



## Tubular vanadium membranes for hydrogen purification

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### ARTICLE INFO

#### Keywords:

Vanadium  
Palladium  
Hydrogen  
Hydride  
Membrane

### ABSTRACT

It is widely accepted that vanadium is unsuitable as a membrane material due to an extreme susceptibility to hydrogen embrittlement. Consequently, the focus of R&D effort towards hydrogen-selective, vanadium-based metal membranes in recent years has been the development of robust alloys with improved embrittlement resistance. What the literature hasn't really addressed, however, is whether vanadium's shortcomings can be overcome through the implementation of suitable controls. This work attempts to address this question by closely examining V-H phase equilibrium and undertaking practical demonstrations of Pd-coated vanadium membranes in a tubular geometry.

Membranes were prepared from a 500 mm-long tubular 99.9% V substrate, coated on each surface with Pd catalyst layers. This single tube was sectioned for several permeation and hydrogen absorption tests. An examination of the V-H phase diagram show that hydride phase transitions ( $\alpha \rightarrow \beta$ ,  $\beta \rightarrow \gamma$ ) and corresponding miscibility gaps can readily be avoided using appropriate operating procedures. Hydrogen permeating testing showed these membranes exhibit very high permeability (initially exceeding  $3.0 \times 10^{-7} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-0.5}$  at 320 °C and above) which allows the use of thick-walled ( $\sim 0.25 \text{ mm}$ ), self-supporting, pinhole-free vanadium tubes as the membrane substrate. These membranes also exhibited robustness, with mechanical integrity being maintained through multiple thermal and hydride cycles and over several hundred hours of testing.

This work shows that the main natural advantages of vanadium (low cost relative to Pd and very high permeability which affords the use of self-supporting, defect-free substrates) can still be exploited if used in conjunction with appropriate geometry and operating procedures.

### 1. Introduction

The high permeability of a number of group IVb and Vb metals, and their alloys, is well reported [1], and they are considered prospective candidates for use in hydrogen-selective metal membranes [2]. Of these metals, vanadium has received most attention due to its relatively high solubility for alloying elements, favourable hydride phase stability, relatively low cost and favourable mechanical properties (e.g., [3–5]). These membranes can potentially produce hydrogen at lower cost than the benchmark Pd-based membrane technology.

The shortcoming of vanadium and other Group IVb and Vb metals, relative to Pd, is that their hydrogen absorption is significantly greater. While this contributes to their high permeability by creating a large concentration gradient of dissolved hydrogen during permeation, it also leads to issues with hydrogen embrittlement due to expansion, decohesion and hydride phase transitions. Hydrogen absorption can be reduced through alloying, but alloying also has implications with respect to hydrogen diffusivity, hydride phase stability and mechanical properties. To date, selection of vanadium alloy compositions for

experimental validation has been largely a trial-and-error affair, which is time and cost prohibitive considering the vast potential compositional space.

This body of work on vanadium alloys is largely driven by the assumptions that vanadium membranes are fundamentally unsuitable for practical applications due to the above-mentioned shortcomings, but it can be argued that the reported literature doesn't address this assumption. This begs the question of whether these assumptions are unfounded, and whether pure V can be used as a reliable membrane material. Here we address this question by exploring vanadium hydride phase equilibrium and observing the performance of vanadium membranes under a range of operating conditions.

Metal membranes are essentially metal hydrides with a geometry which enables hydrogen transfer between adjacent atmospheres of high and low partial pressure of hydrogen. Unlike metal hydrides for hydrogen storage, however, membranes ideally are operated in manner which prevents hydride phase transition, and the degradation of mechanical properties which can occur as a result. This phenomenon is widely classified as hydrogen embrittlement, but is actually the result of

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**Table 1**  
Summary of vanadium hydride phases.

Phase	
$\alpha$	Body-centred cubic (BCC) extending to $\text{VH}_{0.05}$ , $a = 3.037 \text{ \AA}$ [6] H randomly distributed in tetrahedral sites [7]
$\beta$	Body-centred tetragonal (BCT) with $c/a = 1.1$ [6], but also reported to be monoclinic ( $\alpha = 91^\circ$ ) [8] Occupancy in $\text{O}_{z1}$ octahedral sites [7,9] Exists in the range $\text{VH}_{0.41} - \text{VH}_{0.61}$ below $175^\circ \text{C}$ [10]
$\epsilon$	Called $\beta_2$ by Fukai [11] equal occupancy between $\text{O}_{z1}$ and $\text{O}_{z2}$ sites [9,11] $\text{VH}_{0.40}$ to $\text{VH}_{0.80}$ , $a = 3.01 \text{ \AA}$ , $c = 3.295 \text{ \AA}$ [10] The high-temperature form of $\beta$
$\gamma$	Face-centred cubic (FCC) from $\text{VH}_{0.90}$ to $\text{VH}_{2.00}$ [6] $a = 4.27 \text{ \AA}$ [12]
$\delta$	Ordered $\text{V}_3\text{H}_2$ phase in low-temperature region of $\beta$ phase [13] below $-49^\circ \text{C}$ [14]
$\zeta$	VH superstructure achieved by filling empty sites in $\epsilon$ [15]
$\eta$	Probably similar to $\beta$ but with higher degree of order [15]

several phenomena which may or may not involve hydride phase transitions. Despite the perception of vanadium as being prone to embrittlement, any metal membrane can fail due to embrittlement, including Pd membranes. Importantly, this hasn't stopped progress towards commercialisation of Pd membranes, as two strategies (management and modification) exist to minimise the impact of embrittlement on membrane lifetimes.

The “management” approach involves understanding the hydride phase equilibrium, and operating the membrane in a manner which avoids phase transitions. Metal membranes are metal hydrides insofar as hydrogen dissolves chemically into the metal, occupying interstices in the lattice. Hydrogen is therefore an alloying element, donating its electrons to the band structure, altering the electronic and mechanical properties of the host metal. Hydriding can also result in phase transitions which are not characteristic of the host. Therefore, while vanadium may be phase stable below its melting point of  $1910^\circ \text{C}$ , vanadium hydride most certainly is not. This is illustrated in Table 1 which summarises reported vanadium hydride phases.

The “modification” approach to avoiding fracture due to hydride phase transitions is to suppress these transitions to temperatures below those encountered during normal operation. This approach is analogous to that of the Pd-Ag<sub>23</sub> alloy: whereas the  $\alpha + \beta$  miscibility gap for palladium hydride exists below  $297^\circ \text{C}$ , it is well known that alloying Pd with 23 wt% Ag suppresses this miscibility gap to below ambient temperature [16].

We have previously reported that the  $\alpha + \beta$  miscibility gap in vanadium can be suppressed to below ambient temperature through addition of aluminium [17], whereas alloying with nickel increases the temperature at which this miscibility gap exists (up to  $\sim 400^\circ \text{C}$ ). It is the  $\beta + \gamma$  gap, however, which may be of greater concern as it lies within a temperature-pressure region which may be encountered during operation.

This work is in some ways a step back from current thinking on vanadium-based membranes. Numerous studies over the past 15 years have been devoted to understanding the hydrogen permeability of a range of vanadium alloys, but there is inadequate justification in the literature for why unalloyed vanadium is unsuitable. Here we manufacture Pd-coated vanadium membranes with a tubular geometry, measure their hydrogen absorption and permeability, and in doing so, devise strategies for overcoming the main mechanisms by which these membranes can fail.

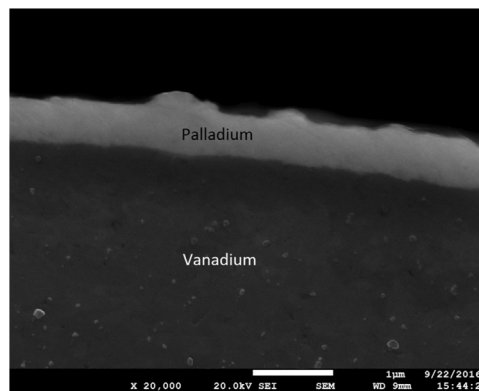


Fig. 1. Cross-section of Pd catalyst layer on vanadium substrate.

## 2. Materials and methods

### 2.1. Membrane preparation

Drawn 99.9% Vanadium tubing (9.54 mm (3/8”) outer diameter, 0.28 mm wall thickness, 500 mm long) was used as the membrane substrate. The inner and outer surfaces were abraded using SiC grit under flowing deionised water. A  $0.5 \mu\text{m}$ -thick Pd layer, shown in Fig. 1, was electroplated onto the inner and outer surfaces using commercial palladium electroplating solution. The tube was cut to 75 mm lengths for testing, and membrane ends were sealed using commercial 3/8” compression fittings with graphite ferrules, giving an exposed area of  $15.0 \text{ cm}^2$ . A sealed membrane is shown in Fig. 2.

### 2.2. Absorption testing

A 0.2 g sample of the Pd-coated tube was sectioned from a membrane and used for hydrogen absorption testing. Absorption was measured using the Sieverts' technique in a Hiden Isochema IMI-HTP instrument. Multiple absorption isotherms were measured for each temperature until duplicate measurements were achieved.

### 2.3. Permeation testing

$\text{H}_2$  flux through the membranes was measured using the constant pressure method under 99.99%  $\text{H}_2$ . Each membrane was sealed inside a 1” outer diameter SS316 tube. One thermocouple was positioned inside the membrane, and another external to the membrane. A constant flow of  $\text{N}_2$  was fed to the outer surface of the membrane, and a vacuum was applied to the inner surface using a diaphragm pump, while the membrane was heated using a tube furnace. When the desired membrane temperature was attained,  $\text{N}_2$  flow was stopped and  $\text{H}_2$  (99.99%) was introduced to the outer surface, and the  $\text{H}_2$  flux was measured using an electronic mass flow meter (Aalborg). Once  $\text{H}_2$  flux stabilised, indicating the activation period had elapsed,  $\text{H}_2$  flux was measured at a series of feed pressures, and a permeate pressure of 0.10 MPa (ambient). This pressure series was repeated at 340, 320, 300 and  $280^\circ \text{C}$ .

Membrane integrity was confirmed before and after the permeability measurements by briefly feeding 25%  $\text{N}_2$  in  $\text{H}_2$  to the membrane,

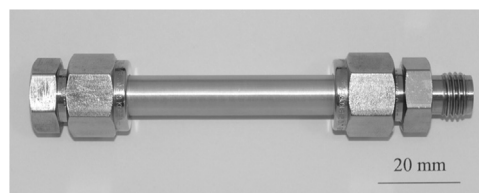


Fig. 2. Membrane prior to testing, with the left end capped, and the right end to be connected to a flow meter and mass spectrometer for flux and purity measurements.

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