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Review of proton conductors for hydrogen separation

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Abstract There is a global push to develop a range of hydrogen technologies for timely adoption of the hydrogen economy. This is critical in view of the depleting oil reserves and looming transport fuel shortage, global warming, and increasing pollution. Molecular hydrogen (H_2) can be generated by a number of renewable and fossil-fuel-based resources. However, given the high cost of H_2 generation by renewable energy at this stage, fossil or carbon fuels are likely to meet the short- to medium-term demand for hydrogen. In view of this, effective technologies are required for the separation of H_2 from a gas feed (by-products of coal or bio-mass gasification plants, or gases from fossil fuel partial oxidation or reforming) consisting mainly of H_2 and CO_2 with small quantities of other gases such as CH_4 , CO , H_2O , and traces of sulphur compounds. Several technologies are under development for hydrogen separation. One such technology is based on ion transport membranes, which conduct protons or both protons and electrons. Although these materials have been considered for other applications, such as gas sensors, fuel cells and water electrolysis, the interest in their use as gas separation membranes has developed only recently. In this paper, various classes of proton-conducting materials have been reviewed with specific emphasis on their potential use as H_2 separation membranes in the industrial processes of coal gasification, natural gas reforming, methanol reforming and the water-gas shift (WGS) reaction. Key material requirements for their use in these applications have been discussed.

Keywords Proton conductors · Hydrogen separation · Hydrogen economy · Coal gasification · Methane reforming

Introduction

Many studies predict that global oil production is likely to peak within the next 5 to 15 years [1–3]. With declining global oil reserves and consequent concern over the supply of liquid fuels for transport application for future generations, increasing pollution and global warming prospects, there is an increasing worldwide interest in the hydrogen economy and hydrogen (H_2) technologies. In this scenario, hydrogen will be the main energy carrier, currency, and storage media.

Currently, world H_2 production is about 500 billion m^3/Y or 42 million tons per annum [4] and would barely meet ~1.5% of total global energy demand or US transportation needs. Most of the H_2 presently generated is via the steam reforming of natural gas. About half of this is used for ammonia, fertilizer, and explosive production and just over 1/3 for the impurity removal and upgrade of heavy oil fractions into lighter and more valuable products. The remainder, in small quantities, is used in methanol production, chemical and metallurgical industries, and space missions as rocket fuel. However, to use hydrogen as the main energy carrier and storage media, H_2 has to be generated in significantly larger quantities. A range of new technologies based on renewable energy (photoelectrolysis, photo-biological processes, water electrolysis, thermolysis, etc.) or fossil fuels (reforming, partial oxidation, coal or bio-mass gasification, etc.) or their combination (e.g., solar thermal reforming of natural gas) are under development or consideration [5–7]. Although generation of H_2 from renewable energy sources has the potential to provide a sustainable energy cycle, there is consensus that fossil fuels would provide a short- to medium-term solution, provided H_2 can be generated without additional adverse environmental impacts [8, 9].

In principle, apart from steam reforming of natural gas, H_2 can also be produced from steam reforming or partial oxidation of a range of other carbon fuels and by the gasification of coal or bio-mass. These processes may be followed by the water-gas shift reaction to convert CO in the reformat into more H_2 and CO_2 . However, to avoid

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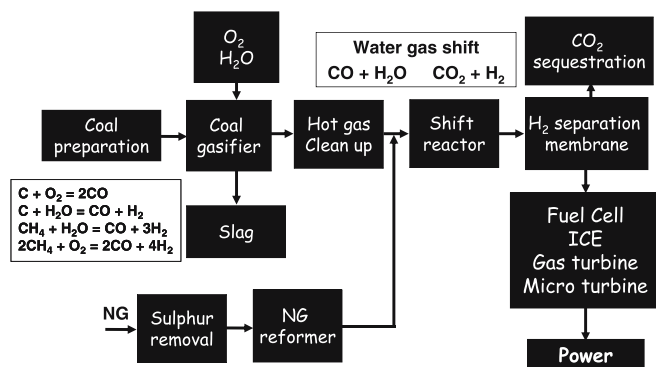


Fig. 1 A schematic of a coal gasification/natural gas reforming plant for H₂ production (NG Natural gas, ICE internal combustion engine)

greenhouse gas emission penalties, the H₂ subsequently needs to be separated from CO₂ and other gases to attain the desired level of purity, followed by CO₂ sequestration (Fig. 1).

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, coal gasification produces syn-gas, which can be used to run a gas turbine, a solid oxide, or a molten carbonate fuel cell to generate power. Syn-gas may also act as a feedstock for the production of liquid fuels and other chemicals. However, coal-based power plants would still be quite greenhouse-gas-intensive and produce CO₂ in a dilute form, which needs to be separated and sequestered to reduce greenhouse gas emissions. Technologies available for post-combustion CO₂ separation are expensive and bulky although they have the advantage of being integrated into existing power plants with minimum penalty on power generation infrastructure. Alternatively, the pre-combustion separation of CO₂ in new coal-based power plants is expected to be more economical, as the gas is in concentrated form and at a high pressure.

For pre-combustion separation of CO₂ for its sequestration, the syn-gas is shift-converted into CO₂ and more H₂. Following separation of H₂ from CO₂, the H₂ then can be combusted in a gas turbine or an internal combustion engine, or used in low temperature fuel cells (e.g., polymer electrolyte membrane or phosphoric acid) at higher electric and system efficiencies. The CO₂ can be transported in a concentrated form for sequestration. The use of hydrogen as a transport fuel, for example, in polymer electrolyte membrane fuel cell engines, would significantly reduce the dependence on oil and reduce the burden on depleting oil reserves.

A range of technologies are available for the separation of H₂ from CO₂ and other gases [10, 11]. The technologies, which can be directly integrated into the reforming or gasification plants (temperature, pressure), are more attractive from operational and economic points of view [10].

Apart from chemical scrubbing, cryogenic, and pressure swing adsorption techniques for CO₂ removal from product

gases, the technologies available specifically for H₂ separation include:

1. Polymer membranes
2. Dense metal membranes
3. Nano-porous ceramic or glass ceramic membranes
4. Dense ion transport membranes
5. Dense cermet membranes consisting of an ion transport material and a metal.

Polymer membranes operate with selective permeation of one or more gases from the feed side to the permeate side under a concentration gradient. The gas separation factor depends on the size of the gases to be separated and the molecular sieving capability of the membrane, which in turn depends on the diffusivity and solubility selectivity factors. Typically, small molecules, such as H₂, move rapidly, compared with bulky CO₂ molecules. These membranes are used in various industrial processes. The major drawbacks are that they cannot be used in aggressive chemical environments or at high temperatures, and gases must be cooled sufficiently for hydrogen separation and reheated—a costly and energy-intensive process. Moreover, the separation factor is low, and it is often difficult to get high purity hydrogen and flux rates are significantly lower [9].

In nano-porous membranes, H₂ is separated from gases such as CO₂, CO, CH₄, etc., by molecular diffusion if the pore size of the membrane material is such that smaller H₂ molecules (diameter=2.83 Å) can move freely while large molecules of other gases are restricted. Therefore, the material acts as a molecular sieve, allowing only H₂ to pass through. Typical membrane materials used are metal oxides and often silica, aluminosilicates, silicalite, and zeolites. The hydrogen flux is directly proportional to the pressure differential across the membrane. The major disadvantages are the difficulty of fabricating thin membranes free of flaws and with a discrete pore structure to achieve a large separation factor. Thus, the H₂ produced is not of high purity.

Metal membranes, such as Pd, Zr, Ta, and Nb or their alloys and many amorphous alloys are known to be effective in separating hydrogen from other gases at high temperatures (300–600 °C) (Phair and Donelson 2006, submitted for publication). The process for H₂ separation relies on their ability to allow only H₂ gas to diffuse through and restrict the flow of all other gases. Hydrogen permeation proceeds in several steps via adsorption and dissociation of H₂ to the atomic form, solution in the metal, diffusion, and re-association and desorption. The hydrogen flux through the membrane is generally proportional to the square root of the pressure differential (assuming fast hydrogen exchange at the gas/metal interface), with hydrogen migrating from the high pressure side to the low-pressure side. The hydrogen permeation flux rates are a function of hydrogen solubility, hydrogen diffusion characteristics, operating temperature, and the membrane thickness. In addition, the metal membrane must have the ability to dissociate and reassociate H₂ at the surface. Alternatively, effective dissociation/association catalytic layers may be required to perform this function. The H₂ produced is of very high purity and can be directly

utilized in a fuel cell. However, the major drawback is that Pd is too expensive and has to be used as a very thin film (few microns) on a porous support structure to reduce cost and increase flux rates. Other metals or alloys are sensitive to hydrogen embrittlement, exhibit low hydrogen flux density or lack stability under operating environments.

In ion transport membranes, H₂ is separated and transported through the material electrochemically by a surface exchange reaction at the feed surface of the membrane to dissociate and ionize H₂ into protons. These protons then migrate through the membrane material and are reduced to form H₂ molecules on the permeate side of the membrane. The driving force for hydrogen migration is the H₂ partial pressure differential across the membrane, with hydrogen migrating from the high-pressure side to the low-pressure side. One of the major advantages of this technology is that the dense membranes are 100% selective with an infinite separation factor. Thus, no secondary purification of the gas is required.

Ideally, the ion transport membrane material must have both proton and electronic conductivity to avoid external electrochemical loading of the cell and to save energy. To optimize proton and electronic conductivity, these materials may be mixed with a metal to enhance electronic conduction. If the metal is also a proton transporting metal, such as Pd, Pd-alloys, or cheaper alternatives, then the hydrogen flux can be substantially enhanced. Major technical issues relate to the availability of suitable proton conductors with high proton flux rates and which are stable at the operating temperatures (300–600 °C), pressures (to 20–30 bar A), and in the presence of other gases and contaminants (CO₂, CO, CH₄, H₂O, H₂S, and metal vapors). Other major challenges relate to ensuring the materials used have adequate mechanical strength and toughness, that chemical and thermal compatibility exists between metal and ceramic phases, and that the fabrication and optimization of the microstructure can provide dense, defect-free thin membranes. To become attractive for use at an industrial scale, H₂ separation rates in excess of 50 ml(stp)/min cm² should be achieved.

Several materials exhibit reasonable proton conductivity in the temperature range of 100 to 900 °C. These materials may have the potential to be used for the construction of electrochemical cells for the separation of H₂ from CO₂. This paper provides an overview of various classes of proton-conducting materials available for H₂ separation,

key criteria they must meet, and application regimes of proton and mixed proton/electron conductors.

Key criteria of proton conductors to separate H₂

A H₂ separation membrane based on dense ceramic proton conductors has similar performance targets to any other hydrogen separation membrane. That is, the membrane must have: (1) high H₂ permeation flux rates; (2) low cost; (3) sufficient lifetime durability in real operating environments; (4) low parasitic power requirements; and (5) low membrane fabrication costs. Specific target values for dense ceramic H₂ separation membranes outlined by the U.S. Department of Energy are described in Table 1.

To operate a H₂ separation membrane, a hydrogen chemical potential gradient must be applied to drive the flow of hydrogen through the membrane. The chemical potential gradient across the membrane may be controlled by the pressure gradient, concentration gradient, temperature gradient, or electric field gradient. Typically, a hydrostatic gradient is used to promote the transport of H₂ through the membrane, so it must be able to withstand extreme pressure (up to 7 MPa Δ P hydrogen partial pressure) and operating temperature between 300 and 900 °C, depending on the specific industrial process (e.g., steam reforming of natural gas, methanol partial oxidation, or coal gasification) in which it is applied.

Overall, the process of hydrogen permeation through a dense ion transport membrane involves several steps (Fig. 2):

1. H₂ diffusion in the gas phase to reaction sites on the surface of the feed side
2. H₂ adsorption, dissociation, and charge transfer at the membrane surface
3. H⁺ diffusion in the bulk of the membrane
4. H⁺ diffusion along and through grain boundaries
5. Proton reduction and hydrogen re-association at the membrane surface
6. H₂ desorption and movement away from the surface on the permeate side.

The hydrogen permeation rate increases with increasing temperature, decreasing membrane thickness—as it is inversely proportional to the thickness of the membrane, and

Table 1 Hydrogen dense ceramic membrane separation targets [120, 121]

Characteristic	Units	2003 status	2007 target	2010 target	2015 target
Flux rate	m ³ /h/m ²	18.3	30.5	61	91.5
Cost	US\$/m ²	1,940	1,620	1,080	<1,080
Durability	Years	<1	1	3	>5
Operating temp	°C	300–600	400–700	300–600	250–500
Parasitic power	kWh/1,000 m ³ H ₂ generated	113	113	105	<100
Δ P operating capability	MPa	0.69	1.38	<2.76	2.76–6.89
Hydrogen recovery	% of total gas	60	70	80	90
Hydrogen purity	% of total (dry) gas	>99.9	>99.9	>99.95	99.99

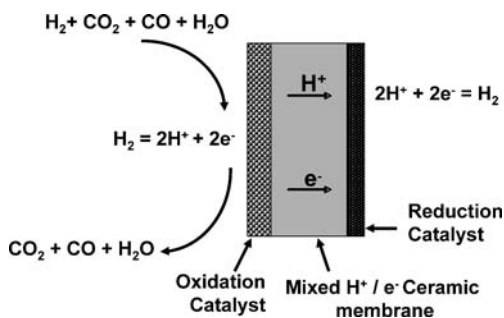


Fig. 2 Process steps for H₂ separation with a mixed proton/electron-conducting membrane

maximum H₂ dissociation and re-association reaction rates at the surface. However, finding a single phase material with both high hydrogen diffusivity in the bulk and which also allows fast surface exchange of hydrogen is not easy.

Achieving high H₂ flux remains the greatest obstacle for developing proton conductors into commercially useful hydrogen separation membranes. Both proton and electron conductivities in excess of 0.1 S cm⁻¹ are required in order for a proton conductor to be useful for hydrogen separation. In materials, which have sufficient proton conductivity, it is the rate of electron transport that is the limiting step in the permeation of hydrogen through a proton conductor [12]. Thus, if the proton conductor cannot conduct sufficient quantity of electrons by itself, it must be capable of forming a composite material with a second phase that can conduct sufficient quantity of electrons.

While hydrogen ion transport membranes may be used as self-supported structures of variable shapes (e.g., flat plates or tubes) and sizes, the manufacture of a very thin membrane (of the order of few microns) on a support structure is attracting significant interest for achieving high hydrogen flux rates and for imparting mechanical integrity to thin-film structures. The porous support may be constructed from a ceramic or metallic alloy and may consist of multiple layers of variable pore structure for ease of gas diffusion (more open microstructure) and deposition of impervious coatings (nano-porous microstructure) of ion transport material at the surface. Several variations to this design are possible, such as a tri-layer structure reported in the literature that consists of a thin-film mixed conducting membrane surrounded by a porous support/catalyst layer on either side [13]. In any case, due consideration needs to be given to match the thermal expansion coefficient of the membrane material with the support structure; otherwise, delamination and cracking of the membrane can occur during fabrication and subsequent use.

Dense thin-film membranes of the proton conductive layer can be deposited on to the porous support by a variety of methods, including spin coating [14, 15], sputtering [16], slip-casting [17], sol-gel methods [18], particulate or vapor phase deposition methods (e.g., chemical or electrochemical vapor phase deposition) [19–21]. Complications with wet dense-film preparative methods can arise due to the impregnation of the membrane materials into the porous

substrate, but this may be controlled by altering the properties of the membrane material and micropores of the porous support structure. A relatively simple and cheap method of thin-film preparation that may avoid these difficulties is dry pressing to prepare dense ceramic membranes on porous substrates [22]. The effect of preparative techniques for proton conductors (liquid-phase or solid state) on the microstructure and the H₂ permeation properties remains to be fully investigated.

Critical to the design of dense H₂ separation membrane is the surface of the membrane, which must catalyze the H₂ dissociation/reassociation reactions necessary for the permeation of hydrogen through the membrane. Generally, the surface properties of proton conductive materials are insufficient to allow for the spontaneous dissociation or re-association of H₂ on the surface. As a consequence, surface modification of the proton-conductive thin film or electrodes may be required to promote hydrogen exchange reactions at the gas/membrane interface. Often, the requirements of having secondary catalytic layers or electrodes are reduced or eliminated if a metal phase (e.g., Ni) is added in sufficient quantities to improve the electron-conducting properties of the material and promote the hydrogen exchange reaction [23]. In addition, the surface must be free of impurities and undesired phases that may form as a result of the membrane preparation methods used, handling, or operation. For example, BaCe_{0.90}Yb_{0.10}O_{3-δ} (BCYb10) thin films synthesized through a combined EDTA-citrate complexing method, underwent phase segregation in an asymmetric atmosphere and failed to maintain a perovskite structure at the surface [24].

Another critical property for a proton conductor to serve as a useful hydrogen separation membrane is high mechanical strength. However, if a proton conductor with high flux capabilities has poor mechanical strength, then it must be incorporated into a composite structure to improve the device's mechanical properties. It may be necessary, for instance, to impregnate the proton-conductive material into a porous ceramic or metal, such that it can withstand the physical demands (e.g., high pressures and temperatures) of its application as a H₂ separation membrane [25]. Alternatively, proton conductors may be combined with a refractory oxide to form a composite material with stronger physical properties upon sintering, which widens its application domain [26].

Chemical stability under conditions in which proton conductors may be used for H₂ separation is another key criterion. Under all situations of practical use, the H₂ separation membrane will be exposed to reducing conditions on both sides of the membrane. Not only must the ceramic be stable under these conditions, but also exhibit stability in the presence of CO, CO₂, H₂O, H₂S, NO_x, and chlorides, as these are typically present in the gases from which the H₂ must be separated. Many oxides with high conductivity (e.g., BaCeO₃-derived compounds) are often unstable and susceptible to reaction with CO₂ and H₂O, forming insulating carbonates and hydroxides [27]. This may be overcome by doping highly conducting oxides to improve stability (e.g., Zr-doped cerates) [28], improving

the conductivity of more chemically stable oxides by reducing grain boundary resistance [29], by composite design, or by developing new alternatives (e.g., pyrochlores without any Ba or Sr) [13].

The proton conductor must also be thermally stable under the operating conditions expected for H₂ separation, and any spontaneously combustible or decomposing phases should be eliminated or modified to remove the potential for thermal degradation.

Compared to dense metal membrane structures on a porous metal support, which may undergo interdiffusion of metals resulting in a reduction of the H₂ transporting ability, proton-conducting ceramics, which can also be manufactured as dense membranes on porous support structures, are expected to be more stable [30]. As a result, there will be less complications in designing thermally compatible support structures for ceramic proton conductors allowing an easy integration into industrial processes. Furthermore, dense ceramic membranes have the potential to exist as self-supported structures at high temperatures (>600 °C).

One other important stage in the integration of a proton-conducting membrane into the overall H₂ separation process is ensuring that the membrane is hermetically sealed to the support structure of the separation chamber by a seal that is both mechanically robust and resistant to high temperatures [31]. Recent attention has focused on brazing as a method to seal ceramic membranes used in the purification of gases derived from gasification processes with certain braze alloys that are stable at high temperature (800 °C) [32]. Inconel 600 has been reported as a useful brazing alloy for joining ceramic membranes to their metal holders [13], while Gold ABA (3% Ni, 0.6% Ti, balance Au by weight) and Niore ABA (16% Ni, 0.75% Mo, 1.25% V, balance Au by weight) have also been tried and, while they undergo oxidative damage in an oxygenated atmosphere [32], their properties in a reducing atmosphere at high temperature are expected to be better. Thus, some proton conductors also have the advantage of being hermetically sealable for practical use in separating hydrogen.

Classes of proton conductors

Solid-state proton conductors may be classified in a variety of ways based, for example, on their chemical structure, composition, preparative method, or cost, to name a few. As high-bulk H₂ flux is a fundamental requirement for any proton conductor to be applied as a hydrogen separation membrane, it is useful to review proton conductors which, as a minimum, are already known to exhibit high proton conductivity. Kreuer has already identified four main groups of compounds as “fast” proton conductors of technological and engineering significance [33]. The challenge now is to review the various “fast” proton conductors based on the Kreuer classification system, with reference to the application as H₂ separation membranes.

Water-containing systems

Hydrated compounds or water-containing systems that may be of potential use as H₂ separation membranes, include a diverse array of inorganic and organic compounds. While relatively few novel compounds have been discovered over the past 20 years with high conductivity, significant advances have been made in the characterization of these materials and the formation and properties of composite-derived materials.

Water-containing proton conductors with high proton conductivity are the hydrated hetero-polyoxo-metallate acids (heteropolyacids), such as hydrated phosphomolybdic acid (H₃PMo₁₂O₄₀·nH₂O, denoted as PMA) and phosphotungstic acid (H₃PW₁₂O₄₀·nH₂O, denoted as PTA), due to three-dimensional conductivity network. Proton conductivities of the order of 10⁻² S cm⁻¹ are routinely achieved at room temperature for pure compounds. However, under conditions of low humidity, the hydrates lose their water of crystallization, leading to a decrease in the proton conductivity. Furthermore, pelletization of the compounds can also force the water of crystallization out of the compound affecting the ionic conductivity. Therefore, novel approaches have been investigated to improve the stability and robustness of such heteropolyacids as protonic conductors, which include the insertion of the heteropolyacids within the pores of SiO₂ gel [34], or the mixing and grinding with a refractory oxide (e.g., Al₂O₃) to form a composite membrane [35, 36].

Of probably greater technological interest, however, have been proton conductors based on sulfonated polymer membranes with hydrated layers, such as sulfonated fluorocarbon NAFION [37], sulfonated polybenzimidazole (S-PBI) [38], and sulfonated polyether ether ketone (S-PEEK) [39], which all exhibit high proton conductivity and reasonable chemical stability. While NAFION is generally considered a stable and robust material, limitations to its use exist due to the fact that its glass transition temperature is at ~105 °C and the membrane loses water and, thus, ionic conductivity at temperatures >80 °C. As a result, recent research has sought to expand the conditions under which they may be used by developing composite materials or polymer-based alternatives to NAFION, which maintain high conductivity at higher temperatures (300–600 °C).

Composite membranes in which NAFION is sorbed onto high-surface-area structures, such as polystyrene microbeads, have been reported to exhibit higher proton flux than ordinary NAFION films [40]. Alternative polymeric membranes also receiving interest include other poly(perfluoro-sulfonic acid) membranes, styrene-based polymers, poly(arylene ether)s, poly(imide)s, polyphosphazene, and polymers containing alternative hydrating moieties, such as the phosphonic group [41]. Success at increasing the maximum operating temperature up to 145 °C has already been achieved by combining perfluorinated ionomers (NAFION) and non-perfluorinated ionomers (silica) to form a hybrid composite membrane [42]. However, significant modifications of present polymeric membranes are still required to demonstrate that their chemical, thermal, and physical sta-

bility can satisfy the demands of an industrial H₂ separation process.

Inorganic acid hydrates with a layered structure, on the other hand, have the advantage of being prepared using more thermally stable acid groups. Thus, it is possible to synthesize a variety of acid hydrates with high proton conductivity that are stable up to around 350 °C. These include H₃OUO₂XO₄·3H₂O [X=P, As], H₃Sb₃P₂O₁₄·10H₂O, H₂Ti₄O₉·1.2H₂O and HSbP₂O₈·10H₂O, using phosphonic groups. Typically, compounds such as H₃

OUO₂AsO₄·3H₂O undergo a phase transition above ~50 °C resulting in at least an order of magnitude increase in conductivity or “superconductivity”. Above 350 °C, however, prevention of complete acid condensation, while maintaining high proton conductivity, becomes extremely difficult, so their use is limited to below this temperature in pure form. Of notable interest are layered acidic zirconium silicates (e.g., K₂ZrSi₃O₉ or wadeite, K₂ZrSi₃O₉ or khibinskite), phosphates (α-Zr(HPO₄)₂·nH₂O and γ-Zr(PO₄)-(H₂PO₄)·2H₂O) and phosphonates (α- and

Table 2 Conductivity of potential proton-conducting materials for hydrogen separation membranes

Material	Optimal conducting temperature (°C)	Proton conductivity (S cm ⁻¹)	Reference
Hydrated sulfonated polymers			
NAFION	<100	5×10 ⁻² at 25 °C, 4×10 ⁻² at 160 °C	[37, 39]
S-PBI	<100	1×10 ⁻² at 25 °C	[38]
S-PEEK	<100	3×10 ⁻² at 25 °C, 4×10 ⁻² at 160 °C	[39]
Heteropolyacid hydrates			
H ₄ SiW ₁₂ O ₄₀ ·28H ₂ O	<100	2×10 ⁻² at 25 °C	[122, 123]
H ₃ PW ₁₂ O ₄₀ ·29H ₂ O	<100	8×10 ⁻² at 25 °C	[122, 123]
H ₃ PMo ₁₂ O ₄₀ ·29H ₂ O	<100	1.7×10 ⁻¹ at 25 °C	[122, 123]
Layered hydrates			
HUO ₂ PO ₄ ·4H ₂ O	<100	5×10 ⁻³ at 25 °C	[124, 125]
α-Zr(HPO ₄) ₂ ·nH ₂ O	<100	1×10 ⁻⁴ at 25 °C	[126]
γ-Zr(PO ₄)(H ₂ PO ₄)·2H ₂ O	<100	3×10 ⁻⁴ at 25 °C	[127]
γ-Zr sulfo phosphonates	<180	1×10 ⁻² at 25, 100 °C	[128]
Oxide hydrates			
Sb ₂ O ₅ ·4H ₂ O	<300	3×10 ⁻⁴ at 25 °C	[47, 49]
V ₂ O ₅ ·nH ₂ O, ZrO ₂ ·nH ₂ O,	<150	1×10 ⁻² at 100 °C	[48]
SnO ₂ ·nH ₂ O	<300	4×10 ⁻⁴ at 25 °C	[129]
Ce(HPO ₄) ₂ ·nH ₂ O	<150	1×10 ⁻³ at 100 °C	[48]
Polyphosphate composite			
NH ₄ PO ₃ /(NH ₄) ₂ SiP ₄ O ₁₃	200–300	8.7×10 ⁻³ (dry atm), 3.3×10 ⁻¹ (wet atm) at 300 °C.	[53, 54]
NH ₄ PO ₃ /TiP ₂ O ₇	150–250	2.4×10 ⁻² at 250 °C	[54]
Layered polyvalent (Zr or Ta) hydrogen phosphate	25 (Ta>Zr)	2×10 ⁻⁴ at 25 °C	[130]
Sr-doped La ₃ P ₃ O ₉	700	7×10 ⁻⁷ to 3×10 ⁻⁴ at 300–700 °C	[131, 132]
Sr-doped LaPO ₄	500–925	6×10 ⁻⁶ to 3×10 ⁻⁴ at 500–925 °C in wet atm	[133, 134]
Perovskites			
BaCe _{0.9} Y _{0.1} O _{3-α} (BCY)	500–900	1.8×10 ⁻² to 7×10 ⁻² at 600–1,000 °C	[135]
BaZr _{0.9} Y _{0.1} O _{3-α} (BZY)	500–900	1.6×10 ⁻³ to 6×10 ⁻³ at 600–1,000 °C	[135]
Ba ₃ Ca _{1.18} Nb _{1.82} O _{8.73} (BCN18)	500–900	5.5×10 ⁻⁴ at 600 °C	[136]
Oxo acid salts			
K ₃ H(SO ₄) ₂	100–200	9.5×10 ⁻⁶ to 2.2×10 ⁻² at 80–250 °C	[137]
CsHSO ₄		2×10 ⁻⁷ to 3×10 ⁻² at 110–190 °C	[138]
H ₃ OCIO ₄		3.5×10 ⁻⁴ at 25 °C	[139]
Oxo acid composites			
MeNO ₄ -SiO ₂ (Me=Rb, Cs)	100–200	1×10 ⁻⁶ to 1×10 ⁻² at 60–280 °C	[140]
Cs ₃ (HSO ₄) ₂ (H ₂ PO ₄)		1×10 ⁻⁶ to 1×10 ⁻² at 40–180 °C	[141]
Pyrochlore			
(La _{1.95} Ca _{0.05})Zr ₂ O _{7-δ}	500–900	6.8×10 ⁻² at 600 °C	[142]
La ₂ Ce ₂ O ₇ , Eu ₂ Zr ₂ O ₇		7×10 ⁻⁷ to 1×10 ⁻² at 300–800 °C	[78]
Chalcogenides			
H ₂ S/(B ₂ S ₃ or Ga ₂ S ₃)/(GeS ₂ , SiS ₂ , As ₂ S ₃ or CsI)	200–500	5×10 ⁻¹¹ to 4×10 ⁻⁷ at 60–300 °C	[94, 143]

γ -Zr sulfophenylphosphonate or sulfoarylphosphonates), which can exhibit good conductivity even in dry form [25]. Moreover, research has shown that novel forms of acidic phosphate and phosphonates intercalated with large molecules, such as imidazoles, pyrazoles, heterocyclic bases and alkyls, have significant proton conductivity [43–45]. These may provide a useful direction for future research along with dispersed systems of hydrated acidic particles and xerogels [46].

A variety of other non-layered hydrated oxides, such as antimonite acid ($\text{Sb}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$) [47], $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$, $\text{SnO}_2 \cdot n\text{H}_2\text{O}$ and $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ demonstrate high proton conductivity in the order of $10^{-2} \text{ S cm}^{-1}$ at $150 \text{ }^\circ\text{C}$ [48]. Although maintaining conditions of saturated water vapor pressure is a requirement for the operation of a number of hydrated compounds as proton conductors, some compounds, such as antimonite acid, are insensitive to humidity [49].

Unfortunately, the use of water-containing systems or acid hydrate compounds as H_2 separation membranes is often restricted, as conductivity is highly related to the water content. To operate most effectively, the membranes must retain H_2O as a hydrate or surface liquid to allow the ion jump mechanism to occur, which restricts their application to temperatures $<100 \text{ }^\circ\text{C}$ in their pure form. Even in fully dense materials, it is difficult to maintain a hydrated state at temperatures above $100 \text{ }^\circ\text{C}$, unless a water-impermeable barrier covers the membrane keeping the water within the material or there is a way of preserving an even and close distribution of water molecules across the surface of the membrane to sustain the necessary surface interactions for proton conduction.

To date, there have been scant reports of water-containing systems or hydrated compounds as proton conductors used as membranes for H_2 separation. While separation membranes constructed from these materials will probably not undergo any structural damage due to the presence of steam in the feed gas, the extent to which the steam may affect the operation and efficiency of such membranes remains unexplored at this stage. Moreover, the effect of other contaminants such as CO , H_2S , particulate, and metal vapor on their chemical stability is largely unknown. Table 2 gives conductivity data for various water-containing materials.

Oxo-acid salt conductors

This group includes the range of salts and acids pertaining to the heteroatom oxo-anions of sulphate, selenate, phosphate, arsenate, nitrate, etc. In the anhydrous state, these compounds are able to conduct protons due to self-dissociation and the hopping or jumping mechanism of protons among hetero-oxo ions (e.g., NO_3^- , SeO_4^{2-} , SO_4^{2-} , PO_4^{3-} , AsO_4^{3-} , etc.) by aid of rotating hetero-oxo ions, from one group to the next. So-called oxo-acid salt “superionic” conductors (e.g., CsHSO_4 , RbHSO_4) are receiving considerable research interest at the moment

for applications in numerous technologies where ionic conductors are required (e.g., fuel cell electrolytes) [50]. Proton conductors based on the hydrosulphate of larger alkali metals tend to exhibit a superprotonic transition with anomalously high conductivities at higher temperatures (usually $>140 \text{ }^\circ\text{C}$). Typically, the conductivity increases and the activation energy decreases with increasing cation radius, whereby Cs^+ provides the highest conductivity, followed by Rb^+ , K^+ , Na^+ and Li^+ . It has been suggested that this increase is not due to the metal cations themselves but due to the softer $\text{M}-\text{O}$ bonds, the resultant crystal structure and proximity of heteroatoms, which promote the rapid reorientations observed in superprotonic phases [51].

A significant advantage of oxo-salts is that they do not necessarily have to exist as a Bronsted acid or with a structural proton to exhibit high conductivity. Proton conductivity will occur in H_2 - or water- rich atmospheres for neutral sulphates [52], phosphates [53, 54], and nitrates [51]. Major limitations of oxo-salts for H_2 separation include the fact that they may decompose at higher temperatures if not properly stabilized. For instance, nitrates may decompose at temperatures above $350 \text{ }^\circ\text{C}$ (e.g., RbNO_3 to NO_2^-) [55], while sulphates may undergo reduction to form H_2S and H_2O [50].

As a consequence of these chemical susceptibilities, oxo-anion systems based on phosphates or complex heteropolyacids are more likely to be of practical use. In particular, polyphosphate glasses, aluminium polyphosphate, ammonium polyphosphate, and polyphosphate composites (e.g., $\text{NH}_4\text{PO}_3/(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$ or $\text{NH}_4\text{PO}_3/\text{TiP}_2\text{O}_7$) [53, 54] have recently attracted interest for applications as proton conductors due to their high conductivities at intermediate temperature ranges. (e.g., 0.1 S cm^{-1} at $300 \text{ }^\circ\text{C}$) [56]. Recent work has examined the dynamics and nature of the species responsible for charge transport, although the full mechanism has not yet been elucidated. On the downside, synthesis of polyphosphates is slightly more complicated than for other oxo-acid salt composites, based on sulphate and nitrate.

Oxo-acid salts also have the distinct advantage that while the physical properties of the salts alone are probably inadequate to form a mechanically useful separation membrane, they may be combined with intergranular oxides (e.g., SiO_2 [57, 58], Al_2O_3 [55, 59], Fe_2O_3 , TiO_2 [60], ZrO_2 , MgO , etc.) to form proton-conducting composite materials, which are stable over a wider temperature range and show an increase in total conductivity due to modifications to the phase boundaries of the pure salt. Oxo-acid salts have also been combined with polymers, such as polyacrylamide [61], poly(ethylene oxide), and poly(benzimidazole) to produce highly conducting hybrid materials [62]. Their applicability to H_2 separation has received limited attention to date, but given their relative cost effectiveness and ease of preparation, compared to a host of other proton conductors, they remain an attractive choice for H_2 separation membranes.

Densely packed oxides

This group of proton conductors is extremely large and encompasses a series of different classes of materials. Their main advantages are that they are generally quite stable and durable materials particularly up to high temperatures (1,000 °C), and may also be able to conduct electrons. Achieving high conductivities and chemical stability at low temperatures remains a challenge for these systems. For most of these materials, ionic defects form the basis for proton transport. The systems, which have potential application to H₂ separation membranes, are outlined below.

Perovskites

Numerous cerate and zirconate perovskite oxides (e.g., SrCeO₃, BaCeO₃, CaZrO₃, or SrZrO₃) have been reported to have reasonable proton conductivity in hydrogen-rich and humid atmospheres, particularly at high temperature when they are doped with a rare earth ion [63, 64]. Their basic formula is AB_{1-x}M_xO_{3-α}, where M is some trivalent dopant like rare earth element (e.g., Nd³⁺, Gd³⁺, Y³⁺, Yb³⁺, La³⁺) and α is the oxygen deficiency in the perovskite-type oxide lattice.

Materials based on BaCeO₃ and SrCeO₃ with the perovskite structure are p-type or hole conductors in atmospheres free of H₂ or water vapor. However, in the presence of hydrogen or water vapor, they develop proton conductivity with a decrease of electronic conductivity. BaCeO₃ and SrCeO₃ are typically doped with an aliovalent cation (Y, Yb, Gd) at the B site to replace some Ce in the lattice and, as a consequence, oxygen vacancies are created to maintain electroneutrality. These vacancies play an important role for proton conduction. Due to the presence of water vapor, mobile protons are created when the water is absorbed into the oxygen vacancies, formed by the presence of the trivalent ion in the lattice structure. A distinct advantage of perovskites is their ability to also conduct electrons in the single phase. While electronic conductivities may typically be relatively low, they can be increased significantly by doping aliovalent ions in the B site. SrCe_{0.95}Yb_{0.05}O_{3-x} has been reported to have proton conductivity of 0.005 S cm⁻¹ at 800 °C and 0.018 S cm⁻¹ at 1,000 °C [64]. This conductivity, however, is not sufficient to achieve the target H₂ flux.

It should be noted that very few perovskites exhibit both high proton conductivity and thermodynamic stability, which are vital pre-requisites for use as a H₂ separation membrane. For example, while cerate oxides (e.g., BaCeO₃) may display reasonable proton conductivity characteristics, their chemical stability is very low under real operating environments (e.g., reaction with CO₂, the major constituent of the gas mixture from which H₂ is to be separated). Research is underway to overcome some of these problems. However, any degradation in the membrane would lead to a decrease in the H₂ flux rate. The reverse may be said to be true of zirconate oxides (e.g., BaZrO₃),

which, despite exhibiting high chemical stability, have low conductivity and require high sintering temperatures to achieve dense structures free of pores [28]. Often, however, it is possible to achieve a compromise between the proton conductivity and chemical stability (for use as H₂ separation membranes), by preparing mixed solid solutions of BaCeO₃ and BaZrO₃.

Furthermore, increased stability of perovskite materials may best be achieved by synthesizing mixed perovskites, such that A₂B'_{1+x}B''_{1-x}M_xO_{6-α} (where A=Ba or Sr, B'= trivalent ion and B''=pentavalent ion) or A₃B'_{1+x}B''_{2-x}M_xO_{9-α} (where A=Ba or Sr, B'=divalent ion and B''=pentavalent ion) [65–68]. In addition to increased thermodynamic stability, off-stoichiometric perovskites, also exhibit higher proton conductivity, for example, Ba₃CaNb₂O₉ exhibits higher proton conductivity than Nd-doped BaCeO₃ [65, 66]. Mixed perovskites have been demonstrated to maintain their structure sitting in boiling water for 5 days, while their simple perovskite counterparts decomposed after a few hours [69, 70]. This has been attributed to lower Madelung (electrostatic) energies [71].

While researchers have examined the effects of A-site doping and stoichiometry on increasing the stability of barium cerates while preserving high conductivity [72], there are very few reports on the possibilities of using mixed perovskites as proton conductors for H₂ separation. Furthermore, recent work comparing polycrystalline conductors to single crystal conductors has demonstrated that the grain boundary interface plays a significant role in controlling the total conductivity [73]. Attaining a high level of understanding of grain-boundary microstructure as a function of composition and sintering conditions is critical to the design of new materials, whereby, the grain boundaries may be manipulated to optimize conductivity [74, 75]. However, there are very few reports in the literature on the relationship between grain boundaries, the ceramic microstructure, and proton conductivity of polycrystalline perovskites.

Efforts are also continually being made to develop perovskites that conduct protons at intermediate temperature ranges (300–700 °C). Recently, significant focus has been given to a class of perovskites with the formula A₃B'_{1+x}B''_{2-x}M_xO_{9-δ}, where A and B' are divalent ions and B'' are pentavalent ions [65]. Initial results indicate that non-stoichiometric compounds of this group (e.g., non-stoichiometric Ba₃CaNb₂O₉) yield promising proton conductivity exceeding that of Nd-doped BaCeO₃ [66]. However, the stability of barium oxides in CO₂ and H₂ is a drawback for practical operations. Other materials considered include strontium zirconates (Sr₃Ca_{1+x+y}Zr_{1-x}Ta_{1-y}O_{9-δ} (SCZT), where δ = (2x + 3y)/2,), although the proton conductivities are slightly lower [76]. The ionic conductivity data are given in Table 2.

Some of the other major issues in relation to the use of these materials as H₂ separation membranes are their poor mechanical strength and toughness, and their preparation as thin and impervious coatings on controlled porosity support structures.

Pyrochlores

Pyrochlores have been attracting growing interest for H₂ separation due to their relatively high resistance to chemical attack by CO₂ and H₂O, compared to strontium and barium cerates [13]. Pyrochlores exist in the stable fluorite-type structure with multiple oxygen vacancies available for proton conduction and do not require strontium or barium, so they are, therefore, more chemically durable. For example, lanthanum zirconate (La₂Zr₂O₇) has been reported to possess reasonable proton conductivity in the 600–1,000 °C temperature range [77, 78], and substitutional doping of Sr for La and Y for Zr in La₂Zr₂O₇ can further increase the conductivity, with the highest gains obtained for a 4 and 8 mol% substitution of Y for Zr [79]. Other pyrochlores, such as (Gd_{0.98}Ca_{0.02})₂Ti₂O₇, have demonstrated high ionic conductivity at high temperature (0.01 S cm⁻¹ at 1,000 °C), as well as good electron conductivity [80], while Gd₂Mo₂O₇ is reported to possess metallic-like electron conductivities at room temperature [81].

The patent literature refers to a series of pyrochlores that may be useful for proton conduction, including A₂Zr_{2-x}Y_xO_{7-δ} (A=La, Nd, Gd, Sm), Y₂Ti_{2-x}M_xO_{7-δ} (M=In, Mg) [82], and A₂(B'_{1+β}B''_{1-β})O_{6-λ} or A₃(B'_{1+β}B''_{2-φ})O_{9-λ}, where A are divalent ions (e.g., Ba²⁺, Sr²⁺, Ca²⁺, La²⁺), B' ions are trivalent (e.g., Y³⁺, Ga³⁺, Sc³⁺, In³⁺, Yb³⁺, Nd³⁺), or tetravalent (e.g., Zr⁴⁺, Ti⁴⁺, Ce⁴⁺), and B'' ions are pentavalent (e.g., Bi⁵⁺, Nb⁵⁺) [83]. However, there are no detailed reports on the proton conductivity of these compounds and pyrochlores in general, as a function of composition in a reducing environment. While there is substantial opportunity for characterizing new proton conductors and mixed conductors based on pyrochlores, initial data seem to indicate that they may not be able to provide high enough proton conductivity to be useful as H₂ separation membranes (certainly not higher than perovskites); thus, interest in these materials is somewhat limited [13]. The ionic conductivity data for various materials are given in Table 2.

Other potential useful proton conductor oxides, sulfides

On hydrogen insertion into WO₃ or MoO₃ or other transition metal oxides, they can act as useful proton conductors. Recently, a series of tetragonal tungsten bronzes, Na_{1-x}H_xNbWO₆ have exhibited conductivities of the order of 10⁻² S cm⁻¹ at 90 °C [84]. Typically, the addition of Nb to the system is done so as to suppress electronic conduction. So, if the goal is to produce a mixed proton and electron conductor, it may not be necessary to substitute W; rather, try to maximize the mixed oxidation states of W. There has been little focus on bronzes to date as mixed proton and electron conductors and whether increased electrical conductivity increases proton conductivity and vice versa. While no startling conductivities have yet been reported, the

stability of these systems over a wide temperature range makes these materials potentially useful candidates for investigation as H₂ separation membranes. At this stage, however, it appears their conductivities are not high enough, and significant microstructural improvements are required before they can become a feasible alternative [85].

In addition to bronzes, a range of other oxides have been suggested as potential useful proton conductors for H₂ separation membranes, including compounds, such as brown millerites [86], fluorites [13, 87–89], and phosphates [90] in the structure of apatite, although data on their proton and electron conductivities, as well as thermal and chemical stability in a reducing environment, are limited. Again, high proton conductivity is normally only attained at high temperatures, which is a significant drawback to the application of such materials [90]. Recently, efforts have been made to prepare so-called intermediate temperature (400–700 °C) mixed electron and proton-conducting composite materials of a fluorite structure, but only limited reports on the proton conductivity of such materials that would be relevant to H₂ separation have surfaced [91, 92].

Structurally modified glasses remain another option for further research with sulfur glasses in particular, offering promise for high conductivity, compared to oxide glasses given the lower bond energies sulfur has with protons, compared to oxygen in anhydrous form. Chalcogenide glasses offer a new method for proton conduction at 100–300 °C, while maintaining good mechanical stability in a reducing atmosphere [93] with PbO-SiO₂, BaO-SiO₂ and CaO-SiO₂ cited for practical potential [94]. The ionic conductivity data for various materials are given in Table 2.

Application of proton conductors as mixed ionic and electronic conductors

Often, materials with high proton conductivity do not have sufficient electron conductivity to be useful as mixed ionic and electronic conductors, unless they are modified in some way. Ideally, the H₂ separation membrane material must have both proton and electronic conductivity to avoid the need to apply external electrical power to the cell. There are two options to enhance the electronic transport. One involves intrinsic doping of the materials with aliovalent cations, and the second involves mixing the materials with a metal or another electronic conducting material to enhance electronic conduction. Achievement of optimum proton/electronic conductivity by the former route may be somewhat more difficult.

Initial attempts to improve the electron conductivity of proton conducting perovskites (e.g., BaCe_{1-x}M_xO₃ and SrCe_{1-x}M_xO₃, where M is a rare earth metal), by replacing the usual univalent dopant with a multivalent dopant cation, such as Eu^{2+/3+} and Sm^{2+/3+}, have been only partially successful [95]. Further work is required to maximize electron conductivity by optimizing the dopant level. A more recent approach to improving the electron conductivity of perovskites has been to introduce a

transition metal (e.g., Ru) as a partial substitute for Ce in Y-doped BaCeO₃. A significant increase in the hydrogen permeation was observed due to an increase in ambipolar diffusion associated with hole conduction [96]. Another challenge is to optimize surface exchange reaction at the membrane/gas interface either by modifying the surface structure of the materials or by using coatings of catalytic materials, which facilitate H₂ dissociation/reassociation reactions.

For a proton conductor, which does not exhibit sufficient electron conduction with or without doping, a second conducting phase must be added forming a composite mixed conductor to function as a useful H₂ separation membrane. Typically, this involves the addition of a metal (e.g., Pd or Ni) in powdered or oxide form. For instance, a mixed conductor based on perovskite as the proton-conducting phase and Pd as the electron-conducting phase, preferably has the Pd added as a coating on the individual particles (size <45 μm) of the proton conducting oxide by wet impregnation of the powder, electroless plating, or chemical vapor deposition [97]. Addition of a metal, such as Ni, to form a dual-phase cermet not only increases the electron flow in cerate or zirconate-based perovskite oxides but improves their mechanical stability. Moreover, as the presence of Ni leads to an increase in the endothermic hydrogen solubility of the membrane, the hydrogen permeability increases due to enhanced H₂ ionization and adsorption at the membrane surface [98].

One further possibility for improving the electron conductivity is by adding a secondary ceramic phase (e.g., an n-type semiconductor) to the proton conducting perovskite oxide. For instance, the addition of doped ceria to perovskite materials above the percolation limit results in a substantial improvement to the electronic conductivity of the composite in a reducing atmosphere as well as improving the thermodynamic stability of the composite in both a CO₂- and H₂O-rich environment [83]. Other ceramic phases which may be added include semi-conductors, such as SnO₂, WO₃, or SiC. While dual-phase ceramics have not been extensively studied for mixed proton and electron conductors for H₂ separation, some reports do exist of dual ceramic-phase mixed oxygen-ion and electron conductors for separating H₂ [99]. These perovskite composites utilize Y- and Al-doped SrTiO₃ (YSTA) as the electron-conducting phase, while Gd-doped CeO₂ (GDC) is the oxygen-conducting phase, and exhibit good stability under reducing conditions associated with H₂ separation.

Critical to the development and improvement of composite mixed electron and proton conductors as a membrane for H₂ separation is a proper understanding of the nature and relative contributions of electron transport and proton transport to the bulk H₂ flux. Recent attempts at modeling the process of hydrogen permeation through mixed ionic-electronic conductor membranes have been based on considering the bulk solid-state diffusion of hydrogen as the rate limiting step [23], and by the resistor network approach [100]. Another important consideration when optimizing membrane design, is to carefully control the microstructure

and fabrication process so that reducing membrane thickness of the composite cermet-mixed conductor may not lead to an increase in the bulk resistivity. It may also be necessary to accompany the reduction in membrane thickness with a reduction in the interfacial resistance at the gas/membrane interface to maximize high levels of H₂ transportation [101]. For example, applying a catalytic layer to the surface can be an important way to maintain the high H₂ flux through a dense cermet membrane [102].

Other significant criteria in designing composite membranes include the chemical and thermal compatibility between metal (or oxide) and ceramic phases, as well as possible thermal expansion mismatch between various phases during fabrication of the membrane and its subsequent use. Also, fabrication process and optimization of the microstructure to obtain dense, defect-free thin membranes are critical issues.

Application regimes of proton conductors for H₂ separation

The application in which the separation membrane is to be used will largely dictate the performance requirements of the proton conductor. The main applications, to date, for H₂ separation membranes are in the industrial processes of coal gasification, natural gas reforming, methanol reforming, and the water-gas shift reaction. While the potential exists for utilizing other fossil fuels (e.g., naphtha and other heavier alkanes), biofuels, or biomass for H₂ generation [103, 104], there is limited immediate demand for developing technology to separate H₂ from these fuels. Conditions of the different industrial processes do vary most notably in the temperature, pressure, likely operating volumes, and composition (including contaminants) of the gas mixture from which H₂ is to be separated.

For example, with regard to operating temperatures, large-scale coal gasification requires temperatures in the range of 1,040–1,540 °C for entrained flow systems (e.g., Texaco, Shell, and E-Gas) or 760–1,040 °C for fluidized bed systems (e.g., U-Gas) [105]. Coal gasification, therefore, requires ceramic membranes with high chemical and mechanical and thermal stability to yield high proton con-

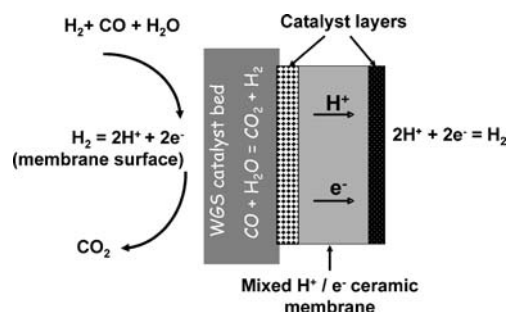


Fig. 3 Incorporation of water-gas shift catalyst in the H₂ separation membrane reactor to reduce overall system cost and to drive the water-gas shift reaction equilibrium forward (CO + H₂O = CO₂ + H₂) with continual removal of H₂

ductivities in this temperature range. Significant work on perovskites has established that they may be well-suited to application in this temperature regime (500–900 °C) [106, 107]. Optimal temperatures for reforming of natural gas occur at 800 to 950 °C for good conversion at 2.6 MPa for large-scale H₂ production [108]. However, low-temperature reforming is gaining increasing interest [109], particularly in membrane reactor applications where the membrane allows sufficiently high H₂ flux and has a high separation factor [110]. Reforming temperatures for methanol, on the other hand, are relatively low (250–350 °C), and methanol has the advantage that it can generally be obtained in consistently high purity (sulfur content <5 ppm), compared to other fuels [111].

Often, the gases from a coal gasifier or natural gas reformer consist of, apart from H₂, significant levels of CO, CO₂, H₂O, and CH₄ as well as small quantities of particulates, sulphur compounds, and metal vapors—especially in the case of coal gasifiers. Following removal of particulates and sulphur compounds, gases are passed through a water–gas shift (WGS) reactor to convert CO to H₂ and CO₂ by reacting it with steam over a catalyst. The WGS reaction is typically a two-stage shift process, with steam being added initially in the high-temperature WGS reactor (300–500 °C), followed by a low-temperature shift reaction (around 200 °C), with each process employing separate catalysts [112, 113]. The gases need to be cooled before entering the low-temperature shift reactor. Alternatively, in next generation membrane reactors under consideration, if the water–gas shift (WGS) catalyst and H₂ separation membrane are incorporated into one unit, continuous removal of H₂ will drive the equilibrium of the shift reaction forward (Fig. 3). Therefore, the requirement to use a two-stage shift reaction and a cooling step in-between can be eliminated and the water–gas shift reaction may be carried out at higher temperatures in the vicinity of 500 °C. Consequently, membranes that can be directly coupled with a shift reactor for pre-combustion H₂ separation and operate in this temperature regime are considered more attractive.

Based on temperature considerations, high-temperature proton conductors (e.g., perovskites) would be well-suited to application in coal gasification and methane reforming. While for methanol reforming and water–gas shift reactions, low-temperature or intermediate-temperature proton conductors, such as oxo-acid salt or heteropolyacid composites, would be more attractive. Another factor for consideration is that for large-scale applications, such as coal gasification, the industrial throughput and, therefore, the membrane dimensions will differ substantially to that required for a natural gas micro-reformer with potential market in domestic or portable applications for distributed H₂ generation. Membrane technology with high H₂ flux capabilities must, therefore, be able to be manufactured on different size scales, depending on the specific process demands.

Clearly, different temperature regimes exist in which proton conductors may be required for the separation of H₂.

Given that most proton conductors have optimal conductivity over a limited temperature range (100–200 °C), the demand to develop proton conductors for a specific temperature range and application will grow as the technological means and sources of H₂ production develop. Significant effort continues to examine alternative reactor conditions [114, 115], catalysts [116, 117], and membrane reactor designs [118], as well as H₂ sources [103, 104], so variations to H₂-separating conditions and, therefore, to membrane material performance requirements, are likely to continue into the future [108].

Other applications of proton conductors

Once proton conductors are developed for use as H₂ separation membranes, there are a host of other applications where such membranes may be used. These include H₂ sensors for process control and monitoring, H₂ leak detectors for safety monitoring, dehumidifiers (water removal from wet gases), water electrolysis for H₂, and oxygen production (with or without coupling to renewable energy sources), electrochemical reactors for chemical production, and fuel cells for power generation [119].

Conclusions

Proton-conducting materials have been reviewed for applications in industrial processes of coal gasification, natural gas reforming, methanol reforming, and the water–gas shift reaction. Key material requirements for their use in these applications have been discussed. Clearly, different temperature regimes exist in which proton conductors may be required for the separation of H₂. Given that most proton conductors have optimal conductivity over a limited temperature range, the demand to develop proton conductors for a specific temperature range and application will grow as the technological means and sources of H₂ production develop. No single class of materials is able to cover all applications for H₂ separation. More critically, no class of materials yet exists which meet the criteria of high H₂ flux rates, thermal and chemical stability, and mechanical properties. The field is at an early stage of development, and considerable resources need to be devoted for the research and development of optimal materials and fabrication of membranes for H₂ separation in the future. It is unlikely that proton conductors will be used as a single-phase material for hydrogen separation. Most likely, they will be used as cermets or mixed phase materials, where the second phase acts as an electronic conductor. For cermets, if the metal phase also transports hydrogen, then higher hydrogen flux rates can be achieved.

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