

Developing a hydrogen impurity enrichment device 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 Information derived from published and unpublished results of others has been acknowledged in the text and in the relevant references included within the thesis.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 thin horizontal line.

Imperial College London

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Executive summary

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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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List of Acronyms, Abbreviations and Symbols

AHF Asymmetric Hollow Fibre

ASTM American Society for Testing and Materials

BCC Body Centered Cubic

CRDS Cavity Ring Down Spectroscopy

CTE Coefficient of thermal expansion

DFT Density Functional Theory

ELP Electroless Plating

EU European Union

EDS Energy-dispersive X-ray spectroscopy

FCC Face-centred cubic

FTIR Fourier-transform infrared spectroscopy

HF Hollow Fibre

ISO International Standards Organisation

GC Gas Chromatography

NPL National Physical Laboratory

NPT National Pipe Thread

MS Mass Spectrometry

PDHID Pulsed discharge helium ionization detector

PEMFC Proton Exchange Membrane Fuel Cell

PID Proportional–integral–derivative

PPB Parts-Per-Billion

PPM Parts-Per-Million

PSA Pressure Swing Adsorption

SMR Steam Methane Reforming

WGS Water Gas Shift

XRD X-ray diffraction

XPS X-ray photoelectron spectroscopy

YSZ Yttrium stabilized zirconium

Ag Silver

Ar Argon

Au Gold

CH₄ Methane

Cu Copper

CO Carbon Monoxide

CO₂ Carbon Dioxide

He Helium

H₂ Hydrogen

HCHO Formaldehyde

HCOOH Formic Acid

H₂O Water

N₂H₄ Hydrazine

HCl Hydrochloric Acid

H₂S Hydrogen Sulphide

NaOH Ammonium hydroxide

Pd Palladium

PdNH₃4Cl₂H₂O Tetra-amminepalladium (II) chloride monohydrate

SnCl₂ Tin(ii)Chloride

Zn Zinc

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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 sale 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 vehicles 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 when developments in lowering the platinum catalyst loading and breakthroughs in the production of thin film electrodes drove the cost of fuel cells down to a level where they were a commercially viable option. As of 2017, a number of auto mobile manufacturers including Toyota,[2] Hyundai, [3] Honda [4] and Daimler [5] now offer hydrogen vehicles commercially. It is also possible to retrofit a petroleum vehicle to run off hydrogen.[6] Many countries both in the EU, and globally have ambitious hydrogen infrastructure plans over the next 10 years. This is 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, however several countries are aiming to deploy 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 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 purity, are adequate to ensure customers vehicles are not inadvertently damaged by fluctuations in hydrogen composition.

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

International standards advise that all hydrogen suppliers should prove that their product is pure enough to prevent degradation of fuel cell components. 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 includes some challenging hydrogen purity specifications mainly due to the impurity limits being below the limits of detection of the standard techniques commonly used to measure the concentration of these compounds.

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 these specifications 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 require a number 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 a GC-MS. Therefore a solution is to increase the

concentration of impurities above the limit of detection of a cheaper, more widespread analyser. 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 semi permeable membrane material, such as palladium, which only allows the passage of hydrogen.[12] As hydrogen leaves the system, the impurities remain, increasing in concentration with 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.

The accuracy, cost and time taken for a hydrogen enrichment device is highly dependent on the membrane material. Different materials will allow hydrogen to permeate at different rates and will interact differently with impurities that may be present in hydrogen.[12] While hydrogen enrichment is a promising technology for hydrogen impurity measurement, more research must be done to properly understand how different membrane materials interact with common hydrogen impurities, and therefore identify the most appropriate material.

1.2 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
- Finalise a protocol for national measurement institutions to follow when enriching a hydrogen sample.
- Convert the experimental set up in to a commercially viable prototype which could be used in analytical laboratories
- 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 tracer enrichment will be tested using a real sample taken from a hydrogen refuelling station.

1.3 Thesis structure and presentation

This thesis consists of 7 chapters, which includes the ‘Introduction’, ‘Literature Review’, experimental chapters and ‘Conclusion’. The thesis structure is visualised in figure 1.1. The experimental chapters address different aspects of development of hydrogen metrology techniques as described above.

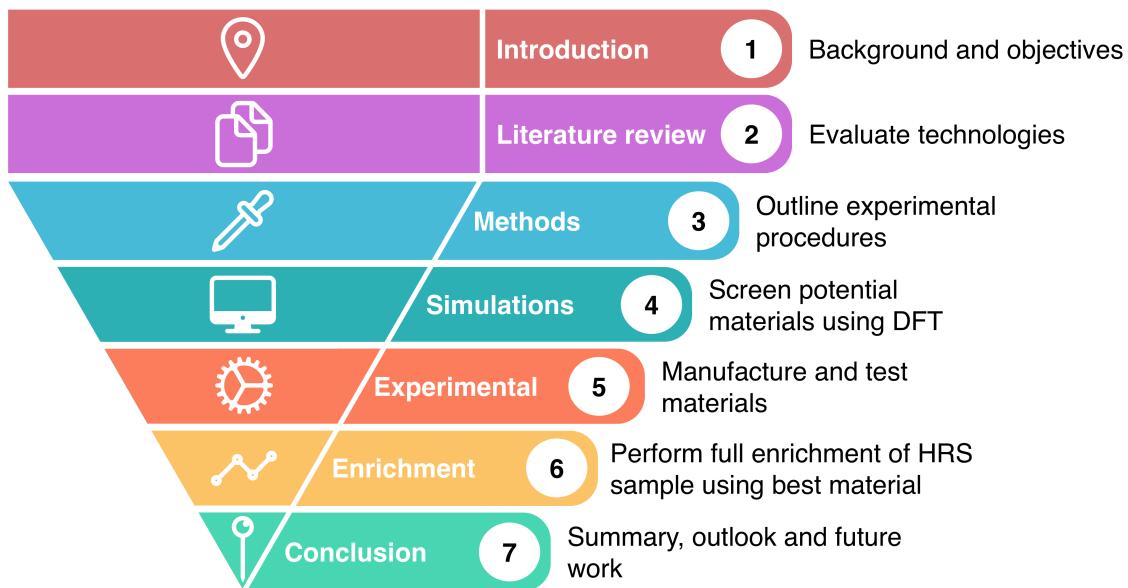


Figure 1.1: Schematic presentation of the thesis structure

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Chapter 2

Literature review

2.1 Fuel cell electric vehicles

A Fuel cell electric vehicle (FCEV) refers to a vehicle which uses a solid state electrochemical device to convert chemical energy into electrical energy for motor power. The most common fuel source for FCEV's is hydrogen, where energy is produced using oxygen from air and compressed hydrogen stored on board.

A fuel cell is made up from an electrolyte and two electrocatalysts at both the anode and cathode sides of the cell. The electrolyte separates the two electrodes and usually defines the type of fuel cell. At the anode side the fuel is oxidised as shown in equation 2.1, creating a positively charged ion and an electron. The electrolyte is designed to only allow the passage of ions, and prevents the passage of electrons. The freed electron travels through a circuit, creating an electric current to provide power for it's desired use. The ions travel through the electrolyte to the cathode side of the fuel cell where they are reunited with the freed electrons, and oxygen to produce water as shown in equation 2.2. The overall process for a hydrogen fuel cell is shown in equation 2.3 and visualised in figure 2.1

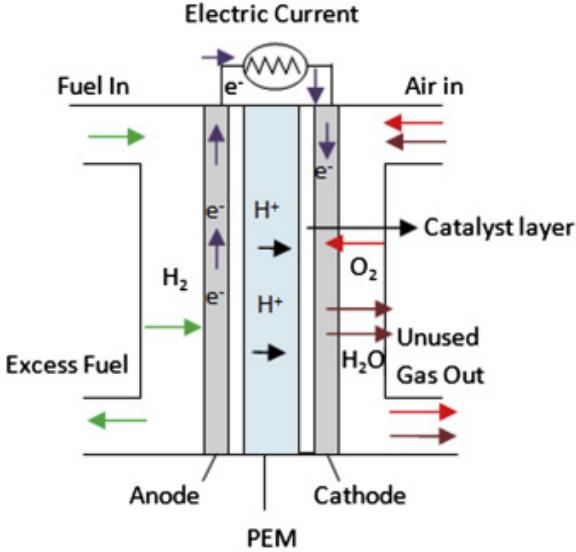


Figure 2.1: Schematic of a PEMFC cell [1]



While a number of fuel cell technologies can use hydrogen as a fuel source, the most suitable for FCEV's, and in particular mass production of affordable vehicles, are proton exchange membrane fuel cells (PEMFC). This is due to their high power density, low start up time, and low operating temperatures. [2]

A PEMFC uses a proton conducting polymer membrane as an electrolyte material, typically naftion. A PEMFC cell consists of two metal bipolar plates which act to distribute the fuel and oxidant within the cell, aid water management within the cell, separate individual cells in a fuel cell stack, and carry current away from the cell. [2] A Membrane electrode assembly (MEA) which consists of the polymer membrane, two dispersed noble metal catalyst layers to enable the anode and cathode reactions, and two gas diffusion layers to ensure uniform access of fuel and oxidant to the catalyst layer. Common materials for the MEA are shown in figure 2.2[3]. The components are wedged between two rubber seals to ensure the cell is gas tight. Individual cells are combined in series to form a fuel cell stack which can provide the desired power as shown in 2.3

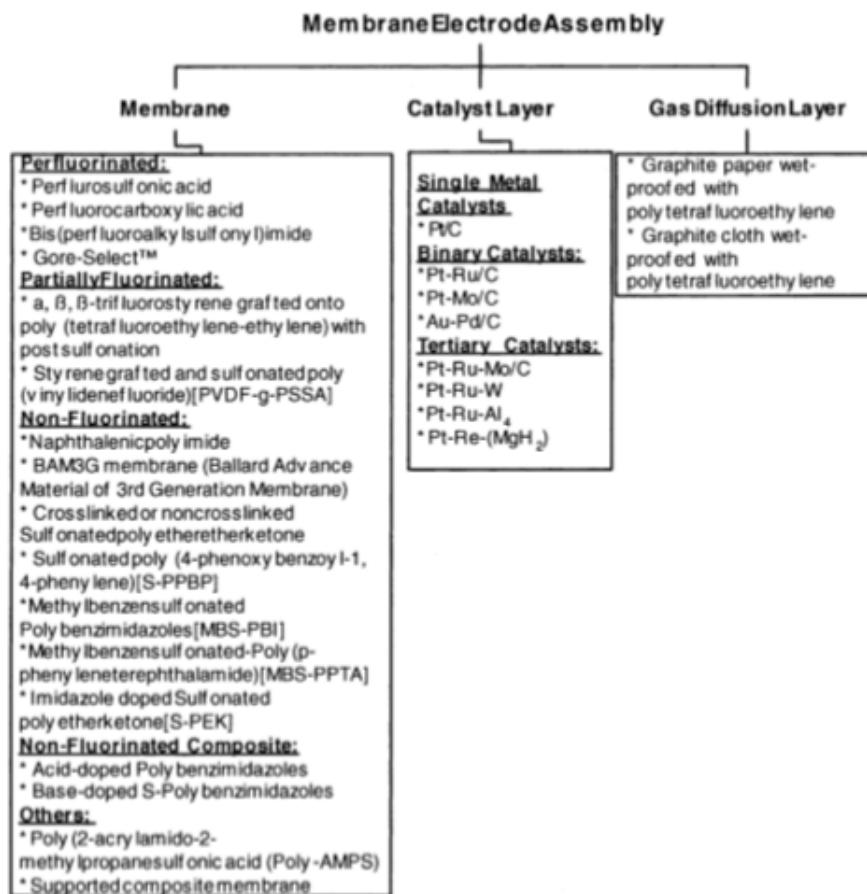


Figure 2.2: Classification of MEA materials [3]

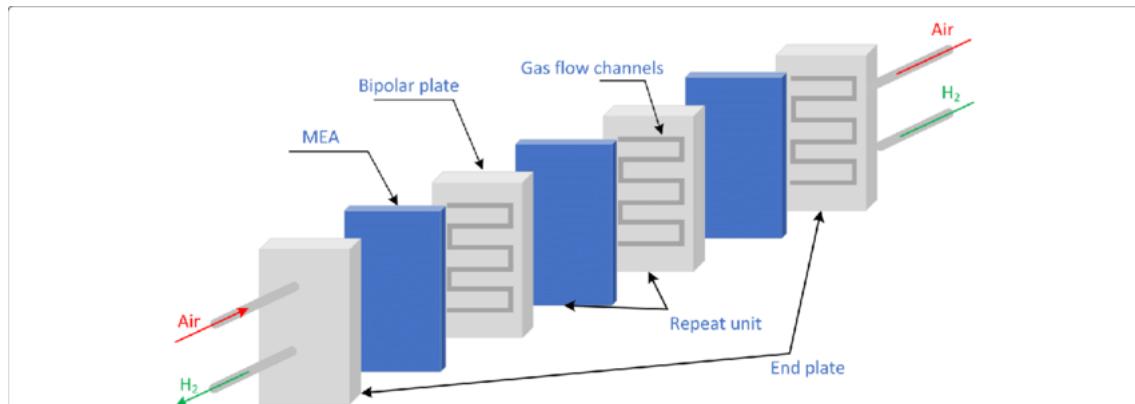


Figure 2.3: Schematic of a PEMFC stack [4]

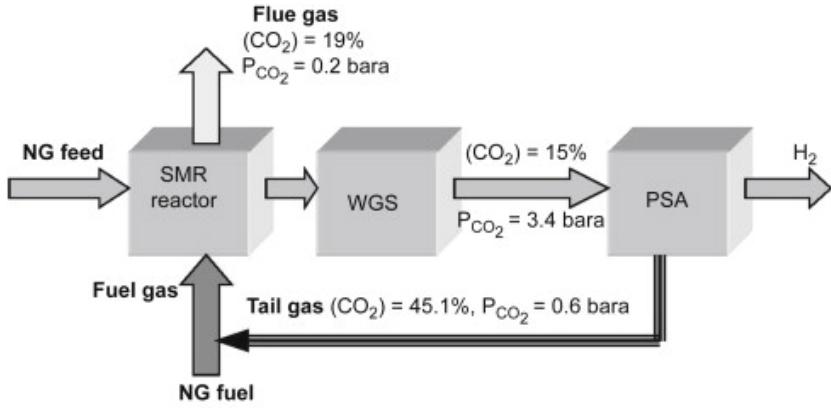


Figure 2.4: Simplified block diagram of a typical modern SMR plant. WGS is a water gas shift reactor. CO₂ concentrations are in mol.%. [8]

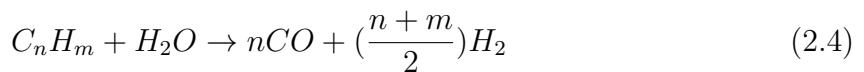
2.2 Hydrogen Production

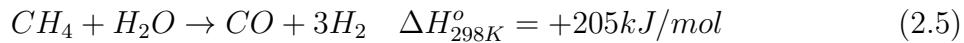
Hydrogen production refers to a range of industrial processes for generating hydrogen. Since there are no natural reserves of hydrogen, it must be obtained through one of these methods. The most important factor for determining the feasibility of a hydrogen production process is the primary source of 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, light; or fossil fuels either through decomposition of the hydrocarbons present in the fuel, or through heat. Currently the primary sources of hydrogen are from fossil fuels: steam reforming of methane accounts for 48% and other hydrocarbons account for 30% of global hydrogen production; gasification of coal accounts for 18%; and electrolysis of water accounting for the remaining 4%. [5] Electrolysis and SMR will be discussed since these are expected to be the most dominant production methods in the future. [6]

2.2.1 Hydrogen from fossil fuels and hydrocarbons

Fossil fuels are the most dominant source of hydrogen production [5] and there are a number of processes which are commonly utilized in industry. The most popular and therefore the ones which will be discussed are steam methane reforming and hydrocarbon decomposition.

Steam Methane Reforming is the conventional and most economical method for producing hydrogen, and it has been predicted by the IEA that this trend will continue despite the emergence of other hydrogen production methods. [7] 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 2.4. A schematic representation of the process can be seen in figure 2.4



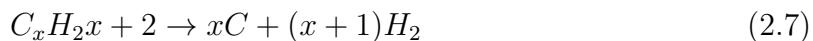


Equation 2.5 takes place in a reactor operating at 700-850°C, at pressures of 3-25 bar, and in the presence of a nickel based catalyst. [8] The result of this step is a mixture of CO and H₂, commonly referred to as syngas. This syngas is further used as a feedstock for the reaction shown in equation 2.6 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 H₂, and a final low-temperature step which operates at 250°C which utilizes a catalyst with higher activity to minimise the remaining CO₂. [8] The final product will be a mixture of CO₂ and H₂.

A number of separation steps are used 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. [8] 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. [8] This step is essential to ensure sulphur is not present and to ensure catalyst poisoning does not occur at any point in the process.

The cost of producing hydrogen through SMR varies but averages at around £2 per kg of hydrogen and therefore costs around £2000 per tonne of hydrogen produced. [9]

Hydrocarbon decomposition is a process by which hydrocarbon molecules are converted into solid carbon and hydrogen. [10] This reaction is typically operated either thermally or by creating a plasma. A metallic catalyst such as nickel or iron is required. The reaction is shown in equation 2.7 [11]

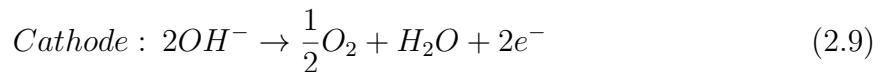
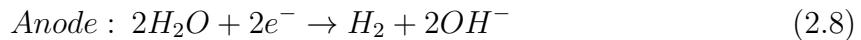


An advantage of this process is that the only feedstock is the hydrocarbon, so presuming that the feedstock is sufficiently pure this method of hydrogen production should remove the needs for further downstream processing. [10] The main disadvantage of this method is since solid carbon is the main by-product the catalyst will be easily deactivated and will require regular maintenance to ensure carbon build up is managed. [10]

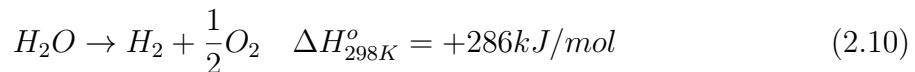
2.2.2 Hydrogen from water

Electrolysis uses an electric current to split water into hydrogen and oxygen using separate anode and cathode chambers isolated using an ion exchange membrane. The anode and cathode reactions are shown in equations 2.8 and 2.9. The main competitive advantage of electrolysis is that reactors are modular and highly scalable, allowing

hydrogen to be produced in a distributed manner. [12] 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. However if a non-renewable source of energy is used the net carbon produced per mole of hydrogen would be higher than that produced by SMR. [13] Electrolysis is 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. [12] Currently most commercial electrolyzers operate at efficiencies of around 80% and therefore requires around 55000 kWh per tonne of hydrogen produced. The average price of industrial electricity in the UK in 2020 is around £0.13 per kWh [14] and therefore the average price of hydrogen produced through electrolysis is around £7150 per tonne. [9]

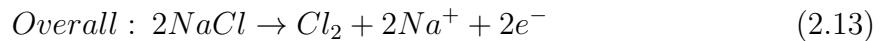
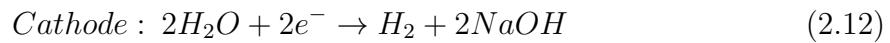
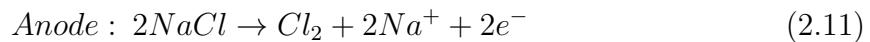


Thermal decomposition of water is the process of splitting water into hydrogen and oxygen at temperatures of 2000°C as shown in equation 2.10. [6] The operating temperature of the reaction can be lowered under the presence of a nickel or iron based catalyst. [6] Due to the high energy demand for this production method water splitting is not a feasible method of commercial hydrogen production.



Chloro Alkali process

The chloro alkali process is an electrolysis process which involves the electrolysis of sodium chloride solutions. The process is already performed on an industrial scale in the production of chlorine and sodium hydroxide. Hydrogen is a by-product of the cathode reaction in the electrolytic cell shown in equation



It is estimated that around 0.4 million tonnes of hydrogen per year and this could potentially contribute to annual demand. [15] The process is extremely energy intensive however, requiring 2500 kWh per tonne of NaOH produced or 99200 kWh per tonne of H₂ produced. [16] Therefore it is unlikely that this process will be used to solely produce hydrogen. As with many waste gases, producers often reuse the gas to power parts of their process, typically through consumption. It may also be the case that producers

Table 2.1: Summary of ISO 14687-2 impurities in the supply chain and their effects on fuel cell operation adapted from [18]

Impurity	Production sources	Contamination source	Contamination barriers	Effect on fuel cell operation
N ₂	SMR	Raw material PSA malfunction Maintenance Leakage	PSA	Reduced energy density of fuel
	Electrolysis	Air intake into water tank Raw materials	Maintainance PEM membrane H ₂ pressure > N ₂ pressure supply PSA	
Ar He	SMR	Generation at the anode Membrane cross over TSA malfunction	TSA operating condition Oxygen sensor	Potential damage to hydrogen storage
	-	By-product Raw materials	PSA CO sensor on line	
O ₂	Electrolysis	By-product Raw materials	PSA	Temporary electrocatalyst poisoning
CO	SMR	By-product Raw materials	PSA	Damage to hydrogen storage medium Could cause formation of CO
CO ₂	SMR	Raw material	CO ₂ filter	
CH ₄	SMR	Raw material	Anodic separator tank Ion exchange resin in closed water loop PEM membrane	Reduced energy density of fuel
	SMR	Raw material Reactant	PSA	
H ₂ O	Electrolysis	Through PEM membrane Hydrogen output water saturated TSA malfunction	TSA dryer Dew point monitor Operating procedure	Ice formation during refilling K ⁺ and Na ⁺ contamination reducing cathode side conductivity
Total sulphur compounds	SMR	Raw material	Sulphur trap in reforming system PSA	Permanent electrocatalyst poisoning
NH ₃	SMR	Raw material	Stainless steel pipe and vessel PSA	Reduced ion exchange capacity
Formaldehyde	SMR	Raw material	Reverse osmosis PEM membrane	Temporary electrocatalyst poisoning
Formic acid	SMR	Raw material	PSA	Temporary electrocatalyst poisoning
Halogenated compounds	SMR	Raw material	Desulfuration unit Chlorinated trap in reforming system PSA	Permanent electrocatalyst poisoning
Monitoring Cl ₂ concentration		Raw material contamination	Stainless steel pipe and vessel Reverse osmosis	

would rather find more efficient methods for performing this rather than selling their hydrogen on the open market. A recent example of this is in 2019 when a chloro alkali plant in Jordan reused their waste hydrogen in a fuel cell situated on site to power their process. [17]

2.3 Hydrogen impurities in the supply chain

The method used to manufacture hydrogen will affect which potential impurities can be present in the final product. While steps are taken in both electrolysis and SMR to ensure a pure product is produced, there is still the chance of impurities reaching the customers fuel cell. This section will explore how ISO 14687-2 impurities can enter the supply chain, and their effect on the operation of a PEMFC. A summary is shown in table 2.1

Water

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 an appropriate barrier to prevent water contaminating the end product. This is due to the molecular sieves commonly used having a high selectivity for water. [8] 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 $\mu\text{mol/mol}$. [18] 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

Modern electrolyzers are fitted with a drier, which is the main barrier for water vapour exiting the process with hydrogen. [18] 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. [18]

Water can also contaminate produced hydrogen in the chloro alkali process since, similar to electrolysis, it is present in the process. Typically the process contains a drier which ensures that a dew point of -20°C is maintained which should prevent any water in the exit stream.

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^+ [19] 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.

Total hydrocarbon content

The presence of hydrocarbons are most likely to result from the SMR process. Hydrocarbons are not expected to be present at all in electrolysis or chloro alkali however could potentially contaminate the system if hydrocarbons are present in any components such as compressors. 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. [18]

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.[19] Methane (CH_4) is generally considered an

inert constituent and it's main effect on fuel cell performance is diluting the hydrogen fuel stream. [19]

Oxygen

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 hydrogen produced 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 $\mu\text{mol/mol}$. [18]

Oxygen can also contaminate the exit stream in the chloro alkali process due to it's presence in ambient air. There are no safeguards in place to prevent oxygen contaminating the hydrogen stream so it is likely that oxygen can be present in any produced hydrogen if given the opportunity.[18]

Oxygen 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. [19]

Helium, nitrogen and argon

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 the natural gas feedstock for SMR. 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. [18]

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.

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 used for hydrogen dispensing. [19]

Carbon dioxide

Like most other impurities which are present in SMR, CO₂ 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. [8]

CO₂ 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 CO₂ filter on the inlet and a reverse osmosis 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 CO₂ has a low crossover potential through the PEM membrane and therefore is unlikely to cross into the cathode side of the system.[18]

Carbon dioxide is not likely to be in the product stream from hydrogen produced in chloro alkali as it remains in the caustic soda lye that is produced. CO₂ could also be formed from oxidation of the membrane material when degraded however no quantitative assessment has been made on this. [18]

CO₂ does not typically affect the function of fuel cells. However, CO₂ may adversely effect on board hydrogen storage systems using metal hydride alloys. With CO₂, at levels higher than the specification, a reverse water gas shift reaction can occur under certain conditions in fuel cell systems to create carbon monoxide. [19]

Carbon monoxide

Carbon monoxide is a main byproduct of SMR which is separated from the exit gas stream through PSA. [8] If this fails SMR processes are fitted with a CO sensor to ensure the concentration in the product does not pass a certain threshold. [18] It is unlikely for CO to be present from electrolysis.

Carbon monoxide (CO) is a severe catalyst poison that adversely effects fuel cell performance by inducing a competitive adsorption effect between itself and hydrogen on the electrocatalyst surface. The result is a temporary reduction in operating efficiency. [19] Although its effect can be reversed through mitigating strategies, such as material selection of membrane electrode assembly (MEA), system design, and operating conditions, its effect on operation is still a concern. Lower catalyst loadings are particularly susceptible to catalyst poisoning contaminants.

Total sulfur compounds

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. [8] This is designed to reduce the concentration of sulphurous compounds to <50 nmol/mol. [18]

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 H₂S will adsorb onto the molecular sieves more strongly than CO. [18]

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. [19]. It is unlikely that sulphur contamination will arise from electrolysis.

Sulfur containing compounds are severe catalyst poisons that at even very low levels can cause irreversible degradation of fuel cell performance due to a permanent reaction taking place between sulphur and the platinum catalyst. The specific sulfur compounds addressed in particular are: hydrogen sulfide (H₂S), carbonyl sulfide (COS), carbon disulfide(CS₂), methyl mercaptan (CH₃SH). [19]

Formaldehyde and formic acid

Formaldehyde (HCHO) and formic acid (HCOOH) is produced through a side reaction in SMR depending on the specific operating conditions of the process.[8] PSA is the main barrier for preventing contamination of the product. [18]

Formaldehyde and formic acid 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. [19] Lower catalyst loadings are particularly susceptible to catalyst poisoning contaminants.

Ammonia

Hydrogen could be contaminated with ammonia through either SMR or electrolysis. Ammonia is a by-product of the reforming steps and PSA should be sufficient to remove ammonium from the exit stream of SMR. Ammonia can also be present in water used in electrolysis however the reverse osmosis step used to purify the water before the process is normally sufficient in removing all ammonia before it is used in the process. [18]

Ammonia (NH₃) causes some irreversible fuel cell performance degradation by affecting the ion exchange capacity of the ionomer of the proton exchange membrane. [19]

Total halogenated compounds

Halogenated compounds can contaminate hydrogen by entering either SMR or electrolysis through the process input, or leaking into the process at other points where they are used. Potential sources include chlor-alkali production processes, refrigerants used in processing, and cleaning agents. [18]

In the chlor-alkali process, the presence of chlorine and hydrochloric acid in hydrogen gas could be likely since they are main feedstocks in the process. Both HCl and Cl₂ are highly soluble in water and are likely to leave the process in solution. Cl₂ and H₂ are also contained separately from each other and not expected to cross contaminate.

Cross contamination could occur in the event that there is not enough liquid water in the system. This would likely be detected as the system would quickly fill with hydrogen gas which is continuously monitored due to risk of explosion, shutting down the system and preventing contaminated hydrogen leaving. Therefore it is unlikely that Cl will be present in the produced hydrogen. Halogenated compounds cause irreversible performance degradation similar to sulphur, reacting with the platinum electrocatalysts to form platinum-halides such as PtCl₄. [20] However the concentrations required to cause this damage has not been well documented in literature.

Other impurities

2.4 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 [21] 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 3.1 and 2.15.

$$CEF_{NI} = \frac{\frac{P_{1,a}V_1}{Z_{1,a}RT_{1,a}} \frac{P_{2,a}V_2}{Z_{2,a}RT_{2,a}} - \frac{P_{1,b}V_1}{Z_{1,b}RT_{1,b}}}{\frac{P_{2,b}V_2}{Z_{2,b}RT_{2,b}}} \quad (2.14)$$

$$y_{i,a} = \frac{y_{i,b}}{CEF} \quad (2.15)$$

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. [22] The non-ideal gas law method used in the previous paper [21] was compared to a novel tracer enrichment method developed by NPL. [22] 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 2.16.

$$CEF_{Tracer} = \frac{y_{Krb}}{y_{Kra}} = \frac{1}{y_{Kra}} \frac{A_{Krb}}{A_{Kra}} y_{Krst} \quad (2.16)$$

The set-up was similar to the one used by Papadias et al [21] 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.[22, 23] 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. [22] 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. [24] 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.

2.4.1 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 [25]. 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 μ 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 [23]. 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.

2.5 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 2.2 and visualized in Figure 5.1.

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 5.1, 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 combination 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

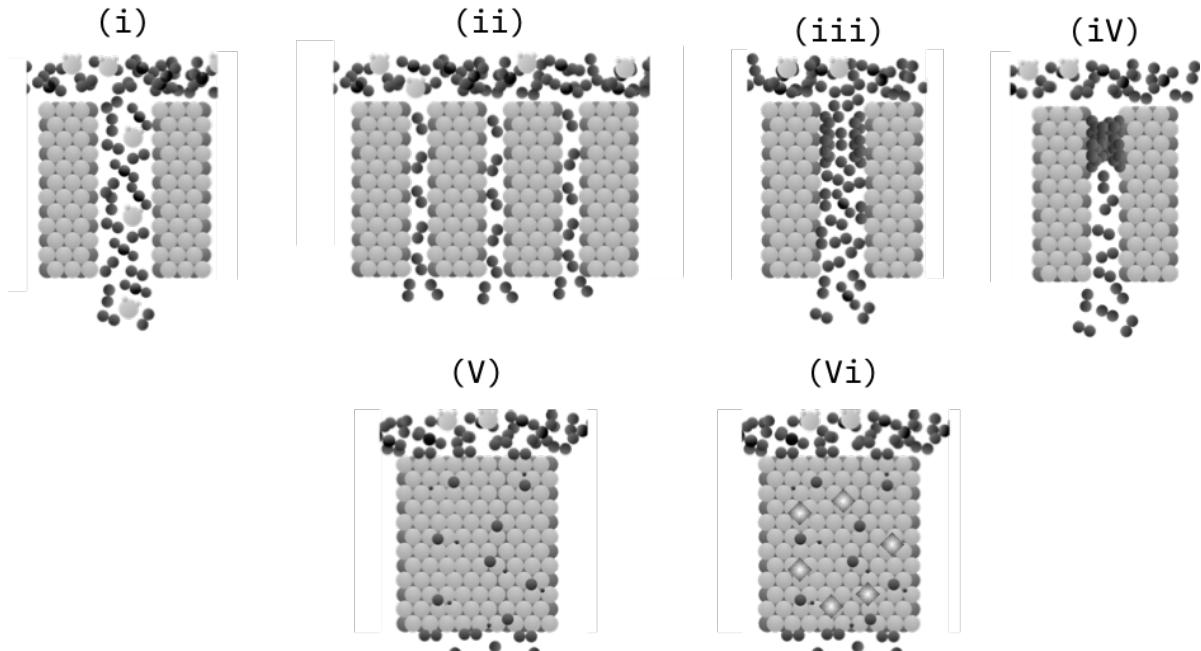


Figure 2.5: Illustration of the five membrane separation mechanisms (i) Poiseuille Flow/Knudsen diffusion, (ii) Molecular Sieving, (iii) Surface diffusion (iV) Capillary condensation (V) Solution diffusion (Vi) Facilitated transport

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 2.17 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.

$$\frac{r}{\lambda} = \frac{2P}{3\eta} \sqrt{\left(\frac{2M_w}{\pi RT}\right)} \quad (2.17)$$

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 (2-50nm) 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 H₂ 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 mechanism. 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 a specific membrane is.

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.

Table 2.2: Types of hydrogen separation membrane

Material	Separation mechanism	Mechanical stability	Chemical Stability	Operating temperature	Selectivity
Polymer (Dense)	Solution diffusion, Facilitated transport Knudsen diffusion, Poiseuille flow, Capillary condensation, Surface diffusion, Molecular sieving	Susceptible to Compaction [26] and Swelling [27]	Low chemical stability, Degrades under H ₂ S, HCl, CO ₂ , SO _x [28]	< 100°C	2.5 [29] – 960 [30]
Nano-porous		Brittle	Good[31]	Ambient -500°C	2.4 [32] - 1000 [31] (H ₂ /N ₂ selectivity)
Dense Metal	Solution Diffusion	Phase transition [33] Dependant on support [33] Surface segregation[33]	Negative interaction with CO, CH ₄ , and H ₂ O. Reacts with H ₂ S and SO _x [33]	300-600 [34]	∞
Dense Ceramic	Solution Diffusion	Brittle Difficult to seal due to high operating temperature	Degrades under CO ₂ [35]	500-1000 [35]	∞

2.5.1 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. H₂/N₂ 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.

$$n_{i_{exit}} = n_{exit_{total}} / \alpha^{H_2/i} \quad (2.18)$$

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.

$$y_i = \frac{(n_{i_{ret}} + n_{i_{exit}})/n_{tot_{ret}}}{CEF} \quad (2.19)$$

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 µmol/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 H₂/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 µmol/mol of Helium a H₂/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 H₂/N₂ selectivity of 2632 [36] 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.

The common thread with all the micro-porous materials discussed here is that they are currently difficult and expensive to synthesise on a large scale, particularly in membrane form. Due to the separation mechanism of micro-porous materials they are not suitable for use in hydrogen impurity enrichment as their selectivity will not produce a viable enrichment medium. However, due to their high surface areas and ability to be modified to promote integration with specific gas species, they may find use in sensor applications for detecting the ISO-14687 impurities. There is a wealth of work on the use of many of these materials as chemical sensors however much of this work has been performed using the gases in non-hydrogen matrix gases and therefore much work is required before their true potential in this area can be realised.

Polymer membranes have a similar issue to micro porous materials in that their selectivity is too low to be effective at enriching impurities in hydrogen samples. The mechanical strength and impurity resistance of polymer membranes also limits their use as hydrogen impurity enrichment mediums. While again there are some successful applications of polymers as sensor materials, the same issues as micro porous materials regarding lack of information of their effectiveness in a hydrogen matrix crops up again. It is likely that polymer membranes will continue to be most effective in industrial separation and will be limited in their use as an analytical material.

Therefore this section will only concern itself with membranes which show permselectivity towards hydrogen therefore making them viable as hydrogen impurity enrichment materials. This section will discuss the performance of dense metallic and dense ceramic membranes, and by comparing their reported metrics, their suitability for hydrogen impurity enrichment will be determined.

Dense metallic

Metallic membranes are comprised of dense metal or alloy sheets which allow the permeation of hydrogen through its constituent electrons and protons. While this is the same separation mechanism seen in dense polymer membranes the hydrogen selectivity is typically a lot higher in these systems since molecules which are not hydrogen are unable to dissociate and permeate through the membrane surface, giving a theoretically infinite selectivity towards hydrogen. The minimum requirement for a dense metal mem-

brane for hydrogen separation is the ability to dissociate and permeate hydrogen. There are a number of metals which have shown varying degrees of suitability for hydrogen separation and these are shown in Table 2.3.

Table 2.3: Metals which show the ability for hydrogen permeation [37]

Structure	Metal	Activation energy for hydrogen permeation (kJ/mol)	Heat of hydride formation (kJ/mol)	Hydrogen permeability at 500°C (mol/ m s pa ^{1/2})
fcc	Ni	40.0	-6	7.8 × 10 ⁻¹¹
	Cu	38.9	-	4.9 × 10 ⁻¹²
	Pd	24.0	20	1.9 × 10 ⁻⁸
	Pt	24.7	26	2.0 × 10 ⁻¹²
bcc	V	5.6	-54	1.9 × 10 ⁻⁷
	Fe	44.8	14	1.8 × 10 ⁻¹⁰
	Nb	10.2	-60	1.6 × 10 ⁻⁶
	Ta	14.5	-78	1.3 × 10 ⁻⁷

The flux of a dense metal membrane is given by Eqn 2.20 and is a function of the metals permeability to hydrogen, the concentration and pressure gradient across the membrane, and the thickness of the dense layer.

$$J = \frac{\phi}{l} (P_{H,ret}^{0.5} - P_{H,perm}^{0.5}) \quad (2.20)$$

From the metals shown in Table 2.3 palladium and its alloys are by far the most popular choice due to a combination of high hydrogen permeability, favourable catalytic activity towards hydrogen dissociation and re-association, and aversion towards hydride formation compared to other metals.[37, 38, 39]

For other metals there is often a trade-off, V, Nb and Ta exhibit higher permeability than palladium but are limited by their low catalytic activity for hydrogen dissociation and typically must be combined with another metal to compensate for this. A common strategy is to deposit palladium particles on both sides of membranes made from these metals to provide this catalytic activity. Embrittlement of pure metal membranes is also an issue, even for metals with a high heat of hydride formation. Embrittlement is a side effect of hydrogen passing through the crystal lattice. During transport a H-M phase will form which has a higher lattice parameter than the original crystal lattice. This change in lattice parameter can cause stress in the overall structure of the dense membrane layer and cause the formation of pin holes, cracks, and eventually membrane failure. Metals with a low heat of hydride formation in Table 2.3 will readily embrittle within hydrogen containing atmospheres.

This section will discuss developments in both palladium and non-palladium membranes and the issues still surrounding the technology.

As previously mentioned palladium is typically the material of choice for dense metallic membranes due to its combination of high stability, permeability, and catalytic activity. Palladium based membranes have been successfully used to provide ultrapure hydrogen for a number of applications including electronics, industrial gas, and fuel cell

industries for a number of years. The main downside to the use of palladium is its high cost of around \$25 per gram. [40] This high cost has pushed researchers into focusing on reducing the amount of palladium used in the membrane in order to find a more economical solution. This is done either by using a traditional membrane approach, whereby the thickness of the membrane layer is reduced as much as possible to maximise the flux while decreasing the overall amount of palladium used, or by alloying palladium with a cheaper metal to reduce the amount of bulk palladium in the manufacturing process.

During operation of a pure palladium membrane at temperatures lower than 300°C, hydrogen embrittlement can occur due to the aforementioned phase transition between interstitial hydrogen within palladium (α phase) and palladium hydride (β phase). The β phase (0.4025 nm) has a lattice parameter bigger than the α phase (0.389nm). [41] The formation of this α - β phase will cause the membrane to distort, become brittle, and eventually results in membrane failure when a leak occurs. [42] The behaviour of hydrogen embrittlement is shown in figure 2.6 Aside from this pure palladium has poor chemical stability, it can be poisoned by a number of impurities which are commonly found in hydrogen. Some of these impurities simply inhibit permeation of hydrogen but do not have a permanent interaction and thus their effects can be mitigated by optimising the operating conditions. Others such as H₂S and CH₄ are known to interact with the membrane through chemisorption and permanently damage the membrane through the formation of compounds with palladium, breaking the crystalline lattice resulting in membrane failure.

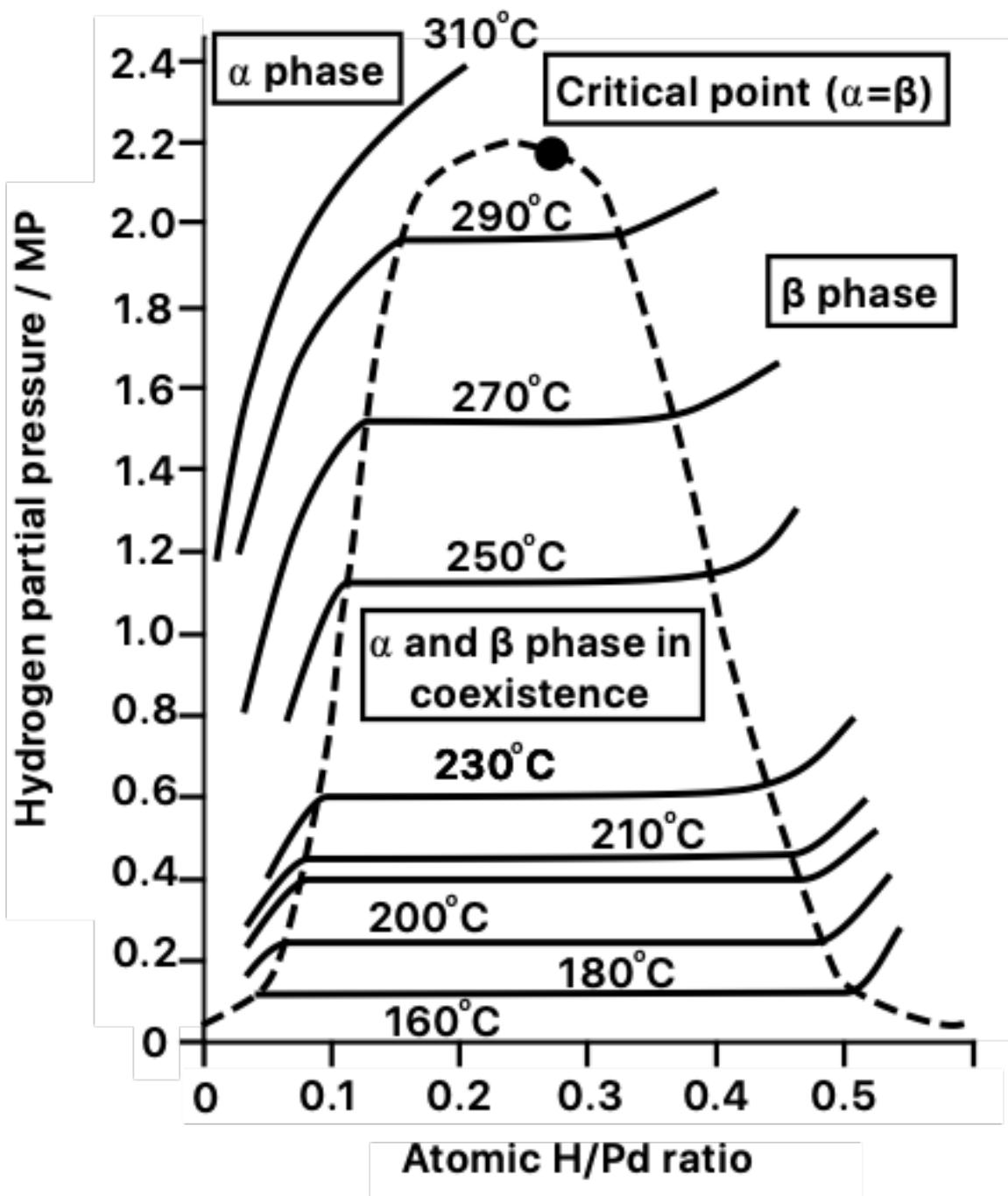


Figure 2.6: Palladium-Hydrogen phase diagram adapted from [42]

From the impurities listed in ISO 14687-2 CO, H₂O, Hydrocarbons and sulphur containing compounds are known to have a physisorption interaction with palladium. Physisorption based poisoning occurs by the impurity inducing a competitive adsorption with hydrogen, blocking active sites for hydrogen dissociation, and hence reducing the active area available for hydrogen permeation.[33] The ultimate effect of this is a

temporary flux reduction which has no long lasting damage on the membrane. Compounds such as H₂S have a more extreme effect on the membrane as adsorption leads to a reaction between palladium and the metal permanently changing the membrane composition and structure. The most commonly studied interaction is the interaction between palladium and H₂S to form palladium sulphide. Palladium sulphide, while still permeable to hydrogen, has an extremely low permeability, drastically reducing the efficiency of the membrane. Palladium sulphide also has a larger lattice constant than that of pure palladium which can lead to membrane failure by creating gaps in the crystal lattice resulting in pinholes. Some of these impurities, in particular those which only exhibit physisorption, can be mitigated by altering the operating conditions. It has been reported that the effects of CO and H₂O poisoning can be completely eliminated by operating at temperatures above 300°C. Another example where this is shown is with H₂S related poisoning. Since the reaction between palladium and H₂S is exothermic, and produces hydrogen as a side product, it can be inhibited by increasing the H₂:H₂S ratio and increasing the temperature.

A combination of cost, easy formation of phase transitions [41, 42] and its low tolerance for common impurities found in hydrogen processes limits pure palladium's use as a hydrogen separation material. Many of these effects however, can be completely mitigated through alloying palladium with another metal. By forming an alloy with a metal which has a lattice parameter similar to that of the β -phase the average difference between the sizes of the two phases is effectively decreased and thus the hydrogen embrittlement effect can be effectively mitigated. The effect of impurities on palladium membranes can also be partially mitigated by alloying with another metal and oftentimes an increase in permeability is reported with certain alloy compositions.

Both binary and ternary alloys of palladium have been reported and is a mature topic in literature. By far the three most popular alloying compounds with palladium are silver, copper and gold. The current literature landscape of palladium alloy membranes are summarised in Table 2.4 and for the purpose of this review studies which looked at the impurity resistance, which is currently the most pressing issue in the field, were focused on.

Silver is the most popular dopant for palladium membranes and forms a stable alloy with palladium at concentrations greater than 20wt %, with the optimal composition occurring at 23%. On top of mitigating the effects of hydrogen embrittlement, a 60% increase in permeability is observed when compared to pure Pd membranes. Despite having enhanced permeation properties, PdAg is still susceptible to poisoning, in particular from sulphurous compounds which can form both Pd₄S and Ag₅Pd₁₀S₅. Several studies exposing PdAg membranes to sulphurous compounds have been performed and in most cases the membranes suffer a large decrease in flux, and are permanently damaged as shown by a permanent decrease in flux when sulphide is removed from the inlet. [43] It has been observed that exposure to 5 $\mu\text{mol mol}^{-1}$ H₂S in the feed stream is enough to induce Pd₄S formation [43] and therefore this composition is only suitable for atmospheres and applications which do not contain any sulphur.

Copper is another widely studied binary alloy which is known to suppress hydrogen embrittlement. Alloying with copper also has the advantage that it reduces the cost

of the membrane by a larger amount than most other metals and through improving the membranes sulphur resistance. The maximum permeability of a palladium copper membrane occurs at the composition $Pd_{60}Cu_{40}$ and this is due to the formation of a bcc lattice rather than the fcc lattice commonly seen in pure palladium and most binary alloys. [44] Temperature cycling has been performed on this alloy composition and it has been found that the bcc crystalline configuration has a higher permeability than the fcc phase. [45] This behaviour is due to the increased number of hcp adsorption sites which hydrogen has a slight preference for.[46] Conversely the fcc structure has a higher impurity resistance than the bcc structure, particularly for H_2S . This has been theorised to be because adsorption of H_2S on a palladium membranes surface is largely controlled by electronic factors.[47] There have been several studies reporting an increased resistance to sulphur poisoning by alloying palladium with copper. A $Pd_{80}Cu_{20}$ membrane exposed to $20 \mu\text{mol mol}^{-1}$ of H_2S for 90 hours results in a 22% drop in flux, performing much better than $Pd_{75}Ag_{25}$ reported in the same paper which became impermeable after 65 hours of exposure in the same conditions.[43] In a similar study, the performance of bcc and fcc alloys in response to H_2S $Pd_{20}Cu_{80}$, $Pd_{40}Cu_{60}$ and $Pd_{53}Cu_{47}$ foils at varying temperatures was tested in hydrogen containing $1000 \mu\text{mol mol}^{-1} H_2S$.[48] It was found that when the alloys were in the fcc phase the reduction in flux was only round 10%, while in the bcc phase the membrane loses around 99% of its permeance. The H_2S concentration required to make a $Pd_{60}Cu_{40}$ membrane completely impermeable was found to be around $300 \mu\text{mol mol}^{-1}$ [49].

PdAu alloys see a slight increase in permeability, up to 30% more than pure Pd, with gold additions up to 20%, after which the permeability rapidly decreases. While alloying with gold does not improve the permeability much compared to silver or copper, gold alloys show greatly improved sulphur resistance. Several studies have been performed which show that PdAu membranes show no permanent permeability loss after exposed to ppm levels of sulphurous compounds implying that permeability decline is only due to H_2S adsorption. It has been reported that a $Pd_{92}Au_8$ membrane exposed to $54.8 \mu\text{mol mol}^{-1}$ of H_2S was able to resist reaction with H_2S and its permeability was completely recoverable. [50]. When tested higher temperatures it was also found that the adsorption effect of H_2S was reduced which is evidence that dissociative adsorption of H_2S on metals is exothermic. [50] In the original patent for palladium membranes by McKinley [51] in 1964 $Pd_{60}Au_{40}$ was found to be the composition which performed best under sulphur containing atmospheres, losing only 9.44% of its flux compared to the 99% and 95% lost by PdAg and PdCu membranes respectively.[51] However under recovery the flux increased to 120% of its original value while the PdCu membrane was fully recovered under the same conditions. This may be evidence that the $Pd_{60}Au_{40}$ membrane used is not completely stable. [51] When comparing the performance of PdCu and PdAu membranes under a number of gases which commonly result from the water gas shift reaction it was found that the PdAu resisted . [52] It was found that from the four membranes tested, the PdAu membranes show no permeability loss under an atmosphere containing CO , CO_2 and H_2O while the PdCu membranes showed considerable permeability loss. [52] The biggest downside to alloying with gold is that due to its high price in recent years alloying palladium with gold drives up the price higher than that

of a pure palladium membrane and is one of the less economic options. [53]

Other metals have been alloyed with palladium although outside of these three metals, studies evaluating the impurity resistance of other binary alloys are rare. The adsorption of CO on Pd₉₂Y₈ membranes under various concentrations has been studied using TDS and XPS and found that CO can react with the Pd-Y allow at 623K, forming YO and solid carbon. [54] Bryden et al studied the poisoning resistance of nanostructured palladium-iron alloys compared to polycrystalline membranes of the same composition. [55] They found that nanostructured membranes not only display higher fluxes, but also exhibit a higher resistance to hydrogen sulphide poisoning. When exposed to ~60 $\mu\text{mol mol}^{-1}$, of H₂S for 2.2 hours there was no permanent reduction in flux. Howard et al studied the performance of PdPt₂₀ membranes under 1000 $\mu\text{mol mol}^{-1}$ H₂S at temperatures between 350°C and 450 °C. [56] The alloy had decent performance on the lower end of the temperature, only losing about 5% of permanent permeability. At higher temperatures the membrane lost around 25% of its permeability, much of this attributed to platinum segregation to the surface of the membrane.[56] The impurity resistance of PdPt membranes has also been studied under common WGS compositions which concluded that small additions of Pt (Between 5-9%) can decrease the flux decline caused by WGS mixtures from 39% for pure Pd, to anywhere between 7%-22%. [56] Platinum however does not appear to be as effective at mitigating the effects of WGS mixtures as alloying with Au which can completely mitigate the flux decline. [57] The use of Pd₉₅Ru₅ membranes in syngas mixtures has been tested in WGS conditions and also showed good resistance to adsorbing compounds, losing only 6% of their flux compared to the 11% lost by a pure Pd membrane under the same conditions.[58]

Ternary alloys are a newly emerging field which aims at utilizing the strengths of a binary alloy while mitigating its weaknesses with another component. Research in this area has mainly focused on ternary alloys based on copper, gold and silver however there are theoretically infinite combinations possible. A Pd₈₀Au₁₀Pt₁₀ membrane manufactured through magnetron sputtering was found to be completely resistant to H₂S poisoning, recovering 100% of its flux prior to exposure to impurity containing gas streams. [59] However after long term testing, the purity of the permeate decreased which implies that pinholes had started to form on the membrane surface. [59] This is most likely due to segregation of the individual components, destabilising the structure. This was not confirmed in the papers analysis however. [59] The most in depth study of PdAgAu membranes under H₂S was performed by Braun et al, who studied the performance of Pd, Pd₉₀Ag₁₀, Pd₇₈Ag₉Au₁₃, Pd₇₅Ag₁₆Au₉, and Pd₉₁Au₉. While all the tested membranes saw a permanent permeability loss under 100 $\mu\text{mol mol}^{-1}$ of H₂S the Pd₉₁Au₉, Pd₇₈Ag₉Au₁₃, and Pd₇₅Ag₁₆Au₉ all resisted bulk corrosion as proven by Energy-dispersive X-ray spectroscopy (EDS), with the Pd₉₁Au₉ sample having the highest resistance to H₂S atmospheres. [60, 61] While this study shows that ternary alloys do offer an increase in impurity resistance over pure Pd and PdAg membranes, the original flux values are not provided so it is difficult to see if there are any inherent advantages over simply using a PdAu alloy. [60, 61] The Materials and Chemistry group at SINTEF have performed the most extensive study into ternary alloys, [62, 63] testing by far the widest range of alloys and using a combination of X-ray Diffraction

(XRD) and X-ray photoelectron spectroscopy to analyse the segregation behaviour of the ternary alloys. [62, 63] Through alloying PdCu alloys with a third transition metal they found that the addition of 1% of a transition metal component always resulted in an increase in permeability, likely due to a phenomenon where the activation energy for hydrogen permeation decreases with increasing fcc lattice constant. [64] In particular the addition of 1% Ta, 1% Y and 14% Ag resulted in an increase in permeability of 10, 45 and 65% respectively when compared with $\text{Pd}_{73}\text{Cu}_{27}$ membranes for Y and Ta, and $\text{Pd}_{65}\text{Cu}_{35}$ membranes for Ag additions. [64] In the follow up paper $\text{Pd}_{75}\text{Ag}_{22}\text{Au}_3$, $\text{Pd}_{76}\text{Ag}_{21}\text{Mo}_3$ and $\text{Pd}_{69}\text{Ag}_{27}\text{Y}_4$ membranes were exposed to $20 \mu\text{mol mol}^{-1}$ of H_2S for 500 hours. The $\text{Pd}_{75}\text{Ag}_{22}\text{Au}_3$ membrane was the only membrane which showed no bulk sulphur formation, with the other two membrane compositions showing large levels of oxidation and segregation when analysed using XPS. [65] The PdAgAu composition has been further studied by Braun et al, [61] who backed up that small additions of Au to PdAg membranes can reduce the membranes reactivity with sulphides and would be suitable for application in a hydrogen impurity enrichment device. Tarditi et al, have done a similar study on the impurity resistance of PdCuAu membranes. [66] While XRD and EDS of this alloy showed no formation of bulk sulphides, the XPS depth profile showed low, but measurable levels of sulphur showing that this composition has some reactivity with impurities. [66]

Table 2.4: Review of palladium alloys and their interactions with impurities

Membrane composition	Support	Susceptability to poisoning compounds				Pressure (bar)	Permeability $molm^{-1}s^{-1}pa^{-\frac{1}{2}}$	Temperature °C	Fabrication technique	Membrane thickness (μm)	Ref	
		Compound concentration	Exposure time	Percentage flux drop	Flux Recovery							
PdAg ₂₃	PSS/Al ₂ O ₃	19.2% CO ₂ , 15.4% H ₂ O, 4% CO, 1.2% CH ₄ 40.5% CO ₂ ,	500h	88.36%	-	990 $cm^3cm^{-2}min^{-1}$	26	2.42×10^{-9}	400	Magnetron Sputtering	2.2	[67]
PdAg ₂₃	PSS/Al ₂ O ₃	25% H ₂ O, 2% CO, 2.5% CH ₄ 60% CO ₂ ,	500h	94.65%	-	990 $cm^3cm^{-2}min^{-1}$	26	2.42×10^{-9}	400	Magnetron Sputtering	2.2	[67]
PdAg ₂₃	PSS/Al ₂ O ₃	25.5% H ₂ O, 2% CO, 2.5% CH ₄	500h	94.65%	-	990 $cm^3cm^{-2}min^{-1}$	26	2.42×10^{-9}	400	Magnetron Sputtering	2.2	[67]
Pd	Self-supported	1000 ppm H ₂ S	6h	90%	-	14 $cm^3cm^{-2}min^{-1}$	3.1	1.2×10^{-8}	350	-	25	[48]
PdCu ₅₃	Self-supported	1000 ppm H ₂ S	6h	90%	-	14 $cm^3cm^{-2}min^{-1}$	3.1	1.3×10^{-8}	350	-	25	[48]
Pd	PSS/Al ₂ O ₃	54.8 ppm H ₂ S	24h	93%	0%	-	2.02	-	400	ELP	10.3	[50]
PdAu ₈	PSS/Al ₂ O ₃	54.8 ppm H ₂ S	24h	85%	54%	-	2.02	-	400	ELP/Electroplating	16	[50]
PdAg ₂₃	PSS	2 ppm H ₂ S	10 minutes	7%	100%	66.7 $cm^3cm^{-2}min^{-1}$	-	1.9×10^{-8}	450	Magnetron Sputtering	10	[68]
PdAg ₂₃	PSS	5 ppm H ₂ S	10 minutes	29%	100%	66.7 $cm^3cm^{-2}min^{-1}$	-	1.9×10^{-8}	450	Magnetron Sputtering	10	[68]
PdAg ₂₃	PSS	2-5-2 ppm H ₂ S	10 minutes at 5ppm	25%	99.4%	51.5 $cm^3cm^{-2}min^{-1}$	-	1.9×10^{-8}	450	Magnetron Sputtering	10	[68]
PdAg ₂₃	PSS	2-6.6-2 ppm H ₂ S	10 minutes at 6.6ppm	25%	36%	51.2 $cm^3cm^{-2}min^{-1}$	-	1.9×10^{-8}	450	Magnetron Sputtering	10	[68]
PdAg ₂₃	PSS	2-10-2 ppm H ₂ S	10 minutes at 10ppm	83%	99.6%	51.2 $cm^3cm^{-2}min^{-1}$	-	1.9×10^{-8}	450	Magnetron Sputtering	10	[68]
PdAg ₂₃	PSS	2-20-2 ppm H ₂ S	10 minutes at 20ppm	85%	100%	51.0 $cm^3cm^{-2}min^{-1}$	-	1.9×10^{-8}	450	Magnetron Sputtering	10	[68]
PdAg ₂₃	PSS	5-20-5 ppm H ₂ S	10 minutes at 6.6ppm	71%	17.99%	18.9 $cm^3cm^{-2}min^{-1}$	-	1.9×10^{-8}	450	Magnetron Sputtering	10	[68]
Pd	PSS/Al ₂ O ₃	111.8% CO ₂ , 5.3% H ₂ O, 14.2% CO, 1.7% CH ₄ 51% N ₂	48h	11%	-	-	0.1	-	350	ELP	6.5	[69]

Pd	PSS/Al ₂ O ₃	11.8% CO ₂ , 5.3% H ₂ O, 14.2% CO, 1.7% CH ₄ 51% N ₂ 120 mg/m ³ tar	24h	66.7%	-	-	0.1	-	350	ELP	6.5	[69]
Pd	PSS/Al ₂ O ₃	11.8% CO ₂ , 5.3% H ₂ O, 14.2% CO, 1.7% CH ₄ 51% N ₂ 240 mg/m ³ tar	24h	100%	-	-	0.1	-	350	ELP	6.5	[69]
PdRu ₅	PSS	11.8% CO ₂ , 5.3% H ₂ O, 14.2% CO, 1.7% CH ₄ 51% N ₂	48h	6%	-	-	0.1	-	350	ELP	7.3	[69]
PdRu ₅	PSS	11.8% CO ₂ , 5.3% H ₂ O, 14.2% CO, 1.7% CH ₄ 51% N ₂ 120 mg/m ³ tar	24h	66.7%	-	-	0.1	-	350	ELP	7.3	[69]
PdRu ₅	PSS	11.8% CO ₂ , 5.3% H ₂ O, 14.2% CO, 1.7% CH ₄ 51% N ₂ 240 mg/m ³ tar	24h	93%	-	-	0.1	-	350	ELP	7.3	[69]
Pd	YSZ	50% NH ₃	75h	0%	-	0.056.0 mol m ⁻² s ⁻¹	2-7	-	400	ELP	1.6	[70]
PdAg ₂₅	PSS	0.5%CO	Until stable	80%	-	-	-	-	400	-	100	[71]
PdAg ₂₅	PSS	0.5%CO	Until stable	4%	-	-	-	-	573	-	100	[71]
PdAg ₂₅	PSS	0.5%CO	Until stable	0%	-	-	-	-	773	-	100	[71]
PdAg ₂₅	PSS	1.5%CO	Until stable	91%	-	-	-	-	400	-	100	[71]
PdAg ₂₅	PSS	1.5%CO	Until stable	7%	-	-	-	-	573	-	100	[71]
PdAg ₂₅	PSS	1.5%CO	Until stable	0%	-	-	-	-	773	-	100	[71]
PdAg ₂₅	PSS	10%CO	Until stable	98%	-	-	-	-	400	-	100	[71]
PdAg ₂₅	PSS	10%CO	Until stable	50%	-	-	-	-	573	-	100	[71]
PdAg ₂₅	PSS	10%CO	Until stable	0%	-	-	-	-	773	-	100	[71]
PdAg ₂₅	PSS	20%CO	Until stable	99.8%	-	-	-	-	400	-	100	[71]
PdAg ₂₅	PSS	20%CO	Until stable	50.5%	-	-	-	-	573	-	100	[71]
PdAg ₂₅	PSS	20%CO	Until stable	0%	-	-	-	-	773	-	100	[71]
Pd	PSS	0.1%H ₂ S	120h	75%	-	8.5cm ³ cm ⁻² min ⁻¹	-	4 × 10 ⁻⁸	350	-	100	[72]
Pd	PSS	0.1%H ₂ S	120h	82%	-	13.5cm ³ cm ⁻² min ⁻¹	-	4 × 10 ⁻⁸	450	-	100	[72]

Pd	PSS	0.1% H ₂ S 12% CO, 12% N ₂	120h	81%	-	27.5 cm ³ cm ⁻² min ⁻¹	-	4 × 10 ⁻⁸	550	-	100	[72]
Pd	PSS	1.6% Steam, 1.6% N ₂	Until stable	22%	-	8.5 cm ³ cm ⁻² min ⁻¹	3	-	380	ELP	10	[73]
Pd	PSS	20 ppm H ₂ S, 40% N ₂	Until stable	17%	-	12.87 cm ³ cm ⁻² min ⁻¹	3	-	380	ELP	10	[73]
Pd	-	10 ppm H ₂ S, 20% N ₂	115h	71.88%	-	-	31	1.5 × 10 ⁻⁸	320	-	100	[43]
PdAg ₂₅	-	20 ppm H ₂ S, 40% N ₂	65h	100%	-	27.5 cm ³ cm ⁻² min ⁻¹	31	1.4 × 10 ⁻⁸	320	-	130	[43]
PdCu ₂₀	-	20 ppm H ₂ S, 40% N ₂	90h	22%	-	-	31	-	320	-	130	[43]
PdCu ₈	PSS	42.7 ppm H ₂ S	2.5h	82%	86.67%	-	2	-	450	ELP	14	[74]
PdAg ₂₇	-	4.4 ppm H ₂ S	48h	99%	67%	3.7 cm ³ cm ⁻² min ⁻¹	5.17	-	350	-	920	[51]
PdCu ₄₀	-	4.5 ppm H ₂ S	72h	95%	100%	2.9 cm ³ cm ⁻² min ⁻¹	5.17	-	350	-	1030	[51]
PdAu ₄₀	-	4.7 ppm H ₂ S	72h	9.4%	120%	0.99 cm ³ cm ⁻² min ⁻¹	5.17	-	350	-	820	[51]
Pd	-	4.7 ppm H ₂ S	96h	70.1%	10%	1.8 cm ³ cm ⁻² min ⁻¹	5.17	-	350	-	900	[51]
PdAu ₄₀	-	20.6 ppm H ₂ S	168h	56.6%	120%	0.99 cm ³ cm ⁻² min ⁻¹	5.17	-	350	-	790	[51]
PdAu ₄₀	-	6.6% H ₂ S	6h	99%	120%	0.99 cm ³ cm ⁻² min ⁻¹	5.17	-	350	-	810	[51]
PdFe ₆	PSS	59.1 ppm H ₂ S	2.2h	75%	100%	8.8 cm ³ cm ⁻² min ⁻¹	1	-	200	Electroplating	10	[55]
PdFe ₆	PSS	59.1 ppm H ₂ S	2.2h	95%	100%	6.4 cm ³ cm ⁻² min ⁻¹	1	-	200	Electroplating	10	[55]
PdFe ₅	PSS	1% CO	4.2h	83.3%	-	5.5 cm ³ cm ⁻² min ⁻¹	1	-	200	Electroplating	18	[55]
PdFe ₅	PSS	1% CO	4.2h	79%	-	3.9 cm ³ cm ⁻² min ⁻¹	1	-	200	Electroplating	18	[55]
PdCu ₄	Accusep	20% CO ₂ , 8% CO	2h	17%	-	5.85 cm ³ cm ⁻² min ⁻¹	1.38	-	350	-	7	[52]
PdAu ₁₃	Accusep	26% CO ₂ , 21% H ₂ O, 2% CO	13h	0%	-	35.56 cm ³ cm ⁻² min ⁻¹	4.96	-	350	-	7	[52]
PdCu ₄	Accusep	50 ppm H ₂ S 26% CO ₂ , 21% H ₂ O, 2% CO	2h	70%	100%	5.85 cm ³ cm ⁻² min ⁻¹	4.96	-	350	-	7	[52]
PdAu ₁₃	Accusep	50 ppm H ₂ S 26% CO ₂ , 21% H ₂ O, 2% CO	2h	0%	-	35.56 cm ³ cm ⁻² min ⁻¹	4.96	-	350	-	7	[52]
PdAu ₁₀	Self-supported	30% CO ₂ , 19% H ₂ O, 1% CO	43h	32%	-	0.28 molm ⁻² s ⁻¹	12.7	-	400	Magnetron Sputtering	-	[59]
PdAu ₁₀	Self-supported	30% CO ₂ , 19% H ₂ O, 1% CO 20ppm H ₂ S	100h	70%	-	0.28 molm ⁻² s ⁻¹	12.7	-	400	Magnetron Sputtering	-	[59]

PdAu ₂₀ Pt ₁₀	Self-supported	30% CO ₂ , 19% H ₂ O, 1% CO	43h	30%	-	0.212 mol m ⁻² s ⁻¹	12.7	-	400	Magnetron Sputtering	-	[59]
PdAu ₂₀ Pt ₁₀	Self-supported	30% CO ₂ , 19% H ₂ O, 1% CO 20 ppm H ₂ S	100h	100%	-	0.28 mol m ⁻² s ⁻¹	12.7	-	400		33	[59]
PdAu _{10.2}	PSS	30% CO ₂ , 19% H ₂ O, 1% CO	350h	36%	-	0.21 mol m ⁻² s ⁻¹	6.27	-	400	Cold working	25	[57]
PdAu _{10.2}	PSS	30% CO ₂ , 19% H ₂ O, 1% CO 20 ppm H ₂ S	350h	72%	-	0.21 mol m ⁻² s ⁻¹	6.27	-	400	Cold working	25	[57]
PdAu ₁₉	PSS	30% CO ₂ , 19% H ₂ O, 1% CO	350h	0%	-	0.25 mol m ⁻² s ⁻¹	6.27	-	400	Cold working	25	[57]
PdAu ₁₉	PSS	30% CO ₂ , 19% H ₂ O, 1% CO 20 ppm H ₂ S	350h	0%	-	0.25 mol m ⁻² s ⁻¹	6.27	-	400	Cold working	25	[57]
PdAu ₇	PSS	30% CO ₂ , 19% H ₂ O, 1% CO	350h	32%	-	0.47 mol m ⁻² s ⁻¹	6.27	-	400	Cold working	11	[57]
PdAu ₇	PSS	30% CO ₂ , 19% H ₂ O, 1% CO 20 ppm H ₂ S	350h	68%	-	0.47 mol m ⁻² s ⁻¹	6.27	-	400	Cold working	11	[57]
PdAu _{10.1}	PSS	30% CO ₂ , 19% H ₂ O, 1% CO	350h	24%	-	0.36 mol m ⁻² s ⁻¹	6.27	-	400	Cold working	31	[57]
PdAu _{10.1}	PSS	30% CO ₂ , 19% H ₂ O, 1% CO 20 ppm H ₂ S	350h	62%	-	0.36 mol m ⁻² s ⁻¹	6.27	-	400	Cold working	31	[57]
PdAg ₁₀	ZrO ₃ /PSS	100 ppm H ₂ S	24h	85%	16%	-	-	1.21×10 ⁻⁸	400	ELP	-	[61]
PdAg ₁₆ Au ₉	ZrO ₃ /PSS	100 ppm H ₂ S	24h	75.7%	33%	-	-	1.65×10 ⁻⁸	400	ELP	-	[61]
PdAg ₉ Au ₁₃	ZrO ₃ /PSS	100 ppm H ₂ S	24h	73%	64.5%	-	-	1.18×10 ⁻⁸	400	ELP	-	[61]
PdAu ₉	ZrO ₃ /PSS	100 ppm H ₂ S	24h	66.67%	81%	-	-	1.34×10 ⁻⁸	400	ELP	-	[61]
PdAg ₂₃	Micro channel stainless steel	10% N ₂ , 20 ppm H ₂ S	1h	97.5%	67.5%	170 cm ³ cm ⁻² min ⁻¹	-	1.3×10 ⁻⁸	450	Magnetron Sputtering	2.2	[63]
PdAg ₂₂ Au ₃	Micro channel stainless steel	10% N ₂ , 20 ppm H ₂ S	1h	87.5%	80%	145 cm ³ cm ⁻² min ⁻¹	-	9.3×10 ⁻⁹	450	Magnetron Sputtering	1.9	[63]

PdAg ₂₇ Y ₄	Micro channel stainless steel	10% N ₂ , 20 ppm H ₂ S	1h	92.5%	65%	140 cm ³ cm ⁻² min ⁻¹	-	1.3×10 ⁻⁸	450	Magnetron Sputtering	2.4	[63]
PdAg ₂₁ Mo ₃	Micro channel stainless steel	10% N ₂ , 20 ppm H ₂ S	1h	97.5%	98%	75 cm ³ cm ⁻² min ⁻¹	-	5.8×10 ⁻⁸	450	Magnetron Sputtering	2.3	[63]
PdAg ₁₁ Mo ₄	Micro channel stainless steel	10% N ₂ , 20 ppm H ₂ S	1h	97.5%	96%	125 cm ³ cm ⁻² min ⁻¹	-	8.8×10 ⁻⁸	450	Magnetron Sputtering	2.2	[63]
PdAg ₂ Au ₁₅	Al ₂ O ₃ /PSS	1000 ppm H ₂ S	30h	-	-	-	-	1.3×10 ⁻⁸	350	ELP	-	[60]
PdAg ₁₄ Au ₁₂	Al ₂ O ₃ /PSS Pd PSS	1000 ppm H ₂ S	30h	-	-	-	-	-	350	ELP	-	[60]
PdCu ₆₅	ZrO ₂ /PSS	Varying	Varying	-	-	-	-	-	450	ELP	10	[49]
PdCu ₇₃	ZrO ₂ /PSS	Varying	Varying	-	-	-	-	-	450	ELP	8	[49]
Pd	ZrO ₂ /PSS	Varying	Varying	-	-	-	-	-	450	ELP	4	[49]
Pd	ZrO ₂ /PSS	Varying	Varying	-	-	-	-	-	450	ELP	3	[49]
PdCu ₃₂	ZrO ₂ /PSS	Varying	Varying	-	-	-	-	-	450	ELP	2	[49]
PdCu ₂₀	ZrO ₂ /PSS	Varying	Varying	-	-	-	-	-	450	ELP	3	[49]
PdCu ₄₀	ZrO ₂ /PSS	Varying	Varying	-	-	-	-	-	450	ELP	15	[49]
PdCu ₄₀	ZrO ₂ /PSS	Varying	Varying	-	-	-	-	-	450	Cast rolled	25	[49]
PdPt ₂₀	Self-supported	1000 ppm H ₂ S	150h	50%	95%	1.85 mLcm ⁻² min ⁻¹	6.2	-	350	Metalurgical	100	[56]
PdPt ₂₀	Self-supported	1000 ppm H ₂ S	125h	80%	75%	2.95 mLcm ⁻² min ⁻¹	6.2	-	400	Metalurgical	100	[56]
PdPt ₂₀	Self-supported	1000 ppm H ₂ S	125h	25%	75%	3.55 mLcm ⁻² min ⁻¹	6.2	-	450	Metalurgical	100	[56]
PdY ₈	-	2-26% CO SO ₂	-	-	-	-	0.06	-	Varying	-	-	[54]
Pd	-	CS ₂ H ₂ S	-	-	-	-	0.07 mBar	-	Varying	-	-	[75]
PdCu ₂₀	Inconel	1000 ppm H ₂ S	-	-	-	-	-	-	Varying	Vacuum arc welding	100	[76]
PdCu ₄₀	Inconel	1000 ppm H ₂ S	-	-	-	-	-	-	Varying	Vacuum arc welding	100	[76]
PdCu ₄₇	Inconel	1000 ppm H ₂ S	-	-	-	-	-	-	Varying	Vacuum arc welding	100	[76]
Pd	PSS	100 ppm H ₂ S	24h	36%	80%	0.0475 molm ⁻² s ⁻¹	0.5	1.2 × 10 ⁻⁸	400	ELP	4	[77]
PdAu ₉	PSS	100 ppm H ₂ S	24h	59%	75%	0.05 molm ⁻² s ⁻¹	0.5	9.9 × 10 ⁻⁹	400	ELP	4	[77]
PdCu ₂₅ Au ₅	PSS	100 ppm H ₂ S	24h	50%	74%	0.01 molm ⁻² s ⁻¹	0.5	1.9 × 10 ⁻⁹	400	ELP	4	[77]
PdCu ₃₇ Au ₃	PSS	100 ppm H ₂ S	24h	54%	70%	0.015 molm ⁻² s ⁻¹	0.5	2.9 × 10 ⁻⁹	400	ELP	4	[77]
PdAu ₂₃	Accusep	20 ppm H ₂ S	96h	29%	97%	1.4 molm ⁻² s ⁻¹	11	1.55 × 10 ⁻⁸	500	ELP	4.8	[78]
PdAu ₂₀ Ag ₁₃	Accusep	20 ppm H ₂ S	96h	50%	89%	0.9 molm ⁻² s ⁻¹	11	1.65 × 10 ⁻⁸	500	ELP	9.3	[78]

Non-palladium

Due to the high cost of palladium there is a particular interest to use alternative materials which still give the high selectivity intrinsic to dense metallic membranes, while reducing the cost, for example, by switching to a cheaper, non-platinum group metal. Non-palladium alloy membranes in the form of amorphous, or crystalline structures generally attract the most research interest.

Crystalline non-palladium membranes are generally based on Group IV based alloys and follow a similar philosophy to the previously discussed palladium membranes. Group IV metals are alloyed with other metals in order to improve their physical properties while maintaining the bcc structure essential for the material to transport hydrogen. Crystalline metals typically have the same advantages and disadvantages as palladium membranes. Recent research activity has focused mainly on studying how the size of the grain boundary affects the permeability of such a membrane, an area which has been mostly neglected in palladium research. [31] This is likely due to the fact that many of these alloys are manufactured through cold work where the grain size can be more easily tailored than in the traditional electroless and sputtering methods used to manufacture palladium membranes. A key aspect of crystalline alloy research is the effect of nano-crystalline structures. Most research in this area has revolved around the addition of small amounts of elements to alloys based on either Zr or Hf to tailor these nano-crystalline structures and study their effects on permeability. Similarly to palladium alloys, dopants are generally chosen based on their effectiveness at suppressing hydride formation, with Zr, Mo, Ru and Rh being popular choices. [79, 80, 81, 82, 83] Alloying in this context would also likely be useful in reducing the membranes interaction with impurities through surface contamination. However this has not been touched upon much in research outside of palladium. The largest drawback to this technology is that crystalline alloys often do not show the catalytic activity necessary for dissociation of hydrogen. This requires an additional coating of palladium to be applied to the surface in order for the material to be viable for hydrogen separation. Interestingly when this was done with some commonly used industrial alloys [84] it was found that they showed reasonable hydrogen permeability which further highlights the importance of catalytic dissociation of hydrogen. Crystalline membranes are also mechanically weak and still susceptible to hydrogen embrittlement through hydride formation in a similar manner to palladium membranes. [31]

On the other hand amorphous metal membranes are generally seen as more attractive than crystalline membranes and are often reported to have greater mechanical strength and hydrogen solubility properties than crystalline structures due to their amorphous structure giving them a more open lattice. Unlike crystalline structures, amorphous metallic membranes can also have high catalytic activity towards hydrogen dissociation which reduces the need for an additional layer to induce this catalytic activity. This property is highly composition dependent and is typically shown by Nickel containing alloys. [85] For example $Zr_{36}Ni_{64}$ in its pure form due to the presence of nickel which is catalytically active for hydrogen dissociation, however when researchers started to dope the material with Ti or Hf, the catalytic properties of the material was drastically

reduced and required a layer of palladium in order to induce permeability.

Amorphous membranes still show some tendency towards hydrogen embrittlement however this is less prevalent than the crystalline alloys previously discussed. This is due to the differences in mechanisms of hydrogen embrittlement between the two classes of materials. Amorphous alloys do not show the α - β phase transition which is the main suspect of embrittlement in crystalline structures [85] and the embrittlement effect is instead due to the filling of free volume within the amorphous structure.

The main disadvantage of amorphous alloys is that given sufficient energy amorphous metallic membranes may crystallise, drastically changing their structure. This has been reported when the material is heated to high temperatures above 500°C. [85] This limits the application of amorphous alloys to low-temperatures however if the material is intended to be used at 300°C, like most palladium membranes, and the material shows a high enough permeability, then this would likely not be an issue.

Judging from the current research landscape on non-palladium membranes, the technology is still in its infancy, with most studies focusing on the fundamental properties of these alloys and with little focus on the practical applications of the technology. Non-palladium dense metal membranes are promising due to the drastic reduction in material cost with, in many cases, an increase in permeability. Of these technologies amorphous membranes appear to be the most appealing, in particular compositions such as Zr₃₆Ni₆₄ which require no precious metals to induce catalytic activity. This has the great advantage of reducing cost of the module and bringing dense metallic membranes, and their high associated selectivity, to a wider market by taking advantage of already established industrial production of amorphous alloys. Further practical research must be performed on these membrane compositions, in particular impurity interactions, thermal stability, and long-term stability to bring this technology to market.

Table 2.5: Hydrogen permeable non-palladium metallic membranes

Membrane composition	Structure	Catalytic coating	Feed pressure	Permeability mol m ² m s	Temperature °C	Membrane thickness (μm)	Ref
(Ni _{0.6} Nb _{0.4}) ₇₀ Zr ₃₀	Amorphous	Pd	7	1.8×10 ⁻⁸	400	40	[86]
(Ni _{0.6} Nb _{0.4}) ₆₀ Zr ₄₀	Amorphous	Pd	7	6×10 ⁻⁹	400	40	[86]
Ni ₆₅ Nb ₂₅ Zr ₁₀	Amorphous	Pd	7	5 ×10 ⁻⁹	400	40	[86]
Ni ₄₅ Nb ₄₅ Zr ₁₀	Amorphous	Pd	7	3 ×10 ⁻⁹	400	40	[86]
Ni ₆₀ Nb ₄₀	Amorphous	Pd	7	2 ×10 ⁻⁹	400	40	[86]
Ni ₄₄ Nb ₄₃ Zr ₁₀ Pd ₃	Amorphous	Pd	7	1×10 ⁻⁹	400	40	[86]
Zr ₃₆ Ni ₆₄	Amorphous	None	1	1.2×10 ⁻⁹	350	30	[87]
(Ni _{0.6} Nb _{0.4}) ₄₅ Zr ₅₀ Al ₅	Amorphous	Pd	3	1.9 ×10 ⁻⁸	400	50	[88]
(Ni _{0.6} Nb _{0.4}) ₄₅ Zr ₅₀ Co ₅	Amorphous	Pd	3	2.46 ×10 ⁻⁸	400	50	[88]
(Ni _{0.6} Nb _{0.4}) ₄₅ Zr ₅₀ Cu ₅	Amorphous	Pd	3	2.34 ×10 ⁻⁸	400	50	[88]
(Ni _{0.6} Nb _{0.4}) ₄₅ Zr ₅₀ Pd ₅	Amorphous	Pd	3	1.36 ×10 ⁻⁸	400	50	[88]
V ₈₅ Ni ₁₅	Crystalline	Pd	0.8	5 ×10 ⁻⁸	300	300-400	[89]
V ₉₅ Ni ₁₅	Crystalline	Pd	0.1-2.0	4 ×10 ⁻⁷	400	2000	[90]
V ₈₅ Ni _{14.91} Al _{0.09}	Crystalline	Pd	0.1-2.0	4.5 ×10 ⁻⁷	400	2000	[90]
V ₈₅ Ni _{14.1} Al _{0.9}	Crystalline	Pd	0.1-2.0	4.5 ×10 ⁻⁷	400	2000	[90]
V ₈₅ Ni _{12.4} Al _{2.6}	Crystalline	Pd	0.1-2.0	6 ×10 ⁻⁷	400	2000	[90]
V ₈₅ Ni _{10.5} Al _{4.5}	Crystalline	Pd	0.1-2.0	7 ×10 ⁻⁷	400	2000	[90]
V ₉₀ Al ₁₀	Crystalline	Pd	0.2 – 2.0	2 ×10 ⁻⁷	900	800-2300	[91]
V ₇₀ Al ₃₀	Crystalline	Pd	0.2 – 2.0	1.8 ×10 ⁻⁹	700	800-2300	[91]
INCOLOY903	Crystalline	Pd	1	1.33 ×10 ⁻⁷	430	200	[84]

WASPALOY	Crystalline	Pd	1	2.99×10^{-7}	430	200	[84]
JBK-75	Crystalline	Pd	1	4.36×10^{-7}	430	200	[84]
GH85A	Crystalline	Pd	1	2.73×10^{-7}	430	200	[84]
INCOLOY907	Crystalline	Pd	1	9.67×10^{-8}	430	200	[84]
INCONEL718	Crystalline	Pd	1	2.22×10^{-7}	430	200	[84]
GH761	Crystalline	Pd	1	1.5×10^{-7}	430	200	[84]
<i>Nb₂₀Zr₃₅Ni₃₅</i>	Crystalline	Pd	1	2.73×10^{-8}	400	500-700	[92]
<i>Nb₁₀Zr₄₅Ni₄₅</i>	Crystalline	Pd	1	2.5×10^{-8}	400	500-700	[92]
<i>Nb₂₉Ti₃₁Ni₄₀</i>	Crystalline	Pd	2	7×10^{-9}	400	550-750	[93]
Nb17Ti42Ni41	Crystalline	Pd	2	0.6×10^{-8}	400	550-750	[93]
Nb10Ti50Ni40	Crystalline	Pd	2	4.5×10^{-9}	400	550-750	[93]
Nb39Ti31Ni30	Crystalline	Pd	2	2.0×10^{-8}	400	550-750	[93]
Nb28Ti42Ni30	Crystalline	Pd	2	1×10^{-8}	400	550-750	[93]
Nb21Ti50Ni29	Crystalline	Pd	2	1×10^{-8}	400	550-750	[93]
<i>Ta₉₅W₅</i>	Crystalline	None	1.4	$52 \text{ mol m}^{-2} \text{s}^{-1}$	500	650	[94]

Dense Ceramic

Dense ceramic membranes operate in a similar manner to metallic membranes, with the key difference being that they are made from ion conducting ceramics rather than metals. Dense ceramic membranes have a selectivity comparable to dense metal membranes since they only allow hydrogen to permeate, however at a lower cost than Pd-based membranes. Unlike dense metallic membranes, most ion conducting materials claim to be intrinsically inert to common hydrogen impurities and hence are stable in CO, CO₂ and H₂S containing atmospheres. [31] The major drawback to ion conducting ceramic membranes is that generally high temperatures are required to achieve any form of H₂ flux. While palladium membranes can achieve a high flux at temperatures between 300-400°C, most Perovskite membranes require temperatures between 700-900°C and generally only achieve a hydrogen permeability <10% compared to a palladium membrane of the same thickness.

The hydrogen separation process in a dense ceramic membrane is near identical to that which occurs in a dense metal membrane with the main driving forces being the pressure and concentration gradients. This is primarily controlled by the catalytic surface effects and bulk diffusion rather than thickness due to ceramic materials intrinsically low catalytic activity for such a process. For practical purposes both sides of the membrane should have sufficient catalytic activity to dissociate hydrogen atoms and the bulk should have high enough proton and electron conductivities to ensure a reasonably high flux can be achieved. More information on the precise mechanism behind proton conducting membranes can be found in the following reviews [95, 96]. The bulk diffusion of a dense ceramic membrane can be described through the Wagner equation written as Eq 2.21

$$J_{H_2} = \frac{RT}{4F^2L} \frac{\theta_H\theta_e}{\theta_H + \theta_e} \ln \left(\frac{P'_{H_2}}{P''_{H_2}} \right) \quad (2.21)$$

Dense ceramic membranes can be split into two broad categories; single phase ceramic membranes are composed of a single material which has the ability to conduct both protons and electrons, and multi-phase ceramic membranes which are normally composed of two or more phases which when combined show proton and electron conductivity. The most common type of multi-phase ceramic membranes is known as ‘cermet’ which combines a proton conducting ceramic and a metal, such as palladium or nickel, as the electron conducting phase.

Single phase ceramic membranes must be given proton conductivity by doping a single phase ceramic material (typically perovskite) in order to create a proton hole within the material. This combined with catalytic dissociation of hydrogen on the surface allows uptake of a certain number of protons, which then diffuse through the material using the proton holes within the material. [95, 96]

Extensive efforts have been placed into developing proton-electron conducting ceramic materials for hydrogen separation however there are still many technical hurdles which must be overcome before the technology can be applied on a useful scale. The

main problem holding back the technology is the incredibly low flux values reported despite operating at such high temperatures. Until this is solved there will be no point in using the technology over faster porous materials, or even dense metal membranes which offer the same selectivity's, at much faster permeation rates. This stems back to a lack of understanding behind the surface kinetics of hydrogen dissociation (which is also an issue for non-palladium dense membranes). Despite claims that ceramic membranes are inert to impurities there is contradictory evidence showing that the materials cannot withstand acidic conditions and degrade under atmospheres containing CO₂ and H²S. Finally, since such high temperatures are required there will be difficulties forming a hermetic seal with ceramic membranes which can withstand the high temperature environments. This is already an issue with ceramic supported metallic membranes which operate at much more mild conditions.

From this it can be concluded that dense ceramic membranes for hydrogen separation are still at a research level and a better understanding of the material science behind the surface interactions with hydrogen and other gases, along with research into new classes of ceramics which can either permeate hydrogen at faster rates, at lower temperatures, or both are key to bringing this technology to market.

Table 2.6: Hydrogen permeable ceramic and cermet membranes which show resistance to common hydrogen impurities

Material	Class	Feed	Temperature °C	Flux	Thickness (μm)	Stability	Notes	Ref
$SrCe_{0.75}Zr_{0.2}Tm_{0.05}O_{3-\alpha}$	Perovskite	100 mLmin ⁻¹ 50% H ₂ + He	900	0.042 mLcm ⁻² min ⁻¹	1200	-	-	[97]
$Nd_{5.5}WO_{12-\alpha}$	Lanthanide tungstate	80% He + 20 % H ₂	1000	0	900	Stable under 115 ppm H ₂ S, 4.43% CO ₂ , 2.12% CO	No flux due to dry conditions	[98]
$La_{5.5}WO_{11.25}$	Lanthanide tungstate	80% He + 20 % H ₂	1000	< 0.005 mLmin ⁻¹ cm ⁻²	900	Stable in 15% CO ₂ for 3 days	Requires humidification for faster permeation	[99]
Nd_6Wo_{12}	Lanthanide tungstate	He + H ₂	1000	0.012 mLmin ⁻¹ cm ⁻²	510	Stable in CO ₂ and CH ₄ after 3 days	Humidified atmosphere	[100]
$La_{5.5}W_{0.8}Re_{0.2}O_{11.25-\alpha}$	Lanthanide tungstate	2.5% H ₂ , 2.5% H ₂ O, H ₂ balance	1000	0.095 mLmin ⁻¹ cm ⁻²	760	Stable in 5% CO ₂ 1000 ppm COS 100 ppm HCN 46% CO 46% H ₂ at 35 bar	Humidified atmosphere	[101]
$(La_{5/6}Nd_{1/6})_{5.5}WO_{12-\alpha}$	Lanthanide tungstate	80% He + 20 %H ₂	1000	0.005 mLmin ⁻¹ cm ⁻²	900	Stable in 15% CO ₂ for 3 days	Requires humidification	[102]
$La_{27}Mo_{1.5}W_{3.5}O_{55.5}$	Lanthanide tungstate	10% H ₂ 90% He	700	0.78×10^4 mLmin ⁻¹ cm ⁻²	650	-	-	[103]
$La_{27}Mo_{1.5}W_{3.5}O_{55.5}$	Lanthanide tungstate	10% H ₂ 90% He	700	0.78×10^4 mLmin ⁻¹ cm ⁻²	650	-	-	[103]
$Nd_{5.5}W_{0.5}Mo_{0.5}O_{11.25-\alpha}$	Lanthanide tungstate	50% H ₂ , 50% He	1000	0.235 mLcm ⁻² min ⁻¹	900	Stable in environments containing 330 ppm H ₂ S and 22% H ₂ in N ₂ . 480 ppm H ₂ S and 32% H ₂ in N ₂ . 705 ppm H ₂ S and 47% H ₂ in N ₂ 1500 ppm H ₂ S and H ₂ .	Values for humidified atmosphere. Stabilised flux value after 3 sets of tests Flux reduction due to Mo reduction	[104]
$Ni - Ba(Zr_{0.7}Pr_{0.1}Y0.2)O_{3-\alpha}$	Cermet	40% H ₂ , 57% N2, 3% H ₂ O	900	1.36×10^8 molcm ⁻² s ⁻¹	400	Stable under 30% CO ₂	Maximum value achieved for humid atmosphere	[105]
$Ni - Ba(Zr_{0.1}Ce_{0.7}Y_{0.2})O_{3-\alpha}$	Cermet	20% H ₂ , 77% N2, 3% H ₂ O	900	1.37×10^{-7} molcm ⁻² s ⁻¹	30	-	Maximum value achieved for humid atmosphere	[106]
$La_{27}W_5O_{55.5} - LaCrO_3$	Dual phase ceramic	50% H ₂ (humid)	700	0.384×10^{-3} mLcm ⁻² min ⁻¹	1210	-	Pt coating	[107]
$La_{5.5}WO_{11.25-\alpha} - La_{0.87}Sr_{0.13}CrO_{3-\alpha}$	Dual phase ceramic	50% H ₂ , 2.5%H ₂ O	700	0.15 mLcm ⁻² min ⁻¹	360	Stable in 15% CO ₂ after 24 hours.	No dry atmosphere testing	[108]
$Ni - La_{0.5}Ce_{0.5}O_{2-\alpha}$	Cermet	20% H ₂ , 80% N2	900	5.64×10^{-8} molcm ⁻² s ⁻¹	48	Stable in CO ₂	Flux increased in humidified conditions	[109]
$Ni - Ca_{0.0125}La_{0.4875}Ce_{0.5}O_{2-\alpha}$	Cermet	20% H ₂ , 77% N2, 3%H ₂ O	900	1.88×10^{-8} molcm ⁻² s ⁻¹	600	Stable in CO ₂	No dry atmosphere testing	[110]
$Ni - La_{0.5}Ce_{0.5}O_{2-\alpha}$	Cermet	20% H ₂ , 80% N2	900	1.57×10^{-8} molcm ⁻² s ⁻¹	600	Stable in CO ₂	No dry atmosphere testing	[110]

$Ni - La_{0.5}Ce_{0.5}O_{2-\alpha}$	Cermet	20% H ₂ , 80% N2	900	$2.87 \times 10^{-8} molcm^{-2}s^{-1}$	600	-	No dry atmosphere testing	[111]
$BaZr_{0.8}Y_{0.15}Mn_{0.05}O_{3-\alpha}$	Perovskite	50% H ₂ , 50% He	1000	$0.01 - 0.03 mLcm^{-2}min^{-1}$	900	-	No dry atmosphere, Pt coated	[102]
$SrCe_{0.75}Zr_{0.2}Tm_{0.05}O_{3-\alpha}$	Perovskite	10% H ₂ , 90% He	900	$0.025 mL(STP)cm^{-2}min^{-1}$	1600	Stable in 20% CO ₂ and 11.3% CO	-	[112]
$SrCe_{0.75}Zr_{0.2}Eu_{0.1}O_{3-\alpha}$	Perovskite	100% H ₂	900	$0.35 cm^3 cm^{-2}min^{-1}$	17	-	Flux improves in humid atmospheres	[113]
$Ni - BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-\alpha}$	Cermet	100% H ₂	700	$0.49 mLcm^{-2}min^{-1}$	44	-	-	[114]
$Ni - BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-\alpha}$	Cermet	100% H ₂	900	$1.12 mLcm^{-2}min^{-1}$	44	-	-	234
$BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-\alpha}$	Perovskite	50% H ₂ 50% He	1000	$0.422 molcm^{-2}s^{-1}$	-	-	Hollow fibre	[114]
$BaCe_{0.85}Tb_{0.05}Co_{0.1}O_{3-\alpha}$	Perovskite	50% H ₂ 50% He	1000	$0.385 mLcm^{-2}min^{-1}$	167	Unstable in H ₂	Hollow fibre. Also shows oxygen permeability	[115]
$Ni - BaCe_{0.7}Y_{0.1}Yb_{0.1}Zr_{0.1}O_{3-\alpha}$	Cermet	20% H ₂ , 20% CO ₂ , 60% N2	1000	$5.5 \times 10^{-8} molcm^{-2}s^{-1}$	44	Unstable in H ₂	Shows reverse WGS catalytic activity, Stable in 60% CO ₂ . CO causes Ni corrosion	[116, 117]
$BaCe_{0.8}Y_{0.2}O_{3-\alpha}$	Perovskite	25% H ₂ 75% He	1050	$0.38 mLcm^{-2}min^{-1}$	1000	Unstable in humid environments and CO ₂	Hollow Fibre	[118]
$La_{28-x}W_{4+x}O_{54+3x/2}(La = W \times 5.6)$	Lanthanum tungstate	10% H ₂ 90% Ar	925	$0.08 NmLcm^{-2}min^{-1}$	30	-	-	[119]
$La_{0.87}Sr_{0.13}CrO_{3-\alpha}$	Lanthanum tungstate	10% H ₂ , 2.5% H ₂ O 87.5% Ar	1000	$10 \times 10^{-4} mLcm^{-2}min^{-1}$	550	Chemically stable under tested conditions	-	[120]
$BaCe_{0.85}Tb_{0.05}Co_{0.1}O_{3-\alpha}$	Perovskite	50% H ₂ , 50% He	700-1000	$0.009 - 0.164 mL(STP)cm^{-2}min^{-1}$	132	-	Hollow fibre	[121]
$BaCe_{0.85}Tb_{0.05}Co_{0.1}O_{3-\alpha}$	Perovskite	50% H ₂ , 50% He	700-1000	$0.018 - 0.269 mL(STP)cm^{-2}min^{-1}$	132	-	Hollow fibre, Ni Coating	[121]
$BaCe_{0.85}Tb_{0.05}Co_{0.1}O_{3-\alpha}$	Perovskite	50% H ₂ , 50% He	700-1000	$0.1 - 0.42 mL(STP)cm^{-2}min^{-1}$	132	-	Hollow fibre, Pd Coating	[121]
$BaCe_{0.95}Tb_{0.05}O_{3-\alpha}$	Perovskite	50% H ₂ , 50% He	900	$0.272 mLcm^{-2}min^{-1}$	100	-	Hollow fibre, Pd Coating	[122]

Viable membrane materials and outlook

While ceramic membranes provide a viable alternative to metallic membranes as an impurity enrichment material, the technology is still in its infancy and the membranes do not show suitable permeabilities to perform impurity enrichment in a reasonable time frame. While many studies on these materials also claim that impurity resistance of these materials outclasses metallic membranes, there is little backing up these claims.

Of the membranes discussed, metallic membranes are the most suitable for hydrogen impurity enrichment. Palladium membranes are the only current material that has successfully been used for hydrogen impurity enrichment however there is still room for improvement which will be discussed in the following section. Non-palladium dense metallic membranes for hydrogen impurity enrichment are the next logical step in development of these membranes for analytical purposes due to their lower costs however more practical research on the materials must first be performed.

2.5.2 Membrane manufacture

Dense metal membranes can either be supported or unsupported. Unsupported membranes are free standing structures, which usually feature high wall thicknesses in order to achieve the required mechanical strength to withstand use in a process. As a result of this the flux seen through these membranes is typically low due to the high transport resistance of the membrane. Self-supported membranes are also typically expensive due to the large amount of materials required. [31]

A more efficient method is to use a support structure to allow a thinner membrane layer to be deposited, while achieving the mechanical strength required by use of another, cheaper material. This allows thinner membranes to be deposited, thereby increasing the achievable flux, and greatly reducing the cost of such a membrane.[31] Because of these clear advantages this thesis will explore the use of self-supported membranes.

Support selection

When selecting a support material there are a number of considerations which should be taken into account prior to deposition:

- Pore size distribution: If the supporting materials pore size distribution is too small then it will provide an added transfer resistance to permeation. The minimum thickness of a membrane deposited on a porous support has been found to be 3x the size of the smallest pore, [123] meaning there is a trade off between these two values
- Support surface: Adhesion of the deposited membrane to the surface of the support is compromised if the support is too smooth
- Thermal stability: The thermal stability of a support material is defined by the melting temperature, coefficient of thermal expansion (CTE) and intermetallic diffusion potential. If the CTE difference between the deposited membrane and

the support is too large it will lead to a difference in the expansion rate which eventually leads to membrane failure. Intermetallic diffusion is defined as the migration of atoms between the membrane and the substrate which can negatively affect its permeability and lead to membrane failure in extreme cases

- Mechanical Stability
- Chemical stability

Of the materials available for use as a support; ceramics, porous stainless steel, and porous glass have been the most widely studied.

Glass

Porous glass supports are generally amorphous solids which feature pores ranging in sizes between the nanometre to micrometre range. They are commonly created through sol-gel synthesis, through metastable phase separation of borosilicate glasses, or by sintering glass powder. Porous glass supports have high thermal stability, and a narrow pore size distribution typically between 4-5 nm [124] [125], theoretically allowing membrane thicknesses of 8-10 nm to be achieved. [123] Despite this they are extremely brittle and highly susceptible to acidic, alkaline or in the presence of metallic solutions. This limits their use in a number of common membrane manufacturing methods.

They are however extremely brittle and are highly susceptible to degradation under acidic, alkaline, or under metallic solutions which limits their use in a number of common membrane synthesis methods. [126]

Porous Stainless Steel (PSS)

Porous stainless steel is widely available in a large number of geometries and mainly see commercial use in a number of filtering applications. A membrane layer can be deposited on top of PSS in order to gain such properties as the high mechanical strength of PSS. PSS also features a similar CTE to palladium which limits the likelihood of membrane failure due to difference in expansion rate. They are however an expensive option, with 70% of the cost in such systems being attributed to the PSS support.

The main problem with using PSS supports revolves around operation during hydrogen separation. Since both the support material, and the membrane materials are metals, at temperatures above 275°C intermetallic diffusion will occur. Intermetallic diffusion is when molecules from the stainless steel support diffuse into the membrane layer and vice versa. The result is a drastic decrease in permeability, and potential compromise of membrane integrity due to the lattice structure of the membrane being changed. A common method for mitigating this effect is to modify the surface of the PSS support with an intermediate layer that is not susceptible to intermetallic diffusion. Common intermetallic diffusion barrier are zirconia, porous silica, and porous Pd-Ag. [34] It is also possible to create an oxide layer on the surface of the PSS support by heating the material to 80°C which achieves the same result. While these methods

are effective at mitigating the effects of intermetallic diffusion; they instead introduce a different problem where, in particular with some ceramic intermetallic diffusion layers, there is a difference in CTE between the material and support. Many of the intermetallic diffusion materials can also be made into supports on their own, at a much lower cost than PSS so it also opens the question of if these materials can be made into satisfactory supports on their own, why bother adding them to costly PSS supports.

Ceramic

Ceramic supports generally consist of porous ceramics manufactured through sintering of ceramic powders. They are a good candidate for supporting metallic membranes due to their uniform pore size distribution (0.1-10 μm) and their high chemical, thermal and mechanical stabilities.

While the materials and processes for manufacturing ceramic supports are cheaper, the overall manufacturing process requires more steps which increases the overall time required. The resulting membranes are also extremely brittle and can easily be damaged during handling.

Al_2O_3 has traditionally been the ceramic support of choice for palladium membranes however in recent years YSZ has become more popular. This is due to the increased mechanical stability of YSZ [127], and the fact that at higher temperatures aluminium can intrude into the active layer from the support through a mechanism similar to intermetallic diffusion.[34] Using ceramic supports solves the problem of intermetallic diffusion with the drawback of increasing the likelihood of delamination occurring due to different CTE values. Ceramic supports also have the advantage of being much cheaper to manufacture the metallic supports. [34]

Membrane deposition methods

There are various methods which can be used to deposit dense metal membranes onto the surface of a support can be carried through a wide number of chemical processes. From our reviews performed in sections 2.5.1 and 2.5.1 the most commonly used methods for deposition of dense metal membranes are PVD (e.g. magnetron sputtering) and ELP. Other methods including such as chemical vapour deposition (CVD) [128, 129, 130], electroplating deposition, atmospheric plasma [131] and spray pyrolysis [132] exist, however they have been omitted due to the inconsistency in final material, unreliability of the method, or cost. Additionally methods used to manufacture self-supporting membranes will not be discussed.

Chemical vapour deposition (CVD)

CVD involves the thermal composition of one or more metal complexes with a high volatility and subsequent deposition through nucleation and on a surface. Commonly used precursor materials are metal carbonyls or organometallic compoints. The method is known for it's ability to reliably deposit thin dense membrane layers typically (<2

μm). The method is held back by its high material costs and the expensive operating conditions required.[128, 133]

Physical vapour deposition (PVD)

PVD is a coating method in which a solid material, usually a pure metal, is vaporized in a vacuum system in the presence of an inert gas. The generated atoms migrate in all directions and condensate when coming in contact with a lower temperature substrate, forming a metallic film. PVD involves using the desired membrane material as a 'target', and a 'coating surface' which in the case of membrane fabrication is the support. [134] The target is bombarded with ions or neutral particles which atomise the material. The inert gas, normally argon, is introduced to the sputtering chamber. The sputtering gas is ionized with a positive charge, while the target is subjected to a negative voltage typically around the magnitude of -300V. This potential difference causes the positively charged ions to impact the surface of the target, as this occurs atoms of the target material are removed and are intended to land on the substrate with enough energy to form a thin, dense, and strongly attached film. Magnetrons are commonly employed in sputtering which use magnetic fields to confine the charged plasma particles as close to the target as possible, which increases the sputter yield.

PVD in the form of Magnetron Sputtering is already an industrially widespread deposition method and is used to deposit metallic films for several applications and products. [134] The method can be used to deposit any metal or alloy. This technique can produce extremely thin nanostructured membrane layers while allowing the alloy composition to be accurately controlled and minimising the presence of impurities. [135, 136] However this method can prove to be expensive and complicated when looking to achieve defect free membranes. [137] The quality of the support is also a limiting factor with this fabrication method, the substrate must be extremely smooth in order for the film to properly adhere to the surface. In addition to this some problems arise due to the small grain sizes created by this technique which can cause grain growth and phase transitions at temperatures as low as 200°C. [138]

Electroplating deposition

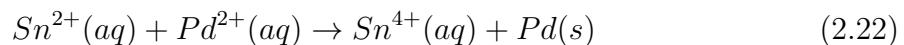
EDP is a simple coating process where a thin metal layer is deposited on a substrate by the reduction of metal ions in solution. An electrical potential promotes the transport of the ions through the plating bath onto the desired support material which acts as a cathode. The thickness of the membrane is normally controlled by the electroplating time and the composition of the plating solution. The electrochemical process is simple and only involves simple and low-cost equipment. However, the support must be conductive, which greatly limits your choice. [128, 31].

Electroless Plating (ELP)

ELP is an autocatalytic deposition method in which a surface is coated with a metallic film through a two step process. The first step, normally referred to as the activation

step, involves preparing the surface by depositing small amounts of a metal with an equal to or higher electropositivity than the metal you desire onto the surface of the support material. Palladium is commonly used as the seeding material since it has the highest electropositivity of metals capable of being deposited through ELP and hence can be used to catalyse the deposition of any other metallic species. [139] The second step is metallization where the reduction/oxidation reactions occur, catalysed by the deposited seeds and initiated by a reducing agent added to the plating bath.

The activation step is required for all non conductive support materials (i.e. ceramics, glass) otherwise the chemical activity of support will be too low and plating will likely be inefficient or will fail. The most common method used is the stannum route which involves immersing the desired support in an acidic solution of SnCl_2 , and subsequent immersion in a solution of the desired seeding metal in the form of a salt (chloride, nitride). The Sn^{2+} ions are adsorbed on the surface of the substrate in a hydrolytic form. The Sn^{2+} ions are then oxidised and replaced with Pd seeds. [139] The process for seeding a support with palladium is shown in equation 2.22 [139].



The metallization or plating step involves placing the activated support material in a bath of a solution containing a metal source, such as a metallic salt, a complexion agent which stabilizes the metallic ions in the solution, and a stabilizing agent which regulates the pH of the plating bath. The bath is heated to the desired plating conditions before addition of a reducing agent which releases electrons and initiates the reaction. As the reaction proceeds metal is continuously deposited on the seed material, growing until eventually a dense, homogenous layer is formed.

Only a select number of metals can be deposited through electroless plating, these are shown in figure 2.7. [139] These metals can be deposited through electroless plating since they have a high reduction activity. While this is commonly seen as a disadvantage, in practice many of the metals were discussed in section 2.5.1 as having advantageous effects on the final membrane, and therefore is not as much of a hindrance as often reported. [139] This method also has the advantages of being extremely cheap, easy to perform, can be used to deposit on practically any geometry imaginable, and easily scalable. Due to the nature of this deposition method it is difficult to control the deposition rate and hence the thickness of the membrane deposited. This becomes an even larger problem when plating alloys as the final composition can be difficult to control has a large effect on the properties of the final membrane. Due to the nature of this deposition method the membranes are also susceptible to impurities which may have been present in the plating solutions or entered the solution in other means.

Figure 2.7: Metals which can be deposited using electro less plating [139]

There are two reported ways of creating palladium alloys through electroless plating; co-plating, and sequential plating. Co-plating has only been reported for Pd-Ag alloys since both palladium and silver have the same reducing agent.[140, 125] Co-plating may seem like the optimal manufacturing method since it cuts down on the number of steps required it is generally unsuitable for membrane production since the silver content of the bath must be lowered to at least 7% in order to prevent dendritical growth, and even then it is difficult to achieve a defect free layer while maintaining plating bath stability. [139]

Sequential plating involves plating layers on top of each other and forming the alloy in a subsequent step. For example if a Pd-Ag membrane is desired a palladium layer would first be plated followed by a silver layer. [139] The membrane would then be annealed under a high temperature in order to achieve a homogeneous alloy.

2.6 Density functional theory for screening of membrane alloy compositions

Density functional theory (DFT) is a computational quantum mechanical modelling method which is used to investigate the electronic structure of many body systems, in particular that of atoms, molecules and condensed phases. The method operates by providing an approximate solution to the Schrödinger equation of many body systems. This allows for prediction and calculation of material behaviour based purely on quantum mechanics, eliminating the need for fundamental material properties or experimental data. DFT techniques evaluate the electronic structure of a system by assuming a potential is acting on each of the systems electrons.

DFT-based methods prove to be useful in applications where a large number of elements and compositions must be investigated to optimize the desired material. For our application DFT calculations can be theoretically used to investigate, and quickly screen the suitability of any atomic configuration in the periodic table in combination with any of the ISO 14687-2 impurities. Much of the work in DFT screening of palladium membranes has been performed by the group of David S. Scholl who have suggested 5 criteria to ensure the application of DFT to the field of palladium membranes are performed in an optimal manner.[141], [142] These five criteria are:

1. The timescale and/or cost for predictions made using DFT should be shorter than it would take to perform the same tests experimentally
2. There should be minimal input from experimental data
3. Predictions must be made on properties relevant to the end-use application
4. Quantitative data should be sufficient to make confident judgements on whether a material is promising or unpromising
5. The drawbacks and assumptions associated with DFT should be clearly stated to allow judgement on the predictions impact on real-world situations

This section will provide a brief overview into DFT. This will include the key concepts required to perform DFT, different assumptions which can be made along with their advantages and disadvantages, and how these relate to our chosen application, screening of metal alloy membranes. Previous work relating to the use of DFT to predict the performance of palladium alloy membranes will be discussed and finally we will tie our planned work back to Scholl's criteria.

2.6.1 Key concepts

Simulating crystalline structures

DFT is focused on applying calculations to arrangements of atoms that are periodic in space. DFT calculations achieve this by defining the shape of the 'cell' which will be repeated periodically in space. [143]

In crystalline solids, which this thesis will focus on, the atoms are arranged in a periodic fashion which repeats after a certain length. In order to explain the crystal structure in this manner a concept called 'reciprocal space' or 'k space' is used. Using this concept planes can be defined as having coordinates within a crystal lattice. These coordinates are referred to as k-points and allow for the structure of a system to be calculated and therefore solved to its lowest energy state. [143]

The most effective and widespread solution was developed by Monkhorst and Pack which is implemented into most DFT packages, allowing users to simply define the number of k-points in each direction of reciprocal space. Frequently the same number of k-points are used in each direction. [144]

The number of k-points used is important to the accuracy of the performed calculation, however higher k-points involve a larger number of calculations across the supercell in reciprocal space and therefore will result in higher calculation times for the whole system. [144] Convergence is often used to find the optimal number of k-points. This concept is visualised in figure 2.8

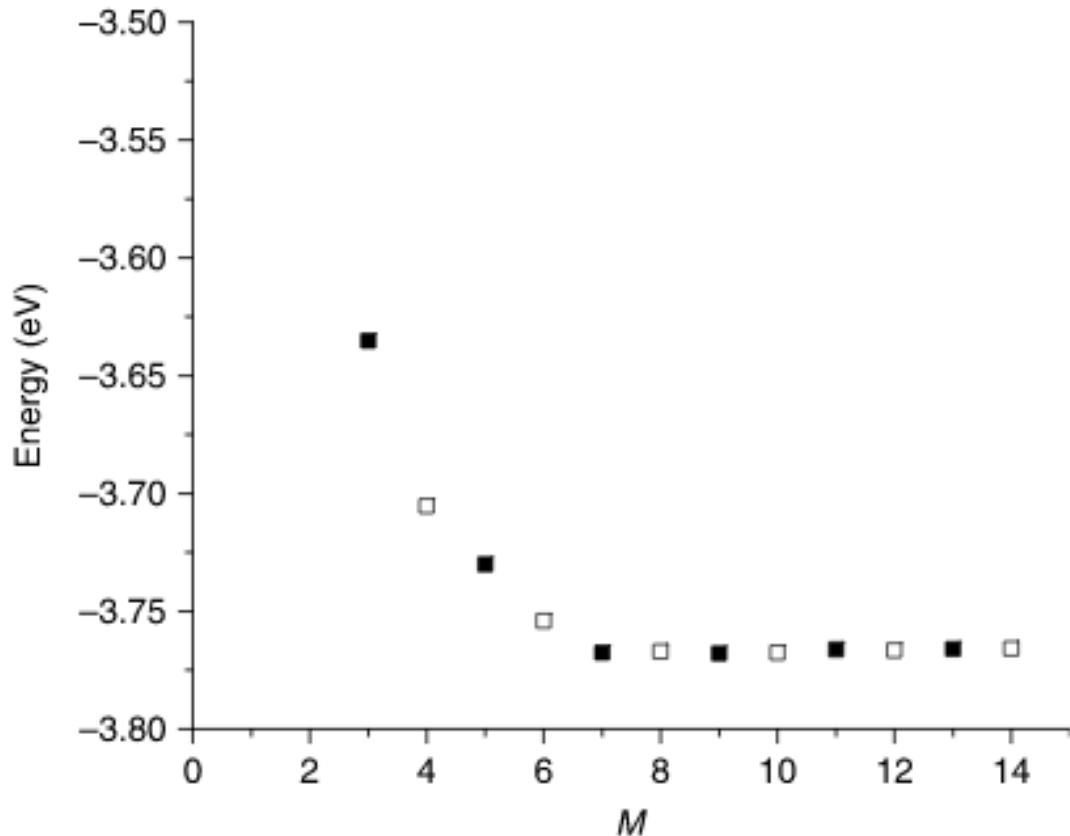


Figure 2.8: Total energies (per atom) for bulk Cu calculated as a function of M for calculations using $M \times M \times M$ kpoints [144]

At lower numbers of k-points the total energy of the system is dependent on the number of k-points used. This value eventually converges and at $M > 8$ k-points becomes completely independent of the number of k-points used. This should be kept in mind when optimising the output values for any simulated system. K-points can be thought of as sampling points within a defined supercell. [143]

Defining the supercell which will be repeated in periodic space is a simple process and involves defining the volume for the supercell, along with the number, and position of the atoms residing within.

Metals are a special case in DFT and require the use of special algorithms to ensure that the energy state of a metallic system can be calculated without a high number of k-values. The two best methods for doing this are the tetrahedron method, or smearing.

The tetrahedron method involves defining a tetrahedron using a discrete set of k-points. This tetrahedron fills the reciprocal space and can be integrated to form at all points in the k space and evaluated. [143]

Smearing involves forcing the function to be continuously integrated to replace any step functions with a smoother function. Ideally the result of the calculation should be a result which can be extrapolated to the limit where smearing is eliminated. [143]

When simulating a membrane often a slab geometry is used in order to avoid 'edge effects' where simulation results are skewed because of unique surface boundaries resulting from being at the edge of a supercell. The geometry of such a model is achieved through the generation of a box containing a multilayer atomic slab representing the membrane material with a vacuum layer in the remaining volume. From literature palladium membranes are normally in the fcc material phase [145] (with the exception being Pd₄₀Cu₆₀ which is in the bcc phase). It is common to represent this using 3-5 atomic layers of palladium. To create alloys random atoms can be substituted for other elements to achieve the desired alloy composition.

In order to determine the adsorption energy of impurities on a palladium membrane using DFT both the slab being used to represent the membrane surface, and the individual gas molecule must first be simulated in order to determine their individual ground energy states. Then the gas molecule must be adsorbed onto the surface of the membrane. In a crystalline structure there are often multiple sites which are available for gas adsorption. In an fcc structure such as Pd there are 4 main sites which can be considered, shown in figure 2.9 [146]. Once the site is chosen the simulation is iterated, slightly changing the distances between molecules until the minimum ground state is found and therefore the ground energy level of the system composed of the palladium membrane, and the adsorbed impurity. The adsorption energy, $E_{i,ads}$, for the adsorption of a gaseous impurity on the surface is calculated equation 2.23. Where E_{slab+i} is the total energy of the relaxed gas-surface system where i is the simulated gas, E_{slab} and E_i are the total energy of relaxed bare surface and gas molecule respectively. Since a system will always tend towards it's lowest energy state, if the total energy of the $E_{i,ads}$ is lower than the sum of it's component energies, it indicates an affinity for the target impurity to adsorb onto the surface of the membrane.

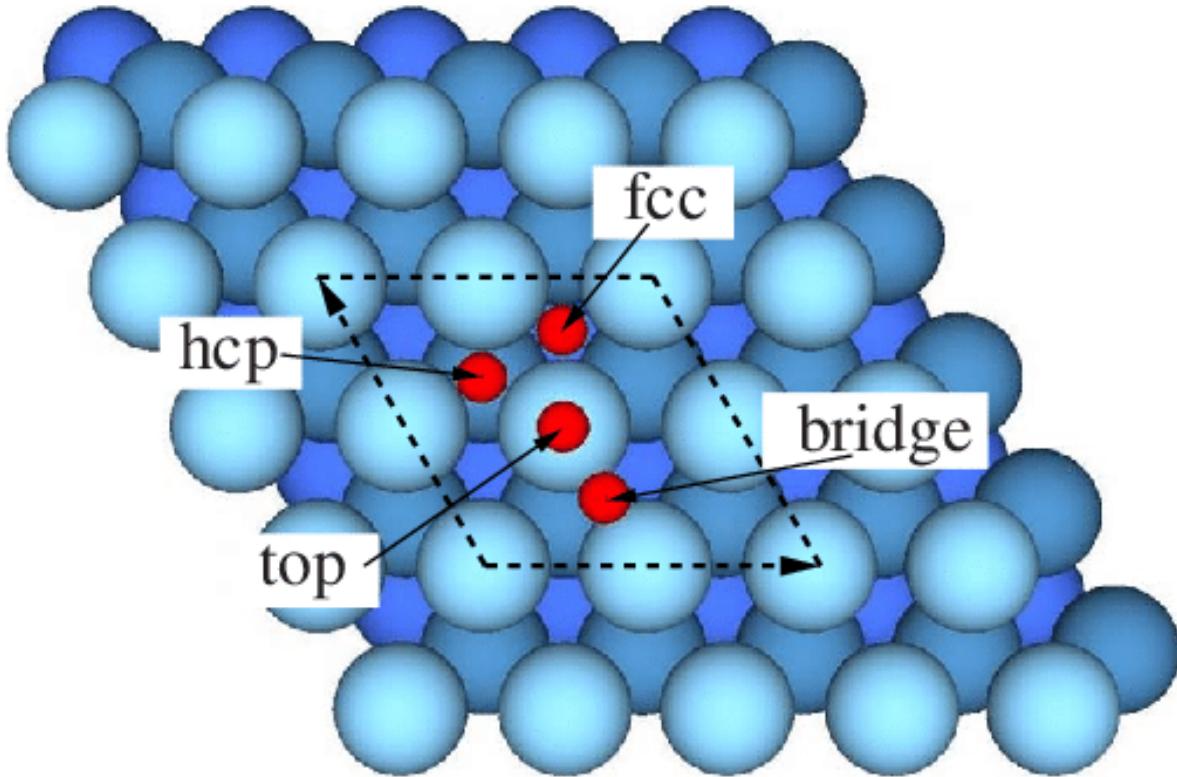


Figure 2.9: Top view of the high-symmetry adsorption sites fcc, hcp, bridge, and top [146]

$$E_{i,ads} = E_{slab} + E_i - E_{slab+i} \quad (2.23)$$

Approximations

The ultimate goal of DFT is to calculate the ground-state energy of the defined system. This was shown by Kohn, Holberg and Sham who discovered that this could be found by finding a self-consistent solution to a set of single particle equations, as an exchange correlation. A major complication to this however is that a guaranteed exchange correlation function simply does not exist, therefore they must be approximated. Two common methods for approximating exchange correlations are local density approximation (LDA) and generalized gradient approximation (GGA)

LDA is where the energy of the system is assumed to depend on the electron density. LDA is able to predict the energy of a structure to within 1-2% of the experimental value. Unfortunately the method fails when looking to predict magnetic properties of materials and the band gaps calculated generally tend to overshoot the bond strengths. [147]

GGA is an improvement over LDA and takes into account the gradient of electron density as well ad the average electron density. This adds an extra layer of computational complexity. it allows for strucural properties to be predicted to within 1% of the experimental values and the total energy to be calculated to 1 kJ/mol. [147] This is also claimed in literature [148].

This thesis will mainly focus on the solid state chemistry in the bulk of the material. For this reason GGA functionals have been chosen as they been shown in numerous publications to perform well.

Pseudopotentials

A pseudopotential is a method used to replace the electron density of a chosen set of core electrons in an atom with a smoothed density chosen to match the physical and mathematical properties of the ionic core of the atom. [147] The use of a pseudopotential is extremely important in reducing computational burden by reducing the number of planes calculated within the atom. This is commonly referred to as the 'frozen core' assumption whereby only the behaviour of the outer most electrons are calculated, and the inner electrons, whose behaviour has previously been calculated, is considered fixed. [147]

The main differentiating feature between different tyypes of pseudopotentials is the mininum energy cutoff for each atom in an equation. The mionimum energy cutoff value refers to the number of plane wave functions which will be used to represent the system, a higher cutoff value means that more plane wave functions are used to represent the bahviour of electrons. The most commonly used pseudopotentials are ultrasoft pseudopotentials which feature a relatively low energy cutoff, making them extremely computationally efficient. A disadvantage of using an ultrasoft pseudopotential is that they require the use of empirical values in defining the properties of the core. However a review of various types of pseudopotentials found that there is virtually no difference in results regardless of what pseudopotential is used and this only becomes a factor whern more complex phenomena such as magnetic properties have to be considered. [147]

Calculations that do not use a pseudopotential are called 'all electron' calculations. However their use is limited due to increased computational burden. [147]

2.6.2 Use cases, and limitations

Most work revolving around the use of DFT to predict the adsorption strength of impurities on palladium and palladium alloy surfaces has focused on catalysis of chemical reactions. As a result there are a limited number of papers focusing on quantifying the interaction between these key hydrogen impurities and membranes. Papers which use DFT to predict the behaviour of hydrogen impurities on the surface of palladium membranes are shown in table 2.7 . The most relevant study performed by Ozdogan et al [149] studied the effect of H₂ and H₂S adsorption energies when small additions of Cu and Nb were added to the membrane composition. The results indicated that while the addition of Cu and Nb hindered hydrogen adsorption, they had a large effect on the

adsorption ennergy of H₂S, concluding that Nb has a higher affinity for H₂S compared to Pd and a lower addinity for Cu. The results were correlated with experimental results and found to be within 1% error which is consistent with results found from using GGA.

Another useful study from Herron et al [150] studied the adsorption of a variety of atomic species (H, O, N, S, and C), molecular species (N₂, HCN, CO, NO, and NH₃), and molecular fragments (CN, NH₂, NH, CH₃, CH₂, CH, HNO, NOH, and OH) on the face of Pd(111) to quantify it's effectivness at catalysing a variety of industrial reactions. Depsite it's target application not being membranes, the results are still relevant to our desired study since a number of the molecular species and molecular fragments tested can be expected to be found in hydrogen. As well as quantifying the binding enmergies of all these molecules, the potential energies also indicated that the only reaction thermochemically preferable is the decomposition of NO. Which gives further evidence that reactions such as water gas shift occurring during catalysis are of no concern.

Outside of these the technique has seen use in predicting the stability of palladium and palladium alloy membranes. A number of studies have successfully combined data from density functional theory to calculate the solubility, diffusivity and permeability of PdCu ([151], [152], [153]), PdAg([154], [155], [156]), PdAu([154], [155], [156]), and ternary alloy ([157], [158],[159] membranes. In particular the study by Morreale et al showed that DFT can be used predict experimental data, although to a limited degree as experimental results were approximately 7 times greater than simulated results. [72]. The greatest challenge when attempting to describe the permeation of hydrogen through metallic membranes is frequent disordering of atoms during the simulation runtime, throwing off results. Other methods such as cluster expansion have been employed in order to overcome this.

The fundamental limitation of using DFT to accurately predict the behaviour of materials is that ultimately such calculation usually calculate, at a maximum, interactions between 10-30 of atoms at a time. This is in no way similar to a physical system where the number of atoms is likely to be in the millions.[147]It must be understood that DFT calculations draw results from extremely small numbers of atoms, and while relevant to phsycal systems, are likely to result in some errors because of this. [147]

DFT is also known to be inaccurate in describing systems where weak van der walls attractions exist between molecules and atoms. [147] This is due to the fact that such attractions are a result of temporary fluctuations in electron density. In order to describe the effect of these interactions on a quantum mechanic level it is necessary to use high level wave function based methods which DFT is unable to accurately predict. This explains why research only focuses on predicting one molecule on a surface at a time, while multiple molecules could theoretically be placed in a simulation, due to the lack of intermolecular forces being taken into account such results are likely to be innacurate. [147]

Despite these drawbacks DFT analysis is a useful tool for screening of potential palladium alloy membrane. The technique is capable of speeding up material development by eliminating options that are unlikely to work, cutting down on trial and error. Due to inaccuracies in the technique however it is unlikely that it will ever become a stan-

dalone technique in membrane research and it's findings should always be backed up by experimental data.

Table 2.7: Review of DFT studies for adsorption of ISO 14687-2 impurites and hydrogen on palladium membrane surfaces

Simulated material	Structure	Approximation	Exchange function	K-points	Adsorbed species	Adsorption site	Binding energy (eV)	ref
Pd	4x4x4 unit cell	GGA	PW91	5x5x1	H ₂	hcp	- 0.5485	[149]
Pd	4x4x4 unit cell	GGA	PW91	5x5x1	H ₂	fcc	- 0.5927	[149]
Pd	4x4x4 unit cell	GGA	PW91	5x5x1	H ₂ S	bridge-fcc-top (H-H-S)	- 0.7	[149]
Pd	4x4x4 unit cell	GGA	PW91	5x5x1	H ₂ S	bridge-bridge-top (H-H-S)	- 0.707	[149]
Pd	4x4x4 unit cell	GGA	PW91	5x5x1	H ₂ S	bridge-hcp-top (H-H-S)	- 0.707	[149]
Pd	4x4x4 unit cell	GGA	PW91	5x5x1	H ₂ S	fcc-hcp-top (H-H-S)	- 0.692	[149]
PdNb _{1.6}	4x4x4 unit cell	GGA	PW91	5x5x1	H ₂	hcp	-0.4259	[149]
PdNb _{1.6}	4x4x4 unit cell	GGA	PW91	5x5x1	H ₂	fcc	-0.4740	[149]
PdNb _{1.6}	4x4x4 unit cell	GGA	PW91	5x5x1	H ₂ S	bridge-fcc-top (H-H-S)	- 0.803	[149]
PdNb _{1.6}	4x4x4 unit cell	GGA	PW91	5x5x1	H ₂ S	bridge-bridge-top (H-H-S)	- 0.704	[149]
PdNb _{1.6}	4x4x4 unit cell	GGA	PW91	5x5x1	H ₂ S	bridge-hcp-top (H-H-S)	- 0.735	[149]
PdNb _{1.6}	4x4x4 unit cell	GGA	PW91	5x5x1	H ₂ S	fcc-hcp-top (H-H-S)	- 0.682	[149]
PdNb _{1.6}	4x4x4 unit cell	GGA	PW91	5x5x1	H ₂ S	hcp-bridge-top (H-H-S)	- 0.602	[149]
PdCu _{1.6}	4x4x4 unit cell	GGA	PW91	5x5x1	H ₂	hcp	-0.4946	[149]
PdCu _{1.6}	4x4x4 unit cell	GGA	PW91	5x5x1	H ₂	fcc	-0.5357	[149]
PdNb _{1.6}	4x4x4 unit cell	GGA	PW91	5x5x1	H ₂ S	bridge-fcc-top (H-H-S)	- 0.429	[149]
PdNb _{1.6}	4x4x4 unit cell	GGA	PW91	5x5x1	H ₂ S	bridge-hcp-top (H-H-S)	- 0.431	[149]
Pd	2x2x4 unit cell	GGA	PW91	3x3x1	N ₂	top	- 0.23	[150]
Pd	2x2x4 unit cell	GGA	PW91	3x3x1	N ₂	fcc	- 0.02	[150]
Pd	2x2x4 unit cell	GGA	PW91	3x3x1	N ₂	bridge	- 0.07	[150]
Pd	2x2x4 unit cell	GGA	PW91	3x3x1	NH ₃	top	- 0.62	[150]
Pd	2x2x4 unit cell	GGA	PW91	3x3x1	NH ₂	top	-1.63	[150]
Pd	2x2x4 unit cell	GGA	PW91	3x3x1	NH ₂	bridge	-2.15	[150]
Pd	2x2x4 unit cell	GGA	PW91	3x3x1	NH	fcc	-3.45	[150]
Pd	2x2x4 unit cell	GGA	PW91	3x3x1	NH	hcp	-3.30	[150]

Pd	2x2x4 unit cell	GGA	PW91	3x3x1	CO	top	-1.29	[150]
Pd	2x2x4 unit cell	GGA	PW91	3x3x1	CO	fcc	-1.95	[150]
Pd	2x2x4 unit cell	GGA	PW91	3x3x1	CO	hcp	-1.96	[150]
Pd	2x2x4 unit cell	GGA	PW91	3x3x1	CO	bridge	-1.77	[150]
Pd	2x2x4 unit cell	GGA	PW91	3x3x1	CH_3	top	-1.67	[150]
Pd	2x2x4 unit cell	GGA	PW91	3x3x1	CH_2	bridge	-3.56	[150]
Pd	2x2x4 unit cell	GGA	PW91	3x3x1	CH	fcc	-5.91	[150]
Pd	2x2x4 unit cell	GGA	PW91	3x3x1	CH	hcp	-5.89	[150]
Pd	2x2x4 unit cell	GGA	PW91	3x3x1	CH	hcp	-5.89	[150]
Pd	2x2x3 unit cell	GGA	PW91	3x3x1	H_2	top	-0.07	[148]
Pd	2x2x3 unit cell	GGA	PW91	3x3x1	H_2	bridge	-0.37	[148]
Pd	2x2x3 unit cell	GGA	PW91	3x3x1	H_2	fcc	-0.49	[148]
Pd	2x2x3 unit cell	GGA	PW91	3x3x1	H_2	hcp	-0.45	[148]
PdAg ₂₅	2x2x3 unit cell	GGA	PW91	3x3x1	H_2	top	0.84	[148]
PdAg ₂₅	2x2x3 unit cell	GGA	PW91	3x3x1	H_2	bridge	-0.27	[148]
PdAg ₂₅	2x2x3 unit cell	GGA	PW91	3x3x1	H_2	fcc	-0.22	[148]
PdAg ₂₅	2x2x3 unit cell	GGA	PW91	3x3x1	H_2	hcp	-0.22	[148]

2.7 Conclusion

This chapter provided a review of the hydrogen process, from how hydrogen is produced and its relationship to the impurities which can end up in the supply chain. The effect of these impurities on the operation of a fuel cell electric vehicle was discussed and the likelihood of these impurities reaching a consumers fuel cell.

Different methods for enriching hydrogen was discussed with one of the most promising methods identified being hydrogen impurity enrichment using a dense metal membrane. From here a number of membrane materials designed to separate hydrogen from multicomponent mixtures. An extensive summary has been provided on the separation performance and stability of these materials with an emphasis on the complications related to transitioning the use of these materials from laboratory and R&D efforts, to industrially relevant processes. The key observation is that while there is a large research focus on new membrane materials, there is a lack of research looking into the engineering of these membranes into functional systems and products. Out of the hundreds of materials being researched for gas separation, commercially only four-eight different polymers are being used, with some niche applications using palladium membranes. Research focus should shift towards focusing on repeatability, scale up, and creating engineered systems where new membrane materials can be used in order to make progress in bringing these new materials to market. Out of the membrane materials reviewed palladium based alloys were the most appropriate to be used for hydrogen impurity enrichment and focus in this thesis will be to find a suitable composition for measuring ISO 14687-2 impurities while minimising interaction with reactants.

DFT based theories were discussed and identified as a method to save time money and cost when attempting to optimise the palladium alloy composition. There is a gap in research on using this technique for palladium alloys specifically targeting ISO 14687-2 impurities. While limited literature exists since many papers address the use of palladium surfaces as catalysts the research is useful for creating a starting base. Palladium alloy membranes can be screened for materials which exhibit the lowest reactivity with ISO 14687-2 impurities, and once identified, they can be manufactured and tested. It is important to note however that there are a number of inaccuracies involved in the technique and should only be used as a rough guide.

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Chapter 3

Experimental methods

3.1 Density functional theory

All DFT calculations were performed using the Quantum Espresso (QE) [1, 2, 3] 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 energy 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/A. A Monkhorst Pack mesh with 5x5x5 k-points was used for all calculations as this was determined to be adequate for achieving convergence from literature in table 2.7 and backed up by initial testing on a Pd system as shown in figure 3.1.

Python with scikit learn, pandas, numpy, and matplotlib packages were used for scripting, data collection and analysis. Sample files can be found in Appendix 3.

3.1.1 ISO 14687-2 Impurities and Hydrogen

ISO 14687-2 impurities were simulated using the above parameters and their structure relaxed until convergence was achieved. The resulting structure was then cross checked using bond lengths from literature to ensure the resulting molecule was an accurate representation.

3.1.2 Palladium and Palladium alloy slab models

The structure of bulk palladium was first created using a lattice parameter of 3.859Å as reported by D. Wheeler [4]. Initially the pure palladium slab model used to represent the periodic supercell was created using this palladium primitive unit cell cleaved using the miller indices $(h, k, l) = (111)$ which is adequate in describing the surface of a palladium membrane. A 2×2 slab was created in order to ensure minimal in-plane interactions between neighbouring molecules adsorbed onto the surface in the periodic simulations. The slab was extended to 5 atom thickness which is adequate to describe the surface of

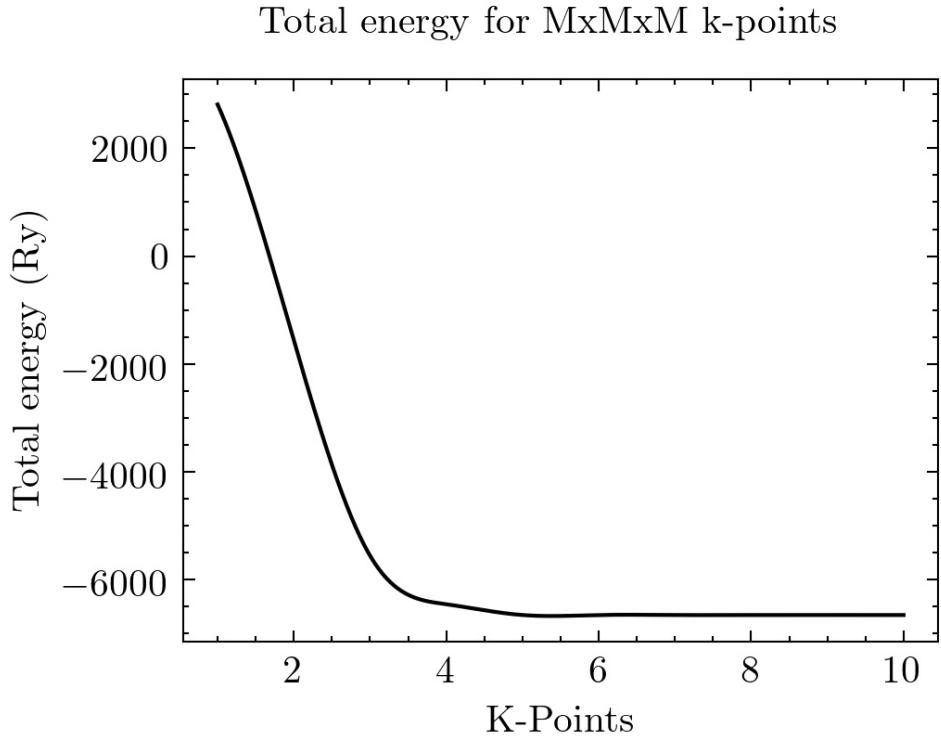


Figure 3.1: Total energy as a function of $M \times M \times M$ k-points across a Pd(111) fcc slab

Pd(111) and a 20Å vaccum layer was placed on top. The resulting supercell consisted of 20 atoms.

When creating palladium alloy systems it was assumed that alloys adopt a 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.

Quantum ATK Virtual NanoLab Builder [5] was used to generate these structures and export to QE input files. Each metal composition was simulated with three random distributions of substituted metal. For each alloy, geometry optimization was performed to get the lattice constant and total energy of each alloy prior to adsorption of gaseous molecules.

Adsorption energy

In order to find the adsorption energy of each ISO 14687-2 impurity on the membrane surfaces the molecules simulated in section 3.1.1 were inserted into the vaccum region of the slab models generated in section 3.1.2. (111) fcc surfaces have 4 available sites for adsorption shown in figure 2.9 A separate system was created for adsorption of each impurity onto each of these sites. Initially the adsorbed molecule was simulated using a rigid constraint to prevent any changes to the impurities molecular structure, and a low cutoff energy in order to get a quick starting point for the basis of the full simulation.

Final geometry relaxation was then performed from this using the parameters described in section 3.1

The adsorption energy, $E_{i_{ads}}$, for the adsorption of a gaseous impurity on the surface is then calculated using equation 2.23 where i is the target ISO 14687-2 impurity or hydrogen molecule.

3.2 Membrane manufacture

3.2.1 Materials used

3.2.2 Support fabrication

The YSZ 3% hollow fibre substrates with a sponge like microstructure were fabricated by a fingering induced phase-inversion process, followed by high temperature sintering. A uniform ceramic suspension, with 60 wt.% solid loading YSZ 3% powder (1 μ m, VWR), 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 excess 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 PdCuZr) were deposited onto the surface of the porous YSZ substrate through electroless plating. The process was performed in the two step activation-plating process discussed in section 2.5.2. Palladium was used due to its high electro positivity compared to other metals commonly plated through electroless deposition.

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 coated at one end with a gas tight glaze and sintered at 900°C for 1 hour. The outer surfaces of the fibres were 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

Table 3.1: Compositions used for activation of YSZ substrate prior to palladium deposition

Compound	Concentration (g/L)			
	Sensitisation	Washing	Activation	Acid Washing
SnCl ₂	1	-	-	-
PdCl ₂	-	-	0.1	-
HCl	1	-	1	0.01

Table 3.2: Compositions used for preparation of palladium based membranes on YSZ substrate through electroless plating and immersion plating

Compound	Deposited metal			
	Pd	Ag	Cu	Au
Metal Source (g/L)				
PdCl ₂	4	-	-	-
AgNO ₃	-	3.4	-	-
CuSO ₄	-	-	10	-
AuCl ₃	-	-	-	0.1
Stabilising agent				
NH ₃ -H ₂ O (mL/L)	198	200	-	-
NaOH (g/L)	-	-	8.63	1
Complexing Agent (g/L)				
Na ₂ EDTA-2H ₂ O	40	35	-	-
Persulfate	-	-	30	-
Reducing agent (mL/L)				
N ₂ H ₄	5.6	4.2	-	-
Formaldehyde	-	-	14	-

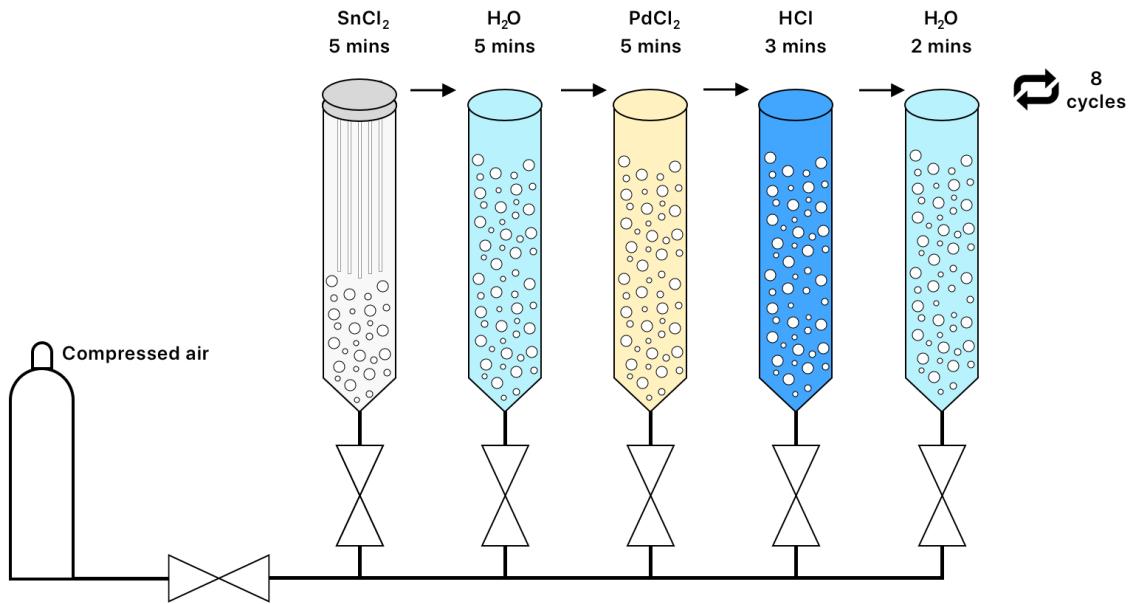


Figure 3.2: Schematic representation of the sequential baths for sensitisation/activation process.

water for 3 mins. All chemical baths were homogenised using compressed air. The sensitisation/activation process was repeated for 8 cycles. The composition of each bath is shown in Table 3.1.

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 3.2 taken from [6] for Pd, [7] for Ag, [8] 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. [9] 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/cm³.

The resulting composite membranes consisting of multiple metal layers stacked were

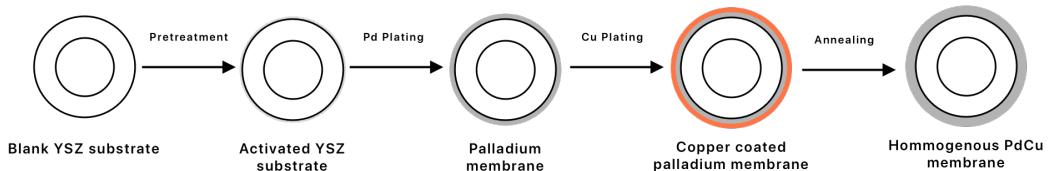


Figure 3.3: Example of ELP procedure when manufacturing a PdCu membrane on YSZ substrate

Table 3.3: Conditions used during magnetron sputtering of palladium membranes on YSZ tubular substrate

Alloy	Target current (A)		
	Pd	Cu	Zr
PdCuZr	1.25	0.65	0.4
PdCu (fcc)	1.25	0.8	-
PdCu (bcc)	1.2	1.0	-

then heat treated at 500°C under an environment containing 25% H₂ in Ar balance for 24 hours in order to alloy the layers into a homogenous membrane and reduce any oxides that were present on the surface.

Magnetron Sputtering

Membranes were deposited using a closed field unbalanced magnetron sputter ion plating system produced by Teer Coatings Ltd. The thin film membranes were deposited onto the YSZ 3% hollow fibres by mounting them vertically inside the sputtering system. The system was then evacuated to 1x10⁻⁶ mBar and subjected to an ion cleaning process with Ar plasma prior to sputtering. Pd, Cu, and Zr targets (99.9% purity) were used to sputter the chosen alloy composition onto the membranes at the target currents shown in. A bias voltage of 50 V was applied to the magnetron during deposition runs. Samples were deposited using pulsed DC, with a constant target to substrate distance and a sample rotation speed of 16 rpm. An Ar flux of 25 (SCC/m) was used during deposition. PdCu membranes in both BCC and FCC phase were manufactured through magnetron sputtering along with PdCuZr ternary alloys.

3.2.4 Materials testing

The thickness of the plated layers was characterised by first using a Focused Ion Beam (FIB) to mill through a section of the hollow fibre to provide a flat, cross sectional surface for analysis. The thickness of the metal later was then measured using high resolution

Table 3.4: Gas mixture composition of the non-sulphur sample used during impurity tests

Impurity	Concentration ($\mu\text{mol/mol}$)
O ₂	10.06
N ₂	10.04
CH ₄	10.01
CO ₂	10
CO	9.98
H ₂	Balance

Scanning Electron Microscopy (SEM) and composition analysed using Energy Dispersive x-ray Spectrometry (EDS) on the same sample.

The surface composition of the membrane was further characterised using X-ray Photoelectron Spectroscopy to provide a more accurate compositional analysis for the top 10 nm of the membrane, the depth which is most relevant for catalytic dissociation of hydrogen and adsorption of impurities.

Prior to the H₂ permeation tests, the integrity of the hollow fibre membranes was evaluated by testing the gas-tightness of the membrane under N₂ atmosphere, up to 10 bar and room temperature and using a gas-tightness apparatus developed in house. [6]

3.3 Membrane testing

3.3.1 Preparation of gas standards

Gas standards of hydrogen were prepared gravimetrically in 10 litre cylinders (BOC, UK) in accordance with [10] from pure hydrogen (Air Products, UK), nitrogen (Air Products), carbon monoxide (Scott Speciality Gases, UK), methane (CK Gases, UK) and krypton (BOC, UK). Any impurities that were detected in these pure gases were quantified and these values were then incorporated into the final determination of the gas mixture compositions and uncertainties.

For the purpose of this thesis the gas standards that were used to perform the permeation tests will be referred to as gas mixtures, and the gas standards that were used to calibrate the analytical instruments will be referred to as calibration gas standards. Before use, the gas mixtures were verified against traceable primary reference materials using Gas Chromatography with either a pulsed helium discharge ionisation detector (PDHID) for samples not containing sulphur [Reference for DN34], and sulphur chemiluminescence detector (SCD) for sulphur containing samples [Reference for B543]. The compositions of the non-sulphur, and sulphur containing gas standards created for the purposes of this thesis are shown in tables 3.4 and 3.5.

Table 3.5: Gas mixture composition of the sulphur sample used during impurity tests

Impurity	Concentration (umol/mol)
Kr	1.1
H ₂ S	0.41
OCS	0.42
CS ₂	0.362
t-BuSH	0.391
THT	0.409
H ₂	Balance

3.3.2 Membrane testing rig

After the membranes were ensured to be gas tight, hydrogen permeation measurements were performed using the experimental apparatus shown in Figure 1. The palladium alloy composite hollow fibre membranes were sealed on to a stainless steel $\frac{1}{4}$ " NPT fitting. The membrane was then placed in a Sulfinert®-treated sample vessel (Thames Restek, UK) with nominal volume of 300 cm³. The vessel was then heated using heavy insulated heating tape (OMEGA STH051-020). The heating was controlled using the temperature of the membrane using a PID temperature controller (OMRON). The feed was supplied from a cylinder either containing BIP+ hydrogen (Air Products) for pure hydrogen permeability tests or one of two gravimetrically prepared gas mixtures for impurity testing shown in tables 3.4 and 3.5. Prior to introducing gas to the membrane the system was evacuated down to 1×10^{-6} mbar. The pressure on the retentate side of the membrane is controlled using a tamper proof pressure reducer. The set-up is shown in figure 3.4. After tests the system was vented and purged 7 times with N₂ to ensure an explosive atmosphere could not build up within the equipment.

The flux and permeability of the membrane were automatically calculated using software developed in house. Each membrane sample was made using the same batch of substrate and cut to the same length prior to testing. The permeability (P) of a dense metal membrane is given by Eqn 3.1 [11] and is a function of the hydrogen flux through the membrane (J), the concentration and pressure gradient across the membrane ($P_{ret}^{0.5} - P_{perm}^{0.5}$), and the thickness of the metallic membrane (l).

$$P = \frac{Jl}{P_{ret}^{0.5} - P_{perm}^{0.5}} \quad (3.1)$$

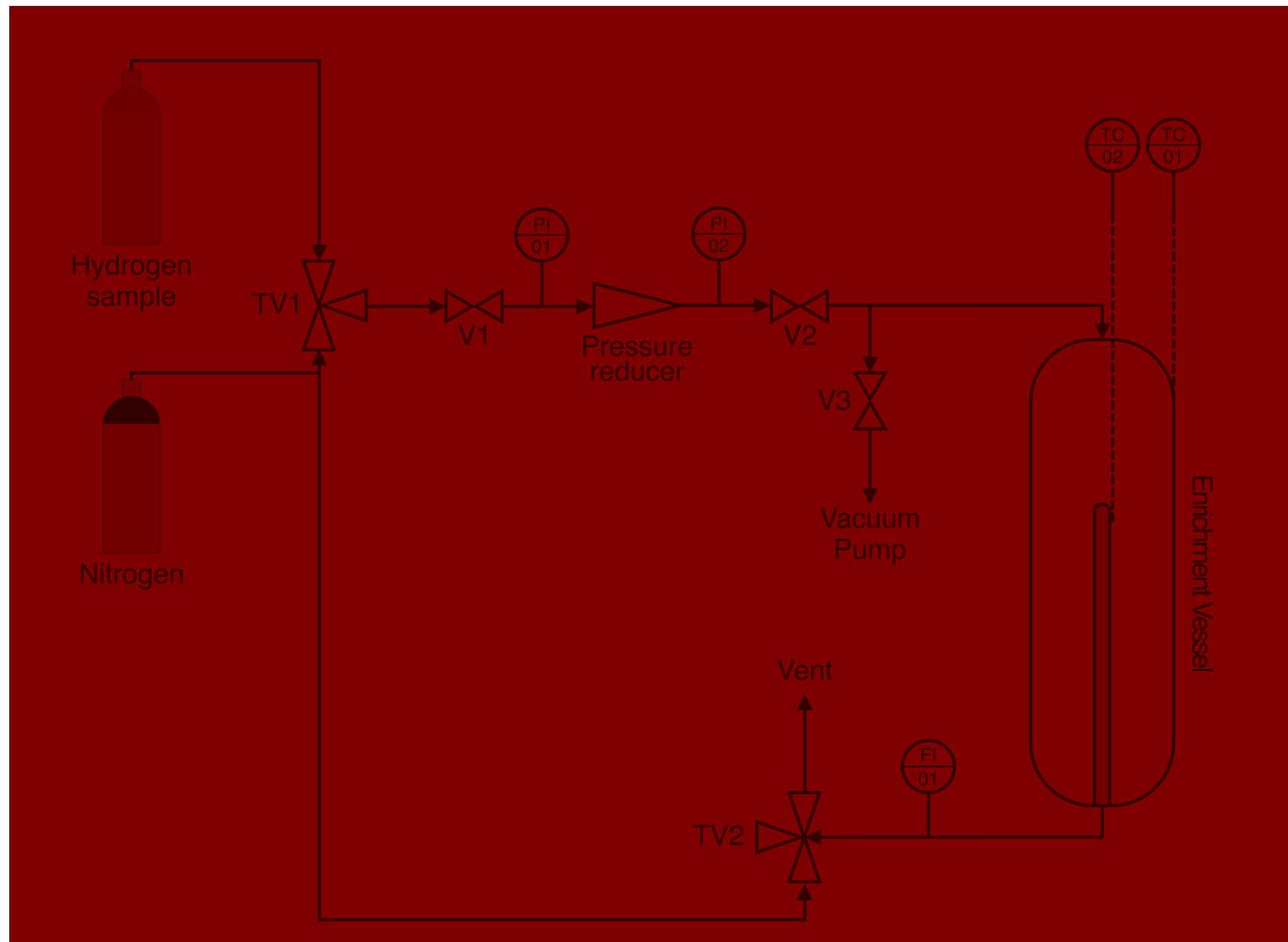


Figure 3.4: Experimental set up used during hydrogen permeation and enrichment experiments, TC: Temperature controller, PI: Pressure indicator, V: Valve, TV: Three-way valve, FI: Flow indicator.

3.4 Hydrogen impurity enrichment

A hydrogen impurity enrichment device was designed and tested, more details on this will be discussed in chapter 6. This section will describe the methodology and testing procedure for the hydrogen impurity enrichment device.

Hydrogen impurity enrichment tests were performed on synthetic samples created using the procedure described in section 3.3.1 and using a sample taken from a hydrogen refuelling station. Regardless of source all samples were tested using a PDHID in order to calculate it's oxygen level for safety reasons. Since only hydrogen can leave the HIED in normal testing conditions, if not checked the concentration of oxygen could rise above a safe level and create an explosive mixture. For the purpose of these tests the enrichment factor was capped at a value that would ensure the oxygen level in the mixture would not surpass 1%.

The enrichment factor was calculated using both non-ideal gas law (equation 2.14), and tracer enrichment (equation 2.15) methods. This was to ensure any leaks in the device could be detected using non-ideal gas law method, while having a low uncertainty on the final value from the tracer enrichment method. Gas composition testing was performed using the same GC procedures discussed in section 3.3.1

3.4.1 Krypton spiking

In order to perform enrichment using the tracer enrichment method a certain quantity of inert gas, not normally present within a hydrogen sample, must be included in the gas. Krypton was used in this study. For synthetic samples this can be added using loop addition along with other impurities using the procedure in section 3.3.1. When taking a sample directly from a hydrogen refuelling station, as would have to be done in real sampling, this approach is not effective as the tracer gas cannot be added to an already pressurised container. The krypton must first be added to the evacuated sampling vessel through loop addition.

Since sampling from a hydrogen refuelling station is dependent on a number of variables, it is difficult to determine the final pressure of the sample. Therefore, a fixed quantity of krypton gas was added to the cylinders. For the purpose of this thesis, since 10L cylinders were used for the purpose of hydrogen sampling, 0.24g of Kr was added through loop addition as this is enough to ensure at a max fill pressure of 100 bar there would be atleast 70 $\mu\text{mol/mol}$, which is well within the range of the GC-PDHID detector, and available gas standards for validation.

3.4.2 Performing enrichment

The protocol for performing hydrogen impurity enrichment is similar to hydrogen permeation tests. After evacuation the gas is introduced to a vessel containing the chosen palladium membrane composition at a set enrichment pressure and the vessel heated to 300°C to begin enrichment. The pressure of the enrichment vessel and sample cylinder were both monitored and their values used to calculate the enrichment factor in real

time using equations 2.14 and 2.15. Once the desired enrichment factor was achieved the heater was switched off and the enrichment vessel isolated. The enrichment vessel was then brought to the desired GC detector and it's composition tested against a gas standard as described in section 3.3.1

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Chapter 4

Density functional theory as a screening method for dense metal membranes

4.1 Abstract

In this chapter 18 different palladium based membrane materials were simulated in order to determine their suitability as a material for hydrogen impurity enrichment. The alloys were represented using $2 \times 2 \times 5$ atomic slab models comprised of palladium, with varying compositions of different metals including common palladium additives (Au, Ag, Cu), and metals known for their resistance against aggressive environments (Zr, Cu). From the alloy compositions tested 16/18 were stable, with Cr containing alloys unable to form a stable system. The 16 remaining alloys were then tested with hydrogen, and each of the ISO 14687-2 impurities adsorbed on the 4 available surface sites for hydrogen adsorption. The results were that the impurities could be split into four broad groups. Inert impurities included NH₃, CO₂, N₂, He, Ar and formic acid, which did not interact with the surface of the alloys. Oxidising impurities included H₂O and O₂, which pure palladium alone was completely resistant against. The effect could be amplified through the addition of Au and Ag, with PdAu₂₀ being the best performing alloy for resisting these impurities. Carbonaceous impurities included CO and CH₄ where PdAu₂₀ was again the best performing alloy, with an average binding energy of CO and CH₄ of around $\times 0.4$ and $\times 0.5$ compared to binding of H. Finally sulphurous atmospheres were tested using H₂S where PdCuZr and PdAuZr alloys were the best performing. These alloys showed an average binding energy of $\times 0.52$ and $\times 0.49$ compared to H. Formaldehyde was a special case where no alloy composition was found to resist binding.

This study shows that DFT can be used to give an indication on the suitability of a palladium alloy membrane for its desired purpose. It also shows that while the effects of some impurities on the surface of a palladium alloy membrane can be completely mitigated, many cannot be inhibited completely. A number of alloys were identified as

the best options for hydrogen impurity detection and will be studied experimentally in the following chapters.

4.2 Introduction

Metal membranes operate by selectively dissociating hydrogen, which then allows the hydrogen atoms to subsequently permeate through the bulk of the separation layer. The problem in using palladium membranes as a material for performing hydrogen impurity enrichment is that many hydrogen impurities are also capable of adsorbing onto, and interacting with palladium membranes. The impact of this adsorption can vary depending on the molecule, Carbon monoxide for example will simply adsorb onto the surface and result in competitive adsorption between the hydrogen and impurity. Sulphur containing impurities present more of a problem since they can potentially react with many metals used for hydrogen separation membranes. The impact of these contaminants can be minimized by designing alloy compositions that have a weaker attraction to the membrane, and therefore will have less of an affect at higher temperatures where these membranes operate.

Physically testing each potential membrane composition would be time consuming and costly due to the high price of palladium, the time required to synthesise specific membrane compositions, and performing the tests. Simulations provide a solution to this, allowing potential alloys to be quickly screened for their interaction strength with each individual ISO 14687-2 impurity, avoiding the costly and time consuming process of manufacturing each alloy composition.

In this chapter, 18 dense metal alloy membranes will be simulated using DFT density functional theory as described in section 3.1 [1, 2, 3]. The metals will first be evaluated in terms of their ability to form a stable alloy, with low risk of segregation, or failure. All stable metals will then be simulated with either hydrogen, or an ISO 14687-2 impurity on the surface, and its binding energy calculated. The results will be evaluated using the ratio of binding energy of adsorbent to binding energy of hydrogen (σ) on the same metal as shown in equation 4.1 where E_{ads} is the binding energy, i is the simulated impurity on the surface of the metal alloy, and H is hydrogen.

$$\sigma = E_{i_{ads}} / E_{H_{ads}} \quad (4.1)$$

The metallic compositions with the lowest value for σ represent the best simulated material for dealing with that impurity. A high value of σ indicates that the metal is more reactive with the impurity molecule, whereas a σ value of 1 or lower indicates that the ability for the impurity to adsorb on the surface is equal to, or lower than that of hydrogen, and therefore has a weaker interaction.

4.3 Results and discussion

4.3.1 Stability of palladium alloy compositions and ISO 14687-2 impurities

In order to perform the simulations, first an appropriate slab model of each alloy must be created. The structure of these slabs is shown in section 3.1.2. The metals chosen to substitute into the palladium lattice were common palladium alloys (Au, Cu, and Ag) and metals which have previously shown a resistance to sulphur. Zr[4] and Cr[5] are commonly used additives in steel to improve it's corrosion resistance in acidic environments and were decided to be ideal candidates. Once simulated the total energy of the system was compared to the sum of the energy levels of the component atoms. The results of this analysis are shown in table 4.1. All alloys were stable except for the Cr containing alloys which could not converge to a suitable solution.

Similarly each ISO 14687-2 impurity was simulated and the results of these can be found in table 4.2. The parameters used to simulate these molecules can be found in the appendix.

Table 4.1: Simulated total energy values of alloy slabs

Alloy/Metal Composition	Total Energy (ry)
Pd	-6653.38
PdAg ₂₃	-6774.37
PdAu ₁₀	-7545.53
PdAu ₂₀	-8437.613
Pd ₆₀ Cu ₄₀	-5703.15
Pd ₈₀ Cu ₂₀	-6178.29
Pd ₇₀ Au ₂₀ Zr ₁₀	-8389.61
Pd ₇₀ Cu ₂₀ Zr ₁₀	-6130.29
Pd ₇₀ Ag ₁₀ Zr ₂₀	-6605.75
PdZr ₁₀	-6605.45
PdZr ₂₀	-6557.46
Pd ₇₀ Au ₂₀ Ag ₁₀	-8485.99
Pd ₇₀ Au ₂₀ Cu ₁₀	-8200.05
Pd ₇₀ Cu ₂₀ Ag ₁₀	-6226.71
PdCr ₁₀	-
PdCr ₂₀	-

Table 4.2: Simulated total energy values of ISO 14687-2 impurities

Gas	Total Energy (kJ × 10 ⁻²¹)
H	-2.01
N ₂	-123.91
O ₂	-180.86
CO	-130.93
CO ₂	-221.95
NH ₃	-1933.22
Ar	-208.10
CH ₄	-50.73
Formaldehyde	-136.13
Formic Acid	-227.08
H ₂ S	-150.36
He	-12.62
H ₂ O	-95.99

4.3.2 Hydrogen and Impurity adsorption on palladium alloy membranes

Hydrogen

The hydrogen binding energy on the surface of palladium is a key value for the purpose of this study. The affinity for a palladium alloy to adsorb on the surface is the initial step for hydrogen permeation, and below a certain thickness becomes the rate limiting step. As expected all alloys had an affinity for hydrogen binding and these values matched what is generally found in literature. These values will be compared to the binding energies of other impurities on the alloys in order to determine their resistance to the impurity. The binding energies of hydrogen on a the Pd slab system is shown in figure 4.1. In a Pd system hydrogen preferentially adsorbs on the FCC and top sites at relativley even energies. At both of these sites hydrogen is able to form a stable system without being affected by other forces. HCP and TOP sites have a lower preference for hydrogen binding and this is likely due to the influence of competition by neighbouring sites which can provide higher stability. The average binding energies of hydrogen on the surface of all palladium alloy slab systems are shown in figure 4.2.

All alloys show a decreased preference towards hydrogen binding compared to pure palladium. This is due to hydrogen adsorption energies being closely related to the catalytic activity for hydrogen dissociation of the individual metal elements. The effect appears to be less prevalent for binary alloys with elements with a larger atomic size such as silver which is likely due to the larger atomic size creating a larger area for hydrogen to adsorb within fcc site of the crystalline lattice, which is one of the preferential sites for H adsorption. Zr and Au do not follow this trend however which indicates that the

Hydrogen adsorption sites on Pd

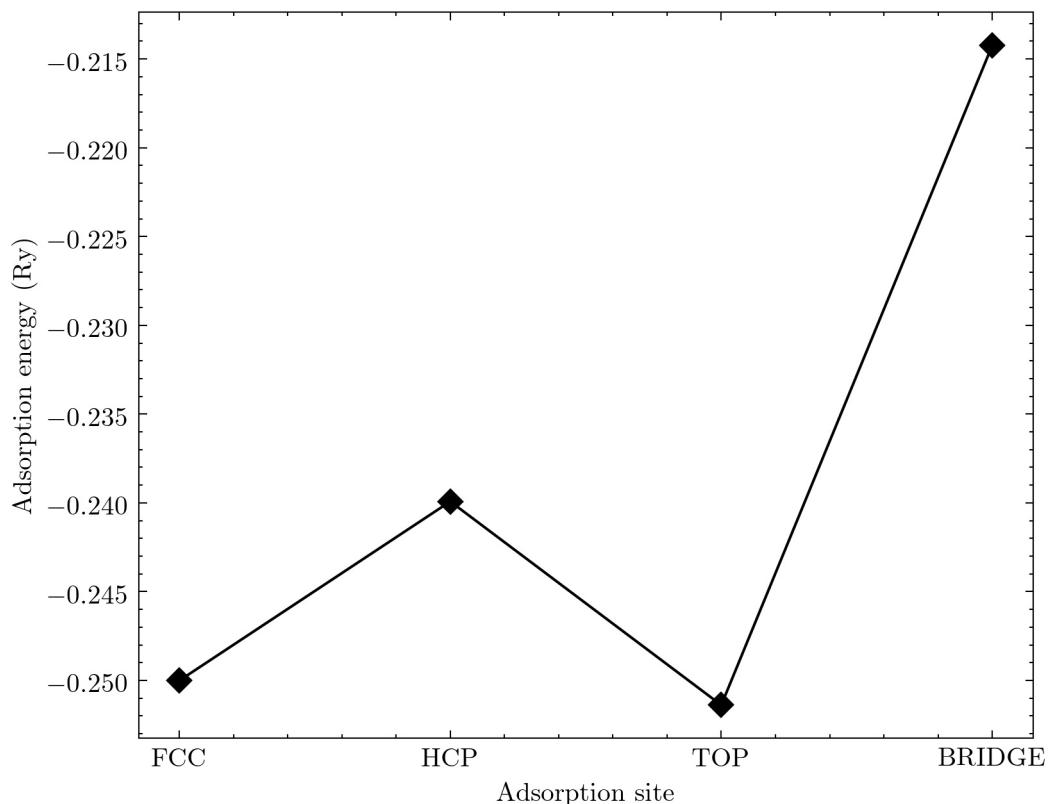


Figure 4.1: Adsorption energy of H for each site on a 2x2x5 Pd slab

Table 4.3: Correlation coefficient of Ag, Au, Cu, Zr addition to Pd with binding energy of H

Metal	Correlation coefficient
Ag	-0.024666
Au	0.259205
Cu	0.019221
Zr	0.347930

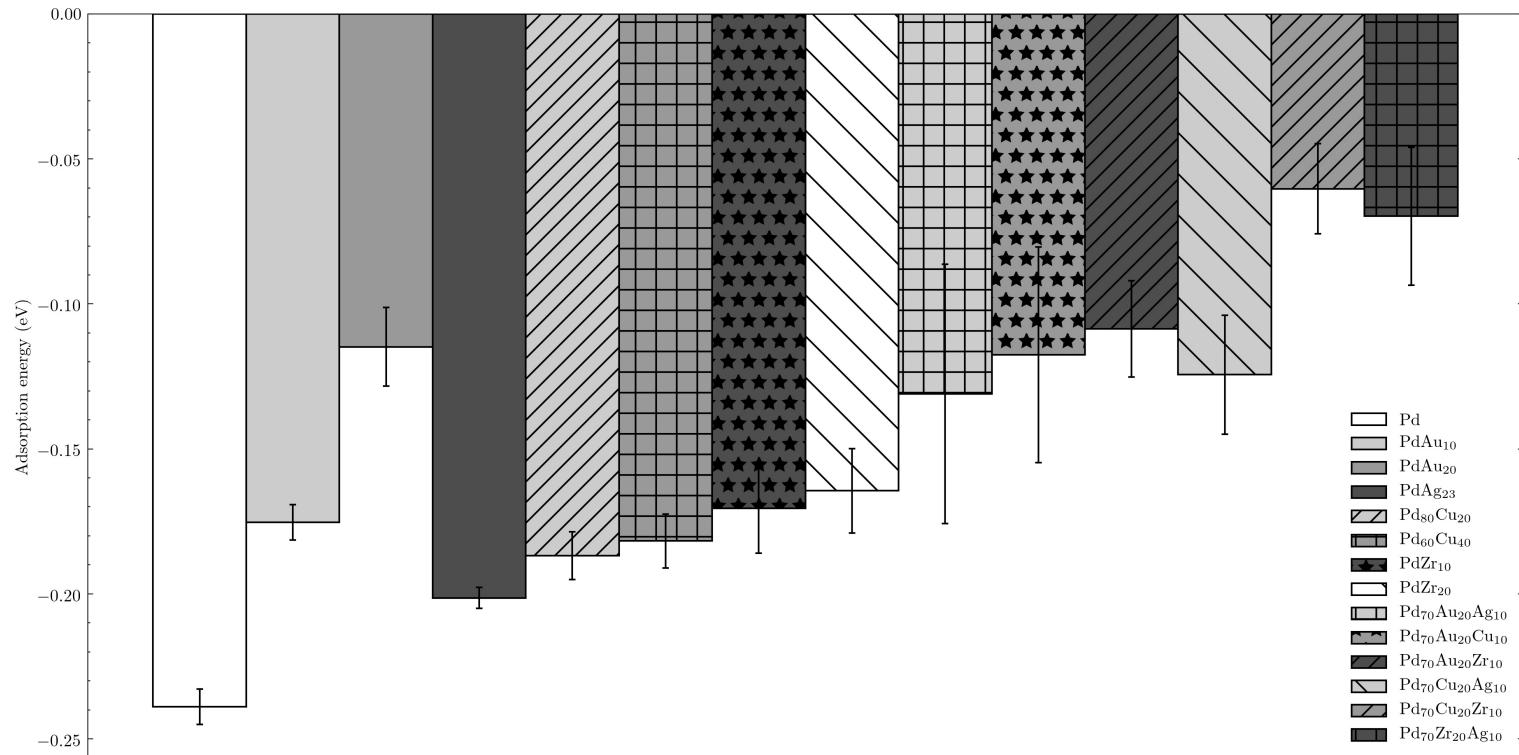
catalytic activity is affected more by electronic interactions than surface geometry. In all cases reduction in palladium from the surface results in lower catalytic activity for hydrogen adsorption which is also likely to be due to the average reduction in number of top sites available for adsorption, which other than FCC is one of the preferential adsorption sites.

The ternary alloys with the highest catalytic activity were PdAuAg and PdCuAg which previous experimental results showing that these alloys have higher permeability than other ternary alloys. All Zr containing alloys had lower catalytic activity showing that for hydrogen permeation Zr has the greatest inhibiting effect. The detrimental effects of Zr to the catalytic activity can be lowered by the addition of Au, Ag, or Cu however all are still lower than binary alloys.

The correlation coefficient for the presence of each metal and it's effect on the resulting adsorption energy was calculated and is shown in table 4.3. It shows that the resulting inhibiting effect of each element follows the order Ag<Cu<Au<Zr.

This binding energy of hydrogen is an important benchmark for the following tests and will be compared to the resulting binding energies for other impurities. If these impurities show a lower binding energy value when compared to hydrogen then they will be preferntially adsorbed and less suitable for use for that type of impurity. It also reveals that the composition of the membrane can largely effect the catalytic activity for dissociation of hydrogen in itself. As membranes become thinner this will result in a shift of the limiting step to catalytic activity and therefore this value must also be optimised to ensure the highest flux can be achieved, however such work is outside the scope of this study.

Hydrogen adsorption

Figure 4.2: Average binding energy of H_2 on the surface of palladium and palladium alloy slabs

Helium, Nitrogen, Carbon Dioxide and Argon

Helium, Nitrogen, Argon, and CO₂ all represent the inert components in fuel cell hydrogen which do not interact with the electrocatalyst and are therefore also likely to be inert to palladium membranes. The binding energies of these molecules on the surface of all the simulated palladium alloy slab systems are shown in figures 4.3 (He), 4.4 (N₂), 4.5 (CO₂) and 4.6 (Ar). All these systems showed a positive binding energy meaning that no competitive adsorption will take place between these gases and hydrogen for the surface adsorption sites.

Carbon Monoxide

CO adsorption was performed by adsorbing the gaseous molecule by the C atom as is normal for CO binding on metallic surfaces [6]. All systems showed binding preference towards CO. The results of the simulations and their binding energies compared to that of hydrogen on the same alloy are shown in figure 4.8. No alloys showed an aversion to CO binding therefore all of the simulated alloys, regardless of their preference to H₂, will likely experience some competitive adsorption and therefore inhibition when CO is present.

The pure Pd system showed a clear preference to CO binding over hydrogen, this matches previous experiments performed to investigate this. [7] Figure 4.7 shows the binding energy on each site compared to that of H calculated in section 4.3.2. The fcc system shows a clear preference for CO on the FCC, HCP and TOP sites, while still preferring to bind to H on the BRIDGE site. This is most prevalent for the FCC site which has a lower binding energy of around -0.55 eV, with HCP and TOP sites showing a drop in around -0.35 and -0.3 eV respectively. However since the top site still shows a preference for H binding which represents around 41% of the binding sites. While this may indicate that these sites are still available for hydrogen permeation, when bulk diffusion is modelled using kinetic monte carlo simulations that hydrogen travels through the bulk by relaxing the lattice around the fcc and hcp sites to facilitate transport. [8] Therefore the blocking of these sites is likely to have a severe effect on hydrogen permeation.

Of the systems tested PdAu₂₀, PdAg₂₃, and Pd₇₀Au₂₀Cu₁₀ all showed marginal preference for hydrogen binding over CO binding. Binding of CO on Au and Ag surfaces has previously been studied and concluded that these metals do not interact with CO under normal circumstances, and will only adsorb through way of material defect or alloying. [9] [10]

By far the worst performing metal for inhibiting the effect of CO were all Zr containing alloys, and Pd₆₀Cu₄₀. Zr readily forms a bond with C, and even has its own unique branch of chemistry referring to such compounds.[11] Zirconium is also a common complex used in homogeneous refractory catalysts for reforming hydrocarbon compounds.[12] Therefore the evidence suggests that Zr naturally has a high affinity towards forming carbon bonds and is not a suitable additive for CO resistant membranes.

Similarly Cu has been previously studied and found to readily adsorb CO on its

He adsorption

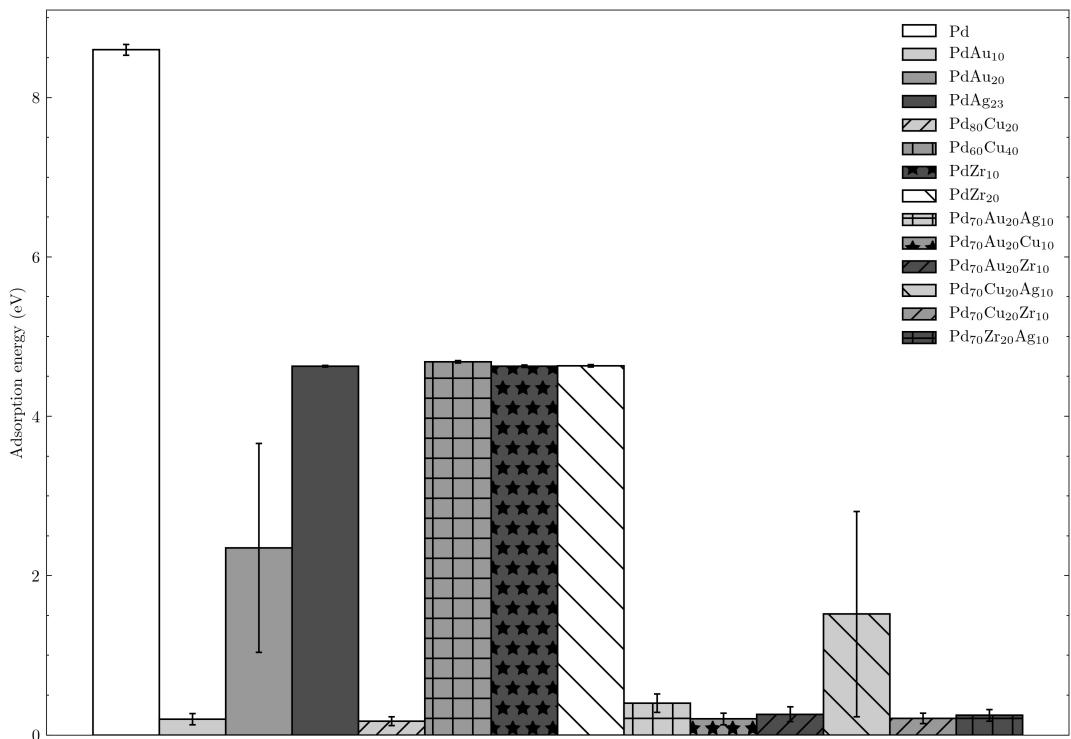


Figure 4.3: Average binding energy of He on the surface of palladium and palladium alloy slabs

N_2 adsorption

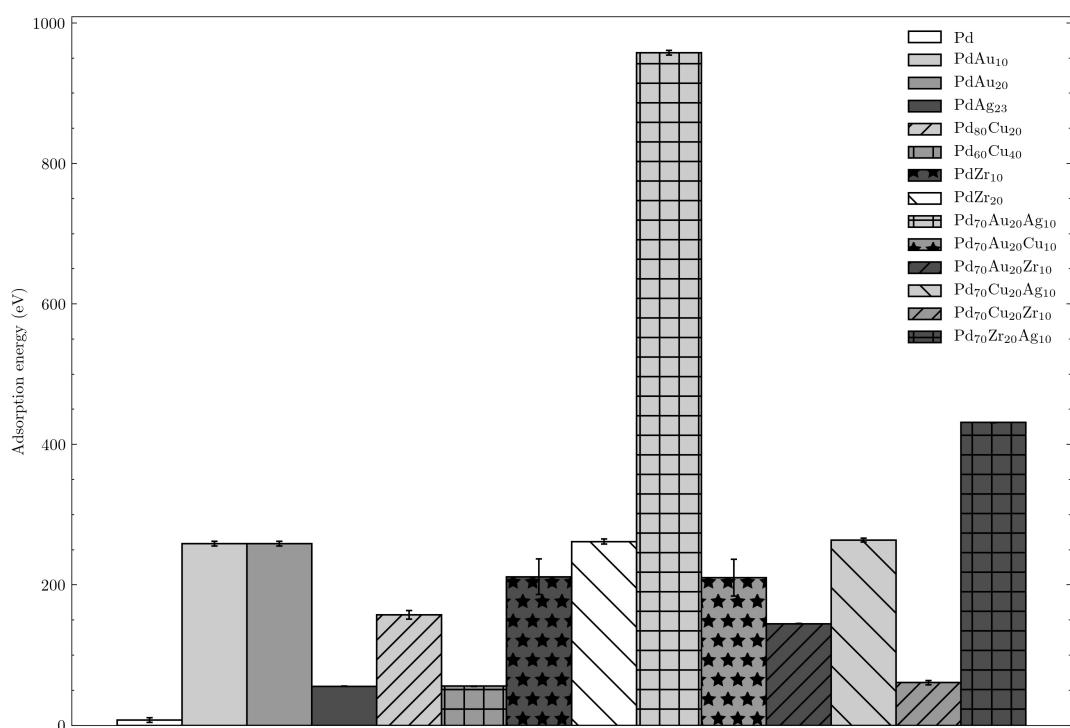


Figure 4.4: Average binding energy of N_2 on the surface of palladium and palladium alloy slabs

CO₂ adsorption

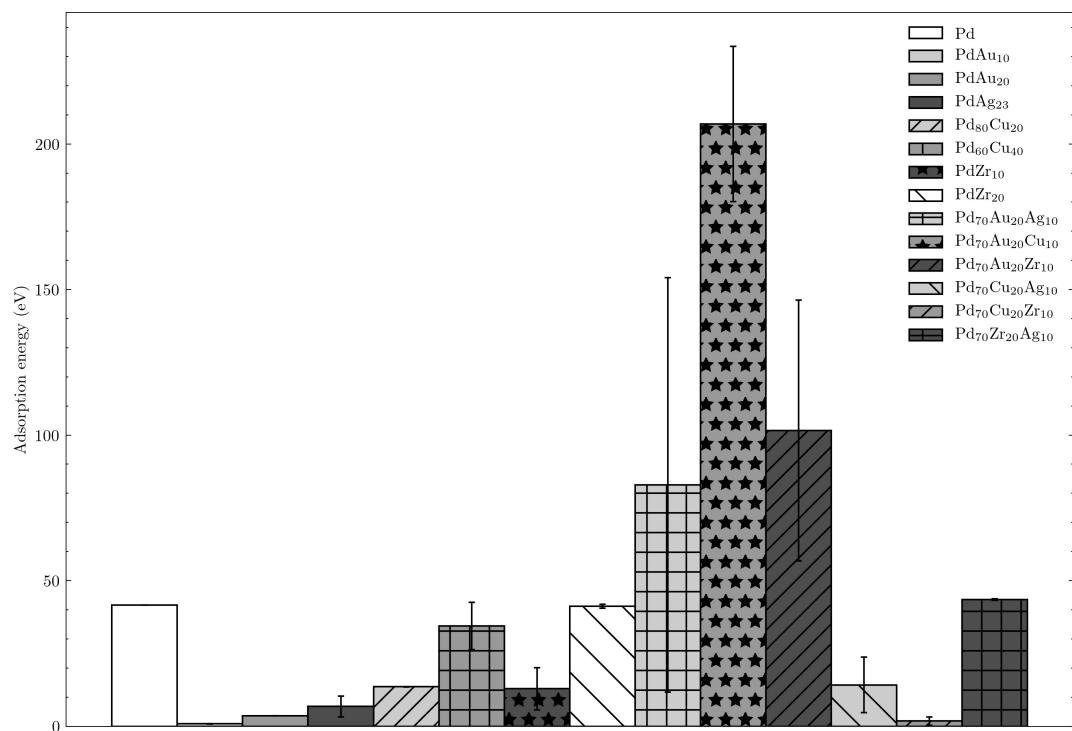


Figure 4.5: Average binding energy of CO₂ on the surface of palladium and palladium alloy slabs

Ar adsorption

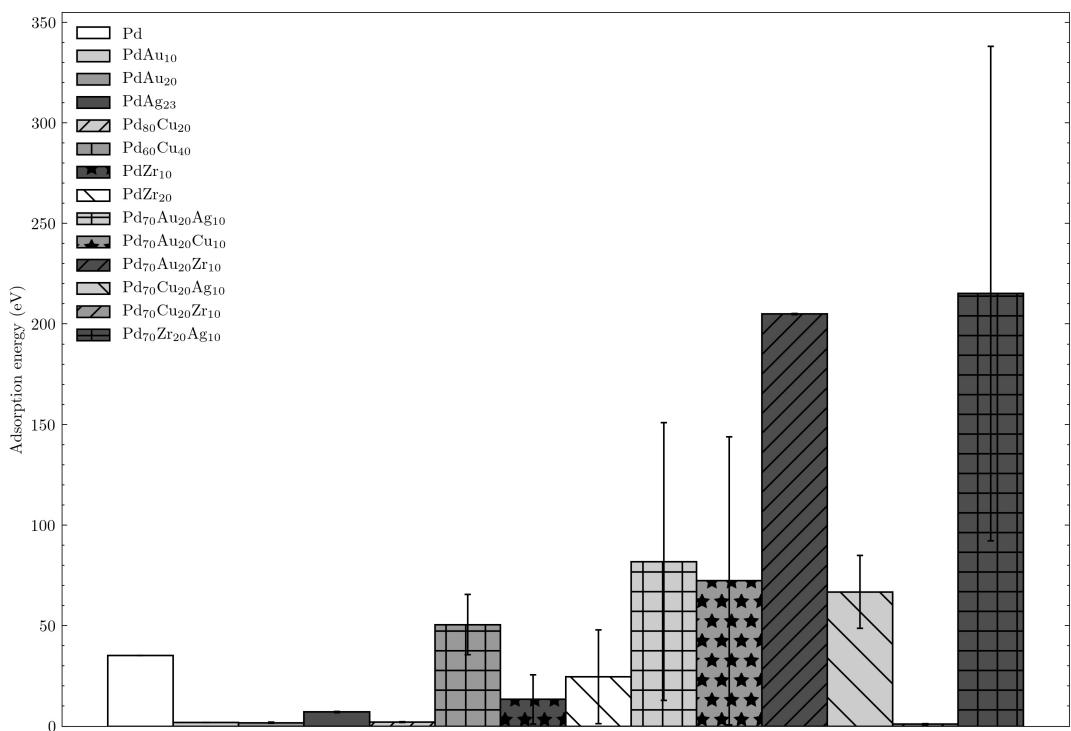


Figure 4.6: Average binding energy of Ar on the surface of palladium and palladium alloy slabs

CO adsorption sites on Pd compared to H

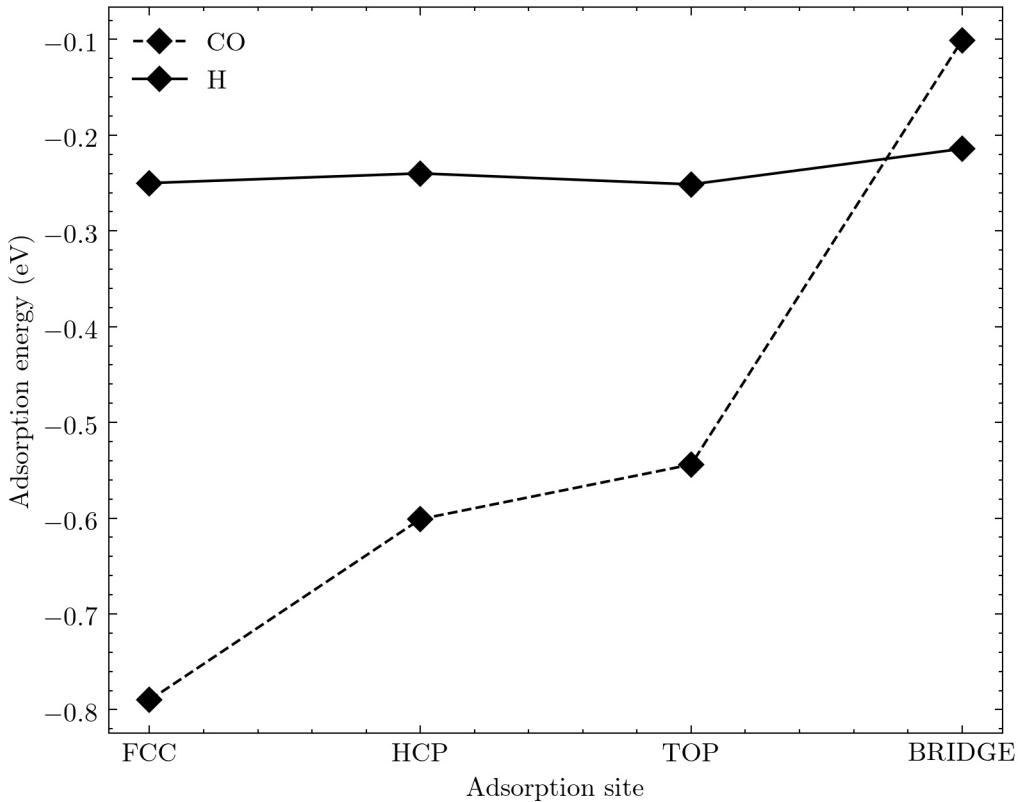


Figure 4.7: binding energy of H and CO for each site on a 2x2x5 Pd slab

surface. [9] This does not appear to be an issue for PdCu_{20} alloys indicating that this level of Cu is too low to have such an effect. The $\text{Pd}_{60}\text{Cu}_{40}$ alloy on the other hand has a much higher binding preference for CO than its sister hydrogen system. $\text{Pd}_{60}\text{Cu}_{40}$ is different from other systems in that the crystalline structure transitions to a BCC lattice. [13] BCC structures only have two different sites available for hydrogen binding, BRIDGE and HCP. [14] This change in structure combined with the Cu's availability to bind with C likely accounts for the large discrepancy.

CO adsorption

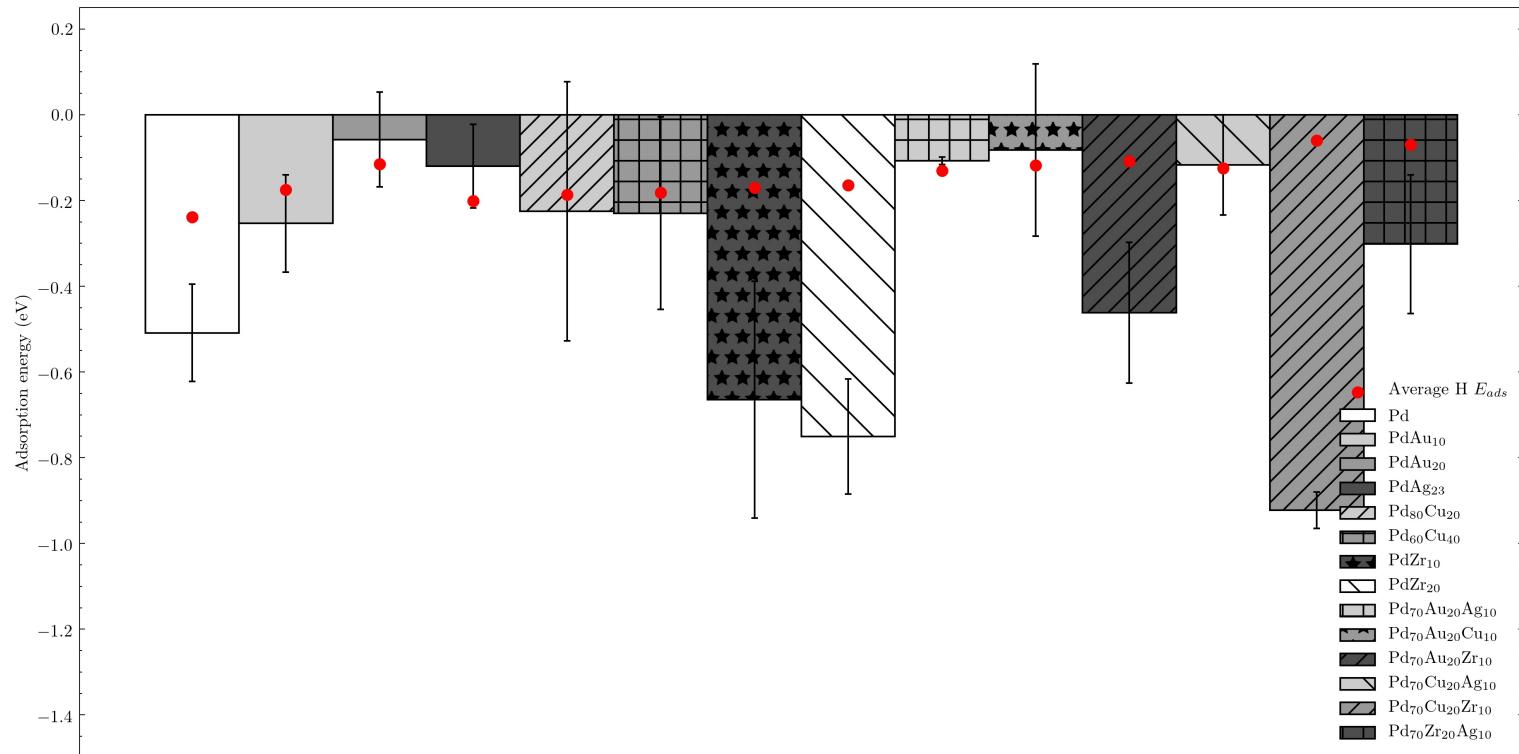


Figure 4.8: Average binding energy of CO on the surface of palladium and palladium alloy slabs

NH₃ adsorption

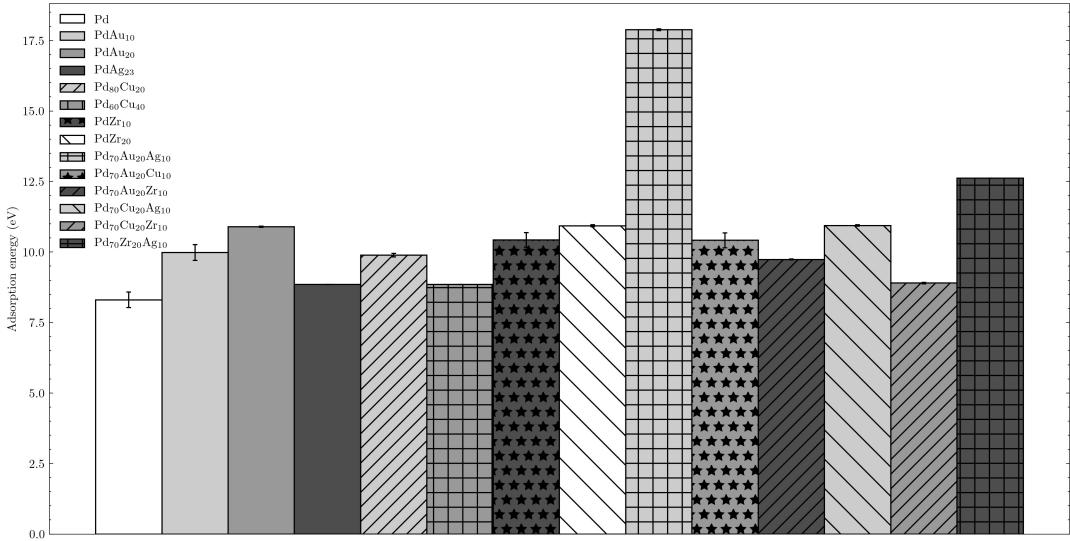


Figure 4.9: Average binding energy of NH₃ on the surface of palladium and palladium alloy slabs

Ammonia

The results of the ammonia simulations are shown in figure 4.9. Of the tested material compositions, neither palladium or any alloy showed an ability to readily bind with Ammonia, this was also true across all sites on the fcc and bcc lattice. This is consistent with the experimental results of Lundin et al [15] and the previous simulations by Herron et al [16]. It should be noted that the paper by Herron [16] found that while ammonia itself did not bind with the surface of palladium, radicals which can be created from ammonia such as imidogen (NH) and azanide (NH₂) will readily form bonds. It is however extremely unlikely that these compounds wil be present in fuel cell hydrogen, and in the unlikely event they are they will likely instantly reform into the more stable NH₃. It can be concluded therfore that NH₃ will create no challenges for the operation of palladium membranes.

Oxygen and Water

Since O₂ is a symetrical molecule binding was performed similarly to H₂ in section 4.3.2, the results of which are shown in figure 4.10. Alloys consisting mainly of noble metals (Pd, Ag, Au) typically did not readily bind with oxygen. Whereas alloys containing non-noble metals (Zr and Cu) showed a preference towards oxygen binding. This can pose an issue during enrichment and will likely lead to either the formation of oxides on the surface of the membrane, or catalyse a reaction between either oxygen and hydrogen, or oxygen and one of the other gaseous impurities. In the former the formation of oxides creates a shift in the lattice parameter, similar to the $\alpha - \beta$ transition seen in pure

palladium membranes (figure 2.6)[17] and cause membrane failure. In the latter results from hydrogen impurity can be thrown off. Therefore if oxygen is expected in the sample Zr and Cu containing alloys should be avoided.

Water adsorption was performed by attaching the O atom to each available site as per previous studies. [18] The results are shown in figure 4.11 and follow the same trend as the O₂ results discussed above. One important caveat when considering water binding on the surface of metals is the ability for H₂O molecule to form hydrogen bonds with neighbouring molecules.[19] While this study only considered the influence of a single water molecule, in real tests the system will likely have a number of water molecules present. The effect of the hydrogen bond would likely result in the further stabilisation of future water molecules onto the surface, creating an exponential increase in adsorbed H₂O. [19] Care should also be taken, as previous studies on other metallic systems have shown that the binding of water often leads to subsequent dissociation, and formation of a metal oxide and hydrogen. Leading to the same problems with oxidation as previously discussed. [20]

In conclusion noble metals appear to be the best alloying compounds to protect against the influence of H₂O and O₂. This is to be expected as these metals are traditionally resistant to oxidation. It should be noted however that while this study focused on binding of water on the membrane, it does not take into account adsorption on any other components and fittings on a system. Water in particular is notoriously difficult to remove from a system due to its availability for binding on metal surfaces.[21] Therefore while reducing its effect on the membrane solves one problem, its effect on the overall system still has to be considered.

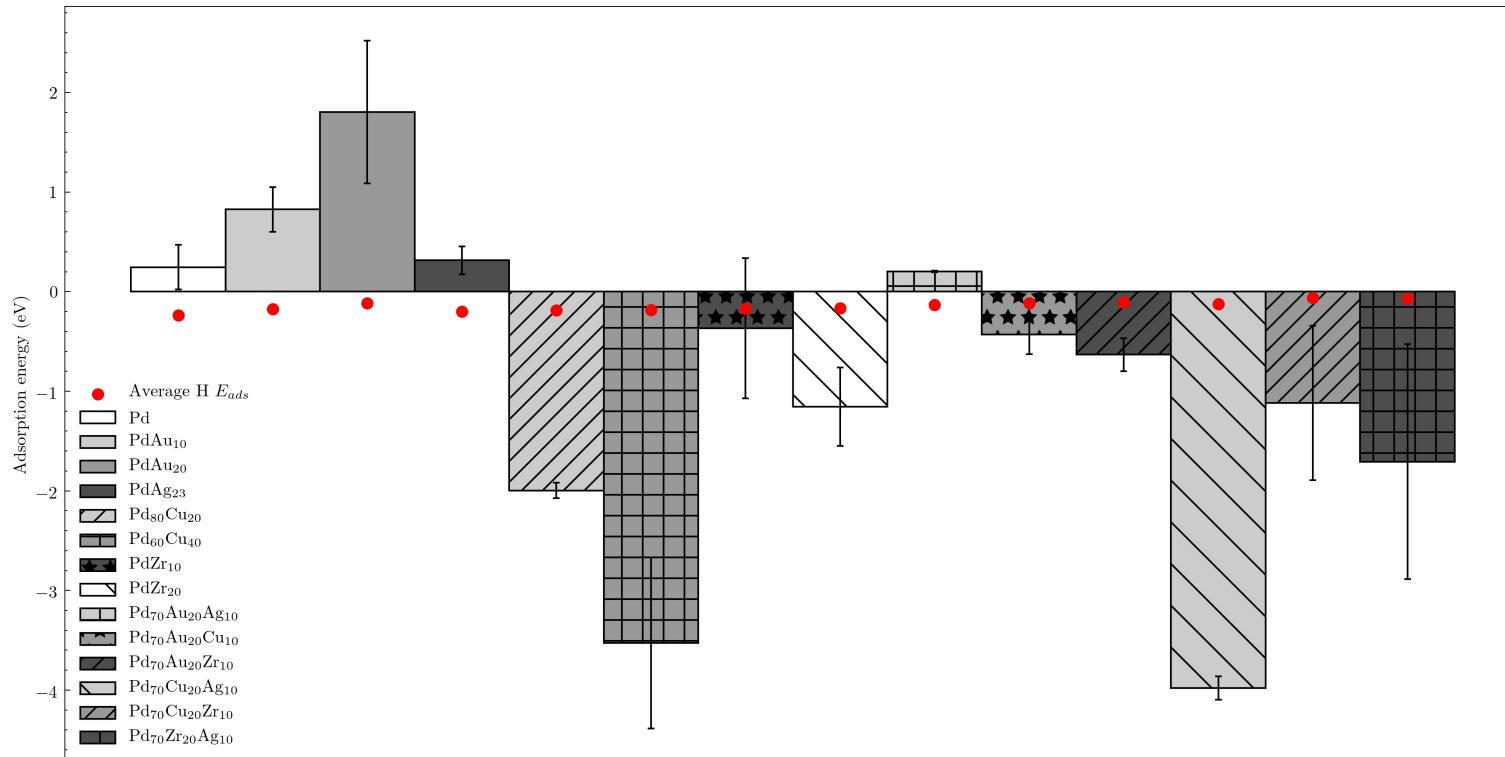
O_2 adsorption

Figure 4.10: Average binding energy of O₂ on the surface of palladium and palladium alloy slabs

H₂O adsorption

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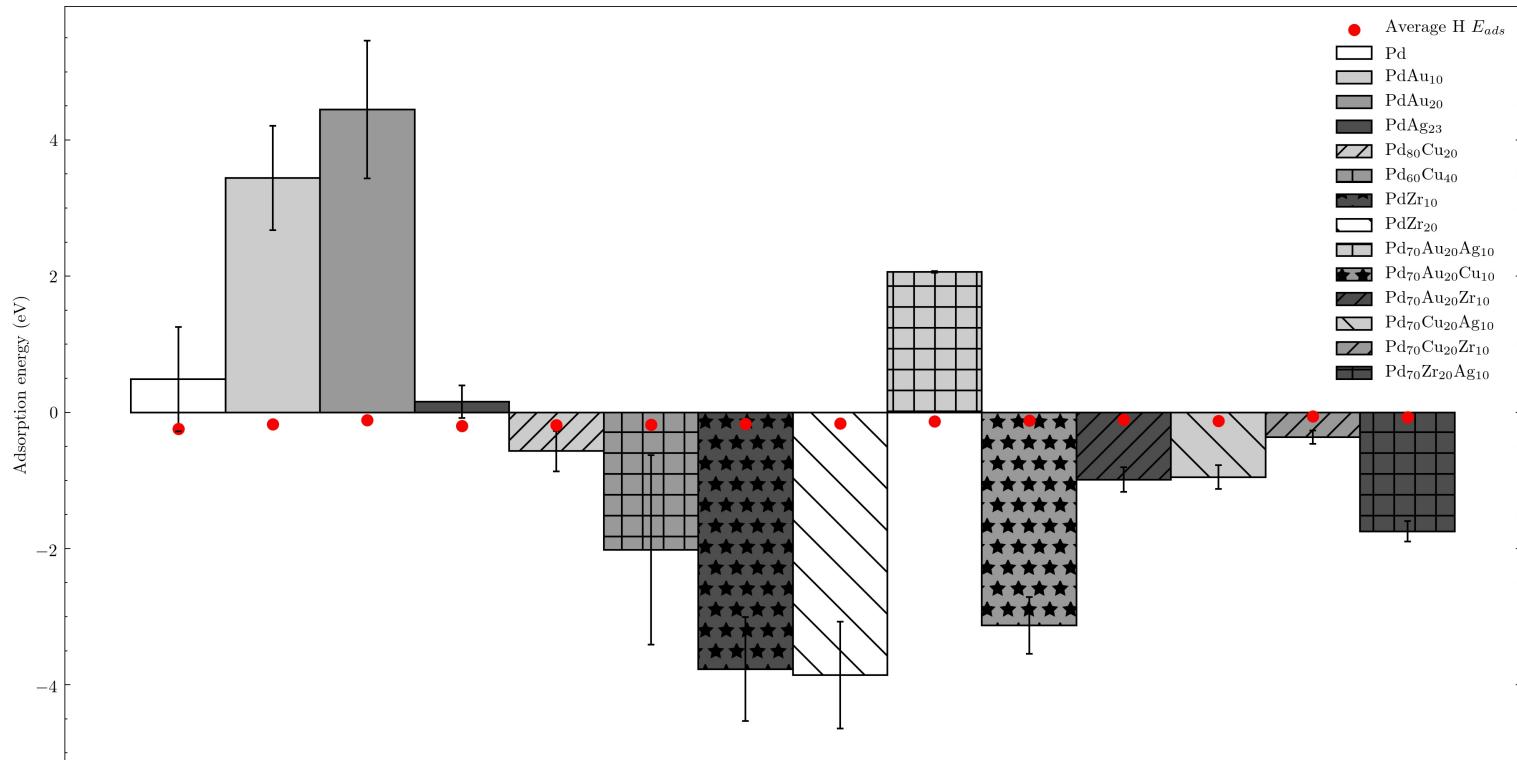


Figure 4.11: Average binding energy of H₂O on the surface of palladium and palladium alloy slabs

Methane

Methane was adsorbed onto the surface of the Pd slab systems using one of the hydrogen molecules as has previously been performed in literature. [22] The results of the simulations are shown in figure 4.13.

All simulated metals seem to have the ability to bind CH_4 to its surface. Intuitively this seems reasonable since the atom binding to the surface is H_2 , which we have already proven has the ability to bind to all Pd alloy models. The molecule also features a carbon molecule which from our CO simulations in figure 4.8 will also preferentially bind to the surface of the Pd slab models, at a higher preference than hydrogen. The results of the CH_4 simulations seem to follow the general trend of it's sister CO results, however at a weaker level. All simulations were unstable which is shown by the large error values showing large swings in the results from each simulation. Therefore it is likely that in many simulations, while CH_4 is stable on the surface, could not find the most stable coordination due to competing forces acting from the hydrogen atoms, and the carbon atom.

The binding energies of CH_4 on each site in the Pd system are shown in figure 4.12. Similarly to CO, the CH_4 molecule has a higher preference to the FCC and HCP sites than H. Unlike CO, CH_4 does not bind as strongly to the TOP site as CO. The reason for the strong binding preference to the FCC and HCP sites is likely due to the fact that while the H atom is bound within the HCP and FCC sites, the C atom and other H atoms will bind to the surrounding metallic atoms in the crystalline lattice, stabilising the molecule in those sites. On the TOP and BRIDGE sites this does not happen, and since the H atom is bound more strongly to C through a covalent bond, the resulting energy available for binding on these sites is lower than it would be if the molecule was pure hydrogen.

In terms of resistance to CH_4 binding, the conclusions reached in the section discussing the results of CO still hold true. All alloy compositions with high percentages of Au and Ag showed higher resistance to CH_4 binding, whereas Cu and Zr containing molecules performed worse.

Past studies performing CH_4 binding on metallic surfaces found that in some cases the H atom could dissociate from the molecule, creating CH_3 and H. [23] In this particular application such a reaction would result in the liberated H atom permeating through the membrane, leaving CH_3 on the retentate side. While this changes the composition of the retentate gas, from a measurement perspective it should not pose much of an issue. The ISO 14687-2[24] standard specifies a total hydrocarbon level and therefore any CH_3 that is produced should be detected using previously outlined techniques. [25]

What may pose a larger issue is that in the study performed by Herron [16], it was found that similar to Ammonia, CH_4 based radicals will bind more strongly to the surface than CH_4 resulting in an increasing poisoning effect. It is unknown whether the hydrogen dissociation effect previously discussed would continue to occur with these radicals, but in the case it does, the result would eventually be carbon deposition on the surface of the membrane. Eventually deactivating the membrane entirely, and throwing off all results due to removal of carbon from the gas.

CH_4 adsorption sites on Pd compared to H

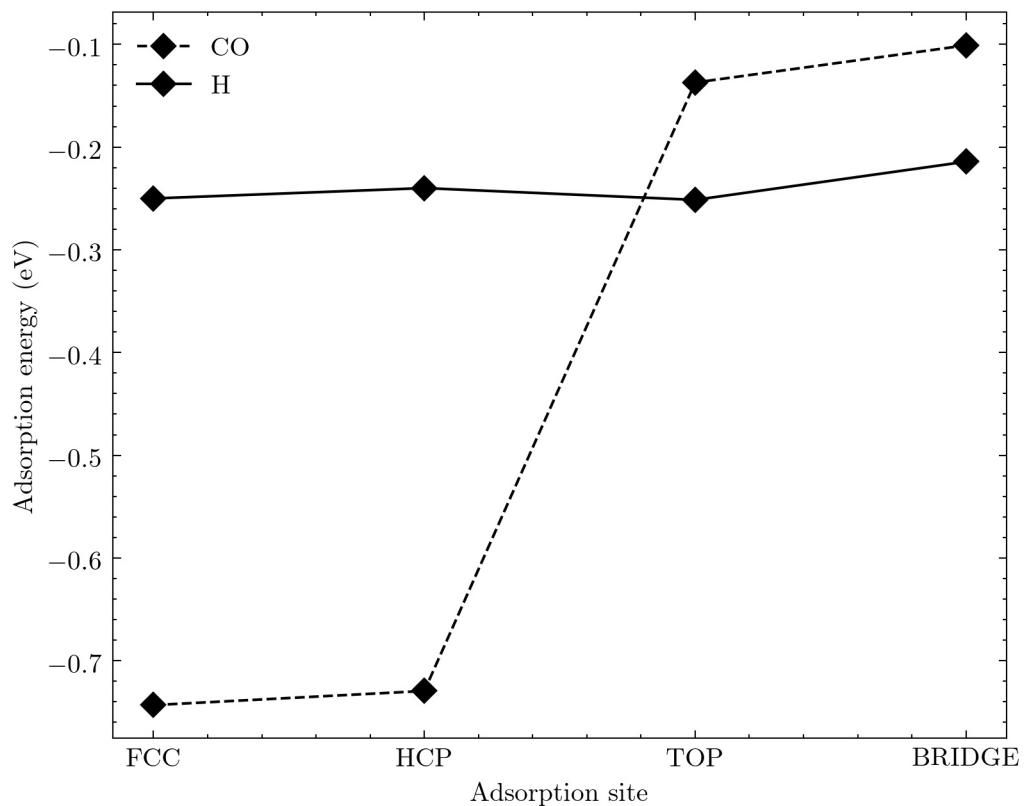


Figure 4.12: binding energy of H and CH_4 for each site on a $2\times 2\times 5$ Pd slab

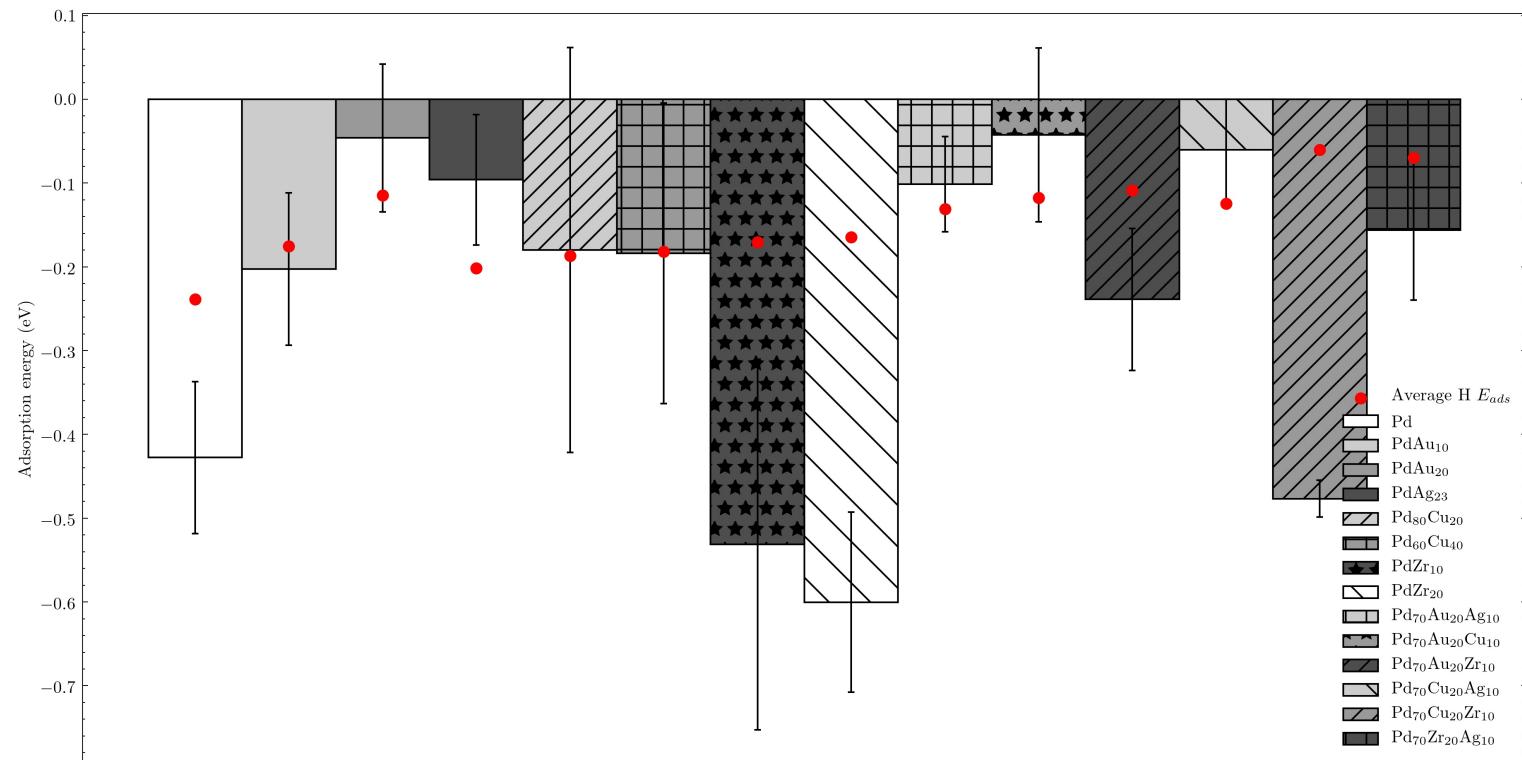
CH_4 adsorption

Figure 4.13: Average binding energy of Methane on the surface of palladium and palladium alloy slabs

Formaldehyde and Formic acid

Formaldehyde and Formic acid are similar molecules, with the only difference being one of the hydrogen atoms being replaced with an OH group on formic acid. Both molecules were adsorbed onto the surface using the double bonded O atom perpendicular to the surface of the slab model.[26] The results for the simulations are shown in both figure 4.14 for formaldehyde and figure 4.15 for formic acid.

The results of these simulations vary widely, with formaldehyde showing strong binding ability with Pd and Pd alloy surfaces, while Formic acid appears to reject binding completely. The systems were also largely unstable as indicated by the large error values, which indicates that there are a number of forces acting on each atom on the molecule and therefore multiple stable arrangements other than the one chosen.

This result for formaldehyde is not surprising as formaldehyde is widely known to be effective catalyst for oxidation of formaldehyde, being able to oxidise formaldehyde under the presence of sunlight alone. [27] Therefore it is likely that any mixture containing both formaldehyde and oxygen under the presence of a palladium membrane will likely react, forming carbon dioxide and hydrogen. Additionally palladium alone may be powerful enough to dissociate the formaldehyde molecule, and depending on the coordination of the molecule from H₂ and CO, or hydrocarbon compounds ranging from CH₂ to C₄ and oxygen,[26] the ramifications of which have been discussed previously. Unfortunately out of the tested alloys there does not appear to be a solution to this and further membrane compositions should be screened in order to determine an appropriate material to suppress the effect of formaldehyde.

Past research evaluating Pd surfaces for formic acid oxidation found that Pd surfaces typically reject COH bindings which lines up well with these results. [28]

Formaldehyde adsorption

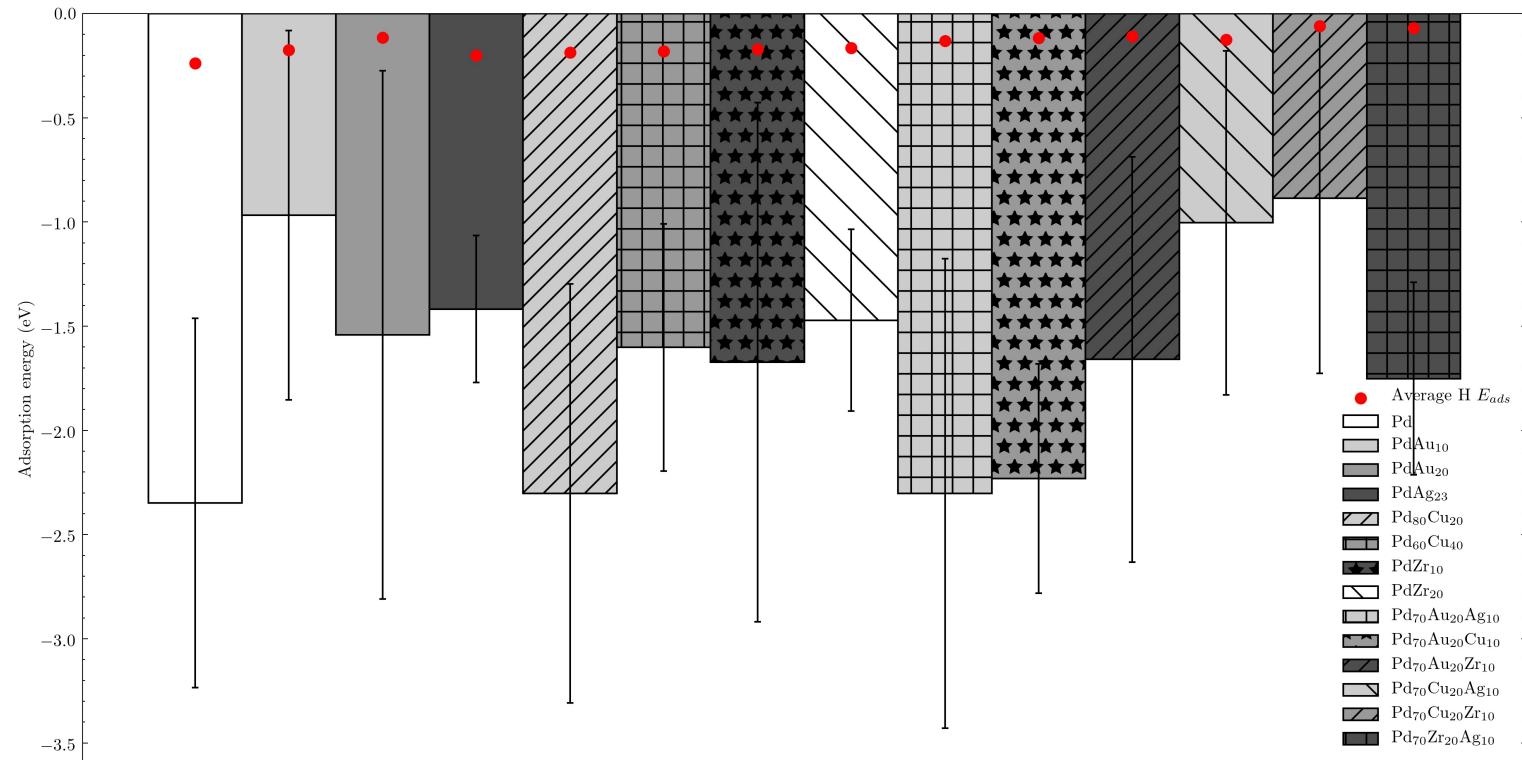


Figure 4.14: Average binding energy of formaldehyde on the surface of palladium and palladium alloy slabs

Formic Acid adsorption

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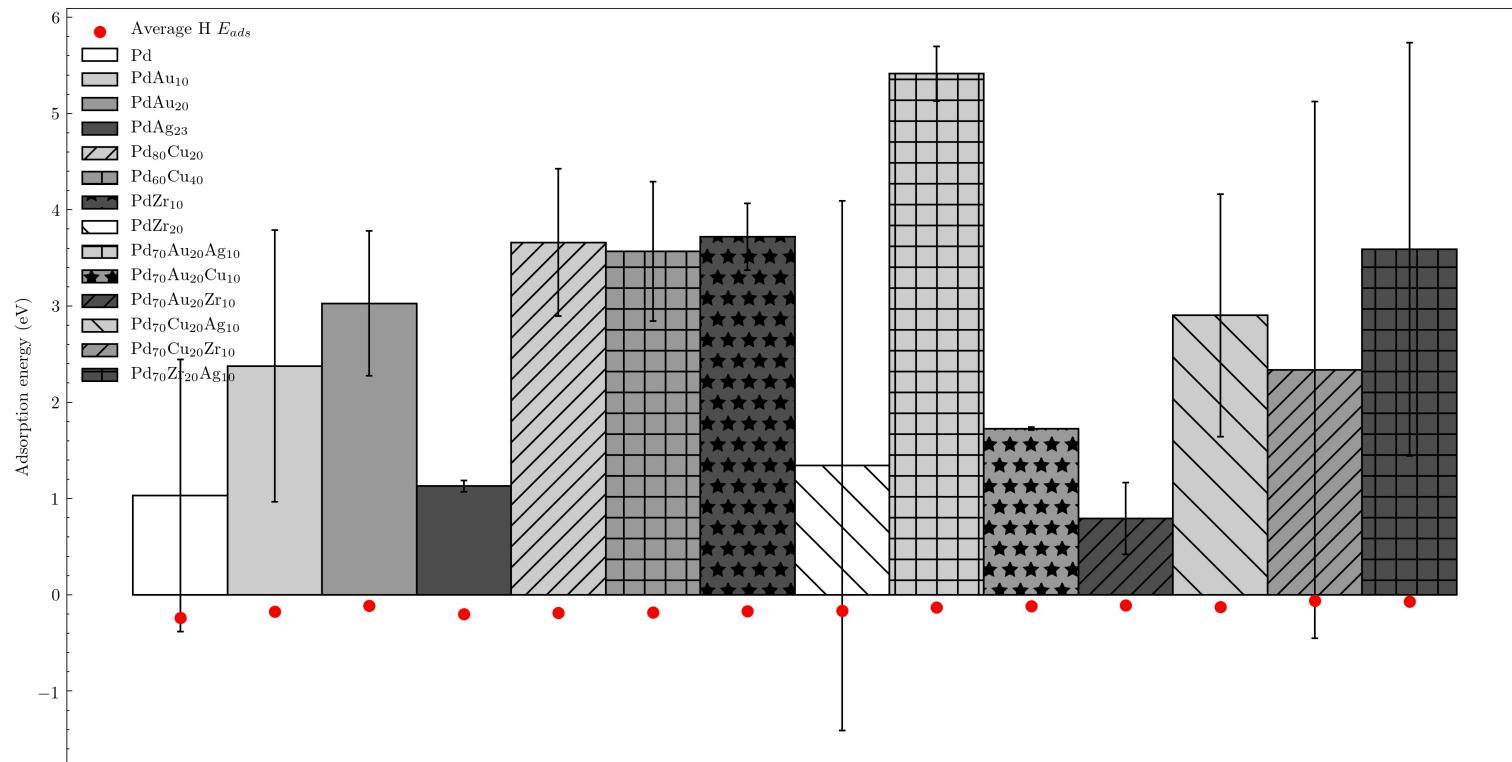


Figure 4.15: Average binding energy of Formic Acid on the surface of palladium and palladium alloy slabs

H₂S adsorption sites on Pd compared to H

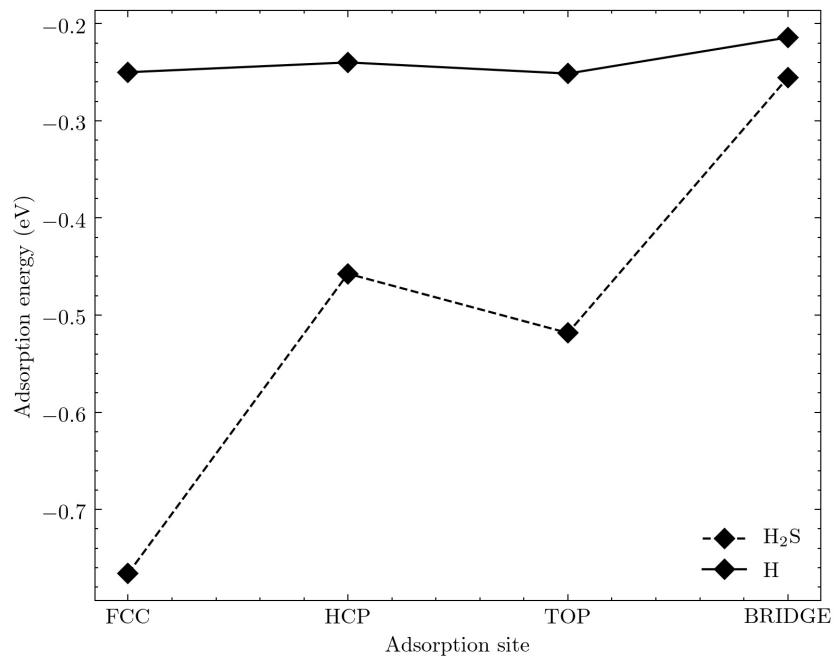


Figure 4.16: binding energy of H and H₂S for each site on a 2x2x5 Pd slab

Hydrogen sulphide

The final molecule that was simulated was H₂S. This molecule was adsorbed using the sulphur atom as this is the known mechanism for H₂S binding on a metallic surface. [29] The results are shown in figure 4.17. As expected all metals showed the ability to bind with the sulphur atom at least as strongly as hydrogen. Additionally the S atom will bind stronger to all active sites for hydrogen dissociation as shown by figure 4.16.

It appears that alloying with most metals will do little to halt the binding of sulphur, except for gold and Zr. Alloying with these metals brings the binding energy to a level where it is around equal to that of hydrogen, and is therefore more manageable. Additionally while alloying with silver on its own appears to infact increase the ability for sulphur to bind onto the surface, the effect is completely negated when gold is present.

Of the alloys tested PdAu₂₀, both Zr binary alloys, PdAuZr, and PdZrCu appear to be the most suitable for mitigating the effects of H₂S. It should be noted that past studies have revealed that Pd₄S is in fact available for hydrogen permeation, albeit at a much slower rate.[29] This may indicate that it is possible to pretreat a palladium membrane with sulphur, to a point where it is no longer reactive to sulphur, but can still permeate hydrogen. Such studies are outside the scope of this thesis however

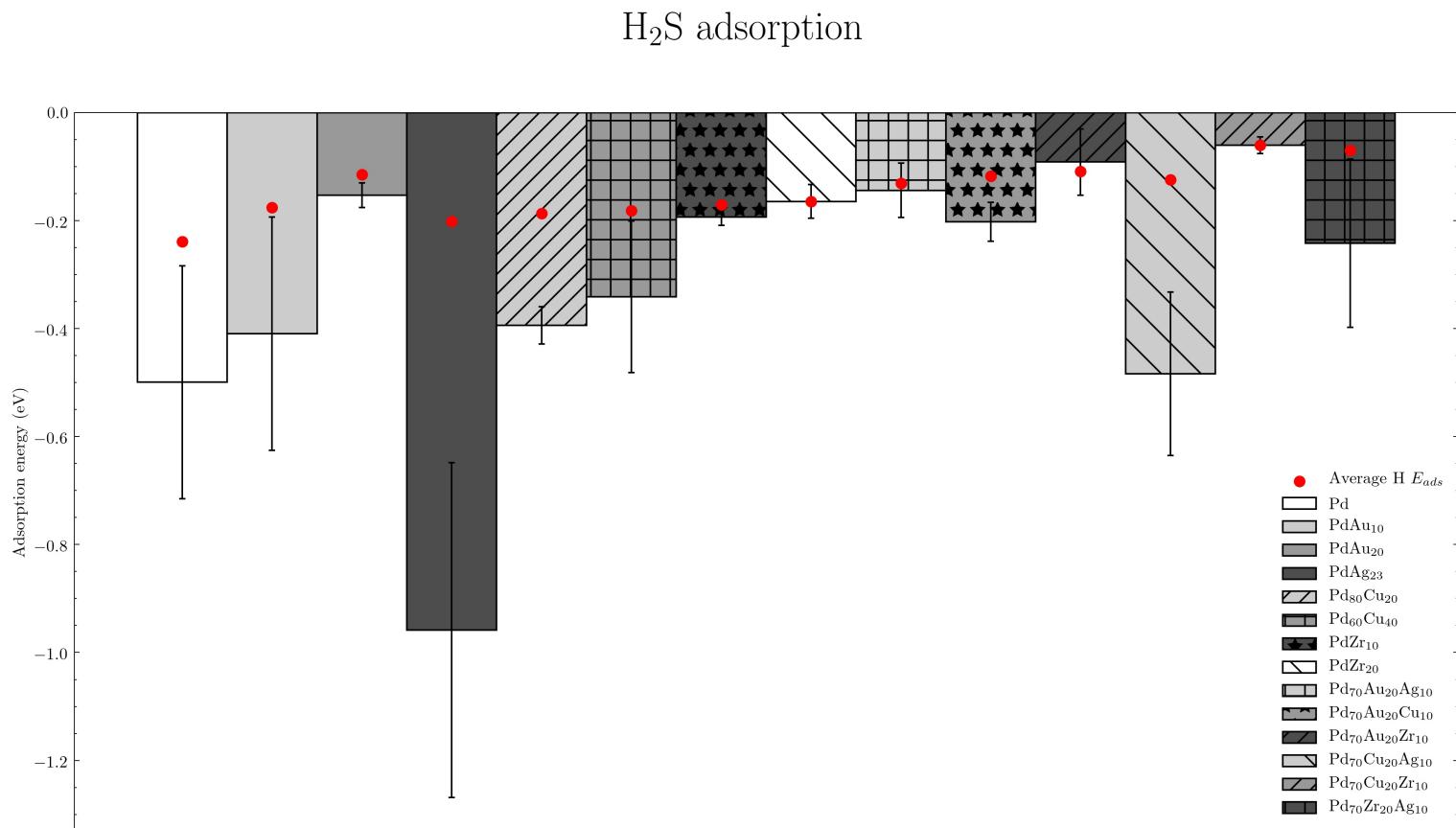


Figure 4.17: Average binding energy of H_2S on the surface of palladium and palladium alloy slabs

Table 4.4: Best performing alloys for each environment with respect to the different between the binding energies with relevant impurities, and the binding energy of hydrogen

Environment	Best performing alloy(s)	$E_{i_{ads}}/E_{H_{ads}}$ ($i=$ impurity)
Oxidising	PdAu20	-38.73 (H ₂ O), -7.18 (O ₂)
Carbonaceous	PdAu ₂₀ PdAuCu PdZr20	0.50(CO) 0.40 (CH ₄) 0.70(CO) 0.36(CH ₄) 0.93
Sulphurous	PdCuZr PdAuZr	0.92 0.98

4.4 Conclusion

DFT simulations were carried out investigating the binding energies of ISO 14687-2 impurities on the surface of palladium and palladium alloy membranes. A number of metals were alloyed, either because they are commonly used in literature, or are known for their resistance to sulphur containing environments which were of key importance to this thesis. Most alloys were found to be stable except for Cr containing alloys, which were eliminated from the study.

After testing the impurities it was clear that the binding of CO, CH₄, O₂, H₂O and H₂S were affected most by the alloy composition. Ar, He, N₂, NH₃, CO₂, and Formic acid were found to be completely inert to all compositions. Formaldehyde strongly adsorbed to all alloys regardless of composition and further research will have to be taken to find a suitable composition to mitigate this.

These impurities can be split into 3 broad groups, oxidising (O₂ and H₂O) carbonaceous (CH₄ and CO) and sulphurous (H₂). The best performing alloys for each of these impurities were decided by comparing the calculated binding energy to that of the same alloy binding with Hydrogen. The most suitable alloys for each class of material is shown in table 4.4.

In the following chapter these membranes will be manufactured and tested under carbonaceous and sulphur containing environments in order to validate the results of this study. Oxygen containing environments will not be tested due to the dangers of heating oxygen in a hydrogen matrix.

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Chapter 5

Impurity resistance of dense metal membranes under hydrogen impurities

5.1 Abstract

In order to further develop hydrogen impurity enrichment as a suitable technique for hydrogen quality assurance more research is required on a suitable membrane material for use within such a device. In this chapter a number of dense palladium alloy membranes were synthesised on a YSZ substrate using a combination of electroless plating and magnetron sputtering.

The permeation of the synthesised membranes, in addition to a commercial membrane were tested under a variety of ISO 14687-2 impurities in order to determine which alloy composition was most suitable for use as a membrane material for hydrogen impurity enrichment, where low reactivity with impurities present in hydrogen samples are required. Of the tested membranes the best performing compositions were PdAuAg, PdAuCu and PdCuZr which only showed a 27%, 25% and 26% drop in permeability under atmospheres containing 10 ppm of non-sulphurous, and 2 ppm of sulphurous impurities typically expected to be found in hydrogen derived from steam methane reforming. This indicates that these alloys are most suitable for metrology purposes due to their low reactivity.

5.2 Introduction

In order to improve the accuracy and the cost of hydrogen impurity enrichment a suitable membrane composition must be found. In addition to this all previous studies used a commercial palladium-based membrane and in all cases it was noted that certain impurities reacted with the membrane. This interaction had the result of changing the composition of the enriched gas mixture and therefore reducing the final accuracy of the measurement. [1, 2] The self-supported commercial membranes used in both studies are

also generally between 20-100 μm in order to provide sufficient mechanical strength for a membrane. However, for palladium membranes to be economical this thickness must be reduced to about 1-5 μm giving the added benefit of greater flux and therefore lower enrichment times.

Palladium alloy membranes are generally created by forming an alloy with silver, copper or gold. By doing this the hydrogen embrittlement effect can be effectively mitigated. Using alloys has the added benefits of decreasing the overall amount of palladium required in the film, driving up their cost effectiveness, and in some cases increasing the flux of the membrane to higher levels achievable than a pure palladium membrane. The addition of extra metallic elements however will affect the membranes catalytic properties with impurities within the hydrogen sample. If the membrane catalyses reactions such as water gas shift, methanation, or CO oxidation, the composition of the gas sample could change, which would lead to inaccurate results during analysis of the enriched sample. In addition to this, it is possible that hydrogen samples contain sulphurous impurities such as H₂S or OCS, if produced from hydrocarbons (steam methane reforming etc.). Sulphurous impurities are known to chemisorb onto the surface of palladium membranes through a permanent reaction, not only changing the composition of the gas mixture and compromising analysis, but also severely reducing flux through the membrane, and potentially leading to membrane failure due to crack formation in the palladium layer.

This study aims to apply recent advances in palladium membrane manufacturing to improve impurity enrichment. Palladium alloy membranes will be deposited onto porous YSZ supports using both electroless plating and closed field unbalanced magnetron sputter ion plating. This will have the combined effect of reducing the amount of palladium used, driving down their cost, and increasing the flux, and therefore reducing the time taken to enrich a hydrogen sample. This work aims to quantify the degree of interaction of impurities with palladium alloy membranes in a three-step experimental procedure. The pure hydrogen flux of each membrane composition will be measured and the membranes hydrogen permeability calculated as a base line. The following two permeation tests will measure the change in permeability resulting from introducing part-per-million level impurities into the gas sample. The change in permeability which results from this will act as a measure for the membranes tendency to interact with different impurity types. Additionally, at all three testing stages, X-ray photoelectron spectroscopy (XPS) will be performed on the surface of the membranes to investigate how the composition on the surface of the membrane changes when exposed to each impurity environment. This will allow the alloy segregation behaviour to be observed, and more importantly, quantify the amount of sulphur which has reacted with the surface of the membrane.

Table 5.1: Membrane compositions analysed by EDS and their thickness measured using FIB-SEM

Membrane ID	Manufacturing technique	Composition (wt%) (+- 1% Relative)					Thickness (um)
		Pd	Cu	Ag	Au	Zr	
PdCu (Fcc)	Magnetron Sputtering	76.24	23.76	-	-	-	1.679
PdCu (Bcc)	Magnetron Sputtering	43.24	56.64	-	-	-	1.664
PdCuZr	Magnetron Sputtering	72.10	14.46	-	-	13.54	1.541
PdAg	Electroless Plating	65.55	-	34.45	-	-	0.573
PdAu	Electroless Plating	74.7	-	-	25.3	-	1.172
PdCuAg	Electroless Plating	72.1	-	8.27	19.58	-	0.867
PdCuAu	Electroless Plating	63.90	13.6	-	22.1	-	1.545
PdAuAg	Electroless Plating	60	-	11.2	28.3	-	0.736

5.3 Results and Discussion

5.3.1 Membrane characterisation

Figure 5.1 (a)-(g) shows the cross-sectional SEM images of the manufactured membranes. Through both electroless plating and magnetron sputtering dense and defect-free separation layers were able to be fabricated for all compositions. Thickness of the fabricated membranes are shown in 5.1 and ranged from 573 nm to 1.579 μm . In general thinner layers were achieved using electroless plating although theoretically sub-micron layers are possible through magnetron sputtering, examples of this being SINTEF's patented sputtering process.[3] The integrity of the manufactured membranes was measured using the procedure laid out in section 3.2.4. All membranes showed no leakage when pressurised to 10 bar indicating that all membranes were uniform, pinhole free and therefore suitable for hydrogen separation. [4]

The surface composition of each membrane was measured by XPS and is shown in Table 5.1. A wide range of compositions were fabricated. From phase data on the PdCu system [5, 6] both varieties of PdCu membranes (bcc phase and fcc phase) were successfully fabricated. In addition to this PdCuZr ternary alloy was fabricated through magnetron sputtering as there is evidence in literature that this alloy composition shows high resistance to impurities and Zr cannot be deposited through electroless plating. [6]

Silver is the most popular dopant for palladium membranes and forms a stable alloy with palladium at concentrations greater than 20 wt%, with the optimal composition occurring at 23 wt%. On top of mitigating the effects of hydrogen embrittlement, a 60% increase in permeability is observed when compared to pure Pd membranes. Despite having enhanced permeation properties, PdAg is still susceptible to poisoning, in particular from sulphurous compounds which can form both Pd_4S and $\text{Ag}_5\text{Pd}_{10}\text{S}_5$. A composition of $\text{Pd}_{64.9}\text{Ag}_{35.1}$ wt% was achieved, which, while higher than the desired composition of $\text{Pd}_{77}\text{Ag}_{23}$ wt%, was determined adequate for the purposes of this study.

Copper is another widely studied binary alloy which is known to suppress hydrogen embrittlement. Alloying with copper also has the advantage that it reduces the cost

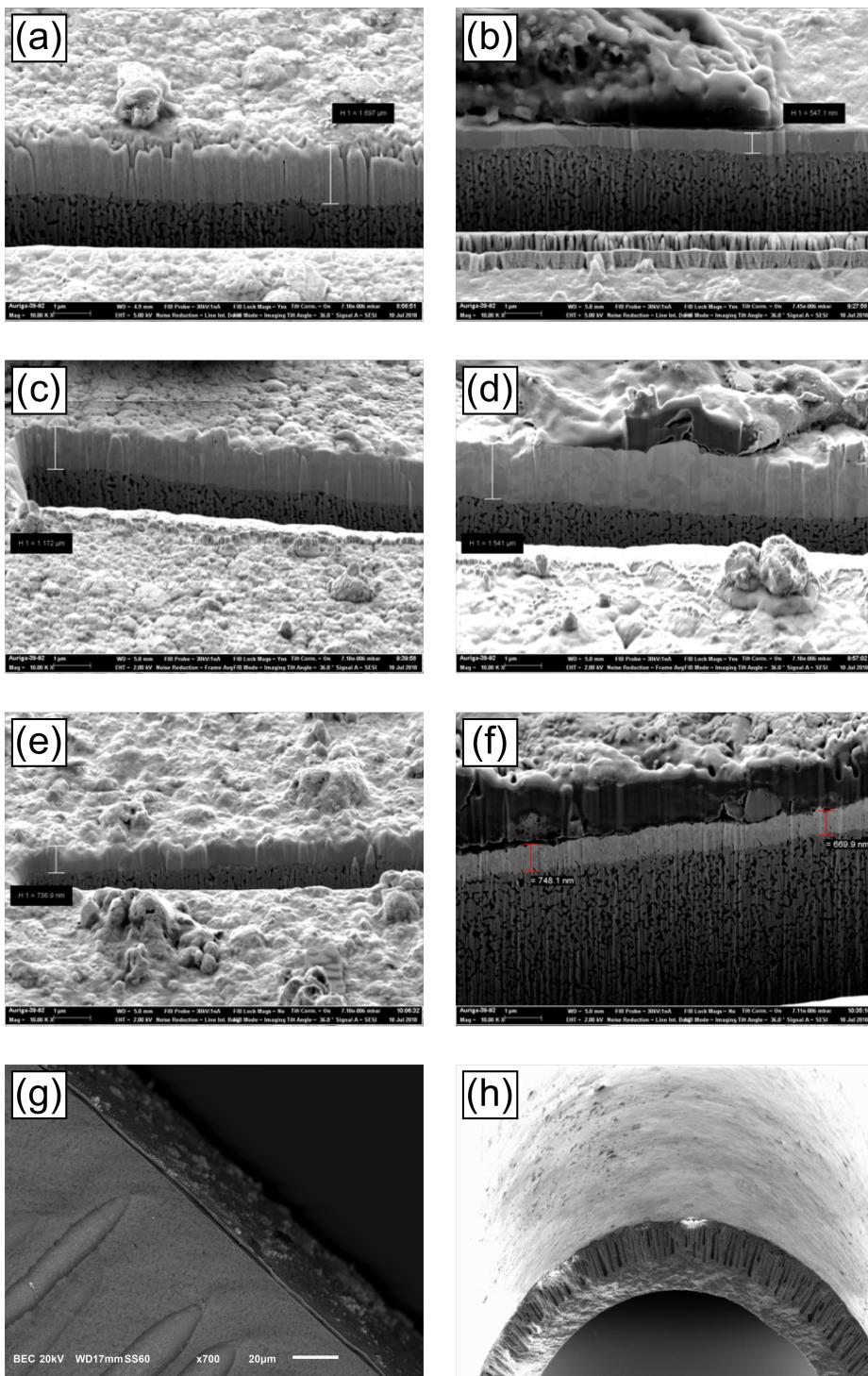


Figure 5.1: SEM images of fabricated membranes (a) PdCu (fcc) (Sputtering) (b) PdAg (ELP) (c) PdAu (ELP) (d) PdCuZr (Sputtering) (e) PdAgAu (ELP) (f) PdCuAg (ELP) (g) PdCu (bcc) (Sputtering) (h) typical cross section

of the membrane by a larger amount than most other metals and through improving the membranes sulphur resistance. The maximum permeability of a palladium copper membrane occurs at the composition $Pd_{60}Cu_{40}$ wt% and this is due to the formation of a bcc lattice rather than the fcc lattice commonly seen in pure palladium and most binary alloys. [7] Temperature cycling has previously been performed on this alloy composition and it has been found that the bcc crystalline configuration has a higher permeability than the fcc phase. [8] This behaviour is due to the increased number of hcp adsorption sites which hydrogen has a slight preference for, and the bcc structure allowing faster diffusion through the bulk of the membrane. [9] Conversely the fcc structure has a higher impurity resistance than the bcc structure, particularly for H_2S . [7, 10] $Pd_{44}Cu_{66}$ and $Pd_{65.5}Cu_{34.5}$ wt % membranes were manufactured using magnetron sputtering which were in the range for bcc and fcc phases respectively.

$PdAu$ alloys see a slight increase in permeability, up to 30% more than pure Pd [11], with gold additions up to 20%, after which the permeability rapidly decreases. While alloying with gold does not improve the permeability much compared to silver or copper, gold alloys show greatly improved sulphur resistance. [12] The synthesised membrane was found to have the composition $Pd_{74.7}Au_{25.3}$ which, while containing a high amount of gold resulting in lower permeation, will have a higher impurity resistance.

5.3.2 Hydrogen permeation

Table 6 shows the hydrogen permeation through the 9 tested membranes at steady state after 12 hours of operation. As expected, hydrogen permeation flux increases with the elevated temperatures. Moreover, the mass transfer resistance of the substrate will not represent major limitations since its gas transport resistance is negligible compared to that of the dense palladium alloy layer¹⁰. Deposited layers were all on the scale of 0.5-2 μm which from previous research indicates the main rate limiting step in hydrogen permeation being the thickness of the membrane layer. [13] The palladium copper alloy which was in the bcc phase showed the highest hydrogen permeability of all the synthesised membranes which was expected as discussed in **section 3.1**. The membrane which showed the lowest hydrogen permeability was the $PdCuZr$ membrane, this is likely due to the combined effects of the alloy having an fcc structure, and the alloy having the lowest concentration of palladium compared to the other synthesised membrane, resulting in the lowest number of sites for hydrogen dissociation and subsequent permeation. The $PdAu$ and $PdAuAg$ membranes both showed low permeabilities. Gold as an alloying material traditionally does not show much increase in permeability [12] but is instead used to suppress the effects of impurities on the membrane, [12] which is the main goal of this study. Despite the fact that the commercial membrane is also based on $PdA-gAu$, the membrane manufactured through electroless plating has a lower permeability due to the high gold concentration. It is likely that the concentration of silver in the commercial membrane is closer to 23%, which is the optimal value for hydrogen permeation, and it's gold concentration is much lower than the electroless plated membrane. Both $PdCuAg$ and $PdCuAu$ had reasonably high hydrogen permeabilities. While none of these membranes showed a hydrogen permeability as high as the commercial alloy, it

Table 5.2: Pure hydrogen permeability of studied alloy membranes under pure hydrogen at 300°C and 1 bar pressure differential

Membrane ID	Permeability ($mol\ m^{-1}s^{-1}pa^{1/2} \times 10^{-8}$)
PdCu (Fcc)	1.30
PdCu (Bcc)	1.68
PdCuZr	0.14
PdAg	0.94
PdAu	0.33
PdCuAg	1.22
PdCuAu	1.43
PdAuAg	0.19
Commercial (REB)	5.71

Table 5.3: Permeability results for all membranes under both impurity conditions

Membrane ID	Permeability ($mol\ m^{-1}s^{-1}pa^{1/2} \times 10^{-8}$)			% Drop	
	Pure H ₂	Non-Sulphur	Sulphur	Non-sulphur	Sulphur
PdCu (Fcc)	1.30	0.22	0.185	80%	86%
PdCu (Bcc)	1.68	0.721	2.47	55%	85%
PdCuZr	0.14	0.12	0.101	12%	26%
PdAg	0.94	0.117	0.007	88%	92%
PdAu	0.33	0.165	0.215	51%	35%
PdCuAg	1.22	0.48	0.299	61%	75%
PdCuAu	1.43	0.789	1.07	45%	25%
PdAuAg	0.19	0.163	0.142	16%	27%

should be noted that the commercial membrane had a much larger thickness resulting in a much higher cost and lower flux values than the composite membranes.

5.3.3 Impurity reactivity

Table 5.3 shows the results of hydrogen permeation under the presence of the two different impurity conditions discussed in Table 5.3 compared to the pure hydrogen permeability values shown in Table 5.2. The permeability data was taken once the flux had reached steady state after 12 hours of operation. For all membranes there was a reduction in permeability when the membranes were exposed to impurities. The magnitude of this reduction compared to the pure hydrogen permeability is used as an indication of the degree of interaction between the membrane and the impurities. Table 5.4 shows the composition of each membrane in between each test in order to measure permanent

surface reactions and segregation behaviour of the alloys under the chosen impurities.

Binary alloys

In non-sulphur tests the PdAg binary alloy was the worst performing, with the permeability dropping by 88% of its original value. This was expected as the addition of silver to a palladium system, while effective at increasing the permeability, does not contribute much to impurity resistance. [14] This was further supported by the results of the sulphur tests where the permeability dropped by 92% and composition analysis in Table 5.4 showing that sulphur was present in 42% of the surface. The PdAg alloy also showed a large degree of segregation behaviour under non-sulphur impurities which likely contributed to the large reduction in flux, with silver concentration increasing to 75% at the top 10 nm of the sample, resulting in a large drop in permeability.

Interestingly the PdCu membrane with a composition in the bcc phase showed higher resistance to non-sulphurous impurities than the fcc phase, with the former only experiencing a 55% drop in permeability compared to an 80% drop in permeability in the latter. This again seems to be a result of the segregation behaviour of the alloy, with the PdCu alloy in the fcc phase experiencing a large amount of segregation, with the palladium concentration increasing to around 90% on the retentate side. Conversely the PdCu composition in the BCC phase membrane only changed slightly. The XPS analysis showed that while the reactivity of sulphur on the surface of both copper based binary membranes was of a similar magnitude, the BCC phase had a slightly lower resistance, with 29% of the surface containing sulphur after exposure to sulphurous impurities as opposed to the 25% shown by the fcc phase alloy.

The PdAu alloy showed the best impurity resistance out of the binary alloys tested under both impurity conditions, with only a 51% and 35% drop in permeability under non-sulphur and sulphur conditions respectively and only a 12% concentration of sulphur was observed on the surface after XPS analysis. The alloy showed slight segregation of gold away from the permeate surface under non-sulphur impurity conditions likely due to the fact the difference in interaction strength between gold and palladium with the components of the gas mixture varies widely, with many gases preferentially adsorbing on palladium [15].

Ternary alloys

Five ternary alloy compositions were tested including the commercial alloy. The commercial alloy had the highest permeability of all ternary alloys with a value of $5.71 \text{ mol m}^{-1} \text{ s}^{-1} \text{ pa}^{-0.5} \times 10^{-8}$ under pure hydrogen and $4.28 \text{ mol m}^{-1} \text{ s}^{-1} \text{ pa}^{-0.5} \times 10^{-8}$ under non-sulphur conditions, a drop in permeability of 25%. However, the commercial membrane nearly lost all of its permeability under sulphurous conditions. The PdAuAg membrane manufactured through electroless plating performed better under both impurity conditions than the commercial alloy despite being based on the same composition, only seeing a 16% and 27% drop in hydrogen permeability under non-sulphur and sulphur conditions respectively compared to a 25% and 96% drop shown by the commercial alloy.

Table 5.4: XPS composition analysis of the palladium alloy membrane surfaces after impurity tests

Membrane ID	Pure Hydrogen Exposure					Non-Sulphur Exposure					Sulphur Exposure					
	Pd	Ag	Au	Cu	Zr	Pd	Ag	Au	Cu	Zr	Pd	Ag	Au	Cu	Zr	S
PdCu (Fcc)	65.5	-	-	35.5	-	92.5	-	-	7.5	-	67.5	-	-	7.5	-	25
PdCu (Bcc)	44	-	-	66	-	54.85	-	-	45.15	-	40	-	-	31	-	29
PdCuZr	63.6	-	-	22.6	13.8	64.4	-	-	27.5	8.5	54.2	-	-	27	8	10.8
PdAg	65.5	34.5	-	-	-	25	75	-	-	-	29	29	-	-	-	42
PdAu	75	-	25	-	-	82.9	-	17.1	-	-	71	-	16	-	-	13
PdCuAg	64.6	9.1	-	26.3	-	8.6	8.9	-	82.5	-	6	5	-	64	-	25
PdCuAu	63.9	-	22.5	13.6	-	84.9	-	1.46	13.6	-	65.3	-	1	18.5	-	15.2
PdAuAg	60	11.7	28.3	-	-	47.2	49.8	3	-	-	52	35	1	-	-	12

The high levels of gold likely contributed to the low levels of sulphur on the surface of the electroless plated PdAuAg membrane. These results indicate that the composition of the commercial membrane, while ideal for separation, does not contain enough gold to withstand the levels of sulphur impurities expected for analytical purposes.

The worst performing ternary alloy was the PdCuAg alloy which showed large permeability drops under all conditions, 61% under non-sulphur and 75% under sulphurous conditions. In addition to these, large degrees of segregation were observed under non-sulphur impurities, with the palladium concentration at the surface dropping to 8.5 wt%, showing that the alloy is not completely stable under the varying conditions expected during analytical purposes.

Both gold containing ternary alloys, PdAuAg and PdCuAu, performed well under sulphur conditions, with the PdCuAu alloy only reducing in permeability by 25% and the PdAgAu membrane by 27%. The PdCuAu membrane however had a stronger interaction with non-sulphur impurities, indicated by the permeability drop of 45% when exposed to the non-sulphur containing gas sample. This drop is likely due to the segregation of palladium to the surface with the XPS data indicating an increase of palladium to the surface to 84.9 wt% from 63.9%. The best performing ternary membrane was the PdCuZr membrane which showed the smallest drop in permeability of only 12% non-sulphur conditions, and a permeability percentage drop of 26% under sulphur conditions which on a similar magnitude to that of the gold containing alloys.

Segregation behaviour

All membranes tested showed some degree of segregation with the two thinnest membrane samples, PdAg (0.573 micron), PdAuAg (0.736 micron) and PdCuAg (0.873 micron) all showing the highest degrees of segregation. While this may still be a property of the alloy compositions it may also indicate that sub-micron palladium alloys layers are unstable and there may be a minimum thickness for alloys, below which the membrane layer is unstable and frequently varies during operation.

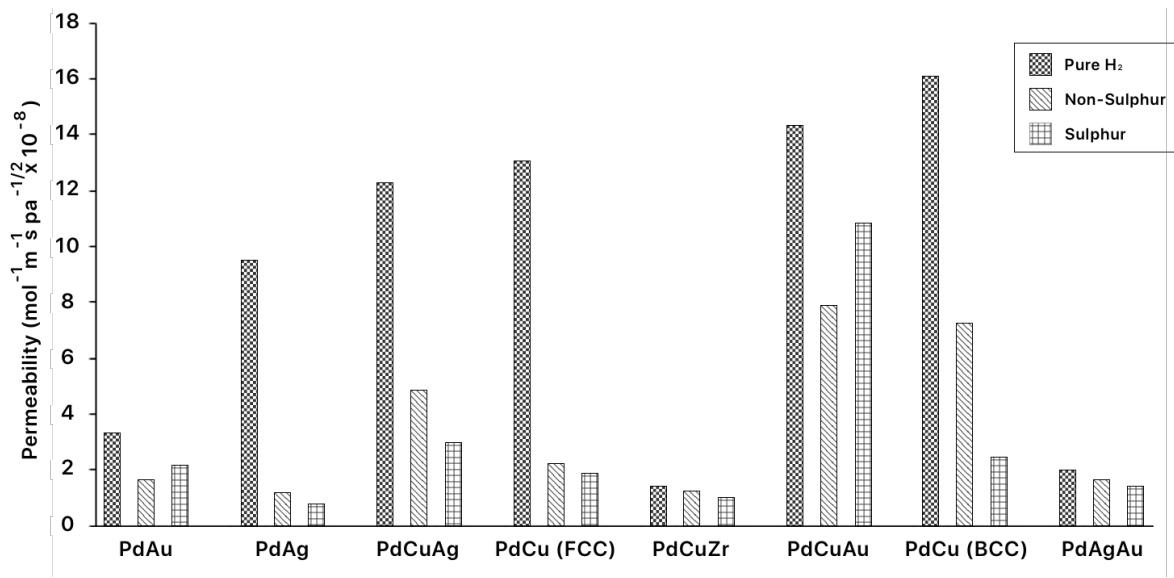


Figure 5.2: Permeability data for pure hydrogen, non-sulphur, and sulphur permeation tests

5.4 Conclusion

In order to identify a suitable palladium alloy composition for hydrogen impurity enrichment, eight different membrane compositions were manufactured and tested under three different hydrogen conditions against a commercial palladium membrane. Two different measures were used to compare the membrane compositions suitability for hydrogen impurity enrichment, the permeability deviation from the pure hydrogen permeability was used as an initial indicator of interaction between the alloy and impurities, and the surface composition was measured to detect any impurities which had permanently reacted with the membrane. The best performing membrane, and therefore the most suitable for hydrogen impurity enrichment was the PdCuZr alloy, which only showed a 12% and 26% drop in permeability under non-sulphur, and sulphur conditions, and low levels of sulphur on the surface. The permeability of this alloy was low, however, surface areas could easily be scaled up to increase the speed of hydrogen enrichment.

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Chapter 6

A hydrogen impurity measurement device for measuring ISO 14687 impurities

6.1 Abstract

In this chapter a device capable of performing hydrogen impurity enrichment is designed and tested under a number of conditions using a commercial membrane compared against the best performing fabricated membranes in chapter 5. The aim of this chapter is to improve upon the designs in literature to provide a more efficient, and safe device which could be sold as a commercial product. A sample was taken from a commercial hydrogen refuelling station, spiked with krypton, and enriched using the device in order to validate the krypton tracer enrichment method using real world conditions, and to quantify the impurity concentrations present in commercial hydrogen fuel.

6.2 Introduction

6.3 Results and discussion

6.4 Conclusion

Chapter 7

Conclusion and future work

7.1 Impurity enrichment devices

7.1.1 Further research

7.1.2 Additional use cases

7.1.3 Commercialisation

7.2 Closing remarks