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Design and operational considerations for a catalytic membrane reactor incorporating a vanadium-based membrane

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ABSTRACT

Self-supporting vanadium-based metal membranes, comprising a vanadium core overlaid with hydrogen dissociation and recombination catalysts, are a low-cost alternative to the current benchmark Pd-based membranes. Absorption of hydrogen, however, significantly degrades the mechanical properties of the host metal, and causes significant volume expansion of the membrane. Consequently, these membranes must be operated within narrow temperature and pressure windows, and must be free to expand upon absorption of hydrogen. These conditions can be attained readily when operating these membranes as hydrogen separators, but the introduction of a catalyst to create a water–gas-shift catalytic membrane reactor (WGS CMR) introduces conditions which may be in conflict with the membrane requirements. Here we have described efforts to develop a scalable vanadium-based, packed-bed CMR which is heated only by the feed gas and the WGS reaction exotherm. Difficulty in achieving a suitable temperature profile along the length of the CMR, and membrane fractures due to the mechanical constraints of the packed catalyst bed proved to be problematic, and we conclude that the packed-bed configuration is unsuitable for this membrane type. While these initial results were less than stellar, they have clearly pointed the way for future iterations with respect to configuration and operation. Three alternative CMR configurations have been proposed.

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1. Introduction

A reduction in CO₂ emissions associated with large-scale, coal-based power systems can be achieved by post-combustion CO₂ capture (PCC), oxy-fuel combustion or pre-combustion CO₂ capture. Pre-CC, unlike PCC and oxy-fuel, is a gasification specific technology, and involves shifting the energy content in coal to H₂ via CO, and separating the resulting H₂/CO₂ mixture prior to H₂ utilisation. Gasification-based power generation offers an inherent efficiency advantage over combustion-based systems [1], and this advantage is magnified when the energy penalty associated with CO₂ capture is accounted for.

Gasification-based pre-CC has yet to be demonstrated on a commercial scale, however several favourable economic analyses were reported in the mid-2000s [2,3]. Around this time, several full-scale demonstrations in the USA (FutureGen 1.0 [4]) and Australian (ZeroGen [5]) reached the advanced stages of planning, but were halted prior to the commencement of construction. These plants were to have been based on modular gasification,

acid gas capture, shift and H₂/CO₂ separation technologies which have all been proven commercially in other industries, but never as part of an integrated gasification-combined cycle power system.

It is the water–gas-shift reaction (CO + H₂O ⇌ CO₂ + H₂, ΔH₂₉₈ = −41.1 kJ mol^{−1} [6]) which makes pre-CC possible by shifting the energy content of CO (the main product of gasification) to H₂. This reaction is kinetically limited, and catalysts are required to achieve acceptable reaction rates. Commercial sweet-shift catalysts (*i.e.*, operating in desulfurised syngas) for the high-temperature (>350 °C) regime are predominantly iron-based [7–9]. Hla [8] derived a power rate law for the WGS reaction over a commercial iron–chromium-based catalyst:

$$R = 10^{0.66} \exp\left(-\frac{88}{RT}\right) p_{\text{CO}}^{0.90} p_{\text{H}_2\text{O}}^{0.31} p_{\text{CO}_2}^{-0.15} p_{\text{H}_2}^{-0.05} \quad (1)$$

The WGS reactants (CO and H₂O) have a strong influence on kinetics, whereas the reaction products (CO₂ and H₂) both have a smaller reverse effect on the reaction rate. As Fig. 1 shows, the rate of the WGS reaction increases by an order of magnitude between 350 and 450 °C. Being exothermic, this can lead to a runaway reaction as the exothermic heat release increases the system

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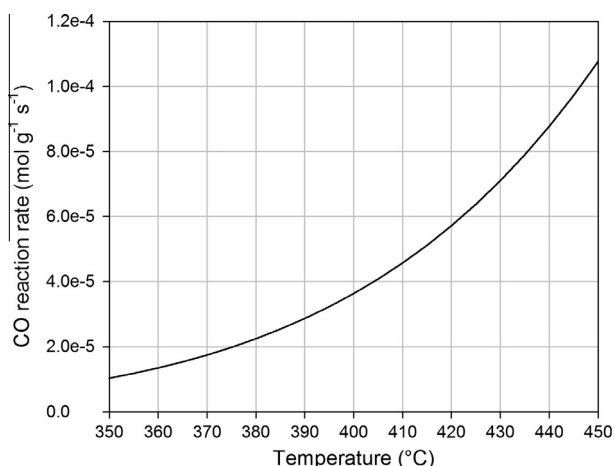


Fig. 1. Rate of CO consumption per mass of catalyst and 3:1 H₂O:C, based on power rate law published by Hla [8].

temperature and the rate, which in turn increase the rate of heat release. The temperature must therefore be carefully managed to prevent such temperature excursions.

The inverse relationship between kinetics and thermodynamics necessitates the use of several reaction stages to achieve acceptable CO conversion: a high-temperature (~400 °C stage which offers fast kinetics but an equilibrium-limited conversion of ~90%), followed by a low-temperature stage (~200 °C) which enables higher conversion but with slower kinetics. This is less than optimal with respect to plant size, cost and thermal efficiency, and is the *raison d'être* for the catalytic membrane reactor (CMR), a device which integrates the shift reaction with in situ H₂ removal via a membrane, thereby creating a conditions which allow this equilibrium barrier to be broken.

The WGS-CMR has been demonstrated by several groups, typically combining a granular, commercial WGS catalyst with palladium-alloy membranes in a planar [10,11] or tubular [12–15] configuration, and operated in the temperature range 350–450 °C. CO conversions well in excess of equilibrium, and H₂ yields in excess of 90% have been routinely reported, depending on reactor geometry, space velocities and pressures. Although not yet proven on a commercial scale, the CMR offers advantages over conventional technology with respect to economics and efficiency, but uncertainties remain around durability and raw materials costs (especially Pd) [16–18].

The issue of high membrane costs is being addressed through the development of self-supporting, layered metal membranes based on vanadium [19], but the robustness (or lack thereof) of these membranes is perhaps the main aspect of this technology which is limiting commercial deployment. Temperature sensitivity is of particular concern. Operation at low temperatures (<300 °C) can result in failure due to hydrogen embrittlement from excessive absorption and $\alpha\beta$ hydride phase transitions [20–22], and although this can be addressed through alloying [23,24], reducing H absorption also reduces hydrogen permeability. At elevated temperatures, degradation can occur through formation of compounds at the interface of the metal and any applied catalyst layers. In the case of V–Pd, these can form at temperatures as low as 400 °C [25].

An additional consideration is the significant volume expansion arising from hydrogen absorption. As shown in Fig. 2, vanadium can expand by almost 10% at 400 °C as a result of hydrogen absorption at hydrogen partial pressures corresponding to WGS CMR conditions [21]. The effect is even more pronounced as temperature is decreased.

Attaining sufficiently long membrane lifetimes to make this technology viable necessitates that membranes be operated in a

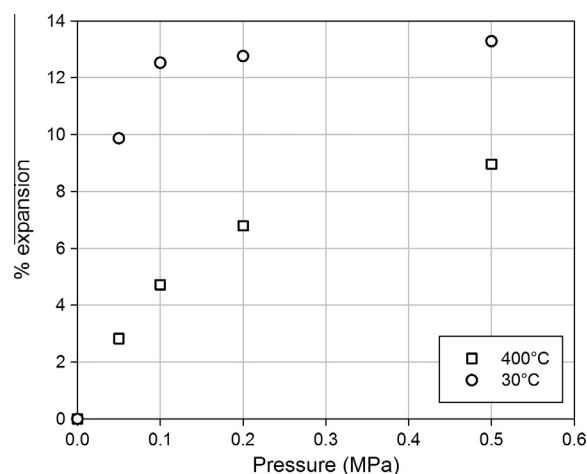


Fig. 2. Volume expansion of vanadium as a function of hydrogen partial pressure at several temperatures [21].

very narrow range of defined operating conditions (including temperature, impurity concentrations, and prescribed start-up and shut-down procedures). The embrittlement tendency, high power output associated with the WGS reaction, and large volume expansion associated with H absorption must be managed appropriately to ensure the performance and durability of the membrane is not impacted. Here we explore these issues further in a prototype tube-in-shell WGS-CMR incorporating a self-supporting, vanadium-based tubular membrane, and discuss their implications respect to CMR design and operation. The lessons learned will inform CMR design and operation as the scale of the technology is increased.

2. Experimental

2.1. Catalyst and membranes

Self-supporting, tubular vanadium membranes were fabricated from 9.52 mm (3/8") OD × 0.200 mm-thick vanadium tube, overlaid by 0.50 μm-thick electroplated Pd films on the inner and outer surfaces. These were sealed using commercial compression fittings. The membranes, shown in Fig. 3, were 0.33 m long which left an area of 0.009 m² after sealing. The surfaces were prepared by degreasing in 1% Alconox detergent, followed by abrasion with 120 grit SiC. The surface was then cathodically etched in 10% HF, followed by immediate electrodeposition of a 0.50 μm-thick Pd layer. The inner and outer surfaces were prepared in separate steps. Finally, coated membranes were annealed under vacuum at 350 °C for 12 h to remove any H absorbed by the vanadium during electroplating.

High-temperature WGS catalyst was obtained from a commercial supplier in the form of 6.0 × 6.0 mm pellets. The catalyst was manually ground and sized to +500–850 μm. The catalyst was diluted with inert media (borosilicate glass beads) of the same particle size in the ratio 10:90 catalyst:inert (g/g).

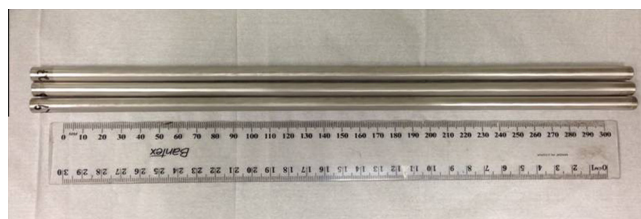


Fig. 3. 9.52 mm OD × 0.33 m-long V-based membranes.

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