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ORIGINAL ARTICLE

A comprehensive review of carbon molecular sieve membranes for hydrogen production and purification

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Abstract
Demand in clean alternative energy source together with fuel cells developments has attracted researchers towards utilization of hydrogen (H_2). Common production of hydrogen from fossil fuels requires further pretreatment prior to the application, which makes separation and purification technology a very crucial component. Membrane reactors for water-gas shift reaction which was used for H_2 generation by conversion of carbon monoxide revealed a good potential in shifting the reaction equilibrium. Two types of inorganic membranes widely studied for H_2 separation and purification are dense phase metal and metal alloys and porous ceramic membranes. Among these two, microporous-type membrane was found to be more advantageous at harsh temperature during water-gas shift reaction. Sol-gel method employed for synthesised of porous ceramic membranes produced membranes with high stability and durability at high temperature and at tough hydrothermal environments. This work presents the critical issues regarding the membranes based on technical and economical perspective. Discussions are made on the significance of membrane technology advancement in order to strive for a clean environment with zero power technologies.

Keywords Carbon molecular sieve membranes · Hydrogen production · Hydrogen purification · Mixed matrix membranes · And zeolite membranes

1 Introduction

Separation technology is well acknowledged for its importance in various energy sectors and chemical industries. Notable progress on separation technology can be seen through the increasing trend of technologies development related to gas separation [1–3]. This matter was likely due to increasing demand for purified natural gas and other gases employed in industrial and pharmaceutical sector [4, 5]. Even with various available gas separation technologies (i.e. cryogenic distillation and pressure swing adsorption), researchers are still making efforts in developing new, low-cost approaches with simplicity in its operation and control process [6]. Emergence of membrane having distinctive inherent properties such as low energy usage, ease of scale up and small footprint has drawn attraction for this technology to be utilised in various gas separation applications [7–10]. Figure 1 shows various application provided from membrane for H_2 purification [11]. Haider et al. [12] stated that separation by membrane technology has achieved $150 million per year from data in 2002 and is expected to keep increasing.

Thus, further scientific research and R&D breakthrough need to be done extensively to overcome the challenges and for advancement in membrane technology. While polymeric-type membranes are gaining attention, carbon membranes also possess similar distinctive properties and excellent gas separation performance. Most notable features of carbon-based membranes are their superior chemical and thermal stability, added with its potential to outpace the permeability-selectivity trade off [13–15]. From technical perspective, carbon-based membranes are proof of the importance of morphology in separation performance, in which porous structure offers high gas permeance while molecular-sieve network offers high selectivity in terms of its efficient size and shape discrimination of molecules [16–18]. Of all existing membranes, carbon molecular sieve (CMS) membranes have garnered attentions as potential candidate for future membrane technology [8, 19].

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Fig. 1 Various applications provided from membrane for H_2 purification [11]

Carbon membranes possess similar distinctive properties and excellent gas separation performance. Most notable features of carbon-based membranes are their superior chemical and thermal stability, added with its potential to outpace the permeability-selectivity trade off [20–22]. From technical perspective, carbon-based membranes are proof of the importance of morphology in separation performance, in which porous structure offers high gas permeance while molecular-sieve network offers high selectivity in terms of its efficient size and shape discrimination of molecules [23–25].

CMS is build up from the arrangement of aromatised strands that is tightly positioned to shaped plates that is further systematised into amorphous cellular structure. The sieving behaviour of the CMS is monitored by the ultramicropores which referred to the slits that present between the strands. Meanwhile, the adsorption of the gas molecules will happen at the sorption site at the micropore area that has the size of 7–20 Å. The micropores appeared between the improperly arranged carbon plates [13]. The complex structure of the CMS can be briefly understood by referring the attached illustration in Fig. 2. In detail, the mechanism for the formation of CMS from the 6FDA:BPDA-DAM precursor is shown in Fig. 3 [26].

Carbon molecular sieve membranes were synthesised from pyrolysis of the polymeric precursors. Pyrolysis reaction to produce CMS will be done in the presence of the inert gases under the controlled temperature ranging from 400 to 1000 °C while escaping completed graphitization for the temperature more than 2500 °C [27]. For instance, Ogieglo et al. (2020) successfully fabricated ultra-thin 100-nm CMS via different ranges of pyrolysis temperatures ranging from 500 to 800 °C and had produced noticeable optical images for the four prepared CMS membranes [28]. As can be referred in Fig. 4, as the pyrolysis temperatures increased, the surface of the top view of the samples became darker.

Vital factors affecting transport properties of resulted carbon membranes were found through extensive studies done by numerous researchers. Some of the factors are the polymer structure itself, precursor's microstructure and parameters of pyrolysis process [13, 16, 17, 29, 30]. These factors determined the structure of membrane, pore distribution with critical dimension and properties of surface with desired characteristics. In addition, another prominent factor which is type of precursor has also been widely investigated, proved by various reported studies in highly performing carbon membranes [18, 31–35]. Selection of material for membrane preparation is essential, not only for carbon-based membranes but for all types of membranes employed for gas separation. Thus, the chosen material should have the prerequisite characteristics in order to produce membrane with desired functionalities. As an example, materials with good chemical stability and thermal stability, accompanied by its competency to maintain macromolecular structures during pyrolysis, are included as additional prerequisites. A novel carbon membrane based on poly-phthalazione ether sulfone ketone (PPESK) developed by Zhang et al. [36] was tested for its separation performance for several gas pairs. It was found that satisfactory separation performance was achieved by resultant carbon membrane in comparison to polyimide-based carbon membranes.

In addition, as presented by Kelly and groups, the fabrication of CMS incorporated on ceramic tubes possess a crack-free–supported carbon membrane [37]. The permeance of H_2 separation is measured through permeation module as visualised in Fig. 5. Based on the fabricated model in Fig. 5, the membrane was fully shaped with Viton O-rings that automatically permitted the membrane to be placed in the module with minimal leakage

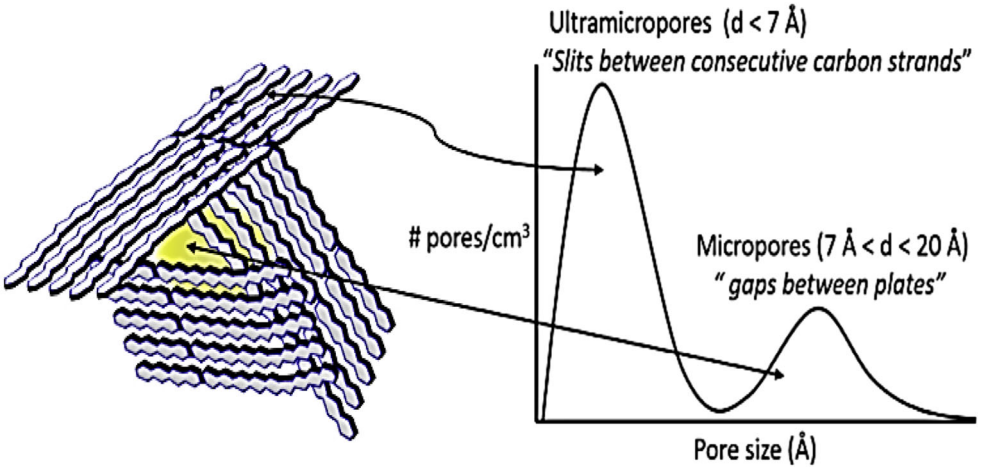

Fig. 2 The complex structure of the CMS [13]

chances. In different approaches, the CMS membrane as published in Fig. 6 constructed from carbon layer supported on porous asymmetric ceramic tubular membrane was found to have H_2/N_2 selectivity of 47.68 [38].

Other than possessing high gas permeance and moderate to high gas selectivity, porous ceramic membrane especially microporous-type membranes are both chemically and thermally stable, which makes them suitable to be utilised in

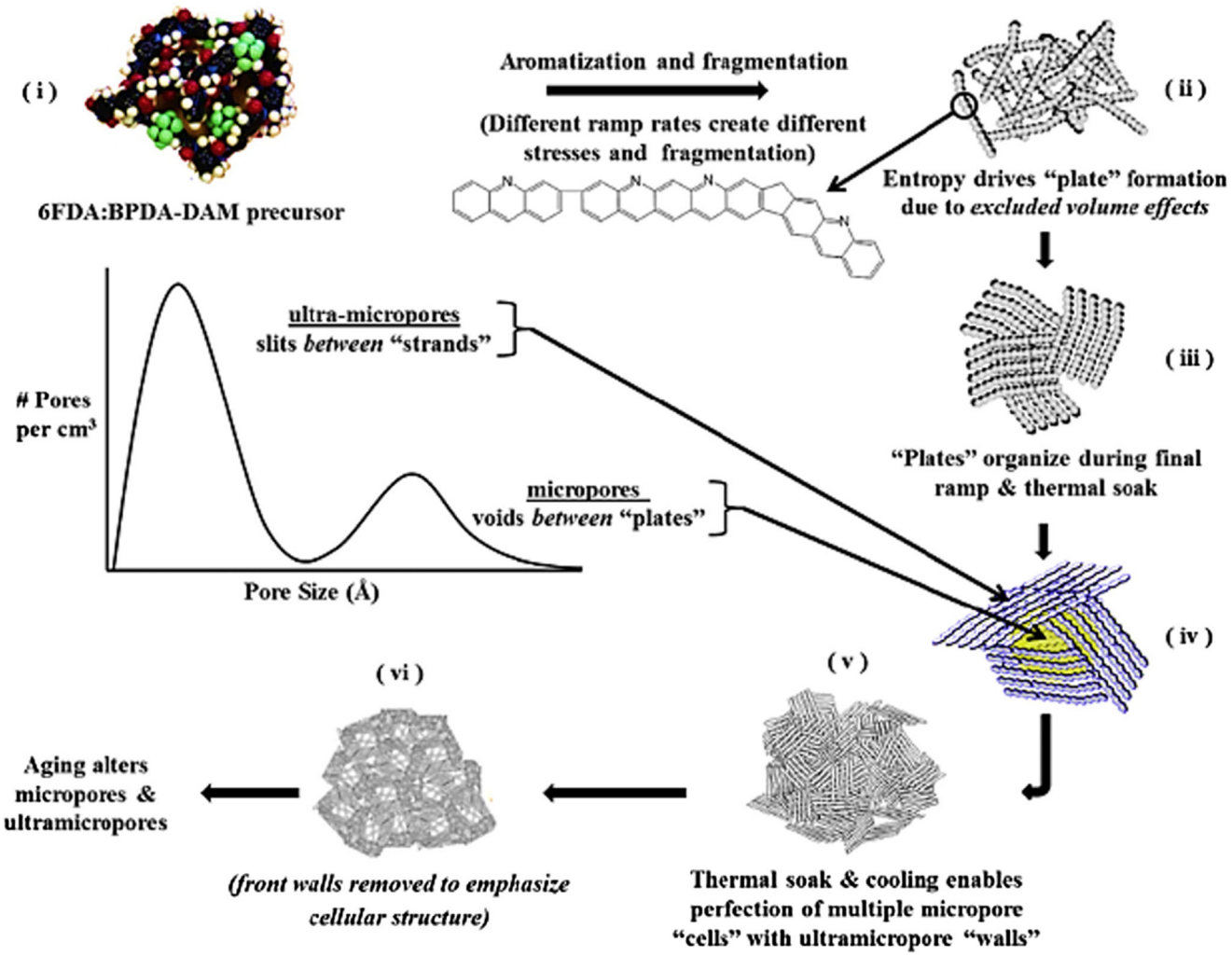

Fig. 3 The mechanism for the formation of complex CMS from 6FDA:BPDA-DAM precursor [26]

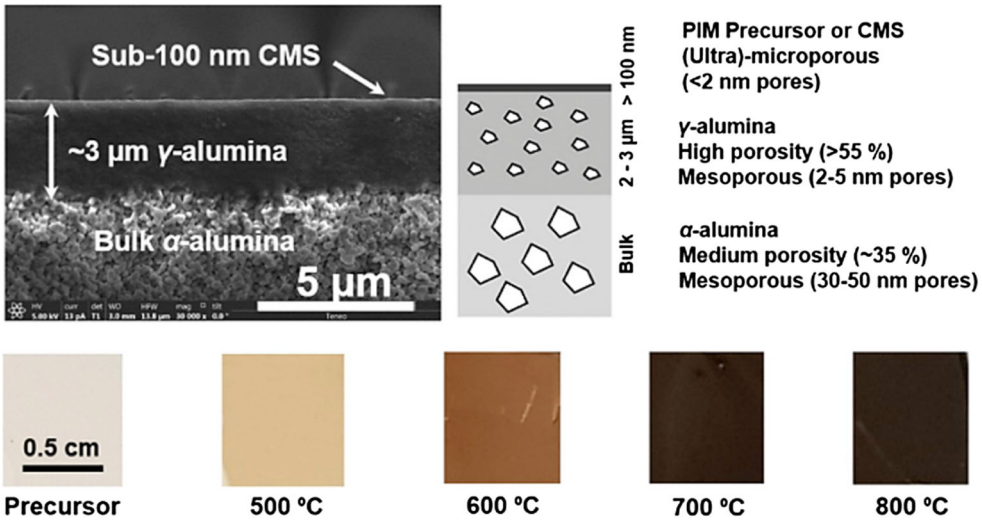

Fig. 4 The fabrication of the CMS from SBFDA-DMN at different pyrolysis temperature ranges from 500 to 800 °C [28]

hydrogen production reactions. Existing literatures have reported several types of porous membranes that were investigated for separation and production of H_2. It includes carbon-based molecular sieve membranes for hydrogen gas recovery and gas separation [39–41]. Laboratory-scale studies have proved the efficacy of carbon molecular sieve membranes in separating H_2 from the refinery gas streams. This technology was employed by Air Products and Chemicals Inc. in enriching H_2 to 56–60% before PSA purification to produce H_2 with purity of 99.99% [42, 43]. However, it was noted that the same type of membrane is not compatible for membrane reactor-related application such as steam reforming and water-gas shift. This is due to surface characteristics of the carbon molecular membrane possessing oxidative nature. Alumina-based mesoporous membranes were also reported for its application in hydrogen gas production, but most of gas separation literatures were for helium and carbon tetrafluoride rather than hydrogen. In helium gas study, selectivity was fairly low around Knudsen flow separation factor in order of 1 to 10. Both silica and surface-modified ceramic membranes with silica have shown promising enhancement for application in separation and production of H_2. Over the decade, a group of researchers mainly from USA, Holland, Germany, Japan and Australia has led the development of silica-based membranes, resulting in a significant development in the particular area. A novel carbon membrane based on poly-phthalazione ether sulfone ketone (PPESK) developed by Zhang and co-workers [36] was tested for its separation performance for several gas pairs. It was found that satisfactory separation performance was achieved by resultant carbon membrane in comparison to polyimide membranes.

In recent years, there are plenty of publications regarding polyimides as potential precursors in fabrication of carbon membranes, showing its prominent position in the area

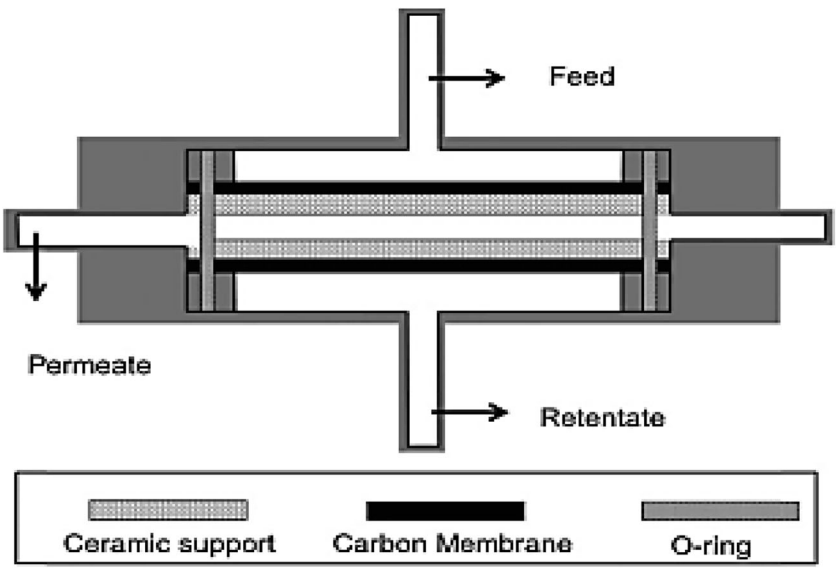

Fig. 5 Permeation model of H_2 separation [37]

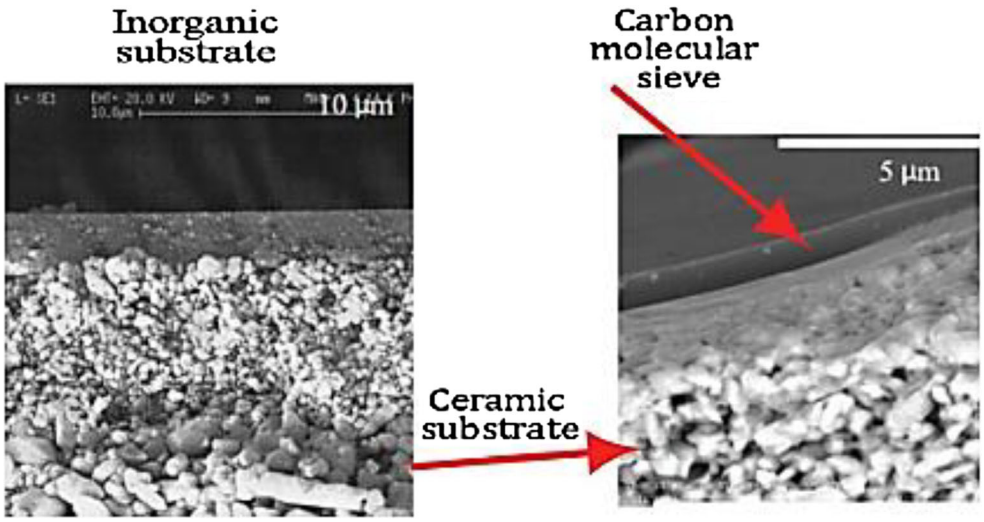

Fig. 6 Fabricated CMS membrane and ceramic substrate [38]

[44–51]. This is due to superior properties of the polyimides itself, possessing good rigidity with high temperature for both melting point and glass transition temperature while retaining its chemical and thermal stability. Few classes of polyimides including a group of hexafluoroisopropylidene (6-FDA) [29, 52–54], P-84 polyimide [50, 55–58], pyromellitic dianhydride (PMDA) [44, 59, 60], benzophenone tetracarboxylic dianhydride (BTDA)-based [3, 8, 15, 55, 57], BPDA-based (3,3,4,4-biphenyltetracarboxylic dianhydride) and 2,4,6-trimethyl-1,3-phenylene diamine have been investigated throughout the years [61]. Comprehensive insights on polyimide-based carbon membranes are tabulated elsewhere [48]. Up to date, the schematic flow presented in Fig. 7 shows that a novel nanohybrid CMS membrane was fruitfully fabricated through vapour phase infiltration (VPI) from PIM-PI precursor with metal organic which is trimethylaluminium possessing excellent H_2/N_2 selectivity of 120 [27].

Out of various polyimide materials, Matrimid has been thoroughly investigated and has been the polymeric model for porosity studies and related effects on gaseous separation characteristic for carbon membranes due to its availability as commercial product. ADDIN EN.CITE Despite all the reported studies, there are scarce information on enhancement of carbon membrane properties by blending but the trend towards this method is increasing recently [62–66]. It is expected that the membrane development approach by blending is simple yet effective and efficient for tailoring the membrane properties. For this approach, material selection needs to be selected accordingly, which enables to form homogenous matrix and fulfil the expectations. The resulting membranes were then analysed with respect to the efficacy of gas separation. The results from the investigations revealed that engineered carbon membranes by blending and suitable set of parameters produced interesting gas permeability and perm selectivity.

Synthesis of carbon molecular sieve membrane occurred at high temperatures under controlled environment during pyrolysis. Preparation of CMS membrane by carbonisation process was first employed by Koresh and Soffer in 1980 [67]. Advantages of CMS membrane are its resistance to corrosion, stability in high temperature and superior permeability and selectivity compared to current conventional (polymeric) membrane. According to Rungta and groups [26], CMS membrane has a "slit-like" structure with two modules pore size distribution known as micropores and ultramicropores, in which the ultramicropores are connected to the micropores. The narrow constrictions are responsible for gas molecule sieving properties while the microporous structure provides sites for gas adsorption [68].

Recently, Parsley et al. (2014) [69] demonstrated the separation and purification of H_2 from biomass-based syngas via CMS membrane. Results from their studies were quite significant, achieving 90% H_2 recovery with 90% of gas purity at dry basis. As aforementioned, CMS membrane was obtained from thermal treatment, and thus, tuning of carbonisation parameters can affect the separation performance by CMS membrane. Relevant study was conducted by Rodrigues et al. (2014) [70] to find out the influence of pyrolysis end temperature to the membrane performance. They prepared an alumina-supported CMS membrane with resorcinol-formaldehyde resin containing boehmite at 550 °C where separation of H_2/N_2 surpassed the Robeson upper limit. From investigation of CMS membrane done by Llosa Tanco et al. (2015) [71], they described that ageing process of membrane which was done for 24 h reduced the permeability of N_2 while H_2 permeability was not affected. In addition, further investigation by the same authors discovered that carbonisation temperature at 1000 °C decreases the membrane pore size. Novel CMS membrane derived from ionic liquid-regenerated cellulose precursor was successfully fabricated by researchers [72–74]. It was reported that the resultant membrane possesses superior separation performance and high stability at humid atmosphere.

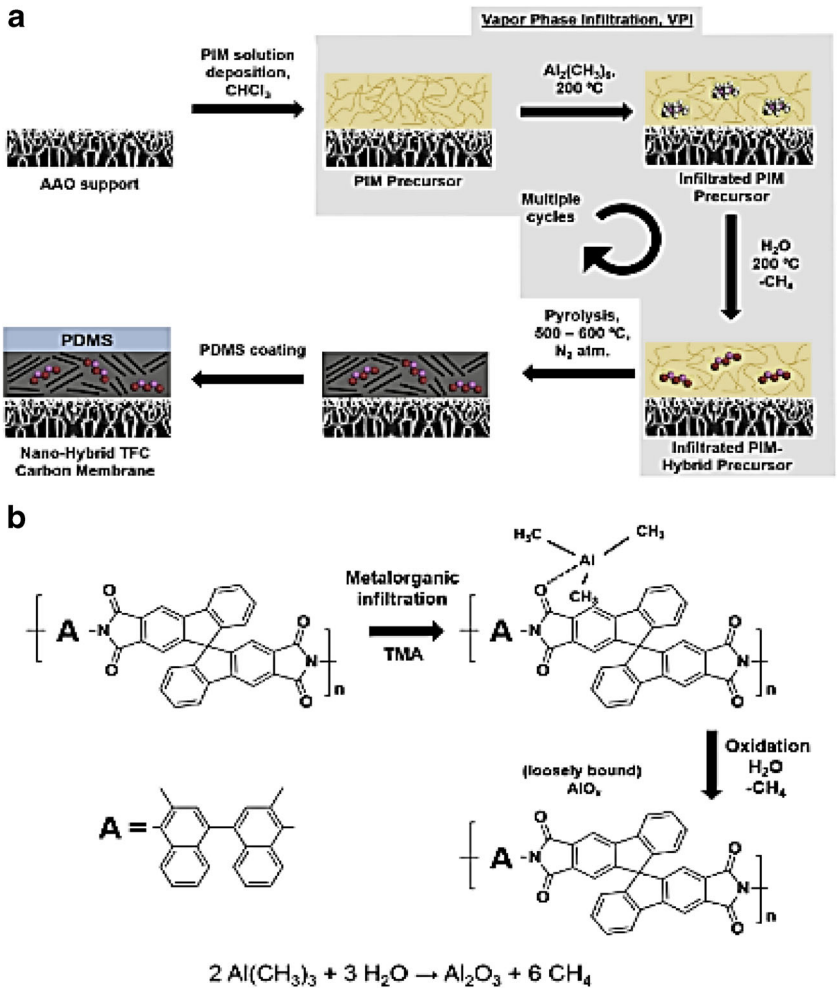

Fig. 7 The schematic flow of **a** the constructed CMS membrane via VPI process and **b** the proposed chemical schematic for the reaction of trimethylaluminium in PIM matrix [27]

2 Hydrogen specialities

The concept of utilizing hydrogen gas as prime energy carrier, or simply known as H_2 economy concept, is well-known among the futurists and policy makers since two centuries ago. It was first employed by Isaac de Rivaz in 1805, in which H_2 was fuelled in the first combustion engine before it was replaced by steam and currently petroleum to power the engines [75]. As displayed in Fig. 8, H_2 acts as vital key role especially in H_2-based sectors such as ammonia and ethanol production plants together with significant industries like electricity grid, transportation, energy storage, residential etc. [76]. H_2 has garnered attentions due to its potential in solving two of the global challenges that affect world economies and achieving energy independence while possessing minimal impact to the environment [77]. However, the realization of H_2 economy can only be achieved after developing four crucial technologies outlined below:

1. Economical production of hydrogen gas in carbon constrained global energy system. Production of hydrogen gas derived from fossil fuels with sequestration of carbon needs to be taken into account. Also, usage of renewable sources will increase
2. Technology for purification and gas storage able to purify hydrogen streams according to subsequent storage requirements and utilization systems. US DOE has defined target of 6.5 wt% for efficient and practical hydrogen storage devices
3. Well-arranged, efficient and worldwide availability for H_2 delivery and distribution
4. Utilization of H_2 in fuel cells and another energy conversion technology

Inorganic membranes are currently gaining attention as a promising material for H_2 gas separation and purification and are important in membrane reactors for H_2 production processes. However, no comprehensive review was found for the membrane status for H_2 applications. Therefore, this work aims to provide insights on recent progress in membrane technology, comparing their separation properties and efficacy in membrane reactor systems for natural gas reforming and water-gas shift reactions. Gas permeance by various

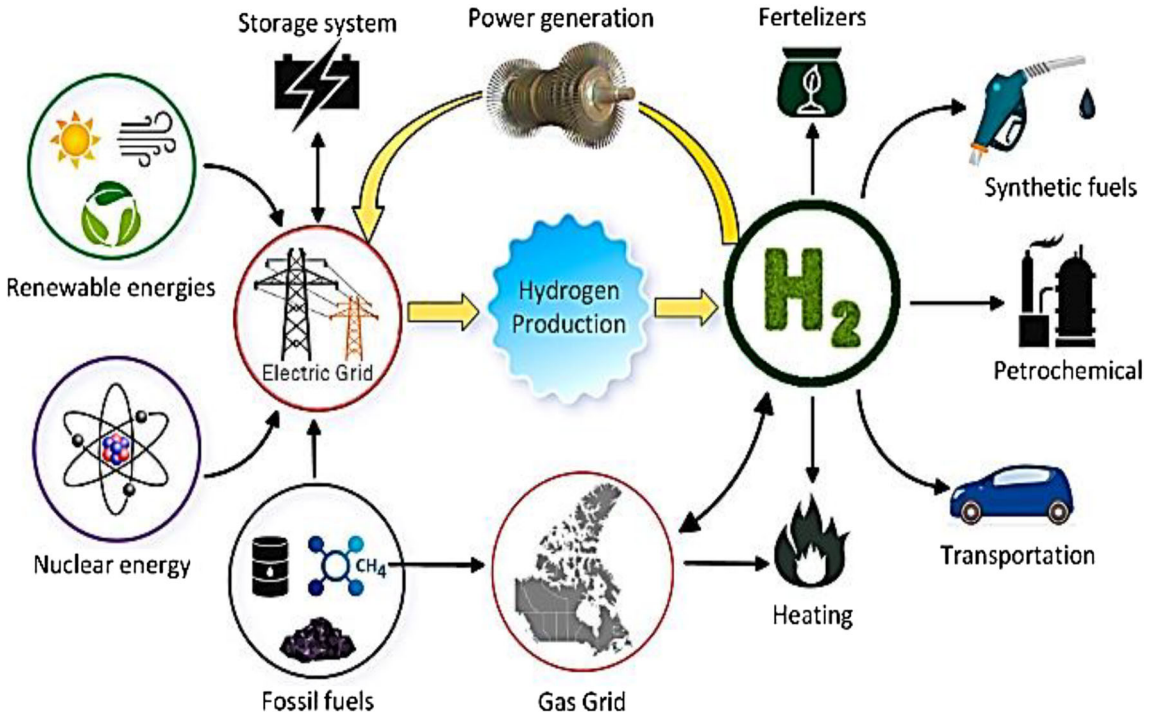

Fig. 8 Key functions of H_2 in related important industries [76]

membranes were presented and discussed further in next subsection.

H_2 is one of the most abundant elements that can be found in earth. Few methods to obtain H_2 are extraction from natural sources: water, biomass or hydrocarbons (i.e. coal and natural gas). It can also be obtained by nuclear energy reaction or from renewable source-derived electricity (e.g. wind, solar and biomass). Globally, the production of H_2 is reported to be majorly sourced from fossil fuel with 71.27%, while only 0.74% of H_2 was purified from renewable sources as tabulated in Fig. 9 [76]. Energy driven by H_2 is often known as 'clean energy' due to production of only water as the by-product after combustion. However, H_2 derived from hydrocarbons yielded a type of greenhouse gas, CO_2. Approximately, annual production of H_2 is 5 billion m^3 around the world in which half of that is used for ammonia production for fertiliser, 37% for oil refineries, and 8% for methanol production and the remaining are utilised in chemical and metallurgical industries.

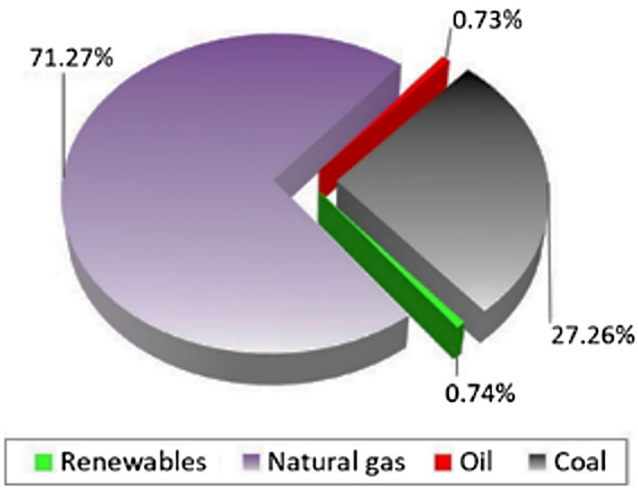

Fig. 9 The current worldwide sources for the production of H_2 [76]

As current movement emphasised more on sustainability of environment, more efforts are put for development of technologies needed in building infrastructure that supports 'H_2 economy' [78]. It was revealed that total worldwide investment in H_2 gas has increased significantly over the years and currently in range of several billion US dollars. To add, Bush Administration had announced a US$1.7 billion project focusing on H_2 technology advancement especially for fuel cell vehicles. Japan also has shared their plans to set up around 4000 H_2 filling stations by 2020. Another best-known example was from the European, where they announced their vision to have a complete transition to H_2 by the year 2050. Figure 10 depicts the plans set by the Europeans in achieving their goal.

From their milestones as seen in Fig. 10, H_2 gas will be generated from Iceland's geothermal and hydro resources. Then, it will be fed into fuel cells for various applications in both stationary (e.g. homes and businesses) and moving transportation (i.e. cars, bus, boats etc). On the other hand, Hawaii conducted a feasibility study in order to assess the practicality for a larger scale of H_2 utilization, fuel cells and renewable energy. Various technological barriers related to storage and distribution of H_2 need to be overcome. It can be noted that pathway to H_2 is still uncertain. Majority of the countries in

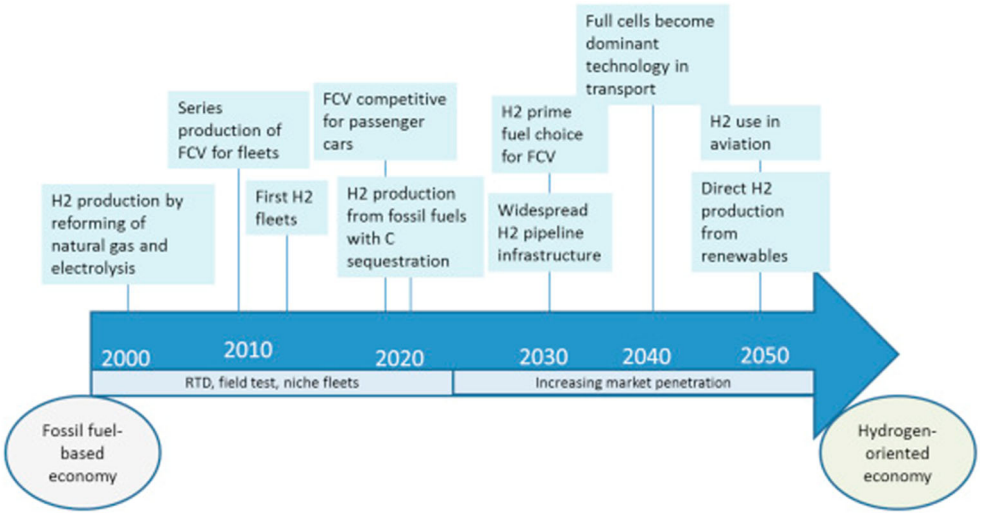

Fig. 10 Major milestones in the European H_2 vision [79]

the world are abundant with coal and gas, which plays an important role for the energy transition. New infrastructures for H_2 transition initiative such as pipelines, storage facilities and fuel stations require a huge investment. It can be assured that usage of H_2 will encourage diversity in the countries' energy mix while offering a better and cleaner environment.

2.1 Reactor for H_2 production

Separation and purification technology is very crucial for H_2 derived from fossil fuels. In the process, water-gas shift (WGS) reaction occurs and CO is converted to H_2 inside a membrane reactor. The WGS reactor was first discovered in 1888 and then became popular since Haber ammonia synthesis process and the introduction of catalyst in 1912. Conceptually, the WGS reaction can be done by two different types of reactors which are high temperature shift reactor labelled as HTSR and low temperature shift reactor known as LTSR. The process in both of the reactors occurred in several steps. The initial stage of the reaction started in HTSR under high pressure which is 60 bar in the range of the temperature recorded at 320 to 360 °C that will speed up the conversion of carbon monoxide, CO. Next, the process will be completely finished in LTSR with lower pressure (40 bar) in between 190 and 250 °C in order to reach higher conversion that is optimised by the WGS equilibrium [80]. The WGS is reversible and an exothermic reaction can be expressed in the following Eq. 1:

$$CO_{(g)} + H_2O_{(g)} \leftrightarrow CO_{2(g)} + H_{2(g)} \; \Delta H^{\circ}_{298K} = -41.1 \text{ kLmol}^{-1} \quad (1)$$

In this context, membrane reactor shows a great potential in shifting the equilibrium. Few properties of a good membrane reactor include high separation selectivity, high gas permeance and the durability and stability of the membrane itself. It should be noted that membranes also play an important role in purification mechanism of H_2.

An economical way to produce H_2 is by stream reforming, where steam reacted with hydrocarbons and nickel is added to accelerate the process [81]. Examples of competitive separating technology for H_2 from the streams are amine absorption [55], pressure swing adsorption (PSA) [43] and membrane separation [16, 34]. Among the list, gas separation using membrane system is more cost-effective than PSA in comparison to the relative capital investment and unit recovery cost [42]. Selective removal of H_2 from the reaction system shifted the reaction equilibrium to the products side, resulting in higher conversion of CH_4 to H_2 and carbon dioxide (CO_2), and it can be obtained at lower temperatures. There are two inorganic membrane classes for production and purification of H_2 which are dense phase metal, metal alloys and ceramics and porous ceramic membranes.

A simulation study for H_2 production which employed Pd-based disk membrane with 100 μm of thickness proved the enhancement of steam reforming performance in a real membrane catalytic system [82]. From their study, the production of H_2 was increased but at high temperature range of 700 or 800 °C. However, available commercial membrane for Pd-based membrane is too thick and does not work effectively at the temperature suggested. Their PSA unit consists of multiple adsorption beds that comprised of molecular sieves and activated carbon. Sequential H_2 production process in water-gas shift reactors and subsequent separation with Pd-alloy–based membranes are illustrated in Fig. 11 [83]. Usually, sol-gel technique or hydrothermal methods are used to prepare porous ceramic membranes. The method will produce membrane with high stability and durability at high temperature, high impurity and at tough hydrothermal environments. To

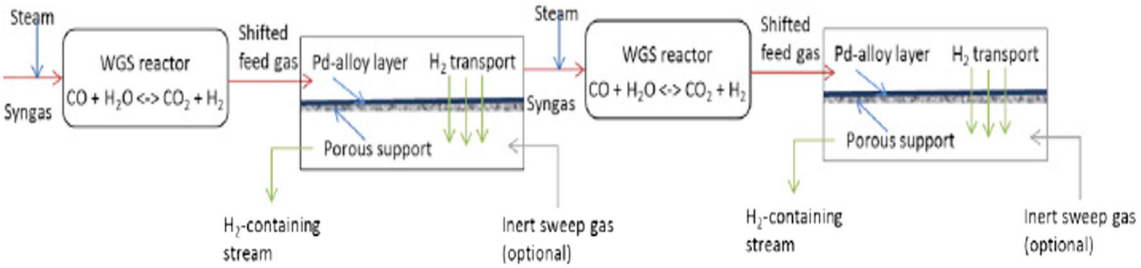

Fig. 11 Schematic illustration of sequential H_2 generation in water-gas shift reactors and subsequent separation with Pd-alloy membranes [83]

simplify, inorganic ceramic membrane has low H_2 selectivity but with higher flux. Microporous membranes show great potential in replacing conventional membrane for water-gas shift reaction at higher temperature [84].

Importance of these requirements differs for each application, but it should be known that selectivity and permeability are the basic features of a membrane. Efficiency of the process can be determined from the higher value of selectivity and lower driving force needed to attain a given separation which then lowers the total operating cost for the separation system. Higher flux requires a small membrane area and thus reduces the total cost of the system. Compared to other type of membranes, inorganic membranes are preferable for applications under extreme temperature and chemical environments whilst polymeric membranes have the advantage of being cost-effective membranes [2]. H_2 polymeric-based membrane is known to be useful for utilization in moderate environment temperature at range of 350 to 450 °C which fits the prerequisite temperature for water-gas shift reaction in natural gas steam regeneration.

2.2 H_2 separation membranes

Membrane can be defined as physical barrier that permits selective transport of mass species, extensively used for separation and purification in various industries, not limited to only gaseous. It can be broken down into three types: organic, inorganic and hybrid of organic/inorganic membrane system. In organic class type, it can be further classified into two which are known as polymeric and biological constituents. For inorganic membranes, it can be divided into metallic (dense phase) and ceramic (porous and non-porous types). IUPAC reports contained the summarised information for basic concepts and its elaboration for particular membranes [85]. Proper selection of membranes is complicated and differs for each application. Few significant considerations that need to be taken into account for candidate membrane type include its productivity and selectivity and durability of membrane, and mechanical principle during the operation must be balanced against its total cost [86]. The needs for energy-efficient technology and ease of operation make H_2 selective membranes a good alternative.

Particularly, mixed matrix membranes are composed of molecular sieving materials that were incorporated in a polymer matrix. Well-known molecular sieving materials usually embedded in the matrix are carbon molecular sieves and zeolite. This type of membranes is highly proposed to be applied in gas separation in efforts to find alternative to current separation membrane. Table 1 shows several H_2 membranes reported from previous study.

For zeolite-based membrane separation, gas molecules bind itself onto active surface of zeolite. Therefore, overall separation efficiency is closely related with the affinity of the adsorption process. Zeolite membrane usually obtain its maximum selectivity at low to moderate operating temperature ranging from 100 to 200 °C, which varies depending on their molecular structure and its polarity. At those temperatures, the membrane remains partially inaccessible as mixture that contains stronger adsorbing molecules block the other components from passing through the channels. This type of separation based on adsorption selectivity is suitable for dewatering and CO_2 capture, where removal of strong adsorbate is needed. Among listed components in Table 1, H_2O and CO_2 are the most adsorbed molecules on zeolites as they have large dipole and quadrupole moments.

As aforementioned, polarity, topology and flexibility of zeolite frameworks are few factors that determine the adsorption performance of zeolite adsorbents. Polarity of zeolite molecules depends on zeolite composition, in which addition of Al helps to increase the polarity of the framework. When polarity increases, the adsorption performance increases due to stronger interaction between adsorbent and the adsorbate. Thus, proper selection of zeolite material is critical for high-efficiency membrane separation. For instance, silicalite-1 is one of the zeolite membranes that are comparable to other conventional inorganic and organic membrane. New breakthrough to high-efficiency H_2 separation membrane could be achieved if development of narrow, pore full SiO_2 6-ring zeolite for molecular sieving (pore size of 0.3 nm) turns out to be a success. Constricted pore structures and its compactness require thin membrane layers for maximum H_2 sieving. Other than silicalite-1 membrane, DDR membranes are also suggested for H_2 separation tools [103]. The process for the purification of H_2 was done by Hang Yin and co-workers through the fabrication of MOF membrane coupled with Cu/

Table 1 Performance of mixed matrix membranes from previous studies

Samples	Performance					References
	Permeability ($\times 10^{-16}$ mol m/ m^2 s Pa)			Ideal selectivity		
	H_2	CO_2	N_2	H_2/N_2	H_2/CO_2	
6FDA-m-PDA	20.3	8.2	0.36	56.39	2.476	[87]
6FDA-2,4-DATr	87.2	28.6	1.31	66.56	3.049	[87]
6FDA-3,5-DBTF	58.6	21.6	1.17	50.09	2.713	[87]
6FDA-4BDAF	46	19	0.98	46.94	2.42	[88]
6FDA-3,3^0-ODA	14	2.1	0.10	140	6.67	[88]
6FDA-3BDAF	21	6.3	0.24	87.5	3.33	[88]
Bisphenol-F polysulfone	10	4.5	0.2	50	2.22	[89]
Bisphenol-O polysulfone	15	4.3	0.2	75	3.49	[89]
Dimethyl bisphenol-A polysulfone	11	2.1	0.09	122.22	5.238	[90]
Dimethyl bisphenol-z polysulfone	9.2	1.4	0.06	153.33	6.57	[91]
MOFs (NH_2-CAU-1 and NH_2-MIL-53)	33	0.622	–	–	53	[92]
NH_2-MIL-53/PI (VTEC)	0.45	0.058	–	–	7.7	[93]
Zeolite FAU/Matrimid	6	0.582	–	–	10.3	[94]
NH_2-CAU-1/PMMA	3.7	0.285	–	–	13	[95]
ZIF/Matrimid	0.6	0.136	–	–	4.4	[96]
UiO-66/PI	2.5	0.490	–	–	5.1	[97]
Cyclic olefin copolymer/GO	0.05	0.0012	–	–	40	[98]
ZIF-11/PBI	1.38	0.197	–	–	7	[99]
Silica/PPO	23	6.38	–	–	3.6	[100]
ZIF-11/Matrimid	0.36	0.08	–	–	4.4	[101]
$Cu_3(BTC)_2$/PI	420	15.11	–	–	27.8	[102]

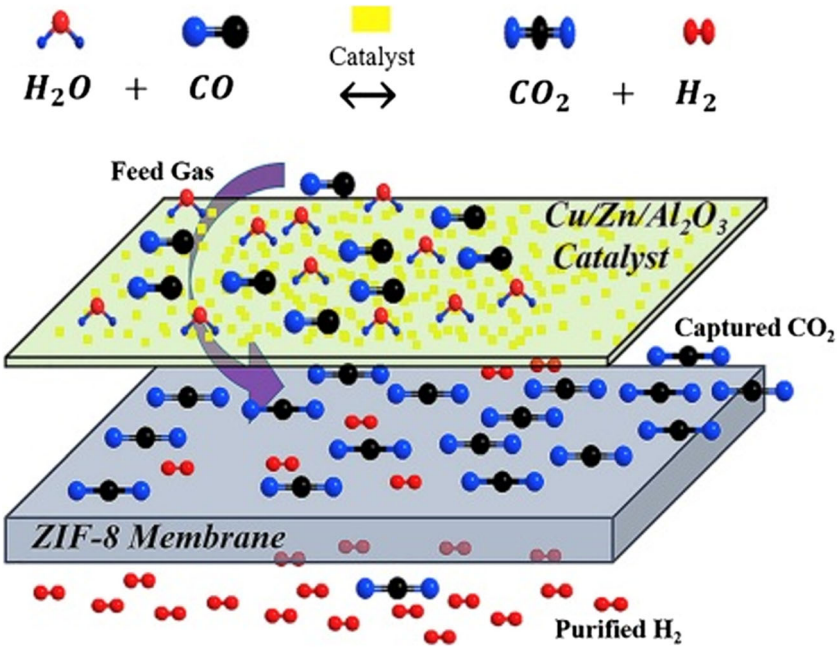

Fig. 12 The proposed illustration of the H_2 purification process using ZIF-8 membrane [104]

Zn/Al_2O_3 catalyst via LTSR as illustrated in Fig. 12 [104]. The membrane recorded a pure H_2 permeance of 9.2×10^{-7} mol m^2 s Pa with selectivity of H_2/CO of 6.13 finished at room temperature.

To operate membrane, two key parameters that have to be considered are hydrogen partial pressure and temperature at both inlet and outlet streams. Contradict to other separation methods, separation by membrane is suitable for small-scale and portable applications. Plus, it can be operated at various ranges of temperature and pressure. Significant advantage for separation by membrane is that it can be employed in membrane reactors that allow synchronised generation and purification of hydrogen [105]. Different type of separation membrane produced different purity of H_2. Porous membrane types are formed from polymer consisting of carbon, ceramic and metals whilst dense membranes include polymeric membrane, ion-conductive ceramic and metallic membranes. Table 2 shows a concise portrayal of different membrane types for separation.

Separation of gas via polymeric membranes was first employed almost two centuries ago by Mitchell for study of hydrogen and carbon dioxide mixture [106]. Then, permeation process was explained by Graham in 1866, in which he described the involvement of solution-diffusion mechanism in the process [107]. Dissolved permeate molecules found in upstream face of membrane were transported through it by the same process that occurs during liquid diffusion. First successful gas separation by membrane was introduced in the 1970s for separation of hydrogen from ammonia purge gas streams and adjustment of H_2/CO ratio in synthesis gas using polymeric-based membrane [77]. Polymeric membrane possesses superior diffusion coefficient of H_2 relative to all other molecules, which led to an excellent separation from highly supercritical gases (i.e. methane, CO and N_2) except for helium. Its excellence diffusion characteristic is dominant in gas separation mechanism and produce high overall selectivity with low H_2 solubility. For instance, newly synthesised polyimide and polyaramide-based membranes showed H_2/CH_4 selectivity of approximately 200.

As aforementioned, basic and important features for separation membranes are its selectivity and permeability. In absence of defects, selectivity is a function of material properties at given operating conditions while productivity is affected by material properties and thickness of membrane film. It was suggested that lower film thickness has a higher productivity. Koros and co-workers [108] stated that requirements for gas separation by membrane can be divided into two: technical and practical requirements. Technical requirement is the properties that need to be present in the system to be considered for application in gas separation while practical requirement is the essential characteristics in producing a technically acceptable system that can compete with existing separation technologies such as cryogenic distillation and pressure swing adsorption technique.

Technical requirements for two main membranes for separation of H_2 are described below:

1. For solution-diffusion membranes either polymeric or metallic membrane, it is vital to obtain a selective layer without any defects such as pin hole or crack in order for the membrane to last longer in long-term pressurization and presence of system upsets.
2. Similar standard features (defect-free) need to be ensured for molecular-sieve–type membrane so that it does not have continuous pores with size that exceeds certain critical size presented between upstream and downstream membrane faces. Maximum pore size for H_2 separation membrane is around 0.3–0.4 nm. Adsorptive pore walls may reduce the effective opening below the 'dry' substrate.
3. Before membrane separation stage, it is suggested that gas streams undergo removal of condensable, adsorptive and reactive components.

Table 2 Concise portrayal of several separation membranes

Membrane types				
	Porous	Polymeric	Ceramic iron conducting	Dense metal
Typical type	Silica, alumina, zeolites, carbon	Polyimide, cellulose acetate	Polyimide, cellulose acetate	Polyimide, cellulose acetate
Diffusion mechanism	Size exclusion	Solution diffusion	Solution diffusion	Solution diffusion
Driving force	Pressure gradient	Pressure gradient	Ionic gradient	Pressure gradient
Operating temperature	≤ 1000 °C	≤ 110 °C	700–1000 °C	150–700 °C
Permeability	Moderate high	Moderate high	Moderate	Moderate
Typical selectivity	Low moderate	Moderate	Very high	Very high
Relative cost	Low	Low	Low	Low

Similar to membrane separation, PSA method also used feed pretreatments. More robust membrane system which allows unconditioned feeds are more attractive as it is flexible and easy to operate. Thus, chemical and thermal stability for every membrane is also essential as it will affect its life cycle and operation. For practical requirements, a membrane should offer commercially viable throughputs (fluxes) which require a defect-free and low value of membrane effective thickness. This is to ensure that intrinsic selectivity of the material is destroyed while retaining its intrinsic permeability. It is not convenient to use a thick membrane film even for a highly permeable membrane due to its high total material cost. Large-scale gas separation system needs to utilise an enormous membrane area which contributes to the increase in total cost. Next, practical membrane systems have to be able to achieve required upstream or downstream H_2 compositions. High ideal separation factor is favourable as it allows flexible configuration of transmembrane pressure difference whilst still acquiring the gas purity requirements. In addition, it determines the energy used for feed gas compression and if multi-stage system design is required. However, the drawback of having high ideal separation factors is that it usually comes with low intrinsic membrane permeability which shows the compromise between productivity and selectivity of membrane. The relationship between intrinsic membrane permeability and selectivity can be considered as major problem that is constantly discussed by researchers in order to strive for a better material in optimizing both properties.

2.3 Existing membrane technologies for hydrogen purification

Commercially available membrane such as dense phase metallic and metallic alloy has garnered great attention. It is available in various compositions and can be modified into a large-scale membrane assembly. However, there are scarce effective metallic membranes for H_2 separation which are mainly palladium-based (Pd) alloys possessing H_2 permselectivity and have satisfactory mechanical stability [109–111]. Initial application of thick, self-supported dense membranes (50–100 μm) in gas separation was found to be unattractive due to high cost with low permeability rate and low chemical stability. Current modification made was by depositing a thin layer of palladium (< 20 μm) onto the porous ceramic membrane or the metal substrate to enhance the resistance to H_2 embrittlement and thus increase H_2 permeability [112–115]. In PdAg-based membrane which is common for H_2 extraction, increase in Ag composition enhanced the H_2 permeance, with reported Ag content to reach maximum permeability at 23 wt% [116]. The diffusivity of the PdAg membrane decreased but H_2 solubility increased. Alloyed membranes have excellent stability with lower total cost. It offers high H_2 fluxes and excellent mechanical properties compare

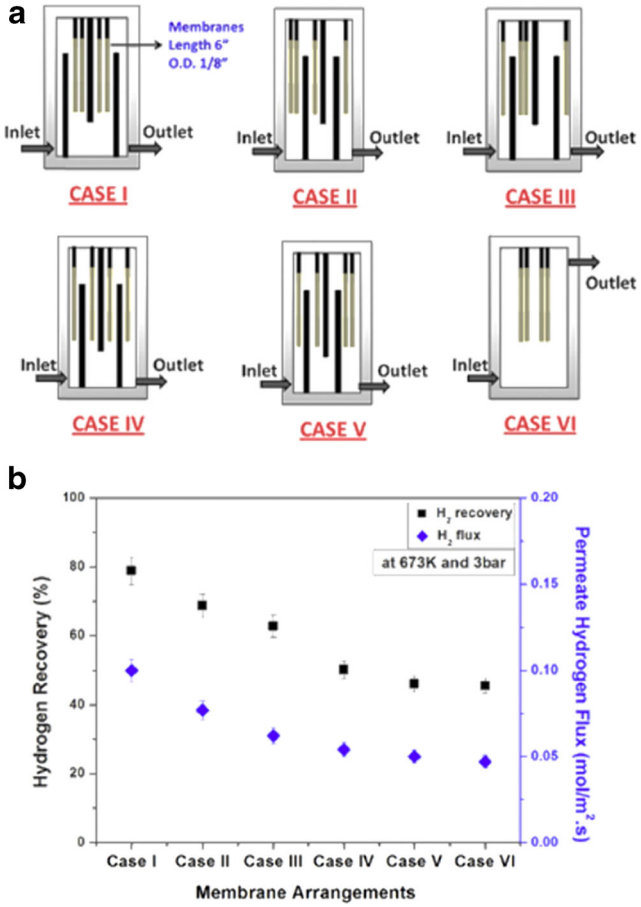

Fig. 13 The schematic for **a** different position of the membrane and **b** H_2 performance for different types of PdAg-based membrane position [117]

to the thick metal membranes. The development of PdAg membrane for H_2 separation was done by Sharma et al. and found that the permeance of H_2 reached 1.78 ×

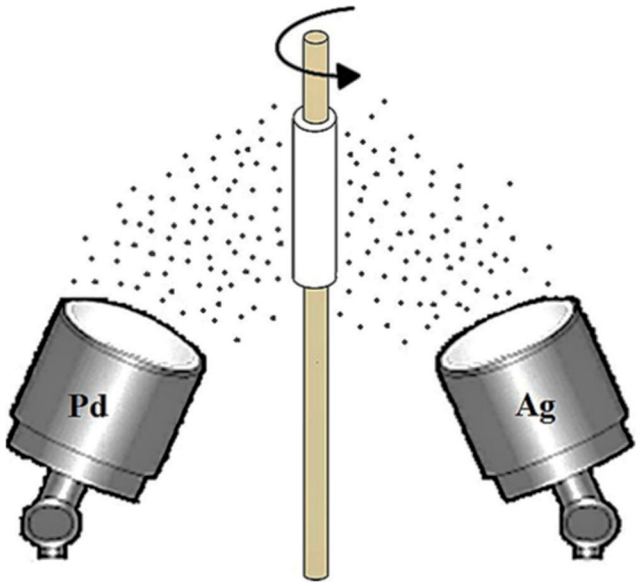

Fig. 14 The process for the fabrication of PdAg to be sputtered onto the surface of the ceramic membrane [119]

10^{-6} mol m^{-2} s^{-1} Pa^{-1} with 74.4% of H^2 recovery [117]. The setup for the H_2 recovery is presented in Fig. 13.

In another work done by Pereira and members, the fabricated PdAg thin film membranes that are incorporated on ceramic support achieved permeance of 0.71×10^{-6} mol m^{-2} s^{-1} Pa^{-1} which resulted in H_2/N_2 selectivity of 10 [118]. The co-sputtering process for the PdAg onto the ceramic surface membrane is illustrated in Fig. 14. Meanwhile, as can be viewed in Fig. 15, the constructed PdAg-based membrane onto porous alumina support yielded good H_2 flux that reached up to 0.62 mol_{H2} m^{-2} s^{-1} at 450 °C at 300 kPa [38].

Three well-established techniques for metal thin films coating onto porous metallic or ceramic supports are electroless plating, chemical vapour deposition and by physical sputtering [120]. Electroless plating approach is the most effective method with various advantages such as simple process, is economical, production of uniform coatings on complex shapes and has high coating adhesion. For chemical vapour deposition, it has the flexibility in coating metal film onto the support of different geometry and easy for scale up test. However, both of the common methods have similar drawback in which it has uncontrolled composition deposition of metal alloy. Previous study has reported the deposition of metal membranes inside alumina support mesopores to solve the mechanical problem concerning alpha-beta phase transformation due to pressure and temperature change of H_2 [121]. It was discovered that metallic membrane formed by pore deposits exhibits lower permeability of H_2 compared to the metal film on the support surface. To prevent H_2 embrittlement, it is suggested that a second element be added into Pd, a process known as alloying.

H_2 permeation process through metallic-based film is a complicated process involving H_2 molecule adsorption on film surface and desorption from ceramic substrate. Molecules of H_2 breakdown into hydrogen atoms located at the feed side of the film before being diffused through the film and re-associate on the permeate side. Due to its fast-forward and reverse reaction, H_2 atom diffusion through metal film became the rate-limiting step. Gas permeance in this context is the product of gas solubility and diffusivity. Li and coworkers [122] in their study employed the new approach to repair defects in Pd/α-Al_2O_3 composite membranes. Comparison regarding membrane microstructure showed that electroless plating for preparation of thin Pd/Ag membranes usually comprises of large crystallites in submicron range while membrane from chemical vapour deposition has polycrystalline or nanocrystalline structure, dependent on deposition conditions in 100 s nm. For sputtering method, it tends to contain nano-sized crystalline structure ranging from 20 to 100 nm. Due to complex system, some discrepancies cannot be described through the differences in thickness and composition of the membrane. Impact of crystallite size to H_2 permeance could be vital.

Separation of H_2 from highly supercritical gases for example CO, CH_4 and N_2 might be effectively achieved through the utilization of polymeric membranes due to H_2's exceptionally high diffusion coefficient compared to other molecules with an exception of He gas. Although solubility aspects are unfavourable for H_2, the influence of diffusion dictates providing high selectivity in overall. As an example, selectivity of H_2/CH_4 of certain new rigid polyaramide and polyimide membranes is around 200. Scaling up the technologies of H_2 membrane is the most complex but is also an important mission for researchers. Development of small-scale membranes with high quality in research is effective in terms of cost as failed units can be ignored easily. Rejection of failed large membranes is costly; thus, the vital challenge that needs to be overcome is to use large surface areas in preparing high-quality membranes fused into process components with high temperature sealing. Nevertheless, industrial implementation was found to be very scarce even with exceptional separation

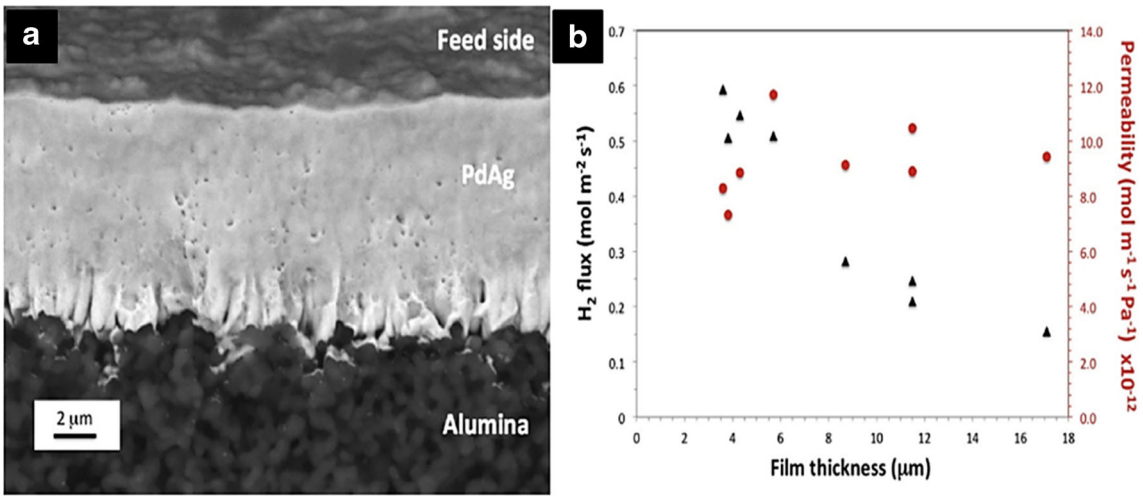

Fig. 15 **a** SEM image of the developed PdAg membrane on porous alumina support and **b** H_2 flux achieved for PdAg-based alumina membrane [38]

performances. Extremely high fabrication cost causes the implementation of dense metallic membranes to be suitable for only small-scale applications, for example, the electronics industry which requires a small quantity concerning H_2 of ultra-high purity.

3 Further improvements

To date, real-scale catalytic membrane reactor data are still scarce. Most of data for condition of reactions and comparison between dense and porous membrane were derived from mathematical model [123–125]. Catalytic membrane reactors can be easily merged with existing plant without having any drastic modifications. Even though there are many available literatures reported on investigation of catalytic membrane reactors, there are small to none that analysed the total devices' cost. This is due to unpopular application of membrane reactor technology with studies reporting the deficiencies and no implementation at real-life scale. Future research should highlight and focus on perfect, defect-free homogenous membranes that are able to last long under high temperature and pressure, and also under aggressive environments. Higher permeability at low thickness of membrane and high selectivity will be required. On the other hand, process of membrane sealing into modules need to be enhanced to overcome stream mixing and bypassing problem during reaction tests.

Lastly, engineering optimization during module preparation can be a critical move in order to increase the efficacy of membrane reactor, producing a high membrane area per unit volume, developing control system for large-scale modules, etc., together with studies on other elements regarding enhancement and application of reactors membrane [126]. However, the authors emphasised that progress in area of film formation and defect-free membrane film preparation has neglected the area of sealing temperature and scale-up membrane reactor. Dixon and co-workers [75] shared his opinion in importance concerning the paradox in membrane reactor. Membranes utilised in real industrial applications have not been reported from data found in the years 1998 to 2002 even though more than 500 articles have been published. Reviews done for membrane reactors suggested that further investigation is needed to enhance the membrane reactor technology, although its potential has been well-recognised since decades ago. In addition, analysis on current and future economy is required in order to stimulate specific technology advancement that has to be made. Economic analysis for water-gas shift reaction on Integrated coal Gasification Combined Cycle (IGCC) employed in microporous silica membranes revealed that highly favourable investment and operation cost can only be attained if more stable and more selective gas separation membrane is used [127].

4 Concluding remarks and perspective

For more than 50 years, Pd-based membranes have been widely studied with varieties of approaches for membrane preparation including the most known method which is via electroless plating [110, 128–130]. Current researchers have put more efforts in enhancing membrane film quality with low membrane thickness in order to reduce total cost. H_2 to N_2 selectivity at high temperature is more promising in Pd membrane with selectivity around 400–4700. However, it was noted that CO reduces the gas permeance of H_2 at temperature below 250 °C. Thus, Pd composite membranes are more suitable to be employed in a higher temperature system, especially membrane reactors. Progress in molecular sieve silica (MSS) membranes in comparison to Pd-based membrane is far more recent, with results of the selectivity only appearing 15 years ago [131, 132]. Comparing ceramic materials with Pd, it has its own pros and cons, in which ceramic materials show a greater stability than Pd under high temperature up to 600 °C but with lower selectivity range of 9–1500. Preparation of membrane commonly used sol-gel method [133, 134] and chemical vapour deposition (CVD) [135–138]. Sol-gel approaches resulted in high permeability and good selectivity whilst the latter method produced a satisfactory permeability with superior selectivity. Natural reactive reaction of silica with water directed researchers to focus on material functionalisations, developing hydrothermally stable membranes. Similar to Pd membrane, producing defect-free membrane and achieving repeatable membrane quality are current topics for MSS membrane development.

Metallic membrane (dense phase) and ceramic membrane (porous and non-porous) classified in inorganic membrane group possessed various advantages including ability to operate in high temperature and high flux. Performance of selective H_2 membrane differs for each type of membrane. Metallic Pd-based membrane offers infinite selectivity but with few drawbacks such as expensive metal cost and low thermomechanical stability of selective film layer. Examples for ceramic membranes are dense ceramics (perovskites) and microporous membrane [139, 140]. Porous membranes are interesting as they are easy to fabricate and have molecular sieving properties that provide high hydrogen permeance. However, challenges in employing carbon-based membrane for future membrane technology are its low mechanical strength for unsupported membrane and complicated membrane reactor design.

Dense and organic-type membrane is driven by solution diffusion as its gas transport mechanism whilst porous-type membrane followed molecule transport by Knudsen flow and activated diffusion. Superior H_2 selective membrane features have shown a promising potential for utilization in membrane reactors, in which constant elimination of reaction products helps to reduce catalyst, decrease the size of operation which

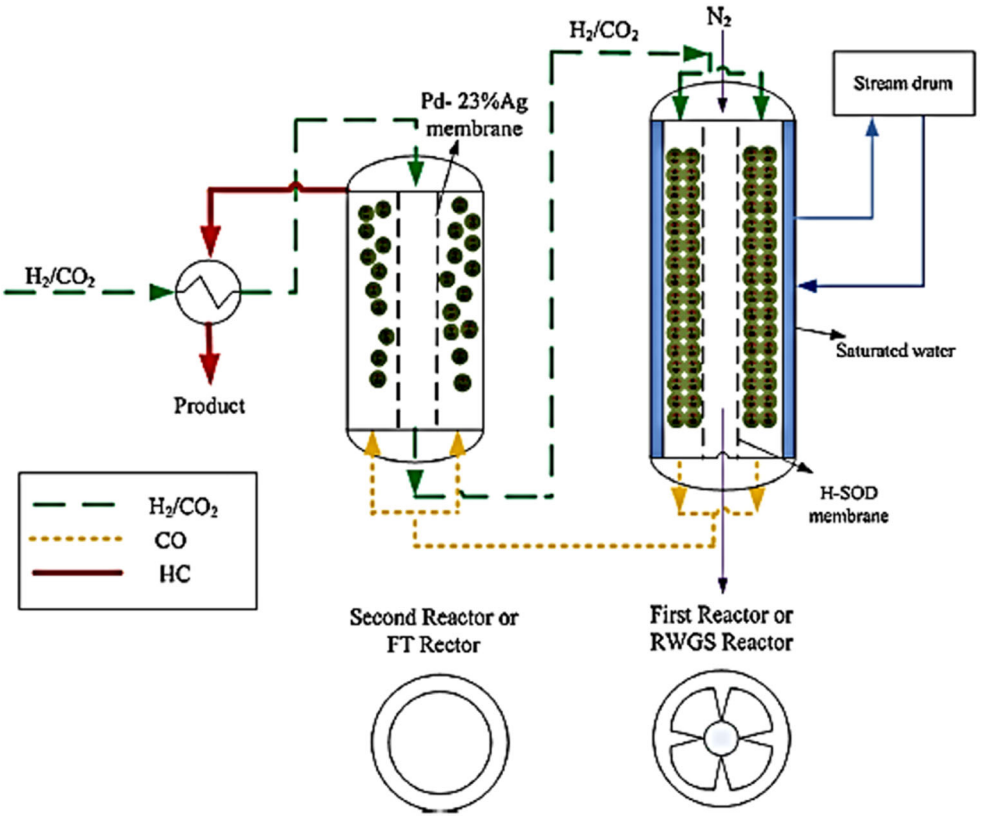

Fig. 16 Illustration of dual-type membrane reactor as future work [141]

later reduces the total cost and also enhances temperature and pressure conditions. In this work, carbon membranes have been shown to be a potential candidate for hydrogen separation and recovery when applied in a membrane reactor. Investigations were done to enhance the separation performance of hydrogen such as blending of polymer precursors. Further research should devote on optimizing the technique in fabrication of flexible carbon membrane for application in hydrogen production membrane reactor. Also, researchers should emphasise more on efficient reactor design to shift reaction towards product side while keeping catalyst active during reaction process by improving the surface area for the first reactor wall as illustrated in Fig. 16 [141].

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