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## Asymmetric layered vanadium membranes for hydrogen separation

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## ABSTRACT

Layered alloy membranes, with sub-micron Pd catalyst layers over a highly permeable vanadium alloy core, provide a low-cost alternative to supported Pd-alloy membranes. Despite the minimal Pd consumption, Pd still comprises a significant fraction of the overall membrane costs, and further cost reductions can be achieved by replacing Pd with suitable alternative catalytic layers. Ni is an obvious candidate, exhibiting high catalytic activity for a range of reactions while being relatively inexpensive, but its instability in syngas renders it unsuitable as a feed-side catalyst. The permeate surface of an alloy membrane is exposed to H<sub>2</sub> only during operation, making Ni of interest as a permeate-side catalyst.

Asymmetric Pd/V/Ni alloy membranes have been fabricated with varying Ni thickness, and hydrogen permeance has been examined over a wide range of pressures and temperatures. Hydrogen permeance increases with decreasing Ni thickness, down to a limiting thickness of 150 nm, beyond which permeance degraded due to incomplete Ni coverage. The permeance was 65% that of a symmetrical Pd/V/Pd membrane with 500 nm Pd layers. The cost-effectiveness is dependent on raw Pd price and manufacturing costs.

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## 1. Introduction

Hydrogen-selective alloy membranes are an emerging technology which allow the continuous separation of hydrogen mixed gas streams at elevated temperatures. With most of the global H<sub>2</sub> production arising from gasification and reforming processes, membrane-based separation has the potential to significantly increase the efficiency and decrease the cost of H<sub>2</sub> production relative to conventional, separate conversion and separation processes.

Palladium-based alloy membranes are the clear benchmark technology, having already entered commercial production as well as being the subject of numerous long-term industrial trials. Pd combines high catalytic activity for hydrogen dissociation and recombination with reasonable permeability, tolerance to CO and in the case of some alloys, tolerance to H<sub>2</sub>S (eg., Pd–Cu [1–3], Pd–Au [4–6]). Palladium's high price (currently \$US 28,710 per kg, or \$US 350 per m<sup>2</sup> per μm thickness) [7] is its main drawback, and commercial viability can only be achieved by minimising Pd consumption though minimising membrane thickness and alloying with less expensive metals (eg, Pd–Cu [8,9], Pd–Ni [10], Pd–Fe [11], Pd–Ag [12,13], Pd–Cu–Ni [14,15]).

A competing approach to minimising membrane thickness is to create membranes from highly permeable but less-expensive metals. The seminal work of Steward [16], presented in graphical form by Buxbaum and Marker [17], shows that Group IV and V metals such as V, Ti, Zr and Nb exhibit hydrogen permeabilities several orders of magnitude greater than Pd. Of these metals, vanadium offers the best combination of performance, cost and formability, but like the others in this series, it is prone to hydrogen embrittlement [18] through strong hydrogen absorption [19] and α→β hydride phase transition [20]. Considerable effort has been expended to identify more robust V-based alloys, and significant advances have been made in improving resistance to hydrogen embrittlement.

The high reported permeability really only takes into account hydrogen transfer through the bulk alloy. Without the ability to exchange hydrogen with the feed and permeate gas streams, however, even the most permeable metals will not function effectively as a membrane. Vanadium forms a tightly held oxide which is a poor catalyst for hydrogen dissociation and recombination. Furthermore, the oxide layer itself acts as a barrier to hydrogen transport such that, even if H<sub>2</sub> were dissociated, it could not penetrate the oxide layer to enter the bulk vanadium metal. Because of this, vanadium-based membranes can only function if this oxide layer is stripped off and replaced with a suitably catalytic material. In most reported cases to date, this applied layer has been palladium [17,19,21,22], or an alloy of palladium [23,24], thereby imparting the favourable properties described above.

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The layered configurations of these V-based membranes gives rise to the option of depositing different catalysts on the feed and permeate surfaces. Whereas the feed catalyst must exhibit tolerance to CO and H<sub>2</sub>S, there is no such requirement for the permeate surface as it is exposed to H<sub>2</sub> only during permeation, and possibly an inert gas during start-up and shut-down. Tolerance to CO and H<sub>2</sub>S is therefore not required, leaving high catalytic activity as the main consideration. This gives rise to the option of using Pd-free catalysts such as Ni [25–27] and Mo<sub>2</sub>C [28]. Ni in particular combines high catalytic activity in the temperature range of interest with low cost and ease of deposition through an electroless plating or electroplating process. Ni is known to bind strongly with CO [29,30] and H<sub>2</sub>S [31,32], rendering it unsuitable for use as a feed-side catalyst, but its high catalytic activity for H<sub>2</sub> dissociation [27] and low cost (~\$US 15 per kg, or just \$US 0.17 per m<sup>2</sup> per μm thickness) [33] make it a leading candidate as a Pd-free permeate-side catalyst.

On the negative side, the permeability of Ni ( $\sim 2 \times 10^{-11}$  mol m<sup>-1</sup> s<sup>-1</sup> Pa<sup>-0.5</sup> at 400 °C) [34] is significantly lower than that of Pd ( $\sim 1.1 \times 10^{-8}$  mol m<sup>-1</sup> s<sup>-1</sup> Pa<sup>-0.5</sup> at 400 °C) [35], meaning a Ni will generate significantly greater transport resistance than Pd. The depth of the Ni layer will therefore strongly influence the overall permeability of an asymmetric membrane.

Based on the above review, it is clear that Ni is worthy of investigation as a permeate-side catalyst for hydrogen recombination. To evaluate this further, we will evaluate the permeability of asymmetric Pd/V/Ni alloy membranes under a range of temperatures, pressures and Ni thicknesses. The observed hydrogen transport will be correlated with physical observations of the pre- and post-permeation membranes.

## 2. Experimental

### 2.1. H<sub>2</sub>-D<sub>2</sub> exchange

Adsorption and desorption kinetics of H<sub>2</sub> in Ni was studied by measuring hydrogen–deuterium dissociation (H<sub>2</sub>+D<sub>2</sub>⇌HD). Ni foil was ultrasonically cleaned and cut into  $\sim 2$  mm × 2 mm squares and loaded into a quartz-lined packed bed reactor. The total area of alloy ribbon used was  $\sim 10$  cm<sup>2</sup>. H<sub>2</sub>-D<sub>2</sub> exchange studies were carried out in the temperature range of 50–400 °C by introducing H<sub>2</sub> and D<sub>2</sub> at flow rates of 10 ml/min, and measuring the relative concentrations of H<sub>2</sub>, D<sub>2</sub> and HD using a mass spectrometer (European Spectrometry Systems). The reactor outlet was connected to the mass spectrometer with Teflon tubing to minimise any background conversion. Background conversion measurements were performed using an empty reactor at all temperatures of interest. Calibration of the mass spectrometer was achieved by loading the reactor with an excess of Pd foil to ensure complete conversion of H<sub>2</sub> and D<sub>2</sub> to HD. Statistically, complete conversion was achieved when the concentrations at the outlet of the reactor were 25% H<sub>2</sub>, 25% D<sub>2</sub> and 50% HD.

### 2.2. Membrane preparation

A drawn vanadium tube, 9.5 mm (3/8") diameter with a wall thickness of 0.2 mm was used as the core for all membranes. The outer (feed) and inner (permeate) surfaces were prepared and electroplated separately. The inner surface was electroplated first, after which the ends of tube were sealed and the outer surface was then electroplated.

The inner surface of the tube was abraded using a SiC impregnated nylon brush with deionised (DI) water as a lubricant. A nylon brush and detergent was then passed through the tube to remove any remaining grinding debris and grease followed by a



Fig. 1. Macrograph of vanadium tube surface as received (top) and after cleaning (bottom).

rinse in DI water. The final preparation step was a cathodic etch in 10% HF in DI water.

The outer surface was prepared by rotating the tube between centres and abrading the surface with SiC paper and DI water lubricant. This was followed by cleaning with detergent and cotton wool and DI water rinse. As with the inner surface, the final step was a cathodic etch in 10% HF in DI water. Fig. 1 shows the surface of the vanadium tube as received with heavy oxide layer, and after mechanical abrasion and cathodic etching in 10% HF.

Commercial electroplating solutions were chosen for both Pd and Ni deposition. The Pd solution contained 2 g l<sup>-1</sup> Pd and was pH neutral ( $\sim 7.2$ ). The acidic Ni solution contained 5 g l<sup>-1</sup> and had a pH of 3.9. Five membranes were prepared for evaluation: four asymmetric Pd/V/Ni membranes (#1–4) were prepared with a 500 nm layer of Pd on the feed surface and varying thicknesses of Ni deposited on the permeate surface. One symmetric Pd/V/Pd membrane (#5) was prepared with a 500 nm layer of Pd on both surfaces and used as a reference in H<sub>2</sub> flux measurements.

Plated tubes were annealed under vacuum at 300 °C for 12 h. Examples of the post-annealed tubes are shown in Fig. 2. 20 mm was then cut from one end of the tubes for pre-permeation analysis. The remaining 80 mm was used for permeation testing.

### 2.3. Hydrogen permeation testing

Membranes were mounted into a tube-in-shell reactor using compression fittings and graphite ferrules. The reactor was then mounted in a custom permeation test rig described previously [36].

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