

High temperature electrochemical hydrogen membrane separation using a PGM-based catalyst

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DECLARATION

I, Leandri Vermaak, hereby declare that the thesis entitled: **“High temperature electrochemical hydrogen membrane separation using a PGM-based catalyst”** is my own original work. All external sources (e.g. text books and journal articles) were referenced accordingly.



Signature

25/11/2019

Date signed

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ABSTRACT

Hydrogen, as energy carrier, is expected to play an indispensable role in the future energy prospects. Subsequently, significant advancements in research and development of hydrogen-based technologies, in the areas of low cost hydrogen production, separation/purification, hydrogen storage (e.g. compression, liquid, chemical compounds etc.), hydrogen distribution and hydrogen transportation, are required. Among several technologies under consideration for hydrogen infrastructure, the use of an electrochemical hydrogen separator is very probable, since both hydrogen purification/separation and hydrogen compression (for storage purposes) are integrated and addressed. Some advances have already been made in this field, including the development of high-temperature membranes, doped with phosphoric acid, to overcome the limitations associated with conventional low-temperature membranes. However, limited studies had been performed on these membranes and their operations under various conditions and feed compositions are largely unexplored.

The first part of the work reported, addresses the aforementioned issue through experimental investigation of the performance of a high-temperature TPS-based membrane under various feed compositions (containing CH₄, CO₂ and NH₃, balance hydrogen) over a temperature range of 100-160°C. The performance parameters used included polarisation curves, electrochemical impedance spectroscopy, hydrogen purity, hydrogen separation selectivity, hydrogen flux/permeability, and general efficiencies (current, voltage and power). Results showed that a high purity hydrogen (>99.9%) was achieved, from a low purity feed (20% H₂) with the H₂/CH₄ mixtures. Also, hydrogen purities of 98-99.5 % were achieved with 10% CO₂ in the feed and 96-99.5% with 50% CO₂ in the feed stream. Moreover, electrochemical hydrogen separation was rendered inappropriate for separating hydrogen-rich streams containing NH₃.

The second part of the work focussed on the poisoning effect of CO on Pt. An integrated approach of high-temperature operation and Pt-Ru as bimetallic catalyst was implemented and tested with a 2% CO (balance hydrogen) inlet. The performance of Pt-Ru/C and Pt/C was compared under the same operating conditions. The electrochemical active surface area was then determined to evaluate the CO poisoning of the two catalysts. In general, Pt-Ru showed better CO tolerance over the entire temperature range (80-160°C). Also, temperature played a crucial role in the mitigation of CO poisoning in the case of Pt-Ru.

Keywords: *Electrochemical hydrogen separation/purification; Proton exchange membrane(PEM); Phosphoric acid (PA)-doped polybenzimidazole (PBI) membrane; TPS membrane; High-temperature; Polarisation curve; Electrochemical impedance spectroscopy (EIS); Gas chromatograph (GC); Pt-based catalyst; Cyclic voltammetry (CV); Electrochemical active surface area (ECSA); CO poisoning; CO-stripping*

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LIST OF SYMBOLS

NOMENCLATURE			
A	Area/surface area, cm ²	x_{N_2}	Molar fraction of nitrogen, (-)
A_{EC}	Electrochemical surface area, cm ²	x_i	Molar fraction of species i in the feed, (-)
A_{geo}	Geometrical area of the electrode, cm ²	x_j	Molar fraction of species j in the feed, (-)
A_{real}	Real surface area of the electrode, cm ²	y_i	Molar fraction of species i in the permeate, (-)
d	Nanoparticle diameter, nm	y_j	Molar fraction of species j in the permeate, (-)
E	Potential, V	Greek symbols	
EC_{SA}	Electrochemical active surface area, cm ² mg ⁻¹	α	Selectivity, (-)
E^0	Standard thermodynamic potential @ 25°C, V	α	Charge transfer coefficient, (-)
E_{Nerst}	Nernst/electrode potential, V	ε_i	Current efficiency, %
E_{ohmic}	Ohmic overpotential, V	ε_p	Power efficiency, %
$E_{polarisation}$	Polarisation overpotential, V	ε_v	Voltage efficiency, %
$E_{theoretical}$	Theoretical potential, V	η	Overpotential, V
ΔG	Gibbs free energy, J mol ⁻¹	δ	Membrane thickness, μ m (unless otherwise specified)
ΔG^0	Standard Gibbs free energy, J mol ⁻¹	Other symbols	
ΔH	Change in enthalpy, J mol ⁻¹	$*$	Resembles an empty catalytic site or an adsorbed species
I	Current, A	e^-	Electron
I_b	Current peak in the reverse direction	Superscripts and subscripts	
I_f	Current peak in the forward direction	⁰	Standard
i	Current density, A cm ⁻²	a	anode
i_0	Exchange current density, A cm ⁻²	b	Backward
i_b	Backward reaction current density, A cm ⁻²	c	cathode
p_c	Cathode partial pressure, kPa	CO	Carbon dioxide
$\dot{n}$	Hydrogen molar flow rate, mol s ⁻¹	EC	Electrochemical
n	Number of electrons	f	Forward
$\dot{m}$	Hydrogen mass flow rate, kg s ⁻¹	geo	geometrical
Q	Charge, μ C or C	H	hydrogen
q	Mass flux of gas through membrane, cm ³ (STP).s ⁻¹	P	Permeate
n_α	Apparent electron number, (-)	pa	Anodic peak
L	Catalyst load, mg cm ⁻²	R	Retentate
Pe_{H_2}	Hydrogen permeability, Barrer	SA	Surface area
i_f	Forward reaction current density, A cm ⁻²	Constants	
p_a	Anode partial pressure, kPa	F	Faraday constant, 96 485 C mol ⁻¹
P	Pressure, bar, atm or kPa	R	Ideal gas constant, 8.314 J mol ⁻¹ K ⁻¹
M	Molecular weight, kg mol ⁻¹	Normal Condition	
Q_{CO}	CO-stripping peak charge, μ C or C	STP	0°C and 1 bar
Q_H	Hydrogen peak charge, μ C or C		
Q_{SA}	Surface area specific charge, μ C cm ⁻²		
R_Ω	Resistance, Ω		
r	Nanoparticle radius, nm		
S	Catalytic site on electrode		
ΔS	Change in entropy, J K ⁻¹ mol ⁻¹		
T	Temperature, °C (unless otherwise specified, K)		
t	Time, s or min.		
$\dot{V}$	Volumetric flow rate, nmL/min		
V	Voltage, V		
v	Scan rate, mV s ⁻¹		
W	Power, Watt		
x_{H_2}	Molar fraction of hydrogen, (-)		

ABBREVIATIONS

atm	<i>Atmospheric</i>
BBPs	<i>Bipolar back plates</i>
BoL	<i>Beginning of life</i>
CE	<i>Counter electrode</i>
CL	<i>Catalyst layer</i>
COS	<i>CO-stripping</i>
CSS	<i>Carbon support surface</i>
CV	<i>Cyclic voltammetry/voltammogram</i>
DHE	<i>Dynamic hydrogen electrode</i>
ECSA	<i>Electrochemical active surface area</i>
EHC	<i>Electrochemical hydrogen compressor</i>
EHP	<i>Electrochemical hydrogen pump</i>
EHS	<i>Electrochemical hydrogen separator</i>
EIS	<i>Electrochemical impedance spectroscopy</i>
FC	<i>Fuel cell</i>
FF	<i>Flow fields</i>
GC	<i>Gas chromatograph</i>
GDE	<i>Gas diffusion electrode</i>
GDL	<i>Gas diffusion layer</i>
GHG	<i>Greenhouse gas emissions</i>
HT	<i>High-temperature</i>
H_{upd}	<i>Underpotentially deposited hydrogen</i>
IPCC	<i>Intergovernmental Panel on Climate Change</i>
IRENA	<i>International Renewable Energy Agency</i>
LT	<i>Low-temperature</i>
Max.	<i>Maximum</i>
MEA	<i>Membrane electrode assembly</i>
Min.	<i>Minimum</i>
MPL	<i>Microporous layer</i>
nmL	<i>Normal milliliter</i>
OCV	<i>Open-circuit voltage</i>
P2G	<i>Power to gas</i>
PA	<i>Phosphoric acid</i>
PBI	<i>Polybenzimidazole</i>
PEHP	<i>Polymer electrolyte hydrogen pump</i>
PEM	<i>Proton exchange membrane fuel cell</i>
PFSA	<i>Perfluorinated sulfonic acid</i>
PGM	<i>Platinum group metal</i>
POX	<i>Partial oxidation</i>
ppm	<i>Parts per million</i>
PSA	<i>Pressure swing adsorption</i>
Pt/C	<i>Platinum supported on carbon</i>
Pt-Ru/C	<i>Platinum-ruthenium bimetallic catalyst supported on carbon</i>
PV	<i>Photovoltaic</i>
RE	<i>Renewable energy</i>
RE	<i>Reference electrode</i>
Ref.	<i>Reference</i>
RES	<i>Renewable energy sources</i>
RH	<i>Relative humidity</i>
RHE	<i>Reversible hydrogen electrode</i>
SD	<i>Standard deviation</i>
SDG	<i>Sustainable Energy Development Goals</i>
SEM	<i>Scanning electron microscopy</i>
SMR	<i>Steam methane reforming</i>
SNG	<i>Synthetic natural gas</i>
SPPEsk	<i>sulfonated poly (phthalazinone ether sulfone ketone)</i>
TCD	<i>Thermal conductivity detector</i>
TEM	<i>Transmission electron microscopy</i>
vol.	<i>Volume</i>
WE	<i>Working electrode</i>
WGS	<i>Water-gas shift</i>
wt.	<i>Weight</i>
X	<i>Foreign metal X</i>

LIST OF CONFERENCES ATTENDED DURING THIS STUDY

Kriek, L., Neomagus, H.W.J.P. & Bessarabov D.G. 2018. Electrochemical hydrogen membrane separation from various gas mixtures. 29th Annual Conference of the Catalysis Society of South Africa, 11-14 November, Legend Golf & Safari Resort, Limpopo, South Africa.

Kriek, L., Kruger, A.J., Neomagus, H.W.J.P. & Bessarabov D.G. 2018. High temperature polybenzimidazole (PBI) electrochemical hydrogen membrane separation. 30th International Partnership for Hydrogen and Fuel Cells in the Economy (IPHE) Conference, 4-7 December, Pretoria, Gauteng, South Africa

NOTE FROM THE AUTHOR

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CHAPTER 1. INTRODUCTION

This chapter serves as an introductory chapter to the experimental work presented in this dissertation. In **Section 1.1** an overview is given of the essential facets pertaining to the background and problem statement of the present work. The project motivation is presented in **Section 1.2**. This is followed by the overall aim and specific objectives of this work, provided in **Section 1.3**, and the project scope and methodology, explained in **Section 1.4**. Finally, the outline of this dissertation is presented in **Section 1.5**.

1.1 BACKGROUND AND PROBLEM STATEMENT

The global energy sector is facing transitional changes based on the need to decrease fossil fuel dependency due to high CO₂ emissions associated with conventional energy generation methods. A convenient way to reduce the global carbon footprint lies in the increased use of renewable energy (RE) (e.g. wind and solar). Storage of the surplus energy produced is required to overcome the limitations related to RE (e.g. unreliable supply due to environmental and seasonal fluctuations, and difficulties with large scale storage (Han *et al.*, 2017; Maddy *et al.*, 2016; Scamman & Newborough, 2016)). Among other previously implemented storage technologies, such as pumped hydro energy storage, electrochemical methods such as batteries, compressed air, flywheels, and capacitors (Han *et al.*, 2017; Judd & Pinchbeck, 2013), capturing and storing surplus energy into chemical components is seen as a promising large scale energy storage alternative. This is known as the power-to-gas (P2G) concept, where the power-to-hydrogen method in particular is attracting great attention.

Although hydrogen is the lightest element, it has the highest gravimetric energy density (122 MJ kg⁻¹) among all the existing fuels (Balat, 2008; Baykara, 2018). Other advantages of hydrogen include its high energy conversion efficiency, it can be generated from water with negligible emissions, it is the most abundant element, it lends itself to a variety of storage methods (e.g. gaseous, liquid, etc.), it can easily be converted to other forms of energy, and it has higher high and low heating values compared to most of the conventional fossil fuels (Abdalla *et al.*, 2018; Acar & Dincer, 2015).

The application of fuel cells (FCs) is widely considered as an enabling technology towards a sustainable 'hydrogen economy'. FCs can be used to produce 'green' electricity for peak energy demand by converting hydrogen into electricity with much higher efficiency than can be achieved with internal combustion engines (Maltosz & Commenge, 2002). Among the

various types of FCs, e.g. proton exchange membrane (PEM)-FCs, phosphoric acid (PA) FCs, alkaline FCs, solid oxide FCs, and direct methanol FCs, PEM-FCs are attracting the most attention. Reasons include the following: their favourable operational characteristics, such as quiet operation; near-zero emissions and high power densities (Holladay *et al.*, 2004). However, for effective operation, high-purity hydrogen (>99.97%) is required (SAE International, 2015). This, in turn, necessitates adequate separation technologies because hydrogen generation processes produce hydrogen rich streams commonly accompanied by impurities such CO₂, CO, N₂ and CH₄, among others (Benicewicz *et al.*, 2008; Chen *et al.*, 2014; Choi *et al.*, 2004).

1.2 RESEARCH MOTIVATION

Currently, advanced technologies exist for the separation of hydrogen from hydrocarbons and other gas mixtures; technologies include pressure swing adsorption (PSA), cryogenic processes and membrane separation technologies (Gardner *et al.*, 2007). Membrane technologies have several advantages, including ease of operation, low investment cost, the possibility of continuous operation, low energy consumption, cost effectiveness (even at low gas volumes), low maintenance requirements and compactness (Adhikari & Fernando, 2006; Groß *et al.*, 2017; Husaini *et al.*, 2015; Kaghazchi *et al.*, 2009). However, additional compression is required for storage applications after the hydrogen is purified. However, the costs related to hydrogen storage remains a challenge due to the low volumetric energy density of hydrogen (Gallucci *et al.*, 2019).

PEM electrochemical hydrogen compressors/separators (EHCs/Ss) are seen as possible substitutes for pressure-driven membrane processes; simultaneous compression and purification can be achieved (Gallucci *et al.*, 2019; Gardner & Ternan, 2007). The process that applies here is an isothermal process which is not energy intensive, it is environmentally friendly with near-zero pollutants, and known for its silent operation, making it a promising technology for hydrogen separation (Benicewicz *et al.*, 2008). However, despite the numerous advantages and growing interest, various drawbacks do hinder its large-scale implementation. Currently, some of the main obstacles are the cost, a lack of adequate understanding of the degradation mechanisms related to this technology and the fact that certain aspects of this technology are as yet unexplored. Very little comprehensive work on experimental investigations into electrochemical hydrogen separation/purification is reported in open literature.

Gaps in available knowledge to an understanding of electrochemical hydrogen separation/purification were identified:

- Generally speaking, little information is available on electrochemical hydrogen separation, including a lack of adequate membrane system characterisation. Most information pertaining to the degradation of the different cell components has been extracted from reports on FCs, which use the same device (electrochemical cell) as an electrochemical hydrogen separation system (Gallucci *et al.*, 2019).
- Although certain limitations associated with low-temperature (LT)-PEMs can be overcome by using high-temperature (HT)-PEMs, including achieving improved tolerance to impurities such as CO and no required pretreatment of the feed gas (e.g. water/relative humidity management), very limited information is available to quantify the performance of these HT-PEMs.
- The effect of temperature on the separation performance of HT-PEMs are unknown. Coupled to this, optimal operational parameters need defining.
- No adequate understanding nor quantitative data on an EHS's ability to separate hydrogen from several individual impurities appears to be available. Studies to date have mainly focussed on reformat gas streams, making it difficult to discern what impurities predominantly contribute to the behaviour and performance of the electrochemical cell (EHS).
- The durability of HT-PEMs after prolonged everyday use is unknown.
- LT-PEMs (e.g. Nafion) are damaged in the presence of ammonia, even at very low concentrations (ppm) thereof. However, the ammonia tolerance of a HT PA-doped PEM remains unexplored.
- HT operation allows the use of less costly metals in the electrocatalyst, such the bimetallic catalyst Pt-Co; however, the separation performance of the membranes utilising Pt-Co as catalyst are not recorded. (See **Appendix A: Section A.3.3 (b)**).
- An understanding of the adsorption characteristics of CO on Pt and Pt-Ru at high temperature is lacking. It is also unclear whether the addition of Ru to the Pt catalyst, or temperature, is more effective in alleviating CO poisoning.

Overall, these gaps in literature motivated the requirement for a thorough research study in this field, to determine how suitable this technology is for hydrogen separation and purification from various industrially relevant gas mixtures.

1.3 PROJECT AIM AND OBJECTIVES

The overall aim of this study is to determine whether HT-PEMs doped with PA, along with a platinum-group metal (PGM-based) catalyst, are suitable candidates for the purification of hydrogen from industrially relevant gas mixtures. This will include investigating, and quantitatively determining, the separation performance and the overall cell performance of an EHS comprising a HT-PEM for hydrogen purification/separation.

The specific objectives of this study are therefore:

- I. To determine the separation performance of HT-PEM with a bimetallic Pt-Co/C anode electrocatalyst from a hydrogen-containing stream in the presence of different concentrations of impurities (NH₃, CH₄ and CO₂).
- II. To determine the effect of temperature (100-160°C) and impurity concentration on the electrochemical performance of the membrane separation system, making use of several performance parameters. These performance parameters include: (i) the voltage-current characteristics (polarisation curves) (e.g. limiting current densities and open-circuit voltage), (ii) the ohmic resistance of the cell components (measured through electrochemical impedance spectroscopy (EIS)), (iii) the general cell efficiencies (current, voltage and power efficiencies), (iv) the hydrogen permeability (Barrer) and (v) the hydrogen purity and selectivity.
- III. To characterise the membrane electrode assemblies (MEAs) making use of electrochemical techniques. These techniques include: polarisation curves and EIS.
- IV. To determine, then compare, the performance of Pt/C and Pt-Ru/C electrocatalysts when exposed to CO at elevated temperatures (>100°C).
- V. To determine which of the following two factors is more dominant in alleviating CO poisoning of PGM-based catalysts: HT operation (>100°C) (utilising HT-PEMs) or making use of Pt-Ru bimetallic catalysts.

Ultimately this dissertation serves to address some of the literature gaps and principal challenges identified, and to add to the current knowledge of electrochemical hydrogen separation/purification.

After obtaining satisfactory experimental results, and drawing conclusions, recommendations will be made for future research in this area.

1.4 PROJECT SCOPE AND METHODOLOGY

Three different MEAs (referred to MEA 1, 2 and 3) were used to achieve the objectives; their properties are tabulated in **Table 1.1**. All three MEAs were first characterised with pure hydrogen to obtain baseline values for each membrane, depicted as Section 1 in **Figure 1.1**.

Table 1.1: Summary of properties of membrane electrode assemblies (MEAs) used in this study

	MEA 1	MEA 2	MEA 3
Membrane type	PBI-based	PBI-based	TPS® (pyridine-based)
Membrane thickness (μm)	± 58.9 (determined)	± 58.9 (determined)	60-65 (specified)
Anode catalyst	Pt/C	Pt-Ru/C	Pt-Co/C
Cathode catalyst	Pt/C	Pt/C	Pt/C
Total catalyst loading (equally divided between anode and cathode) (mg cm^{-2})	2	2	1.8
Active area (cm^2)	25	25	25
Temperature range ($^{\circ}\text{C}$)	120-180	120-180	120-200
Proton conductivity (specified by supplier at temperature range mentioned above) (S cm^{-1})	10×10^{-2}	10×10^{-2}	8×10^{-2}

MEA 3 was used for the baseline experiments, including hydrogen separation from H_2/CH_4 ; H_2/CO_2 and H_2/NH_3 (see **Chapter 3**). These gas mixtures were chosen due to their industrial relevance in processes related to syngas, the water-gas shift (WGS) reaction, the P2G concept and ammonia production. From the experimental results presented in **Chapter 3**, it was observed that although good separation was achieved for H_2/CH_4 , the membranes were not as effective in the presence of CO_2 . This was attributed to the formation of CO from CO_2 that underwent the reverse WGS reaction (Araya *et al.*, 2016). Due to this, preliminary tests were performed and another array of polybenzimidazole (PBI) membranes were chosen to investigate the mitigation of CO poisoning. It was decided to investigate the adsorption characteristics of CO on Pt/C in a temperature range of 80-160 $^{\circ}\text{C}$. According to Bessarabov & Tokarev (2014), besides HT operation (>100 $^{\circ}\text{C}$), the bimetallic catalyst Pt-Ru/C can be used

to improve CO tolerance: therefore, similar investigations were performed on Pt-Ru/C, for the purpose of comparison. The same PBI membranes, denoted as MEA 1 and MEA 2, were used for comparative reasons (see **Figure 1.1**).

Figure 1.1 indicates the order in which the experiments were conducted. This is highly relevant since some of the impurities harm certain cell components and could therefore contribute to the experimental results obtained for the following experiments. The characterisation methods used for the respective experiments are indicated in the form of numbers with the legend provided in the top right corner. All three PEMs were first characterised using pure hydrogen (no impurities), as seen in Section 1 in **Figure 1.1**.

For MEA 1 and MEA 2, a hydrogen diffusion measurement step is included. After the pure hydrogen characterisation experiments, the gas mixtures were tested, in the experimental order indicated in the orange region in Section 2. The first three gas mixtures (H_2/CH_4 ; H_2/CO_2 and H_2/NH_3) with varying compositions, were tested on MEA 3 (presented in **Chapter 3**), whilst the final gas mixtures (H_2/CO) were only tested on MEAs 2 and 3 (presented in **Chapter 4**).

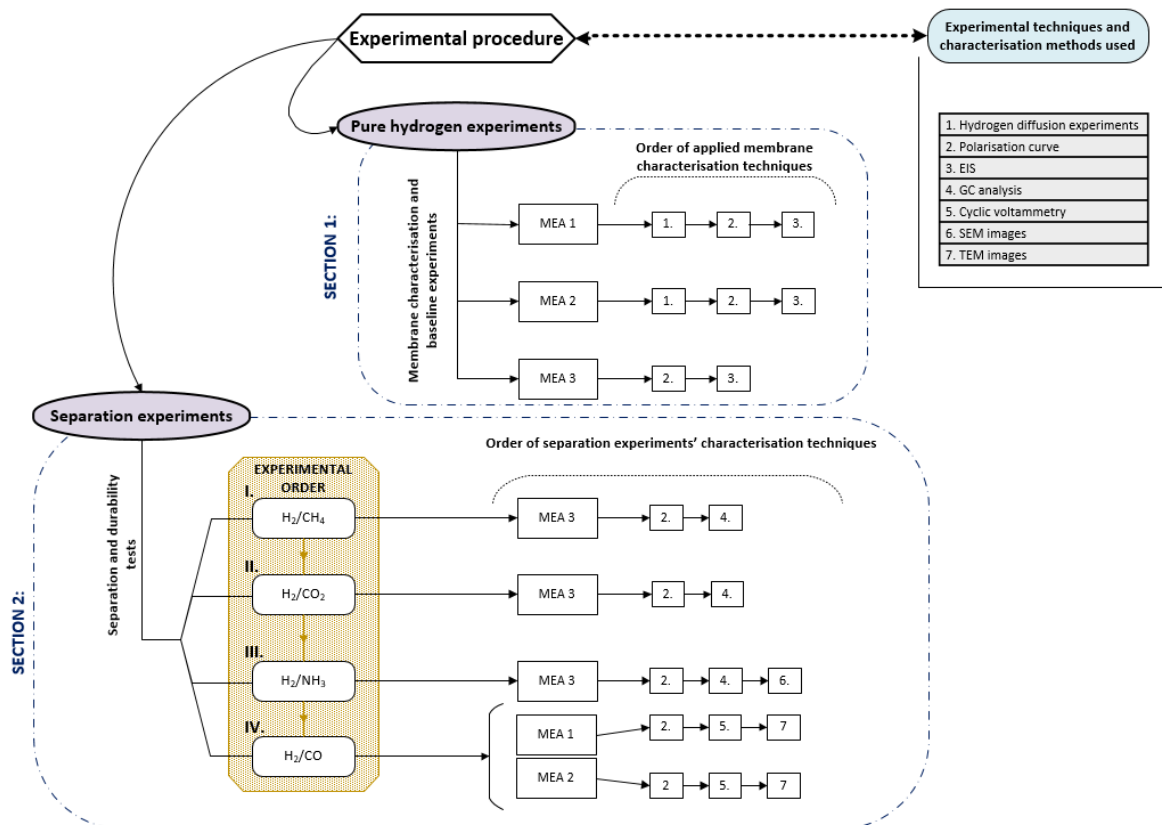


Figure 1.1: Project scope

1.5 OUTLINE

This thesis is done and presented in six chapters.

- **Chapter 1** presents a background to this study and motivation for the research work carried out. The overall aim and objectives were stated and the methodology described.
- **Chapter 2** presents a literature review on the current state of the energy sector, mentioning a low carbon energy system—known as the ‘hydrogen economy’. The focus then moves to the need for hydrogen purification/separation systems to realise the full potential of a ‘hydrogen economy’. Special attention is given to different separation methods, focussing on electrochemical separation technologies, highlighting their advantages and limitations.
- **Chapter 3** presents an evaluation of the hydrogen separation performance of a HT-EHS from H_2/CH_4 , H_2/CO_2 and H_2/NH_3 gas mixtures at 120-160°C/1 atm. The effect of the cell temperature and inlet composition on key performance parameters (e.g. gas permeability (Barrer), hydrogen purity and selectivity, and the general cell efficiencies (current, voltage and power efficiency) were investigated.
- **Chapter 4** compares the performance of Pt/C and Pt-Ru/C electrocatalysts in the presence of CO. This was done with an inlet stream comprising 2% CO (balance hydrogen). The CO adsorption and oxidation on Pt and Pt-Ru catalysts were examined at a temperature range of 80-160°C. The electrochemical active surface area (ECSA) was estimated, making use of the hydrogen underpotential deposition peaks. Cyclic voltammetry (CV) was used as the characterisation method of choice.
- **Chapter 5** first summarises the results of the experimental work performed in this study. Conclusions to the specified objectives are specified. The contributions of the information gathered in this study to the current available literature are mentioned. Some suggestions for future studies are included.
- **References.** References cited in all five chapters are included in this (final) chapter.

Some information, especially pertaining to the experimental sections in **Chapter 3** and **Chapter 4**, is unavoidably repeated.

CHAPTER 2. ELECTROCHEMICAL HYDROGEN SEPARATION AND PURIFICATION – A REVIEW

This chapter encloses a review of open literature. **Section 2.1** serves as an introduction to the possibility of transitioning to a fully functional ‘hydrogen economy’. **Section 2.2** focus on hydrogen generation and application, whilst **Section 2.3** concentrates on hydrogen purification and separation technologies. Electrochemical hydrogen purification/separation is also introduced in this section. This is followed by a discussion on the current status of electrochemical hydrogen separation. Lastly, this chapter is concluded in **Section 2.4**, with a summary of limitations related to previous studies and literature gaps identified in the current research knowledge of electrochemical hydrogen separation. This served as a basis for the experimental work performed and presented in this dissertation (see **Chapter 3-Chapter 4**).

Supplementary literature to this chapter is available in **Appendix A**.

2.1 INTRODUCTION: THE POSSIBILITY OF TRANSITIONING TO A HYDROGEN ECONOMY

2.1.1 THE NEED FOR GLOBAL ENERGY TRANSFORMATION HIGHLIGHTED

The continued expansion of the commercial and industrial sectors raises concerns regarding the supply capacity of existing energy resources, paired with environmental concerns related to the CO₂ emissions connected with conventional fossil fuel utilisation methods (Maddy *et al.*, 2016). Energy-related CO₂ emissions are known to comprise two-thirds of all greenhouse gases (GHGs) (IPCC, 2014) and, according to trends in global energy use, the estimated percentage of emitted CO₂ will increase yearly by at least 1.7% until 2030, reaching an approximated 38 billion tons in 2030 (Chakraborty & Laha, 2017). Against this background it is evident that a transition from fossil fuels to a low-carbon energy system is imperative (Wang *et al.*, 2011).

The Paris Agreement of 2015 states the global ambition to accomplish a balance between anthropogenic discharges by source and removal of GHGs in the second half of this century—the goal of the agreement is to maintain the increase in the average universal temperature to <2°C above pre-industrial levels and, secondly to attempt to limit the temperature to 1.5°C. However, the ambitions of the Paris agreement might not be fully captured by existing energy scenarios. The Intergovernmental Panel on Climate Change (IPCC), commissioned by the

United Nations (UN), highlights, in a special report, the significant gap between aspiration and reality in undertaking climate change: global warming of 1.5°C (IPCC, 2018).

The solution to achieve these ambitions lies in the reduction of GHG emissions from fossil fuels, by implementing large-scale renewable energy (RE) supply in energy systems (Breyer *et al.*, 2019; Holttinen *et al.*, 2019). The Sustainable Energy Development Goals (SDGs) adapted by the United Nations General Assembly (UNGA) in 2015, provides a powerful framework for international cooperation towards a sustainable future. SDG 7 states three main targets: ensure affordable, reliable and international access to up-to-date energy services; increasing the RE percentage of the worldwide energy mix by 2030; and double the rate of global energy efficiency. The focus of recent studies were on global transition, to complete renewable-based power systems—indicating that these systems are feasible (Aghahosseini *et al.*, 2019).

2.1.2 ENERGY TRANSITION: TOWARDS RENEWABLE ENERGY

Until very recently, electricity generation from solar and wind has not been cost competitive compared with other leading methods of electricity generation (e.g. fossil fuels based). However, according to the latest report from the International Renewable Energy Agency (IRENA; 2019), the cost of RE is rapidly decreasing, to such an extent that RE should be cost competitive with fossil fuels by 2020. The organisation, involving >150 associate countries, states that the cost of producing power from onshore wind has decreased by approximately 23% since 2010 and the global average cost of solar photovoltaic (PV) electricity by 73% over the same period (IRENA, 2018d), with Europe's offshore wind already able to compete with market prices (IRENA, 2019).

Despite the fact that the energy policies of many countries are not properly aligned to the global climate goals, the recent Conference of Parties (COP21) in Paris indicated that most countries are willing to alleviate their carbon footprint. Germany, being a bellwether, has taken the lead in RE transition—known as the *Energiewende*. Furthermore, complete renewable electricity targets by 2045-2050 have been set by, for example, California, Hawaii, Vietnam, Bangladesh, Barbados, Colombia, Cambodia, Ethiopia, Ghana and Mongolia (REN21, 2018). Some countries, such as Costa Rica and Norway, already supply almost all of their electricity from renewable energy sources (RES) (predominantly hydropower) (REN21, 2018). Companies that are involved in similar renewable trends include IKEA, BMW and Walmart, and technology companies such as Apple, Google, Sony, Facebook and eBay, amongst several others (Breyer *et al.*, 2019).

2.1.3 HYDROGEN AS ENERGY CARRIER: A POSSIBLE SOLUTION

Although RES is seen as a very promising solution to the current energy crisis, with very positive developments in the continuous decrease in wind and solar electricity generation costs, a few limitations threaten to reverse this trend. The main limitation is the high levels of variable RE, mainly due to seasonal and weather fluctuations (Han *et al.*, 2017; Maddy *et al.*, 2016; Scamman & Newborough, 2016). RE is not available on demand and, traditionally, it cannot be stored on large scale (excess energy needs to be shifted), nor can it be used in times of limited supply (Han *et al.*, 2017; Maddy *et al.*, 2016; Scamman & Newborough, 2016). Germany has already faced significant losses due to this in their integrated wind and PV energy (IRENA, 2019).

There is, however, a solution to this problem—it lies in adequate energy storage. Energy storage can provide flexibility and will reduce the global dependence on fossil fuel backup power. To date, the storage of energy has been implemented using technologies such as pumped hydro-storage (PHS), electrochemical cells (e.g. batteries), compressed air energy storage (CAES), flywheels, capacitors and others (e.g. thermal energy storage) (Han *et al.*, 2017; Judd & Pinchbeck, 2013) (**Figure 2.1**). Alternative methods for large-scale energy storage are being researched, including renewable hydrogen and synthetic natural gas (SNG), with storage capability in the GWh range (Han *et al.*, 2017; Judd & Pinchbeck, 2013). See **Figure 2.1**.

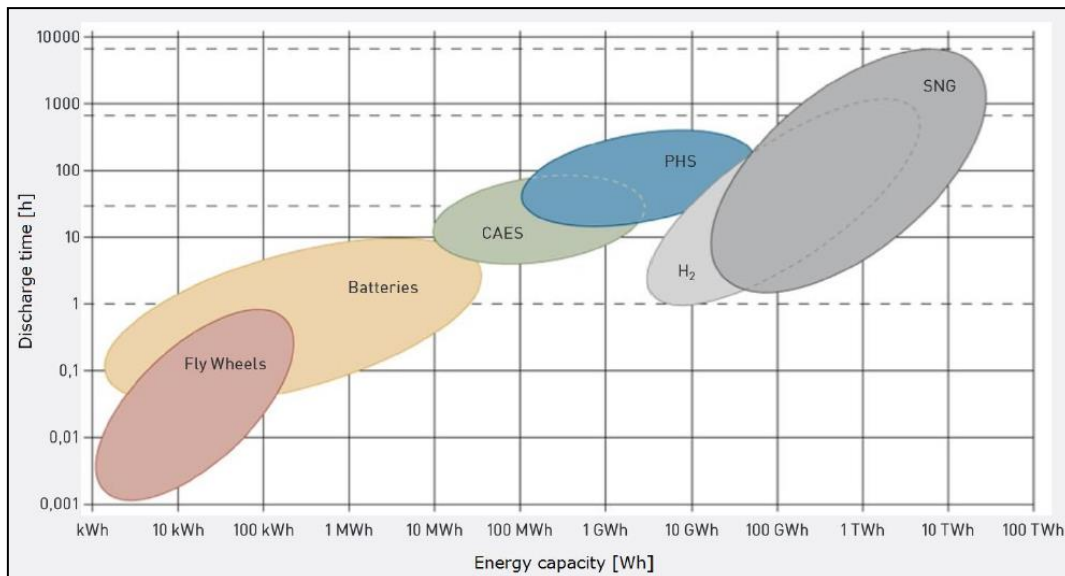


Figure 2.1: Discharge time and capacity of different energy storage technologies (taken from Judd & Pinchbeck, 2013).

Hydrogen is part of an industrial concept known as the power-to-gas (P2G) technology, which is a power grid balancing mechanism used to capture and store surplus energy to use at times of limited supply (e.g. night time or at times of low wind speed, when solar and wind is used as energy source) (Scamman & Newborough, 2016). Principally in the P2G concept, excess RE is converted into a chemical carrier such as hydrogen or methane (Scamman & Newborough, 2016). Hydrogen, in particular, is attracting great interest as an energy carrier. It can be stored as compressed gas, cryogenic liquid and chemical compounds (e.g. NH_3 and liquid organic hydrogen carriers (LOHCs)) (Maddy *et al.*, 2016). It has great potential to provide energy to the main sectors of the economy, including transportation, buildings and industry (Ghoshal & Sharma *et al.*, 2015). This, in turn, may lead to a low-carbon energy system known as the “hydrogen economy”, which was introduced in 1972 (Maddy *et al.*, 2016).

2.1.4 TECHNOLOGICAL ADVANCES: A HYDROGEN ECONOMY MADE POSSIBLE

Steven Chu, former US Secretary of Energy, winner of the 1997 Nobel prize in Physics, and the new president of the American Association for the Advancement of Science, recently stated (in Chicago): “Get ready for the 1.5 cent per kilowatt hour (kWh) renewable electricity,” a cost that “could unleash the hydrogen economy.” Earlier, in 2009, he had stated “In order to get significant hydrogen deployment, you need four significant technological breakthroughs” in the areas of efficient production, storage, distribution infrastructure, and conversion (via fuel cells (FCs)).

Great technological advances already seen in the hydrogen transportation industry include the following:

- Toyota, Hyundai, and Honda hydrogen cars available in Japan, Germany, South Korea and California
- The hydrogen mobility programme in Europe—Germany aims to have 100 hydrogen refuelling stations installed by the end of 2019
- Cities in China converted their entire bus fleets to electricity (IRENA, 2019)
- Integrated hydrogen fuel cell systems for ships are available
- The first hydrogen-powered passenger aircraft, named Element one, from an aviation company in Singapore, HES Energy Systems—the first prototype is expected in 2025

- Sustainable Innovations, Inc. (Skyre Inc.) has developed a helium/hydrogen recovery system for NASA, based on their proprietary H2RENEW™ technology.

Furthermore, several companies around the globe have been working to advance the technologies, specifically those involving hydrogen, including: HyET Hydrogen, Fuel Cell Technologies, Nuvera Hydrogen Fuel Cells, FuelCell Energy, California Fuel Cell Systems, Shell, Hydrogenious Technologies, and Xergy Inc., to name a few.

Research projects pertaining to hydrogen advancement have also been launched globally. Examples include the following:

- The Reduction Industrial Research (RICE) initiative of the Energy Safety Research Institute (ESRI), based at Swansea University (UK)
- The membrane-based purification of hydrogen system (MEMPHYS) project, based on electrochemical hydrogen purification—with the ability to recover hydrogen from gas mixtures (Schmitz *et al.*, 2019)
- Research at Princeton University, where a team has devised an inexpensive way to harness sunlight for the purpose of hydrogen isolation from industrial waste water—doubling the previous standard for splitting hydrogen from water in a scalable manner.

2.2 HYDROGEN GENERATION AND APPLICATION

Currently, hydrogen is a very important industrial commodity, as it is a key reactant and/or by-product of several industrial processes, including the food industry, petrochemical and petroleum refining, ammonia production, methanol production, hydrogenation processes, hydrometallurgical processes, and metal refining (mainly nickel, tungsten, molybdenum, copper, zinc, uranium and lead) (Benicewicz *et al.*, 2008; Bessarabov & Millet, 2017; Ghoshal & Sharma *et al.*, 2015; Maddy *et al.*, 2016). Although hydrogen has many applications, it is mainly used for the synthesis of ammonia and other nitrogenated fertilizers. Various hydrogen production process technologies exist such as chemical, biological, electrolytic, PV and thermochemical (Ghoshal & Sharma, 2015). Presently, fossil fuels constitute the main source for the production of hydrogen—approximately 95% of the hydrogen that is produced is produced from fossil fuels (Baykara, 2018; Maddy *et al.*, 2016). **Figure 2.2** shows the most widely employed methods currently used to produce hydrogen, starting with the primary energy source (Acar & Dincer, 2014; Collins-Martinez *et al.*, 2016; da Costa Rubim Messeder dos Santos *et al.*, 2017).

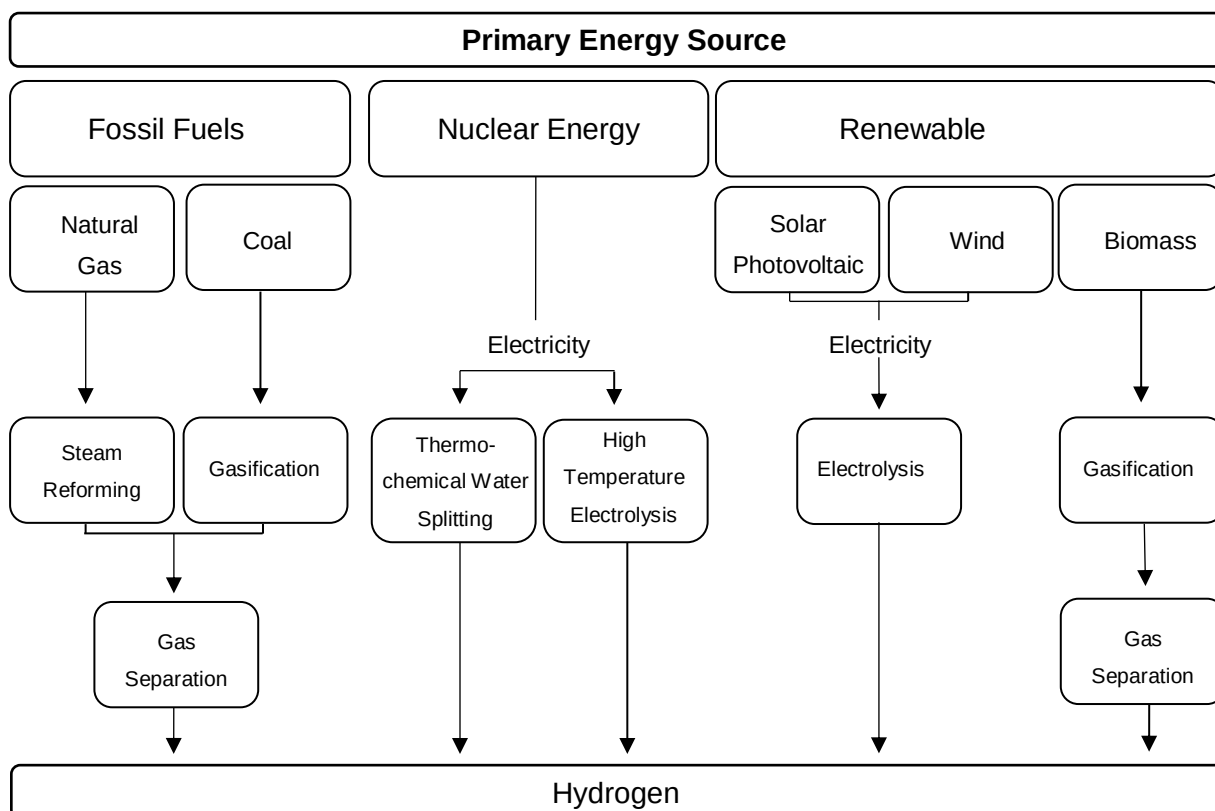


Figure 2.2: Hydrogen production methods (Acar & Dincer, 2014; Collins-Martinez *et al.*, 2016; da Costa Rubim Messeder dos Santos *et al.*, 2017).

Steam methane reforming (SMR) from natural gas (predominantly methane) is the most widely implemented hydrogen production method; efficiency is in the range 65-75 % (Abdalla *et al.*, 2018; Baykara, 2018; David, 2012). Typical hydrogen-rich streams are generated from SMR with compositions of 70-75% hydrogen, 2-6% methane, 7-10% CO and 6-14% CO₂ (Ghoshal & Sharma, 2015). Another fossil fuel-based hydrogen production method, known as partial oxidation (POX)/gasification, generates hydrogen from a broad range of hydrocarbons, including coal, heavy residual oils, as well as low-value refinery products (Acar & Dincer, 2014; Ghoshal & Sharma, 2015). The CO₂ emissions associated with coal, are, however, substantially higher than those associated with other feedstocks. POX mainly yields a mixture of CO and H₂, with small amounts of CO₂ and SNG, at an efficiency of 50% (Acar & Dincer, 2014; Baykara, 2018; Ghoshal & Sharma, 2015).

Although not widely implemented, hydrogen can also be produced from biomass using processes such as pyrolysis/gasification, but this is commonly accompanied by large amounts of impurities (Baykara, 2018). The efficiency of biomass gasification processes lies in the range 35-50 % (Husaini *et al.*, 2015). Several methods of hydrogen production from water are also available, including electrolysis, thermochemical processes, photolysis and direct thermal

decomposition or thermolysis (Baykara, 2018). The efficiency of electrolysis can vary in the range 70-90 % (Baykara, 2018). Thermochemical cycles can also be used to produce hydrogen from water, with efficiencies of 40-50% (Baykara, 2018). Furthermore, hydrogen can be produced from RES such as wind and PV. These methods are in early stages of development, however, and still have very low efficiency levels (Baykara, 2018).

The benefits of hydrogen as a fuel, which is clean and efficient, can however only be fully recognized when hydrogen is produced from RES (Han *et al.*, 2017). Most of the current hydrogen production methods yield hydrogen-rich streams, which is commonly accompanied by contaminant gases including CO₂, CO and N₂ (Benicewicz *et al.*, 2008) (**Table 2.1**). High-grade hydrogen (>99.97%) is required for FCs (SAE International, 2015), the chemical industry and stationary power production. It is therefore abundantly clear that hydrogen should be efficiently purified after generation to ensure its widespread usage.

Table 2.1: Common hydrogen sources and their accompanying impurities (adapted from Nenoff & Ockwig, 2007; David, 2012)

SOURCE	IMPURITIES
Electrolysis	CH ₄ , O ₂ , N ₂ , CO
Steam methane reforming	CO, CO ₂ , CH ₄
Dry shifted syngas	N ₂ , CO ₂ , CO, CH ₄ , H ₂ S
Hot shifted syngas	N ₂ , CO, H ₂ S
Petroleum refining	C ₁ -C ₆ , benzene, toluene, xylene
NH ₃ purge gas	NH ₃ , N ₂ , CH ₄
Coke oven gas	CH ₄ , N ₂ , benzene, toluene, xylene, CO, CO ₂ , O ₂

2.3 HYDROGEN SEPARATION/PURIFICATION

For hydrogen to be realised as a widespread energy carrier (especially a RE carrier), its purification and compression are unavoidable industrial processes. Several technological approaches are used to extract hydrogen from gas mixtures, utilising various characteristics of hydrogen, under different industrial conditions. Common approaches for hydrogen recovery include the following: adsorbing the impurities (pressure swing adsorption (PSA)), condensing the impurities (cryogenic distillation) or by using permselective membranes (Adhikari & Fernando, 2006; Benicewicz *et al.*, 2008; Kvello *et al.*, 2010). PSA and cryogenic distillation technologies all require multiple units and, in some instances, may involve supplementary

wash columns to remove CO and CO₂ (Binicewicz *et al.*, 2008). Although PSA and cryogenic distillation processes are both commercial processes used in hydrogen separation, pressure-driven membrane processes are considered to be a better candidate for hydrogen production because they are not as energy intensive and they yield high-purity hydrogen (Adhikari & Fernando, 2006). However, although membrane technologies are very advantageous over the other purification methods mentioned, they commonly depend on high-pressure feed streams and hydrogen embrittlement is often experienced (Benicewicz *et al.*, 2008). Properties of the various hydrogen purification technologies are summarised in **Table 2.2**, for the purpose of comparison, after which a brief discussion on each technology follows.

Table 2.2: Properties of different hydrogen purification processes (adapted from Chu *et al.*, 2014; Groß *et al.*, 2017; Kaghazchi *et al.*, 2009; Liu & Zhang, 2004)

PROPERTIES	PSA	MEMBRANE	CRYOGENIC
Min. feed purity [vol. %]	>40	>25	15-80
Max. product purity [vol. %]	>99.9	>98	~97
Max. hydrogen recovery [%]	Up to 90	Up to 95	Up to 98
Inlet pressure [bar]	10-70	14-138	14-83
Outlet pressure [bar]	Similar to feed	Substantially less than feed	Similar to feed

2.3.1 PRESSURE SWING ADSORPTION

PSA is the most extensively used state-of-the-art industrial process for hydrogen separation. It is most frequently used in the chemical/petrochemical industry, as well as to recover hydrogen from industrial-rich exhaust gases, including reforming off-gases, coke oven gases and ethylene effluent gases (Adhikari & Fernando, 2006; Bénard *et al.*, 2016; Groß *et al.*, 2017). Currently about 85% of the produced hydrogen is purified by PSA (Schmitz *et al.*, 2019). PSA systems purify hydrogen-rich gas streams by means of adsorbent beds that are used to remove the impurities (Husaini *et al.*, 2015; Kvello *et al.*, 2010). PSA units are designed to adsorb a large amount of impurities at high partial pressures (Adhikari & Fernando, 2006).

Although the system is mainly classified as a batch system, continuous operation can be achieved by implementing multiple adsorbers (Adhikari & Fernando, 2006; Groß *et al.*, 2017; Kvello *et al.*, 2010). The system can be divided into five primary steps: (i) adsorption, (ii) concurrent depressurization, (iii) counter-current depressurization, (iv) purge and (v) counter-current pressurization (Groß *et al.*, 2017). PSA offers two great advantages: the ability to

reduce the impurities to a low level and to produce high purity hydrogen (up to 99.999%) (Schmitz *et al.*, 2019). The quantity of recovered hydrogen is dependent on the feed and purge gas pressures and hydrogen-to-impurity ratio (Adhikari & Fernando, 2006). However, the hydrogen recovery only lies in the range 60-90% (Schmitz *et al.*, 2019).

2.3.2 CRYOGENIC DISTILLATION

Cryogenic distillation is a widely used separation process at low temperature (LT); it is used to separate gas components based on differences in their boiling points (Adhikari & Fernando, 2006; Groß *et al.*, 2017; Kvello *et al.*, 2010). Hydrogen's low boiling point of -252.9°C (below that of almost all other substances) is used as a measure to separate it from other components, where the collected hydrogen can be stored as a liquid (Schmitz *et al.*, 2019). The gas needs to be cooled down, to condense, resulting in large energy consumption (Adhikari & Fernando, 2006; Groß *et al.*, 2017).

If significant amounts of CO, CO₂ and N₂ are found in the feed stream, a methane wash column is needed to lower the concentrations of these gases (Adhikari & Fernando, 2006; Kvello *et al.*, 2010). The feed gas is also in need of pretreatment to remove the components that might freeze, therefore water should be reduced to <1 ppm and CO₂ to <100 ppm (Groß *et al.*, 2017). It is not practical to use this method to obtain high-purity hydrogen; yet higher hydrogen recovery can be achieved at moderate hydrogen purity yields ($\leq 95\%$) (Adhikari & Fernando, 2006; Groß *et al.*, 2017).

2.3.3 MEMBRANE TECHNOLOGIES

The advantages offered by the membrane technologies, over the PSA and cryogenic distillation processes, include the following: ease of operation, low energy consumption, possibility of continuous operation, cost effectiveness, low maintenance, and compactness (Adhikari & Fernando, 2006; Groß *et al.*, 2017; Husaini *et al.*, 2015; Kaghazchi *et al.*, 2009). Hydrogen selective membranes can be broadly divided into four categories namely: polymeric (organic), metallic, carbon based, and ceramic based (**Table 2.3**) (Adhikari & Fernando, 2006; Husaini *et al.*, 2015). Membranes can further be divided into porous and dense membranes (Adhikari & Fernando, 2006).

Table 2.3: Comparison of selected hydrogen separation membrane properties (adapted from Adhikari & Fernando, 2006; Corengia *et al.*, 2013; Nenoff & Ockwig, 2007).

	MEMBRANE TYPES						
	METALLIC		CERAMIC		CARBON	POLYMERIC	
	DENSE	POROUS	DENSE	MICROPOROUS	POROUS	DENSE	POROUS
Materials	Pd, Ta, V, Nb, and alloys		Proton conducting ceramics, silica, alumina, zirconia, titania, metal organic frameworks (MOF) and zeolites		Carbon	Polymers: polyimide, cellulose acetate, polysulfone, polyesters, ethers, imides, urethanes etc.	
T range [°C]	300-700		600-900	200-600	500-900	<100	
H₂ Selectivity	>1 000		>1 000	5-139	4-20	low	
H₂ flux^a	60-300		6-80	60-300	10-200	low	
Stability	Phase transitions (cause embrittlement)		Brittle, stability in CO ₂	Brittle, Stability in H ₂ O	Very brittle, oxidising	Swelling and compacting	
Poisoning issues	H ₂ S, HCl, CO ₂ , SO _x , CO		Potential degradation with H ₂ O, H ₂ S or CO ₂		Oxidizing and susceptible to organic vapours	H ₂ S, HCl, CO ₂ , SO _x , CO	
Transport Mechanism^b	Sol-D	Sol-D/MS	Sol-D	MS	Sol-D/MS	Sol-D	MS
Cost	Moderate to high	Moderate	Low	Low	Low	Low	Low

^a 10⁻³ mol m⁻² s⁻¹ at ΔP = 1 bar; ^b Sol-D, Solution diffusion; MS, Molecular sieving

Table 2.3 gives a comparison of the different membrane types suitable for hydrogen separation, and the membrane properties (Adhikari & Fernando, 2006; Corengia *et al.*, 2013; Nenoff & Ockwig, 2007). Dense metal membranes (mainly palladium alloys) are seen as the most appropriate construction materials due to their high hydrogen selectivity (Adhikari *et al.*, 2006; Corengia *et al.*, 2013; Groß *et al.*, 2017; Oyama & Yun, 2011). Dense ceramic membranes are also seen as a favourable option, for the same reason (Corengia *et al.*, 2013). The greatest disadvantage of membrane processes is that, compression is required after hydrogen purification, for the purpose of transport and storage (Schmitz *et al.*, 2019).

2.3.4 ELECTROCHEMICAL HYDROGEN PURIFICATION/SEPARATION

Electrochemical membranes are seen as a promising alternative to pressure-driven membranes (Groß *et al.*, 2017). Electrochemical membranes are known to generate electricity (FCs) or to apply it (water electrolysis); they are also used to purify/enrich and compress hydrogen streams (Groß *et al.*, 2017). Electrochemical hydrogen pumping has the following advantages over other conventional separation systems (Bessarabov, 1998; Hashimoto *et al.*, 2008):

- Hydrogen, in the form of protons, is selectively transferred through the proton conducting electrolyte
- One-step operation provides pure hydrogen
- The hydrogen separation rate can be controlled by the current (Faraday's Law)
- High hydrogen collection rate is achieved
- Simultaneous purification and compression of hydrogen is possible, in principle
- High hydrogen separation is achieved at low cell voltages, with a high separation efficiency (Gardner & Ternan, 2007)
- High selectivity and low permeability results in pure hydrogen (up to 99.99 vol. %) (Fateev *et al.*, 2011)

An additional benefit of this electrochemical method is that CO₂ is concentrated, and it can be captured and stored, without any further treatment—hence, reducing GHG emissions (Benzinger *et al.*, 2012; Gardner & Ternan, 2007). In terms of application, electrochemical hydrogen separation could be beneficial in numerous industrial fields, including: (i) hydrogen purification for the use in FC technologies, (ii) cooling agent in turbines, (iii) for the application in nuclear reactors (separation and concentration of hydrogen isotopes), and (iv) separation of hydrogen from natural gas mixtures (e.g. transportation of hythane through gas pipelines) (Fateev *et al.*, 2011). Also, compressed high purity hydrogen is required for FCs (>99.97%) (SAE International, 2015) and hydrogen mobility (e.g. Hydrogen Mobility Europe (H2ME) (Hydrogen Europe, 2015; Speers, 2018)).

2.3.5 CURRENT STATUS OF ELECTROCHEMICAL HYDROGEN SEPARATION

A summary of previously reported literature addressing electrochemical hydrogen purification technologies is presented in **Table 2.4** (in chronological order of applicable references). The type of membrane, the electrocatalyst, as well as the gas mixtures that was used in the articles listed are included. A brief discussion on each contribution follows.

Table 2.4: Summary of electrochemical hydrogen purification technologies reported in literature

MEMBRANE TYPE	CATALYST USED	GAS MIXTURE ^a	CELL T ^b	SOURCE
Nafion 115	0.4 mg Pt cm ⁻²	Hydrogen composition between 10-90%, balance N ₂ to CO ₂ ratio of 1:1	30-70°C	Choi <i>et al.</i> (2004:92-98)
Not specified	Not specified	H ₂ /N ₂ mixtures (99.99, 10 and 1% H ₂ with balance N ₂)	60°C	Araki <i>et al.</i> (2007:1-8)
Nafion 115	Carbon supported Pt and Ru on anode and cathode (1 mg Pt, 0.5 mg Ru cm ⁻²)	Pure H ₂	20°C	Gardner & Ternan (2007:836-840)
		80% hydrogen, 1000-ppm CO, and 20% CO ₂		
		80% H ₂ , 20% CO ₂		
Nafion 115	Pt (loading: 1 mg Pt cm ⁻²) or Pt/Ru (1 mg Pt, 0.5 mg Ru cm ⁻²) catalyst on both anode and cathode	H ₂ /CH ₄ mixtures	20-70°C	Gardner <i>et al.</i> (2007:908-914)
		H ₂ /Ar mixtures		
Self-manufactured PBI membrane	1 mg Pt cm ⁻²	35.8% H ₂ , 1906 ppm CO, 11.9% CO ₂ , and balance N ₂	120-160°C	Benicewicz <i>et al.</i> (2008:479-483)
		1.03% CO, 29.8% CO ₂ , balance H ₂		
Nafion 117	0.1 mg Pt cm ⁻²	H ₂ /N ₂ gas mixture	25 and 60°C	Bianchi <i>et al.</i> (2008:103-113)

^a vol. %; ^b Temperature, °C

Table 2.4 (continued): Summary of electrochemical hydrogen purification technologies reported in literature

MEMBRANE TYPE	CATALYST USED	GAS MIXTURE ^a	CELL T ^b	SOURCE
Not specified	Not specified	1-99.99% H ₂ diluted in N ₂ or CO ₂	60°C	Araki <i>et al.</i> (2009:1-7)
Nafion 115	Carbon supported Pt on both anode and cathode with catalyst loading 1 mg Pt cm ⁻²	H ₂ / Ar mixtures H ₂ /ethylene mixtures		Doucet <i>et al.</i> (2009:998-1007)
Commercially available PBI with fibre reinforced Teflon gaskets	Not specified	H ₂ diluted in N ₂ (80-40% H ₂) 75% H ₂ , 23.5% CO ₂ , 1.36% CO, and 0.36% CH ₄ 44% H ₂ , 35% N ₂ , 21% CO ₂ , and 100 ppm CO	160-180°C	Kvello <i>et al.</i> (2010:229-234)
Nafion membrane modified by addition of zirconyl phosphate	0.4 mg Pt cm ⁻² for both anode and cathode	H ₂ /N ₂ mixtures (62%, 76% and 100% H ₂)	35-75°C	Fateev <i>et al.</i> 2011:4148-4155
Nafion 115	Air-brushing a suspension of 20 wt% Pt/C catalyst and solubilized Nafion in methanol – loading of 0.4 mg Pt cm ⁻²	Mixtures of CO ₂ , H ₂ O and H ₂	50-70°C	Abdulla <i>et al.</i> 2011: 1767-1779
Solubilized Nafion in methanol onto Nafion 115 membrane	Airbrushed 20 wt. % Pt/C and 20 wt. % Pd/C catalysts	CO ₂ /H ₂ reformat mixtures	30-50°C	Benziger <i>et al.</i> (2012:424-434)
Home-made PBI/PA membranes	Commercial Pt/C catalyst (46 wt.% Pt/C) Pt loading of 0.4 mg cm ⁻² to 2.2 mg cm ⁻²	80% CO ₂ and 20% H ₂	160°C	Ahn <i>et al.</i> (2013:14816-14823)
PBI-based PA doped fuel cell membrane	Pt/C catalyst (unknown loading)	Simulated reformat gases with different H ₂ , N ₂ and CO concentrations	140-160°C	Chen <i>et al.</i> (2014:13757-13762)

^a vol. %; ^b Temperature, °C

Table 2.4 (continued): Summary of electrochemical hydrogen purification technologies reported in literature

MEMBRANE TYPE	CATALYST USED	GAS MIXTURE ^a	CELL T ^b	SOURCE
Nafion based	Ir/C nanocatalysts (unknown loading)	H ₂ /CO ₂ gas mixtures	70°C	Ahn <i>et al.</i> (2014:348-354)
SPPEsk membrane, Nafion 212, Nafion/PTFE and Nafion 115	0.2 mg Pt cm ⁻² at the anode and 0.4 mg Pt cm ⁻² at the cathode	H ₂ /CO ₂ gas mixtures	20-60°C	Chen <i>et al.</i> (2016:178-186)

^a vol. %; ^b Temperature, °C

Choi *et al.* (2004) investigated the electrochemical membrane separation of hydrogen from a H₂/N₂/CO₂ mixture. They reported that an increase in cell temperature resulted in enhanced hydrogen purity and energy efficiency. Applying pressure on the feed gas side increased the performance and the amount of hydrogen produced but decreased the hydrogen purity, as the permeation flux of impurities increased. The performance decreased with higher concentration of impurities in the feed gas stream. The permeability of CO₂ is greater than that of N₂, therefore the hydrogen purity is more dependent on CO₂. At a current density of 0.7 A cm⁻², a hydrogen purity of 98.6 and 99.73% can be achieved from a low purity feed (30% H₂) using a one-stage and two-stage process, respectively.

Araki *et al.* (2007) carried out preliminary investigations into the separation and compression efficiencies, and performance, of a hydrogen pump, and found that >98% of hydrogen in the feed could be separated, at cell voltage 0.06-0.15 V and current efficiencies ~100%.

Gardner & Turner (2007) investigated hydrogen separation from hydrogen-rich streams containing CO₂ and 1000 ppm CO. The cell resistance was ~17 mΩ (using pure hydrogen to plot a polarisation curve). It was found that pure hydrogen yielded efficiencies of >80%. When extracting hydrogen from a H₂/CO₂ mixture, the extraction efficiency was ~80%. However, when the hydrogen feed stream contained CO, the efficiency was relatively poor. CO severely contaminates the anode, raising the anode potential by up to 300 mV. In attempt to improve the efficiency in the presence of CO, periodic pulsing was examined. It was determined that pulsing can substantially mitigate the problem of CO contamination and reduce the anode potential, although the anode potential is still very high when compared with that of an unpoisoned cell. The maximum current densities observed were ~0.2 A cm⁻².

Gardner *et al.* (2007) investigated hydrogen separation from H_2/CH_4 mixtures with both Pt and Pt/Ru anode catalysts. Little energy is consumed and CH_4 seems to be inert at LT, which results in negligible fouling of the anode electrocatalyst. It was found that if the hydrogen recovery is smaller than 80%, a small portion of the hydrogen energy is required for separation. A mathematical model was developed to simulate the electrochemical separation process. It proved to be in good agreement with the experimental data obtained.

Benicewicz *et al.* (2008) investigated and reported on the performance of a HT polybenzimidazole (PBI) membrane (processed by the sol-gel process). The electrochemical cell was operated at 120-160°C with various gas reformat feed streams, with and without humidification. This was done in order to evaluate key parameters such as the power requirements of the cell, the electrochemical efficiency, the durability, the CO tolerance and the hydrogen purification efficiency. They found that almost faradic flows (correlating to the law of Faraday) were achieved and little power was required to operate the hydrogen pump; durability in long-term tests was excellent. Polarisation curves were constructed to investigate the power requirements. For a typical current density of 0.2 A cm^{-2} , low voltages of $\sim 45 \text{ mV}$ were achieved at 160°C for pure hydrogen. These low voltages are an indication of facile oxidation and reduction of hydrogen and low resistance of the MEA and the cell hardware components. With a stoichiometric hydrogen feed of 1.2 (without humidification), an increase in linearity of the outlet flow rates to current density was observed.

The current efficiencies for current densities between 0 and 2 A cm^{-2} were $>83\%$ and $>90\%$ for current densities $\geq 0.4 \text{ A cm}^{-2}$. Premixed natural gas reformat (35.8% H_2 , 1906 ppm CO and 11.9% CO_2 , with the balance N_2) and methanol reformat (1.03% CO and 29.8% CO_2 , with the balance H_2) were used to investigate the CO tolerance and the cells' tolerance to impurities. Nearly faradic flows were achieved, irrespective of the feed composition. The effect of CO on the Pt catalyst were completely reversible at 120-160°C. Furthermore, the CO concentrations were reduced from 1 906 ppm to $\sim 12 \text{ ppm}$, and CO_2 concentrations were reduced from 11.9% to 0.37% at 0.4 A cm^{-2} and 0.19% at 0.8 A cm^{-2} . Results of these experiments justify the use of PBI membrane-based hydrogen purification at HT from feed streams containing relatively high CO and CO_2 concentrations and low concentrations of hydrogen—which is not observed at LT ($<100^\circ\text{C}$), due to catalyst poisoning and water management issues.

Bianchi *et al.* (2008) investigated the concentration of hydrogen achieved electrochemically from a lean hydrogen-inert gas mixture under galvanostatic and potentiostatic conditions. Results of the experimental runs suggested that galvanostatic operating conditions were

unstable, whereas operation at potentiostatic conditions appears to be more stable. They reported that the hydrogen recovery increased with applied potential and the coefficient of performance (defined as the ratio of the hydrogen produced over the hydrogen consumed) decreased with the applied potential difference. Furthermore, the feed flow rate had a noteworthy effect on the recovered hydrogen. They proposed an optimum energy efficiency for separation, but did not identify its dependency on the process parameters.

Araki *et al.* (2009) measured the voltage–current characteristics of an electrochemical hydrogen pump (EHP) and PEM-FCs; they changed the hydrogen concentration from 99.99% to 1%. Nearly all of the hydrogen could be separated and recovered, even when the hydrogen feed mixture flow rate or feed gas concentration was changed (impurity concentration in the treated gas stream: max. 1 000 ppm). The hydrogen released at the anode side were approximately 50 ppm, which is well below the permissible limit, 1%. The cell voltage became unstable for CO₂ gas mixtures.

Doucet *et al.* (2009) investigates the feasibility of separating hydrogen from H₂/ethylene gas mixtures. Experimental results showed that, a large amount of the ethylene reacted with the H₂ to form ethane. In spite of this reaction taking place, results still show that it is possible to obtain reasonable separation. Results indicated that if Pt is used as electrocatalyst to separate alkenes and H₂, the consumption of hydrogen is somewhat less than the amount of alkenes in the inlet. The suggestion was made that another catalyst (which has a lower hydrogenation rate and different selectivities for H₂ and ethylene adsorption) should be used when alkenes are present, as it might improve the general efficiency of the process. The authors concluded that electrochemical hydrogen separation by means of PEM-FC technology is not suitable for large quantities of ethylene.

Kvello *et al.* (2010) investigated simultaneous hydrogen separation and compression using PBI-based PEM-FC technology. The tests were performed using pure hydrogen, N₂/H₂ mixtures and reformat feed gas mixtures containing CO, CO₂ and CH₄. The energy efficiency of the compression process was found to be 80-90% based on the lower heating value of separated hydrogen, at hydrogen fluxes of 5-7 Nm³ m⁻² h⁻¹. Furthermore, a CO tolerance of ±1.5% was reported, with a reduction in the other gas components in the separated hydrogen of up to 99%. Stable compression was reported up to 0.65 bar differential pressure over the PBI membrane with almost no increase in the energy consumption.

Fateev *et al.* (2011) investigated the extraction and compression of hydrogen from a H₂/N₂ mixture. They found that a lower hydrogen content in mixtures resulted in high mass transport

limitations and that the compression efficiency decreased as the hydrogen content decreased. The current density of the compressor must be reduced in order to match mass transport limitations that result from lower hydrogen concentrations in the feed, in order to avoid low concentration and compression efficiencies. They concluded that this system could not be used to effectively extract hydrogen from diluted hydrogen streams.

Abdulla *et al.* (2011) investigated the recovery and energy efficiency of hydrogen separation from mixtures of CO₂, H₂O and H₂ using a polymer electrolyte hydrogen pump (PEHP). Measurements were recorded as functions of the operating parameters: gas flow rate, gas composition, applied potential difference and temperature. High-purity hydrogen (>99.99%) was recovered in single-stage PEHP experiments, at energy efficiencies of 45%. Experimental analysis showed that energy efficiencies of >90% with >98% hydrogen recovery is possible with a programmed voltage profile multistage PEHP and 90% hydrogen recovery is achievable with 75% energy efficiency if a fixed applied potential difference multistage PEHP is used. The experimental results obtained were used as a basis for predictive models in single-stage and multistage PEHPs.

Benziger *et al.* (2012) compared carbon-supported Pt/C and Pd/C catalysts in the electrochemical recovery of hydrogen from H₂/CO₂ reformat mixtures. Electrochemical activity and separation efficiency were evaluated using CV, polarisation and potentiostatic hydrogen pumping. The results showed that the MEA resistance increased as the dilution of hydrogen in CO₂ increased. In addition, the effective resistance of the Pd/C catalyst was greater than that of the Pt/C catalyst. The CO₂ adsorbed more strongly to the surface of the Pd/C catalyst, impairing the electrochemical active surface area available for hydrogen oxidation/reduction—hence resulting in lower separation efficiencies. Furthermore, the Pd/C catalyst showed lower resistance to CO₂ poisoning, higher effective ohmic resistance and a lower mass transport coefficient of hydrogen. Benzinger *et al.* (2012) concluded that it would be possible to replace Pt with Pd as catalyst to reduce costs, however, this will be accompanied by reduced energy efficiencies.

Ahn *et al.* (2013) investigated the effects of Pt loading on the cell performance of a PBI-based electrochemical hydrogen pump (EHP) by means of polarisation curves. This was paired with an investigation into electrochemical impedance characteristics, utilizing MEAs with various Pt loadings on the anode and the cathode. In addition, the gas separation of H₂/CO₂ was investigated, with no humidification, at a cell operating temperature of 160°C. The cell voltage was reported to be a mere 80 mV at 0.8 A cm⁻² for a pure hydrogen feed. This was lower than that achieved with PFSA cells at a relative humidity (RH) of ≤43%. The cell voltage increased

by 72% when the anode Pt loading was decreased from 1.1 mg Pt cm⁻² to 0.2 mg Pt cm⁻². The effect of various catalyst loadings on the cathode proved to be insignificant.

Chen *et al.* (2014) investigated PBI-based PA-doped FCs under simulated reformat gases with various H₂, N₂ and CO concentrations. In the absence of CO, the dilution effect of N₂ had little to no effect on the performance of the cell. CO poisoning, however, increased the charge transfer resistance, which substantially decreased the performance. Experimental results indicated that higher operating temperatures suppresses the Pt-CO binding reaction, resulting in improved tolerance towards CO.

Ahn *et al.* (2014) investigated the replacement of Pt electrocatalysts with Ir-based electrocatalysts and carried out electrochemical hydrogen separation from H₂/CO₂ mixtures. The Ir-based catalysts were characterised using x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and thermogravimetric analysis (TGA). CO₂ stripping indicated that the Ir catalyst were unaffected by CO₂, unlike the Pt catalyst. Furthermore, the performance of the Ir catalyst were better than that of the Pt catalyst when the focus was placed on H₂/CO₂ separation. The operating voltage to separate hydrogen from the CO₂ mixture was less for Ir300 (0.18 V at a current density of 0.8 A cm⁻²) than for Pt (0.20 V at a current density of 0.8 A cm⁻²).

Chen *et al.* (2016) investigated the possibility of coupling H₂/CO₂ separation with hydrogenation of biomass-derived butanone in an EHP, and replacing Nafion membranes with non-fluorinated SPPEK (sulfonated poly (phthalazinone ether sulfone ketone)) membranes. Due to higher resistance, caused by swelling, the SPPEK-based EHP reactor had exceptional reaction rates at elevated temperatures (60°C). It also had a higher butanone concentration of 270 nmol cm⁻² s⁻¹, compared to that of a Nafion-based EHP reactor which had a butanone concentration of 240 nmol cm⁻² s⁻¹. Furthermore, the SPPEK-based EHP exhibited better hydrogenation than an EHP with Nafion membranes due to lower CO₂ permeation; however, efficiencies of the former approximately 20% lower than those of the latter. With H₂/CO₂ as feed stream, an efficiency of 40% was reached with the EHP, with a power consumption of 0.3 kWh per Nm³ hydrogen, which is superior to what is reached with alternative processes such as PSA and water electrolysis. The separation efficiencies of the membranes used in this study are tabulated in **Table 2.5**.

Table 2.5: Hydrogen purity of the product gas (inlet stream properties: 56.7 mA cm⁻², 40 °C, 1 atm, 75 vol. % CO₂)

Gas	Composition [%]			
	SPPEsk-0.71	Nafion 115	Nafion 212	Nafion/PTFE
H ₂	>99.99	>99.99	99.79	99.25
CO ₂	<0.01	<0.01	0.21	0.75

2.4 SUMMARY AND CONCLUSIONS

In conclusion, some limitations of the earlier studies that have been carried out by others (studies included in this literature chapter) are now mentioned (**Section 2.4.1**) and gaps that still exist in knowledge pertaining to electrochemical hydrogen separation are highlighted (**Section 2.4.2**).

2.4.1 LIMITATIONS OF PREVIOUS STUDIES IN THE FIELD OF ELECTROCHEMICAL HYDROGEN SEPARATION AND AREAS REQUIRING FURTHER RESEARCH AND DEVELOPMENT

- Contribution/s of various impurities (considered separately) to the performance parameters. **Table 2.1** shows the impurities that commonly accompany hydrogen streams generated from various traditional hydrogen generation methods. Impurities typically include CH₄, O₂, N₂, CO, CO₂, H₂S, benzene, toluene, xylene and NH₃. However, as is evident from **Table 2.4**, research articles are only available on electrochemical hydrogen separation from mixtures containing CO, N₂, CO₂, CH₄, Ar, ethylene and H₂O, and the HT research mainly included reformat gases. Therefore, the contribution of each impurity, separately, on the performance parameters is largely unknown.
- Electrochemical hydrogen separation from NH₃-containing feed streams. The presence of small amounts of NH₃ (ppm concentrations) was found to be detrimental to LT-PEM-FCs; however, to the best of the author's knowledge, no literature/articles are available in open literature on the performance of a HT electrochemical cell at HT (100-200°C) in the presence of ammonia. It is therefore unknown whether higher temperatures will also alleviate this effect, as in the case when CO is present.
- Limited number of articles pertaining to HT electrochemical hydrogen separation. From **Table 2.4** it is evident that more information is available on LT separation than HT separation. Further research is required to achieve a broader understanding of the

expected extent of separation with respect to the various performance parameters—such as limiting currents, hydrogen recovery, selectivities and fluxes achieved.

2.4.2 GAPS IN RESEARCH KNOWLEDGE IN THE FIELD OF ELECTROCHEMICAL HYDROGEN SEPARATION

- In general, there are very few research articles and very little information available on electrochemical hydrogen separation, largely because the technology is not yet mature. Most information regarding component degradation and cell component interactions has been extracted from the existing knowledge of FCs, since the same cells and components are used for different purposes.
- The influence of CO₂ on the performance of an EHS has hardly been analysed; it has mostly been studied together with the presence of CO.
- No articles were found on the determination of the ECSA of a hydrogen pump when separating hydrogen from a stream containing CO. Nor were any articles found that report whether temperature or bimetallic catalysts are more dominant when obtaining improved tolerance to CO.
- More information is required on hydrogen separation from streams containing ammonia.
- It is considered important to obtain a broad understanding of the lifetime cycle of an electrochemical hydrogen membrane and how an aged membrane's performance compare to that of a membrane at the beginning of its life. This is, however, lacking in open literature.
- It was stated that one of the advantages that HT membranes present is the possibility of being able to use catalysts such as iron and cobalt. More information on this topic is required, in efforts to determine how beneficial this would be—besides only focusing on the cost reduction.

CHAPTER 3. HIGH-TEMPERATURE ELECTROCHEMICAL HYDROGEN SEPARATION BY MEANS OF PROTON EXCHANGE MEMBRANE TECHNOLOGY

This chapter encloses an experimental investigation on the performance of a high-temperature TPS[®]-based membrane used to electrochemically separate hydrogen from various gas mixtures. Herein reported is a study on the electrochemical separation of hydrogen from H₂/CH₄, H₂/CO₂ and H₂/NH₃ gas mixtures. The effect of temperature and impurity concentration on the performance was investigated.

Section 3.1 serves as an introductory chapter, which encloses aspects regarding the background and motivation for this work. **Section 3.2** describes the experimental apparatus used and protocol followed during the experimental investigation of the electrochemical hydrogen separator. The experimental set-up, and the equipment and materials used is described in **Section 3.2.1**. This is followed by the experimental procedure found in **Section 3.2.2**, and a definition of the performance parameters given in **Section 3.2.3**. The results obtained from the experimental evaluation is presented and discussed in **Section 3.3**. Finally, **Section 3.4** highlights the conclusions made during this experimental investigation.

Supplementary information pertaining to the membrane durability and operational stability is included in **5.4Appendix C: Section 5.4C.5**.

3.1 INTRODUCTION

This chapter describes an experimental investigation on the performance of a high-temperature (HT) TPS[®]-based membrane used to electrochemically separate hydrogen from various gas mixtures. The focus was on the electrochemical separation of hydrogen from H₂/CH₄, H₂/CO₂ and H₂/NH₃ gas mixtures. The effects of temperature and impurity concentration on the performance were investigated.

From the background presented in **Chapter 1** and literature reported in **Chapter 2**, it is evident that alternative energy generation methods are indispensable and that hydrogen as energy carrier is seen as a favourable solution to the current energy crisis. Consequently, many are promoting the vision of a low-carbon energy system known as the 'hydrogen economy' (see **Section 2.1**), based on energy from electricity and hydrogen (Doucet *et al.*, 2009). However, according to Diniz da Costa *et al.* (2007), the development of four critical technologies are necessary before a 'hydrogen economy' can be fully realised:

- Production of hydrogen in a carbon-constrained global energy system in a cost effective manner. The challenges include (a) the production of H_2 from fossil fuels, taking carbon sequestration into account and (b) increasing hydrogen utilization from renewable sources.
- Development of hydrogen infrastructure, including hydrogen purification, separation, compression, and storage technologies.
- Efficient hydrogen delivery and distribution infrastructure.
- The development of efficient fuel cell (FC) technologies as well as other energy conversion technologies that utilize hydrogen.

Currently, the greatest impediment towards a fully functional ‘hydrogen economy’ lies in the lack of infrastructure to deliver hydrogen, especially to FCs (Diniz da Costa *et al.*, 2007). It would therefore be of significant economic interest to use existing natural gas infrastructure for hydrogen distribution rather than constructing a dedicated hydrogen pipeline, which will be very expensive (Gardner *et al.*, 2007). If this route is taken, hydrogen will then either be introduced, and mixed with natural gas, at the point of production, or transported through the pipeline (Gardner *et al.*, 2007).

Hydrogen separation/purification technology is therefore of great importance, since hydrogen must be separated from H_2/CH_4 gas mixtures. Besides utilizing the existing natural gas infrastructure for hydrogen distribution, the on-demand hydrogen generation from an easily stored fuel such as NH_3 (Dolan *et al.*, 2019) could also be considered a promising solution to overcoming the challenges that hydrogen storage and transportation presents. These challenges include high storage costs and the low volumetric energy density of hydrogen, which exacerbate transportation and storage difficulties. However, if this method is to be considered, then the separation of hydrogen from H_2/NH_3 is unavoidable.

In terms of hydrogen generation, the efficient use of industrial sources of hydrogen should be a key focus because thousands of tons of surplus hydrogen are produced each year in various industrial processes (Doucet *et al.*, 2009). This surplus hydrogen is not recovered, but it is vented or utilised for its heating value (Doucet *et al.*, 2009). Moreover, hydrogen production methods are commonly accompanied by several impurities (see **Table 2.1**) (Benicewicz *et al.*, 2008; Chen *et al.*, 2014; Choi *et al.*, 2004). An example is the syngas produced from coal gasification and steam reforming of natural gas—it includes H_2 , CH_4 , H_2O , and CO_2

(Benicewicz *et al.*, 2008; Cho *et al.*, 2014; Choi *et al.*, 2004; Doucet *et al.*, 2009). The development of technologies and techniques for effective hydrogen separation from these streams is of global interest, especially for FC application, as high purity hydrogen (>99.97%) is required (Benziger *et al.*, 2012; Cao *et al.*, 2015; SAE International, 2015). Hydrogen fuel quality specifications are presented elsewhere (see **Appendix G**).

Conventional advanced hydrogen purification technologies, and a promising alternative separation technology known as the electrochemical hydrogen separator (EHS), have been discussed earlier (**Section 2.3**). One of the most beneficial advantages of the EHS is the integration between hydrogen recovery and CO₂ capture and storage, without further treatment, hence reducing greenhouse gas (GHG) emissions (Benziger *et al.*, 2012; Gardner & Ternan, 2007).

Against this background, it is obvious that the role of hydrogen separation technologies in the potential 'hydrogen economy' is inevitable. Therefore, in view of the demand and the promising nature of EHSs, research in this field is motivated.

Although high-temperature (HT) proton exchange membranes (PEMs) have been developed to overcome the limitations associated with low-temperature (LT)-PEMs (see **Appendix A: Section A.3.3**), not much has been reported on HT electrochemical hydrogen separation (see **Table 2.4**). Experimental work was therefore carried out to quantify, and properly define, the general performance (voltage-current characteristics (e.g. limiting current density and open-circuit voltage), hydrogen permeability and general performance efficiencies: power efficiency, voltage efficiency and current efficiency) and hydrogen separation performance (hydrogen purity and selectivity) of a HT TPS[®]-based PEM in a temperature range of 100-160°C. The TPS[®]-based membrane has the ability to comfortably operate at temperatures up to 200°C, which is higher than what is achievable with the polybenzimidazole (PBI) membranes from the same supplier (see **Table 1.1** in **Section 1.4**). However, no open literature was found on the separation performance of a TPS[®]-based membrane. Therefore, the TPS[®]-based membrane was selected as the membrane of choice. The electrocatalyst of choice, Pt-Ru/C, were selected based on the literature gaps identified in the available knowledge; summarised on **page 3** (in **Section 1.2**). The gas mixtures used were different concentrations of H₂/CH₄, H₂/CO₂ and H₂/NH₃. The mixtures were selected based on their industrial relevance in processes related to syngas, the water–gas shift (WGS) reaction, the power-to-gas (P2G) concept, ammonia production and also the separation of hydrogen from hythane.

3.2 EXPERIMENTAL

3.2.1 TEST RIG, EQUIPEMENT AND MATERIALS USED

3.2.1.1 Description of the test rig

The test set-up used for the experimental performance evaluation of the TPS[®]-based membrane is illustrated in **Figure 3.1**. The anode compartment accommodates two inlet streams, whilst the cathode inlet is sealed off (no inlet). The anode inlet streams comprise a hydrogen feed, with an allowance of impurities (hydrogen mixture with impurities CO₂, CH₄ and NH₃), and a nitrogen feed. The nitrogen feed acts as a purge gas to clean the cell of impurities. All feed gasses were stored in high-pressure gas cylinders, controlled by pressure regulators, and connected to the cell making use of small-diameter (1/4") plastic tubing. Mass flow controllers (Brooks Delta Smart II) were used to regulate the flow of the feed streams. The mass flow controllers were controlled making use of LabVIEW software (National Instruments, Austin, TX) and exhibit a rate accuracy of $\pm 0.7\%$ and a rate repeatability of 0.25 % (Brooks instruments, 2008).

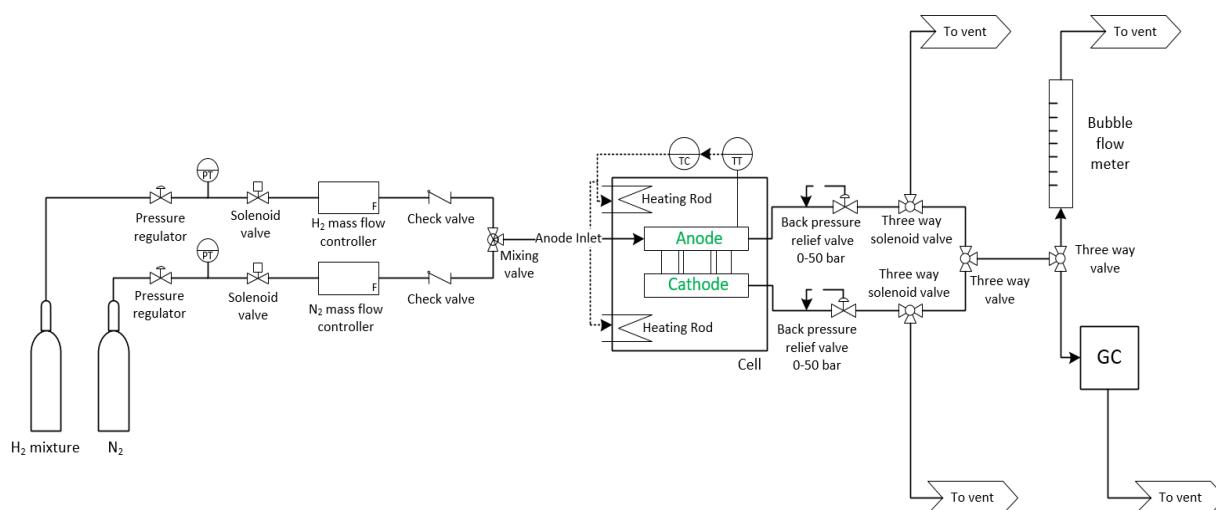


Figure 3.1: Experimental set-up used for electrochemical hydrogen separation.

An external DC power supply was connected, in parallel, to the bus plates of the electrochemical cell and operated in constant current mode. The current and voltage were recorded with an electronic load attached to a computer, making use of LabVIEW software. The cell temperature was maintained making use of two Watlow FIREROD[®] heating rods, one at the anode side and one at the cathode side, with incorporation of a K-type thermocouple (anode side) and PID controller (DCL-33A). The cell was enclosed in a heat insulation jacket to reduce heat losses. The temperature at the centre of the anode back plate was taken as

the cell temperature. All fittings used in the system are standard fittings, supplied by Swagelok (Modderfontein, Johannesburg, South Africa).

The permeate volumetric flow rate was measured using a soap flow meter and the composition of the permeate was determined with an online gas chromatograph (GC) (SRI 8610C-GC; SRI Instruments, Torrance, CA). Refer to **Appendix D** for the curves used to calibrate the GC, situated downstream from the cell, with no pressurisation.

Furthermore, a voltage limit was instated to prevent damage to the catalyst layer (CL) (Belhadj *et al.*, 2016). Experiments were terminated when the anode potential exceeded the set voltage limit of 1.1 V. The experiments were also terminated when a limiting current density was reached.

3.2.1.2 The electrochemical cell

Experiments were carried out using a single, square-shaped, off-the-shelf electrochemical cell with an active area of 25 cm² (Fuel Cell Technologies, Inc., Albuquerque, NM) making use of a multipath serpentine flow field design for gas distribution. The cell comprised a proton conducting membrane, placed between two pieces of carbon cloth (acting as gas diffusion layers (GDLs)), copper current collectors, sealed off with high temperature PFA gaskets (used to properly compress the membrane electrode assembly (MEA)), and aluminium back plates used for assembly (**Figure 3.2**).

The cell was compressed using a torque wrench to ensure a uniform pressure distribution over the compressed MEA and to minimize the electrochemical and thermal resistance of the GDLs. The assembly torques for the 8 bolts was 6 Nm.

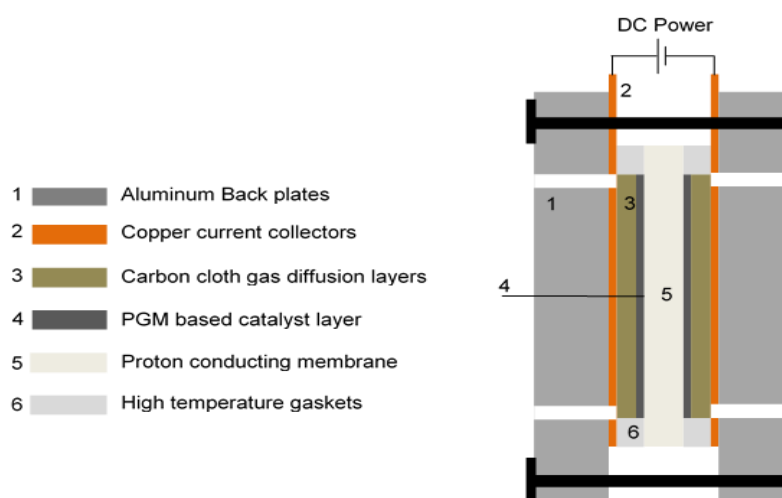


Figure 3.2: Cross section of the electrochemical cell.

The properties of the TPS[®]-based MEA used to conduct the experiments are summarised in **Table 3.1**. The exact nature of the TPS[®]-based membrane cannot be disclosed due to the non-disclosure agreement with the supplier—hence limited information is presented (information as received from the supplier).

Table 3.1: Properties of the TPS[®]-based membrane (as received from the supplier)

Membrane type	TPS [®] -based
Membrane thickness	60-65 μm
Catalyst used anode	Pt-Co/C
	Atomic ratio 1:1 (Pt:Co)
Catalyst used cathode	Pt/C
Total catalyst loading	1.8 mg cm^{-2}
Membrane area	25 cm^2
Temperature range	120-200°C
Proton conductivity	$8 \times 10^{-2} \text{ S cm}^{-1}$

3.2.1.3 Materials used

The compositions of the feed gas mixtures used in the experiments described in this chapter are given in **Table 3.2**.

Table 3.2: Feed compositions of tested gas mixtures

	Vol.% H ₂	Vol.% CH ₄	ppm NH ₃	Vol.% CO ₂
CH₄-10	90	10	-	-
CH₄-50	50	50	-	-
CH₄-80	20	80	-	-
CO₂-10	90	-	-	10
CO₂-50	50	-	-	50
NH₃-1500	99.85	-	1500	-
NH₃-3000	99.7	-	3000	-

3.2.2 EXPERIMENTAL PROCEDURE

All experiments were carried out at room and atmospheric pressure (~86 kPa). The cell operating temperature, was varied over the range 100-160°C for pure hydrogen, and over the range 120-160°C for the gas mixtures, used for hydrogen separation. All experiments were conducted in hysteretic order as per assessment of the performance deterioration during

experimentation. The flow rates herein reported are all given in normal milliliters per minute (nmL/min), with 0°C and 1 bar taken as reference. The experimental performance parameters by which the generated data was analysed are given in **Section 3.2.3**.

3.2.2.1 Pure hydrogen experiments

Experiments were first conducted using pure hydrogen. The effect of temperature on the performance of the cell was investigated by varying the temperature between 100 and 160°C, in 20°C steps, for hydrogen flow rates 50, 100, and 150 nmL/min. Polarisation curves were drawn for each temperature and flow rate, commencing at the lowest temperature and flow rate. The flow rate was then raised to the second lowest flow rate and the process was repeated until the highest flow rate was reached, after which the temperature was again raised by 20°C and the process repeated once again.

Furthermore, the polarisation curves were drawn, starting at 0 A cm⁻², then raising the current density with a step change of 0.02 A cm⁻² every 10 min, whilst the respective voltage output of the cell was recorded every 5 sec. (performed in constant current mode). This was done until a limiting current was reached or until the voltage limit (1.1 V) was reached, after which the run was terminated.

The volumetric flow rate of the permeate was recorded for each set current density value at the respective temperatures and flow rates, making use of soap flow meters to determine the current efficiency. Experimental results are presented in **Appendix C**.

To determine the resistance of the MEA *in situ* electrochemical impedance spectroscopy (EIS) was performed in constant current/galvanostatic mode (1 A), frequency range 100 kHz to 0.1 Hz, at 100-160°C in hydrogen pumping mode. For feed streams containing impurities, the hydrogen flow rate was held constant for all EIS experiments at 100 nmL/min H₂. The AC current amplitude were a standard 10% of the applied direct current (Chen *et al.*, 2014). A Nyquist plot was generated of the impedance spectrum.

3.2.2.2 Gas mixtures: separation experiments

The effect of temperature on the performance of the cell was investigated by varying the temperature at a step of 20°C between 120 and 160°C. The minimum operating temperature was raised in the case where impurities were present, to avoid degradation due to poisoning at lower temperatures (Andreasen *et al.*, 2017). For the separation experiments, the hydrogen flow rate was kept constant at 100 nmL/min (and not the overall flow rate). The operating procedure for drawing polarisation curves remained consistent throughout (see **Section**

3.2.2.1) Test were performed starting at the lowest concentration of impurities and moving toward the highest impurity concentration (hysteretic order), in the order as given in **Table 3.2** (top to bottom).

3.2.3 PERFORMANCE PARAMETERS

The cell and membrane performance were evaluated based on the following performance parameters: voltage–current characteristics (e.g. limiting current densities and open-circuit voltage (OCV)), hydrogen permeability Pe_{H_2} (in Barrer), hydrogen purity (%) and hydrogen selectivity (α), which is a dimensionless parameter; and the general performance efficiencies: current efficiency, voltage efficiency and power efficiency. These parameters are defined by **Eq. 3.1-3.7**.

$$OCV = E_{Nernst} = \frac{RT}{nF} \ln \left(\frac{p_c}{p_a} \right) \quad (\text{Eq. 3.1})$$

$$Pe_{H_2} = q \cdot \delta / A \cdot \Delta P \quad (\text{Eq. 3.2})$$

$$1 \text{ Barrer} = \left[10^{-10} \frac{\text{cm}^3(\text{STP}) \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg}} \right] \quad (\text{Eq. 3.3})$$

$$\alpha_{ij} = \frac{y_i/x_i}{y_j/x_j} \quad (\text{Eq. 3.4})$$

$$\varepsilon_i = \frac{\text{Experimental } H_2 \text{ product}}{\text{Theoretical } H_2 \text{ product}} \quad (\text{Eq. 3.5})$$

$$\varepsilon_v = 1 - \frac{V}{1.484} \quad (\text{Eq. 3.6})$$

$$\varepsilon_p = \varepsilon_i \times \varepsilon_v \quad (\text{Eq. 3.7})$$

Refer to **Appendix B: Section B.2.2**, for an explanation of, and discussion of, each of the performance parameters. Note that the OCV is discussed elsewhere (Refer to **Eq. B.7**).

3.3 RESULTS AND DISCUSSION

3.3.1 PURE HYDROGEN EXPERIMENTS: MEMBRANE CHARACTERISATION

3.3.1.1 Polarisation curves

The voltage-current characteristics of the EHS at different cell temperatures and hydrogen flow rates are shown in **Figure 3.3**. In general, the relationship appears to be linear, up until

the point where a limiting current density is reached/approached (vertical lines). Variations from this trend is observed at 160°C with hydrogen flow rates of 100 and 150 nmL/min. The limiting current densities, that was reached in the high current density region ($\geq 0.3 \text{ A cm}^{-2}$), indicate that the overall cell reaction rate (mass transfer limitations) dominate in the high current density region (Gallucci *et al.*, 2019). This behaviour can be explained by the depletion of reactants at the surface of the anode electrode (Choi *et al.*, 2004).

The linear nature of the majority of the plot indicate the ohmic losses (IR_{Ω} losses) dominate the voltage losses, and that the activation overpotentials of the electrodes can be considered negligible. This behaviour is very common in FCs and EHSs (Barbir & Görgün, 2007; Choi *et al.*, 2004; Gardner & Ternan, 2007), and suggests that the membrane-, and contact resistance play a crucial role in the general performance of the cell. Therefore, to improve the general performance of the cell, both the membrane resistance and contact resistance should be minimised.

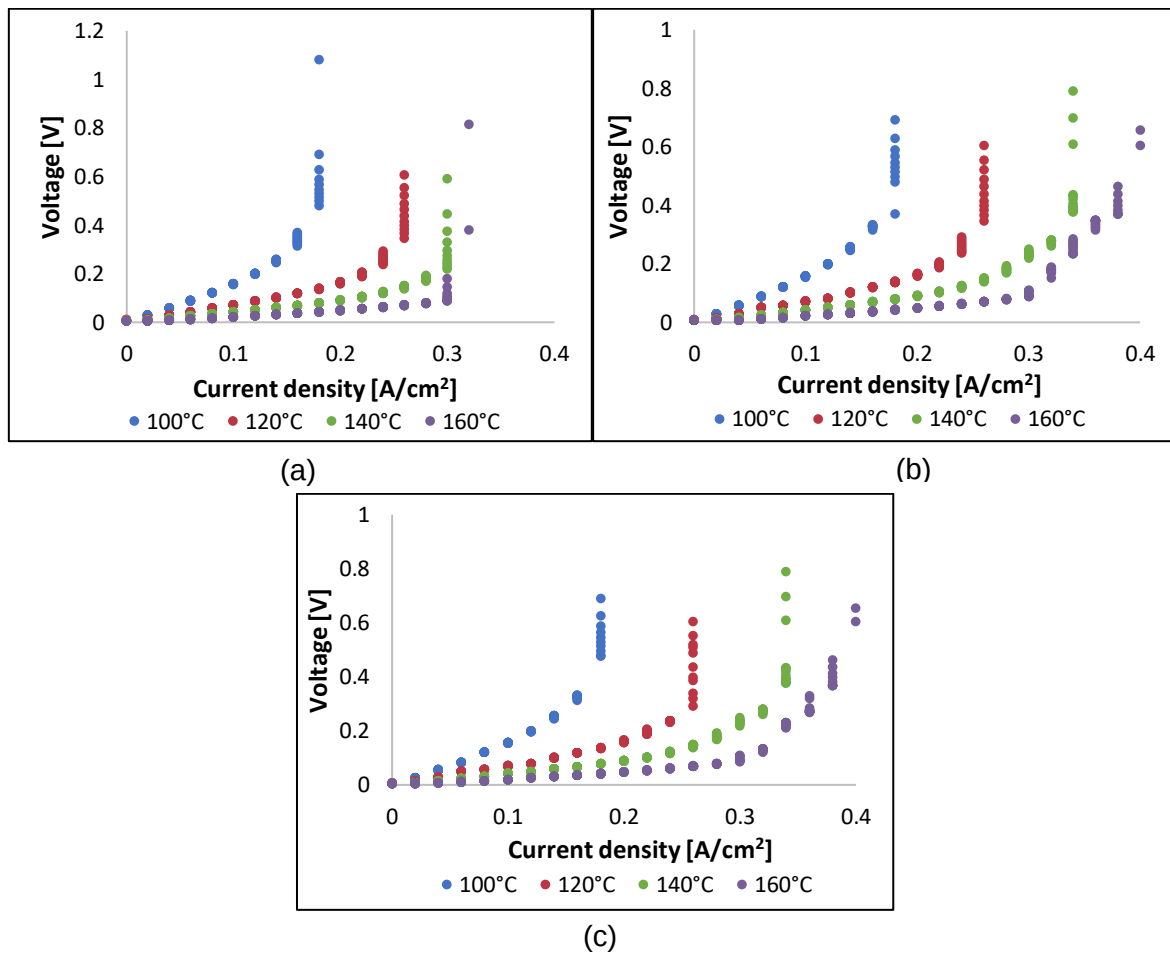


Figure 3.3: Polarisation curves for pure H₂ at various flow rates: (a) 50 nmL/min, (b) 100 nmL/min and (c) 150 nmL/min.

The ohmic resistance was determined by calculating the slope of the polarisation curve between 0.02 and 0.04 A cm⁻² and multiplying the value by area of the membrane (conversion from current density to current). In **Table 3.3**, the values obtained from the slope of the polarisation curves are compared to those obtained from the Nyquist plot of the impedance spectra, which is discussed in detail later in this chapter.

Table 3.3: Membrane resistance comparison, EIS vs polarisation curves

	EIS resistance [mohm]	Polarisation curve resistance [mohm]
120°C	15.2	30
140°C	14.1	16
160°C	9.2	8

The values determined from the polarisation curves correlate well with those determined from the EIS data, with the exception of the values obtained at 120°C. Here, the polarisation curves exhibit a value that is two times greater than that obtained through EIS measurements. It is however evident, from both the polarisation resistance and EIS resistance, that the ohmic resistance decrease with temperature.

The effect of the cell temperature on the general performance of the EHS was investigated using three different hydrogen flow rates (**Figure 3.3**). The performance of the TPS[®]-based PEM was very sensitive to changes in the operating temperature. In all three cases, the general performance of the cell increased significantly with minor temperature changes (20°C). Lower voltages were reached at the same current densities when the temperature was increased. Consequently, higher limiting currents were reached at higher temperatures. The highest limiting current density (0.4 A cm⁻²) was observed at 160°C, with flow rates 100 and 150 nmL/min. When the hydrogen flow rate was increased (>150 nmL/min), insignificant changes in the performance resulted; the effect on the limiting current density was negligible. It can, therefore, be concluded that the membrane was not capable of reaching current densities in the range of practical interest (≥ 1 A cm⁻²) (Fateev *et al.*, 2011).

Additionally, the space between the polarisation curves (**Figure 3.3**), for two neighbouring temperatures, decreased slightly when the temperature was increased. For example, at a fixed hydrogen flow rate of 50 nmL/min and current density of 0.1 A cm⁻², the voltage difference between 100 and 120°C was 85 mV, while the voltage differences between 120 and 140°C, and 140 and 160°C were 30 and 21 mV, respectively. This was observed for all three of the hydrogen flow rates and indicate that the effect of temperature on the cell's performance was

more definite at lower temperatures than at higher temperatures. This is consistent with previous work performed on HT PBI-membrane-based FCs in the temperature range 120-200°C (Song *et al.*, 2007).

With a flow rate of 50 nmL/min (**Figure 3.3 (a)**), fuel starvation was observed at 140 and 160°C and a current density of $\sim 0.3 \text{ A cm}^{-2}$. This is explained by Faraday's law, according to which, for a hydrogen feed flow rate of 50 nmL/min a current density of $\leq 0.3 \text{ A cm}^{-2}$ can be reached. At a flow rate of 100 nmL/min, much higher current densities are reached, resulting in higher hydrogen permeation rates (hydrogen permeability). The highest current density achieved was 0.4 A cm^{-2} , resulting in Faradic flows of up to $\pm 70 \text{ nmL/min}$, indicating that hydrogen is supplied in excess throughout.

Insignificant performance variations were observed between 100 nmL/min and 150 nmL/min (**Figure 3.3 (b) and (c)**). It was, therefore, concluded that the flow rate is no longer the performance limiting factor ($\geq 100 \text{ nmL/min}$) and that sufficient fuel is supplied. The low limiting current densities might therefore be attributed to other limiting factors, such as the limitations presented by the MEA itself (e.g. acid distribution or acid leaching). No further attention was given to the performance limiting factors.

3.3.1.2 Hydrogen permeation and general efficiencies

In an ideal cell, the hydrogen permeation flux is given a function of current, according to the law of Faraday, which is derived by assuming that the hydrogen is an ideal gas (Choi *et al.*, 2004). However, the real value is always smaller than that depicted by an ideal process, due to some losses in the system. In this particular case, the losses can be determined by the current efficiency, which is defined as the ratio of the actual hydrogen permeation rate and the theoretical hydrogen permeation rate (see **Eq. 3.5**).

A visual correlation between the theoretical hydrogen permeation rate and the measured hydrogen permeation rates are given in **Figure 3.4**. Only the 50 nmL/min and 100 nmL/min flow rate curves were shown in the figure, since the behaviour of 100 nmL/min and 150 nmL/min are similar, as mention previously. In general, the measured data show good correlation to the theoretical values. Nearly faradic flows were achieved throughout. Moreover, the permeability of hydrogen increased from ~ 25 Barrer to ~ 30 Barrer, when the hydrogen flow rate was increased from 50 nmL/min to 100 nmL/min at 160°C. This increase in hydrogen flux confirms the fuel starvation at 50 nmL/min, mentioned earlier.

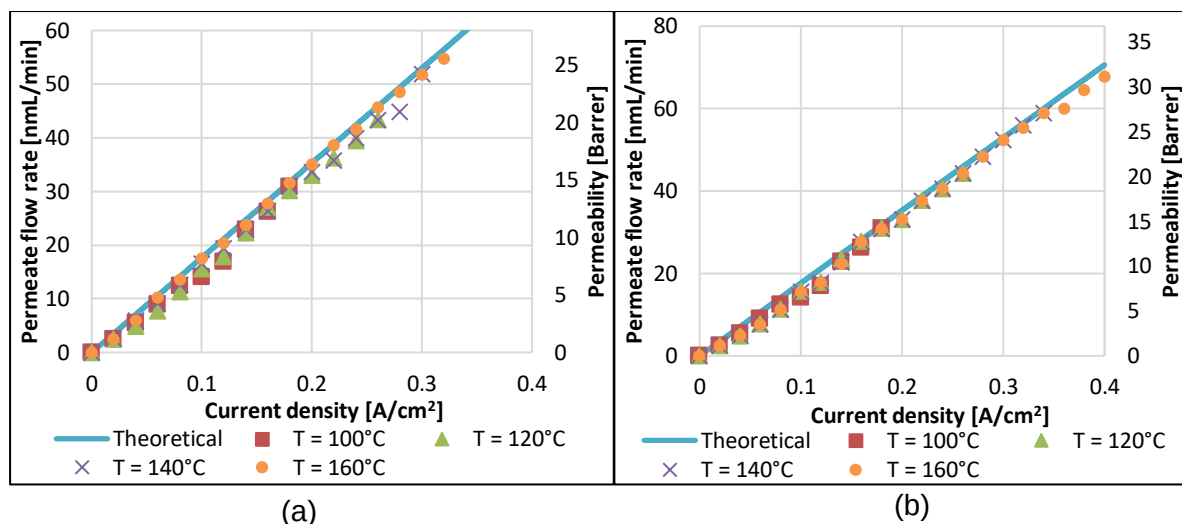


Figure 3.4: Hydrogen flux and permeation rate vs current density at hydrogen flow rates: (a) 50 nml/min and (b) 100 nml/min.

The measured current-, voltage- and power efficiencies as a function of temperature and current density, at a hydrogen flow rate of 100 nml/min, is given in **Table 3.4** (refer to **Appendix C** for the data of the other flow rates). At a low current density of 0.02 A cm^{-2} , the current efficiency was relatively low ($\sim 70\%$), for all the temperatures. The low current efficiencies, in this case, can either be attributed to the back diffusion of hydrogen or to gas leakages through the gaskets or the tube fittings. As the current density was increased, and therefore also the hydrogen flux, the current efficiency was increased to levels $>95\%$. Due to the fact that high current efficiencies are seen at higher current densities, the assumption was made that no major leakages are present within the system. Therefore, the low current efficiencies observed at lower current densities, were assumed to be caused by the back diffusion of hydrogen, due to the low hydrogen fluxes at these current densities.

Based on Choi *et al.* (2004), the current efficiency should increase with current density at constant temperature and pressure. This trend was confirmed at lower and moderate current densities, with variations seen at higher current densities. Additionally, Choi *et al.* (2004) concluded that the voltage efficiency will increase with an increase in temperature and decrease with an increase in current density. This is also confirmed by the experimental work performed, as seen in **Table 3.4**. Moreover, higher power efficiencies were reached when the temperature was increased. The maximum power efficiencies at the respective temperatures being 80.17% (100°C); 90.75% (120°C); 93.10% (140°C) and 95.29% (160°C) (The highest power efficiency for each temperature is highlighted in grey; **Table 3.4**). At temperatures $\geq 120^\circ\text{C}$, the power efficiencies were seen to reach a maximum at $\sim 0.16 \text{ A cm}^{-2}$. Therefore, this current density was considered the optimum operating current density with regards to the power consumption at $\geq 120^\circ\text{C}$.

Furthermore, the effect of the feed flow rate on the voltage efficiency was recorded at constant temperature. An insignificant increase in the voltage efficiency was observed (see **Appendix C**); it was considered negligible.

Table 3.4: Current-, voltage- and power efficiencies as a function of current density at 100-160°C; hydrogen flow rate 100 nmL/min

Current density (A cm ⁻²)	Current efficiency (%)				Voltage efficiency (%)				Power efficiency (%)			
	100°C	120°C	140°C	160°C	100°C	120°C	140°C	160°C	100°C	120°C	140°C	160°C
0.02	70.73	70.66	70.4	70.28	98.13	99.19	99.46	99.60	69.4	70.09	70.02	70.00
0.04	80.61	68.56	70.4	70.03	96.15	98.18	98.92	93.11	77.51	67.31	69.64	65.20
0.06	85.01	72.99	72.57	72.39	94.10	96.56	98.38	99.22	79.99	70.48	71.40	71.82
0.08	87.28	80.46	78.87	78.76	91.85	96.29	97.84	98.92	80.17	77.47	77.17	77.91
0.10	79.79	89.26	88.03	87.91	89.42	95.22	97.17	98.65	71.35	84.99	85.54	86.73
0.12	79.98	84.02	83.64	83.45	86.59	94.47	96.50	98.38	69.26	79.37	80.71	82.10
0.14	92.49	95.83	91.61	90.65	82.95	93.39	96.09	97.98	76.72	89.50	88.03	88.82
0.16	93.19	98.51	97.7	97.70	77.76	92.12	95.28	97.53	72.47	90.75	93.10	95.29
0.18	97.36	97.75	96.98	96.98	62.29	90.84	94.81	97.10	60.64	88.80	91.94	94.17
0.20	-	93.63	93.63	93.63	-	89.22	93.97	96.73	-	83.54	87.98	90.57
0.22	-	97.14	96.99	96.99	-	86.73	92.99	96.29	-	84.25	90.19	93.40
0.24	-	95.86	95.86	95.86	-	82.34	91.98	95.96	-	78.93	88.17	91.98
0.26	-	96.53	96.53	96.53	-	69.53	90.57	95.28	-	67.11	87.42	91.98
0.28	-	-	97.79	97.79	-	-	88.07	94.61	-	-	86.13	92.52
0.3	-	-	98.96	98.96	-	-	84.25	93.40	-	-	83.37	92.42
0.32	-	-	99.03	97.87	-	-	81.46	88.13	-	-	80.67	86.26
0.34	-	-	98.20	98.20	-	-	68.58	82.87	-	-	67.35	81.37
0.36	-	-	-	94.28	-	-	-	77.21	-	-	-	72.80
0.38	-	-	-	96.14	-	-	-	73.26	-	-	-	70.43
0.40	-	-	-	95.91	-	-	-	57.51	-	-	-	55.16

3.3.1.3 Electrochemical impedance spectroscopy

In order to obtain a better understanding of the temperature effect on the performance of the EHS, EIS was used to diagnose the cell. **Figure 3.5** shows the *in situ* AC impedance spectrum of the EHS operated at 0.1 A cm⁻² with variations in the temperature and the hydrogen flow rate. Similar spectra have been widely reported in literature for both FCs (Chen *et al.*, 2014; Song *et al.*, 2007) and EHSs (Ahn *et al.*, 2013; Fateev *et al.*, 2011; Hao *et al.*, 2016). The intercept of the real axis (x-axis) represents the ohmic resistance, which is defined as the sum of the contact resistance, electrical resistance and the proton conduction resistance in the membrane (Chen *et al.*, 2014).

Figure 3.5 shows that the impedance spectra move towards the left as the temperature is increased. The leftwards movement indicates that the ohmic resistance of the cell decrease with temperature. This is in agreement with literature—the membrane can be considered an electric insulator, which means that theoretically its resistance should decrease with temperature (Andreasen *et al.*, 2017). Furthermore, at 100°C and 120°C a slight shift towards the right in the frequency range of 100 kHz to 1 Hz is observed, as the flow rate is increased in the range 50-150 nmL/min. Larger incremental shifts towards the right are observed at 140°C and 160°C. This indicates that the ohmic resistance increases with the flow rate.

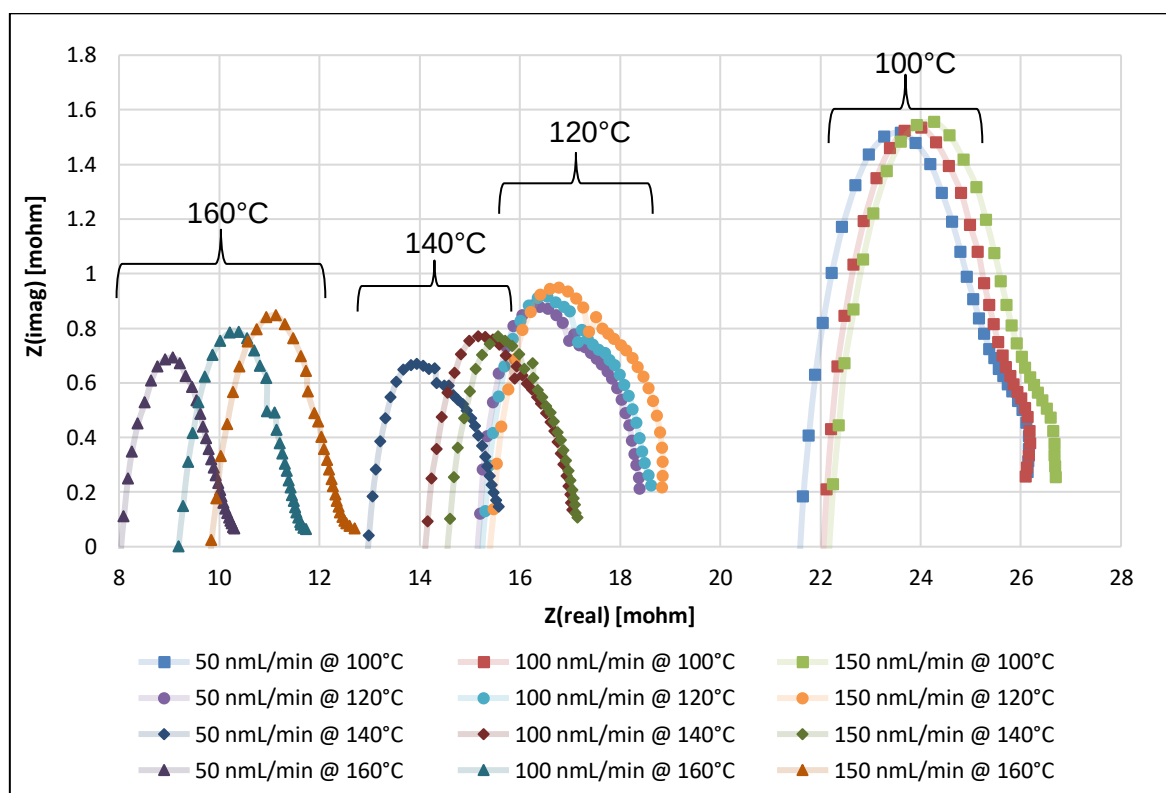


Figure 3.5: EIS results for TPS[®]-based membrane at 0.1 A cm⁻² using pure H₂, determined at various temperature and flow rates.

Furthermore, the diameter of the impedance arc depicts the sum of the charge transfer and mass transfer resistance. Therefore, the reduction in the arc diameter at higher temperatures indicates that there is a slight improvement in mass transport and high frequency charge transfer, which is in accordance with the literature (Andreasen *et al.*, 2017). According to Ferng *et al.* (2012), an increase in temperature enhances the cell performance due to an increase in the reaction and the mass transfer rate, and a lower cell resistance. This is confirmed in the present work.

Furthermore, the overall improvement in performance achieved when the temperature is increased, as observed in the polarisation curves, can be attributed to a slight decrease in ohmic resistance and improvements in mass transport and high frequency charge transfer observed in the EIS tests (Andreasen *et al.*, 2017). According to literature, excess fuel during EIS analysis should minimise the mass transport resistance, and differentiate between the ohmic and activation resistances (Kim *et al.*, 2015). This is partly confirmed in this work; the mass transport resistance seems to increase when excess hydrogen is supplied (the diameter of the arcs increases).

3.3.2 HYDROGEN SEPARATION FROM H_2/CH_4 MIXTURES

3.3.2.1 Polarisation curves

The EHS was evaluated for the electrochemical hydrogen separation from H_2/CH_4 gas mixtures (10% CH_4 , 50% CH_4 and 80% CH_4 , with the balance hydrogen), where the hydrogen flow rate was kept constant at 100 nmL/min. The voltage–current characteristics of the H_2/CH_4 mixtures at different cell temperatures and feed concentrations are shown in **Figure 3.6** and were compared to that of pure hydrogen (refer to **Figure 3.3 (b)**).

The curves presented in **Figure 3.6** can be divided into two regions; (i) the initial portion of the curves, which exhibit linear behaviour, and (ii) the final portion of the curve, which has a curved profile. These two regions are separated with a dashed line in **Figure 3.6 (a)** and **(b)**. For **(c)**, the overvoltage characteristics seems to be linear up until the point where limiting current density is approached (0.1 A cm^{-2} (120°C); 0.12 A cm^{-2} (140°C) and 0.14 A cm^{-2} (160°C)). The limiting current density values, indicating where most of the hydrogen in the H_2/CH_4 mixtures has been consumed and where the hydrogen partial pressure at the anode become small (Gardner *et al.*, 2007), were seen to increase with temperature and decrease with methane concentration.

In all three cases, the linear nature of the initial portion of the curves suggest that, the ohmic losses (IR_Ω) dominate in this region (**Figure 3.6**) (Barbir & Görgün, 2007; Gardner *et al.*, 2007). This is in accordance with literature; the ohmic losses are expected to dominate in the intermediate current density region (especially when a linear trend is observed) (Gallucci *et al.*, 2019; Choi *et al.*, 2004). However, when compared to the voltage–current characteristics of pure hydrogen, a clear deviation is observed, although the temperature dependencies were similar. The increase in non-linear behaviour (curved profile region) seems to originate from the mass transport losses, due to the change of reactants at the surface of the electrode (depletion of the reactants) (Gallucci *et al.*, 2019; Barbir & Görgün, 2007; Choi *et al.*, 2004).

Since CH_4 occupy a substantial amount of the inlet gas composition, a great portion of the reaction zone is occupied with CH_4 . This leads to a decrease in the effective active area and consequently the dispersion of hydrogen is hindered.

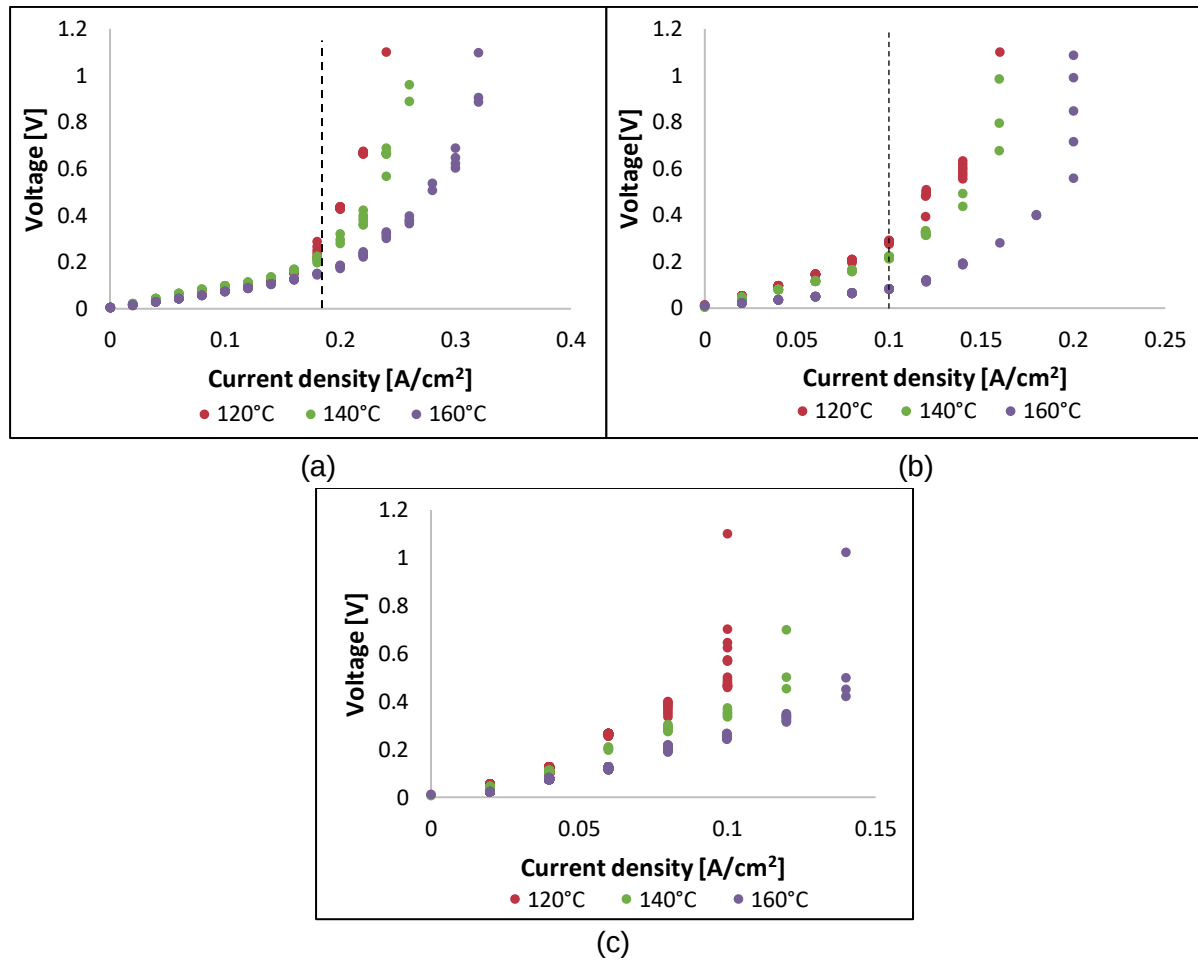


Figure 3.6: Polarisation curves for H_2/CH_4 gas mixtures with a fixed hydrogen flow rate of 100 nmL/min: (a) 10% CH_4 , (b) 50% CH_4 and (c) 80% CH_4 methane.

In general, higher voltages were reached with the H_2/CH_4 gas mixtures, compared to that of pure hydrogen. Here, it should be noted that the OCV, determined by the Nernst equation (**Eq. 3.1**), is not zero, as is the case with pure hydrogen, due to the differences in partial pressures. The OCVs were calculated for the different feed compositions and temperatures at a fixed current density of 0.1 A cm^{-2} . See **Table 3.5**. These values were compared to the cell voltages corresponding to pure hydrogen at the same current density; 0.071 V (120°C), 0.042 V (140°C) and 0.021 (160°C), respectively.

Based on Ahn *et al.* (2013) the actual operating voltage for the gas separation can be estimated by subtracting the OCV from the measured cell voltage. However, from **Table 3.5**,

it can be observed that these values are still much higher than the cell voltages corresponding to pure hydrogen.

Table 3.5: Hydrogen purity and cell voltage values as a function of temperature for the H₂/CH₄ inlet mixtures, measured at 0.1 A cm⁻²

Temperature	Hydrogen purity (%)		OCV [V]	Measured voltage [V]	Measured – OCV [V]
	Inlet (anode)	Permeate (cathode)			
120°C	20	99.978	0.027	0.564	0.537
	50	99.980	0.012	0.284	0.272
	90	99.997	0.002	0.077	0.075
140°C	20	99.982	0.029	0.352	0.323
	50	99.976	0.012	0.219	0.207
	90	99.994	0.002	0.075	0.074
160°C	20	99.856	0.030	0.253	0.233
	50	99.952	0.013	0.083	0.070
	90	99.992	0.002	0.074	0.072

General conclusions can be made from the performance curves (**Figure 3.6**), one of which is that at constant inlet composition, the general performance of the cell increased with temperature. This is explained by the enhanced reaction activity of the electrodes at higher temperatures. Similar results have been reported by Choi *et al.* (2004). However, at constant temperature, an increase in methane concentration leads to a decrease in the performance of the cell. This performance decrease shows that the partial pressure of the hydrogen influences the general performance of the cell. Moreover, the hydrogen flux is seen to increase with an increase in the current density, explained by Faraday's law.

3.3.2.2 Separation performance: hydrogen selectivity and purity

From **Table 3.5** it can be concluded that the hydrogen to impurity ratio of the inlet gas had a negligible effect on the purity of hydrogen in the permeate stream. However, the hydrogen purity seems to decrease slightly as the temperature is increased.

The properties of pressure swing adsorption (PSA), membrane technologies and cryogenic distillation, as conventional hydrogen purification technologies, were tabulated and compared in **Chapter 2: Table 2.2**. Maximum hydrogen product purities of >99.9% (PSA), >98% (membrane) and ~97 (cryogenic) were achievable from feed purities of >40%, >25% and 15-80%, respectively. In comparison to these technologies, EHSs show great potential, particularly in the case where hydrogen is separated from H₂/CH₄ gas mixtures. High grade hydrogen (>99.9%) was achievable for all the inlet methane concentrations (10; 50 and 80%

CH₄) (refer to **Appendix E**). This implies that a high purity hydrogen can be achieved from H₂/CH₄ gas mixtures in a single-stage process regardless of the inlet methane concentration. Additionally, this high purity hydrogen was obtained without pressurisation or humidification of the inlet stream.

The relationship between the hydrogen selectivity and current density is illustrated in **Figure 3.7** (as a function of methane concentration) and in **Figure 3.8** (as a function of temperature). At fixed temperature (at 1 atm) and impurity concentration, the hydrogen purity of the permeate stream was enhanced with an increase in current density. This is because, according to the law of Faraday, the proton flux through the membrane increases with current density, while the impurities (in this case CH₄) are not influenced by the current density. The conclusion can, however, be made that the permeation of the impure gas species (CH₄) through the membrane were proportional to/dependent on the change in partial pressure. When the hydrogen partial pressure at the anode side decreased, the selectivity and the hydrogen purity of the permeate (cathode outlet) increased. This has been reported elsewhere (Choi *et al.*, 2004).

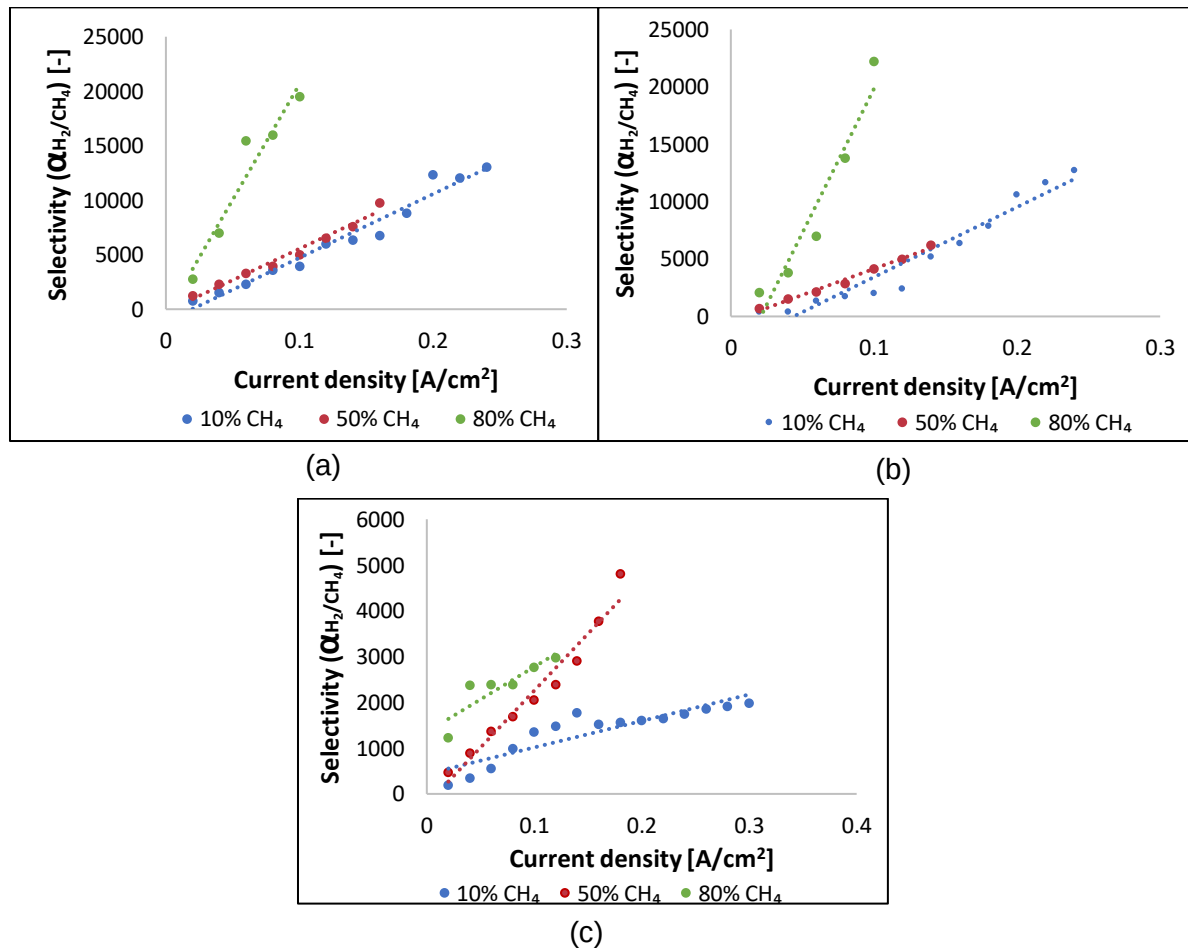


Figure 3.7: H₂/CH₄ selectivity, in terms of temperature versus current density: (a) 120°C, (b) 140°C and (c) 160°C.

According to Freeman *et al.* (2010), the separation performance of a membrane can be improved by reducing the temperature, as explained by the Arrhenius equation. This was confirmed in this work. From **Figure 3.7** it can collectively be observed that much higher hydrogen selectivity values were achieved at lower temperatures. For the 10% methane feed stream the hydrogen selectivity decreased from ~13 000 to ~12 750 and then to ~1 980 as temperature was increased from 120°C to 140°C and then to 160°C. For the 50% methane feed stream the selectivity reduced from ~9 800 (120°C) to ~6 250(140°C) to ~4 800 (160°C). The highest hydrogen selectivity (~22 200) was achieved with the 80% methane feed stream at 140°C. It was, therefore, concluded here that the selectivity values increase with both methane concentration and current density, and decrease when the temperature is increased.

Further examination of **Figure 3.8**, suggest that the temperature effect on the hydrogen selectivity of the PEM was more severe at higher temperatures. This conclusion/assumption was made based on the large difference in hydrogen selectivity values observed between 140 and 160°C, which was much higher than the difference existing between 120 and 140°C. This was true for all the H₂/CH₄ inlet compositions.

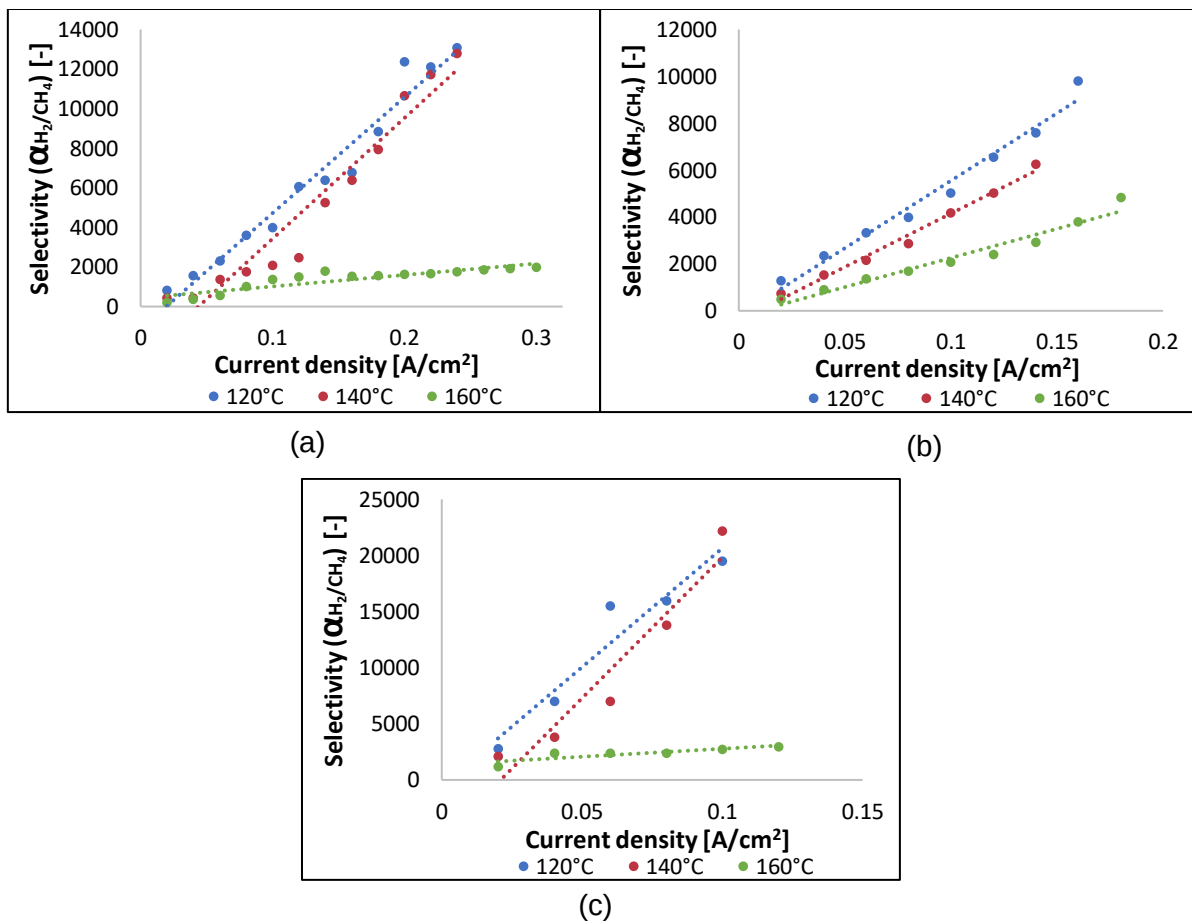


Figure 3.8: H₂/CH₄ selectivity, in terms of CH₄ concentration in the feed stream versus current density: (a) 10% CH₄, (b) 50% CH₄ and (c) 80% CH₄.

The selectivity values for dense metallic (>1 000), dense ceramic (>1 000), microporous ceramic (5-139), porous carbon (4-20), and dense polymeric (low) membranes were compared in **Chapter 2: Table 2.3**. In comparison to these membrane technologies, the hydrogen selectivity values achieved were 22 higher than those obtained with traditional dense metallic and dense ceramic membranes. Therefore, it is evident that in terms of H₂/CH₄ separation (selectivity), the EHS far exceeds its competitors.

3.3.2.3 General efficiencies

The current-, voltage- and power efficiencies of the H₂/CH₄ gas mixtures were also compared to those of pure hydrogen. The experimental results obtained for 10%, 50% and 80% CH₄ are tabulated in **Table 3.6**, **Table 3.7** and **Table 3.8**, respectively. In general, the initial current efficiencies were much lower than that obtained with pure hydrogen. The current efficiencies for H₂/CH₄ ranged between 46.86-51.42% at 0.02 A cm⁻², whereas those for pure hydrogen were ~70%. The current efficiencies of the H₂/CH₄ mixtures, did however, also, increased with current density as was the case with pure hydrogen. Slight variations from this trend was, however, observed at higher current densities.

The voltage efficiencies decreased with an increase in current density, which correlates well with the pure hydrogen experiments. Moreover, the voltage efficiencies seemingly increased with temperature, observed with the 50% and 80% CH₄ inlet mixtures. However, in the case of the 10% CH₄, this trend was only visible at current densities above 0.16 A cm⁻².

The power efficiencies showed a maximum value at 0.12 A cm⁻² with 10% CH₄ (**Table 3.6**), 0.08-0.1 A cm⁻² with 50% CH₄ (**Table 3.7**) and 0.04-0.08 A cm⁻² with 80% CH₄ (**Table 3.8**). This depicts the optimum current density for hydrogen separation from the H₂/CH₄ mixtures at the respective operating conditions, with regards to the power consumption (Choi *et al.*, 2004). Additionally, the power efficiencies decreased with an increase in methane concentration and increased with temperature. The highest power efficiency was, therefore, observed with the 10% CH₄ mixture at 160°C, this being 89.27%. Overall, the power efficiencies obtained with the respective H₂/CH₄ mixtures, were much lower than in the case with pure hydrogen, especially when the hydrogen-to-methane ratio of the inlet decreased.

It can, therefore be concluded that, although the overall/general performance of the cell decrease when the inlet gas mixture contains methane, similar trends with regards to the current-, voltage- and power efficiencies were seen when compared to the case of pure hydrogen.

Table 3.6: Current-, voltage- and power efficiencies of the 10% CH₄ (balance H₂) inlet mixture as a function of current density at 120-160°C; hydrogen flow rate 100 nL/min

Current density (A cm ⁻²)	Current efficiency (%)			Voltage efficiency (%)			Power efficiency (%)		
	120°C	140°C	160°C	120°C	140°C	160°C	120°C	140°C	160°C
0.02	47.22	47.19	47.24	98.91	98.45	98.93	46.71	46.50	46.74
0.04	72.90	72.93	73.44	97.98	97.04	97.98	71.43	70.77	71.96
0.06	85.30	85.34	86.12	96.97	95.62	97.01	82.72	81.60	83.54
0.08	87.99	88.97	90.11	95.96	94.46	96.02	84.44	84.04	86.52
0.10	91.97	91.84	92.46	94.83	93.40	95.01	87.22	85.78	87.85
0.12	93.84	95.43	94.99	93.58	92.33	93.98	87.82	88.11	89.27
0.14	95.43	95.70	95.02	91.92	90.98	92.83	87.71	87.07	88.21
0.16	96.30	96.82	95.43	89.30	88.83	91.46	86.00	86.01	87.28
0.18	95.11	94.72	95.66	83.01	85.64	89.91	78.95	81.12	86.01
0.20	96.32	95.51	95.98	70.79	79.83	87.78	68.19	76.25	84.25
0.22	96.85	97.13	96.72	54.92	74.02	84.21	53.19	71.88	81.45
0.24	97.11	96.85	97.77	25.88	55.83	78.64	25.13	54.07	76.89
0.26	-	96.98	98.12	-	37.63	74.39	-	36.49	72.99
0.28	-	-	98.55	-	-	64.76	-	-	63.82

Table 3.7: Current-, voltage- and power efficiencies of the 50% CH₄ (balance H₂) inlet mixture as a function of current density at 120-160°C; hydrogen flow rate 100 nL/min

Current density (A cm ⁻²)	Current efficiency (%)			Voltage efficiency (%)			Power efficiency (%)		
	120°C	140°C	160°C	120°C	140°C	160°C	120°C	140°C	160°C
0.02	49.11	50.22	47.23	96.47	97.09	98.46	47.38	48.76	46.50
0.04	75.98	75.55	68.33	93.49	94.63	97.57	71.03	71.49	66.67
0.06	85.34	85.34	85.34	90.23	92.16	96.65	77.00	78.65	82.48
0.08	92.03	95.88	92.00	86.16	89.09	95.65	79.29	85.42	88.00
0.10	94.12	94.56	93.84	80.83	85.24	94.42	76.08	80.60	88.60
0.12	95.91	93.30	93.04	67.74	78.27	92.02	64.97	73.03	85.62
0.14	95.49	95.49	96.51	59.93	68.67	87.14	57.23	65.57	84.10
0.16	96.93	98.05	95.44	25.74	44.79	81.00	24.95	43.91	77.31
0.18	-	98.20	96.32	-	-	73.07	-	-	70.38
0.20	-	-	95.51	-	-	43.36	-	-	41.41

Table 3.8: Current-, voltage- and power efficiencies of the 80% CH₄ (balance H₂) inlet mixture as a function of current density at 120-160°C; hydrogen flow rate 100 nmL/min

Current density (A cm ⁻²)	Current efficiency (%)			Voltage efficiency (%)			Power efficiency (%)		
	120°C	140°C	160°C	120°C	140°C	160°C	120°C	140°C	160°C
0.02	51.42	48.20	46.86	96.8	97.23	98.58	49.77	46.86	48.41
0.04	79.02	76.08	70.60	92.39	92.80	94.89	73.01	70.60	72.10
0.06	85.42	85.33	73.73	82.31	86.41	91.87	70.31	73.73	78.40
0.08	89.02	90.00	72.62	74.86	80.69	86.18	66.64	72.62	79.31
0.10	94.30	96.10	73.29	61.97	76.26	82.96	58.44	73.29	78.08
0.12	-	95.19	59.86	-	62.89	77.67	-	59.86	73.93
0.14	-	-	46.86	-	-	59.75	-	-	57.62

3.3.3 HYDROGEN SEPARATION FROM H₂/CO₂ MIXTURES

3.3.3.1 Polarisation curves

The voltage–current characteristics of electrochemical hydrogen separation from various H₂/CO₂ gas mixtures, as a function of temperature, are shown in **Figure 3.9**. Compared to the performance of pure hydrogen, the cell showed significantly larger voltages for H₂/CO₂ separation. For the 10% CO₂ (balance hydrogen) separation mixture, the maximum achievable current density at 160°C was 0.16 A cm⁻². This is a large drop from 0.4 A cm⁻² that was reached with pure hydrogen. Furthermore, at 120 and 140°C the limiting current densities decreased from 0.28 and 0.32 A cm⁻², obtained with pure hydrogen, to 0.12 and 0.16 A cm⁻², respectively. For the 50% CO₂ inlet stream, the limiting current densities were 0.14, 0.14 and 0.12 A cm⁻², respectively at 160, 140 and 120°C.

The methane polarisation curves showed a curved profile, as opposed to the polarisation curves of hydrogen which mainly showed a linear profile. The curved profile of the polarisation curves, suggest that the electrode reaction dominate the overpotential. Similar tests were performed on PBI membranes with H₂/CO₂ mixtures and the same conclusion was made (Ahn *et al.*, 2013). The change in the overpotential characteristics can be explained by the hydrogen to impurity ratio of the inlet stream. Since the impurity (CO₂) make up a large portion of the gas mixture, a large amount of the active sites was covered by impurities, and consequently the reaction sites were ‘blocked’ by the impurities. This was also observed with the H₂/CH₄ gas mixtures. However, the performance decay was more severe in the presence of CO₂ when compared to that of CH₄, which might be ascribed to possible CO formation by the reverse WGS reaction (**Eq. 3.8**):



This was reported by Araya *et al.* (2016), in similar experiments. The CO attach to the Pt sites and therefore hinder Pt-H binding; hence, a voltage increase result. Theoretically, the electrode tolerance to CO should increase with temperature, which is confirmed by the present work; the performance increased when the temperature was raised. However, in terms of carbon dioxide concentration, no significant performance variations were observed when the CO₂ inlet percentage changed from 10% to 50%.

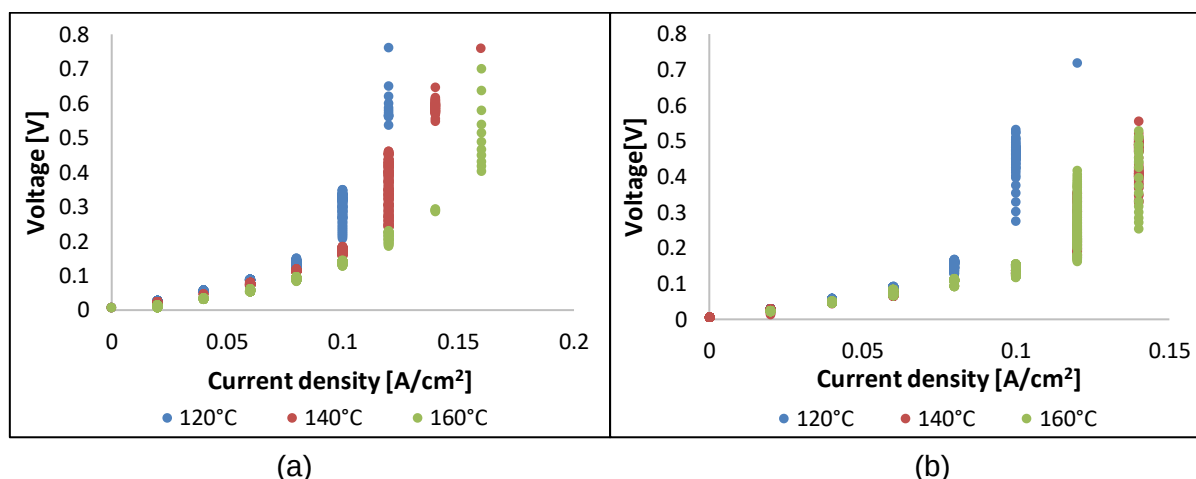


Figure 3.9: Polarisation curves for H₂/CO₂ gas mixtures with a fixed hydrogen flow rate of 100 nmL/min: (a) 10% CO₂ and (b) 50% CO₂.

Here, as was the case with the methane-containing mixtures, the OCV is not zero, explained by the difference in partial pressures. See **Table 3.9**. The OCVs obtained, were much higher than those obtained with the H₂/CH₄ mixtures at the same conditions. This might be due to the fact that CH₄ only act as a hydrogen diluent (Gardner *et al.*, 2007), whilst CO₂ actually affects the electrode.

Table 3.9: Hydrogen purity and cell voltage values as a function of temperature for the H₂/CO₂ inlet mixtures, measured at 0.1 A cm⁻²

Temperature	Hydrogen purity (%)		OCV [V]	Measured voltage [V]	Measured – OCV [V]
	Inlet (anode)	Permeate (cathode)			
120°C	50	99.391	0.012	0.454	0.442
	90	99.597	0.002	0.300	0.298
140°C	50	99.285	0.012	0.132	0.120
	90	99.440	0.002	0.170	0.168
160°C	50	99.344	0.013	0.125	0.112
	90	99.631	0.002	0.138	0.136

3.3.3.2 Separation performance: hydrogen selectivity and purity

Hydrogen purities of 98-99.5% could be reached with 10% CO₂ in the feed and 96-99.5% with 50% CO₂ in the feed stream (refer to the selectivity tables in **Appendix E**). Therefore, it can be drawn that a hydrogen purity up to 99.5% can be reached with a H₂/CO₂ ratio of 1:1. No correlation was found between the hydrogen purity of the permeate and the temperature. The hydrogen purity did, however, increase with current density. Refer to **Appendix E: Section E.2**.

The selectivity values are given in terms of inlet concentration (**Figure 3.10**) and set temperature (**Figure 3.11**). Reasonable separation can be achieved from the 1:1 H₂/CO₂ mixture, with selectivities up to ~200. This is much lower than the hydrogen selectivity values obtained with the H₂/CH₄ gas mixtures (up to ~22 000). However, a similar trend was observed for both the H₂/CH₄ and H₂/CO₂ mixtures in terms of current density and impurity concentration; the hydrogen selectivity increased with current density and impurity concentration. However, the trend of the selectivity in terms of temperature varied from that of the H₂/CH₄ mixtures. The the selectivity did not increase with a decrease in temperature; the best selectivity was achieved at 160°C. This can be explained by the catalyst poisoning that occurs (CO-poisoning), where the catalyst deactivation is alleviated at higher temperatures.

Compared to other membrane technologies, the hydrogen selectivities were lower than those of dense metallic and dense ceramic membranes (>1 000), but higher than those obtained by microporous ceramic, porous carbon and dense polymeric membranes (see **Chapter 2: Table 2.3**).

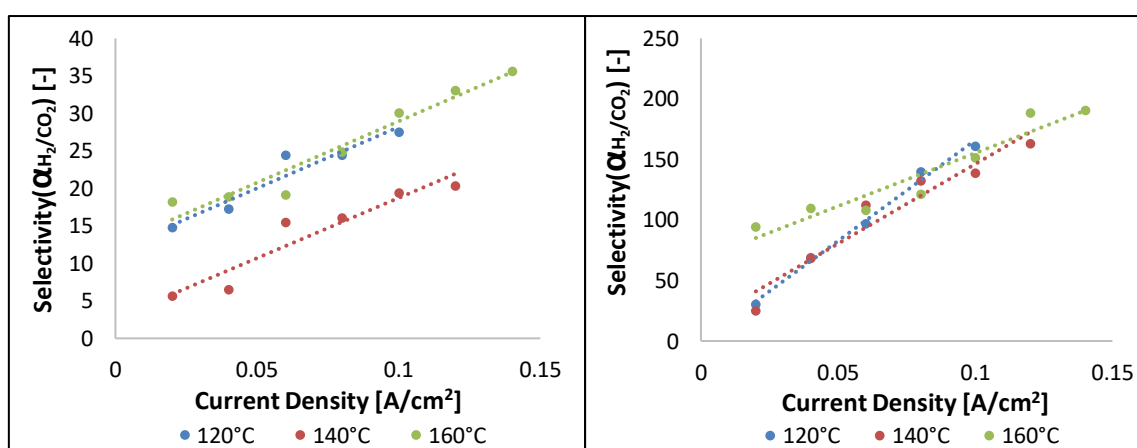


Figure 3.10: H₂/CO₂ selectivity, in terms of CO₂ concentration in the feed stream versus current density: (a) 10% CO₂ and (b) 50% CO₂.

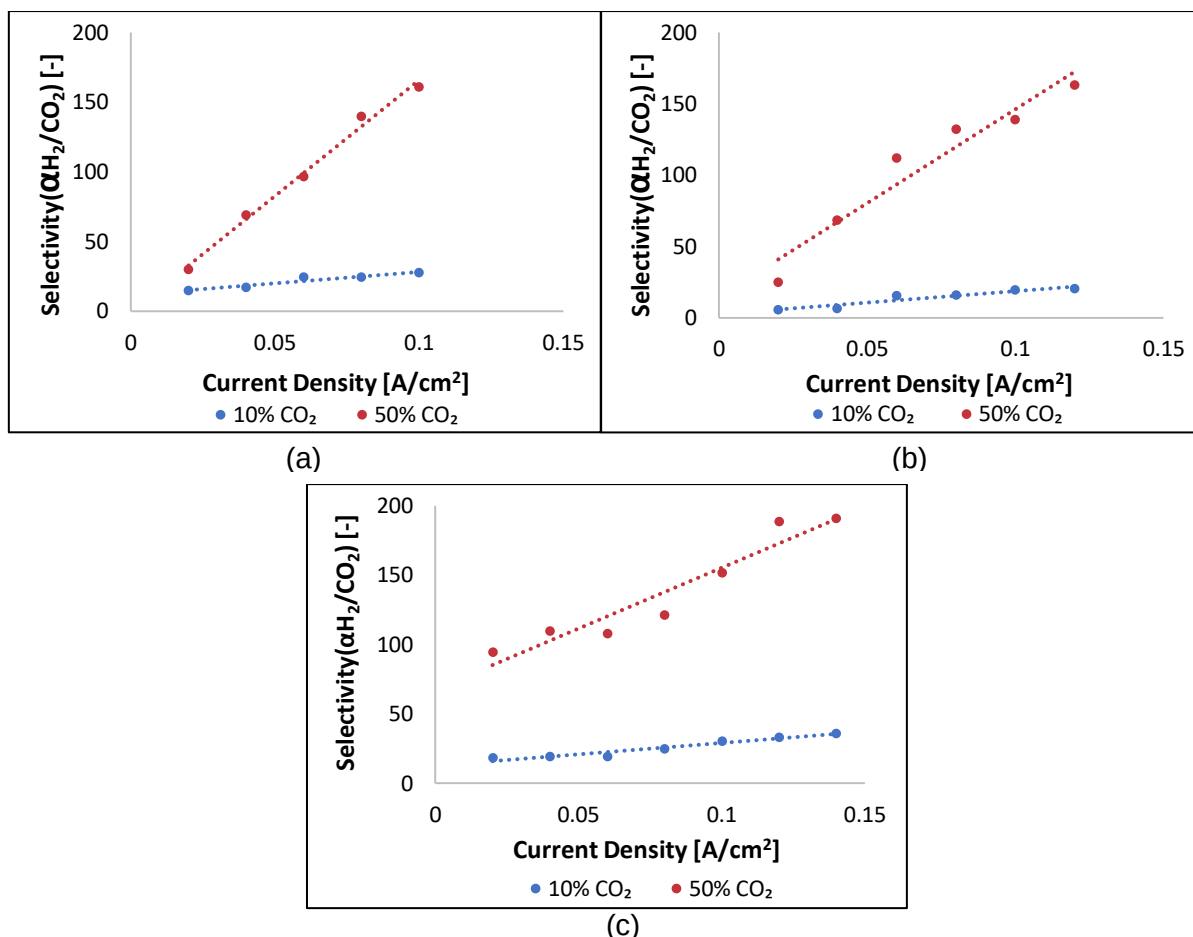


Figure 3.11: H_2/CO_2 selectivity, in terms of temperature versus current density: (a) 120°C, (b) 140°C and (c) 160°C.

3.3.3.3 General efficiencies

The current; voltage and power efficiencies of the H_2/CO_2 gas mixtures are tabulated in **Table 3.10** and **Table 3.11**. In general, the current efficiencies increased with current density. The lower current efficiencies at lower current densities can be attributed to hydrogen cross over. The current efficiencies at lower current densities were lower than that of pure hydrogen ($\sim 70\%$ at $0.02 A cm^{-2}$). In terms of voltage efficiencies, an increase was observed when the temperature was raised. Also, the voltage efficiencies showed a decrease with an increase in current density. The same trend was seen in both the pure hydrogen and hydrogen-methane mixture cases.

The power efficiencies showed a maximum value between 0.08 - $0.10 A cm^{-2}$ for both the 10% (**Table 3.10**) and 50% CO_2 (**Table 3.11**) inlet mixtures. This depicts the optimum current density for hydrogen separation from the H_2/CO_2 mixtures at the respective operating conditions, with regards to the power consumption (Choi *et al.*, 2004). Similar to the methane-containing mixtures, the power efficiencies decreased with an increase in carbon dioxide concentration and increased with temperature.

Table 3.10: Current-, voltage- and power efficiencies of the 10% CO₂ (balance H₂) inlet mixture as a function of current density at 120-160°C; hydrogen flow rate 100 nmL/min

Current density (A cm ⁻²)	Current efficiency (%)			Voltage efficiency (%)			Power efficiency (%)		
	120°C	140°C	160°C	120°C	140°C	160°C	120°C	140°C	160°C
0.02	51.42	51.42	51.43	98.23	98.65	99.23	50.51	50.73	51.04
0.04	79.02	69.02	69.92	96.30	96.91	97.80	76.10	66.89	68.38
0.06	85.42	83.42	83.42	94.12	94.99	96.18	80.40	79.24	80.23
0.08	89.02	89.02	89.02	90.97	92.30	93.90	80.98	82.17	83.59
0.10	94.30	94.33	92.30	79.81	88.58	90.72	75.26	83.56	83.74
0.12	95.02	95.05	93.02	59.84	76.27	85.77	56.86	72.50	79.78
0.14	-	94.13	94.04	-	60.21	80.51	-	56.62	75.71
0.16	-	95.23	93.32	-	48.92	65.60	-	46.59	61.16

Table 3.11: Current-, voltage- and power efficiencies of the 50% CO₂ (balance H₂) inlet mixture as a function of current density at 120-160°C; hydrogen flow rate 100 nmL/min

Current density (A cm ⁻²)	Current efficiency (%)			Voltage efficiency (%)			Power efficiency (%)		
	120°C	140°C	160°C	120°C	140°C	160°C	120°C	140°C	160°C
0.02	54.14	54.14	54.13	98.11	98.29	98.50	53.10	53.21	50.51
0.04	70.22	70.22	68.98	96.30	96.92	96.97	67.62	68.06	76.10
0.06	72.93	73.00	73.00	94.09	95.12	95.37	68.62	69.44	80.40
0.08	77.02	79.05	79.02	89.70	93.67	93.76	69.09	74.04	80.98
0.10	83.42	87.42	87.43	69.42	91.08	91.61	57.91	79.62	75.26
0.12	90.02	90.03	89.99	51.55	83.09	83.49	46.41	74.81	56.86
0.14	-	91.04	91.00	-	70.24	70.75	-	63.95	50.51

3.3.4 HYDROGEN SEPARATION FROM H₂/NH₃ MIXTURES

3.3.4.1 Polarisation curves

The voltage–current characteristic of the H₂/NH₃ inlet mixtures are presented in **Figure 3.12**. The cell performance is severely impaired in the presence of ammonia in very low concentrations (ppm range) when compared to the performance of pure hydrogen (**Figure 3.3**). The limiting current densities achieved were 0.1, 0.12 and 0.12 A cm⁻² for 120, 140 and 160°C respectively, when 1 500 ppm ammonia was present. When the cell is operated in the presence of 3 000 ppm ammonia, the cell performance deteriorated completely, even with an increase in temperature. The limiting current densities in the presence of 3 000 ppm NH₃ were 0.04, 0.04 and 0.02 A cm⁻² for 120, 140 and 160 °C, respectively. The limiting current densities seemingly indicate that the performance of the cell decrease as the temperature is raised. A reverse trend is, however, seen in the presence of 1 500 ppm NH₃. Based on the order of

experiments, the results indicated that the performance of the cell deteriorates in the presence of ammonia (continuous exposure to ammonia) rather than with temperature, as observed in **Figure 3.12 (b)**.

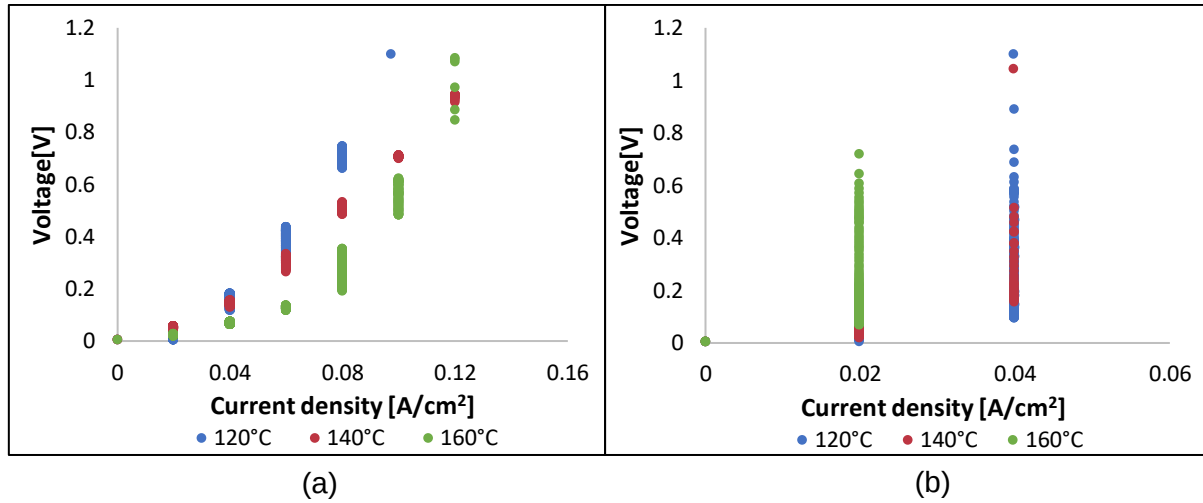


Figure 3.12: Polarisation curves for H₂/NH₃ gas mixtures with a fixed hydrogen flow rate of 100 nmL/min: (a) 1 500 ppm NH₃ and (b) 3 000 ppm NH₃.

3.3.4.2 Separation performance: hydrogen selectivity and purity

The selectivity graphs presented in **Figure 3.13** show that very poor selectivities (<2) are achieved for feed streams containing both 1 500 ppm and 3 000 ppm ammonia. Ammonia and hydrogen seem to compete with each other. In the cases where the selectivity values <1, ammonia transport through the membrane is favoured, whereas hydrogen is favoured at selectivities >1. Since hydrogen is split into its constituents, more specifically, protonated to H⁺ ions, ammonia protonation results:



NH₃⁺ is then also transported through the membrane.

The anode reaction can be depicted as:



At lower current densities however, the reaction seems to be:



where ammonia is favoured and not hydrogen.

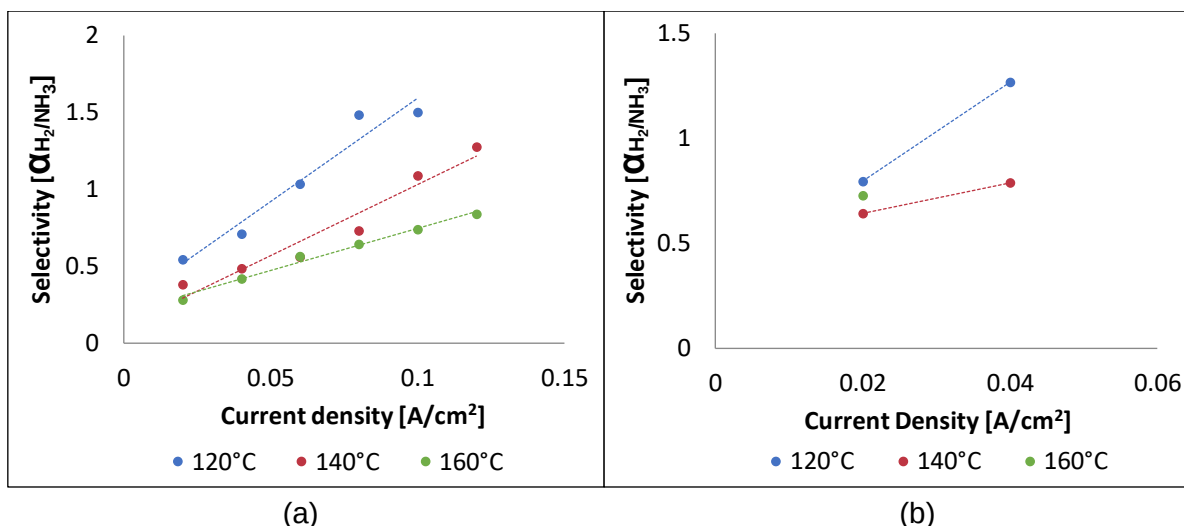


Figure 3.13: H_2/NH_3 selectivity versus current density with a hydrogen flow rate of 100 nmL/min, at fixed ammonia concentrations: (a) 1 500 ppm and (b) 3 000 ppm

The effect of ammonia on the performance of FCs have been tested and reported in literature. Overall, the effect was detrimental; some sources even report a decrease in FC catalytic activity when only 1 ppm NH_3 is present, over a short one-week period. These tests were performed with Nafion® membranes. The loss in activity can be attributed to the alkaline nature of ammonia. The formed NH_4^+ ions (Eq. 3.10 and Eq. 3.11) react with the sulphonic groups (SO_3^-) which is characteristic of Nafion membranes. Consequently, the water content and the conductivity of the membrane decreases, resulting in reduced FC performances (Gottesfield *et al.*, 2002; Halseid *et al.*, 2004). As for the sulphonic groups of Nafion® membranes, so too the phosphoric acid (PA) used in HT membranes (usually PBI- based membranes), resulting in phosphate groups (PO_4^-). The performance losses observed in Figure 3.12 can attributed to the alkaline nature of NH_4^+ that reacts with the PA on the membrane. More specifically the formed NH_4^+ ions therefore react with the PO_4^- groups, consequently resulting in a loss of conductivity.

Although it is the anode side that is expected to be predominantly affected by the NH_4^+ , diffusion of NH_4^+ ions the cathode side is also noteworthy, since the membrane are typically only 10-100 μm thick (Halseid *et al.*, 2006). Furthermore, transport of ammonia through the membrane was observed in GC analysis. Results of studies carried out with Nafion membranes to determine the effect of ammonia on the performance of FCs revealed that, although substantial poisoning effects were observed in the presence of ammonia in the feed gas, the cell performance was recoverable with time (in the order of days) when neat hydrogen is introduced to the anode side (Halseid *et al.*, 2004). In the present study, however, this did not apply—the membrane was damaged beyond recovery. Membrane cracks occurred, rendering the membrane useless. Figure 3.14 shows a visual representation of the state of

the membrane at beginning of life and after experiments with ammonia. Clear cracks are visible. The damage of the PBI membrane here, caused by ammonia, was completely irreversible. Scanning electron microscopy (SEM) images of the microscopic morphological changes on the surface of the membrane and GDLs are shown elsewhere (**Appendix F**).

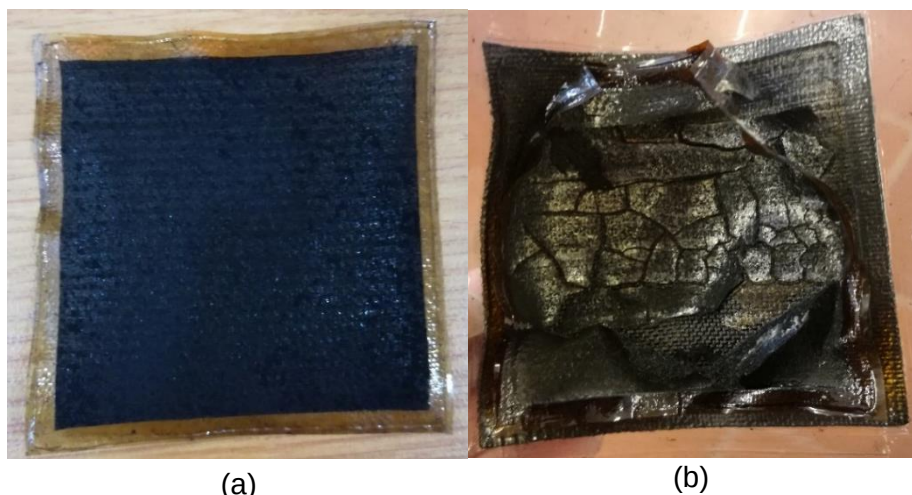


Figure 3.14: Digital images of (a) undamaged membrane and (b) damaged (cracked) membrane after ammonia exposure.

3.3.4.3 General efficiencies

The general efficiencies, being the current-, voltage- and power efficiencies, for the H_2/NH_3 inlet mixtures are tabulated in **Table 3.12** (1 500 ppm NH_3) and **Table 3.13** (3 000 ppm NH_3). The current efficiencies were very similar to those obtained using pure hydrogen. The same trend of increasing current efficiency with current density observed in the pure hydrogen experiments, was also observed with the H_2/NH_3 feed mixtures. The voltage efficiencies seemingly decreased with temperature and current density. The voltage efficiency trend with temperature, observed here, can be explained by the membrane deterioration that takes place during continuous ammonia exposure.

In terms of power efficiency, the same trend that was observed throughout was still visible here; the power efficiency increased with temperature. The maximum power efficiencies achieved were 70.30 (120°C), 73.66 (140°C) and 78.59 (160°C) with 1 500 ppm NH_3 and 69.10 (120°C), 69.75 (140°C) and 62.46 (160°C) with 3 000 ppm NH_3 . The maximum power efficiencies were, however, achieved in the current density region where ammonia transport through the membrane is favoured instead of hydrogen transport.

Table 3.12: Current-, voltage- and power efficiencies of the 1 500 ppm NH₃ (balance H₂) inlet mixture as a function of current density at 120-160°C; hydrogen flow rate 100 nmL/min

Current density (A cm ⁻²)	Current efficiency (%)			Voltage efficiency (%)			Power efficiency (%)		
	120°C	140°C	160°C	120°C	140°C	160°C	120°C	140°C	160°C
0.02	70.68	71.68	71.99	99.28	96.97	87.45	70.17	69.51	70.78
0.04	78.85	81.70	81.45	89.16	90.16	98.33	70.30	73.66	77.58
0.06	85.61	86.16	86.10	73.65	79.25	95.25	63.05	68.28	78.59
0.08	89.04	88.46	89.16	51.68	65.36	91.27	46.02	57.82	72.38
0.10	80.82	80.87	81.30	25.88	52.29	81.19	20.91	42.29	50.51
0.12	-	81.06	80.58	-	36.59	62.13	-	29.66	26.74

Table 3.13: Current-, voltage- and power efficiencies of the 3000 ppm NH₃ (balance H₂) inlet mixture as a function of current density at 120-160°C; hydrogen flow rate 100 nmL/min

Current density (A cm ⁻²)	Current efficiency (%)			Voltage efficiency (%)			Power efficiency (%)		
	120°C	140°C	160°C	120°C	140°C	160°C	120°C	140°C	160°C
0.02	70.60	72.06	71.42	97.87	96.79	87.45	69.10	69.75	62.46
0.04	79.31	81.50	-	82.38	78.74	-	65.33	64.18	-

3.4 CONCLUSION

In this chapter, the feasibility and efficiency of electrochemically separating hydrogen from various H₂/CH₄, H₂/CO₂ and H₂/NH₃ gas mixtures were examined. Experiments were carried out to evaluate both pure hydrogen, and the separation of hydrogen from streams containing CH₄, CO₂ and NH₃ as impurities. The effect of temperature and impurity concentration on the separation and general cell performance of the PEM and EHS were evaluated.

For pure hydrogen, the voltage–current characteristics showed that the ohmic losses dominated the overpotential. From this, it was concluded that the membrane- and contact resistance of the cell play a major role in the efficacy of the EHS, and should, therefore, be minimised. Overall, the general performance of the cell increased with minor temperature changes (20°C). This temperature effect was more pronounced at lower temperatures. EIS results showed that this effect can be attributed to the decrease of the ohmic resistance and also the increase of the reaction kinetics at higher temperatures.

Moreover, the current efficiencies for the pure hydrogen inlet ranged from ~70% to to levels >95%. The current efficiency increased with current density, whilst the voltage efficiency increased with temperature and decreased with current density. This resulted in higher power

efficiencies as the temperature was raised. The optimal current density with regards to power consumption, was $\sim 0.16 \text{ A cm}^{-2}$ at temperatures $\geq 120^\circ\text{C}$. A hydrogen permeability of up to ~ 30 Barrer was achieved and the highest limiting current density was 0.4 A cm^{-2} , which is well below a current density of practical interest, 1 A cm^{-2} .

From the experimental results obtained with the H_2/CH_4 gas mixtures, it can be concluded that hydrogen can be effectively recovered from H_2/CH_4 mixtures, yielding a hydrogen purity $>99.9\%$. In terms of the voltage–current characteristics, the mixtures showed higher voltages compared to that of pure hydrogen. Since the OCV is not zero in the case of the gas mixtures, as was the case with pure hydrogen, the OCV was subtracted from the measured cell voltage to determine the actual cell voltage. The values obtained were still much higher than that of pure hydrogen. Additionally, the limiting current density values were lower than those obtained for pure hydrogen at the same operating conditions, which decreased as the methane concentration increased. This, together with the increase in cell voltage indicate that the cell performance is influenced by the hydrogen partial pressure, which had an effect on the concentration overpotential (loss). This was confirmed with the CO_2 -containing mixtures.

However, although the performance of the cell was influenced by the methane concentration, the temperature effect was still visible; a performance increase with temperature was observed. The hydrogen selectivity decreased with temperature, whilst the overall cell efficiency (power efficiency) is increased, therefore the selectivity and cell efficiency behaves antagonistically towards one another. The highest selectivity achieved was ca. 22 000. Similar trends with regards to current-, voltage- and power efficiencies were visible when compared to that of the pure hydrogen experiments.

In the H_2/CO_2 experiments the Pt/Co catalyst efficiency is severely influenced by CO_2 even at elevated temperatures. Hydrogen purities of 98-99.5 % can be achieved when 10% CO_2 is in the feed and 96-99.5% when 50% CO_2 is in the feed stream. Overall, poor selectivities were reached for the CO_2 containing stream, with poor overall cell performances due to catalyst deactivation explained by CO formation by the reverse water gas shift reaction. The selectivity values reached, were up to ± 200 . Moreover, the curved profile of the polarisation curve suggest that the electrode reaction dominate the overpotential. This is expected since the catalyst is directly affected by the presence of CO_2 . Similar to the methane-containing mixtures, the power efficiencies decreased with an increase in carbon dioxide concentration and increased with temperature. The power efficiencies were, however, lower than that obtained by pure hydrogen and the methane containing mixtures. The maximum power efficiency obtained were 83.74% for the 10% CO_2 mixture and 80.98% for the 50% CO_2

mixture, respectively. This is lower than the maximum power efficiencies at the same methane concentrations; 89.27% and 88.60%, respectively.

Furthermore, ammonia was seen to have detrimental effects on the membrane, as ammonia reacted with the membrane acid. Ammonia and hydrogen was found to compete, where ammonia transport was favoured at low current densities and hydrogen transport was favoured at higher current densities. The membrane was irreversibly damaged and was rendered insufficient for the separation of hydrogen from feed streams containing ppm concentrations of ammonia. Therefore, if ammonia is used as measure to store H_2 , or used as a transport medium specifically for FCs, completed decomposition of NH_3 to N_2 and H_2 is required before electrochemical separation can be applied to remove the contaminants.

CHAPTER 4. CO TOLERANCE OF Pt/C AND Pt-Ru/C ELECTRO-CATALYSTS: WITH A POLYBENZIMIDAZOLE-BASED PROTON EXCHANGE MEMBRANE

This chapter evaluates the practicality of implementing Pt-Ru/C electro-catalysts for high-temperature (100-160°C) electrochemical hydrogen separators to alleviate CO poisoning. This was done by comparing the performance of a pure Pt/C catalyst with that of Pt-Ru/C catalyst (Pt:Ru atomic ratio 1:1) under pure hydrogen and a H₂/CO gas mixture at 80-160°C.

Section 4.1 is an introductory section; it includes background to this aspect of research, the research motivation and the objective of the work carried out here. **Section 4.2** provides a theoretical background relevant to this study, particularly pertaining to cyclic voltammetry and its use for/in evaluating the electrochemical active surface area. In **Section 4.3**, the experimental apparatus and equipment used, and methods followed during the experimental procedures are explained. The experimental results are reported and discussed in **Section 4.4**, after which this chapter is concluded with **Section 4.5**.

4.1 INTRODUCTION

Electrochemical hydrogen separators (EHSs), just like fuel cells (FCs), show good potential for future hydrogen-based energy prospects. EHSs can be used to simultaneously purify and compress hydrogen streams for FC application and storage purposes (see **Section 2.3.4**). Perfluorinated sulfonic acid (PFSA) membranes (mainly Nafion based), typically operated at 60-80°C, are commonly used as proton exchange membranes (PEMs) in these cells, due to their high proton conductivity, mechanical integrity and chemical stability (Benicewicz, *et al.*, 2008). Although the focus of current research is on alternative catalysts, Pt-based materials are still the most preferred electrocatalyst because of their effectiveness, high chemical stability and current density, and high activities for hydrogen oxidation/evolution reactions in EHSs and oxygen reduction reaction in FCs (Adroher *et al.*, 2011; Haque *et al.*, 2017). However, Pt does have some disadvantages, such as limited resources, its costly nature and the fact that it is easily poisoned (Bracchini *et al.*, 2001; Haque *et al.*, 2017; Ihm *et al.*, 2004). Pt is poisoned by low concentrations of carbon monoxide (CO) (>10 ppm) (Benicewicz *et al.*, 2008; Bracchini *et al.*, 2001; Chen *et al.*, 2014). Oetjin *et al.*, (1996) explained this behaviour by the two competing reactions of H₂ and CO adsorption:





From the equations, it is evident that the performance deterioration of the cell can be partly attributed to the CO adsorption, which consequently blocks a great number of Pt sites used for the adsorption and oxidation of hydrogen (Bracchini *et al.*, 2001). It is reported that the CO tolerance of Pt-based catalysts can be enhanced by either increasing the operating temperature or by making use of bimetallic catalysts (Araya *et al.*, 2016; Chen *et al.*, 2014). To this end, platinum alloy catalysts such as Pt-Ru have been developed and utilised (Araya *et al.*, 2016; Orhan & Sharaf, 2014). Ru is known to weaken the Pt–CO bond whilst strong binding of Ru–CO occurs, and Ru atoms adsorb oxygen-containing atoms, oxidising CO to CO₂, as seen in FCs (Bessarabov & Tokarev, 2014). However, operating the anode at a potential that is high enough to oxidise CO to CO₂ results in substantial losses in cell efficiency (Gardner & Ternan, 2007).

High-temperature (HT) proton exchange membranes (PEMs) (operating temperatures: 100-200°C) with concentrated phosphoric acid (PA) as electrolyte have been developed to overcome the limitations associated with low-temperature (LT) membranes (Haque *et al.*, 2017; Huth *et al.*, 2009; Kwon *et al.*, 2009). Polybenzimidazole (PBI) membranes are the most widely studied HT-PEMs. They have high proton conductivity due to their high PA doping capabilities (Kwon *et al.*, 2009). PA-doped PBI membranes conduct protons well, even in anhydrous conditions, which significantly simplifies the electrochemical system as the need for humidification steps is eliminated, hence reducing water management issues (Araya *et al.*, 2016). Additional advantages include fast electrode kinetics, enhanced mass transport, higher tolerance to impurities such as CO (up to 3 vol. %) and better sustainability (Alegre *et al.*, 2018; Benicewicz, *et al.*, 2008; Chippar *et al.*, 2014; Kim *et al.*, 2015).

Moreover, an increase is expected in the transport of gases through the flow fields (FFs) as well as their diffusion in the gas diffusion layer (GDL) due to the absence of liquid water. This, in turn, allows simplified FF designs as well as improved interaction between reactants and reaction sites (Araya *et al.*, 2016). However, the higher Pt loadings required, due to the free nature of the acid, undermine these advantages (Araya *et al.*, 2016). In efforts to reduce costs, whilst maintaining efficiency, noble metals are combined with carbon particles (Ihm *et al.*, 2004). To achieve further cost reduction, highly porous nanostructured catalysts, known as Pt black, have been implemented in the electrodes to maximise the surface area and to achieve ideal contact between the gas phase, electrode (electrically conductive) and the electrolyte (ion-conductive), for optimal performance (Ahn *et al.*, 2014; Kwon *et al.*, 2009).

Although both Pt-Ru and HT operation are both considered to be valuable methods to alleviate CO poisoning, uncertainty prevails regarding which method is more effective. Since bimetallic Pt-Ru catalysts are only common in LT Nafion membranes (Bessarabov & Tokarev, 2014), and elevated temperatures are only used in HT-PEM application, the two methods cannot be effectively compared.

Therefore, a combined approach of using both HT-PEMs and Pt-Ru catalysts is now proposed. To effectively evaluate the practicality of this method, the performance of a Pt-Ru/C nanoparticle-sized catalyst was compared to that of a Pt/C nanoparticle-sized catalyst using the same PA-doped PBI membrane, in the temperature range 80-160°C.

Cyclic voltammetry (CV) is a very popular technique that can be used to determine the electrochemical active surface area (ECSA) (also known as the real surface area) of the electrode. The ECSA is a key performance parameter that assesses the catalytic activity of the electrode (e.g. the catalyst/electrode degradation) (Kwon *et al.*, 2009; Wu *et al.*, 2013), especially when the electrode has a low Pt content (Carpenter *et al.*, 2017; Czerwiński *et al.*, 2016). In general, the ECSA values can be used as a measure for electrocatalyst utilisation in electrochemical cells such as fuel cells, electrolyzers and hydrogen pumps (Bayer *et al.*, 2012).

For carbon supported Pt, two common methods for measuring ECSA exist: Hydrogen underpotential deposition (H_{upd}) and CO-stripping (COS) (Binninger *et al.*, 2014). The former is a very popular method used for ECSA determination, and has been widely applied (from rotating disk electrode (RDE) systems to electrochemical cells, where the electrode is integrated with the membrane electrode assembly (MEA)) (Carpenter *et al.*, 2017; Czerwiński *et al.*, 2016; Morimoto *et al.*, 2011). However, despite being a widely implemented method, several concerns related to the accuracy of these methods have been highlighted in previous papers (Carpenter *et al.*, 2017; Cardellini *et al.*, 2002). Some concerns include the H_2 adsorption/desorption characteristics that may be masked by the carbon (e.g. the double layer charging behaviour of surface groups on carbon (Wu *et al.*, 2013) and severe corrosion of Pt nanoparticles at potentials $>1.1V$ due to oxidation of the carbon support (Binninger *et al.*, 2014). In the case of HT ($>100^\circ C$) additional concerns arise, such as (i) the strongly adsorbed PA anions from the dissociation of concentrated PA (mainly $H_2PO_4^-$) that may inhibit the adsorption of hydrogen (Engl *et al.*, 2014) and (ii) the high Faradic currents from the hydrogen evolution reaction (the electrochemical reduction of H^+ ions which leads to the formation of H_2 molecules that can superimpose the pseudocapacitive currents from the hydrogen underpotential deposition layer (Engl *et al.*, 2014). Improved methods to obtain baselines for

the H_{upd} signal and the COS peak, does, however, allow reproducible and consistent values for Pt-based ECSA (Arenz *et al.*, 2008).

In the case of Pt alloys, the ratio of the H_{upd} -based and COS-based ECSAs ($ECSA_{CO}/ECSA_{H_{upd}}$) can disclose some electronic properties of the surface structure of the catalyst. Becknell *et al.* (2015) found that pure Pt and rough acid leached Pt alloy surfaces exhibited a charge ratio of $Q_{CO}/2Q_H \sim 1$, whilst skin type Pt-alloy surfaces showed high oxygen reduction reaction activity with charge ratios of $Q_{CO}/Q_H \sim 1.5$. Based on this, the authors advised to use CO-stripping (COS) alongside H_{upd} for ECSA evaluations, to avoid the underestimation of the specific area of the electrodes, associated with the overestimation of the surface area normalised catalytic activity.

In open literature, *in situ* measurements (MEA) of the electro-oxidation kinetic parameters of CO adsorbed on Pt-based catalysts are rarely seen due to the complex overlapping of the different oxidation mechanisms, *ex situ* measurements (e.g. RDE) are preferred and either measured from electrode in solution mechanisms or deduced from fitting a model to the CO performance loss data (Balasubramanian *et al.*, 2011). It is common for catalytic properties measured from *ex situ* measurements (e.g. RDE) to disagree with those measure in MEAs (Carpenter *et al.*, 2017). Therefore, in order to develop and design improved electro-catalytic materials particularly for fuel cells and related processes, the fundamental aspects of CO oxidation on real electro-catalyst needs to be understood. Since *ex-situ* and *in-situ* result vary greatly, this can only be achieved when the *in-situ* methods are applied. Therefore, this investigation will focus on *in-situ* measurement.

Benchmark tests were first performed with pure hydrogen by evaluating the hydrogen pumping performance of the cell for Pt/C and Pt-Ru/C (see **Appendix H: Section H.2**), after which the CO-tolerance of the two catalysts were investigated and compared through cyclic voltammograms/voltammetry (CV) scans.

COS scans are typically performed with CO/N₂ gas mixtures, but since the focus of this study is placed on electrochemical hydrogen separation, a H₂/CO gas mixture (2% CO, balance H₂) was used in the present work. Three types of electrochemical active surface areas (ECSAs) methods were compared: H_{upd} -based ECSA, COS-based ECSA, and H_{upd} /COS-based ECSA. The three ECSAs were evaluated from COS and H_{upd} stripping steps applied. The hydrogen charge was obtained through a N₂ saturated baseline, where the saturation refers to the cathode feed stream. For improving the H_{upd} analysis, Arenz *et al.*, (2008) have suggested that the CV currents obtained from the CO saturated baseline be subtracted from the H_{upd} signal instead of the traditional standard baseline currents (N₂ saturated baseline). This was also

performed by Binninger *et al.*, (2014). However, in both these references, these methods were applied *ex situ*, therefore, the reliability of *in situ* measurements remains as yet unknown; clarity is still required. This method was nonetheless considered, but preliminary test revealed that this method was not very reliable and it was therefore disregarded.

The COS-based ECSA determination proved to be ineffective in the presence of H_2 due to the complex overlapping of the oxidation mechanisms and therefore the $CO-H_{upd}$ peak was used to estimate the ECSA from the COS CV data. For HT-PEM electrochemical cells, the distribution of the electrolyte in the MEA determines the availability of the triple phase boundary and therefore influences the ECSA. The mobility of the PA results in lower catalyst utilisation, and ultimately a lower ECSA (Kwon *et al.*, 2009). This is expected to have an unavoidable effect on the experimental ECSA results. However, this effect was considered to be minimal.

4.2 THEORETICAL BACKGORUND: CYCLIC VOLTAMMETRY

CV is an electrochemical technique that records the current response to a potential scan applied to the working electrode (WE) in the forward and reverse directions (Joshi & Sutrave, 2018). This is carried out at a constant scan rate and can be performed once or several times. The cyclic sweep of the potentials generates a current vs. potential curve called a CV, which is depicted in **Figure 4.1**.

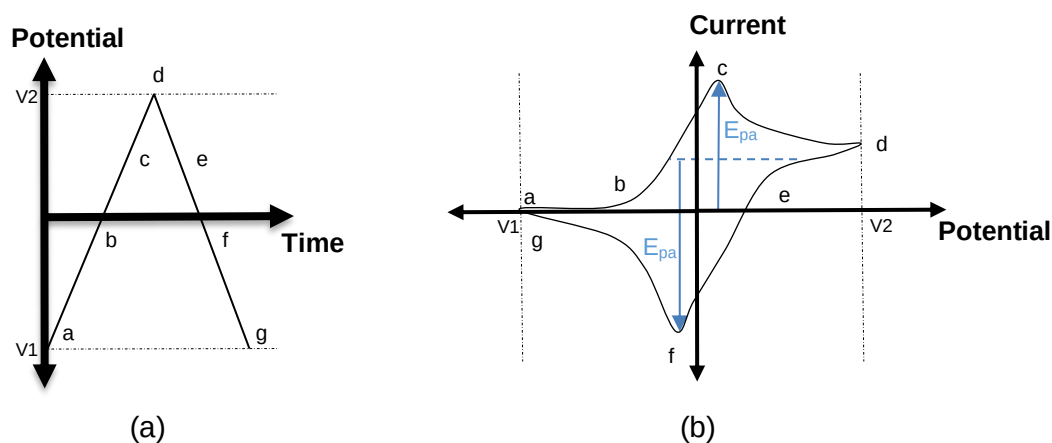


Figure 4.1: A schematic representation of a CV waveform and typical current response. (a) Representation of applied potentials swept linearly back and forth between the voltage limits [V₁ and V₂]. (b) The resulting current given as a function of the voltage (Adapted from Gouws (2012)).

Figure 4.1 shows that the oxidation process occurs from the (a) initial potential (V₁) to (d) the upper potential (V₂). First, the potential is scanned positively, starting at V₁ and linearly increasing the potential over time (scan rate in $mV s^{-1}$) until V₂ is reached, as depicted in

Figure 4.1 (a) as (d). The corresponding peak potential is reached at (c), and is known as the anodic peak potential (E_{pa}). The E_{pa} is reached when all the substrate at the surface of the electrode is oxidised. Hereafter, the cycle is completed by sweeping the potential in the reverse direction (negatively) from the (d) V2 to the (g) V1 (Joshi & Sutrave, 2018). This results in a reduction at the cathode electrode. The cathodic peak potential (f) is reached when all of the substrate at the surface of the electrode has been reduced. The shape of the voltammograms and magnitude of the oxidation and reduction peaks are highly dependent on the analyte concentration, scan rate and experimental conditions, and provides information on the relative kinetic rate and diffusion coefficients of the electrochemical system (Gouws, 2012; Quiroga, 2018). The scan rate controls speed at which the potential is scanned. Faster scanning rates result in a smaller diffusion layer and, consequently, higher currents are achieved (Dempsey *et al.*, 2017).

The flow of current in a CV can be divided in two: (i) the electrical double layer charging current and (ii) the non-linear current response (Binniger *et al.*, 2014). The former flows in response to the linealy changing voltage, whilst the latter corresponds to the hydrogen adsorption/desorption reaction occurring on the ECSA. The value of the ECSA is directly associated with the amount of electrolyte in contact with the catalyst (Binniger *et al.*, 2014).

For illustrative purposes a CV curve recorded for a Pt electrode in contact with a 0.5 M H_2SO_4 solution at 25°C, well known and discussed in literature (Czerwiński *et al.*, 2016; Doña Rodríguez *et al.*, 2000), is presented in **Figure 4.2**. Three potential regions are distinguished in the CV curve of a Pt electrode in contact with an acid solution (Czerwiński *et al.*, 2016):

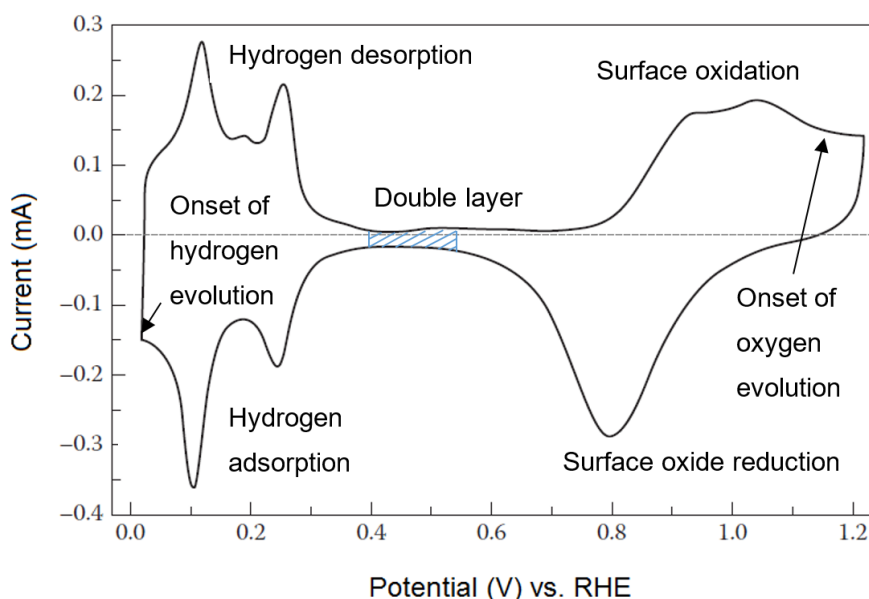


Figure 4.2: CV recorded for a Pt electrode in 0.5 M H_2SO_4 at 25°C (Czerwiński *et al.*, 2016).

- a) The 'hydrogen region' – a region of hydrogen adsorption/desorption
- b) The 'double layer region' – a region free from Faradic processes (only capacitive processes present)
- c) The 'oxygen region' – a region of surface oxide formation/reduction.

The hydrogen adsorption/desorption peaks are used to quantify the ECSA by converting the area under the peak into the total charge for the hydrogen reaction, excluding the capacitive charging current distribution (Binniger *et al.*, 2014). The working principle is similar when COS is used to determine the ECSA. The major disadvantage of this technique, however, is that the carbon support may alter the hydrogen adsorption and desorption characteristics by increasing the double-layer current and the redox reactions of the surface active groups on carbon. To avoid carbon oxidation, the voltage limit of the WE should be set to <1 V (vs. DHE) (Cardellini *et al.*, 2002; Wu *et al.*, 2013).

4.3 EXPERIMENTAL

4.3.1 EXPERIMENTAL RIG

A flow diagram of the experimental set-up used in this study is shown in **Figure 4.3**.

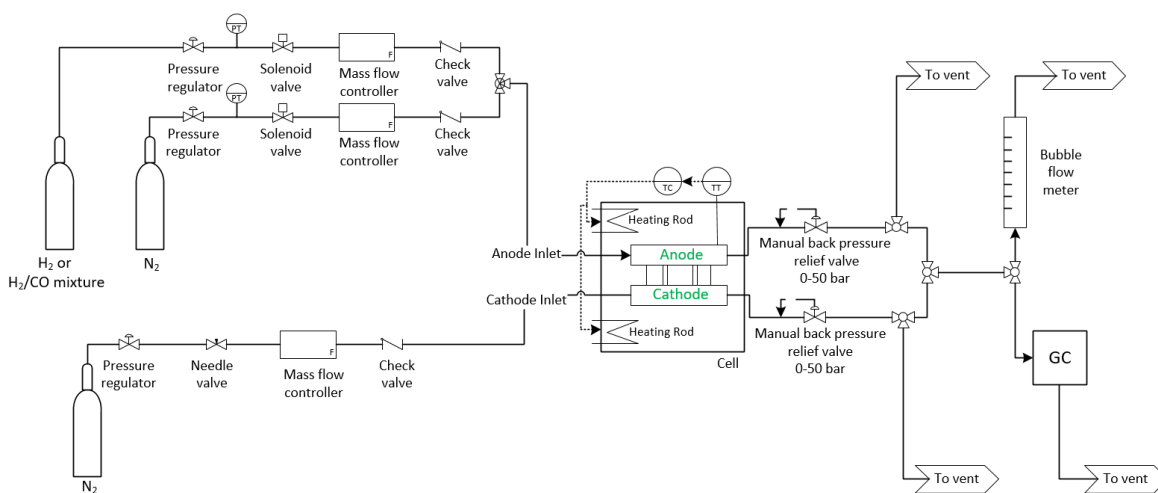


Figure 4.3: Schematic of the test set-up.

Three gas mixtures were used for the various experiments conducted. Pure H_2 was used to characterise the performances of the Pt/C and Pt-Ru/C MEAs, and also to determine the H_{upd} -based ECSA. A 2 vol. % CO (balance H_2) gas mixture was used for the COS-based ECSA determination, for both the Pt/C and Pt-Ru/C MEAs. Dry N_2 was used to flush the cathode

compartment and to purge the system, cleaning it from unwanted impurities. Refer to **Appendix M** for the gas quality specifications of all the gases used in this study. All gases were stored in high-pressure gas cylinders, regulated by pressure regulators, and connected to the rig through small-diameter (1/4") plastic tubing. Mass flow controllers (Brooks Delta Smart II) were used to regulate the flow of the feed streams: rate accuracy $\pm 0.7\%$ and a rate repeatability 0.25% (Brooks instruments, 2008). The mass flow controllers were controlled making use of LabVIEW software.

4.3.2 EXPERIMENTAL CONDITIONS

All experiments were carried out at atmospheric pressure. The cell operating temperature was varied over the temperature range 80-160°C. The cell temperature was maintained by two Watlow FIREROD® heating rods (one at the anode side and one at the cathode side). A K-type thermocouple (anode side) and PID controller (DCL-33A) were incorporated. The cell was enclosed in a heat insulation jacket to reduce heat losses. The temperature at the centre of the anode back plate was taken as the cell temperature.

All experiments were conducted in hysteretic order as per assessment of the performance deterioration during experimentation. The flow rates herein reported are all given in normal milliliters per minute (nmL/min), with 0°C and 1 bar taken as reference. All potentials reported in this chapter are referred to the dynamic hydrogen electrode (DHE) at the specified temperature.

4.3.3 EQUIPMENT

4.3.3.1 Electrochemical cell

A two-electrode system was used, with the anode acting as the WE, whilst the cathode acts as both the counter electrode (CE) and reference electrode (RE), illustrated in **Figure 4.4**. The cathode also acts as a DHE. The same cell was used here as the one described earlier in **Section 3.2.1.2**.

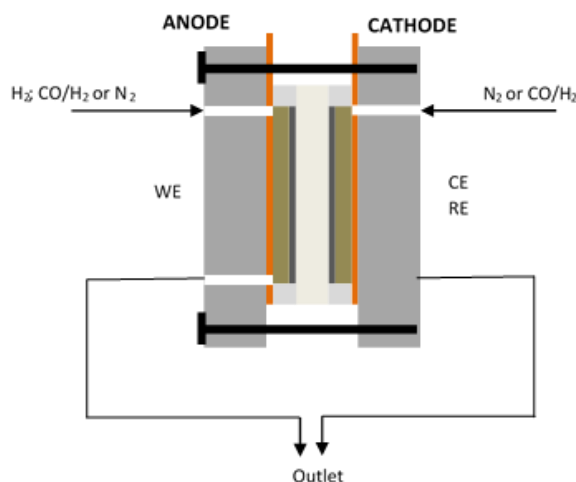


Figure 4.4: Schematic electrochemical cell.

The cell was compressed using a torque wrench to ensure a uniform pressure distribution over the compressed MEA and to minimise the electrochemical and thermal resistance of the GDLs. The assembly torque for each of the 8 bolts was 6 Nm. The properties of the MEAs used in the experiments are given in **Table 4.1**. In the case of the Pt-Ru catalyst, the Pt:Ru atomic ratio was 1:1. The total metal loading for both Pt and Pt-Ru was 2 mg cm^{-2} .

Table 4.1: Properties of the MEAs used in CV experiments

	MEA 1	MEA 2
Membrane type	PBI membrane	PBI membrane
Membrane thickness	Approximately $58.90 \mu\text{m}$ (determined)	Approximately $58.90 \mu\text{m}$ (determined)
Anode catalyst	Pt/C	Pt-Ru/C
Cathode catalyst	Pt/C	Pt/C
Catalyst loading	2 mg cm^{-2}	2 mg cm^{-2}
Active area	25 cm^2	25 cm^2
Temperature range	$120\text{-}180^\circ\text{C}$	$120\text{-}180^\circ\text{C}$
Proton conductivity	$10 \times 10^{-2} \text{ S cm}^{-1}$	$10 \times 10^{-2} \text{ S cm}^{-1}$

4.3.3.2 Gamry equipment

The electrochemical techniques used in this study included electrochemical impedance spectroscopy (EIS) (data presented in **Appendix H**), CV and polarisation curves. The latter were logged making use of LabVIEW software, incorporated into the user interface. The other two electrochemical techniques were conducted making use of Gamry Instruments. The

Gamry Reference 3000 K is a precision electrochemical instrument and is accompanied by a current booster (Gamry 30K current booster) to achieve the desired current. The specifications of the Gamry reference 3000 and the 30K booster is summarised in **Table 4.2**.

Table 4.2: Gamry equipment specifications

Gamry Reference 3000		
Operating modes	Potentiostatic, galvanostatic	
Possible cell connections	2,3 or 4 electrodes	
Current range	3 A	
Voltage range	15 V	
Voltage resolution	1 μ V	
EIS measurement	Waveform	Sine
	Frequency range	10 μ Hz-1 Mhz
	Max amplitude	1.425 V
	Min amplitude	2.75 μ V
Gamry 30K Booster		
Compliance Voltage	20 V, -2.5 V	
Output current	30 A	
Accuracy	0.3 mA	
Frequency range	200 Hz	

4.3.4 ECSA EVALUATION METHODS

4.3.4.1 H_{upd} : ECSA evaluation

Voltammetric measurements undertaken to study the ECSA were conducted using dry H_2 at the anode (the WE). The cathode, acting as both the CE and RE, was flushed with dry N_2 . The H_{upd} -based ECSA values were determined making use of the third cycle of a total of three CV scans. The CVs were recorded at a scan rate of 50 $mV s^{-1}$, the upper and lower potential chosen as 1.0 and -0.025 V vs DHE. This was done to see the onset of hydrogen evolution in the CV. The currents obtained in the CV scan were used to estimate the ECSA.

4.3.4.2 CO-stripping: ECSA evaluation

The CO adsorption was accomplished with 2 vol. % CO in H_2 ; hydrogen flow rate 100 nmL/min. The CO experiments were conducted based on the following procedure: (1) the anode was purged with 2% CO mixture for 10 min with a constant electrode potential of 0.1 V vs. DHE. Successively, (2) the monolayer of adsorbed CO was stripped off; a CV scan was conducted at 20 $mV s^{-1}$, from 0.1 V vs. DHE, to 1.0 V vs. DHE. Three cycles were performed.

Then, (3) the CO reference baseline experiments were executed according to the same procedure, the only difference being that the tests were performed in N₂ saturated electrolyte (CO is not present in the experiment). Here the potential is initially held at 0.1 V for 30 min followed by a CV scan at 20 mV s⁻¹.

4.3.5 METHOD DEVELOPMENT

For the application of all CV methods it is important to define a baseline for the determination of the H_{upd} and CO oxidation charge. This is essential for reproducibility and diagnostically conclusive results. Consequently, two additional parameters need to be defined: the upper and lower potential limit. The methods considered to define the baselines are now described.

$H_{\text{upd}} - \text{ECSA}_{(\text{Capacitive charge baseline})}$: In the capacitive charge baseline CV analysis, the double layer region is used as the subtraction baseline for the hydrogen adsorption/desorption peaks (Binninger *et al.*, 2014). The potential at the current density minimum before the hydrogen evolution peak is taken as the lower potential limit for the integration of the charges. The upper limit is the potential after the hydrogen adsorption/desorption peak. This baseline method is referred to as the ‘standard baseline’.

$\text{COS} - \text{ECSA}_{(\text{Ref. CV baseline})}$: The reference CV is used to obtain a correct integration baseline without the adsorption of CO. This is crucial, since contributions from sources other than CO oxidation are possible, hence correction is required. Therefore, the reference CV peak is used as a baseline, where the integration boundaries can be defined as the potentials where the reference CV peak and the COS CV peak (cycle 1) intersects.

4.3.6 EXPERIMENTAL PROCEDURE

During the electrochemical measurements, the cell temperature was controlled in the range 80-160°C. As a basic characterisation step, pure hydrogen was used. The operational sensitivities and performance were investigated for both Pt/C and Pt-Ru/C electrocatalysts (see **Appendix H**). This was followed by the ECSA determination tests, where the experiments on the electrodes were organised as follows. First the cleaning step was performed. The anode and cathode were initially completely purged with N₂, after which the CE was purged with H₂. To ensure that all contaminants on the WE were removed, potential cycles between -0.025 and 1 V vs. DHE were conducted for 30 cycles at a scan rate of 50 mV s⁻¹. In the case of Pt-Ru, preconditioning is completed within narrower potential limits, with the upper potential limit set to 0.8 V. This was done to avoid irreversible oxidation or possible Ru dissolution (Christov *et al.*, 2007).

In the second step, referred to as the reference CV scan, N₂ was fed to the cell and the baseline for the CO-ECSA_{Ref. CV} was obtained at the different temperatures. Following this, the H_{upd} CV scan was performed at 50 mVs⁻¹. The final step was the actual COS measurement. The reason for this organisation is that once CO is introduced into the system, the entire removal thereof is challenging, and then interferences from oxidation of residual CO are possible. Hydrogen separation of the gas mixtures were also carried out to determine, and compare, the separation efficiency of both Pt/C and Pt-Ru/C.

4.3.7 ECSA CALCULATION

Evaluation of the ECSAs of Pt and Pt-based electrocatalysts firstly involves the measurement of the charge of the adsorbed species (Q_H or Q_{CO}), determined from the CV scans:

$$I = \frac{dQ}{dt} \quad (\text{Eq. 4.3})$$

$$\therefore Q = \int_{t_i}^{t_f} I dt = \frac{1}{v} \int_{E_i}^{E_f} I dE \quad (\text{Eq. 4.4})$$

where t_i is the time at which the hydrogen adsorption commences and t_f is the moment at which the monolayer is completed; E and I depict the potential [V] and current [A], respectively; and v is the applied scan rate [mV s⁻¹]. Gamry Echem Analyst software was used to determine the charge area for all the respective CV peaks. Accordingly, the charge was normalised using a surface area specific charge (Q_{SA}) of an ideal one-electron transfer 210 $\mu\text{C cm}^{-2}$ (H_{upd}) or two-electron transfer 420 $\mu\text{C cm}^{-2}$ (CO), which yield the electrochemical surface area (A_{EC} ; cm²) (Friedrich *et al.*, 2008):

$$A_{EC} = \frac{Q_H/Q_{CO}}{Q_{SA}} \quad (\text{Eq. 4.5})$$

The electrochemical surface area (A_{EC}), in **Eq. 4.5**, is not the same value as the specific/real surface area of the catalyst. The real surface area being the most important parameter when characterising an electrode, since the real surface area will determine the catalyst activity (Doña Rodríguez *et al.*, 2000). Since the surface of the electrode is not always smooth and the real area will always exceed the geometric area (Czerwiński *et al.*, 2016; Doña Rodríguez *et al.*, 2000). For nanoparticles the real surface area, A_{real} (cm² mg⁻¹), is a function of the catalyst load, L (mg cm⁻²) and the geometric area of the electrode, A_{geo} (cm²) (Friedrich *et al.*, 2008; Korstdottir *et al.*, 2009):

$$A_{real} = \left(\frac{A_{EC}}{A_{geo}} \right) \left(\frac{1}{L} \right) \quad (\text{Eq. 4.6})$$

Therefore, since the electrodes used in this study exhibit an active electrode area of 25 cm², the H_{upd}-based and COS-based ECSA of the anode can be calculated using the following equations (Cardellini *et al.*, 2002; Engl *et al.*, 2014; Korstdottir *et al.*, 2009):

$$ECSA_{(H)} \left(\frac{cm^2 Pt}{mg Pt} \right) = \frac{Q_H (\mu C)}{210 \left(\frac{\mu C}{cm^2 Pt} \right) \times L \left(\frac{mg Pt}{cm^2} \right) \times 25 cm^2} \quad (\text{Eq. 4.7})$$

$$ECSA_{(CO)} \left(\frac{cm^2 Pt}{mg Pt} \right) = \frac{Q_{CO} (\mu C)}{420 \left(\frac{\mu C}{cm^2 Pt} \right) \times L \left(\frac{mg Pt}{cm^2} \right) \times 25 cm^2} \quad (\text{Eq. 4.8})$$

4.4 RESULTS AND DISCUSSION

4.4.1 H_{upd}-BASED ECSAs

The CV scans obtained for the N₂ saturated electrolyte for Pt/C and Pt-Ru/C are plotted in **Figure 4.5**. As the temperature increased, the H_{upd} peak moved to the left (lower potential region), for both Pt/C and Pt-Ru/C. The shift was more severe in the case of Pt/C. This is indicative of the temperature dependency of the H_{upd} peak, which also influence the size and shape of the peak (Behm *et al.*, 1999; Engl *et al.*, 2014). For both Pt/C and Pt-Ru/C, the peak height increased with temperature, whilst the peak width appeared to become narrower. Broader smaller peaks are observed at 80°C, whilst sharper narrower peaks are witnessed at 160°C.

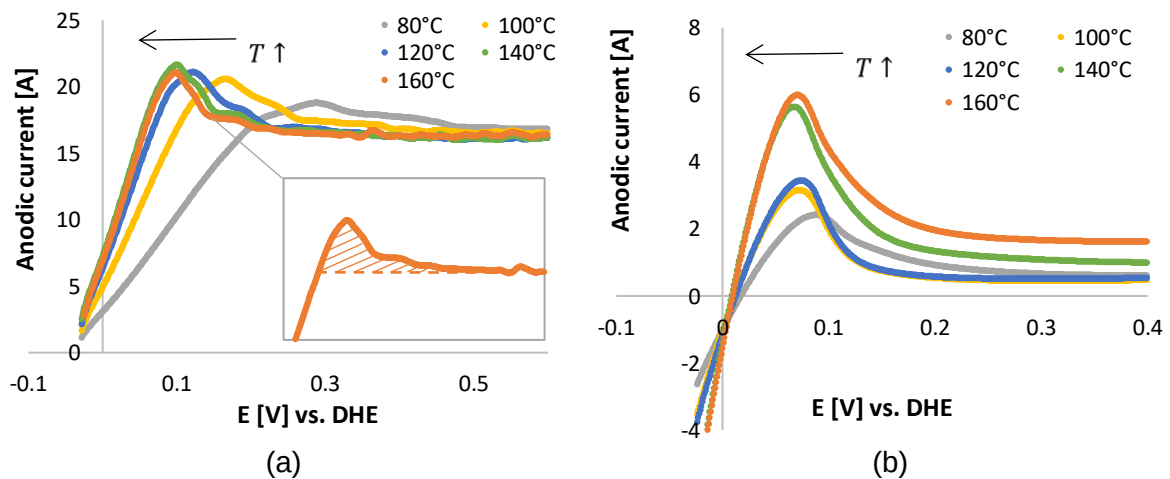


Figure 4.5: *In situ* CVs performed in N₂ saturated electrolyte (PA) with a scan rate of 50 mV s⁻¹. (a) Pt/C. (Inset) The filled area represents the charge related to the H_{upd} peak after applying the standard baseline correction at 160°C. (b) Pt-Ru/C.

The capacitive currents for the Pt/C catalyst (**Figure 4.5 (a)**) were far above the zero current region, and exhibited higher values compared to the Pt-Ru/C catalyst. This can be described by the diffusion characteristics of nanoparticles, where circular/convergent diffusion is present (Banks *et al.*, 2009). See **Figure 4.6**. The effect of convergent/circular diffusion poses the benefit of improvements in mass transport to an extent where the current density is greater than that of a macro-electrode under planar diffusion (Banks *et al.*, 2009). This was evident for both Pt/C and Pt-Ru/C, since the anodic current peaks range between approximately 16-22 A and 2-6 A, respectively, whereas bulk current values are commonly expressed on a μA or mA scale (Arenz *et al.*, 2008; Binninger *et al.*, 2014; Czerwiński *et al.*, 2016; Engl *et al.*, 2014).

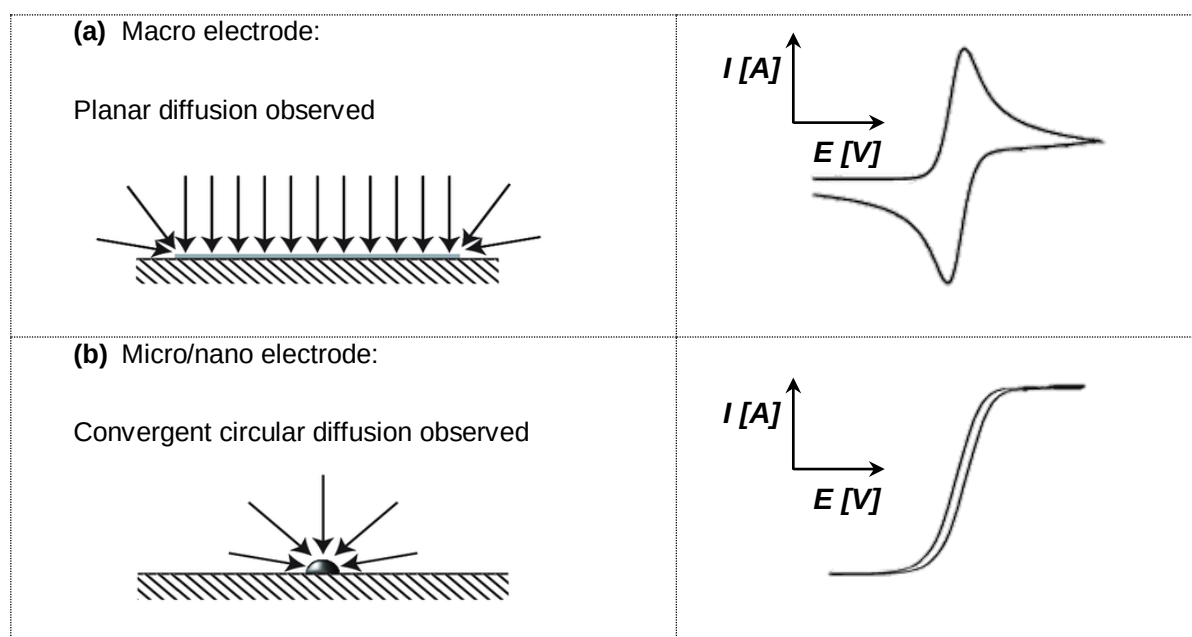


Figure 4.6: (a) Macro electrode: planar diffusion with the resulting CV curve shape; (b) Micro/nano electrode: convergent/circular diffusion with the resulting CV curve shape (based on Banks *et al.*, 2009).

Results for the ECSA estimation by means of the standard baseline method for Pt/C and Pt-Ru/C are tabulated in **Table 4.3** and **Table 4.4**, respectively (ECSA data column highlighted in grey). The tables show that the estimated ECSA values, in $\text{cm}^2 (\text{mg catalyst})^{-1}$, for Pt/C and Pt-Ru/C are similar, with Pt/C exhibiting slightly higher ECSA values than the Pt-Ru/C at the same temperatures. For both Pt/C and Pt-Ru/C, the apparent ECSA increased with temperature. This may be explained by enhanced electrode kinetics (Alegre *et al.*, 2018; Benicewicz, *et al.*, 2008; Benicewicz, *et al.*, 2018; Chippar *et al.*, 2014; Kim *et al.*, 2015).

Table 4.3: Pt/C H_{upd} -based ECSA estimation data at different temperatures, determined via the standard baseline method

Temp. [°C]	Q_H [C]	A_{EC} [cm ²]	ECSA [cm ² mg _{Pt} ⁻¹]
80	7.39 ± 0.05	35190 ± 240	704 ± 5
100	10.56 ± 0.05	50286 ± 240	1006 ± 5
120	10.82 ± 0.05	51524 ± 240	1030 ± 5
140	11.03 ± 0.05	52524 ± 240	1050 ± 5
160	12.28 ± 0.05	58476 ± 240	1170 ± 5

Table 4.4: Pt-Ru/C H_{upd} -based ECSA estimation data at different temperatures, determined via the standard baseline method

Temp. [°C]	Q_H [C]	A_{EC} [cm ²]	ECSA [cm ² mg _{Pt-Ru} ⁻¹]
80	6.61 ± 0.05	31462 ± 240	629 ± 5
100	9.96 ± 0.05	47433 ± 240	949 ± 5
120	10.45 ± 0.05	49762 ± 240	995 ± 5
140	11.00 ± 0.05	52381 ± 240	1048 ± 5
160	12.11 ± 0.05	57667 ± 240	1153 ± 5

The ECSA values obtained are comparable to that obtained for LT Nafion membranes, as reported by Garsany *et al.* (2014), for 50 wt. % Pt/C. See **Figure 4.7**.

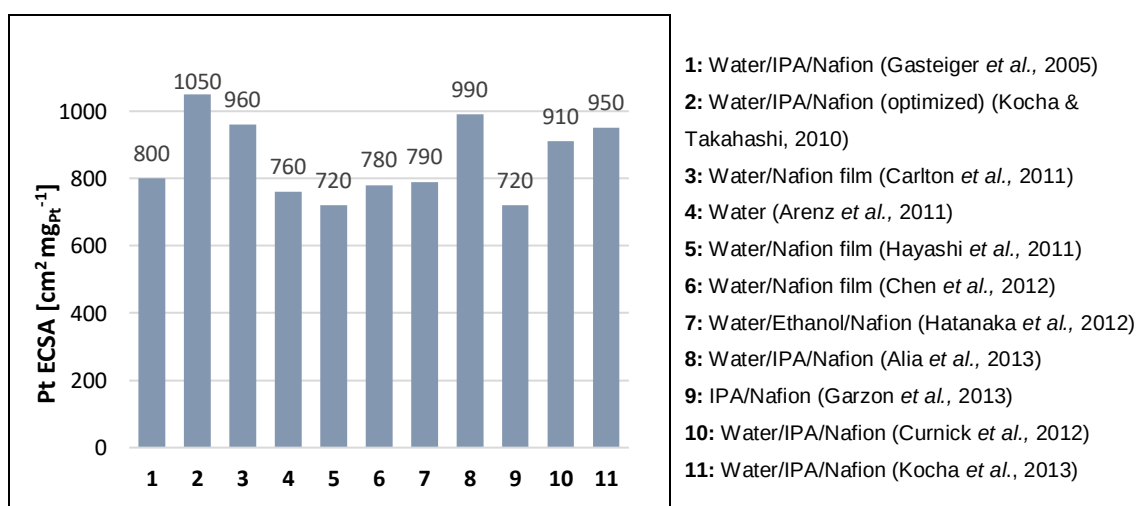


Figure 4.7: Pt ECSA values for a ~50 wt. % Pt/C standard (TKK-TEC-10E50E). Nafion indicates Nafion ionomer (reproduced from Garsany *et al.*, 2014).

4.4.2 CO-BASED ECSAs

The CO-stripping CV curves for Pt/C and Pt-Ru/C in the presence of H₂ (98 vol. %) are presented in **Figure 4.8 (a)-(e)** and **Figure 4.9 (a)-(e)**, respectively.

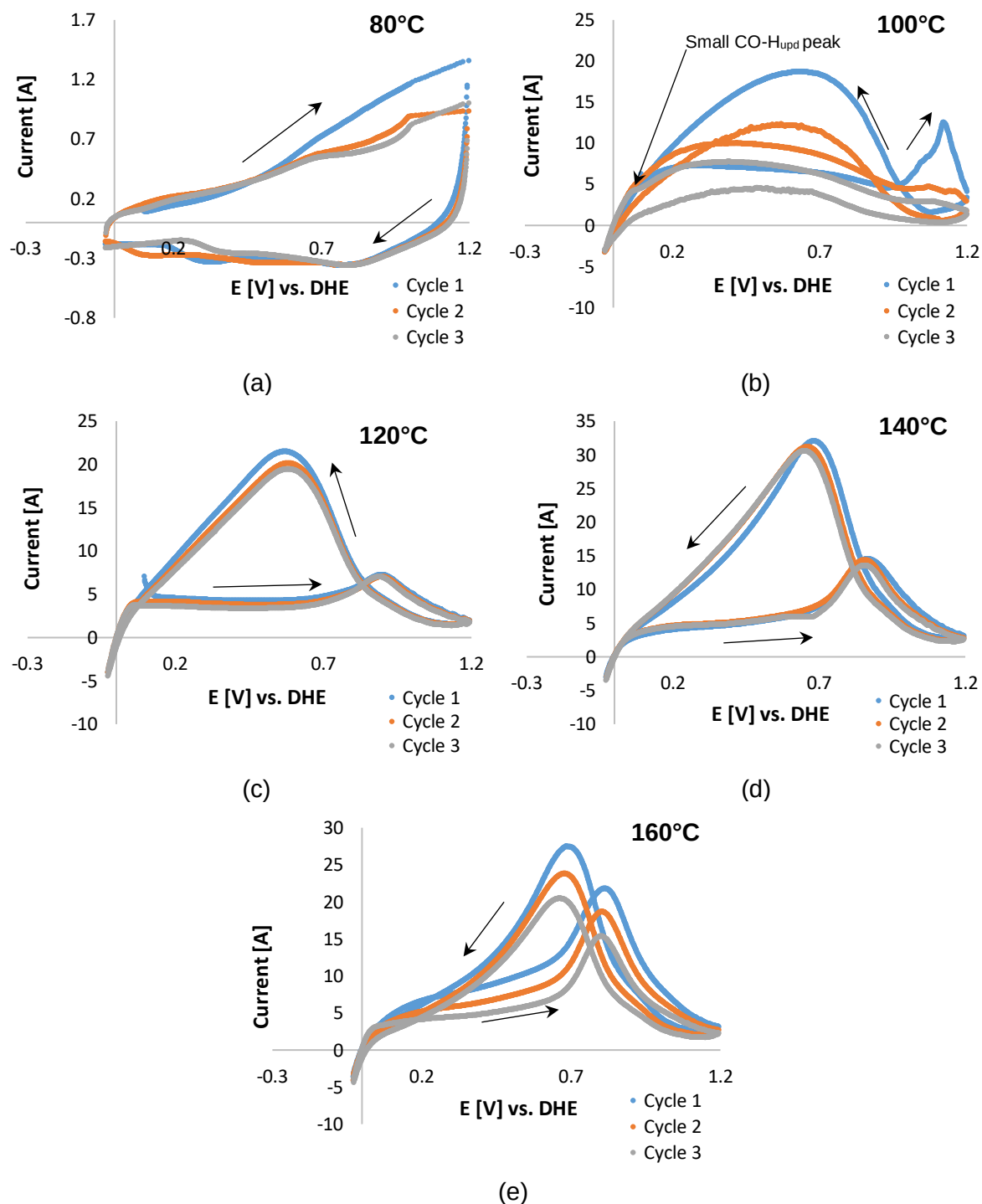


Figure 4.8: COS CVs of the Pt/C catalyst, 2 % CO (balance hydrogen), performed with a scan rate of 20 mV s⁻¹ with potential limits -0.025 and 1.2 V vs. DHE at (a) 80°C, (b) 100°C, (c) 120°C, (d) 140°C and (e) 160°C.

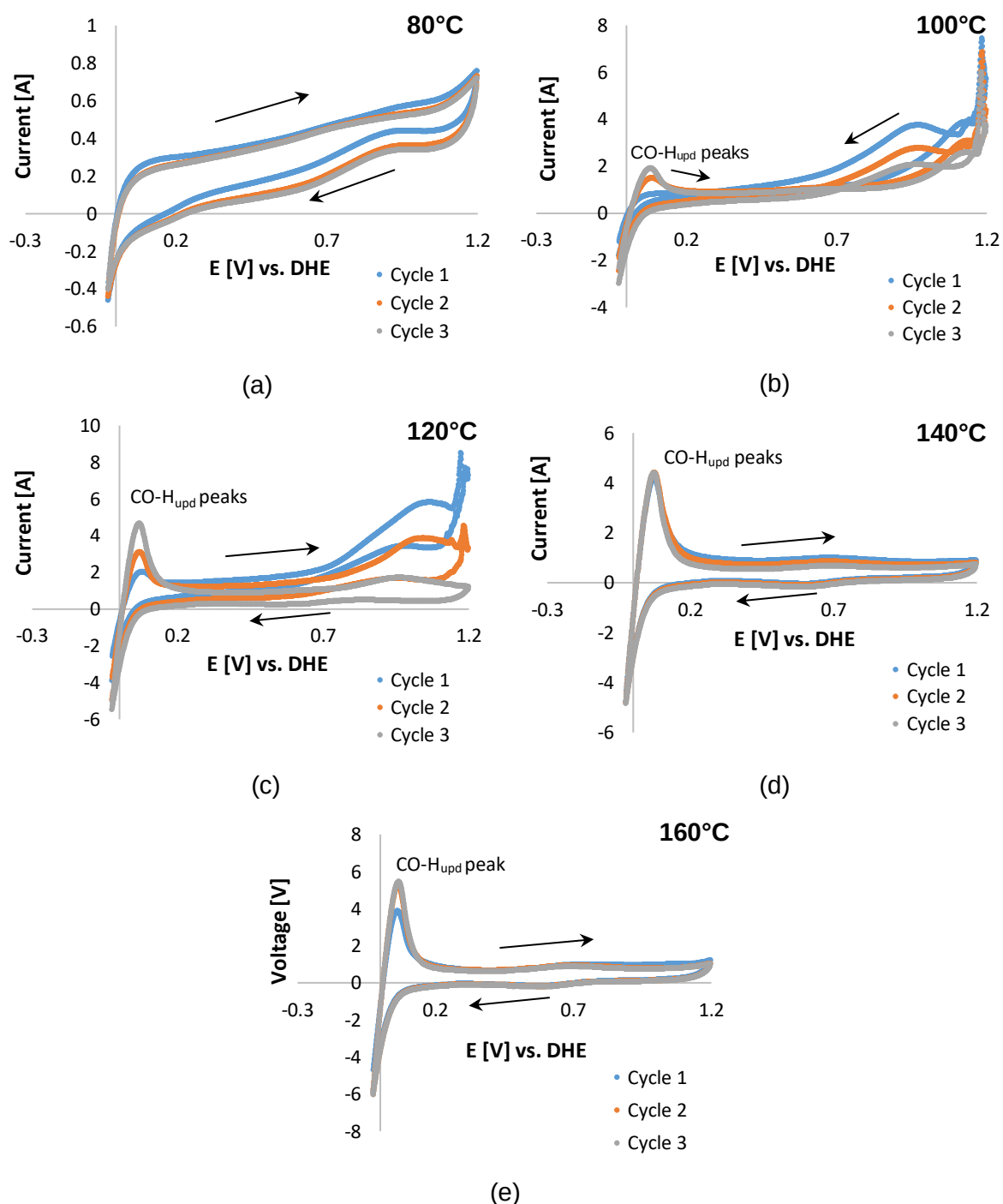


Figure 4.9: COS CVs of the Pt-Ru/C catalyst, 2 % CO (balance hydrogen), performed with a scan rate of 20 mV s^{-1} potential limits -0.025 and 1.2 V vs. DHE at (a) 80°C, (b) 100°C, (c) 120°C, (d) 140°C and (e) 160°C.

The absence of peaks at 80°C (**Figure 4.8 (a)**) indicated that the Pt catalytic sites were deactivated by CO. This was also seen in the case of Pt-Ru/C at 80°C (**Figure 4.9 (a)**), which means that a large amount of the catalytic surface is blocked by CO. This is in agreement with literature; the CO tolerance for LTs (70-80°C) is 50 ppm maximum (Haque *et al.*, 2017), and, since 2 vol. % CO is used to test the CO-based ECSAs, the catalytic sites become deactivated.

Peak formation was observed at 100°C (**Figure 4.8 (b)**), with one large peak seen in the first potential cycle (forward direction) at ~1.1 V. In the succeeding cycles, this peak disappeared, which is what is expected from COS experiments because the monolayer of adsorbed CO is removed. Although the entire peak disappeared by cycle 3, only a small CO-H_{upd} peak was formed, which indicated that a large number of the catalytic sites might still be deactivated by CO. Typical CO oxidation potentials on Pt were reported around 0.5-0.8 V vs. DHE (Binninger *et al.*, 2014; Engl *et al.*, 2014), which is in disagreement with the peak potential observed in cycle 1.

Furthermore, a peak was seen in the reverse direction; this was repeated at higher temperatures. This peak became sharper and seemed to shift to lower potentials as the temperature was increased beyond ≤120 °C. The same peak was also visible in the Pt-Ru/C CVs (**Figure 4.9**) at 100-120°C, but it decreased as the temperature increased. Only CO-H_{upd} peaks were visible at 140-160°C. Similar behaviour has been reported for the methanol electro-oxidation reaction (Chen *et al.*, 2012; Huang *et al.*, 2011), where the CO tolerance of Pt-based electrocatalysts was compared by means of the peak current ratio in the reverse (I_b) and forward (I_f) directions, as illustrated in **Figure 4.10**.

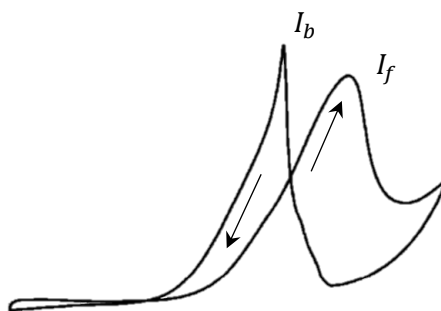


Figure 4.10: CV illustrating the reverse (I_b) and forward (I_f) current peaks.

Both Chen *et al.* (2012) and Huang *et al.* (2011) have studied the frequently invoked method to mitigate CO poisoning by introducing a foreign metal (X) to Pt, forming a Pt alloy, to facilitate the removal of adsorbed CO on the Pt surface, either by a bifunctional mechanism or by an electronic effect. Chen *et al.* (2012) studied Pt-Ru/C and Huang *et al.* (2011) studied Pt-Au. The current ratio criterion implemented in both these papers stated that the smaller the I_b/I_f ratio of an electrocatalyst the greater is the improvement in its CO tolerance and catalytic activity (Chen *et al.*, 2012). Goodenough & Manoharan (1992) introduced this criterion of Chen *et al.* (2012) and speculated that the I_b peak is associated with residual carbon species, rather than originating from the newly oxidised chemisorbed species. This means that I_b presumably does not have the same chemical origin as I_f . However, the accuracy of this method was

considered ambiguous for the curves considered, since the forward and reverse peaks seemed to be related in some or other manner. This conclusion was drawn from the Pt/C data, which showed that a decrease in one peak (forward/reverse) is accompanied by a decrease in the other peak (reverse/forward).

Although the origin of the reverse peak is vague, the peaks found in the potential region 0.7–1.2 V for Pt-Ru/C were expected to be related to CO adsorption on the catalyst, since a decrease in these peaks seemed to be directly related to an increase in the CO- H_{upd} peaks. This increase indicates that as the CO-related peaks decreased the Pt sites become reactivated for hydrogen adsorption to take place, hence a hydrogen peak resulted. Furthermore, since the forward current peak does not decrease with temperature, as expected, and seemingly increases as the temperature is increased, the assumption was made that this peak originated from side reactions (as reported by Engl *et al.* (2014)). Two possible side reactions were identified: one being the complex overlap of mechanisms, and the other presumably originating from the oxidation of the carbon support (Binninger *et al.*, 2014). Both these reactions were considered and investigated.

Beginning with the latter, the Pt nanoparticle catalyst supported on high-surface-area carbon suffers from severe corrosion at potentials >1.1 V. It is for this reason that Wu *et al.* (2013) suggested that the anodic limit be set to < 1.0 V vs. DHE. Following this suggestion, Pt/C COS scans in the presence of H_2 and small amounts of H_2O (from dilute PA) were repeated with an upper potential limit of 1 V vs. DHE. The curves at 100°C were similar in shape to those reported by Binninger *et al.* (2014) for pure hydrogen in nitrogen-saturated electrolyte; which suggested that the CO peak was not present. The forward peak disappeared almost completely at 120 and 140°C, and was once again visible at 160°C (**Figure 4.11**). At 160°C the forward and reverse peaks decreased with each subsequent cycle, along with the CO- H_{upd} peak formation observed in cycle 3. The H_{upd} peaks were considered insignificant in terms of size. The reverse peak disappeared almost completely, which is to be expected because CO is no longer adsorbed onto Pt at 140-160°C (Haque *et al.*, 2017). However, Carpenter *et al.* (2017) stated that the HT suppresses the COS-based ECSA more than the H_{upd} -based ECSA, due to the shift in the equilibrium of CO adsorption/desorption on the Pt surface.

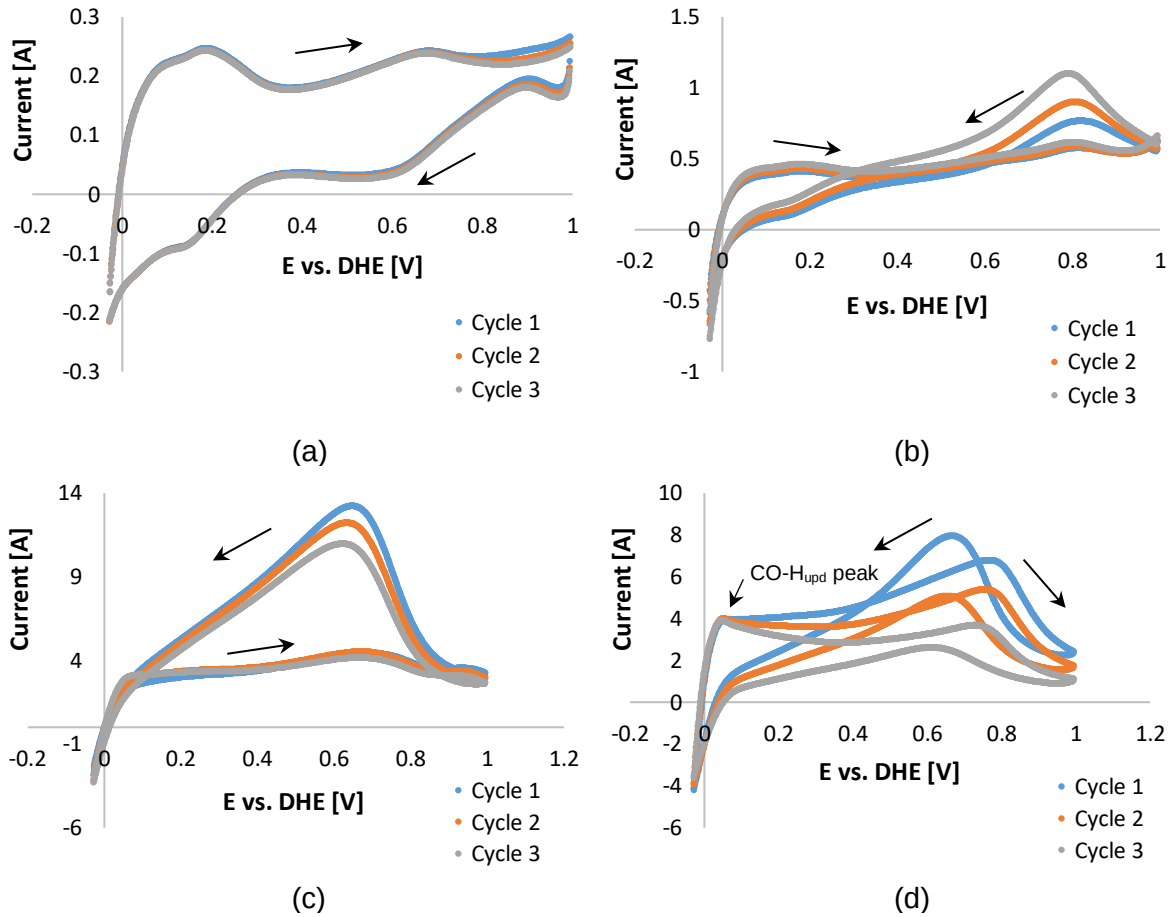
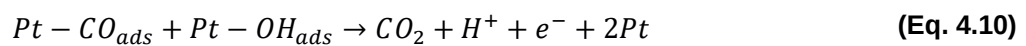
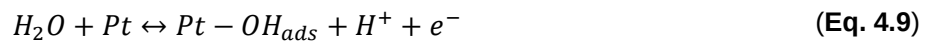


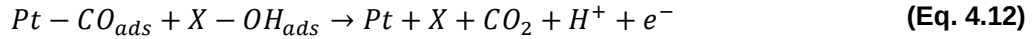
Figure 4.11: COS CVs of the Pt/C catalyst, 2 % CO (balance hydrogen), performed with a scan rate of 20 mV s^{-1} with potential limits -0.025 and 1 V vs. DHE at (a) 100°C , (b) 120°C , (c) 140°C and (d) 160°C .

Upon comparing the results in **Figure 4.11 (d)** and **Figure 4.8 (e)**, the oxidation of the carbon support was observed when the potential limit is set to $>1 \text{ V}$. The peaks in **Figure 4.8 (d)** are much larger, yet both CVs do show improvement (decrease in peak size) with each cycle. Results observed in **Figure 4.11** led to the conclusion that oxidation of the carbon support, although not completely disregarded, was not the origin of the reverse peaks. Therefore, the theory of overlapping mechanisms was investigated.

From a mechanistic point of view, the adsorbed CO is believed to be electrochemically oxidised by an oxygen-containing species (generally OH) (Cardellini *et al.*, 2002; Ciapina *et al.*, 2018):



In the case of bi-metallic catalysts (e.g. Pt-Ru) the reaction is suggested to change in the following manner:



where X denotes the foreign metal added to Pt.

In the case of PEM-FCs, water is the only possible oxygen source, due to the low partial pressure of oxygen (Ioroi *et al.*, 2002). Here the activation of the water molecule is considered imperative for the oxidation of adsorbed CO on Pt-based electrocatalysts. However, although water is considered an important factor for CO electrooxidation, most studies on the oxidation of CO_{ad} have been conducted in aqueous electrolyte (e.g. dilute H₂SO₄ or HClO₄ solution) (Ioroi *et al.*, 2002). Since the electrolyte used consists of 85 wt. % PA, diluted in water, the water present was considered to be sufficient for the oxidation of CO.

In other studies, it has been observed that the presence of H₂ has promotional effects on CO oxidation similar to H₂O; H₂ can be oxidised to H₂O or hydroxyl (OH) groups (Calla & Davis, 2005; Kohyama *et al.*, 2018). Since the anode feed gas consists of a mixture of hydrogen and CO, hydrogen is expected to have a promotional effect on the CO oxidation. Furthermore, coupling chemistries arises from the use of gas mixtures containing H₂ and CO or CO, O, and H₂O (Mhadeshwar & Vlachos, 2004). An example of such coupling is the production of oxygenates (e.g. COOH*) through a recombination reaction, as proposed by Mhadeshwar & Vlachos (2004):



with its subsequent decomposition:



or



where, the asterisk (*) resembles either an empty site or an adsorbed species. HCOO** also undergoes similar reactions (**Appendix I, Table I.2:R39-46**). These coupling chemistries are important when considering surface reactions on Pt-based catalysts and needs to be accounted for. Therefore, a surface reaction mechanism consisting of three sub mechanisms (CO oxidation, H₂ oxidation and CO-H₂ coupling steps) was developed, as illustrated in **Figure 4.12**. The individual steps are elaborated on in **Appendix I**.

The surface reaction mechanism was constructed based on the assumption that the PA used is stable and do not partake in any of the reactions. Moreover, the reactions were based on the surface reactions presented by Mhadeshwar & Vlachos (2004).

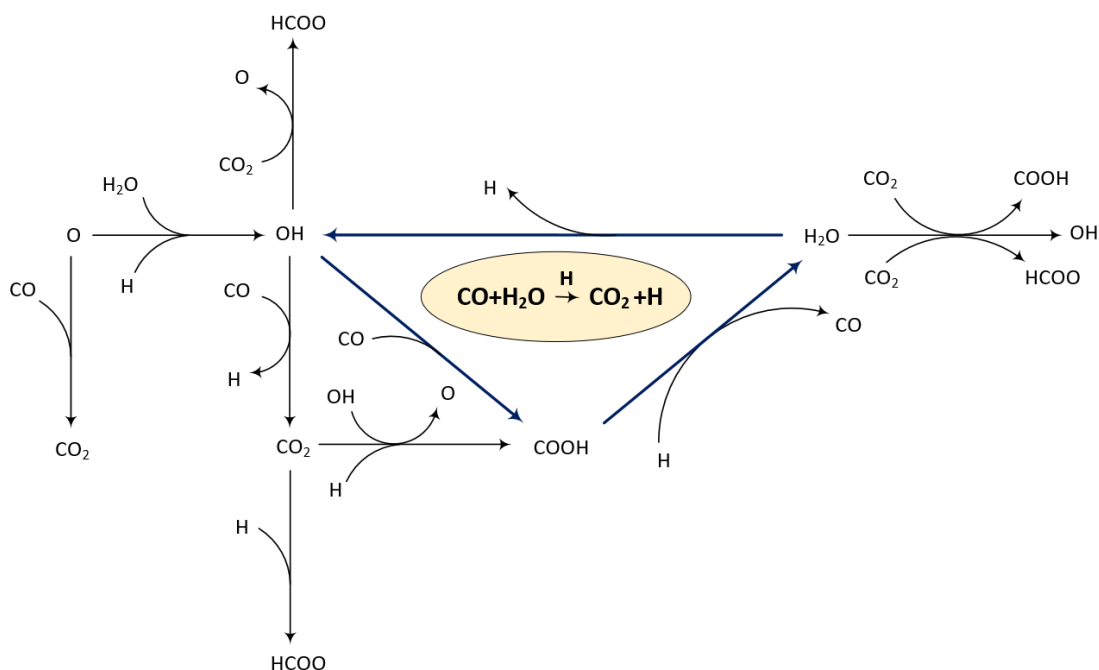


Figure 4.12: The reaction mechanisms of CO oxidation on Pt in the presence of H₂ and water.

The reaction mechanism presented in **Figure 4.12** indicates that the surface reaction is more complex than previously thought. From this, the possibility of subsequent oxidation or the formation of intermediate carboxyl species (COOH) was identified, which might explain the reverse peak previously mentioned. The facile formation of intermediate carboxyl species has been reported previously, and subsequently confirmed, by experiments performed on Au surfaces (Kohyama *et al.*, 2018). Results of tests performed with 1 vol. % CO (balance N₂; no H₂ present) (see **Figure 4.13**) also serve as confirmation (for the coupling mechanisms in the presence of H₂); no reverse peak is present and only one CO peak was seen in the first potential cycle. Therefore, no side reactions were evident in the absence of H₂. No further attention was given to the identification of the side reactions, since this aspect did not form part of the initial project scope.

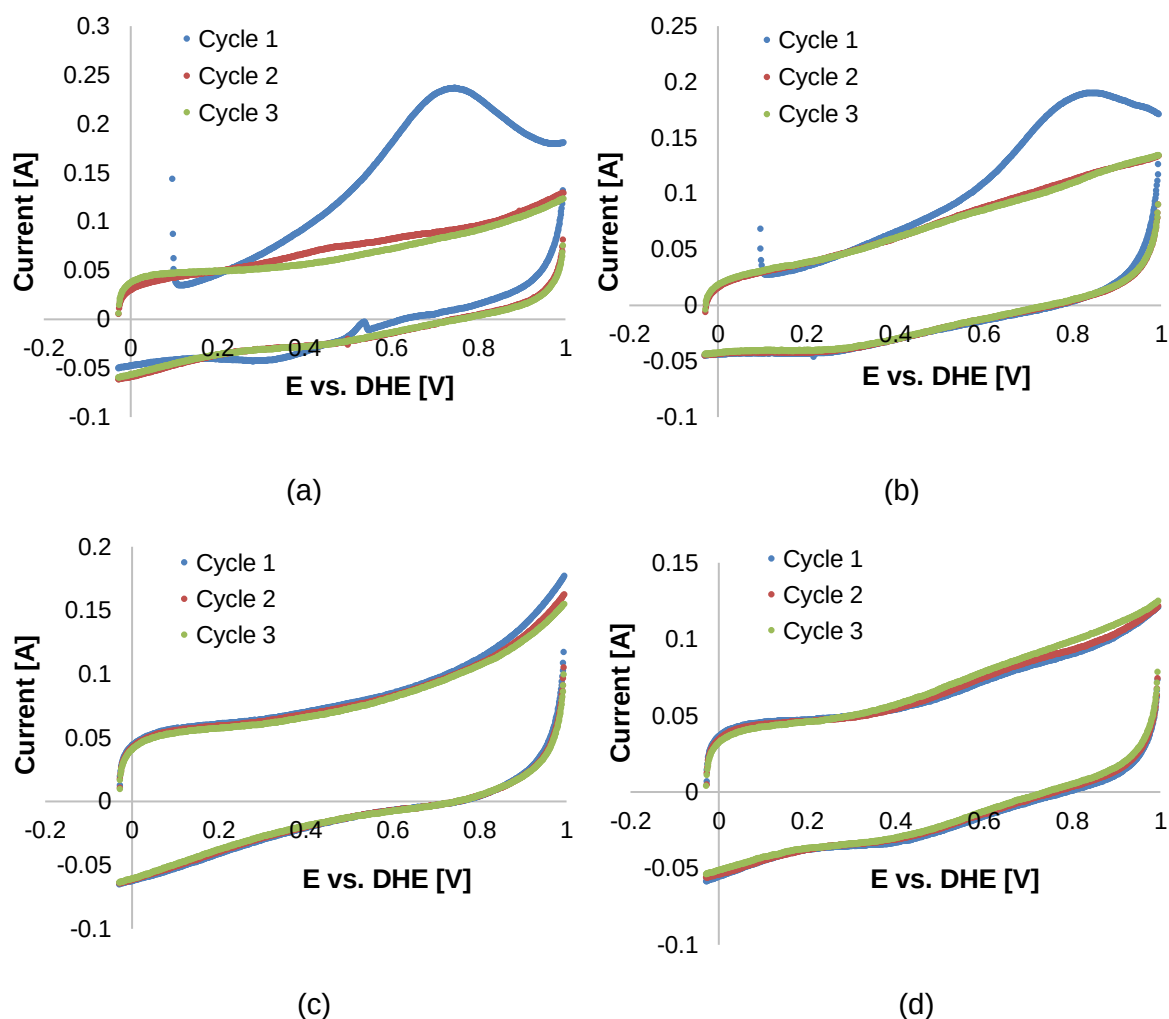


Figure 4.13: Cyclic voltammetry scans of 1% CO in N₂ at: (a) 100°C, (b) 120°C, (c) 140°C and (d) 160°C.

Since the ECSA could not be evaluated from the CO peaks, the decision was made to evaluate the ECSA from the CO-H_{upd} peaks instead. The latter were considered to resemble the reactivated Pt sites. Since no CO-H_{upd} peaks were present in the CV scans performed on Pt/C, the ECSA values for only Pt-Ru/C could be analysed. See **Table 4.5**. The values presented are not considered the real ECSA values, but are rather seen as an estimation.

Table 4.5: Pt-Ru/C (CO-H_{upd})-based ECSA estimation in terms of cm²/mg catalyst (100-160°C)

	100°C	120°C	140°C	160°C
Cycle 1	7 ± 0.5	166 ± 2	586 ± 5	624 ± 5
Cycle 2	161 ± 1	318 ± 3	632 ± 5	781 ± 5
Cycle 3	239 ± 2	654 ± 5	705 ± 5	874 ± 5

Table 4.5 clearly shows that the CO/ H_{upd} -based ECSA values increase with each consecutive cycle at the temperatures that were used in this study. Moreover, the ECSA values also increased as the temperature increased (also seen previously for H_{upd} -based ECSA values). However, the values obtained were lower than those depicted in **Table 4.4**. This could be explained by the change in acid distribution or the deactivation of Pt sites upon CO exposure. At temperatures $<140^{\circ}\text{C}$, other peaks, originating from CO as a source, were visible. Therefore, the lower ECSA values at these lower temperatures might be considered to be caused by CO poisoning. However, at temperatures $\geq 140^{\circ}\text{C}$, no peaks other than H_{upd} /CO are visible, and therefore CO poisoning was not considered to be the cause behind the lowered ECSA values for temperatures above 140°C .

The transmission electron microscopy (TEM) images displayed in **Figure 4.14** reveal that particle agglomeration/aggregation after heat treatment, could have caused the decrease in the ECSA. The scale size of the different TEM images are not the same (scale indicated in the lower left corner of each image), hence the images are not indicative of the exact size difference; rather, they provide an indication of the agglomeration/aggregation evident after heat exposure. See **Figure 4.15** for the particle size distribution before and after heat treatment (where ‘heat treatment’ is referred to as HT in the figure).

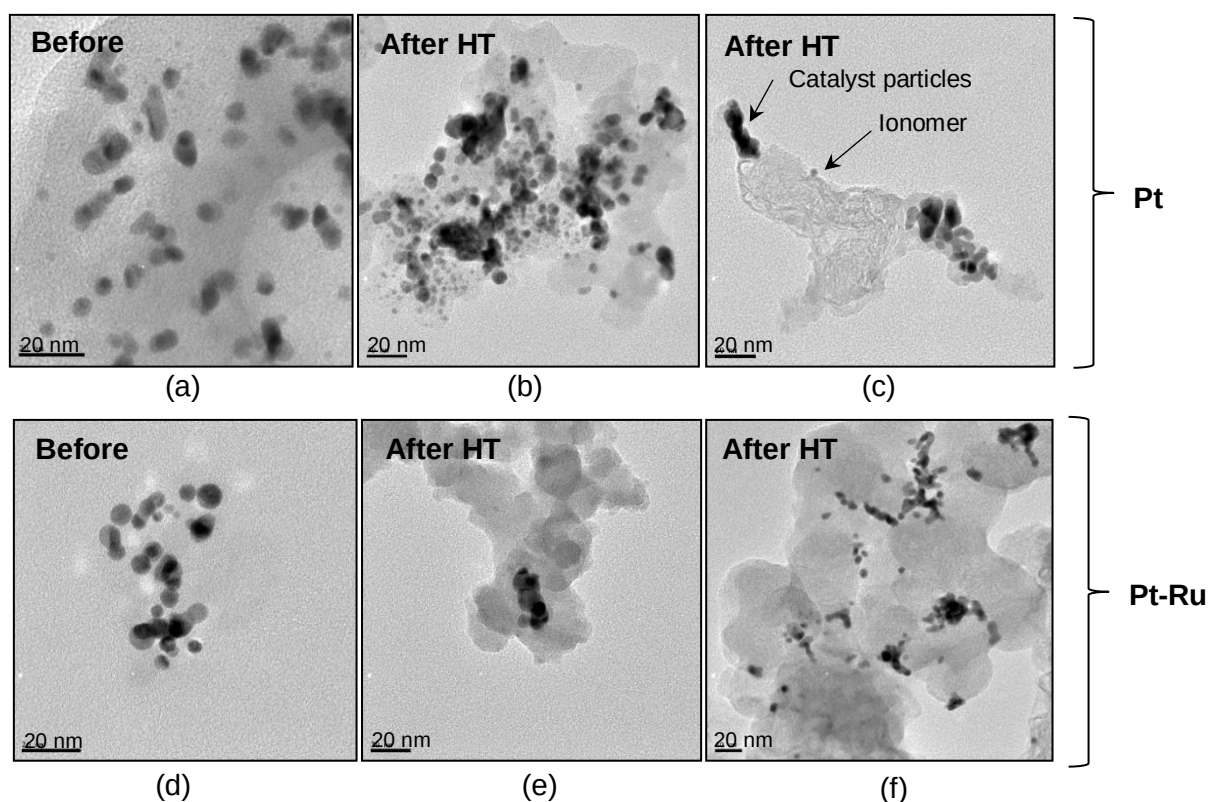


Figure 4.14: Transmission electron microscopy (TEM) images of Pt/C and Pt-Ru/C catalysts, before and after, CO and heat treatment (HT): (a) Pt; (b) Pt-HT, (c) Pt-HT, (d) Pt-Ru, (e) Pt-Ru-HT and (f) Pt-Ru-HT.

Figure 4.14 (a) and (d) (TEM images before heat treatment) show that there was almost no aggregation of particles, although major particle size differences was evident. The individual particles were clearly observed (the darkened sections indicate overlapping particles). Most of the particles in **(d)** appeared to be spherical, whereas the particles in image **(a)** exhibited odd shapes. The porosity of these particles could be seen (light particles) but could not be quantified by TEM. The Pt and Pt-Ru nanoparticle aggregates are observed in **(b), (c), (e) and (f)**. The extent of the particle agglomeration differs in the four images. The shape of the particles changed from small spherical to larger elongated particles. The most severe aggregation was seen in **(b)**, where irregular particle lumps were formed.

In **Figure 4.15**, a box and whiskers diagram of the particle size distribution (based on the particle diameter) for both Pt/C and Pt-Ru/C, before and after heat exposure, is given. A very similar particle size distribution is seen for both Pt and Pt-Ru, before heat treatment. The average particle sizes for Pt and Pt-Ru were ~5.8 nm and ~6.5 nm, respectively.

The Pt particles before heat treatment were in the range 2.3-9.7 nm, whereas the Pt-Ru particle sizes, before heat treatment were in the range 2.9-10.4 nm. After heat treatment, the minimum particle size increased by 1 nm for Pt and by 0.8 nm for Pt-Ru. The values for Q_1 (upper boundary for quartile one) and the median were very closely related before and after heat treatment for both Pt and Pt-Ru. The Q_3 values increase by 0.7 and 1.5 nm for Pt and Pt-Ru, respectively. There was a large difference in the maximum particle size (max.); the maximum particle size before heat treatment changed from 9.7 and 10.4 nm to 39.2 and 31.4 nm after heat treatment respectively for Pt and Pt-Ru. This means that, for the Pt-Ru particles, almost a quarter of the heat-treated particles were larger than the maximum particle size before heat treatment.

Moreover, for Pt the average particle size before heat treatment changed from 5.7 to 7.35 nm after heat treatment. Similar results were seen for Pt-Ru, where the average particle sizes changes from 6.53 nm to 8.91 nm. Hence, the aggregation of the nanoparticles was confirmed. Refer to **Appendix J** for the raw data generated. It is known that the aggregation of particles have an impact on the surface area, as larger particles reduce the available surface, therefore resulting in lower ECSA values (discussed in **Appendix A** on **page 144**). This could, therefore, explain the reduction in ECSA seen in **Table 4.5**. However, this was only considered to influence the ECSA at higher temperatures. CO poisoning is expected to be the greatest contributor to loss of ECSA at LT. It remains uncertain, however, at what temperature the particle agglomeration commences. Overall, it was concluded that analysis of the ECSA is

more complex at HT than initially thought. No further attention was given to explaining the reduction in ECSA.

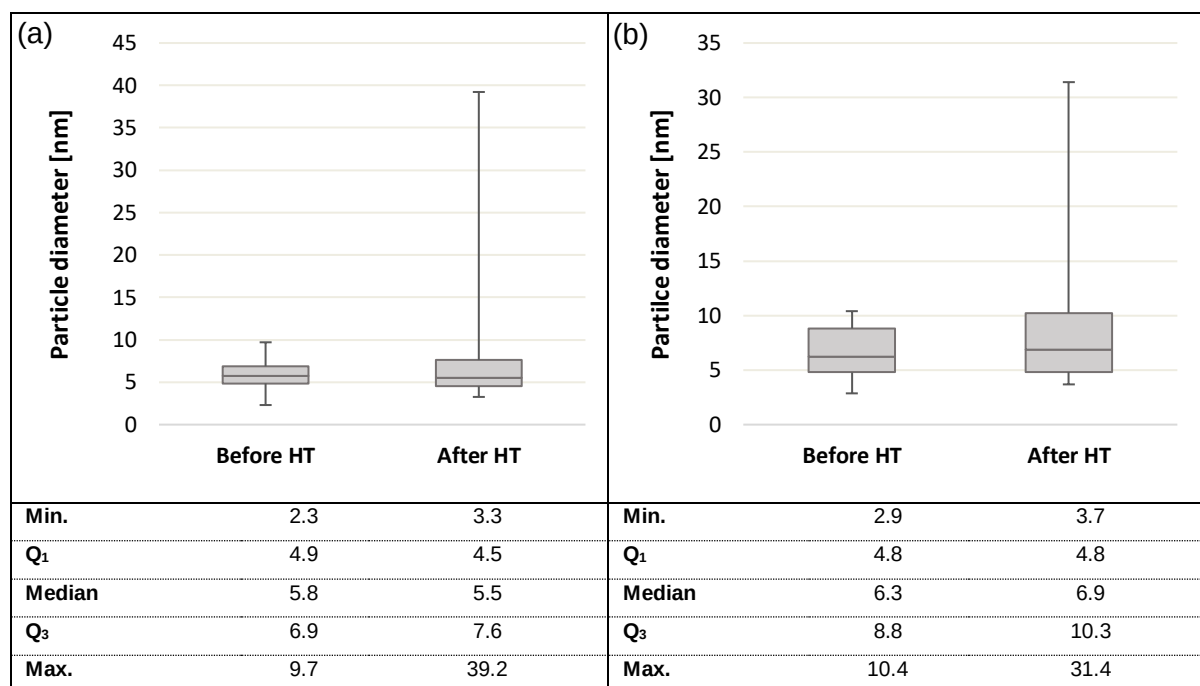


Figure 4.15: Box and whiskers diagram of the particle size distribution based on the particle diameters for (a) Pt and (b) Pt-Ru, before and after heat treatments (HT).

4.5 CONCLUSION AND RECOMMENDATIONS

In this chapter the CO tolerance of Pt/C and Pt-Ru/C electrocatalysts was evaluated using CV. This was done in the temperature range 80-160°C. Three types of CV peaks were considered to evaluate the ECSA: the COS-based ECSA, the H_{upd} -based ECSA and the H_{upd} /COS-based ECSA.

For the H_{upd} -based ECSA evaluation, it was found that the ECSA is temperature dependent and it increases with an increase in temperature, for both Pt/C and Pt-Ru/C. The COS CV scans, performed with a 2 % CO (balance hydrogen) gas mixture, showed that both Pt and Pt-Ru were deactivated by CO at 80°C; therefore, the ECSA could not be evaluated at this temperature. Moreover, Pt was seen to be strongly affected by the coupling chemistries existing between CO and H_2 . These overlapping mechanisms were so significant that the ECSA could not be evaluated by the H_{upd} /COS-based method. Since no CO peaks were seen (whereas other peaks were seen), COS could also not be used to analyse the ECSA. However, upon the addition of Ru to Pt, the 'side' reactions brought about by H_2 and CO were suppressed, and H_{upd} /CO peaks were observed for Pt-Ru. At temperatures $\geq 140^\circ\text{C}$ no side

reactions were seen. Only $H_{\text{upd}}/\text{COS}$ peaks are visible. This is what was expected for Pt, since CO should not adsorb onto the surface of Pt above 140°C.

Hence, the conclusion was drawn that Pt-Ru is ultimately more tolerant to the coupling chemistries existing between CO and H_2 . Furthermore, the assumption was made that Pt-Ru is more tolerant to CO even at these elevated temperatures. It is recommended that the same COS tests be performed with CO/N_2 as anode feed gas mixture to evaluate the CO tolerance in the absence of the coupling chemistries brought about by H_2 . These results could then be used to verify the results presented in this chapter.

The ECSA results obtained from the H_{upd} peaks were compared with those obtained from the $H_{\text{upd}}/\text{COS}$ peaks. The $H_{\text{upd}}/\text{COS}$ -based values were lower. This was explained by the CO poisoning of the catalyst at LT. Since no peaks other than the $H_{\text{upd}}/\text{COS}$ peaks are visible for the COS scans performed on Pt-Ru at temperatures $\geq 140^\circ\text{C}$, CO poisoning is not expected to influence the ECSA above 140°C. TEM images revealed that particle agglomeration takes place after heat exposure. This is considered to be the cause of the lower ECSA values at HTs. The TEM images were recorded after the CV experiments were carried out, hence it is uncertain at what temperature the particle agglomeration commences.

Although no major performance differences were detected between Pt and Pt-Ru in the presence of pure hydrogen (data presented in **Appendix H: Section H.2**) the lifetime of the Pt-Ru catalyst is expected to be longer. This conclusion is drawn from the ability of Ru to suppress the surface reactions taking place on Pt in the presence of CO and H_2 (coupling chemistries).

To conclude, it is well known that CO alters the performance of Pt-based electrocatalyst, also, Ru is known to alleviate the poisoning effect that CO has on Pt at low temperatures. However, from the work presented it is also clear that Ru serves to be valuable for CO mitigation even at high temperatures ($>100^\circ\text{C}$). Pt-Ru might be a possible solution to keeping active sites free for hydrogen pumping in this temperature range. However, this technique will require some research to validate the effect, to find optimal operating conditions and to quantify the extent of the alleviation of CO poisoning. It is suggested that future research should include carrying out CV scans and using an analytical method, such as gas chromatography (GC) analysis, under the same operational conditions, to try to identify the products formed from the coupling chemistries between H_2 and CO. It should, however, be taken into consideration that if the operating temperature is increased, improved reaction will result, and this may cause

immediate conversion from one chemical component to another. Therefore, GC analysis might not include all the reactions that are taking place on the Pt surface.

CHAPTER 5. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

This chapter recapitulates the experimental results obtained and main outcomes as defined by the objectives of this dissertation. A summary of the present work is presented in **Section 5.1**. The conclusions made during the experimental investigation are included in **Section 5.2**. Contributions to the current knowledge in the field of electrochemical hydrogen separation emanating from this work are presented in **Section 5.3**. The chapter concludes with **Section 5.4**, in which recommendations are made for future studies related to electrochemical hydrogen separation/purification processes.

5.1 SUMMARY

A review of open literature (**Chapter 2**) related to electrochemical hydrogen separation revealed that there are many advantages associated with this technology, especially as related to application in the low-carbon energy scenario, known as the 'hydrogen economy'. High-temperature (HT)-proton exchange membranes (PEMs), in particular, are gaining increasing attention due to their ability to overcome certain limitations associated with low-temperature (LT) operation. However, not much appears to be reported on HT electrochemical hydrogen separation involving mixtures containing various impurities. More specifically, the literature review highlighted the paucity of information on the HT electrochemical hydrogen separation of specific industrially relevant impurities, such as NH_3 and CO_2 (CO_2 was mostly studied together with CO , while NH_3 was only investigated at LT operation). Only few articles on reformat gas mixtures and HT operation were found. Moreover, the performance parameters (e.g. limiting currents, hydrogen purity, selectivities and hydrogen fluxes) of HT-PEMs under various operating conditions are largely unknown. The present work addresses these shortcomings by investigating the performance of an EHS under HT operation, using various gas mixtures, of various inlet compositions and impurities (CH_4 , CO_2 and NH_3). From the work presented it is advised to benchmark more membranes, specifically to identify membranes that have low resistance and low cross-over. Also, research should focus on minimising the catalyst load, without altering the catalyst utilisation. More research is also required to understand the mechanisms involved on the Pt surface when gas mixtures such as H_2/CO and H_2/CO_2 is used. This would allow performance optimisation and technologic evolvement in the area of electrocatalyst used for electrochemical cells. Also, various uncertainties such as the durability of this technology and the exact cost related to implementation could be addressed in order to aim at commercialisation.

5.2 CONCLUSIONS

Detailed conclusions are included at the end of preceding chapters (**Chapter 2**, **Chapter 3** and **Chapter 4**). This section only summarises the key concluding remarks of the results obtained and main outcomes related to the specific aims and objectives of this dissertation:

- This investigation successfully demonstrated the electrochemical separation of hydrogen from various gas mixtures (H_2/CH_4 ; H_2/NH_3 and H_2/CO_2) under various operational conditions (different cell operating temperature, inlet compositions, and hydrogen flow rates), making use of a laboratory-scale single-cell EHS.
- Generally, the performance of the EHS was higher temperatures. The best performance was achieved for a pure hydrogen inlet. Hydrogen was effectively recovered from H_2/CH_4 gas mixtures with 10-80% CH_4 in the inlet, yielding a hydrogen purity of >99.9%. The performance of the cell was severely influenced when CO_2 was introduced. Hydrogen purities of 98-99.5% was achieved with 10% CO_2 in the inlet and 96-99.5% when 50% CO_2 was in the inlet. In the case of hydrogen separation from H_2/NH_3 gas mixtures, NH_3 permeation (as NH_4^+) was favoured at low current densities; therefore, the hydrogen purity was lower than that of the inlet. At higher current densities, hydrogen permeation through the membrane was favoured. However, the purity of hydrogen was not greatly enhanced at higher current densities. The maximum hydrogen to ammonia ratio of the permeate was achieved at 0.1 A cm^{-2} and 140°C , where 66.92% percent of the initial ammonia was still found in the permeate stream.
- The effect of temperature had a promotional effect on the general performance of the cell, including the voltage efficiency and power efficiencies (with a few variations from this trend observed). The promotional effects were ascribed to the enhance electrode kinetics existing at higher temperatures. However, temperature had a reverse effect on the hydrogen selectivity of the membrane.
- The inlet composition influenced the overall efficacy of the system, due to the difference of partial pressures. The current efficiency was lower in the presence of impurities, although no major hydrogen flux changes were observed compared to in the case of a pure hydrogen inlet. The hydrogen selectivity increased with an increase in impurity concentration, for both CH_4 and CO_2 .
- Ammonia had adverse and irreversible effects on the membrane. The membrane was completely damaged, even by low concentrations of ammonia (ppm levels). However,

the possibility of an electrochemical ammonia pump/separator was realised, working on the same principal as the current EHS (here, the ammonia will be protonated).

- The CO tolerance of Pt/C and Pt-Ru/C was compared by means of electrochemical active surface area (ECSA) evaluations through cyclic voltammetry (CV) scans. A 2% CO (balance hydrogen) feed was used to determine the CO-stripping (COS)-based ECSA. However, no CO peaks resulted; rather, a mixture of coupling chemistries were observed between CO and H₂ on the Pt surface. The addition of Ru suppressed these coupling chemistries at temperatures $\geq 140^{\circ}\text{C}$.

The conclusion was therefore made that the integration of Ru addition to Pt and operation at HT shows promise in terms of mitigating CO poisoning effects. Pt appears to play a significant role in the coupling chemistries that exist between CO and H₂ in the presence of H₂O (H₂O originating from the 85 wt. % dilute phosphoric acid (PA)).

- ECSA evaluation of the H_{upd} peak of the CV scan performed on the Pt/C and Pt-Ru/C catalysts, showed that the ECSA is temperature dependent. The actual effect of CO on the ECSA could not be evaluated due to the absence of COS peaks. However, in the case of Pt-Ru/C the H-Pt binding sites were reactivated as the temperature was raised.

Therefore, the COS/H_{upd}-based ECSA was used to evaluate the ECSA after introducing CO to Pt-Ru/C. Lower ECSA resulted, due to CO poisoning (at lower temperatures) and particle agglomeration. Particle agglomeration was observed after heat treatment of the cell and was therefore considered to lower the available surface area of the catalyst.

5.3 CONTRIBUTION TO CURRENT KNOWLEDGE

The following were considered valuable contributions to the current knowledge in the field of electrochemical hydrogen separation—more specifically, in the field of HT electrochemical hydrogen separation.

- A single-cell electrochemical hydrogen separator was successfully designed and operated (**Chapter 3**). Its operation and the separation performance was evaluated under HT operation. The knowledge gathered during investigations into the performance of the EHS under HT, under HT, with various inlet compositions and

impurities (CH_4 , CO_2 and NH_3) offers a valuable contribution to the limited literature/available knowledge pertaining to HT EHSs

- Evaluation of the CO tolerance of both Pt/C and Pt-Ru/C, by means of CV, resulted in an important contribution to the current knowledge, specifically, discovery of the coupling chemistries that exist between CO and H_2 on the surface of Pt (**Chapter 4**). The addition of Ru to Pt appears to suppress the coupling reactions as the temperature is increased.
- The CO tolerance of an EHS can therefore be mitigated by integrating both HT operation and the bimetallic Pt-Ru catalyst approach, to alleviate CO poisoning.

5.4 RECOMMENDATIONS

Whilst this thesis proved to be useful in quantifying the general performance of a HT EHS, there is a significant research scope that still needs to be exploited before widespread commercialisation can be considered. The possible research prospects are summarised in this section:

- The durability of the membranes should be evaluated under HT conditions. Long-term operation with pure hydrogen as well as various inlet compositions should be evaluated. This could be integrated with accelerated stress testing to evaluate the overall durability of the membrane.
- Due to the limited availability of membranes and the timely nature of experiments, the reproducibility of the data was not completely validated. This is recommended for future work. Also, more benchmark tests of a variety of membranes should be conducted in the future. This is necessary for system optimisation and also to fill the literature gap regarding the operational parameters of these membranes at high temperatures.
- The simultaneous compression and separation of various inlet streams should be evaluated. This is especially applicable to H_2/CO_2 inlet streams, in order to evaluate the hydrogen separation and compression capability (storage capability) of the system, as well as the system's ability to sequester CO_2 (the retentate).
- The utilisation of multiple cells can be considered and investigated for the separation of hydrogen from H_2/CO_2 gas mixtures, in order to improve the hydrogen purity.

- A separate characterisation study should be performed on industrially simulated reformat inlet streams, specifically to evaluate the hydrogen separation capability of the EHS, based on the hydrogen quality specifications of fuel cells (FCs).
- In **Chapter 3**, the ohmic resistance was seen to play a major role in the general performance of the cell. It was also mentioned that membrane resistance should be minimised to obtain maximum performance. Therefore, it is recommended that the membrane and contact resistance, as well as the resistance originating from the electrolyte distribution, be analysed and evaluated as a separate study. The effect of the clamping pressure/torque of the bolts should be investigated to determine the optimum assembly pressure, in order to minimise the contact resistance. This study can be extended to investigating different PA doping levels (to maximise the ECSA) and the Pt loading of the anode to obtain optimal electrode functionality.
- The possibility of an electrochemical ammonia pump/separator became evident. Studies should be performed on PEMs that could facilitate the transport of ammonia, without being damaged beyond recovery. This work could lay a foundation for a whole new field in electrochemistry.
- The Brunauer, Emmett and Teller (BET)-based surface area should be determined and used to aid in the ECSA evaluation of CO-poisoned catalysts. Results could then be compared to results of the CV-based ECSA evaluations.
- To promote widespread commercialisation of PEM electrochemical cells, the amount of electrocatalyst used should be minimised, without altering the electrochemical performance. For this purposes, it is essential to not only utilise Pt efficiently in terms of a large surface area per unit mass, but also to maximise the ECSA per unit surface area of the catalyst (Morimoto *et al.*, 2011). Electrocatalyst utilisation (u) is an indicator of the latter. The author, therefore, suggests that future work should include data on electrocatalyst utilisation (u) under various operating conditions. The following equation should be used to calculate the catalyst utilisation:

$$u = \frac{ECSA_{MEA}}{ECSA_{cat}}$$

where $ECSA_{MEA}$ in m^2/g is the electrochemically active catalyst surface area in the MEA and $ECSA_{cat}$ in m^2/g is the catalyst surface area of the carbon supported catalyst powder used for the MEA. The $ECSA_{MEA}$ can be determined from the H_{upd} -charge

obtained by CV (Durst *et al.*, 2015; Gasteiger *et al.*, 2005; Li & Pickup, 2003) and the $ECSA_{cat}$ could be determined from the particle sizes obtained through TEM or XRD analysis of the powder (Durst *et al.*, 2015; Morimoto *et al.*, 2011). From TEM measurements of the catalyst the surface-averaged diameter ($\bar{d}_s$) of the catalytic particles can be determined and used together with the density (ρ) to calculate $ECSA_{cat}$:

$$ECSA_{cat} = ECSA_{TEM} = \frac{6}{\rho \bar{d}_s}$$

by assuming that:

- All particles are spherical (morphological assumption)
 - All particles are the same size and are uniformly and equally distributed (lattice structure)
 - The surface area of a single particle is smooth (nano scale)
 - The particle size distribution reflects the distribution of the entire catalyst
 - Aggregation is negligible since the contact area of the spherical particles are assumed to be strictly point like (practically no area)
 - Enough PA is present. All the metal surface sites are covered with PA and the PA is equally distributed. Therefore, the entire surface is electrochemically available.
- An extended study on the experimental results presented in **Chapter 4** should be carried out to further investigate the coupling chemistries seen between CO and H₂ on the surface of Pt. These experiments should be carried out with the same experimental conditions, with the addition of an analytic evaluation method, e.g. gas chromatography, to determine the actual surface reactions taking place. Also, the hypothesised effects highlighted in **Chapter 4** should be estimated and quantified by, for example, a visual representation of the Arrhenius effects. To do this, the exchange current densities (i_o), transfer coefficients ($\alpha_{a/c}$, representing the anodic (HOR) and cathodic (HER) transfer coefficients) and the activation energy (E_a) should be extracted. The Butler-Volmer equation can then be fitted to the current *versus* HER/HOR overpotential semi-log plots as seen in Durst *et al.* (2015). See **Eq. B.12**. Hereafter,

the activation energies, in kJ/mol, can be fitted for the i_o -values of the different metals over a set temperature range, using (Durst *et al.*, 2015):

$$\frac{\partial \log(i_o)}{\partial \log(1/T)} = \frac{E_a}{2.303R}$$

From the visual Arrhenius trend, it can then be determined whether temperature was the only effect/contributor. IV and EIS data can then be used to further analyse and determine what is happening within the cell. From the EIS data a cathode and anode effects could be identified separately, perhaps together with trends regarding membrane thickness (e.g. conductivity measurements).

- In terms of a review article, or maybe even an article that focusses on commercialisation of this technology, a reflection on the commercial value could be a welcome addition.

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Appendix A. SUPPLEMENTARY LITERATURE

This appendix serves as supplementary literature to **Chapter 1. Section A.1** serve as an introduction to the literature study presented. The working principal of an electrochemical hydrogen separator is discussed and illustrated in **Section A.2**, after which the electrochemical cell components are discussed in **Section A.3**. Lastly, this appendix is concluded with the degradation mechanism of the respective cell components discussed in **Section A.4**.

A.1 INTRODUCTION

Despite the great advances that have been made regarding proton exchange membrane fuel cell (PEM-FC) technologies, there are still several issues associated with this concept that limits their widespread commercialization (Alegre *et al.*, 2018). These limitations include the high cost (especially related to Pt-based catalysts with high Pt loadings), durability and performance degradation (Alegre *et al.*, 2018). Although degradation cannot be avoided yet, it can be minimised by understanding the cell components and degradation mechanisms (Haque *et al.*, 2017). Limited information is available on high-temperature (HT) electrochemical hydrogen separation (polybenzimidazole (PBI) membranes), compared to low-temperature (LT) separation (e.g. Nafion membranes). Therefore, in this appendix, the focus is placed on understanding PEM electrochemical hydrogen separation (especially HT PBI-based PEMs), with special attention given to the cell components used and the degradation mechanisms taking place inside these cells.

A.2 ELECTROCHEMICAL HYDROGEN SEPARATOR: PURIFICATION/SEPARATION

In principal, an electrochemical hydrogen separator (EHS) is based on the following process (**Figure A.1**). Molecular gaseous hydrogen at low pressure is injected at the anode side of the PEM electrochemical cell. When the hydrogen makes contact with the anode electrode, hydrogen is oxidized into its constituents (protons and electrons) achieved with a Pt-based catalyst (**Table A.1**). The electrons then travel through an electrical circuit, whilst the protons move through the PEM to the cathode compartment. Finally, the protons and electron reduce to H₂, at the cathode compartment (**Table A.1**). This can be carried out at high pressure to improve the specific volumetric energy density, for storage.

In the case of hydrogen purification and separation, a hydrogen-rich gas enters the anode compartment and hydrogen is selectively transferred through the PEM. This reaction does not occur spontaneously. An external voltage (DC power source) is required to drive the chemical

reaction (electrolytic mode) (Bard & Faulkner, 2001). According to literature, minimal power is required to operate the cell. The oxidation and reduction reactions of hydrogen are facile and nearly Nernstian/Faradic in their electrochemical behaviour (Benicewicz *et al.*, 2008).

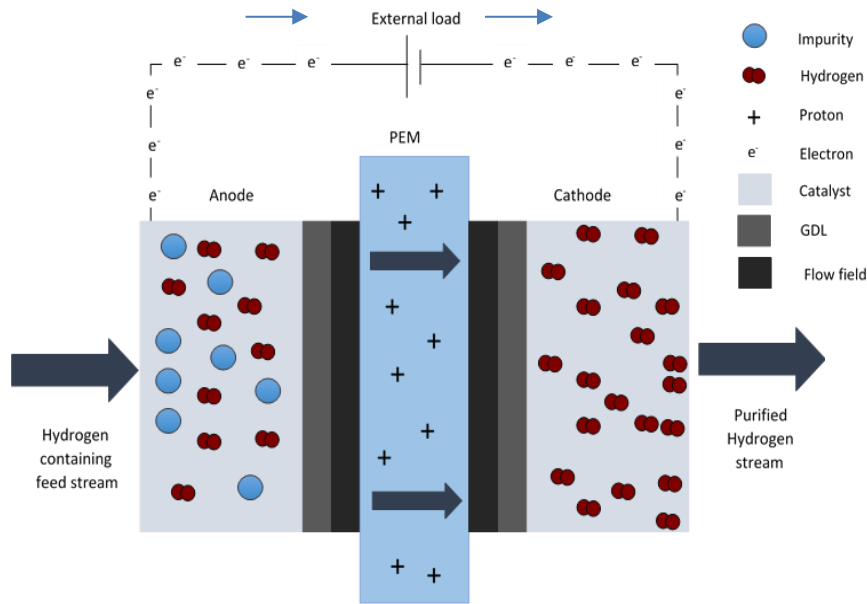


Figure A.1: Schematic of the working principal of an electrochemical hydrogen separator.

Unlike conventional membrane systems that rely on pressure or concentration differentials, the hydrogen permeation of an EHS is only dependent on the applied current as driving force. This is called the law of Faraday (**Eq. A.1**).

$$I = nF\dot{n} \quad (\text{Eq. A.1})$$

where, $\dot{n}$ depicts the flow of hydrogen, I is the current (A), n depicts the number of electrons and F is Faraday's constant ($96,485 \text{ C mol}^{-1}$). Faraday's law can also be rewritten in terms of the hydrogen mass flow rate ($\dot{m}$), which is proportional to the current (Barbir & Görgün, 2007):

$$\dot{m} = \frac{MI}{nF} \quad (\text{Eq. A.2})$$

where, M is the molecular weight in kg mol^{-1} .

Although the cell overvoltage in this process is normally quite low, high hydrogen separation efficiencies can be achieved (Gardner & Ternan, 2007). The purity of the hydrogen that is produced at the cathode side is high and highly dependent on several factors, for example: (i) the permeability of the membrane with respect to the feed gas composition; (ii) the integrity of

the membrane; and (iii), in the case of LT gas separation (<100°C), when Nafion is used, the water content of the membrane (Benicewicz *et al.*, 2008).

Table A.1: Hydrogen pump half-cell reactions

HALF CELL REACTIONS OF A HYDROGEN PUMP	
Anode reaction	$H_2 \rightarrow 2H^+ + 2e^-$
Cathode reaction	$2H^+ + 2e^- \rightarrow H_2$
Overall reaction	$H_2(\text{Anode}) \rightarrow H_2(\text{Cathode})$

A.3 ELECTROCHEMICAL CELL COMPONENTS

A.3.1 MEMBRANE ELECTRODE ASSEMBLY AND GAS DIFFUSION ELECTRODES

MEAs are the core components of electrochemical cells such as FCs and electrolyzers (Ha *et al.*, 2015; Manomayidhikarn *et al.*, 2007; Omrani & Shabani, 2017). MEAs consist of a PEM with a catalyst layer (CL) and gas diffusion layer (GDL) on both sides (Cindrella *et al.*, 2009), covered gaskets and back plates, which is compressed to prevent gas leakage and to obtain low contact resistance (**Figure A.2**) (Ha *et al.*, 2015; Omrani & Shabani, 2017).

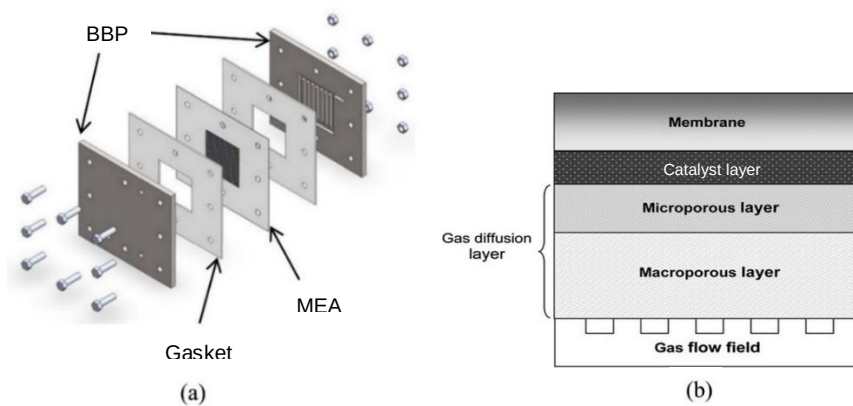


Figure A.2: Schematic illustration of: (a) exploded view of a single electrochemical cell (Omrani & Shabani, 2017); (b) basic structure of electrochemical cell electrode (dual-layer GDL) (Belhadj *et al.*, 2016; Ha *et al.*, 2015; Haque *et al.*, 2017 and Lee *et al.*, 2012).

A.3.2 ELECTRODES: GAS DIFFUSION LAYER AND ELECTROCATALYST

An electrochemical cell electrode essentially consists of a GDL and a CL/active layer (Haque *et al.*, 2017; Ihm *et al.*, 2004). The GDL, known to be a highly porous medium (Ihm *et al.*, 2004; Omrani & Shabani, 2017), has as primary function the effective distribution/transportation of the reactant gas from/to the flow fields (FFs) towards/from the CL (Cindrella *et al.*, 2009; Ha

et al., 2015; Heo *et al.*, 2017; Hussain *et al.*, 2017; Lee *et al.*, 2012; Omrani & Shabani, 2017). The GDL further serves to provide electron flow pathways and heat transfer between the FFs and the CL on the PEM to maintain the desired temperature (Omrani & Shabani, 2017) and provide physical support for the membrane and CL (Hussain *et al.*, 2017). The key factors that dictate the GDL performance include the thickness, porosity and permeability (Cindrella *et al.*, 2009). A GDL typically consist of a twofold layered structure, the macroporous substrate (MPS), also known as the gas diffusion backing (Belhadj *et al.*, 2016; Haque *et al.*, 2017) and the microporous layer (MPL) (Ha *et al.*, 2015) (see **Figure A.2 (b)**). The MPS is regarded as the core of the GDL. It is usually constructed of carbon fibre substrate (e.g. carbon paper or carbon cloth) or carbon nanotubes (Ha *et al.*, 2015; Omrani & Shabani, 2017) due to their high porosity and electric conductivity (Heo *et al.*, 2017). The substrate, which is in contact with the FFs or back plates, serves as the gas distributor and current collector (Ha *et al.*, 2015; Lee *et al.*, 2012; Omrani & Shabani, 2017). The second layer (microporous layer) consist of a carbon powder (carbon black) and a hydrophobic/hydrophilic agent (Ha *et al.*, 2015; Heo *et al.*, 2017; Lee *et al.*, 2012).

The electrocatalysts for both the anode and the cathode are crucial elements as they serve as electrochemical reaction sites (Haque *et al.*, 2017). This is known as the three-phase interface, where the catalyst comes into contact with both the membrane and the reaction gas (Ihm *et al.*, 2004; Lee & Hwang, 2008). PEM-FC catalysts can be divided into three categories: (i) Pt-based catalysts, (ii) Pt-modified catalysts (combined with other metals such as Cr, Cu, Co or Ru), and (iii) non-Pt-based catalysts (e.g. non-noble metal or organometallic catalysts) (Haque *et al.*, 2017). Typical electrocatalyst construction materials are noble metals, especially Pt (Ihm *et al.*, 2004), Ir, Pd or Ru (Ahn *et al.*, 2014). The catalysts that are usually used vary from single metal catalyst such as Pt/C or Ir/C, to binary catalysts—especially platinum and its alloys (Pt-Ru, Pt-Co, Pt-Cr, Pt-Ru/C or Pt-Mo/C)—then to tertiary catalyst such as Pt-Ru-Mo/C, Pt-Ru-Co, Pt-Co-Cr and combinations of Pt with Fe, Co, Cu and Ni (Adroher *et al.*, 2011; Araya *et al.*, 2016; Haque *et al.*, 2017; Ihm *et al.*, 2004). Although the focus of current research is largely on an alternative catalyst, platinum (Pt, Pt/C or Pt-based materials) is still the most preferred electrocatalyst due to its effectiveness, high chemical stability and large current density (Adroher *et al.*, 2011; Haque *et al.*, 2017).

However, despite its advantages, Pt exhibits some severe disadvantages, including its costly nature and limited resources, and the fact that it is easily poisoned (Haque *et al.*, 2017; Ihm *et al.*, 2004). The Pt catalyst in the anode can be severely deactivated when H₂/CO₂ gas mixtures are fed to the EHS (especially with Nafion membranes). The Pt surface becomes poisoned by

the CO generated from the reverse water–gas shift (WGS) reaction of CO₂ and adsorbed H₂ (Ahn *et al.*, 2014). Pt catalysts are known to be poisoned by small amounts of CO, whereas Ar, N₂ and CH₄ only act as diluents (Ahn *et al.*, 2014). CO poisoning of the catalyst occurs when CO covers the active sites of the catalyst (reducing the ECSA). It adsorbs onto the carbon matrix, followed by a reduction in the rate of hydrogen adsorption onto the electrode surface (Haque *et al.*, 2017).

Pt-alloys are used in efforts to reduce the Pt content of the catalyst whilst minimising effect on the catalytic performance (Haque *et al.*, 2017). It has been reported that the use of bimetallic alloys with Pt can enhance the performance of an electrochemical cell as the size of the active catalyst site is increased (Haque *et al.*, 2017). To minimise CO poisoning, bifunctional Pt-alloy catalysts such as Pt-Ru have been developed and utilised (Araya *et al.*, 2016; Orhan & Sharaf, 2014). Gardner & Ternan (2007) reported that CO poisoning can also be alleviated by periodic pulsing. As noble metals are mainly used for the electrocatalysts, associated costs are very high. To reduce costs whilst still maintaining efficiency, the noble metals are deposited onto carbon particles (Ihm *et al.*, 2004). Carbon-supported Pt (Pt/C) nanoparticles have been widely used as electrocatalysts for hydrogen compression and separation from various gas mixtures (Ahn *et al.*, 2014).

Great progress in cell performance enhancement is achieved by the following:

- Reducing the catalyst loading (Hwang & Lee, 2008; Ihm *et al.*, 2004) (typical loadings of 0.01-5 mg cm⁻², depending on the electrode layer thickness) (Haque *et al.*, 2017)
- using platinum supported on carbon (high surface area) as an electrocatalyst rather than pure platinum black
- impregnating a GDE CL with a proton conductor (Nafion ionomer), to increase the three-dimensional reaction zone of catalytic activity (Hwang & Lee, 2008)
- depositing platinum (thin layer) on the front side of the electrode
- utilising thinner membranes
- adopting alternative electrode preparation procedures, such as spraying, rolling and screen printing, and
- depositing a thin layer of electrocatalyst and proton conductor (Nafion ionomer) on an uncatalysed electrode or on a proton conducting membrane (Ihm *et al.*, 2004).

A.3.3 PROTON EXCHANGE MEMBRANES

The key functions of the PEM include; (i) transporting the protons, (ii) preventing electron transportation, and (iii) acting as separator of the electrodes (Dafalla & Jiang, 2018). Numerous PEMs are commercially available, including various perfluorosulfonic acid (PFSA) types (e.g. Nafion), as well as PBI membranes and membranes of PBI derivatives. Essential properties of a PEM include the following: (i) stability, as conditions are highly oxidative and reductive (Pan *et al.*, 2007); (ii) high proton conductivity; and (iii) excellent mechanical stability (Millet *et al.*, 2009).

(a) Low-temperature PFSA membranes

PFSA ionomers are commonly used in PEM-FCs due to their high proton conductivity, mechanical integrity and chemical stability (Benicewicz *et al.*, 2008). Properties such as chemical stability and thermal stability are attributed to the presence of fluorine atoms in the main chain of these polymers (Bessarabov, 2019). See **Figure A.3**.

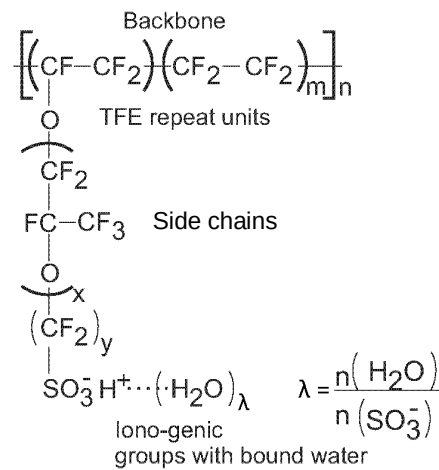


Figure A.3: General chemical structure of common PFSA ionomers (Bessarabov, 2019).

The mechanical properties of the PFSA membrane are directly related to the water uptake; as the degree of hydration strongly influences the mechanical and physical properties (Benicewicz *et al.*, 2008). The proton conductivity is substantially enhanced by membrane hydration (Benicewicz *et al.*, 2008). Furthermore, swelling-induced stresses results from water adsorption of a partially constrained membrane during FC operation (Cleghorn *et al.*, 2010). A major disadvantage is poisoning of the catalyst when small amounts of CO (10-1000 ppm) are present (Benicewicz *et al.*, 2008; Chen *et al.*, 2014), resulting in a significant performance drop of the electrochemical cell (Chen *et al.*, 2014). CO does not only bind to the vacant Pt sites, but also to Pt-H sites (**Eq. A.6**) (Chen *et al.*, 2014). CO-Pt bindings are stronger than Pt-

H, therefore CO-Pt bindings act as a barrier for Pt-H binding (Chen *et al.*, 2014). The mechanism for CO poisoning is illustrated in **Eqs A.3- Eq. A.6** (Gardner & Ternan, 2007; Chen *et al.*, 2014):



where S represents a catalytic site on the electrode.

These elementary reactions show that CO competes with hydrogen for the active sites on the platinum surface. According to Garner & Ternan (2007), about 98% of the active Pt sites are blocked if the gas mixture contains 1% CO at 25°C (Garner & Ternan, 2007). The adsorbed CO can also be removed by increasing the anode potential to approximately 700 mV vs RHE. At this potential the CO reacts with hydroxyl species (formed on the Pt surface) to form CO₂ (**Eq. A.7** and **Eq. A.8**) (Gardner & Ternan, 2007):



Currently, many methods exist to enhance CO tolerance of Pt-based catalyst, including the following: (i) increasing operating temperature, (ii) introducing the air-bleeding method, and (iii) making use of bimetallic catalysts (Araya *et al.*, 2016; Chen *et al.*, 2014). Periodic pulsing has also been shown to alleviate CO poisoning (Gardner & Ternan, 2007). The air-bleeding method is, however, not seen as a very reliable method (Chen *et al.*, 2014). This method entails the introduction of a low concentration of oxidant (e.g. air or hydrogen peroxide) to the H₂ stream, which then counteracts CO poisoning by selective oxidation of CO (especially in the case of LT-PEM-FC) (Araya *et al.*, 2016).

To enhance the CO tolerance, bimetallic catalysts are commonly used, together with Nafion membranes, in particular, Pt-Ru as Ru is known to increase CO tolerance (Bessarabov & Tokarev, 2014). There are two general explanations for this phenomenon: (i) Ru weakens the Pt-CO binding whilst strong binding of Ru-CO occurs; (ii) Ru atoms adsorb oxygen-containing species, which oxidise CO to CO₂ (Bessarabov & Tokarev, 2014). However, operation of the anode of an electrochemical separation cell or a FC at a potential that is high enough to oxidise

CO to CO₂ results in substantial losses of cell efficiency (Gardner & Ternan, 2007). Furthermore, bimetallic metals are known to raise the cost of the MEA (Chen *et al.*, 2014).

(b) High-temperature PBI membranes

Operation at elevated temperatures (>100°C) requires thermally and chemically stable membrane. PBI PEMs doped with PA have attracted great attention because of their high operating temperatures, ranging between 100 and 200°C (Benicewicz *et al.*, 2008). In addition to their high CO and CO₂ tolerance (Ahn *et al.*, 2013; Benicewicz *et al.*, 2008), HT PBI membranes are also associated with faster electrode kinetics, as seen with HT-PEM-FCs (Ahn *et al.*, 2013; Benicewicz *et al.*, 2008). Moreover, PBI membranes doped with PA exhibit good proton conductivity, thermal stability, low gas permeability and negligible electro-osmotic drag at elevated temperatures (100-200°C), without humidification of the feed gas (Ahn *et al.*, 2013; Araya *et al.*, 2016; Chippar *et al.*, 2014).

Despite the numerous advantages that PBI membranes offer, the issue of durability still remains a major problem. It has been reported that catalyst degradation and the evaporation of PA are the main causes of cell degradation (Araya *et al.*, 2016). Studies have revealed that cracks in the PBI membranes, after long operating hours, alter the performance of the entire system. This is because these cracks lead to gas crossover from the anode to the cathode, which further degrades the performance of the cell. Gas crossover is an indication of degradation of the membrane (Araya *et al.*, 2016).

Table A.2: Comparison between LT-PEM-FC and HT-PEM-FC (adapted from Haque *et al.*, 2017)

	LT-PEM-FC	HT-PEM-FC
Electrolyte/membrane	PFSA-based	PBI-based polymer
Electrode	Carbon support Pt catalyst and/or Pt-alloys	Carbon support Pt catalyst and/or Pt-alloys
Pt loading [mg cm⁻²]	0.2-0.5	1.0-2.0
Cell operating temperature [°C]	70-80	120-180
Efficiency [%]	40	45-50
Operating pressure [bar]	Ambient pressure	Ambient pressure
Proton transport medium	Water (humidification pre-treatment)	Inorganic acids
CO tolerance	<50 ppm	1-3 vol. %
Other impurity tolerance	Low	Higher
Water management	Complex	None
Heat management	Complex	None
Electrode kinetics	Low	High

HT-PEM-FCs offer several advantages over LT PFSA PEM-FCs (**Table A.2**). These advantages include: fast electrode kinetics, enhanced mass transport, simple water and thermal management, higher CO tolerance at the elevated temperatures, and better sustainability (Alegre *et al.*, 2018; Benicewicz, *et al.*, 2008; Chippar *et al.*, 2014; Kim *et al.*, 2015;). Furthermore, reduced cost is also associated with PBI membranes (they are known to be cheaper than Nafion-based membranes) and operation at higher temperatures presents the possibility of using alternative noble metal catalysts, such as iron and cobalt (Haque *et al.*, 2017).

A.3.4 BACK PLATES

Bipolar back plates (BBPs) are responsible for three functions: (i) mechanical support for the MEA, (ii) conduction of the current and (ii) removal of heat from the active area (Abdollahzadeh *et al.*, 2018). The properties of BBPs that influence the performance of the electrochemical cell include, primarily, the corrosion and contact resistance (Alegre *et al.*, 2018).

The application of the cell dictates the construction material of the back plates. Common construction materials of BBPs mainly include the following: carbon-based compounds (e.g. graphite and carbon composites), and metals and metallic alloys (e.g. stainless steel, aluminium and titanium, among others) (Alegre *et al.*, 2018). Metallic plates should however should be coated to increase their resistance to corrosion (Alegre *et al.*, 2018). In cases where PBI membranes are used, special care should be taken in terms of corrosion because PA is present (Alegre *et al.*, 2018). It has been proven that graphite become porous in HT operation, consequently allowing more a higher uptake of electrolyte (PA), which results in faster degradation of the MEA due to redistribution of the acid (Alegre *et al.*, 2018). The use of metallic plates is a promising alternative to graphite plates as they minimise the effects of PA uptake, and also reduce the cost and total weight of the cell/stack (Alegre *et al.*, 2018). Aluminium is a lightweight and inexpensive metal that has been widely used in LT-PEM-FC application.

A.3.5 FLOW FIELDS

The flow channel design in the BBP influences the mass, heat and current transport in a complex manner (Abdollahzadeh *et al.*, 2017). Serpentine FF designs are known to have very poor performance due to disadvantages such as clogged FFs, linear flow and pressure drops that can occur over the inlet to the outlet (Hoek, 2013). The parallel design is the simplest design; it comprises a number of distinct parallel flow channels linked to the gas inlet and outlet (Abdollahzadeh *et al.*, 2018).

A.3.6 GASKETS

Similar to the bipolar plates, gaskets are multifunctional—they therefore have to fulfil multiple requirements, for example: (i) prevent leakage of gases, (ii) to compensate for dimensional changes during temperature variations, (iii) provide electrical insulation, to prevent a shortage occurring within the cell, and (iii) sufficient assembly torque should be applied to minimise the contact resistance between components (e.g. back plates and the GDLs) (Araya *et al.*, 2016). Gaskets should be able to withstand an acid environment, originating from the PA, at temperatures $\leq 200^{\circ}\text{C}$. Chemical stability is also a critical prerequisite to take into account as the gaskets are exposed to hot PA (Araya *et al.*, 2016). Typical gaskets materials that have proven to be satisfactory in the fulfilment of the gaskets' requirements include silicon rubber, perfluoroelastomer, tetrafluoroethylenepropylene, ethylene propylene rubber and fluorocarbon (Araya *et al.*, 2016). PTFE gaskets are commonly used for HT operation due to their ability to provide gas tightness with good chemical stability (Araya *et al.*, 2016).

A.4 DEGRADATION MECHANISMS

Over the past two decades, the degradation of FC components has been widely investigated (Behadj *et al.*, 2016) and findings used as a basis to arrive at a better understanding of the component degradation mechanisms. The information available (from various literature sources) was used to construct a degradation mechanism chart (**Figure A.4**) (the HT-FC degradation chart provided by Araya *et al.* (2016) was used as a basis). The performance of an electrochemical cell is known to decrease from the beginning of its lifetime (Haque *et al.*, 2007) and is severely influenced by parameters such as feed flow rate, and operating pressure and temperature (Benli & Taymaz, 2010). The lifespan of FCs is affected by many factors, including mainly the operating conditions and component degradation (Dafalla & Jiang, 2018). Although no moving parts are present in the cell, several degradation mechanisms tend to shorten the lifespan (Dafalla & Jiang, 2018). Rapid changes in operation (e.g. changes in the load cycle, /shutdown cycles and high power operation) are known to severely harm the lifespan of an electrochemical cell (Haque *et al.*, 2017). Durability degradation is primarily caused by the failure of components, the membrane thinning/deforming, pinhole formation in the membrane, catalyst support corrosion, or non-homogenous catalyst dilution and acid leaching (HT membranes), or, through unstable operating parameters including insufficient reactant supply and impurities inside the feed stream, pressure, high operating temperatures and transient loading (Haque *et al.*, 2017).

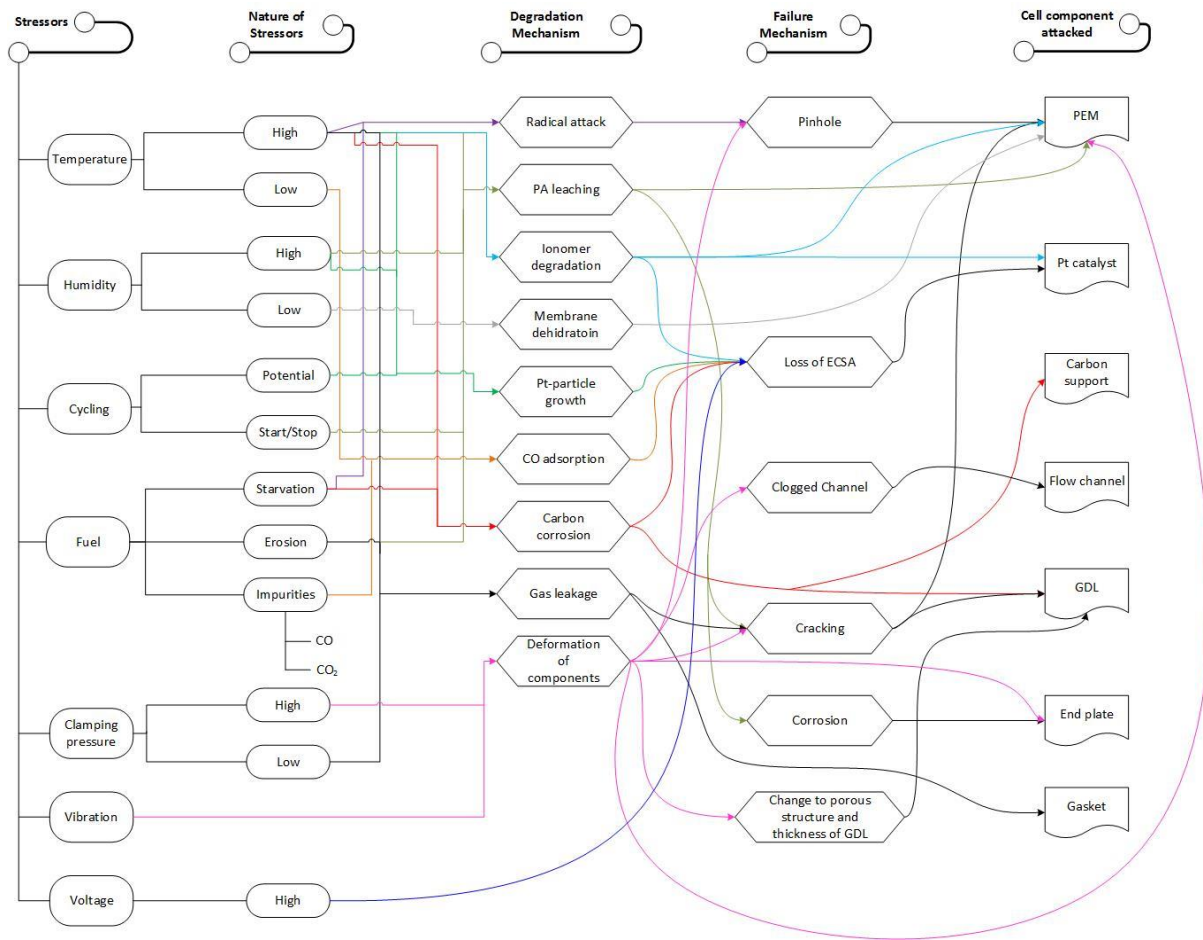


Figure A.4: HT electrochemical cell degradation flowchart (adapted from Alegre *et al.*, 2018; Araya *et al.*, 2016; Benli & Taymaz, 2010; Ha *et al.*, 2015; Hu *et al.*, 2009).

Degradation of an electrochemical cell often originates in the GDL, Pt catalyst and the CL, carbon support, membranes and the bipolar plates (Haque *et al.*, 2017). The most often discussed topics (related to degradation mechanisms) include the degradation of components such as the ionomer material forming the membrane and the CL (i.e. Pt particles and their carbon support) (Belhadj *et al.*, 2016).

Degradation processes are sub-divided into three categories: (i) baseline degradation due to long-term application, which is unavoidable and irreversible; (ii) degradation due to experimental repetition and operating conditions; and (iii) degradation due to adverse operating conditions, such as insufficient fuel supply (Haque *et al.*, 2017). Various degradation effects are discussed in the next five subsections.

A.4.1 INSUFFICIENT FUEL SUPPLY

An insufficient supply of fuel can be attributed to either gas starvation or excess gas supply, which may erode some of the cell components (Araya *et al.*, 2016). Overall gas starvation may

be caused by factors such as uneven gas distribution, faulty gas supply system/control, and a sudden increase in the current load (Araya *et al.*, 2016).

A.4.2 COMPRESSION EFFECTS

Several stress sources can contribute to MEA damage, the first of which is the initial stresses that occur during the assembly phase of the cell (Dafalla & Jiang, 2018). Bolt assembly was introduced as an effort to optimise the cell assembly procedure (Dafalla & Jiang, 2018). In the assembly phase, a pressure should be applied to the cell components to ensure stability when operating the cell (Benli & Taymaz, 2010). The applied pressure influences the membrane, GDL, the CL/GDL interface (Dafalla & Jiang, 2018; Ha *et al.*, 2015) and the bipolar plate interface itself—consequently affecting the cell performance (Benli & Taymaz, 2010; Dafalla & Jiang, 2018; Ha *et al.*, 2015). During operation, the membrane is compressed by the BBPs and can undergo deformation, such as membrane creep and microcrack fracture (Araya *et al.*, 2016). Membrane deformation can cause membrane thinning, which in turn can lead to pinhole creation and membrane deterioration (Araya *et al.*, 2016). Compression effects can be reversible—each component returning to its pristine thickness when the pressure is released—if the compression is of minor intensity (Belhadj *et al.*, 2016). However, this is unlikely; in most cases (as observed by hysteresis in pressure cycles) the deformation of the cell components, in particular the GDL, is irreversible (Belhadj *et al.*, 2016).

A.4.3 GAS DIFFUSION LAYER DEGRADATION

Although carbon paper is widely used as a GDL construction material, there are several drawbacks associated with it, in addition to the cost (Hussain *et al.*, 2017). Due to the material characteristics of the GDL, the core abilities (hydrophobicity, conductivity and mechanical strength) of the GDL decreases during operation (Ha *et al.*, 2015). This material exhibits a poorly controlled variation in porosity, resulting in a random microstructure. This random structure results in typical intrinsic variation in local physical properties, leading to severe performance variations (Hussain *et al.*, 2017). It is also well known that the surface of MPL-coated GDLs contains numerous cracks (Heo *et al.*, 2017). Because these cracks exhibit a non-uniform nature regarding location, pore width and length, it is very difficult to quantify the effect on mass transport through the GDL (Heo *et al.*, 2017). Depending on the stress applied to the GDL, several types of damage result, e.g. loss of porosity and permeability (Hussain *et al.*, 2017), carbon fibre breakage, delamination of layers, dissolution of carbon materials and surface oxidation of carbon components (Belhadj *et al.*, 2016).

The degradation of GDLs is often characterised as being either mechanical or chemical (Belhadj *et al.*, 2016; Ha *et al.*, 2015; Haque *et al.*, 2017). The former is a physical damage that comprises mechanical breakdown caused by compression, erosion due to gas circulation at high velocity, and the effects of freeze-thaw conditions (Belhadj *et al.*, 2016; Ha *et al.*, 2015). Continuous gas flow can contribute to mechanical degradation of the GDL (Ha *et al.*, 2015). The latter mainly comprises degradation of the GDL constituents or the chemical dissolution upon soaking in liquid solutions (Belhadj *et al.*, 2016). Chemical degradation of a GDL mainly consists of carbon corrosion (Ha *et al.*, 2015), where the GDL constructed of carbon reacts with water inside the FC. In special cases, including startup/shutdown cycles and fuel starvation, this would lead to structural damage (Ha *et al.*, 2015). As the GDL has a structure of randomly oriented carbon fibres, and is the most porous component in an electrochemical cell, the GDL is more prone to global and localised deformation, i.e. shrinking under the clamping pressure applied to mount the cell (Belhadj *et al.*, 2016; Dafalla & Jiang, 2018; Ha *et al.*, 2015; Hu *et al.*, 2009; Hussain *et al.*, 2017).

Most of the critical material parameters of a GDL are influenced by the compression behaviour of the GDL, such as thermal and electrical conductivities, permeability, and diffusivity (Belhadj *et al.* 2016; Dafalla & Jiang, 2018). When the GDL is compressed by the applied pressure to the back plates, the GDL protrudes into the cavities of the FF channels (**Figure A.5**) (Hu *et al.*, 2009). A high assembly pressure could therefore cause damage to the porous structure and affect the thickness of the GDL, leading to changes in the mass, and heat and charge transfer properties of the cell (Benli & Taymaz, 2010; Hu *et al.*, 2009).

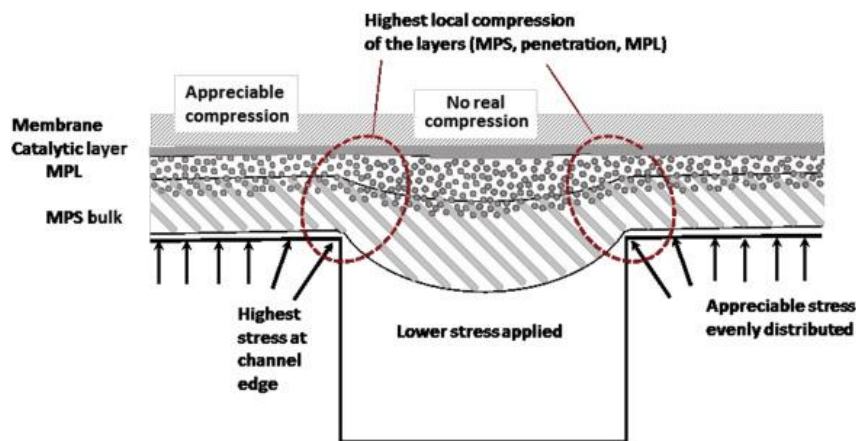


Figure A.5: Localised compression of GDL caused by flow channel (for simplicity, only one channel is indicated) (Belhadj *et al.*, 2016).

When the pressure is too high, the cell components (BBPs, GDLs, PEM, and CL) may be deformed (Benli & Taymaz, 2010; Hu *et al.*, 2009). Compressive deformation has implications

on the durability of the GDL and MEA components (Hussain *et al.*, 2017). Over-compression of the GDL elevates the mechanical stresses within the FC, which may result in damage to the GDL and uneven distribution of the contact pressure, subsequently influencing the overall cell performance and structure (Dafalla & Jiang, 2018). Adequate assembly pressure can increase the GDLs overall electrical conductivity and improve the contact resistance between the GDLs and the bipolar plates, leading to reduced electrical resistance inside the cell (Hu *et al.*, 2009; Belhadj *et al.*, 2016). However, if the pressure is too low, then gas leakage and higher contact resistance could occur, leading to performance loss (Benli & Taymaz, 2010). Low compression will result in higher diffusion overpotentials and lower limiting current densities (Belhadj *et al.*, 2016).

Metal-based GDLs are considered as an alternative to carbon-paper-based GDLs. Hence, they are currently being investigated, in an attempt to alleviate some of the limitations associated with GDLs (Hussain *et al.*, 2017). Metal-based GDLs are associated with superior performance, especially when considering the high current density region (Hussain *et al.*, 2017). The metal-based GDLs offer a non-compressibility property, which eliminates the reduction of the porosity effect of carbon-based GDLs. The same property (non-compressibility) leads to negative effects, including cell leakage issues, due to sealing issues, and the inability of the non-compressible GDL to deal with issues such as thermal expansion. This has the potential to damage the internal MEA components (e.g. the membrane) (Hussain *et al.*, 2017).

Additional mechanical stresses, when the cell is operated, contribute severely to the lifetime limitations of MEAs (Dafalla & Jiang, 2018). The durability of the MEA is greatly dependent on cell potential, humidity, temperature, feed gas contaminants and the stability of the carbon support; durability is mainly influenced by the catalyst and carbon support (Ha *et al.*, 2015).

A.4.4 CATALYST DEGRADATION

The CL degradation severely impact the lifespan of the cell (Dafalla & Jiang, 2018); it can be accelerated by dynamic operating conditions, such as load cycles, thermal cycles, and startup/shutdown cycles (Araya *et al.*, 2016). The CL suffers much more from high potential accelerated stress tests than the GDL does (Belhadj *et al.*, 2016). The extent of degradation can be determined from the polarisation curve variations, from the reduction in limiting current density reached by the FC or by the decay of the ECSA (Belhadj *et al.*, 2016). The degradation of the catalyst/CL includes catalyst contamination through fuel impurities, losses in activity due to the sintering process, catalyst maturation, loss of catalyst transfer, carbon corrosion, catalyst migration to the carbon substrate, catalyst dissolution to the membrane, electrolyte

and interface degradation, and a decrease in ECSA due to catalyst agglomeration (Haque *et al.*, 2017), which consequently leads to lower performance (Ha *et al.*, 2015).

During long-term operation, the nanoscale Pt particles tend to undergo a slow increase in diameter (Araya *et al.*, 2016). Pt ions form, followed by re-deposition on the existing Pt particles, leading to larger diameter particle formation which result in a decrease in the available active area (Araya *et al.*, 2016). The dissolved particles might migrate to other MEA components not accessible to the reactant gas (Araya *et al.*, 2016). This dissolution, migration and reprecipitation process which leads to Pt particle growth is known as Ostwald ripening (Araya *et al.*, 2016). Likewise, an increase in Pt particle growth could also occur when adjacent Pt particles sinter to form bigger particles—known as Pt agglomeration. This process is more rapid when the Pt particles are smaller, due to higher Gibbs free energy values (Araya *et al.*, 2016).

Therefore, the catalyst degradation is responsible for performance decay mainly in the early stages of the cells' lifespan. The Pt particles are then still small in diameter and properly distributed on the carbon support surface (CSS). As the particle size increase, the performance decay is not so extreme, which clarifies the lower deterioration rate experienced at advanced stages of the cells' lifecycle (Araya *et al.*, 2016). Successively, the ECSA of the electrodes decrease (Araya *et al.*, 2016).

Pt or Pt-alloys, or carbon, are widely used in both HT and LT applications (Araya *et al.*, 2016). The degradation mechanism associated with Pt in HT operation is similar to that in LT. Despite the numerous competitive advantages that HT-PEM-FCs offer, several challenges still remain, including thermal, mechanical and electrochemical fluctuations which can cause the cell to become severely degraded during start and stop procedures, due to their high operating temperatures. HT operation introduces more challenges to the operation of conventional PEM cells. In addition to the corrosion of Pt particles and a decrease in the thickness of the CL, HT operation may cause: exacerbation of the mechanisms mentioned above (especially severe Pt dissolution and aggravated carbon corrosion), as well as of acid leaching as a more acidic and higher operating temperature environment is created (Araya *et al.*, 2016; Haque *et al.*, 2017). At elevated temperatures, a faster increase in Pt particles size and decrease in ECSA is experienced, which leads to a higher performance deterioration rate (Araya *et al.*, 2016). Therefore, the electrocatalyst of HT MEAs are subject to greater challenges compared to LT MEAs. Furthermore, the kinetics of Pt dissolution, migration, agglomeration and carbon corrosion is enhanced by the higher temperatures resulting in accelerated degradation of the CL (Araya *et al.*, 2016). Pt particle attachment on the CSS is weakened by high operating

temperatures, leading to more Pt particle detachment from the CSS (Araya *et al.*, 2016). Furthermore, the adsorption of CO on the Pt particles is highly dependent on temperature and the catalyst can be easily poisoned when the cell operation ceases (Lee *et al.*, 2006).

Performance decay of HT PA-doped PBI membranes can mainly be ascribed to two key factors: (i) reduction in the ECSA of the catalyst (caused by catalyst poisoning, agglomeration of metallic particles and carbon corrosion) and (ii) PA migration/leaching (Alegre *et al.*, 2018). Contamination in the reformat can cause performance loss and degradation. The reformat gas generated from steam reforming almost always contains 20 vol. % CO₂ as by-product. When the reformat stream is used as a feed stream to an electrochemical cell, the CO₂ is responsible for a reduced H₂ partial pressure (Araya *et al.*, 2016). Moreover, CO₂ can form CO by obeying the reverse water-gas shift (WGS) reaction:



The overall effect of impurities on the performance of a HT-PEM-FC can be summarised as follows: preferential adsorption on the catalyst surface; decomposition into CO or other by-products, which adsorb onto the catalyst surface; and dilution of reactant gases (Araya *et al.*, 2016). More specifically, the main contaminants causing performance decay are known to be CO₂ and CO. The main mechanism of CO poisoning in HT-PEM-FCs includes its strong affinity to adsorb onto the Pt catalyst surface, leading to catalyst deactivation—there will be a decrease in the catalytic sites available for H₂ adsorption (Araya *et al.*, 2016). Due to the exothermic nature of the process, HT can effectively alleviate the adsorption of CO on the catalytic sites—thus higher tolerance towards impurities can be observed during HT operation compared to LT (Araya *et al.*, 2016). However, the presence of CO, in low percentage concentration (by volume), could result in severe performance decay of the cell (Araya *et al.*, 2016). Furthermore, increasing the operating temperature could cause degradation of other cell components, which may result in a shorter lifespan of the cell (Araya *et al.*, 2016).

Further research on the optimal temperature range which accounts for both CO tolerance and durability is required (Araya *et al.*, 2016). Elevated temperatures, together with high relative humidity (RH), can influence the PEM cell polarisation losses in numerous ways, including: the catalyst activity, membrane electrical and mechanical properties, and gas transport (Hu *et al.*, 2009). As the RH increases, the membrane absorbs water, resulting in swelling of the membrane, hence increasing pressure to the electrodes. This results in further GDL deformation/compression, and protrusion of the GDL into the flow channels increases (Hu *et al.*, 2009).

A.4.5 MEMBRANE DEGRADATION

It is highly unlikely that a PBI membrane will experience significant thermal damage. TGA has shown that no substantial weight loss occurs between 150-500°C (Araya *et al.*, 2016). Pristine PBI is known to have good mechanical strength, with a tensile strength range 60-70 MPa when dry and 100-160 MPa when it is saturated with water (Araya *et al.*, 2016). However, when PBI membranes are doped with PA to achieve acceptable proton conductivity, the backbones of the polymer may become disconnected by the free acid, and result in a severe decrease in the mechanical strength, particularly when operated at HT (Araya *et al.*, 2016).

Therefore, the PA doping level should be carefully considered, taking into account the mechanical strength and the proton conductivity (Araya *et al.*, 2016). In a PA-doped PBI membrane, only two acid molecules directly interact with the basic pyridinic nitrogen of PBI (**Figure A.6**). This means that when the acid doping level is >2, free mobile acids are present. Their mobility causes difficulty, specifically, in ensuring that they are fixed to the membranes or electrodes. This can lead to migration of the free mobile acids to the CL and/or other components of the cell, or even out of the cell—causing an inevitable decrease in performance (Araya *et al.*, 2016). It has been reported that the PA leaching rate is enhanced by high operating temperatures and current densities (Benicewicz *et al.*, 2008). The loss of PA causes a decrease in the ionic conductivity of the membrane and brings about a malfunctioning cell (Alegre *et al.*, 2018). This can cause degradation of additional cell components, e.g. the BBPs (Alegre *et al.*, 2018).

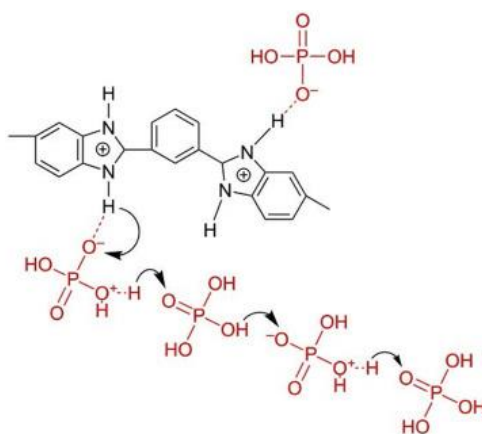


Figure A.6: Interaction between PBI and PA (Araya *et al.*, 2016).

The mechanism for PA loss, which has a negative effect in a HT-PEM cell, can be summarised as follows: (i) removal of surplus PA at the initial stages of the membrane's lifespan, (ii) PA migration originating from load cycling, (iii) squeezing out PA due to compression, (iv) acid

uptake by the FFs, and (V) the dilution effect caused by high RH (Araya *et al.*, 2016). Membrane dehydration is expected to be less common in HT-PEM than in LT-PEM cells (Araya *et al.*, 2016). Membrane dehydration seriously affects the durability of the cell—this can become quite severe at the end of the cell's life (Araya *et al.*, 2016). The PA in a HT-PEM-FC membrane, when it is operated at typical operating temperatures (140-180°C), is prone to gradually dehydrate to form polyphosphoric acid, which results in a continuous decrease in proton conductivity (Araya *et al.*, 2016). Sources of degradation of PA-doped PBI membranes include chemical oxidative degradation, mechanical degradation and thermal stress (Araya *et al.*, 2016).

Appendix B. THEORETICAL AND EXPERIMENTAL BACKGROUND

This appendix provides the theoretical and experimental background needed to understand the functionality of an electrochemical cell (e.g. Fuel cells (FCs) and electrochemical hydrogen separators (EHS)). **Section B.1** gives some theoretical background, and fundamental equations pertaining to electrochemical cells. This is followed by experimental background presented in **Section B.2**.

B.1 THEORETICAL BACKGROUND

The Nernst equation is a useful tool to understand the thermodynamic aspects of electrochemical cells, whilst the Butler-Volmer equation is useful to understand the reaction rates of the electrochemical reactions. The overpotential is a term used to describe the thermodynamic potential of electrochemical cells.

B.1.1 NERNST EQUATION

At equilibrium, the Nernst equation can be used to postulate the oxidation-reduction potential. The Gibbs free energy of cell can be expressed by **Eq. B.2**, for electrochemical cells that follow the chemical reaction found in **Eq. B.1**.



$$\Delta G = \Delta H - T\Delta S \quad (\text{Eq. B.2})$$

where ΔH refers to the change in enthalpy [J mol^{-1}], ΔS is the change in entropy [$\text{J K}^{-1} \text{mol}^{-1}$] and T is the absolute temperature [K].

An alternative equation for the Gibbs free energy (for fuel cells (FCs)), in terms of the anode and cathode partial pressures, p_a and p_c , respectively [kPa], is given in **Eq. B.3**:

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{p_c}{p_a} \right) \quad (\text{Eq. B.3})$$

where ΔG° depicts the standard Gibbs free energy [J mol^{-1}] and R is the universal gas constant [$8.314 \text{ J mol}^{-1} \text{K}^{-1}$].

Since the Gibbs free energy is a measure of the electrical work of the electrochemical reaction, the electrical potential of the same reaction is dependent on the Gibbs free energy. This is given by **Eq. B.4**:

$$\Delta G = -nFE_{Nernst} \quad (\text{Eq. B.4})$$

where $-nFE_{Nernst}$ represents the electrochemical work done by the reaction, n refers to the number of electrons present in the reaction, F is the Faraday constant [96 485 C mol⁻¹] and E_{Nernst} is the electrode potential [V].

The cell voltage between the anode and the cathode electrodes is given by **Eq. B.5**.

$$E = E_{Nernst} + E_{polarisation} + E_{ohmic} \quad (\text{Eq. B.5})$$

The Nernst potential found (electrode potential) found in **Eq. B.6** (E_{Nernst}) is given by the Nernst equation (for FCs):

$$E_{Nernst} = E^0 - \frac{RT}{nF} \ln \left(\frac{p_c}{p_a} \right) \quad (\text{Eq. B.6})$$

where, E^0 is the standard thermodynamic potential [V] at 25°C.

Since E^0 for pure hydrogen is 0 V, theoretically the required potential to pump hydrogen across an electrochemical cell membrane is given by an adapted Nernst equation (**Eq. B.7**):

$$E_{theoretical} = \frac{RT}{nF} \ln \left(\frac{p_c}{p_a} \right) \quad (\text{Eq. B.7})$$

The actual cell voltage will however always be higher than that predicted by the Nernst equation. This is due to losses such as (i) activation, (ii) overpotential and (iii) ohmic resistance (Barbir & Görgün, 2007).

The polarisation overpotential is the sum of the cathode and anode polarisation overpotentials, expressed by the Butler–Volmer equation (Huth *et al.*, 2009). At low overpotential values, the polarisation potential is approximated and expressed by **Eq. B.8**, where i is the current density [A cm⁻²] and i_0 is the exchange current density (Benicewicz *et al.*, 2016).

$$E_{polarisation} = \frac{RT}{nF} \frac{i}{i_0} \quad (\text{Eq. B.8})$$

The ohmic overpotential is given by ohm's law (**Eq. B.9**):

$$E_{ohmic} = iR_{\Omega} \quad (\text{Eq. B.9})$$

where R_{Ω} is the ohmic cell resistance in Ohm. The ohmic cell resistance include the membrane resistance, electrode and hardware resistance (Benicewicz *et al.*, 2016).

B.1.2 BUTLER–VOLMER EQUATION

The Butler–Volmer equation meets a shortcoming of the Nernst equation, specifically, the interrelationship between the reaction rate and the electrode potential. Therefore, the Butler–Volmer equation is only valid when the electrical charge transfer at the electrode controls the electrode reaction. For the chemical reaction given in **Eq. B.1**, the forward and backward reaction rates, in terms of current density, are expressed by **Eq. B.10** and **Eq. B.11**, respectively.

$$i_f = i_0 e^{\left(\frac{\alpha F \eta}{RT}\right)} \quad (\text{Eq. B.10})$$

$$i_b = i_0 e^{\left(\frac{(1-\alpha) F \eta}{RT}\right)} \quad (\text{Eq. B.11})$$

where i_f depicts the forward reaction current density, i_b depicts the backwards reaction current density, η is the overpotential and α is the charge transfer coefficient (usually ranging between 0.3 and 0.7) (Martinson, 2012).

The Butler–Volmer equation is obtained by subtracting **Eq. B.11** from **Eq. B.10**, to give:

$$i = i_f - i_b = i_0 \left(e^{\left(\frac{\alpha F \eta}{RT}\right)} - e^{\left(\frac{(1-\alpha) F \eta}{RT}\right)} \right) \quad (\text{Eq. B.12})$$

The Butler–Volmer equation changes when multi-electron transfer occurs within the electrochemical reaction, as follows:

$$i = i_0 \left(e^{\left(\frac{\alpha n_a F \eta}{RT}\right)} - e^{\left(\frac{(1-\alpha) n_a F \eta}{RT}\right)} \right) \quad (\text{Eq. B.13})$$

where n_a is the apparent electron number.

From the Butler–Volmer equation it is evident that the overpotential and the current density are directly related; therefore, if the overpotential increases so will the current density. The overpotential of an electrochemical cell should therefore be kept at a minimum to ensure that a high efficiency is achieved (Martinson, 2012).

B.1.3 REQUIRED POWER

Power, by definition, is the product of the current and voltage; the power required for the pumping of hydrogen also follows this principal. The theoretical power is therefore

$$W_{theoretical} = IV_{theoretical} \quad (\text{Eq. B.14})$$

where

$$V_{theoretical} = E_{theoretical} \quad (\text{Eq. B.15})$$

Combining **Eq. B.7** and **Eqs. B.14-Eq. B.15**, the theoretical power required to pump hydrogen at a mass flow rate $\dot{m}$ can be expressed as (Barbir & Görgün, 2007):

$$W_{theoretical} = \frac{\dot{m}RT}{M} \ln\left(\frac{p_c}{p_a}\right) \quad (\text{Eq. B.16})$$

where, M is the molecular weight in kg mol⁻¹.

B.2 EXPERIMENTAL BACKGROUND

B.2.1 EXPERIMENTAL PREPARATIONS: TESTING THE EXPERIMENTAL SET-UP

Before conducting any experiments, the cell was initially purged with nitrogen and then pure hydrogen, through the anode inlet (nothing was fed to the cathode inlet). This was done in efforts to ensure that the cell was clean/free of unnecessary impurities that could influence the experimental results.

The cell was operated using pure nitrogen to check whether the membrane was functioning in an acceptable manner and that there were no pinholes present. Even at a low current density of 0.02 A cm⁻² the voltage limit (1.1 V) was reached with a nitrogen flow rate of 50 nmL/min. The voltage limit is reached because hydrogen starvation occurs, as here no hydrogen is fed. This indicated that the membrane was indeed functioning satisfactorily and that no pinholes/cracks are present. Moreover, a mass balance was performed over the entire cell to ensure that there were no leakages.

Theoretically, the volumetric flow of the feed stream should be equal to the sum of the permeate (F_P) and retentate (F_R) volumetric flows (nmL/min) (**Eq. B.17**). This was tested using a hydrogen flow rate of 50 nmL/min and a current density of 0.28 A cm⁻², since approximately 49.43 nmL/min of hydrogen (~98.86% of the fed hydrogen) should exit at the cathode compartment according to Farady's law. The mass balance was repeated 3 times to test the repeatability of the cell; the data were relatively consistent, with 96.37, 96.94 and 97.08% of the hydrogen fed, exiting at the cathode outlet. The flow measurement was taken with a soap/bubble flow meter. Negligibly small flow fluctuations occurred. The mass balance over

the cell indicated that no major leakages were present. The assumption was therefore made that the mass balance is valid throughout the entire experimental period.

$$F_{Feed} = F_P + F_R \quad (\text{Eq. B.17})$$

Furthermore, it was visually observed, and then measured, that the cathode outlet stream almost immediately stopped flowing when the current density was set to 0 A cm⁻², which indicated that the gas diffusion through the membrane and crossover leaks were minimal/negligible.

B.2.2 PERFORMANCE PARAMETERS

i. Permeability

The permeability coefficient, Pe_{H_2} , is generally expressed as follows:

$$Pe_{H_2} = q \cdot \delta / A \cdot \Delta P \quad (\text{Eq. B.18})$$

where q represents the mass flux of gas through a membrane area A of thickness δ , under a partial pressure gradient ΔP across the membrane (Stern, 1968). Here, generally, q is expressed in cm³ (STP).s⁻¹, A in cm², δ in cm or mm, and ΔP in either cm. Hg or atm (Stern, 1968). Permeability is commonly expressed in terms of the unit Barrer:

$$1 \text{ Barrer} = \left[10^{-10} \frac{\text{cm}^3(\text{STP}).\text{cm}}{\text{cm}^2.\text{s.cm Hg}} \right] \quad (\text{Eq. B.19})$$

ii. Selectivity

The selectivity/separation factor of a membrane is a measure that reports the permeability difference of two components. It can be defined as the ratio of the permeability of component i with relation to component j (Cao *et al.*, 2015). This is illustrated in **Eq. B.24**,

$$\alpha_{ij} = \frac{y_i/x_i}{y_j/x_j} \quad (\text{Eq. B.20})$$

where y_i and y_j are the molar fraction of gas species i and j on the permeate side, while x_i and x_j are the molar fraction of gas species i and j on the feed side.

iii. General performance efficiencies

To achieve meaningful conclusion regarding separation performance, certain efficiencies need to be taken into consideration: the current efficiency, voltage efficiency and power efficiency.

(a) Current efficiency

The ratio between the theoretical expected Faradic flow and the measured flow value is defined as the current efficiency (**Eq. B.21**) (Benicewicz *et al.*, 2008; Lee *et al.*, 2004)

$$\varepsilon_i = \frac{\text{Experimental } H_2 \text{ product}}{\text{Theoretical } H_2 \text{ product}} \quad (\text{Eq. B.21})$$

Thus, **Eq. B.21** gives an indication of how efficient the cell is performing to produce hydrogen. According to Lee *et al.*, (2004), the current efficiency will increase with an increase in current density if the cell temperature and pressure remain constant.

(b) Voltage efficiency

The voltage efficiency is defined in terms of the thermal energy that the obtained hydrogen contains. This is calculated with the voltage equivalent of the heat of combustion of hydrogen being 1.484 (Lee *et al.*, 2004), which is known as the higher heating value of hydrogen (Barbir, 2011). The voltage efficiency can be calculated by **Eq. B.22**,

$$\varepsilon_v = 1 - \frac{V}{1.484} \quad (\text{Eq. B.22})$$

where V depicts the voltage value obtained experimentally.

(c) Power efficiency

The power efficiency can be defined as the product of both the voltage and current efficiencies (Lee *et al.*, 2004)

$$\varepsilon_p = \varepsilon_i \times \varepsilon_v \quad (\text{Eq. B.23})$$

Appendix C. THE TPS®-BASED MEMBRANE: EXPERIMENTAL DATA

The raw data for the commercially available TPS®-based HT-PEM is given in the following tables. The voltage column in these tables refers to the average voltage for each set current density. The abbreviations used in the tables are explained in **Table C.1**, together with the units of the properties reported in the raw data tables.

Table C.1: Abbreviations and units of the properties presented in the raw data tables

Abbreviations	
CD	Current density
CE	Current
P	Permeability
PE	Power efficiency
VE	Voltage efficiency
Units	
^a	A cm ⁻²
^b	Volt
^c	nm ³ m ⁻² hr ⁻¹
^e	%
^f	mol cm cm ⁻² s ⁻¹ kPa ⁻¹

C.1 EXPERIMENTS WITH PURE HYDROGEN

Experimental data for pure hydrogen at various temperatures and flow rates are tabulated below (**Tables C.2-C.13**).

Table C.2: Experimental data for pure hydrogen at 100°C, flow rate 50 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.028	0.08	0.06	2.2E-07	69.74	98.11	68.42	3.7E-15	1.13
0.04	0.058	0.17	0.13	5.0E-07	77.80	96.09	74.76	8.3E-15	2.53
0.06	0.088	0.25	0.21	8.2E-07	84.47	94.07	79.46	1.4E-14	4.12
0.08	0.121	0.34	0.30	1.1E-06	87.86	91.85	80.70	1.9E-14	5.71
0.10	0.158	0.42	0.34	1.3E-06	79.74	89.35	71.25	2.1E-14	6.47
0.12	0.200	0.51	0.41	1.5E-06	79.89	86.52	69.12	2.57E-14	7.78
0.14	0.256	0.59	0.55	2.1E-06	92.40	82.75	76.64	3.5E-14	10.50
0.16	0.342	0.68	0.63	2.4E-06	92.98	76.95	71.55	4.0E-14	12.08
0.18	0.612	0.76	0.74	2.8E-06	97.23	58.76	57.13	4.7E-14	14.21

Table C.3: Experimental data for pure hydrogen at 100°C, flow rate 100 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.024	0.08	0.06	2.3E-07	70.73	98.13	69.40	3.8E-15	1.15
0.04	0.046	0.17	0.14	5.2E-07	80.61	96.15	77.51	8.6E-15	2.62
0.06	0.088	0.25	0.22	8.2E-07	85.01	94.10	79.99	1.4E-14	4.14
0.08	0.121	0.34	0.30	1.1E-06	87.28	91.85	80.17	1.9E-14	5.67
0.10	0.157	0.42	0.34	1.3E-06	79.79	89.42	71.35	2.1E-14	6.48
0.12	0.199	0.51	0.41	1.5E-06	79.98	86.59	69.26	2.57E-14	7.79
0.14	0.253	0.59	0.55	2.1E-06	92.49	82.95	76.72	3.5E-14	10.51
0.16	0.330	0.68	0.63	2.4E-06	93.19	77.76	72.47	4.0E-14	12.11
0.18	0.560	0.76	0.74	2.8E-06	97.36	62.29	60.64	4.7E-14	14.23

Table C.4: Experimental data for pure hydrogen at 100°C, flow rate 150 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.027	0.08	0.06	2.3E-07	71.03	98.16	69.70	3.8E-15	1.15
0.04	0.056	0.17	0.14	5.2E-07	80.37	96.21	77.28	8.6E-15	2.61
0.06	0.085	0.25	0.22	8.2E-07	84.96	94.27	79.94	1.4E-14	4.14
0.08	0.122	0.34	0.30	1.1E-06	87.97	91.78	80.80	1.9E-14	5.71
0.10	0.157	0.42	0.34	1.3E-06	80.22	89.42	71.74	2.2E-14	6.51
0.12	0.202	0.51	0.40	1.5E-06	79.51	86.39	68.85	2.56E-14	7.75
0.14	0.252	0.59	0.55	2.1E-06	92.31	83.02	76.57	3.5E-14	10.49
0.16	0.339	0.68	0.63	2.4E-06	93.50	77.15	72.14	4.0E-14	12.15
0.18	0.552	0.76	0.74	2.8E-06	97.23	62.84	61.10	4.7E-14	14.21

Table C.5: Experimental data for pure hydrogen at 120°C, flow rate 50 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.013	0.08	0.06	2.3E-07	70.88	99.12	70.25	3.8E-15	1.15
0.04	0.028	0.17	0.12	4.4E-07	68.52	98.11	67.23	7.4E-15	2.23
0.06	0.043	0.25	0.19	7.1E-07	73.16	97.10	71.04	1.2E-14	3.56
0.08	0.057	0.34	0.27	1.0E-06	80.43	96.16	77.34	1.7E-14	5.22
0.10	0.072	0.42	0.38	1.4E-06	88.67	95.16	84.38	2.4E-14	7.20
0.12	0.086	0.51	0.43	1.6E-06	84.21	94.20	79.32	2.71E-14	8.20
0.14	0.101	0.59	0.54	2.0E-06	90.22	93.18	84.07	3.4E-14	10.26
0.16	0.118	0.68	0.65	2.5E-06	95.64	92.05	88.04	4.1E-14	12.42
0.18	0.137	0.76	0.72	2.8E-06	95.06	90.76	86.28	4.6E-14	13.89
0.20	0.163	0.85	0.79	3.0E-06	93.37	89.02	83.12	5.0E-14	15.16
0.22	0.196	0.93	0.87	3.3E-06	93.27	86.79	80.95	5.5E-14	16.66
0.24	0.262	1.02	0.95	3.6E-06	93.14	82.35	76.70	6.0E-14	18.15
0.26	0.452	1.10	1.04	4.0E-06	94.58	69.54	65.77	6.6E-14	19.97

Table C.6: Experimental data for pure hydrogen at 120°C, flow rate 100 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.012	0.08	0.06	2.3E-07	70.66	99.19	70.09	3.8E-15	1.15
0.04	0.027	0.17	0.12	4.4E-07	68.56	98.18	67.31	7.4E-15	2.23
0.06	0.051	0.25	0.19	7.0E-07	72.99	96.56	70.48	1.2E-14	3.56
0.08	0.055	0.34	0.27	1.0E-06	80.46	96.29	77.47	1.7E-14	5.23
0.10	0.071	0.42	0.38	1.4E-06	89.26	95.22	84.99	2.4E-14	7.25
0.12	0.082	0.51	0.43	1.6E-06	84.02	94.47	79.37	2.7E-14	8.19
0.14	0.098	0.59	0.57	2.2E-06	95.83	93.39	89.50	3.6E-14	10.89
0.16	0.117	0.68	0.67	2.5E-06	98.51	92.12	90.75	4.2E-14	12.80
0.18	0.136	0.76	0.75	2.8E-06	97.75	90.84	88.80	4.7E-14	14.29
0.20	0.160	0.85	0.79	3.0E-06	93.63	89.22	83.54	5.0E-14	15.20
0.22	0.197	0.93	0.91	3.4E-06	97.14	86.73	84.25	5.7E-14	17.35
0.24	0.262	1.02	0.97	3.7E-06	95.86	82.34	78.93	6.2E-14	18.68
0.26	0.452	1.10	1.06	4.0E-06	96.53	69.53	67.11	6.7E-14	20.38

Table C.7: Experimental data for pure hydrogen at 120°C, flow rate 150 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.013	0.08	0.06	2.3E-07	70.62	99.11	69.99	3.8E-15	1.15
0.04	0.028	0.17	0.12	4.4E-07	68.31	98.09	67.01	7.3E-15	2.22
0.06	0.050	0.25	0.19	7.0E-07	72.87	96.63	70.41	1.2E-14	3.55
0.08	0.057	0.34	0.27	1.0E-06	80.54	96.16	77.45	1.7E-14	5.23
0.10	0.071	0.42	0.38	1.4E-06	88.67	95.22	84.43	2.4E-14	7.20
0.12	0.080	0.51	0.43	1.6E-06	83.89	94.61	79.37	2.7E-14	8.17
0.14	0.101	0.59	0.57	2.2E-06	96.80	93.18	90.19	3.6E-14	11.00
0.16	0.120	0.68	0.67	2.5E-06	98.57	91.93	90.61	4.2E-14	12.81
0.18	0.137	0.76	0.76	2.9E-06	99.25	90.76	90.08	4.8E-14	14.50
0.20	0.163	0.85	0.82	3.1E-06	96.39	89.05	85.84	5.2E-14	15.65
0.22	0.196	0.93	0.91	3.4E-06	97.14	86.81	84.33	5.7E-14	17.35
0.24	0.237	1.02	0.98	3.7E-06	96.52	84.04	81.12	6.2E-14	18.81
0.26	0.441	1.10	1.03	3.9E-06	93.63	70.26	65.79	6.5E-14	19.77

Table C.8: Experimental data for pure hydrogen at 140°C, flow rate 50 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.008	0.08	0.06	2.3E-07	70.88	99.46	70.50	3.8E-15	1.15
0.04	0.016	0.17	0.14	5.4E-07	68.52	98.92	67.78	7.4E-15	2.23
0.06	0.025	0.25	0.22	8.3E-07	72.06	98.32	70.85	3.9E-15	1.17
0.08	0.033	0.34	0.30	1.2E-06	83.79	97.78	81.93	9.0E-15	2.72
0.10	0.042	0.42	0.40	1.5E-06	86.33	97.17	83.89	1.4E-14	4.21
0.12	0.051	0.51	0.47	1.8E-06	89.42	96.56	86.34	1.9E-14	5.81
0.14	0.059	0.59	0.55	2.1E-06	93.79	96.01	90.05	2.5E-14	7.62
0.16	0.069	0.68	0.63	2.4E-06	91.53	95.37	87.29	2.95E-14	8.92
0.18	0.079	0.76	0.74	2.8E-06	92.49	94.70	87.59	3.5E-14	10.51
0.20	0.090	0.85	0.81	3.1E-06	93.19	93.97	87.57	4.0E-14	12.11
0.22	0.103	0.93	0.86	3.3E-06	94.36	93.03	87.78	4.7E-14	14.23
0.24	0.121	1.02	0.96	3.6E-06	95.25	91.83	87.47	5.1E-14	15.47
0.26	0.145	1.10	1.04	3.9E-06	92.21	90.24	83.21	5.4E-14	16.47
0.28	0.180	1.19	1.07	4.1E-06	94.32	87.87	82.88	6.1E-14	18.38
0.30	0.317	1.27	1.24	4.7E-06	94.40	78.64	74.24	6.6E-14	19.93

Table C.9: Experimental data for pure hydrogen at 140°C, flow rate 100 nml/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.008	0.08	0.06	2.3E-07	70.40	99.46	70.02	3.8E-15	1.14
0.04	0.016	0.17	0.12	4.5E-07	70.40	98.92	69.64	7.6E-15	2.29
0.06	0.024	0.25	0.18	7.0E-07	72.57	98.38	71.40	1.2E-14	3.54
0.08	0.032	0.34	0.27	1.0E-06	78.87	97.84	77.17	1.7E-14	5.12
0.10	0.044	0.42	0.37	1.4E-06	88.03	97.17	85.54	2.4E-14	7.15
0.12	0.052	0.51	0.43	1.6E-06	83.64	96.50	80.71	2.69E-14	8.15
0.14	0.058	0.59	0.54	2.1E-06	91.61	96.09	88.03	3.4E-14	10.41
0.16	0.070	0.68	0.66	2.5E-06	97.70	95.28	93.10	4.2E-14	12.69
0.18	0.077	0.76	0.74	2.8E-06	96.98	94.81	91.94	4.7E-14	14.17
0.20	0.090	0.85	0.79	3.0E-06	93.63	93.97	87.98	5.0E-14	15.20
0.22	0.104	0.93	0.90	3.4E-06	96.99	92.99	90.19	5.7E-14	17.33
0.24	0.119	1.02	0.97	3.7E-06	95.86	91.98	88.17	6.2E-14	18.68
0.26	0.140	1.10	1.06	4.0E-06	96.53	90.57	87.42	6.7E-14	20.38
0.28	0.177	1.19	1.16	4.4E-06	97.79	88.07	86.13	7.3E-14	22.23
0.30	0.234	1.27	1.26	4.8E-06	98.96	84.25	83.37	8.0E-14	24.11
0.32	0.275	1.36	1.34	5.1E-06	99.03	81.46	80.67	8.5E-14	25.73
0.34	0.466	1.44	1.41	5.4E-06	98.20	68.58	67.35	9.0E-14	27.11

Table C.10: Experimental data for pure hydrogen at 140°C, flow rate 150 nml/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.007	0.08	0.06	2.3E-07	70.32	99.47	69.95	3.8E-15	1.14
0.04	0.015	0.17	0.12	4.5E-07	70.54	98.97	69.81	7.6E-15	2.29
0.06	0.024	0.25	0.19	7.0E-07	72.87	98.40	71.70	1.2E-14	3.55
0.08	0.032	0.34	0.27	1.0E-06	80.54	97.84	78.80	1.7E-14	5.23
0.10	0.043	0.42	0.38	1.4E-06	88.55	97.10	85.98	2.4E-14	7.19
0.12	0.049	0.51	0.43	1.6E-06	83.89	96.69	81.11	2.7E-14	8.17
0.14	0.059	0.59	0.54	2.1E-06	91.61	96.02	87.95	3.4E-14	10.41
0.16	0.068	0.68	0.65	2.5E-06	95.86	95.42	91.47	4.1E-14	12.45
0.18	0.078	0.76	0.74	2.8E-06	97.49	94.74	92.36	4.7E-14	14.25
0.20	0.089	0.85	0.82	3.1E-06	96.39	94.00	90.61	5.2E-14	15.65
0.22	0.103	0.93	0.89	3.4E-06	95.62	93.10	89.02	5.6E-14	17.08
0.24	0.121	1.02	0.98	3.7E-06	96.52	91.83	88.63	6.2E-14	18.81
0.26	0.145	1.10	1.03	3.9E-06	93.63	90.24	84.49	6.5E-14	19.77
0.28	0.179	1.19	1.15	4.4E-06	96.80	87.88	85.07	7.3E-14	22.01
0.30	0.233	1.27	1.24	4.7E-06	97.66	84.25	82.28	7.9E-14	23.79
0.32	0.269	1.36	1.31	5.0E-06	96.30	81.87	78.84	8.3E-14	25.02
0.34	0.457	1.44	1.40	5.3E-06	96.88	69.21	67.05	8.8E-14	26.74

Table C.11: Experimental data for pure hydrogen at 160°C, flow rate 50 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.006	0.08	0.06	2.3E-07	70.62	99.60	70.33	3.8E-15	1.15
0.04	0.007	0.17	0.14	5.4E-07	83.79	96.53	80.88	9.0E-15	2.72
0.06	0.012	0.25	0.25	9.3E-07	96.81	99.19	96.03	1.6E-14	4.72
0.08	0.016	0.34	0.33	1.2E-06	96.32	98.92	95.29	2.1E-14	6.26
0.10	0.021	0.42	0.42	1.6E-06	99.18	98.58	97.78	2.7E-14	8.05
0.12	0.026	0.51	0.49	1.9E-06	96.27	98.25	94.58	3.1E-14	9.38
0.14	0.031	0.59	0.57	2.2E-06	95.73	97.90	93.72	3.6E-14	10.88
0.16	0.037	0.68	0.67	2.5E-06	98.16	97.53	95.74	4.2E-14	12.75
0.18	0.042	0.76	0.76	2.9E-06	99.25	97.14	96.41	4.8E-14	14.50
0.20	0.048	0.85	0.84	3.2E-06	99.33	96.73	96.08	5.3E-14	16.13
0.22	0.055	0.93	0.93	3.5E-06	99.53	96.31	95.86	5.9E-14	17.78
0.24	0.062	1.02	1.00	3.8E-06	98.31	95.82	94.19	6.3E-14	19.16
0.26	0.070	1.10	1.10	4.2E-06	99.41	95.31	94.75	6.9E-14	20.99
0.28	0.078	1.19	1.16	4.4E-06	98.09	94.73	92.92	7.4E-14	22.30
0.30	0.108	1.27	1.24	4.7E-06	97.77	92.70	90.63	7.9E-14	23.81
0.32	0.596	1.36	1.31	5.0E-06	96.97	59.84	58.02	8.3E-14	25.19

Table C.12: Experimental data for pure hydrogen at 160°C, flow rate 100 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.006	0.08	0.06	2.3E-07	70.28	99.60	70.00	3.8E-15	1.14
0.04	0.010	0.17	0.12	4.5E-07	70.03	93.11	65.20	7.5E-15	2.27
0.06	0.013	0.25	0.18	7.0E-07	72.39	99.22	71.82	1.2E-14	3.53
0.08	0.016	0.34	0.27	1.0E-06	78.76	98.92	77.91	1.7E-14	5.12
0.10	0.020	0.42	0.37	1.4E-06	87.91	98.65	86.73	2.4E-14	7.14
0.12	0.024	0.51	0.42	1.6E-06	83.45	98.38	82.10	2.69E-14	8.13
0.14	0.030	0.59	0.54	2.0E-06	90.65	97.98	88.82	3.4E-14	10.30
0.16	0.037	0.68	0.66	2.5E-06	97.70	97.53	95.29	4.2E-14	12.69
0.18	0.043	0.76	0.74	2.8E-06	96.98	97.10	94.17	4.7E-14	14.17
0.20	0.048	0.85	0.79	3.0E-06	93.63	96.73	90.57	5.0E-14	15.20
0.22	0.054	0.93	0.90	3.4E-06	96.99	96.29	93.40	5.7E-14	17.33
0.24	0.060	1.02	0.97	3.7E-06	95.86	95.96	91.98	6.2E-14	18.68
0.26	0.074	1.10	1.06	4.0E-06	96.53	95.28	91.98	6.7E-14	20.38
0.28	0.080	1.19	1.16	4.4E-06	97.79	94.61	92.52	7.3E-14	22.23
0.30	0.098	1.27	1.26	4.8E-06	98.96	93.40	92.42	8.0E-14	24.11
0.32	0.176	1.36	1.33	5.0E-06	97.87	88.13	86.26	8.4E-14	25.43
0.34	0.254	1.44	1.41	5.4E-06	98.20	82.87	81.37	9.0E-14	27.11
0.36	0.338	1.53	1.44	5.5E-06	94.28	77.21	72.80	9.1E-14	27.56
0.38	0.397	1.61	1.55	5.9E-06	96.14	73.26	70.43	9.8E-14	29.66
0.40	0.631	1.69	1.63	6.2E-06	95.91	57.51	55.16	1.0E-13	31.15

Table C.13: Experimental data for pure hydrogen at 160°C, flow rate 150 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.006	0.08	0.06	2.3E-07	70.10	99.60	69.82	3.8E-15	1.14
0.04	0.009	0.17	0.12	4.6E-07	71.37	99.39	66.82	7.7E-15	2.32
0.06	0.012	0.25	0.19	7.0E-07	72.87	99.22	72.29	1.2E-14	3.55
0.08	0.016	0.34	0.27	1.0E-06	80.16	98.92	79.29	1.7E-14	5.21
0.10	0.021	0.42	0.37	1.4E-06	88.32	98.58	87.07	2.4E-14	7.17
0.12	0.026	0.51	0.43	1.6E-06	83.64	98.32	82.18	2.69E-14	8.15
0.14	0.031	0.59	0.54	2.1E-06	91.34	97.98	89.42	3.4E-14	10.38
0.16	0.037	0.68	0.65	2.5E-06	95.75	97.44	93.38	4.1E-14	12.44
0.18	0.042	0.76	0.73	2.8E-06	96.23	97.14	93.48	4.6E-14	14.06
0.20	0.048	0.85	0.81	3.1E-06	95.71	96.90	92.58	5.1E-14	15.54
0.22	0.055	0.93	0.88	3.4E-06	94.87	96.50	91.37	5.6E-14	16.95
0.24	0.062	1.02	0.97	3.7E-06	95.69	95.81	91.69	6.2E-14	18.65
0.26	0.070	1.10	1.03	3.9E-06	93.21	95.42	88.83	6.5E-14	19.68
0.28	0.078	1.19	1.14	4.3E-06	95.83	94.81	90.77	7.2E-14	21.79
0.30	0.098	1.27	1.24	4.7E-06	97.66	93.33	91.24	7.9E-14	23.79
0.32	0.130	1.36	1.31	5.0E-06	96.30	91.22	87.84	8.3E-14	25.02
0.34	0.223	1.44	1.40	5.3E-06	96.88	84.94	82.29	8.8E-14	26.74
0.36	0.273	1.53	1.48	5.6E-06	97.36	81.60	79.45	9.4E-14	28.46
0.38	0.397	1.61	1.59	6.0E-06	98.83	73.26	72.40	1.0E-13	30.49
0.40	0.631	1.69	1.65	6.3E-06	97.16	57.51	55.88	1.0E-13	31.56

C.2 EXPERIMENTS WITH H₂/CH₄

Experimental data for H₂/CH₄, expressed as the CH₄ percentage of the inlet mixture (the balance being H₂), at various temperatures are tabulated below (**Tables C.14-C.22**). The hydrogen flow rate was kept constant throughout, at 100 nmL/min.

Table C.14: Experimental data: 80% methane at 120°C

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.047	0.08	0.08	3.1E-07	51.42	96.8	49.77	5.1E-15	1.55
0.04	0.113	0.17	0.16	6.2E-07	79.02	92.39	73.01	1.0E-14	3.10
0.06	0.262	0.25	0.24	9.2E-07	85.42	82.31	70.31	1.5E-14	4.62
0.08	0.373	0.33	0.00	2.6E-09	89.02	74.86	66.64	1.8E-14	5.36
0.10	0.564	0.42	0.00	1.5E-09	94.30	61.97	58.44	2.0E-14	6.21

Table C.15: Experimental data: 80% methane at 140°C

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.041	0.08	0.08	3.0E-07	48.20	97.23	46.86	5.0E-15	1.50
0.04	0.107	0.17	0.16	5.9E-07	76.08	92.80	70.60	9.9E-15	3.00
0.06	0.202	0.25	0.23	8.8E-07	85.33	86.41	73.73	1.5E-14	4.44
0.08	0.287	0.33	0.33	1.3E-06	90.00	80.69	72.62	2.1E-14	6.34
0.10	0.352	0.42	0.40	1.4E-06	96.10	76.26	73.29	2.3E-14	7.07
0.12	0.551	0.50	0.48	1.8E-06	95.19	62.89	59.86	3.0E-14	9.15

Table C.16: Experimental data: 80% methane at 160°C

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.021	0.08	0.08	2.9E-07	49.11	98.58	48.41	4.8E-15	1.45
0.04	0.076	0.17	0.16	5.9E-07	75.98	94.89	72.10	9.8E-15	2.98
0.06	0.121	0.25	0.24	9.1E-07	85.34	91.87	78.40	1.5E-14	4.61
0.08	0.205	0.33	0.32	1.2E-06	92.03	86.18	79.31	2.0E-14	6.08
0.10	0.253	0.42	0.41	1.5E-06	94.12	82.96	78.08	2.6E-14	7.77
0.12	0.331	0.50	0.49	1.9E-06	95.19	77.67	73.93	3.1E-14	9.36
0.14	0.597	0.59	0.56	2.1E-06	96.44	59.75	57.62	3.6E-14	10.81

Table C.17: Experimental data: 50% methane at 120°C

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.052	0.08	0.08	3.1E-07	49.11	96.47	47.38	5.2E-15	1.56
0.04	0.097	0.17	0.16	6.2E-07	75.98	93.49	71.03	1.0E-14	3.15
0.06	0.145	0.25	0.25	9.5E-07	85.34	90.23	77.00	1.6E-14	4.80
0.08	0.205	0.33	0.32	1.2E-06	92.03	86.16	79.29	2.0E-14	6.19
0.10	0.284	0.42	0.40	1.5E-06	94.12	80.83	76.08	2.6E-14	7.76
0.12	0.479	0.50	0.48	1.8E-06	95.91	67.74	64.97	3.0E-14	9.22
0.14	0.595	0.59	0.56	2.1E-06	95.49	59.93	57.23	3.5E-14	10.71
0.16	1.102	0.67	0.65	2.5E-06	96.93	25.74	24.95	4.1E-14	12.42

Table C.18: Experimental data: 50% methane at 140°C

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.043	0.08	0.08	3.1E-07	50.22	97.09	48.76	5.2E-15	1.58
0.04	0.080	0.17	0.17	6.3E-07	75.55	94.63	71.49	1.0E-14	3.18
0.06	0.116	0.25	0.25	9.3E-07	85.34	92.16	78.65	1.6E-14	4.70
0.08	0.162	0.33	0.32	1.2E-06	95.88	89.09	85.42	2.0E-14	6.15
0.10	0.219	0.42	0.40	1.5E-06	94.56	85.24	80.60	2.5E-14	7.58
0.12	0.323	0.50	0.47	1.8E-06	93.30	78.27	73.03	3.0E-14	8.97
0.14	0.465	0.59	0.58	2.2E-06	95.49	68.67	65.57	3.6E-14	11.04
0.16	0.819	0.67	0.66	2.5E-06	98.05	44.79	43.91	4.2E-14	12.57

Table C.19: Experimental data: 50% methane at 160°C

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.023	0.08	0.08	3.1E-07	47.23	98.46	46.50	5.2E-15	1.58
0.04	0.036	0.17	0.15	5.8E-07	68.33	97.57	66.67	9.7E-15	2.95
0.06	0.050	0.25	0.24	8.9E-07	85.34	96.65	82.48	1.5E-14	4.51
0.08	0.065	0.33	0.31	1.2E-06	92.00	95.65	88.00	2.0E-14	5.96
0.10	0.083	0.42	0.40	1.5E-06	93.84	94.42	88.60	2.6E-14	7.73
0.12	0.118	0.50	0.49	1.9E-06	93.04	92.02	85.62	3.1E-14	9.39
0.14	0.191	0.59	0.57	2.2E-06	96.51	87.14	84.10	3.6E-14	10.89
0.16	0.282	0.67	0.67	2.5E-06	95.44	81.00	77.31	4.2E-14	12.80
0.18	0.400	0.75	0.74	2.8E-06	96.32	73.07	70.38	4.7E-14	14.26
0.20	0.841	0.84	0.81	3.1E-06	95.51	43.36	41.41	5.1E-14	15.49

Table C.20: Experimental data: 10% methane at 120°C

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.016	0.08	0.06	2.1E-07	47.22	98.91	46.71	3.5E-15	1.07
0.04	0.030	0.17	0.15	5.4E-07	72.90	97.98	71.43	8.9E-15	2.70
0.06	0.045	0.25	0.24	8.5E-07	85.30	96.97	82.72	1.4E-14	4.27
0.08	0.063	0.33	0.32	1.1E-06	87.99	95.96	84.44	1.8E-14	5.54
0.10	0.077	0.42	0.42	1.4E-06	91.97	94.83	87.22	2.4E-14	7.32
0.12	0.095	0.50	0.49	1.7E-06	93.84	93.58	87.82	2.8E-14	8.60
0.14	0.120	0.59	0.57	2.0E-06	95.43	91.92	87.71	3.3E-14	9.97
0.16	0.159	0.67	0.63	2.2E-06	96.30	89.30	86.00	3.7E-14	11.13
0.18	0.252	0.75	0.74	2.6E-06	95.11	83.01	78.95	4.3E-14	13.08
0.20	0.433	0.85	0.80	2.8E-06	96.32	70.79	68.19	4.6E-14	14.01
0.22	0.669	0.93	0.89	3.1E-06	96.85	54.92	53.19	5.1E-14	15.55
0.24	1.100	1.02	0.95	3.3E-06	97.11	25.88	25.13	5.5E-14	16.75

Table C.21: Experimental data: 10% methane at 140°C

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.016	0.08	0.08	2.9E-07	47.23	98.92	46.50	4.8E-15	1.46
0.04	0.032	0.17	0.16	5.7E-07	72.93	97.84	70.77	9.4E-15	2.86
0.06	0.044	0.25	0.23	8.1E-07	85.34	96.87	81.60	1.4E-14	4.10
0.08	0.062	0.33	0.33	1.2E-06	88.97	95.96	84.04	1.9E-14	5.85
0.10	0.075	0.42	0.41	1.4E-06	91.84	93.40	85.78	2.3E-14	7.11
0.12	0.090	0.50	0.50	1.7E-06	95.43	92.33	88.11	2.9E-14	8.75
0.14	0.111	0.59	0.58	2.0E-06	95.70	90.98	87.07	3.4E-14	10.25
0.16	0.135	0.67	0.65	2.3E-06	96.82	88.83	86.01	3.8E-14	11.42
0.18	0.213	0.75	0.74	2.6E-06	94.72	85.64	81.12	4.3E-14	12.91
0.20	0.299	0.85	0.82	2.8E-06	95.51	79.83	76.25	4.7E-14	14.35
0.22	0.386	0.93	0.88	3.1E-06	97.11	74.02	71.88	5.1E-14	15.45
0.24	0.655	1.02	0.97	3.4E-06	96.85	55.83	54.07	5.6E-14	17.05
0.26	0.926	1.10	1.03	3.6E-06	96.98	37.63	36.49	6.0E-14	18.08

Table C.22: Experimental data: 10% methane at 160°C

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.016	0.08	0.08	2.8E-07	47.24	98.93	46.74	4.7E-15	1.41
0.04	0.030	0.17	0.16	5.7E-07	73.44	97.98	71.96	9.5E-15	2.89
0.06	0.044	0.25	0.25	8.6E-07	86.12	97.01	83.54	1.4E-14	4.33
0.08	0.059	0.33	0.32	1.1E-06	90.11	96.02	86.52	1.9E-14	5.63
0.10	0.074	0.42	0.41	1.4E-06	92.46	95.01	87.85	2.4E-14	7.20
0.12	0.089	0.50	0.48	1.7E-06	94.99	93.98	89.27	2.8E-14	8.44
0.14	0.106	0.59	0.58	2.0E-06	95.02	92.83	88.21	3.4E-14	10.27
0.16	0.127	0.68	0.66	2.3E-06	95.43	91.46	87.28	3.8E-14	11.60
0.18	0.150	0.76	0.74	2.6E-06	95.66	89.91	86.01	4.3E-14	12.95
0.20	0.181	0.85	0.82	2.9E-06	95.98	87.78	84.25	4.8E-14	14.41
0.22	0.234	0.93	0.89	3.1E-06	96.72	84.21	81.45	5.2E-14	15.71
0.24	0.317	1.02	0.95	3.3E-06	97.77	78.64	76.89	5.5E-14	16.60
0.26	0.380	1.10	1.02	3.5E-06	98.12	74.39	72.99	5.9E-14	17.91
0.28	0.523	1.19	1.11	3.9E-06	98.55	64.76	63.82	6.4E-14	19.45

Table C.22 (continued): Experimental data: 10% methane at 160°C

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.30	0.642	1.27	1.21	4.2E-06	94.65	56.77	53.73	7.0E-14	21.28
0.32	0.964	1.36	1.31	4.5E-06	96.65	35.03	33.86	7.6E-14	22.95

C.3 EXPERIMENTS WITH H₂/CO₂

Experimental data, expressed as CO₂ percentage of the inlet mixture (the balance being H₂), are presented in **Tables C.23-C.28**. The hydrogen flow rate was kept constant throughout, at 100 nmL/min.

Table C.23: Experimental data: 50% carbon dioxide at 120°C

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.028	0.08	0.06	2.1E-07	54.12	98.11	53.10	3.5E-15	1.07
0.04	0.055	0.17	0.14	5.0E-07	69.02	96.30	66.47	8.3E-15	2.52
0.06	0.088	0.25	0.23	8.4E-07	72.93	94.09	68.62	1.4E-14	4.23
0.08	0.153	0.34	0.31	1.1E-06	77.02	89.70	69.09	1.9E-14	5.64
0.10	0.454	0.42	0.40	1.4E-06	83.42	69.42	57.91	2.3E-14	7.11
0.12	0.719	0.51	0.49	1.7E-06	90.02	51.55	46.41	2.9E-14	8.66

Table C.24: Experimental data: 50% carbon dioxide at 140°C

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.025	0.08	0.08	2.7E-07	54.14	98.29	53.21	4.5E-15	1.36
0.04	0.046	0.17	0.16	5.4E-07	70.22	96.92	68.06	9.0E-15	2.73
0.06	0.072	0.25	0.24	8.1E-07	73.00	95.12	69.44	1.4E-14	4.09
0.08	0.094	0.34	0.32	1.1E-06	79.05	93.67	74.04	1.8E-14	5.53
0.10	0.132	0.42	0.40	1.4E-06	87.42	91.08	79.62	2.3E-14	7.11
0.12	0.251	0.51	0.49	1.7E-06	90.03	83.09	74.81	2.9E-14	8.64
0.14	0.442	0.59	0.58	2.0E-06	91.04	70.24	63.95	3.4E-14	10.26

Table C.25: Experimental data: 50% carbon dioxide at 160°C

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.022	0.08	0.08	2.8E-07	54.13	98.50	53.32	4.7E-15	1.41
0.04	0.045	0.17	0.16	5.7E-07	68.98	96.97	66.89	9.5E-15	2.89
0.06	0.069	0.25	0.25	8.6E-07	73.00	95.37	69.62	1.4E-14	4.33
0.08	0.093	0.34	0.32	1.1E-06	79.02	93.76	74.09	1.9E-14	5.64
0.10	0.125	0.42	0.41	1.4E-06	87.42	91.61	80.09	2.4E-14	7.17
0.12	0.245	0.51	0.49	1.7E-06	89.99	83.49	75.13	2.8E-14	8.57
0.14	0.434	0.59	0.58	2.0E-06	91.00	70.75	64.38	3.4E-14	10.27

Table C.26: Experimental data: 10% carbon dioxide at 120°C

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.026	0.08	0.06	2.1E-07	51.42	98.23	50.51	3.5E-15	1.07
0.04	0.055	0.17	0.15	5.3E-07	79.02	96.30	76.10	8.9E-15	2.70
0.06	0.087	0.25	0.24	8.5E-07	85.42	94.12	80.40	1.4E-14	4.27
0.08	0.134	0.34	0.32	1.1E-06	89.02	90.97	80.98	1.8E-14	5.53
0.10	0.300	0.42	0.42	1.5E-06	94.30	79.81	75.26	2.4E-14	7.33
0.12	0.596	0.51	0.49	1.7E-06	95.02	59.84	56.86	2.9E-14	8.66

Table C.27: Experimental data: 10% carbon dioxide at 140°C

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.020	0.08	0.08	2.7E-07	51.42	98.65	50.73	4.5E-15	1.36
0.04	0.046	0.17	0.16	5.4E-07	69.02	96.91	66.89	9.0E-15	2.72
0.06	0.074	0.25	0.23	8.1E-07	83.42	94.99	79.24	1.4E-14	4.10
0.08	0.114	0.34	0.31	1.1E-06	89.02	92.30	82.17	1.8E-14	5.52
0.10	0.170	0.42	0.41	1.4E-06	94.33	88.58	83.56	2.3E-14	7.11
0.12	0.352	0.51	0.49	1.7E-06	95.05	76.27	72.50	2.9E-14	8.65
0.14	0.590	0.59	0.58	2.0E-06	94.04	60.21	56.62	3.4E-14	10.27
0.16	0.758	0.68	0.66	2.3E-06	95.23	48.92	46.59	3.8E-14	11.60

Table C.28: Experimental data: 10% carbon dioxide at 160°C

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.011	0.08	0.08	2.8E-07	51.43	99.23	51.04	4.7E-15	1.41
0.04	0.033	0.17	0.16	5.7E-07	69.92	97.80	68.38	9.5E-15	2.89
0.06	0.057	0.25	0.25	8.6E-07	83.42	96.18	80.23	1.4E-14	4.33
0.08	0.091	0.34	0.32	1.1E-06	89.02	93.90	83.59	1.9E-14	5.63
0.10	0.138	0.42	0.41	1.4E-06	92.30	90.72	83.74	2.4E-14	7.20
0.12	0.211	0.51	0.48	1.7E-06	93.02	85.77	79.78	2.8E-14	8.44
0.14	0.289	0.59	0.58	2.0E-06	94.04	80.51	75.71	3.4E-14	10.27
0.16	0.511	0.68	0.66	2.3E-06	93.23	65.60	61.16	3.8E-14	11.60

C.4 EXPERIMENTS WITH H₂/NH₃

Experimental data, expressed in terms of the ammonia percentage of the inlet mixture (the balance being H₂), are presented in **Tables C.29-C.34**. The hydrogen flow rate was kept constant throughout, at 100 nmL/min.

Table C.29: Experimental data: 3000 ppm ammonia at 120°C

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.032	0.08	0.06	2.2E-07	70.60	97.87	69.10	3.7E-15	1.13
0.04	0.262	0.17	0.13	5.0E-07	79.31	82.38	65.33	8.4E-15	2.54

Table C.30: Experimental data: 3000 ppm ammonia at 140°C

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.048	0.08	0.06	2.3E-07	72.06	96.79	69.75	3.8E-15	1.15
0.04	0.315	0.17	0.14	5.2E-07	81.50	78.74	64.18	8.6E-15	2.61

Table C.31: Experimental data: 3000 ppm ammonia at 160°C

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.186	0.08	0.06	2.3E-07	71.42	87.45	62.46	3.8E-15	1.14

Table C.32: Experimental data: 1500 ppm ammonia at 120°C

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.011	0.08	0.06	2.2E-07	70.68	99.28	70.17	3.7E-15	1.13
0.04	0.161	0.17	0.13	5.0E-07	78.85	89.16	70.30	8.3E-15	2.53
0.06	0.391	0.25	0.21	8.2E-07	85.61	73.65	63.05	1.4E-14	4.12
0.08	0.717	0.33	0.30	1.1E-06	89.04	51.68	46.02	1.9E-14	5.71
0.10	1.100	0.42	0.34	1.3E-06	80.82	25.88	20.91	2.1E-14	6.47

Table C.33: Experimental data: 1500 ppm ammonia at 140°C

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.045	0.08	0.06	2.3E-07	71.68	96.97	69.51	3.8E-15	1.15
0.04	0.146	0.17	0.14	5.2E-07	81.70	90.16	73.66	8.6E-15	2.62
0.06	0.308	0.25	0.22	8.2E-07	86.16	79.25	68.28	1.4E-14	4.14
0.08	0.514	0.33	0.30	1.1E-06	88.46	65.36	57.82	1.9E-14	5.67
0.10	0.708	0.42	0.34	1.3E-06	80.87	52.29	42.29	2.1E-14	6.48
0.12	0.941	0.50	0.41	1.5E-06	81.06	36.59	29.66	2.57E-14	7.79

Table C.34: Experimental data: 1500 ppm ammonia at 160°C

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.02	0.025	0.08	0.06	2.3E-07	71.99	98.33	70.78	3.8E-15	1.15
0.04	0.071	0.17	0.14	5.2E-07	81.45	95.25	77.58	8.6E-15	2.61
0.06	0.130	0.25	0.22	8.2E-07	86.10	91.27	78.59	1.4E-14	4.14
0.08	0.279	0.33	0.30	1.1E-06	89.16	81.19	72.38	1.9E-14	5.71
0.10	0.562	0.42	0.34	1.3E-06	81.30	62.13	50.51	2.2E-14	6.51
0.12	0.992	0.50	0.40	1.5E-06	80.58	33.19	26.74	2.56E-14	7.75

C.5 MEMBRANE DURABILITY AND STABILITY

In this section the durability (e.g. aging effects) and stability (e.g. voltage stability) of the membrane is discussed. To evaluate the durability of the membrane to some extent, the performance of a membrane at beginning of life (BoL) was compared to that of an aged membrane (used in the lab for ca. 12 months). The aged membrane was exposed to a variety of gas mixtures in the laboratory, including H₂, N₂, CH₄, Ar, and CO₂. Due to the timely nature of the experiments and the magnitude of the work scope, only pure hydrogen and hydrogen-methane mixtures were used to evaluate the membrane durability. The hydrogen-methane mixtures were also used to report on the separation durability of the membranes by comparing the separation performance (hydrogen selectivity) of the BoL and aged membranes.

The voltage stability graphs contained within this section include the graphs of pure hydrogen, hydrogen-methane gas mixtures and hydrogen-carbon dioxide gas mixtures. The V-t graphs of the cell under hydrogen-ammonia operation is not included in this section, due to voltage shutdown in the initial stages of the experiments.

C.5.1 PURE HYDROGEN

The polarisation curves for the BoL membrane and aged membrane are compared in **Figure C.10**. In general, it can be drawn that the membrane performance is subject to aging, since the performance at BoL is substantially higher than the performance of the aged membrane. In the case of the aged membrane, the maximum current density values that could be reached with a hydrogen feed of 100 nmL/min was roughly 0.1 A cm⁻² lower than that of the membrane at BoL.

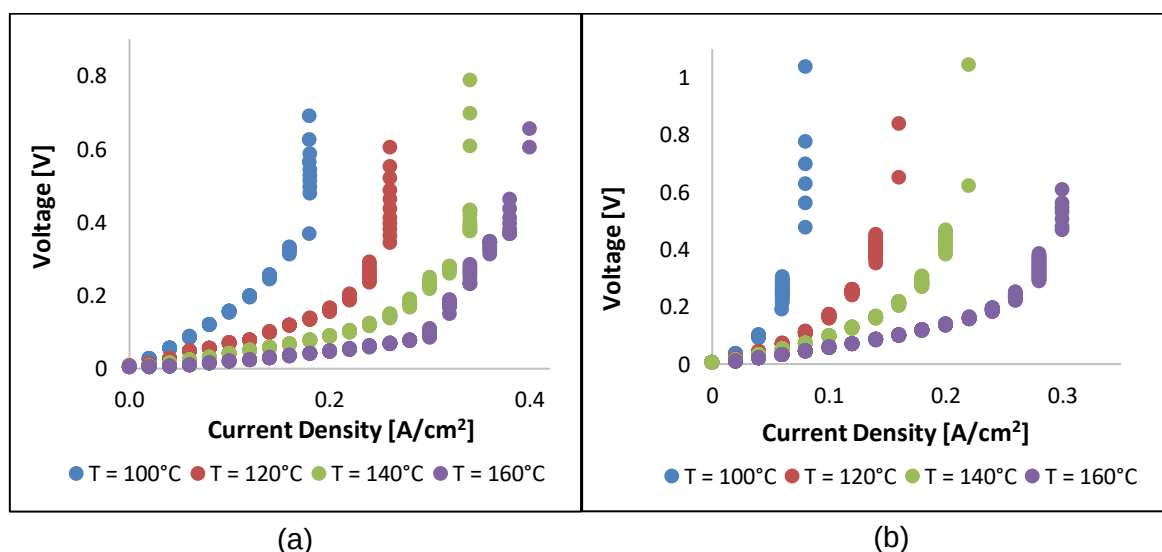


Figure C.1: Polarisation curves of pure hydrogen at 100 nmL/min (a) beginning of life membrane; (b) aged membrane.

Figure C.10 shows the average cell voltage at the respective current densities, prior to the limiting current density values. The voltage losses can be divided into three regions: the active, ohmic and mass-transfer limiting regions (Gallucci *et al.*, 2019). Gallucci *et al.* (2019) state that the active overpotential is expected predominate at low current densities, whilst the ohmic losses (due to the cell internal resistance) are expected to dominate in the intermediate region especially (when a linear trend is observed) and in the high current density region the overall cell reaction rate is expected to dominate due to the depletion of reactants. The activation polarisation effects are however, expected to be minimal (Gallucci *et al.*, 2019; Barbir & Görgün, 2007; Fasil *et al.*, 2002). From **Figure C.10** a linear trend is visible for the membrane at BoL, indicating that the Ohmic losses (IR) are predominant (Barbir & Görgün, 2007; Gardner *et al.*, 2007) which is visible in **Figure C.10 (a), (c) and (e)** where the weight of the different contributors to the cell voltage losses are illustrated. The polarisation losses (defined as the sum of the activation polarisation and concentration (mass transfer limiting) losses (Gallucci *et al.*, 2019)) in **Figure C.10** was calculated by simply deducting the measured ohmic losses (IR) and the Nernst/theoretical potential (0 V) from the measured cell voltage.

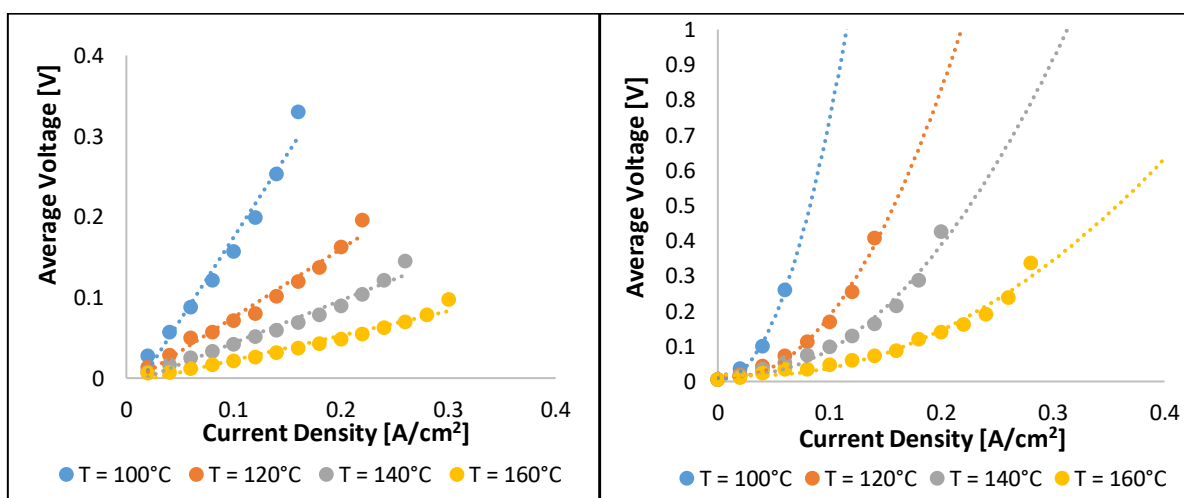


Figure C.2: The average cell voltage as a function of current density for pure hydrogen at 100 nmL/min: (a) beginning of life membrane; (b) aged membrane.

Figure C.10 (b) shows that a polynomial curve is more fitting for the relationship between the average pump cell voltage and the current applied for the aged membrane, before the limiting current is approached. This indicate that the voltage losses is dominated by the mass-transfer limitations which improves at 160°C (See **Figure C.3**). This can be explained by catalytic particles that might be poisoned from previous tests performed on CO_2 , which gets reactivated at higher temperatures. **Figure C.3** proves to be very valuable in understanding the weight of the different contributing factors to the voltage losses within the cell. At 140-160°C, the membrane at BoL was dominated by the ohmic losses, with minimal polarisation effects.

However, at 120°C the ohmic and polarisation losses seems to contribute equally. This is explained by the mass transfer kinetic rate, which is reduced at lower temperatures. The aged membrane, on the other hand, show that the mass-transfer limitations dominate the voltage losses at 120-140°C (mentioned earlier). The reaction kinetics improve at 160°C, where the voltage losses are seemingly dominated by the ohmic losses for the majority of the curve.

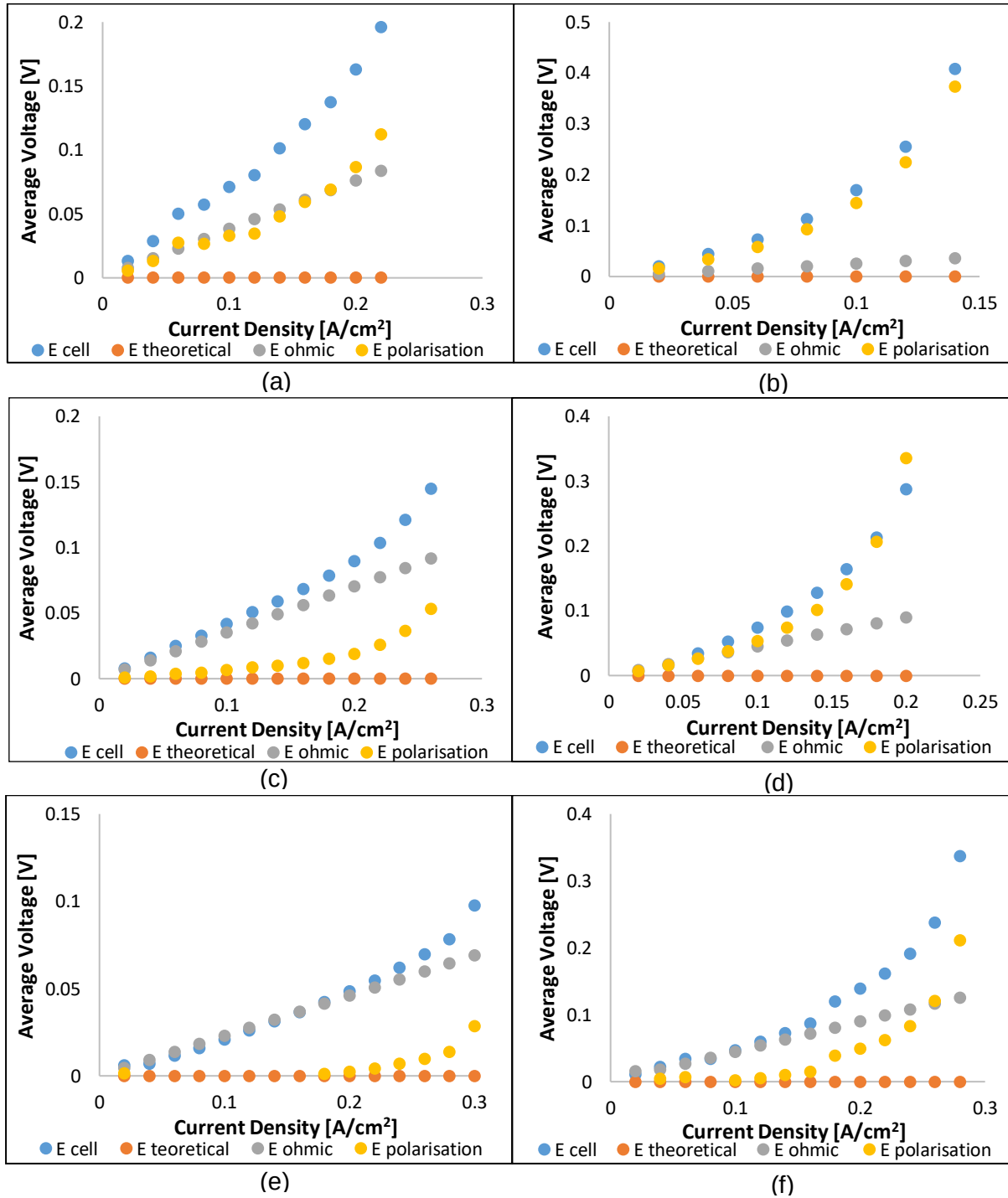


Figure C.3: Components of electrochemical pump average voltage: (a) new membrane at 120°C; (b) aged membrane at 120°C; (c) new membrane at 140°C; (d) aged membrane at 140°C; (e) new membrane at 160°C; (f) aged membrane at 160°C.

In terms of stability, voltage-time (V-t) curves were extracted and evaluated. V-t curves were performed with a pure hydrogen feed (100 nmL/min) at temperatures 100-160°C with a step of 20°C and an arbitrary chosen benchmark current density of 0.1 A cm⁻² for 30 minutes. See **Figure C.10**. At 100°C a current density of 0.1 A cm⁻² could not be reached with the aged membrane and is therefore not reported in the graph. The V-t curves for the BoL membrane shows that lower voltage values were obtained at higher temperatures. Also, the voltage values obtained by the aged membrane were significantly higher than that obtained by the BoL tests. The voltage increased from approximately 0.02; 0.03 and 0.07 A cm⁻² at the BoL test for 160; 140 and 120°C respectively to 0.025; 0.07 and 0.14 A cm⁻² in the first minute of experimentation. In **Figure C.10 (b)** it can be observed that the voltage keeps on inclining with time. This shows that the voltage is not very stable when an aged membrane is used.

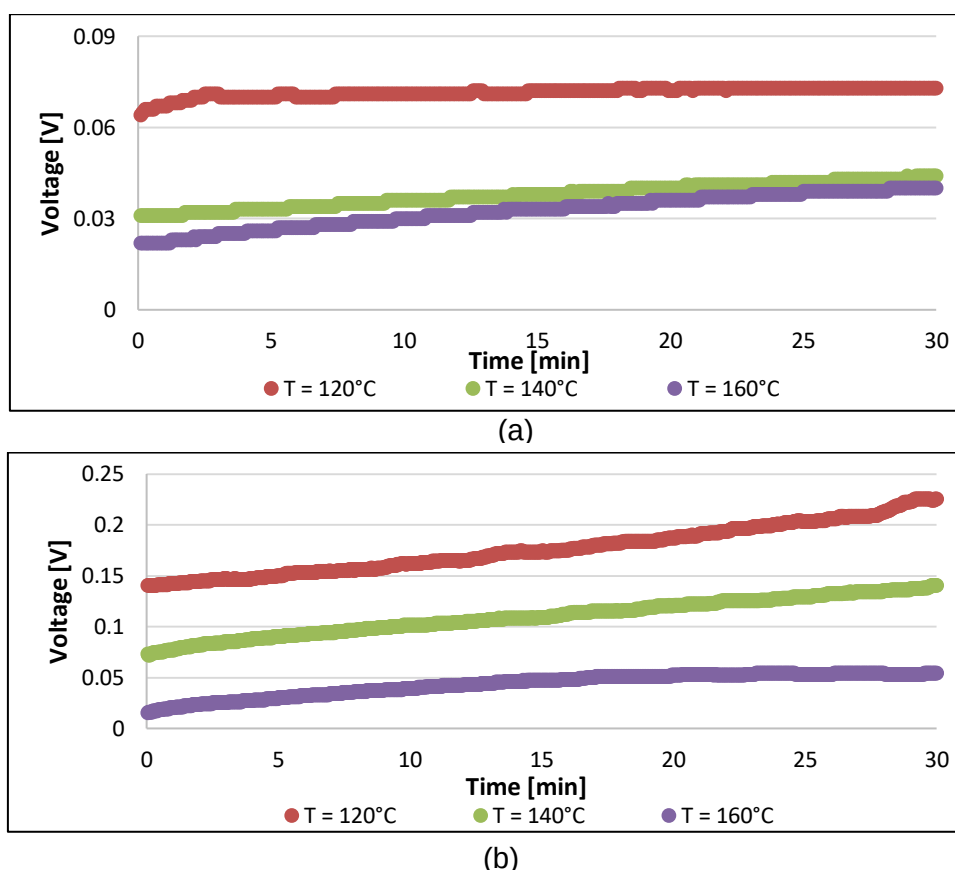


Figure C.4: Voltage–time (V-t) curves of Advent TPS aged membrane with pure hydrogen at a flow rate of 100 nmL/min at 0.1 A cm⁻².

Moreover, from **Figure C.5** it can be seen that nearly Faradic flow rates were achieved for both the aged membrane and the new membrane, with slight deviations observed for the aged membrane at 0.18-0.22 A cm⁻². This indicate that the performance losses were not caused by leakages inside the system and can therefore be attributed solely to membrane or component degradation.

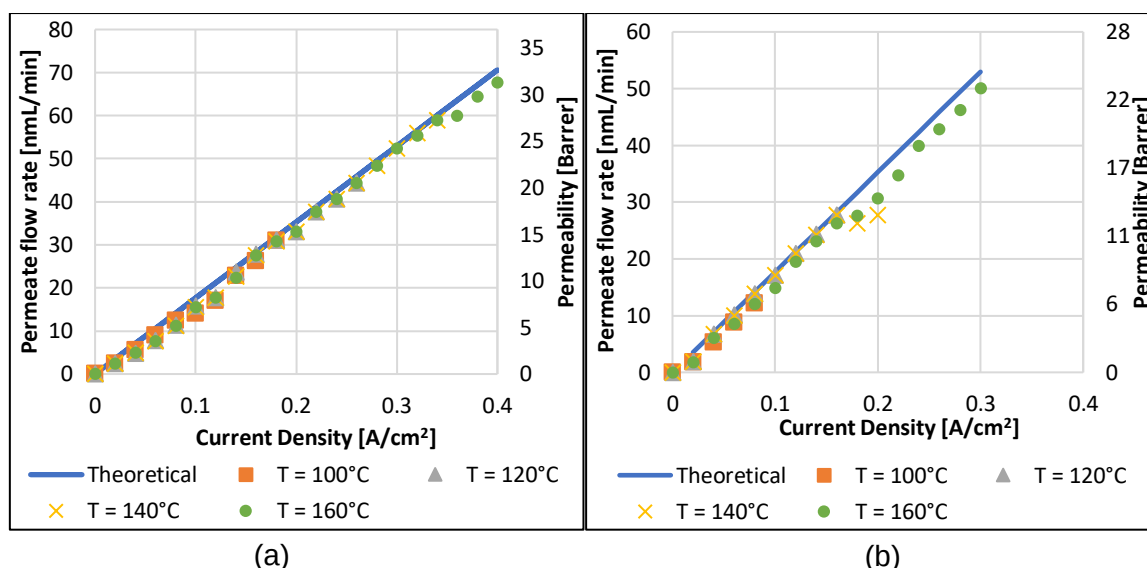


Figure C.5: Hydrogen permeation rate and permeability for a hydrogen feed flow rate of 100 nmL/min: (a) beginning of life membrane; (b) aged membrane.

C.5.2 H_2/CH_4 SEPARATION

The voltage–current characteristics of the hydrogen/methane mixtures at different cell temperatures and feed concentrations are shown for both the BoL and aged membranes in **Figure C.10**. Since the hydrogen flow rate is kept constant at 100 nmL/min three possible factors were identified to influence the shape of the curves: the temperature effects, the methane concentration of the feed stream and the differences in hydrogen partial pressure at the anode and cathode. While the hydrogen partial pressure remains relatively constant at the cathode compartment at 1 atm, the hydrogen partial pressure at the anode is dependent on the mixture used and the current density applied, which depletes the hydrogen at the anode and thus changes the composition of the mixture.

The performance of the cell was influenced by the methane concentration; the cell performance decreased with an increase in methane concentration even at BoL. In the case where 10% methane is present slight performance losses occur at 120°C when compared to that of pure hydrogen (**Figure C.10 (a)**). The same current density value was reached, with much higher voltages, which means that the power efficiencies are poorer in the presence of methane. The performance losses increased with temperature and larger performance losses are observed at 140 and 160°C, where the achieved current densities for pure hydrogen were 0.34 and 0.4 A cm⁻² at 140 and 160°C respectively and reduces to 0.26 and 0.32 A cm⁻² in the presence of 10% methane. This effect worsens as the methane percentage increase from 10% to 50% and 80%. At a methane concentration of 50 % and a temperature of 160°C the maximum current density was 0.2 A cm⁻² and further reduces to a mere 0.14 A cm⁻² when 80% methane is present in the feed. The performance of the aged membrane is further impaired,

where the maximum achievable current density for 10 % methane streams reduces from 0.32, 0.26 and 0.24 A cm⁻² for 160, 140 and 120°C to 0.26, 0.18 and 0.14 A cm⁻² respectively. For the 50 and 80 % methane feed stream the maximum achievable current densities also decrease from 0.2, 0.16 and 0.16 A cm⁻² to 0.14, 0.12 and 0.12 A cm⁻² and from 0.14, 0.12 and 0.1 A cm⁻² to 0.06, 0.08 and 0.06 A cm⁻² for 160, 140 and 120°C respectively

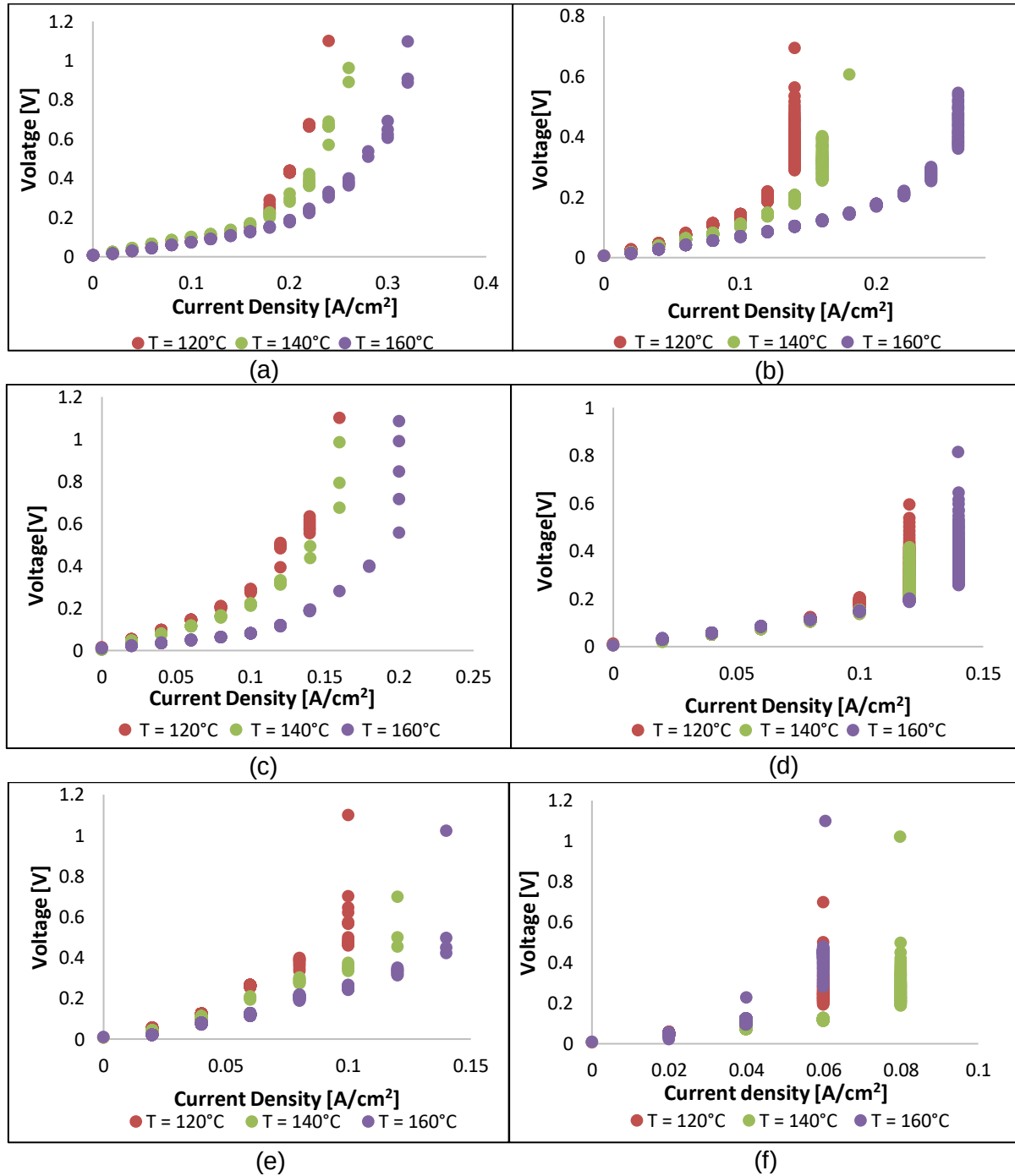


Figure C.6: Polarisation curves for the old and new membrane for hydrogen/methane separation with a fixed hydrogen flow rate of 100 nmL/min at 1 atm (a) 10% methane (new); (b) 10% methane (aged); (c) 50% methane (new); (d) 50% methane (aged); (e) 80% methane (new) and (f) 80% methane (aged).

The limiting current values reached by the aged membrane might be due to catalyst poisoning/deactivation since the cell was exposed to various concentrations of CO₂. CO has been reportedly formed from CO₂, obeying the reverse water gas shift reaction (Araya *et al.*, 2016):



The voltage-time curves of the BoL membrane are shown in **Figure C.10**. From the figure it is evident that the cell is influenced by the methane concentration and is also influenced by the amount of methane in the feed stream; the voltage increased with an increase in the methane concentration. The 80% methane mixture was not able to reach 0.1 A cm⁻² and therefore no graph is shown for this mixture. For the 10% methane feed stream, the voltage values seemed to be quite stable between 0.06 and 0.08 V for all temperatures. However, the different temperatures' voltage values cannot be greatly distinguished as the variations were very small. For the feed stream containing 50% methane the temperature effects could be better distinguished. The voltage values at 120°C was not very stable and had a continuous increase. However, when the temperature was raised, the voltage declined and was more stable due to the electrode kinetics that was enhanced at higher temperatures.

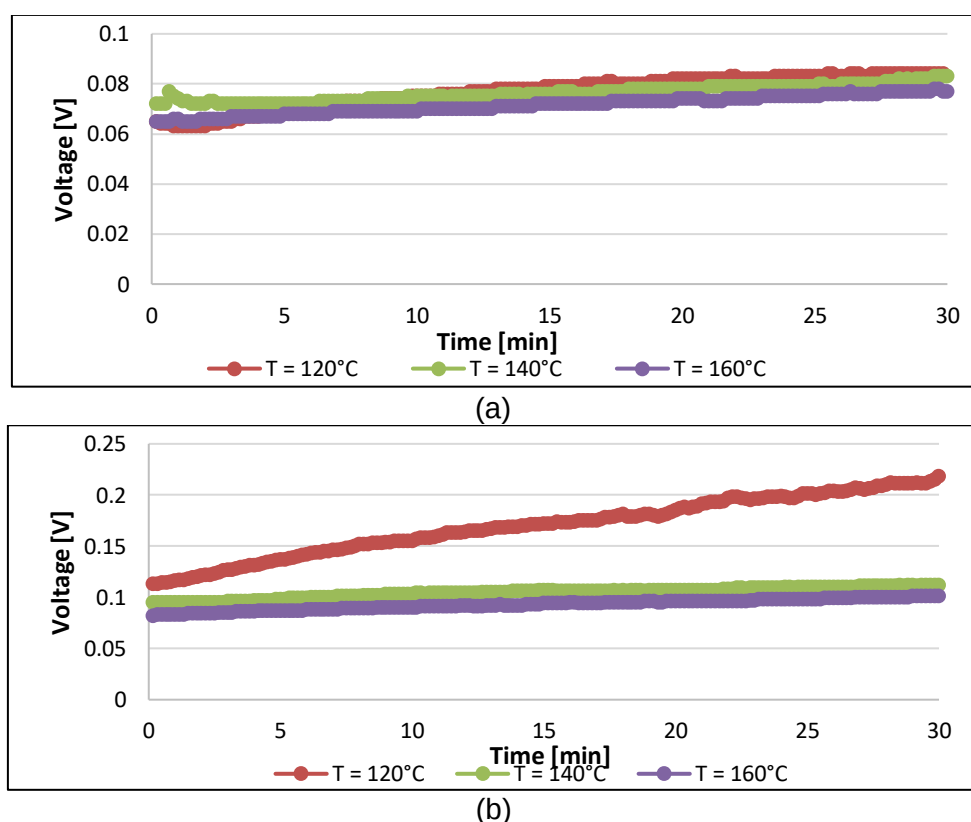


Figure C.7: Voltage–time (V-t) curves of TPS[®]-based membrane with a hydrogen flow rate of 100 nL/min at 0.1 A cm⁻²: (a) 10% and (b) 50% methane in the feed stream (balance hydrogen).

The GC analysis of the permeate stream for the CH₄ experiments conducted with the BoL membrane show that high grade hydrogen (>99.9%) can be achieved for all the tested methane concentrations (10; 50 and 80% methane), whereas further purification will be needed for the aged membrane. In **Figure C.8**, at fixed temperatures the selectivity improves with an increase in methane concentration and current density. This can be observed throughout, including both the BoL tests as well as aged membrane tests. Literature state that the separation performance of a membrane can be improved by reducing the temperature explained by the Arrhenius equation (Freeman *et al.*, 2010), which is confirmed in this work. From **Figure C.10** it can collectively be observed that, at the BoL tests (graphs at the left-hand side), much higher selectivities is reached at lower temperatures. For the 10% methane feed stream a selectivity decrease can be observed from 13048.43 to 12758.46 and then to 1979.66 as temperatures is increased from 120°C to 140 and then to 160°C. For the 50% methane feed stream this is also true as the selectivity reduces from 9802.92 to 6249 to 4806.69.

For the 80% methane feed stream the highest selectivity (~22218.22) is achieved at 140°C and this is merely because the feed stream is subject to a limiting current density at 120°C of 0.1 A cm⁻² and therefore has an influence on the separation efficiency. Furthermore, it is evident in **Figure C.8** and **Figure C.10** that the separation performance is severely impaired when the cell reaches then end of its lifetime as the separation factor values experience an immense drop from achievable values in the 20 000s to values in the 70s. However, although the separation performance of the cell is severely impaired when the membrane is aged, the trend of the current density, methane concentration effect and the temperature dependency is still there. Very poor selectivity values are achieved with the aged membrane and the membrane can be classified as incapable of sufficient separation. From this the conclusion was made that a lot of time and researching effort should still be implemented in the durability studies of this technology before large scale application can be fully considered.

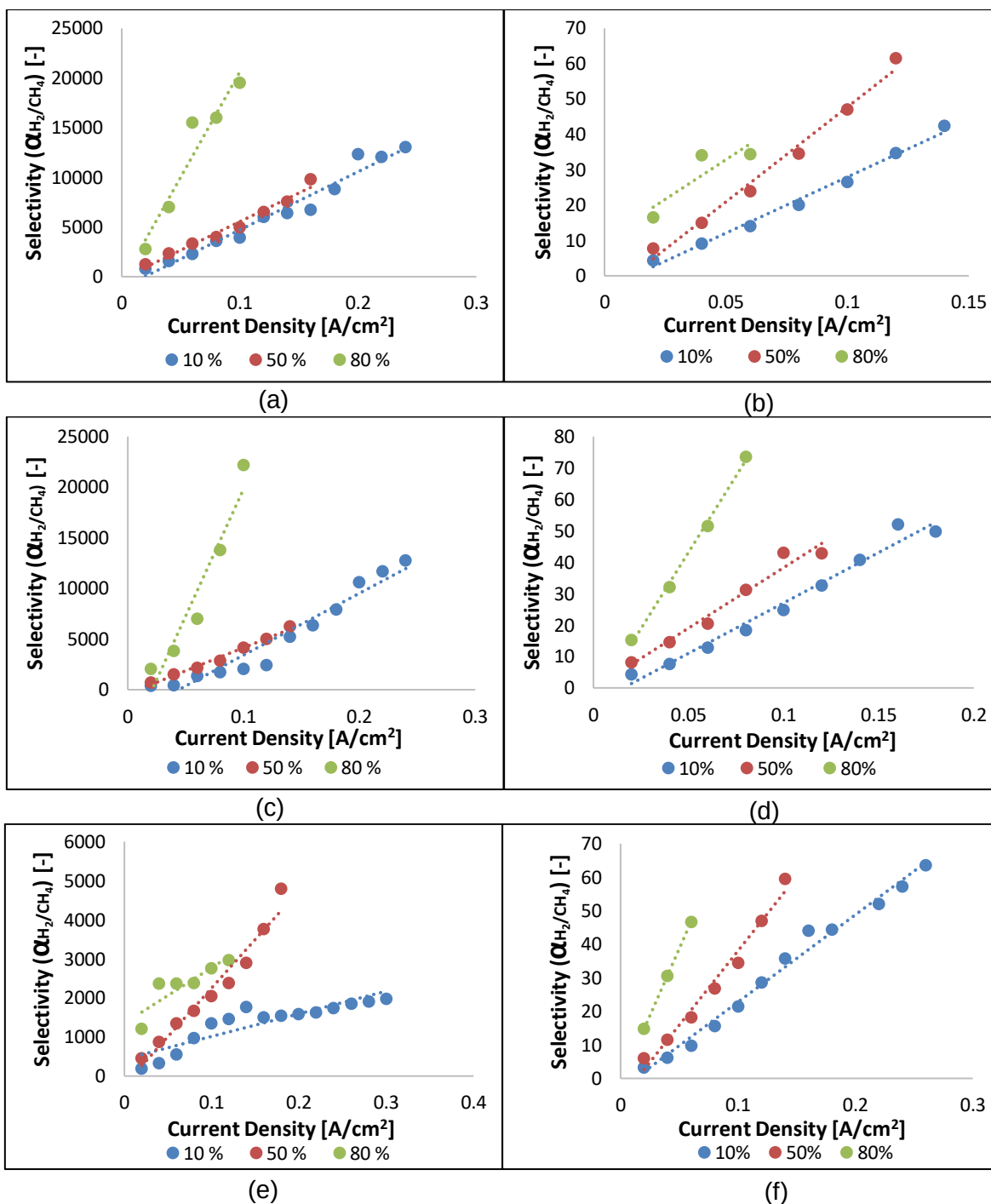


Figure C.8: Hydrogen/methane selectivity in terms of temperature versus current density at a hydrogen feed rate of 100 nmL/min: (a) 120°C (new); (b) 120°C (aged); (c) 140°C (new); (d) 140°C (aged); (e) 160°C (new) and (f) 160°C (aged).

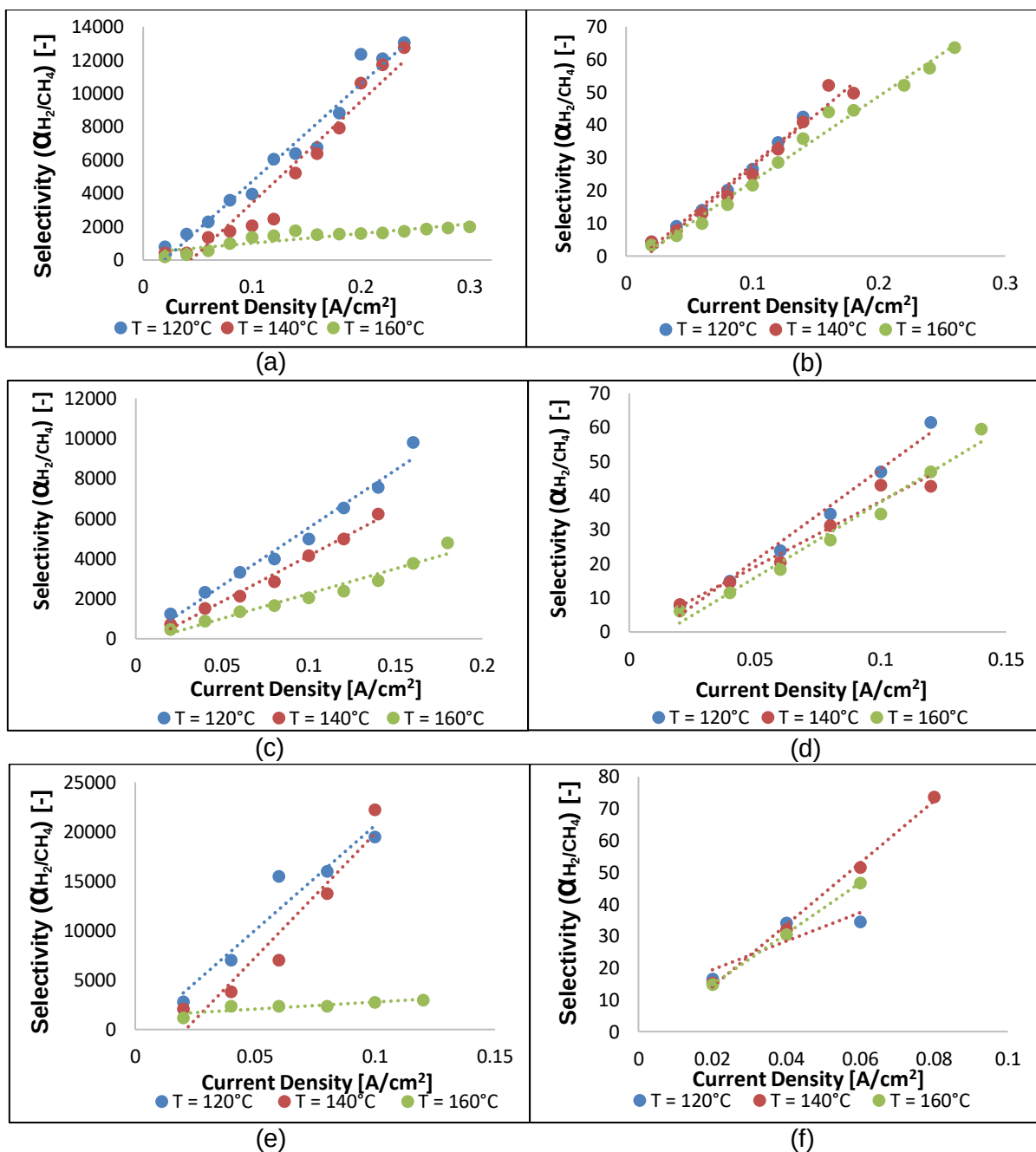
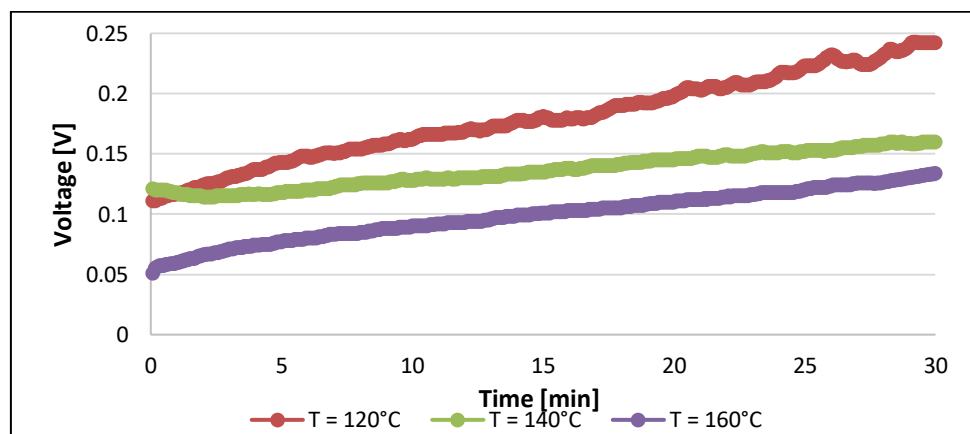


Figure C.9: Hydrogen/methane selectivity in terms of methane concentration in the feed stream versus current density, at a hydrogen feed rate of 100 nmL/min: (a) 10% (new); (b) 10% (aged); (c) 50% (new); (d) 50% (aged); (e) 80% (new) and (f) 80% (aged).

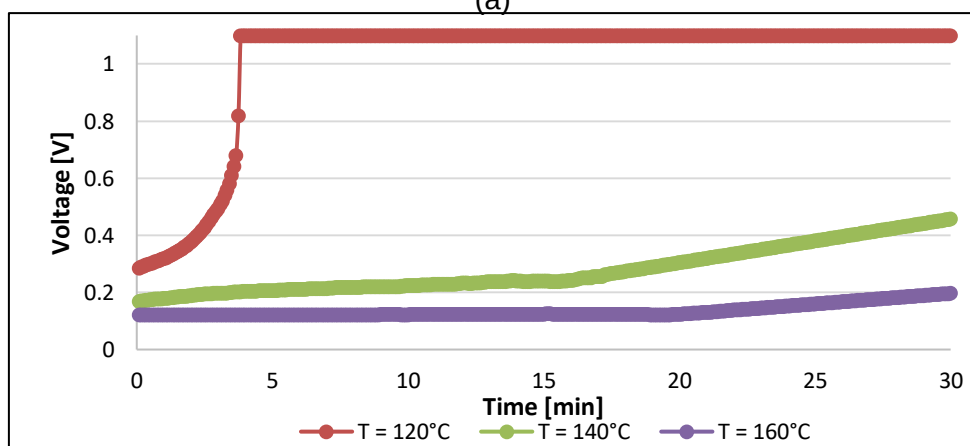
C.5.3 H_2/CO_2 V-t CURVES

From the voltage stability curves depicted in **Figure C.10** it can be collected that the voltage values obtained with H_2/CO_2 gas mixtures were much higher than that obtained with pure hydrogen. Where the starting voltage values and ending values are ± 0.125 ; 0.12 ; 0.05 V and ± 0.24 ; 0.16 ; 0.135 V at 120; 140 and 160°C respectively when 10% carbon dioxide is used and 0.3; 0.2; 0.26 V and 1.1 (voltage limit); 0.48; 0.2 V when 50% carbon dioxide is used. In

the presence of 50% methane the voltage limit is reached at 120°C after approximately 4 minutes, this is caused by the poor performance associated with lower temperatures especially when high vol. % impurities are present. A voltage incline is observed after 15 and 20 minutes at 140 and 160°C. The voltage incline might be due to poisoning of the electro-catalyst, where the active sites are deactivated by CO that is formed by the reverse water gas shift reaction. The same explanation can also be used for the smaller voltage inclines that is observed in the presence of 10% carbon dioxide.



(a)



(b)

Figure C.10: Voltage –time (V-t) curves of TPS[®]-based membrane with a hydrogen flow rate of 100 nmL/min at 0.1 A cm⁻²: (a) 10% and (b) 50% carbon dioxide in the feed stream (balance hydrogen).

Appendix D. GAS CALIBRATION CURVES

For gas chromatography (GC) analyses of the permeate streams, a SRI 8610C GC instrument was used (SRI Instruments, Torrance, CA). The average time for a single sample analysis was 10 minutes. The GC chamber was fitted with a molecular sieve (MS) 10X column (1.8 m) and a 0.9 m HayeSep-D column, in series. The instrument was equipped with a thermal conductivity detector (TCD). Ar was used as carrier gas. In GC analysis, use was made of a load/injection loop. A valve opens (load mode) at $t = 0.05$ s, introducing 1 mL sample gas, which is carried to the MS column. There, H_2 , CH_4 and CO are separated, and then carried to the HayeSep-D column where the larger molecules, such as CO_2 and NH_3 , are trapped. Hereafter, the separated molecules are carried to the TCD. The valve is then switched to 'inject mode'. The carrier gas is then used to remove the trapped molecules from the HayeSep-D column and then send to the TCD. Analysis, by means of TCD, is based on the difference in thermal conductivity of the different chemical species; it is able to effectively detect a minimum of 200-500 ppm with an accuracy of $\pm 90\%$ (Chromotech, 2013; EPA, 2001).

Standard gas mixtures (supplied by Afrox, South Africa) were used to obtain the GC calibration curves for CH_4 , NH_3 , CO, CO_2 , N_2 and H_2 . Subsequently, the compositions of the permeate streams (cathode outlet) obtained during experiments on the electrochemical hydrogen separator (EHS) were determined, making use of these gas calibration curves (based on peak area counts).

The respective gas calibration curves are illustrated for the following: CH_4 low concentrations (**Figure D.1**), CH_4 high concentrations (**Figure D.3**), NH_3 (**Figure D.5**), CO_2 low concentrations (**Figure D.7**), CO_2 high concentrations (**Figure D.9**), CO (**Figure D.11**) and N_2 (**Figure D.13**). These are accompanied by the calibration curve statistics for the following: CH_4 low concentrations (**Figure D.2**), CH_4 high concentrations (**Figure D.4**), NH_3 (**Figure D.6**), CO_2 low concentrations (**Figure D.8**), CO_2 high concentrations (**Figure D.10**), CO (**Figure D.12**) and N_2 (**Figure D.14**). In addition, two calibration curves are supplied for CH_4 and CO_2 , as high concentrations of CH_4 (up to 80%) and up to 50% CO_2 are fed to the EHS, resulting in larger quantities of methane and carbon dioxide in the product stream. In an effort to ensure that accurate readings were obtained for the lower concentrations of methane, two calibration curves were created. Lastly, the calibration curve for the H_2 diffusion experiments is given in **Figure D.15**, accompanied by the calibration curve statistics in **Figure D.16**.

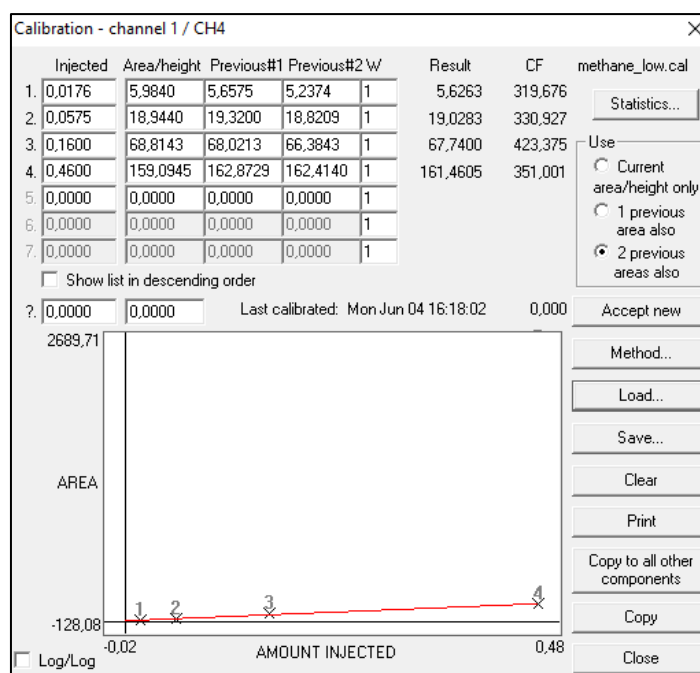


Figure D.1: Methane calibration curve used to calculate small quantities of CH₄ (mole fractions) of the product gas.

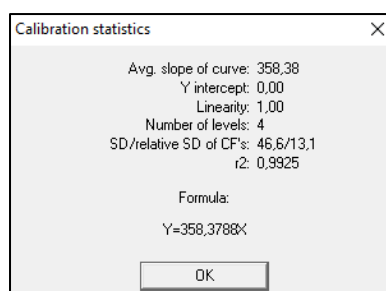


Figure D.2: Statistics for methane (low concentrations) calibration curve.

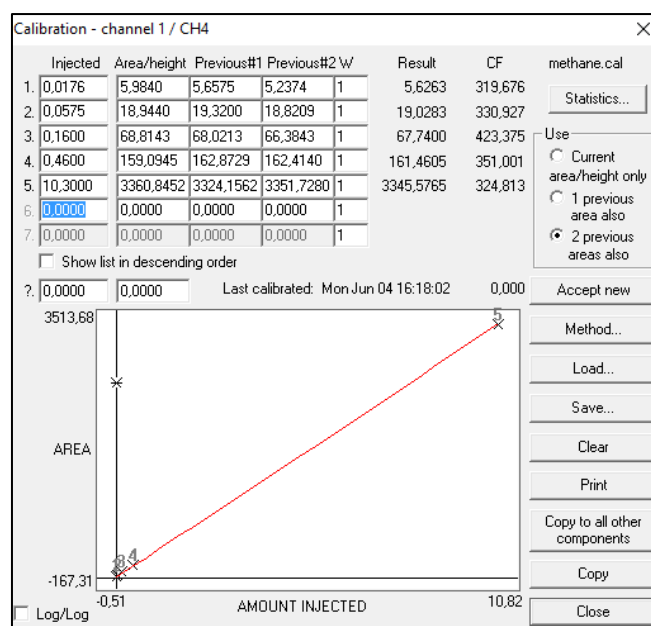


Figure D.3: Methane calibration curve used to calculate large quantities of CH₄ (mole fractions) of the product gas.

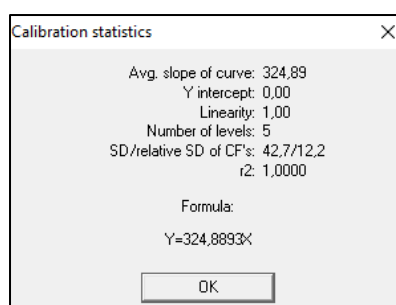


Figure D.4: Statistics for methane (large quantities) calibration curve.

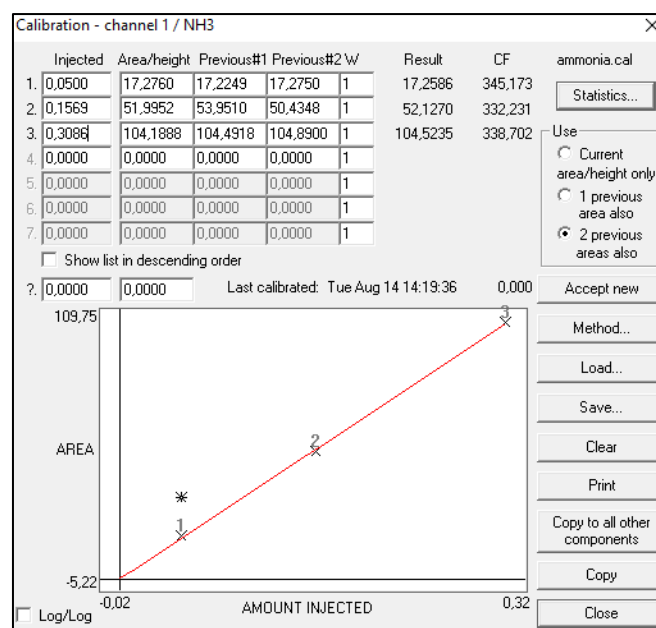


Figure D.5: Ammonia calibration curve used to calculate quantities of NH₃ (mole fractions) in the product gas.

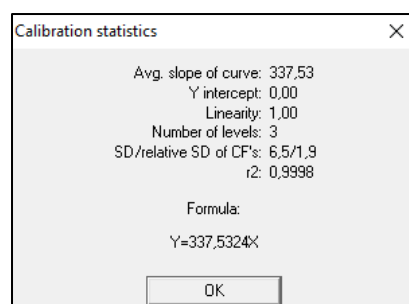


Figure D.6: Statistics for ammonia calibration curve.

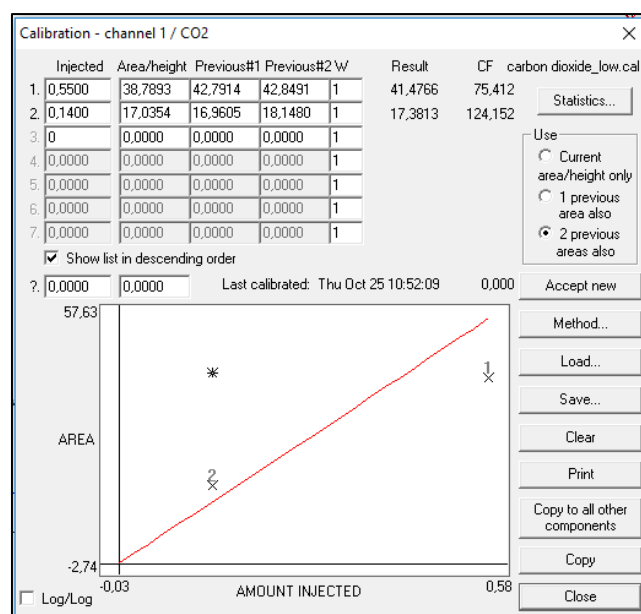


Figure D.7: Carbon dioxide calibration curve used to calculate small quantities of CO₂ (mole fractions) of the product gas.

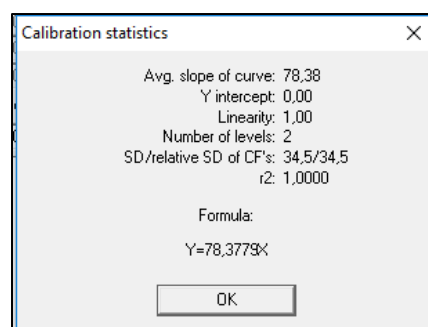


Figure D.8: Statistics for carbon dioxide (low concentrations) calibration curve.

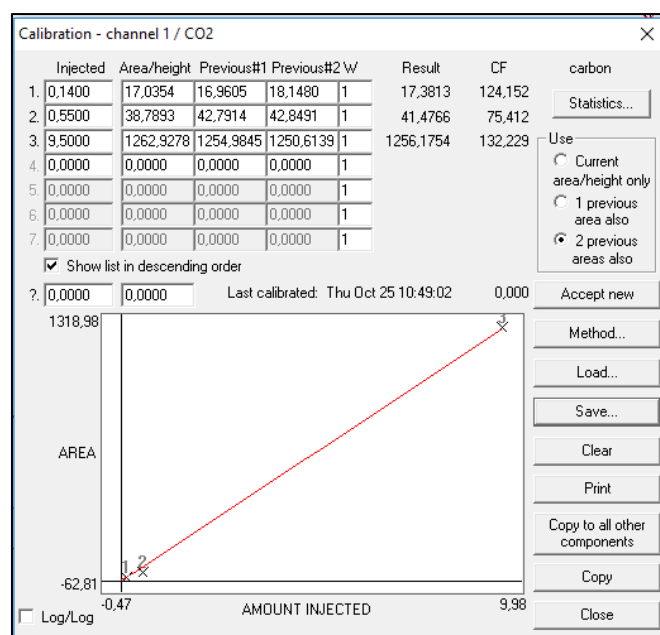


Figure D.9: Carbon dioxide calibration curve used to calculate large quantities of CO₂ (mole fractions) of the product gas.

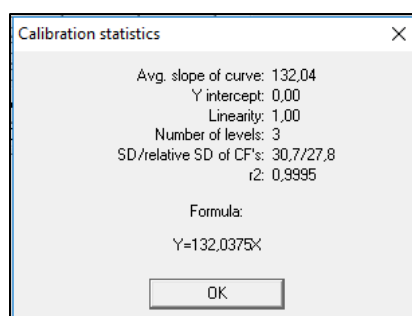


Figure D.10: Statistics for carbon dioxide (large quantities) calibration curve.

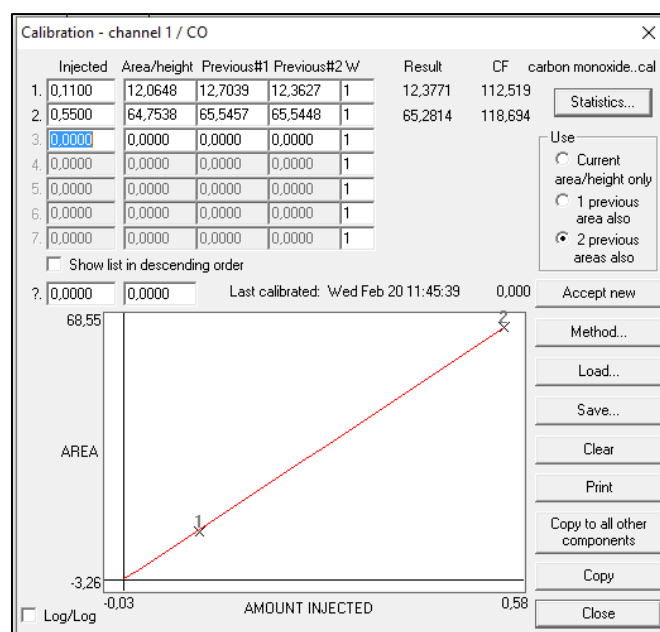


Figure D.11: Carbon monoxide calibration curve used to calculate quantities of CO (mole fractions) in the product gas.

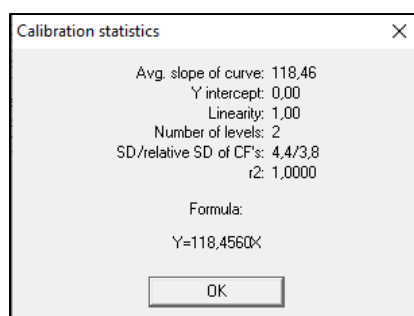


Figure D.12: Statistics for carbon monoxide calibration curve.

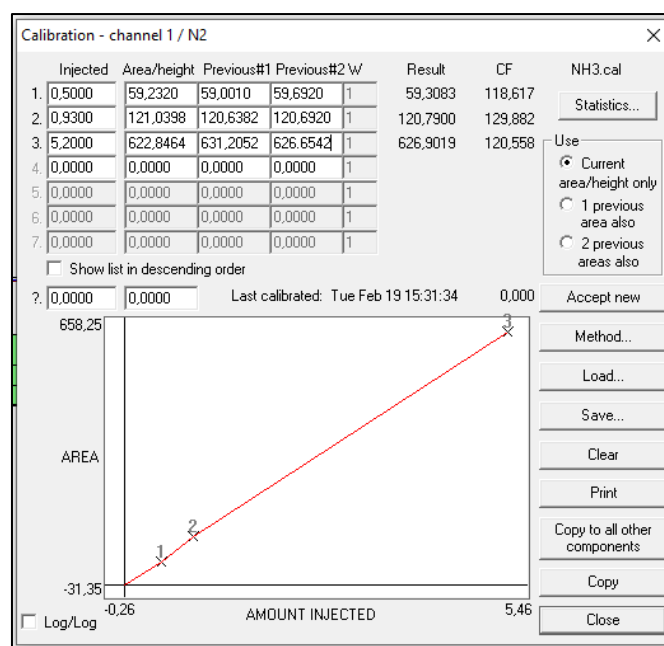


Figure D.13: Nitrogen calibration curve used to calculate quantities of N₂ (mole fractions) in the product gas during experiments.

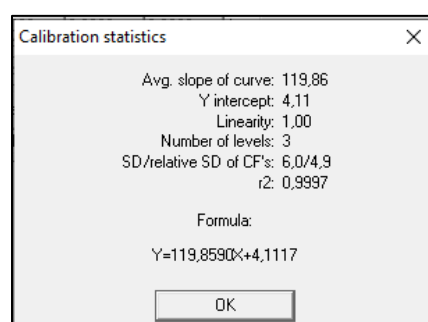


Figure D.14: Statistics for nitrogen calibration curve.

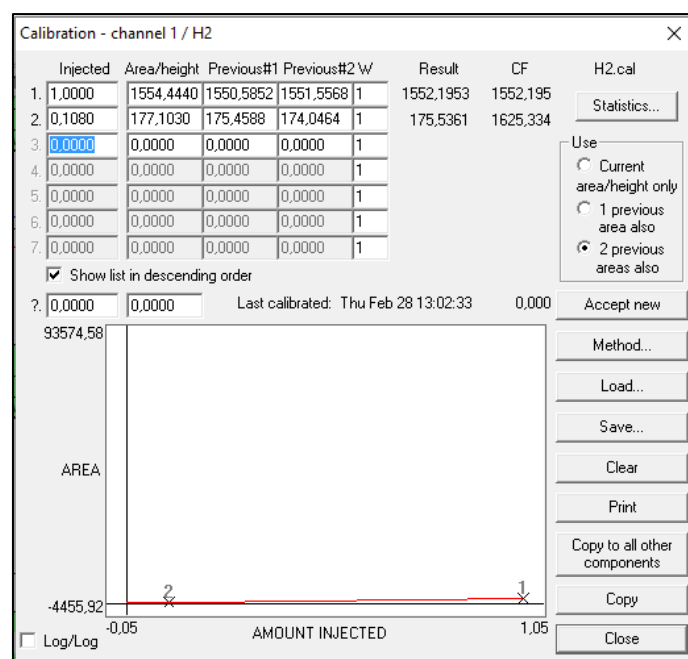


Figure D.15: Hydrogen calibration curve used to calculate quantities of H₂ (mole fractions) in the gas diffusion experiments.

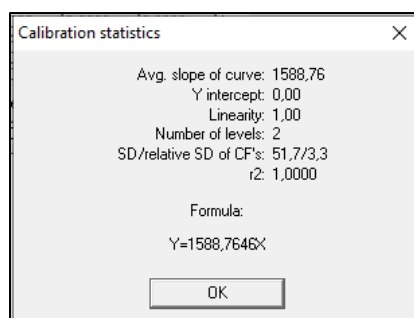


Figure D.16: Statistics for hydrogen calibration curve.

Appendix E. TPS[®]-BASED PEM: SELECTIVITY DATA

E.1 H₂/CH₄ SEPARATION

Table E.1: H₂/CH₄ selectivity at 120°C

Current Density (A cm ⁻²)	T = 120 °C		
	CH ₄ inlet (vol. %)	CH ₄ outlet (vol. %)	Hydrogen selectivity (α)
0.02	10	0.01440	797.30
	50	0.07945	1257.65
	80	0.14220	2808.94
0.04	10	0.00740	1551.60
	50	0.04300	2324.58
	80	0.05700	7013.54
0.06	10	0.00500	2296.43
	50	0.03010	3321.26
	80	0.02580	15499.88
0.08	10	0.00320	3588.24
	50	0.02511	3981.48
	80	0.02500	15996.00
0.10	10	0.00290	3959.44
	50	0.02000	4999.00
	80	0.02050	19508.20
0.12	10	0.00190	6043.42
	50	0.01530	6534.95
0.14	10	0.00180	6379.17
	50	0.01320	7574.76
0.16	10	0.00170	6754.43
	50	0.01020	9802.92
0.18	10	0.00130	8832.75
0.20	10	0.00093	12346.90
0.22	10	0.00095	12086.96
0.24	10	0.00088	13048.43

Table E.2: H₂/CH₄ selectivity at 140°C

Current Density (A cm ⁻²)	T = 140 °C		
	CH ₄ inlet (vol. %)	CH ₄ outlet (vol. %)	Hydrogen selectivity (α)
0.02	10	0.02740	418.96
	50	0.13675	730.26
	80	0.19110	2089.14
0.04	10	0.02710	423.60
	50	0.06590	1516.45
	80	0.10380	3849.56
0.06	10	0.00850	1350.79
	50	0.04650	2149.54
	80	0.05700	7013.54
0.08	10	0.00660	1739.69
	50	0.03500	2856.14
	80	0.02900	13789.10
0.10	10	0.00560	2050.37
	50	0.02400	4165.67
	80	0.01800	22218.22
0.12	10	0.00470	2443.02
	50	0.02000	4999.00
0.14	10	0.00220	5219.30
	50	0.01600	6249.00

Table E.2 (continued): H₂/CH₄ selectivity at 140°C

Current Density (A cm ⁻²)	CH ₄ inlet (vol. %)		CH ₄ outlet (vol. %)	Hydrogen selectivity (α)
	0.16	10	0.00180	6379.17
	0.18	10	0.00145	7919.00
	0.20	10	0.00108	10632.03
	0.22	10	0.00098	11716.95
	0.24	10	0.00090	12758.46

Table E.3: H₂/CH₄ selectivity at 160°C

Current Density (A cm ⁻²)	T = 160 °C		
	CH ₄ inlet (vol. %)	CH ₄ outlet (vol. %)	Hydrogen selectivity (α)
	T = 160 °C		
0.02	10	0.0605	189.68
	50	0.2141	466.07
	80	0.3278	1216.26
0.04	10	0.0341	336.62
	50	0.1130	884.35
	80	0.1681	2375.54
0.06	10	0.0206	557.30
	50	0.0736	1357.70
	80	0.1678	2379.79
0.08	10	0.0117	981.31
	50	0.0595	1679.67
	80	0.1675	2384.06
0.10	10	0.0085	1350.79
	50	0.0487	2052.39
	80	0.1444	2766.08
0.12	10	0.0078	1472.03
	50	0.0419	2385.63
	80	0.1344	2972.19
0.14	10	0.0065	1766.46
	50	0.0344	2905.98
0.16	10	0.0076	1510.77
	50	0.0265	3772.58
0.18	10	0.0074	1551.60
	50	0.0208	4806.69
0.20	10	0.0072	1594.71
0.22	10	0.0070	1640.27
0.24	10	0.0066	1739.69
0.26	10	0.0062	1851.94
0.28	10	0.0060	1913.67
0.30	10	0.0058	1979.66

E.2 H₂/CO₂ SEPARATION

Table E.4: H₂/CO₂ selectivity at 120°C

Current Density (A cm ⁻²)	<i>T</i> = 120 °C		
	CO ₂ inlet (vol. %)	CO ₂ outlet (vol. %)	Hydrogen selectivity (α)
0.02	10	0.748	14.74
	50	3.223	30.03
0.04	10	0.641	17.22
	50	1.428	69.04
0.06	10	0.453	24.40
	50	1.024	96.66
0.08	10	0.453	24.40
	50	0.709	140.02
0.10	10	0.403	27.49
	50	0.617	161.00

Table E.5: H₂/CO₂ selectivity at 140°C

Current Density (A cm ⁻²)	<i>T</i> = 140 °C		
	CO ₂ inlet (vol. %)	CO ₂ outlet (vol. %)	Hydrogen selectivity (α)
0.02	10	1.918	5.68
	50	3.813	25.23
0.04	10	1.680	6.50
	50	1.437	68.59
0.06	10	0.711	15.50
	50	0.883	112.25
0.08	10	0.687	16.07
	50	0.751	132.21
0.10	10	0.560	19.41
	50	0.715	138.86
0.12	10	0.544	20.31
	50	0.609	163.20

Table E.6: H₂/CO₂ selectivity at 160°C

Current Density (A cm ⁻²)	<i>T</i> = 160 °C		
	CO ₂ inlet (vol. %)	CO ₂ outlet (vol. %)	Hydrogen selectivity (α)
0.02	10	0.608	18.17
	50	1.048	94.44
0.04	10	0.585	18.87
	50	0.919	109.47
0.06	10	0.578	19.13
	50	0.905	107.83
0.08	10	0.446	24.81
	50	0.818	121.28
0.10	10	0.369	30.02
	50	0.656	151.51
0.12	10	0.335	33.09
	50	0.527	188.65
0.14	10	0.311	35.64
	50	0.522	190.75

E.3 H₂/NH₃ SEPARATION

Table E.7: H₂/NH₃ selectivity at 120°C

Current Density (A cm ⁻²)	T = 120 °C		
	NH ₃ inlet (vol. %)	NH ₃ outlet (vol. %)	Hydrogen selectivity (α)
0.02	0.1569	0.288	0.54
	0.3086	0.387	0.80
0.04	0.1569	0.220	0.71
0.06	0.1569	0.151	1.04
0.08	0.1569	0.106	1.48
0.10	0.1569	0.105	1.50

Table E.8: H₂/NH₃ selectivity 140°C

Current Density (A cm ⁻²)	T = 140 °C		
	NH ₃ inlet (vol. %)	NH ₃ outlet (vol. %)	Hydrogen selectivity (α)
0.02	0.1569	0.412	0.38
	0.3086	0.479	0.64
0.04	0.1569	0.322	0.49
	0.3086	0.391	0.79
0.06	0.1569	0.280	0.56
	0.3086	0.304	1.02
0.08	0.1569	0.214	0.73
0.10	0.1569	0.144	1.09
0.12	0.1569	0.123	1.28

Table E.9: H₂/NH₃ selectivity at 160°C

Current Density (A cm ⁻²)	T = 160 °C		
	NH ₃ inlet (vol. %)	NH ₃ outlet (vol. %)	Hydrogen selectivity (α)
0.02	0.1569	0.552	0.28
	0.3086	0.424	0.73
0.04	0.1569	0.372	0.42
	0.3086	0.310	1.00
0.06	0.1569	0.278	0.56
0.08	0.1569	0.244	0.64
0.10	0.1569	0.212	0.74
0.12	0.1569	0.186	0.84

Appendix F. TPS®-BASED PEM BEFORE AND AFTER AMMONIA EXPOSURE: SEM IMAGES

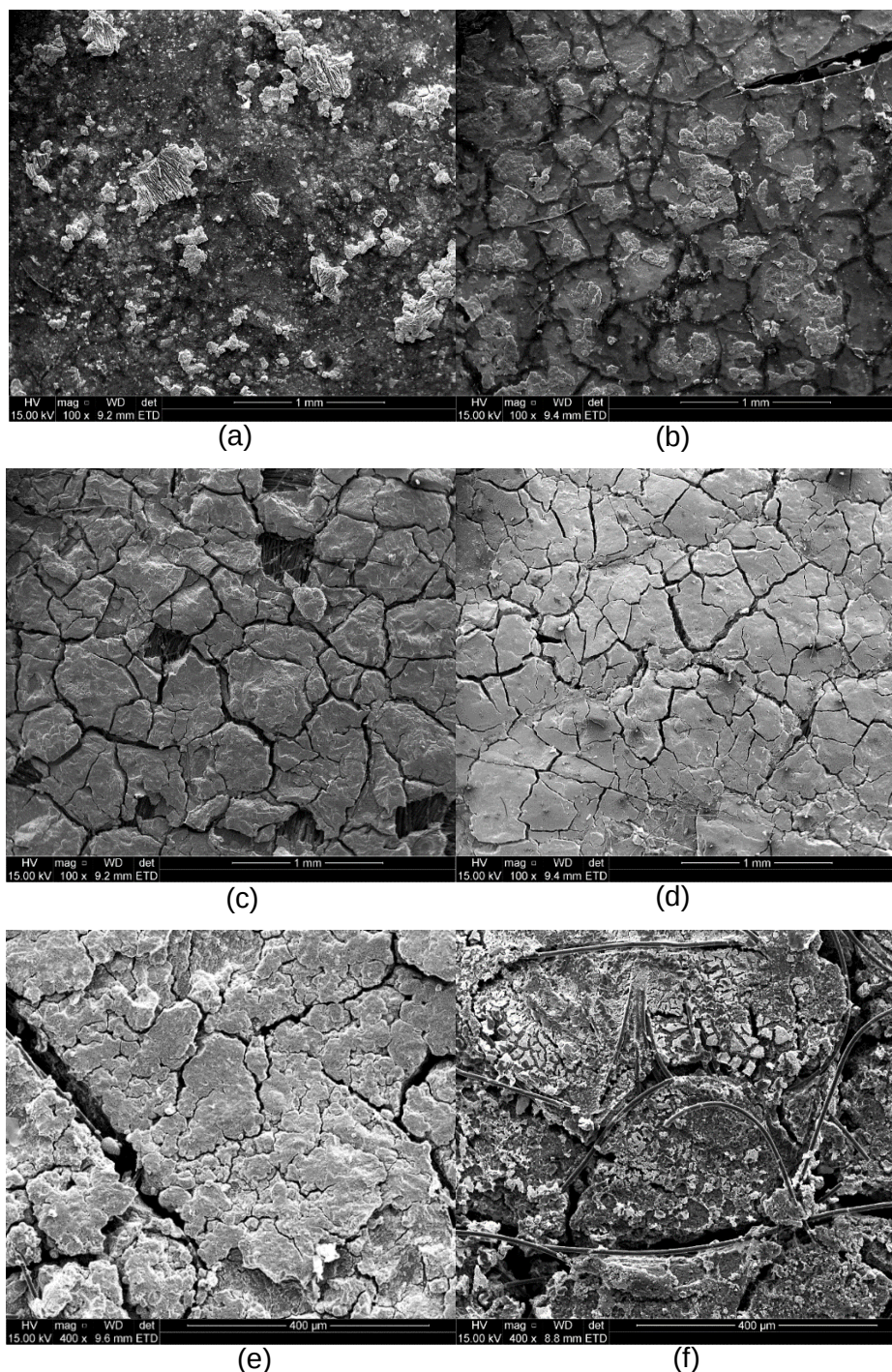


Figure F.1: SEM images/surface morphologies of MEA components: (a) membrane before ammonia exposure, (b) damaged membrane after ammonia exposure, (c) cathode GDL (Pt catalyst) before ammonia exposure, (d) cathode GDL (Pt catalyst) after ammonia exposure, (e) anode GDL (Pt/Co catalyst) before ammonia exposure and (f) anode GDL (Pt/Co catalyst) after ammonia exposure (MEA: membrane electrode assembly; GDL: gas diffusion layer).

Appendix G. HYDROGEN FUEL QUALITY: SPECIFICATIONS

The hydrogen fuel quality specifications are given in **Table G.1**. The units of the constituent limits are given in $\mu\text{mol/mol}$ unless otherwise specified. The limits given are all upper limits, with the exception of hydrogen which specifies the lower limit.

Table G.1: Hydrogen fuel quality specifications (SAE International (2015))

Constituent	Chemical formula	Limits	Minimum Analytical detection limit
Hydrogen fuel index	H ₂	>99.97%	
Water ^a	H ₂ O	5	0.12
Total hydrocarbons ^b (C ₁ basis)		2	0.1
Oxygen	O ₂	5	1
Helium	He	300	100
Nitrogen, Argon	N ₂ , Ar	100	5
Carbon dioxide	CO ₂	2	0.1
Carbon monoxide	CO	0.2	0.01
Total sulfur ^c		0.004	0.00002
Formaldehyde	HCHO	0.01	0.01
Formic acid	HCOOH	0.2	0.02
Ammonia	NH ₃	0.1	0.02
Total halogenates ^d		0.05	0.01
Particulate Concentration		1 mg/kg	0.005 mg/kg

^a Due to the water threshold level, the following should be tested for if there is a question regarding water content:

- Sodium (Na⁺) < 0.05 $\mu\text{mol/mol}$ H₂ or < 0.05 $\mu\text{g/L}$
- Potassium (K⁺) < 0.05 $\mu\text{mol/mol}$ H₂ or < 0.08 $\mu\text{g/L}$
- Potassium hydroxide (KOH) < 0.05 $\mu\text{mol/mol}$ H₂ or < 0.12 $\mu\text{g/L}$

^b e.g. ethylene, propylene, acetylene, benzene, phenol (paraffins, olefins, aromatic compounds, alcohols, aldehydes). The summation of methane, nitrogen and argon is not to exceed 100 ppm.

^c e.g. hydrogen sulfide (H₂S), carbonyl sulfide (COS), carbon disulphide (CS₂) and mercaptans.

^d e.g. hydrogen bromide (HBr), hydrogen chloride (HCl), Chlorine (Cl₂) and organic halide (R-X).

Appendix H. SUPPLEMENTARY EXPERIMENTS: CO TOLERANCE OF Pt/C AND Pt-Ru/C ELECTROCATALYST SUPPORTED ON A PBI-BASED PEM (CHAPTER 4)

H.1 HYDROGEN DIFFUSION THROUGH THE MEMBRANE

The cross-section of a proton exchange membrane (PEM) sandwiched between the Pt catalyst layers (CLs) is shown in **Figure H.1**.

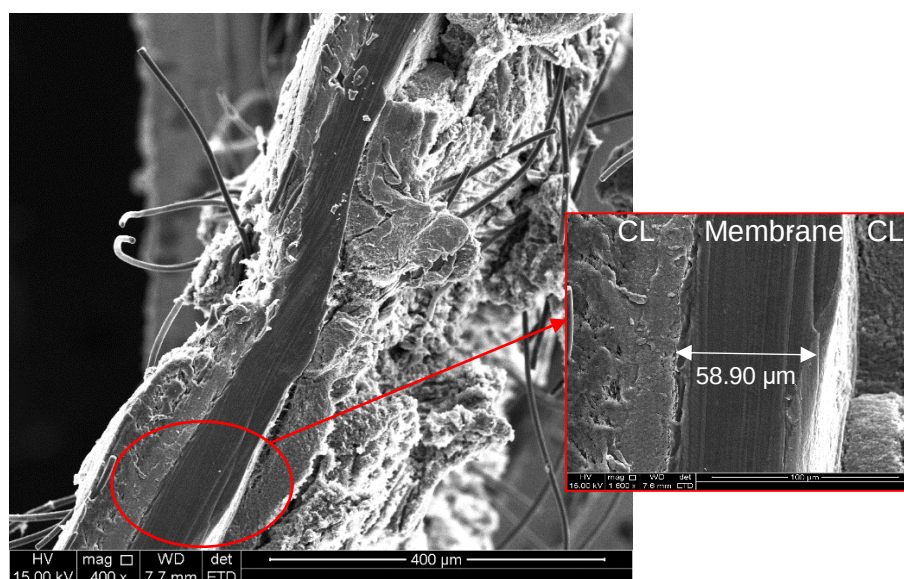


Figure H.1: Cross section of the PEM sandwiched between the Pt catalyst layers

The diffusion of hydrogen through the PEM was determined for various hydrogen feed flow rates. Hydrogen was fed to the anode inlet, whilst nitrogen was simultaneously fed to the cathode inlet, at a controlled flow rate of 5 nmL/min. This was done in the absence of an external DC load, and at atmospheric pressure and cell operating temperatures of 120-160°C. The nitrogen was used to transport the diffused hydrogen to the gas chromatograph (GC), where the composition of the cathode outlet gas mixture was determined. The total cathode feed flow rate (determined using a soap flow meter), gas composition and the nitrogen feed flow rate are known, hence the flow rate of the diffused hydrogen can be calculated by

$$F_{total} = x_{H_2}F_{H_2} + x_{N_2}F_{N_2} \quad (\text{Eq. H.1})$$

F_{total} , F_{H_2} and F_{N_2} depict the total, hydrogen and nitrogen flow rates of the cathode outlet stream, respectively, in nL/min, and x_{H_2} and x_{N_2} resemble the fractional compositions of hydrogen and nitrogen of the same stream. From the hydrogen diffusion data given in **Figure H.2**, the molecular diffusional contributions to the experiments were considered to be negligibly small and the electrochemical Faradic law were considered the only driving force for hydrogen transport through the PEM.

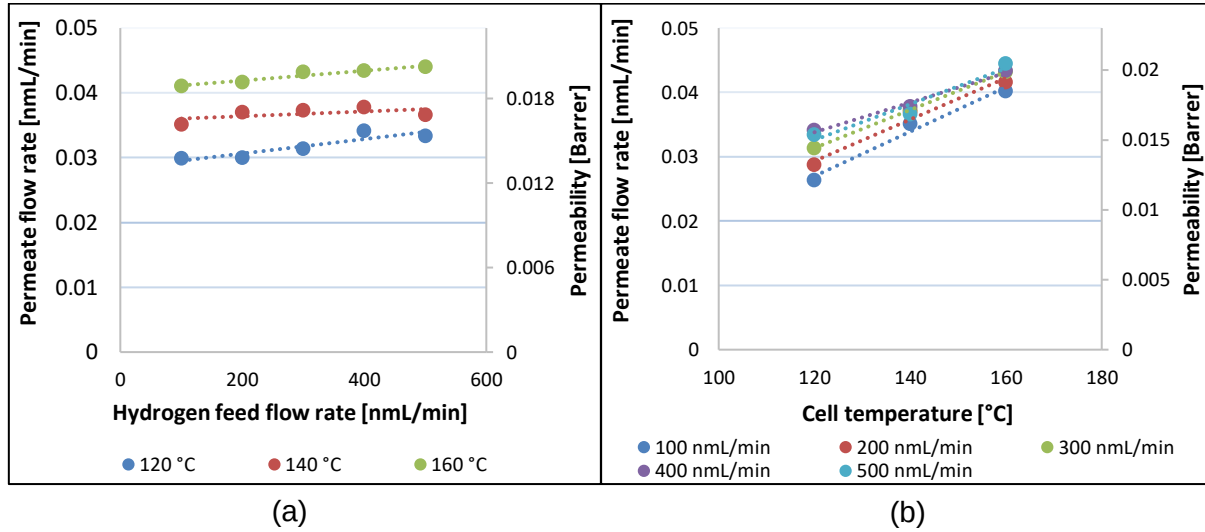


Figure H.2: Hydrogen diffusion through the membrane in the absence of an applied load in terms of (a) hydrogen flow rate; (b) cell temperature

From **Figure H.2** it is apparent that the hydrogen flow rate increases with temperature at a constant flow rate and there is a very small increase in the hydrogen diffusion when the flow rate increases, at constant temperature.

H.2 PURE HYDROGEN EXPERIMENTS: MEMBRANE CHARACTERISATION

In **Figure H.3**, the voltage–current characteristic of the MEA with Pt/C and MEA with Pt-Ru/C are compared for pure hydrogen fed to the cell at various flow rates and cell operating temperatures in the range 120-160°C. The linear nature of the initial and intermediate section of the plots indicate that the ohmic (IR_{Ω}) losses dominate the cell overpotential in this region, whilst the overall cell reaction rate dominate in the high current density region (horizontal lines), due to the depletion of reactants (Barbir & Görgün, 2007; Gardner *et al.*, 2007; Gardner & Ternan, 2007). The activation polarisation effects are considered minimal (Barbir & Görgün, 2007; Fasil *et al.*, 2002; Gallucci *et al.*, 2019). The vertical lines in **Figure H.3**, indicate the current density at which most of the supplied hydrogen has been consumed, defined as the limiting current density, which, in this case, is dependent on the hydrogen supplied to the cell. Higher limiting current densities were reached when higher feed flow rates were used. This

can be explained by Faraday's law, which state that the flow of hydrogen is directly proportional to the current.

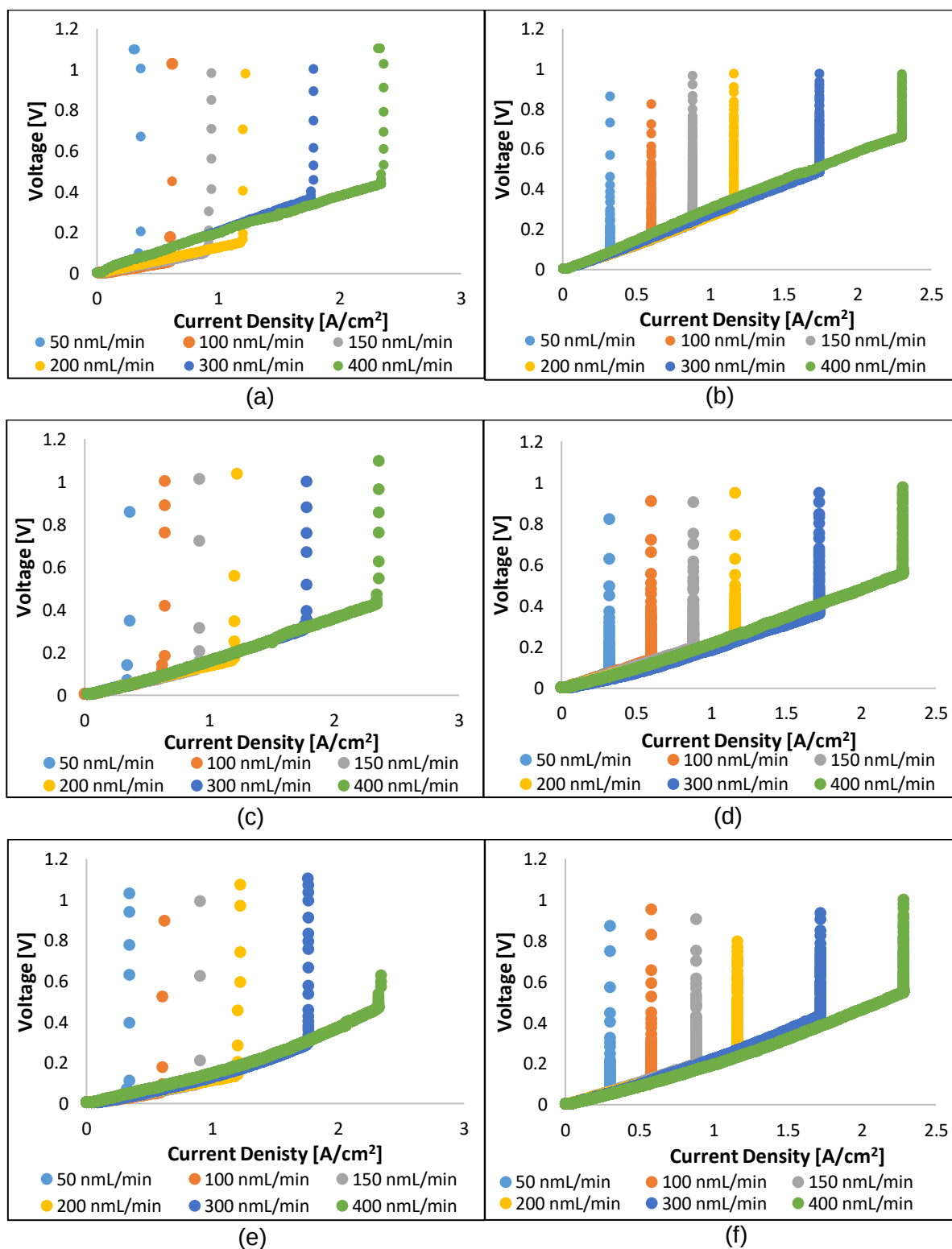


Figure H.3: Polarisation curves for (a) Pt/C at 120°C; (b) Pt-Ru/C at 120°C; (c) Pt/C at 140°C; (d) Pt-Ru at 140°C; (e) Pt/C at 160° and (f) Pt-Ru at 160°C

In general, similar limiting current densities were reached for the two MEAs although Pt/C shows better overall performance, as lower voltages are achieved at the respective current densities when compared with the Pt-Ru/C. This means higher power efficiencies result when Pt/C is used (Refer to **Appendix K**). Since IR_{Ω} -losses, defined as the sum of the contact resistance, electrical resistance and the proton conducting resistance (Chen *et al.*, 2014), dominate the largest part of the polarisation curves, the ohmic resistance is expected to be higher for the Pt-Ru/C since higher voltages are observed with this MEA. This is verified by EIS experiments.

From the Nyquist plots of the impedance data presented in **Figure H.4** and **Figure H.5**, with the x-intercept resembling the ohmic resistance of the membrane, it can be clearly observed that higher values are obtained with the MEA containing Pt-Ru/C. In **Figure H.4** the x-intercept values for the Pt/C MEA range between 5 and 5.5 mohm at 120°C; 3.9 and 4.1 mohm at 140°C; and 3.3 and 3.7 mohm at 160°C. Whereas the Pt-Ru/C MEAs ohmic resistance range between 7 and 7.5 ohm at 120°C; 5.2 and 5.5 at 140°C; and 5.1 and 5.4 at 160°C (**Figure H.5**). Further investigation of the EIS data indicate that the mass and charge transfer resistance (diameter of the impedance arc) is higher for the Pt-Ru/C MEA. A possible explanation for both the higher ohmic resistance and the higher mass and transfer resistances seen for the Pt-Ru/C MEA might be explained by the distribution of the PA acid in the membrane, since the ohmic resistance is mainly related to the resistance of the electrolyte (Baek *et al.*, 2012) and the ECSA should be directly related to the amount of the electrolyte contacting the catalyst (Kwon *et al.*, 2009). Due to the mobile nature of the PA, lower catalyst utilisation results and ultimately lower ECSA, which might be the case with the Pt-Ru/C (Kwon *et al.*, 2009). However, it is uncertain whether the higher resistances are due to the poor distribution of the acid inside the membrane or whether it can be explained by the bifunctional mechanism involving Pt and Ru as active sites or an electronic effect of Ru on Pt. The opposite is seen to be true in an alkaline environment: the oxidation of hydrogen on Pt is sluggish and Pt-Ru alloys shows exceptionally higher HOR activity (Dietz *et al.*, 2018). No reports were found on the comparison of HER and HOR on Pt and Pt-Ru at high temperatures in an acidic environment. It is however known that hydrogen oxidation and evolution on Pt in acid are facile processes (Durst *et al.*, 2014).

Further, general observations can be made from the EIS data presented for both the Pt/C and Pt-Ru/C containing MEAs. Temperature is seen to enhance ohmic and mass and charge transfer resistances. The reduction in the arc diameter at higher temperatures indicate that there is a slight improvement in mass transport and high frequency charge transfer, which is

confirmed in literature (Andreasen *et al.*, 2017). Ferng *et al.* (2012) revealed that an increase in temperature enhances the cell performance due to the increase in the reaction and the mass transfer rate and a lower cell resistance, which is confirmed in this work.

Another observation made is the influence of the hydrogen feed flow rate on the ohmic resistance and electrode kinetics. Both the Pt/C and Pt-Ru/C MEAs indicate that the ohmic resistance increase with the applied flow rate at temperatures $\geq 140^{\circ}\text{C}$, whilst and electrode kinetics seems to be independent of the applied flow rate. At 120°C the resistance increase in terms of hydrogen feed flow rate (nmL/min) for Pt/C and Pt-Ru/C is $200 < 150 < 100 < 50$ and $200 < 150 < 50 < 100$ respectively. Similarly, tests performed at 100°C (not indicated in the graphs) showed the resistance dependence on the feed flow rate in nmL/min for both MEAs to be $200 < 150 < 100 < 50$. According to literature excess fuel during EIS should minimise the mass transport resistance (Kim *et al.*, 2015). This is however partly confirmed in this work as this was only observed at lower temperatures, where the resistance was seen to decrease with an increase in the fuel supply.

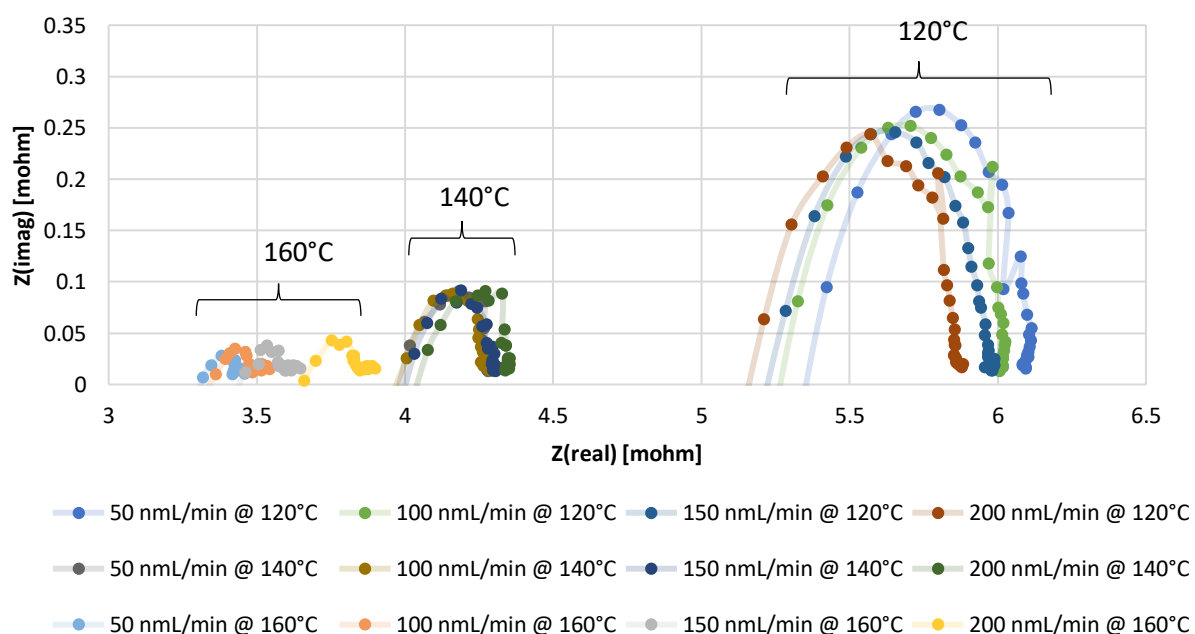


Figure H.4: EIS results for PBI membrane (Pt/C catalyst) with pure hydrogen at temperature and flow rate variations

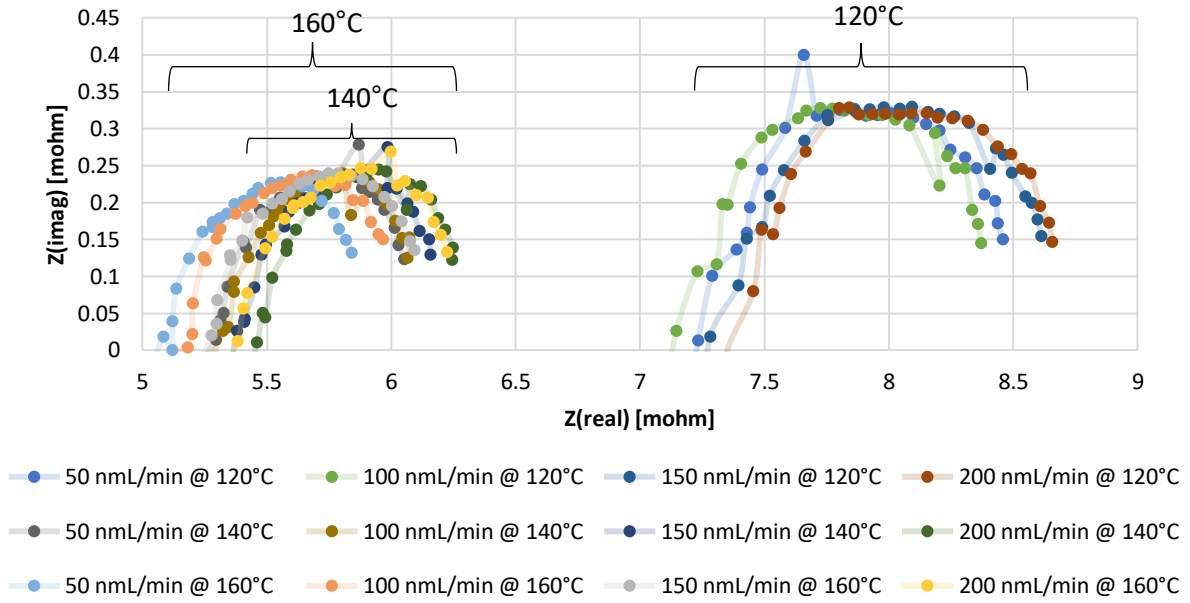


Figure H.5: EIS results for PBI membrane (Pt-Ru/C catalyst) with pure hydrogen at temperature and flow rate variations

To conclude this section, the hydrogen flux measured with a bubble flow meter indicated that nearly Faradic flow rates were achieved throughout, which indicate that no major system or cell leakages were present. The graph for a hydrogen feed flow rate of 100 nmL/min is demonstrated in **Figure H.6**. Here the theoretical line illustrates the law of Faraday. Refer to **Appendix K** for the remaining data.

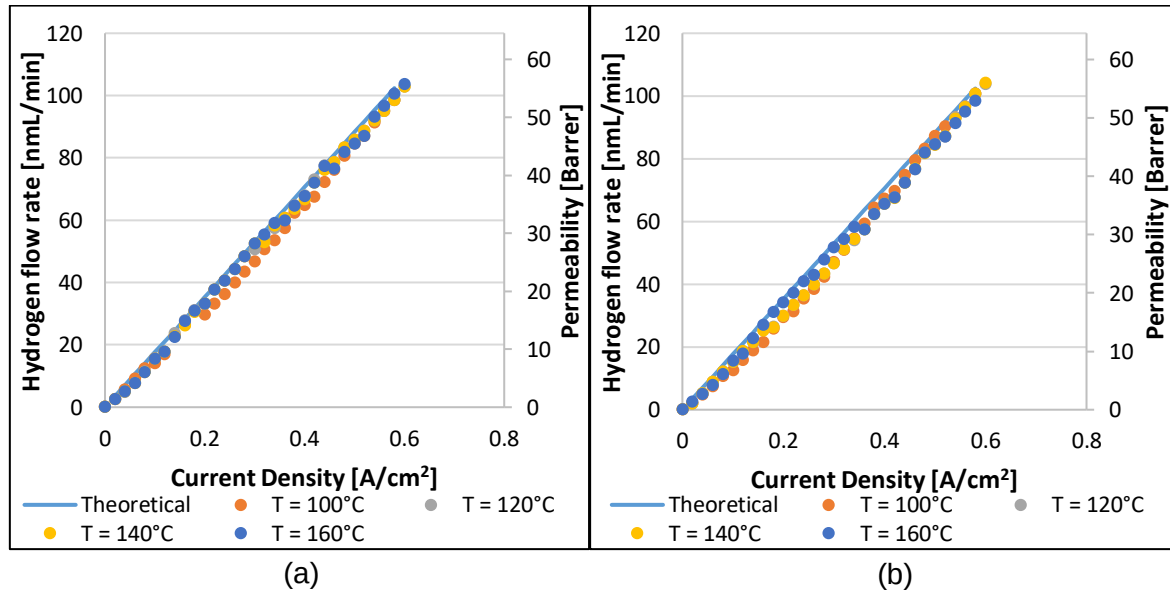


Figure H.6: Hydrogen flux and permeation rate for a hydrogen feed flow rate of 100 nmL/min: (a) Pt/C MEA; (b) Pt-Ru/C MEA.

Appendix I. SURFACE REACTION MECHANISMS FOR H₂ OXIDATION, CO OXIDATION AND CO-H₂ COUPLING ON Pt

Table I.1: Surface reaction mechanisms for CO and H₂ oxidation on Pt (Mhadeshwar & Vlachos, 2004)

Reaction no.	Reaction	Sticking coefficient [-] or pre-exponential [s ⁻¹]	Temperature exponent, β	Activation energy @ 300 K [kcal/mol]
<u>CO oxidation on Pt:</u>				
R ₁	$CO + * \rightarrow CO^*$	1.00×10^0	0.000	0.0
R ₂	$CO^* \rightarrow CO + *$	5.66×10^{15}	-0.500	$40 - 15\theta_{CO} + f(T)$
R ₃	$CO_2 + * \rightarrow CO_2$	1.95×10^{-1}	0.250	0.0
R ₄	$CO_2^* \rightarrow CO_2 + *$	3.63×10^{12}	-0.250	$3.6 + f(T)$
R ₅	$CO_2^* + * \rightarrow CO^* + O^*$	4.18×10^{10}	0.177	$26.4 + f(\theta_0, \theta_{CO}, T)$
R ₆	$CO^* + O^* \rightarrow CO_2^* + *$	2.39×10^{11}	-0.177	$20.6 + f(\theta_0, \theta_{CO}, T)$
<u>H₂ oxidation on Pt:</u>				
R ₇	$H_2 + 2^* \rightarrow 2H^*$	1.29×10^{-1}	0.858	0.0
R ₈	$2H^* \rightarrow H_2 + 2^*$	7.95×10^{12}	-0.001	$19.8 - 6\theta_H + f(T)$
R ₉	$O_2 + 2^* \rightarrow 2O^*$	5.42×10^{-2}	0.766	0.0
R ₁₀	$2O^* \rightarrow O_2 + 2^*$	8.41×10^{12}	-0.796	$50.9 - 32\theta_O + f(T)$
R ₁₁	$OH^* + * \rightarrow H^* + O^*$	1.95×10^{12}	1.872	$27.1 + f(\theta_0, \theta_H, \theta_{H_2O}, T)$
R ₁₂	$H^* + O^* \rightarrow OH^* + *$	6.33×10^{12}	0.624	$8.8 + f(\theta_0, \theta_H, \theta_{H_2O}, T)$
R ₁₃	$H_2O^* + * \rightarrow H^* + OH^*$	9.36×10^{12}	-0.118	$17.8 + f(\theta_0, \theta_H, \theta_{OH}, \theta_{H_2O}, T)$
R ₁₄	$H^* + OH^* \rightarrow H_2O + *$	9.99×10^{12}	-1.049	$13.5 + f(\theta_0, \theta_H, \theta_{OH}, \theta_{H_2O}, T)$
R ₁₅	$H_2O^* + O^* \rightarrow 2OH^*$	4.32×10^9	0.082	$8.8 + f(\theta_0, \theta_{OH}, \theta_{H_2O}, T)$
R ₁₆	$2OH^* \rightarrow H_2O^* + O^*$	1.70×10^9	0.325	$22.7 + f(\theta_0, \theta_{OH}, \theta_{H_2O}, T)$
R ₁₇	$OH + * \rightarrow OH^*$	9.99×10^{-1}	2.000	0.0
R ₁₈	$OH^* \rightarrow OH + *$	1.44×10^{14}	2.000	$63.0 - 33\theta_O + 25\theta_{H_2O} + f(T)$
R ₁₉	$H_2O + * \rightarrow H_2O^*$	1.08×10^{-1}	1.162	0.0
R ₂₀	$H_2O^* \rightarrow H_2O + *$	2.03×10^{12}	1.372	$10.0 - 2.5\theta_{H_2O} + 25\theta_{H_2O} + f(T)$
R ₂₁	$H + * \rightarrow H^*$	3.84×10^{-1}	1.832	0.0
R ₂₂	$H^* \rightarrow H + *$	4.37×10^{13}	1.890	$62.0 - 3\theta_H + f(T)$
R ₂₃	$O + * \rightarrow O^*$	4.91×10^{-2}	0.250	0.0
R ₂₄	$O^* \rightarrow O + *$	1.44×10^{13}	-0.250	$85.0 - 16\theta_O + f(T)$

Table I.2: Surface reaction mechanisms for the CO-H₂ coupling on Pt (Mhadeshwar & Vlachos, 2004)

Reaction no.	Reaction	Sticking coefficient [-] or pre-exponential [s ⁻¹]	Temperature exponent, β	Activation energy @ 300 K [kcal/mol]
<u>Coupling between H₂ and CO chemistries on Pt:</u>				
R ₂₅	$CO_2^* + H^* \rightarrow CO^* + OH^*$	8.03×10^{10}	-0.531	$6.0 + f(\theta_O, \theta_H, \theta_{H_2O}, \theta_{CO}, T)$
		8.03×10^8		
R ₂₆	$CO^* + OH^* \rightarrow CO_2^* + H^*$	1.25×10^{11}	0.531	$18.5 + f(\theta_O, \theta_H, \theta_{H_2O}, \theta_{CO}, T)$
		1.25×10^9		
R ₂₇	$COOH + * \rightarrow COOH^*$	6.34×10^{-2}	-0.089	0.0
R ₂₈	$COOH^* \rightarrow COOH + *$	1.12×10^{13}	0.089	$55.3 + f(T)$
R ₂₉	$COOH^* + * \rightarrow CO^* + OH^*$	8.43×10^{10}	0.024	$5.3 + f(\theta_O, \theta_{H_2O}, \theta_{CO}, T)$
		8.43×10^8		
R ₃₀	$CO^* + OH^* \rightarrow COOH^* + *$	1.19×10^{11}	-0.024	$19.1 + f(\theta_O, \theta_{H_2O}, \theta_{CO}, T)$
		1.19×10^9		
R ₃₁	$COOH^* + * \rightarrow CO_2 + H^*$	1.06×10^{11}	0.549	$1.0 + f(\theta_H, T)$
R ₃₂	$CO_2^* + H^* \rightarrow COOH^* + *$	9.45×10^{10}	-0.549	$2.4 + f(\theta_H, T)$
R ₃₃	$CO^* + H_2O^* \rightarrow COOH^* + H^*$	1.10×10^{11}	0.492	$23.7 + f(\theta_H, \theta_{OH}, \theta_{H_2O}, \theta_{CO}, T)$
R ₃₄	$COOH^* + H^* \rightarrow CO^* + H_2O^*$	9.07×10^{10}	-0.492	$5.6 + f(\theta_H, \theta_{OH}, \theta_{H_2O}, \theta_{CO}, T)$
R ₃₅	$CO_2^* + OH^* \rightarrow COOH^* + O^*$	5.35×10^{10}	0.097	$26.5 + f(\theta_O, \theta_{H_2O}, T)$
R ₃₆	$COOH^* + O^* \rightarrow CO_2 + OH^*$	1.87×10^{11}	-0.097	$7.0 + f(\theta_O, \theta_{H_2O}, T)$
R ₃₇	$CO_2^* + H_2O^* \rightarrow COOH^* + OH^*$	8.64×10^{10}	-0.031	$17.5 + f(\theta_O, \theta_{OH}, \theta_{H_2O}, T)$
R ₃₈	$COOH^* + OH^* \rightarrow CO_2^* + H_2O^*$	1.16×10^{11}	0.031	$11.9 + f(\theta_O, \theta_{OH}, \theta_{H_2O}, T)$
R ₃₉	$HCOO + 2 * \rightarrow HCOO^{**}$	1.46×10^{-1}	0.201	0.0
R ₄₀	$HCOO^{**} \rightarrow HCOO + 2 *$	4.83×10^{12}	-0.201	$53.0 + f(T)$
R ₄₁	$CO_2 + H^* \rightarrow HCOO^{**}$	1.12×10^{11}	-0.422	$18.5 + f(\theta_H, T)$
R ₄₂	$HCOO^{**} \rightarrow CO_2^* + H^*$	8.96×10^{10}	0.422	$f(\theta_H, T)$
R ₄₃	$CO_2^* + OH^* + * \rightarrow HCOO^{**} + O^*$	6.17×10^{10}	0.236	$36.8 + f(\theta_O, \theta_{H_2O}, T)$
R ₄₄	$CHOO^{**} + O^* \rightarrow CO_2^* + OH^* + *$	1.62×10^{11}	-0.236	$f(\theta_O, \theta_{H_2O}, T)$
R ₄₅	$CO_2^* + H_2O^* + * \rightarrow HCOO^{**} + OH^*$	1.02×10^{11}	0.095	$25.8 + f(\theta_O, \theta_{OH}, \theta_{H_2O}, T)$
R ₄₆	$HCOO^{**} + OH^* \rightarrow CO_2^* + H_2O^* + *$	9.78×10^{10}	-0.095	$3.0 + f(\theta_O, \theta_{OH}, \theta_{H_2O}, T)$

Appendix J. TEM IMAGES FOR THE PARTICLE SIZE ANALYSIS OF Pt AND Pt-Ru CATALYSTS, BEFORE AND AFTER HEAT TREATMENT

The particle sizes of both Pt/C and Pt-Ru/C, were manually determined using TEM images and ImageJ software. The white dots observed in **Figure J.1** indicate the particles that were analysed. From the TEM images, the area, radius and diameter of each particle (tabulated in **Table J.2-Table J.5**) was determined using ImageJ software. The tables presented corresponds to the images displayed in **Figure J.1**. The results obtained was used to quantify the onset of particle agglomeration after heat treatment. The mean, standard deviation, maximum and minimum of each parameter is included at the end of each table.

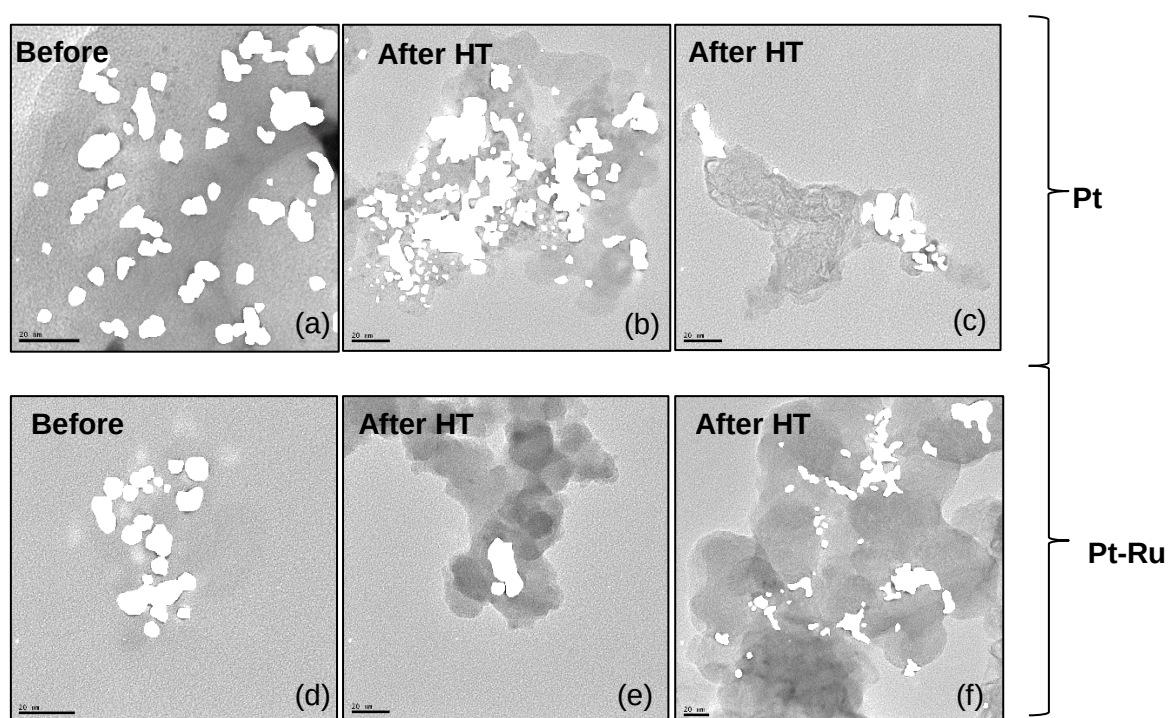


Figure J.1: Transmission electron microscopy (TEM) images of Pt/C and Pt-Ru/C catalysts, before and after, CO and heat treatment (HT): (a) Pt; (b) Pt-HT; (c) Pt-HT; (d) Pt-Ru; (e) Pt-Ru-HT; (f) Pt-Ru-HT.

A list of the symbols used in the particle size tables below is summarized in **Table J.1**:

Table J.1: List of symbols used in the particle size tables

Symbol	
#	number
A	area
r	radius
d	diameter

J.1 Pt PARTICLE SIZE ANALYSIS, BEFORE AND AFTER HEAT TREATMENT

Table J.2: Particle size data for Pt particles before experimental heat treatment (data corresponds to **Figure J.1 (a)**)

Particle #	A [nm ²]	r ² [nm ²]	r [nm]	d [nm]	Particle #	A [nm ²]	r ² [nm ²]	r [nm]	d [nm]
1	14.25	4.53	2.13	4.26	41	21.06	6.70	2.59	5.18
2	38.84	12.36	3.52	7.03	42	43.88	13.97	3.74	7.47
3	13.51	4.3	2.07	4.15	43	8.78	2.79	1.67	3.34
4	13.66	4.35	2.09	4.17	44	31.80	10.12	3.18	6.36
5	24.63	7.84	2.8	5.6	45	21.19	6.74	2.60	5.19
6	17	5.41	2.33	4.65	46	20.72	6.60	2.57	5.14
7	27.96	8.9	2.98	5.97	47	41.89	13.33	3.65	7.30
8	9.34	2.97	1.72	3.45	48	39.92	12.71	3.56	7.13
9	19.01	6.05	2.46	4.92	49	29.86	9.50	3.08	6.17
10	29.4	9.36	3.06	6.12	50	26.81	8.53	2.92	5.84
11	39.51	12.58	3.55	7.09	51	56.45	17.97	4.24	8.48
12	9.83	3.13	1.77	3.54	52	64.93	20.67	4.55	9.09
13	10.63	3.38	1.84	3.68	53	21.50	6.84	2.62	5.23
14	9.57	3.05	1.75	3.49	54	25.18	8.01	2.83	5.66
15	19.42	6.18	2.49	4.97	55	43.95	13.99	3.74	7.48
16	45.15	14.37	3.79	7.58	56	33.41	10.63	3.26	6.52
17	38.91	12.38	3.52	7.04	57	32.82	10.45	3.23	6.46
18	35.62	11.34	3.37	6.73	58	28.64	9.12	3.02	6.04
19	23.57	7.5	2.74	5.48	59	32.36	10.30	3.21	6.42
20	18.91	6.02	2.45	4.91	60	11.94	3.80	1.95	3.90
21	18.3	5.83	2.41	4.83	61	45.20	14.39	3.79	7.59
22	33.24	10.58	3.25	6.51	62	24.57	7.82	2.80	5.59
23	18.28	5.82	2.41	4.82	63	11.10	3.53	1.88	3.76
24	34.55	11	3.32	6.63	64	45.22	14.39	3.79	7.59
25	23.72	7.55	2.75	5.5	65	63.64	20.26	4.50	9.00
26	17.79	5.66	2.38	4.76	66	28.17	8.97	2.99	5.99
27	20.48	6.52	2.55	5.11	67	46.67	14.85	3.85	7.71
28	24.08	7.67	2.77	5.54	68	5.12	1.63	1.28	2.55
29	23.2	7.38	2.72	5.43	69	22.07	7.03	2.65	5.30
30	26.54	8.45	2.91	5.81	70	7.60	2.42	1.56	3.11
31	26.09	8.31	2.88	5.76	71	6.47	2.06	1.44	2.87
32	23.53	7.49	2.74	5.47	72	4.19	1.33	1.15	2.31
33	48.7	15.5	3.94	7.87	73	19.24	6.13	2.47	4.95
34	74.02	23.56	4.85	9.71	74	16.79	5.34	2.31	4.62
35	40.93	13.03	3.61	7.22	75	32.06	10.20	3.19	6.39
36	26.99	8.59	2.93	5.86					
37	34.34	10.93	3.31	6.61	Mean	32.09	8.93	2.89	5.77
38	29.88	9.51	3.08	6.17	SD	20.88	4.59	0.78	1.56
39	42.23	13.44	3.67	7.33	Min	4.19	1.33	1.15	2.31
40	43.29	13.78	3.71	7.42	Max	123.57	23.56	4.85	9.71

Table J.3: Particle size data for Pt particles after experimental heat treatment (data corresponds to **Figure J.1 (b)** and **(c)**)

Particle #	A [nm ²]	r ² [nm ²]	r [nm]	d [nm]	Particle #	A [nm ²]	r ² [nm ²]	r [nm]	d [nm]
1	15.95	5.08	2.25	4.51	58	15.94	5.07	2.25	4.50
2	16.24	5.17	2.27	4.55	59	23.18	7.38	2.72	5.43
3	14.37	4.57	2.14	4.28	60	9.83	3.13	1.77	3.54
4	26.48	8.43	2.90	5.81	61	15.85	5.05	2.25	4.49
5	22.89	7.29	2.70	5.40	62	15.59	4.96	2.23	4.46
6	8.38	2.67	1.63	3.27	63	14.63	4.66	2.16	4.32
7	40.59	12.92	3.59	7.19	64	10.70	3.41	1.85	3.69
8	45.94	14.62	3.82	7.65	65	16.74	5.33	2.31	4.62
9	203.27	64.70	8.04	16.09	66	18.56	5.91	2.43	4.86
10	9.99	3.18	1.78	3.57	67	19.26	6.13	2.48	4.95
11	16.57	5.28	2.30	4.59	68	15.07	4.80	2.19	4.38
12	29.81	9.49	3.08	6.16	69	21.99	7.00	2.65	5.29
13	23.84	7.59	2.75	5.51	70	23.51	7.48	2.74	5.47
14	15.80	5.03	2.24	4.49	71	20.89	6.65	2.58	5.16
15	21.05	6.70	2.59	5.18	72	25.02	7.97	2.82	5.64
16	9.14	2.91	1.71	3.41	73	23.45	7.46	2.73	5.46
17	16.23	5.17	2.27	4.55	74	23.37	7.44	2.73	5.46
18	10.38	3.30	1.82	3.64	75	34.33	10.93	3.31	6.61
19	18.08	5.76	2.40	4.80	76	49.25	15.68	3.96	7.92
20	24.83	7.90	2.81	5.62	77	227.83	72.52	8.52	17.03
21	9.59	3.05	1.75	3.49	78	34.25	10.90	3.30	6.60
22	15.95	5.08	2.25	4.51	79	42.38	13.49	3.67	7.35
23	15.83	5.04	2.24	4.49	80	271.24	86.34	9.29	18.58
24	45.25	14.40	3.80	7.59	81	20.11	6.40	2.53	5.06
25	26.13	8.32	2.88	5.77	82	49.86	15.87	3.98	7.97
26	35.65	11.35	3.37	6.74	83	215.42	68.57	8.28	16.56
27	284.45	90.54	9.52	19.03	84	22.06	7.02	2.65	5.30
28	15.63	4.97	2.23	4.46	85	23.45	7.46	2.73	5.46
29	21.30	6.78	2.60	5.21	86	17.53	5.58	2.36	4.72
30	48.63	15.48	3.93	7.87	87	12.75	4.06	2.01	4.03
31	37.81	12.04	3.47	6.94	88	17.06	5.43	2.33	4.66
32	40.66	12.94	3.60	7.20	89	15.26	4.86	2.20	4.41
33	14.97	4.77	2.18	4.37	90	38.23	12.16	3.49	6.98
34	664.79	211.61	14.55	29.09	91	26.26	8.35	2.89	5.78
35	25.71	8.18	2.86	5.72	92	26.26	8.35	2.89	5.78
36	308.86	98.31	9.92	19.83	93	37.47	11.92	3.45	6.91
37	8.82	2.81	1.68	3.35	94	124.46	39.60	6.29	12.59
38	14.69	4.68	2.16	4.32	95	134.19	42.70	6.53	13.07
39	10.11	3.22	1.79	3.59	96	189.24	60.21	7.76	15.52
40	45.40	14.45	3.80	7.60	97	56.41	17.95	4.24	8.47
41	80.51	25.63	5.06	10.12	98	115.31	36.69	6.06	12.11
42	14.59	4.64	2.16	4.31	99	138.85	44.18	6.65	13.29
43	25.15	8.01	2.83	5.66	100	32.05	10.20	3.19	6.39
44	1208.35	384.63	19.61	39.22	101	23.16	7.37	2.71	5.43
45	51.60	16.43	4.05	8.11	102	15.04	4.78	2.19	4.37
46	284.69	90.62	9.52	19.04	103	27.47	8.74	2.96	5.91
47	30.45	9.69	3.11	6.23	104	75.54	24.03	4.90	9.80
48	20.21	6.43	2.54	5.07	105	17.62	5.61	2.37	4.74
49	61.53	19.58	4.43	8.85	106	35.55	11.31	3.36	6.73
50	16.65	5.30	2.30	4.60	107	167.44	53.28	7.30	14.60
51	727.00	231.41	15.21	30.42	108	32.26	10.26	3.20	6.41
52	28.57	9.09	3.02	6.03					
53	64.30	20.47	4.52	9.05	Mean	54.73	22.76	3.68	7.35
54	54.41	17.32	4.16	8.32	SD	155.27	53.77	3.06	6.12
55	16.06	5.11	2.26	4.52	Min	1.36	2.67	1.63	3.27
56	18.11	5.76	2.40	4.80	Max	1208.35	384.63	19.61	39.22
57	16.09	5.12	2.26	4.53					

J.2 Pt-Ru PARTICLE SIZE ANALYSIS, BEFORE AND AFTER HEAT TREATMENT

Table J.4: Particle size data for Pt-Ru particles before experimental heat treatment (data corresponds **Figure J.1 (d)**)

Particle #	A [nm ²]	r ² [nm ²]	r [nm]	d [nm]
1	63.19	20.11	4.48	8.97
2	24.30	7.73	2.78	5.56
3	67.68	21.54	4.64	9.28
4	6.46	2.06	1.43	2.87
5	43.39	13.81	3.72	7.43
6	30.79	9.80	3.13	6.26
7	22.68	7.22	2.69	5.37
8	28.58	9.10	3.02	6.03
9	11.26	3.58	1.89	3.79
10	6.60	2.10	1.45	2.90
11	10.16	3.23	1.80	3.60
12	85.05	27.07	5.20	10.41
13	33.73	10.74	3.28	6.55
14	30.66	9.76	3.12	6.25
15	42.37	13.49	3.67	7.35
16	81.11	25.82	5.08	10.16
17	35.34	11.25	3.35	6.71
18	66.23	21.08	4.59	9.18
19	55.33	17.61	4.20	8.39
20	10.28	3.27	1.81	3.62
21	67.90	21.61	4.65	9.30
22	26.84	8.54	2.92	5.85
23	14.28	4.54	2.13	4.26
24	26.74	8.51	2.92	5.83
25	16.60	5.28	2.30	4.60
26	68.16	21.70	4.66	9.32
Mean	43.37	11.94	3.27	6.53
SD	43.00	7.71	1.15	2.31
Min	6.46	2.06	1.43	2.87
Max	220.16	27.07	5.20	10.41

Table J.5: Particle size data for Pt-Ru particles after experimental heat treatment (data corresponds to **Figure J.1 (e)** and **(f)**)

Particle #	A [nm ²]	r ² [nm ²]	r [nm]	d [nm]	Particle #	A [nm ²]	r ² [nm ²]	r [nm]	d [nm]
1	35.59	11.33	3.37	6.73	32	11.88	3.78	1.94	3.89
2	18.98	6.04	2.46	4.92	33	18.23	5.80	2.41	4.82
3	20.16	6.42	2.53	5.07	34	49.39	15.72	3.97	7.93
4	76.15	24.24	4.92	9.85	35	29.85	9.50	3.08	6.16
5	105.80	33.68	5.80	11.61	36	20.64	6.57	2.56	5.13
6	50.38	16.04	4.00	8.01	37	34.87	11.10	3.33	6.66
7	66.99	21.32	4.62	9.24	38	14.45	4.60	2.14	4.29
8	82.48	26.25	5.12	10.25	39	14.45	4.60	2.14	4.29
9	13.85	4.41	2.10	4.20	40	564.16	179.58	13.40	26.80
10	10.70	3.40	1.85	3.69	41	85.17	27.11	5.21	10.41
11	13.96	4.44	2.11	4.22	42	39.31	12.51	3.54	7.07
12	12.11	3.86	1.96	3.93	43	59.28	18.87	4.34	8.69
13	18.36	5.84	2.42	4.83	44	203.71	64.84	8.05	16.10
14	147.91	47.08	6.86	13.72	45	160.05	50.94	7.14	14.28
15	15.33	4.88	2.21	4.42	46	38.07	12.12	3.48	6.96
16	37.10	11.81	3.44	6.87	47	286.54	91.21	9.55	19.10
17	32.60	10.38	3.22	6.44	48	54.56	17.37	4.17	8.33
18	46.14	14.69	3.83	7.66	49	24.84	7.91	2.81	5.62
19	16.60	5.28	2.30	4.60	50	12.45	3.96	1.99	3.98
20	18.28	5.82	2.41	4.82	51	26.19	8.34	2.89	5.77
21	297.78	94.79	9.74	19.47	52	22.13	7.04	2.65	5.31
22	11.53	3.67	1.92	3.83	53	774.92	246.66	15.71	31.41
23	104.77	33.35	5.77	11.55	54	89.12	28.37	5.33	10.65
24	12.97	4.13	2.03	4.06	55	41.69	13.27	3.64	7.29
25	20.55	6.54	2.56	5.11	56	43.46	13.84	3.72	7.44
26	126.38	40.23	6.34	12.68	57	337.62	107.47	10.37	20.73
27	52.19	16.61	4.08	8.15					
28	61.83	19.68	4.44	8.87	Mean	82.16	29.60	4.45	8.91
29	670.74	213.50	14.61	29.22	SD	138.92	49.61	3.15	6.30
30	14.98	4.77	2.18	4.37	Min	7.33	3.40	1.85	3.69
31	30.31	9.65	3.11	6.21	Max	674.92	246.66	15.71	31.41

Appendix K. PBI MEMBRANES: RAW DATA

K.1 EXPERIMENTAL DATA FOR Pt/C CATALYST

K.1.1 PURE HYDROGEN EXPERIMENTS AT 100°C

Table K.1: Pure hydrogen experimental data for Pt/C at 100°C, flow rate 50 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.06	2.1E-07	64.93	99.60	64.67	3.5E-15	1.05
0.04	0.008	0.17	0.12	4.4E-07	68.66	99.47	68.30	7.4E-15	2.23
0.06	0.012	0.25	0.21	7.9E-07	81.84	99.19	81.18	1.3E-14	3.99
0.08	0.016	0.34	0.28	1.1E-06	82.85	98.92	81.96	1.8E-14	5.38
0.10	0.020	0.42	0.36	1.4E-06	85.28	98.65	84.13	2.3E-14	6.92
0.12	0.024	0.51	0.44	1.7E-06	85.83	98.38	84.44	2.8E-14	8.36
0.14	0.028	0.59	0.51	1.9E-06	85.39	98.11	83.78	3.2E-14	9.71
0.16	0.032	0.68	0.56	2.1E-06	83.22	97.82	81.41	3.6E-14	10.81
0.18	0.037	0.76	0.63	2.4E-06	82.60	97.51	80.54	4.0E-14	12.07
0.20	0.041	0.85	0.73	2.8E-06	86.38	97.21	83.98	4.6E-14	14.03
0.22	0.046	0.93	0.81	3.1E-06	86.76	96.92	84.09	5.1E-14	15.50
0.24	0.049	1.02	0.91	3.5E-06	89.69	96.69	86.73	5.8E-14	17.48
0.26	0.054	1.10	1.01	3.8E-06	91.47	96.36	88.14	6.4E-14	19.31
0.28	0.058	1.19	1.05	4.0E-06	88.72	96.09	85.25	6.7E-14	20.17
0.30	0.155	1.27	1.16	4.4E-06	91.18	89.54	81.64	7.3E-14	22.21

Table K.2: Pure hydrogen experimental data for Pt/C at 100°C, flow rate 100 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.05	1.9E-07	60.34	99.60	60.09	3.2E-15	0.98
0.04	0.007	0.17	0.11	4.3E-07	67.15	99.53	66.83	7.2E-15	2.18
0.06	0.011	0.25	0.18	6.7E-07	68.95	99.24	68.43	1.1E-14	3.36
0.08	0.015	0.34	0.25	9.7E-07	75.08	98.98	74.32	1.6E-14	4.88
0.10	0.020	0.42	0.30	1.1E-06	70.54	98.65	69.59	1.9E-14	5.73
0.12	0.024	0.51	0.38	1.4E-06	74.38	98.40	73.20	2.4E-14	7.25
0.14	0.028	0.59	0.45	1.7E-06	76.48	98.11	75.04	2.9E-14	8.69
0.16	0.032	0.68	0.51	2.0E-06	75.97	97.84	74.33	3.3E-14	9.87
0.18	0.036	0.76	0.62	2.4E-06	81.34	97.57	79.37	3.9E-14	11.89
0.20	0.040	0.85	0.71	2.7E-06	83.58	97.30	81.33	4.5E-14	13.57
0.22	0.044	0.93	0.75	2.9E-06	80.77	97.04	78.37	4.8E-14	14.43
0.24	0.048	1.02	0.85	3.2E-06	83.33	96.77	80.63	5.4E-14	16.24
0.26	0.053	1.10	0.92	3.5E-06	83.53	96.46	80.57	5.8E-14	17.63
0.28	0.057	1.19	1.02	3.9E-06	85.70	96.16	82.40	6.4E-14	19.48
0.30	0.061	1.27	1.13	4.3E-06	88.82	95.89	85.17	7.1E-14	21.63
0.32	0.065	1.36	1.22	4.6E-06	90.17	95.62	86.23	7.7E-14	23.43
0.34	0.070	1.44	1.31	5.0E-06	90.74	95.28	86.46	8.3E-14	25.05
0.36	0.074	1.53	1.42	5.4E-06	93.10	95.01	88.45	9.0E-14	27.21
0.38	0.079	1.61	1.54	5.9E-06	95.88	94.68	90.77	9.8E-14	29.58
0.40	0.083	1.69	1.61	6.1E-06	95.23	94.41	89.90	1.0E-13	30.93
0.42	0.087	1.78	1.67	6.3E-06	93.84	94.13	88.34	1.1E-13	32.00
0.44	0.091	1.86	1.79	6.8E-06	96.22	93.86	90.31	1.1E-13	34.38
0.46	0.096	1.95	1.90	7.2E-06	97.74	93.53	91.42	1.2E-13	36.51

Table K.2 (continued): Pure hydrogen experimental data for Pt/C at 100°C, flow rate 100 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.48	0.101	2.03	1.99	7.6E-06	98.10	93.21	91.44	1.3E-13	38.23
0.50	0.105	2.12	2.09	7.9E-06	98.81	92.94	91.84	1.3E-13	40.12
0.52	0.109	2.20	2.17	8.2E-06	98.28	92.65	91.06	1.4E-13	41.49
0.54	0.114	2.29	2.23	8.5E-06	97.62	92.32	90.12	1.4E-13	42.80
0.56	0.118	2.37	2.32	8.8E-06	97.79	92.04	90.00	1.5E-13	44.46
0.58	0.228	2.46	2.41	9.2E-06	98.23	84.67	83.17	1.5E-13	46.26

Table K.3: Pure hydrogen experimental data for Pt/C at 100°C, flow rate 150 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.05	1.9E-07	58.52	99.60	58.28	3.1E-15	0.95
0.04	0.007	0.17	0.12	4.5E-07	70.62	99.53	70.28	7.6E-15	2.29
0.06	0.011	0.25	0.20	7.6E-07	78.52	99.25	77.93	1.3E-14	3.83
0.08	0.015	0.34	0.28	1.1E-06	83.68	98.98	82.83	1.8E-14	5.44
0.10	0.020	0.42	0.36	1.4E-06	85.28	98.67	84.15	2.3E-14	6.92
0.12	0.024	0.51	0.44	1.7E-06	86.76	98.39	85.36	2.8E-14	8.45
0.14	0.028	0.59	0.52	2.0E-06	87.70	98.11	86.05	3.3E-14	9.97
0.16	0.032	0.68	0.59	2.3E-06	87.63	97.84	85.74	3.8E-14	11.38
0.18	0.036	0.76	0.64	2.4E-06	83.48	97.57	81.46	4.0E-14	12.20
0.20	0.041	0.85	0.71	2.7E-06	84.26	97.26	81.95	4.5E-14	13.68
0.22	0.045	0.93	0.80	3.0E-06	85.48	96.97	82.89	5.0E-14	15.27
0.24	0.049	1.02	0.87	3.0E-06	85.70	96.70	82.87	5.1E-14	15.30
0.26	0.054	1.10	0.96	3.6E-06	86.89	96.36	83.73	6.1E-14	18.34
0.28	0.058	1.19	1.06	4.0E-06	89.45	96.10	85.96	6.7E-14	20.34
0.30	0.061	1.27	1.12	4.3E-06	88.11	95.86	84.46	7.1E-14	21.46
0.32	0.066	1.36	1.23	4.7E-06	90.47	95.56	86.45	7.8E-14	23.51
0.34	0.070	1.44	1.30	4.9E-06	90.01	95.28	85.77	8.2E-14	24.85
0.36	0.074	1.53	1.38	5.2E-06	90.27	95.01	85.77	8.7E-14	26.39
0.38	0.078	1.61	1.49	5.7E-06	92.84	94.74	87.96	9.5E-14	28.65
0.40	0.083	1.69	1.57	6.0E-06	92.72	94.41	87.54	9.9E-14	30.11
0.42	0.087	1.78	1.62	6.2E-06	91.08	94.12	85.73	1.0E-13	31.06
0.44	0.092	1.86	1.73	6.6E-06	93.06	93.80	87.29	1.1E-13	33.25
0.46	0.096	1.95	1.84	7.0E-06	94.20	93.53	88.10	1.2E-13	35.18
0.48	0.101	2.03	1.97	6.8E-06	96.69	93.19	90.11	1.1E-13	34.52
0.50	0.110	2.12	2.03	7.7E-06	95.81	92.59	88.71	1.3E-13	38.90
0.52	0.110	2.20	2.09	7.9E-06	94.66	92.59	87.65	1.3E-13	39.97
0.54	0.115	2.29	2.23	8.5E-06	97.62	92.25	90.05	1.4E-13	42.80
0.56	0.119	2.37	2.32	8.8E-06	97.79	91.98	89.95	1.5E-13	44.46
0.58	0.124	2.46	2.41	9.2E-06	98.23	91.64	90.02	1.5E-13	46.26
0.60	0.129	2.54	2.49	9.4E-06	97.87	91.31	89.37	1.6E-13	47.68
0.62	0.134	2.63	2.49	9.5E-06	94.92	90.97	86.35	1.6E-13	47.79
0.64	0.139	2.71	2.63	1.0E-05	96.85	90.63	87.78	1.7E-13	50.33
0.66	0.144	2.80	2.77	1.1E-05	98.96	90.30	89.36	1.8E-13	53.03
0.68	0.148	2.88	2.84	1.1E-05	98.45	90.00	88.60	1.8E-13	54.36
0.70	0.152	2.97	2.92	1.1E-05	98.34	89.74	88.25	1.8E-13	55.89
0.72	0.157	3.05	2.92	1.0E-05	95.86	89.42	85.71	1.7E-13	51.34
0.74	0.162	3.14	2.94	1.1E-05	93.75	89.12	83.55	1.9E-13	56.33
0.76	0.165	3.22	3.12	1.2E-05	96.96	88.88	86.18	2.0E-13	59.83
0.78	0.169	3.30	3.30	1.3E-05	99.80	88.61	88.43	2.1E-13	63.21
0.80	0.173	3.39	3.32	1.3E-05	97.87	88.33	86.45	2.1E-13	63.58
0.82	0.178	3.47	3.36	1.3E-05	96.62	88.01	85.03	2.1E-13	64.33
0.84	0.183	3.56	3.52	1.3E-05	99.00	87.65	86.78	2.2E-13	67.52

Table K.4: Pure hydrogen experimental data for Pt/C at 100°C, flow rate 200 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.04	1.7E-07	52.90	99.60	52.69	2.8E-15	0.86
0.04	0.006	0.17	0.12	4.6E-07	71.03	99.60	70.74	7.6E-15	2.31
0.06	0.008	0.25	0.20	7.7E-07	80.24	99.45	79.80	1.3E-14	3.91
0.08	0.012	0.34	0.27	1.0E-06	80.17	99.19	79.53	1.7E-14	5.21
0.10	0.016	0.42	0.36	1.4E-06	85.86	98.92	84.93	2.3E-14	6.97
0.12	0.020	0.51	0.45	1.7E-06	87.86	98.67	86.68	2.8E-14	8.56
0.14	0.023	0.59	0.52	2.0E-06	86.94	98.45	85.60	3.3E-14	9.88
0.16	0.027	0.68	0.61	2.3E-06	89.50	98.18	87.87	3.8E-14	11.63
0.18	0.030	0.76	0.63	2.4E-06	82.70	97.98	81.02	4.0E-14	12.09
0.20	0.034	0.85	0.71	2.7E-06	84.26	97.71	82.33	4.5E-14	13.68
0.22	0.037	0.93	0.80	3.0E-06	85.54	97.51	83.40	5.0E-14	15.28
0.24	0.041	1.02	0.87	3.3E-06	85.70	97.24	83.33	5.5E-14	16.70
0.26	0.045	1.10	0.96	3.6E-06	86.89	96.97	84.26	6.1E-14	18.34
0.28	0.049	1.19	1.04	4.0E-06	87.82	96.72	84.94	6.6E-14	19.97
0.30	0.052	1.27	1.12	4.3E-06	88.11	96.50	85.02	7.1E-14	21.46
0.32	0.056	1.36	1.21	4.6E-06	89.50	96.23	86.12	7.7E-14	23.25
0.34	0.060	1.44	1.28	4.9E-06	88.99	95.96	85.40	8.1E-14	24.57
0.36	0.064	1.53	1.38	5.2E-06	90.27	95.69	86.38	8.7E-14	26.39
0.38	0.068	1.61	1.49	5.7E-06	92.84	95.44	88.61	9.5E-14	28.65
0.40	0.072	1.69	1.55	5.9E-06	91.71	95.16	87.27	9.8E-14	29.78
0.42	0.075	1.78	1.62	6.2E-06	91.08	94.95	86.48	1.0E-13	31.06
0.44	0.079	1.86	1.73	6.6E-06	93.06	94.68	88.10	1.1E-13	33.25
0.46	0.083	1.95	1.82	6.9E-06	93.59	94.41	88.36	1.2E-13	34.96
0.48	0.087	2.03	1.93	7.3E-06	95.04	94.14	89.47	1.2E-13	37.04
0.50	0.091	2.12	2.03	7.7E-06	95.81	93.87	89.93	1.3E-13	38.90
0.52	0.095	2.20	2.09	7.9E-06	94.66	93.60	88.60	1.3E-13	39.97
0.54	0.100	2.29	2.19	8.3E-06	95.73	93.28	89.30	1.4E-13	41.97
0.56	0.104	2.37	2.28	8.7E-06	96.02	92.99	89.29	1.4E-13	43.66
0.58	0.108	2.46	2.36	9.0E-06	96.19	92.72	89.19	1.5E-13	45.30
0.60	0.211	2.54	2.43	9.2E-06	95.77	85.77	82.14	1.5E-13	46.66
0.62	0.117	2.63	2.49	9.5E-06	94.92	92.14	87.47	1.6E-13	47.79
0.64	0.121	2.71	2.63	1.0E-05	96.85	91.85	88.96	1.7E-13	50.33
0.66	0.125	2.80	2.77	1.1E-05	98.96	91.58	90.62	1.8E-13	53.03
0.68	0.130	2.88	2.84	1.1E-05	98.45	91.25	89.84	1.8E-13	54.36
0.70	0.134	2.97	2.92	1.1E-05	98.34	90.96	89.45	1.8E-13	55.89
0.72	0.138	3.05	2.92	1.1E-05	95.86	90.70	86.94	1.9E-13	56.04
0.74	0.143	3.14	3.02	1.1E-05	96.24	90.37	86.97	1.9E-13	57.83
0.76	0.147	3.22	3.12	1.2E-05	96.96	90.07	87.33	2.0E-13	59.83
0.78	0.152	3.30	3.30	1.3E-05	99.80	89.76	89.58	2.1E-13	63.21
0.80	0.157	3.39	3.32	1.3E-05	97.87	89.43	87.53	2.1E-13	63.58
0.82	0.162	3.47	3.36	1.3E-05	96.62	89.10	86.08	2.1E-13	64.33
0.84	0.166	3.56	3.52	1.3E-05	99.00	88.81	87.93	2.2E-13	67.52
0.86	0.171	3.64	3.57	1.4E-05	97.92	88.49	86.65	2.3E-13	68.37
0.88	0.176	3.73	3.70	1.4E-05	99.12	88.15	87.37	2.3E-13	70.82
0.90	0.181	3.81	3.78	1.4E-05	99.18	87.83	87.11	2.4E-13	72.48
0.92	0.186	3.90	3.86	1.5E-05	99.00	87.47	86.60	2.4E-13	73.96
0.94	0.191	3.98	3.98	1.5E-05	99.96	87.13	87.09	2.5E-13	76.29
0.96	0.196	4.07	4.07	1.5E-05	99.98	86.79	86.77	2.6E-13	77.93
0.98	0.202	4.15	4.14	1.6E-05	99.73	86.42	86.18	2.6E-13	79.35
1.00	0.206	4.24	4.20	1.6E-05	99.18	86.12	85.41	2.7E-13	80.53
1.02	0.211	4.32	4.23	1.6E-05	97.96	85.78	84.03	2.7E-13	81.13
1.04	0.216	4.41	4.30	1.6E-05	97.53	85.44	83.33	2.7E-13	82.36
1.06	0.222	4.49	4.36	1.7E-05	97.16	85.06	82.65	2.8E-13	83.63

Table K.4 (continued): Pure hydrogen experimental data for Pt/C at 100°C, flow rate 200 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
1.08	0.227	4.58	4.45	1.7E-05	97.23	84.70	82.36	2.8E-13	85.27
1.10	0.232	4.66	4.63	1.8E-05	99.36	84.37	83.83	2.9E-13	88.75
1.12	0.237	4.75	4.67	1.8E-05	98.39	84.03	82.68	3.0E-13	89.48
1.14	0.243	4.83	4.71	1.8E-05	97.47	83.63	81.52	3.0E-13	90.22
1.16	0.411	4.91	4.83	1.8E-05	98.23	72.28	71.00	3.1E-13	92.52

K.1.2 PURE HYDROGEN EXPERIMENTS AT 120°C

Table K.5: Pure hydrogen experimental data for Pt/C at 120°C, flow rate 50 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.05	1.8E-07	56.88	99.60	56.65	3.1E-15	0.92
0.04	0.009	0.17	0.12	4.4E-07	68.87	99.40	68.45	7.4E-15	2.24
0.06	0.013	0.25	0.21	7.9E-07	82.13	99.12	81.41	1.3E-14	4.00
0.08	0.018	0.34	0.28	1.1E-06	83.30	98.79	82.29	1.8E-14	5.41
0.10	0.023	0.42	0.37	1.4E-06	88.35	98.45	86.98	2.4E-14	7.17
0.12	0.028	0.51	0.42	1.6E-06	82.65	98.11	81.09	2.7E-14	8.05
0.14	0.032	0.59	0.51	1.9E-06	85.39	97.84	83.55	3.2E-14	9.71
0.16	0.037	0.68	0.56	2.1E-06	83.22	97.51	81.15	3.6E-14	10.81
0.18	0.042	0.76	0.63	2.4E-06	82.60	97.17	80.27	4.0E-14	12.07
0.20	0.047	0.85	0.73	2.8E-06	86.38	96.85	83.66	4.6E-14	14.03
0.22	0.051	0.93	0.81	3.1E-06	86.76	96.56	83.78	5.1E-14	15.50
0.24	0.056	1.02	0.91	3.5E-06	89.69	96.23	86.31	5.8E-14	17.48
0.26	0.061	1.10	1.01	3.8E-06	91.47	95.89	87.71	6.4E-14	19.31
0.28	0.065	1.19	1.05	4.0E-06	88.72	95.62	84.83	6.7E-14	20.17
0.30	0.071	1.27	1.16	4.4E-06	91.18	95.24	86.84	7.3E-14	22.21
0.32	0.161	1.36	1.26	4.8E-06	93.08	89.12	82.95	8.0E-14	24.19

Table K.6: Pure hydrogen experimental data for Pt/C at 120°C, flow rate 100 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.04	1.6E-07	50.74	99.60	50.53	2.7E-15	0.82
0.04	0.009	0.17	0.13	4.8E-07	74.33	99.41	73.89	8.0E-15	2.41
0.06	0.013	0.25	0.21	8.0E-07	82.68	99.12	81.96	1.3E-14	4.03
0.08	0.018	0.34	0.29	1.1E-06	85.78	98.79	84.74	1.8E-14	5.57
0.10	0.023	0.42	0.36	1.4E-06	85.86	98.45	84.52	2.3E-14	6.97
0.12	0.027	0.51	0.45	1.7E-06	87.86	98.18	86.26	2.8E-14	8.56
0.14	0.032	0.59	0.52	2.0E-06	86.94	97.84	85.07	3.3E-14	9.88
0.16	0.037	0.68	0.61	2.3E-06	89.50	97.51	87.27	3.8E-14	11.63
0.18	0.041	0.76	0.63	2.4E-06	82.70	97.23	80.41	4.0E-14	12.09
0.20	0.046	0.85	0.71	2.7E-06	84.26	96.90	81.65	4.5E-14	13.68
0.22	0.051	0.93	0.80	3.0E-06	85.54	96.56	82.60	5.0E-14	15.28
0.24	0.056	1.02	0.87	3.3E-06	85.70	96.23	82.46	5.5E-14	16.70
0.26	0.061	1.10	0.96	3.6E-06	86.89	95.89	83.32	6.1E-14	18.34
0.28	0.065	1.19	1.04	4.0E-06	87.82	95.59	83.95	6.6E-14	19.97
0.30	0.070	1.27	1.12	4.3E-06	88.11	95.28	83.96	7.1E-14	21.46
0.32	0.075	1.36	1.23	4.7E-06	90.47	94.95	85.90	7.8E-14	23.51

Table K.6 (continued): Pure hydrogen experimental data for Pt/C at 120°C, flow rate 100 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.34	0.080	1.44	1.30	4.9E-06	90.01	94.61	85.16	8.2E-14	24.85
0.36	0.085	1.53	1.38	5.2E-06	90.27	94.27	85.10	8.7E-14	26.39
0.38	0.090	1.61	1.49	5.7E-06	92.84	93.94	87.21	9.5E-14	28.65
0.40	0.096	1.69	1.57	6.0E-06	92.72	93.56	86.75	9.9E-14	30.11
0.42	0.101	1.78	1.62	6.2E-06	91.08	93.19	84.88	1.0E-13	31.06
0.44	0.106	1.86	1.73	6.6E-06	93.06	92.86	86.41	1.1E-13	33.25
0.46	0.110	1.95	1.84	7.0E-06	94.20	92.58	87.21	1.2E-13	35.18
0.48	0.116	2.03	1.97	6.8E-06	96.69	92.20	89.14	1.1E-13	34.52
0.50	0.121	2.12	2.03	7.7E-06	95.81	91.85	88.00	1.3E-13	38.90
0.52	0.126	2.20	2.09	7.9E-06	94.66	91.51	86.63	1.3E-13	39.97
0.54	0.131	2.29	2.23	8.5E-06	97.62	91.17	89.00	1.4E-13	42.80
0.56	0.137	2.37	2.32	8.8E-06	97.79	90.78	88.77	1.5E-13	44.46
0.58	0.142	2.46	2.41	9.2E-06	98.23	90.43	88.83	1.5E-13	46.26
0.60	0.274	2.54	2.49	9.4E-06	97.87	81.50	79.77	1.6E-13	47.68

Table K.7: Pure hydrogen experimental data for Pt/C at 120°C, flow rate 150 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.04	1.5E-07	48.08	99.60	47.88	2.6E-15	0.78
0.04	0.009	0.17	0.12	4.5E-07	70.67	99.39	70.24	7.6E-15	2.30
0.06	0.013	0.25	0.20	7.6E-07	78.52	99.11	77.82	1.3E-14	3.83
0.08	0.018	0.34	0.28	1.1E-06	83.96	98.79	82.94	1.8E-14	5.45
0.10	0.023	0.42	0.34	1.3E-06	80.22	98.45	78.98	2.2E-14	6.51
0.12	0.028	0.51	0.40	1.5E-06	79.51	98.11	78.01	2.6E-14	7.75
0.14	0.032	0.59	0.55	2.1E-06	92.31	97.84	90.32	3.5E-14	10.49
0.16	0.037	0.68	0.63	2.4E-06	93.50	97.51	91.17	4.0E-14	12.15
0.18	0.042	0.76	0.74	2.8E-06	97.23	97.17	94.48	4.7E-14	14.21
0.20	0.047	0.85	0.73	2.8E-06	86.38	96.83	83.65	4.6E-14	14.03
0.22	0.052	0.93	0.81	3.1E-06	86.76	96.50	83.72	5.1E-14	15.50
0.24	0.057	1.02	0.91	3.5E-06	89.69	96.16	86.25	5.8E-14	17.48
0.26	0.061	1.10	1.01	3.8E-06	91.47	95.86	87.68	6.4E-14	19.31
0.28	0.067	1.19	1.05	4.0E-06	88.72	95.50	84.72	6.7E-14	20.17
0.30	0.072	1.27	1.16	4.4E-06	91.18	95.15	86.75	7.3E-14	22.21
0.32	0.077	1.36	1.26	4.8E-06	93.08	94.81	88.25	8.0E-14	24.19
0.34	0.081	1.44	1.36	5.2E-06	94.66	94.53	89.48	8.6E-14	26.13
0.36	0.086	1.53	1.46	5.5E-06	95.49	94.17	89.92	9.2E-14	27.91
0.38	0.092	1.61	1.52	5.8E-06	94.59	93.82	88.74	9.6E-14	29.19
0.40	0.096	1.69	1.60	6.1E-06	94.29	93.53	88.19	1.0E-13	30.62
0.42	0.101	1.78	1.73	6.6E-06	97.04	93.19	90.43	1.1E-13	33.09
0.44	0.107	1.86	1.86	7.1E-06	99.61	92.79	92.43	1.2E-13	35.59
0.46	0.112	1.95	1.84	7.0E-06	94.20	92.45	87.09	1.2E-13	35.18
0.48	0.117	2.03	1.97	6.8E-06	96.69	92.09	89.04	1.1E-13	34.52
0.50	0.123	2.12	2.03	7.7E-06	95.81	91.71	87.87	1.3E-13	38.90
0.52	0.128	2.20	2.09	7.9E-06	94.66	91.40	86.52	1.3E-13	39.97
0.54	0.133	2.29	2.23	8.5E-06	97.62	91.04	88.87	1.4E-13	42.80
0.56	0.138	2.37	2.32	8.8E-06	97.79	90.69	88.68	1.5E-13	44.46
0.58	0.144	2.46	2.41	9.2E-06	98.23	90.30	88.70	1.5E-13	46.26
0.60	0.149	2.54	2.49	9.4E-06	97.87	89.96	88.05	1.6E-13	47.68
0.62	0.155	2.63	2.49	9.5E-06	94.92	89.57	85.03	1.6E-13	47.79
0.64	0.160	2.71	2.63	1.0E-05	96.85	89.19	86.38	1.7E-13	50.33
0.66	0.166	2.80	2.77	1.1E-05	98.96	88.81	87.89	1.8E-13	53.03

Table K.7 (continued): Pure hydrogen experimental data for Pt/C at 120°C, flow rate 150 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.68	0.171	2.88	2.84	1.1E-05	98.45	88.48	87.11	1.8E-13	54.36
0.70	0.177	2.97	2.92	1.1E-05	98.34	88.07	86.61	1.8E-13	55.89
0.72	0.183	3.05	2.92	1.1E-05	95.86	87.69	84.05	1.9E-13	56.04
0.74	0.188	3.14	3.02	1.1E-05	96.24	87.33	84.05	1.9E-13	57.83
0.76	0.193	3.22	3.12	1.2E-05	96.96	86.99	84.35	2.0E-13	59.83
0.78	0.199	3.30	3.30	1.3E-05	99.80	86.59	86.42	2.1E-13	63.21
0.80	0.205	3.39	3.32	1.3E-05	97.87	86.19	84.35	2.1E-13	63.58
0.82	0.211	3.47	3.36	1.3E-05	96.62	85.81	82.90	2.1E-13	64.33
0.84	0.216	3.56	3.52	1.3E-05	99.00	85.44	84.59	2.2E-13	67.52
0.86	0.222	3.64	3.57	1.4E-05	97.92	85.04	83.27	2.3E-13	68.37
0.88	0.402	3.73	3.70	1.4E-05	99.12	72.91	72.27	2.3E-13	70.82

Table K.8: Pure hydrogen experimental data for Pt/C at 120°C, flow rate 200 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.04	1.6E-07	51.18	99.60	50.97	2.7E-15	0.83
0.04	0.009	0.17	0.10	3.8E-07	59.51	99.43	59.17	6.4E-15	1.93
0.06	0.013	0.25	0.20	7.5E-07	77.93	99.12	77.25	1.3E-14	3.80
0.08	0.033	0.34	0.28	1.1E-06	81.64	97.81	79.85	1.8E-14	5.30
0.10	0.023	0.42	0.37	1.4E-06	87.51	98.45	86.15	2.3E-14	7.11
0.12	0.028	0.51	0.43	1.6E-06	83.89	98.11	82.31	2.7E-14	8.17
0.14	0.033	0.59	0.57	2.2E-06	96.80	97.78	94.65	3.6E-14	11.00
0.16	0.038	0.68	0.67	2.5E-06	98.57	97.46	96.06	4.2E-14	12.81
0.18	0.042	0.76	0.76	2.9E-06	99.25	97.17	96.44	4.8E-14	14.50
0.20	0.047	0.85	0.82	3.1E-06	96.39	96.83	93.34	5.2E-14	15.65
0.22	0.052	0.93	0.91	3.4E-06	97.14	96.50	93.74	5.7E-14	17.35
0.24	0.057	1.02	0.98	3.7E-06	96.52	96.16	92.81	6.2E-14	18.81
0.26	0.062	1.10	1.03	3.9E-06	93.63	95.82	89.72	6.5E-14	19.77
0.28	0.067	1.19	1.14	4.3E-06	95.83	95.49	91.50	7.2E-14	21.79
0.30	0.072	1.27	1.24	4.7E-06	97.66	95.15	92.92	7.9E-14	23.79
0.32	0.077	1.36	1.31	5.0E-06	96.30	94.81	91.30	8.3E-14	25.02
0.34	0.082	1.44	1.40	5.3E-06	96.88	94.47	91.52	8.8E-14	26.74
0.36	0.087	1.53	1.48	5.6E-06	97.36	94.13	91.64	9.4E-14	28.46
0.38	0.093	1.61	1.59	6.0E-06	98.83	93.73	92.64	1.0E-13	30.49
0.40	0.098	1.69	1.65	6.3E-06	97.16	93.40	90.75	1.0E-13	31.56
0.42	0.103	1.78	1.62	6.2E-06	91.08	93.06	84.76	1.0E-13	31.06
0.44	0.108	1.86	1.73	6.6E-06	93.06	92.72	86.29	1.1E-13	33.25
0.46	0.113	1.95	1.82	6.9E-06	93.59	92.38	86.46	1.2E-13	34.96
0.48	0.118	2.03	1.93	7.3E-06	95.04	92.04	87.47	1.2E-13	37.04
0.50	0.124	2.12	2.03	7.7E-06	95.81	91.64	87.80	1.3E-13	38.90
0.52	0.129	2.20	2.09	7.9E-06	94.66	91.30	86.43	1.3E-13	39.97
0.54	0.135	2.29	2.19	8.3E-06	95.73	90.92	87.04	1.4E-13	41.97
0.56	0.140	2.37	2.28	8.7E-06	96.02	90.54	86.94	1.4E-13	43.66
0.58	0.146	2.46	2.36	9.0E-06	96.19	90.16	86.72	1.5E-13	45.30
0.60	0.151	2.54	2.43	9.2E-06	95.77	89.80	86.00	1.5E-13	46.66
0.62	0.157	2.63	2.49	9.5E-06	94.92	89.41	84.87	1.6E-13	47.79
0.64	0.163	2.71	2.63	1.0E-05	96.85	89.02	86.22	1.7E-13	50.33
0.66	0.168	2.80	2.77	1.1E-05	98.96	88.68	87.76	1.8E-13	53.03
0.68	0.173	2.88	2.84	1.1E-05	98.45	88.34	86.97	1.8E-13	54.36
0.70	0.179	2.97	2.92	1.1E-05	98.34	87.92	86.47	1.8E-13	55.89
0.72	0.185	3.05	2.92	1.1E-05	95.86	87.53	83.91	1.9E-13	56.04

Table K.8 (continued): Pure hydrogen experimental data for Pt/C at 120°C, flow rate 200 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.74	0.190	3.14	3.02	1.1E-05	96.24	87.20	83.92	1.9E-13	57.83
0.76	0.196	3.22	3.12	1.2E-05	96.96	86.77	84.14	2.0E-13	59.83
0.78	0.203	3.30	3.30	1.3E-05	99.80	86.35	86.18	2.1E-13	63.21
0.80	0.209	3.39	3.32	1.3E-05	97.87	85.93	84.10	2.1E-13	63.58
0.82	0.214	3.47	3.36	1.3E-05	96.62	85.58	82.68	2.1E-13	64.33
0.84	0.220	3.56	3.52	1.3E-05	99.00	85.18	84.33	2.2E-13	67.52
0.86	0.227	3.64	3.57	1.4E-05	97.92	84.73	82.96	2.3E-13	68.37
0.88	0.232	3.73	3.70	1.4E-05	99.12	84.39	83.65	2.3E-13	70.82
0.90	0.237	3.81	3.78	1.4E-05	99.18	84.03	83.34	2.4E-13	72.48
0.92	0.243	3.90	3.86	1.5E-05	99.00	83.63	82.79	2.4E-13	73.96
0.94	0.248	3.98	3.98	1.5E-05	99.96	83.29	83.25	2.5E-13	76.29
0.96	0.254	4.07	4.07	1.5E-05	99.98	82.88	82.87	2.6E-13	77.93
0.98	0.260	4.15	4.14	1.6E-05	99.73	82.48	82.25	2.6E-13	79.35
1.00	0.265	4.24	4.20	1.6E-05	99.18	82.14	81.47	2.7E-13	80.53
1.02	0.271	4.32	4.23	1.6E-05	97.96	81.74	80.07	2.7E-13	81.13
1.04	0.276	4.41	4.30	1.6E-05	97.53	81.38	79.37	2.7E-13	82.36
1.06	0.282	4.49	4.36	1.7E-05	97.16	81.00	78.70	2.8E-13	83.63
1.08	0.288	4.58	4.45	1.7E-05	97.23	80.59	78.36	2.8E-13	85.27
1.10	0.294	4.66	4.63	1.8E-05	99.36	80.21	79.69	2.9E-13	88.75
1.12	0.299	4.75	4.67	1.8E-05	98.39	79.85	78.57	3.0E-13	89.48
1.14	0.306	4.83	4.71	1.8E-05	97.47	79.41	77.40	3.0E-13	90.22
1.16	0.454	4.91	4.83	1.8E-05	98.23	69.42	68.20	3.1E-13	92.52

K.1.3 PURE HYDROGEN EXPERIMENTS AT 140°C

Table K.9: Pure hydrogen experimental data for Pt/C at 140°C, flow rate 50 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.06	2.3E-07	70.32	99.60	70.04	3.8E-15	1.14
0.04	0.007	0.17	0.12	4.5E-07	70.54	99.52	70.21	7.6E-15	2.29
0.06	0.013	0.25	0.19	7.0E-07	72.87	99.15	72.25	1.2E-14	3.55
0.08	0.017	0.34	0.27	1.0E-06	80.54	98.85	79.62	1.7E-14	5.23
0.10	0.022	0.42	0.38	1.4E-06	88.55	98.52	87.24	2.4E-14	7.19
0.12	0.027	0.51	0.43	1.6E-06	83.89	98.18	82.37	2.7E-14	8.17
0.14	0.031	0.59	0.54	2.1E-06	91.61	97.89	89.67	3.4E-14	10.41
0.16	0.036	0.68	0.65	2.5E-06	95.86	97.57	93.53	4.1E-14	12.45
0.18	0.041	0.76	0.74	2.8E-06	97.49	97.24	94.80	4.7E-14	14.25
0.20	0.046	0.85	0.82	3.1E-06	96.39	96.90	93.41	5.2E-14	15.65
0.22	0.051	0.93	0.89	3.4E-06	95.62	96.56	92.33	5.6E-14	17.08
0.24	0.056	1.02	0.98	3.7E-06	96.52	96.23	92.88	6.2E-14	18.81
0.26	0.061	1.10	1.03	3.9E-06	93.63	95.89	89.78	6.5E-14	19.77
0.28	0.066	1.19	1.15	4.4E-06	96.80	95.58	92.52	7.3E-14	22.01
0.30	0.071	1.27	1.24	4.7E-06	97.66	95.20	92.97	7.9E-14	23.79
0.32	0.152	1.36	1.31	5.0E-06	96.30	89.78	86.46	8.3E-14	25.02

Table K.10: Pure hydrogen experimental data for Pt/C at 140°C, flow rate 100 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.04	1.6E-07	50.74	99.60	50.53	2.7E-15	0.82
0.04	0.008	0.17	0.13	4.8E-07	74.33	99.45	73.92	8.0E-15	2.41
0.06	0.013	0.25	0.21	8.0E-07	82.68	99.12	81.96	1.3E-14	4.02
0.08	0.018	0.34	0.29	1.1E-06	85.78	98.79	84.74	1.8E-14	5.56
0.10	0.022	0.42	0.36	1.4E-06	85.77	98.52	84.50	2.3E-14	6.96
0.12	0.027	0.51	0.45	1.7E-06	87.92	98.18	86.32	2.8E-14	8.57
0.14	0.032	0.59	0.52	2.0E-06	86.86	97.85	84.99	3.3E-14	9.87
0.16	0.036	0.68	0.61	2.3E-06	89.26	97.57	87.10	3.8E-14	11.60
0.18	0.041	0.76	0.63	2.4E-06	82.65	97.24	80.37	4.0E-14	12.08
0.20	0.046	0.85	0.71	2.7E-06	84.37	96.90	81.76	4.5E-14	13.70
0.22	0.050	0.93	0.80	3.0E-06	85.72	96.63	82.83	5.1E-14	15.31
0.24	0.055	1.02	0.87	3.3E-06	85.70	96.29	82.52	5.5E-14	16.70
0.26	0.059	1.10	0.96	3.6E-06	86.91	96.02	83.46	6.1E-14	18.35
0.28	0.064	1.19	1.04	4.0E-06	87.74	95.69	83.96	6.6E-14	19.95
0.30	0.069	1.27	1.12	4.3E-06	88.12	95.36	84.02	7.1E-14	21.46
0.32	0.073	1.36	1.23	4.7E-06	90.47	95.08	86.02	7.8E-14	23.48
0.34	0.078	1.44	1.30	5.0E-06	90.01	94.74	85.28	8.3E-14	24.99
0.36	0.083	1.53	1.38	5.2E-06	90.27	94.41	85.22	8.7E-14	26.36
0.38	0.088	1.61	1.49	5.7E-06	92.84	94.07	87.34	9.4E-14	28.61
0.40	0.090	1.69	1.57	6.0E-06	92.85	93.94	87.22	1.0E-13	30.16
0.42	0.095	1.78	1.62	6.1E-06	90.82	93.60	85.01	1.0E-13	30.97
0.44	0.102	1.86	1.74	6.6E-06	93.20	93.13	86.79	1.1E-13	33.30
0.46	0.106	1.95	1.84	7.0E-06	94.66	92.86	87.90	1.2E-13	35.35
0.48	0.111	2.03	1.96	6.8E-06	96.52	92.51	89.29	1.1E-13	34.46
0.50	0.116	2.12	2.03	7.7E-06	95.64	92.18	88.16	1.3E-13	38.83
0.52	0.121	2.20	2.09	7.9E-06	95.01	91.85	87.27	1.3E-13	40.12
0.54	0.126	2.29	2.22	8.4E-06	97.23	91.51	88.98	1.4E-13	42.63
0.56	0.132	2.37	2.32	8.8E-06	97.59	91.11	88.92	1.5E-13	44.37
0.58	0.136	2.46	2.41	9.2E-06	98.23	90.81	89.20	1.5E-13	46.26
0.60	0.236	2.54	2.50	9.5E-06	98.31	84.08	82.65	1.6E-13	47.89

Table K.11: Pure hydrogen experimental data for Pt/C at 140°C, flow rate 150 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.04	1.5E-07	48.08	99.60	47.88	2.6E-15	0.78
0.04	0.008	0.17	0.12	4.5E-07	70.67	99.46	70.29	7.6E-15	2.30
0.06	0.012	0.25	0.20	7.6E-07	78.52	99.19	77.88	1.3E-14	3.83
0.08	0.016	0.34	0.28	1.1E-06	83.96	98.92	83.05	1.8E-14	5.45
0.10	0.021	0.42	0.34	1.3E-06	80.22	98.58	79.09	2.2E-14	6.51
0.12	0.025	0.51	0.40	1.5E-06	79.51	98.32	78.17	2.6E-14	7.75
0.14	0.029	0.59	0.55	2.1E-06	92.31	98.05	90.51	3.5E-14	10.49
0.16	0.033	0.68	0.63	2.4E-06	93.50	97.78	91.42	4.0E-14	12.15
0.18	0.038	0.76	0.74	2.8E-06	97.04	97.44	94.56	4.7E-14	14.18
0.20	0.042	0.85	0.73	2.8E-06	86.16	97.17	83.72	4.6E-14	13.99
0.22	0.046	0.93	0.81	3.1E-06	86.63	96.90	83.95	5.1E-14	15.48
0.24	0.051	1.02	0.91	3.5E-06	89.69	96.56	86.61	5.8E-14	17.48
0.26	0.055	1.10	1.01	3.8E-06	91.47	96.29	88.08	6.4E-14	19.31
0.28	0.059	1.19	1.06	4.0E-06	89.46	96.02	85.91	6.7E-14	20.34
0.30	0.064	1.27	1.17	4.4E-06	91.93	95.69	87.96	7.4E-14	22.39
0.32	0.068	1.36	1.26	4.8E-06	93.08	95.42	88.82	8.0E-14	24.19

Table K.11 (continued): Pure hydrogen experimental data for Pt/C at 140°C, flow rate 150 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.34	0.073	1.44	1.36	5.2E-06	94.66	95.08	90.01	8.6E-14	26.13
0.36	0.077	1.53	1.46	5.5E-06	95.49	94.81	90.53	9.2E-14	27.91
0.38	0.082	1.61	1.52	5.8E-06	94.59	94.47	89.36	9.6E-14	29.19
0.40	0.086	1.69	1.60	6.1E-06	94.29	94.20	88.83	1.0E-13	30.62
0.42	0.090	1.78	1.70	6.5E-06	95.73	93.94	89.93	1.1E-13	32.65
0.44	0.095	1.86	1.76	6.7E-06	94.50	93.60	88.45	1.1E-13	33.76
0.46	0.100	1.95	1.84	7.0E-06	94.20	93.26	87.85	1.2E-13	35.18
0.48	0.104	2.03	1.97	6.8E-06	96.69	92.99	89.91	1.1E-13	34.52
0.50	0.109	2.12	2.03	7.7E-06	95.81	92.65	88.77	1.3E-13	38.90
0.52	0.113	2.20	2.09	7.9E-06	94.66	92.39	87.46	1.3E-13	39.97
0.54	0.118	2.29	2.23	8.5E-06	97.62	92.05	89.86	1.4E-13	42.80
0.56	0.122	2.37	2.32	8.8E-06	97.79	91.78	89.75	1.5E-13	44.46
0.58	0.127	2.46	2.41	9.2E-06	98.23	91.44	89.83	1.5E-13	46.26
0.60	0.132	2.54	2.49	9.4E-06	97.87	91.11	89.17	1.6E-13	47.68
0.62	0.136	2.63	2.55	9.7E-06	97.06	90.84	88.16	1.6E-13	48.86
0.64	0.141	2.71	2.63	1.0E-05	96.85	90.50	87.65	1.7E-13	50.33
0.66	0.146	2.80	2.77	1.1E-05	98.96	90.20	89.26	1.8E-13	53.03
0.68	0.150	2.88	2.84	1.1E-05	98.45	89.89	88.49	1.8E-13	54.36
0.70	0.155	2.97	2.92	1.1E-05	98.34	89.58	88.09	1.8E-13	55.89
0.72	0.159	3.05	2.92	1.1E-05	95.86	89.27	85.57	1.9E-13	56.04
0.74	0.164	3.14	3.02	1.1E-05	96.24	88.96	85.61	1.9E-13	57.83
0.76	0.169	3.22	3.12	1.2E-05	96.96	88.65	85.95	2.0E-13	59.83
0.78	0.173	3.30	3.30	1.3E-05	99.80	88.34	88.16	2.1E-13	63.21
0.80	0.178	3.39	3.32	1.3E-05	97.87	88.03	86.15	2.1E-13	63.58
0.82	0.182	3.47	3.36	1.3E-05	96.62	87.72	84.75	2.1E-13	64.33
0.84	0.187	3.56	3.52	1.3E-05	99.00	87.41	86.53	2.2E-13	67.52
0.86	0.192	3.64	3.60	1.4E-05	98.85	87.10	86.09	2.3E-13	69.03
0.88	0.306	3.73	3.70	1.4E-05	99.12	79.38	78.69	2.3E-13	70.82

Table K.12: Pure hydrogen experimental data for Pt/C at 140°C, flow rate 200 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.04	1.6E-07	51.18	99.60	50.97	2.7E-15	0.83
0.04	0.007	0.17	0.10	3.8E-07	59.51	99.53	59.23	6.4E-15	1.93
0.06	0.011	0.25	0.20	7.5E-07	77.93	99.26	77.36	1.3E-14	3.80
0.08	0.015	0.34	0.28	1.1E-06	81.64	98.99	80.82	1.8E-14	5.30
0.10	0.019	0.42	0.37	1.4E-06	87.51	98.72	86.39	2.3E-14	7.11
0.12	0.023	0.51	0.43	1.6E-06	83.89	98.45	82.59	2.7E-14	8.17
0.14	0.027	0.59	0.56	2.1E-06	94.60	98.18	92.88	3.6E-14	10.75
0.16	0.031	0.68	0.65	2.5E-06	96.30	97.91	94.29	4.1E-14	12.51
0.18	0.035	0.76	0.72	2.7E-06	94.28	97.65	92.06	4.6E-14	13.78
0.20	0.039	0.85	0.82	3.1E-06	96.39	97.40	93.89	5.2E-14	15.65
0.22	0.042	0.93	0.91	3.4E-06	97.14	97.16	94.39	5.7E-14	17.35
0.24	0.046	1.02	0.98	3.7E-06	96.52	96.89	93.52	6.2E-14	18.81
0.26	0.050	1.10	1.03	3.9E-06	93.63	96.63	90.48	6.5E-14	19.77
0.28	0.054	1.19	1.14	4.3E-06	95.83	96.36	92.34	7.2E-14	21.79
0.30	0.058	1.27	1.24	4.7E-06	97.66	96.09	93.84	7.9E-14	23.79
0.32	0.062	1.36	1.31	5.0E-06	96.30	95.82	92.27	8.3E-14	25.02
0.34	0.066	1.44	1.40	5.3E-06	96.88	95.55	92.57	8.8E-14	26.74
0.36	0.070	1.53	1.48	5.6E-06	97.36	95.31	92.80	9.4E-14	28.46
0.38	0.073	1.61	1.59	6.0E-06	98.70	95.08	93.84	1.0E-13	30.45

Table K.12 (continued): Pure hydrogen experimental data for Pt/C at 140°C, flow rate 200 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.40	0.077	1.69	1.64	6.2E-06	96.60	94.79	91.57	1.0E-13	31.38
0.42	0.082	1.78	1.73	6.6E-06	97.34	94.50	91.98	1.1E-13	33.20
0.44	0.085	1.86	1.73	6.6E-06	93.06	94.27	87.73	1.1E-13	33.25
0.46	0.089	1.95	1.82	6.9E-06	93.59	94.00	87.98	1.2E-13	34.96
0.48	0.093	2.03	1.93	7.3E-06	95.04	93.73	89.08	1.2E-13	37.04
0.50	0.097	2.12	2.03	7.7E-06	95.81	93.46	89.55	1.3E-13	38.90
0.52	0.101	2.20	2.09	7.9E-06	94.66	93.19	88.22	1.3E-13	39.97
0.54	0.105	2.29	2.19	8.3E-06	95.73	92.92	88.96	1.4E-13	41.97
0.56	0.109	2.37	2.28	8.7E-06	96.02	92.65	88.97	1.4E-13	43.66
0.58	0.113	2.46	2.36	9.0E-06	96.19	92.37	88.85	1.5E-13	45.30
0.60	0.118	2.54	2.43	9.2E-06	95.77	92.05	88.16	1.5E-13	46.66
0.62	0.122	2.63	2.49	9.5E-06	94.92	91.78	87.12	1.6E-13	47.79
0.64	0.126	2.71	2.63	1.0E-05	96.85	91.51	88.63	1.7E-13	50.33
0.66	0.130	2.80	2.77	1.1E-05	98.96	91.24	90.29	1.8E-13	53.03
0.68	0.134	2.88	2.84	1.1E-05	98.45	90.97	89.56	1.8E-13	54.36
0.70	0.138	2.97	2.92	1.1E-05	98.34	90.70	89.20	1.8E-13	55.89
0.72	0.142	3.05	2.92	1.1E-05	95.86	90.43	86.68	1.9E-13	56.04
0.74	0.146	3.14	3.02	1.1E-05	96.24	90.15	86.76	1.9E-13	57.83
0.76	0.151	3.22	3.12	1.2E-05	96.96	89.82	87.09	2.0E-13	59.83
0.78	0.155	3.30	3.30	1.3E-05	99.80	89.56	89.38	2.1E-13	63.21
0.80	0.159	3.39	3.32	1.3E-05	97.87	89.29	87.39	2.1E-13	63.58
0.82	0.163	3.47	3.36	1.3E-05	96.62	89.02	86.00	2.1E-13	64.33
0.84	0.168	3.56	3.52	1.3E-05	99.00	88.70	87.81	2.2E-13	67.52
0.86	0.172	3.64	3.57	1.4E-05	97.92	88.41	86.57	2.3E-13	68.37
0.88	0.177	3.73	3.70	1.4E-05	99.12	88.11	87.33	2.3E-13	70.82
0.90	0.181	3.81	3.78	1.4E-05	99.18	87.80	87.08	2.4E-13	72.48
0.92	0.186	3.90	3.86	1.5E-05	99.00	87.47	86.59	2.4E-13	73.96
0.94	0.191	3.98	3.98	1.5E-05	99.96	87.13	87.09	2.5E-13	76.29
0.96	0.195	4.07	4.07	1.5E-05	99.98	86.83	86.81	2.6E-13	77.93
0.98	0.201	4.15	4.14	1.6E-05	99.73	86.48	86.25	2.6E-13	79.35
1.00	0.205	4.24	4.20	1.6E-05	99.18	86.19	85.48	2.7E-13	80.53
1.02	0.210	4.32	4.23	1.6E-05	97.96	85.85	84.10	2.7E-13	81.13
1.04	0.214	4.41	4.30	1.6E-05	97.53	85.58	83.47	2.7E-13	82.36
1.06	0.219	4.49	4.36	1.7E-05	97.16	85.24	82.82	2.8E-13	83.63
1.08	0.224	4.58	4.45	1.7E-05	97.23	84.91	82.56	2.8E-13	85.27
1.10	0.228	4.66	4.63	1.8E-05	99.36	84.64	84.10	2.9E-13	88.75
1.12	0.233	4.75	4.67	1.8E-05	98.39	84.30	82.94	3.0E-13	89.48
1.14	0.238	4.83	4.71	1.8E-05	97.47	83.96	81.84	3.0E-13	90.22
1.16	0.344	4.91	4.83	1.8E-05	98.23	76.79	75.44	3.1E-13	92.52

K.1.4 PURE HYDROGEN EXPERIMENTS AT 160°C

Table K.13: Pure hydrogen experimental data for Pt/C at 160°C, flow rate 50 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.06	2.3E-07	70.40	99.60	70.11	3.8E-15	1.14
0.04	0.007	0.17	0.12	4.5E-07	70.40	99.54	70.07	7.6E-15	2.29
0.06	0.010	0.25	0.18	7.0E-07	72.57	99.32	72.08	1.2E-14	3.54
0.08	0.014	0.34	0.27	1.0E-06	78.87	99.06	78.13	1.7E-14	5.12

Table K.13 (continued): Pure hydrogen experimental data for Pt/C at 160°C, flow rate 50 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.10	0.018	0.42	0.37	1.4E-06	88.03	98.79	86.96	2.4E-14	7.15
0.12	0.022	0.51	0.43	1.6E-06	83.64	98.52	82.40	2.7E-14	8.15
0.14	0.025	0.59	0.54	2.1E-06	91.61	98.31	90.06	3.4E-14	10.41
0.16	0.029	0.68	0.59	2.3E-06	87.49	98.05	85.78	3.8E-14	11.37
0.18	0.033	0.76	0.69	2.6E-06	91.05	97.78	89.02	4.4E-14	13.31
0.20	0.036	0.85	0.79	3.0E-06	93.63	97.57	91.36	5.0E-14	15.20
0.22	0.040	0.93	0.90	3.4E-06	96.99	97.30	94.37	5.7E-14	17.33
0.24	0.043	1.02	0.97	3.7E-06	95.86	97.09	93.07	6.2E-14	18.68
0.26	0.047	1.10	1.06	4.0E-06	96.53	96.83	93.47	6.7E-14	20.38
0.28	0.051	1.19	1.16	4.4E-06	97.79	96.56	94.43	7.3E-14	22.23
0.30	0.120	1.27	1.26	4.8E-06	98.96	91.89	90.93	8.0E-14	24.11

Table K.14: Pure hydrogen experimental data for Pt/C at 160°C, flow rate 100 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.06	2.3E-07	50.74	99.60	50.53	3.8E-15	1.14
0.04	0.006	0.17	0.12	4.5E-07	74.33	99.60	74.03	7.6E-15	2.29
0.06	0.010	0.25	0.19	7.0E-07	82.68	99.33	82.12	1.2E-14	3.55
0.08	0.013	0.34	0.27	1.0E-06	85.78	99.10	85.01	1.7E-14	5.23
0.10	0.017	0.42	0.38	1.4E-06	88.55	98.85	87.54	2.4E-14	7.19
0.12	0.021	0.51	0.43	1.6E-06	83.89	98.58	82.70	2.7E-14	8.17
0.14	0.025	0.59	0.54	2.1E-06	91.61	98.32	90.06	3.4E-14	10.41
0.16	0.028	0.68	0.65	2.5E-06	95.86	98.11	94.05	4.1E-14	12.45
0.18	0.032	0.76	0.74	2.8E-06	97.49	97.84	95.39	4.7E-14	14.25
0.20	0.036	0.85	0.82	3.1E-06	96.39	97.57	94.06	5.2E-14	15.65
0.22	0.039	0.93	0.89	3.4E-06	95.62	97.37	93.10	5.6E-14	17.08
0.24	0.043	1.02	0.98	3.7E-06	96.52	97.10	93.72	6.2E-14	18.81
0.26	0.047	1.10	1.03	3.9E-06	93.63	96.83	90.67	6.5E-14	19.77
0.28	0.050	1.19	1.15	4.4E-06	96.80	96.63	93.54	7.3E-14	22.01
0.30	0.054	1.27	1.24	4.7E-06	97.66	96.36	94.11	7.9E-14	23.79
0.32	0.058	1.36	1.31	5.0E-06	90.47	96.09	86.93	8.3E-14	25.02
0.34	0.062	1.44	1.40	5.3E-06	90.01	95.85	86.27	8.8E-14	26.74
0.36	0.065	1.53	1.38	5.2E-06	90.27	95.62	86.32	8.7E-14	26.39
0.38	0.069	1.61	1.49	5.7E-06	92.84	95.35	88.53	9.5E-14	28.65
0.40	0.073	1.69	1.57	6.0E-06	92.72	95.08	88.16	9.9E-14	30.11
0.42	0.077	1.78	1.62	6.2E-06	91.08	94.81	86.36	1.0E-13	31.06
0.44	0.080	1.86	1.73	6.6E-06	93.06	94.61	88.04	1.1E-13	33.25
0.46	0.084	1.95	1.84	7.0E-06	94.20	94.34	88.87	1.2E-13	35.18
0.48	0.088	2.03	1.97	6.8E-06	96.69	94.07	90.95	1.1E-13	34.52
0.50	0.092	2.12	2.03	7.7E-06	95.81	93.80	89.87	1.3E-13	38.90
0.52	0.096	2.20	2.09	7.9E-06	94.66	93.53	88.54	1.3E-13	39.97
0.54	0.100	2.29	2.19	8.3E-06	95.73	93.26	89.28	1.4E-13	41.97
0.56	0.104	2.37	2.28	8.7E-06	96.02	92.98	89.28	1.4E-13	43.66
0.58	0.194	2.46	2.36	9.0E-06	96.19	86.91	83.59	1.5E-13	45.30

Table K.15: Pure hydrogen experimental data for Pt/C at 160°C, flow rate 150 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.04	1.5E-07	48.08	99.60	47.88	2.6E-15	0.78
0.04	0.008	0.17	0.12	4.5E-07	70.67	99.46	70.29	7.6E-15	2.30
0.06	0.012	0.25	0.20	7.6E-07	78.52	99.19	77.88	1.3E-14	3.83
0.08	0.016	0.34	0.28	1.1E-06	83.96	98.92	83.05	1.8E-14	5.45
0.10	0.021	0.42	0.34	1.3E-06	80.22	98.58	79.09	2.2E-14	6.51
0.12	0.025	0.51	0.40	1.5E-06	79.51	98.32	78.17	2.6E-14	7.75
0.14	0.029	0.59	0.55	2.1E-06	92.31	98.05	90.51	3.5E-14	10.49
0.16	0.031	0.68	0.63	2.4E-06	93.50	97.91	91.55	4.0E-14	12.15
0.18	0.035	0.76	0.74	2.8E-06	97.23	97.64	94.94	4.7E-14	14.21
0.20	0.038	0.85	0.73	2.8E-06	86.38	97.44	84.17	4.6E-14	14.03
0.22	0.042	0.93	0.81	3.1E-06	86.76	97.17	84.30	5.1E-14	15.50
0.24	0.051	1.02	0.91	3.5E-06	89.69	96.56	86.61	5.8E-14	17.48
0.26	0.055	1.10	1.01	3.8E-06	91.47	96.29	88.08	6.4E-14	19.31
0.28	0.059	1.19	1.05	4.0E-06	88.72	96.02	85.19	6.7E-14	20.17
0.30	0.064	1.27	1.16	4.4E-06	91.18	95.69	87.24	7.3E-14	22.21
0.32	0.068	1.36	1.26	4.8E-06	93.08	95.42	88.82	8.0E-14	24.19
0.34	0.073	1.44	1.36	5.2E-06	94.66	95.08	90.01	8.6E-14	26.13
0.36	0.077	1.53	1.46	5.5E-06	95.49	94.81	90.53	9.2E-14	27.91
0.38	0.082	1.61	1.52	5.8E-06	94.59	94.47	89.36	9.6E-14	29.19
0.40	0.086	1.69	1.60	6.1E-06	94.29	94.20	88.83	1.0E-13	30.62
0.42	0.090	1.78	1.73	6.6E-06	97.04	93.94	91.16	1.1E-13	33.09
0.44	0.095	1.86	1.86	7.1E-06	99.61	93.60	93.23	1.2E-13	35.59
0.46	0.100	1.95	1.84	7.0E-06	94.20	93.26	87.85	1.2E-13	35.18
0.48	0.104	2.03	1.97	6.8E-06	96.69	92.99	89.91	1.1E-13	34.52
0.50	0.109	2.12	2.03	7.7E-06	95.81	92.65	88.77	1.3E-13	38.90
0.52	0.113	2.20	2.09	7.9E-06	94.66	92.39	87.46	1.3E-13	39.97
0.54	0.118	2.29	2.23	8.5E-06	97.62	92.05	89.86	1.4E-13	42.80
0.56	0.122	2.37	2.32	8.8E-06	97.79	91.78	89.75	1.5E-13	44.46
0.58	0.127	2.46	2.41	9.2E-06	98.23	91.44	89.83	1.5E-13	46.26
0.60	0.132	2.54	2.49	9.4E-06	97.87	91.11	89.17	1.6E-13	47.68
0.62	0.136	2.63	2.49	9.5E-06	94.92	90.84	86.23	1.6E-13	47.79
0.64	0.141	2.71	2.63	1.0E-05	96.85	90.50	87.65	1.7E-13	50.33
0.66	0.146	2.80	2.77	1.1E-05	98.96	90.20	89.26	1.8E-13	53.03
0.68	0.150	2.88	2.84	1.1E-05	98.45	89.89	88.49	1.8E-13	54.36
0.70	0.155	2.97	2.92	1.1E-05	98.34	89.58	88.09	1.8E-13	55.89
0.72	0.159	3.05	2.92	1.1E-05	95.86	89.27	85.57	1.9E-13	56.04
0.74	0.164	3.14	3.02	1.1E-05	96.24	88.96	85.61	1.9E-13	57.83
0.76	0.169	3.22	3.12	1.2E-05	96.96	88.65	85.95	2.0E-13	59.83
0.78	0.173	3.30	3.30	1.3E-05	99.80	88.34	88.16	2.1E-13	63.21
0.80	0.178	3.39	3.32	1.3E-05	97.87	88.03	86.15	2.1E-13	63.58
0.82	0.182	3.47	3.36	1.3E-05	96.62	87.72	84.75	2.1E-13	64.33
0.84	0.187	3.56	3.52	1.3E-05	99.00	87.41	86.53	2.2E-13	67.52
0.86	0.292	3.64	3.57	1.4E-05	97.92	80.33	78.66	2.3E-13	68.37

Table K.16: Pure hydrogen experimental data for Pt/C at 160°C, flow rate 200 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.05	1.8E-07	56.88	99.60	56.65	3.1E-15	0.92
0.04	0.008	0.17	0.12	4.4E-07	68.87	99.48	68.51	7.4E-15	2.24
0.06	0.012	0.25	0.21	7.9E-07	82.13	99.19	81.47	1.3E-14	4.00
0.08	0.016	0.34	0.28	1.1E-06	83.30	98.92	82.41	1.8E-14	5.41
0.10	0.021	0.42	0.37	1.4E-06	88.35	98.58	87.10	2.4E-14	7.17
0.12	0.025	0.51	0.42	1.6E-06	82.65	98.32	81.26	2.7E-14	8.05
0.14	0.029	0.59	0.51	1.9E-06	85.39	98.05	83.72	3.2E-14	9.71
0.16	0.033	0.68	0.56	2.1E-06	83.22	97.78	81.37	3.6E-14	10.81
0.18	0.037	0.76	0.63	2.4E-06	82.60	97.51	80.54	4.0E-14	12.07
0.20	0.041	0.85	0.73	2.8E-06	86.38	97.24	84.00	4.6E-14	14.03
0.22	0.045	0.93	0.81	3.1E-06	86.76	96.97	84.13	5.1E-14	15.50
0.24	0.049	1.02	0.91	3.5E-06	89.69	96.70	86.73	5.8E-14	17.48
0.26	0.053	1.10	1.01	3.8E-06	91.47	96.43	88.20	6.4E-14	19.31
0.28	0.057	1.19	1.05	4.0E-06	88.72	96.16	85.31	6.7E-14	20.17
0.30	0.061	1.27	1.16	4.4E-06	91.18	95.89	87.43	7.3E-14	22.21
0.32	0.065	1.36	1.26	4.8E-06	93.08	95.62	89.01	8.0E-14	24.19
0.34	0.069	1.44	1.36	5.2E-06	94.66	95.35	90.26	8.6E-14	26.13
0.36	0.073	1.53	1.46	5.5E-06	95.49	95.08	90.79	9.2E-14	27.91
0.38	0.077	1.61	1.52	5.8E-06	94.59	94.81	89.68	9.6E-14	29.19
0.40	0.081	1.69	1.60	6.1E-06	94.29	94.54	89.14	1.0E-13	30.62
0.42	0.085	1.78	1.73	6.6E-06	97.04	94.27	91.49	1.1E-13	33.09
0.44	0.089	1.86	1.86	7.1E-06	99.61	94.00	93.63	1.2E-13	35.59
0.46	0.093	1.95	1.82	6.9E-06	93.59	93.73	87.73	1.2E-13	34.96
0.48	0.097	2.03	1.93	7.3E-06	95.04	93.49	88.85	1.2E-13	37.04
0.50	0.100	2.12	2.03	7.7E-06	95.81	93.26	89.35	1.3E-13	38.90
0.52	0.104	2.20	2.09	7.9E-06	94.66	92.99	88.03	1.3E-13	39.97
0.54	0.109	2.29	2.19	8.3E-06	95.73	92.67	88.71	1.4E-13	41.97
0.56	0.113	2.37	2.28	8.7E-06	96.02	92.39	88.71	1.4E-13	43.66
0.58	0.117	2.46	2.36	9.0E-06	96.19	92.12	88.60	1.5E-13	45.30
0.60	0.122	2.54	2.43	9.2E-06	95.77	91.81	87.93	1.5E-13	46.66
0.62	0.126	2.63	2.49	9.5E-06	94.92	91.51	86.87	1.6E-13	47.79
0.64	0.130	2.71	2.63	1.0E-05	96.85	91.24	88.37	1.7E-13	50.33
0.66	0.134	2.80	2.77	1.1E-05	98.96	90.97	90.02	1.8E-13	53.03
0.68	0.138	2.88	2.84	1.1E-05	98.45	90.70	89.29	1.8E-13	54.36
0.70	0.142	2.97	2.92	1.1E-05	98.34	90.43	88.93	1.8E-13	55.89
0.72	0.146	3.05	2.92	1.1E-05	95.86	90.16	86.42	1.9E-13	56.04
0.74	0.151	3.14	3.02	1.1E-05	96.24	89.84	86.47	1.9E-13	57.83
0.76	0.155	3.22	3.12	1.2E-05	96.96	89.56	86.83	2.0E-13	59.83
0.78	0.159	3.30	3.30	1.3E-05	99.80	89.29	89.11	2.1E-13	63.21
0.80	0.163	3.39	3.32	1.3E-05	97.87	89.02	87.12	2.1E-13	63.58
0.82	0.168	3.47	3.36	1.3E-05	96.62	88.67	85.67	2.1E-13	64.33
0.84	0.173	3.56	3.52	1.3E-05	99.00	88.34	87.46	2.2E-13	67.52
0.86	0.178	3.64	3.57	1.4E-05	97.92	88.03	86.19	2.3E-13	68.37
0.88	0.183	3.73	3.70	1.4E-05	99.12	87.67	86.90	2.3E-13	70.82
0.90	0.188	3.81	3.78	1.4E-05	99.18	87.35	86.63	2.4E-13	72.48
0.92	0.192	3.90	3.86	1.5E-05	99.00	87.04	86.18	2.4E-13	73.96
0.94	0.198	3.98	3.98	1.5E-05	99.96	86.68	86.64	2.5E-13	76.29
0.96	0.203	4.07	4.07	1.5E-05	99.98	86.30	86.28	2.6E-13	77.93
0.98	0.209	4.15	4.14	1.6E-05	99.73	85.92	85.68	2.6E-13	79.35
1.00	0.215	4.24	4.20	1.6E-05	99.18	85.52	84.82	2.7E-13	80.53
1.02	0.219	4.32	4.23	1.6E-05	97.96	85.22	83.48	2.7E-13	81.13
1.04	0.225	4.41	4.30	1.6E-05	97.53	84.85	82.76	2.7E-13	82.36
1.06	0.230	4.49	4.36	1.7E-05	97.16	84.50	82.10	2.8E-13	83.63

Table K.16 (continued): Pure hydrogen experimental data for Pt/C at 160°C, flow rate 200 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
1.08	0.235	4.58	4.45	1.7E-05	97.23	84.16	81.84	2.8E-13	85.27
1.10	0.240	4.66	4.63	1.8E-05	99.36	83.83	83.29	2.9E-13	88.75
1.12	0.245	4.75	4.67	1.8E-05	98.39	83.49	82.15	3.0E-13	89.48
1.14	0.250	4.83	4.71	1.8E-05	97.47	83.15	81.05	3.0E-13	90.22
1.16	0.378	4.91	4.83	1.8E-05	98.23	74.52	73.20	3.1E-13	92.52

K.2 EXPERIMENTAL DATA FOR PT-RU/C CATALYST

K.2.1 PURE HYDROGEN EXPERIMENTS AT 100°C

Table K.17: Pure hydrogen experimental data for Pt-Ru/C at 100°C, flow rate 50 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.06	2.2E-07	69.74	99.60	69.45	3.7E-15	1.13
0.04	0.011	0.17	0.13	5.0E-07	77.80	99.26	77.22	8.3E-15	2.53
0.06	0.017	0.25	0.21	8.2E-07	84.47	98.85	83.51	1.4E-14	4.12
0.08	0.023	0.34	0.30	1.1E-06	87.86	98.45	86.49	1.9E-14	5.71
0.10	0.030	0.42	0.34	1.3E-06	79.74	97.98	78.13	2.1E-14	6.47
0.12	0.360	0.51	0.41	1.5E-06	79.89	75.74	60.51	2.6E-14	7.78
0.14	0.042	0.59	0.55	2.1E-06	92.40	97.17	89.79	3.5E-14	10.50
0.16	0.048	0.68	0.63	2.4E-06	92.98	96.77	89.97	4.0E-14	12.08
0.18	0.054	0.76	0.74	2.8E-06	97.23	96.36	93.70	4.7E-14	14.21
0.20	0.061	0.85	0.81	3.1E-06	95.25	95.89	91.33	5.1E-14	15.47
0.22	0.067	0.93	0.86	3.3E-06	92.21	95.49	88.05	5.4E-14	16.47
0.24	0.074	1.02	0.96	3.6E-06	94.32	95.01	89.61	6.1E-14	18.38
0.26	0.080	1.10	1.04	3.9E-06	94.40	94.61	89.31	6.6E-14	19.93
0.28	0.087	1.19	1.07	4.1E-06	90.59	94.14	85.28	6.8E-14	20.60
0.30	0.093	1.27	1.24	4.7E-06	97.87	93.73	91.74	7.9E-14	23.84
0.32	0.238	1.36	1.31	5.0E-06	96.30	83.93	80.82	8.3E-14	25.02

Table K.18: Pure hydrogen experimental data for Pt-Ru/C at 100°C, flow rate 100 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.06	2.3E-07	70.73	99.60	70.44	3.8E-15	1.15
0.04	0.009	0.17	0.14	5.2E-07	80.61	99.43	80.15	8.6E-15	2.62
0.06	0.016	0.25	0.22	8.2E-07	85.01	98.92	84.09	1.4E-14	4.14
0.08	0.024	0.34	0.30	1.1E-06	87.28	98.38	85.87	1.9E-14	5.67
0.10	0.031	0.42	0.34	1.3E-06	79.79	97.91	78.13	2.1E-14	6.48
0.12	0.038	0.51	0.41	1.5E-06	79.98	97.44	77.93	2.6E-14	7.79
0.14	0.044	0.59	0.55	2.1E-06	92.49	97.04	89.75	3.5E-14	10.51
0.16	0.051	0.68	0.63	2.4E-06	93.19	96.56	89.98	4.0E-14	12.11
0.18	0.058	0.76	0.74	2.8E-06	97.36	96.09	93.56	4.7E-14	14.23
0.20	0.064	0.85	0.71	2.7E-06	83.89	95.69	80.27	4.5E-14	13.62
0.22	0.071	0.93	0.80	3.0E-06	85.54	95.22	81.44	5.0E-14	15.28
0.24	0.078	1.02	0.87	3.3E-06	85.70	94.74	81.19	5.5E-14	16.70

Table K.18 (continued): Pure hydrogen experimental data for Pt-Ru/C at 100°C, flow rate 100 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.26	0.085	1.10	0.96	3.6E-06	86.89	94.27	81.91	6.1E-14	18.34
0.28	0.092	1.19	1.04	4.0E-06	87.82	93.80	82.38	6.6E-14	19.97
0.30	0.099	1.27	1.12	4.3E-06	88.11	93.33	82.23	7.1E-14	21.46
0.32	0.105	1.36	1.21	4.6E-06	89.50	92.92	83.17	7.7E-14	23.25
0.34	0.112	1.44	1.28	4.9E-06	88.99	92.45	82.28	8.1E-14	24.57
0.36	0.119	1.53	1.38	5.2E-06	90.27	91.98	83.03	8.7E-14	26.39
0.38	0.125	1.61	1.49	5.7E-06	92.84	91.58	85.02	9.5E-14	28.65
0.40	0.131	1.69	1.55	5.9E-06	91.71	91.17	83.61	9.8E-14	29.78
0.42	0.138	1.78	1.62	6.2E-06	91.08	90.70	82.61	1.0E-13	31.06
0.44	0.145	1.86	1.73	6.6E-06	93.06	90.23	83.97	1.1E-13	33.25
0.46	0.152	1.95	1.82	6.9E-06	93.59	89.76	84.01	1.2E-13	34.96
0.48	0.158	2.03	1.93	7.3E-06	95.04	89.35	84.92	1.2E-13	37.04
0.50	0.165	2.12	2.03	7.7E-06	95.81	88.88	85.16	1.3E-13	38.90
0.52	0.170	2.20	2.09	7.9E-06	94.66	88.54	83.82	1.3E-13	39.97
0.54	0.176	2.29	2.19	8.3E-06	95.73	88.14	84.38	1.4E-13	41.97
0.56	0.182	2.37	2.28	8.7E-06	96.02	87.74	84.24	1.4E-13	43.66
0.58	0.343	2.46	2.36	9.0E-06	96.19	76.91	73.98	1.5E-13	45.30

Table K.19: Pure hydrogen experimental data for Pt-Ru/C at 100°C, flow rate 150 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.06	2.3E-07	71.03	99.60	70.74	3.8E-15	1.15
0.04	0.012	0.17	0.14	5.2E-07	80.37	99.19	79.72	8.6E-15	2.61
0.06	0.019	0.25	0.22	8.2E-07	84.96	98.72	83.87	1.4E-14	4.14
0.08	0.025	0.34	0.30	1.1E-06	87.97	98.32	86.49	1.9E-14	5.71
0.10	0.032	0.42	0.34	1.3E-06	80.22	97.84	78.49	2.2E-14	6.51
0.12	0.038	0.51	0.40	1.5E-06	79.51	97.44	77.47	2.56E-14	7.75
0.14	0.045	0.59	0.55	2.1E-06	92.31	96.97	89.51	3.5E-14	10.49
0.16	0.051	0.68	0.63	2.4E-06	93.50	96.56	90.29	4.0E-14	12.15
0.18	0.057	0.76	0.73	2.8E-06	95.98	96.16	92.29	4.6E-14	14.03
0.20	0.063	0.85	0.81	3.1E-06	95.71	95.75	91.64	5.1E-14	15.54
0.22	0.069	0.93	0.88	3.4E-06	94.87	95.35	90.46	5.6E-14	16.95
0.24	0.075	1.02	0.97	3.7E-06	95.69	94.95	90.86	6.2E-14	18.65
0.26	0.081	1.10	1.03	3.9E-06	93.21	94.54	88.12	6.5E-14	19.68
0.28	0.088	1.19	1.14	4.3E-06	95.83	94.07	90.15	7.2E-14	21.79
0.30	0.094	1.27	1.24	4.7E-06	97.66	93.67	91.47	7.86E-14	23.79
0.32	0.100	1.36	1.31	5.0E-06	96.30	93.26	89.81	8.3E-14	25.02
0.34	0.106	1.44	1.40	5.3E-06	96.88	92.86	89.96	8.8E-14	26.74
0.36	0.113	1.53	1.48	5.6E-06	97.36	92.39	89.95	9.4E-14	28.46
0.38	0.119	1.61	1.59	6.0E-06	98.83	91.98	90.91	1.0E-13	30.49
0.40	0.126	1.69	1.65	6.3E-06	97.16	91.51	88.91	1.0E-13	31.56
0.42	0.132	1.78	1.62	6.1E-06	90.82	91.11	82.74	1.0E-13	30.97
0.44	0.138	1.86	1.74	6.6E-06	93.20	90.70	84.53	1.1E-13	33.30
0.46	0.145	1.95	1.84	7.0E-06	94.66	90.23	85.41	1.2E-13	35.35
0.48	0.151	2.03	1.96	6.8E-06	96.52	89.82	86.70	1.14E-13	34.46
0.50	0.156	2.12	2.03	7.7E-06	95.64	89.49	85.58	1.3E-13	38.83
0.52	0.162	2.20	2.09	7.9E-06	95.01	89.08	84.64	1.3E-13	40.12
0.54	0.168	2.29	2.22	8.4E-06	97.23	88.68	86.23	1.4E-13	42.63
0.56	0.175	2.37	2.32	8.8E-06	97.59	88.21	86.08	1.5E-13	44.37
0.58	0.181	2.46	2.41	9.2E-06	98.23	87.80	86.25	1.5E-13	46.26
0.60	0.187	2.54	2.50	9.5E-06	98.31	87.40	85.92	1.6E-13	47.89

Table K.19 (continued): Pure hydrogen experimental data for Pt-Ru/C at 100°C, flow rate 150 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.62	0.192	2.63	2.50	9.5E-06	95.13	87.06	82.83	1.6E-13	47.89
0.64	0.197	2.71	2.63	1.0E-05	96.85	86.73	84.00	1.7E-13	50.33
0.66	0.202	2.80	2.76	1.0E-05	98.72	86.39	85.28	1.75E-13	52.90
0.68	0.208	2.88	2.86	1.1E-05	99.19	85.98	85.29	1.8E-13	54.77
0.70	0.213	2.97	2.88	1.1E-05	97.09	85.65	83.16	1.8E-13	55.19
0.72	0.218	3.05	2.92	1.1E-05	95.61	85.31	81.56	1.8E-13	55.89
0.74	0.224	3.14	2.92	1.1E-05	93.27	84.91	79.19	1.9E-13	56.04
0.76	0.230	3.22	3.02	1.1E-05	93.71	84.50	79.19	1.9E-13	57.83
0.78	0.236	3.30	3.12	1.2E-05	94.47	84.10	79.45	2.0E-13	59.83
0.80	0.240	3.39	3.30	1.3E-05	97.30	83.83	81.57	2.1E-13	63.21
0.82	0.245	3.47	3.32	1.3E-05	95.49	83.49	79.72	2.1E-13	63.58
0.84	0.250	3.56	3.36	1.3E-05	94.32	83.15	78.43	2.12E-13	64.33
0.86	0.322	3.64	3.52	1.3E-05	96.70	78.32	75.73	2.2E-13	67.52

Table K.20: Pure hydrogen experimental data for Pt-Ru/C at 100°C, flow rate 200 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.06	2.3E-07	71.03	99.60	70.74	3.8E-15	1.15
0.04	0.011	0.17	0.14	5.2E-07	80.37	99.26	79.77	8.6E-15	2.61
0.06	0.017	0.25	0.22	8.2E-07	84.96	98.85	83.98	1.4E-14	4.14
0.08	0.023	0.34	0.30	1.1E-06	87.97	98.45	86.61	1.9E-14	5.71
0.10	0.029	0.42	0.34	1.3E-06	80.22	98.05	78.65	2.2E-14	6.51
0.12	0.035	0.51	0.40	1.5E-06	79.51	97.64	77.63	2.6E-14	7.75
0.14	0.041	0.59	0.55	2.1E-06	92.31	97.24	89.76	3.5E-14	10.49
0.16	0.047	0.68	0.63	2.4E-06	93.50	96.83	90.54	4.0E-14	12.15
0.18	0.053	0.76	0.73	2.8E-06	95.98	96.43	92.55	4.6E-14	14.03
0.20	0.059	0.85	0.81	3.1E-06	95.71	96.02	91.90	5.1E-14	15.54
0.22	0.065	0.93	0.88	3.4E-06	94.87	95.62	90.72	5.6E-14	16.95
0.24	0.071	1.02	0.97	3.7E-06	95.69	95.22	91.11	6.2E-14	18.65
0.26	0.077	1.10	1.03	3.9E-06	93.21	94.81	88.37	6.5E-14	19.68
0.28	0.083	1.19	1.14	4.3E-06	95.83	94.41	90.47	7.2E-14	21.79
0.30	0.089	1.27	1.24	4.7E-06	97.66	94.00	91.80	7.9E-14	23.79
0.32	0.094	1.36	1.31	5.0E-06	96.30	93.67	90.20	8.3E-14	25.02
0.34	0.100	1.44	1.40	5.3E-06	96.88	93.26	90.35	8.8E-14	26.74
0.36	0.105	1.53	1.48	5.6E-06	97.36	92.92	90.47	9.4E-14	28.46
0.38	0.111	1.61	1.59	6.0E-06	98.83	92.52	91.44	1.0E-13	30.49
0.40	0.117	1.69	1.65	6.3E-06	97.16	92.12	89.50	1.0E-13	31.56
0.42	0.123	1.78	1.62	6.1E-06	90.82	91.71	83.30	1.0E-13	30.97
0.44	0.129	1.86	1.74	6.6E-06	93.20	91.31	85.10	1.1E-13	33.30
0.46	0.134	1.95	1.84	7.0E-06	94.66	90.97	86.11	1.2E-13	35.35
0.48	0.140	2.03	1.96	6.8E-06	96.52	90.57	87.41	1.1E-13	34.46
0.50	0.145	2.12	2.03	7.7E-06	95.64	90.23	86.29	1.3E-13	38.83
0.52	0.150	2.20	2.09	7.9E-06	95.01	89.89	85.41	1.3E-13	40.12
0.54	0.156	2.29	2.22	8.4E-06	97.23	89.49	87.01	1.4E-13	42.63
0.56	0.161	2.37	2.32	8.8E-06	97.59	89.15	87.00	1.5E-13	44.37
0.58	0.167	2.46	2.41	9.2E-06	98.23	88.75	87.18	1.5E-13	46.26
0.60	0.173	2.54	2.50	9.5E-06	98.31	88.34	86.85	1.6E-13	47.89
0.62	0.177	2.63	2.50	9.5E-06	95.13	88.07	83.79	1.6E-13	47.89
0.64	0.183	2.71	2.63	1.0E-05	96.85	87.67	84.91	1.7E-13	50.33
0.66	0.188	2.80	2.76	1.0E-05	98.72	87.33	86.21	1.7E-13	52.90
0.68	0.194	2.88	2.86	1.1E-05	99.19	86.93	86.23	1.8E-13	54.77

Table K.20 (continued): Pure hydrogen experimental data for Pt-Ru/C at 100°C, flow rate 200 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.70	0.199	2.97	2.88	1.1E-05	97.09	86.59	84.07	1.8E-13	55.19
0.72	0.203	3.05	2.92	1.1E-05	95.61	86.32	82.53	1.8E-13	55.89
0.74	0.206	3.14	2.92	1.1E-05	93.27	86.12	80.32	1.9E-13	56.04
0.76	0.210	3.22	3.02	1.1E-05	93.71	85.85	80.45	1.9E-13	57.83
0.78	0.215	3.30	3.12	1.2E-05	94.47	85.51	80.79	2.0E-13	59.83
0.80	0.221	3.39	3.30	1.3E-05	97.30	85.11	82.81	2.1E-13	63.21
0.82	0.226	3.47	3.32	1.3E-05	95.49	84.77	80.95	2.1E-13	63.58
0.84	0.231	3.56	3.36	1.3E-05	94.32	84.43	79.64	2.1E-13	64.33
0.86	0.235	3.64	3.52	1.3E-05	96.70	84.16	81.39	2.2E-13	67.52
0.88	0.239	3.73	3.61	1.4E-05	96.91	83.89	81.30	2.3E-13	69.24
0.90	0.242	3.81	3.78	1.4E-05	99.18	83.69	83.01	2.4E-13	72.48
0.92	0.246	3.90	3.86	1.5E-05	99.00	83.42	82.59	2.4E-13	73.96
0.94	0.251	3.98	3.98	1.5E-05	99.96	83.09	83.05	2.5E-13	76.29
0.96	0.256	4.07	4.07	1.5E-05	99.98	82.75	82.73	2.6E-13	77.93
0.98	0.261	4.15	4.14	1.6E-05	99.73	82.41	82.19	2.6E-13	79.35
1.00	0.265	4.24	4.20	1.6E-05	99.18	82.14	81.47	2.7E-13	80.53
1.02	0.268	4.32	4.23	1.6E-05	97.96	81.94	80.27	2.7E-13	81.13
1.04	0.272	4.41	4.30	1.6E-05	97.53	81.67	79.66	2.7E-13	82.36
1.06	0.275	4.49	4.36	1.7E-05	97.16	81.47	79.16	2.8E-13	83.63
1.08	0.278	4.58	4.45	1.7E-05	97.23	81.27	79.02	2.8E-13	85.27
1.10	0.281	4.66	4.63	1.8E-05	99.36	81.06	80.55	2.9E-13	88.75
1.12	0.285	4.75	4.67	1.8E-05	98.39	80.80	79.50	3.0E-13	89.48
1.14	0.288	4.83	4.71	1.8E-05	97.47	80.59	78.55	3.0E-13	90.22
1.16	0.364	4.91	4.83	1.8E-05	98.23	75.49	74.16	3.1E-13	92.52

K.2.2 PURE HYDROGEN EXPERIMENTS AT 120°C

Table K.21: Pure hydrogen experimental data for Pt-Ru/C at 120°C, flow rate 50 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.06	2.3E-07	70.88	99.60	70.59	3.8E-15	1.15
0.04	0.007	0.17	0.12	4.4E-07	68.52	99.53	68.20	7.4E-15	2.23
0.06	0.011	0.25	0.19	7.1E-07	73.16	99.26	72.62	1.2E-14	3.56
0.08	0.016	0.34	0.27	1.0E-06	80.43	98.92	79.56	1.7E-14	5.22
0.10	0.020	0.42	0.38	1.4E-06	88.67	98.65	87.47	2.4E-14	7.20
0.12	0.024	0.51	0.43	1.6E-06	84.21	98.38	82.85	2.71E-14	8.20
0.14	0.028	0.59	0.54	2.0E-06	90.22	98.11	88.52	3.4E-14	10.26
0.16	0.032	0.68	0.65	2.5E-06	95.64	97.84	93.57	4.1E-14	12.42
0.18	0.037	0.76	0.72	2.8E-06	95.06	97.51	92.69	4.6E-14	13.89
0.20	0.041	0.85	0.79	3.0E-06	93.37	97.24	90.79	5.0E-14	15.16
0.22	0.045	0.93	0.87	3.3E-06	93.27	96.97	90.44	5.5E-14	16.66
0.24	0.049	1.02	0.95	3.6E-06	93.14	96.70	90.06	6.0E-14	18.15
0.26	0.054	1.10	1.04	4.0E-06	94.58	96.36	91.13	6.6E-14	19.97
0.28	0.058	1.19	1.16	4.4E-06	97.69	96.09	93.87	7.3E-14	22.21
0.30	0.063	1.27	1.22	4.6E-06	95.67	95.75	91.61	7.7E-14	23.30
0.32	0.339	1.36	1.29	4.9E-06	95.42	77.16	73.62	8.2E-14	24.79

Table K.22: Pure hydrogen experimental data for Pt-Ru/C at 120°C, flow rate 100 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.06	2.3E-07	70.66	99.60	70.37	3.8E-15	1.15
0.04	0.006	0.17	0.12	4.4E-07	68.56	99.60	68.28	7.4E-15	2.23
0.06	0.006	0.25	0.19	7.0E-07	72.99	99.60	72.69	1.2E-14	3.56
0.08	0.007	0.34	0.27	1.0E-06	80.46	99.53	80.08	1.7E-14	5.23
0.10	0.009	0.42	0.38	1.4E-06	89.26	99.39	88.72	2.4E-14	7.25
0.12	0.011	0.51	0.43	1.6E-06	84.02	99.26	83.40	2.7E-14	8.19
0.14	0.013	0.59	0.57	2.2E-06	95.83	99.12	94.99	3.6E-14	10.89
0.16	0.015	0.68	0.67	2.5E-06	98.51	98.99	97.51	4.2E-14	12.80
0.18	0.017	0.76	0.75	2.8E-06	97.75	98.85	96.63	4.7E-14	14.29
0.20	0.019	0.85	0.79	3.0E-06	93.63	98.72	92.43	5.0E-14	15.20
0.22	0.021	0.93	0.91	3.4E-06	97.14	98.58	95.77	5.7E-14	17.35
0.24	0.023	1.02	0.97	3.7E-06	95.86	98.45	94.37	6.2E-14	18.68
0.26	0.025	1.10	1.06	4.0E-06	96.53	98.32	94.90	6.7E-14	20.38
0.28	0.027	1.19	1.16	4.4E-06	97.69	98.18	95.91	7.3E-14	22.21
0.30	0.029	1.27	1.22	4.6E-06	95.67	98.05	93.80	7.7E-14	23.30
0.32	0.031	1.36	1.29	4.9E-06	95.42	97.91	93.43	8.2E-14	24.79
0.34	0.033	1.44	1.38	5.2E-06	95.47	97.78	93.34	8.7E-14	26.36
0.36	0.035	1.53	1.46	5.5E-06	95.49	97.64	93.23	9.2E-14	27.91
0.38	0.037	1.61	1.56	5.9E-06	96.67	97.51	94.26	9.85E-14	29.83
0.40	0.039	1.69	1.63	6.2E-06	96.05	97.37	93.52	1.0E-13	31.20
0.42	0.042	1.78	1.75	6.7E-06	98.54	97.04	95.62	1.1E-13	33.61
0.44	0.044	1.86	1.86	7.1E-06	99.93	96.90	96.84	1.2E-13	35.70
0.46	0.046	1.95	1.88	7.2E-06	96.70	96.77	93.57	1.2E-13	36.12
0.48	0.048	2.03	2.00	7.6E-06	98.39	96.63	95.08	1.3E-13	38.35
0.50	0.050	2.12	2.06	7.8E-06	97.20	96.50	93.79	1.3E-13	39.46
0.52	0.052	2.20	2.12	8.1E-06	96.44	96.36	92.93	1.3E-13	40.72
0.54	0.054	2.29	2.21	8.4E-06	96.48	96.23	92.84	1.4E-13	42.30
0.56	0.056	2.37	2.28	8.7E-06	96.02	96.02	92.20	1.4E-13	43.66
0.58	0.059	2.46	2.36	9.0E-06	96.19	96.02	92.36	1.5E-13	45.30
0.60	0.278	2.54	2.47	9.4E-06	97.02	81.25	78.83	1.6E-13	47.27

Table K.23: Pure hydrogen experimental data for Pt-Ru/C at 120°C, flow rate 150 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.06	2.3E-07	70.62	99.60	70.33	3.8E-15	1.15
0.04	0.006	0.17	0.12	4.4E-07	68.31	99.60	68.04	7.3E-15	2.22
0.06	0.006	0.25	0.19	7.0E-07	72.87	99.60	72.57	1.2E-14	3.55
0.08	0.007	0.34	0.27	1.0E-06	80.54	99.53	80.16	1.7E-14	5.23
0.10	0.010	0.42	0.38	1.4E-06	88.67	99.33	88.07	2.4E-14	7.20
0.12	0.012	0.51	0.43	1.6E-06	83.89	99.19	83.21	2.7E-14	8.17
0.14	0.015	0.59	0.57	2.2E-06	96.80	98.99	95.82	3.6E-14	11.00
0.16	0.017	0.68	0.67	2.5E-06	98.57	98.85	97.44	4.2E-14	12.81
0.18	0.019	0.76	0.76	2.9E-06	99.25	98.72	97.97	4.8E-14	14.50
0.20	0.021	0.85	0.82	3.1E-06	96.39	98.58	95.03	5.2E-14	15.65
0.22	0.024	0.93	0.91	3.4E-06	97.14	98.38	95.57	5.7E-14	17.35
0.24	0.026	1.02	0.98	3.7E-06	96.52	98.25	94.83	6.2E-14	18.81
0.26	0.028	1.10	1.03	3.9E-06	93.63	98.11	91.86	6.5E-14	19.77
0.28	0.031	1.19	1.06	4.0E-06	89.45	97.91	87.58	6.7E-14	20.34
0.30	0.033	1.27	1.12	4.3E-06	88.11	97.78	86.15	7.1E-14	21.46
0.32	0.035	1.36	1.23	4.7E-06	90.47	97.64	88.33	7.8E-14	23.51

Table K.23 (continued): Pure hydrogen experimental data for Pt-Ru/C at 120°C, flow rate 150 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.34	0.037	1.44	1.30	4.9E-06	90.01	97.51	87.77	8.2E-14	24.85
0.36	0.039	1.53	1.38	5.2E-06	90.27	97.37	87.90	8.7E-14	26.39
0.38	0.042	1.61	1.49	5.7E-06	92.84	97.17	90.22	9.5E-14	28.65
0.40	0.044	1.69	1.57	6.0E-06	92.72	97.04	89.97	9.9E-14	30.11
0.42	0.046	1.78	1.62	6.2E-06	91.08	96.90	88.26	1.0E-13	31.06
0.44	0.048	1.86	1.73	6.6E-06	93.06	96.77	90.05	1.1E-13	33.25
0.46	0.050	1.95	1.84	7.0E-06	94.20	96.63	91.02	1.2E-13	35.18
0.48	0.052	2.03	1.97	6.8E-06	96.69	96.50	93.30	1.1E-13	34.52
0.50	0.054	2.12	2.03	7.7E-06	95.81	96.36	92.32	1.3E-13	38.90
0.52	0.057	2.20	2.09	7.9E-06	94.66	96.16	91.03	1.3E-13	39.97
0.54	0.059	2.29	2.23	8.5E-06	97.62	96.02	93.74	1.4E-13	42.80
0.56	0.061	2.37	2.32	8.8E-06	97.79	95.89	93.77	1.5E-13	44.46
0.58	0.063	2.46	2.41	9.2E-06	98.23	95.75	94.06	1.5E-13	46.26
0.60	0.065	2.54	2.49	9.4E-06	97.87	95.62	93.59	1.6E-13	47.68
0.62	0.068	2.63	2.49	9.5E-06	94.92	95.42	90.58	1.6E-13	47.79
0.64	0.070	2.71	2.63	1.0E-05	96.85	95.28	92.29	1.7E-13	50.33
0.66	0.073	2.80	2.77	1.1E-05	98.96	95.08	94.09	1.8E-13	53.03
0.68	0.075	2.88	2.84	1.1E-05	98.45	94.95	93.47	1.8E-13	54.36
0.70	0.078	2.97	2.92	1.1E-05	98.34	94.74	93.17	1.8E-13	55.89
0.72	0.080	3.05	2.92	1.0E-05	95.86	94.61	90.69	1.7E-13	51.34
0.74	0.083	3.14	2.94	1.1E-05	93.75	94.41	88.51	1.9E-13	56.33
0.76	0.085	3.22	3.12	1.2E-05	96.96	94.27	91.40	2.0E-13	59.83
0.78	0.087	3.30	3.30	1.3E-05	99.80	94.14	93.95	2.1E-13	63.21
0.80	0.090	3.39	3.32	1.3E-05	97.87	93.94	91.94	2.1E-13	63.58
0.82	0.092	3.47	3.36	1.3E-05	96.62	93.80	90.63	2.1E-13	64.33
0.84	0.095	3.56	3.52	1.3E-05	99.00	93.60	92.67	2.2E-13	67.52
0.86	0.206	3.64	3.57	1.4E-05	97.92	86.14	84.34	2.3E-13	68.37

Table K.24: Pure hydrogen experimental data for Pt-Ru/C at 120°C, flow rate 200 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.06	2.3E-07	70.62	99.58	70.32	3.8E-15	1.15
0.04	0.006	0.17	0.12	4.4E-07	68.31	99.60	68.04	7.3E-15	2.22
0.06	0.007	0.25	0.19	7.0E-07	72.87	99.53	72.52	1.2E-14	3.55
0.08	0.009	0.34	0.27	1.0E-06	80.54	99.39	80.05	1.7E-14	5.23
0.10	0.012	0.42	0.36	1.4E-06	84.37	99.19	83.69	2.3E-14	6.85
0.12	0.015	0.51	0.43	1.6E-06	83.89	98.99	83.04	2.7E-14	8.17
0.14	0.017	0.59	0.52	2.0E-06	87.02	98.85	86.02	3.3E-14	9.89
0.16	0.020	0.68	0.63	2.4E-06	92.36	98.65	91.12	4.0E-14	12.00
0.18	0.022	0.76	0.71	2.7E-06	93.21	98.52	91.83	4.5E-14	13.62
0.20	0.025	0.85	0.71	2.7E-06	83.89	98.32	82.48	4.5E-14	13.62
0.22	0.027	0.93	0.80	3.0E-06	85.54	98.18	83.98	5.0E-14	15.28
0.24	0.030	1.02	0.87	3.3E-06	85.70	97.98	83.96	5.5E-14	16.70
0.26	0.033	1.10	0.96	3.6E-06	86.89	97.78	84.96	6.1E-14	18.34
0.28	0.035	1.19	1.04	4.0E-06	87.82	97.64	85.75	6.6E-14	19.97
0.30	0.038	1.27	1.12	4.3E-06	88.11	97.44	85.86	7.1E-14	21.46
0.32	0.040	1.36	1.21	4.6E-06	89.50	97.30	87.09	7.7E-14	23.25
0.34	0.043	1.44	1.28	4.9E-06	88.99	97.10	86.42	8.1E-14	24.57
0.36	0.046	1.53	1.38	5.2E-06	90.27	96.90	87.47	8.7E-14	26.39
0.38	0.048	1.61	1.49	5.7E-06	92.84	96.77	89.84	9.5E-14	28.65
0.40	0.051	1.69	1.55	5.9E-06	91.71	96.56	88.55	9.8E-14	29.78

Table K.24 (continued): Pure hydrogen experimental data for Pt-Ru/C at 120°C, flow rate 200 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.42	0.053	1.78	1.62	6.2E-06	91.08	96.43	87.83	1.0E-13	31.06
0.44	0.056	1.86	1.73	6.6E-06	93.06	96.23	89.55	1.1E-13	33.25
0.46	0.058	1.95	1.82	6.9E-06	93.59	96.09	89.93	1.2E-13	34.96
0.48	0.061	2.03	1.93	7.3E-06	95.04	95.89	91.13	1.2E-13	37.04
0.50	0.063	2.12	2.03	7.7E-06	95.81	95.75	91.74	1.3E-13	38.90
0.52	0.066	2.20	2.09	7.9E-06	94.66	95.55	90.45	1.3E-13	39.97
0.54	0.069	2.29	2.19	8.3E-06	95.73	95.35	91.28	1.4E-13	41.97
0.56	0.071	2.37	2.28	8.7E-06	96.02	95.22	91.43	1.4E-13	43.66
0.58	0.074	2.46	2.36	9.0E-06	96.19	95.01	91.39	1.5E-13	45.30
0.60	0.076	2.54	2.43	9.2E-06	95.77	94.88	90.87	1.5E-13	46.66
0.62	0.079	2.63	2.49	9.5E-06	94.92	94.68	89.87	1.6E-13	47.79
0.64	0.082	2.71	2.63	1.0E-05	96.85	94.47	91.50	1.7E-13	50.33
0.66	0.084	2.80	2.77	1.1E-05	98.96	94.34	93.36	1.8E-13	53.03
0.68	0.087	2.88	2.84	1.1E-05	98.45	94.14	92.68	1.8E-13	54.36
0.70	0.090	2.97	2.92	1.1E-05	98.34	93.94	92.38	1.8E-13	55.89
0.72	0.092	3.05	2.92	1.1E-05	95.86	93.80	89.91	1.9E-13	56.04
0.74	0.095	3.14	3.02	1.1E-05	96.24	93.60	90.08	1.9E-13	57.83
0.76	0.097	3.22	3.12	1.2E-05	96.96	93.46	90.62	2.0E-13	59.83
0.78	0.100	3.30	3.30	1.3E-05	99.80	93.26	93.07	2.1E-13	63.21
0.80	0.102	3.39	3.32	1.3E-05	97.87	93.13	91.15	2.1E-13	63.58
0.82	0.105	3.47	3.36	1.3E-05	96.62	92.92	89.78	2.1E-13	64.33
0.84	0.107	3.56	3.52	1.3E-05	99.00	92.79	91.86	2.2E-13	67.52
0.86	0.110	3.64	3.57	1.4E-05	97.92	92.59	90.66	2.3E-13	68.37
0.88	0.113	3.73	3.70	1.4E-05	99.12	92.39	91.57	2.3E-13	70.82
0.90	0.115	3.81	3.78	1.4E-05	99.18	92.25	91.49	2.4E-13	72.48
0.92	0.118	3.90	3.79	1.4E-05	97.35	92.05	89.61	2.4E-13	72.72
0.94	0.120	3.98	3.94	1.5E-05	98.92	91.91	90.92	2.5E-13	75.50
0.96	0.123	4.07	4.01	1.5E-05	98.57	91.71	90.40	2.5E-13	76.83
0.98	0.125	4.15	4.08	1.5E-05	98.29	91.58	90.01	2.6E-13	78.21
1.00	0.128	4.24	4.20	1.6E-05	99.18	91.37	90.62	2.7E-13	80.53
1.02	0.131	4.32	4.23	1.6E-05	97.96	91.17	89.31	2.7E-13	81.13
1.04	0.133	4.41	4.30	1.6E-05	97.53	91.04	88.79	2.7E-13	82.36
1.06	0.136	4.49	4.36	1.7E-05	97.16	90.84	88.26	2.8E-13	83.63
1.08	0.138	4.58	4.45	1.7E-05	97.23	90.70	88.19	2.8E-13	85.27
1.10	0.140	4.66	4.57	1.7E-05	98.16	90.57	88.90	2.9E-13	87.67
1.12	0.143	4.75	4.67	1.8E-05	98.39	90.36	88.91	3.0E-13	89.48
1.14	0.146	4.83	4.71	1.8E-05	97.47	90.16	87.88	3.0E-13	90.22
1.16	0.251	4.91	4.83	1.8E-05	98.23	83.10	81.63	3.1E-13	92.52

K.2.3 PURE HYDROGEN EXPERIMENTS AT 140°C

Table K.25: Pure hydrogen experimental data for Pt-Ru/C at 140°C, flow rate 50 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.06	2.3E-07	72.06	99.60	71.77	3.9E-15	1.17
0.04	0.006	0.17	0.14	5.4E-07	83.79	99.60	83.45	9.0E-15	2.72
0.06	0.008	0.25	0.22	8.3E-07	86.33	99.46	85.86	1.4E-14	4.21
0.08	0.011	0.34	0.30	1.2E-06	89.42	99.26	88.76	1.9E-14	5.81
0.10	0.014	0.42	0.40	1.5E-06	93.79	99.06	92.91	2.5E-14	7.62
0.12	0.017	0.51	0.47	1.8E-06	91.53	98.85	90.48	2.9E-14	8.92
0.14	0.020	0.59	0.55	2.1E-06	92.49	98.65	91.25	3.5E-14	10.51

Table K.25 (continued): Pure hydrogen experimental data for Pt-Ru/C at 140°C, flow rate 50 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.16	0.023	0.68	0.63	2.4E-06	93.19	98.45	91.74	4.0E-14	12.11
0.18	0.026	0.76	0.74	2.8E-06	97.36	98.25	95.66	4.7E-14	14.23
0.20	0.030	0.85	0.81	3.1E-06	95.25	97.98	93.32	5.0E-14	15.16
0.22	0.033	0.93	0.86	3.3E-06	92.21	97.78	90.16	5.5E-14	16.66
0.24	0.036	1.02	0.96	3.6E-06	94.32	97.57	92.03	6.0E-14	18.15
0.26	0.039	1.10	1.04	3.9E-06	94.40	97.37	91.92	6.6E-14	19.97
0.28	0.042	1.19	1.07	4.1E-06	90.59	97.17	88.03	7.3E-14	22.21
0.30	0.126	1.27	1.24	4.7E-06	97.87	91.50	89.56	7.7E-14	23.30

Table K.26: Pure hydrogen experimental data for Pt-Ru/C at 140°C, flow rate 100 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.06	2.3E-07	70.40	99.60	70.11	3.8E-15	1.14
0.04	0.006	0.17	0.12	4.5E-07	70.40	99.60	70.11	7.6E-15	2.29
0.06	0.070	0.25	0.18	7.0E-07	72.57	95.28	69.15	1.2E-14	3.54
0.08	0.010	0.34	0.27	1.0E-06	78.87	99.33	78.34	1.7E-14	5.12
0.10	0.013	0.42	0.37	1.4E-06	88.03	99.12	87.26	2.4E-14	7.15
0.12	0.015	0.51	0.43	1.6E-06	83.64	98.99	82.80	2.7E-14	8.15
0.14	0.018	0.59	0.54	2.1E-06	91.61	98.79	90.50	3.4E-14	10.41
0.16	0.021	0.68	0.63	2.4E-06	92.31	98.58	91.01	4.0E-14	11.99
0.18	0.023	0.76	0.73	2.8E-06	95.73	98.45	94.25	4.6E-14	13.99
0.20	0.026	0.85	0.79	3.0E-06	93.63	98.25	91.99	5.0E-14	15.20
0.22	0.029	0.93	0.90	3.4E-06	96.99	98.05	95.09	5.7E-14	17.33
0.24	0.032	1.02	0.97	3.7E-06	95.86	97.84	93.79	6.2E-14	18.68
0.26	0.034	1.10	1.06	4.0E-06	96.53	97.71	94.31	6.7E-14	20.38
0.28	0.037	1.19	1.16	4.4E-06	97.79	97.51	95.35	7.3E-14	22.23
0.30	0.040	1.27	1.26	4.8E-06	98.96	97.30	96.29	8.0E-14	24.11
0.32	0.043	1.36	1.27	4.8E-06	93.50	97.10	90.79	8.0E-14	24.29
0.34	0.045	1.44	1.40	5.3E-06	96.99	96.97	94.05	8.8E-14	26.78
0.36	0.048	1.53	1.46	5.5E-06	95.49	96.77	92.40	9.2E-14	27.91
0.38	0.051	1.61	1.52	5.8E-06	94.59	96.56	91.34	9.6E-14	29.19
0.40	0.054	1.69	1.60	6.1E-06	94.29	96.36	90.86	1.0E-13	30.62
0.42	0.056	1.78	1.73	6.6E-06	97.04	96.23	93.38	1.1E-13	33.09
0.44	0.059	1.86	1.83	6.9E-06	98.00	96.02	94.11	1.2E-13	35.01
0.46	0.062	1.95	1.88	7.2E-06	96.70	95.82	92.66	1.2E-13	36.12
0.48	0.065	2.03	2.00	7.6E-06	98.39	95.62	94.08	1.3E-13	38.35
0.50	0.067	2.12	2.06	7.8E-06	97.20	95.49	92.81	1.3E-13	39.46
0.52	0.700	2.20	2.12	8.1E-06	96.44	52.83	50.95	1.3E-13	40.72
0.54	0.073	2.29	2.21	8.4E-06	96.48	95.08	91.73	1.4E-13	42.30
0.56	0.075	2.37	2.28	8.7E-06	96.02	94.95	91.17	1.4E-13	43.66
0.58	0.078	2.46	2.36	9.0E-06	96.19	94.74	91.13	1.5E-13	45.30
0.60	0.241	2.54	2.47	9.4E-06	97.02	83.76	81.26	1.6E-13	47.27

Table K.27: Pure hydrogen experimental data for Pt-Ru/C at 140°C, flow rate 150 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.06	2.3E-07	70.32	99.59	70.03	3.8E-15	1.14
0.04	0.006	0.17	0.12	4.5E-07	70.54	99.60	70.26	7.6E-15	2.29
0.06	0.007	0.25	0.19	7.0E-07	72.87	99.53	72.52	1.2E-14	3.55
0.08	0.010	0.34	0.27	1.0E-06	80.54	99.33	80.00	1.7E-14	5.23
0.10	0.013	0.42	0.38	1.4E-06	88.55	99.12	87.78	2.4E-14	7.19
0.12	0.016	0.51	0.43	1.6E-06	83.89	98.92	82.99	2.7E-14	8.17
0.14	0.018	0.59	0.54	2.1E-06	91.61	98.79	90.50	3.4E-14	10.41
0.16	0.021	0.68	0.64	2.4E-06	93.71	98.58	92.38	4.0E-14	12.17
0.18	0.024	0.76	0.70	2.6E-06	91.49	98.38	90.01	4.4E-14	13.37
0.20	0.027	0.85	0.82	3.1E-06	96.39	98.18	94.64	5.2E-14	15.65
0.22	0.029	0.93	0.89	3.4E-06	95.62	98.05	93.75	5.6E-14	17.08
0.24	0.032	1.02	0.98	3.7E-06	96.52	97.84	94.44	6.2E-14	18.81
0.26	0.035	1.10	1.03	3.9E-06	93.63	97.64	91.42	6.5E-14	19.77
0.28	0.038	1.19	1.15	4.4E-06	96.80	97.44	94.32	7.3E-14	22.01
0.30	0.040	1.27	1.24	4.7E-06	97.66	97.30	95.03	7.9E-14	23.79
0.32	0.043	1.36	1.31	5.0E-06	96.30	97.10	93.51	8.3E-14	25.02
0.34	0.046	1.44	1.40	5.3E-06	96.88	96.90	93.87	8.8E-14	26.74
0.36	0.049	1.53	1.48	5.6E-06	97.36	96.70	94.15	9.4E-14	28.46
0.38	0.051	1.61	1.59	6.0E-06	98.70	96.56	95.30	1.0E-13	30.45
0.40	0.054	1.69	1.64	6.2E-06	96.60	96.36	93.09	1.0E-13	31.38
0.42	0.057	1.78	1.73	6.6E-06	97.34	96.16	93.60	1.1E-13	33.20
0.44	0.059	1.86	1.73	6.6E-06	93.06	96.02	89.36	1.1E-13	33.25
0.46	0.062	1.95	1.82	6.9E-06	93.59	95.82	89.68	1.2E-13	34.96
0.48	0.065	2.03	1.93	7.3E-06	95.04	95.62	90.88	1.2E-13	37.04
0.50	0.068	2.12	2.03	7.7E-06	95.81	95.42	91.42	1.3E-13	38.90
0.52	0.070	2.20	2.09	7.9E-06	94.66	95.28	90.20	1.3E-13	39.97
0.54	0.073	2.29	2.19	8.3E-06	95.73	95.08	91.02	1.4E-13	41.97
0.56	0.076	2.37	2.28	8.7E-06	96.02	94.88	91.10	1.4E-13	43.66
0.58	0.079	2.46	2.36	9.0E-06	96.19	94.68	91.07	1.5E-13	45.30
0.60	0.082	2.54	2.43	9.2E-06	95.77	94.47	90.48	1.5E-13	46.66
0.62	0.085	2.63	2.49	9.5E-06	94.92	94.27	89.49	1.6E-13	47.79
0.64	0.087	2.71	2.63	1.0E-05	96.85	94.14	91.18	1.7E-13	50.33
0.66	0.090	2.80	2.77	1.1E-05	98.96	93.94	92.96	1.8E-13	53.03
0.68	0.092	2.88	2.84	1.1E-05	98.45	93.80	92.35	1.8E-13	54.36
0.70	0.095	2.97	2.92	1.1E-05	98.34	93.60	92.05	1.8E-13	55.89
0.72	0.098	3.05	2.92	1.1E-05	95.86	93.40	89.53	1.9E-13	56.04
0.74	0.101	3.14	3.02	1.1E-05	96.24	93.19	89.69	1.9E-13	57.83
0.76	0.104	3.22	3.12	1.2E-05	96.96	92.99	90.16	2.0E-13	59.83
0.78	0.106	3.30	3.30	1.3E-05	99.80	92.86	92.67	2.1E-13	63.21
0.80	0.109	3.39	3.32	1.3E-05	97.87	92.65	90.69	2.1E-13	63.58
0.82	0.113	3.47	3.36	1.3E-05	96.62	92.39	89.26	2.1E-13	64.33
0.84	0.115	3.56	3.52	1.3E-05	99.00	92.25	91.33	2.2E-13	67.52
0.86	0.230	3.64	3.57	1.4E-05	97.92	84.53	82.76	2.3E-13	68.37

Table K.28: Pure hydrogen experimental data for Pt-Ru/C at 140°C, flow rate 200 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.06	2.3E-07	70.62	99.60	70.33	3.8E-15	1.15
0.04	0.006	0.17	0.12	4.4E-07	68.31	99.60	68.04	7.3E-15	2.22
0.06	0.008	0.25	0.19	7.0E-07	72.87	99.46	72.47	1.2E-14	3.55
0.08	0.011	0.34	0.27	1.0E-06	80.54	99.26	79.94	1.7E-14	5.23
0.10	0.014	0.42	0.36	1.4E-06	84.37	99.06	83.57	2.3E-14	6.85
0.12	0.017	0.51	0.43	1.6E-06	83.89	98.85	82.93	2.7E-14	8.17
0.14	0.019	0.59	0.52	2.0E-06	87.02	98.72	85.91	3.3E-14	9.89
0.16	0.022	0.68	0.63	2.4E-06	92.36	98.52	91.00	4.0E-14	12.00
0.18	0.025	0.76	0.74	2.8E-06	96.98	98.32	95.35	4.7E-14	14.17
0.20	0.028	0.85	0.82	3.1E-06	96.39	98.11	94.58	5.2E-14	15.65
0.22	0.031	0.93	0.91	3.4E-06	97.14	97.91	95.11	5.7E-14	17.35
0.24	0.034	1.02	0.98	3.7E-06	96.52	97.71	94.31	6.2E-14	18.81
0.26	0.037	1.10	1.03	3.9E-06	93.63	97.51	91.30	6.5E-14	19.77
0.28	0.040	1.19	1.14	4.3E-06	95.83	97.30	93.25	7.2E-14	21.79
0.30	0.042	1.27	1.24	4.7E-06	97.66	97.17	94.90	7.9E-14	23.79
0.32	0.045	1.36	1.31	5.0E-06	96.30	96.97	93.38	8.3E-14	25.02
0.34	0.048	1.44	1.40	5.3E-06	96.88	96.77	93.74	8.8E-14	26.74
0.36	0.050	1.53	1.48	5.6E-06	97.36	96.63	94.08	9.4E-14	28.46
0.38	0.054	1.61	1.59	6.0E-06	98.83	96.36	95.24	1.0E-13	30.49
0.40	0.057	1.69	1.65	6.3E-06	97.16	96.16	93.43	1.0E-13	31.56
0.42	0.060	1.78	1.73	6.6E-06	97.34	95.96	93.40	1.1E-13	33.20
0.44	0.063	1.86	1.79	6.8E-06	95.99	95.75	91.92	1.1E-13	34.29
0.46	0.066	1.95	1.85	7.0E-06	95.12	95.55	90.89	1.2E-13	35.53
0.48	0.069	2.03	1.93	7.3E-06	95.04	95.35	90.62	1.2E-13	37.04
0.50	0.072	2.12	2.03	7.7E-06	95.81	95.15	91.16	1.3E-13	38.90
0.52	0.075	2.20	2.09	7.9E-06	94.66	94.95	89.88	1.3E-13	39.97
0.54	0.078	2.29	2.19	8.3E-06	95.73	94.74	90.70	1.4E-13	41.97
0.56	0.081	2.37	2.28	8.7E-06	96.02	94.54	90.78	1.4E-13	43.66
0.58	0.084	2.46	2.36	9.0E-06	96.19	94.34	90.74	1.5E-13	45.30
0.60	0.087	2.54	2.43	9.2E-06	95.77	94.14	90.16	1.5E-13	46.66
0.62	0.089	2.63	2.49	9.5E-06	94.92	94.00	89.23	1.6E-13	47.79
0.64	0.092	2.71	2.63	1.0E-05	96.85	93.80	90.85	1.7E-13	50.33
0.66	0.094	2.80	2.77	1.1E-05	98.96	93.67	92.69	1.8E-13	53.03
0.68	0.097	2.88	2.84	1.1E-05	98.45	93.46	92.01	1.8E-13	54.36
0.70	0.100	2.97	2.92	1.1E-05	98.34	93.26	91.71	1.8E-13	55.89
0.72	0.103	3.05	2.92	1.1E-05	95.86	93.06	89.20	1.9E-13	56.04
0.74	0.106	3.14	3.02	1.1E-05	96.24	92.86	89.37	1.9E-13	57.83
0.76	0.108	3.22	3.12	1.2E-05	96.96	92.72	89.90	2.0E-13	59.83
0.78	0.110	3.30	3.30	1.3E-05	99.80	92.59	92.40	2.1E-13	63.21
0.80	0.114	3.39	3.32	1.3E-05	97.87	92.32	90.36	2.1E-13	63.58
0.82	0.117	3.47	3.36	1.3E-05	96.62	92.12	89.00	2.1E-13	64.33
0.84	0.120	3.56	3.52	1.3E-05	99.00	91.91	91.00	2.2E-13	67.52
0.86	0.123	3.64	3.57	1.4E-05	97.92	91.71	89.80	2.3E-13	68.37
0.88	0.125	3.73	3.70	1.4E-05	99.12	91.58	90.77	2.3E-13	70.82
0.90	0.128	3.81	3.78	1.4E-05	99.18	91.37	90.62	2.4E-13	72.48
0.92	0.130	3.90	3.86	1.5E-05	99.00	91.24	90.33	2.4E-13	73.96
0.94	0.133	3.98	3.98	1.5E-05	99.96	91.04	91.00	2.5E-13	76.29
0.96	0.135	4.07	4.07	1.5E-05	99.98	90.90	90.88	2.6E-13	77.93
0.98	0.138	4.15	4.14	1.6E-05	99.73	90.70	90.45	2.6E-13	79.35
1.00	0.141	4.24	4.20	1.6E-05	99.18	90.50	89.76	2.7E-13	80.53
1.02	0.143	4.32	4.23	1.6E-05	97.96	90.36	88.52	2.7E-13	81.13
1.04	0.145	4.41	4.30	1.6E-05	97.53	90.23	88.00	2.7E-13	82.36
1.06	0.148	4.49	4.36	1.7E-05	97.16	90.03	87.47	2.8E-13	83.63

Table K.28 (continued): Pure hydrogen experimental data for Pt-Ru/C at 140°C, flow rate 200 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
1.08	0.151	4.58	4.45	1.7E-05	97.23	89.82	87.34	2.8E-13	85.27
1.10	0.153	4.66	4.63	1.8E-05	99.36	89.69	89.12	2.9E-13	88.75
1.12	0.156	4.75	4.67	1.8E-05	98.39	89.49	88.05	3.0E-13	89.48
1.14	0.159	4.83	4.71	1.8E-05	97.47	89.29	87.02	3.0E-13	90.22
1.16	0.270	4.91	4.83	1.8E-05	98.23	81.78	80.33	3.1E-13	92.52

K.2.4 PURE HYDROGEN EXPERIMENTS AT 160°C

Table K.29: Pure hydrogen experimental data for Pt-Ru/C at 160°C, flow rate 50 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.05	2.1E-07	63.88	99.60	63.62	3.4E-15	1.04
0.04	0.006	0.17	0.13	5.1E-07	79.23	99.60	78.91	8.5E-15	2.57
0.06	0.006	0.25	0.20	7.7E-07	79.56	99.60	79.23	1.3E-14	3.88
0.08	0.008	0.34	0.29	1.1E-06	84.21	99.46	83.75	1.8E-14	5.47
0.10	0.010	0.42	0.37	1.4E-06	88.28	99.33	87.69	2.4E-14	7.17
0.12	0.012	0.51	0.45	1.7E-06	88.62	99.19	87.91	2.85E-14	8.63
0.14	0.015	0.59	0.53	2.0E-06	90.05	98.99	89.14	3.4E-14	10.24
0.16	0.017	0.68	0.63	2.4E-06	92.72	98.85	91.66	4.0E-14	12.05
0.18	0.019	0.76	0.71	2.7E-06	93.04	98.72	91.85	4.5E-14	13.60
0.20	0.021	0.85	0.79	3.0E-06	93.76	98.58	92.43	5.0E-14	15.23
0.22	0.024	0.93	0.89	3.4E-06	95.62	98.38	94.07	5.6E-14	17.08
0.24	0.026	1.02	0.94	3.6E-06	92.59	98.25	90.97	6.0E-14	18.04
0.26	0.028	1.10	1.03	3.9E-06	93.12	98.11	91.37	6.5E-14	19.66
0.28	0.031	1.19	1.15	4.4E-06	96.80	97.91	94.78	7.3E-14	22.01
0.30	0.034	1.27	1.24	4.7E-06	97.77	97.71	95.53	7.9E-14	23.81
0.32	0.304	1.36	1.31	5.0E-06	96.97	79.51	77.10	8.3E-14	25.19

Table K.30: Pure hydrogen experimental data for Pt-Ru/C at 160°C, flow rate 100 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.06	2.3E-07	70.28	99.57	69.98	3.8E-15	1.14
0.04	0.006	0.17	0.12	4.5E-07	70.03	99.60	69.74	7.5E-15	2.27
0.06	0.006	0.25	0.18	7.0E-07	72.39	99.60	72.10	1.2E-14	3.53
0.08	0.006	0.34	0.27	1.0E-06	78.76	99.60	78.44	1.7E-14	5.12
0.10	0.008	0.42	0.37	1.4E-06	87.91	99.46	87.44	2.4E-14	7.14
0.12	0.010	0.51	0.42	1.6E-06	83.45	99.33	82.89	2.69E-14	8.13
0.14	0.012	0.59	0.54	2.0E-06	90.65	99.19	89.92	3.4E-14	10.30
0.16	0.014	0.68	0.66	2.5E-06	97.70	99.06	96.78	4.2E-14	12.69
0.18	0.015	0.76	0.74	2.8E-06	96.98	98.99	96.00	4.7E-14	14.17
0.20	0.017	0.85	0.79	3.0E-06	93.63	98.85	92.56	5.0E-14	15.20
0.22	0.019	0.93	0.90	3.4E-06	96.99	98.72	95.75	5.7E-14	17.33
0.24	0.021	1.02	0.97	3.7E-06	95.86	98.58	94.50	6.2E-14	18.68
0.26	0.023	1.10	1.06	4.0E-06	96.53	98.45	95.03	6.7E-14	20.38
0.28	0.025	1.19	1.16	4.4E-06	97.79	98.32	96.14	7.3E-14	22.23
0.30	0.027	1.27	1.26	4.8E-06	98.96	98.18	97.16	8.0E-14	24.11
0.32	0.029	1.36	1.33	5.0E-06	97.87	98.05	95.96	8.4E-14	25.43

Table K.30 (continued): Pure hydrogen experimental data for Pt-Ru/C at 160°C, flow rate 100 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.34	0.031	1.44	1.41	5.4E-06	98.20	97.91	96.15	9.0E-14	27.11
0.36	0.033	1.53	1.44	5.5E-06	94.28	97.78	92.18	9.1E-14	27.56
0.38	0.035	1.61	1.55	5.9E-06	96.14	97.64	93.87	9.8E-14	29.66
0.40	0.037	1.69	1.63	6.2E-06	95.91	97.51	93.52	1.0E-13	31.15
0.42	0.039	1.78	1.73	6.6E-06	97.04	97.37	94.49	1.1E-13	33.09
0.44	0.041	1.86	1.86	7.1E-06	99.61	97.24	96.85	1.2E-13	35.59
0.46	0.043	1.95	1.84	7.0E-06	94.20	97.10	91.47	1.2E-13	35.18
0.48	0.045	2.03	1.97	6.8E-06	96.69	96.97	93.75	1.1E-13	34.52
0.50	0.047	2.12	2.03	7.7E-06	95.81	96.83	92.77	1.3E-13	38.90
0.52	0.049	2.20	2.09	7.9E-06	94.66	96.70	91.54	1.3E-13	39.97
0.54	0.051	2.29	2.23	8.5E-06	97.62	96.56	94.26	1.4E-13	42.80
0.56	0.053	2.37	2.32	8.8E-06	97.79	96.43	94.30	1.5E-13	44.46
0.58	0.056	2.46	2.41	9.2E-06	98.23	96.23	94.53	1.5E-13	46.26
0.60	0.269571	2.54	2.49	9.4E-06	97.87	81.83	80.09	1.6E-13	47.68

Table K.31: Pure hydrogen experimental data for Pt-Ru/C at 160°C, flow rate 150 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.06	2.3E-07	70.10	99.60	69.82	3.8E-15	1.14
0.04	0.006	0.17	0.12	4.6E-07	71.37	99.60	71.08	7.7E-15	2.32
0.06	0.006	0.25	0.19	7.0E-07	72.87	99.60	72.57	1.2E-14	3.55
0.08	0.007	0.34	0.27	1.0E-06	80.16	99.53	79.78	1.7E-14	5.21
0.10	0.009	0.42	0.37	1.4E-06	88.32	99.39	87.78	2.4E-14	7.17
0.12	0.011	0.51	0.43	1.6E-06	83.64	99.26	83.02	2.7E-14	8.15
0.14	0.013	0.59	0.54	2.1E-06	91.34	99.12	90.54	3.4E-14	10.38
0.16	0.015	0.68	0.65	2.5E-06	95.75	98.99	94.78	4.1E-14	12.44
0.18	0.018	0.76	0.73	2.8E-06	96.23	98.79	95.06	4.6E-14	14.06
0.20	0.020	0.85	0.81	3.1E-06	95.71	98.65	94.42	5.1E-14	15.54
0.22	0.022	0.93	0.88	3.4E-06	94.87	98.52	93.46	5.6E-14	16.95
0.24	0.024	1.02	0.97	3.7E-06	95.69	98.38	94.14	6.2E-14	18.65
0.26	0.026	1.10	1.03	3.9E-06	93.21	98.25	91.57	6.5E-14	19.68
0.28	0.028	1.19	1.14	4.3E-06	95.83	98.11	94.02	7.2E-14	21.79
0.30	0.031	1.27	1.24	4.7E-06	97.66	97.91	95.62	7.9E-14	23.79
0.32	0.033	1.36	1.31	5.0E-06	96.30	97.78	94.16	8.3E-14	25.02
0.34	0.035	1.44	1.40	5.3E-06	96.88	97.64	94.59	8.8E-14	26.74
0.36	0.037	1.53	1.48	5.6E-06	97.36	97.51	94.93	9.4E-14	28.46
0.38	0.039	1.61	1.59	6.0E-06	98.83	97.37	96.24	1.0E-13	30.49
0.40	0.041	1.69	1.65	6.3E-06	97.16	97.24	94.48	1.0E-13	31.56
0.42	0.043	1.78	1.62	6.1E-06	90.82	97.10	88.19	1.0E-13	30.97
0.44	0.045	1.86	1.74	6.6E-06	93.20	96.97	90.37	1.1E-13	33.30
0.46	0.048	1.95	1.84	7.0E-06	94.66	96.77	91.59	1.2E-13	35.35
0.48	0.050	2.03	1.96	6.8E-06	96.52	96.63	93.27	1.1E-13	34.46
0.50	0.052	2.12	2.03	7.7E-06	95.64	96.50	92.29	1.3E-13	38.83
0.52	0.054	2.20	2.09	7.9E-06	95.01	96.36	91.56	1.3E-13	40.12
0.54	0.057	2.29	2.22	8.4E-06	97.23	96.16	93.50	1.4E-13	42.63
0.56	0.059	2.37	2.32	8.8E-06	97.59	96.02	93.71	1.5E-13	44.37
0.58	0.062	2.46	2.41	9.2E-06	98.23	95.82	94.13	1.5E-13	46.26
0.60	0.064	2.54	2.50	9.5E-06	98.31	95.69	94.07	1.6E-13	47.89
0.62	0.066	2.63	2.50	9.5E-06	95.13	95.55	90.90	1.6E-13	47.89
0.64	0.068	2.71	2.63	1.0E-05	96.85	95.42	92.42	1.7E-13	50.33
0.66	0.071	2.80	2.76	1.0E-05	98.72	95.22	94.00	1.7E-13	52.90

Table K.31 (continued): Pure hydrogen experimental data for Pt-Ru/C at 160°C, flow rate 150 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.68	0.073	2.88	2.86	1.1E-05	99.19	95.08	94.31	1.8E-13	54.77
0.70	0.075	2.97	2.88	1.1E-05	97.09	94.95	92.19	1.8E-13	55.19
0.72	0.078	3.05	2.92	1.1E-05	95.61	94.74	90.58	1.8E-13	55.89
0.74	0.080	3.14	2.92	1.1E-05	93.27	94.61	88.24	1.9E-13	56.04
0.76	0.083	3.22	3.02	1.1E-05	93.71	94.41	88.47	1.9E-13	57.83
0.78	0.085	3.30	3.12	1.2E-05	94.47	94.27	89.06	2.0E-13	59.83
0.80	0.087	3.39	3.30	1.3E-05	97.30	94.14	91.60	2.1E-13	63.21
0.82	0.090	3.47	3.32	1.3E-05	95.49	93.94	89.70	2.1E-13	63.58
0.84	0.092	3.56	3.36	1.3E-05	94.32	93.80	88.47	2.1E-13	64.33
0.86	0.209	3.64	3.52	1.3E-05	96.70	85.94	83.10	2.2E-13	67.52

Table K.32: Pure hydrogen experimental data for Pt-Ru/C at 160°C, flow rate 200 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0	0	0	0	0	0	0	0	0	0
0.02	0.006	0.08	0.05	1.8E-07	56.47	99.60	56.24	3.0E-15	0.92
0.04	0.006	0.17	0.11	4.2E-07	65.51	99.60	65.24	7.0E-15	2.13
0.06	0.006	0.25	0.20	7.5E-07	77.40	99.60	77.09	1.2E-14	3.77
0.08	0.008	0.34	0.27	1.0E-06	79.37	99.46	78.94	1.7E-14	5.16
0.10	0.011	0.42	0.35	1.3E-06	82.89	99.26	82.28	2.2E-14	6.73
0.12	0.013	0.51	0.42	1.6E-06	82.65	99.12	81.93	2.7E-14	8.05
0.14	0.015	0.59	0.50	1.9E-06	84.82	98.99	83.96	3.2E-14	9.64
0.16	0.017	0.68	0.56	2.1E-06	83.22	98.85	82.27	3.6E-14	10.81
0.18	0.020	0.76	0.63	2.4E-06	82.60	98.65	81.49	4.0E-14	12.07
0.20	0.022	0.85	0.73	2.8E-06	85.83	98.52	84.56	4.6E-14	13.94
0.22	0.025	0.93	0.80	3.0E-06	85.54	98.32	84.10	5.0E-14	15.28
0.24	0.027	1.02	0.89	3.4E-06	87.17	98.18	85.58	5.6E-14	16.99
0.26	0.029	1.10	0.98	3.7E-06	89.09	98.05	87.35	6.2E-14	18.81
0.28	0.031	1.19	1.05	4.0E-06	88.72	97.91	86.86	6.7E-14	20.17
0.30	0.033	1.27	1.16	4.4E-06	91.18	97.78	89.15	7.3E-14	22.21
0.32	0.036	1.36	1.26	4.8E-06	93.08	97.57	90.83	8.0E-14	24.19
0.34	0.038	1.44	1.36	5.2E-06	94.66	97.44	92.24	8.6E-14	26.13
0.36	0.041	1.53	1.46	5.5E-06	95.49	97.24	92.85	9.2E-14	27.91
0.38	0.043	1.61	1.52	5.8E-06	94.59	97.10	91.85	9.6E-14	29.19
0.40	0.045	1.69	1.60	6.1E-06	94.29	96.97	91.43	1.0E-13	30.62
0.42	0.047	1.78	1.65	6.3E-06	92.81	96.83	89.87	1.0E-13	31.65
0.44	0.050	1.86	1.80	6.8E-06	96.45	96.63	93.20	1.1E-13	34.46
0.46	0.052	1.95	1.82	6.9E-06	93.59	96.50	90.31	1.2E-13	34.96
0.48	0.054	2.03	1.93	7.3E-06	95.04	96.36	91.58	1.2E-13	37.04
0.50	0.057	2.12	2.03	7.7E-06	95.81	96.16	92.13	1.3E-13	38.90
0.52	0.059	2.20	2.09	7.9E-06	94.66	96.02	90.90	1.3E-13	39.97
0.54	0.061	2.29	2.19	8.3E-06	95.73	95.89	91.80	1.4E-13	41.97
0.56	0.064	2.37	2.28	8.7E-06	96.02	95.69	91.88	1.4E-13	43.66
0.58	0.066	2.46	2.36	9.0E-06	96.19	95.55	91.91	1.5E-13	45.30
0.60	0.068	2.54	2.43	9.2E-06	95.77	95.42	91.39	1.5E-13	46.66
0.62	0.070	2.63	2.49	9.5E-06	94.92	95.28	90.45	1.6E-13	47.79
0.64	0.073	2.71	2.63	1.0E-05	96.85	95.08	92.09	1.7E-13	50.33
0.66	0.075	2.80	2.77	1.1E-05	98.96	94.95	93.96	1.8E-13	53.03
0.68	0.078	2.88	2.84	1.1E-05	98.45	94.74	93.28	1.8E-13	54.36
0.70	0.080	2.97	2.92	1.1E-05	98.34	94.61	93.04	1.8E-13	55.89
0.72	0.082	3.05	2.92	1.1E-05	95.86	94.47	90.56	1.9E-13	56.04
0.74	0.085	3.14	3.02	1.1E-05	96.24	94.27	90.73	1.9E-13	57.83

Table K.32 (continued): Pure hydrogen experimental data for Pt-Ru/C at 160°C, flow rate 200 nmL/min

CD ^a	Voltage ^b	Theoretical Flux ^c	Calculated flux ^{c,d}		CE ^e	VE ^e	PE ^e	P ^f	Barrer
0.76	0.087	3.22	3.12	1.2E-05	96.96	94.14	91.27	2.0E-13	59.83
0.78	0.089	3.30	3.25	1.2E-05	98.37	94.00	92.47	2.1E-13	62.30
0.80	0.090	3.39	3.32	1.3E-05	97.87	93.94	91.94	2.1E-13	63.58
0.82	0.092	3.47	3.34	1.3E-05	96.05	93.80	90.09	2.1E-13	63.95
0.84	0.094	3.56	3.52	1.3E-05	99.00	93.67	92.73	2.2E-13	67.52
0.86	0.096	3.64	3.57	1.4E-05	97.92	93.53	91.58	2.3E-13	68.37
0.88	0.099	3.73	3.70	1.4E-05	99.12	93.33	92.51	2.3E-13	70.82
0.90	0.101	3.81	3.78	1.4E-05	99.18	93.19	92.43	2.4E-13	72.48
0.92	0.104	3.90	3.86	1.5E-05	99.00	92.99	92.06	2.4E-13	73.96
0.94	0.106	3.98	3.98	1.5E-05	99.96	92.86	92.82	2.5E-13	76.29
0.96	0.108	4.07	4.07	1.5E-05	99.98	92.72	92.70	2.6E-13	77.93
0.98	0.110	4.15	4.14	1.6E-05	99.73	92.59	92.33	2.6E-13	79.35
1.00	0.113	4.24	4.20	1.6E-05	99.18	92.39	91.63	2.7E-13	80.53
1.02	0.012	4.32	4.23	1.6E-05	97.96	99.23	97.20	2.7E-13	81.13
1.04	0.118	4.41	4.30	1.6E-05	97.53	92.05	89.78	2.7E-13	82.36
1.06	0.120	4.49	4.36	1.7E-05	97.16	91.91	89.31	2.8E-13	83.63
1.08	0.122	4.58	4.45	1.7E-05	97.23	91.78	89.24	2.8E-13	85.27
1.10	0.124	4.66	4.63	1.8E-05	99.36	91.64	91.06	2.9E-13	88.75
1.12	0.127	4.75	4.67	1.8E-05	98.39	91.44	89.97	3.0E-13	89.48
1.14	0.130	4.83	4.71	1.8E-05	97.47	91.24	88.93	3.0E-13	90.22
1.16	0.270	4.91	4.83	1.8E-05	98.23	81.83	80.39	3.1E-13	92.52

Appendix L. MINI HAZOP

A risk assessment on the possible risks that could be encountered while working on the test set-up is now presented (**Table L.1**). In the section entitled 'Chemicals', all the risks are described after taking the material safety data sheets (MSDSs) of the chemicals into consideration.

Table L.1: Risk assessment table

Electrical			
Description	Yes/No	Possible Risk / Issue	Suggested Safety Procedure / installation
Open connections	Yes	Electrocution	The voltage and current are manually controlled making use of LabVIEW. Ensure that the power supply is switched off when no experiments are being conducted and do not touch the cell or other equipment when the experiments are running.
Special/Custom power supply	Yes	Shortage, equipment damage	Shutdown procedure should be initiated.
UPS	Yes	Data will be lost when power interruptions occur	-
High-voltage components	No	-	-
Additional electrical installations	Yes	Faulty data readings (e.g. thermocouple readings)	Check manually, on a regular basis, that the readings are in fact correct. As part of the starting procedure, ensure that all readings are correct before commencing with actual experiments.

Table L.1 (continued): Risk assessment table

Pressure			
Description	Yes/No	Possible Risk / Issue	Suggested Safety Procedure / installation
Gas installations required	Yes	Leakage	Ensure that all fittings to the gas cylinder are tight and sealed before starting an experiment. Check that all gas cylinders are closed when experiments are done.
Special cylinders required	Yes	Gas cylinder could fall or leakage could occur	Ensure that special care is taken when working with all gas cylinders. Ensure that all fittings to the gas cylinder are tight, and sealed, before starting an experiment.
Flow meters	Yes	Faulty equipment	Check beforehand that equipment is in good working condition. Check equipment regularly for any irregularities.
Regulators	Yes	Faulty equipment	Check beforehand that equipment is in good working condition. Check equipment regularly for any irregularities
Pressure hoses and piping	Yes	Leakage, at extreme conditions a small scale explosion	Check piping for any possible leakages. Ensure that all fittings are tight before starting experiments
High operating pressures (above 2 bar)	Yes	At extreme conditions, the gas cylinder could explode or leak	Ensure that special care is taken when working with the gas cylinder.
Thermal			
Description	Yes/No	Possible Risk / Issue	Suggested Safety Procedure / installation
Specific heating / cooling installations	Yes	Burn	Do not touch the cell at any time during the experiments. Allow the cell to cool off and check the thermo-couple readings before making any adjustments to the cell (e.g. changing the membrane).
Thermal requirements	No	-	-

Table L.1 (continued): Risk assessment table

Material Compatibility			
Description	Yes/No	Possible Risk / Issue	Suggested Safety Procedure / installation
Corrosion specific materials	No	-	-
Special material installations	No	-	-
Chemicals			
Description	Yes/No	Possible Risk / Issue	Suggested Safety Procedure / installation
Toxic / Hazardous gasses	Yes	Inhalation	Ensure that the ventilation system is working properly. Consider installing a sensor with an alarm that would signal if any leakage occurs. Gas cylinders should be stored outdoors.
Special installations	Yes	Leakage	Ensure that all fittings are tight, and sealed, before starting with experiments. Test the system with a non-toxic gas to ensure that the system do not pose any hazards. Consider installing a sensor with an alarm that would signal if any leakage does occur.
Corrosive chemicals	Yes	Irritating or corrosive to exposed tissue	If there is the possibility of exposure to eyes (particularly when the amounts could be large), an eye rinsing area must be installed.
Flammable Gas	Yes	Explosion	Ensure that there are no open flames near the gas cylinder. Ensure that all fittings to the gas cylinder are tight, and sealed, before starting the experiments. Ensure that the cylinder is in a fixed position.

Additional Comments:

CO	2% CO in N₂ will be diluted with H₂ before experimentation commences, hence the CO value will be greatly reduced. The ceiling limit for CO is 35 ppm and therefore an alarm should be installed to signal when this limit is reached. The source of CO will then immediately be shut off. Another option, applicable to extreme conditions, is to make use of an approved mask. There is a door that leads to the outside of the building and it should be kept open when operating with CO, to ensure that the area is well ventilated, thus minimising the amount of CO that is inhaled. The retentate stream should be vented outside of the building. Before commencing with any experiments, the gas bottle, regulator, and systems should be checked for possible leakages.
N₂	N₂ alone poses no environmental hazard, therefore if a leakage does occur outside of the building there will be no harmful environmental effects. However, N₂ does pose a concerns for human health in a confined space. Inhalation of large concentrations of N₂, without dilution with air, can be very dangerous. A N₂ sensor should, therefore, be installed in case the N₂ levels increase to such an extent that it becomes hazardous, due to leakage.
NH₃	Flammable. In the event of a fire, suitable extinguishing equipment should be used. Appropriate PPE clothing should be worn when carrying out experiments (i.e. a coat and protective glasses). An alarm should be installed in the laboratory to alert to any leakages that may occur. A vent is installed so that the ammonia can be vented, ensuring that ammonia does not build up in a confined space. If inhalation of a large amount of ammonia does perhaps occur, workers should move out of/away from the ammonia-rich area, into an area where they can inhale pure air or oxygen.
CH₄	Flammable. Keep away from heat, sparks, open flames, etc. If an open flame does occur, it should be extinguished immediately.
CO₂	The only potential hazard associated with CO₂ at the concentrations that will be used is CO₂ build-up in a confined space, where inhalation for a prolonged period could result in symptoms such as headaches.
H₂	Highly flammable. H₂ sensors are installed to indicate when a leakage does occur. If a fire does occur it should be extinguished immediately, with a fire extinguisher.

Appendix M. GAS QUALITY SPECIFICATIONS

The gas quality specifications of the different gas mixtures used in this study are specified in **Table M.1**.

Table M.1: Gas quality specifications of the gas mixtures used for experimental evaluation

Impurity	Concentration (vol.)	Specified quality
CH ₄	10%	10.3% CH ₄ , balance hydrogen
	50%	50.2% CH ₄ , balance hydrogen
	80%	80% CH ₄ , balance hydrogen
CO ₂	10%	9.5% CO ₂ , balance hydrogen
	50%	49.9% CO ₂ , balance hydrogen
NH ₃	1 500 ppm	1 569 ppm NH ₃ , balance hydrogen
	3 000 ppm	3 086 ppm NH ₃ , Balance hydrogen
CO	2%	2.1% CO, balance hydrogen