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Hydrogen separation from blended natural gas and hydrogen by Pd-based membranes

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Abstract

Hydrogen separation membranes based on a heated metal foil of a palladium alloy, offer excellent permeability for hydrogen as a result of the solution-diffusion mechanism. Here, the possibility to separate hydrogen from the mixture of Natural Gas (NG) and hydrogen (NG+H₂) with various NG concentrations using Pd, PdCu₅₃ and PdAg₂₄ hydrogen purification membranes is demonstrated. Hydrogen concentrations above ~ 25% (for Pd and PdCu₅₃) and ~ 15% (for PdAg₂₄) were required for the hydrogen separation to proceed at 400 °C and 5 bar pressure differential. Hydrogen permeability of the studied alloys could be almost fully recovered after switching the feed gas to pure hydrogen, indicating no significant interaction between the natural gas components and the membranes surface at the current experimental condition. Hydrogen flux of the membranes at various pressure differential was measured and no changes in the hydrogen permeation mechanism could be noticed under (NG 50%+H₂) mixture. The hydrogen separation capability of the membranes is suggested to be mainly controlled by the operating temperature and the hydrogen partial pressure.

Keywords: *Hydrogen purification, Pd-based membranes, blending, Natural gas, hydrogen*

1. Introduction

The fluctuating and intermittent nature of power generated from renewable energy sources mandates the development of economic and scalable energy storage solutions. Excess electricity can be used to produce hydrogen by electrolysis, which can be stored, distributed and converted back into electricity using a fuel cell when needed. With 'power-to-gas' [1], [2], a low concentration of hydrogen is blended into the existing natural gas pipeline network hence, storing and delivering renewable energy to the market. This can also result in lowering the cost of building hydrogen delivery infrastructure if pure hydrogen can be effectively extracted.

The widespread application of hydrogen as a sustainable energy carrier strongly depends on the development of infrastructure, transportation and storage facilities. Blending a low concentration of hydrogen with natural gas appears to be a viable method to transport hydrogen using the existing natural gas pipeline [3]. Blending can eliminate the requirements for building a dedicated hydrogen infrastructure, enabling hydrogen transport through existing pipelines, rather than through the vehicular transportation of stored hydrogen, potentially producing a more economically favourable and environmentally friendly method of hydrogen transportation. In addition, a significant reduction in greenhouse gas emissions can be also achieved if hydrogen is produced from renewable sources. Also, a large scale transportation of hydrogen produced from renewable sources showed to be economically favourable when using an existing natural gas infrastructure [4]

This strategy can be also used for delivering high purity hydrogen using separation and purification technologies. The blended hydrogen may be directly used for applications such as heating, cooking with less CO₂ emission or hydrogen can be separated for Fuel Cell Electric Vehicles (FCEVs) and stationary fuel cell systems for power generation. However,

there are several interrelated key issues to hydrogen blending that should be properly addressed. Various significant studies, predominantly a study from the Gas Technology Institute (GTI) conducted within the NaturalHy project [5] and information from Green House Gas R&D [6] are reviewed and summarised by Melaina et al. [7]. The interrelated key issues mainly involve the benefit of blending, the extent of the natural gas pipeline network and its durability, safety, the possible impact of the end-use systems, leakage and downstream extraction of hydrogen [7]. The practicality of blending was demonstrated by the pilot project proposed by Kippers et al. [8], indicating that pipeline systems and home applications do not hinder the blending of hydrogen of up to 20% into the gas grid pipeline network. It was concluded that aside from the production of hydrogen, blending small quantities of hydrogen into the gas grid system would be free from cost, however technical and logistic obstacles would need to be solved [6]. The H21 Leeds City Gate project [9] also suggested the possibility of switching the current natural gas grid in Leeds to 100% hydrogen, estimating the cost of 10p/kWh, including modifications made to utility appliances. However, the existing natural gas transmission and distribution systems may not be suitable for the delivery of pure hydrogen due to its different physical and chemical properties. Moreover, the impact of the higher hydrogen blend levels on the end-use appliances requires careful consideration. In fact, hydrogen concentrations up to 28% were suggested [10] to be safely used with no or minor end-use appliances adjustments. The acceptable hydrogen concentration was also suggested [11] to be determined according to the tolerance of each elements of the natural gas infrastructure. For example, in the transmission network the maximum hydrogen concentration is limited by the compressors to 10%, whilst distribution network, storage elements and end-use appliances allow a range of 20- 50% hydrogen concentration. Therefore, it seems that technological restrictions such

as durability of transmission and distribution pipelines, leakage hazards and adaptability of the end-use appliances hamper the delivery of pure hydrogen by the existing gas network systems at near future. Nevertheless, a low concentration of blended hydrogen can be still directly used in the end-use appliance or as pure hydrogen by selective extraction from the mixture.

Various methods including Pressure Swing Adsorption (PSA) and membranes were suggested to purify hydrogen from the gas mixture [7]. A hybrid approach using a polymeric membrane and PSA was also studied to separate hydrogen (99.97 %) from the (NG+H₂) mixture with hydrogen contents lower than 10% [12]. A membrane separation step was used to pre-enrich hydrogen which was then upgraded to the required purity by PSA method. Whilst, PSA is a well-established technology, it requires large scale units and operates best with high hydrogen concentration (higher than 50%). In contrast, membranes and in particular Pd-based metallic membranes [13]–[16] appear to be the most effective high purity hydrogen separation method from gas mixtures with low hydrogen concentration (<30%). Yet, the efficient operation of Pd-based membranes requires elevated temperatures (>350 °C) and a large pressure differential across the membrane surface. For this reason, membranes technology were proposed to be only cost effective for the high-pressure transmission pipelines rather than the distribution networks [7]. In addition, the surface of Pd-membranes are highly sensitive to the gas impurities, especially sulphur species in the gas stream [17]–[19] Nevertheless, Hydrogen flux and the resistant to the surface poisoning showed to be improved by alloying [13], [20]–[22].

The superior hydrogen permeability of Pd, PdCu₅₃ (bcc structure) and PdAg₂₄ (at.%) membranes may facilitate hydrogen separation from the dilute (NG+H₂) mixtures [16], [23]. Here, the possibility of using commercially available Pd, PdCu₅₃ and PdAg₂₄ membranes to

separate hydrogen from gas mixtures containing natural gas of various concentrations is studied. The possible interaction between the membranes and the natural gas components, when mixed with hydrogen, is also investigated.

2. Materials and Methods

Cold-rolled foils of Pd, PdCu₅₃ and PdAg₂₄ membranes (nominal composition in at. %) were purchased from Alfa Aesar. The thickness of the membranes was measured by a micrometer and the membranes compositions were determined by JEOL 6060 Scanning Electron Microscopy (SEM) equipped with an INCA 300 Energy Dispersive Spectroscopy (EDS) (Table 1). Structural analyses of the foils before and after the mixed gas exposure were performed by X-Ray Diffraction (XRD) measurements using a Bruker D8–Advanced diffractometer with monochromatic CuK α radiation ($\lambda = 1.54056 \text{ \AA}$).

Hydrogen permeation through the foils under pure hydrogen and mixed gases was measured by a hydrogen permeation system designed and built in the Author's group [24], which can be seen in Figure 1. Membrane disks with an area of 2.54 cm^2 were cut off the rolled foils, washed in acetone and sealed by a copper gasket and a knife-edge. Nitrogen gas (99.95%, BOC) was used at a pressure differential of 5 bar for a leak test. A pressure transducer with an accuracy of $\pm 0.25\%$ was used on the downstream side of the membrane to monitor any pressure increase as a result of the leak. All samples were leak tight before starting the experiments. A vacuum of 10^{-5} mbar was applied on both sides of the membranes prior to hydrogen (99.99995%, BOC) and natural gas (grid gas from BOC) admittance. The composition of the natural gas is given in Table 2 according to the gas supplier. The hydrogen permeation system is equipped with four Brooks 5850S Mass Flow Controller (MFC) calibrated over a range of $6\text{-}600 \text{ ml min}^{-1}$ with an accuracy of $\pm 6 \text{ ml min}^{-1}$. A constant upstream pressure of 6 bar was applied by continuous gas flow and bled using

another Brooks 5850S MFC. The upstream pressure was also increased up to 10 bar (in 1 bar steps) to investigate the hydrogen permeation mechanism. Downstream pressure was maintained at 1 bar at all times using a back-pressure regulator. The permeated gas flow was measured by Brooks 5850S MFC placed after the back-pressure regulator. The temperature of both the membrane and the upstream atmosphere was increased using an Elite Thermal Systems Ltd. split furnace with a ramp rate of 2 °C min⁻¹. Hydrogen flux was first measured under pure hydrogen and the natural gas concentration was increased in steps after achieving a steady flux at each step. Hydrogen permeability was calculated according to equation 1, assuming hydrogen diffusion through the bulk of the membrane as the rate-limiting step for thick Pd and Pd alloy membranes [25].

$$J = \emptyset \frac{P_1^n - P_2^n}{l}$$

Where J is the hydrogen flux (mol m⁻² s⁻¹), \emptyset is hydrogen permeability (mol m⁻¹ s⁻¹ Pa^{-0.5}), P_1 and P_2 are hydrogen pressures (Pa) on the upstream and downstream side of the membrane respectively, n is pressure exponent, which is 0.5 for bulk diffusion in this study, and l is the membrane thickness (m).

3. Results and discussion

The XRD patterns of the Pd, PdCu₅₃ and PdAg₂₄ membranes before the gas exposure are shown in Figure 2 a, c and e respectively. Whilst XRD peaks for the Pd and PdAg₂₄ membranes correspond to fcc structure, XRD patterns for the PdCu₅₃ membrane demonstrates the existence of a dual phase (bcc+fcc) in the as-received membranes. The phase diagram of the PdCu₅₃ alloy [25] suggests that the composition of this alloy should fall within the bcc region at room temperature. The coexistence of bcc and fcc phases at room temperature indicates some deviation from the nominal composition (as seen by the EDS

results in Table 1). Also, a preferential orientation along the (220) plane can be observed for the fcc phase in all the membranes as a result of cold rolling during the fabrication process.

Hydrogen permeability of the Pd membrane at 400 °C under pure hydrogen and (NG+H₂) mixtures is given in Figure 3. Hydrogen permeability of the Pd membrane under pure hydrogen is comparable to the previously reported literature value [25]. Once a stable hydrogen flux was established, the (NG+H₂) mixture was admitted and the natural gas concentration increased at different steps from 9% to 75%. A hydrogen flux reduction was observed at each step of the mixed gas admittance (Table 3) and the hydrogen flux was fully ceased by increasing the natural gas concentration to 75% at 400 °C and 5 bar pressure differential. Hydrogen flux recovery was also performed after exposing the Pd membrane to (NG 75% +H₂) mixture by switching the gas inlet to pure hydrogen. Hydrogen flux could be recovered after allowing a sufficient recovery time but slightly lower than the original value.

Hydrogen permeability of the PdCu₅₃ membrane at 400 °C under pure hydrogen and (NG+H₂) mixtures is given in Figure 4. The hydrogen permeability of the PdCu₅₃ membrane under pure hydrogen is lower compared to the previously reported value [25]. The high hydrogen permeability of PdCu₅₃ is known to be a characteristic of the bcc phase (CsCl-type ordered structure) [25] with high hydrogen diffusion rate [26], [27]. Hence, the lower hydrogen permeability value observed for the PdCu₅₃ membrane may be due to the observed compositional variation and the coexistence of bcc and fcc phases. After establishing a stable hydrogen flux under pure hydrogen, (NG+H₂) mixture was admitted and the natural gas concentration increased from 9% to 75% at different steps. Similar to the Pd membrane, hydrogen flux was reduced (Table 3) by admitting and increasing the natural gas concentration until the hydrogen flux was fully ceased after increasing the natural gas concentration to 75% at 400 °C and 5 bar pressure differential. Similar to the Pd

membrane, hydrogen flux could be recovered by switching to pure hydrogen but slightly lower than the original value.

Hydrogen permeability of the PdAg₂₄ membrane at 400 °C under pure hydrogen and (NG+H₂) mixtures is given in Figure 5. Hydrogen permeability of Pd-Ag alloys strongly depends on their composition [28]. The hydrogen permeability of the PdAg₂₄ membrane under pure hydrogen seems to be within the reported range [28], [29] with respect to its actual composition (Table 1). After achieving a stable hydrogen flux under pure hydrogen, (NG+H₂) mixture was admitted and the natural gas concentration increased from 9% to 85%. Hydrogen flux was reduced at each step by increasing the natural gas concentration (Table 3). Unlike the Pd and PdCu₅₃ membranes, hydrogen flux is sustained at 75% and only stops when the natural gas concentration increased to 85%. In order to investigate the effect of the pressure differential on the hydrogen separation capability of the PdAg₂₄ membrane, the overpressure was increased from 6 bar to 10 bar while maintaining the natural gas concentration at 85%. This led hydrogen flux to resume in PdAg₂₄ even at the natural gas concentration of 85% (Figure 5), denoting the possibility to separate even low concentration of hydrogen at an appropriate pressure differential. Hydrogen flux could be recovered, but not to the original value, by switching to pure hydrogen and the initial upstream pressure of 6 bar.

In addition, hydrogen flux of the membranes under (NG 50%+H₂) mixture was measured as a function of hydrogen differential pressures and temperatures in Figure 6. It can be seen that hydrogen flux of the Pd membrane linearly increases by increasing the differential pressure at various temperatures (Fig. 6 a), denoting the noticeable effect of hydrogen partial pressure in the gas mixture on the hydrogen separation process. Similar trends can

be seen for the PdCu₅₃ and PdAg₂₄ membranes in Fig 6 b after rising the feed side pressure at 400 °C

Also, a good linear relationship between the hydrogen flux and the pressure differential is observed in Fig 6 a and b with a pressure exponent equal to 0.5, indicating no changes in the rate of the surface reactions occur under the (NG 50%+H₂) mixed gas condition. Hence, hydrogen concentration beneath the membrane surface is proportional to the square root of the hydrogen pressure (Sievert's law) and no changes in the hydrogen permeation mechanism is observed at the studied temperature range. Surface interaction of the studied membranes with the (NG+H₂) mixture was also examined by XRD after the mixed gas exposure in Figure 2 b, d and f. Whilst after the mixed gas exposure Pd and PdAg₂₄ membranes show peaks corresponding to fcc structure (Figure 2 b and f), the PdCu₅₃ structure transforms mainly to fcc structure (Figure 2 d), possibly due to the heat treatment effect during the hydrogen flux measurement at 400 °C. The natural gas components in the (NG+H₂) mixture do not seem to have any significant interaction with the membrane surface and the formation of any new phase/s cannot be observed. Carbide formation as a result of dissociative chemisorption of CH₄ on the Pd surface was shown to occur at low temperatures [30], [31]. However, the process appeared to be very slow (also concentration and temperature dependent) in the presence of H₂ due to the high reactivity of the carbidic surface carbon which facilitates its rehydrogenation to form CH₄. Our hydrogen flux recovery measurements showed that hydrogen flux could not be fully recovered in the studied membranes after switching the mixed gas to pure hydrogen. This may imply a very weak interaction between the surface of the membranes and the natural gas components at the experimental condition used in this study. The extent of the surface reactions, their

reversibility and the durability of the membranes should be investigated after long-term exposure to (NG+H₂) mixtures at varying concentrations.

In addition, hydrogen flux reduction observed in the studied membranes under mixed gas condition may originate from the i) formation of surface carbides and/or dissolved carbon into the Pd layer and hence reducing the hydrogen solubility, ii) competitive surface adsorption of other gases and therefore blocking available sites for hydrogen adsorption and iii) a reduction in hydrogen partial pressure and hydrogen mass transport limitation known as concentration polarisation [32]–[34]. Although surface carbide formation was suggested to be favourable on the Pd surface, the formation of stable carbides seemed to be strongly temperature dependent [33]. In fact, hydrogen flux remained stable after 6 h exposing a Pd membrane to the mixtures of (CH₄+H₂) [33] with various concentrations at 450 °C, indicating the absence of stable surface carbide formation. In addition, here we showed (in Fig. 6) that the hydrogen permeation mechanism remains unaffected by the surface processes after exposing the membranes to (NG 50%+H₂) mixture at 400 °C.

Therefore, the significant hydrogen flux reduction in the studied membranes is less likely to originate from the carbide formation due to the experimental condition in this study.

Concentration polarisation is normally caused by rapid depletion of hydrogen molecules adjacent to the surface of the membrane. This leaves an impermeable laminar gas boundary above the membrane surface causing mass transport limitation for hydrogen. However, concentration polarisation problem appears to be more significant for scale-up membrane modules [32]. The effect of the concentration polarisation was also mitigated in our experiments by using a continuous gas flow and bled to avoid the gas impurities built-up above the membrane surface. Hence, hydrogen flux reduction in the studied membranes as a function of natural gas concentration seems to be primarily due to the reduction in

hydrogen partial pressure and the competitive surface adsorption of other gas species on the membrane surface. Increasing the natural gas concentration effectively lowers the hydrogen partial pressure on the feed side and results in a lower hydrogen feed rate. This trend was observed in all the studied membranes and the strong correlation between the hydrogen flux and the gas feed pressure was demonstrated in Fig. 5 and 6. Consequently, hydrogen separation at higher natural gas concentrations could be achieved by the PdAg₂₄ membrane due to its higher hydrogen permeability and the lower required driving force for hydrogen permeation.

Hydrogen has the potential to play an important role in long-term decarbonisation of the energy system. Deployment of hydrogen at scale may be achieved by blending hydrogen into the natural gas grid. This will offer using hydrogen produced via low-carbon routes to reduce harmful emissions without the need for significant infrastructure development at near future. Furthermore, blending can help to develop the hydrogen supply chain, creating subsequent opportunities for wider deployment of hydrogen [35]. Nevertheless, switching the natural gas grid to pure hydrogen seems to be impractical at the current stage due to many technical hurdles. Here, we showed that hydrogen can be effectively separated from the (NG+H₂) mixture by Pd-based membranes even with hydrogen concentrations as low as 15%. The effectiveness of the hydrogen separation process strongly depends on the pressure differential and the operation temperature. These requirements make the membrane technology more suitable for hydrogen separation at transmission lines where high pressure and temperature can be supplied as suggested previously [7]. Using membrane technology to separate hydrogen from the low hydrogen content gas mixtures at these points may create local high purity hydrogen distribution centres, particularly beneficial to the mobile applications.

4. Conclusions

Pd, PdCu₅₃ and PdAg₂₄ membranes were used to investigate the possibility to separate hydrogen when blended with natural gas at various concentrations. The possibility to separate hydrogen by Pd, PdCu₅₃ and PdAg₂₄ membranes at 400 °C with 5 bar pressure differential was confirmed. Whilst Pd and PdCu₅₃ membranes required a minimum hydrogen concentration over 25% in the (NG+H₂) mixture to be capable of separating hydrogen, the PdAg₂₄ membrane could still separate hydrogen from the (NG+H₂) mixture until hydrogen concentration drops to 15% at the studied experimental conditions. It was shown that the hydrogen separation capability of the membranes strongly depends on the operating temperature and the hydrogen partial pressure. The surface properties of the Pd membrane did not alter after the mixed gas exposure, indicating the lack of noticeable reaction between the membrane surface and the natural gas components took place at the current experimental condition. Structural analysis of the alloys after the mixed gas exposure also did not show the formation of any new phases on the surface of the membranes. However, the durability of the membrane at long-term exposure and the possible surface and bulk interactions with natural gas components needs further investigation. The capability of membrane technology to effectively separate pure hydrogen from the blended (NG+H₂) is demonstrated; creating a platform for wider deployment of hydrogen into the energy system and promoting hydrogen-related technologies.

5. Acknowledgments

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6. References

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Figures:

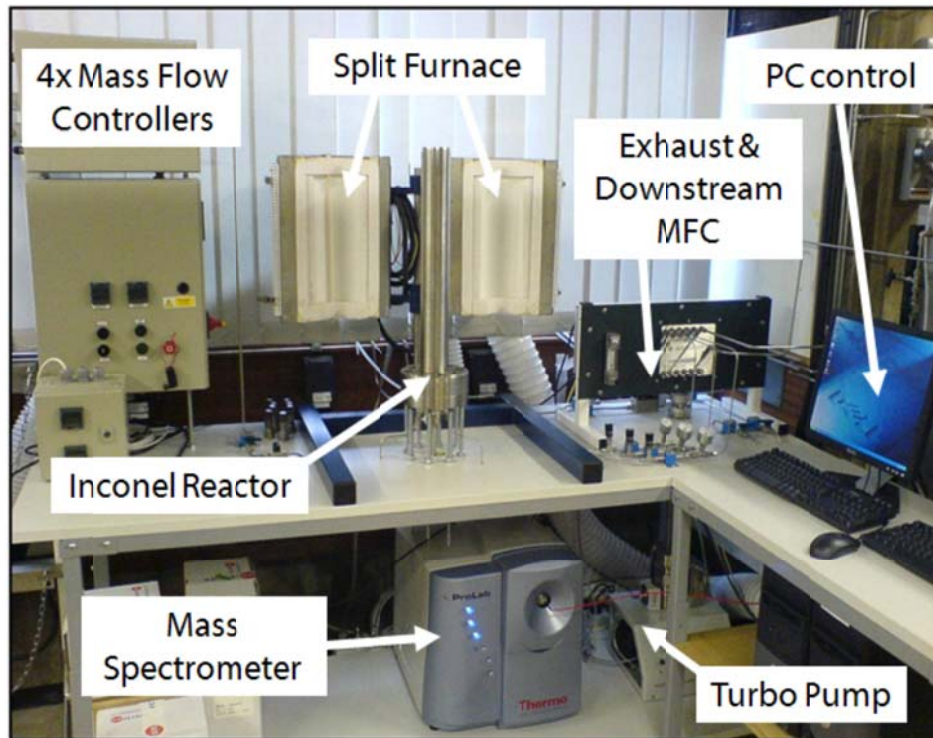


Figure 1: Hydrogen permeation systems design and built at the School of Metallurgy and Materials Science, University of Birmingham

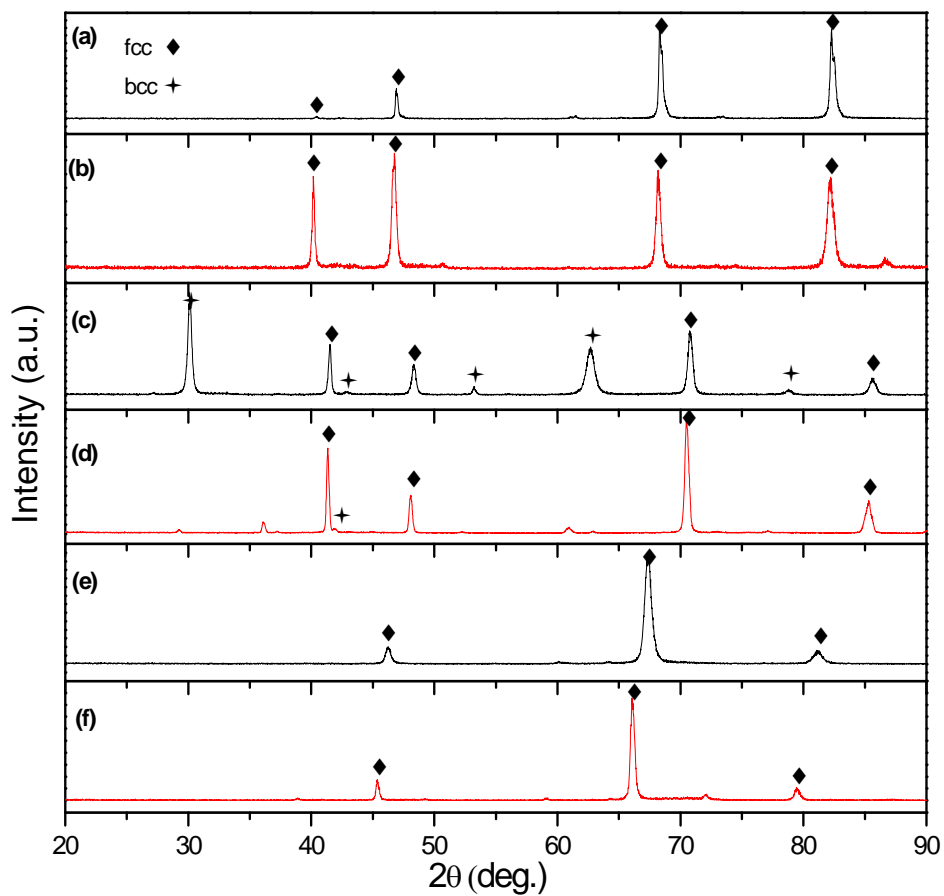


Figure 2: XRD patterns of the Pd membrane (a) before and (b) after the mixed gas exposure, PdCu₅₃ membrane (c) before and (d) after the mixed gas exposure and PdAg₂₄ (e) before and (f) after the mixed gas exposure.

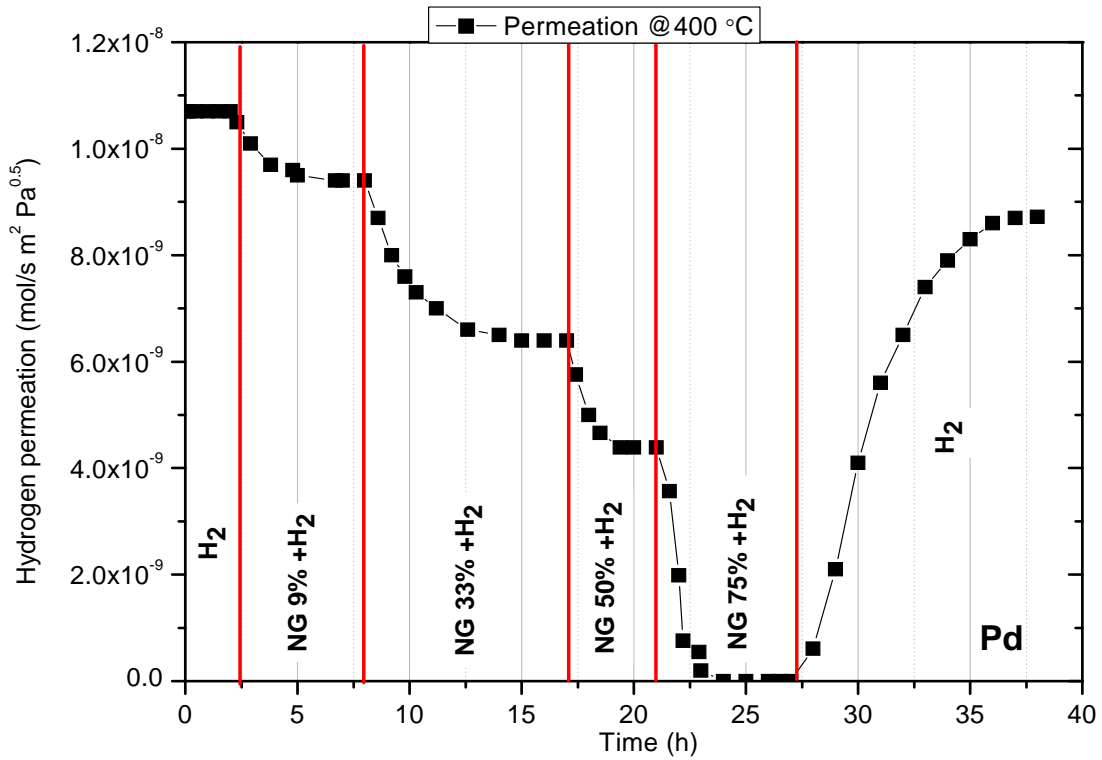


Figure 3: Hydrogen permeation of the Pd membrane as a function of natural gas concentration at 400 °C and 5 bar pressure differential.

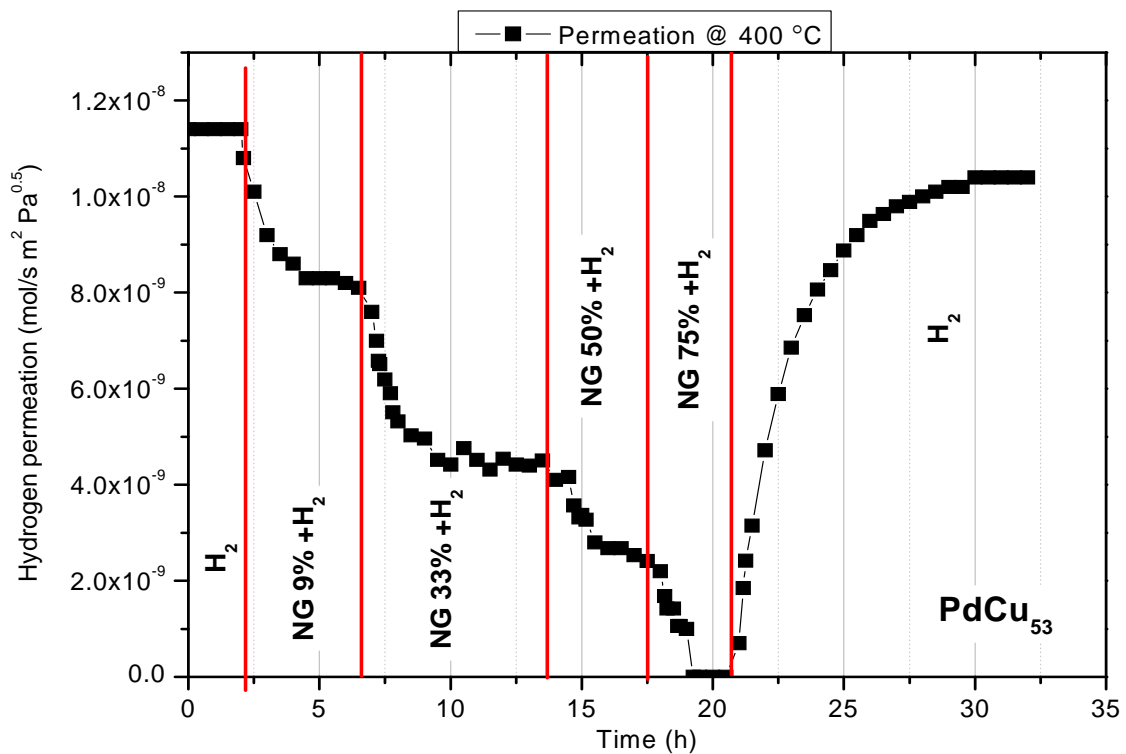


Figure 4: Hydrogen permeation of the PdCu_{53} membrane as a function of natural gas concentration at 400 °C and 5 bar pressure differential.

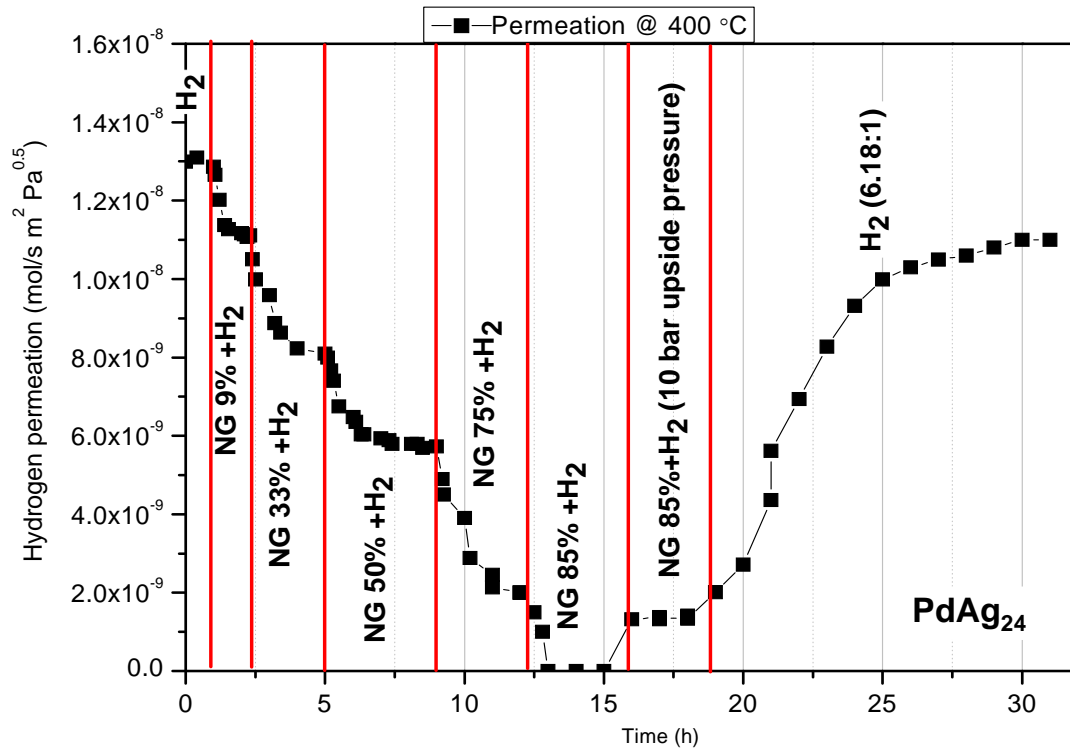


Figure 5: Hydrogen permeation of the PdAg₂₄ membrane as a function of natural gas concentration at 400 °C and 5 bar pressure differential. Effect of pressure differential at a high natural gas concentration (85%) was examined by increasing it to 9 bar.

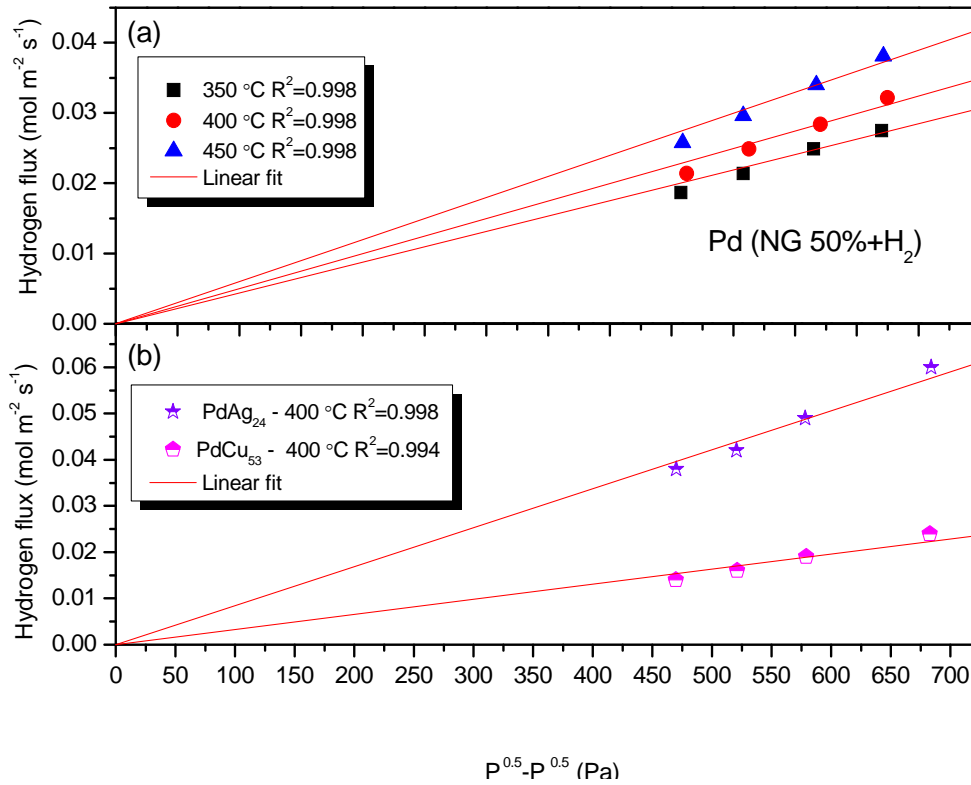


Figure 6: (a) hydrogen permeation of Pd membrane as a function of temperature and pressure differential and (b) hydrogen permeation of PdCu₅₃ and PdAg₂₄ membranes as a function of pressure differential under (NG 50%+H₂) mixed gas. A linear fit is used to study the hydrogen permeation mechanism with a pressure exponent of 0.5. The quality of the linear fit is given by the R² values in each case.

Tables

Table 1: EDS compositional analysis of the membrane and their thicknesses.

| Membrane | Composition (at. %) | Thickness (μm) |
|---------------------|---|----------------|
| Pd | - | 25 |
| Pd-Cu ₅₃ | Pd _{47.5±0.4} Cu _{52.5±0.4} | 40 |
| Pd-Ag ₂₄ | Pd _{73.9±0.5} Ag _{26.1±0.5} | 50 |

Table 2: Natural gas composition used in this study.

| Component | Range (mole %) |
|----------------|----------------|
| Methane | 87-97 |
| Ethane | 1.5-7 |
| Propane | 0.1-1.5 |
| Iso-Butane | 0.01-0.3 |
| Iso-Pentane | 0.01-0.3 |
| Normal Pentane | Trace-0.04 |
| Hexanes plus | Trace-0.06 |
| Nitrogen | 0.2-5.5 |
| Carbon dioxide | 0.1-1 |
| Oxygen | 0.01-0.1 |
| Hydrogen | Trace-0.02 |

Table 3: Hydrogen permeation values of the studied membranes as a function of natural gas concentration

| Hydrogens permeation (mol/sm ² Pa ^{0.5}) at different NG concentrations | | | | | | | |
|--|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|---|-----------------------|
| | 0% NG | 9% NG | 33% NG | 50% NG | 75% NG | 85% NG | Recovery |
| Pd | 1.07x10 ⁻⁸ | 9.41x10 ⁻⁹ | 6.42x10 ⁻⁹ | 4.39x10 ⁻⁹ | 0 | - | 8.76x10 ⁻⁹ |
| PdCu ₅₃ | 1.14x10 ⁻⁸ | 8.3x10 ⁻⁹ | 4.46x10 ⁻⁹ | 2.68x10 ⁻⁹ | 0 | - | 1.04x10 ⁻⁸ |
| PdAg ₂₄ | 1.30x10 ⁻⁸ | 1.11x10 ⁻⁹ | 8.16x10 ⁻⁹ | 5.75x10 ⁻⁹ | 1.98x10 ⁻⁹ | 0 (1.32 x10 ⁻⁹ at 9 bar PD*) | 1.10x10 ⁻⁸ |

*PD: Pressure Differential