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Hydrogen selective membranes: A review of palladium-based dense metal membranes

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ABSTRACT

High purity hydrogen has many applications one of which is in the hydrogen fuel cell industry. Hydrogen can be easily produced from water electrolysis; however, the most economical method is steam reforming of methane. This delivers a mixture of gaseous compounds from which hydrogen can be extracted. Besides various techniques such as pressure swing adsorption and cryogenic distillation, dense metal membranes offer an energy efficient and highly selective method for separating hydrogen from a hot gas mixture achieving high purity levels.

This review article covers the fundamentals of hydrogen selective membranes for both the porous and dense kind. An in-depth look at dense and porous membranes is taken to establish their current development and a comparison is drawn between both types showing that dense metal membranes have the best hydrogen flux and selectivity. A variety of commercial dense metal membranes are compared revealing the Group V elements such as vanadium (V), niobium (Nb) and tantalum (Ta) to have the highest hydrogen permeability. A major limitation with these metals is their tendency to form a stable oxide layer under ambient conditions. Palladium (Pd) does not suffer this problem at typical membrane operating conditions and with relatively high hydrogen permeability is a suitable alternative as a dense metal membrane. Over the years it has been discovered that alloying Pd with elements such as silver (Ag), yttrium (Y) and copper (Cu) results in marked improvements in hydrogen permeability, mechanical durability and in some cases resistance to contamination by sulphur containing compounds. Nevertheless, there are still opportunities to improve the performance of the existing commercial Pd-based membranes by investigating the endless scope of unexplored Pd binary and ternary alloys.

Contents

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1. Introduction

The current fossil fuel based economy has presented many global issues in recent times, most notably rising energy prices and climate change. As a result, efforts have been focussed towards developing a renewable, sustainable and environmentally friendly energy system to reduce reliance on fossil fuels. A hydrogen based economy has shown potential to be a key part of the solution. With heavy research activity underway to optimise means of producing hydrogen from renewable sources, the realisation of a hydrogen economy appears imminent.

Nowadays, steam methane reforming (SMR) is the most common method for hydrogen production. The composition of the SMR product stream is typically 74% H_2, 18% CO_2, 7% CH_4 and 1% CO [1]. The water gas shift reaction involving steam is used to convert CO to CO_2 and H_2; however, contamination of the gas stream with CO remains. While CO_2 and H_2O can be removed from the gas stream via condensation, CO requires a further purification step. A majority of applications need a minimum hydrogen purity of 99.99%, whereas, polymer electrolyte fuel cells (PEFCs) require ultra-pure hydrogen (99.9995%) and can only tolerate contaminants in the parts per million within the feed stream. Any higher would be sufficient to poison the platinum catalyst used by PEFCs. Thus, hydrogen separation is an essential process constituting up to half of the production cost [2].

Membrane technology has been in strong development over the past 50 years and during this period has established a time and tested manufacturing method. Nowadays, membranes can be used in a variety of applications including micro-filtration of bacteria to reverse osmosis for water clean-up. Membranes hold many advantages such as [3]:

- Typically low energy consumption;
- ability to carry out separation continuously;
- mild process conditions;
- ease of scaling up;
- absence of additives; and
- possibility to combine with other separation technologies.

Important disadvantages are, depending on the specific membrane type, as follows:

- Fouling tendency;
- low membrane lifetime;
- low selectivity or flux; and
- more or less linear scaling up factor (whereas competing processes exhibit economies of scale).

Pure Pd and its various alloys have the innate ability to allow monatomic hydrogen to selectively diffuse through its structure to produce purities in excess of $\geq$99.9999% [4]; this process is depicted in Fig. 1. Pd and its alloys are relatively expensive; so there is a growing need to investigate materials that contain as little Pd as possible without sacrificing the membrane properties.

Dense Pd-based metal membranes offer a convenient way to separate hydrogen from a hot gas mixture to purity levels required by PEFCs either as a standalone device or combined with the SMR process as a membrane reactor. Commercial dense metal membranes are commonly based on the Pd–Ag binary alloy system that are either cold rolled into a foil or drawn into a tube with an approximate thickness of 50 μm. The hydrogen flux through such membranes is roughly an order of magnitude lower than that set out by the U.S. DoE targets [5].

It is possible to meet the U.S. DoE flux rate target for dense metal membranes by utilising thin film membranes that are less than 5 μm thick. Using thin films has the added advantage of lowering material cost although at such low thicknesses the tensile strength of the membrane is reduced resulting in less resistance to thermal and mechanical stresses during operation. In order to remedy this, thin films are deposited onto a substrate for mechanical support.

A broad range of porous supports have been investigated over the years such as alumina [6], silicon [7], nickel [8], glass [9] and stainless steel [10]. Porous stainless steel (PSS) substrates are the preferred choice for supporting Pd alloys due to their strength, robustness, similar thermal expansion coefficient as well as ease of welding and sealing [11]. Depositing defect-free Pd and Pd alloy thin films of <5 μm thickness onto PSS is highly complex. Laser-melting of the PSS reduces the surface roughness and porosity which can facilitate the deposition of a defect-free thin film. Furthermore, dense metal membranes typically operate at approximately 400 °C which is a temperature that can promote intermetallic diffusion of Fe from the PSS substrate into the Pd-based thin film membrane which in turn can drastically reduce hydrogen permeability [12].

2. Hydrogen separation techniques

Methods for hydrogen separation will be reviewed to understand the advantages and disadvantages they present for the application of purifying hydrogen from a hot gas mixture. There currently exists three commercial methods that give varying purity levels some of which are used on large industrial scales, whilst others can be scaled down for portable applications.

2.1. Pressure swing adsorption

Pressure swing adsorption (PSA) works by passing a gas mixture through a high surface area adsorber which has the ability to adsorb impurity gases whilst allowing hydrogen to permeate through the material. Impurity gas species are adsorbed onto an adsorbent material at high gas partial pressures and conversely desorbed at lower partial pressures. A common adsorbent material used is Zeolite. The impurities can be removed by swinging the system pressure from the feed to the tail gas (exhaust) pressure coupled with a high purity hydrogen purge. The process is cyclic and more than one adsorber is used in order to maintain a constant flow for the feed, product and tail gas. Each adsorbent material undergoes the same process of swinging; however, the steps are staggered during the procedure. The driving force behind PSA is the impurity gases' partial pressure difference between the feed and tail gas.

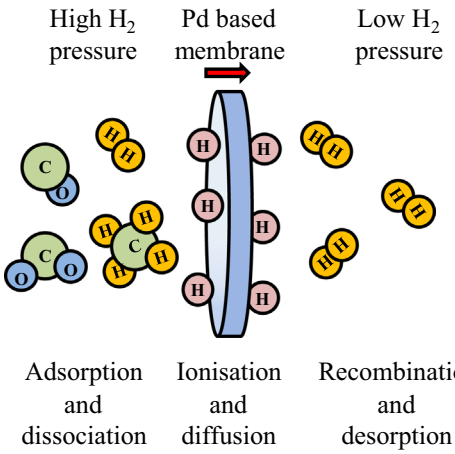

Fig. 1. Schematic representation of hydrogen separation from a hot gas mixture using a Pd based membrane.