Advancement in Palladium Membrane Hydrogen Purification

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Introduction

Hydrogen has the potential to become a significant vector of clean energy. All of the major car manufacturers are already involved in the development of cars powered by proton exchange membrane (PEM) fuel cells, with thousands of cars being introduced to the market starting in 2015. This technology will be a great step ahead in the introduction of clean cars because the exhaust consists of only water vapor. A necessary requirement for the mass adoption of this new vehicle technology is the development of a suitable infrastructure capable of filling car tanks at high pressure, 700 bar, with high purity hydrogen. The specification limits listed in the ISO Standards, ISO14687-2, for some impurities are very low: less than 200 ppb for impurities such as carbon monoxide (CO) and sulphur compounds. These strict limits are required because of their ability to deplete the efficiency of the fuel cells. Purification is often required because traditional hydrogen manufacturing techniques contain CO and Sulphur levels above the ISO Standards.

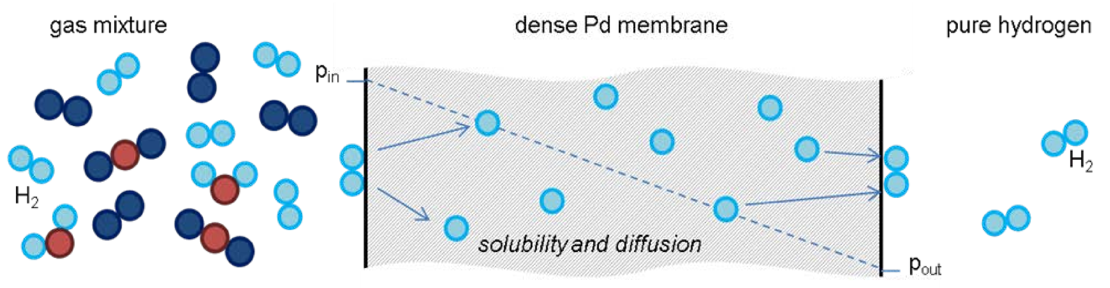
The use of purification provides many advantages such as: consistent gas quality over time, elimination of any impurity coming from the supply chain, elimination of variation in gas cylinder quality, mitigation of impurities introduced during the replacement of gas cylinders, and other random sources of contamination.

Due to the chemical and physical properties of hydrogen, several purification technologies have been developed over the years, some of them specific only to hydrogen, like palladium (Pd) membrane purifiers.

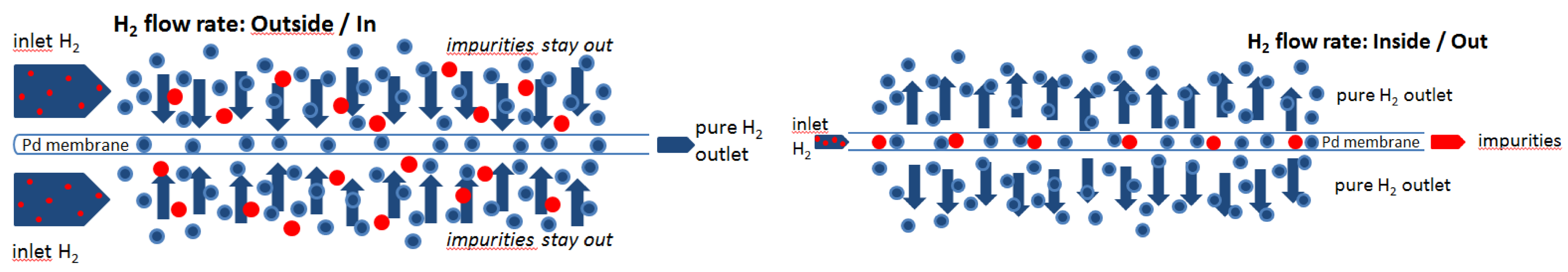
The development of thin film Pd supported membranes compared to self-standing Pd membranes have two main advantages: a drastic reduction in the amount of expensive precious metals and a large increase in H_2 flux. Leak tightness and the elimination of pinholes are the challenges for these type of purifiers.

Pd membrane Purification Technology

Palladium-based membranes are mainly used for ultra-high H_2 purification due to their high H_2 permeances and selectivities compared to other materials. The mechanism behind this technology is depicted in the figure below and it is called solution-diffusion.



Molecular hydrogen dissociates into atomic hydrogen through chemisorption on the Pd surface, followed by its dissolution in the Pd lattice. Diffusion to the other side of the membrane and recombination into molecular species results into permeation, driven by the difference in (the square root of) H_2 partial pressure on both sides of the membrane, as described by Sievert's law.



Pd membrane H_2 Purifiers: Main Characteristics

- Removes all impurities: O_2, H_2O, CO, CO_2, N_2, NH_3, organics and inert gases (Ar, He, etc.) down to < 1 ppb
- Only allows hydrogen molecules to pass through to the outlet; infinite efficiency
- Inlet gas purity: 3N or even lower grade
- Available for flow rates up to 100 m^3/h
- About 2-5% of the incoming H_2 is used to purge out the impurities
- Unlimited lifetime, no regeneration or replacement due to consumable components
- Small footprint and inexpensive installation
- High pressure drop
- Work at relatively high temperature

Self-Standing Pd based membranes

Self-standing Pd membrane must be sufficiently thick in order to accept the high H_2 pressure, especially in the configuration where H_2 is passing from the inside of the membrane tube to the outside. In the reverse configuration, where the H_2 flows from the outside of the membrane, since the membrane must be supported by a stainless steel spring, its thickness is less critical. To handle high flow rates, in the range of many tens of m^3/h, many membranes of cylindrical shape are fixed on a suitable manifold to maximize the Pd surface.

The main advantage of this type of membranes is their leak integrity which allows a very efficient H_2 purification.

Supported Pd based membranes

It is similar to the self-standing Pd purifiers but it uses thinner layers of Pd.

The lower thickness has two main advantages:

- the need of a small quantity of a very expensive precious metal
- high H_2 permeance across the membrane

Results

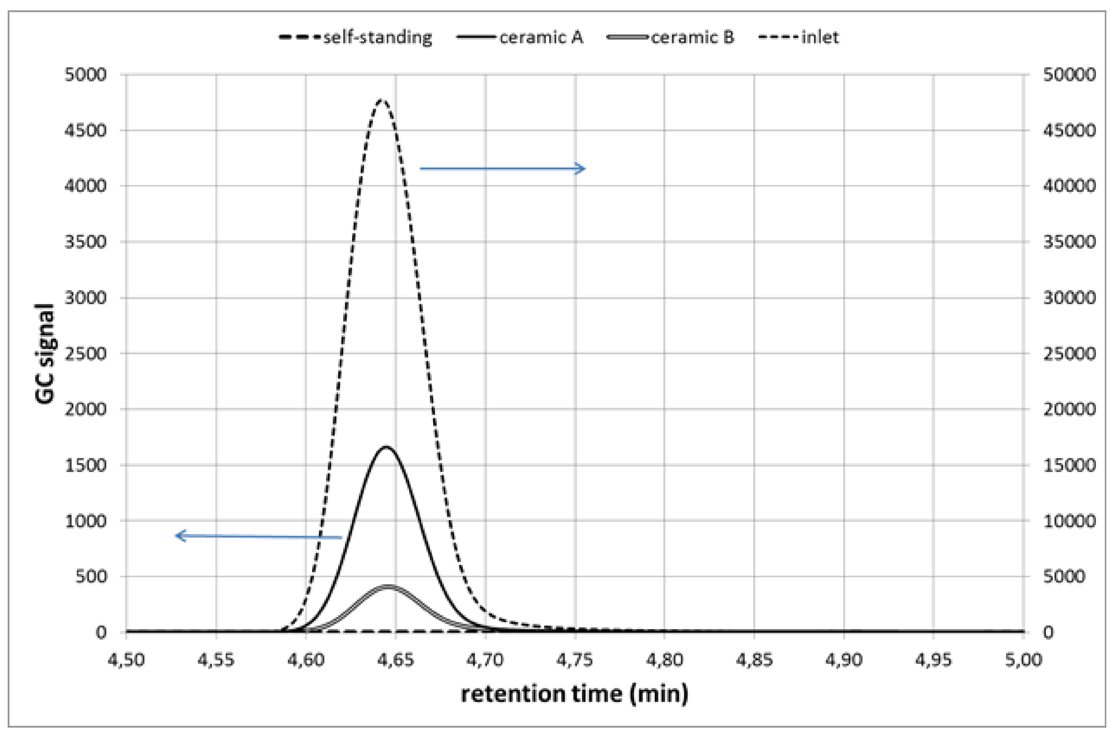
The supported membranes have a measurable leak rate probably coming from microdefects of the Pd layers, the quality of the support and the connection between the porous and the solid part. The improvements in the brazing and Pd deposition process introduced during the manufacturing of membrane B have already been able to decrease the leak rate by more than a factor of 10 compared to membrane A.

Type of membrane	He leak rate (mbar l s^{-1})
self-standing Pd membrane	<1 x 10^{-8}
porous ceramic, sample A	7.0 x 10^{-2}
porous ceramic, sample B	3.0 x 10^{-3}

The H_2 permeance of the self-standing membrane is the lowest and it is directly related to the thickness of Pd while the H_2 permeance of the supported membranes is defined by a combination of the contribution of the porous support and the Pd thickness.

Type of membrane	H_2 permeance (mol m^{-2} s^{-1} Pa^{-1})
self-standing Pd membrane	0.4 x 10^{-6}
porous ceramic, sample A	1.8 x 10^{-6}
porous ceramic, sample B	2.3 x 10^{-6}

The figure shows the N_2 peak of the chromatograms collected at the outlet of the tested membranes



The following tables show the results obtained using each membrane to purify a stream of H_2 with a known content of N_2 in the thousands of ppm range.

Due to the high pressure drop of the self-standing membrane and the limitation of the maximum H_2 line pressure, this membrane was tested only at a flow of 620 sccm.

Self-standing Pd membrane

inlet flow (sccm)	bleed flow (sccm)	inlet p (mbarg)	outlet p (mbarg)	p drop (mbar)	inlet N_2 conc. (ppmV)	outlet N_2 conc. (ppmV)	selectivity
625.3	81	4970	690	4280	27.9	< 0.03	> 1000
618.4	81	4970	690	4280	2898	< 0.03	> 100000

Porous ceramic sample A

inlet flow (sccm)	bleed flow (sccm)	inlet p (mbarg)	outlet p (mbarg)	p drop (mbar)	inlet N_2 conc. (ppmV)	outlet N_2 conc. (ppmV)	selectivity
617.4	56	1794	690	1104	1267	34	38
618.0	56	1794	690	1104	2174	80	27
1201	104	2346	690	1656	1306	39	33
1201	152	3174	1380	1794	1306	42	31

Porous ceramic sample B

inlet flow (sccm)	bleed flow (sccm)	inlet p (mbarg)	outlet p (mbarg)	p drop (mbar)	inlet N_2 conc. (ppmV)	outlet N_2 conc. (ppmV)	selectivity
617.4	56	1311	690	621	1267	8.5	149
618.0	53	1242	690	552	2174	19	112
1201	87	1725	690	1035	1306	10	130
1201	104	2553	1380	1173	1306	10	127

Conclusions

Different types of Pd membranes, self-standing and supported, have been compared to understand their applicability to improve industrial H_2 purity and to make it compatible with ISO14687-2 specifications to be used to power fuel cell cars. While self-standing Pd membranes are well satisfactory to improve H_2 quality at the desired level, their high cost and pressure requirement limit their use to occasional adoption; on the contrary supported Pd membranes have the potential to be widely used since the Pd content is very low, about 5% compared to self-standing membranes, and the pressure drop about 2- 5 times less thanks to the reduced Pd film thickness.

Sample B shows a better selectivity compared to sample A after having improved both the brazing process and the Pd deposition.

Unlike other sealing techniques for ceramic supported Pd-based membranes such as the one based on Swagelok-graphite connectors, brazing allows the mounting of several membranes in parallel to achieve a H_2 flow rate in the range of hundreds of m^3/h and a reliable industrialization.

Further improvements of the brazing process, quality of the support and Pd deposition are expected to give selectivity well above 1000.

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