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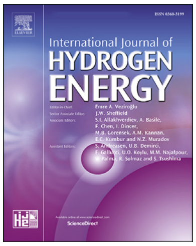

# Ultra-pure hydrogen production via ammonia decomposition in a catalytic membrane reactor

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## HIGHLIGHTS

- Ultra-pure hydrogen production via ammonia decomposition in membrane reactors.
- Fuel cell grade hydrogen can be obtained in a single step.
- For thin membranes, low cost hydrogen polishing can be integrated in the system.

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## ABSTRACT

In this work two alternatives are presented for increasing the purity of hydrogen produced in a membrane reactor for ammonia decomposition. It is experimentally demonstrated that either increasing the thickness of the membrane selective layer or using a small purification unit in the permeate of the membranes, ultra-pure hydrogen can be produced. Specifically, the results show that increasing the membrane thickness above 6 μm ultra-pure hydrogen can be obtained at pressures below 5 bar. A cheaper solution, however, consists in the use of an adsorption bed downstream the membrane reactor. In this way, ultra-pure hydrogen can be achieved with higher reactor pressures, lower temperatures and thinner membranes, which result in lower reactor costs. A possible process diagram is also reported showing that the regeneration of the adsorption bed can be done by exploiting the heat available in the system and thus introducing no additional heat sources.

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## Introduction

Although the primary use of ammonia is nowadays for the fertilizers industry [1], ammonia has been recently regarded as a valuable alternative for long term hydrogen storage [2–9]. Despite hydrogen is considered as the ideal energy carrier, mainly due to the fact that carbon-free emissions result from its combustion [10], there are in fact some unresolved challenges related to its storage and distribution which could be solved by storing its energy in the chemical bonds of ammonia [3,8,11]. Compared to compressed hydrogen, ammonia shows several advantages such as a higher volumetric density, a relatively lower cost and a higher ease of liquefaction which would ultimately solve the problems related to hydrogen storage and transportation [3–7]. Hydrogen stored in ammonia can then be recovered and used as fuel for applications that require pure hydrogen as feedstock. Specifically, the carbon-free nature of ammonia makes this molecule attractive for the production of hydrogen to be used as fuel for proton exchange membrane fuel cells (PEMFCs) [12–20]. The PEMFC electrodes suffer in fact from poisoning when exposed to $CO_x$ concentration even at ppm level [21]. To produce hydrogen from ammonia, first ammonia has to be decomposed into hydrogen and nitrogen according to Eq. (1) and, subsequently, hydrogen has to be separated from nitrogen and possible traces of unconverted ammonia.

$$NH_3 \rightleftarrows 1/2N_2 + 3/2H_2 \quad \Delta H_f^o = 45.92\ \frac{kJ}{mol} \tag{1}$$

In this regard, the membrane reactor has been recently demonstrated to be a promising technology for hydrogen recovery from ammonia, as it allows for both ammonia decomposition into hydrogen and nitrogen and high purity hydrogen separation to simultaneously occur within a single device [11,22–32]. This technology has also been proven to show other benefits compared to conventional systems for ammonia conversion into pure hydrogen, such as a lower investment cost due to the lower number of process steps as well as higher efficiencies due to the lower operating temperatures. As $NH_3$ decomposition is limited by the thermodynamic equilibrium, the selective separation of hydrogen through the membranes walls shifts in fact the thermodynamic equilibrium towards the reaction products ($H_2$ and $N_2$) according to the Le Chatelier's principle, allowing the membrane reactor to circumvent the thermodynamic constraint of conventional reactors [28]. Hydrogen production via ammonia decomposition in a membrane reactor has already been experimentally investigated in literature, especially using a ruthenium-based (Ru-based) catalyst [11,22,33] and Pd-based membranes. Pd-based membranes show in fact outstanding performance in terms of hydrogen separation as well as good stabilities [28,29,34–38]. In our previous work [11], it was demonstrated that, when choosing a membrane reactor technology over a conventional system, it is possible not only to achieve higher ammonia conversion, but also to simultaneously recover part of the hydrogen produced. As a result, when the membrane reactor technology is selected, virtual full conversion of $NH_3$ into ultra-pure hydrogen is achieved within a single device. However, to be able to use $NH_3$-derived hydrogen for fuel cell applications, some specifications regarding the fuel cell limit on residual ammonia concentration must be met. Specifically, residual $NH_3$ concentrations above 0.1 ppm in the permeated hydrogen would prevent hydrogen from being directly used as fuel in fuel cell as such concentrations would be responsible for the cell electrodes poisoning [5,39]. From the results of our previous work [11], the hydrogen purity achieved with the membrane reactor technology seems not to be always sufficiently high to directly feed the hydrogen produced to the fuel cell. To meet the specifications regarding the fuel cell limit on residual ammonia concentration in the hydrogen stream, strategies have therefore to be implemented to increase hydrogen purity.

Higher performance in terms of purity of hydrogen can be achieved in the membrane reactor by optimizing the reactor operating conditions and improving the membrane selectivity towards hydrogen, for example by increasing the thickness of the selective layer of the membrane. Another possible strategy to achieve higher hydrogen purities consists in the addition of a hydrogen purification step downstream the membrane reactor to remove the undesired unconverted $NH_3$ that permeates through the membrane (and sealings) defects. This solution makes the system more complex, but could be a more economically viable option compared to an increase of membrane thickness. It is in fact expected that an increased thickness of the membrane selective layer not only results in an increase of the membrane selectivity, but also is responsible for a decrease in the hydrogen permeation through the membrane. Consequently, the cost associated to this solution would be higher as a higher number of membranes would be needed as well as more palladium would be used.

Objective of this work is to experimentally demonstrate that either increasing the thickness of the membrane selective layer or forcing the produced hydrogen with traces of ammonia to pass through a $NH_3$ removal unit it is possible to produce ultra-pure hydrogen. By "ultra-pure" in this work we consider a $H_2$ stream containing ammonia traces below 0.75 ppm which represents the detection limit of the analytical equipment used. For the experimental investigation, ammonia decomposition has been performed over a conventional Ru-based catalyst, while double-skin Pd-based membranes and zeolite 13X were used for hydrogen separation and hydrogen purification from residual $NH_3$, respectively.

## Material and methods

### *Membrane preparation*

The preparation of the Pd–Ag membranes tested in this work is carried out into two steps. The first step consists in the coating of the porous supports and, specifically, it is carried out by co-depositing a Pd–Ag layer onto porous tubular alumina ($\alpha$-$Al_2O_3$) asymmetric supports (14/7 mm OD/ID) with a top layer pore size of 100 nm from Rauschert Kloster Veilsdorf [40]. The co-deposition has been performed via electroless plating, a technique which consists of a first activation of the support with Pd seeds and a subsequent immersion of the support in a bath containing a Pd–Ag solution to produce the selective layer. The thickness of this layer proportionally increases with the plating time, therefore different plating times are set in order to obtain membranes with different permeation properties. In this work two membranes have been used, one with selective layer of ~ 1 μm and one with selective layer of ~ 6–8 μm. The second step of the membrane preparation consists in the deposition of a porous protective layer by dip-coating over the selective layer [35,41]. This protective layer, which is a porous $Al_2O_3$-YSZ (yttria-stabilized zirconia) layer of 50 wt% of YSZ with thickness of ~ 1 μm, aims at improving the membrane stability as it avoids any possible interaction between the selective layer and the catalyst in which the membrane will be immersed during application.

## *Experimental setup*

A schematic representation of the experimental setup is reported in Fig. 1. The Pd–Ag membrane was sealed to the flange of the reactor and assembled into a stainless-steel reactor. The reactor has an inner diameter of 4.5 cm, an active length of 28 cm and is located inside an electrical split oven with three heating sections (one at the top, one at the middle and one at the bottom of the reactor) independently controlled. Ammonia decomposition is in fact an endothermic reaction and is therefore favored by high temperatures. A porous stainless steel plate has been welded at the bottom of the reactor in order to enhance the gas distribution at the reactor inlet, whereas at the freeboard of the catalytic bed the reactor has a conical shape which allows to reduce the gas velocity and therefore minimize the risk of catalyst particle escaping from the reactor during experimental tests under reactive conditions. The Pd-based membrane was fully immersed in a packed bed of 250 g of a Ru-based catalyst, which according to several literature studies is the most active single metal catalyst in high $NH_3$ concentrations [42]. A product available in pelleted form from Alfa Aesar was selected as catalyst, specifically a Ru-based catalyst 2 wt% supported on alumina pellets of 3 mm.

The feed gases were controlled by mass flow controllers from Bronkhorst and a back-pressure controller was used for system pressure regulation. The permeate side of the membrane was sent to a mass flow meter (Bronkhorst) to determine the permeation flux through the membrane and to a hydrogen purification stage, in which a bed of zeolite 13X at ambient conditions was used as adsorbent material for residual $NH_3$ removal. The experimental setup was also equipped with a Fourier-Transform Infrared Spectrometer (FTIR) from Shimadzu mounting a 5 m gas cell from Specac and an MCT (Mercury–Cadmium-Telluride) detector capable of determining the ammonia concentration in the hydrogen permeate. The $NH_3$ concentration in the permeate was measured both upstream and downstream the hydrogen purification stage. The retentate was first sent through a gas filter which aims at protecting the downstream equipment from fine particles, then to a μ-GC (Varian CP- 4900) to measure the retentate composition. All the lines connecting the permeate side of the membrane to the FTIR are made of SilcoNert and PEFT in order to prevent any possible $NH_3$ absorption phenomenon in the gas line which would influence the FTIR reading. The retentate and permeate lines were subsequently mixed and sent to a water absorption unit where possible traces of unconverted $NH_3$ are absorbed. During the experimental study, two Pd-based membranes with double-sealing configuration have been used for selective $H_2$ separation: one with thickness of the selective layer of ~ 1 μm and a total active length of 200 mm and one with thickness of the selective layer of ~ 6–8 μm and a total active length of 195 mm. Each membrane was tested first for single gas $H_2$ and $N_2$ permeation, then for ammonia decomposition.

## *Experimental methods*

Before their integration in the reactor, the membranes were sealed with graphite gaskets and Swagelok connectors as described in the work of Fernandez et al. [43]. Subsequently, the membranes were tested with helium/ethanol in order to

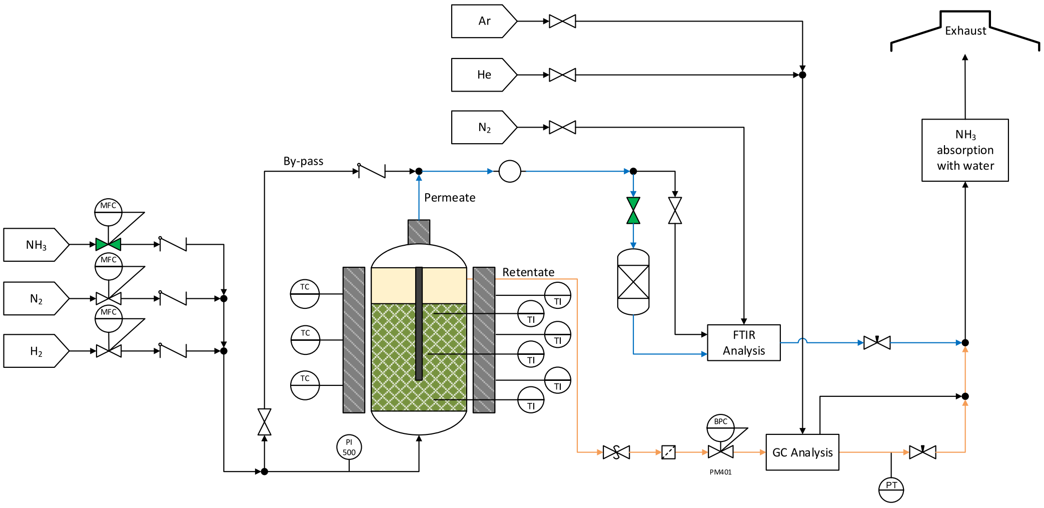

Fig. 1 – Process flow diagram of the experimental setup used in this work.

detect potential leakages from both the sealing and the Pd–Ag surface. As no leakages were detected during the leakages test, the membranes have then been installed one at the time in the reactor. Single gas permeation tests for $H_2$ and $N_2$ were carried out to determine the ideal $H_2/N_2$ perm-selectivity of the Pd-based membranes. The experiments were carried out at different pressures and temperatures, and with the permeate side of the membrane at atmospheric pressure. Specifically, the gas permeation was measured for temperatures ranging between 425 °C and 500 °C and pressures in the range between 2 and 6 bar(a). For a given temperature, the permeance of $N_2$ and $H_2$ as well as the $H_2/N_2$ ideal perm-selectivity were then calculated. Before starting an experiment, the reactor was heated up to the desired temperature at a heating rate of 2 °C/min in $N_2$ atmosphere. Once the desired operating temperature was achieved, the membrane was activated by feeding the reactor with hydrogen. This step is meant to increase the hydrogen permeance of the non-activated membrane as the continuous flow of hydrogen serves for the removal of impurities which are present on the surface of the Pd layer as residues of chemicals that are used during membrane preparation [44,45]. The setup was left under hydrogen atmosphere until hydrogen permeation was stable and then pure nitrogen and hydrogen permeation tests were performed (see Table 1).

After single gas $N_2$ and $H_2$ permeation tests, both the membranes used in this work have been tested under reactive conditions. In this work, ammonia decomposition has been performed in the temperature range between 425 °C and 500 °C, for pressures ranging between 2 and 6 bar(a) and feed flow rates between 0.5 and 0.9 $L_N$/min. An overview of the experiments carried out in this work is presented in Table 2.

Before starting an experiment, the reactor was heated up to the reaction temperature at a heating rate of 2 °C/min in $N_2$ atmosphere. Once the desired operating temperature was achieved, pure $NH_3$ was fed into the reactor and the operating pressure was adjusted. The reaction, and specifically $NH_3$ conversion, was then monitored for 1 h until steady state operation was observed. The permeate flow rate, the ammonia concentration in the permeate and the composition of the retentate side of the membrane were measured 5 times. $NH_3$ conversion was then calculated as the ratio between the amount of ammonia that decomposes into hydrogen and nitrogen and the amount of ammonia fed to the reactor (Eq. (2)), whereas $H_2$ recovery was calculated as the ratio between total amount of pure hydrogen separated through the membrane and the total amount of hydrogen fed into the reactor in the form of ammonia (Eq. (3)).

$$\text{Ammonia conversion}: \; X_{NH_3} = \frac{NH_{3,in} - NH_{3,out}}{NH_{3,in}} \tag{2}$$

$$H_2 \text{ recovery}: \; HRF = \frac{H_{2,\,permeated}}{3/2\,NH_{3,in}} \tag{3}$$

**Table 1 – Overview of the experimental conditions investigated in this work.**

| | |
|---|---|
| Single gas permeation test | |
| Single gas investigated | $N_2$, $H_2$ |
| Permeation temperature [°C] | 425, 450, 475, 500 |
| Pressure feed [bar] | 2–6 |
| Pressure permeate [bar] | 1 |
| Ammonia decomposition | |
| Ammonia decomposition reaction | $2NH_3 \leftrightarrow N_2 + 3H_2$ |
| Permeation temperature [°C] | 425, 450, 475, 500 |
| Pressure feed [bar] | 2–6 |
| Pressure permeate [bar] | 1 |
| Feed flow rate [$L_N$/min] | 0.5–0.9 |

## Results and discussion

### *Single gas permeation tests*

The measured hydrogen permeance and the ideal perm-selectivity at 450 °C and 1 bar pressure difference across the membrane are listed in Table 2 for each tested membrane.

From the experimental results, it is possible to notice that the thicker the membrane selective layer, the lower the hydrogen permeance through the membrane and the higher the membrane selectivity towards hydrogen. Accordingly, due to its thinner selective layer, A-2 has relatively high hydrogen permeance and low $H_2/N_2$ perm-selectivity, whereas A-3, given its thicker selective layer, has lower hydrogen permeance but a significantly higher $H_2/N_2$ perm-selectivity compared to A-2. This trend is due to the role played by palladium. When contacted by hydrogen molecules, palladium acts in fact as a catalyst for hydrogen splitting into hydrogen atoms which then cross the membrane due to the difference in the hydrogen partial pressure across the membrane. The thicker the selective layer, the fewer the membrane defects and the lower is then the nitrogen flow, which results in higher membrane selectivity; at the same time, the thicker the selective layer the lower the hydrogen flow, which results in lower hydrogen permeance.

### *Permeation tests under reactive conditions*

In order to show that ultra-pure hydrogen can be produced via ammonia decomposition in a membrane reactor, ammonia decomposition was performed in a composite palladium membrane reactor where a commercial Ru-based catalyst was selected and double-skin Pd-based membranes were used for hydrogen separation. Since increasing the thickness of the membrane selective layer it is expected to reduce the $NH_3$ concentration in the hydrogen produced, two membranes with respectively ~ 1 μm and ~ 6–8 μm thick selective layer were tested under reactive conditions. Table 3 presents the hydrogen recovery and the ammonia concentration in the permeate that have been achieved performing ammonia decomposition with the two different membranes. For these experiments, ammonia decomposition has been carried out at 500 °C and 4 bar(a) under a feed flow rate of 0.5 $L_N$/min of pure ammonia. A temperature of 500 °C was chosen as a trade-off between the endothermic nature of ammonia decomposition, which results in higher conversion and consequent lower ammonia concentration in the permeate at high temperature, and the maximum operating temperature at which a Pd-based membrane can work prior deterioration. In

**Table 2 – Hydrogen permeance at 450 °C and 1 bar pressure difference across the membrane, and ideal $H_2/N_2$ selectivity for the double-skin Pd-based membranes which have been tested in this work.**

| Membrane code | Thickness selective layer [μm] | $H_2$ permeance [mol/s/m$^2$/Pa] | $N_2$ permeance [mol/s/m$^2$/Pa] | Pressure exponent [–] | $H_2/N_2$ ideal perm-selectivity |
|---|---|---|---|---|---|
| A-2 | ~ 1 | $2.22 \cdot 10^{-6}$ | $4.26 \cdot 10^{-10}$ | 0.80 | 5210 |
| A-3 | ~ 6 – 8 | $1.15 \cdot 10^{-6}$ | $1.66 \cdot 10^{-11}$ | 0.72 | 68960 |

**Table 3 – $H_2$ recovery and $NH_3$ concentration in the permeate achieved with membranes with selective layer with thickness 1 μm and 6–8 μm. The experiments have been carried out performing ammonia decomposition at 500 °C and 4 bar(a) under a feed flow rate of 0.5 $L_N$/min of pure ammonia.**

| Membrane code | Thickness selective layer [μm] | $H_2$ recovery [%] | $NH_3$ concentration in the permeate [ppm] |
|---|---|---|---|
| A-2 | ~1 | 93.2 | 47 (±2.1) |
| A-3 | ~6-8 | 84.8 | <0.75 |

Temperature 500 °C, reaction pressure 4 bar(a), ammonia feed flow rate 0.5 $L_N$/min.

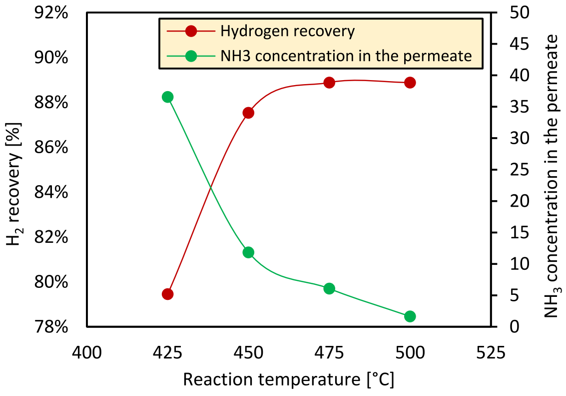

**Fig. 2 – Influence of the reaction temperature on hydrogen recovery and $NH_3$ concentration in the permeate at 5 bar(a) for a feed flow rate of 0.5 $L_N$/min of pure $NH_3$. The experimental results have been obtained with a Pd-based membrane with thickness of the selective layer of 6–8 μm.**

agreement with the results of the single gas permeation tests, from Table 3 it is possible to notice that a thicker membrane selective layer results in a lower hydrogen recovery as well as in a lower $NH_3$ concentration in the permeate. Specifically, increasing the membrane thickness from ~ 1 μm to ~ 6–8 μm, hydrogen recovery decreases from 93.2% to 84.8%, while ammonia concentration in the permeate drastically reduces from 47 ppm to a value which is below the detection limit of 0.7 ppm of the FTIR used to measure the $NH_3$ content in the $H_2$ stream. From these results it is possible to conclude that while the use of A-2 membrane requires a $NH_3$ removal downstream the membrane reactor to reach the FTIR detection limit of 0.7 ppm, it is on the other hand possible to directly achieve this threshold with an adequately thicker membrane. It should be noted that this result is ensured if the increase in the membrane thickness is coupled with a selection of process operating conditions capable of minimizing the targeted low ammonia concentration in the permeate while at the same time ensuring high ammonia conversion as well as good recover.

The influence of the reactor operating conditions on $NH_3$ conversion, $H_2$ recovery and $H_2$ purity achieved when installing the membrane with ~ 6–8 μm thick selective layer was investigated. Fig. 2 and Table 4 illustrate the influence of temperature on the reaction performance for the reactor operated at 5 bar(a) under a feed flow rate of 0.5 $L_N$/min of pure ammonia and with the permeate at atmospheric pressure. The experiments were carried out at 425 °C, 450 °C, 475 °C and 500 °C as in our previous work [11] we demonstrated that for temperatures from and above 425 °C full ammonia conversion can be achieved, whereas at lower temperatures the kinetic limitations result in relatively low ammonia conversion as well as low hydrogen recovery. In agreement with literature results, the experimental results achieved in this work show that temperature has an impact on the reaction performance. Specifically, a temperature increase results in higher ammonia conversion as well as in higher recovery. An increase in conversions results in fact in higher $H_2$ partial pressures in the reactor which in turn leads to higher driving force for hydrogen separation and therefore higher recovery. It is worth nothing that despite the increase in ammonia conversion is limited, the $NH_3$ concentration in the permeate significantly decreases. As temperature increases from 425 °C to 500 °C, the $NH_3$ concentration in the permeate in fact decreases from 36.6 ppm to 1.6 ppm. A further temperature increase would certainly allow to decrease $NH_3$ concentration in the permeate; however, as for temperatures above 500 °C Pd-based membranes undergo deterioration phenomena, it was chosen to evaluate if it is possible to lower the $NH_3$ concentration in the permeated hydrogen stream (possibly beneath 0.1 ppm) by varying the reaction pressure and the ammonia feed flow rate. The results of this investigation are presented in Fig. 3 (and Table 5) and Fig. 4 (and Table 6), respectively.

In line with the results of our previous study [11], as it is possible to notice from Fig. 3 and Table 5, while pressure does not have a major impact on $NH_3$ conversion at 500 °C, as in the entire pressure range it is higher than 99.5%, significantly higher hydrogen recovery as well as slightly lower hydrogen purities are achieved with increasing pressure as a consequence of a higher driving force for separation. Although the hydrogen purity remains very high in the entire investigated pressure range (>99.993%), the $NH_3$ concentration in the hydrogen stream increases with increasing recovery. A trade-off between hydrogen recovery and $NH_3$ concentration in the permeate is therefore needed when choosing for the reactor operating pressure. The experimental results confirm the

**Table 4 – $NH_3$ conversion, $H_2$ recovery, $H_2$ purity and $NH_3$ conversion in the permeate at various reaction temperatures.**

| Temperature [°C] [°C] | $NH_3$ conversion [%] | $H_2$ recovery [%] | $H_2$ purity [%] | $NH_3$ concentration in the permeate [ppm] *(std dev.)* |
|---|---|---|---|---|
| 425 | 96.5 | 79.5 | 99.994 | 36.6 (±0.254) |
| 450 | 99.7 | 87.5 | 99.994 | 11.8 (±0.415) |
| 475 | 99.8 | 88.9 | 99.994 | 6.1 (±0.124) |
| 500 | 99.8 | 88.9 | 99.994 | 1.6 (±0.206) |

Reaction pressure 5 bar(a), ammonia feed flow rate 0.5 $L_N$/min.

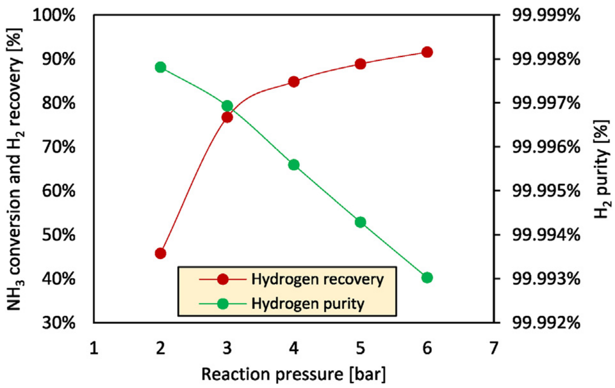

**Fig. 3 – Influence of the reaction pressure on hydrogen recovery and hydrogen purity at 500 °C for a feed flow rate of 0.5 $L_N$/min of pure $NH_3$. The experimental results have been obtained with a Pd-based membrane with thickness of the selective layer of 6–8 μm.**

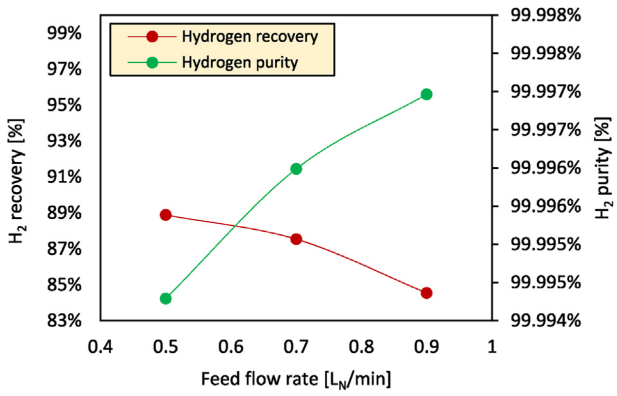

**Fig. 4 – Influence of the feed flow rate of ammonia on hydrogen recovery and hydrogen purity at 500 °C and 5 bar(a). The experimental results have been obtained with a Pd-based membrane with thickness of the selective layer of 6–8 μm.**

decreasing trend of $NH_3$ concentration in the permeate with decreasing pressure and it is therefore possible to conclude that, even if perhaps with this specific membranes $NH_3$ concentrations might have been above the fuel cell limit, this limit could anyway be overcome with further thickening of the selective membrane layer.

Fig. 4 and Table 6 show how $NH_3$ conversion, $H_2$ recovery and $H_2$ purity are affected by a variation of the ammonia feed flow rate for the reactor operated at 500 °C and 5 bar(a).

As ammonia feed flow rate increases, the residence time in the reactor decreases and this results in slightly lower hydrogen recovery and higher hydrogen purity in the permeate. The results show that an optimized reactor design, optimizing the membrane area installed over the ammonia residence time, would result in a very high purity of hydrogen. $NH_3$ concentrations below the FTIR detection limit were detected for the reactor working under feed flow rate of 0.7 and 0.9 $L_N$/min of pure ammonia. Nevertheless, if on one hand the use of a thicker membrane allows to avoid the addition of a purification stage which would ultimately increase the system complexity, on the other hand the resulting disadvantage

**Table 6 – $NH_3$ conversion, $H_2$ recovery, $H_2$ purity and $NH_3$ conversion in the permeate at various ammonia feed flow rate.**

| Feed flow rate [$L_N$/min] | $NH_3$ conversion [%] | $H_2$ recovery [%] | $H_2$ purity [%] | $NH_3$ concentration in the permeate [ppm] *(std dev.)* |
|---|---|---|---|---|
| 0.5 | 99.8 | 88.9 | 99.994 | 1.6 (±0.254) |
| 0.7 | 99.7 | 87.5 | 99.996 | <0.75 |
| 0.9 | 99.7 | 84.5 | 99.997 | <0.75 |

Temperature 500 °C, reaction pressure 5 bar(a).

**Table 5 – $NH_3$ conversion, $H_2$ recovery, $H_2$ purity and $NH_3$ conversion in the permeate at various reaction pressures.**

| Pressure [bar] | $NH_3$ conversion [%] | $H_2$ recovery [%] | $H_2$ purity [%] | $NH_3$ concentration in the permeate [ppm] *(std dev.)* |
|---|---|---|---|---|
| 2 | 99.5 | 45.8 | 99.998 | <0.75 |
| 3 | 99.7 | 76.8 | 99.997 | <0.75 |
| 4 | 99.8 | 84.8 | 99.996 | <0.75 |
| 5 | 99.8 | 88.9 | 99.994 | 1.6 (±0.254) |
| 6 | 99.8 | 91.6 | 99.993 | 3.7 (±0.078) |

Temperature 500 °C, ammonia feed flow rate 0.5 $L_N$/min.

would be associated to the higher costs of the materials for membranes preparation. In this context, the introduction of an $NH_3$ removal unit downstream the reactor could therefore represent a more economically feasible solution compared to the membrane reactor implementing thick membranes.

In order to show the feasibility of producing $NH_3$-free hydrogen while using thin and therefore relatively inexpensive membranes, ammonia decomposition has been performed at 450 °C and 3 bar(a) under a feed flow rate of 0.5 $L_N$/min of pure ammonia and the permeate side of the membrane with ~ 1 μm thick selective layer was connected to a purification stage, in which a bed of zeolite 13X at ambient conditions was used as adsorbent material for $NH_3$. Zeolite is in fact described in literature as one of the relevant materials that are used for $NH_3$ adsorption both at lab- and pilot-scale, next to other options such as bentonite, clay, biochar and activated carbon [46]. According to the Le Chatelier's principle, adsorption is favored at low temperatures and high pressures. Being the permeate side of the membrane kept in this study at atmospheric pressure, it was chosen to operate the adsorbent bed at this pressure as an increase in the pressure, whilst being beneficial in terms of adsorbent capacity of the reactor, would require an additional hydrogen compressor, which would increase both investment and variable costs associated to the supply of electricity. The $NH_3$ concentration in the hydrogen stream was monitored in a 3 h experiment in which after 90 min of operation the hydrogen permeate stream was connected to the hydrogen cleaning unit. The results of this experiment, which are presented in Fig. 5 shows that when the produced hydrogen with traces of ammonia is forced to pass through a zeolite 13X bed, it is possible to sharply reduce the ammonia content of the stream. In fact, while in the first part of the experiment the $NH_3$ concentration in the permeate is detected to be in the range between 70 and 80 ppm, when the hydrogen purification unit is connected to the hydrogen permeation stream the $NH_3$ concentration decreases to levels below the detection limit of the FTIR. As it is possible to see from Fig. 5 a slight decrease in the $NH_3$ concentration is detected shortly after the application of the hydrogen cleaning unit. This decrease is due to the fact that, during the first measurements after the introduction of the hydrogen cleaning unit, the gas cell of the FTIR is not completely filled with $NH_3$-free gas. In other words, as they are affected by the presence in the gas cell of residual traces of $NH_3$ from the non-purified stream, the first measurements after the introduction of the hydrogen cleaning unit are not representative of the actual $NH_3$ concentration of the stream leaving the adsorption column. The actual $NH_3$ concentration in the produced hydrogen stream can therefore be considered to be the one measured once the measurements become stable, that is the one measured about 10 min after the hydrogen permeate stream was connected to the hydrogen cleaning unit. Nevertheless, it must be noted that $NH_3$ concentration was detected to be below the FTIR detection limit, proving that zeolite 13X is a suitable sorbent for the production of ultra-pure $H_2$.

From a comparison between the results achieved with A-2 and A-3, it is possible to conclude that while with A-3 it is possible to achieve a high hydrogen purity level which can be possibly the target level for fuel cell application when performing ammonia decomposition at 500 °C, with A-2 this result cannot be achieved even with any temperature increase within the deterioration limits of the membrane and therefore a hydrogen purification stage is required. The introduction of a hydrogen purification stage offers not only the possibility to produce ultra-pure (possibly $NH_3$-free) hydrogen, but also to work at lower temperatures compared to the case in which hydrogen is produced within a single unit with thicker membranes. As hydrogen purity depends in this case on the performance of the adsorbent bed and not entirely on the reaction temperature, it is in fact possible to operate the reactor at lower temperatures and to accept higher $NH_3$ concentration at the reactor outlet. This brings benefits from an energetic point of view, albeit at the expenses of a slight decrease in the hydrogen recovery.

## *Process flow diagram of a system for ultra-pure hydrogen production from ammonia*

A detailed process flow diagram of the pure hydrogen production system including a hydrogen purification unit downstream the membrane reactor for ammonia decomposition is depicted in Fig. 6. In this system the ammonia feed is preheated up to the reactor operating temperature and then enters the reaction unit in which ammonia decomposes into hydrogen and nitrogen after contacting a suitable catalyst for ammonia decomposition. As the membranes are immersed in the catalyst bed, hydrogen containing traces of unconverted ammonia permeates through the membranes and leaves the

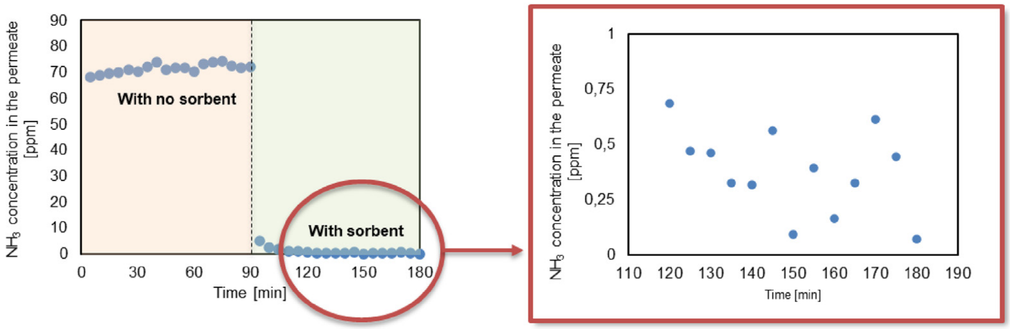

**Fig. 5 – Influence of the introduction of a $H_2$ cleaning unit consisting of a bed of zeolite 13X at ambient conditions on the purity of $H_2$ produced from $NH_3$ decomposition at 450 °C, 3 bar(a) and for a feed flow rate of 0.5 $L_N$/min of pure $NH_3$.**

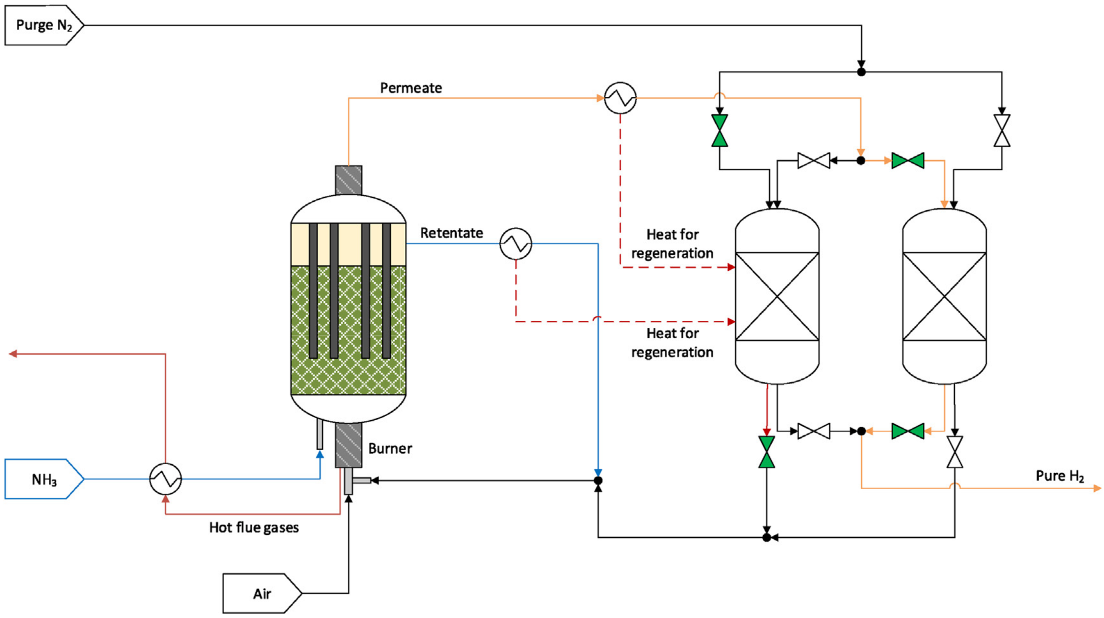

**Fig. 6 – Process flow diagram of a system for ultra-pure hydrogen production from ammonia consisting of a membrane reactor and a hydrogen purification unit.**

reactor at high temperature. Nitrogen resulting from ammonia decomposition, unrecovered hydrogen and unconverted ammonia leave the reactor at the retentate side at the reactor operating pressure and temperature. As ammonia decomposition is an endothermic reaction, and therefore heat must be supplied to maintain the reactor at the desired operating conditions, the retentate stream is first cooled down in a heat exchanger and then combusted in presence of air in a burner. The heat released by combustion is used to supply heat to the reaction. As the flue gases resulting from the retentate combustion leave the burner at high temperature, their heat content is exploited to pre-heat the ammonia stream to be sent to the reactor inlet and they leave then the system at relatively low temperatures (<150 °C). The permeate stream containing hydrogen and traces of ammonia is cooled down in a heat exchanger and sent to the hydrogen purification unit, specifically an adsorption column, where traces of unconverted ammonia which unavoidably permeates through the membrane are captured and ultra-pure hydrogen is produced. The hydrogen production unit includes two columns, which are simultaneously working, but into two different modes. While one column works as just described allowing for the removal of ammonia from the hydrogen stream, the other one works in regeneration mode. The one-time use of adsorbent materials is in fact not economically viable, and therefore the cyclability of adsorbents is paramount. The heat recovered from the cooling of both the permeate and retentate stream is exploited for the saturated sorbent regeneration, as high temperature favors ammonia desorption from the adsorbent material. The off-gas leaving the regeneration column is sent to the burner to be combusted together with the retentate stream. When working in regeneration mode, a column may also be fed with inert gas (nitrogen for instance) which could serve as a purge for ammonia that desorbs from the adsorbent material. Once the column working in adsorption mode is saturated with ammonia, its functioning is switched to regeneration mode, and at the same time the column working in regeneration mode is switched to adsorption mode. The continuous switching of the columns from adsorption to regeneration mode ensures a continuous pure hydrogen purification process.

## Conclusions

As the purity of hydrogen produced with the membrane reactor technology is not always sufficiently high to directly feed $H_2$ to fuel cells, strategies to decrease the $NH_3$ content of the permeated hydrogen stream must be implemented. In this work is has been experimentally demonstrated that either increasing the thickness of the membrane selective layer or forcing the produced $H_2$ with traces of ammonia to pass through a hydrogen purification unit it is possible to produce hydrogen which can be used as suitable fuel for systems requiring ultra-pure hydrogen. Two double-skin Pd–Ag membranes, with respectively $\sim 1$ μm and $\sim 6$–$8$ μm thick selective layer, have been tested for hydrogen separation during ammonia decomposition and the $NH_3$ content of the produced hydrogen stream was monitored. It was demonstrated that increasing the membrane thickness from $\sim 1$ μm to $\sim 6$–$8$ μm during ammonia decomposition hydrogen recovery decreases from 93.2% to 84.8%, while ammonia concentration in the permeate significantly decreases from 47 ppm to a value which is below the detection limit of the FTIR that was used to measure the $NH_3$ content of the hydrogen stream. It is therefore possible to conclude that by adequately increasing the thickness of the membrane selective layer it is possible to achieve hydrogen purities compatible with the specifications imposed by fuel cells. The influence of a variation in the reactor operating conditions on

$NH_3$ conversion, $H_2$ recovery and $H_2$ purity achieved when installing the membrane with ~ 6–8 μm thick selective layer was also investigated and the results of this study demonstrate that the targeted $H_2$ purity can be increased by properly tuning the reactor operating conditions. It was demonstrated that an operating temperature increase is always beneficial when performing ammonia decomposition as it results in higher hydrogen recovery, ammonia conversion as well as hydrogen purity. Nevertheless, as Pd-based membranes suffer from deterioration phenomena when exposed to temperatures higher than 500 °C, when operating a membrane reactor for hydrogen production from ammonia decomposition it is not possible to overcome this temperature and it is therefore necessary to tune the other membrane reactor operating condition - namely pressure and feed flow rate - to achieve the targeted hydrogen purity, especially in terms of ammonia concentration in the permeate. The experimental results show that an increase in the reaction operating pressure, while not showing a major impact on $NH_3$ conversion, is responsible for a significant increase in the hydrogen recovery as well as for an increase in the $NH_3$ concentration in the permeate. The reactor operating pressure must therefore be selected as a trade-off pressure capable of minimizing the $NH_3$ concentration in the permeate while at the same time guaranteeing a good hydrogen recovery. On the other hand, it was demonstrated that an increase in the ammonia feed flow rate results in slightly lower hydrogen recovery and lower $NH_3$ concentration in the permeate. The reactor feed flow rate should be hence selected in such a way to compensate for the decrease in the reaction performance that are detected when a specific reaction pressure is selected.

The introduction of an $NH_3$ removal unit downstream the reactor could however represent a more economically feasible solution compared to the membrane reactor implementing thick membranes. In this study, a bed of zeolite 13X at ambient conditions was tested as adsorbent material for $NH_3$ removal downstream the membrane reactor equipped with the membrane with ~ 1 μm thick selective layer and operated at 450 °C and 3 bar(a) under a feed flow rate of 0.5 $L_N$/min of pure ammonia. The experimental results show that zeolite 13X can be regarded as a suitable sorbent for hydrogen purification from ammonia. However, as the same result could be achieved with any other sorbent capable of adsorbing $NH_3$, future work should be addressed in the investigation of the performance of other materials. Furthermore, since one-time use of adsorbent materials is not economically viable, further work should also be addressed to investigate the regeneration process and the cyclability of adsorbent materials as well as on the evaluation of the economic impact given by the introduction of a hydrogen purification stage in the $NH_3$-to-$H_2$ system.

## Disclaimer

The present publication reflects only the author's views and the Commission is not responsible for any use that may be made of the information it contains.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2022.04.240.

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