Membrane reactor for hydrogen production

Project 3-0510-0040: Milestone Report #3

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Glossary

CFD	Computational fluid dynamics
CMR	Catalytic membrane reactor
Flux	Flow of hydrogen per unit area per time (usually ml/cm^2/min or mol/m^2/s)
HF	Hydrofluoric acid
Pd	Palladium
Permeability	A measure of the intrinsic rate at which hydrogen migrates through a material. Constant for a given material at a given temperature(usually mol m^{-1} s^{-1} Pa$^{-0.5}$), and independent of membrane thickness and pressure
Raffinate	The gas stream at the outlet of a membrane reactor which is depleted with respect to H$_2$. Also referred to as 'retentate'.
SiC	Silicon carbide
SS316	Stainless steel 316
V	Vanadium
WGS	Water-gas-shift reaction (CO + H$_2$O $\rightleftharpoons$ CO$_2$ + H$_2$)

Executive summary

Through ANLEC project 3-0510-0040 (Alloy CMR for hydrogen production), CSIRO is developing a catalytic membrane reactor (CMR), incorporating a H_2-selective alloy membrane, which intensifies the process of hydrogen production by combining water gas shift (WGS) conversion and H_2/CO_2 separation reactors. Applied to the processing of coal-derived syngas, a membrane reactor can potentially achieve near-complete CO to H_2 conversion, H_2 purification and pre-combustion CO_2 capture in a single device.

This report describes progress in the 18-25 month period of this 36 month project. As detailed in the funding agreement, this report summarises testing of single-module CMR, and provides a determination of whether subsequent testing is viable or not when assessed against the outlined reactor performance criteria.

This report describes progress in the 18-25 month period of this 36 month project. Effort has centred on the following key areas:

- Membrane surface preparation: The process for depositing a catalyst on the surface of vanadium alloy tubes has been further refined. Significant improvements in quality, consistency and hydrogen throughput have been demonstrated. The process has been applied to the preparation of 33 cm-long membrane tubes, significantly greater than the previous 15 cm-long tubes.

- When operated as a hydrogen separator, hydrogen flux exceeding 60 cm^3 H_2 cm^{-2} min^{-1} at 400°C has been achieved using a 0.20 mm-thick tube. This is approximately 5 times greater than the leading palladium alloy of equivalent thickness, twice the value reported in the previous milestone report, and 40% of the DOE flux target.

- H2 flux in excess of 10 L/min has been demonstrated using a 180 cm^2 membrane module. A H_2 yield in excess of 80% has been demonstrated with a feed of shifted syngas (33% H_2 + 22% CO_2 + 44% H_2O) at 400°C.

- A patent which covers CSIRO's embrittlement-resistant alloy composition, and tube manufacturing method, has been drafted. Once submitted, CSIRO's IP will be suitably protected and CSIRO will be in a position to engage with potential commercial partners.

- Accompanying this milestone is a decision point on whether further R&D is viable. The results demonstrated in the present reporting period (membrane size doubled from 45 to 90 cm^2, membrane flux doubled from 30 to 60 ml/cm^2/min, high yield and stability in steam-laden syngas) show the promise of this technology, and a continuation of funding for the remaining 11 months of the project is sought by CSIRO.

1   Introduction

1.1   Project overview

Through ANLEC project 3-0510-0040 (Alloy CMR for hydrogen production), CSIRO is developing a catalytic membrane reactor (CMR), incorporating a H_2-selective alloy membrane, which intensifies the process of hydrogen production by combining water gas shift (WGS) conversion and H_2/CO_2 separation. Applied to the processing of coal-derived syngas, a membrane reactor can potentially achieve near-complete CO to H_2 conversion, H_2 purification and pre-combustion CO_2 capture in a single device.

A CMR is depicted in Figure 1, illustrating the close coupling of the water-gas-shift conversion catalyst and H_2-selective membrane. By continuously extracting H_2 in situ as it is formed, an artificially high chemical equilibrium is created within the reactor, allowing CO conversions of almost 100 %. Additional benefits include reduced energy consumption and plant volume compared to conventional, separate shift and separation processes.

This report describes progress towards this ultimate aim achieved during the 18-25 month period of this 36-month project.
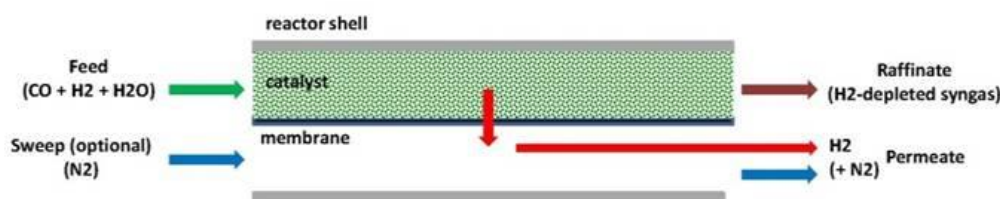
Figure 1: Schematic of catalytic membrane reactor

1.2   Membrane types

The aim of this project is to develop a CMR incorporating CSIRO-developed vanadium-based alloy membranes. CSIRO has developed embrittlement-resistant alloys and a patent is being prepared which will claim this composition and the manufacturing process. Until this patent is submitted, vanadium tubing is being used in the preparation of membranes. Vanadium offers comparable performance in terms of hydrogen throughput, but is poorer with respect to embrittlement.

1.3   Planar versus tubular

The planar membrane geometry was evaluated during the first 12 months of this project, and the tubular configuration has been used in all subsequent trials. The membranes developed in the course of this project are tubular with an outer diameter of 3/8" (9.52 mm) and wall thickness of 0.20 mm.

1.4   Performance targets

Establishing performance targets for membranes is difficult because they cannot be considered as a stand-along technology, but rather, as part of a broader gasification-based system. One set of performance benchmarks which are often referred to, however, are those established by the US Department of Energy for H_2-selective membranes. These are listed in Table 1. These consider the membrane performance characteristics in isolation, and hot the performance of any integrated pre-combustion capture process.

Table 1. Performance targets for alloy membranes established by the US Department of Energy

Performance criterion	Units	2015 target
Flux (100 psi ΔP)	$ft^3\ ft^{-2}\ hr^{-1}$	300
	$cm^3\ cm^{-2}\ min^{-1}$	152
	$mol\ m^{-2}\ s^{-1}$	1.13
Temperature	°C	$250 - 500$
Sulfur tolerance	ppmv	> 100
Cost	$/ft^2	< 100
	$/m^2	< 1076
WGS activity		Yes
ΔP operating capability	psi	$800 - 1000$
	MPa	$5.16 - 6.89$
CO tolerance		Yes
Hydrogen purity	%	99.99%
Stability/Durability	years	5

1.5   Project plan and report Scope

The plan for this project is shown in Figure 2. Running for a total of 36 months, the focus during 18-25 month period has been increasing the size and quality of the tubular membrane elements. This milestone report (#3) will describe progress towards these goals during this period.

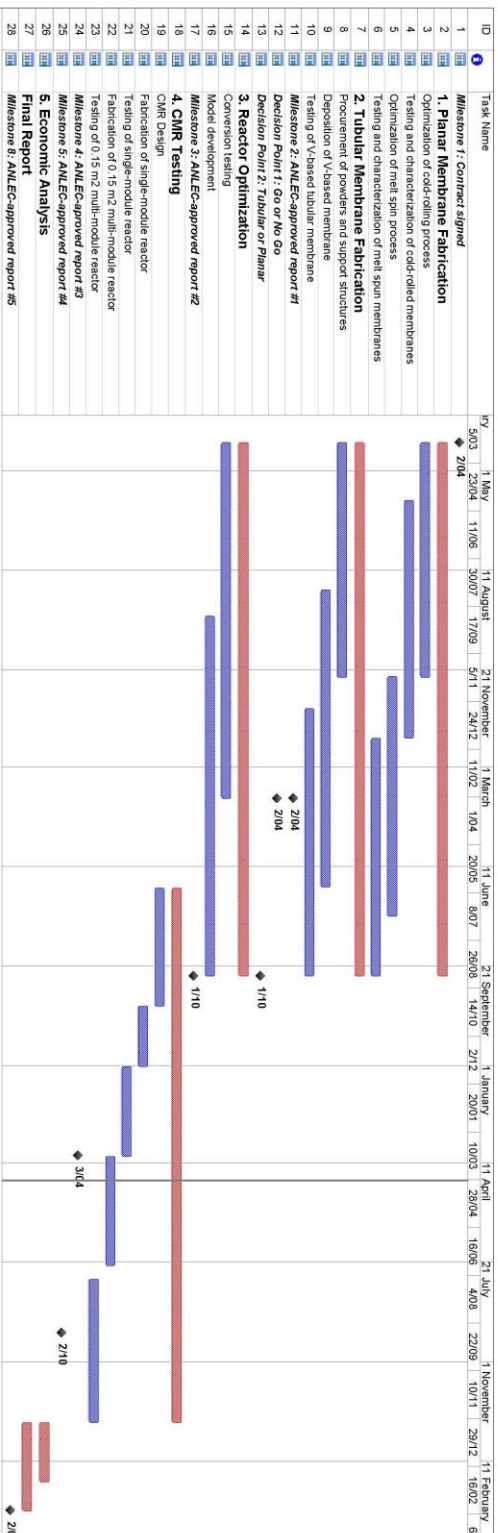| ID	Task Name
1	*Milestone 1: Contract signed*
2	**1. Planar Membrane Fabrication**
3	Optimization of cold-rolling process
4	Testing and characterization of cold-rolled membranes
5	Optimization of melt spin process
6	Testing and characterization of melt spun membranes
7	*Milestone 2: ANLEC-approved report #1*
8	*Decision Point 1: Go or No Go*
9	**2. Tubular Membrane Fabrication**
10	Procurement of powders and support structures
11	Deposition of V-based membrane
12	Testing of V-based tubular membrane
13	*Milestone 2: ANLEC-approved report #1*
14	*Decision Point 2: Tubular or Planar*
15	**3. Reactor Optimization**
16	Conversion testing
17	Model development
18	*Milestone 3: ANLEC-approved report #2*
19	**4. CMR Testing**
20	CMR Design
21	Fabrication of single-module reactor
22	Testing of single-module reactor
23	Fabrication of 0.15 m2 multi-module reactor
24	Testing of 0.15 m2 multi-module reactor
25	*Milestone 4: ANLEC-approved report #3*
26	*Milestone 5: ANLEC-approved report #4*
27	**5. Economic Analysis**
28	**Final Report**
	Milestone 8: ANLEC-approved report #5

Figure 2: Work plan for project 3-0510-0040

2   Membrane fabrication

2.1   Overview

CSIRO's optimised V-based alloy is the subject of a patent application, and engagement with a commercial tube manufacturer for supply of these membranes will not be undertaken until the intellectual property is secure. In the current term, vanadium tubing with outer diameter of 9.52 mm (3/8 ") and wall thickness of 0.20 mm has been procured for testing during this period. This alloy is unoptimised with respect to embrittlement resistance, but is satisfactory with respect to hydrogen permeability and as a substrate for surface optimisation.

The key challenge with respect to surface preparation is achieving a V-Pd interface free of oxide or other contaminants. Vanadium, however, spontaneously forms a continuous oxide on contact with air, and achieving an oxide-free interface is probably not achievable in an aqueous-based deposition process. The only acid known to dissolve vanadium oxide is hydrofluoric (HF) acid, and therefore the oxide layer thickness can be minimised through use of a HF etching step prior to plating, and reducing the time between etching and plating. Significant improvements in the quality, consistency and hydrogen permeability of Pd-overlayers has been achieved in the present reporting period, and the length of the membranes which can be routinely prepared has been increased from 15 to 33 cm (45 to 99 cm2).

2.2   Surface preparation

The surface of as-received vanadium tubing is impermeable to hydrogen due to the presence of oxide scale, oil and grease, and metallic contaminants. In order to permeate hydrogen, the vanadium surface must be stripped of oxide and other contamination, and a catalytic layer must be applied to promote the rate at which molecular hydrogen exchanges with the alloy. A process which was reported in the previous period for preparing the surfaces of vanadium tube has been further refined, and the number of steps reduced, resulting in an improvement of quality and hydrogen throughput.

Inner surface preparation

Abrasion: A rotating stainless steel brush is passed through the tube several times followed a SiC-impregnated brush with water lubrication.

Cleaning and degreasing: The tube is submerged in an Alconox solution and cotton wool is passed through the bore several times. The tube is then ultrasonically cleaned for 5 minutes followed by a rinse with DI water.

Anodic etching: Anelectrode is inserted into the bore of the tube, and the tube is submerged in a HF acid solution. A voltage is applied across the solution, causing vigorous gas evolution at the vanadium surface. The effervescence acts to thoroughly

clean the surface by carrying away any solid material, and the HF acid acts to dissolve vanadium oxide at the surface.

Plating: The tube is thoroughly rinsed and transferred to a custom plating cell. Plating solution, heated to 30°C, is circulated through the tube. The resulting Pd layer is ~ 0.5 micrometres thick.

The length of the anodes available commercially has limited the length of membrane tubes which could be coated. This has been addressed by threading the ends of several 200 mm-long electrodes and joining them by a conducting sleeve. Plastic spacers have also been manufactured to ensure the electrode remains centred during plating.
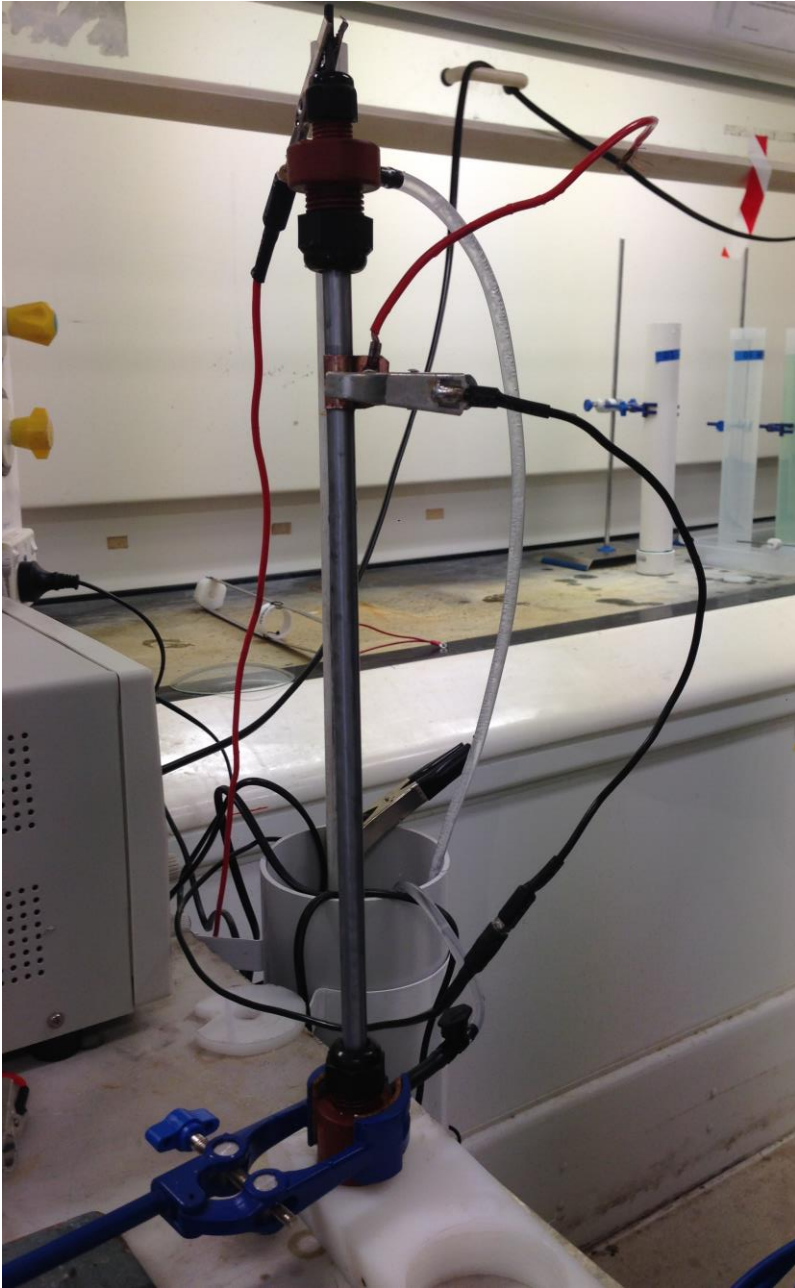
Figure 3: Apparatus for electroplating Pd onto the inner surface of 33 cm-long (99 cm^2) vanadium tube

Outer surface preparation

Abrasion: The tube is rotated between centres in a lathe and abraded with SiC paper and DI water lubrication.

Cleaning and degreasing: The ends of the tube are plugged (to prevent contamination of the prepared inner surface), and the outer surface is wiped with cotton wool dipped in an Alconox solution, followed by a DI water rinse.

Anodic etching: The tube is submerged in HF acid and cleaned electrolytically under the same conditions described above. This removes any residual particulate matter and vanadium oxide.

Plating: The tube is transferred to a custom plating apparatus and and a ~0.5 micrometre-thick Pd layer is deposited electrolytically.

Post plating procedure

After coating, the membrane tubes are annealed under vacuum for two hours at 400°C to i) remove any residual hydrogen from the plating process, and ii) promote bonding by diffusion between the vanadium tube and palladium overlayer.

Several examples of 33 cm-long (99 cm^2) membrane tubes are shown in Figure 4.
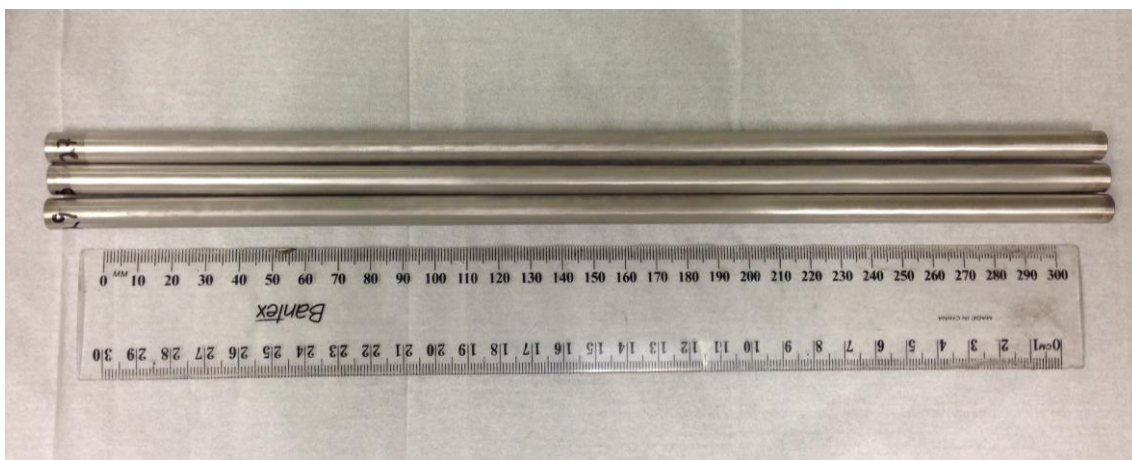

Figure 4: 3/8" x 33 cm-long (99 cm^2) membranes with inner and outer Pd layers

Continued development

The following aspects of membrane fabrication and assembly will be explored further during the remaining term of the project:

- *Increasing the length:* the plating process will be adapted for 50 cm-long tubes (~150 cm^2). This is dependent on increasing the length of the anodes used in plating the tube bore, and in procuring suitable HF-resistant tanks for the etching stage.

- *H_2S-tolerant surface coatings:* A procedure for deposition of sulfur-tolerant Pd-Cu and Pd-Au surface coatings is under development. These coatings will be required before any slipstream testing can be undertaken.

- *Asymmetric coatings:* Pd and Pd-based alloys are required for the outer surface as they offer tolerance to CO, steam and as described above, H_2S. The inner surface, however, is only ever exposed to H_2 and therefore has less stringent requirements. There are other less expensive metals (eg, Ni, Co, Cu) which are known to catalyse hydrogen dissociation and recombination, and these could potentially be used on the inner surface. This would dramatically decrease the overall cost of the membrane.

- Joining and sealing: The current SS316-graphite compressive seals, while reliable, are imperfect as i) they are heavy which places the membrane under tension during use when suspended vertically, ii) there is a large expansion mismatch between the fitting and the membrane, and iii) they limit the shell diameter to 1" when ¾" would be preferred. Issues i) and ii) may be addressed by using commercial aluminium compression fittings: aluminium has much lower density than SS316 (2.7 versus 8 g/cm^3) meaning less weight is supported by the membrane. Also, aluminium has a much higher coefficient of thermal expansion (13 x 10^{-6} versus 9 x 10^{-9} K^{-1}) meaning the expansion mismatch between the fitting and the hydrided membrane is reduced. Commercial aluminium fittings will be trialled in the next reporting period. Issue iii) can be addressed by fittings which are welded to the vanadium tubing, and trials of a laser welding process were reported previously. Welded joins remain the preferred option as they will reduce the weight and will allow use of a 3/4" reactor shell. Considerable work will be required to develop a reliable technique and this will not be achieved in the current project.

3 Performance of Pd-coated V-based membranes

3.1 Overview

This section describes the hydrogen permeability characteristics of tubular vanadium membranes prepared according to the procedure described in Chapter 2.

3.2 Module assembly

Membranes were incorporated into a shell-in-tube module for permeation testing. A compressive sealing system, demonstrated previously, was used for all tests. This makes use of commercial 3/8" compression fitting and nut, combined with a deformable graphite ferrule and a stainless steel insert to strengthen the tube around the fitting. When using membrane tubes with a total length of 33 cm, the exposed membrane length after assembly is 30 cm, giving an area of approximately 90 cm^2.

3.3 Permeation testing

Membrane activation and stability

Fresh membranes require a period of activation before full performance is achieved. For these vanadium-based membranes, exposure to H_2 at 400°C for 6 hours results in a 40% increase in permeability, as shown in Figure 5. This can be attributed to the diminishing of transport resistances at the surface due to reduction of the Pd.

The membrane was then shutdown (cooled and purged of hydrogen) before being started up again. Permeability didn't recover to the same value, but steadily increased over a 20 hour period.

These membranes are designed to be indefinitely stable at 400°C, but exposure to higher temperatures causes an irreversible degradation in performance due to diffusion of vanadium into the catalytic Pd layer, and oxidation of V to form a non-catalytic oxide layer. In order to observe this degradation under accelerated conditions, the H_2 permeability was measured at 450°C over several days, the results of which are shown in Figure 6. At regular intervals, the membrane surface was reactivated by exposure to air, a process which enhances surface activity by roughening the Pd layer, thereby increasing its surface area.

Permeability began to degrade slowly after around 10 hours, and dropped to around half its maximum value after the 40 hours. 450°C can therefore be tolerated temporarily, but will cause irreversible degradation if the exposure time is greater. Care must therefore be taken when operating these membranes in a CMR so that the WGS reaction exotherm does not cause localised heating adjacent to the membrane surface. As shown in previous reports, this excursion can be as high as 100°C above

the CMR inlet temperature if the catalyst is not diluted appropriately. The edevlopment of a CFD model of the reactor will assist in determining the optimum operating conditions from the perspective of both overall efficiency and membrane stability.
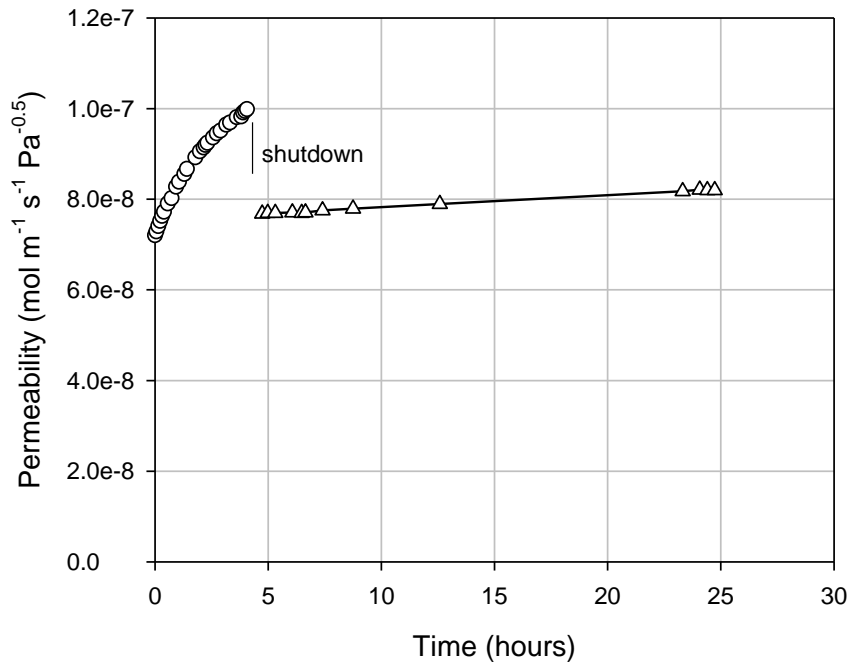

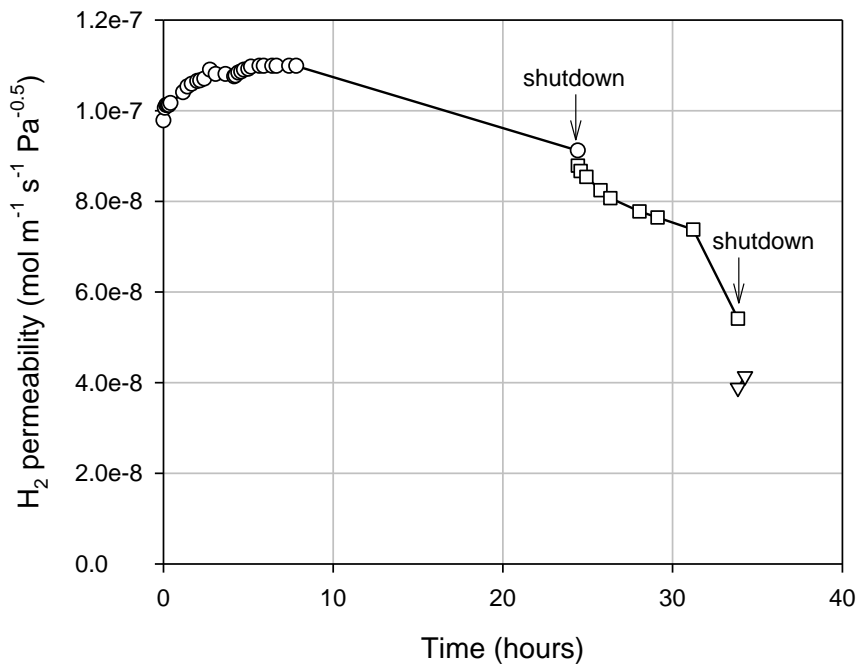**Figure 5: Permeability of vanadium membrane at 400°C**

Figure 6: Permeability of vanadium membrane at 450°C

10 LPM Module

With the aim of demonstrating a module with a H_2 flow rate of at least 10 litres per minute, a 180 cm^2 membrane was created by joining two 30 cm-long membranes in series, as shown in Figure 7. In a feed of pure H_2 at 400°C, this module achieved a total H_2 flow rate of 11 litres per minute at a feed pressure of 9.6 bar (Figure 8). This equates to a H_2 flux of 60 ml/cm^2/min, and is the greatest flow rate yet achieved during the course of this project. The highest flux reported in milestone report #2 was ~ 30 ml/cm^2/min.

Despite this significant increase, the measured flux is still only half the theoretical value for a membrane of this thickness. The most likely reason for this is the formation of an oxide layer at the interface during plating which acts as a barrier to hydrogen transport. Vanadium tends to oxidise spontaneously and rapidly, and despite the introduction of the anodic HF etching step, it is unlikely that oxide formation can be eliminated in an aqueous electroplating procedure unless a protective layer can be applied in the presence of HF.

This same module was exposed to mixed gas feed representative of a shifted syngas (*i.e.*, downstream of a shift reactor) with the composition 33.3% H_2, 22.2% CO_2 and 44.4% H_2O, and a total feed rate of 16 L/min, and a reactor temperature of 400°C. Hydrogen flow rate and yield (the fraction of the H_2 in the feed extracted through the membrane) both increased with increasing feed pressure, as shown in Figure 9. This is an important demonstration of the ability of the membrane to operate in the high-steam environment of a shift reactor. The H_2 yield at 10 bar exceeded 80%.
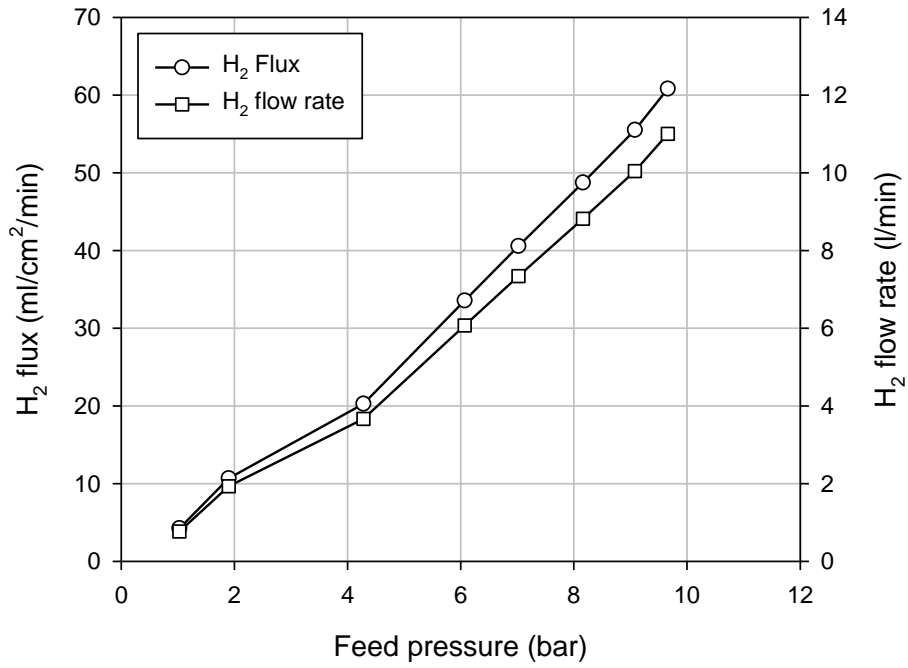

Figure 7: 180 cm^2 membrane module

Figure 8: Flux (H_2 flow per cm^2 per minute) and total flow rate (L/min) through 180 cm^2 membrane at 400°C
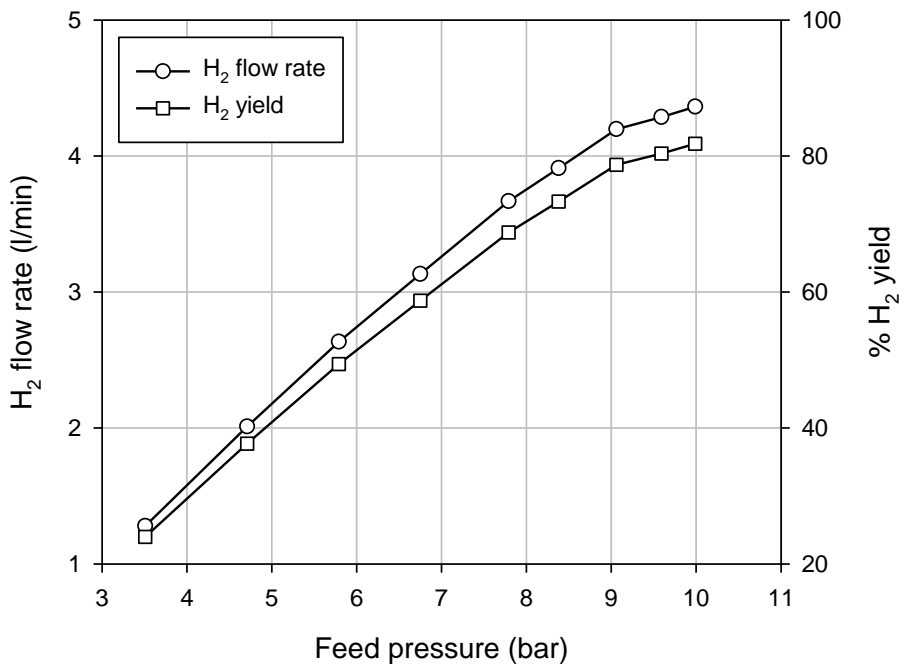

Figure 9: H_2 flow rate (L/min) and yield (H_2 flow relative to feed rate) for 180 cm^2 membrane at 400°C with a feed of 16 L/min shifted syngas (33% H_2 + 22% CO_2 + 55% H_2O)

Catalytic membrane reactor testing

The overall aim of this project is the demonstration of a catalytic membrane reactor, a device which can perform CO shift (via a catalyst) and H_2 extraction (via a membrane) in a single device. The previous report described validation experiments which incorporated a commercial Pd-Ag-based tubular membrane, surrounded by a packed bed of granular catalyst and inert material.

Several trials, incorporating the CSIRO-developed V membranes, have been undertaken in the present reporting period.

Vanadium-based membranes expand significantly as the absorption of hydrogen causes the vanadium lattice to swell. This expansion can be as much as 5%, which over a 1 m length of membrane tube, equates to an increase in length of 5 cm. A packed-bed configuration offers advantages of easy assembly and catalyst dilution (through the introduction of inert packing), but it creates a fairly rigid barrier around the membrane which opposes hydrogen-induced expansion, and places the membrane under compression during operation.

The several trials undertaken using the packed-bed configuration experienced very similar failures, typically adjacent to the compressive seal at the end farthest from the reactor inlet. An example is shown in Figure 10.

When unimpeded, these membranes can be reliably operated and shut down repeatedly, as demonstrated in milestone report #2 and also in this report. The obvious solution is therefore to shift to a CMR in which the catalyst is deposited on the inside of the reactor shell, as depicted in Figure 11, which will leave the membrane free to expand without resistance. The outcome of trials to prepare and test coated reactor tubes will be reported in the next milestone report.

Figure 10: Fractured membrane after CMR test due to physical restriction caused by the catalyst bed against membrane expansion
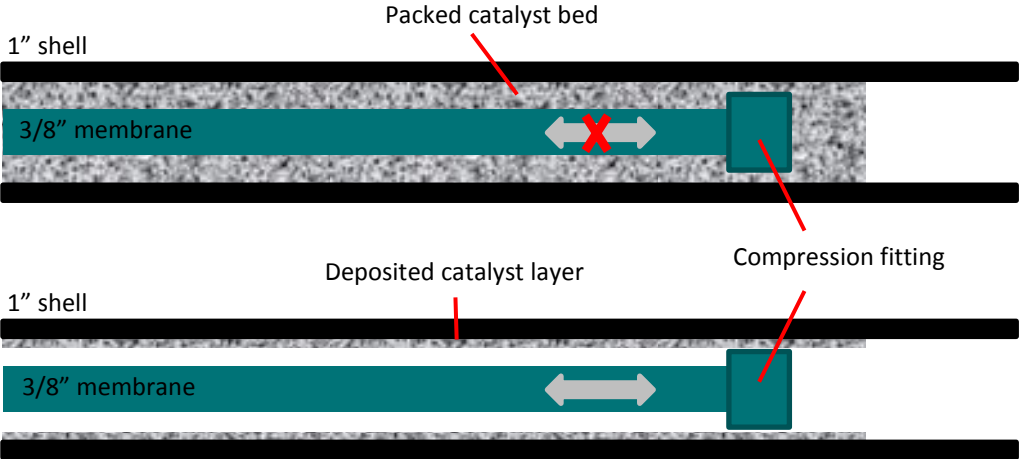

Figure 11: Membrane reactors with packed bed (top) and coated tube (bottom) configurations

Performance and cost benchmarking

The 2015 US DOE targets for H_2 flux and cost are 150 ml H_2 cm^{-2} min^{-1} (1.00 mol m^{-2} s^{-1}) and \$1000 m^2 respectively [1]. This can be reduced to a cost per throughput value of \$1000 per (mol s^{-1}).

As described in milestone report #2, and based on raw materials costs and expected manufacturing costs, our expectation that these vanadium-based alloy membranes will cost significantly less than the DOE target, and probably closer to \$600 m^{-2}. The flux reported in Figure 8 is only 40% of the DOE target value, but this was achieved with a relatively thick (0.20 mm) membrane. The simplest route to achieving greater performance is to reduce the thickness of the tube. With H_2 flux being inversely proportional to thickness, halving the tube thickness would result in a doubling of hydrogen flux. With thinner tube batches in the future, combined with incremental increases in performance due to the quality of the deposited surface layers, a hydrogen flux value of 100 ml/cm^2/min is expected. Thus, the cost per throughput will be almost identical to the DOE value.

The main competing technology in the alloy membrane field is the thin Pd-based membrane deposited on a porous support. Such membrane modules developed by HYSEP have entered the market, and these are based on 5 micrometre-thick $Pd_{77}Ag_{23}$ alloy on high quality porous substrates (http://www.hysep.com/technology/). Published data shows a H_2 flux of 3.9 mol m^{-2} s^{-1}, or ~ 4x the DOE target, but although no costs are provided, these are known to be prohibitively expensive at this early stage of commercialisation. As of 2010 the Pall Corp., the leading US-based developer, claim a price of 2x the DOE target with a flux slightly less than the DOE flux target (http://www.hydrogen.energy.gov/pdfs/review11/pd005_damle_2011_p.pdf). Other developers in the pre-commercial stage are reluctant to divulge prices at this stage, so making an informed comparison against the CSIRO membrane technology is difficult.

In terms of raw materials, the Pd required for HYSEP membrane will cost around \$1200/m^2 based on current prices. Porous support tubes of the quality required for thin membranes were recently purchased by this group at a price of \$400 for each 60 cm^2 tube, making the supports more expensive that the Pd. Obviously this cost will reduce with economies of scale, but it does illustrate that the support tubes will be a significant cost.

De Falco et al [2] proposed an experience curve for alloy membranes for which membrane costs decreased from 9000 euro per m^2 to 1000 euro per m^2 after cumulative production of 10,000,000 m^2. While manufacturing costs can be reduced through mass production, precious metal costs will likely increase and will remain the single greatest determining factor for this technology. Importantly, the CSIRO approach uses less Pd than any supported membrane technology.

4 Commercial engagement

CSIRO does not typically commercialise technology directly, but relies on partnerships, licensing and spin-offs to achieve commercial outcomes. Commercial deployment of CMR technology will require commercial engagement in the near term to meet the following requirements:

- Increased scale of membrane manufacture

- Provision of supplementary technologies (eg, desulfurisation, catalysts)

- Conduct slipstream testing program

4.1 Membrane composition and fabrication

A patent is presently being prepared which will claim the CSIRO-developed, embrittlement-resistant alloy, and a process for refining the grain structure for optimum deformability during tube production. This patent will secure CSIRO's IP, and CSIRO will then be sufficiently protected to engage commercial tube suppliers for the procurement of tubes made from CSIRO's optimised alloy.

4.2 Catalyst and sorbent supply

A Materials Transfer Agreement between CSIRO and Johnson Matthey has been executed, and JM has supplied CSIRO with water-gas-shift catalyst material. This material will be used in subsequent CMR testing.

4.3 Slipstream testing

Slipstream testing of CSIRO-developed CMR modules will be an essential aspect of any future R&D strategy. CSIRO is developing agreements with one European and three American institutions which will allow the testing of CSIRO membrane materials in coal-derived syngas environments. It is expected that the first trials will be undertaken before the completion of the present project.

5   **Summary**

Effort in the current period has focused on increasing the quality of the Pd catalyst overlayer, and increasing the size of the membranes which can be prepared. As evidence of an improvement in overlayer quality, the highest flux recorded (60 ml cm^{-2} min^{-1}) is around twice the value reported in milestone report #2. A reliable procedure for preparing 33 cm-long tubes has been developed, exceeding the previous size of 15 cm. A module with a H_2 production rate in excess of 10 L/min has been demonstrated, in contrast to the previous value of 0.9L/min. These increases in size and performance illustrate that the project is on track to achieve its aim of a 0.15 m^2, multi-module CMR with an 85% H_2 yield.

References

[1] Miller CL, Cicero DC, Ackiewicz M, Hydrogen from coal program: Research, development and demonstration plan for the period 2007 through 2016, The United States Department of Energy, National Energy Technology Laboratory; 2007.

http://fossil.energy.gov/programs/fuels/hydrogen/2010_Draft_H2fromCoal_RDD_final.pdf

[2] De Falco M, Marrelli L, Iaquaniello G, Membrane reactors for hydrogen production processes. London: Springer. 2011.