REVIEW ARTICLE

The opportunity of membrane technology for hydrogen purification in the power to hydrogen (P2H) roadmap: a review

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Abstract The global energy market is in a transition towards low carbon fuel systems to ensure the sustainable development of our society and economy. This can be achieved by converting the surplus renewable energy into hydrogen gas. The injection of hydrogen ($\leqslant 10\%$ v/v) in the existing natural gas pipelines is demonstrated to have negligible effects on the pipelines and is a promising solution for hydrogen transportation and storage if the end-user purification technologies for hydrogen recovery from hydrogen enriched natural gas (HENG) are in place. In this review, promising membrane technologies for hydrogen separation is revisited and presented. Dense metallic membranes are highlighted with the ability of producing 99.9999999% (v/v) purity hydrogen product. However, high operating temperature ($\geqslant 300$ °C) incurs high energy penalty, thus, limits its application to hydrogen purification in the power to hydrogen roadmap. Polymeric membranes are a promising candidate for hydrogen separation with its commercial readiness. However, further investigation in the enhancement of H_2/CH_4 selectivity is crucial to improve the separation performance. The potential impacts of impurities in HENG on membrane performance are also discussed. The research and development outlook are presented, highlighting the essence of upscaling the membrane separation processes and the integration of membrane technology with pressure swing adsorption technology.

Keywords power to hydrogen, membrane technology, hydrogen, energy

1 Introduction

1.1 Energy outlook to 2040

Energy plays a crucial role in the global economy growth. From the BP Energy Outlook [1], world population will reach 9.2 billion in 2040 and the global gross product is proposed to grow 3.2% per annum in the 2017–2040 period assuming that government policies, technology development and social preferences will remain at the current pace and manner of evolution. The expansion of world economy will drive the global energy demand by an increase of 0.8%–1.2% per annum with 16.4–17.9 Gtoe (gigatonnes of oil equivalent) of primary energy consumption in 2040 [1].

Although energy demand fluctuates with major changes in global economy or our society [2], it is clear that the overall global energy demand tends to increase from a long term perspective. The global energy consumption showed recovery from the 2008 global economy crisis [2], however, the outbreak of the severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) in 2019–2020 added extra uncertainty to the fuel demand. The recent Global Oil Demand Report published by International Energy Agency (IEA) predicts that the global oil demand will drop by 90000 barrels per day in 2020 in comparison with that in 2019 [3]. However, with the SARS-CoV-2 being under control in China, which accounts for more than 80% of the global oil demand growth in 2019, the global oil demand will rebound in 2021 and grow by 5.7 million barrels per day over 2019–2025 [3].

One of the greatest challenges for the energy system is to meet the fast-growing energy demand simultaneously with less or no greenhouse gas emissions, which is the major driver for climate change. The breakdown of primary

energy consumption in 2017 (Fig. 1) shows that traditional energy sources such as coal, oil and gas remain to be the major fuels in the global energy market [1]. The production and consumption of fossil fuels produce anthropogenic greenhouse gas. The global plans set out in the 2015 at the United Nations Conference of the Parties targeted at an increase of global average temperature to be well below 1.5 °C by 2050 via effective carbon mitigation approaches etc. [4]. One major approach is carbon capture, utilization and storage (CCUS), which utilises gas separation technologies, such as solvent absorption, membrane separation and adsorption, to capture the CO_2 from the processing gas streams and then either converts the captured CO_2 into fuels or chemicals [5,6], or stores it underground in geological reservoirs safely and permanently [7]. Globally, 37 large-scale CCUS projects are operating, commissioning or in progress with a total CO_2 capture capacity of 65 Mt per annum (mega tons per annum) [5,8]. Another approach for carbon removal and storage is bioenergy with carbon capture and storage, which uses biomass to produce energy for CCUS facilities and the whole process results in negative net CO_2 emission [6]. However, both technologies require extremely high capital investment, land footprint and energy consumption [9]. Hence, many other proposals have been made to decarbonise the energy sector such as implementing more renewables, developing better energy storage systems and enhancing energy usage efficiency [1].
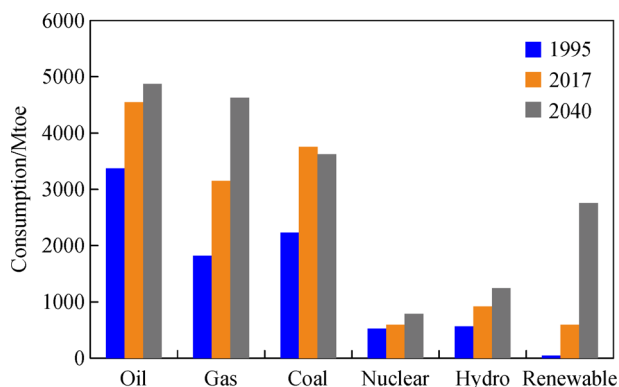

Fig. 1 The breakdown of primary energy consumption by fuel in 1995, 2017 and an outlook to 2040 based on the Evolving transition scenario (Renewable includes wind, biomass, solar, biofuels and geothermal) [1]. Source: BP Energy Outlook 2019. Adapted with permission.

1.2 Renewables

Renewables, such as wind, solar, hydro, biomass and geothermal energy, is expected to play a key role in the clean energy transition process [1,10,11]. The IEA estimated that the share of renewables in primary energy consumption would be 12.4% by 2023 (Fig. 2) [11]. Generally, the renewables are abundant to meet the global energy demand, however, their deployment highly relies on the readiness of energy generation, transportation and storage infrastructures and technologies. For instance, the net global wave energy is around 2–3 terawatt [12] which approximates to the global electricity consumption in 2018 [13]. However, the fluid corrosion and the voltage limit in electricity grid (i.e., ±10% of the nominal value) [14] to resist the fluctuation of renewable energy supply in accordance with weather change are some of the challenges to overcome for deploying the wave energy in large scale. Similarly, wind and solar energy are experiencing a gap in electricity supply between daytime and nighttime and among seasons resulting in the waste of surplus electricity due to the lack of energy storage solutions [15].
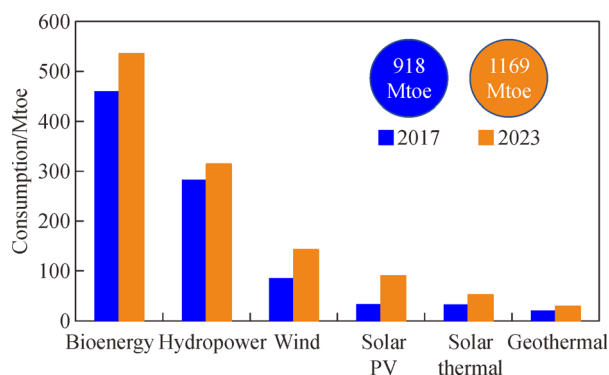

Fig. 2 The consumption of renewable energy categorised by technology in 2017 and an outlook to 2023 [11]. Source: IEA (2018). Market Report Series: Renewables 2018: Analysis and Forecasts to 2023, All rights reserved. As modified by Lu et al.

1.3 Power to hydrogen (P2H)

One approach to enhance the storage and reserve the production capacity of renewable energy is the power to hydrogen (P2H) process chain, in which surplus electricity is used to convert water to H_2 via technologies such as alkaline electrolysis [16], proton exchange membrane electrolysis [17] and solid oxide electrolysis [18], thereafter, hydrogen can be transported and consumed by end-users for combustion, carbon hydrogenation or methanation etc. [19]. Hydrogen is preferable for renewable energy storage due to its higher mass energy density ($142 \ MJ \cdot kg^{-1}$) in comparison with other fuels such as natural gas and gasoline (energy density at around 40–$60 \ MJ \cdot kg^{-1}$) [20]. Hydrogen can also be used in several industries such as hydrocarbon reforming and ammonia synthesis [21]. The minimum hydrogen purity requirements in fuel gas, polymer electrolyte fuel cells and rocket engine fuel industries are 54%–60% (v/v), 99.97% (v/v) and 99.999999% (v/v), respectively [22,23]. The major challenge for hydrogen transportation and storage is its low volumetric density and the possibility of hydrogen-induced fracture on the pipelines and storage facilities

[24,25]. Around 88% of reported hydrogen projects utilised compressed gas tanks for storage and a minority utilised metal hydrides storage [24].

The recent cost assessment for hydrogen delivery pathways suggested that the pipeline networks is the most cost effective and environmental-friendly approach for large scale hydrogen stations (around 80000 kg hydrogen capacity required per day) [26]. However, the construction of hydrogen distribution pipelines can cost USD 320–1000 per metre for the 20–61 cm pipelines at 68 bars [27,28], which is at least 10% more expensive than natural gas pipelines [27,29].

A more cost-effective option for hydrogen transport, especially in the market development phase, is to inject hydrogen into the existing natural gas pipelines [30] as the global natural gas pipelines are well built and distributed (>2.7 million kilometres in 2016) [31]. However, since the traditional natural gas pipelines are commonly made of ferritic stainless steel (SS) [32], plastic and cast iron [33], the suggested hydrogen injection concentration in natural gas pipelines is 6%–10% (v/v) at up to 40 bar pipeline pressure [34,35] to minimise the ignition risks, leakage issues and pipeline fatigues [30,36].

The hydrogen/natural gas mixture, also called hydrogen enriched natural gas (HENG), can be utilised directly for power generation [30] and household appliances [37]. However, the increasing displacement of hydrogen in natural gas stream will lower the heating value of gas mixture [38]. In fact, HENG could be used as a carrier to transport hydrogen from production sites to the renewable energy end users if the technologies for purifying hydrogen from HENG are in place.

Studies on hydrogen separation from methane reformed off gas and syngas have been reported extensively in literature [15,30,39,40]. These gas streams, however, commonly have 10%–80% (v/v) H$_2$, 2%–30% (v/v) CO$_2$ and up to 60% (v/v) N$_2$ in balance of methane [15,30,39,41] while the HENG is a H$_2$/CH$_4$ mixture with up to 15% (v/v) H$_2$ and less than 2%–4% (v/v) CO$_2$ [30]. There are very few investigations on hydrogen recovery from HENG at low temperature (e.g., ambient temperature). Therefore, the development of high efficiency and cost-effective technologies for the recovery of H$_2$ from its low concentration streams is a key to extend the P2H technology.

Membrane technology is one of the most proven economically viable approach for gas separation and has been commercialised in natural gas sweetening [42] and hydrogen recovery from ammonia purge gas [43] since 1980s. Recently, membrane technology is also implemented in carbon capture studies [44,45] and plasma technology to convert N$_2$ and CO$_2$ into value-added chemicals [46,47]. The advantages of membrane technology in comparison with other hydrogen separation technologies such as cryogenic distillation and pressure swing adsorption (PSA) processes are having high energy efficiency, high surface area-to-volume ratio [41], low environmental impact [41,48,49] and potential to achieve high purity hydrogen ($>99.5\%$ (v/v)) [30,40,48,50].

Several review articles have been published to assess the role of membrane separation technology in hydrogen purification. For instance, Adhikari and Fernando reviewed the use of different membrane types, mainly focusing on inorganic membranes, in hydrogen separation from hydrogen-rich gas streams [40]. The relationships of structure and property of membranes and hydrogen separation ability was also reported by Ockwig and Nenoff [51]. In addition, a book chapter about the advances in hydrogen separation and purification using membrane technology was also presented by Zornoza et al. that summarised the hydrogen separation performance of different membrane materials and membrane reactors [50]. A comparison between H$_2$-selective membranes and CO$_2$-selective membranes for hydrogen purification was also reported [49]. However, most of these reviews targeted at steam reforming of hydrocarbons that contained high hydrogen concentration (up to 80% (v/v) in the balance of CO$_2$ and minor CH$_4$) at high temperature (>350 °C) [50,51]. Hence, the scope of this review is to critically assess the role of membrane technologies for hydrogen recovery from HENG and highlight its potential in the P2H pathway.

2 Membrane for hydrogen separation

2.1 Fundamental of hydrogen transport in membranes

A membrane is a barrier that selectively separates some components from a mixture based on the physical nature of penetrants and the interactions between penetrants and penetrant-membrane [49,50]. The transport mechanism of H$_2$ and CH$_4$ through membranes varies depending upon the membrane types and generally follows one or a combination of the following 4 mechanisms: Knudsen diffusion, surface diffusion, molecular sieving and solution-diffusion model (Fig. 3) [40,49,50,52,53]. Knudsen diffusion applies when the mean free path of penetrant (i.e., the average travelling distance of a penetrant molecule inside the pores) is larger than the pore diameter [52,54]. The gas selectivity via the Knudsen mechanism is proportional to the inverse square root ratio of the molecular weight of transported gases (i.e., Selectivity A/B $\propto \sqrt{\dfrac{\text{Molecular weight of component B}}{\text{Molecular weight of component A}}}$) [54]. This ratio for H$_2$/CH$_4$ systems is 2.8 that is not attractive in commercial scale due to the low gas selectivity [52].

The diffusion of hydrogen through the membrane could be enhanced if the gas molecules absorbed on the pore surface, which is defined as surface diffusion [55]. This mechanism is mainly applied in porous membranes
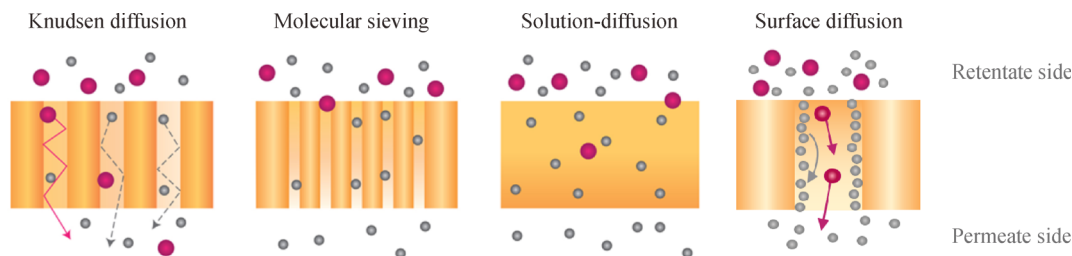
Fig. 3 The penetration mechanism of penetrants through membranes. Photo courtesy of CO2CRC.

[40,56]. When the pore size of membranes and kinetic diameter of penetrants are similar, the gas transport primarily follows the molecular sieving mechanism. According to the kinetic diameters of H_2 and CH_4 (Table 1), the preferred pore diameter for the separation of H_2 from HENG is between 2.89 and 3.80 Å such as ultra-microporous membranes [52].

Table 1 Physical properties of hydrogen and methane gas molecules [57]

Item	Molecular weight /(g·mol^{-1})	Kinetic diameter /Å	Critical temperature /K
H_2	2	2.89	33.24
CH_4	16	3.80	191.05

The widely-accepted mechanism of gas transport in polymeric and dense metallic membranes is solution-diffusion. This mechanism typically involves three steps: 1) the penetrants dissolve into the membrane on the feed side; 2) diffuse through the membrane; 3) desorb on the permeate side of the membrane [41,52]. The permeation and selectivity of H_2/CH_4 by solution-diffusion mechanism rely on the solubility and diffusivity of penetrants in the membrane [43].

The driving force for gas permeation through membranes is the chemical potential difference of H_2 and CH_4 on the two sides of the membrane, which is mainly in the form of gas partial pressure. The performance of H_2/CH_4 separation membrane can be expressed in term of permeance (Q) or permeability (P) of hydrogen and selectivity (α) of H_2 versus CH_4 (Eqs. (1) and (2)). The hydrogen permeability in metallic membrane follows the Sievert's law (Eq. (3)) with the flux being dependent on pressure exponent 'n' at around 0.5 [58]. The hydrogen separation efficiency is often limited by the pressure ratio across the membrane as shown in Eq. (4) [59], which is not a barrier for hydrogen purification from HENG stream as its operation pressure can be as high as 68 bar [30].

$$P_i = Q_i l = \frac{J_i l}{(p_{i,\text{feed}} - p_{i,\text{permeate}})}, \quad (1)$$

$$\alpha_{H_2/CH_4} = \frac{P_{H_2}}{P_{CH_4}}, \quad (2)$$

where Q is the gas permeance of gas component i (e.g., H_2 or CH_4); l is the membrane thickness; J is the gas flux (flowrate per membrane area); $p_{i,\text{feed}}$ and $p_{i,\text{permeate}}$ are partial pressure of gas component i in the feed and permeate sides of the membrane, respectively.

$$P_{H_2} = \frac{J_{H_2} \cdot l}{(p_{H_2,\text{feed}}^n - p_{H_2,\text{permeate}}^n)}, \quad (3)$$

$$\frac{\text{Feed pressure}}{\text{Permeate pressure}} \geqslant \frac{H_2 \text{concentration in permeate}}{H_2 \text{concentration in feed}}. \quad (4)$$

2.2 Dense metallic membranes

Several types of membranes have been extensively studied for hydrogen separation including dense metallic membranes, porous inorganic membranes, metal organic membranes and polymeric membranes. Among these, dense metallic membranes have attracted great interests due to their high hydrogen selectivity and commercial availability [50,60]. In the presence of catalytic membrane surfaces, hydrogen is transported through the membrane in form of proton, hydride ion or neutral atoms [50]. This mechanism is unique for hydrogen and cannot occur for other gas components in HENG like CH_4 and CO_2, therefore, the hydrogen purity in metallic membranes can reach up to 99.9999999% (v/v) [30].

Pd membranes are the most common metallic membranes for hydrogen separation with hydrogen permeability on the order of 1000 times greater than other metals such as Fe, Ni and Pt [61]. Several studies (Table 2) on the Pd membranes showed that the H_2/CH_4 selectivity could be extremely high ($\geqslant 1000$). However, there are some challenges for using the Pd membranes such as low mechanical resistance of the membrane in high pressure and the poison effects of impurities such as H_2S and CO in the feed gas [50,62,63]. An effective method to increase the hydrogen recovery is depositing thin Pd membranes on the supports such as Vycor glass [64,65], ceramics [66,67], porous alumina [68,69] or SS [69–71]. This is because thinner membrane enhances the hydrogen flux (Eq. (3)) while the support increases the mechanical strength of

Table 2 A shortlist of palladium membranes for hydrogen separation

Membrane material /support	Preparation method [a]	Thickness of active layer/μm	Experiment conditions	Hydrogen permeance /(mol·m^{-2}·s^{-1}·Pa^{-1})	Hydrogen selectivity [b]	Ref.
Pd/SS [a]	ELP	3.5	3.5 bar 500 °C–550 °C	1.7–9.4×10^{-7}	∞	[71]
Pd/PPO polymer [a]	ELP	5	1 bar 500 °C	1×10^{-6}	∞	[96]
Pd/α-Al$_2$O$_3$	MOCVD	2	1–2 bar 300 °C–500 °C	1×10^{-6}	1000	[68]
Pd/α-Al$_2$O$_3$	ELP	0.9	1.1 bar 500 °C	4×10^{-6}	9200	[69]
Pd/YSZ/SS	ELP	27.7	4 bar 350 °C–450 °C	1.5×10^{-7}	∞	[78]
Pd-Ag alloy/α-Al$_2$O$_3$	ELP	11	4 bar 550 °C	1.3×10^{-6}	1000–10000	[76]
Pd-Cu alloy	ELP	7.2	2.2 bar 400 °C	1.4×10^{-6}	40000	[77]

a) Metal-organic chemical vapor deposition (MOCVD), Electroless plating (ELP), poly(2,6-dimethyl-1,4-phenylene oxide) (PPO); b) due to the limited application of metallic membrane in literature, the hydrogen selectivity is based on H$_2$/N$_2$ system. However, in the solution-diffusion mechanism, the transportation behaviour of N$_2$ and CH$_4$ through the membrane are proved to be identical [57]. Hence, the trends of H$_2$/N$_2$ and H$_2$/CH$_4$ selectivity are proposed to be identical.

membranes. In addition, the mechanical strength of the membrane has been successfully increased by incorporating Pd with other metals in group IB, IVB, VB and VIB of the periodic table to form alloy membranes without affecting the H$_2$ selectivity of the membrane [72–78].

It should be noted that low operating temperatures ($\leqslant 300$ °C) lead to hydrogen-induced embrittlement phenomenon in Pd membranes [49,79], which limits its application significantly. Another barrier restricting the application of metallic membranes is the high cost of membrane materials [51,80]. Although several palladium membrane modules have been introduced in industrial scale, premium in steam methane reforming and water-gas shift industry (e.g., the Pd alloy Micro-Channel™ Technology (Power & Energy Inc., USA [81]), the Hysep® module (Energy Research Centre of Netherland [82]) and the two-step process of Pd-based membrane module (SINTEF, Norway [82])), dense metallic membranes are not particularly suitable for the purpose of separating hydrogen from HENG pipelines at low temperatures.

2.3 Ceramic mixed protonic-electronic conducting membranes

Dense ceramic mixed protonic-electronic conducting membranes have been intensively studied for hydrogen separation with advantages including high mechanical stability and lower manufacturing cost than dense metallic membranes [83,84]. The H$_2$ transport through dense ceramic proton conducting membranes follows solution-diffusion mechanism [85,86], in which H$_2$ in the feed gas diffuses through the membrane in form of H$^+$ along with the electrons. The flux of hydrogen can be described by the Wagner theory as shown in Eq. (5) [87].

$$J_{\mathrm{H}_2} = -\frac{RT}{2F^2l} \int_{\mathrm{Feed}}^{\mathrm{Permeate}} (\sigma_{\mathrm{H}^+} \times t_{\mathrm{e}^-})d\ln p_{\mathrm{H}_2}, \qquad (5)$$

where J_{H_2} is the H$_2$ flux; R is the universal gas constant; T is the absolute temperature; F is the Faraday constant; l is the membrane thickness; σ_{H^+} is the proton conductivity; t_{e^-} is the electronic transport number and p_{H_2} is partial pressure of H$_2$.

These ceramic materials, such as perovskite-type oxides, pyrochlores, niobates, tantalates and tungstates, often have a large number of protons and high electronic conductivity [88]. The crystal structures of these ceramic materials have been well studied in the literature [88,89]. Perovskites based oxides (e.g., BaCeO$_3$, SrZrO$_3$ and SrCeO$_3$) are the most common proton conducting materials with proton conductivity in range of 10^{-3}–10^{-2} S·cm^{-1} (400 °C–1000 °C) [90]. Various methods have been applied to enhance the proton conductivity to achieve high H$_2$ flux, for instance, the doping of trivalent ions (i.e., Yb and Y) into perovskites to partially replace tetravalent ions (i.e., Ce and Zr) [91–93] and the doping of Ca(II) into La$_2$Zr$_2$O$_{7-\delta}$ pyrochlores [94]. Another approach is dispersing metallic materials (i.e., Pd, Pt and Ni) into ceramic matrix (called cermet) or combining two ceramic proton conducting materials to form a composite membrane (called cercer) [86,88].

A range of ceramic mixed protonic-electronic conducting membranes has been highlighted in Table 3 to address their performance for hydrogen separation. The fabrication techniques of these membranes are similar to metallic membranes, with $\geqslant 20$ μm in membrane thickness and 10^{-8}–10^{-9} mol·m^{-2}·Pa^{-1}·s^{-1} in hydrogen permeance [83,95]. However, the major drawback of this type of membranes is the requirement of high temperature for hydrogen separation. The hydrogen conductivities of most

Table 3 A shortlist of ceramic mixed protonic-electronic conducting membranes for hydrogen separation

Membrane	Type	Thickness of active layer/mm	Temperature/°C	Feed gas	Sweep gas	Hydrogen flux /(10^{-4} mol·m^{-2}·s^{-1})	Ref.
$BaCe_{0.8}Y_{0.2}O_{3-\alpha}$	Perovskites	0.20	1050	25% H_2/He	N_2	28.30	[91]
$Sr(Ce_{0.6}Zr_{0.4})_{0.85}Y_{0.15}O_{3-\delta}$	Perovskites	0.17	800	Pure H_2	Ar	130	[92]
$Sr_{0.97}Ce_{0.9}Yb_{0.05}O_{3-\delta}$	Perovskites	1.16	804	10% H_2/N_2	Ar	3.30	[93]
$Nd_{5.5}W_{0.5}Mo_{0.5}O_{11.25-\delta}$	Tungstates	0.90	1000	50% H_2/He	Ar	22.30	[97]
$La_{26.78}W_{5.22}O_{55.83}$	Tungstates	0.03	1000	10% H_2/Ar 2.5% H_2O	Ar	10.40	[98]
$La_{0.5}Ce_{0.5}O_{2-\delta}$ (P)/Ni (E) [a]	Cermets	0.05	900	20% H_2/Ar 3% H_2O	Ar	6.83	[99]
$Pd(Zr_{0.9}Y_{0.1}O_{2-\delta})$ (P)/Pd (E)	Cermets	0.02	900	Pure H_2	N_2	1410	[100]
$BaCe_{0.95}Tb_{0.05}O_{3-\delta}$ (P)/Ni (E)	Cermets	0.09	850	50% H_2/N_2	He	67.90	[101]
$BaCe_{0.65}Zr_{0.2}Y_{0.15}O_{3-\delta}$ (P)/ $Ce_{0.85}Gd_{0.15}O_{2-\delta}$ (E)	Cercers	0.65	755	50% H_2/He	Ar	21.00	[102]

a) P/E: protonic phase/electronic phase.

ceramic proton conducting materials were reported to decrease by 100–1000 times (i.e., $< 10^{-5}$ S·cm^{-1}) at low temperature (< 250 °C) [88]. To the best knowledge of authors, the study on H_2/CH_4 separation using this type of membranes is very rarely seen. In addition, CH_4 can be dimerised on the surface of ceramic proton conducting membranes such as $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$-Pt [89]. Hence, ceramic mixed protonic-electronic conducting membranes are not suitable for hydrogen separation from HENG.

2.4   Inorganic microporous membranes

Inorganic microporous membranes are commonly used for separating light gas in the mixed gas such as H_2 from H_2/ CH_4 gas mixtures. In comparison with dense metallic membranes, inorganic microporous membranes can resist broader temperatures (25 °C–900 °C) and are more cost effective [40,50]. The flux of hydrogen (J_{H_2}) in dense metallic membranes is proportional to the square root of partial pressure of hydrogen (Eq. (3)) while J_{H_2} is proportional to partial pressure of hydrogen directly for other membrane materials (Eq. (1)). Therefore, inorganic microporous membranes are preferred to operate at high pressure of hydrogen. The H_2 transport mechanism in inorganic microporous membranes is mainly molecular sieving which separates H_2, the smaller kinetic diameter component, from CH_4, the larger component in the mixture (Table 1). Thus, the pore diameter of porous membranes must be under 2 nm (e.g., microporous) to separate hydrogen effectively [50]. However, H_2 may also transport through the membranes by the Knudsen diffusion mechanism in presence of defects [103]. This mechanism is less effective in H_2 separation as discussed in Section 2.1 [49,50,52]. Therefore, the inevitable challenge for microporous membrane is to form a defect-free membrane to gain high purity hydrogen product.

2.4.1   Zeolite membranes

Zeolite membranes are well studied due to their strong chemical, thermal and mechanical stability. A typical zeolite membrane is built with a crystallised microporous zeolite (e.g., aluminosilicates) deposited on a porous support such as alumina, porous ceramic, SS or polymeric membranes [49]. Recent studies showed that zeolite membranes can separate H_2 at various temperatures (25 °C–700 °C), however, with much lower H_2/CH_4 selectivity than dense metallic membranes (Table 4). The low hydrogen selectivity might be due to the presence of inter-crystalline mesopores on the zeolite layer that were formed during the aggregation of nanocrystals [104,105]. These mesopores (2–50 nm) drive the gas separation towards Knudsen diffusion mechanism. Recently, some advanced fabrication techniques were studied which successfully reduced the defects in zeolite membranes in particular layer-by-layer seeding free hydrothermal synthesis [106,107], catalyst cracking deposition hydrothermal synthesis [108] and functionalising the zeolite pores by amorphous materials [109]. However, these studies on zeolite membranes remain mainly in laboratory scale that will require a lot of efforts to scale up and commercialize.

2.4.2   Silica membranes

Silica membranes is favoured as they are often cost effective and easy to fabricate [49,82]. Most study on silica membrane showed high H_2 permeance and selectivity (Table 5). This is due to the amorphous property of ceramic that makes it easy to form nano-scale membrane thickness and pore diameter [49,82]. Particularly, a silica modified membrane deposited on Vycor glass called Nanosil exhibited an outstanding H_2/CH_4 selectivity at up to

Table 4   A shortlist of zeolite membranes for hydrogen separation

Zeolite type/support	Synthesis method	Thickness of active layer/μm	Experiment conditions	Hydrogen permeance /(mol·m^{-2}·s^{-1}·Pa^{-1})	Hydrogen selectivity [a]	Ref.
MFI/ceramic	Hydrothermal	3	1–4 bar 25 °C–500 °C	5×10^{-8}	4.9–7.9	[126]
LTA/α-Al$_2$O$_3$	Seeding free hydrothermal	3.5	1 bar 100 °C	2×10^{-7}	5–6.5	[106]
FAU/α-Al$_2$O$_3$	Seeding free hydrothermal	3	1 bar 100 °C	8×10^{-7}	3.5–5.6	[107]
CHA/α-Al$_2$O$_3$	Hydrothermal	3–4	2.7 bar 27 °C–200 °C	2.4×10^{-8}	25–10	[127]
La$_2$NiO$_4$ MFI/α-Al$_2$O$_3$	Hydrothermal	60	400 °C–700 °C	5.5×10^{-7}	9.2	[128]
MFI/α-Al$_2$O$_3$	Hydrothermal	2–3	2 bar 500 °C	5.3×10^{-7}	4	[108]
	Hydrothermal with CCD [b]	2–3	2 bar 500 °C	3.9×10^{-7}	180	

a) H$_2$/CH$_4$ ideal selectivity; b) CCD: catalyst cracking deposition.

Table 5   A shortlist of silica membranes for hydrogen separation

Silica type/support	Synthesis method	Thickness of active layer/nm	Experiment conditions	Hydrogen permeance /(mol·m^{-2}·s^{-1}·Pa^{-1})	Hydrogen selectivity [a]	Ref.
SiO$_2$/ceramic	Sol-gel	20–30	1 bar 100 °C–600 °C	10^{-7}	2800	[129]
CoSiO$_2$/ZrO$_2$SiO$_2$/α-Al$_2$O$_3$	Sol-gel	20	1–3 bar 200 °C–500 °C	1.8×10^{-7}	480–730	[111]
ZrO$_2$Y$_2$OSiO$_2$/ceramic	Sol-gel	–	1–1.5 bar 150 °C	1×10^{-8}	4	[112]
MTES-SiO$_2$/α-Al$_2$O$_3$[b]	Sol-gel	–	1–6 bar 50 °C–200 °C	3.4×10^{-9}	24–46	[130]
SiO$_2$/γ-Al$_2$O$_3$/α-Al$_2$O$_3$	Sol-gel	20–30	2 bar 600 °C	5×10^{-7}	5900	[131]
SiO$_2$ modified/Vycor glass (called Nanosil)	High temperature atmosphere CVD [c]	–	1.2 bar 200 °C–700 °C	1.8×10^{-8}	23000–27000	[110]

a) H$_2$/CH$_4$ ideal selectivity; b) MTES: methyltriethoxysilane; c) CVD: chemical vapour deposition.

23000–27000 [110]. The drawback of silica membranes is its low resistance to water [49,82]. This challenge could be resolved by introducing metallic oxides such as oxides of cobalt [111] and zirconia [111,112] into the membrane fabrication stage as the metal ions may reduce the interactions between water-silica matrix and minimise the movement of silanol groups [111]. Certainly, due to the low content of water in natural gas (< 0.012% (v/v) [42,59]), the impact of water on silica membranes in H$_2$ separation from HENG is less significant than that in syngas industry, which contains up to 40% (v/v) H$_2$O [15,30,39,41]. To the best of our knowledge, investigation on the large scale H$_2$/CH$_4$ separation using silica membranes, especially from HENG streams, has been very limited. Thus, more investigations on mixed gas measurement and pilot scale study on H$_2$/CH$_4$ separation are needed to verify its performance in industry.

2.4.3   Carbon molecular sieve (CMS) membranes

CMS membranes have also been widely studied (Table 6) for H$_2$ separation. The gas transport in CMS membranes mostly follows the molecular sieving mechanism. However, some large pores (0.6–2 nm in diameter) could more preferably adsorb CH$_4$ than H$_2$ that leads to a reduction in H$_2$ permeability and H$_2$/CH$_4$ selectivity [49,113,114]. Thus, it is critical to control the pore size in CMS membranes to be less than 0.6 nm in diameter. The CMS membranes is fabricated via the pyrolysis process of carbonaceous precursors [49,50,115]. The pore dimensions of CMS membranes can be controlled via the types of precursors, pyrolysis conditions and pre- and post-treatment processes [51,113]. It can be seen from Table 6 that the hydrogen permeance and H$_2$/CH$_4$ selectivity at ambient pressure may reach 10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1} and 1200, respectively. The CMS membranes were also proven to

Table 6   A shortlist of carbon-based membranes for hydrogen separation

Precursor	Synthesis method	Thickness of active layer/µm	Experiment conditions	Hydrogen permeance /(mol·m^{-2}·s^{-1}·Pa^{-1})	Hydrogen selectivity	Ref.
6FDA/BPDA-TMPDA[a]	Pyrolysis	30–35	1–8.3 bar 25 °C	3.4–7.5×10^{-8}	400–500 [b]	[132]
Kapton polyimide	Pyrolysis	0.3–0.5	Up to 6 bar 30 °C–250 °C	3.1×10^{-10}	150 [c]	[133]
Phenol-formaldehyde novolac resin	Pyrolysis	45	2 bar 25 °C	1.7×10^{-9}–1.2×10^{-7}	5–558 [b]	[134]
Polyimide	Pyrolysis	–	10.8 bar 30 °C–120 °C	3.4×10^{-7}–6.0×10^{-8}	132–631[b]	[135]
Polyimide	Pyrolysis	–	10 bar 80 °C	1.4×10^{-7}	540 [b]	[136]
Polypyrrolone	Pyrolysis	40–50	1 bar 35 °C	1.3–4.9×10^{-8}	270–1200 [b]	[137]

a) 6FDA: 5,5-[2,2,2-trifluoro-1-(trifluoromethyl) ethylidene-1,3-isobenzofurandione; BPDA: 3,3′,4,4′-biphenyl tetra carboxylic acid dianhydride; TMPDA: 2,4,6-trimethyl-1,3-phenylenediamine; b) H_2/CH_4 mixed gas selectivity; c) H_2/N_2 ideal selectivity.

separate H_2 effectively (e.g., achieving 98% recovery) from 50% H_2–50% CH_4 (v/v) mixed gas feeding condition [30]. The challenges for commercialising the CMS membranes are the membrane brittleness and high fabrication costs [40,50] which require further improvement.

2.4.4   Other inorganic microporous membranes

Recently, two-dimensional nanomaterials have been integrated into membrane technology and showed the promising H_2/CH_4 separation performance. For instance, the study on graphene-based membranes, which could theoretically achieve single-atom thickness, showed high mechanical and chemical stability and high H_2 separation performance (e.g., 1 mol·m^{-2}·s^{-1}·Pa^{-1} H_2 permeance and 10^8 H_2/CH_4 selectivity) [116]. The studies on hydrogen purification by layered double hydroxides (LDHs)-based membranes, which is formed by positively charged brucite-like layers and an interlayer region containing charge compensating molecules [117,118], also reached 10^{-7}–10^{-8} mol·m^{-2}·s^{-1}·Pa^{-1} H_2 permeance and ~80 H_2/CH_4 selectivity, respectively [119,120]. Although the two-dimensional membrane materials are a promising breakthrough in H_2 separation, the major challenges for these membranes are to control the microstructures and to scale up the process [118].

2.5   Metal organic framework (MOF) membranes

Over recent decades, several studies focused on MOF membranes due to their ultrahigh porosity in comparison with other porous membranes [49,121,122], which enhances the gas sorption capacity and gas transport as a sequence. Some highlighted MOF membranes for hydrogen separation are summarised in Table 7, which indicates that H_2 permeance in the MOF membranes is averagely 10–100 times higher than other porous membranes (e.g., 10^{-6}

mol·m^{-2}·s^{-1}·Pa^{-1} versus 10^{-7}–10^{-8} mol·m^{-2}·s^{-1}·Pa^{-1}). As organic linkers in MOF membranes cannot provide an additional linkage to surrounding MOF crystals and the membrane support, the major challenge is the fabrication of continuous and defect-free membranes [49,122,123]. This can be achieved via better pore shape and size control in the membrane fabrication process. For instance, Huang et al. fabricated a continuous defect-free ZIF-90 membrane on Al_2O_3 support by using 3-aminopropyltriethoxysilane as covalent linkers between ZIF-90 and Al_2O_3 support [122]. In a different approach, Liu et al. used the ZnAl-LDHs as a buffer for connecting the zeolitic-imidazolate framework-8 (ZIF-8) seed layer onto the Al_2O_3 support and the well-intergrown ZIF-8 membrane was formed during the secondary growth [120]. Recently, ZIF-8 is incorporated on hollow fibre membrane in a laboratory scale continuous process [124,125], which shows a promising signal for commercial scale application of MOF membranes in the future.

2.6   Polymeric membranes

Polymeric membranes are the most mature membranes for hydrogen separation with the first industrial application reported in 1980s [42]. Some commercial membrane modules such as Prism® (Air products and Chemicals, Inc.) [142] and polyaramid module (Dupont) [143] could achieve up to 97% hydrogen recovery. The low costs, ease of fabricating a large area/volume ratio hollow fibre or spiral wound module makes polymeric membranes very competitive. Recently, polyimide-based membranes such as 6FDA and Matrimid® introduced on an industrial scale showed even better H_2 transport than conventional polysulfone and cellulose acetate membranes [42,50].

A critical limitation in polymer membrane performance is the trade-off between gas permeability and selectivity, also known as Robeson's upper bound (Fig. 4) [144,145]. However, the empirical upper bound relationship between

Table 7 A shortlist of MOF membranes for hydrogen separation

MOF type/support	Synthesis method	Thickness of active layer/μm	Experiment conditions	Hydrogen permeance /(mol·m^{-2}·s^{-1}·Pa^{-1})	Hydrogen selectivity [a]	Ref.
Cu$_3$(BTC)$_2$/Cu net	Hydrothermal	60	1 bar 25 °C	10^{-6}	5.9	[138]
ZIF-90/α-Al$_2$O$_3$	Hydrothermal	20	1 bar 25 °C–200 °C	1.4 × 10^{-7} –2.5 × 10^{-7}	7–16	[122]
ZIF-8/Titania	Hydrothermal and microwave heating	30–50	1.1–2 bar 25 °C	6 × 10^{-8}	11.2	[139]
ZIF-8/ZnAl-NO$_3$ LDHs/γ-Al$_2$O$_3$	Hydrothermal (*in-situ* growth)	1.3	1 bar 25 °C	1.4 × 10^{-7}	12.5	[119]
ZIF-95/α-Al$_2$O$_3$	Hydrothermal (*in-situ* growth)	30	1 bar 325 °C	1.9 × 10^{-6}	11.0	[140]
Ni-MOF-74	Hydrothermal (*in-situ* growth)	10–25	1 bar 25 °C	10^{-6}	2.9	[141]
NH$_2$-MIL-53(Al) /Glass frit	Colloidal assembly of MOF seeds	15	1 bar 15 °C–80 °C	1.5 × 10^{-6}	20.7	[123]

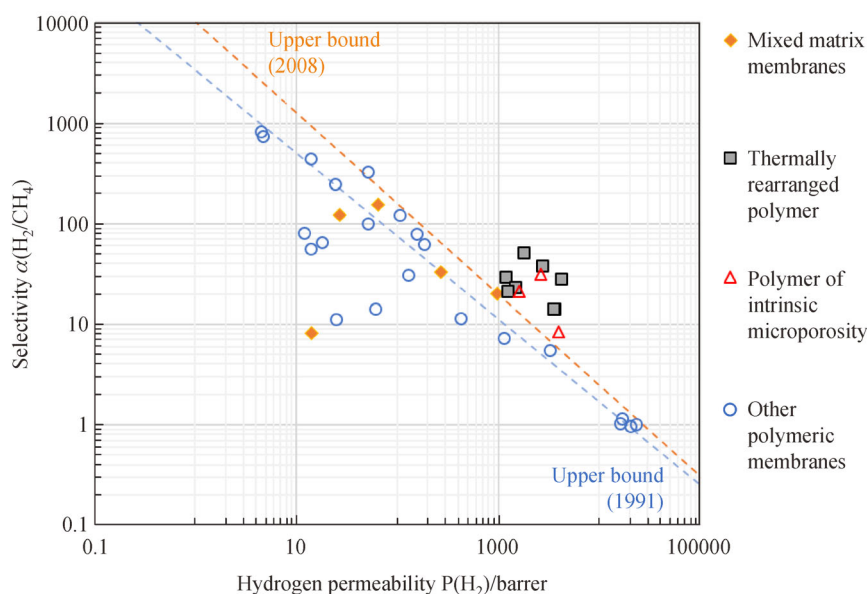a) H$_2$/CH$_4$ mixed gas selectivity.

Fig. 4 Robeson's upper bound for H$_2$/CH$_4$ separation of polymeric membranes. Data from [142,144,145,149–157]. Updated based on Ref. [159], with permission. Copyright 2020, Chinese Academy of Engineering and Higher Education Press.

H$_2$ permeability and H$_2$/CH$_4$ selectivity is a temporary figure that will be shifted to the higher limit with more advanced membrane structures and properties discovered [144,145]. In fact, several approaches have been investigated to crossover the upper bound. In last decades, many laboratory scale membranes have been reported to cross the upper bound such as polymer of intrinsic microporosity (PIM) membrane [146–148] and thermally rearranged (TR) polymer membranes [149–153]. The incorporation of CMS [154], ZIF [155,156], UiO-66 [156] and multi-walled carbon nanotube [157] into polymeric membranes, which is called mixed matrix membrane (MMM), also demonstrated the potential to enhance the H$_2$ permeability without reducing or even increasing the

H$_2$/CH$_4$ selectivity. Simultaneously, researchers have fabricated the defect-free ultra-thin polymeric membranes (~30 nm) by continuously assembly of polymer (CAP) technique [158] that showed a breakthrough in gas permeance. Certainly, most of the advanced H$_2$ selective membranes and fabrication techniques are on laboratory scales that require more investigations and efforts to convert them into industry.

2.7 Impact of minor impurities in natural gas grid on membrane performance

The typical gas standard regulations in many areas still allow the presence of minor impurities such as CO$_2$, H$_2$S,

water, C_{3+} hydrocarbons and inert gases in the natural gas pipeline grids [59,160]. Organosulfur compounds such as dimethyl sulphide and tetrahydrothiophene are also injected into the commercial natural gas stream at concentrations around 0.00002% (v/v) as a legislative practice for detecting natural gas leakage [161,162]. These compounds are commonly removed via the hydrodesulfurization process prior to entering the methane reforming reactors [163]. However, such desulfurization process requires high energy inputs to maintain high reaction pressure and temperature [30]. Hence, an essential factor in selecting the membrane materials for hydrogen recovery from HENG is to consider their resistance to potential minor impurities in natural gas. Generally, the presence of these impurities could alter the membrane performance by following four ways: 1) competing with hydrogen to permeate through the membrane; 2) occupying and blocking the membrane free volume; 3) plasticising the membrane; 4) degrading or poisoning the membrane materials [41].

2.7.1   Dense metallic membranes

Due to the special hydrogen transport mechanism, hydrogen permeation through dense metallic membranes is not affected by most of impurities except H_2S. It was reported that H_2S at concentrations ~0.0002% (v/v) can react with conventional Pd and Pt membranes to form the metal sulphide on the membrane surface, which then completely inhibit the H_2 permeation through the membrane [63,164,165]. Such limitation can be minimised by fabricating the Pd alloy membranes with metals in group IB, IVB, VB and VIB of the periodic table. Peters et al. [164] observed only 20%–30% loss in H_2 flux when exposing a $Pd_{77}Ag_{23}$ membrane (thickness 10 μm) to 5 × 10^{-7}–0.002% (v/v) H_2S/H_2 mixed gas for 265 h. Recent studies further demonstrated that the close to full recovery of H_2 flux through Pd alloy membranes were obtained when removing the H_2S in the feed gas [164,165]. This suggested that the dominant interaction of H_2S and alloy

membranes was reversible adsorption rather than sulfidation reaction.

2.7.2   Molecular sieve membranes

Figure 5 showed that the kinetic diameter of H_2 is much smaller than most of potential impurities. Thus, these impurities retain in the retentate side of the molecular sieving mechanism driving membranes, along with CH_4. Figure 5 also showed that H_2O is more permeable than H_2 that could reduce the purity of hydrogen product stream. H_2O was also reported to densify the silica membrane at temperature above 500 °C [88,166]. However, the impact of H_2O on the purity of H_2 product stream is often negligible due to the strict control of H_2O content in natural gas grids (e.g., commonly in 10^{-7}–10^{-4} % (v/v) level [59,160]) to avoid the formation of hydrates. The water-resistance of silica membrane could also be overcome by doping the metal oxides into silica matrix [166,167] or replacing hydroxyl functional group (–OH) on the pore surfaces by methyl (–CH_3) [168] or perfluorodecyl functional groups [169].

In addition, impurities with high condensation temperature such as C_{3+} hydrocarbon, sulfur compounds and water on microporous membranes may condense and block the membrane pores, which can potentially reduce the hydrogen permeability but enhance the H_2/CH_4 selectivity [88,170–172].

2.7.3   Dense polymeric membranes

The effects of impurities on hydrogen separation depend on their solubility and diffusivity in the materials for those membranes relying on solution-diffusion gas transport mechanism. In comparison with H_2, most impurities have larger kinetic diameter (lower gas diffusivity) and higher condensation temperature (higher gas solubility) (Fig. 5). As the preferred membrane materials (Section 2.6) for H_2 recovery from HENG are mostly relying on diffusivity selection such as glassy polymer (e.g., cellulose acetate
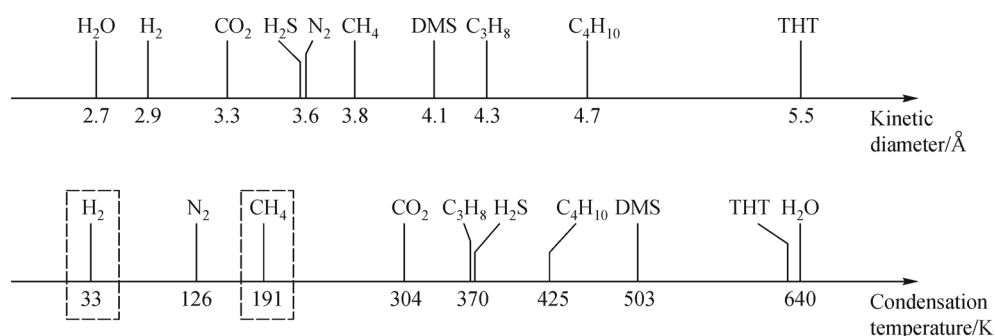

Fig. 5 The kinetic diameter and critical temperature of some potential components in natural gas [59,173] (data for dimethyl sulphide and tetrahydrothiophene obtained from [174] and conductor like screening model, respectively). Updated based on Ref. [59], with permission. Copyright 2008, American Chemical Society.

[173] and polysulfone [51]), impurities with high condensation temperature may condense and block the membrane free volume. Schell et al. [172] reported that the presence of 0.12% (v/v) water vapour (80/20 (v/v) H$_2$/CH$_4$ feed gas at 60 °C and 2410 kPa) supressed the H$_2$ flux through cellulose acetate membranes by 6% and enhanced the H$_2$/CH$_4$ selectivity by 4%. The researchers also observed the similar phenomenon (i.e., 15% decrease in H$_2$ flux and 10% increase in H$_2$/CH$_4$ selectivity) when introducing aromatic hydrocarbons into H$_2$/CH$_4$ mixed gas.

The condensates inside the membrane may also plasticise the membrane matrix and lead to an increase in permeation of all penetrants and decrease in gas selectivity [59]. However, most studies have shown that polymeric membranes have strong resistance to impurities such as H$_2$S, C$_{3+}$, etc. in crude natural gas [51,172,173], which is beneficial for the H$_2$ separation from HENG. Nevertheless, the impacts of impurities in commercial natural gas, specially added odorants, on this membrane materials are not yet clear and need further investigation.

3 Discussion and outlook

3.1 Discussion

Overall, the pathway of converting P2H is a prospective solution for storing and redistributing surplus renewable energy to ensure a clean, secure and sustainable energy supply future. Recent techno-economic analysis estimated that the bulk energy storage cost (USD per kW) of P2H technology can be 1.5–4.3 times less than other energy storage technologies such as batteries, supercapacitors, pumped hydro and flywheels [175]. Although the delivery and temporary storage of hydrogen in natural gas pipelines inherit the advantages of the existing natural gas distribution network, efficient and cost-effective technologies that purifies hydrogen from HENG is the key to push P2H into practice. Hydrogen separation has been well investigated in syngas and methane reformed off gas industries [15,30,39,40], however, very few studies were conducted for H$_2$ separation from HENG.

The hydrogen separation performance of different membrane materials has been discussed and summarised in Table 8 and Fig. 6. Although dense metallic membranes are promising to achieve an extremely high hydrogen purity and comparative hydrogen permeance or recovery in comparison with other membrane materials, the high operating temperature ($\geqslant 300$ °C) hinders its application in hydrogen recovery from HENG. Ceramic mixed protonic-electronic conducting membranes are not suitable for hydrogen purification from HENG due to high operating temperature ($\geqslant 400$ °C) requirement and the ability to dimerising CH$_4$. Polymeric membranes are leading in the

commercially readiness compared to other hydrogen separation membranes with only low operating temperature required. The challenges for these membranes are the moderate H$_2$ selectivity which limits the hydrogen purity in product stream. In addition, inorganic microporous and metal organic framework membranes are also promising for hydrogen separation at low operating temperatures such as ambient temperature. The key to these membranes is to improve the reproductivity in membrane fabrication and performance, especially on pilot- and industrial-scale.

3.2 Research and development (R&D) outlook

Many promising membrane materials for hydrogen recovery from HENG, including their fabrications and separation performance, have been highlighted and discussed. On this basis, we would like to address the R&D outlook to achieve the high hydrogen purification membranes and drive membrane separation into HENG industry.

3.2.1 Development of novel membrane materials and membrane fabrication technologies

To the greatest extent, the development of hydrogen purification membranes will remain focusing on the following key approaches: 1) design and synthesis of novel membrane materials with high H$_2$/CH$_4$ selectivity and permeability; 2) modification of the structure and morphology of existing membranes; 3) incorporation of different membranes into a copolymer, composite or MMM to combine the best features of each membrane material; 4) development of advanced membrane fabrication technologies to produce ultrathin membranes.

The gas transport mechanisms for H$_2$/CH$_4$ separation membranes are dominant by molecular sieving and solution-diffusion (with diffusion selectivity). Both mechanisms require the well control of membrane morphology such as pore sizes and shapes, fractional free volume distribution etc., to enhance H$_2$/CH$_4$ selectivity. Thus, the R&D is expected to shift towards membrane materials that either have uniform pore size such as MOF and two-dimensional membranes (i.e., graphene-based membranes, LDHs membranes, etc.) or the ability to tune or crosslink the membrane free volume such as TR polymers and PIMs membranes. Simultaneously, the incorporation of advanced membrane materials with commercialised membrane materials will also attract great interests. The incorporation could combine the best features of each membrane material and overcome current challenges in fabricating large defect-free membranes. The commercial readiness of conventional membranes could also potentially reduce the time consumption for scaling up the incorporated membranes.

Another crucial approach for enhancing the hydrogen

recovery is to reduce the thickness of active membrane layer but maintain its selectivity and mechanical strength. Along with the conventional thin film composite membranes, the ultra-thin film coating techniques such as CAP and metal-induced ordered microporous polymer thin film composite membranes are able to reduce the membrane thickness to nanometre scale without affecting the gas selectivity. Therefore, it is worthwhile to drive the R&D in H_2 selective membrane fabrication towards this field, starting with investigations on precursor selection for CAP processes of advanced membrane materials.

3.2.2   Pilot scale and economic assessment studies

The development of membrane technologies in hydrogen purification has been relying on conventional polymeric membrane materials and palladium membranes (Table 8). Although several membrane materials have been introduced for H_2/CH_4 separation, there are very few membrane modules introduced into practice such as Vaporsep-H_2™ solution developed by Membrane Technology and Research (USA) [177] and Micro-Channel™ Technology developed by Power and Energy Inc. (USA) [81]. Beside the lack of technology to support the fabrication of large defect-free membranes as addressed above, the lack of pilot scale studies is another major obstacle for commercialising advanced membrane materials. Therefore, more investigations on pilot-scale membranes studies are recommended.

The cost of H_2 separation from 10/90 (v/v) H_2/CH_4 at 20 bar and 80% recovery was estimated to be 3.3–8.3 USD·kg^{-1} H_2 using the PSA [30]. The target of H_2 cost is proposed to be 1.5 USD·kg^{-1} H_2 [84]. However, there is lack of techno-economic study on hydrogen recovery from HENG using membrane technologies. Data collected from pilot scale studies will also be valuable for economic assessments and further upscale of these membranes.

The majority of laboratory studies on hydrogen purification membranes focused on pure H_2 and CH_4 separation performance at low operating pressures and a few on H_2/CH_4 mixtures. In the real world, membranes for hydrogen recovery from HENG may expose to several impurities (section 2.7) and high pressures (68 bar and ambient temperature). Thus, it is worthwhile to investigate the performance of candidate membranes in real HENG conditions, particularly for pilot studies.

3.2.3   Membrane modelling

The transition of technology from laboratory to industry requires extraordinary efforts and resources, especially for membranes in the new P2H energy sector. Hence, developing robust membrane models validated with experiments is essential to minimise the R&D costs and accelerate the technology transition. Several mathematical models have been developed for CO_2/H_2 separation in integrated gasification combined cycle process [178–181]. By counting that CH_4 behaving more inert than CO_2 in membrane separation [57], these models will be the valuable resources for the process development of hydrogen purification from HENG.

3.2.4   Technology integration

While membrane technology has advantages of cost effectiveness and small facility footprint, purify H_2 stream up to 99.99% (v/v) from HENG at low temperatures is a critical challenge. Another technology that can achieve 99.99% (v/v) H_2 purity is the PSA, which is a mature technology for hydrogen separation [182]. However, PSA requires large land footprint to accommodate the adsorption and frequent regeneration cycles for hydrogen separation from its low concentration mixtures [50]. Therefore, an integrated membrane-adsorption process (Fig. 7) is a promising approach to combine the best of both technologies [23,159,183]. Recently, Liemberger et al. reported an integrated process of an aromatic polyimide hollow fibre membrane module with a PSA that could recover at least 60% H_2 at purity 98.0%–99.3% (v/v) from 1/99–10/90 (v/v) H_2/CH_4 feed gas at 21–51 bar and

Table 8   Summary of hydrogen separation performance of some common membrane materials [40,49–51,88,159,176]

Item	Dense metallic membranes	Ceramic mixed protonic-electronic conducting membranes	Inorganic microporous membranes [a]			MOF membranes	Polymeric membranes
			Zeolite	Silica	Carbon based		
Temperature/°C	300–600	400–1000	25–700	50–700	25–900	15–325	25–200
H_2/CH_4 selectivity	1000–∞ [b]	– [c]	4–25 [d]	Up to 5900 [e]	Up to 1200	3–21	Up to 730
Hydrogen permeance /(mol·m^{-2}·s^{-1}·Pa^{-1})	2×10^{-7} –4×10^{-6}	10^{-8}–10^{-9}	2×10^{-8} –8×10^{-7}	3×10^{-9} –5×10^{-7}	2×10^{-9} –3×10^{-7}	6×10^{-8} –2×10^{-6}	$\sim 10^{-9}$ –3×10^{-7}
Development stage	Small commercial scale	Lab-scale membrane modules	Lab-scale membrane modules	Lab-scale membrane modules	Lab-scale membrane modules	Lab-scale membrane modules	Large commercial scale

a) The summary excludes some advanced membrane materials that require more database to make the conclusion; b) H_2/N_2 selectivity with assumption that selectivity of H_2/N_2 and H_2/CH_4 being identical [57]; c) the selectivity of H_2 in ceramic mixed protonic-electronic conducting membrane is proposed to similar to dense metallic membrane. However, there is limited data reported in literature [88]; d) MFI type zeolite membrane prepared by catalyst cracking deposition hydrothermal synthesis could achieve up to 180 H_2/CH_4 selectivity [108]; e) nanosil membrane could achieve 23000–27000 H_2/CH_4 selectivity [110].
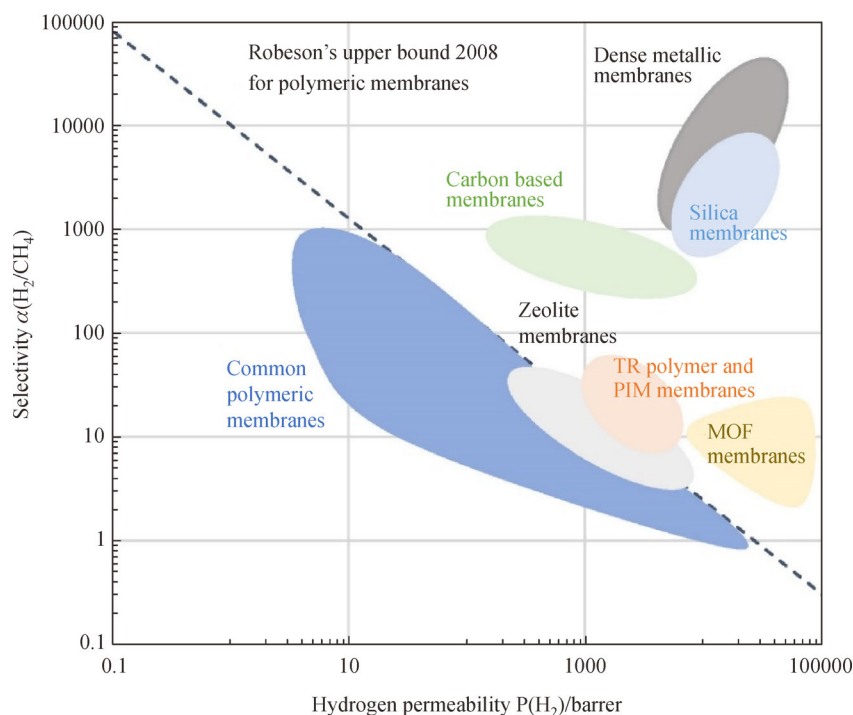
Fig. 6 Summary of H$_2$ permeability versus H$_2$/CH$_4$ selectivity of some common membrane materials based on the literature data summarised in this review. Since the membrane thickness were not fully reported in literature, the H$_2$ permeation is presented in term of H$_2$ permeability instead of permeance. (α(H$_2$/CH$_4$) selectivity in dense metallic membranes was based on H$_2$/N$_2$ selectivity by assuming the identical performance of N$_2$ and CH$_4$ through the membrane [57]).
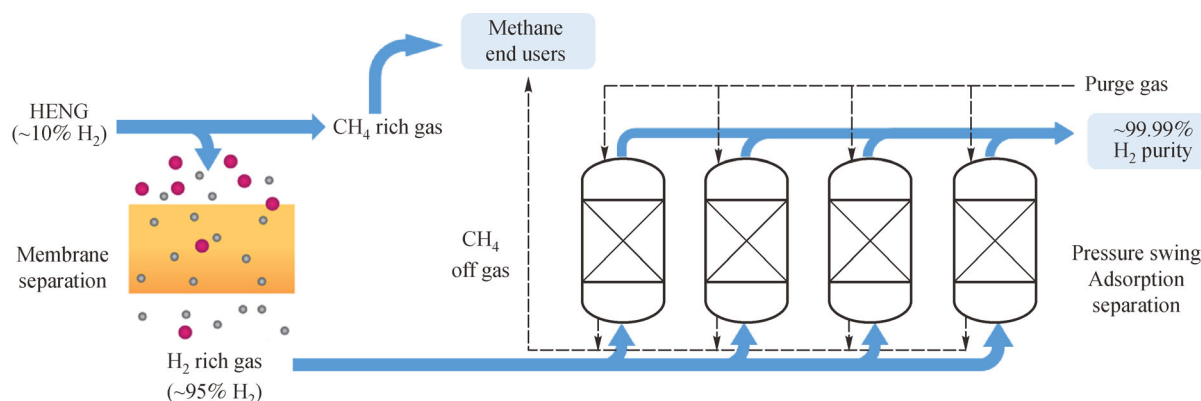
Fig. 7 The integrated module of membrane-adsorption process for hydrogen purification [159]. Adapted with permission from Ref. [159]. Copyright 2020, Chinese Academy of Engineering and Higher Education Press.

ambient temperature [23]. Certainly, the technology integration opportunity will also be open to other hydrogen purification technologies such as cryogenic and solvent absorption. Hence, more investigations on the integrated hydrogen separation units such as material development, process optimisation and economic analysis are suggested to testify its industry potential.

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