pt-S_{ads} species. The elemental sulphur adsorbed on Pt blocks the catalyst, which prevents the HOR from occurring (Lopes, Paganin and Gonzales, 2011). The activation energy for the adsorption of sulphur on Pt has been calculated to be equal to 28.2 ± 5.5 kJ/mol (Mohtadi, Lee and Van Zee, 2005). Shi, et al. (2007) showed that the H₂S dissociation reached a maximum at 0.4 V/DHE at 90°C, 0.5 V at 60°C and 0.6 V at 30°C. He also showed that the desorption of S_{ads} species starts at 0.8 V at 90°C, 0.9 V at 60°C and 1.0 V at 30°C. The adsorption/desorption of sulphur are performed according to the following equations:



Because of the involved potentials, which are very high for the anode side, electrodesorption of S_{ads} species are almost impossible in the operation conditions of the PEMFC. Thus, the impact of H₂S is not reversible and no steady state is observed during H₂S poisoning in normal operation condition.

2.1.2 Effect of the temperature on the sulphur pollution

Working in a potentiostatic mode (0.6 V) on Pt, Mohtadi showed that an increase of temperature accelerates the catalyst poisoning. In these conditions with 5 ppm H₂S in H₂, the Pt-S formation is 69% lower at 50°C than at 90°C. These results are convenient with the H₂S dissociation potential which is lower at higher temperature, in other words H₂S dissociation rate increase with temperature.

In galvanostatic mode, Shi, et al. (2007) showed that the lost of performance is faster at 35°C than at 90°C which seems to contradict the results of Mohtadi, Lee and Van Zee (2005). But in these operating conditions the temperature of the cell can probably have an effect on the electrode potential. And an increase of the anode potential is known to increase the Pt-S_{ads} formation.

Noda et al have shown that the drop in performance of H₂S under galvanostatic mode, is faster at 30°C than at 80 °C.

2.1.3 Effect of the concentration on the sulphur pollution

An increase in the concentration of H₂S in hydrogen accelerates the loss of performance of PEMFC.

In most of the studies the levels of H₂S have been so high that the real dependency on the concentration is difficult to determine. If all H₂S is always adsorbed and adsorption is completely irreversible, then degradation is dependent only on the total amount of H₂S (or sulphur).

The results in the literature indicate that some very slow recovery can take place after poisoning (Mohtadi, et al., 2003). This indicates that sulphur adsorption is not completely irreversible. It can be expected that desorption of sulphur is temperature dependent and therefore the limit for H₂S could be increased if operation temperature of the fuel cell is increased.

There are very few fuel cell studies in which the exhaust concentrations of sulphur compounds are measured. In the measurements of Imamura et al. it was detected that only part of the H₂S or SO₂ were adsorbed and compounds could be detected from the exhaust (Imamura, et al., 2007). In addition, H₂S desorption could be detected after operating with neat hydrogen and switching the cell to open potential. This also indicates that some desorption of sulphur is possible to achieve. This also indicates it is possible to achieve some desorption of sulphur.

In the measurements of Imamura, et al. (2007a) the measured level of sulphur at exhaust was tens of percentage points of initial concentration. The impurity levels were 2 ppm and the gas utilization ratio for fuel only 17%. These results seriously question the assumption that most of the sulphur (practically all) is adsorbed and compounds are not enriched in the anode gas.

If this is true, then gas recirculation on the anode should also be applied in the research of sulphur compounds. The repetition of measurements of Imamura et al. with much lower concentrations could solve this issue.

2.1.3 Mitigation strategies for the sulphur pollution

Unfortunately, the methods used to diminish the CO poisoning effect are (almost) useless in the case of pollution by the H₂S. For example, Mohtadi et al. (2003), showed that the use of a Pt-Ru alloy does not improve the tolerance to H₂S.

Recently, Lopes Paganin and Gonzales (2011) showed that the use of air bleeding could have a beneficial impact on H₂S tolerance but this is not as satisfying as for the CO poisoning.

In general, removal of sulphur is based on its conversion back to H₂S or SO₂ and desorption in conditions in which adsorption is hindered. The promotion of adsorption can be done by applying high or low electrochemical potential and possibly by changing the gas composition.

Electrochemical method

As the oxidation potential of sulphur that is adsorbed on Pt is too high to be reached in the PEMFC operation conditions, the recovery of the initial performance of the cell after H₂S poisoning requires specific electrochemical procedure. Shi applied pulsed potential at 1.5 V for 20s follow by 0.2 V for 20s for a single cell, the time is raised to 2 min in the case of a 10-cell stack (Shi, et al., 2007). During 10 poisoning-recovery cycles of a single cell, the initial performance was recovered after each cycle. However, the poisoning effect increased with the number of cycles, which probably shows an irreversible effect of the H₂S poisoning or an impact of the recovery process on the cell due to too high potential being applied.

This method of high potential oxidation may become more relevant for both anode and cathode if carbon based catalyst supports can be replaced by metal oxides such as tungsten oxide (WO₃), which tolerate higher potentials without oxidation of the catalyst support.

Sethuraman and Weidner (2010) showed that CV between 50 and 1400 mV vs.DHE at 5 mV.s⁻¹ allows recovering the performance of the cell even if CO stripping experiment does not show the recovery of the entire initial active surface area. They proposed the formation of 2 adsorbed species with one hard to oxidize. The adsorption of this hard-to oxidize species is observed when the anode overpotential is maintained at 500 mV during the poisoning step.

Another method to recover the performance of the PEMFC is to reduce the elemental sulphur adsorbed on the catalyst in H₂S. It is possible by applying at the anode a potential close to zero. In that case, the following reaction is favoured:



Imamura and Hashimasa (2007b) used hyper humidified gas at the anode to favour H₂S desorption from the catalyst.

Chemical method

In 2012, Zhai et al have shown that the impact of SO₂ at the cathode led to plateau of the cell voltage drop. The authors explain that this is due to the formation of H₂O₂ that in situ oxidize the adsorbed S onto Pt. The formed SO₄²⁻ is then released from the catalyst.

More recently in 2014, Kakati and Kucernak report that the use of ozone (O_3) allows the oxidation of the S adsorbed species at the anode. The yield of cleaning is higher by using O_3 than electrochemical methods (CV).

The use of external H_2O_2 or O_3 to clean an catalyst is hard to handle in a working system. However, it seems that there could be internal mechanism that would help to move sulphur from the catalyst during the start/stop phase where some jumps of electrode potential are sometimes observed.

References

Garzon, F.H., Rockward, T., Urdampilleta, I.G., Brosha, E.L. & Uribe, F.A. 2006, "The impact of hydrogen fuel contaminants on long-term PMFC performance", ECS Transactions, pp. 695.

Imamura, D., Ebata, D., Hashimasa, Y., Akai, M. & Watanabe, S. 2007a, "Impact of Hydrogen Fuel Impurities on PEMFC Performance", SAE Paper 2007-01-2010, .

Imamura, D. & Hashimasa, Y. 2007b, "Effect of sulfur-containing compounds on fuel cell performance", ECS Transactions, pp. 853.

Knights, S., Jia, S., Chuy, C. & Zhang, J. 2005, "Fuel Cell Reactant Supply - Effects of Reactant Contaminants", Fuel Cell Seminar 2005, November 14-18, 2005.

Kakati B. K., Kucernak A. R. J., "gas phase recovery of hydrogen sulphide contaminated polymer electrolyte membrane fuel cells", J. Power Sources, 252 (2014) 317-326.

Lopes, T., Paganin, V.A. & Gonzalez, E.R. 2011, "The effects of hydrogen sulfide on the polymer electrolyte membrane fuel cell anode catalyst: H_2S -Pt/C interaction products", Journal of Power Sources, vol. 196, no. 15, pp. 6256-6263.

Lopes, T., Paganin, V.A. & Gonzalez, E.R. "The effects of hydrogen sulfide on the polymer electrolyte membrane fuel cell anode catalyst: H_2S -Pt/C interaction products", Journal of Power Sources, vol. In Press, Corrected Proof.

Mohtadi, R., Lee, W.-., Cowan, S., Van Zee, J.W. & Murthy, M. 2003, "Effects of Hydrogen Sulfide on the Performance of a PEMFC", Electrochemical and Solid-State Letters, vol. 6, no. 12, pp. A272-A274.

Mohtadi, R., Lee, W.-. & Van Zee, J.W. 2005, "The effect of temperature on the adsorption rate of hydrogen sulfide on Pt anodes in a PEMFC", Applied Catalysis B: Environmental, vol. 56, no. 1-2 SPEC. ISS., pp. 37-42.

Noda Z., Hirata, K. Hayashi. A. Taniguchi S., Nakazato N., Seo A., Yasuda I., Ariura S., Shinkai H., Sasaki K. " PEFC type impurity sensors for hydrogens fuels" Int. J. Hydrogen Energy 37 (2012) 16256-16263.

Rockward, T., Davey, J., Fernandez, A. & Garzon, F. 2010, "Investigating the Impact of Very Low Levels of Sulfur Compounds on Fuel Cell Performance", ECS Meeting Abstracts, vol. 1002, no. 10, pp. 825.

Sethuraman, V.A. & Weidner, J.W. 2010, "Analysis of sulfur poisoning on a PEM fuel cell electrode", Electrochimica Acta, vol. 55, no. 20, pp. 5683-5694.

Shi, W., Yi, B., Hou, M., Jing, F. & Ming, P. 2007, "Hydrogen sulfide poisoning and recovery of PEMFC Pt-anodes", Journal of Power Sources, vol. 165, no. 2, pp. 814-818.

Y. Zhai, K Bethune, G. Bender, R. Rocheleau J. Electrochem. Soc. 2012, 159 (5), B524-B530

2.2 Multiple contaminants

In 2008, Dorn et al studied the impact of a mixture of toluene and CO on PEMFC performance (Dorn, et al., 2008). They used a system equipped with a gas chromatography (GC) to identify and quantify the gases present in the exhaust stream of the anode. When H₂ containing 20 ppm of toluene was supplied to the cell, a negligible overpotential of 8 mV is detected. At the exhaust no toluene only methyl cyclohexane. This suggests that all the toluene was hydrogenated. The imbalance between the amount of toluene entering the cell and the methyl cyclohexane exiting the cell is attributed to a bad calibration of the detector. When a mixture of toluene (20 ppm) and CO (2 ppm) was used, the anode overvoltage reached 341 mV. It was only 241 mV with 2 ppm CO as the only impurity. The analysis of the exhaust shows that the toluene is no longer hydrogenated at this anode potential. So the toluene might be adsorbed on the catalyst, which increases the overpotential. The analysis of the exhaust gas also show that at the steady state, a part of CO is not adsorbed on the catalyst, which can be explained by the existence of equilibrium between the H₂ adsorption and CO adsorption.

In 2006, Garzon, et al., tested the impact of a mixture of impurities, shown in the table below (Garzon, et al., 2006). A voltage drop and an increase of high frequency resistance determined by EIS were observed. The increase of high frequency resistance is due to the exchange of H⁺ by NH₄⁺ in the ionomer. The overvoltage is attributed by the adsorbed sulfur species. A CV made after 1000 hours of operating clearly shows the poisoning by sulphur whereas the wave of CO oxidation is very small. The presence of H₂S seems to limit the adsorption of CO.

Composition of the mixture tested by Garzon et al.

Component	Level
Hydrogen	> 99.9
Sulfur (as H ₂ S)	10 ppb
CO	0.1 ppm
CO ₂	5 ppm
NH ₃	1 ppm

In 2007, the same group (Rockward, et al., 2007) clearly demonstrated that the use of H₂S tends to diminish the effect of CO poisoning. For that, they performed CV of a cell feed with a mixture of H₂S and CO.

Jing et al have studied the impact of air impurities with a contaminant mixture (1 ppm SO₂ and 1 ppm NO₂). The impact of the mixture was higher then the impact of 1 ppm NO₂ only but lower than 1 ppm SO₂ only. In that case NO₂, which is reversibly adsorbed on Pt acts as a protective agent toward sulfur pollution.

References

Dorn, S., Bender, G., Bethune, K., Angelo, M. & Rocheleau, R., 2008, "The Impact of Trace Carbon Monoxide / Toluene Mixtures on PEMFC Performance, ECS Transactions", vol. 16, no. 2, pp. 659-667.

Garzon, F.H., Rockward, T., Urdampilleta, I.G., Brosha, E.L. & Uribe, F.A. 2006, "The impact of hydrogen fuel contaminates on long-term PMFC performance", ECS Transactions, pp. 695.

F. Jing, M. Hou, W. Shi, J. Fue, H. Yu, P. Ming, B. Yi J. Power Sources 2007, 166, 172-176

Rockward, T., Urdampilleta, I.G., Uribe, F.A., Brosha, E.L., Pivovar, B.S. & Garzon, F.H. 2007, "The effects of multiple contaminants on polymer electrolyte fuel cells", ECS Transactions, pp. 821.

2.3 Contamination by carbon monoxide

In 2012, Noda et al. have studied the use of MEA as an impurity sensor for CO, H₂S and NH₃. For that, they have studied the voltage drop of MEA depending on the concentration of impurities, the temperature and the current profile. They stated that the OCV has completely recovered from the CO poisoning.

CO poisoning is a reversible process. As soon as the CO level is reduced or stopped there is a rapid recovery of performance. It should be, however, noted that while most of the recovery takes place in minutes, the last part from the recovery of serious poisoning takes several hours, as shown by Bonnet, et al. (2010).

Recovery for Pt-catalyst is much more dependent on temperature than on the Pt-Ru, as shown by Narusawa, et al. (2003).

Since the CO desorption rate as well as oxygen permeability (internal bleed) are increased with temperature, CO coverage should decrease when the system is operated at low power (low CO in feed).

From the mitigation methods, the air bleed method also has a very rapid effect. Within minutes, most of the CO is removed from the catalyst surface (Tingelöf, et al., 2008; Chung, Chen and Weng, 2009).

Both in the measurements of Tingelöf, et al. (2008) and Chung, Chen and Weng (2009), somewhat more air bleed was needed for the recovery of *steady-state* performance. However, in these measurements the CO level is about two orders of magnitude higher than what is in standard ISO 14687-2:2012.

It would be of great interest to study air bleed of 0.1% level (or lower) together with ppm-level CO. Air bleed could be in the same order of magnitude as "internal air bleed". In this method the air bleed would help in the beginning of the cell and would allow CO to adsorb but only to extend that it does not affect cell performance (current distribution). In other words, partial bleeding would help to distribute the CO more evenly and increase the amount of time before a more complete recovery process is needed. Optimisation of air bleed in steady state conditions has been done for Pt-Ru catalyst by Du, Pollard and Elter (2006). In their measurements, the temperature was only 65° C and the lowest concentration of CO was 10 ppm.

References:

- Bonnet, C., Franck-Lacaze, L., Ronasi, S., Besse, S. & Lopicque, F. 2010, "PEM fuel cell Pt anode inhibition by carbon monoxide: Non-uniform behaviour of the cell caused by the finite hydrogen excess", Chemical Engineering Science, vol. 65, no. 10, pp. 3050-3058.
- Chung, C.-., Chen, C.-. & Weng, D.-. 2009, "Development of an air bleeding technique and specific duration to improve the CO tolerance of proton-exchange membrane fuel cells", Applied Thermal Engineering, vol. 29, no. 11-12, pp. 2518-2526.
- Du, B., Pollard, R. & Elter, J.F. 2006, "CO-air bleed interaction and performance degradation study on proton exchange membrane fuel cells", ECS Transactions, pp. 705.
- Noda Z., Hirata, K. Hayashi. A. Taniguchi S., Nakazato N., Seo A., Yasuda I., Ariura S., Shinkai H., Sasaki K. Int. J. Hydrogen Energy 37 (2012) 16256-16263.
- Tingelöf, T., Hedström, L., Holmström, N., Alvfors, P. & Lindbergh, G. 2008, "The influence of CO₂, CO and air bleed on the current distribution of a polymer electrolyte fuel cell", International Journal of Hydrogen Energy, vol. 33, no. 8, pp. 2064-2072.

2.4 Cross-contamination issue

In 2011, J. Zhai et al studied the impact of the cross-over of SO₂ from the cathode to the anode on the performance of the PEMFC. It is reported that for the specified condition:

- cathode pressure: 0.1 MPa
- RH: 100% both sides
- Current: 500 mA/cm² for 2 hrs
- Pt loading : 0.4mg/cm² both sides
- membrane Nafion 212
- T 70°C
- Flow: H₂: 50 sscm, Air : 1000 sscm

The use of 15 ppm, 20 ppm and 30 ppm SO₂/Air respectively lead to a loss of ECSA of 2%, 13%, 20%. Only the impact of ECSA (determine by CV) are reported and the authors do not report the impact on the cell voltage.

This result is outside of the scope of HyCoRA, as it deals with the cross contamination from the air to the H₂ side. However, it shows the feasibility for the impurities to cross the membrane to pollute the other side. In literature, no study regarding the cross contaminant of sulphur species from the anode to the cathode has been found.

In 2002, Qi, He and Kaufman studied the impact of a CO contamination on the anode and on the cathode side. By using a synthetic reformat H₂ (10 or 50 ppm CO/ 70 % H₂/ 30% CO₂) to feed a single for stationary application (PtRu 0.6 mg/cm² @ anode and Pt 0.4 mg/Cm² @ cathode), they measure overvoltages on both sides (270mV at the anode and 320 mV at the cathode @ 600 mA/cm²). Here, the overvoltage represents the voltage difference under pure and polluted H₂ in the same conditions. The CV performed at the cathode shows CO oxidation peaks. The authors concluded here that the CO contained in H₂ could also poison the cathode. However, according to the study of Alavrez (2006), it is known that the impact of CO is not homogenous along the hydrogen distribution channel. That creates inhomogeneity in the MEA and could be responsible for a cathode overpotential increase. In these conditions the MEA might have an accelerated degradation, which can lead to the formation of oxidized species at the cathode which have the same signature as CO oxidation.

Considering the low concentration of CO in the H₂, the inhibition of the cathodic active site by CO cross over is highly unlikely.

References:

Alvarez, M.V.S. 2006, Investigations of current density inhomogeneities in polymer electrolyte fuel cells , ETH/PSI <http://e-collection.library.ethz.ch/view/eth:29322>.

Zhai J., Hou M. Zhang H., Zhou Z., Fu J., Shao Z., Yi B., J. Power Sources, 196 (2011) 3172-3177.

3. A review of analytical methods for measuring impurity levels in automotive grade (ISO 14687-2:2012) hydrogen

The different methods advised by the standard ISO 14687-2:2012 for impurity determination in H₂ are described in the following table:

Component	ISO/DIS 14687-2 specification (μmol/mol)	Method 1	Approx. limit of detection (μmol/mol)	Method 2	Approx. limit of detection (μmol/mol)
Water	5	CRDS	0.01	GC-MS	0.8
Total hydrocarbon cmpds	2	Meth. GC-FID	0.01	-	-
Oxygen	5	GC-TCD	3	GC-PDHID	0.002
Helium	300	GC-TCD	13	-	-
Nitrogen	100	GC-TCD	8	GC-PDHID	0.003
Argon	100	GC-TCD	5	GC-PDHID	0.01
Carbon dioxide	2	Meth. GC-FID	0.015	GC-PDHID	0.015
Carbon monoxide	0.2	Meth. GC-FID	0.04	GC-PDHID	0.012
Total sulphur compounds	0.004	GC-SCD	0.001	-	-
Formaldehyde	0.01	GC-MS	0.2	-	-
Formic acid	0.2	-	-	-	-
Ammonia	0.1	GC-MS	0.5	-	-
Total halogenated cmpds	0.05	-	-	-	-
Particulate concentration	1 mg/kg	-	-	-	-

* Note: The specification for nitrogen and argon in ISO 14687-2:2012 is a sum of these impurities.

According to that table, there is currently no appropriate method to measure the formic acid concentration in H₂. However, for that family of small oxidized carbon species (HCOOH, HCOH, CO, CH₃OH), when H₂ is produced by SMR (steam methane reforming) and purified by PSA (pressure swing adsorption) carbon monoxide plays the role of a canary species. It means that if CO reaches the targets, the other oxidized carbon molecules would reach the target too.

For the halogenated data, there is no current method that allows measurements of the total amount of halogenated species, as it is possible to do with sulphur. A better definition of the total halogenated species is required to reduce the scope of halogenated impurities to quantify. Quantified chloride anion could be a solution (Cl⁻). The impact of HCl has been studied by Li et al (2011), and it is reported that only 1 ppm HCl in the anode stream could have a detrimental effect for automotive application (15% loss in 60 hours).

References :

H. Li, H. Wang, W. Qian, S. Zhang, S. Wessel, T. T. H. Chang, J. Sen, S. Wu, "Chloride contamination effects on proton exchange membrane fuel cell" *J. Power Sources* 196 (2011) 6249-6255.

Brown A., Vargha G., Downey M. Hart N. Ferrier G., Hall K. "Methods for the analysis of trace level impurities in hydrogen for fuel cell applications", NPL report AS 64 (2011).

4. Strategy for experimental fuel cell research in HyCoRA project

Based on the results of the reviewed literature and experimental methods applied in those studies, it can be concluded that there is a significant lack of data and understanding. The limits in standard ISO 14687-2:2012 are mostly based on insufficient experimental data. Therefore, conservative assumptions have been applied. As a consequence, there are significant possibilities for the revision of the contaminant limits.

When the effects of various individual contaminants are considered, then enrichment, conversion and washout should be considered when planning the measurements. If the reaction product of the impurity is also a contaminant, the analysis should include this product as well. The Figure 2 illustrates the procedure.

This procedure is applicable only for the contaminants that poison the catalyst. In case the contaminant poisons the membrane (NH_3) or causes accelerated platinum dissolution (Cl^-), the procedure becomes more complicated.

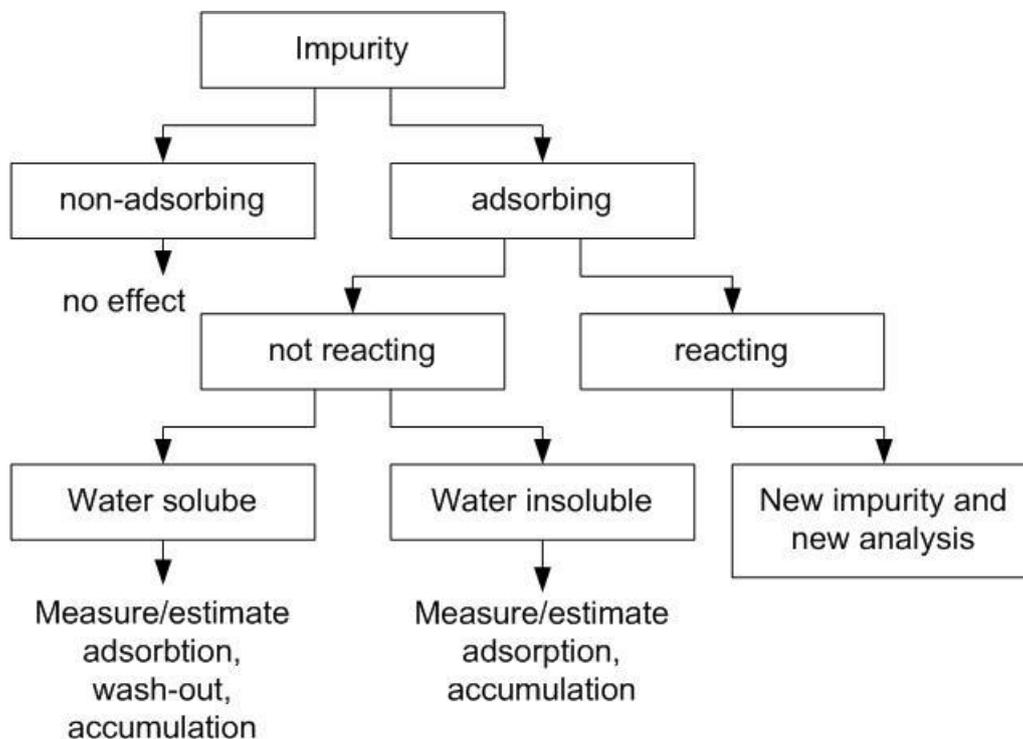


Figure 2: The logical tree, when the effect of impurity is studied.

In the HyCoRA project the work has been started with CO as the main impurity to be studied during the first 6 months. In addition, sulphur has been selected as a topic of interest. Based on the literature review, these seem to be good choices, because there is a significant lack of data concerning the impact of these impurities in real automotive systems, including start and stop.

It also seems possible that the limits of the less detrimental and less probable contaminants formaldehyde (HCHO), formic acid (HCOOH) and ammonia (NH_3) have been determined to be an order of magnitude too high when all the effects of real FC system operation in FCEV are taken in to account. These components could become topics of interest if the change of acceptable levels could make quality assurance instrumentation less expensive.

In the following table the analysis of this review is summarised as a strategy for experimental fuel cell research in the HyCoRA project.

Impurity	Level in ISO 14687-2:2012 in ppm(v)	Issue(s), known and unknown in gas analysis and catalyst and/or membrane poisoning	Strategy in HyCoRA fuel cell research	Possible consequences concerning 14687-2:2012
Total non-hydrogen gases	300	No issues	N/A	N/A
Water (H ₂ O)	5	No issues	N/A	N/A
Total hydrocarbons (C1 basis)	2	Issues largely unknown. The existence of hydrocarbons (excl. CH ₄ , HCHO, HCOOH) depends on the hydrogen production and purification method.	Analyse risk of existence for relevant impurities, if any.	Some specific hydrocarbons may need their own limit.
Helium (He)	300	No issues	N/A	N/A
Total nitrogen (N ₂), argon (Ar)	100	No issues	N/A	N/A
Oxygen (O ₂)	5	No issues	N/A	N/A
Carbon dioxide (CO ₂)	2	The importance of reverse water gas shift (RWGS) in FCEV conditions is largely unknown. The combined effect of sub-ppm level CO and 10-500 ppm CO ₂ is unknown.	Quantify RWGS with low loadings. Quantify combined effect of CO and CO ₂ .	More precise info about CO level. The benefit of in-situ filtering of enriched CO ₂ could be quantified.
Carbon monoxide (CO)	0,2	What is the acceptable level when taking into account the real automotive drive cycle including start and stop (S/S) effects?	Quantify CO (0.5-5 ppm) effect with S/S and expected drive cycles.	The level of CO could be increased 2-5 times.
Total sulphur compounds	0.004	What is the acceptable level when desorption and washout are taken into account?	Contaminate cell with sulphur and measure desorption/washout	The level of total sulphur compounds could be increased tenfold.
Formaldehyde (HCHO)	0.01	What is the acceptable level when possible conversion to HCOOH and washout are taken into account?	Quantify effect with conversion and washout.	The level of HCHO could be increased tenfold or even more.
Formic acid (HCOOH)	0.2	What is the acceptable level when possible conversion to CO ₂ and washout are taken into account?	Quantify effect with conversion and washout.	The level of HCOOH could be increased tenfold or even more.
Ammonia (NH ₃)	0.1	What is the acceptable level when washout is taken into account?	Quantify long-term effect with washout.	The level of NH ₃ could be increased 2-5 times.
Total halogenated compounds	0.05	What is the importance of conversion to other component and washout for possible halogenated compounds?	Quantify long-term effect with conversion and washout.	The levels could be determined for some specific halogenates.
Maximum particulates concentration	1 mg/kg(H ₂)	N/A	N/A	N/A