

Developing quality assurance techniques for measuring impurities in fuel-grade hydrogen

Marc Plunkett

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Declaration of Originality

I hereby declare that the work reported in this thesis was composed and originated entirely by me. Information derived from published and unpublished results of others has been acknowledged in the text and in the relevant references included within the thesis.

Marc Plunkett

A handwritten signature in black ink, appearing to read 'M. Plunkett', followed by a long horizontal line extending to the right.

Imperial College London

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Executive summary

Acknowledgements

List of Publications and Presentations

Publications

1. **M. Plunkett**, K.Li, A. Murugan; Review of membrane technologies for hydrogen impurity enrichment; International Journal of Hydrogen Energy, 163 (2016), pp. F3119-F3124, 10.1149/2.0141611jes
2. **M. Plunkett**, K.Li, A. Murugan; Review of membrane technologies for hydrogen impurity enrichment; International Journal of Hydrogen Energy, 163 (2016), pp. F3119-F3124, 10.1149/2.0141611jes
3. **M. Plunkett**, K.Li, A. Murugan; Review of membrane technologies for hydrogen impurity enrichment; International Journal of Hydrogen Energy, 163 (2016), pp. F3119-F3124, 10.1149/2.0141611jes

Oral Presentations

1. **M. Plunkett**, A. Murugan, K. Li; A hydrogen impurity enrichment device using Pd-Alloy membranes to support the hydrogen economy. Presented at International Conference for Membrane and Electromembrane Processes 2018, 13th – 16th May 2018, Prague, Czech Republic.
2. **M. Plunkett**, A. Murugan, K. Li; A hydrogen impurity enrichment device using Pd-Alloy membranes to support the hydrogen economy. Presented at 15th International Conference on Inorganic Membranes, 18th – 22nd June 2018, Dresden, Germany.
3. **M. Plunkett**; The use of hydrogen selective materials for quality assurance of fuel grade hydrogen to ISO 14687-2 . Presented at 2nd bi-annual Gas and Particle Metrology symposium, 14th August, 2018, Teddington, United Kingdom

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Chapter 1

Introduction

1.1 Problem statement

Due to the damaging environmental effects of using fossil fuels in the transport sector, national and international targets have been set in order to reduce global CO₂ emissions. In the UK for example, there is a plan to completely ban the sales of new conventional petroleum vehicles by as early as 2040. [1] One proposed solution is further adoption of fuel cells and other energy generation methods which utilize hydrogen as a carbon free energy source.

Despite the fact that the technology for hydrogen powered fuel cells, in particular proton exchange membrane fuel cells, has existed since the early 1960's their application has been limited to providing power for space missions and other niche applications. It wasn't until the late 90's where developments in lowering platinum catalyst loading and the production of thin film electrodes drove the cost of fuel cells down to a level where they were a realistic option for transportation. As of 2017, a number of auto mobile manufacturers including Toyota,[2] Hyundai, [3] Honda [4] and Daimler [5] now offer hydrogen vehicles commercially and it is becoming increasingly possible to retrofit a petroleum vehicle to run off hydrogen.[6] Many countries in the EU and globally have ambitious hydrogen infrastructure plans over the next 10 years in an effort to become less reliant on importing fossil fuels, increase their energy security, and transition to a carbon free energy system.

The development of the hydrogen economy is still in its infancy in Europe, but several countries are aiming to employ sizable hydrogen fuelling infrastructures over the next few decades. National reports state that Europe's position in 2030 will be: UK - 1,100 hydrogen refuelling stations and 1.6 million fuel cell vehicles [7] France – 600 hydrogen refuelling stations and

Table 1.1: Concentration limits for ISO-14687 impurities

Characteristics	Regulation
Minimum mole fraction of hydrogen	99.97%
Total non-hydrogen gases	300 $\mu\text{mol mol}^{-1}$
Maximum concentration of individual components	
Total Hydrocarbons (Methane basis)	5 $\mu\text{mol mol}^{-1}$
Water	2 $\mu\text{mol mol}^{-1}$
Oxygen	5 $\mu\text{mol mol}^{-1}$
Helium	300 $\mu\text{mol mol}^{-1}$
Carbon dioxide	2 $\mu\text{mol mol}^{-1}$
Carbon monoxide	0.2 $\mu\text{mol mol}^{-1}$
Total sulphur compounds (H_2S basis)	0.004 $\mu\text{mol mol}^{-1}$
Formaldehyde	0.01 $\mu\text{mol mol}^{-1}$
Formic acid	0.2 $\mu\text{mol mol}^{-1}$
Ammonia	0.1 $\mu\text{mol mol}^{-1}$
Total halogenated compounds	0.05 $\mu\text{mol mol}^{-1}$
Maximum particulate concentration	1 mg/kg

0.8 million fuel cell vehicles [8], Germany – 1,180 hydrogen refuelling stations [9] and 1.8 million fuel cell vehicles and the Netherlands – 200 hydrogen refuelling stations and 0.2 million fuel cell vehicles. [9] The fuel cell system in a hydrogen vehicle can easily degrade if even parts-per-billion to parts-per-million level of some impurities are present in the hydrogen. Therefore, it is imperative that hydrogen purity, and techniques for verifying the purity, are adequate to ensure customers vehicles are not inadvertently damaged by fluctuations in hydrogen composition.

International standards dictate that it is mandatory for all hydrogen suppliers to prove that their product is pure enough to prevent degradation of fuel cell components. The international standard ISO 14687-2:2012 [10] shown in Table 1.1 specifies the maximum impurity levels of 13 impurities that are permissible in fuel cell hydrogen. ISO 14687-2:2012 include some challenging hydrogen purity specifications mainly due to the low limits of detection of standard techniques used to measure the compounds included in the standard.

Existing hydrogen purity laboratories are unable to perform traceable analysis to ISO 14687 specifications because appropriate methods and standards have not been developed. The consequence of this is that hydrogen suppliers cannot provide evidence that their fuel meets the International

Standard and therefore are not permitted to supply hydrogen. Of the 13 gaseous impurities listed in ISO 14687-2, there is no single method for measuring all impurities. Laboratories must therefore use several instruments to perform such an analysis. In 2015 Murugan et al published a review of methods for analysing the purity of fuel grade hydrogen [11]. They concluded that in order for a single laboratory to provide full hydrogen analysis to ISO 14687-2 specifications it would need to comprise a variety of instruments including GCs, FTIR and CRDS. The capital cost of purchasing the gas analysers to perform analysis on the measurable impurities in a hydrogen sample can amount to >€500,000 [11] and hence performing analysis would be out of reach for many of the smaller laboratories.

While the impurities listed in ISO 14687-2 are specified at extremely low amount fractions, many can be analysed at higher amount fractions through the use of cheap and routine gas analysers such as GC-MS. A potential solution to this would be to increase the concentration above the limit of detection of one of these cheaper analysers. These techniques are referred to as enrichment or pre-concentration. The most commonly used technique for pre-concentration of hydrogen fuel samples is referred to as ‘Hydrogen Impurity Enrichment’. This method involves passing the sample through a palladium or palladium alloy membrane which is heated to 400°C. Palladium as a membrane material only allows the passage of hydrogen, and as hydrogen leaves the system, the impurities remain, increasing in time as more hydrogen permeates through the membrane. This increase in concentration is referred to as the enrichment factor and. Once the enrichment is complete the sample can then be analysed at these higher concentrations, and using the enrichment factor, the original composition of the sample can be found.

In order for these devices to provide accurate results the behaviour of the membrane material, and its interaction with any impurities present in the hydrogen same, must be properly understood.

1.2 Research Background

1.2.1 Hydrogen Production

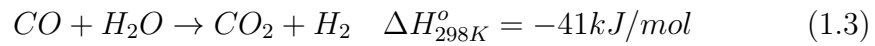
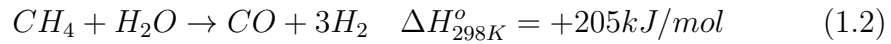
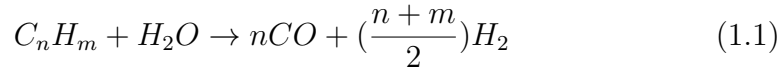
Hydrogen production refers to a range of industrial processes for generating hydrogen. Since there are no natural reserves of hydrogen all hydrogen must be obtained through one of these methods. The most important factor for determining the feasibility of a hydrogen production process is the primary source of energy that is used. Currently the options for this are nuclear energy in the form of heat, renewable energy in the form of heat, electricity,

or light, or fossil fuels. Currently the primary sources of hydrogen are from steam reforming of methane and other hydrocarbons which in total accounts for 96% of global hydrogen production, with electrolysis of water accounting for the remaining 4%.

Hydrogen from fossil fuels and hydrocarbons

Fossil fuels are the most dominant source of hydrogen production and there are a number of processes which utilize fossil fuels to produce hydrogen. The most popular and therefore the ones which will be discussed are steam methane reforming, hydrocarbon decomposition

Steam Methane reforming is the conventional and most economical method for producing hydrogen, and it has been predicated by the IEA that this trend will continue despite the emergence of other hydrogen production methods. Steam methane reforming occurs through a two-step chemical process. If another hydrocarbon other than methane is being used it must first be pre-reformed into methane as shown in equation 2.1

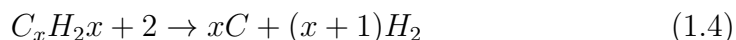


Equation 2.2 takes place in a reactor operating at 700-850°C, at pressures of 3-25 bar, and in the presence of a nickel based catalyst. The result of this step is a mixture of CO and H₂, commonly referred to as syngas. This syngas is used as a feedstock for the reaction shown in equation 2.3 known as water gas shift in order to produce greater hydrogen yields. This step is carried out in a two-step reaction. An initial high temperature stage at 350°C which converts majority of the syngas to CO₂ and hydrogen, and a final low-temperature step which operates at 250°C which utilizes a catalyst with higher activity to minimise the remaining CO₂. The final product will be a mixture of CO₂ and H₂.

A number of separation steps are utilised in order to prevent impurities from contaminating the resulting gas mixture. The traditional separation step is pressure swing adsorption (PSA) which takes advantage of adsorption of gaseous molecules onto a molecular sieve at high pressures. Hydrogen purities of 99.9% are achievable using this method however the cost is high and typically contributes to around 20-30% of the total production cost. The other main separation step is desulphurization which uses a combination of

CoMo and ZnO catalysts in series at 450-550°C to remove sulphur. This step is essential to ensure sulphur is not present in the gas exit stream and also to ensure catalyst poisoning does not occur at any point in the process.

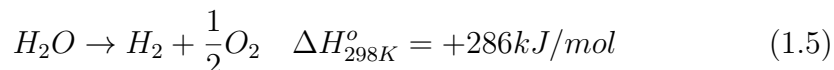
Hydrocarbon decomposition is a process by which hydrocarbon molecules are converted into solid carbon and hydrogen. This reaction is typically operated either thermally or by creating a plasma. Both methods require a metallic catalyst such as nickel or iron. The reaction is shown in equation 1.4



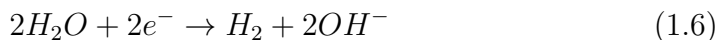
An advantage of this process is that the only feedstock is the hydrocarbon, so presuming that the feedstock is sufficiently pure this method of hydrogen production should remove the needs for further downstream processing. The main disadvantage of this method is the since solid carbon is the main by-product the catalyst will easily be deactivated and will require regular maintenance.

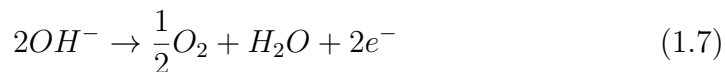
Hydrogen from water

Thermal decomposition of water is the process of splitting water into hydrogen and oxygen at temperatures of 2000°C, this can be lowered under the presence of a nickel or iron based catalyst. Due to the high energy demand for this production method water splitting is not a feasible method of commercial hydrogen production.



Electrolysis is the second most popular method for producing pure hydrogen after SMR. This method uses an electric current to split water into hydrogen and oxygen. The main competitive advantage of electrolysis is that they are modular and highly scalable, allowing hydrogen to be produced in a distributed manner. The main input to the process is electricity and if this electricity is produced using renewable sources then the process can be considered carbon neutral. This is further incentivised by the increasing price of natural gas and the decreasing price of electricity, which some predict will result in electrolysis becoming more economically feasible than SMR in the future.





1.2.2 Hydrogen impurities in the supply chain

Effect on operation of a fuel cell

Water generally does not affect the function of a fuel cell, however; it provides a transport mechanism for water-soluble contaminants such as K^+ and Na^+ to pass through the electrolyte and have a negative long-term effect on the conductivity of the cathode side of the membrane. In addition, water may increase the risk of ice formation within vehicle fuel storage and hydrogen dispensing systems under certain conditions.

Water can be present from both SMR and electrolysis due to it being a main by-product of SMR reactions, and the main reactant in electrolysis. The PSA process used in SMR is considered an appropriate barrier to water in the end product due to the high selectivity to removing water of the molecular sieves used. When a PSA system is designed to produce an output of CO below 0.2 $\mu\text{mol/mol}$, the concentration of water will be less than 0.1 $\mu\text{mol/mol}$. This makes it unlikely for H_2O to be present in hydrogen produced using this method.

There are three potential pathways for water to contaminate hydrogen through electrolysis. These are:

- Electro-osmosis through the proton exchange membrane
- Hydrogen water saturated at 60°C
- Drier malfunction

The drier should remove most of the water from the produced hydrogen. In the event of drier failure most systems are fit with a dew point analyser that will trip, shutting off production until the issue can be fixed.

Total hydrocarbon content Different hydrocarbons have different effects on fuel cell performance. Generally aromatic hydrocarbons adsorb more strongly on the catalyst surface than other hydrocarbons inhibiting access to hydrogen. Methane (CH_4) is considered an inert constituent since its effect on fuel cell performance is to dilute the hydrogen fuel stream.

The presence of hydrocarbons are most likely to result from the SMR process. Hydrocarbons are not expected to be present at all in electrolysis. Similar to water contamination through SMR, the most likely reason for hydrocarbon contamination is due to malfunction of the PSA system used

to purify the product hydrogen. A PSA system designed to deliver hydrogen with a CO concentration $<0.2 \mu\text{mol/mol}$ should be sufficient to reduce the amount fraction of hydrocarbons to below the $5 \mu\text{mol/mol}$ required by ISO 14687. Therefore the probability of hydrocarbons being present is rare.

Oxygen Oxygen (O_2) in low concentrations does not adversely affect the function of the fuel cell system; however, it may be a concern for some on-board vehicle storage systems, for example, by reaction with metal hydride storage materials. In SMR processes oxygen is not used as a raw material, nor is it stable during the process conditions, readily reacting with hydrogen to produce water. In addition to this the oxygen content of the feedstock to the PSA separation stage must be below a certain level for safety reasons. Therefore oxygen contamination from SMR is unlikely. Oxygen is a main by-product of electrolysis, although is generated at the anode side of the electrolysis stack. Likely methods of contamination are through cross over through the PEM membrane. Due to the danger of high oxygen levels in hydrogen streams most electrolysis systems are fit with an oxygen sensor that trips the system if the concentration of oxygen in the hydrogen stream surpasses $5 \mu\text{mol/mol}$.

Helium, nitrogen and argon Inert constituents, such as helium (He), nitrogen (N_2) and argon (Ar) do not adversely affect the function of fuel cell components or a fuel cell system. However, they dilute the hydrogen gas. N_2 and Ar especially can affect system operation and efficiency and can also affect the accuracy of mass metering instruments for hydrogen dispensing. Helium is not present as a feed material in any of the discussed processes, however there is also no barrier to Helium in the exit stream and therefore any helium that enters a SMR or electrolysis process will not be removed. Despite this it is unlikely that helium will be present in a hydrocarbon feedstock, or water. Argon is similar to helium, however it is more likely for Argon to be present in natural gas. Unlike helium, the PSA step in SMR can act as a barrier for Argon, however this will depend on the specific molecular sieve used in the system. Nitrogen is the most likely inert impurity to be present in fuel cell hydrogen, this is due to the abundance of nitrogen in the air which the system could be exposed to, and the frequency at which nitrogen is used as a functional gas in processes for purging chambers, actuating valves etc.

Carbon dioxide does not typically affect the function of fuel cells. However, CO_2 may adversely effect on board hydrogen storage systems using metal hydride alloys. With CO_2 , at levels very much higher than the specifi-

cation, a reverse water gas shift reaction can occur under certain conditions in fuel cell systems to create carbon monoxide. Like most other impurities CO_2 is likely to be removed from the SMR process at the PSA step, with most commonly used molecular sieves being able to remove carbon dioxide during normal operation. CO_2 can be present in the water used for electrolysis although there are several interlocks to prevent it reaching the exit stream. Most electrolysis systems have a CO_2 filter on the inlet and a reverse osmosis purification unit to ensure the purity of the inlet water. An anodic separation tank which features an ion exchange resin in a closed water loop also acts as an additional barrier, and finally CO_2 has a low crossover potential through the PEM membrane and therefore is unlikely to cross into the cathode side of the system.

Carbon monoxide Carbon monoxide (CO) is a severe catalyst poison that adversely affects fuel cell performance and needs to be kept at very low levels in hydrogen fuel. Although its effect can be reversed through mitigating strategies, such as material selection of membrane electrode assembly (MEA), system design and operation, the life time effects of CO on performance is a strong concern. Lower catalyst loadings are particularly susceptible to catalyst poisoning contaminants. Carbon monoxide can be present in gas produced from SMR through PSA malfunction, which is the main barrier to CO contamination. It is unlikely for CO to be present from electrolysis.

Total sulfur compounds Sulfur containing compounds are severe catalyst poisons that at even very low levels can cause irreversible degradation of fuel cell performance. The specific sulfur compounds that are addressed are in particular: hydrogen sulfide (H_2S), carbonyl sulfide (COS), carbon disulfide (CS_2), methyl mercaptan (CH_3SH). Lower catalyst loadings are particularly susceptible to catalyst poisoning contaminants. Sulphur contamination is most likely to come from hydrogen produced from hydrocarbon sources. Since the SMR process also uses catalysts that are susceptible to poisoning from sulphur compounds all plants are fit with a desulphurisation unit upstream from the main process. This is designed to reduce the concentration of sulphurous compounds to <50 nmol/mol. Should the desulphurisation unit fail the catalysts used in both reforming steps will be deactivated, preventing the process from operating and will likely result in shut down of the plant. PSA also acts as a final barrier, since H_2S will adsorb onto the molecular sieves more strongly than CO . The other potential source of sulphur contamination is the potential release from any gasket materials used in the process. This can be easily prevented by ensuring only materials that do not

contain sulphur are used. It is unlikely that sulphur contamination will arise from electrolysis.

Formaldehyde and formic acid Formaldehyde (HCHO) and formic acid (HCOOH) have a similar effect on fuel cell performance as CO and are thus considered as reversible contaminants. The effect of HCHO and HCOOH on fuel cell performance can be more severe than that of CO due to slower recovery kinetics and their specifications are lower than that for CO. Lower catalyst loadings are particularly susceptible to catalyst poisoning contaminants. Formaldehyde is a by-product from the reform steps in SMR and depending on the specific operating conditions of the process however PSA should act as a sufficient barrier to formaldehyde contaminating the product.

Ammonia Ammonia (NH₃) causes some irreversible fuel cell performance degradation by affecting the ion exchange capacity of the ionomer of the proton exchange membrane and/or electrode. Hydrogen could be contaminated with Ammonia either through SMR, ammonia can be a by-product of the reforming steps and should be removed by PSA. It can also be present in water used in electrolysis however the reverse osmosis step should be sufficient in removing all ammonia before it is used in the process

Total halogenated compounds Halogenated compounds cause irreversible performance degradation. Potential sources include chlor-alkali production processes, refrigerants used in processing, and cleaning agents.

Particulates A maximum particulate concentration is specified to ensure that filters are not clogged and/or particulates do not enter the fuel system and affect operation of valves and fuel cell stacks. A maximum particulate size diameter is not specified but should be addressed in fuelling station and/or component standards. Particulate sizes should be kept as small as possible. It is noted that a specific threshold for particulate size which causes degradation has not been made clear and it is influenced by the particulate in ambient air while sampling and refuelling process.

1.3 Research Objectives

This thesis will focus on developing hydrogen impurity enrichment as a low-cost technique for measuring the impurities in fuel grade hydrogen to ISO 14687-2 specification. This study will revolve around the membrane materials used to concentrate the impurities in hydrogen samples and will aim

to determine the best material, and conditions for the hydrogen impurity enrichment device. The thesis aims are as follows:

- Identify the best material for enriching impurities based on the degree of interaction and reactivity with the impurities shown in Table 1
- Convert the experimental set up in to a commercially viable prototype which could be used in analytical laboratories
- Finalise a protocol for national measurement institutions to follow when enriching a hydrogen sample.
- Perform full enrichment using these three conclusions on a real sample taken from a hydrogen refuelling station

In order to determine suitable enrichment material ‘Density Functional Theory (DFT) will be used to screen a number of materials for their suitability as an impurity enrichment membrane on their simulated interaction strength with ISO 14687 impurities. The best performing membrane materials simulated in Chapter 3 will then be synthesised in Chapter 4. The hydrogen permeability of each material under a number of ISO 14687-2 impurities will be measured to validate the simulation results and further narrow down the most suitable membrane composition. Following from this the best membrane will be used in Chapter 5 which will describe the design and commercialisation of the final hydrogen impurity enrichment device. The design of the enrichment device will include an uncertainty budget of the technique, automation of the device, and compliance to European standards. Finally the new device, featuring the most suitable membrane, redesigned process, and protocols for krypton spiking will be tested using a real sample taken from a hydrogen refuelling station.

1.4 Thesis structure and presentation

This thesis consists of 6 chapters, which includes the ‘Introduction’, ‘Literature Review’, experimental chapters and ‘Conclusion’. The thesis structure is visualised in figure 2.1. The experimental chapters address different aspects of development of hydrogen metrology techniques as described above.

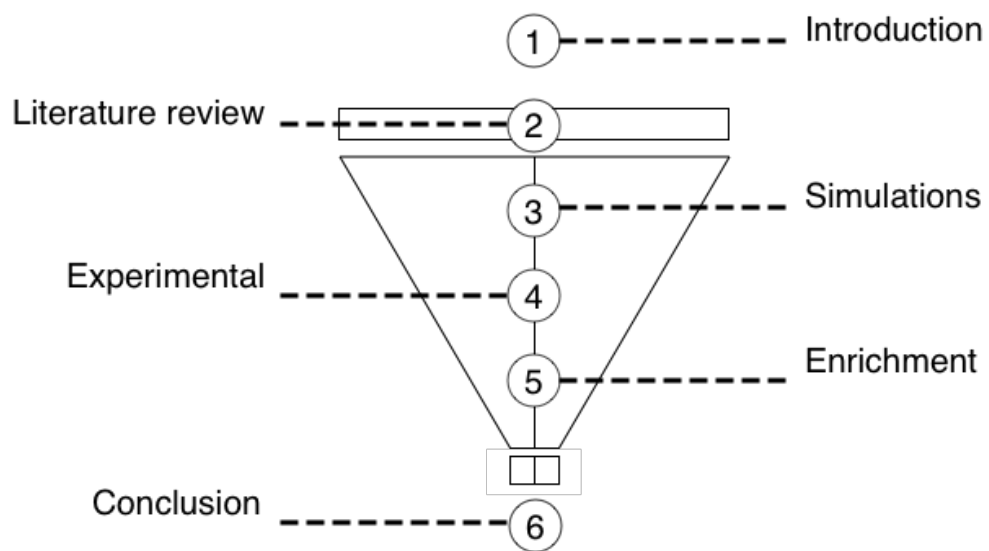


Figure 1.1: Schematic presentation of the thesis structure

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Chapter 2

Literature review

2.1 Hydrogen impurity enrichment

'Hydrogen impurity enrichment' is a term for any technique which involves increasing the concentration of impurities within a hydrogen sample by means of removing the hydrogen matrix gas. There are two previous reports of impurity enrichment being used as a technique for hydrogen impurity analysis. The first report by Papadis et al at Argonne National Laboratory used a Pd/Cu [1] coated Pd/Ag membrane for non-sulphur containing hydrogen samples and a Pd/Au coated Pd/Ag membrane for sulphur containing hydrogen samples to enrich impurities in a 50 bar sample. The analyte gas used contained N₂, CH₄ and CO₂ at 100 µmol/mol and an additional 2 µmol/mol of H₂S during sulphur tests sulphur. The enrichment was calculated by using measured values of temperature and pressure along with the non-ideal gas law, this was represented through a 'calculated enrichment factor' as shown in equations 2.1 and 2.2.

$$CEF_{NI} = \frac{\frac{P_{1,a}V_1}{Z_{1,a}RT_{1,a}} \frac{P_{2,a}V_2}{Z_{2,a}RT_{2,a}} - \frac{P_{1,b}V_1}{Z_{1,b}RT_{1,b}}}{\frac{P_{2,b}V_2}{Z_{2,b}RT_{2,b}}} \quad (2.1)$$

$$y_{i,a} = \frac{y_{i,b}}{CEF} \quad (2.2)$$

The set-up was able to reach enrichment factors of around 32 for non-sulphur tests and 15 for sulphur tests. The non-sulphur tests closely matched with the actual component concentrations, however in the second set of tests there was some loss of sulphur observed, most likely due to the formation of palladium sulphide on the surface of the membrane, or through wall catalysed reactions.

A similar experiment was performed by National Physical Laboratory with the aim of decreasing the uncertainty of using such a device. [2] The

non-ideal gas law method used in the previous paper [1] was compared to a novel tracer enrichment method developed by NPL. [2] The tracer enrichment method involves spiking the hydrogen sample with a known quantity of krypton prior to enrichment. The enrichment factor is then calculated using the change in concentration of the krypton as shown in equation 2.3.

$$CEF_{Tracer} = \frac{y_{kr_b}}{y_{kr_a}} = \frac{1}{y_{kr_a}} \frac{A_{kr_b}}{A_{kr_a}} y_{kr_{st}} \quad (2.3)$$

The set-up was similar to the one used by Papadimas et al [1] and was used to enrich a 50 bar 10L hydrogen sample containing 1.5-2 $\mu\text{mol/mol}$ of CO, Kr, CH₄ and N₂. Use of the tracer enrichment method reduced the associated uncertainty from 2.6% to 1%. Two tests were performed, with the second test resulting in membrane failure.

When operating the hydrogen impurity enrichment device it was found that both methods should be used to calculate the CEF.[2][3] While the tracer enrichment method has a lower uncertainty due to it being dependant on fewer variables, it is impossible to tell if a leak has occurred in the device due to the covariance phenomena. [2] Leaks in the enrichment device could occur due to thermal expansion of components due to heating to the required operating temperature or cracks forming in the membrane. The stability of membranes used in such a device will be discussed in the following section. During a leak it will be expected that the ratio of krypton, along with other impurities which are not naturally present in air, will remain constant, resulting in no change in the CEF. A leak will allow oxygen and nitrogen to enter the system and throw off the measurement of these two impurities. While the tracer enrichment method could still be used to calculate the amount fraction of other impurities, the non-ideal gas law method would have to be used to provide an accurate measurement for Oxygen and Nitrogen.

A device similar to the HIED is the Hydrogen Elimination Mass Spectrometer (HEMS) designed by Power + Energy USA. [4] The principle behind the HEMS is the same as the HIED, where a palladium membrane is used to selectively remove the hydrogen matrix gas and thus concentrate the impurities within the hydrogen sample. The output is directly fed into a mass spectrometer which allows in-situ measurements to be performed. The limit of detection specified by the manufacturer claims to be in the range of pmol/mol however there is no published information regarding the accuracy or uncertainty associated with the device. As of 2016 the device was discontinued by the manufacturer.

2.1.1 Criteria for a hydrogen impurity enrichment material

In order for a membrane to be suitable for hydrogen impurity enrichment material it must be able to increase the concentration of low-level impurities in a hydrogen sample. Although all past examples of hydrogen impurity enrichment have used dense membranes with an infinite selectivity towards hydrogen, it is theoretically possible to use a membrane which has a lower selectivity to perform enrichment. This would have the advantage of allowing membranes with faster flux to be used, greatly reducing the amount of time required for an enrichment run, while allowing cheaper materials to be used in place of the palladium membranes used in past studies. In order to perform this calculation, the following must be known:

- Selectivity of the membrane must be known to a high accuracy
- Total number of moles leaving the system
- Concentration of enriched impurities

Since the selectivity shows the ratio of substances passing through the membrane (i.e. H_2/N_2 selectivity of 2 represents 2 moles of hydrogen for every 1 mole of nitrogen passing through the membrane) if both quantities are known the number of moles of impurity leaving the system through permeation could be easily estimated.

$$n_{i_{exit}} = n_{exit_{total}} / \alpha^{H_2/i} \quad (2.4)$$

The concentration, and therefore the number of moles of impurity on the retentate side of the membrane could then be analysed using suitable instrumentation. These values could then be added together and divided by the enrichment factor in order to give the original number of moles that would be in the vessel.

$$y_i = \frac{(n_{i_{ret}} + n_{i_{exit}}) / n_{tot_{ret}}}{CEF} \quad (2.5)$$

In practice however this may not be feasible due to the low concentrations of impurities expected to be present in these hydrogen samples. In order for an enrichment calculation to work there must be an analysable concentration of impurity remaining in order to back calculate. Since the level of expected impurities in a hydrogen sample is so low, and the selectivity of many membranes also low, there is a high risk of either all impurities simply leaving the sample during the enrichment run, or only achieving a lower enrichment

factor. Take the example of enriching a sample containing $0.2 \mu\text{mol/mol}$ of CO by 100 in order to analyse its composition on a GC-MS. If the sample is a standard 10L cylinder containing 100 bar a H_2/CO selectivity of ~ 4950000 is required to simply prevent all of the CO leaving the enrichment device, which is effectively the same as the selectivity's seen in dense metal membranes. However, for the same sample containing $0.3 \mu\text{mol/mol}$ of Helium a H_2/He selectivity of 330 is the minimum required which is more feasible. However, both these values are the exact values required by the standard, in reality they would be much lower. The highest reported selectivity of a non-infinitely selective membrane was Liquid crystalline polyester which had a H_2/N_2 selectivity of 2632 [5] which indicates that this method may be suitable for enriching some of the higher concentration impurities in hydrogen samples, it is not a solution for lower concentration. It is also unlikely that the selectivity of a membrane material will stay constant throughout its lifespan. Any drift in selectivity would throw off the calculation and either require regular changing of the membrane, driving up cost, or regular calibration to recalculate the selectivity of the membrane at a given time, which would be time consuming. It is however likely that infinitely selective membranes are the only feasible enrichment material due to their ability to enrich every impurity in hydrogen, whereas non-infinitely selective membranes may be applied to analysis of individual impurities, it is unlikely such a scenario would occur in reality which makes them a non-ideal solution.

2.1.2 Other enrichment methods

Sorbent tubes

The use of traps and sorbent tubes to pre-concentrate impurities in gases is very common in gas analysis, but only two hydrogen purity analysis standards have incorporated this technique to facilitate purity analysis. A method for concentrating the impurities in a sample of hydrogen using a zeolite- packed chromatographic column has been described in a paper by Hille [6]. The method involves flowing the gas sample into the column using a pump and cooling the column to a temperature that allows the impurities to remain trapped whilst the matrix gas passes through. The sample is then transferred to GC-MS for analysis. The enrichment factor for this method is determined by the flowrate and amount of time that the gas is sampled into the column. The method was validated by analysing gas mixtures of hydrogen containing 8.7 mmol/mol of silane. By enriching the sample, the signal- to-noise for the same measurement was increased by a factor of 2000 indicating that levels in the range of 4 nmol/mol of silane would easily be measured using this method

whereas the usual limit of detection (without pre-concentration) would have been 1 $\mu\text{mol/mol}$

Cryo-focusing

A method for performing pre-concentration by cryo-focusing has been detailed in ASTM WK34574 where the device is used to concentrate the impurities in a sample of hydrogen before introducing the gas to a GC-MS [3] The pre-concentration method involves trapping the impurities onto a glass bead trap at -150°C . By increasing the temperature of the trap all of the impurities apart from water are transferred to a separate Tenax trap which is cooled to -170°C . Upon heating once again the enriched sample is introduced to the analyser. Very high enrichment factors can be achieved using this method by flowing a high volume of the sample gas through the pre-concentration device to allow capture of the impurities whilst the hydrogen is removed. No information was provided in the standard to indicate the accuracy or limitations of this method.

2.2 Review of hydrogen selective membranes

The term membrane is used to describe a semipermeable barrier which selectively allows certain species to pass through it, while preventing or inhibiting the passage of others. The driving force for gas separation through a membrane is the pressure and component concentration gradients across the chosen material. In the context of hydrogen separation, the trans-membrane pressure and hydrogen concentration gradient across the feed and permeate, combined with the unique properties of the chosen separation material, will allow hydrogen to pass through the membrane, while preventing or inhibiting the transport of impurities which the membrane is not selective or less selective towards. A large number of materials have been studied for hydrogen separation. For the purpose of this review they will be split into four broad categories based on their material type and separation mechanism which is related to their pore structure (dense or porous); these categories are shown in Table 2 and visualized in Figure 2.1.

The material, its structure with regards to pore size and pore size distribution, and surface chemistry, all contribute to the separation mechanism for removing hydrogen from its constituent gas mixture. The six main membrane separation mechanisms are visualised in Figure 2.1, with (i) – (iv) showing the four separation mechanisms for gases in porous media, and (V)- (Vi) showing gas separation through dense media. For porous materials typically a combi-

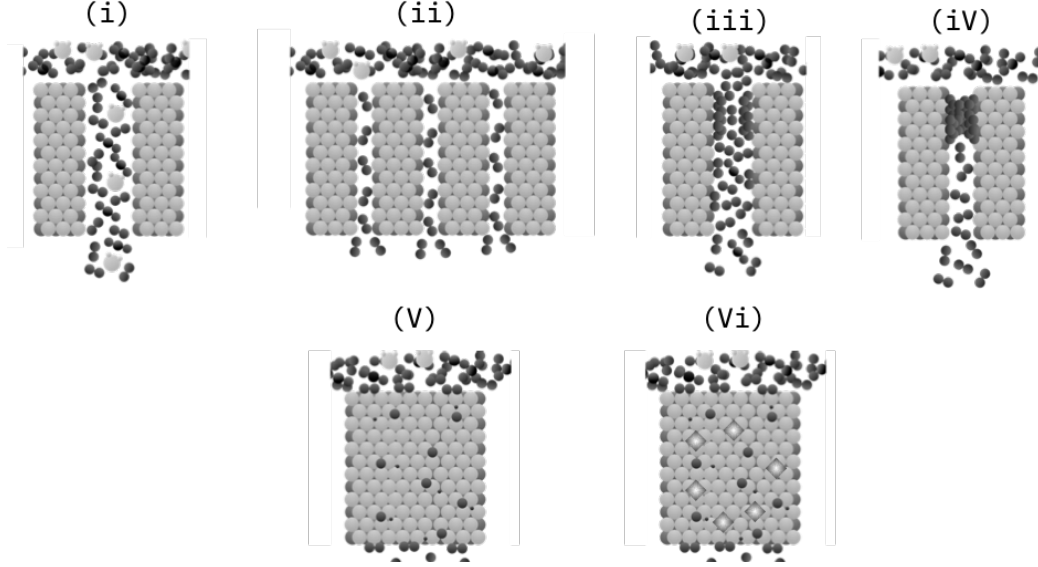


Figure 2.1: Illustration of the five membrane separation mechanisms (i) Poiseuille Flow/Knudsen diffusion, (ii) Molecular Sieving, (iii) Surface diffusion (iv) Capillary condensation (v) Solution diffusion (vi) Facilitated transport

nation of these mechanisms dictates the overall separation performance due to imperfections in the membranes structure. All dense membranes should be dictated by the solution diffusion mechanism and the presence of any other mechanisms are evidence of imperfections in the membrane.

For most porous media, the separation mechanism is dominated by Poiseuille flow or Knudsen Diffusion. The precise separation mechanism can be determined by calculating the ratio between the mean free path of the gas molecules (λ) and the pore radius (r) as shown in Equation 2.6 where η is the viscosity of the gas, P is the pressure, T is the temperature, M_w is the molecular weight of the gas, and R is the universal gas constant.

$$\frac{r}{\lambda} = \frac{2P}{3\eta} \sqrt{\left(\frac{2M_w}{\pi RT}\right)} \quad (2.6)$$

This ratio determines the contribution of Knudsen and Poiseuille flow. If $r/\lambda > 1$ it would indicate that the main gas transport rate limiting step is due to molecule-molecule collisions indicating that Poiseuille flow is the dominant transport mechanism. Likewise if $r/\lambda < 1$ it indicates that molecule-wall collisions govern the rate limiting step showing that Knudsen diffusion is the dominant mechanism. If the transport is purely Knudsen diffusion

the H_2/CO_2 selectivity of the membrane will be equal to around 4.7. Since this value is relatively low, it has pushed researchers into fabricating membranes with smaller pore structures, and to modify their membranes to take advantage of specific surface interactions. Both of these developments allow researchers to surpass the selectivity achievable with purely Knudsen diffusion.

Molecular sieve materials can be classed as macroporous ($>50\text{nm}$), mesoporous ($2\text{-}50\text{nm}$) and microporous ($<2\text{nm}$) with microporous materials being the most relevant for hydrogen separation processes. These membranes are fabricated in such a way that the passageways are small enough that the entrance of molecules with large kinetic diameters is not possible. This results in higher permeation of smaller components in a gas mixture such as H_2 or He while slowing, or completely preventing the passage of bulkier molecules. This mechanism, while effective for some gas mixtures, may not be feasible when looking to perform separation on similar sized gas pairs; selectivity is often hindered by competitive adsorption between the species due to the surface chemistry of the material. Fabrication of these membranes can also be difficult and manufacturing large scale membranes with a tight enough pore size distribution to ensure molecular sieving still proves to be a difficult task. Common microporous materials which are able to be fabricated into molecular sieving membranes are zeolites, metal organic frameworks, activated carbon, and amorphous silica.

Surface diffusion and capillary condensation are similar in that the surface chemistry of the pores in the membrane has a large effect on the separation efficiency. Surface diffusion occurs when the walls of the pore either intrinsically, or following modification, provides adsorption sites for the desired gas molecule. The gas molecule will adsorb onto the walls resulting in faster diffusion through the pore structure than other gases in the mixture. Similarly, capillary condensation typically follows on from surface diffusion and involves the gas species condensing within the pore of the membrane, either due to stronger molecule-wall interactions, or a smaller pore radius. The condensation of the molecule results in further selectivity improvements towards this component by providing an added transport barrier to other gas species.

Gas transport in dense media is typically harder to categorise due to the unique material chemistry present in each material, however all dense membranes perform separation through some variation of the solution diffusion model. Typically, the following steps are always present in some form:

1. Adsorption of gas species onto the surface of the membrane
2. Diffusion of gas species through the bulk of the membrane

3. Desorption and diffusion of the gas species in the downstream.

More details will be provided on the precise features of solution diffusion in each material in the following sections. Facilitated transport is a sub section of solution diffusion and occurs in dense membranes which have a selected chemical species added into the bulk of the membrane. These materials are chosen based on the presence of a particular interaction with components of a gas species. These interactions are typically reversible reactions between the added species and the gas intended for separation and is intended to enhance the diffusion of the selected gas, this additive could either be fixed species (solid) or mobile (liquid).

The most commonly reported metrics for membrane performance is the flux or permeability coefficient and selectivity. The flux (J) of a membrane is a measure of the amount of gas the membrane is allowing to pass per unit time per unit surface area and is typically used as a measure for how effective the fabricated membrane performs. The permeability coefficient (P) can be derived from the flux and is a quantitative expression which gives a specific measure of the separation properties of a material independent of operational and manufacturing constraints such as operating pressure and membrane thickness. While flux and permeability are similar and tied to each other they are both useful in their own way. The permeability coefficient is typically tied to the material and is useful for comparing different materials to each other, while the flux offers a measure on how effective the material is when fabricated into a membrane.

The selectivity ($\alpha_{i/j}$) represents the separating ability of the membrane for a specific gas species (i) with respect to another gas species (j). This is common notation for porous membranes and membranes which are not completely selective towards one component. For membranes which are only selective towards one component such as dense metal and dense ceramic, the selectivity is not reported since any presence of another component in the exit stream is generally an indication of a manufacturing defect.

While these values are reported for all membranes in order to allow for a direct comparison of performance, this is where the similarities end. The fundamental separation mechanism, manufacturing techniques, and unique material chemistry are often different for each material. In addition to this there are other important metrics for the usefulness of a membrane such as mechanical stability, lifespan, and chemical resistance which are more difficult to quantify.

2.2.1 Types of hydrogen separation membrane

Table 2.1: Types of hydrogen separation membrane

Material	Separation mechanism	Mechanical stability	Chemical Stability	Operating temperature	Selectivity
Polymer (Dense)	Solution diffusion, Facilitated transport	Susceptible to Compaction 6 and Swelling 7	A	A	A
Polymer (Porous)	Knudsen diffusion, Molecular sieving, Surface diffusion, Capillary condensation, Poiseuille flow	Susceptible to Compaction 6 and Swelling 7	Low chemical stability, Degrades under H ₂ S, HCl, CO ₂ , SO _x 8	<100°C	2.5 - 960 (H ₂ /N ₂ selectivity) 10
Nano-porous	Knudsen diffusion, Poiseuille flow, Capillary condensation, Surface diffusion, Molecular sieving	Brittle	Good 11	Ambient -500°C	2.4 - 1000 (H ₂ /N ₂ selectivity) 13
Dense Metal	Solution Diffusion	Phase transition 14 Dependant on support 14 Surface segregation 14	Negative interaction with CO, CH ₄ , and H ₂ O. Reacts with H ₂ S and SO _x 14	300-600 °C 15	-
Dense Ceramic	Solution Diffusion	Brittle Difficult to seal due to high operating temperature	Degrades under CO ₂ 16	500-1000 °C 16	-

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Chapter 3

Experimental methods

3.1 Simulations

Density functional theory calculations were performed using the Quantum Espresso (QE) ab initio simulation package using the generalized gradient approximation with the PW91 functional to describe electron-correlation effects. Ion-electron interactions were described using ultra-soft pseudopotentials. A plane-wave expansion with a cut-off of 233.73 eV was used in all calculations. Geometry relaxations were performed with a conjugate gradient method until the forces on all unconstrained atoms were less than 0.03 eV/Å. A Monkhorst Pack mesh with 4x4x4 k-points was used for all calculations.

The supercell used contained 20 metal atoms and one gaseous molecule located on one of four available sites on the metal lattice. It was assumed that all palladium systems adopt the substitutional; random fcc structure. Metal atoms were randomly distributed among the fcc lattice in the supercell. All atoms were allowed to relax during the calculation, with the volume of the super cell fixed at the optimised volume of the super cell without adsorbed molecules.

Geometry optimization was performed to get the lattice constant and total energy of each alloy prior to adsorption of gaseous molecules.

3.2 Membrane manufacture

3.2.1 Materials used

3.2.2 Support fabrication

The YSZ 3% hollow fibre substrates with a desired micro-structure were fabricated by a fingering induced phase-inversion process, followed by high temperature sintering. A uniform ceramic suspension, with 60 wt.% solid loading, was prepared by ball milling. After degassing, the ceramic suspension was transferred into 200 mL stainless steel syringes and extruded through a tube-in-orifice spinneret (outer diameter 3 mm, inner diameter 1.2 mm) into a coagulation bath with no air gap. An extrusion rate of 7 and 5 mL min⁻¹ was adopted for ceramic suspension and bore fluid (15 wt.% 1,4-dioxane in n-hexane), respectively. The formed precursor fibres were kept in deionized water for a minimum of 12 h, in order to remove the excessive solvent. After being gently washed with deionized water, the precursor fibres were dried at room temperature and sintered at 1400°C in a tubular furnace (Elite, Model TSH 17/75/450).

3.2.3 Membrane deposition

Electroless Plating

Palladium silver, copper, gold, and ternary alloy compositions (except for Pd-CuZr) were deposited onto the surface of the porous YSZ substrate through electroless plating. The process was performed in two steps; the first involves ‘activating’ the surface of the material intended for deposition by seeding the surface with particles of a metal with a higher electro positivity than the metal intended to be plated. Normally palladium is used due to its high electro positivity compared to other metals commonly plated through electroless deposition. This activation step is required for non-conductive supports such as ceramics and glass but may not be required for conductive supports depending on the specific support material and intended plating layer. The ‘activation’ step is followed by the ‘plating’ step where a solution containing a metallic salt, complexing agent, and stabilising agent is reduced through the use of a reducing agent, causing solid metal to be displaced from the solution, and due to the catalytic activity of the seeds placed in the prior step, forming a dense metal layer on the intended surface. Electroless plating results in a strongly adhered, dense metallic layer which can be deposited easily on a large range of morphologies.

Prior to deposition, the outer surface of the fibre was cleaned by sequential washings with a 1:1 mixture of ethanol and water for 10 min in an ultrasonic bath, and were then dried overnight at 120°C.

Preceding electroless plating, the substrates were coated at one end with a gas tight glaze and sintered at 900°C for 1 hour. Prior to deposition, the outer surface of the fibre was cleaned by sequential washings with a 1:1 mixture of ethanol and water for 10 min in an ultrasonic bath, and were then dried overnight at 120 °C.

The substrates were then activated with Pd nuclei via sensitisation in an acidic SnCl₂ solution, followed by activation in an acidic PdCl₂ solution. The sensitisation/activation process was carried out by immersing the glazed hollow fibre substrates sequentially in five chemical baths, i.e. acidic SnCl₂ solution for 5 min; deionised water for 5 min, acidic PdCl₂ solution for 5 min; 0.01 M HCl solution for 2 min; and finally deionised water for 3 mins. All chemical baths were homogenised by stirring. The sensitisation/activation process was repeated for 6 cycles. The composition of each bath is shown in Table 2.

The substrates were then immersed in a Pd electroless plating (ELP) solution, at 60°C, in order to deposit metallic Pd layers onto the activated surface. The Pd ELP solution was prepared according to the composition presented in Table 2 and left to stabilize for 1 h in an ultrasonic bath prior to use. The volume of Pd ELP solution was fixed at 4 mL per cm² of substrate surface area. The electroless plating procedure was performed twice, with a total plating time of 60 mins.

After the palladium coating the membranes were then subjected to one, or multiple, other plating steps of silver, gold, or copper. The plating time for silver was 30 minutes for one cycle and the volume of plating solution to substrate was the same as the palladium steps.

It should be noted that the deposition of gold is through immersion plating rather than electroless plating. Immersion plating is the process of applying adhering layers of nobler metals to another metal's surface by dipping the material in a heated nobler metal solution ion to produce a replacement reaction. This causes the deposition of a metallic coating on a base metal from solutions that contain coating metal. One metal is typically displaced by metal ions that have lower levels of oxidation potential, relative to the metal ion being displaced. The plating time for gold was 3 hours and the volume of plating solution to substrate was 4mL per cm³.

The resulting composite membranes consisting of multiple metal layers stacked were then heat treated at 500oC under an environment containing 25% H₂ in Ar balance for 24 hours in order to alloy the layers into a homogeneous metal membrane.

3.2.4 Materials testing

3.3 Membrane testing

3.3.1 Preparation of gas standards

3.3.2 Membrane testing rig

3.4 Hydrogen impurity enrichment

3.4.1 Device design

References

Chapter 4

Density functional theory as a screening method for dense metal membranes

Chapter 5

Impurity resistance of dense metal membranes under hydrogen impurities

Chapter 6

A hydrogen impurity
measurement device for
validating ISO 14687 standard

Chapter 7

Conclusion and future work