

# Development of dense membranes for high-density hydrogen production from ammonia catalytic decomposition (cracking) for PEM fuel cells power in Long-haul Passenger Aircraft Transportation

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## ABSTRACT

Aviation is a major greenhouse gas contributor responsible for around 3.2% of global CO<sub>2</sub> emissions to the atmosphere. That corresponds to over than 1 billion metric tons of carbon (A metric ton is slightly smaller than the American imperial ton—but to be precise, it is 1,000 kilograms—however the two are comparable) being added to the atmosphere yearly. Therefore, the race to find alternatives to fossil fuels for planes is being intensified and in recent years, new and more highly efficient engines have contributed to reducing fuel consumption and harmful emissions. However, despite the impact of the COVID-19 pandemic, global passenger and cargo air traffic is projected to grow by 4% per year to 2040. Biofuels, hydrogen, and electricity are three ways in which the aviation industry can respond to rising emissions and sustainability. The aim is to develop a more compact design for hydrogen production from ammonia to offer a viable means for hydrogen air transportation and storage in the form of ammonia. More importantly, we are considering this approach to be a viable solution for long-haul aviation powered by hydrogen. We will present results demonstrating our world-class expertise in membrane development (hydrogen-nitrogen separation).

**Keywords:** Greenhouse gas, CO<sub>2</sub> emissions, aviation, fuel, long-haul, transport, hydrogen, fuel cell, ammonia, membranes.

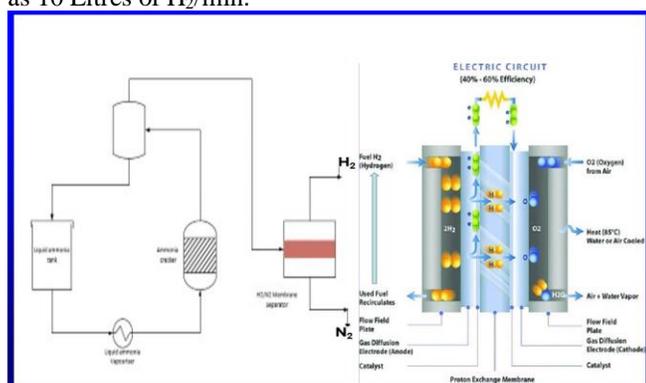
## 1 INTRODUCTION

The aviation sector is a major greenhouse gas contributor that is responsible for around 3.2% of global CO<sub>2</sub> emissions to the atmosphere. That corresponds to over 1 billion metric tons of carbon (A metric ton is slightly smaller than the American imperial ton—but to be precise,

it is 1,000 kilograms—however the two are comparable) being added to the already existing atmospheric CO<sub>2</sub> yearly. Therefore, the race to find alternatives to fossil fuels for planes is being intensified and in recent years, new and more highly efficient engines have contributed to reducing fuel consumption and harmful emissions. However, despite the impact of the COVID-19 pandemic, global passenger and cargo air traffic is projected to grow by 4% per year to 2040. Biofuels, hydrogen, and electricity are the three ways in which the aviation industry can respond to rising emissions and sustainability. The first involves using biofuels and if you flew with one of the world's major airlines during the past ten years, your aircraft may have been partially fuelled by biofuels. Although biofuels are not in regular use, many airlines around the world have conducted extensive test flights on scheduled services using biofuels. The second is hydrogen and fuel cells are already providing power for buses in several cities across the globe although there are concerns as to raise whether hydrogen which the most volatile gas can be the solution to zero-carbon flying. The third option is electricity where there is agreement amongst experts that the current battery technology will have to significantly advance in terms of both weight and storage to enable large, commercial long-haul electric aircraft become a reality although smaller electric passenger aircrafts are currently already flying and may be certified for revenue-earning use in the not very distant future. With significant development being seen in larger-plane aviation projects our proposed fuelling process looks as shown in Figure 1. The aim is to develop a compact design for H<sub>2</sub> production from NH<sub>3</sub>. This will offer a viable means for H<sub>2</sub> transport and storage in the form of ammonia. More importantly, we are considering this to be a solution for long haul aviation powered by hydrogen using membrane for H<sub>2</sub>-N<sub>2</sub> separation (Figure 1).

The current interest in the use of ammonia as a clean replacement to fossil fuels is festered from global ambition

to transition from carbon-intensive fossil fuels that are largely responsible for CO<sub>2</sub> emissions responsible for causing global warming. Ammonia is increasing being viewed the bridge that will link the current carbon-intensive fossil-based economy and the net-zero hydrogen-based economy. In the net-zero hydrogen-based economy, CO<sub>2</sub> emissions would be eliminated. Ammonia itself belongs to a group of energy-dense liquid fuels and therefore can be stored much easier and transported in a fashion that hydrogen cannot. Furthermore, when ammonia is decomposed or cracked it disintegrates to generate hydrogen and nitrogen through only a single reaction step which does not produce any by-products such as carbon oxide nor sulphur in the product stream. Ammonia, therefore, is considered as one of the most promising future zero-carbon liquid fuels (CNLFs) if the feedstocks H<sub>2</sub> and N<sub>2</sub> are produced from renewable energy. With this and under continuous cracking of ammonia hydrogen can thus be made available to smaller size compressors for the smaller high-pressure tanks that will allow modular high-density capability and increased reassurance of hydrogen refuelling stations. Such low-cost and assured on-demand hydrogen generation technology will also find widespread application in many other industrial areas such as glass purification, aerospace, fertilizer production, semiconductor manufacturing welding, and heat-treating metals, pharmaceuticals, annealing, the hydrogenation of unsaturated fatty acids in vegetable and in coolant in power plant generators oil (1,2.). The membrane purifier will allow low temperature, on-site hydrogen generation from ammonia and then by combining the cracking and hydrogen separation in one unit allow low temperature ammonia cracking membrane reactor system using non-precious metal ammonia cracking catalyst, a unique heating approach, a convoluted feed delivery pathway to reduce mass transfer to achieve a high-density hydrogen delivery cost at target pressure (20bar) < \$4.0/kg, at a scale as small as 10 Litres of H<sub>2</sub>/min.



**Figure 1: An onboard ammonia storage and cracker with membrane separation for high-purity hydrogen for fuel cell power production**

## 2 MATERIALS AND METHODS

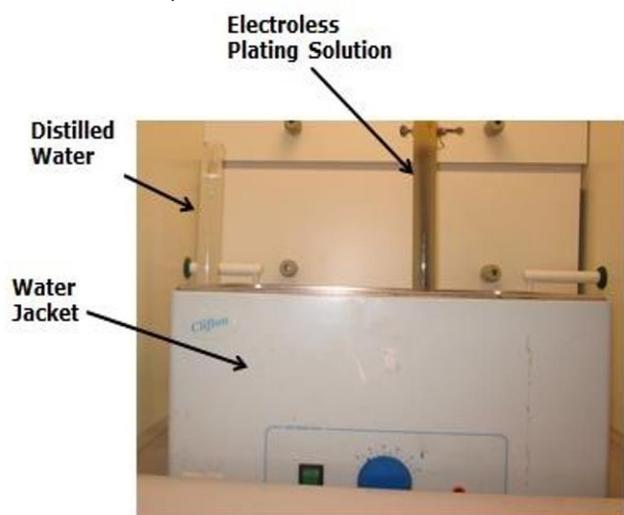
Porous alumina tube (manufactured by SCTI, FRANCE) and are composed of macroporous  $\alpha$ -alumina support with a 30 nm pore diameter and i.d.= 7mm, o.d.= 10 mm, effective length= 0.34 m. Another 30 nm pore diameter  $\alpha$ -alumina support was graded with AlOOH sol and converted to  $\gamma$ -alumina by 5 sequential dipping using the dip coating method. The tubes were cleaned by washing sequentially with water, ethanol, and acetone respectively under ultrasonic irradiation. The surface of both tube ends 5mm in each case was coated by enamelled glass and blanked with Teflon prior to palladium deposition and /or palladium/silver. The porous part left for the Pd or Pd–Ag membrane was fixed 24 cm in length. Palladium acetate, palladium chloride, silver nitrate, ammonia solution, EDTA, and hydrazine monohydrate all of reagent grade were used without further purification. Other chemicals were also of reagent grade.

## 3 EXPERIMENTAL PROCEDURE

Gas permeation through palladium composite membranes was investigated for five single gases including hydrogen. The membranes were fabricated using the electroless deposition method and their hydrogen permeation behaviour investigated at different temperatures and transmembrane pressure drops. The membrane integrity was quantitatively observed through a leak test experiment using helium gas over various transmembrane pressure drops. In all the investigations carried out for the Pd3 palladium alloy membrane, prepared using the co-deposition Pd/Ag electroless plating method at same conditions with the Pd1 and Pd2 membranes,  $n = 0.5$  in accordance with Sievert's Law. For the non-palladium-based silica and ceramic alumina membranes, investigations were carried out for hydrogen permeation and five other single gases: He, CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub> and Ar. For the silica membranes, a maximum hydrogen permeance of  $3.12 \cdot 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  at 573 K and 0.4 bar was observed, which increased to  $4.05 \cdot 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  at 573 K and 0.4 when the membrane was modified with Boehmite sol prior to deposition of the silica layer. The permeance for hydrogen and the five single gases was investigated for the alumina membrane at five successive coatings. It was observed that the commercial alumina membrane displayed a maximum hydrogen permeance of  $9.72 \cdot 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  at 573 K and 0.4 bar, which increased to  $9.85 \cdot 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  at the same temperature and pressure when the membrane was modified with Boehmite sol.

A thin palladium (Pd1) membrane with a thickness of 2  $\mu\text{m}$  was prepared over porous ceramic alumina support using the electroless plating method and a maximum hydrogen flux of  $80.4 \text{ cm}^3 \text{ cm}^{-2} \text{ min}^{-1}$  was observed at 873 K and 0.4 bar after annealing the membrane. The hydrogen flux increased to  $94.5 \text{ cm}^3 \text{ cm}^{-2} \text{ min}^{-1}$  at the same temperature and pressure for the palladium membrane (Pd2), prepared using the modified electroless plating method. The

hydrogen flux increased to  $98.1 \text{ cm}^3 \text{ cm}^{-2} \text{ min}^{-1}$  for the palladium/silver (Pd/Ag) membrane prepared using the co-deposition electroless plating method and the Pd/Ag membrane avoided the hydrogen embrittlement at low temperature. Hydrogen purity for the membrane was also investigated for a reformat gas mixture and a maximum hydrogen purity of 99.93% was observed at 873 K and 0.4 bar. Single and mixed gas permeation tests were conducted for the Pd2 membrane. Prior to the test, the membrane was reduced in flowing hydrogen at  $350^\circ \text{C}$  for 10 minutes to activate the palladium layer just as was done for the Pd1 membrane. Figure 2 shows the Hydrogen flux as a function of the partial pressure difference on the feed and permeate sides at 723, 673 and 623 K. It can be observed that there is a deviation from Sievert's law with the value of the pressure exponential  $n=1$ . At unity, the rate limiting step for hydrogen permeation through the membrane are the surface processes involving hydrogen dissociative adsorption on the palladium layer and/or atomic hydrogen recombination and desorption at the permeate side. The  $n$  value at unity indicates a fast rate of hydrogen permeation through the membrane normally associated with thin palladium membranes ( $<5 \mu\text{m}$ ).



**Figure 2: Schematic diagram of the electroless plating process**



**Figure 3: Photograph of the uncoated support**



**Figure 4: Photograph of the Palladium-coated support**

Chemical	Amount
$\text{PdCl}_2$	2.1 g
$\text{AgNO}_3$	0.7 g
NaEDTA	31 g
$\text{NH}_4\text{OH}$	200 mL
1M $\text{N}_2\text{H}_4$	10 mL
Figure Text	Normal

**Table 1: Palladium plating bath composition.**

## 4 ERESULTS AND DUSCUSSION

He leaks test was carried out after the fabrication of the Pd membrane and the results shown in Figure 5 Helium was used to check for any defects or leaks because helium should not permeate a dense palladium membrane. Hence if it is detected in the permeate stream, then it means either the membrane is porous or there is a leak in the seals. The maximum He permeance after deposition of the Pd layer was lower than the  $3.13 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  which was the maximum permeance for the fresh unmodified alumina support before deposition of the Pd layer. The lower He permeance for the composite Pd membrane indicates that the deposition of the metallic Pd layer was successful. Albeit for a defect free and dense Pd membrane, only  $\text{H}_2$  should permeate through when it is dense as confirmed by adherence of Sievert's Law in Figure 6. Figure 7 shows the Arrhenius plot of the permeability against the reciprocal of the absolute temperature. From the slope it can be observed that the temperature dependence on hydrogen permeation follows the Arrhenius-vant Hoff behaviour with a correlation coefficient of 0.9989. The activation energy was calculated from the slope as 10.77 kJ/mol and represents the effect of temperature on hydrogen permeation through the membrane. Our observed value agrees with values reported by several authors [3-5]. These results suggest a solution-diffusion transport of hydrogen in the palladium membrane in which mmolecular hydrogen dissociates at the membrane surface and dissolves into palladium followed by transport through the metallic matrix and then emerges as molecular hydrogen upon re-association as shown in Figure 8. A modified method for electroless plating was developed which skips the sensitization step during support modification. The maximum hydrogen flux achieved was slightly above  $40 \text{ cm}^3 \text{ cm}^{-2} \text{ s}^{-1}$  using the method compared to the conventional method which involves the 2-step sensitization and activation. In the single-gas hydrogen permeation investigation for the Pd1 membrane, prepared using the conventional electroless plating method, the value of the exponential factor  $n = 0.5$  in accordance with Sievert's Law. However, for the mixed-gas hydrogen separation investigation  $n = 0.62$  at 573 K, which decreased to 0.55 when the membrane was annealed at 873 K. For the

Pd2 membrane, prepared using the modified electroless plating method,  $n = 1$  at 573 K - but the value decreased to 0.76 for the mixed-gas hydrogen separation investigation at the same temperature, which depicts a deviation from Sievert's Law. The susceptibility of the membrane to hydrogen embrittlement when cold hydrogen is allowed to contact its surface is currently being studied. Work is also ongoing to optimize the preparation of the membrane avoiding Tin impurities arising from seeding, reducing the overall time duration of the electroless plating process and preparing palladium membranes of better quality with greater adhesion of the palladium film on the substrate for enhanced hydrogen permeation and durability,

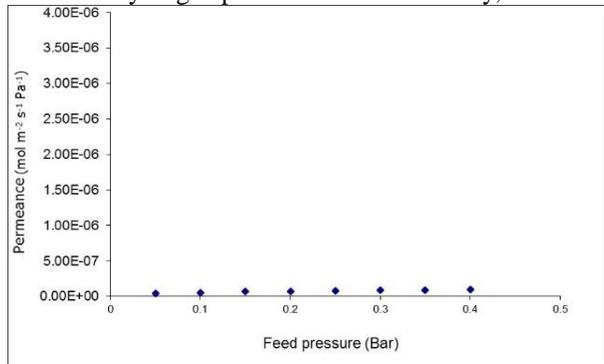


Figure 5: Helium permeance against inlet pressure difference for the Pd1 membrane

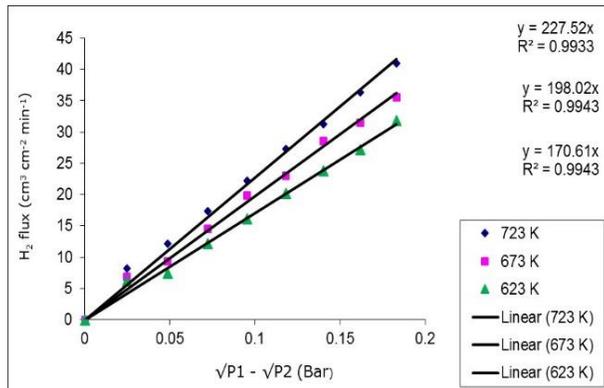


Figure 6: Hydrogen flux against square root of the partial difference of hydrogen across the Pd1 membrane

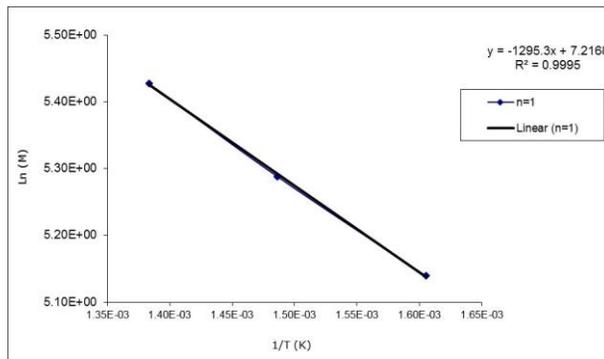


Figure 7: Pd1 Arrhenius plot for hydrogen permeation

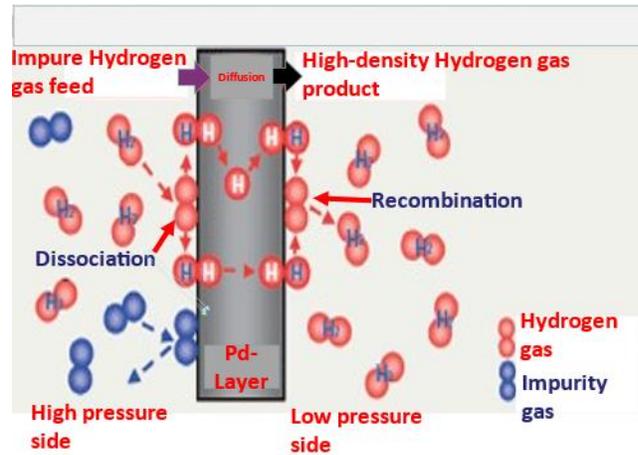


Figure 8: Hydrogen transport mechanism through Palladium

## 5 CONCLUSIONS AND FUTURE WORK

The application of a membrane process for the purification of hydrogen resulting from the cracking of ammonia has been investigated. Mathematical simulations are being conducted for an experimental reactor combining cracking and separation in a single unit to achieve process intensification and further reduce the reactor volume by shifting the cracking reaction to completion and thus operate at significantly reduced temperatures and pressures. We are also evaluating various substrates for enhanced hydrogen permeation and Palladium adhesion/durability.

## 6. ACKNOWLEDGEMENTS

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