



# PEMBeyond

**PEMFC system and low-grade bioethanol processor unit development for back-up and off-grid power applications**

**Grant Agreement no: 621218**

## **Deliverable 5.2**

# **Report on feasibility evaluation of composite palladium membrane for H<sub>2</sub> purification**

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<b>Summary</b>	
<p>Feasibility of alternative H<sub>2</sub> separation and purification techniques has been studied. Focus has been on the composite palladium membranes as they possess great potential in H<sub>2</sub> separation and purification.</p> <p>Present state-of-the-art of palladium membranes were studied through a literature survey. Feasibility of H<sub>2</sub> separation and purification by membrane for PEMBeyond project was evaluated.</p>	
<b>Confidentiality</b>	PU

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## 1. Feasibility evaluation of Pd membrane – a system concept

In PEMBeyond project a PEMFC based power system operating on hydrogen produced from low-grade (crude) bioethanol will be developed. The overall system concept is presented in Figure 1.

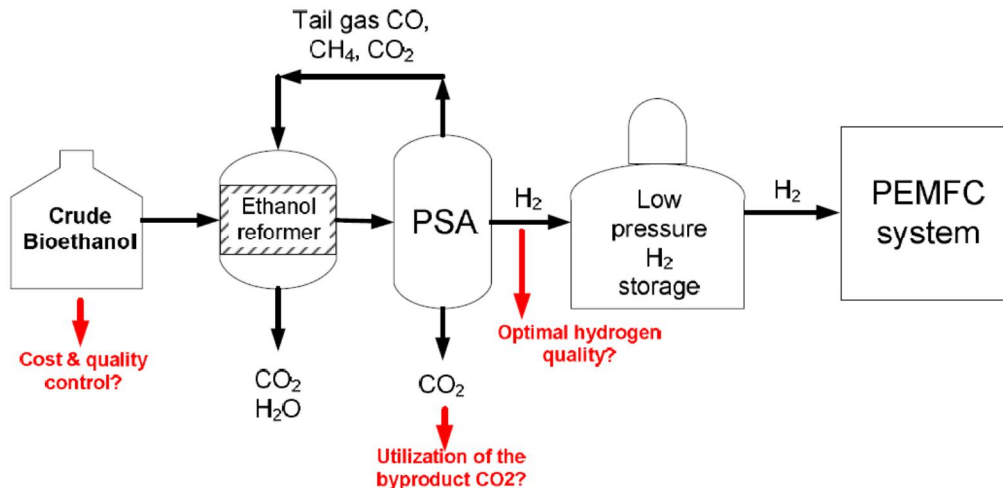


Figure 1. Basic scheme of the complete system in PEMBeyond project.

The economic benefit of the PEMBeyond concept is based on the savings in diesel fuel and battery maintenance. Therefore, in the concept of PEMBeyond, the hydrogen quality is optimised for the local use in PEMFC system.

In work package 5 of PEMBeyond project it is defined that in parallel to the PSA market analysis, feasibility of alternative H<sub>2</sub> separation and purification techniques shall be studied with focus on composite palladium membranes.

If Pd-membrane would replace PSA, the base concept would be as in Figure 2. In this concept all the hydrogen would be purified by Pd-membrane. Pd based membrane shows very high selectivity for H<sub>2</sub> permeation<sup>1</sup>. Commercial palladium membrane purifiers are available for production of hydrogen with purity of 99.9999999%<sup>2</sup>.

Therefore, if there is no damage of the Pd membrane, the expected hydrogen purity will exceed the ISO 14687-2:2012 grade and be unnecessary pure for the stationary power generation by PEMFC in PEMBeyond project.

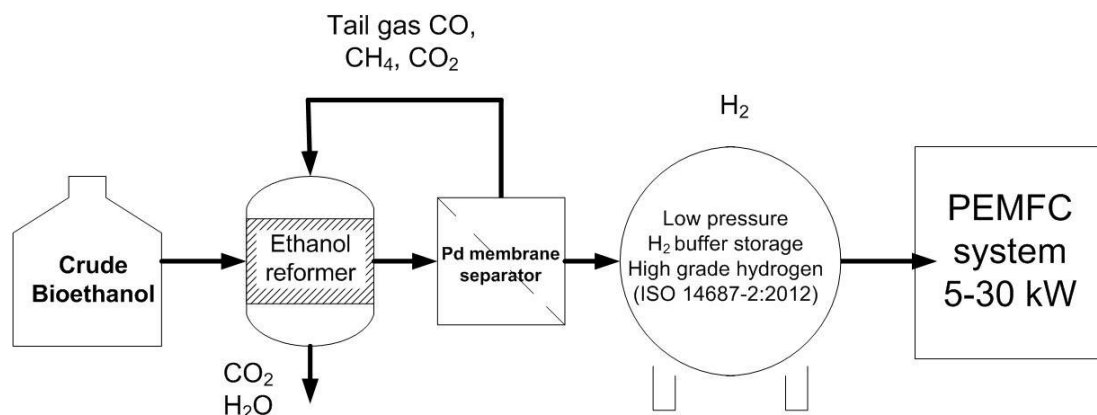


Figure 2. Process concept for ISO 14687-2:2012 grade hydrogen production.

<sup>1</sup> F. Gallucci, E. Fernandez, P. Corengia, M. van Sint Annaland, Recent advances on membranes and membrane reactors for hydrogen production, Chemical Engineering Science. 92 (2013) 40–66.

<sup>2</sup> <http://www.saespuregas.com/Products/Gas-Purifier/Hydrogen/Palladium-Membrane/Home.html>

Another option would be produce ISO 14687-2:2012 grade hydrogen using membrane separation after PSA.

In this concept, which is shown in Figure 3, only a part of the hydrogen is upgraded to high value (ISO 14687-2:2012 grade or better), while rest of the hydrogen is stored to be used in stationary PEMFC system.

One of the advantages of this concept compared to the one in Figure 2 is that PSA will also reduce the level of contaminants, which could damage the Pd membrane.

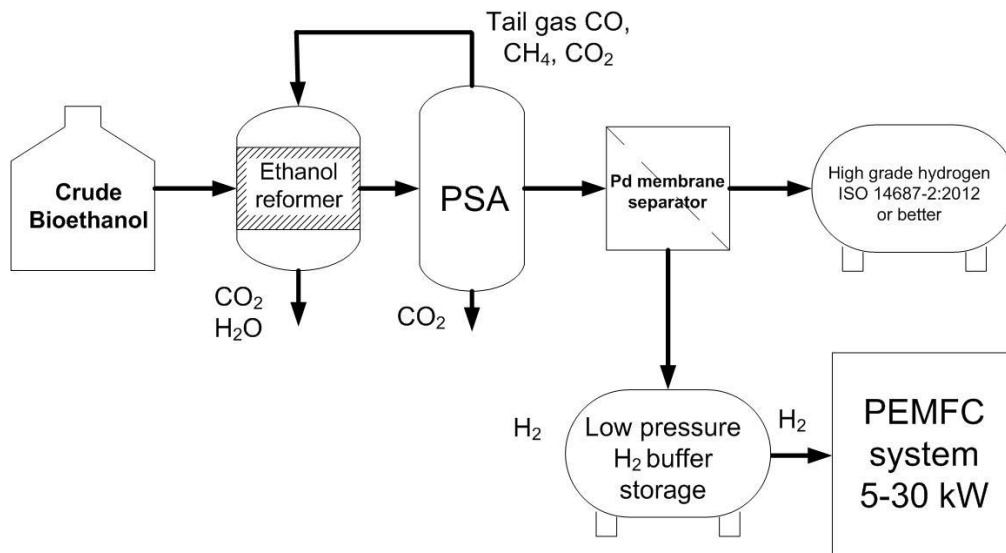


Figure 3. Process concept for both low grade and ISO 14687-2:2012 grade hydrogen production.

If hydrogen is produced for the use in vehicle applications, the compression of hydrogen to 350 bar or 700 bar is not economically viable in small scale with current compressor technology.

Automotive grade (ISO 14687-2:2012) hydrogen could, however, to be used in fleet vehicle applications using metal hydride (MH) storage. Examples of these approaches are scooter application in Taiwan<sup>3</sup> and development of low cost metal hydride hydrogen storage system for forklift applications<sup>4</sup>.

When metal hydride storage is used, then the pressure level in the storage can be 10 bar or even less, depending on the MH storage material, storage vessel design and required charging time.

Hydrogen, used as transportation fuel, has a value of 5-10 €/kg (150-300 € / MWh) depending on the location and application. When feasibility of ISO 14687-2:2012 grade (or better) hydrogen production and use is considered by membrane separation, then the value of this hydrogen should be much higher than the value of hydrogen for stationary

<sup>3</sup> [http://www.apfct.com/goods\\_cat.php?act=view&no=31](http://www.apfct.com/goods_cat.php?act=view&no=31)

<sup>4</sup> [http://www.hydrogen.energy.gov/pdfs/review14/st095\\_narvaez\\_2014\\_p.pdf](http://www.hydrogen.energy.gov/pdfs/review14/st095_narvaez_2014_p.pdf)

## 1.1 The use of Pd membrane for upgrading H<sub>2</sub> quality

The cost of automotive grade hydrogen (ISO 14687-2:2012) is currently too high due to purification and quality assurance (QA) requirements. This is especially true for a small scale production of hydrogen, when QA requirements may become too costly.

In order to minimise these costs there is ongoing FCH JU project HyCoRA (Grant agreement no: 621223) in which risk assessment is used for defining right QA requirements.<sup>5</sup>

One of the major questions is if so called “canary species” could be used for the quality assurance purposes. When the contaminant matrix in the hydrogen to be purified is known, and one contaminant (“canary species”) can be measured accurately in both unpurified and purified hydrogen, the rest of the contaminant levels in the purified hydrogen can be predicted within well-defined error margins. If this is possible, then QA for hydrogen can become highly cost efficient.

With purifier based on Pd membrane the use of “canary species” (tracer gas) could be easier to use compared to PSA. In Pd membrane purifier all the contaminants should permeate with the same ratio through the possible pinholes in Pd membrane. If there also is easily measurable inert gas (N<sub>2</sub>, Ar, He, CH<sub>4</sub>) always present in the primary fuel, then measuring this in primary and secondary hydrogen (and possibly in tail gas) would give the enrichment factor for Pd membrane separation and function also as a “canary species”. Therefore, the commercialisation of low cost Pd membrane purifier could significantly help to reduce the cost of ISO 14687-2:2012 grade hydrogen in small scale production.

A novel tracer enrichment method has been developed by Murugan and Brown (2014) with Krypton as an added tracer gas<sup>6</sup>. For a small scale hydrogen production monitoring of a single contamination or inert gas component by an inexpensive sensor would be needed.

When Pd membrane purifier is applied as in Figure 3, high enrichment of inert gases in the primary side can be allowed, due to high selectivity of Pd membrane (in the order of 1000 or better<sup>7</sup>), while still keeping the hydrogen quality within the specification of standard ISO 14687-2:2012.

When the inert gas content increases, the contribution of mass transfer resistance in gas phase becomes comparable to mass transfer resistance in bulk Pd film<sup>8</sup>. This is true especially when the Pd film thickness is reduced and flux is increased. For supported Pd-membranes the gas phase mass transfer in porous support may also become important<sup>9</sup>.

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<sup>5</sup> <http://hycora.eu/>

<sup>6</sup> Murugan, A., Brown, A.S. Advancing the analysis of impurities in hydrogen by use of a novel tracer enrichment method (2014) *Analytical Methods*, 6 (15), pp. 5472-5482.

<sup>7</sup> Hydrogen Membrane Separation Techniques Sushil Adhikari and Sandun Fernando *Industrial & Engineering Chemistry Research* 2006 45 (3), 875-881.

<sup>8</sup> Yun, S., Ted Oyama, S. Correlations in palladium membranes for hydrogen separation: A review (2011) *Journal of Membrane Science*, 375 (1-2), pp. 28-45

<sup>9</sup> Sanz, R., Calles, J.A., Ordóñez, S., Marín, P., Alique, D., Furones, L. Modelling and simulation of permeation behaviour on Pd/PSS composite membranes prepared by "pore-plating" method (2013) *Journal of Membrane Science*, 446, pp. 410-421.

## 2. Literature review of hydrogen separation membranes

### 2.1 Membrane technologies for hydrogen separation

Hydrogen membranes can be classified to maximum six different types, as done by Doong (2012)<sup>10</sup>. These membrane types are discussed here and compared against palladium based metallic membranes, which are mostly discussed in Chapter 2.2. The classification of membranes in this Chapter is according to Doong (2012).

#### 2.1.1 Metallic membranes (dense)

Palladium and its alloys are the only commercial metallic materials for hydrogen separation and purification. In these materials hydrogen is dissociated, dissolved and diffused through the membrane to the side of lower hydrogen partial pressure. The process is illustrated in Figure 4. In this Figure are also the different steps for solution diffusion hydrogen transport through the Pd membrane marked (Yun and Oyama, 2009)<sup>11</sup>.

- 1) Diffusion of molecular hydrogen to the surface of the palladium membrane.
- 2) Reversible dissociative adsorption on the palladium surface.
- 3) Dissolution of atomic hydrogen into the bulk metal.
- 4) Diffusion of atomic hydrogen through the bulk metal.**
- 5) Association of hydrogen atom on the palladium surface.
- 6) Desorption of molecular hydrogen from the surface.
- 7) Diffusion of molecular hydrogen away from the surface.

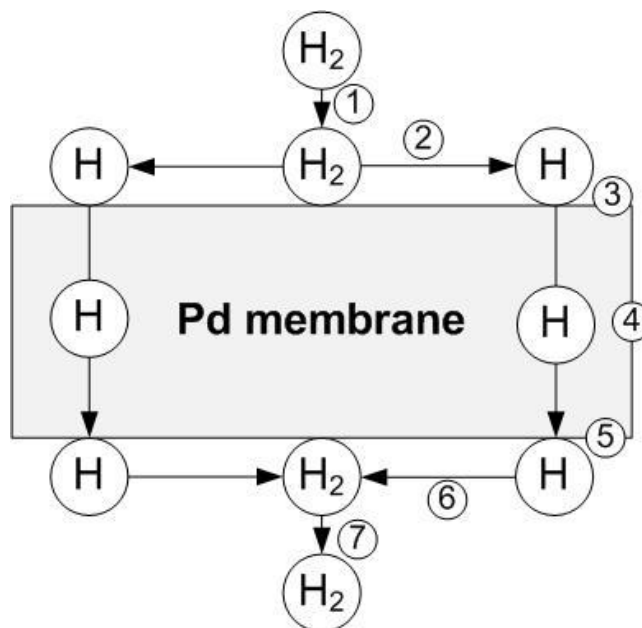


Figure 4. Hydrogen transport in palladium membrane.

Of these processes diffusion of atomic hydrogen is usually the rate determining step. However, other steps may become rate determining, when Pd film thickness is reduced to less than 10  $\mu\text{m}$ .

<sup>10</sup> Doong, S.J. *Membranes, Adsorbent Materials and Solvent-Based Materials for Syngas and Hydrogen Separation in Functional Materials for Sustainable Energy Applications* by S Skinner; S Irvine; J A Kilner; J Kilner; S J C Irvine; P P Edwards; S J Skinner; P Edwards Published by Elsevier Science; Woodhead Publishing, 2012

<sup>11</sup> Yun, S., Ted Oyama, S. Correlations in palladium membranes for hydrogen separation: A review (2011) *Journal of Membrane Science*, 375 (1-2), pp. 28-45.

Pure palladium has a problem of hydrogen embrittlement due to the  $\alpha$ - $\beta$  phase transition of palladium hydride. Therefore, Pd alloy membranes are also used<sup>12</sup>. Different Pd membranes are discussed more in Chapter 2.2.

### 2.1.2 Polymeric membranes (dense)

Polymeric membranes were commercialised for hydrogen separation in 1980s. Separation in polymeric membranes is based on higher permeability (solubility and diffusion) of hydrogen compared to other molecules in the gas mixture. The process is illustrated in Figure 5.

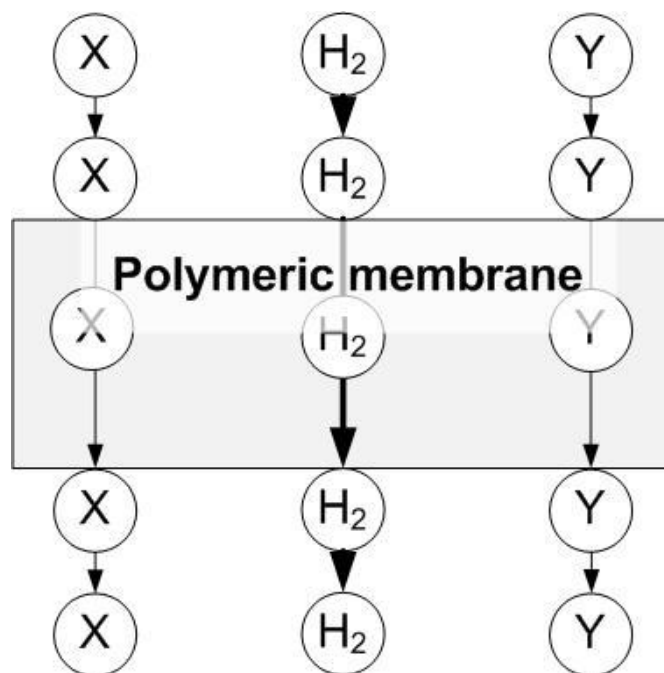


Figure 5. Hydrogen transport in polymeric membrane.

Since all the other gas components can dissolve and diffuse in polymer, there is always a trade-off between selectivity and permeability. The higher the permeability the lower the selectivity. Especially difficult for  $H_2/CO_2$  due to similar kinetic diameter (Doong, 2012).

The applicability of polymeric membranes depends on the contaminant mixture in the gas. If initial levels of critical contaminants, such as CO in ISO 14687-2:2012, are high, then it seems that upgrade of hydrogen to the quality of ISO 14687-2:2012 may be difficult to achieve with polymeric membranes.

Problems of polymeric membranes for hydrogen separation are swelling, and poor chemical stability in presence of some aggressive chemicals (HCl, SO<sub>x</sub>). The maximum operating temperature is also low. However, the tolerance for differential pressure can be up to 100 bar (Doong, 2012).

<sup>12</sup> Doong, S.J. *Membranes, Adsorbent Materials and Solvent-Based Materials for Syngas and Hydrogen Separation in Functional Materials for Sustainable Energy Applications* by S Skinner; S Irvine; J A Kilner; J Kilner; S J C Irvine; P P Edwards; S J Skinner; P Edwards Published by Elsevier Science; Woodhead Publishing, 2012



### 2.1.3 Mixed ionic-electronic membranes (dense)

Hydrogen permeable ceramic membranes are mainly of perovskite type mixed ionic-electronic conductors. The hydrogen permeation process is illustrated in Figure 6.

Hydrogen molecule dissociates into two protons and electrons on the surface. These species are transported through the membrane to its opposite side where they recombine to a hydrogen molecule. Since this process is selective for the hydrogen, also the selectivity of the membrane is very good, if ceramic material is non-porous and pin-hole free.

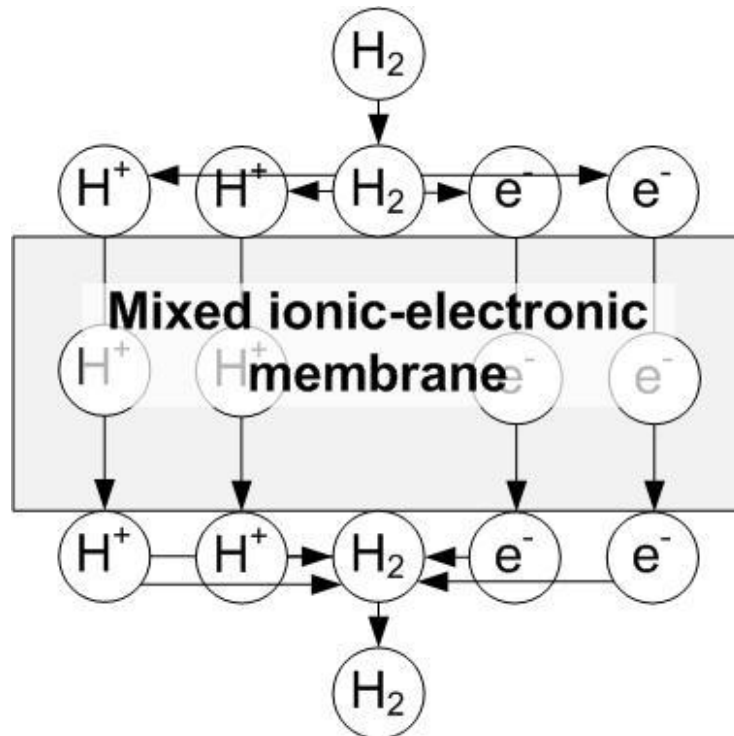


Figure 6. Hydrogen transport in mixed ionic ceramic membrane.

The issue with ionic-electronic membrane is high operating temperature (600-1000 °C). High operation temperature means that there are similar serious material problems as in solid oxide fuel cells and solid oxide electrolysis cells (SOFC and SOEC). On the other hand, the rapid material development of SOFC/SOEC components may help the development of mixed ionic ceramic membranes for H<sub>2</sub> separation.

### 2.1.4 Ceramic membranes (porous)

The use of porous ceramic membranes for hydrogen separation is based on the molecular sieving. The materials are alumina, silica, zirconia or titania in a form of metal oxide. The active layer has a pore size small enough (nm) to work as a molecular sieve. The nanoporous active layer is supported by a supporting membrane with large pore size.

The principle of gas separation by molecular sieving is presented in Figure 7.

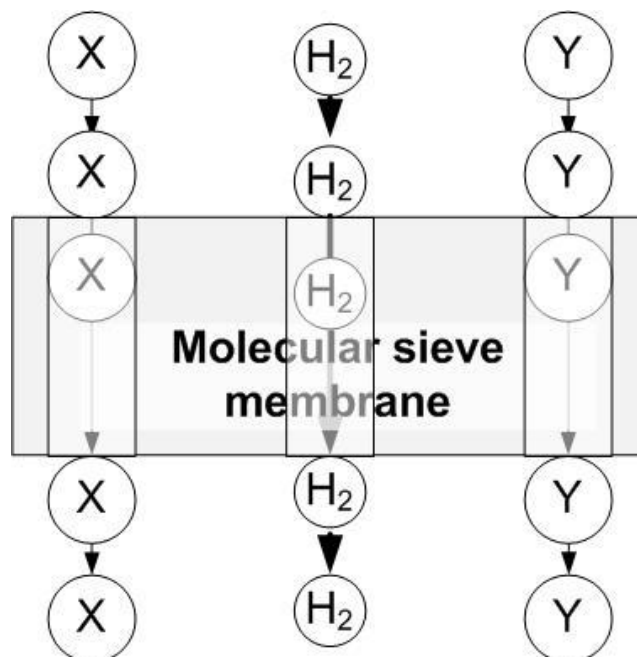


Figure 5. Hydrogen enrichment by molecular sieving.

The problem of ceramic molecular sieves is poor selectivity and difficulty to make uniform and defect-free active layers. The other problems include the tendency of active layer to densify at higher temperature and also hydrothermal stability in case of silica is used as material. Additional problems are delamination and structural instability.

### 2.1.5 Zeolite membranes

Zeolite membranes are another class of molecular sieves. Compared to porous ceramic membranes the uniform pore size is easier to achieve. Due to  $\text{CO}_2$  adsorption is an issue and high temperature operation is needed to improve  $\text{H}_2/\text{CO}_2$  separation factor.

### 2.1.6 Carbon molecular sieve membranes

Carbon molecular sieve membranes have similarly to zeolites narrow pore size distribution. These membranes are typically produced by pyrolysis of organic precursors. The main problem of carbon molecular sieve membranes is poor selectivity for hydrogen separation.

## 2.2 Pd membrane technologies for hydrogen separation

Palladium membranes may be classified into unsupported and supported membranes. Unsupported membranes are thick self-standing films. Thickness exceeding 50  $\mu\text{m}$  thick is needed to have a minimum mechanical stability.

The main drawback of unsupported Pd membranes is their low hydrogen permeability and high palladium usage. Since Pd is an expensive material the cost of the whole membrane will be considerably increased by increasing the membrane thickness<sup>13</sup>.

For these reasons, supported Pd membranes have gained much attention and are considered as viable candidates to replace thick self-standing films. Supported membranes consist of a planar or tubular support with a thin selective film deposited onto it. Support provides mechanical stability, while very thin (order of 1  $\mu\text{m}$  or less) palladium film is sufficient to provide the separation function.

Palladium membranes have been applied for production of ultrapure hydrogen in different niche applications. For these applications of purifiers based on thick Pd membranes is feasible as the value of the ultrapure hydrogen is high.

On the other hand, Helmi et al.<sup>14</sup> have shown that the large scale use of Pd membranes for the pre-combustion  $\text{CO}_2$  capture (CCS) is not possible with Pd membranes, which are several micrometres thick.

Pure Pd membranes are often damaged due to  $\alpha$ - $\beta$  transition at low temperature. Due to this problem, number of alloys with better properties have been also manufactures and characterised. For example, Pd-Ag alloy membranes have better durability and have higher hydrogen permeability<sup>15</sup>. Pure Pd membranes are very sensitive to sulphur poisoning leading to the decrease of membrane performance<sup>16</sup>. With copper alloying sulphur tolerance can also be significantly enhanced<sup>17</sup>.

The use Palladium is a major cost concern in the membrane. Lanning et al. (2009)<sup>18</sup> have estimated that a thickness of 5  $\mu\text{m}$  or less is needed for Pd membrane so that the technology would be competitive with other methods for hydrogen separation in energy applications.

Lanning et al. (2009) give the following equation for the raw material cost ( $\$/\text{ft}^2$ ).

$$R = 1.2 \times 10^{-2} P W (W+3) T$$

P = price of palladium ( $\$/\text{oz}$ )

W = weight-% of palladium in Pd alloy membrane

T = Pd film thickness in microns

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<sup>13</sup> F. Gallucci, E. Fernandez, P. Corengia, M. van Sint Annaland, Recent advances on membranes and membrane reactors for hydrogen production, *Chemical Engineering Science*. 92 (2013) 40–66.

<sup>14</sup> Helmi, A., Gallucci, F., Van Sint Annaland, M. Resource scarcity in palladium membrane applications for carbon capture in integrated gasification combined cycle units (2014) *International Journal of Hydrogen Energy*, 39 (20), pp. 10498-10506.

<sup>15</sup> S.N. Paglieri, J.D. Way, Innovations in Palladium Membrane Research, *Separation & Purification Reviews*. 31 (2002) 1–169.

<sup>16</sup> M.V. Mundscha, X. Xie, C.R. Evenson, A.F. Sammells, Dense inorganic membranes for production of hydrogen from methane and coal with carbon dioxide sequestration, *Catalysis Today*. 118 (2006) 12–23.

<sup>17</sup> Lanning, B.R., Ishteiwy, O., Way, J.D., Edlund, D., Coulter, K. Un-supported palladium alloy membranes for the production of hydrogen (2009) *Inorganic Membranes for Energy and Environmental Applications*, pp. 203-219

<sup>18</sup> Lanning, B.R., Ishteiwy, O., Way, J.D., Edlund, D., Coulter, K. Un-supported palladium alloy membranes for the production of hydrogen (2009) *Inorganic Membranes for Energy and Environmental Applications*, pp. 203-219

On the other hand, hydrogen permeation in palladium is described with an equation (Yun and Oyama, 2011)<sup>19</sup>

$$J = P(p_h^n - p_l^n)/L$$

In which,

J = Hydrogen flux

P = permeability

L = thickness of the membrane

Palladium cost is proportional to Pd film thickness, as seen in the first equation. Therefore, if these equations are combined, then it could be seen that cost per palladium per hydrogen flux is proportional to square of the Pd film thickness. With other words, Pd cost would be reduced by factor of 100 if film thickness can be reduced from 10  $\mu\text{m}$  to 1  $\mu\text{m}$  and the latter equation applies.

However, in the latter equation n is a function of membrane thickness, as illustrated by Yun and Oyama (2011). When Film thickness is reduced from 10  $\mu\text{m}$  to 1  $\mu\text{m}$ , n is changing from 0.5 to 1.0, as diffusion of atomic hydrogen through Pd is not anymore the rate determining step.

### 2.2.1 Pd membrane manufacturing methods for self-standing films

Un-supported (self-standing) films have been reviewed by Lanning et al. (2009)<sup>20</sup>. Traditional thin film palladium metal membranes have been fabricated by cold-rolling. However, the practical thickness limit has been 25  $\mu\text{m}$  and the maximum membrane width 100 mm due to difficulties controlling the thickness and deformation issues.

Vacuum deposition technologies have been applied for manufacturing unsupported Pd and Pd alloy membranes. According to Lanning et al. (2009) vacuum deposition by magnetron sputtering is much better than the electron beam evaporation, especially when Pd alloy membranes are manufactured.

Yun and Oyama (2011) claim that equipment cost for magnetron sputtering is a significant cost issue, while according to Lanning et al. (2009) the main cost is still in Pd raw material cost, when 4  $\mu\text{m}$  films are fabricated.

Lanning et al. (2009) succeeded manufacture defect free under 5  $\mu\text{m}$  thick PdCu films using silicon substrate. The same method has been developed and applied successfully at SINTEF, Norway and thinnest films studied by Mejdell et al. (2009)<sup>21</sup> have been in the range of one  $\mu\text{m}$ . With one  $\mu\text{m}$  film thickness concentration polarization (mass transfer limitation in gas phase) was evident.

Even if these  $\mu\text{m}$  thick unsupported films show very promising results in the laboratory environment, the use of magnetron sputtered for the production of ultrathin Pd films in industrial scale may be challenging. Thinnest feasible thickness for industrial production by magnetron sputtering is to be determined, but it will most probably be several micrometres.

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<sup>19</sup> Yun, S., Ted Oyama, S. Correlations in palladium membranes for hydrogen separation: A review (2011) Journal of Membrane Science, 375 (1-2), pp. 28-45.

<sup>20</sup> Lanning, B.R., Ishteiwy, O., Way, J.D., Edlund, D., Coulter, K. Un-supported palladium alloy membranes for the production of hydrogen (2009) Inorganic Membranes for Energy and Environmental Applications, pp. 203-219

<sup>21</sup> Mejdell, A.L., Jøndahl, M., Peters, T.A., Bredesen, R., Venvik, H.J. Experimental investigation of a microchannel membrane configuration with a 1.4  $\mu\text{m}$  Pd/Ag23 wt.% membrane-Effects of flow and pressure (2009) Journal of Membrane Science, 327 (1-2), pp. 6-10.

However, industrial production of un-supported Pd alloy films by magnetron sputtered seems to be a very attractive option. It could serve as one of the benchmarks, when the feasibility of other Pd membrane methods is evaluated.

## 2.2.2 Existing ultra-thin supported membranes for high flux and low Pd usage

### ***Support materials***

When supported membranes are fabricated, three main support types have been used; Vycor glass, ceramic and metallic (Yun and Oyama 2011)<sup>22</sup>.

Vycor glass was one of the first supports for Pd membrane. The main issue in the industrial use is poor mechanical properties.

Porous ceramic supports have been widely used as supports for Pd membranes. The most common support material is alumina, which is available both in flat and tubular form. Advanced alumina supports with asymmetrical structure have been used to achieve optimal structure (Yun and Oyama, 2011). In asymmetric support there is a gradient in pore size, which provide smooth outer surface, while keeping the flow resistance in the bulk material.

Alumina support has an issue of thermal expansion as the thermal expansion coefficient is about half of that of Pd. In the review of Yun and Oyama (2011) different methods to solve this issue have been analysed. When Alumina supported Pd films are fabricated with electroless plating (ELP), a common problem is pinholes. (Yun 2011).

Porous metal supports are another widely applied porous support for the Pd membrane. The most common metal is porous stainless steel (PSS) due to good availability and low cost. The main benefit of PSS and other metallic support is that the thermal expansion coefficient is much closer to Pd. Thereby the problems of poor adhesion and delamination are not issues (Yun and Oyama, 2011).

The smallest pore size for commercial PSS is 0.2 mm and the required film thickness is 15 mm, when ELP is used (Yun and Oyama, 2011). The required film thickness is 3 times the largest pore in the material.

These issues of surface roughness and large pore size distribution can be mitigated by mechanically altering the surface, depositing other metals (Ni, Cu) on the surface and sintering the surface (Yun and Oyama, 2011). The reported reductions in the Pd film thicknesses are up to order of magnitude. The thinnest films have been in the order of  $\mu\text{m}$ .

Intermetallic diffusion is a problem for PSS and therefore diffusion barriers have been used (Yun and Oyama, 2011). Diffusion barriers can also be used for reduction of the pore size, thereby enabling thinner defect free Pd films.

### ***Supported Pd film fabrication methods***

The methods for the fabricating supported palladium films are.

- 1) Electroless plating (ELP)
- 2) Electroplating (EPD)
- 3) Chemical Vapour deposition (CVD)
- 4) Physical Vapour deposition magnetron sputtering (PVD-MS)

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<sup>22</sup> Yun, S., Ted Oyama, S. Correlations in palladium membranes for hydrogen separation: A review (2011) Journal of Membrane Science, 375 (1-2), pp. 28-45.

Here, the focus is in ultra-thin ( $<1 \mu\text{m}$ ) film fabrication using porous supports. In practice, the pores of the Pd support are filled and this provided the gas tightness. The nano-size effect of the Pd in pores could make the membrane strong against  $\alpha$ - $\beta$  PdH transition and it can be used at low temperatures where conventional Pd membranes are destroyed. The amount of Pd in pore filled membranes is a fraction of the equivalent conventional thin membrane.

In addition, interesting alternative for Pd membrane fabrication, Atomic Layer Deposition (ALD), is discussed.

### **Electroless plating (ELP)**

Electroless plating is the most used method for the preparation of thin Pd based membranes. It can be applied to non-conductive materials of any shape.

ELP is an autocatalytic reaction where Pd is the catalyst. The plating reaction will take place where Pd(0) is present, therefore, the first step in the ELP is the deposition of Pd(0) seeds on the substrate. Pacheco Tanaka et. al have developed this method<sup>23,24,25</sup>. Pacheco Tanaka et. al have prepared thin (3-4  $\mu\text{m}$ ) highly selective ( $\text{H}_2/\text{N}_2 > 10000$ ) membranes exceeding all the DOE targets for the years 2015-2020.

### **Electroplating deposition (EPD)**

In electrochemical deposition the palladium film is formed by reducing palladium ions to the porous support surface, which is a cathode in the electrochemical process. The benefit of this method is that the film thickness can be controlled accurately by controlling the amount of current and time. As discussed by Yun and Oyama (2011) the main drawback is that the process requires conductive support, such as stainless steel.

### **Chemical Vapour deposition (CVD)**

In chemical vapour deposition volatile precursors are deposited on the surface of the support, where they react forming the film. The film thickness can be controlled by controlling the amount of precursors (Yun and Oyama, 2011).

The films formed by CVD have high selectivity and controlled thickness. The main challenge for the industrial production of Pd films is to find suitable volatile precursors, which have reasonable processing times and high yield. In addition, the precursors should not have decomposition products, which may contaminate the produced Pd film.

### **Physical Vapour deposition magnetron sputtering (PVD-MS)**

Physical Vapour deposition magnetron sputtering is a very attractive deposition technology also for supported membranes. It could provide ultrathin uniform layers (down to only few hundred nanometres), which is much lower than the thickness achieved with the ELP technique.

Other important advantage of PVD versus ELP is its environmental friendly operation, without producing waste liquids from chemical baths<sup>26</sup>. As discussed in the section of

<sup>23</sup> D.A. Pacheco Tanaka, M.A. Llosa Tanco, S. Niwa, Y. Wakui, F. Mizukami, T. Namba, et al., , Journal of Membrane Science. 247 (2005) 21–27.

<sup>24</sup> J. Okazaki, D. Tanaka, M. Tanco, Y. Wakui, F. Mizukami, T. Suzuki, , Journal of Membrane Science. 282 (2006) 370–374.

<sup>25</sup> T.M. Suzuki, D.A.P. Tanaka, Composite palladium membranes with improved durability toward hydrogen embrittlement, in: S. V. Gorley (Ed.), Handbook of Membrane Research: Properties, Performance and Applications, Nova Science Publishers, Inc, 2009: pp. 1–10.

<sup>26</sup> H. Klette, R. Bredesen, Sputtering of very thin palladium-alloy hydrogen separation membranes, Membrane Technology. 5 (2005) 7–9.

unsupported Pd membranes SINTEF (Norway) has developed a two-step technique for manufacturing very thin defect free unsupported palladium-based membranes<sup>27</sup>.

Direct one-step deposition of Pd-alloy membranes onto porous support are being developed in TECNALIA. Preliminary results showed that the support pore size has a considerable effect in the permeation properties of the Pd-based membrane. Supports with small pore size are required to obtain defect-free membranes<sup>28</sup>.

### 2.2.3 Potential of Atomic layer deposition (ALD) for fabrication of supported Pd membranes

Atomic layer deposition (ALD) is a common deposition technique in which the reactants are individually fed in the reaction surface so that the reactions are taken place sequentially. A recent paper of Johnson, Hultqvist and Bent (2014) reviews the fundamentals to applications of ALD<sup>29</sup>.

Atomic layer deposition (ALD)<sup>30,31</sup> is an interesting option for Pd membrane fabrication. It is a chemical thin film deposition method in the gas phase for the controlled deposition of high quality thin films. ALD may offer superior conformality in coating the nanoporous structures while tailoring processing parameters and shortening diffusion times also pore sealing can be obtained.

In ALD, the film growth is self-limiting and occurs in a layer-by-layer manner, which gives accurate control of both film thickness and composition. It also enables the deposition of conformal thin films over large areas and on complex-shaped and porous substrates. Due to these unique features ALD enables the deposition of ultra-thin, continuous Pd films<sup>32,33</sup> into the porous structure of gas membranes.

The use of ALD can lead to material savings of the material (Pd) and most likely to increased performance of membranes in gas purification. The self-limited nature of ALD growth produces high quality, dense and nearly pinhole-free films with thickness control at the nm scale, excellent thickness uniformity and unprecedented conformality.

The main issue for the application of ALD is that only ultra-thin films (in the range of 200-300 nm) are feasible. The growth of films in micrometer thickness takes too long for ALD to be an economic industrial process. In addition, adhesion of ALD films may not be sufficient, but this depends on the support. An upper limit to the thickness of ALD film is still to be defined. Possible challenges, therefore, exist in manufacturing suitable low cost membrane support with uniform enough pore diameter distribution and combining this with efficient ALD process on them.

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<sup>27</sup> T.A. Peters, M. Stange, R. Bredesen, On the high pressure performance of thin supported Pd-23%Ag membranes—Evidence of ultrahigh hydrogen flux after air treatment, *Journal of Membrane Science*. 378 (2011) 28–34.

<sup>28</sup> [http://elsevier.conference-services.net/resources/247/2576/pdf/ICIM12\\_0010.pdf](http://elsevier.conference-services.net/resources/247/2576/pdf/ICIM12_0010.pdf)

<sup>29</sup> Richard W. Johnson, Adam Hultqvist, Stacey F. Bent, A brief review of atomic layer deposition: from fundamentals to applications, *Materials Today*, Volume 17, Issue 5, June 2014, Pages 236-246

<sup>30</sup> R.L. Puurunen, *J. Appl. Phys.* 97, 121301 (2005).

<sup>31</sup> V. Miiikkulainen, M. Leskelä, M. Ritala, R.L. Puurunen, *J. Appl. Phys.* 113, 021301 (2013).

<sup>32</sup> J. Hämäläinen, E. Puukilainen, T. Sajavaara, M. Ritala and M. Leskelä, *Thin Solid Films* 531 (2013) 243-250.

<sup>33</sup> E. Sairanen, R. Karinen, M. Borghei, E.I. Kauppinen, J. Lehtonen, *ChemCatChem* 4, 2055-2061 (2013).

When ALD is used both ceramic membrane and PSS could be possible as support candidates. However, PSS pore size is far too large and some of methods reviewed by Yun and Oyama (2011)<sup>34</sup> should be used to smoothen the surface and reduce the pore size.

An important issue to be addressed is how the mechanical flexing of the membrane will affect the Pd film cracking. It is also expected that high number of small pores sealed by ALD. The thickness of Pd membrane is determined by diffusion time of Pd precursors to filled pore and not the film thickness thus ensuring faster ALD processing and lower materials costs.

### 3. Conclusions

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Feasibility of alternative H<sub>2</sub> separation and purification techniques has been studied. The Pd membranes are the most feasible material for the hydrogen separation and purification. Hydrogen purification units based on Pd membrane are also commercially available.

Based on the finding of this review, palladium membrane purifier would be an interesting alternative to demonstrate in PEMBeyond project. However, hydrogen produced by Pd membrane is unnecessary pure for the stationary PEMFC.

If there is added value for the ISO 14687-2:2012 or ultrapure hydrogen, then part of the hydrogen purified by PSA could be upgraded to higher quality providing extra revenues.

As a final conclusion, a palladium membrane purifier could be evaluated in the very end of the PEMBeyond project, if such a purifier would be available from another project. Otherwise the effort and cost for constructing or purchasing such a purifier is not justified.

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<sup>34</sup> Yun, S., Ted Oyama, S. Correlations in palladium membranes for hydrogen separation: A review (2011) Journal of Membrane Science, 375 (1-2), pp. 28-45