Journal of Electrical Engineering 5 (2017) 262-269
doi: 10.17265/2328-2223/2017.05.005

High Purity Hydrogen: Guidelines to Select the Most Suitable Purification Technology

Marco Succi[1], Giorgio Macchi[1] and Sarah Riddle Vogt[2]

1. SAES Getters SpA, Viale Italia 77, Lainate 20020, Milan, Italy

2. Saes Pure Gas Inc., 4175 Santa Fe Rd., San Luis Obispo, CA 93401, the United States

Abstract: Hydrogen is a gas widely used in a number of industrial applications. For example, in the electronic industry it is utilized to manufacture highly advanced devices like microprocessors, LEDs (light-emitting diodes) and solar cells. Hydrogen usage will be expanding as it is the main fuel for fuel cell technology and is used to store the excess energy generated by renewable sources such as solar and wind. In these applications the degree of purity of hydrogen is crucial and advanced purification systems are typically used to guarantee the purity. This article will review the types of purification technologies that are currently available to generate high purity hydrogen, starting from an already clean source that is at least 99.9% pure. Other technologies also widely used in gas purification, like PSA (pressure swing adsorption) and polymeric membrane separation, which are more suitable to handle a lower degree of hydrogen purity will not be discussed. This article will review the advantages and disadvantages of adsorbers, getters, cryogenic and palladium purification technologies with guidelines on how to select the most appropriate technology depending on the application and the experimental conditions.

Key words: Hydrogen purification, palladium membrane, cryogenic.

1. Introduction

Hydrogen is one of the bulk gases needed for semiconductor processes; it is widely used to grow epitaxial layers to make devices on silicon and in the compound semiconductor industry [1-3].

An increase in the use of hydrogen is also taking place for the adoption of EUV (extreme ultraviolet lithography) to make smaller and smaller geometrical patterns [4]. The purity of hydrogen needed for these processes is typically down to 10 ppb or preferably 1 ppb level; thus, gas purifiers at bulk, area or at the point of use are used to achieve this very high degree of purity. The use of purification maintains the same quality of gas over time and also eliminates any impurity contribution coming from the gas distribution system, eliminates variation in gas batch quality, mitigates impurities introduced during the replacement of gas batches, and other random sources of contamination [5].

Hydrogen has the potential to become a significant source of clean energy [6, 7]. All the major car manufacturers are already involved in the development of cars powered by PEM (proton exchange membrane) 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 bars, with high purity hydrogen. The specification limits for some impurities, such as carbon monoxide (CO) and sulphur compounds, are very tight, down to 200 ppb or even less, because of their ability to deplete the lifetime of the fuel cells [8-10].

Due to the chemical and physical properties of hydrogen, several purification technologies have been developed over the years, some of them are specific only to hydrogen. This article will review the most

Corresponding author: Marco Succi, business development manager.

common technologies used to improve hydrogen quality down to at least 8 nines quality, explaining where each technology has advantages over the others.

2. Purification Technologies

The technologies widely used for hydrogen purification that will be discussed in this paper are:

- Adsorber
- Getter
- Cryogenic
- Palladium

2.1 Adsorber Purifiers

The purifiers based on this technology consist of a cylindrical column filled with high surface area materials that are suitable for the chemisorption and physisorption of impurities. An example of an adsorber purifier is shown in Fig. 1.

It is operated at room temperature and removes reactive impurities such as O_2, H_2O, CO, CO_2, NMHC, NH_3, NO_x and sulphur compounds to ppb_v or sub-ppb_v levels. It is completely transparent to, and thus not suitable for removing N_2, CH_4 and rare gases. If these gases are considered to be critical impurities in hydrogen, other purification technologies should be considered.

Fig. 2 demonstrates a typical application of these purifiers to maintain a low and constant concentration of H_2O and O_2 in H_2 from a high pressure cylinder. When H_2 is progressively used from a gas cylinder, there is a continual decrease of the pressure which affects

Fig. 1 Adsorber purifiers.

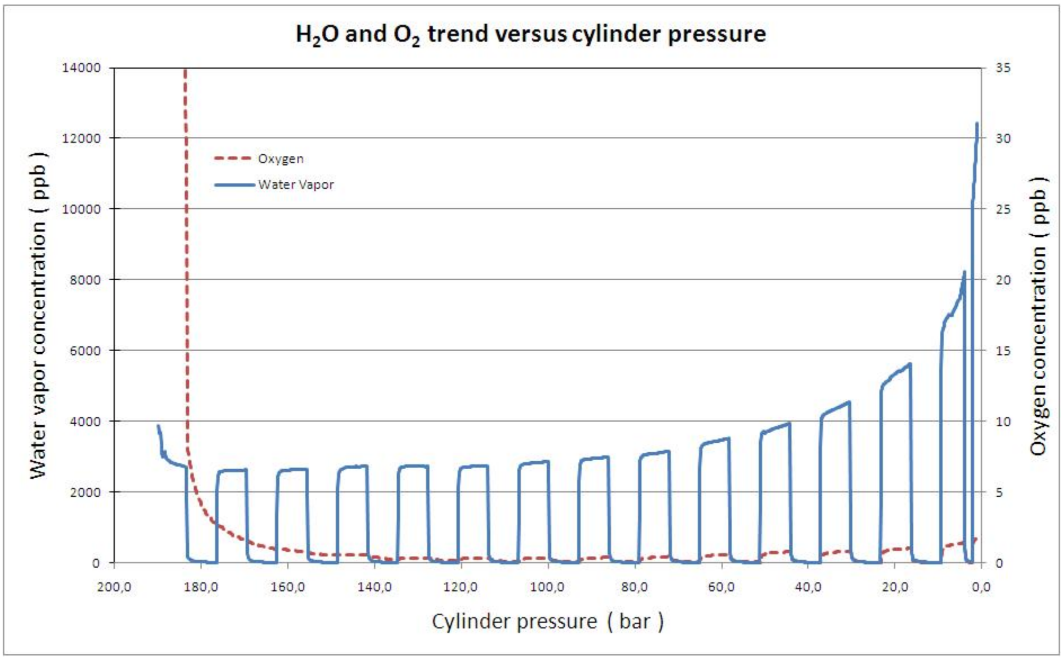

Fig. 2 Water vapor and oxygen trend vs. cylinder pressure.

the moisture content in the delivered gas. The graph shown in Fig. 2 shows the water vapor and oxygen content in H_2 vs. cylinder pressure when a constant flow of 4.6 L/min from a 4.5 N cylinder is delivered.

The H_2O and O_2 content in H_2 was analyzed by means of a Delta F DF-760E; every 30 minutes an adsorber Microtorr H_2 purifier was switched between bypass and on-line to continuously monitor the delivered gas and the purified gas. It is clear that when the cylinder is approaching 80 bar, the water vapor concentration in H_2 starts significantly increasing. Simultaneously the H_2 from the purifier remains below 1 ppb independent of the inlet concentration guaranteeing not only a high degree of purity but also consistency.

Once saturated with impurities, the purifier can be regenerated to fully recover the initial capacity and efficiency to sorb impurities. If this technology is used with relatively clean inlet gas, e.g. 5 nines or preferably 6 nines, the purifier is normally regenerated off-line at the factory. Since the quality of the inlet gas is already fairly good, the lifetime estimation of an adsorber purifier could be several years. An accurate estimation of the lifetime is possible if the average impurity level, the average flow rate, and the duty cycle are known.

The cost of ownership of these purifiers is low: in fact they do not require any power to operate or any loss of hydrogen due to venting. However, if the loading of impurities is high, the purifier could be saturated in a very short period of time. Mishandling, such as lack of purging of the gas lines during installation, could easily contaminate the purifier due to residual air saturating the active sites of the purifier drastically reducing the estimated lifetime.

The flow rate managed by these purifiers typically ranges from a few sccm up to thousands of slpm.

If the hydrogen purity is not as high, such as 4.5 nines or 5 nines, and/or the flow rate is higher than 50-100 standard m^3/h, it could be more convenient to use the same purification technology with 2 columns mounted in parallel in a so-called automatically regenerable purifier. Such a purifier assembly includes valves, heaters and a microprocessor to continuously cycle between the 2 columns, seen in Fig. 3. The purification logic is very simple and effective: while one column purifies the gas, the other is either undergoing regeneration or is in standby mode. This type of purifier is used when the hydrogen flow rates are relatively high ranging from 10 m^3/h to many hundreds of m^3/h. The higher the flow rate handled by the purifier is, the further justified is the use of a more complex unit.

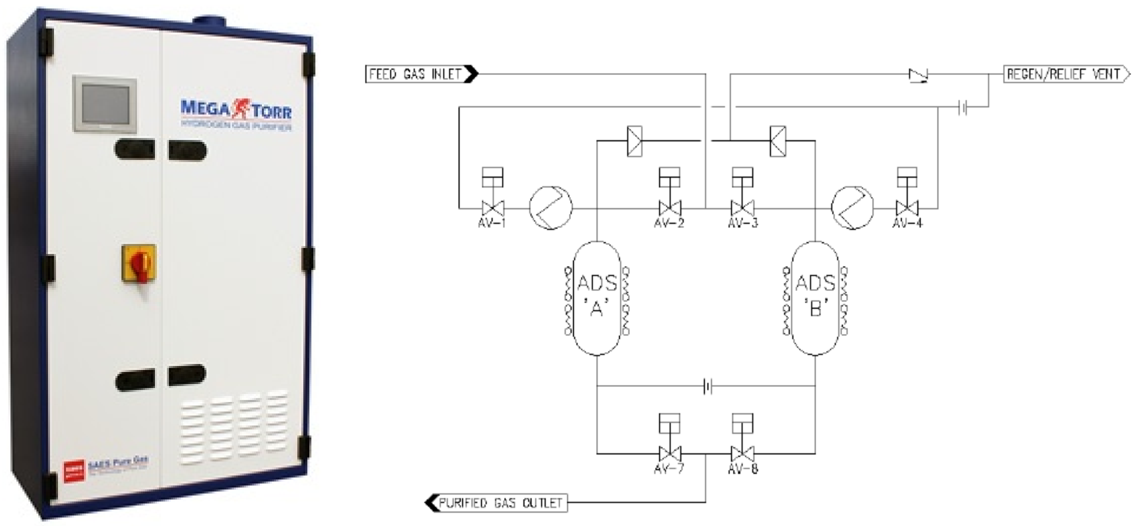

Fig. 3 A two-column purifier assembly and its layout.

The cost of ownership of this purifier is also low: it requires energy to heat up the vessel under regeneration for a period of about 8-12 hours every week or whenever it is necessary to regenerate the purifier. During this process about 5% of the purified hydrogen is used to purge the column under regeneration to remove previously sorbed impurities.

In the high flow rate purifiers, it is also convenient to use nitrogen for the regeneration gas in order to minimize the amount of hydrogen consumed in every regeneration cycle.

The final achievable purity and the impurities removed are the same for the single column and the dual column regenerable purifiers, down to less than 1 ppb, as shown in Table 1.

2.2 Getter Purifiers

Getter purifiers are another widely used technology for the purification of hydrogen based on zirconium alloys. They must be run at high temperature and can remove O_2, H_2O, CO, CO_2, NH_3, NO, NO_2, N_2, CH_4 and other hydrocarbons while they are transparent to rare gases. The zirconium alloy forms stable compounds like oxides, carbides and nitrides and, differently from the adsorber technology, cannot be regenerated. Once the getter column has been saturated with impurities it has to be replaced.

Capacity of a getter column is much higher than the capacity of an adsorber column of the same volume; as a reference, in the case of O_2 and H_2O impurities, the getter column has a capacity 10 to 50 times higher.

Table 1 Comparison of purifier technologies under general conditions.

Technology	Inlet gas purity	Impurities removed	Impurities not removed	Flow range (m^3/h)	Operating temperature	Pressure drop	Maintenance	Comment
Adsorber	5 nines	O_2, H_2O, CO, CO_2, HC > C_5, NO_x, sulphur	N_2, CH_4, rare gas	0.01-120	Room temperature	Low	Regeneration every 1-3 years	The better the inlet gas purity, the longer the lifetime Less expensive technology with limited performance
Regenerable adsorber	4.5 nines	O_2, H_2O, CO, CO_2, HC >C5, NO_x, sulphur	N_2, CH_4, rare gases	10-1,000	Room temperature	Low	None	Suitable for very high flow rate Low running cost No N_2 removal
Getter	6 nines	O_2, H_2O, CO, CO_2, N_2, CH_4, NO_x, sulphur	rare gases	0.1-300	300-600 °C	Low	Getter column replacement every 3-8 years	Good when the gas is relatively clean Removes all impurities, N_2 included
Cryogenic	4 nines	O_2, H_2O, CO, CO_2, N_2, CH_4, NO_x, sulphur	He	20-1,000	-180 °C	Low	None	Requires complex infrastructure to manage liquid N_2 High running cost Removes all impurities except He Competitive for high flow rates
Palladium membrane	3.5 nines	O_2, H_2O, CO, CO_2, N_2, CH_4, rare gases, NO_x, sulphur	none	0.1-100	400 °C	High	None	Removes all impurities, rare gases included Very compact Compatible with high inlet gas purity Sensitive to S contamination
Supported Pd membrane	3.5 nines	O_2, H_2O, CO, CO_2, N_2, CH_4, rare gases, NO_x, sulphur	none	0.1-500	400 °C	Medium -low	None	Removes all impurities, rare gases included Very compact Compatible with high inlet gas purity Sensitive to S contamination

While the use of heat exchangers helps to save energy, since the gas must be heated 100% of the time, the cost of ownership of a getter purifier is higher compared to the adsorber technology.

Depending on the impurity concentration in hydrogen, the lifetime of a typical getter based column is in the range of 3-5 years. However, it is not uncommon for a getter-based cartridge to last more than 8 years.

To minimize the consumption of the getter-based cartridge, an adsorber column could be installed upstream of the getter column. In this way all of the getter capacity will be used to trap nitrogen and methane impurities.

The flow rates for a getter-based purifier (Fig. 4) range from a few L/min up to hundreds of m^3/h.

Fig. 5 shows the typical very low concentration of impurities at the outlet of a getter purifier measured by a Thermo Scientific APIMS (atmospheric pressure ionization mass spectrometry) [11].

2.3 Cryogenic Purifiers

In the cryogenic purification of hydrogen, the stream is cooled down to cryogenic temperatures through a column filled with a high-surface media. In this manner all impurities with the exception of helium are trapped onto the cryogenic column.

The cryogenic purifier works with 2 columns in parallel so that one is in operation while the other is under regeneration, similarly to the adsorber purifier but at different operating temperatures.

This technology is quite efficient but requires a high cost infrastructure because it is necessary to continuously supply liquid nitrogen to maintain the columns' low operation temperature. If the vaporized N_2 is used in the plant for equipment purging, the running cost is reduced. It also requires power to warm up the column during the regeneration and uses a small percentage of the purified hydrogen during regeneration.

This technology can also reduce Ar in H_2 from ppbs down to ppts.

Potentially this technology can be used starting from medium flow rates, e.g. 10 m^3/h, but the high cost of the infrastructure and the consumption of liquid nitrogen make it practical only when the flow rates are at least 100 m^3/h. The running cost of the purifier is strongly influenced by the location and the availability of liquid nitrogen.

Fig. 6 shows the impurities trend at the outlet of a cryogenic purifier; the downward trend of moisture is due to the clean-up of the sample line.

Fig. 4 Getter purifier: examples of purifiers up to 10 m^3/h and 100 m^3/h.

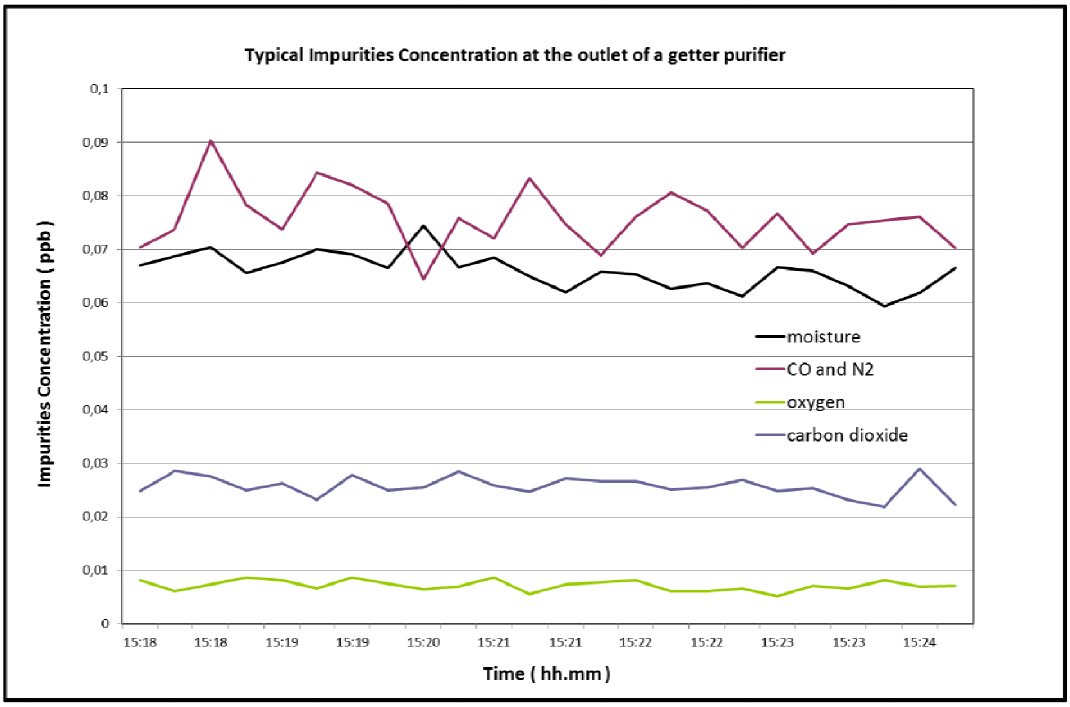

Fig. 5 Typical impurities concentration at the outlet of a getter purifier.

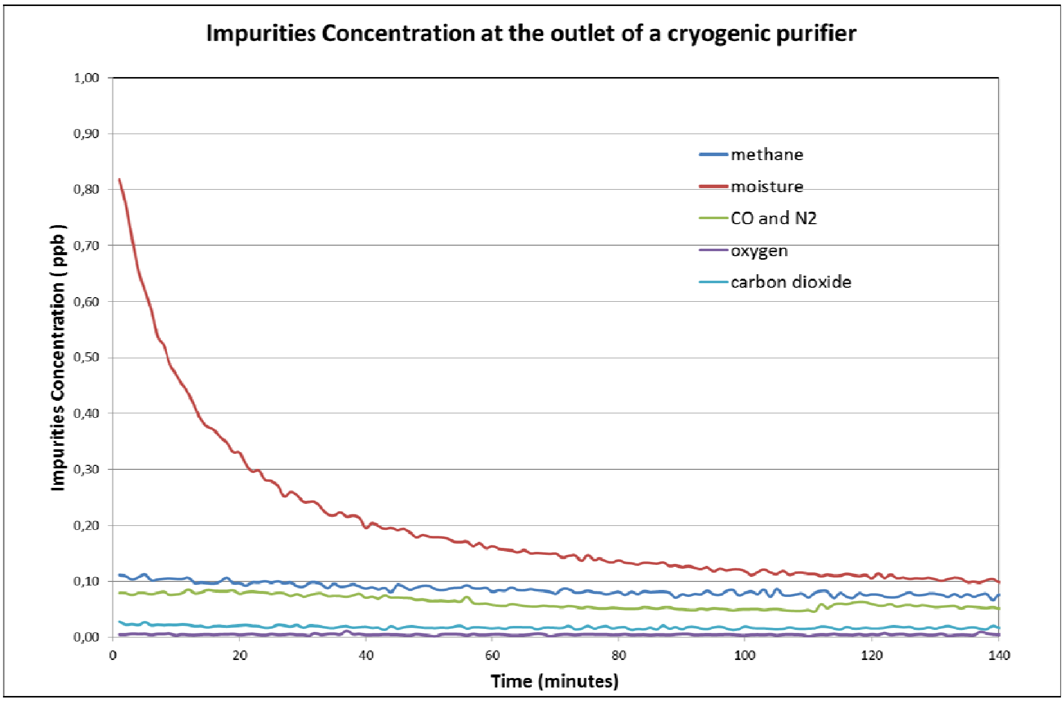

Fig. 6 Typical impurities concentration at the outlet of a cryogenic purifier.

2.4 Palladium Purifiers

This technology is specific for hydrogen purification because hydrogen is the only atom capable of diffusing across a hot palladium membrane (Fig. 7). This technology allows the removal of all impurities from hydrogen even included the rare gases such as helium and argon. Hydrogen diffusion is driven by the inlet gas pressure and by the palladium membrane operating temperature, 350-400 °C, with no need of cycling or switching valves during operation [12].

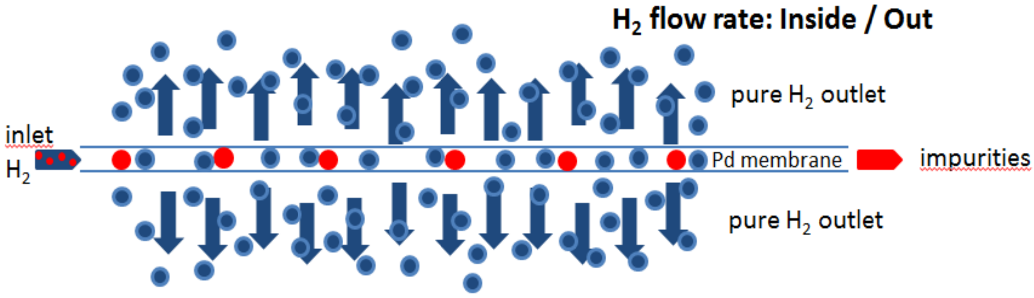

Fig. 7 Principle of operation of a Pd purifier.

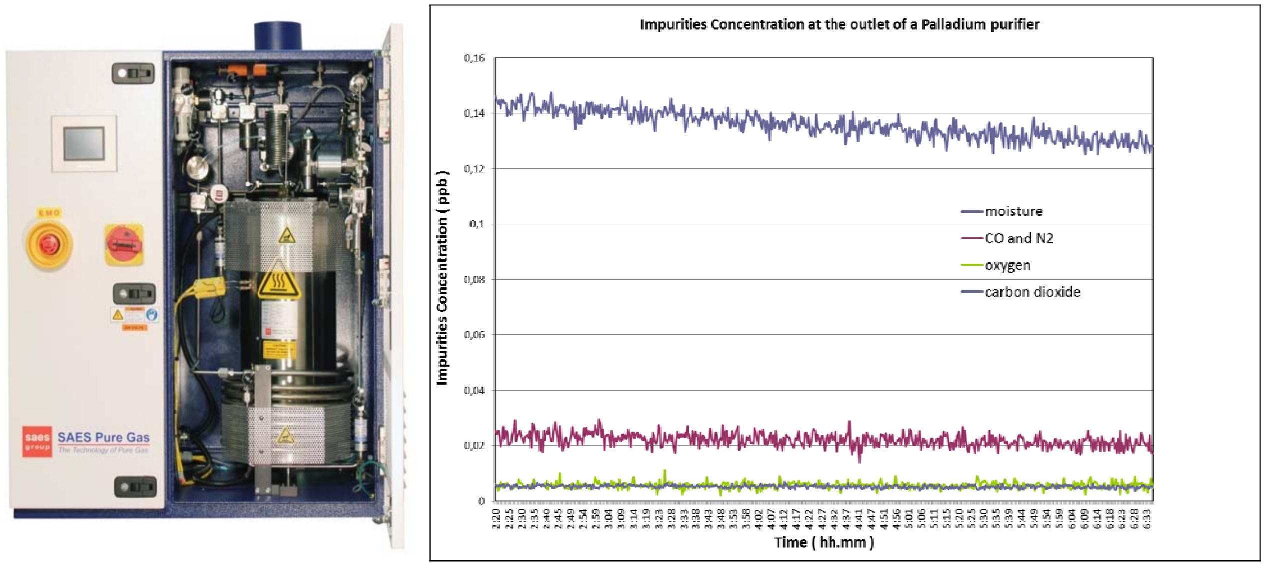

Fig. 8 Palladium purifier and the typical impurities concentration at its outlet.

The Pd purifiers have unlimited lifetime as long as the Pd membrane integrity is maintained and, in terms of footprint, these purifiers are also significantly more compact compared to the other purifier technologies.

In order to keep removing the impurities upstream of the palladium membrane and prevent their build-up, a few percent of the incoming hydrogen flow, typically 2%, is vented along with the impurities [13].

Fig. 8 shows a realization of a palladium purifier using multiple palladium tubes mounted in parallel to achieve a high surface area in a small volume and the typical impurities concentration. The running cost of this purifier is determined by the power consumption and the loss of hydrogen from the bleed flow. In general terms and compared to heated getter or cryogenic purifiers, the cost of ownership will be relatively low if the unit is well engineered with heat exchangers to recover a large part of the energy.

New generations of Pd purifier based on supported membranes are currently under development [14-16]. They have characteristics similar to the self-standing Pd purifiers but use thinner Pd layers in the 2-10 micron range. The lower Pd thickness has two main advantages:

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

3. Comparison among the Technologies

Table 1 directly compares the main characteristics of each technology. This table provides general purification conditions because the specifications of purifiers based on the same technology, but made by different manufacturers, could be different.

4. Conclusions

The purification technologies that are suitable to purify Hydrogen and reduce the impurities concentration down to the ppb and ppt range have been briefly discussed and compared. Each one has its own peculiarities and it is up to the customer to decide on the most appropriate purifier technology for the application based on the inlet hydrogen purity, the desired specifications and the target purity levels.

The reason to install a gas purifier is not only to get a very low concentration of the impurities of concern but to maintain it over time even when the incoming purity of hydrogen is not consistent.

References

[1] Henry, et al. 2012. "SiC Epitaxy Growth Using Chloride-based CVD." *Physica B Condensed Matter* 407 (10): 1467-71. http://dx.doi.org/10.1016/j.physb.2011.09.063.

[2] Leeson, N. 2011. "Developments in the Market for UHP Hydrogen Purifiers." *Semiconductor TODAY* 6 (4).

[3] Ostrander, Solcia. 2001 "The Presence of Impurities in Ultra-high Purity Gas Distribution Systems: Case History Studies." *Semiconductor Fabtech* 13th Edition, 195-8.

[4] Landoni. 2015. "EUV Tools: Hydrogen Gas Purification and Recovery Strategies." *Proceedings of the SPIE*, 7.

[5] Briot. 2011. "Managing Gas Purity in Epitaxial Growth." *Cryst. Res. Technol.* 46 (8): 809-12.

[6] The Fuel Cell Industry Review 2013. Fuel Cell Today. http://www.fuelcelltoday.com/mwg-internal/de5fs23hu73ds/progress?id=y6wD5z6kvkvO8kf7Zbo2y-B34pVtYjmXaCZ4V0jSkNA.

[7] Ahluwalia, R. 2004. "Fuel Economy of Hydrogen Fuel Cell vehicles." *Journal of Power Sources* 130 (1): 192-201.

[8] Rodrigues. 1997. "Carbon Monoxide Poisoning of Proton-Exchange Membrane Fuel Cells." *Proceedings of the Honolulu, HI.*

[9] International Standard ISO 14687-2:2012. Proton Exchange Membrane (PEM) Fuel Cell Applications for Road Vehicles.

[10] Angelo, M. 2008. "The Impacts of Repetitive Carbon Monoxide Poisoning on Performance and Durability of a Proton Exchange Membrane Fuel Cell." *ECS Transactions* 16 (2): 669-76.

[11] Brieasacher, J. 1991. "Gas Purification and Measurement at the PPT Level." *J. Electrochem. Soc.* 138 (12): 3717-23.

[12] Succi, M. 2015. "Hydrogen Gas Purifiers for Fuel Cells." *J. of Electrical Engineering* 3: 91-7.

[13] Burkhanov, G. 2011. "Palladium-Based Alloy Membranes for Separation of High Purity Hydrogen from Hydrogen-Containing Gas Mixtures." *Platinum Metals Rev.* 55 (1): 3-12.

[14] Arratibel, D., Pacheco Tanaka, A., Van Sint Annaland, M., and Gallucci, F. 2017. "Recent Advances in Pd-based Membranes for Membrane Reactors." *Molecules* 22: 51.

[15] Gallucci, F., Fernandez, E., Corengia, P., and van Sint Annaland, M. 2013. "Recent Advances on Membranes and Membrane Reactors for Hydrogen Production." *Chem. Eng. Sci.* 92: 40-66. http://dx.doi.org/10.1016/j.ces.2013.01.008.

[16] Helmi, F., Gallucci, M., and van Sint, A. 2014. "Resource Scarcity in Palladium Membrane Applications for Carbon Capture in Integrated Gasification Combined Cycle Units." *Int. J. Hydrogen Energy* 39 (20): 10498-506.