HYGRID

FLEXIBLE HYBRID SEPARATION SYSTEM FOR H2 RECOVERY FROM NG GRIDS

FCH-2 GRANT AGREEMENT NUMBER: 700355

Start date of project: 01/05/2016 **Duration: 3 years**

WP3 – Membrane development

D.3.2
Report on development of the membranes for lab-scale

Topic: Development of technology to separate hydrogen from low-concentration hydrogen streams
Funding scheme: Research and Innovation Action
Call identifier: H2020-JTI-FCH-2015-1

Due date of deliverable: 30-04-17	**Actual submission date:** 26-05-17	**Reference period:** 01-05-2016 – 31-10-17
Document classification code (*): HYGRID-WP3-D32-TECNALIA-08052017.docx		**Prepared by (**):** TECNALIA

Version	DATE	Changes	CHECKED	APPROVED
v0.1	26-05-2017	First Release	TECNALIA	Ekain Fernandez

Project funded by the FCH-2 JU within the H2020 Programme (2014-2020)		
Dissemination Level		
PU	Public	X
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Content

1. EXECUTIVE SUMMARY

1.1. Description of the deliverable content and purpose

This deliverable reports the development of different types of membranes for hydrogen separation from H_2-CH_4 mixtures carried out during the first 12 months of the project. In this period, thin and ultra-thin Pd-based supported membranes and thin carbon-based supported membranes have been developed. In addition, different porous tubes have been assessed as membrane supports.
The prepared supported membranes have been delivered to SAES and TUE for WP6 (Lab-scale testing) and some preliminary characterization results are presented in this deliverable.

1.2. Brief description of the state of the art and the innovation brought

Palladium-based membranes have received a growing interest for the separation and purification of hydrogen from various resources. Palladium membranes have comparatively very high hydrogen flux and exclusive perm-selectivity for hydrogen due to the unique permeation mechanism. Since the permeation flux is inversely proportional to the membrane thickness, development of composite membranes with a thickness of less than 5 µm have been intensively studied in order to attain high hydrogen flux and to minimize the material cost. Within DEMCAMER and ReforCELL projects, 3-4 microns thick Pd-Ag membranes supported on porous alumina tubes were prepared by TECNALIA; the membranes show good stability up to 500 ºC[1], as well as high hydrogen permeance and high H_2/N_2 permselectivity (>10,000). Within ReforCELL project, TECNALIA prepared 5 microns thick Pd-Ag membranes supported on ceramic coated metallic supports (15 cm long membranes) showing extremely high ideal H_2/N_2 selectivity (>150,000) and moderate H_2 permeance (9.0×10^{-7} mol m^{-2} s^{-1} Pa^{-1}) at 400 ºC and 3 bar of pressure difference for 1,200 h [2]. In FLUIDCELL project, TECNALIA developed ultra-thin Pd-Ag membranes having a hydrogen permeance of 9.0-9.4 x 10^{-6} mol m^{-2} s^{-1} Pa^{-1} (one of the highest supported Pd membrane reported) and H_2/N_2 selectivity of 1,900 for a 1.3 µm thick membrane at 400°C and after 1000 hours of operation[3].

On the other hand, carbon molecular sieves membranes (CMSMs) have been considered as the next generation of gas separation membrane technology to work between 100 and 250 °C were polymeric membranes are not stable and Pd membranes have low permeation and stability and higher cost. CMSM are produced by the carbonization of a polymeric precursor under an inert atmosphere or vacuum. TECNALIA prepared 3 microns thick composite alumina-carbon membranes showing a H_2/N_2 ideal perm-selectivity of 725 and H_2 permeance of 1.45 x 10^{-7} mol m^{-2} s^{-1} Pa^{-1} at room temperature, values comparable with the best performing Pd membranes[4].

Three types of membranes with superior performance compared to state of the art polymeric membranes have been developed by TECNALIA in previous projects and are being optimised in HyGrid:

a) Thin Pd-Ag membranes of 3-5 µm over different supports (metallic or ceramic). These membranes will provide very high H_2/N_2 selectivity and high H_2 permeation.

b) Ultra-thin Pd-Ag membranes (≈ 1 µm). These membranes will provide high H_2/N_2 selectivity and very high H_2 permeation.

c) Carbon molecular sieve membranes (CMSM). Based on cheap polymers (phenolic resins) used on the selective layer, these membranes will provide moderate selectivity and permeation at low costs.

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[1] E. Fernandez et al., Int. Journal of Hydrogen Energy 40 (2015) 3506-3519.

[2] E. Fernandez et al., Chem. Eng. Journal 305 (2016) 182-190.

[3] J. Melendez et al., Journal of Membr. Sci. 528 (2017) 12-23.

[4] M. Llosa et al., Int. Journal of Hydrogen Energy 40 (2015) 5653-5663.

1.3. Deviation from objectives

There are no deviations.

1.4. If relevant: corrective actions

N/A

1.5. If relevant: Intellectual property rights

Patent application on sealing submitted by SAES.

2. Preparation and characterization of porous supports for membrane preparation

During these first months, the permeation properties of porous symmetric and asymmetric alumina, supports have been measured and compared. Four configurations of symmetric supports were studied (see Figure 1): a) o-o where both ends are open, b) c-o similar to o-o but one end was closed with a planar porous disc, c) f-o one end was open and the other one closed having a finger type configuration and d) f-d one end finger type closed and the other end was attached to a dense alumina tube.
Table 1 shows the H_2 and N_2 single gas permeation properties of the supports tested at room temperature and 400 ºC. The asymmetric supports present higher permeation properties than the symmetric tubes. For example, if 10/9 (outer and inner diameter) mm f-d of symmetric alumina is compared with the one asymmetric alumina, it has 3 times lower H_2 permeance. Both type of supports could be used for thin Pd-based membranes (3-5 µm thick), but for the ultra-thin membranes (<3 µm thick) the asymmetric supports would be the suitable option so far since the symmetric ones would apply higher gas resistance to the permeation through the supported membrane.

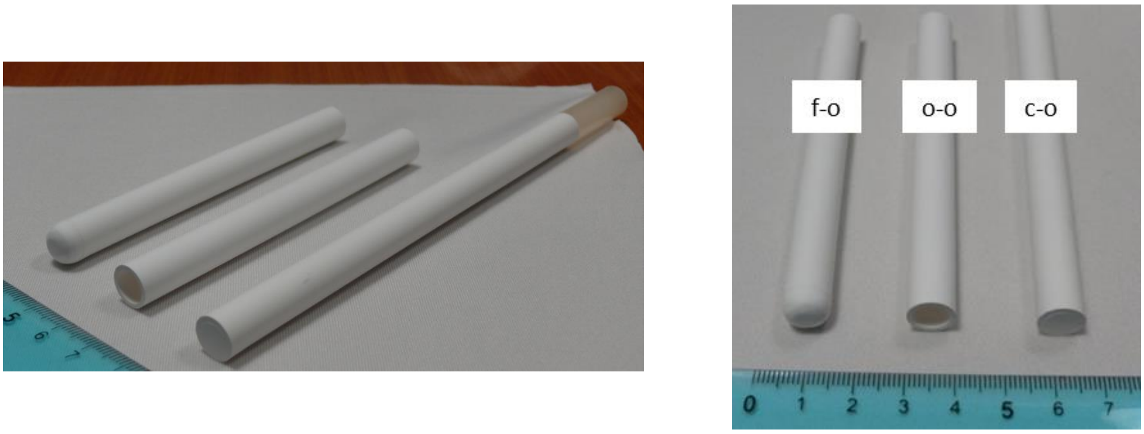

Figure 1. Different support configurations of symmetric supports.

Table 1. Gas permeation properties of supports at room temperature and 400 °C.

sample code	**Configuration**	**Gas permeance (x 10^{-6} mol m^{-2} s^{-1} Pa^{-1}) at room temperature (RT)**			**Gas permeance (x 10^{-6} mol m^{-2} s^{-1} Pa^{-1}) at 400°C**			**Ratio of gas permeance between RT and 400 °C**	
		H_2	N_2	H_2:N_2	H_2	N_2	H_2:N_2	H_2	N_2
10/7 o-o	**open-open (symmetric)**	9.3	3.1 ± 0.2	3.0	5.1	1.6	3.2	1.8	1.9
10/7 c-o	**closed-open (symmetric)**	7.2 ± 0.14	2.4	3.0	n.a.	n.a.	n.a.	n.a.	n.a.
10/8 f-o	**finger type – open (symmetric)**	12.9	4.20± 0.2	3.1	6.5	2.1	3.1	2.0	2.0
10/9 f-d	**finger type – thicker/dense (symmetric)**	23.1	7.2 ± 0.2	3.2	14.2	4.3	3.3	1.6	1.7
10/4 o-o	**open-open (asymmetric)**	77 ± 4	27.7 ± 1.4	2.8	33.8 ± 0.1	14.1 ± 1.0	2.4	2.3	2.0
10/7 o-o	**open-open (asymmetric)**	67.1	20.1 ± 0.6	3.3	40 ± 2	14.4 ± 0.1	2.8	1.7	1.4

3. Development of thin Pd-based supported membranes

TECNALIA prepared and delivered thin Pd-based membranes deposited onto different porous supports: symmetric ceramic porous supports and metallic porous supports (Figure 2). The N_2 permeation values of these membranes have been measured. The results in Table 2 show low N_2 leakage values for the membranes ($\leq 3 \times 10^{-10}$ mol m^{-2} s^{-1} Pa^{-1}), being suitable for obtaining high purity hydrogen streams. Afterwards, the membranes have been delivered to SAES for further testing.

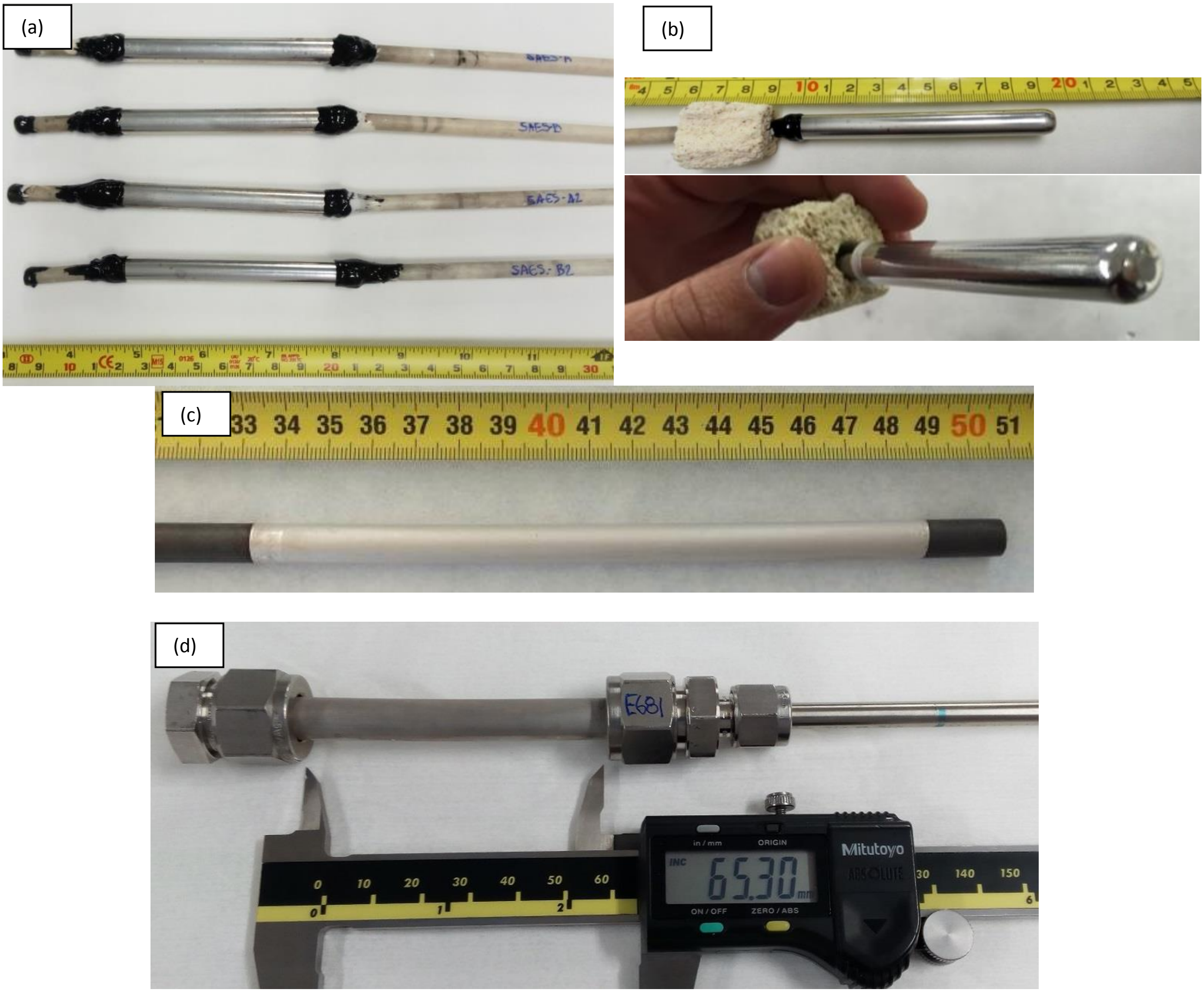

Figure 2. Thin Pd-based membranes deposited onto different supports: a) Open-end (o-o) and b) finger-like (f-o). c and d) porous metallic support (M31 and E681, respectively).

Table 2. N_2 permeation (at room temperature) of thin Pd-Ag membranes deposited on different supports and delivered to SAES and TU/e for further testing.

Membrane code	OD/ID (mm)	Length (cm)	N_2 permeance (mol m^{-2} s^{-1} Pa^{-1}) at room temperature
SAES-A1	10/7 Symmetric	*8.1*	***1.95 x 10^{-10}***
SAES-B1	10/8 Symmetric	*7.6*	***1.28 x 10^{-10}***
SAES-A2	10/7 Symmetric	*7.8*	***3.54 x 10^{-10}***
SAES-B2	10/8 Symmetric	*8.0*	***1.68 x 10^{-10}***
SAES-C	10/8 finger-like symmetric	9.4	**3.07 x 10^{-10}**
M31	Metallic support	13.7	**<8.53 x 10^{-11}**
E681	Metallic support	6.5	**1.10 x 10^{-11}**

4. Development of ultra-thin Pd-based supported membranes

Ultra-thin Pd-based membranes have been prepared at TECNALIA using different plating times and they have been delivered to TU/e for lab-scale tests. The N_2 permeance at room temperature of each membrane is presented in

Table 3. N_2 permeation (at room temperature) of the ultra-thin Pd-Ag membranes deposited on asymmetric 10/7 mm supports and delivered to TU/e for further testing.

Membrane code	Plating time (min)**	Length (cm)	N_2 permeance @ 25°C (mol m^{-2} s^{-1} Pa^{-1})
E633*	t4	4.9	6.50 x 10^{-10}
E634*	t2	3.0	3.59 x 10^{-9}
E635	t3	14.4	9.70 x 10^{-10}
E636	t5	10.0	5.92 x 10^{-9}
E689	t2	24.2	1.70 x 10^{-9}
E690	t1	22.4	4.60 x 10^{-9}

, and two of the delivered membranes can be observed in Figure 3. The E635 membrane is ~1.5 µm thick according to the SEM cross-section image presented in Figure 4.

Table 3. N_2 permeation (at room temperature) of the ultra-thin Pd-Ag membranes deposited on asymmetric 10/7 mm supports and delivered to TU/e for further testing.

Membrane code	Plating time (min)**	Length (cm)	N_2 permeance @ 25°C (mol m^{-2} s^{-1} Pa^{-1})
E633*	t4	4.9	6.50 x 10^{-10}
E634*	t2	3.0	3.59 x 10^{-9}
E635	t3	14.4	9.70 x 10^{-10}
E636	t5	10.0	5.92 x 10^{-9}
E689	t2	24.2	1.70 x 10^{-9}
E690	t1	22.4	4.60 x 10^{-9}

* Membrane sealed before delivery.

** t5>t4>t3>t2>t1

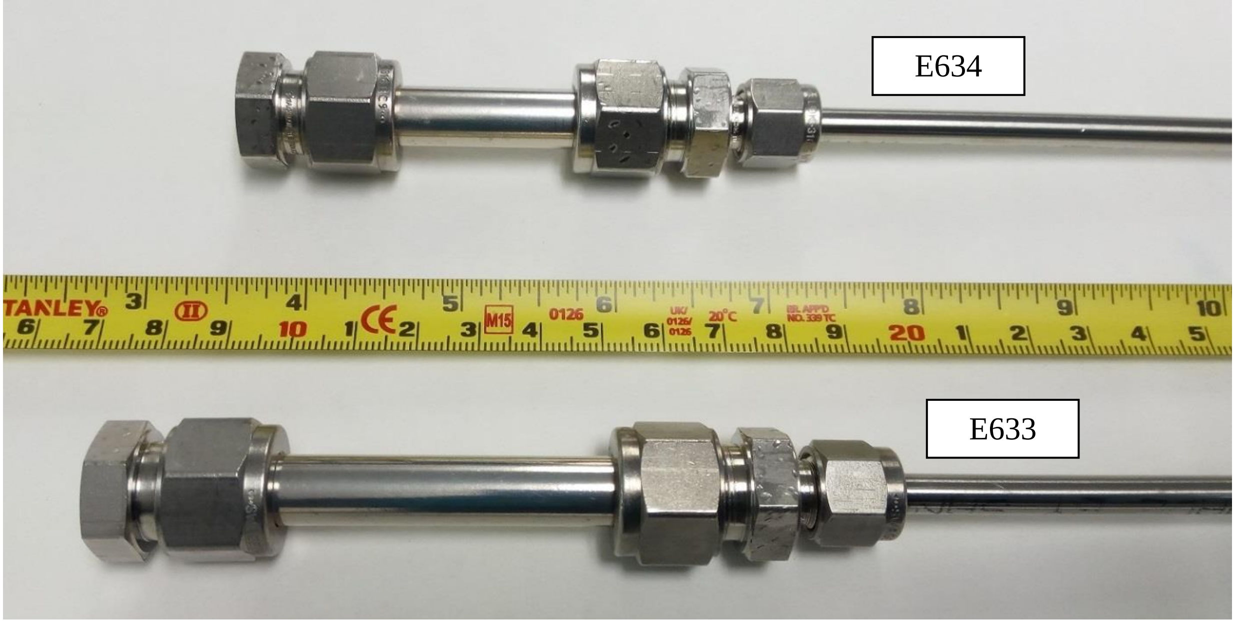

Figure 3. Ceramic supported ultra-thin Pd-based membrane after sealing.

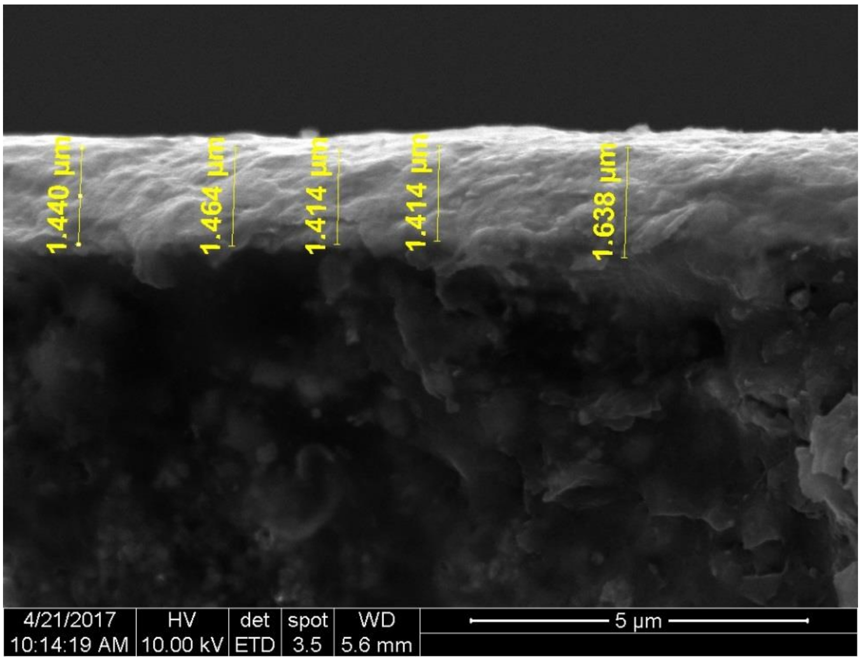

Figure 4. SEM cross-section image of a ceramic supported ultra-thin Pd-Ag membrane (code: E635).

5. Development of thin CMSM supported membranes

Composite-carbon molecular sieve membranes have been prepared onto porous alumina supports. Five membranes have been prepared by TECNALIA and delivered to TU/e for testing. The length of each membrane is around 15 cm, the supports were 10/7 mm asymmetric α-alumina with 200 nm pore size. Membranes with codes 302-N and 304-N have been carbonized at 500 ºC, and membranes with codes 305-N, 306-N and 308-N have been carbonized at 450 ºC. In Figure 5 some of the supported composite-carbon membranes can be observed.

Table 4. Characteristics of the thin composite-carbon membranes deposited on asymmetric 10/7 mm supports and delivered to TU/e for further testing.

Membrane code	Carbonization temperature (°C)	Length (cm)	N_2 permeance @ 25°C (mol m^{-2} s^{-1} Pa^{-1})
302-N	500	15.0	0.38×10^{-9}
304-N	500	15.0	0.41×10^{-9}
305-N	450	15.0	$< 0.17 \times 10^{-9}$
306-N	450	15.0	0.19×10^{-9}
308-N	450	15.0	0.17×10^{-9}

Figure 5. Thin composite-carbon membrane supported on porous alumina support.

Single gas and mixed gas permeation tests of one of the delivered carbon membranes have been conducted at TU/e. Figure 6 shows the H_2 (a) and CH_4 (b) flows as a function of temperature (up to 80 ºC) and pressure (up to 4 bar) for 302-N membrane. It is observed that when increasing the pressure the H_2 flow increases (due to a higher partial pressure), and also when increasing the temperature the H_2 flow increases. However, the improvement in the permeation is not proportional with the temperature; for CH_4, the relative increase is higher (significantly increased at 80 °C). The H_2 and CH_4 permeance values range between 1.09-1.49 x 10^{-7} mol m^{-2} s^{-1} Pa^{-1} and 2.46-41.0 x 10^{-10} mol m^{-2} s^{-1} Pa^{-1}, respectively. As shown in Figure 7a, the H_2/CH_4 ideal perm-selectivity decreases when increasing the temperature (from 443 to 36, when increasing from 30 to 80 °C).

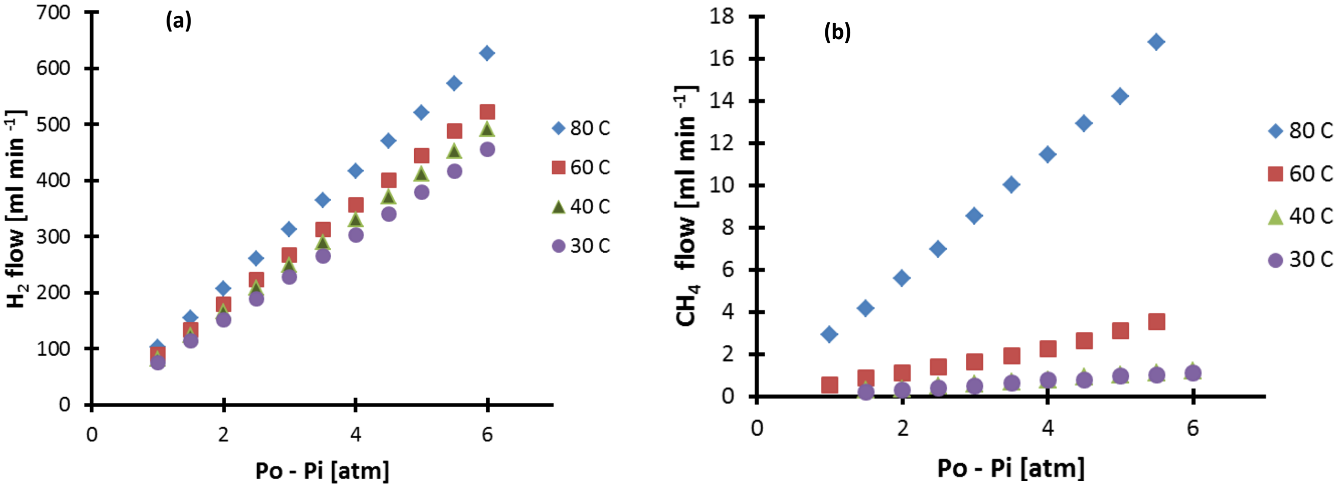

Figure 6. H_2 (a) and CH_4 (b) flows of a supported carbon membrane (code: 302-N) as a function of operating temperature and pressure.

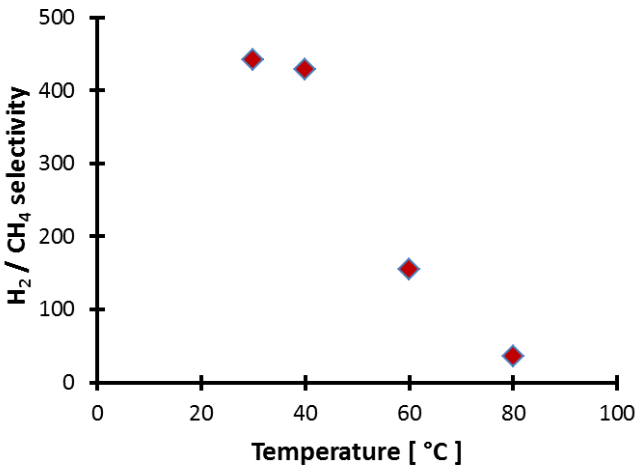

Figure 7. H_2/CH_4 ideal perm-selectivity of a supported carbon membrane (code: 302-N) as a function of temperature.

The H_2 purity of the permeate stream has been measured by Gas Chromatography as a function of the H_2 content (ranging between 5 and 20) in the H_2-CH_4 feed mixture and at 40 and 80 °C at 7.5 bara total pressure and applying vacuum in the permeate. The results are presented in Figure 8a and Table 5. H_2 purities ranging from 93.3 to 96.7 have been obtained at 40 °C at a H_2 content between 5 and 20%; and H_2 purities ranging from 65.2 and 84.8 % at 80 ºC at the same H_2 content range. At 40 °C, The H_2 purities calculated using the single gas tests results match rather well with the experimentally measured H_2 purities. Then, an additional test has been performed with the same carbon membrane at 10% H_2 content of H_2-CH_4 feed mixture and varying the temperature between 30 and 80 °C (see Figure 8b and Table 6). At 30 °C a H_2 purity of 99.4% has been obtained.

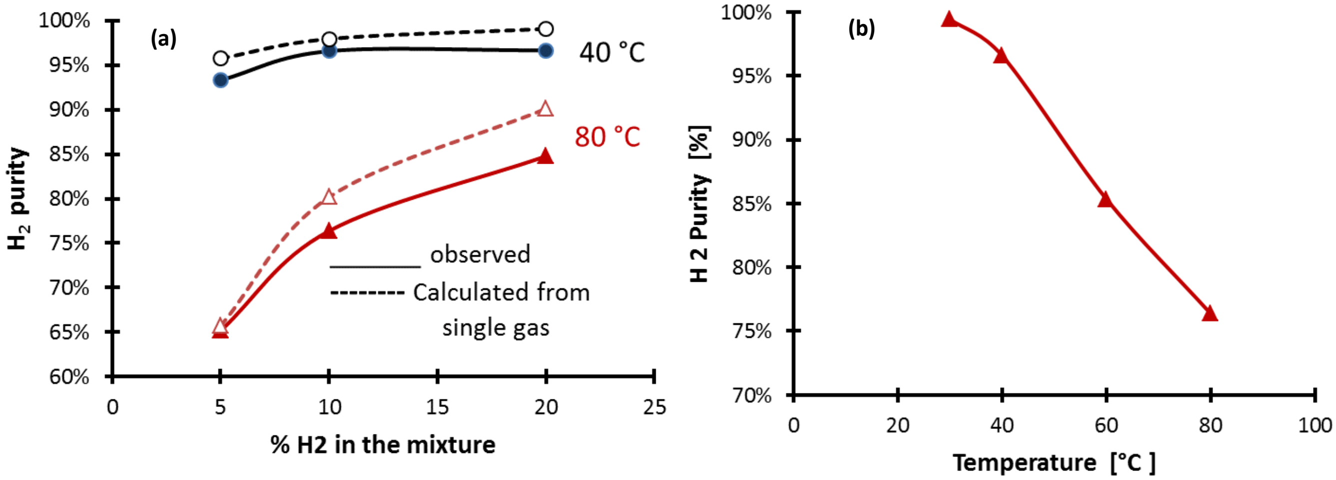

Figure 8. H_2 purity in the permeate of a supported carbon membrane (code: 302-N): (a) as a function of H_2 content in feed stream and at 40 and 80 °C, (b) as a function of temperature and at 10% H_2 content in the feed mixture.

Table 5. H_2 purity of permeate (measured and calculated) of a supported carbon membrane (code: 302-N)as a function of the H_2 content in the feed mixture and at 40 and 80 °C.

Testing temperature (°C)	H_2 in feed mixture (%)	H_2 purity in the permeate (%)	
		Measured	Calculated
40	5	93.3	95.7
	10	96.6	98.0
	20	96.7	99.0
80	5	65.2	65.7
	10	76.4	80.2
	20	84.8	90.1

Table 6. H_2 purity of permeate of a supported carbon membrane (code: 302-N) as a function of the temperature and at 10% H_2 content in the feed mixture.

Testing temperature (°C)	H_2 purity in the permeate (%)
80	76.4
60	85.4
40	96.6
30	99.4

6. Conclusions and future work

Three types of membranes have been prepared and preliminary characterized by TECNALIA for hydrogen separation from H_2-CH_4 mixtures: thin and ultra-thin Pd-based supported membranes and thin carbon-based supported membranes. The prepared supported membranes have been delivered to SAES and TUE for WP6 (Lab-scale testing). In addition, different porous tubes have been assessed as membrane supports. Both symmetric and asymmetric ceramic supports could be used for thin Pd-based membranes (3-5 µm thick), but for the ultra-thin membranes (<3 µm thick) the asymmetric supports would be the suitable option so far since the symmetric ones would apply higher gas resistance to the permeation through the supported membrane. Thin Pd-Ag supported membranes present low N_2 leakage ($\leq 3 \times 10^{-10}$ mol m^{-2} s^{-1} Pa^{-1}), being suitable for obtaining high purity hydrogen streams. On the other hand, one of the thin composite-carbon supported membrane delivered to TU/e has been characterized by single gas and mixed gas permeation tests. Regarding single gas tests, H_2 and CH_4 permeance values range between 1.09-1.49 x 10^{-7} mol m^{-2} s^{-1} Pa^{-1} H_2 and 2.46-41.0 x 10^{-10} mol m^{-2} s^{-1} Pa^{-1} CH_4 have been obtained at 30-80 °C. In the case of mixed gas tests feeding a H_2-CH_4 feed mixture containing a H_2 content ranging between 5 and 20, H_2 purities in the permeate of 93.3-96.7 % and 65.2-84.8 % have been obtained at 40 and 80 °C, respectively. At 30 °C and 10% of H_2 content, a H_2 purity of 99.4% has been obtained.

Depending on the results obtained at WP6 (lab-scale testing), additional supported membranes will be prepared (optimized if needed) and delivered to the WP6 partners in order to meet the targets of the project.