Materials for separation membranes in hydrogen and oxygen production and future power generation

J.W. Phair, S.P.S. Badwal*

CSIRO Manufacturing and Infrastructure Technology, Private Bag 33, Clayton, Victoria 3169, Australia

Received 10 July 2006; received in revised form 24 October 2006; accepted 1 November 2006
Available online 29 December 2006

Abstract

Future fossil fuel power generation is likely to include technologies which increase process efficiency and reduce its impact on the environment, for example, CO2 sequestration. Some of the key technologies identified for clean coal and natural gas combustion to produce power or hydrogen or both include O2 generation/separation, H2 and CO2 separation. Hydrogen is considered as a potentially excellent substitute for transport fuels due to the concern over dwindling oil reserves and global warming. This paper discusses various separation processes that may be used in the industrial production of hydrogen from fossil fuels, with an emphasis on membrane separation technologies. Membrane separation has the advantage over other separation methods in that it is simple and potentially less energy intensive. Depending on the particular separation process utilised, however, the membrane materials can differ substantially. The materials used for H2, O2 and CO2 separation are discussed and the major similarities and differences between the membranes highlighted. Critical design aspects of the membrane such as multiple phase design, nano-structure control, the need for surface layers and fabrication processes are also reviewed as they represent the areas where most research and development effort is likely to be directed in the future.

Keywords: Hydrogen separation; Oxygen production; Carbon dioxide separation; Membranes; Clean power generation

1. Introduction

There is a major global emphasis on developing zero emission coal technologies for power generation and hydrogen production. In the overall CO2 capture, compression, transportation and sequestration chain, CO2 separation is the major cost item at this stage. CO2 can be captured in dilute form (typical CO2 concentration 5–15%) at temperatures below 300°C and ambient pressure from existing power plants (post-combustion separation), using air for coal combustion and steam raising. However, coal gasification for power generation is being actively pursued to improve the competitiveness and environmental performance of coal-based power generation. Instead of burning coal directly, gasification produces syngas which, after particulate and sulphur removal, can be shift converted to H2 and CO2. Following H2 and CO2 separation, H2 can be combusted in a fuel cell, an internal combustion engine, a turbine or used as feedstock for other industrial chemical processes. US Department of Energy (DOE)’s—Vision 21 programme has objectives to develop highly efficient power and co-generation technologies that close the carbon cycle and discharge almost no pollution [1]. Australia’s ‘Coal 21—a national action plan’ calls for the reduction of greenhouse gas emissions arising from the use of coal for electricity generation [2]. Some of the key technologies for near zero emission fossil fuel power generation and hydrogen production are:

- low-cost O2 separation,
- H2 and CO2 separation,
- disposal/recycling of CO2,
- partial oxidation reactors for coal gasification with O2 instead of air,
- gas cleaning,
- ultra clean coal and lignite dewatering and drying.
Low-cost O₂, H₂ and CO₂ separation have been targeted as some of the key research goals in the US DOE’s Vision 21 Programme.

For these new-generation power plants, air separation units (ASUs) which mass produce O₂ for coal gasification, along with CO₂ and H₂ separation membranes, are considered as essential parts of the overall plant (Fig. 1). When O₂ is used in the gasifier instead of air, a smaller gasifier would be required. This reduces costs associated with downstream gas separation/heat recovery and CO₂ sequestration significantly. The CO₂ produced by the process is in a concentrated form, making it much easier and less expensive to separate and sequester. Moreover, the generation of NOₓ’s and other potential pollutants is substantially reduced.

Similarly, auto-thermal process for H₂ or power generation from natural gas, combining steam reforming (endothermic reaction) and partial oxidation (exothermic reaction), require the use of O₂.

Conventional methods of O₂ separation (cryogenic and pressure swing) are less economical for large-scale O₂ production with increasing emphasis now on developing membrane-based technologies. Many economic studies indicate that ion transport membrane technology based on mixed ionic and electronic conductors (MIECs) has the potential to cut cost for oxygen production by about 30–35% for large-scale (tonnage) oxygen production for coal gasification plants [3].

Furthermore, downstream processing of product gases from a coal gasifier or an auto-thermal reformer requires separation of CO₂ and H₂ for CO₂ sequestration. Pre-combustion separation of CO₂ is considered to be more economical as the gas stream is at high pressure (up to 10 MPa) and in the concentrated form. Again membrane separation technologies, which can be directly integrated into the plant, are the subject of active research and development.

In this paper, materials and technologies for O₂ production/separation, H₂ and CO₂ separation have been discussed including their current status, R&D challenges and future directions.

2. Gas separation processes

2.1. Hydrogen (H₂) separation

Three main technologies available for H₂ separation include pressure swing adsorption (PSA), cryogenic distillation and selective permeation through a membrane [4,5]. PSA produces pure H₂ from a gas mixture by subjecting it to high pressures (>10 MPa) in confined chambers containing molecular adsorbing beds, to separate gases. This can be achieved in a batch or continuous process. Cryogenic distillation, on the other hand, involves freezing the gas mixture and then using the difference in gas boiling points of the components to achieve the separation. H₂ separation by permeation selective membranes essentially involves supplying an H₂-enriched gas mixture under pressure to one side of the membrane. This creates a potential gradient which drives the transport of H₂ through the membrane to the low pressure or H₂ poor side.

Determining the optimal technique for H₂ separation depends on factors such as integration into an existing process such as coal gasification or natural gas reforming, the conditions to which the hydrogen separation materials (temperature, pressure, impurities, etc.) will be exposed, flexibility, efficiency as well as cost and purity of the final product. At this stage, H₂ separation by selective permeation membranes is the preferred option since it is considered to be potentially more cost-effective, utilises less energy and it is simpler in operation compared to the other two technologies. Separation membranes are already being used for the separation of H₂ and N₂ in ammonia.
production and for separating H₂ from hydrocarbons in petrochemical plants [6].

Hybrid membrane reactors combining H₂ separation membranes with water–gas shift (WGS) reactor can drive the equilibrium of water shift reaction forward (e.g. in coal gasification, methane partial-oxidation or steam reforming processes), thereby increasing the hydrogen yield and resulting in significant cost reductions in the generation of hydrogen. For instance, a H₂ separation membrane reactor integrated for the steam reforming of methane would not only increase methane to H₂ conversions at lower operating temperatures (250–400 °C), but also reduce steam consumption.

2.2. Oxygen (O₂) separation

As mentioned previously, the production of H₂ from fossil fuels often requires the controlled use of O₂. Therefore, a cheap, reliable and clean supply of O₂ is desirable. Large-scale production of O₂ is commonly achieved by cryogenic separation, i.e. by the fractional distillation of liquid air which yields O₂ of high purity (>99 vol%) or by temperature and PSA for smaller applications, which produces O₂ of lower purity (<95%). There are three basic processes for adsorptive enrichment of O₂ from air using zeolites: PSA, vacuum swing adsorption (VSA) and a combined PSA/VSA (PVSA). The PSA technique involves compressing the air and passing it through canisters filled with molecular sieves to remove impurities resulting in O₂ of 90–95% purity. Once the full length of the adsorbent bed is utilised, it must be regenerated by desorption or purging of the adsorbed gas, by reducing the pressure inside the canister and back flushing with a small quantity of the product (O₂ concentrated) gas. The process is reversible and can be carried out a number of times. For a continuous supply of O₂, two or more separate beds can be used. This allows for the simultaneous removal of impurities from O₂ by fresh beds and regeneration of spent beds. Another process available for O₂ enrichment is the electrolysis of water; however, this has only been used in very restricted applications (e.g. life support on submarines, space travel and for heavy water production).

However, all of these processes are relatively cumbersome, energy and capital-intensive. The supply of O₂ in liquid form also requires special storage facilities, and for coal gasification, this route is unlikely to be cost competitive. O₂ separation membranes, on the other hand, offer a simpler and flexible alternative and there is an increasing global interest in such membranes based on pure or mixed oxygen-ion and electronic conducting materials. These membranes can be used for separating O₂ from air or in syngas production, by combining O₂ generation with the partial oxidation of methane in a single reactor [7–9]. Such membranes have also been considered for the production of H₂ by the electrolysis of steam [10].

2.3. Carbon dioxide (CO₂) separation/capture

CO₂ separation membranes are required in the production of power and H₂ in two main ways. Firstly, they may be used to directly remove the CO₂ from the reaction products from coal gasification or methane reforming, leaving H₂ gas in a pressurised state. This may be advantageous where a compressed H₂ source is required, saving costly re-compression. Alternatively, if the H₂ has already been removed from the reaction gas, then CO₂ must be separated from the remaining un-wanted gas products for sequestration. CO₂ sequestration is a critical stage for ensuring a net ecological advantage in utilising hydrogen as a fuel. Without carbon sequestration, hydrogen generation from fossil fuels will do little to abate global CO₂ emissions, which have been established as a significant contributor to global warming [11]. By separating or capturing CO₂ in a concentrated form, it can then be compressed and transported before being stored indefinitely in geological formations, the ocean, as mineral carbonates or being used in industrial processes [12,13].

A major challenge in CO₂ capture is that it must be reduced to a highly pure (>99%) form before it can be transported to the storage site [12,13]. A multitude of techniques have been developed and already used for CO₂ separation including wet scrubbing, dry regenerable solvents, cryogenics, pressure and temperature swing adsorption (TSA), chemical adsorption and gas separation membranes [13]. A recent survey of the various CO₂ separation/capture technologies demonstrated that advanced polymer separation membranes are favourable to monoethanolamine (MEA) absorption, cryogenics and TSA in terms of costs and energy demands [14]. However, slexol adsorption and PSA both produce a CO₂ of higher purity than polymer separation membranes [15].

Separation membranes continue to offer considerable advantages for process integration, ease of operation and have a smaller environmental impact than other separation techniques, which often result in pollutant by-products (e.g. spent adsorbents, contaminated solutions and solids) requiring costly treatment and removal. Currently, membranes are being considered for separating CO₂ from natural gas.

3. Types of materials for membranes

3.1. Hydrogen separation membranes

H₂ separation membranes may be classified into the following categories:

- dense metals,
- nano-porous inorganic materials (e.g. ceramics, oxides, glasses, etc.),
- organic polymers,
- dense ion transport membranes based on proton conducting materials.
Composites consisting of combinations of these main material groups are also becoming more common.

There has been considerable growth in the research and development of H₂ separation membranes. In line with the commercial potential, over 400 patents have been issued from 2000 to 2005 on hydrogen selective membranes according to a recent study by the US DOE [16].

Major performance criteria that are desirable for membranes are high flux rates, stability at the operating temperatures and pressures and in the presence of other gases and contaminants (e.g., CO₂, CO, CH₄, H₂O, H₂S and metal vapours), high selectivity, ease of fabrication and low cost. US DOE has set stringent targets for hydrogen separation membranes to reach by 2015 [17] as summarised in Table 1. Most of these targets appear to be achievable by 2015 given the growth of research in the area, although the durability/stability of the membrane remains the most difficult target to reach according to Table 1.

3.1.1. Dense metal membranes

Dense metal membranes used in the separation of hydrogen at the temperatures (300–600 °C) typically encountered during gas processing in power generation are traditionally based on Pd [18]. Recent work, however, has focused on Zr-, V- and Nb-based alloys and many amorphous alloys as cheaper alternatives to hydrogen separation such as Ni–Nb–Zr amorphous alloys [19], V–Al alloys [20] or V–Ni alloys [21]. The mechanism for H₂ separation by a metal membrane is often referred to as the "solution-diffusion" mechanism. Hydrogen is transported through the metal membrane in a series of steps that include the adsorption of H₂ onto the surface, its dissociation into ions and electrons, its absorption or dissolution into the metal, its diffusion through the bulk of the metal, its re-association on the metal surface before desorption as a gas. The metal structure is sufficiently dense that it greatly restricts the ability of other gas molecules to diffuse through the metal, thereby separating the H₂.

The permeation of hydrogen through a metal membrane is a function of the solubility and diffusion of hydrogen in the metal in addition to the membrane thickness and temperature. The permeation flux is typically proportional to the square root of the pressure differential, ignoring surface effects. Notwithstanding, a catalytic surface capable of dissociating and re-associating H₂ at the membrane surface is a critical requirement for the operation of a metal membrane. If these reactions occur too slowly, then a catalytic layer must be added to the membrane to enhance hydrogen dissociation and re-association reactions. While metals highly permeable to hydrogen are sought for separations since they offer the greatest flux, greater susceptibility to hydrogen embrittlement often accompanies high permeability. Therefore, a balance must be struck between a metal which offers high permeability but good resistance to hydrogen embrittlement, when selecting an optimal metal for a hydrogen separation membrane. Table 2 provides a list of the permeabilities and enthalpies of hydride formation for selected metals.
poisoned by CO. Pd is known to have reasonable permeation flux through it and catalyses both hydrogen dissociation and re-association reactions. Pd, nevertheless, is expensive and is considered to be a strategic metal in terms of its low availability. Pd (or its alloys)-based membrane reactors for H₂ separation are quite expensive unless the reactor is constructed using a thin film (thickness of a few microns) supported by a porous structure so as to improve flux rates and limit costs. These reactors, however, have limited life and are subject to failure with time. Most alternative metals to Pd with high permeability to hydrogen such as Zr, Ta, Nb and V are sensitive to hydrogen embrittlement and surface oxidation in their pure form and have restricted stability over wide operating environments. Therefore, the search is on to modify existing Pd-based membranes or develop new alloys to minimise hydrogen embrittlement and increase stability under conditions of use (temperatures in the 300–600 °C range, differential pressures to >2.8 MPa, presence of contaminants such as CO, C₅H₁₀, metal vapours and sulphur compounds) [18,19,22].

3.1.2. Nano-porous membranes

Nano-porous membranes made from ceramics, glasses, organic polymers or carbon can separate H₂ from other gases such as CO₂, CO, CH₄, etc. by only allowing the smaller H₂ molecules (diameter = 2.83 Å) to diffuse through the pores of the membrane thus leaving behind larger molecules. Thus, the membrane essentially acts as a molecular sieve whose efficiency is determined by the pore size and distribution relative to the molecule's size. An advantage of porous membranes is that the H₂ flux is directly proportional to the pressure difference across the membrane. However, difficulties arise in the preparation of defect-free thin membranes which can achieve a sufficiently high separation factor through a discrete pore structure. As a result, the purity of H₂ produced is not always of the highest grade (<95%). A summary of the general properties of the different classes of materials for non-porous hydrogen separation membranes is provided in Table 3.

While porous glassy membranes have received limited attention to date for H₂ separation, porous vycor glass membranes have already been made successfully at a commercial scale [23] and have been reported to have good chemical and thermal stability for gas separations up to 850 °C with a pore size of ~4.7 nm [24]. Carbon membranes, typically derived from pyrolyzing polymer membrane or thin films (e.g. PVC, cellulose and phenolic resin), often exhibit much greater chemical and thermal stability than their organic polymer alternatives [25]. A drawback of carbon membranes is that they may be more brittle or mechanically weak compared to other materials.

Porous ceramics have by far seen the most application as membranes for hydrogen separation than any other material. Such membranes are generally based on silica or crystalline structure but may also include a range of zeolite structures including silicalite, aluminosilicates and MFI-type zeolites [26]. Recently, a new breed of membranes consisting of almost-dense SiO₂ thin-films deposited onto a porous Al₂O₃ support by chemical vapour deposition (CVD) has been developed. Since the membrane support has size-graded layers, it is possible to produce a thin film less than 1 μm in thickness. Such a membrane structure is thought to comprise of a network of solubility sites rather than connected pores and consequently, is expected to exhibit a different permeation mechanism to normal porous membranes [27].

While porous organic membranes for hydrogen separation are rare, recent work has examined the potential of polymers with intrinsic microporosity (PIMs) for hydrogen gas separations [28]. PIMs exhibit a structure which is likened to an organic zeolite which is rigid, yet highly voided consisting of randomly distributed and interconnected pores. This structure is expected to allow for greater selectivity and flux of H₂ through a molecular sieving separation mechanism than that which can be achieved through the traditional solution-diffusion mechanism for dense polymer membranes. Rather than traditional methods for porous polymer preparation such as sintering stretching, track etching, phase separation or solution casting, PIMs are prepared by the polymerisation of hydroxylated aromatic monomers with fluorinated or chlorinated aromatic monomers [28].

A summary of the permeabilities and selectivities of selected different types of nano-porous membranes for hydrogen separation is provided in Table 4.

---

Table 3

| General classification of nano-porous materials [113] |
|-----------------------------------------------------|
| **Polymeric** | **Carbon** | **Glass** | **Aluminosilicate** | **Oxides** | **Metal** |
| Pore size | Meso-macro | Micro-meso | Meso-macro | Micro-meso | Micro-meso | Meso-macro |
| Surface area/porosity | Low > 0.6 | High 0.3–0.6 | Low 0.3–0.6 | High 0.3–0.7 | Medium 0.3–0.6 | Low 0.1–0.7 |
| Permeability | Low-medium | Low-medium | High | Low | Low–medium | High |
| Strength | Medium | Low | Strong | Weak | Medium–high | Weak–medium | Strong |
| Thermal stability | Low | High | Good | Medium–high | Medium–high | High |
| Chemical stability | Low–medium | High | High | Very high | High | High |
| Costs | Low | High | High | Low–medium | Medium | Medium |
| Life | Short | Long | Long | Medium–long | Long | Long |

*Microporous = pore radius < 1 nm, mesoporous = 1 nm < pore radius < 25 nm, macroporous = pore radius > 25 nm.*
3.1.3. Non-porous organic polymer membranes

Non-porous polymer membranes have been used considerably in industry for various gas separation processes. The permeation of H₂ through the membrane is achieved through a solution-diffusion mechanism; however, it does not require the H₂ dissociation and reassociation steps unlike dense metal or mixed electron and proton conducting membranes for hydrogen separation. The typical temperature for operation of polymeric membranes is ~100 °C although in certain cases this may extend up to 200 °C [29]. The best example of proton conducting polymer membranes with high conductivities (>10⁻³ S/cm at 50 °C) includes sulfonated fluorocarbons (Nafion) [30], sulfonated polybenzimidazole (S-PBI) [31] and sulfonated polyether ketone (S-PEEK) [32]. However, operation is restricted to below 80 °C since the hydrated layers necessary for the proton conduction dehydrate at higher temperatures (>100 °C).

Non-porous organic membranes useful for gas separation are generally classified into either rubbery or glassy polymer categories [33]. The distinction is based on their temperature of formation relative to their glass transition temperature (Tg): those polymers formed at temperatures below the Tg are glassy while those formed above are referred to as rubbery. In contrast to porous organic membranes, the process of separation by polymer membranes is largely dictated by the relative solubility of the gases to be separated. Gas properties which affect its solubility in the polymer include its chemical affinity (e.g. molecule polarisation) with the polymer, its condensability and kinetic diameter (Table 5) [34]. Major properties of the polymer affecting the permeability of the gas include the free volume content, degree of crystallisation, cross-linking, molecular weight and glass transition temperature.

Glassy polymers are the generally preferred option for removing H₂ from a gaseous mixture stream, since permeation is controlled by diffusion selectivity rather than solubility selectivity as for rubbery polymers [35]. However, there is limited information on their H₂ selectivity over CO₂ [36]. Given that CO₂ is usually highly permeable in polymeric membranes, the selectivity for H₂ is not expected to be all that good. In addition, polymeric membranes have restricted applications due to their limited stability at temperatures greater than 150–200 °C and in aggressive chemical environments (e.g. excess HCl and SO₃ environments) [29,33]. Therefore, it may be necessary to cool the process gases before satisfactory H₂ separation can occur which would require the use of extra energy and add cost to the power and/or H₂ production process. Moreover, if it is not possible to obtain higher purity H₂ gas (because of low separation factors) or higher H₂ flux rates, then polymeric membranes are less attractive for potential applications [37]. The H₂ permeabilities and H₂/CO₂ selectivities for choice polymer membranes are provided in Table 6.

3.1.4. Dense ion transport membranes

Dense ceramic membranes with mixed ion and electron transport capabilities are gaining greater interest for separating H₂. The mechanism for hydrogen transfer is via dissociation of hydrogen to protons and electrons on the high partial pressure side, migration of both electrons and protons through the dense membrane and re-association on the low partial pressure side. The membrane surface must have capability for charge transfer reactions to take place at both external surfaces or alternatively catalytic layers or electrodes are required to facilitate H₂ dissociation and re-association reactions. Similar to metal membranes, the H₂ selectivity is very high (>99%) and no secondary purification of the separated H₂ is required.

| Membrane | Preparative method | Support | H₂ permeance 10⁻⁸ mol/m²/s/Pa | H₂ selectivity | Ref. |
|----------|-------------------|---------|-------------------------------|----------------|-----|
| Silica   | CVD (SiCl₄ + H₂O) | Porous vycor | 5.0 (at 500 °C) | H₂/N₂ = 500–1000 | [114] |
|          | CVD (SiH₄ + O₂)  | Porous vycor | 3.2 (at 500 °C) | H₂/N₂ = 2000–3000 | [115] |
|          | CVD (TEOS)       | Alumina  | 2.2 (at 500 °C) | H₂/N₂ = 1000 | [116] |
|          | Sol-gel          | Alumina  | 112 (at 200 °C) | H₂/H₂O = 5000 | [117] |
| SiC      | CVD              | Alumina  | 60 (400 °C) | H₂/H₂O = 5 | [118] |
| Carbon   | UD (PFFA)        | S. steel | 0.06 (22 °C) | H₂/N₂ = 331 | [119] |
|          | VDP (FA)         | Alumina/glass | 10.6 (150 °C) | H₂/N₂ = 30 | [120] |
| Zeolite  | ZSM-5 in situ synthesis | Alumina | 4.4 (190 °C) | H₂/n-C₄H₁₀ = 14 | [121] |

| Property | H₂ | CO₂ | O₂ |
|----------|----|----|----|
| Molecular weight | 2.02 | 44.01 | 31.98 |
| Kinetic diameter (Å) | 2.89 | 3.30 | 3.46 |
| Specific volume at 21 °C, 1 atm, ml/g | 1.1967 | 547 | 755 |
| Density, at 0 °C, 1 atm, g/l | 0.0899 | 1.977 | 1.4291 |
| Condensability (K) | 60 | 195 | 107 |
| Solubility in water at 25 °C, 1 atm, ml/l water | 19 | 759 | 31 |
| Critical temperature (°C) | -240.2 | 31.0 | -118.4 |
Most of the work to date has been performed on perovskite-type proton conducting phase such as Ba and Sr cerates, doped at A- and/or B-sites [38-41]. Such materials are well suited for operation at high temperatures (> 500 °C). However, there are several other categories of materials which also show promising proton conductivities. These include the range of hydrated or water containing compounds (e.g. polyoxometallates: \( \text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O} \)), compounds containing structural protons (e.g. oxo salts, oxo acid salts: \( \text{CsH}_2\text{PO}_4, \text{Li}_2\text{SO}_4, \text{CsNO}_3 \)), and other dense oxides (e.g. pyrochlores, and mixed phase perovskites) and sulphides [42]. A significant distinction between these major categories is the different temperature range at which they achieve their highest proton conductivities and the requirement of a second phase (e.g. metal or electron conducting oxide) to conduct electrons. The strength and chemical stability of the materials, in general, varies as a function of the composition and temperature, and must be considered when selecting the optimum dense membrane for a specific H₂ separation application. Table 7 provides an overview of the optimal temperatures and conductivities for hydrogen separation membranes based on dense proton conducting materials.

### 3.2. Oxygen separation membranes

Oxygen-ion conducting ceramic membrane materials (pure ionic or mixed ionic/electronic conductors) have the ability to selectively transport oxygen in the form of an ionic flux at high temperatures producing \( \text{O}_2 \) of extremely high purity [8,9,43]. Dense membranes constructed from such materials are highly selective to oxygen with a separation factor approaching infinity.

#### Table 6

Hydrogen permeabilities and \( \text{H}_2/\text{CO}_2 \) selectivities for chosen polymer membranes. [36,124]

| Polymer                                      | \( \text{H}_2 \) Permeabilitya (Barrer)b | \( \text{H}_2/\text{CO}_2 \) selectivity |
|----------------------------------------------|----------------------------------------|---------------------------------------|
| Cellulose acetate                            | 2.63                                   | 0.4                                   |
| Ethyl cellulose                              | 87                                     | 3.3                                   |
| Eval film (co-polymer of polyethylene and polyvinyl alcohol) | 0.5                                    | 2.5                                   |
| Polybenzyl methacrylate                      | 11.0                                   | 1.4                                   |
| Polydimethyl siloxane (ref)                  | 375                                    | 0.3                                   |
| Polyetherimide                               | 7.8                                    | 5.9                                   |
| Polyethylene low density film                | 17.3                                   | 0.9                                   |
| Polymide (Matrimid)                          | 28.1                                   | 1.5                                   |
| Polymethyl methacrylate                     | 2.4                                    | 4                                     |
| Polymethylpentene                            | 125                                    | 1.5                                   |
| Polystyrene                                | 113                                    | 1.5                                   |
| Polystyrene MW 280 K                        | 23.8                                   | 2.3                                   |
| Polystyrene-co-butadiene                    | 7.9                                    | 0.5                                   |
| Polysulfone                                 | 12.1                                   | 2.0                                   |
| Polyvinyl acetate                            | 15.1                                   | 1.2                                   |
| Polyvinylidene fluoride (Kynar)             | 2.4                                    | 2.0                                   |

aPermeabilities determined at 30 °C and at 30 psi feed pressure.
b\( \text{Barrer} = 10^{-10}\text{cm}^2/(\text{cm}^2\text{s cmHg}) \) where STP = standard temperature and pressure.

#### Table 7

Conductivities of potential proton conducting materials for \( \text{H}_2 \) separation membranes [125]

| Material                                               | Optimal conducting temperature (°C) | Proton conductivity (S/cm) |
|--------------------------------------------------------|-------------------------------------|---------------------------|
| \( \text{H}_2\text{SiW}_{12}\text{O}_{40} \cdot 28\text{H}_2\text{O} \) | <100                                | 2 \times 10^{-2} at 25 °C  |
| \( \text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O} \) | <100                                | 8 \times 10^{-2} at 25 °C  |
| \( \text{H}_3\text{PMO}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O} \) | <100                                | 1.7 \times 10^{-1} at 25 °C |
| \( \text{H}_2\text{O}_2\text{PO}_4 \cdot 4\text{H}_2\text{O} \) | <100                                | 5 \times 10^{-3} at 25 °C  |
| \( \alpha\text{-Zr(HPO}_4)_2 \cdot \text{nH}_2\text{O} \) | <100                                | 1 \times 10^{-4} at 25 °C  |
| \( \gamma\text{-Zr sulfo phosphonates} \) | <180                                | 1 \times 10^{-5} at 25, 100 °C |
| \( \text{Sb}_2\text{O}_5 \cdot 4\text{H}_2\text{O} \) | <300                                | 3 \times 10^{-4} at 25 °C  |
| \( \text{V}_2\text{O}_5 \cdot \text{nH}_2\text{O}, \text{Zr}_2\text{O}_5 \cdot \text{nH}_2\text{O} \) | <150                                | 4 \times 10^{-4} at 25 °C  |
| \( \text{SnO}_2 \cdot \text{nH}_2\text{O} \) | <300                                | 1 \times 10^{-3} at 100 °C |
| \( \text{Cr(HPO}_4)_2 \cdot \text{nH}_2\text{O} \) | <150                                | 3.3 \times 10^{-1} (wet atm.) at 300 °C |
| \( \text{NH}_4\text{PO}_3 \cdot (\text{NH}_4)_2\text{SiP}_2\text{O}_{13} \) | 200-300                             | 2.4 \times 10^{-2} at 250 °C |
| \( \text{NH}_4\text{PO}_3 \cdot \text{TiP}_2\text{O}_7 \) | 150-250                             | 7 \times 10^{-7}-3 \times 10^{-4} at 300-700 °C |
| \( \text{Sr} \) doped \( \text{La}_2\text{P}_2\text{O}_7 \) | 700                                 | 6 \times 10^{-6}-3 \times 10^{-4} at 500-925 °C |
| \( \text{Ba}_2\text{Ce}_0\text{Y}_2\text{O}_{3+\delta} \) (BCY) | 500-900                             | 1.8 \times 10^{-2}-7 \times 10^{-2} at 600-1000 °C |
| \( \text{Ba}_2\text{Ga}_0\text{Y}_2\text{O}_{3+\delta} \) (BZY) | 500-900                             | 1.6 \times 10^{-3}-6 \times 10^{-3} at 600-1000 °C |
| \( \text{Ba}_2\text{Ca}_{1.8}\text{Nb}_{0.2}\text{O}_{17} \) (BCN18) | 500-900                             | 5.5 \times 10^{-4} at 600 °C |
| \( \text{K}_2\text{H(SO}_4)_2 \) | 100-200                             | 9.5 \times 10^{-6}-2.2 \times 10^{-2} at 80-250 °C |
| \( \text{CsH}_2\text{O}_4 \) | 100-200                             | 2 \times 10^{-7}-3 \times 10^{-6} at 110-190 °C |
| \( \text{H}_2\text{OCl}_4 \) | 100-200                             | 3.5 \times 10^{-4} at 25 °C |
| \( \text{MeNO}_3 \cdot \text{SiO}_2 \) (Me = Rb, Cs) | 100-200                             | 1 \times 10^{-6}-1 \times 10^{-5} at 60-280 °C |
| \( \text{Cs}_3\text{(HOSO}_4)_2 \cdot \text{H}_2\text{PO}_4 \) | 100-200                             | 1 \times 10^{-6}-1 \times 10^{-5} at 40-180 °C |
| \( \text{La}_2\text{Ce}_0\text{Ga}_0\text{Zr}_2\text{O}_{17} \) | 500-900                             | 6.8 \times 10^{-2} at 600 °C |
| \( \text{La}_2\text{Si}_{2}\text{O}_{16} \cdot 3\text{Zr}_2\text{O}_7 \) | 500-900                             | 7 \times 10^{-7}-1 \times 10^{-5} at 300-800 °C |
| \( \text{H}_2\text{S}/(\text{BaS}_2 \text{or GaS}_2) \)\((\text{GeS}_2, \text{SiS}_2, \text{As}_2\text{S}_3 \text{or CsI}) \) | 200-500                             | 5 \times 10^{-11}-4 \times 10^{-7} at 60-300 °C |
Typically, the gas separation devices based on solid electrolyte systems can be divided into two categories. The first type of devices (also referred to as electric voltage driven) are based on pure or mainly oxygen-ion conducting solid electrolyte membranes (non-porous). By application of a voltage signal across the solid electrolyte cell, ionic conductivity data for selected oxygen-ion conducting materials are given in Table 8.

The O$_2$ permeation is dependent on the membrane thickness, temperature, bulk diffusion rates, surface O$_2$ exchange rates and the O$_2$ partial pressure gradient across the membrane. Oxygen-ion mobility is a highly activated process and for a given material, O$_2$ flux through the membrane increases with increasing temperature, decreasing membrane thickness and increasing partial pressure differential across the membrane.

It is difficult to make a valid comparison of the flux rates reported in the literature for mixed ionic/electronic conducting materials as the conditions used for evaluating materials (including specimen thickness, operating temperature, cell design, differential partial pressure across the membrane and how the partial pressure is achieved on the low pressure side (Ar, He, syngas, CH$_4$, etc.) fluctuate across different studies. The most optimistic targets for O$_2$ flux vary between 10 and 25 cm$^3$/min/cm$^2$. There are extensive R&D efforts funded by both industry and government for the development of effective ceramic membranes and fabrication technology for large-scale O$_2$ separation in syngas production and coal gasification [3]. These efforts are mainly directed at the use of non-porous mixed oxygen-ion and electron conducting membrane materials, which can be shaped into tubular, monolithic or planar-type reactors.

### 3.3. Carbon dioxide separation membranes

Depending on the specific use of the CO$_2$ membrane in the production of power or hydrogen, the required material properties of the membrane may differ significantly. The materials for a CO$_2$ separation membrane for its pre-combustion separation from H$_2$ would be quite different from those required for a membrane for post-combustion separation of CO$_2$ (different temperatures, pressures and gas composition). For instance, the pre-combustion separation of CO$_2$ involves the initial conversion of a fossil fuel into H$_2$ and CO$_2$ (e.g. gasification, followed by,}

| Material | $\sigma$ (S/cm) 700 °C | $\sigma$ (S/cm) 800 °C | $\sigma$ (S/cm) 900 °C | $\sigma$ (S/cm) 1000 °C | Conducting species | Structure |
|----------|------------------------|------------------------|------------------------|------------------------|--------------------|-----------|
| (ZrO$_2$)$_{0.9}$(Y$_2$O$_3$)$_{0.1}$ | 0.052 | 0.18 | O$^{2-}$ | Fluorite |
| (ZrO$_2$)$_{0.9}$(Sc$_2$O$_3$)$_{0.1}$ | 0.12 | 0.32 | O$^{2-}$ | Fluorite |
| (CeO$_2$)$_{0.8}$(SmO$_1.3$)$_{0.2}$ | 0.10 | 0.25 | O$^{2-}$ | Fluorite |
| (Bi$_2$O$_3$)$_{0.6}$(Er$_2$O$_3$)$_{0.4}$ | 0.37 | | | |
| (La$_{0.9}$Sr$_{0.1}$)(Ga$_{0.8}$Mg$_{0.2}$)O$_3-x$ | 0.121 | 0.32 | O$^{2-}$ | Perovskite |
| (La$_{0.9}$Sr$_{0.1}$)(Co$_{0.8}$Mn$_{0.2}$)O$_3-x$ | 0.8 | | O$^{2-}$/e | Perovskite |
| (La$_{0.9}$Sr$_{0.1}$)(Ga$_{0.8}$Fe$_{0.2}$)O$_3-x$ | >1.0 | | O$^{2-}$/e | Brownmillerite |
particulate removal in the case of coal, and water gas shift reaction). The CO₂ must be separated at very high pressures (up to 7 MPa ΔP) and high temperatures (300–700 °C) in these circumstances. Post-combustion separation on the other hand, involves the separation of CO₂ from the flue gas following the combustion of fossil fuels. Typically, the flue gas is at atmospheric pressure and the CO₂ is present in low concentrations (~5–15%) if air is used during combustion (N.B. air contains significant quantities of nitrogen which limits the amount of CO₂ produced.) SO₂, NO₂ and O₂ may also be present in small amounts. Here a membrane is required which provides high CO₂ fluxes at low CO₂ partial pressures and lower temperatures (<300 °C), for efficient separation.

The types of materials already demonstrated to be useful for CO₂ separation membranes include porous carbon, silica and zeolites or non-porous polymers. At this stage, although polymeric membranes are more developed and available commercially for CO₂ separation, more useful membranes during the power generation process are likely to exhibit greater stability at the higher temperatures (>300 °C) encountered during gas processing.

Out of the non-porous organic polymers available for CO₂ separation, rubbery polymers generally have higher CO₂ permeability than glassy polymers; however, their gas selectivity is low. Glassy polymers such as cellulose acetate, polyacetylene, polyamide, polyarylates, polycarbonates, polyimides, poly(phenylene oxide) and polysulphones have dominated industrial CO₂ separation applications due to their high gas selectivity and good mechanical properties. Their greatest application has been found in the separation of CO₂ from CH₄, CO, N₂ or other hydrocarbons. Polyimides, in particular, have attracted considerable attention due to their relatively high thermal, chemical and mechanical stability combined with high selectivity and permeability for CO₂ [48]. Cross-linking has been investigated as a method for reducing the occurrence of swelling and plasticisation resulting from the exposure of polyimides to CO₂. This, in fact, has led to significant improvement without reducing CO₂ permeability [49,50]. There are a limited number of reports related to separating CO₂ from H₂, although polyacetylenes [51,52] and glassy organosilanes [53] have been cited for potential CO₂/H₂ selectivity at low temperatures (25–40 °C).

Rubbery polymeric membranes, on the other hand, have attracted greater interest for the separation of CO₂ from H₂ due to higher flux rates and high selectivity. Recently, a series of cross-linked and highly branched polyethylene oxides (PEO) have been demonstrated to be strongly selective to CO₂ or H₂S (gases with solubility), but not to H₂ which is insoluble in the material [54]. By preferential absorption of the polar CO₂ molecules onto the surface of the membrane, it can be selectively separated from other non-polar molecules (e.g. H₂). This allows the passage of polar molecules CO₂ or H₂S through the membrane while preventing the passage of non-polar molecules, including those of a smaller dimension (e.g. H₂). Thus, these membranes are often referred to as being reverse selective H₂ separation membranes. However, the affinity of the membrane material for CO₂ must not be too high such that a strong bond is formed with CO₂, or else the CO₂ flux will suffer detrimentally. Other rubbery polymers that may be of interest for CO₂ separation (reverse H₂ separation) include polyphosphazenes [55,56] and poly(ethylene glycol) [57–59], although, substantial work is required in this area before commercialisation can occur. A disadvantage of these membranes is that although they are more permeable to condensable gases such as CO₂ or H₂S at lower temperatures (25 °C), with increasing temperature H₂ becomes more mobile and these membranes may also allow H₂ to migrate through [60].

Porosity inorganic (i.e. silica, carbon, zeolites, etc.) membranes have the significant advantage of greater thermal and mechanical stability compared to organic polymers, resistance to harsh environments including high-pressure drops, inertness to microbial degradation, and easy catalytic activation and cleanability after fouling [21]. However, some of the drawbacks of inorganic membranes include high expected cost (including fabrication), high brittleness, low membrane surface area to module volume ratio, insufficient selectivity or separation factor, low permeability of highly selective dense membranes, particularly metal oxides at temperatures below 400 °C and difficult membrane-to-module sealing at temperatures greater than 600 °C.

For separating CO₂ at temperatures greater than 300 °C, membranes based on alumina, zeolites, silica and carbon have received considerable attention in both amorphous and crystalline forms [61,62]. For instance, Y-type zeolites, C and SiO₂ microporous membranes have been demonstrated as potentially useful for separating CO₂ from a mixture with N₂ [63]. The main research challenges remain to synthesise thin membranes that are sufficiently chemically and thermally stable at 300–600 °C which is typically encountered in the process gases during power generation. Similar to proton and oxygen-ion conducting membranes, materials which conduct CO₂⁻ ions (e.g. molten Li₂CO₃ formed from the reaction of Li₂ZrO₃ with CO₂), have also been examined recently for CO₂ separation from a mixture with CH₄ at temperatures up to 600 °C [64,65]. Inorganic membranes based on molten carbonate for CO₂ separation is an area which has received limited attention but may provide an economically efficient, stable and robust separation membrane, in applications where excess heat/energy is readily available to melt the carbonate.

4. Critical material aspects of membrane design

4.1. Composite/multiple phase membranes

It is often necessary to use composite or multiple-phase membrane structures which combine the best properties of individual phases to maximise their overall gas separation performance. Dense inorganic membranes used to separate
H₂, CO₂ or O₂ may all be improved by the use of multiple phases. For instance, dense H₂ separation membranes must have optimum proton and electron conductivities to reduce or eliminate the need to apply an external electrical power and save energy. The electronic conductivity of commonly known proton conducting perovskites may be improved by intrinsic doping of the smaller cation sites (e.g. substituting M in BaCe₁₋ₓMₓO₃ and SrCe₁₋ₓMₓO₃) with a multivalent dopant cation such as Eu²⁺/³⁺ and Sm²⁺/³⁺ or transition metal (e.g. Ru), but until now this has been achieved only to a limited degree of success [66,67]. In general, it is difficult to find materials with reasonable proton and electron conduction in a single phase to give sufficiently high overall H₂ flux to be used as H₂ separation membranes. However, a better and simpler approach, to achieve desired proton and electronic conductivity in a single membrane separation material, is to combine individual proton and electron conducting phases of high respective conductivities. Of course, due consideration must be given to their chemical and thermal compatibilities during fabrication and under conditions of use. Addition of materials with high electron conductivity to the proton conducting phase has indeed been investigated [68]. This phase may be a metal (e.g. Pd or Ni) in powdered or oxide form or a ceramic phase (e.g. an n-type semiconductor such as SnO₂, WO₃, SiC or doped-CeO₂) [69]. If the secondary phase metal preferably also has hydrogen transporting abilities, then the overall hydrogen flux rate through the membrane may also be enhanced. The secondary phase is selected not only for high electron conductivity, but for its ability to improve the thermodynamic or mechanical stability of the membrane in CO₂- and H₂O-rich atmospheres.

For large-scale oxygen separation, mixed oxygen-ion/ electronic conducting materials are preferred as this eliminates the need for external power source and perhaps catalytic layers. The driving force for oxygen separation is the temperature and oxygen partial pressure differential. However, it may not be possible to achieve all desired properties (ionic and electronic conductivity, mechanical strength, stability in operation, etc.) in a single-phase material. Thus, to optimise these properties, often a second phase which may be a metal or metal oxide with high electronic conductivity is added to the oxygen-ion conducting material. For example, mixed conduction in mainly O²⁻ conductors (such as doped zirconia or bismuth oxides and ceria) is achieved by adding a metal (e.g. Ag or Pd) or a metal oxide with high electronic conductivity (e.g. Ba₀.₅Sr₀.₅Fe₀.₂Co₀.₈O₃₋₋₆, La₀.₇Sr₀.₃MnO₃₋₋₆, etc.) [70,71]. CO₂ separating membranes based on molten carbonate as the ion conducting phase, utilise a metal phase to not only support the carbonate but also to provide for the electron conduction [72].

At a bare minimum, the secondary phase must be thermally compatible with the ion conducting phase and/or any other materials in the membrane including the support structure where required. Mismatches in the thermal expansion coefficients or other physical properties (e.g. degradation, chemical susceptibility) of the phases must be minimised in order to prolong membrane durability. Often, the secondary phase may be added as a coating on the individual component particles of the membrane by electroless plating, CVD or wet impregnation of the powder. For instance, a two-phase proton and electron conductor has recently been described for the separation of H₂ in which the proton conducting phase, a perovskite-type metal oxide, was wet impregnated with a saturated PdCl₂ solution. Thus, a Pd electron conducting phase covering the oxide particles of loadings of around 15–30 vol% could be obtained after sintering above 800°C [68].

Considerable opportunity exists to develop MIECs for H₂, O₂, and CO₂ separation. An aspect of considerable importance in the development of composite mixed conductors is a proper assessment of the relative contributions of the individual components to the electron transport, ion transport and overall flux rate through the membrane. Hydrogen permeation through mixed ion-electronic conductor membranes has recently been modelled by the resistor network approach [73] and by assuming the bulk solid-state diffusion of hydrogen as the rate-limiting step [41]. However, as the membrane thickness decreases, surface reactions between the gas and the membrane surface may become rate limiting. Thus, it is essential to have a good understanding not only of the mechanisms of ion and electron transport through the membrane but also of interfacial reactions to ensure optimal flux rates through the membrane are achieved [74]. If the membrane surface has low activity for facilitating surface reactions, then often a catalytic layer is added to the surface of the membrane to ensure good flux rates [75].

H₂ and CO₂ separation membranes must be stable not only under reducing conditions, but also in the presence of CO, CO₂, H₂O, H₂S, NOₓ and chlorides which may be found in the gas mixture. H₂ separation membrane materials such as cerium-based oxides (e.g. BaCeO₃), may be susceptible to the formation of insulating carbonates and hydroxides in the presence of CO₂ and H₂O, respectively. Methods of improving the chemical stability in ion conducting ceramics include doping highly conductive oxides with more stable oxide forming metals (e.g. Zr-doped cerates), reducing the grain boundary resistance in chemically stable but less conducting materials, or developing new compounds (e.g. pyrochlores without any Ba or Sr).

4.2. Membrane nano-structure

Nano-structure control in organic membranes typically involves the dispersion of porous or non-porous inorganic nano-sized particles within the organic matrix to enhance the conductivity, mechanical toughness or catalytic activity of the material. Porous inorganic particles (e.g. zeolites,
molecular sieves) may act as a separating phase within the organic matrix while non-porous particles (e.g. metal oxides, silica) may alter the polymer packing and subsequent gas permeation properties of the organic phase. Common inorganic fillers that have been used in polymers include nano-sized metal oxides (e.g. Al2O3, TiO2, ZnO), silicas, carbon blacks, molecular sieves, zeolites, aluminium powders and mica (see Table 9) [76]. Furthermore, hybrid inorganic–organic materials may be formed by the sol–gel process for the purpose of creating a new network structure or modifying the existing structure. Although, initial results are promising with considerable opportunities for further work in this area, little success has been achieved so far in producing commercially successful nano-structure-modified organic membranes. Especially, it has been a real challenge to produce a membrane with high permeability, high selectivity and robust chemical stability.

Nano-structure control within dense metal membranes for H2 separation is another area of growing interest. This is because nano-crystalline and nano-quasicrystalline alloys have been reported to have greater resistance to degradation and it may also be possible to achieve higher hydrogen permeation rates [77]. Nano-crystalline metals may be prepared either by electrodeposition [77], high-energy ball milling, laser ablation, melt-quenching [78], or devitrification [79,80]. Nano-quasicrystalline particles may be formed within a bulk glassy alloy by adding small amounts of elements (e.g. Ag, Pd, Au, Pt, Ir, Re, Zn, Mo, V, Nb, Ta and Cr) to an alloy (e.g. Zr or Hf based) that allow the precipitation of a primary nano-scale icosahedral phase [81,82].

Initial data indicates that the method of nano-crystalline formation can greatly affect the nano-structure and overall performance properties of the H2 separation membrane. In particular, nano-crystalline metals prepared from the crystallisation of metallic glasses not only exhibit superior physical properties to their glassy alloy and crystalline counterparts, but their properties exceed those of nano-crystalline metals prepared in an alternative manner (e.g. compaction of nano-crystalline powders) [83,84]. Studying the effect of the method of nano-crystalline formation on the grain size distribution, resultant grain boundaries and free volume is central to better understanding and controlling the permeation of hydrogen through these metals. For instance, McCool and Lin [85] reported that the H2 permeation actually increased with increasing grain size due to lower Ag content in CVD-prepared ultra-thin Pd-alloy membranes (thickness: <1 μm). Bryden and Ying [77], however, observed that nano-structured Pd–Fe supported membranes prepared by pulsed electrodeposition exhibited higher hydrogen fluxes than coarse-grained membranes of similar compositions due to the substantial grain boundary regions of smaller grain sizes. Minimising the occurrence of defect leakages, chemical degradation by contaminants and hydrogen embrittlement in dense metal alloys, remain the greatest hurdles to improving their performance for wide-scale use. Nano-crystalline metals offer significant opportunity for improvements to be made in these areas.

Nano-structure control is also a useful approach for improving the performance of dense inorganic membranes for H2 or O2 separation. For instance, dispersion of nanosized refractory oxides such as SiO2 [86,87], Al2O3 [88,89], Fe2O3, TiO2 [90], ZrO2, MgO, etc. within pure oxo-acid salt phases allows considerable improvement to both the thermal stability and proton conductivity of the material. The nano-sized particles provide a surface upon which metastable phases of the pure salt may be stabilised and alter the phase boundaries of the pure salt. Combination of polymers such as polyacrylamide [91], poly(ethylene oxide) and poly(benzimidazole) with oxo acid salts has also been another way for improving the conductivity of the salt phase [92].

Other dense inorganic membranes for hydrogen or oxygen separation which may be prepared as nano-composites are mixed electronic and ionic conducting oxides of a perovskite, fluorite or pyrochlore structure [93–96]. For instance, nano-powders of BaTiO3, LaGaO3 and LaMnO3-based complex perovskites and CeO2-based fluorites doped with Gd, have been prepared by milling in a high-energy planetary mill, also known as mechanosynthesis [93,95]. Mechanosynthesis can result in a solid solution of metastable oxides that may have different lattice structures, and may be stabilised by complex doping before sintering, to produce nano-composites of these complex oxides [97].

4.3. Membrane surface layers

Surface layers are a critical component particularly in dense membranes for the separation of H2 or O2 as the

| Filler type | Examples | Surface chemistry | Primary particle size (nm) | Common uses |
|------------|----------|-------------------|---------------------------|-------------|
| Mineral oxides | Al2O3, TiO2, ZnO | Hydrophilic | 1–100 | Catalysis, tailoring mechanical properties |
| Carbon blacks | Spheron 9, Spheron 4 | Hydrophilic or hydrophobic (treated) | 10–100 | Modifying mechanical properties, toughness, coloring |
| Silicas | Hi-Sil | Hydrophilic or hydrophobic (treated) | 7–50 | Rheology control |
|          |          |                   |                          |             |
surface reactions between the gas phase and the membrane surface may be a potential rate-limiting step in the permeation process. Surface layers in dense membranes serve two main purposes: (i) catalyse the $\text{H}_2$ or $\text{O}_2$ dissociation/re-association reactions fast enough to allow sufficient flux of $\text{H}_2$ or $\text{O}_2$ through the membrane, and (ii) to minimise the effects of any contamination, degradation or oxidation process on membrane surface and the catalytic rate. If the surface of the dense metal, ceramic or cermet membrane does not rapidly catalyse the surface dissociation or re-association of $\text{H}_2$ or $\text{O}_2$ for the required flux rates, then it may be necessary to modify the surface structure or provide an additional catalytic layer.

Pd and its alloys such as Pd–Cu and Pd–Ag, and Ni–P have traditionally been used as combined catalytic and protective layers against surface oxidation on dense metals and they can be prepared as thin-film layers by a variety of methods including vapour deposition, electroplating, electroless plating or by roll cladding [98–101]. However, to reduce capital costs, alternatives to Pd-based coatings are being investigated. Surface layers other than precious metals (e.g. Pd or Pd-alloy) that may prevent oxidation on the surface of the membrane include porous metal oxides (e.g. $\text{Al}_2\text{O}_3$, $\text{ZrO}_2$, iron oxide, nickel oxide and manganese oxide), titanium aluminide, molybdenum silicide, glass-ceramics based on barium oxide, silica and alumina positioned on top of the catalytic layer while sulphide-forming oxides may be used for protection in sulphur-containing feed streams (e.g. $\text{ZnO}$, $\text{La}_2\text{O}_3$, $\text{SrO}$ or $\text{CeO}_2$).

4.4. Membrane construction and preparation

Dense and porous membranes may be manufactured in a variety of shapes and sizes that are self-supporting including flat plates or tubes which can be prepared by a variety of metal or ceramic forming methods. Thin membranes (a few microns thick) are of specific interest for achieving high flux rates and require a support structure to provide mechanical strength. The support structure is porous in nature, which allows easy diffusion of gases containing $\text{H}_2$ or $\text{O}_2$ to the membrane surface and unconsumed gases to diffuse out. The materials for the support structure can be a ceramic or a metal with similar thermal expansion properties to the membrane material, to reduce thermal expansion mismatch and de-lamination and cracking of the membrane during fabrication and use. The porosity of the support structure needs to be controlled by constructing the support in multiple layers each with different pore structures and gas diffusion properties, with the uppermost layer being sufficiently dense to allow the deposition of thin and impervious membrane material.

Fabrication of a dense defect-free thin membrane and optimisation of this process is quite critical. The main methods available for depositing a dense membrane layer onto the support structure include sputtering [102], spin coating [103,104], slip-casting [105], sol–gel methods [106], particulate or vapour phase deposition methods (e.g. chemical or electrochemical vapour phase deposition [107,108]. Other methods such as melt spinning [109] and electroless plating [110] may be more useful for preparing thin metal films. Wet dense-film preparative methods are simple, however, full impregnation of the membrane material into the porous substrate and to achieve desired density are significant challenges.

Another recent trend in dense membrane design has been the construction of multiple layer membrane structures such as that shown in Fig. 2. Further barrier layers may be added in between metal layers to address the specific problem of atomic inter-diffusion which can dramatically affect the $\text{H}_2$ transportation ability of the membrane, particularly in metal membranes.

Ceramic membrane development is somewhat limited by the availability of techniques to fabricate complex designs. Again these membranes may be self-supporting or supported in thin film form on a porous ceramic or metal structure to enhance flux rates and to provide mechanical strength to the thin film structure. Simple membrane reactor designs (e.g. flat plate and tubular) can be fabricated by traditional ceramic processing techniques such as dry pressing, tape casting, screen printing, spraying, calendar rolling, etc. Often flat plate and some tubular designs require seals which can withstand extreme temperatures (>600 °C) and pressures (>10 MPa). A number of new novel designs have been reported in the literature. For example, a hollow fibre ceramic membrane design possesses a significantly larger area per unit volume than disk-shaped membranes and avoids complications associated with high temperature (>600 °C) sealing by keeping the sealing ends away from the high-temperature (>600 °C) area of the separation module [111,112]. An alternative high surface-to-volume membrane module design that is useful for reducing the footprint of the membrane is the spiral-wound module [113].

5. Conclusion

Membrane separation technologies (for $\text{O}_2$, $\text{H}_2$ and $\text{CO}_2$ separation) have the potential to play a key role in future clean power generation and $\text{H}_2$ production from fossil fuels, increase fuel conversion efficiency and reduce the negative environmental impact of power generation via
coal or natural gas power plants. However, the current generation materials and membranes have limitations with respect to the flux, mechanical strength and durability. Major effort is still required to optimise materials, their composition, chemical stability as well as device design and fabrication processes.

Key issues and challenges for using gas separation membranes in future power plants and the production of hydrogen are: choice of the material to suit an application; optimum operating temperature of the membrane material for integration in to a process; fast surface exchange kinetics (catalyst layers, electrodes) with gases; long-term reliability in operation and during thermal cycling;

Acknowledgements

Authors would like to thank Dr. Sarbjit Giddey and Fabio Ciacchi for reviewing this manuscript.

References

[1] US Department of Energy’s Office of Fossil Energy, Vision 21 Program. <http://www.fossil.energy.gov/programs/powersystems/vision21/1>.
[2] Australia’s Coal 21 program <http://www.coal21.com-au/1>.
[3] S. Benson, IEA Clean Coal Centre—Ceramics for advanced power generation. Report CCC/37. ISBN: 92-9029-349-7, (2000) 64pp. <http://www.iea-coal.org.uk/templates/ieaccc/report_detail.asp?LogDocId=80582&PageId=600>.
[4] S. Sircar, T.C. Golden, Sep. Sci. Technol. 35 (2000) 667.
[5] P.N. Dyer, R.E. Richards, S.L. Russek, D.M. Taylor, Solid State Ion. 134 (2000) 21.
[6] R.W. Spillman, Chem. Eng. Prog. 85 (1989) 41.
[7] R.F. Service, Science 305 (2004) 963.
[8] C.J. Orme, F.T. Ciacchi, Adv. Mater. 13 (2001) 993.
[9] T.J. Mazanec, Electrochem. Soc. Interf. (1996) 46.
[10] J. Padin, T.N. Veziroglu, A. Shahin, Int. J. Hydrogen Energy 25 (2000) 295.
[11] I.R. Summerfield, S.H. Goldthorpe, C.J. Bower, Proc. Inst. Mech. Eng. Pt. A—J. Power Energy 207 (1993) 81.
[12] J.C. Chow, J.G. Watson, A. Herzog, S.M. Benson, G.M. Hidy, W.D. Gunter, S.J. Penkala, C.M. White, J. Air Waste Manage. Assoc. 53 (2003) 1172.
[13] C.M. White, B.R. Strazisar, E.J. Granite, J.S. Hoffman, H.W. Pennline, J. Air Waste Manage. Assoc. 53 (2003) 645.
[14] R.F. Service, Science 305 (2004) 965.
[15] S.P. Kaldis, G. Skodras, G.P. Sakellariopoulou, Fuel Process. Technol. 85 (2004) 337.
[16] J.A. Ritter, A.D. Ebner, Separation Technology R&D Needs for Hydrogen Production in the Chemical and Petrochemical Industries, 2005.
[17] J.W. Phair, R. Donelson, Ind. Eng. Chem. Res. 45 (2006) 3657.
[18] S.N. Paglieri, J.D. Way, Sep. Purif. Methods 31 (2002) 1.
[19] S.-I. Yamaura, Y. Shimpo, H. Okouchi, M. Nishida, O. Kajita, H. Kimura, A. Inoue, Mater. T. JIM 44 (2003) 1885.
[20] Y. Zhang, T. Ozaki, M. Komaki, C. Nishimura, Scripta Mater. 47 (2002) 601.
