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NATURALHY

"Preparing for the hydrogen economy by using the existing natural gas system as a catalyst"

Integrated Project

6.1.ii Call 1 Sustainable Energy Systems

Deliverable

D0032-WP5-P-O

Overview Summary for reports:

R0027-WP5-C-0
R0028-WP5-C-0
R0029-WP5-C-0
R0030-WP5-C-0

Work Package No.5

Deliverable No.D-15
Interim report on membrane development for hydrogen separation

Prepared by

UOXF.DF, NTUN, CETH.

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Overview

Deliverable D15 is comprised of different aspects of membrane development within WP5 of the NATURALHY project:

1. *Specifications and targets for membrane development (Task 5.3)*
2. *Development of thin Pd-based membranes (Task 5.4)*
3. *Performance envelope of composite metallic substrate membranes (Task 5.5)*
4. *Intermediate report on low temperature carbon molecular sieve membranes (Task 5.6)*

The partners involved are the University of Oxford, the Norwegian University of Science and Technology (NTNU) and Compagnie Europeenne des Technologies del'Hydrogene (CETH). Together the partners have been working on different aspects of membrane development, with the aim of providing validated data and options for hydrogen separation relevant to the NATURALHY scenario. The ability to separate hydrogen is an important aspect of the project, since it will provide a route to initiating local hydrogen centres, hence 'greening' end-use operations.

Various membrane materials can be considered for hydrogen separation. Since hydrogen is a relatively small molecule compared to the other NATURALHY gas components, it generally exhibits higher flux rates through the membrane and is enriched in the permeate stream, while the heavy components are retained in the high-pressure retentate stream.

Membranes can be classified into two major types, depending on the details of their operating mechanisms. These are the dense membranes and the microporous membranes. In dense membranes (e.g. metallic membranes), the fluid molecules dissolve into the body of the membrane, diffuse across the membrane film, and desorb at the low-pressure (permeate) side. Thus the molecules are separated according to their solubility and diffusion rate in the membrane material.

In the case of microporous membranes (e.g. carbon molecular sieves), the constituent molecules find a path through the interconnected pores and are separated according to their size, shape and mass. In the case of molecular sieves, molecules that are too large can theoretically be excluded entirely, allowing only the smallest ones through.

Within WP5 both types of membranes are being investigated. Palladium based membranes are attractive because of their complete selectivity towards hydrogen but current membranes are very expensive, whilst carbon molecular sieves, although not totally selective for hydrogen have advantages in terms of high flux, low cost and packaging. Nevertheless, development of high performance membranes is technically challenging, and there is worldwide interest in development of new more efficient and cheaper membranes. The challenges for development of new membranes are:

- For carbon based membranes, achieving optimum pore size distribution and presenting the membrane in a usable form are major objectives.
- For Palladium-based membranes, the aim is to develop ultra-thin membranes that allow higher hydrogen permeation rates. However the considerable technical challenge is to fabricate Pd membranes with no defects such as "pin holes", since the presence of any defects will reduce the purity of hydrogen delivered across the membrane. It is worth mentioning that many research organisations and chemicals companies are working to develop efficient hydrogen membranes, and an important issue for NATURALHY is awareness of new developments in this area.

The three partners working on membranes have clear and complementary activities: NTNU is developing more efficient membranes based o carbon molecular sieves, CETH is examining the performance envelope of composite metallic membranes, while the University of Oxford is developing ultra- thin Pd based membranes supported on porous substrates.

The interim reports that comprise D15 highlight technical achievements to date within the project.

Report No. R0027-WP5-C-0: Specifications and Targets for Membrane Development

Targets and specifications for membrane development have been devised against the aims of the Naturalhy project, by considering three different scales and scenarios for separation of hydrogen from the gas network, and by taking into account the changing requirements such as:

- Level of hydrogen in the NATURALHY gas mixture
- Operating Pressure available in specific locations in the network system
- Requirements for appliances
- Changing performance of fuel cells their ability to accept wider range of feeds
- On-going work by ISO and other organisations regarding classification of hydrogen grades and purity

In addition to the performance targets for both metallic and non-metallic membranes, the impact of natural gas composition on the membrane duty is considered, as is the impact of hydrogen quality supplied to the grid.

Report No.R0028-WP5-C-0: Interim Report on Membrane Development- Pd based membranes

Electroless plating of Palladium onto a porous alumina substrate has given membranes that have good hydrogen flux at 400C, meeting or exceeding the 2010 US DOE targets for membrane hydrogen flux. Similar routes to palladium alloyed with silver and copper have not yet given successful membranes. Manufacturing defects in the ceramic supports have been shown to give rise to pin-hole leaks and mechanical problems. The application of a fine pore (20nm) surface coating smoothes out most substrate defects, but improved substrates are still required. Preparation of a coherent, defect-free membrane on a support is a demanding technical objective, since the smallest defect such as a pin hole will reduce the selectivity and effectiveness of the membrane.

Magnetron vacuum sputtering is proposed as an alternative route to membranes, concentrating on using perfectly smooth surfaces such as silicon wafers and polymers as the forming surface, and techniques to their removal from the deposited metal films. Lithography combined with sputtering offers the opportunity to develop cheap sealing/gasketing methods.

Report No. R0029-WP5-C-0: Interim report on Membrane Development-Carbon based membranes

The objective for the membrane development within the membrane research group, Memfo, at NTNU, is the development of two types of new membrane materials suitable for the recovery of hydrogen from the natural gas net as defined in the project NATURALHY. The two identified materials were 1) carbon molecular sieves (CMS) and 2) a mixed matrix (MM) material.
It is critical to the success of the NaturalHy project that the end-user separation is feasible. The hydrogen for end-use components such as fuel cells, require relatively pure hydrogen. Palladium membranes are commonly seen as the bench mark membrane technology for the recovery of hydrogen from feed streams with a low (<30 vol%) hydrogen concentration. In order for these membranes to function efficiently, the entire gas feed stream must be heated to temperatures higher than 350°C, incurring a capital and energy penalty. By contrast, separation at lower or ambient temperature will not be an obstacle for the two membrane materials CMS and MM; however the efficiency with respect to flux and selectivity may vary depending on temperature and pressure – this is documented in the current report.

The separation of hydrogen from a natural gas mixture requires, both for the CMS- and MM-membrane, a very fine tuning of membrane properties such as pore tailoring (CMS) and successful blending of organic/inorganic phase (MM).
Work has been performed on both membrane materials, and the current status is that the development is successful for the carbon membrane, while this is not the case for the mixed matrix membrane. Carbon membranes have been developed that show very good performance at low temperatures (from 30-80C), and a great deal of work has been carried out to optimise the pore structure development during pyrolysis of the precursor materials. Addition of metal oxides (silver for example) improves performance. The membranes have been tested in the form of flat sheets, but for practical membranes, hollow fibres will be more usable, and work on spinning fibres has begun.

The development of the MM-membrane is very challenging, and the results obtained indicate that there is a long way to go to achieve satisfactory separation. Since the financial resources for the project are limited, the recommendation at this point is that work on the MM-membrane is stopped, and focus is set on further development of the CMS-membrane.

Report No. R0030-WP5-C-0: Interim report on Membrane Development –Composite metallic membranes

Composite metallic Pd based membranes have been tested to determine operating envelope.

The table below summarizes the characteristics of CETH membranes:

Alloy	Pd content (% wt)	Thickness (µm)	Minimum operation temperature (°C)	Standard* flux cm^3 H2/cm^2.min	Standard(*,**) flux cm^3 H2/cm^2.min	Sulphur tolerance
Pd	100	20	300	57	57	No

Pd/Ag	77	20	70	93	121	No
Pd/Ag	77	10	70	129	168	No
Pd/Cu	60	20	70	60	100	yes

* : 400°C , $P_{upstream}$=10bar, $P_{downstream}$=1bar
** : Standard flux divided by weight-percentage of palladium.

The conclusions are that:

- At 21 bar and 400°C, using 15% H2, 85% CH4, 20 µm
  - The palladium membrane works well , feasibility is OK
  - H2 flux is very low :
    - 0,7 W/cm² (7 kW/m²) ⇔ 20 µm thickness
    - Compared to ECN (50 – 100 kW /m²) ⇔ 3 µm thick : good agreement
- At 21 bar and 400°C, using 15% H2, 85% CH4, 10 µm
  - H2 flux is directly proportional to the surface area
    - 14 kW / m² ⇔ 10 µm thickness

Thus the thick membranes (10-40 µm) are restricted in terms of flux.CETH results are generally in good agreement with literature (ECN, Idatech, NETL,etc.).
An interesting point is that

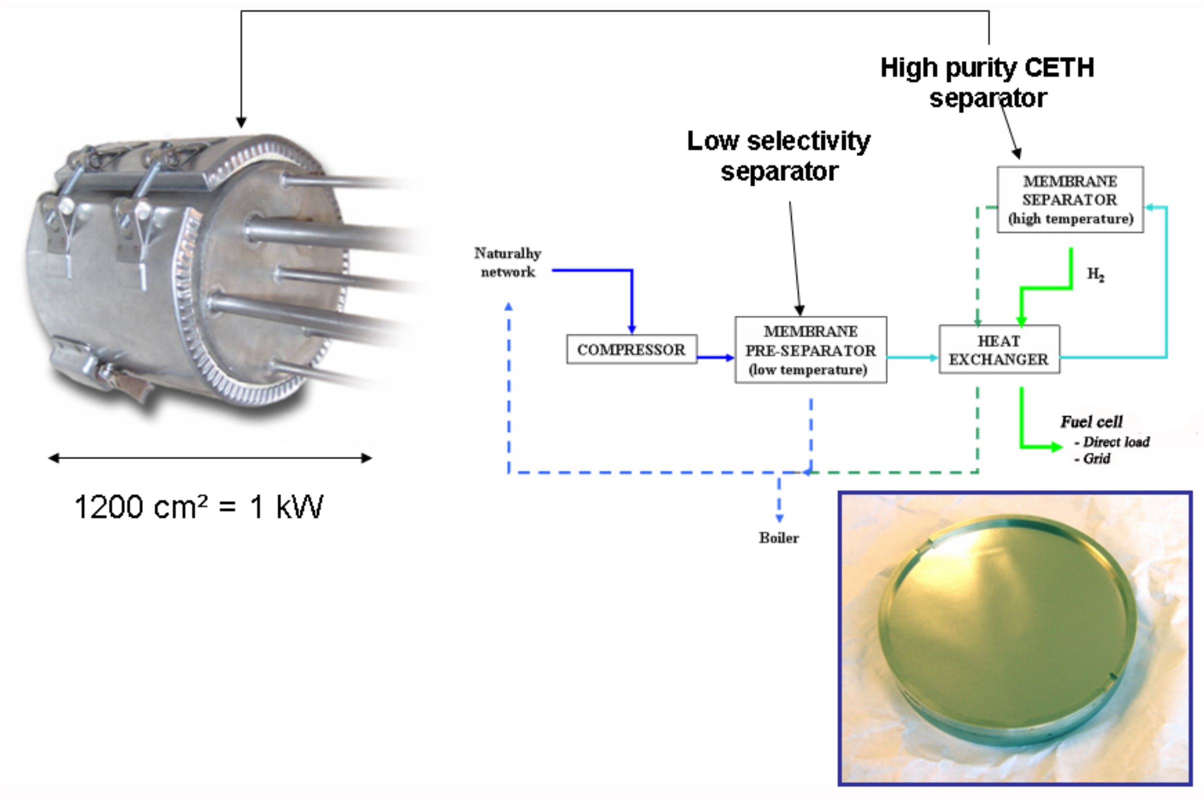
- Investment costs do not necessarily depend on thickness
  - Low thickness equates to low initial cost but potentially low lifetime
  - Higher thickness gives potentially longer lifetime and lower maintenance costs

The technology developed by CETH makes it possible to produce high purity hydrogen at high temperature. The indications are that further developments are required in order to improve the effectiveness of the membranes:

- o by lowering the membrane thickness,
- o By increasing the stability at higher temperatures,
- o By system design of the separators.

The membrane separator developed by CETH is designed to produce very pure hydrogen at high temperature. CETH separators are suited very well for ultimate purification of hydrogen for specific application such as PEM fuel cells or any other applications which requires very pure hydrogen.

For the requirements of the Naturalhy application, it is suggested that a combination of a Pd membrane separator with another less selective separator working at lower temperature may be an effective solution. The scheme shown below could comprise for example, a low cost carbon-based membrane in the first stage, with a Pd alloy membrane for final purification of hydrogen. Further work will be carried out to consider this scheme.


High purity CETH separator
Low selectivity separator
MEMBRANE SEPARATOR (high temperature)
Naturalhy network
COMPRESSOR
MEMBRANE PRE-SEPARATOR (low temperature)
HEAT EXCHANGER
H_2
Fuel cell
- Direct load
- Grid
Boiler
1200 cm² = 1 kW