



Engineering Advance

## Development of Palladium-Alloy Membranes for Hydrogen Separation and Purification

Anwu Li <sup>1,2,\*</sup>, Tony Boyd <sup>1</sup>, Jim Lim <sup>2</sup>, John R. Grace <sup>2</sup><sup>1</sup> NORAM Engineering and Constructors, 200 Granville St., Vancouver, Canada V6C 1S4<sup>2</sup> Chemical and Biological Engineering, University of British Columbia, 2360 East Mall, Vancouver, Canada V6T 1Z3

## Article info

Received 2019-07-04

Revised 2019-10-01

Accepted 2019-10-02

Available online 2019-10-02

## Keywords

Hydrogen separation  
Hydrogen generation  
Composite membranes  
Palladium alloys  
Foil  
Electroless plating

## Highlights

- Thin palladium and Pd-alloy membranes were prepared by electroless plating
- Pd, Ag, Ru and other metals were coated onto flat and cylindrical surfaces
- Novel composite membrane configuration improved robustness and facilitated welding
- A mixed bath was developed for simultaneously depositing Pd and Ru
- Foil modules were prepared and tested in membrane reactors and purifiers

## Abstract

This paper summarizes R&D activities and progress at NORAM Engineering and the University of British Columbia (UBC) on preparation and testing of thin palladium-based membranes and their applications. Most of these activities were carried out internally at NORAM, some jointly with UBC and their spin-off company, Membrane Reactor Technology (MRT) through a wide range of projects. Key results outlined in this paper include: 1) modularization and applications of foil-based Pd alloy membranes with inter-diffusion barriers; 2) preparing and characterizing thin Pd composite membranes; 3) development of Pd-Ru membranes by electroless plating for enhanced stability at higher temperatures; 4) production of palladium membranes for application in hydrogen separation and hydrogen production by fluidized bed membrane reactors.

© 2020 MPRL. All rights reserved.

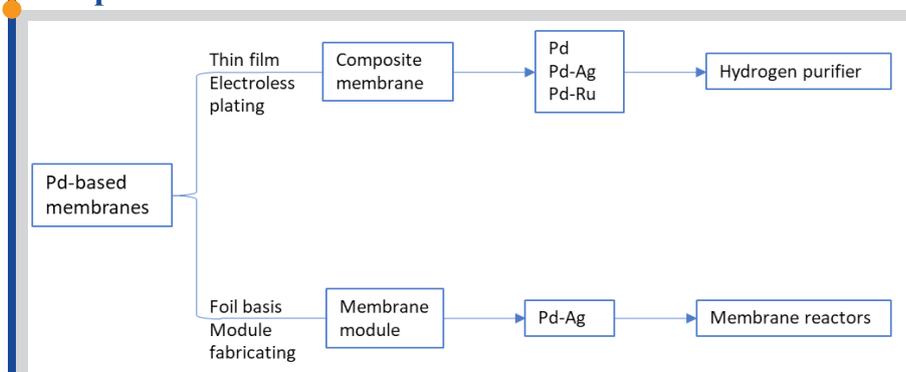
## 1. Introduction

Excessive use of fossil fuels is causing such problems as climate change, reduced air quality and acid rain [1]. With advances in fuel cell technologies, hydrogen has the potential to be an attractive alternative to conventional fossil fuels, improving energy efficiency and reducing environmental impact [2]. Hydrogen is predominantly derived currently from fossil fuels, but it can also be produced from other sources, most notably biomass [3]. However, hydrogen from these sources also contains small amounts of carbon monoxide and sulphur compounds, which are poisonous to fuel cells. Therefore, it is essential to purify the hydrogen by removing these contaminants prior to its oxidation in fuel cells. For example, hydrogen produced in conventional reforming reactors may go through complicated purification steps, including high- and low-temperature shift reactions at low and high temperatures and pressure swing adsorption, to produce hydrogen of the required purity [4]. These steps make the entire hydrogen production process more complicated, less compact and less energy- and cost-effective. Hydrogen-selective membranes can directly

separate hydrogen from hydrogen-containing source without requiring energy-intensive pressure swing adsorption. Selective membranes can also be deployed in hydrogen production to combine reaction and separation processes, thereby improving the efficiencies of both reaction and separation processes and making the entire production/separation system more compact and efficient.

Since 2000, substantial efforts have been made by NORAM, UBC and their affiliated company, Membrane Reactor Technologies Limited (MRT), to prepare Pd-based membranes and to test them for industrial applications [5–16]. These include development of thin palladium-based composite membranes, improvement of their high-temperature stability and hydrogen selectivity, development of hydrogen purifiers and hydrogen production in membrane reactors via steam reforming of natural gas. The most notable results and progress are summarized in this paper.

## Graphical abstract



\* Corresponding author at: Phone: +1-604-4153570; fax: +1-604-6839164  
E-mail address: ali@noram-eng.com (A. Li)

## 2. Preparation of thin composite membranes based on electroless plating

### 2.1. Palladium alloy metallic composite membranes

Both niobium and tantalum have 10 times higher hydrogen permeability and much lower cost than palladium. However, neither of these two metals has the catalytic activity for hydrogen dissociation or recombination. Both these metals also lack resistance to oxidation and hence generally have oxide layers on their surfaces. These drawbacks prevent Ta and Nb from being applied as membranes in hydrogen separation applications. In an effort to solve these problems, we coated thin layers of Pd on the outside surfaces of base Nb/Ta foils by electroless plating. These Pd layers catalyse hydrogen dissociation and recombination, while also protecting against oxidation. The sandwiched composite membrane had high hydrogen permeability, low cost, appropriate strength and high selectivity. The following results were obtained:

- A plating bath and electroless plating technique were developed to deposit thin (~0.5-2  $\mu\text{m}$  thickness) Pd layers onto both sides of Nb and Ta foil of 25-75  $\mu\text{m}$  thickness.
- The thin Pd layers were continuous and dense. SEM images confirmed that no Pd coating peeled off from the substrate, indicating that Pd layers adhered well with base metals Nb and Ta.
- Prior to hydrogen permeation, the composite membranes were mechanically more robust than Pd and Pd-Ag alloy foils of similar thickness.
- Upon permeation, the composite membrane showed perfect hydrogen selectivity and better permeability than Pd or Pd-Ag alloy foil of the same thickness, but cracks developed in the composite membranes over time.

### 2.2. Pd/Pd-Ag alloy foil/Pd metallic composite membranes

Pd-25%Ag alloy membranes provide higher hydrogen diffusion rates and more resistance to hydrogen embrittlement than pure Pd membranes. However, because Ag is less active than Pd for hydrogen dissociation and recombination, Pd-25%Ag alloy with lower Pd content on the alloy foil surface has lower hydrogen permeability than pure Pd membranes at lower temperatures at which dissociation or recombination of hydrogen on Pd-25%Ag membrane becomes rate-determining in the multiple hydrogen permeation steps. Thus, coating thin Pd layers on the surface of Pd-25%Ag alloy foil improved the catalytic activity of the surface, thereby enhancing hydrogen permeability. The following accomplishments were achieved:

- Pd layers of thickness 0.5-1  $\mu\text{m}$  were coated onto both sides of Pd-25%Ag alloy foil of thickness 25-50  $\mu\text{m}$  by electroless plating.
- These thin Pd layers were continuous and dense, and they had good adhesion with Pd-25%Ag alloy, as confirmed by SEM observations.
- Hydrogen permeability at lower temperatures (250 to 450°C) improved significantly (up to 20% at 250°C) after Pd coating. However, the improvement disappeared at temperatures  $\geq 550^\circ\text{C}$ .

### 2.3. Thin Pd-based/porous substrate composite membranes by electroless plating

Substantial R&D efforts were made to develop thin Pd-based/porous substrate composite membranes in recent years at NORAM/UBC. Know-how and propriety technologies have been attained related to synthesis of thin palladium-based composite membranes. These include new bath recipes, and techniques for depositing Pd, Ag, Ru and other metals onto cylindrical and flat substrates, pre-treatment techniques for membrane substrates and testing of membranes under various conditions.

#### 2.3.1. Flat pure Pd/ceramic/PMS composite membranes

##### a. Pre-treatment of porous stainless steel

Porous metallic substrates (PMS) were obtained from the Mott Corporation. The smallest pore size of the commercially available PMS was 0.2  $\mu\text{m}$ , with surface roughness of ~20  $\mu\text{m}$ . This roughness is too high for coating of thin and continuous Pd films onto PMS by electroless plating. In addition to preventing inter-diffusion between Pd film and metallic substrates at high temperatures, which would decrease permeability of hydrogen through the composite membrane over time, a layer which prevents inter-diffusion must be introduced as a barrier between the Pd film and substrate. A comprehensive technique was successfully developed to pre-treat the metallic substrate, including four major steps: polishing, etching, initial coarse-particle coating and subsequent fine-particle coating. After this pre-treatment process,

both surface roughness and the maximum size of PMS pore openings were significantly reduced. Ceramic layers were coated onto the surface of PMS, serving as inter-diffusion barrier layers. Figure 1 compares SEM images before and after pre-treatment.

##### b. Preparation of Pure Pd/ceramic/PMS composite membranes

Pd composite membranes commonly encounter two potential issues in gas separation applications. One is gas leakage through the edges of the porous ceramic layers of the porous substrate. Another is that it is difficult to weld Pd/ceramic/PMS composite membranes onto stainless steel modules, without the high temperature required for welding destroying the Pd film at the edge, leading to membrane leakage. A novel configuration of the composite membrane, shown in Figure 2, was found to respond well to these two critical challenges [5].

Pd films were deposited onto PMS by electroless plating, with three major steps in series: (a) surface activation via pre-seeding, (b) electroless plating, and (c) post-plating treatment. The pre-seeded was by impregnation by a PdCl<sub>2</sub> solution. This was followed by H<sub>2</sub> reduction at 400-450°C. The plating temperature was maintained at 60°C. Immediately after the plating was finished, the membrane was washed with deionized water in order to remove any salts which might be adsorbed on the substrate pores or trapped in the Pd coating layer. The composite membrane was then dried at 120°C in an oven. The membrane was next treated thermally, to coalesce deposited palladium crystals, leading to a continuous impervious film. The thermal treatment was carried out in an inert gas or in a hydrogen environment to promote atomic diffusion, thereby reducing the temperature and time required for thermal treatment. Our composite membranes were first heated to 350°C in N<sub>2</sub> and then immersed for several hours in hydrogen at 400 to 450°C.

##### c. Properties and performance of pure Pd/ceramic/PMS composite membranes

Figure 2 shows the typical configuration of our pure Pd/ceramic/PMS composite membranes. The effective membrane surface area of a typical Pd composite membrane was ~5 cm<sup>2</sup>. The morphology of a deposited Pd film is portrayed in Figure 3. The properties and hydrogen permeation/separation performance were investigated under various operating conditions. Some important observations and results were as follows:

- Dense continuous Pd films were attached to the surfaces of pre-treated porous metallic substrates. The Pd film thickness was controlled to be in the 2-8  $\mu\text{m}$  range by controlling the plating time.
- Both SEM characterization and gas permeation results confirmed that thin Pd films deposited by electroless plating were continuous and defect-free. The ideal H<sub>2</sub>/N<sub>2</sub> separation factor was up to 100,000.
- Many pure Pd/ceramic/PMS composite membranes were prepared with the novel configuration. The preparation procedure was controllable and reproducible.
- No decline in hydrogen permeability of the composite membrane were observed at 550°C or higher temperatures (up to 600°C), suggesting that the intermediate ceramic layers were successful in preventing inter-diffusion.
- The selectivity of the composite membranes was stable at 350-450°C. However, the selectivity of the composite membrane was found to decrease with time at 500°C or higher, indicating that the pure Pd film was not sufficiently mechanically robust, instead developing micro-cracks at high temperatures.
- The flat Pd/ceramic/PMS composite membrane was scaled up to 50 mm  $\times$  50 mm (i.e. 25 cm<sup>2</sup>) surface area.

#### 2.3.2. Flat Pd-Ag alloy/ceramic/PMS composite membranes

Alloying Ag with Pd improves the resistance to hydrogen embrittlement of palladium membranes. It also reduces the cost of the membrane, since silver is much less costly than palladium. Composite Pd-Ag alloy membranes were therefore prepared on PMS, with the same configuration as above. The main achievements were:

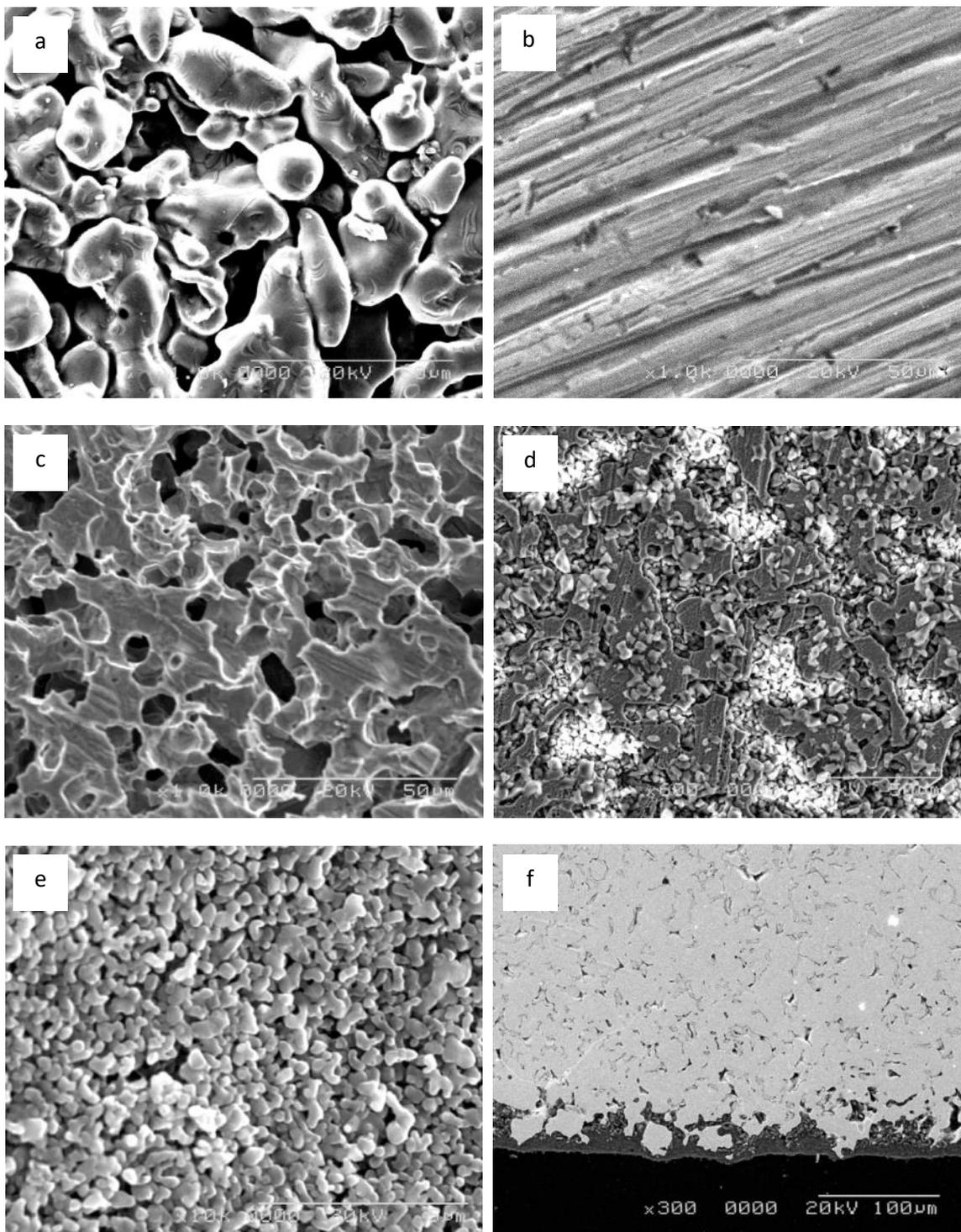
- Pd film was generally first electroless plated on pre-treated PMS, followed by Ag plating. The thickness of Pd or Ag was controllable by the plating times and conditions, so that the alloy composition was controllable. The total thickness of the Pd-Ag films was 2-8  $\mu\text{m}$ .
- Alloying of the Pd and Ag layer was fast in hydrogen at 500°C or higher, so that homogeneous alloying of Pd-Ag was readily achieved.
- Pd-25%Ag alloy composite membranes had higher hydrogen permeability than that of the Pd composite membranes and negligible

hydrogen embrittlement, as long as the temperature exceeded 250°C.

### 2.3.3. Thin Pd-Ru composite membranes on various substrates

The prepared thin defect-free Pd-based composite membranes possessed very good stability for hydrogen permeation in terms of permeability and selectivity at 400°C. However, when we increased the temperature to 550°C,

hydrogen selectivity decreased with time. This was likely caused by insufficient mechanical strength of the Pd and Pd-Ag alloy films. It is widely accepted that adding ruthenium to palladium significantly increases the thermal stability since Ru has a much higher melting point (2333°C) than Pd (1555°C), with greater hardness as well. Ru was also deposited by electroless plating.



**Fig. 1.** SEM photos of PMS before and after pre-treatment: a) surface of original PMS; b) surface after polishing; c) surface after etching; d) surface after initial coarse-particle coating; e) surface after fine-particle coating; f) cross-section after fine-particle coating.

### a. Ru electroless plating bath and plating conditions

Few reports have been published on the deposition of Ru by electroless plating because it is extremely difficult to obtain a stable Ru electroless bath from which Ru can be deposited under proper conditions. It has been reported that the addition of Ru onto Pd membrane substantially enhanced hydrogen permeability, even though the typical Ru content of a membrane was less than 1%. These results were surprising given the very low Ru content. We doubt that the benefits of this negligible amount of Ru in Pd membrane originated from Ru electroless plating. More likely it resulted from impregnation or entrainment from the bath solution. Several Ru bath recipes were successfully developed at NORAM/UBC, and Ru could be deposited from these baths under relatively mild conditions [6,9,10]. The surface of pure Ru film from our Ru bath is shown in Figure 4.

Our main results and findings include:

- Several recipes for Ru electroless plating bath were developed successfully. Ru was deposited under mild conditions, with the Ru film thickness up to 2-5  $\mu\text{m}$  for a single plating. The plating rate and thickness of Ru were both controllable.
- The pH of the Ru bath was adjusted using NaOH solution. The plating rate and Ru quality were greatly affected by the pH of the Ru bath. No Ru deposition was observed at  $\text{pH} < 12$ , and the bath became unstable after adding hydrazine as a reducing agent at  $\text{pH} > 14$ . The pH of the bath must be strictly controlled for Ru plating.
- The ratio of ammonia to Ru was important for Ru plating, affecting both the plating rate of Ru and the stability of the bath.
- Excess reducing agent hydrazine was essential for deposition of Ru, whereas excess hydrazine destabilized Pd baths.
- Several baths were confirmed to be very stable during Ru plating or long-term post-plating storage at ambient temperatures.
- A mixed bath was developed for simultaneously depositing Pd and Ru, allowing Pd-Ru alloy to be formed under mild alloying conditions.

### b. Preparation of Pd-Ru composite membranes

As noted above, the Pd-Ru composite membranes were prepared by in-series electroless plating, with the film of Pd deposited first, followed by Ru deposition. After deposition of Pd and Ru, the composite membrane was subjected to thermal treatment in hydrogen in order to form Pd-Ru alloy.

- Thin Pd-Ru composite membranes were successfully prepared on pre-treated PMS discs, with the Ru layer having good adhesion to the substrate.
- An electroless plating apparatus was designed and constructed for the manufacture of tubular composite membranes. Because the tubular ceramic substrate had lower surface roughness and smaller pores than the planar substrate, thin Pd-Ru composite membranes were easily achieved on this kind of substrate. It was found that the Pd-Ru layer could be as thin as 2  $\mu\text{m}$  without defects or pinholes.
- The preparation technique for tubular Pd-Ru composite membranes (OD, 12.5 mm) was scaled up to a length of 0.45 m (membrane area  $\sim 200 \text{ cm}^2$ ). No problem is anticipated for scaling up to tubes of length 0.9 m.

- More than ten 0.45 m-long tubular Pd-Ru composite membranes were fabricated with a membrane thickness of 3-5  $\mu\text{m}$ . All passed our internal quality control tests, requiring that  $\text{N}_2$  leakage be less than 0.01 ml/min at a pressure difference of 3 bar. The preparation process was reproducible.
- Six tubular Pd-Ru composite membranes (0.45 m long x 12.5 mm OD) with a thickness of 4  $\mu\text{m}$  were sold to a European customer for hydrogen separation applications.

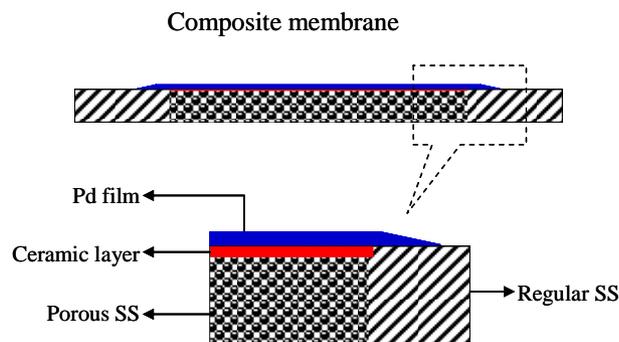


Fig. 2. Schematic diagram of novel composite membrane configuration.

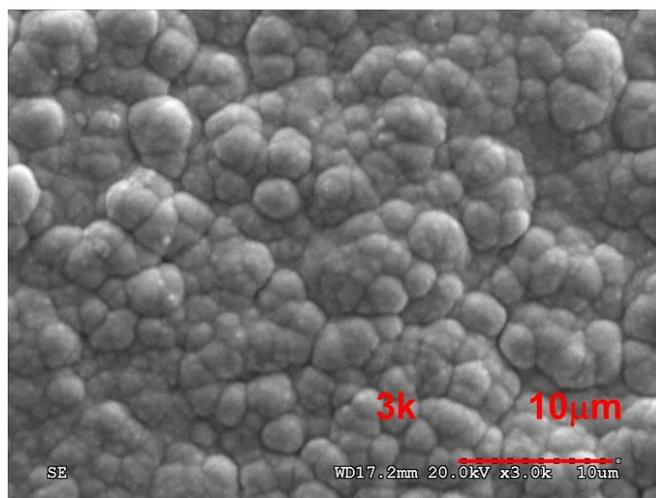


Fig. 3. Morphology of Pd film deposited on pre-treated PMS by electroless plating.

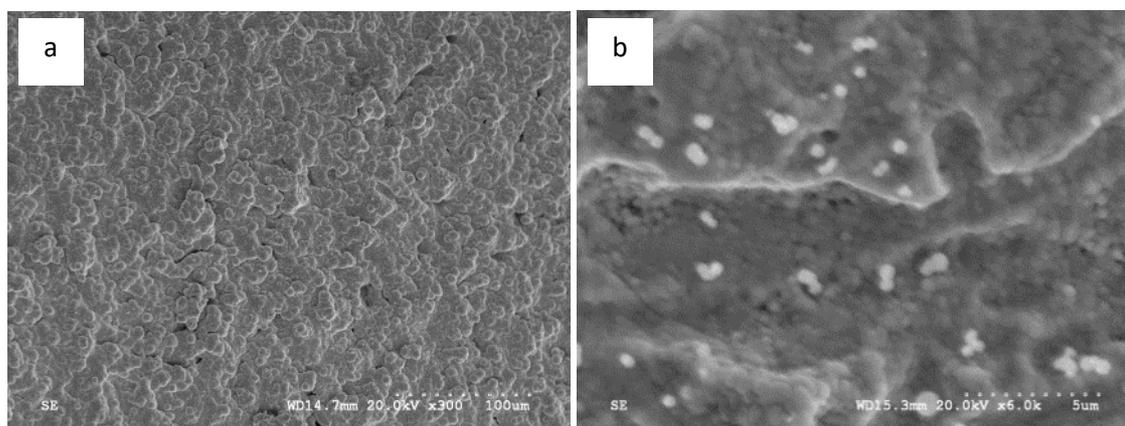


Fig. 4. Surface of pure Ru film achieved by electroless plating, a) limited magnification; b) 20 times greater magnification.

### c. Characterization and testing of Pd-Ru composite membranes

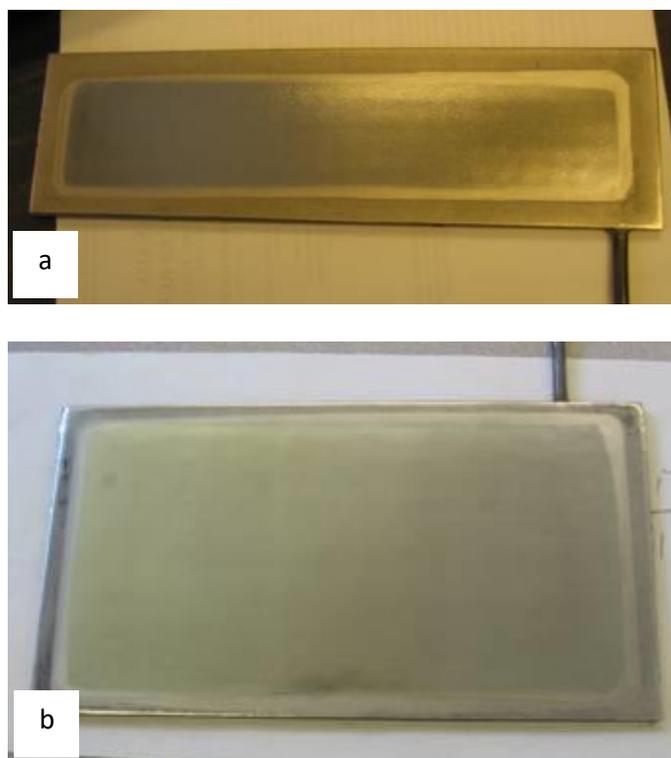
- Pd-Ru composite membranes with 5% Ru content reached maximum hydrogen permeability ~10% higher than for a pure Pd membrane.
- Alloying of Pd-Ru was difficult at a temperature of 600°C or lower because the Tammann temperature of Ru is 1030°C, much higher than the alloying temperature.
- Pd-Ru composite membranes showed much greater resistance to hydrogen embrittlement than pure Pd membranes. Pd-Ru composite membranes survived in hydrogen at temperatures as low as 180°C, at which pure Pd membranes rapidly developed cracks.
- H<sub>2</sub>S was damaging to both pure Pd and Pd-Ru composite membranes. At 350°C, 25 ppm H<sub>2</sub>S significantly inhibited hydrogen permeation through both types of membrane. Pd membranes developed cracks after being exposed to H<sub>2</sub>S for 5 h and broke after ~10 h. In contrast, no cracks were detected after Pd-Ru was exposed to 25 ppm H<sub>2</sub>S for more than 30 h, and its hydrogen permeability was recoverable after terminating the H<sub>2</sub>S exposure.
- Long-term performance tests of Pd-Ru composite membranes on PMS discs (25.4 mm OD) showed that the Pd-Ru membranes had high stability and excellent ideal separation factors. A membrane maintained an ideal separation factor of more than 14,000 at 450°C and 1,000 kPa for 5,000+ hours.
- Tubular Pd-Ru composite membranes of surface area 180 cm<sup>2</sup> were tested at 350-450°C and 200-1000 kPa for more than 4000 h. Both hydrogen permeability and selectivity remained stable throughout this testing.
- Pd-Ru composite membranes on PMS discs were also tested in an industrial environment, using a slip stream of the synthesis gas product of UBC's biomass gasifier before clean-up. Tar from the gas gradually coated the surface of the membrane, physically blocking hydrogen permeation, and thereby substantially reducing hydrogen permeability. However, the hydrogen permeability was fully recovered when tar was removed from the surface.

### 3. R&D of Pd-Ag alloy foil-based membranes

NORAM/MRT/UBC made efforts to commercialize its proprietary membrane technology, in particular the fluidized-bed membrane reactor (FBMR) for generation of hydrogen via steam reforming of natural gas [11–13]. This process needs *in situ* hydrogen-selective membranes to extract hydrogen from the reactor at high temperature. Pd-based membranes on porous stainless steel supports with alumina interlayers were tested extensively for this purpose. Unfortunately, the performance of our thin Pd-based composite membranes, prepared by electroless plating, was found to degrade with time at temperatures  $\geq 550^\circ\text{C}$  and at large trans-membrane pressure differences. Therefore, thicker (25  $\mu\text{m}$ ) Pd-Ag foil was selected to separate hydrogen in FBMR under the adverse conditions. Substantial work was carried out to develop Pd-25%Ag foil membranes for hydrogen separation and purification applications in both reactors and purifiers.

#### 3.1. Modularization of Pd-Ag foil membranes for high-temperature and high-pressure applications

- A membrane module box of complex configuration was designed, manufactured and tested. This included porous stainless steel substrates, their supporting structure, gas flow channels and collecting tubes. The box was designed for temperatures as high as 600°C and pressures up to 25 bar.
- A proprietary bonding technique was developed for sealing Pd-Ag foil with regular stainless steel parts. The bonding was strong, with excellent gas-tightness, without any delamination or gas leakage issues. It was also found that the bonding became stronger with time when the membrane modules were used under various operating conditions, especially high temperatures [14].
- A related pre-treatment technique for membrane modularization was also developed. This includes polishing and cleaning of porous stainless steel substrates and inter-diffusion barrier layer coating.
- More than 200 membrane modules were manufactured. The manufacturing process was reproducible. Standard module sizes included 3"x6" (76 x 152 mm), 3"x12" (76 x 305 mm) and 6"x12" (152 x 305 mm), with one- or double-sided membranes. Figure 5 shows photos of two membrane modules.



**Fig. 5.** Membrane modules, a) 25  $\mu\text{m}$  Pd-25%Ag foil, 75 x 280 mm, double-sided; b) 25  $\mu\text{m}$  Pd-25%Ag foil, 152 x 305 mm, double-sided.

#### 3.2. Membrane purifier applications of Pd-Ag foil-based module

Tanaka (Japan) was our main supplier of Pd-25%Ag alloy foil. 25  $\mu\text{m}$  thick Pd-25%Ag alloy foil was generally used for our applications. During the period of our research, Tanaka improved its manufacturing equipment, giving it the capacity to produce thinner (15-20  $\mu\text{m}$ ) Pd-Ag alloy foil with quality similar to that of its 25  $\mu\text{m}$  foil. The newer foil could be up to 300 mm in width, with no limit on length.

Pd-25%Ag foil modules were tested under various conditions. Several commercial units were sold for hydrogen purification applications.

- Our proprietary bonding technique was used to seal Pd-based foil with regular module boxes. Several hundred modules were tested or used in various gas environments at various temperatures (350-600°C). Some modules were tested for up to 14,000 h without detectable leakage through seals.
- A double-sided 3"x6" (76 x 152 mm) membrane module with 25  $\mu\text{m}$  thick Pd-Ag alloy was tested in a H<sub>2</sub>/N<sub>2</sub> mixture at 550°C for more than 1000 h. No degradation in the permeability and selectivity of the module was observed.
- A membrane module with 50  $\mu\text{m}$  Pd-Ag alloy was cycled from 240°C to 565°C in a 36% H<sub>2</sub>/N<sub>2</sub> mixture at 5 bar-a on the feeding side and 1 bar-a on the permeation side for 10+ cycles. The membrane module remained stable, with no detectable leakage after the cycling.
- A membrane purifier prototype with an effective membrane area of 0.12 m<sup>2</sup>, as shown in Figure 6, was designed and built to extract hydrogen from town gas. The molar composition of the town gas was 60.4% H<sub>2</sub>, 19.9% CH<sub>4</sub>, 5.0% CO, 14.7% CO<sub>2</sub> at temperatures of ~300-400°C and pressures up to 20 bar. The purifier was tested for seven start-up/shut-down cycles, with no observable leakage, nor degradation in membrane performance.

Two membrane purifiers of 25  $\mu\text{m}$  Pd-25%Ag foil were sold to European customers for extraction of hydrogen from reformat streams with effective membrane areas of 0.7 m<sup>2</sup> and 1.1 m<sup>2</sup>. Both purifiers met the requirements specified by the customers at delivery, and the customers were satisfied with the performance of the purifiers. Figure 7 shows a photograph of one of these purifiers.

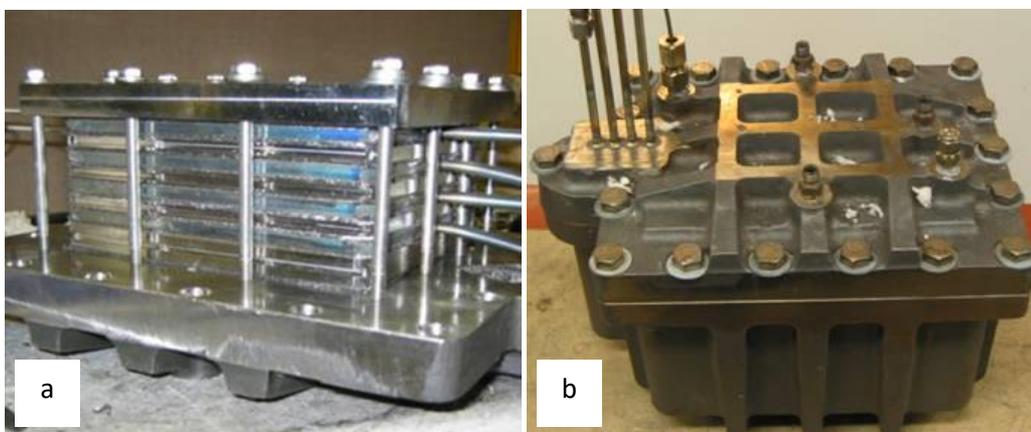


Fig. 6. Purifier for town gas, a) Membrane stack; b) Purifier prototype.

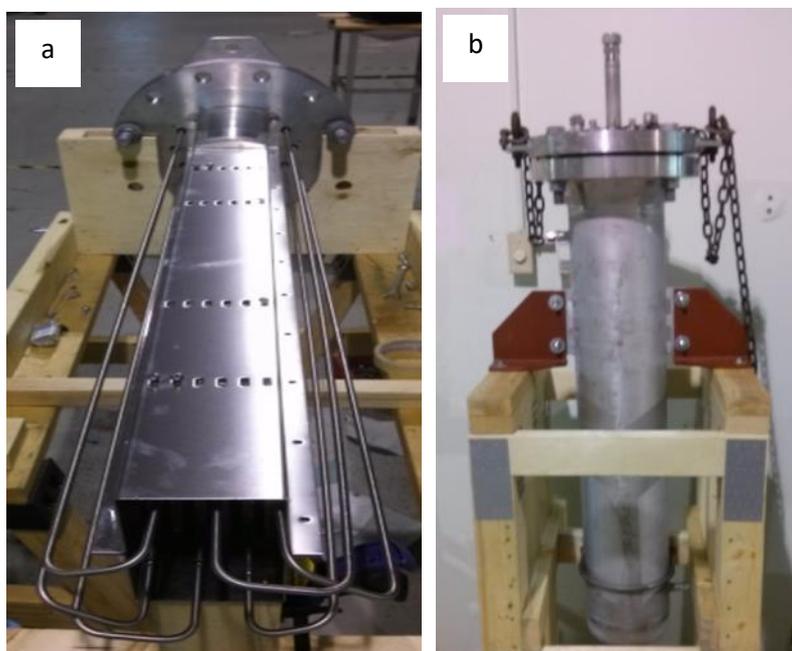


Fig. 7. Commercial membrane purifier, a) Membrane stack; b) Purifier.

### 3.3. Fluidized-bed membrane reactor applications of Pd-Ag alloy foil module

In situ Pd-25%Ag alloy foil-based membrane modules were employed in fluidized-bed membrane reactors (FBMR), a propriety technology developed by NORAM/MRT/UBC for the generation of pure hydrogen from natural gas (as well as other hydrocarbon feedstocks, such as propane) via auto-thermal steam reforming. This reactor technology was tested at various scales during the commercialization efforts. The technologies and major membrane reactor test results are summarized as follows:

#### 1) Internally circulating FBMR (see Figure 8) [7, 15, 16]

- Planar membrane modules were used in a draft box for hydrogen extraction.
- Feed gas flowed upward in the core, with catalyst transported upwards in the core, then descending in the annulus.
- Membranes were located in a region well removed from the oxidant addition zone.
- The solid catalyst particles circulated from the oxidant addition zone, forcing nitrogen to exit from the reactor without reducing the hydrogen concentration needed to maximize the membrane permeation.
- Internal circulation worked, but complicated the mechanical design at

smaller scale.

- Startup and shutdown conditions were critical to achieve membrane longevity.

#### 2) FBMR-demonstration unit for hydrogen production [8,17,18]

Figure 9 consists of both a schematic of a FBMR and a photograph of the demonstration unit built to generate pure hydrogen in a fluidized-bed membrane reactor via steam methane reforming [19,20]. This unit was designed, built and operated at MRT and NORAM, sponsored by the US Department of Energy. The main results were:

- The membrane reactor was designed for 15 Nm<sup>3</sup>/h H<sub>2</sub> production capacity.
- Hydrogen could be pressurized up to 100 bar using a metal hydride compressor.
- Improved 25 μm Pd-25%Ag alloy membrane modules (2.2 m<sup>2</sup>) were used.
- The reactor operated for >500 h, including 1 week of unattended operation.
- The operation was stable.
- Vacuum-assisted permeation was proven.

- Results were generally in good agreement with reactor model predictions.
- Some deactivation of the commercial catalyst was observed, demonstrating that some improvement is required in this aspect of the process.
- The product H<sub>2</sub> purity exceeded 99.99% under normal operating conditions.

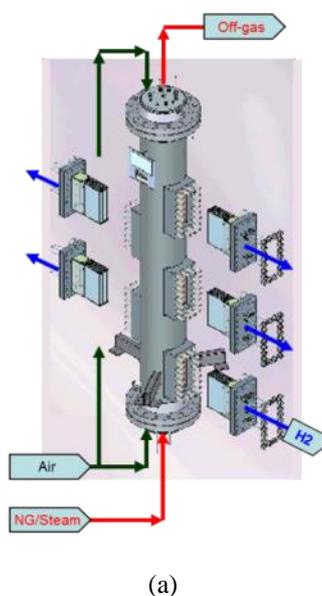
### 3) Sorbent enhanced FBMR technology [21,22]

Figure 10 shows a simple flow-chart and a photograph of the pilot plant built for hydrogen production in a sorption-enhanced membrane reactor. Combining the capture of CO<sub>2</sub> by a sorbent such as CaO with the withdrawal of H<sub>2</sub> could be a process of considerable future interest. This project was jointly carried out by NORAM and Tokyo Gas, with financial support from NEDO Japan and active participation of UBC. The main findings include:

- Some tests were carried out in which membrane separation of hydrogen was coupled with sorption capture of carbon in a steam methane reforming process.
- The hydrogen production capacity was designed to be 1 Nm<sup>3</sup>/h.
- CaO and catalyst solids circulated between the two reactors.
- The best results showed 80% CO<sub>2</sub> capture and > 99.99% pure H<sub>2</sub> produced.
- The results confirmed that CO<sub>2</sub> removal increased H<sub>2</sub> production.
- It was difficult to match temperatures and pressures in the FBMR/carbonator and calcination reactors.
- It was also challenging to circulate solids reliably at this small scale.



Fig. 8. Internally circulating FBMR for hydrogen production.



(a)



(b)

Fig. 9. FBMR demonstration unit for pure hydrogen production at a capacity of 15 Nm<sup>3</sup>/h. (a) Schematic. (b) Photograph

## 4. Conclusions

Hydrogen permeability, selectivity and stability are important properties of membranes for hydrogen separation applications. This paper summarizes work performed to improve key properties of perm-selective membranes and to develop reactors and processes which utilize the membranes. Notable findings included: i) Although both niobium and tantalum offer higher H<sub>2</sub> permeability and lower cost than palladium, their poor resistance to oxidation and hydrogen embrittlement, even after being coated with Pd on their surfaces, prevented their practical application for hydrogen separation. ii) 2-5 μm thick Pd/porous metal composite membranes containing interdiffusion barrier layers of alumina were successfully prepared by electroless plating. These thin Pd composite membranes provided high hydrogen permeability and selectivity, with ideal H<sub>2</sub>/N<sub>2</sub> separation factors up to 100,000. They remained stable at temperatures up to 450°C, with pressure difference of 500 kPa across the membrane. However, the selectivity of the composite

membrane decreased with time at 50 °C or higher, indicating that a pure Pd film was not sufficiently mechanically robust, with micro-cracks developing at high temperatures or high pressures. iii) Palladium/Ruthenium composite membranes were produced with the aid of electroless plating. Compared with Pd and Pd-Ag alloy composite membranes, Pd-Ru composite membranes showed better resistance to hydrogen embrittlement and contaminants, in addition to greater mechanical strength, leading to increased stability at high temperature and high pressure.

A standard manufacturing process was developed for large Pd-Ag alloy foil-based membrane modules, including a suitable sealing technique. The largest membrane module was a double-sided panel of 0.15 m x 0.3 m surface area. This membrane module was immersed in a fluidized bed reactor for hydrogen production from natural gas by steam reforming, where the Pd-Ag alloy membrane area was 2.2 m<sup>2</sup> and the hydrogen production capacity was 15 Nm<sup>3</sup>/h. This membrane was also used with sorbent-enhanced reforming for hydrogen production coupled with CO<sub>2</sub> sequestration.

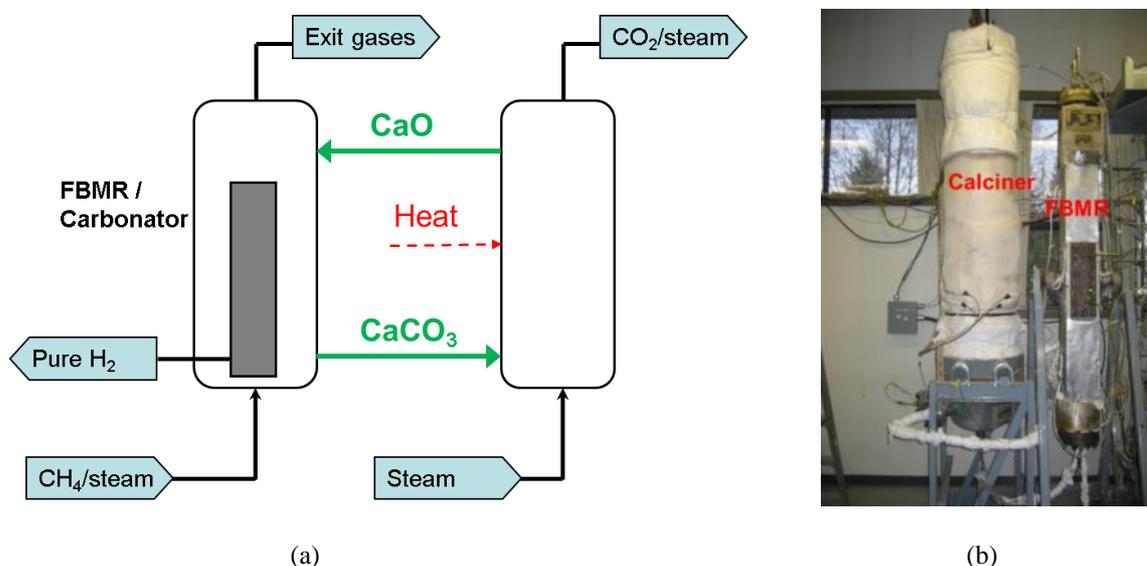


Fig. 10. Sorbent-enhanced FBMR technology for hydrogen production: (a) Simplified flowsheet; (b) Photo of pilot unit built to test the concept.

## References

- [1] R.S. El-Emam, H. Ozcan, Comprehensive review on the techno-economics of sustainable large-scale clean hydrogen production, *J. Clean. Prod.* 220 (2019) 593–609.
- [2] C. Acar, I. Dincer, Review and evaluation of hydrogen production options for better environment, *J. Clean. Prod.* 218 (2019) 835–849.
- [3] G. Solowski, M.S. Shalaby, H. Abdallah, A.M. Shaban, A. Cenian, Production of hydrogen from biomass and its separation using membrane technology, *Renew. Sustain. ENERGY Rev.* 82 (2018) 3152–3167.
- [4] M.R. Rahimpour, F. Samimi, A. Babapoor, T. Tohidian, S. Mohebi, Palladium membranes applications in reaction systems for hydrogen separation and purification: A review, *Chem. Eng. Process. Intensif.* 121 (2017) 24–49.
- [5] A. Li, J.R. Grace, C.J. Lim, Preparation of thin Pd-based composite membrane on planar metallic substrate. Part II. Preparation of membranes by electroless plating and characterization, *J. Memb. Sci.* 306 (2007) 159–165.
- [6] S.M. Lee, N. Xu, S.S. Kim, A. Li, J.R. Grace, C.J. Lim, T. Boyd, S.-K. Ryi, A. Susdorf, A. Schaadt, Palladium/ruthenium composite membrane for hydrogen separation from the off-gas of solar cell production via chemical vapor deposition, *J. Memb. Sci.* 541 (2017) 1–8.
- [7] J. Grace, C. Lim, A.-E. Adris, D. Xie, D. Boyd, W. Wolfs, C. Brereton, Internally circulating fluidized bed membrane reactor system, US patent 7,141,231 (2006), (2005).
- [8] J. Grace, S.S.E.H. Elnashaie, C.J. Lim, Hydrogen Production in Fluidized Beds with In-Situ Membranes, *Int. J. Chem. React. Eng.* 3 (2005).
- [9] X. Li, A. Li, C.J. Lim, J.R. Grace, Hydrogen permeation through Pd-based composite membranes: Effects of porous substrate, diffusion barrier and sweep gas, *J. Memb. Sci.* 499 (2016) 143–155.
- [10] S.-K.K. Ryi, A. Li, C.J. Lim, J.R. Grace, Novel non-alloy Ru/Pd composite membrane fabricated by electroless plating for hydrogen separation, *Int. J. Hydrogen Energy.* 36 (2011) 9335–9340.
- [11] A.M. Adris, C.J. Lim, J.R. Grace, The fluidized bed membrane reactor system: A pilot scale experimental study, *Chem. Eng. Sci.* 49 (1994) 5833–5843.
- [12] A.E.M. Adris, J.R. Grace, Characteristics of Fluidized-Bed Membrane Reactors: Scale-up and Practical Issues, *Ind. Eng. Chem. Res.* 36 (1997) 4549–4556.
- [13] A.-E. Adris, J. Grace, C.J. Lim, S. Elnashaie, Fluidized bed reaction system for steam hydrocarbon gas reforming to produce hydrogen, US patent 5,326,550, 1994.
- [14] A. Li, Diffusion bonding for metallic membrane joining with metallic module, US Patent 7,353,892, 2008.
- [15] T. Boyd, J. Grace, C.J. Lim, A.E.M. Adris, Hydrogen from an internally circulating fluidized bed membrane reactor, *Int. J. Chem. React. Eng.* 3 (2005).
- [16] D. Xie, C.J. Lim, J.R. Grace, A.-E.M. Adris, Gas and particle circulation in an internally circulating fluidized bed membrane reactor cold model, *Chem. Eng. Sci.* 64 (2009) 2599–2606.
- [17] M.A. Rakib, J.R. Grace, C.J. Lim, S.S.E.H. Elnashaie, Steam reforming of heptane in a fluidized bed membrane reactor, *J. Power Sources.* 195 (2010) 5749–5760.
- [18] M.A. Rakib, J.R. Grace, C.J. Lim, S.S.E.H. Elnashaie, Modeling of a Fluidized Bed Membrane Reactor for Hydrogen Production by Steam Reforming of Hydrocarbons, *Ind. Eng. Chem. Res.* 50 (2011) 3110–3129.
- [19] Z. Chen, J.R. Grace, C.J. Lim, A. Li, Experimental studies of pure hydrogen production in a commercialized fluidized-bed membrane reactor with SMR and ATR catalysts, *Int. J. Hydrogen Energy.* 32 (2007) 2359–2366.
- [20] A. Mahecha-Botero, T. Boyd, A. Gulamhusein, N. Comyn, C.J. Lim, J.R. Grace, Y. Shirasaki, I. Yasuda, Pure hydrogen generation in a fluidized-bed membrane reactor: Experimental findings, *Chem. Eng. Sci.* 63 (2008) 2752–2762.
- [21] K. Johnsen, H.J. Ryu, J.R. Grace, C.J. Lim, Sorption-enhanced steam reforming of methane in a fluidized bed reactor with dolomite as CO<sub>2</sub>-acceptor, *Chem. Eng. Sci.* 61 (2006) 1195–1202.
- [22] Y. Chen, A. Mahecha-Botero, C.J. Lim, J.R. Grace, J. Zhang, Y. Zhao, C. Zheng, Hydrogen Production in a Sorption-Enhanced Fluidized-Bed Membrane Reactor: Operating Parameter Investigation, *Ind. Eng. Chem. Res.* 53 (2014) 6230–6242.