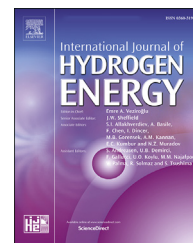


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Review Article

Advances in materials process and separation mechanism of the membrane towards hydrogen separation



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HIGHLIGHTS

- The mechanism associated with polymer membrane and MMMs were discussed.
- Hydrogen separation membranes and associated mechanisms are assessed.
- Current challenges and perspectives in hydrogen separation membranes are presented.
- Various membrane fabrication approaches are compared.

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ABSTRACT

The increased demand for a reliable and sustainable renewable energy source encourages the hydrogen-based economy. For the same, membrane separation approaches were reviewed as an advantageous process over contemporary techniques due to the environmentally friendly nature, economically viable pathway, and easily adaptable technology. A comprehensive assessment for the advancements in the type of membranes namely, polymeric and mixed matrix membranes (MMMs) has been delineated in the present article with the fabrication methodologies and associated mechanism for hydrogen separation. In hydrogen separation mechanism of the membrane, depends on the morphology of the membrane (dense or porous). The existence of pores in membranes offers various gas transport mechanisms such as Knudsen diffusion, surface diffusion, capillary condensation, molecular sieving mechanisms were observed, depending on the pore size of membranes and in dense membrane gas transport through the solution-diffusion mechanism. In polymer membrane, hydrogen separation occurs mainly due to solubility and diffusivity of gases. The hydrogen separation mechanism in MMMs is very complex due to the combining effect of polymer and inorganic fillers. So, the gas separation performance of MMMs was evaluated using the modified Maxwell model. Moreover, adequate polymeric material and inorganic fillers have been summarised for MMMs synthesis and highlighting the mechanism for gas transport phenomena in the process. Several types of materials implemented with polymeric matrix examined in the literature, amongst these functionally aligned CNTs with Pd-nanoparticles dispersed in polymer matrix were observed to reveal the best outcome for the hydrogen separation membrane due to the

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uniform distribution of inorganic material in the matrix. Henceforth, the agglomeration gets reduced promoting hydrogen separation.

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Introduction

The drastically increased global warming and depletion of fossil fuels need an alternative renewable energy source [1]. Hydrogen is a renewable energy source that reduces greenhouse emissions, energy diversification, and noise pollution [2]. The various processes used for hydrogen production like pressure swing adsorption (PSA), amine absorption, and cryogenic distillation [3,4] etc. These conventional methods face many barriers due to their high-price, large power consumption, and adverse environmental effect [5]. The hydrogen generation unit worldwide devoted to the hydrogen energy sector is currently under construction, needing a cost-effective and efficient technique for the separation of hydrogen [6]. Membrane separation is a promising technology to produce ultra-pure hydrogen due to its advantages such as operational versatility, high energy efficiency, compactness, minimal footprints, environment friendly, low operating costs, and simple integration with existing industrialized processes [7].

The development of hydrogen-selective membranes various types of materials used, such as polymer membranes (PI, PBI, PC, etc.), inorganic membrane (Carbon, Zeolite, and silica), and metallic membrane (Pd, Pt, etc.) [6,8]. The polymer membranes have their excellent mechanical strength and versatility to transform into different modules, economically

feasible, and reproducible [9]. Nonetheless, the consistency of the “upper bound” trade-off curve plotted between gas permeability and selectivity denoted by the Robeson plot has limited further advancement of the polymeric membrane separation process [10]. To fulfill the industrial requirements, polymeric membranes require needs improvements in terms of permeability and selectivity that can attempt by integrating the development of membrane materials applied for advancements in membrane manufacturing technology.

On the other side, excellent hydrogen separation performance has been recorded on certain inorganic materials. Inorganic membranes for hydrogen separation usually be categorized into two types: porous (zeolite, carbon, and silica) and non-porous (dense) (metallic) membranes [11]. Many researchers attempted to fabricate inorganic membranes for hydrogen separation due to its advantages, like high chemical, mechanical and thermal stabilities, tuneable allocation of pore size, and less plasticization [11]. These membranes show high H₂ separation performance, such as 3.5×10^{11} GTU, for zeolite [12], 5.46×10^6 GTU for CMS [13]. In metal-based inorganic membranes, developed from palladium [6] and platinum [14] belonging to group 10 and certain metals belong groups 3–5 of the periodic table are capable of dissociating and dissolving hydrogen [15]. Among this palladium, membranes demonstrate an excellent capacity to separate hydrogen from the other gases due to its properties like more excellent solubility of H₂ in a broad temperature range. Abate

et al. (2009) prepared a Pd membrane for hydrogen separation, and these membranes show stability at high temperatures up to 400 °C and good hydrogen separation performance [16]. Nevertheless, for large-scale manufacturing, the expense of these membranes and their risk of processability are serious problems.

To resolve these problems, researchers tried to incorporate the advantages of inorganic materials and polymeric materials to create a new category of membranes. Such a concept was realized with the invention of mixed-matrix membranes (MMMs) in the mid-1980s [17]. In an MMMs, the bulk continuous polymeric phase and the scattered inorganic nanoparticle phase are used. By integrating inorganic nanoparticles within the polymeric matrix, the MMMs obtain a few of the inorganic nanoparticles' features, particularly their excellent separation efficiency [18]. Riasat et al. (2019) used the PDMS polymer membrane for the incorporation of zeolite-A nanoparticles. The H₂ permeability of PDMS membranes was obtained 999.01 barriers, and it enhanced by incorporating zeolite-A up to 92% [19]. In the meantime, the disadvantages of inorganic nanoparticles, like the lack of processability and brittleness, can be compensated by the flexibility of polymeric materials [6,20].

Type of hydrogen separation membrane

Polymeric membrane

Polymeric membrane plays a crucial role in hydrogen separation. Polymeric membranes suitable material for hydrogen separation because of their advantages like high energy-efficient, relatively low environmental impacts compared to conventional separation methods, low cost, and convenience of use. The polymeric membranes are classified into two categories: 1) glassy polymer, 2) rubbery polymer [21]. Glassy polymers having medium to the high free volume are typically used to manufacture membranes since they have adequate voids to help the transportation of gas through the membrane [22,23].

The optimal characteristics for choosing polymeric membrane material are high permeability, high selectivity, mechanical stable, and thermally stable [7]. The high permeability polymer membranes usually offer low selectivity and vice versa—the hydrogen separation characteristics of polymeric membranes directly correlate with the material's microstructure. The permeability is directly affected by the size distribution and free volume present in membranes [24]. Polymeric membranes are also divided based on porosity, such as porous membrane and non-porous membranes. A porous membrane has a solid, widely void framework with pores that are spread at random. The separation of such membranes depends on the size of the molecules and the distribution of pores. A non-porous membrane consist of dense film from which the gas molecules permeated through the fine film are adsorbed. Then diffusion occurs under the driving force (pressure difference, concentration difference, electric potential gradient). Solubility and diffusivity of the permeate gas molecules through the membrane material play an important role in deciding the gas transport process [23].

L. M. Robeson improves the upper bound limit for the hydrogen separation membrane from 1991 to 2008. Fig. 1 indicates the upper limits of Robeson for H₂-selective polymeric membranes at a temperature of 25 °C. The data demonstrated that most of the current polymeric membrane has separation properties under the trade-off limit [25,26]. This trade-off relation is connected to an upper bound agreement. The separation factor versus the higher permeability yielded a limit to achieve the desired result of a high separation factor combined with high permeability for polymeric membranes [27]. Many researcher work on the trade-off limit of polymeric membranes including Polyimide (1,1-6FDA-DIA) [28], polybenzimidazoles [29], and Poly (etherimide) [30], and Poly (silylpropynes) [31], etc. It has been observed that the separation factor typically declines because the more permeable gas component increases its permeability [11].

Among several polymer forms that demonstrate gas separation properties form a gas mixture. Glassy polymers are promising materials due to their strong gas selectivity and superior mechanical strength as well as these types of membranes suitable for Small-sized gas molecules (H₂) have high permeability than large-sized molecules (CO₂, N₂) for gas separation [7]. The various type of polymeric material used for hydrogen separation by researchers such as polyimide (PI), polycarbonate (PC), polysulfone (PSF), polyethersulfone (PES), Polybenzimidazole (PBI), and polyetherimide (PEI) [32]. Among these, PI and PBI are promising materials used for commercialized purposes for hydrogen separation because of these membranes' structure as well as these membranes close to exceeding the Robeson trade-off limit.

Polyimides exhibit strong mechanical properties. These membrane materials show high selectivity and permeability. The membrane's permeability can be increased by changing the intersegment chain packaging and mobility without any reduction in selectivity [33,34]. Alterations in polymers' composition improve the solubility or diffusivity of the target gas; due to this, the gas permeability increases [35]. Many types of polyimide structures use for hydrogen separation, such as Matrimid, Kapton, IP-2080, LARC-TPI [23]. Many researchers work on a polyamide membrane for hydrogen separation from a gas mixture. Shishatskiy et al. (2006) developed and optimized the polyimide (Matrimid 5218) membranes for technological scale processing and hydrogen isolation from other gases. This membrane stable up to a temperature of 200 °C. The non-woven fabric uses for the support provided excellent strength to the membrane. Results show that the selectivity of H₂/CH₄ is approx. 100 [36]. Chung et al. (2006) developed a modified polyimide membrane that cross-linked with propane-1,3-diamine (PDA) for improving gas separation performance. The Crosslinking agent changes the membrane's polymer structural morphology that changes the diffusivity pathway of highly soluble membranes. The outcomes showed that 10 min PDA cross-linking obtained selectivity of H₂/CO₂ was 101 [34].

Polybenzimidazole (PBI) is a heterocyclic polymer and identical to aromatic PI. Recently it is in demand due to it offers excellent thermal stability and good chemical resistance as well as fabricated into fiber and membrane with outstanding stability [37]. PBI is a thermoplastic glassy polymer with a transition temperature (T_g = 427 °C) and is not hydrolyzing.

This polymeric material has good structural stability, resistance to the chemical agent, and acts as proton donors and acceptors. These characteristics of polymer make suitable material for hydrogen separation [38]. Kumbharkar et al. (2011) developed an asymmetric hollow fiber membrane by synthesizing M-PBI using the polycondensation process. The membrane performance was checked at a temperature of 100 °C to 400 °C. The outcomes of membrane performance showed high selectivity of H₂/CO₂ [39]. At low-temperature, the permeability of hydrogen gas low in M-PBI membranes, due to the low free volume of m-PBI arising, resulting from the interaction between strong H-bonding [29]. Despite their appropriateness for numerous operations in research and commercial purposes, polymer membranes are still inadequate in fulfilling specialized current membrane technology requirements, as such membrane materials do not exceed Robeson's upper bound limit. As shown in Fig. 4.

Inorganic membranes

For hydrogen separation, the inorganic membranes especially interesting, as these materials can withstand elevated temperatures and pressure. Inorganic membranes are categorized into two forms porous and dense (non-porous) membranes. Silica, zeolite, and carbon molecular sieve are categories in a porous material. In porous material, Fractionation depends on variations in size, shape, and affinity between the permeable gas molecules and the membrane [40].

Silica membranes are gradually gaining attention, especially in the H₂ separation. Due to their adsorption phenomenon and pore size, these membranes can separate tiny molecules of gas like H₂ and He. Besides, these membranes well-established, scalable, and straightforward synthesis techniques combined with low manufacturing costs [40,41]. Lee and Oyama et al. (2002) conducted a series of systematic studies on the preparation of silica-based membranes by CVD recording enhanced hydrogen permeability and selectivity. They employed porous vector glass material as a support material. The membrane showed high permeability of H₂ $\sim 10^{-8}$ mol m⁻² s⁻¹ Pa⁻¹ and high selectivity ($\sim 10^{-8}$) over large gas molecules (CO₂, CO, and CH₄) at 873 K. Stability of these types of membranes observed by the author up to 900 K [42]. In another study by Gu et al. (2008) Reported the performance of silica-alumina composite membrane of thickness 30–40 nm, it showed high H₂/CO₂ selectivity of 590 and H₂ permeability $2-3 \times 10^{-7}$ mol m⁻² s⁻¹ Pa⁻¹ at 600 °C. These membranes show high H₂ separation performance. Nevertheless, Its hydrothermal instability is the biggest issue with the microporous silica-based membranes. When subjected to moist gas streams at elevated temperatures, the H₂ permeability and separation performance of the silica-based membranes decrease due to changes in the membrane structure as a result of continuous exposure [41].

Zeolites give uniform pores for catalytic, ion exchange, adsorption, and membrane applications with molecular dimensions and unique properties. Zeolite membranes have also naturally emerged as a possible alternative to the separation of hydrogen as well as the well-known Robeson upper

limit is often exceeded [12]. Zeolite membranes, including MFI [41], DDR [43], and SAPO-34 [44] have outstanding hydrothermal durability and chemical resistance; however, due to the presence of intercrystalline micro defects and relatively wide zeolite pores compared to the small and very near kinetic diameters of H₂ and CO₂ (0.289 and 0.330 nm, respectively), they displayed low H₂/CO₂ separation factors. To improve H₂/CO₂ separation, post-treatment modification, and pore size engineering are typically required [27].

Carbon-based membranes are processed in an inert environment by converting polymer layers through pyrolysis/carbonization at elevated temperatures. In particular, the pore-diameter and adsorption capacities of carbon-based membranes can be controlled to a certain degree by changing pyrolysis parameters and the polymer precursor. Ngamou et al. (2019) developed a CMS membrane on alumina support using pyrolysis of polyimide precursor at 700 °C. These membranes show high H₂ permeability up to 1.1×10^{-6} mol m⁻² s⁻¹ Pa⁻¹ and selectivity of 24, 130, and 228 were H₂/CO₂, H₂/N₂, and H₂/CH₄, respectively at 200 °C. These membranes exceed the Robeson trade-off limit [45]. Nevertheless, carbon-based H₂ separation membranes are typically fragile, moderate to highly adsorbent components, and have variable size distribution pores, making it hard to apply for any related gas-separation [12,27].

Metallic membranes are typically dense, which offer excellent selectivity, high diffusivity, and high thermal stability [7]. The dense structure prevents the passage of big gas molecules (CH₄, CO₂, N₂, etc.) due to smaller gas molecules (H₂) enhanced. For the development of hydrogen separation membrane, group V metals such as vanadium, tantalum, and niobium having BCC structure are attractive. These membranes material have high permeability as compare to the Pd-based membrane [46]. The biggest concern with group 5 metals is their excessive solubility to hydrogen, which makes the membranes sensitive to excessive hydrogen embrittlement that may result in pinholes and cracks [7]. Nowadays, Palladium metal gained exposure for the development of hydrogen separation membranes due to its properties like High resistance over hydrogen flow, self-catalyzing nature, and high permeability. The Pd membranes notable feature was its incredible tolerance to hydrogen embitterment and catalytic capacity for recombining hydrogen [47]. The investigator Weber et al. (2020) prepared hydrogen separation Pd membranes using alumina support. These membranes provide high hydrogen permeability above 1000 GTU. The excellent separation factor H₂/N₂ is 16, H₂/CO₂ is 9 obtained. Pd-membranes provide excellent separation performance [48]. Despite the advantage, high price and uncertainty of palladium prices are the most significant obstacles to the use of palladium (Pd) membrane technology, and ultra-thin defect-free palladium membranes that have long-term thermal resilience, and chemical stability remains a challenge. Inorganic membranes associated various challenges to hydrogen separation from a gas mixture such as high cost, structure defect, fragile, and difficulty to fabricate defect-free membrane. Due to these disadvantages, researchers need to develop a new type of material preparing for hydrogen separation membranes.

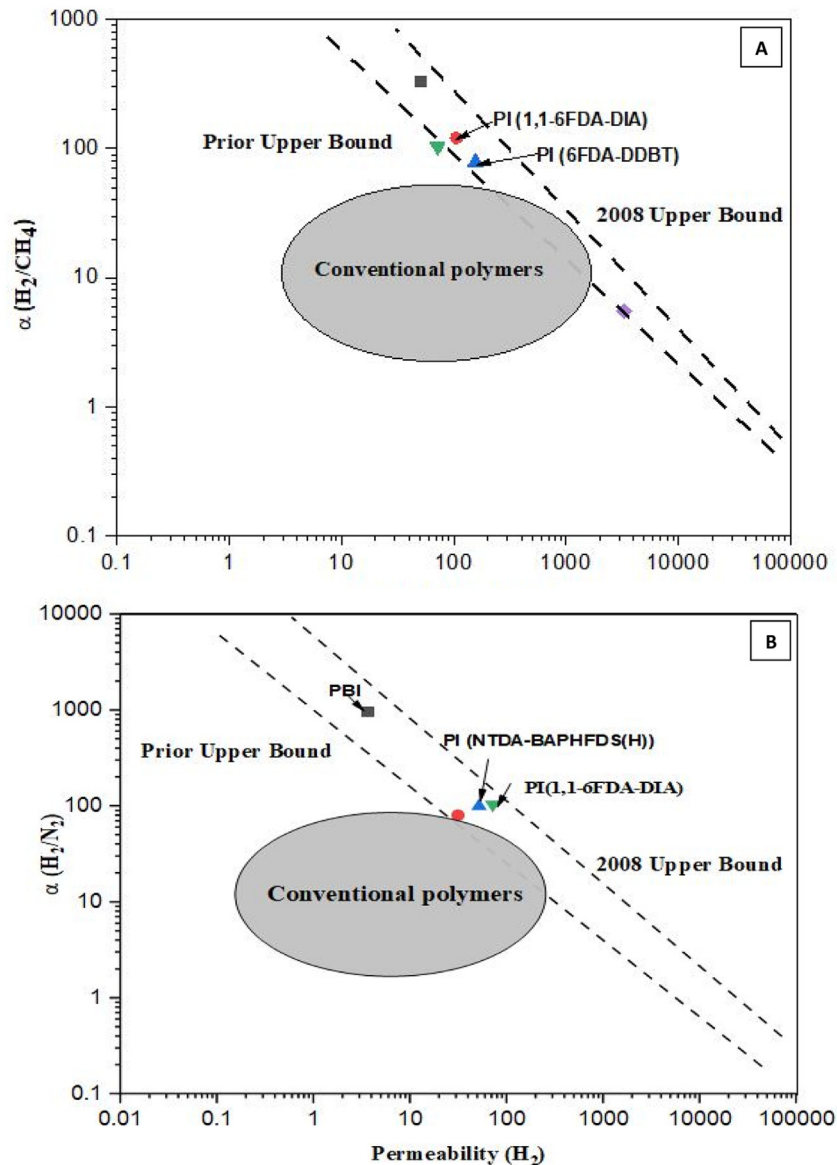


Fig. 1 – The upper limits of Robeson for H₂-selective polymeric membranes A) H₂/CH₄, B) H₂/N₂.

Mixed matrix membrane (MMMs)

Improving the efficiency of the gas separation using polymer membranes barely reaches the trade-off limit defined by the Robeson plot. The prices and the inadequacy of the durability of inorganic materials are significant challenges for large-scale production. To fix these problems, inorganic fillers distributed at a nanometre scale in a polymer matrix have been established as a possible solution to the polymeric membrane's trade-off issues, as well as addressing the inherent brittleness problems found in inorganic membranes [51]. The researchers tried to incorporate the advantages of polymeric and inorganic materials to create a unique membrane class called a mixed matrix membrane, is illustrated in Fig. 2. Inorganic fillers are distributed in a polymeric matrix to theoretically solve the trade-off challenges of the polymer membrane and the

significant issues of fragility present in the inorganic membrane. Fig. 3 shows the trade-off limited of MMMs for hydrogen separation. There are two ways to integrate inorganic sieve fillers into the polymeric matrix by mixing them with the solution or by adding the fillers to the surface using different techniques [52]. A researcher Zhuang et al. (2014) prepared a PPO/silica membrane for H₂ separation from CO₂ by using integrate inorganic sieve filler into the polymeric matrix. This membrane is prepared using the sol-gel method. In this, silica solution and polymer solution added, and mixing occurs. Due to adding both components in solution form, silica partials are uniformly distributed in the membranes [53]. Another investigation of Kamakshi et al. (2017) prepared a track-etched poly(ethylene terephthalate) (PET) with Pd-nanoparticle dispersed in the matrix by using adding the filler to the surface by using the dip-coating method. In this work, functionalized track-

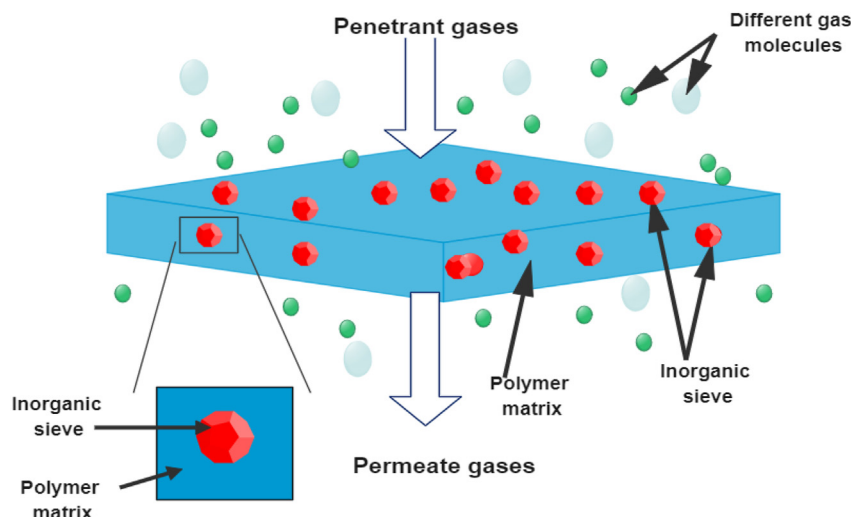


Fig. 2 – Mixed matrix membrane.

etched PET membranes dipped into the Pd-nanoparticle solution due to functionalized surface Pd-nanoparticles attach to the pore walls as well as the surface of the membranes [54].

Selecting the appropriate inorganic filler was a crucial problem in the early stages of fabrication of MMMs; it was noticed that selecting an appropriate polymer material as the matrix is also critical in evaluating the performance of the MMMs for hydrogen separation. Depending on their pores and particle size, the inorganic material is divided into several classes. Generally, porous inorganic partials with polymeric material provide high permeability due to this desire gas selectivity achieved. In non-porous inorganic filler restrict the larger molecules and gives a tortuous structure of the polymeric matrix. The mesoporous inorganic filler shows healthy pores that can penetrate the polymer chain, providing improved moisture and dispersion. Inorganic nano-sized materials can modify the polymer packaging chain by raising the volume of the void [61]. For hydrogen separation, various researchers work for developing MMMs using

different inorganic fillers such as zeolite-based, silica, carbon-based, and metal nanoparticles. Table 2 indicated the advantages and disadvantages of inorganic material used for preparing hydrogen separation MMMs.

Silica-based MMMs

Silica is a promising inorganic material for MMMs due to its high thermal stability, water content retention, ease of fabrication, and cheap cost. Silica particles are divided into many groups depending on their pore and particle size. Each silica form has different chemical, physical, and gas separation properties with the polymeric material.

The silica incorporated in a polymeric matrix disturbed the trade-off relationship between permeability and selectivity of the polymeric membrane. Many researchers work on silica-based MMMs for hydrogen separation. Zhuang et al. (2014) develop a membrane for hydrogen separation from CO₂. The silica particles were incorporated into the Poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) polymer matrix using the sol-gel method. In this work, different acidic and basic-catalyzed silica particles are used to enhance the diffusivity and solubility of PPO/silica MMMs. The porosity of pure polymeric membranes increases due to this membrane mechanism shift from solution diffusion to molecular sieve, causing hydrogen permeability to increase. The permeability of the pure polymer matrix is 82.1, it enhanced up to 548.9 Barrer. The selectivity of MMMs H₂/CO₂ was observed at 3.56. Different silica loading is incorporated in the polymer matrix. Uniform and defect-free membranes were obtained up to the 10 wt% loading of silica partial after enhancing the silica loading interfacial voids creates; causing membranes creates a high degree of aggregation. Robeson's trade-off limit between the permeability of H₂ and H₂/CO₂ cross only 10 wt% silica loading MMMs [53].

For improving the performance silica-MMMs at high loading Patel & Acharya et al. (2019) developed a TR HAB-6FDA polyamide incorporated with silica nanocomposites. In this work, 15% silica loading incorporated in HAB-6FDA enhanced the gas permeability of all the gasses. In that situation, the

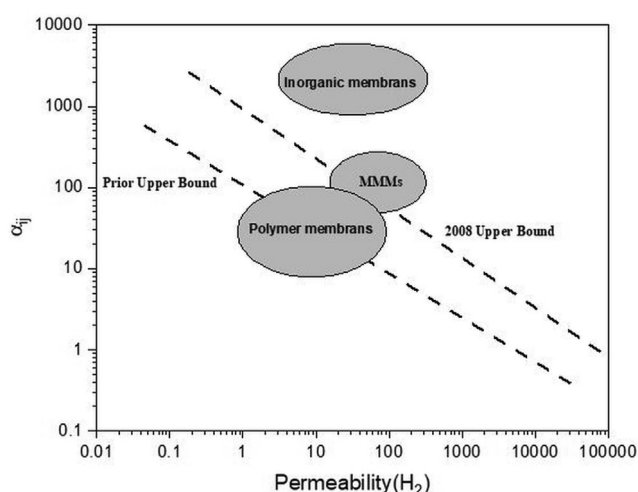


Fig. 3 – Trade-off limit of MMMs.

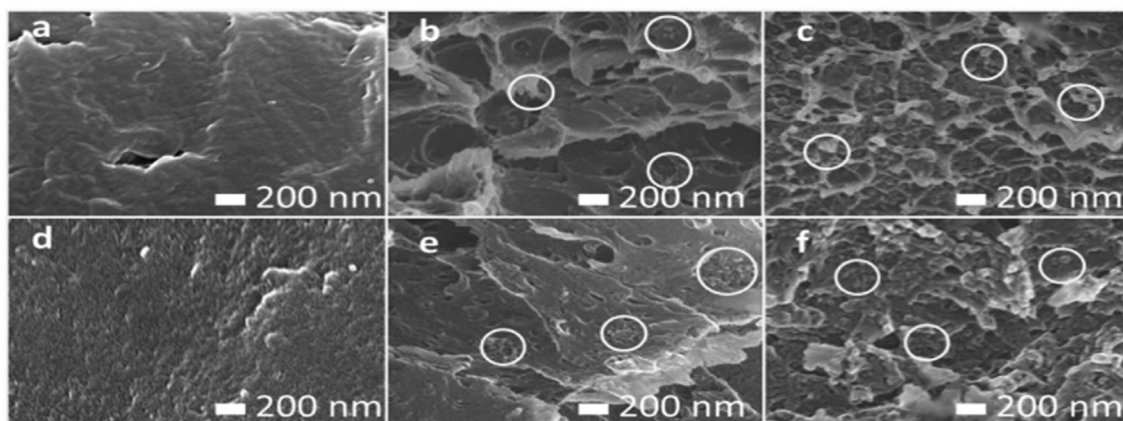


Fig. 4 – Cross-sectional SEM images of (a) HPI, (b) HPI-ZIF8-10, (c) HPI-ZIF8-20, (d) TR-90, (e) TR-90-ZIF8-10, and (f) TR-90-ZIF8-20 showing morphology change about incorporating ZIF-8 on HPI and TR. The circles represent ZIF-8 nanoparticles in MMMs [84].

solution diffusion mechanism shifted from molecular sieve/Knudsen diffusion depending on the pore size of silica particles and the interfacial void created during the preparation of membranes. The interfacial voids created, during the membrane casting, cause a rigidified polymer chain. The established rigid layer surrounding the polymer is correlated with polymer chain mobility restraint by a uniform distribution of stress effects. The presence of interfacial void and nanofiller aggregates provides the extra free volume excluding the fractional free volume that increases the larger molecule [23]. Thermally regenerated (TR) glassy polymer control the pore size of the polymer matrix and block interfacial void, which is suitable for permeating small size gas molecules and restrict large gas molecules. Due to this these membranes show high hydrogen separation performance from other gas molecules such as CH_4 , N_2 , and CO_2 . In TR MMMs molecular sieve mechanism control the gas separation. The results showed that at 350 °C, the selectivity of H_2/CO_2 , H_2/N_2 , H_2/CH_4 were obtained 1.9, 43.2 and 86.4, respectively [62]. The interfacial voids are formed during the membrane fabrication that rigidifies polymer chains due to distinct phase properties and filler and polymeric material densities. The developed rigid layer across silica nanofiller is relevant by a uniform distribution of stress results in the restriction of polymeric chain mobility [63]. TR membranes not successfully eliminated all the interfacial voids as well as the agglomeration problem, at high loading of inorganic partials also a big issue for silica-based MMMs [53]. Therefore these membranes not suitable for industrial purposes for hydrogen separation.

Metallic-based MMMs

Metal-based membranes for hydrogen separation are typically dense, offering hydrogen and permeability via protons and electrons. The metallic membrane provides high selectivity, high diffusiveness, and high-temperature stability. The dense structure restricts the membrane pores to allow large gas molecules for this selectivity of hydrogen to enhance other gas molecules such as CO_2 , CH_4 , and N_2 . Generally, group 5 metallic materials used for hydrogen separation, such as palladium (Pd), vanadium (V), Niobium (Nb), and tantalum

having BCC structure [7]. Among these metals, Pd metal is more promising due to its advantages such as auto-catalyzed nature for hydrogen dissociation, high resistance towards hydrogen gas, and outstanding permeability [64]. Nevertheless, these membranes are very expensive, and low membrane durability due to this metallic is not economical for industrial purposes [64].

Metal nanoparticle incorporated in a polymeric matrix is a promising technique for developing an economical membrane for hydrogen separation. A nanoparticle membrane consists of particles smaller than 100 nm, with at least one dimension. The introduction of nanoparticles into the polymer matrix enables one to eliminate some of the polymer membranes' drawbacks and to grow membranes with greater flexibility, enhanced processability, and enhanced mechanical and thermal characteristics [65]. The existence of nanoparticles in polymer-based membranes affects the structure, physical and chemical properties, including porosity, hydrophilicity, electrical, thermal, and mechanical stability [65]. Many researchers work on this phenomenon, such as Suhaimi et al. (2014) work on Pd-nanoparticles dispersed in Polysulfone polymeric matrix to prepare a hydrogen separation membrane that offers high hydrogen separation towards large molecules such as CO_2 , N_2 , and CH_4 . The increase in Pd loading can be attributed to the enhance in the casting solution's viscosity due to this size of the sponge structure decrease. Thus, the changes in the composition of the membrane led to the development of a fine, thick membrane layer. Therefore, the membrane structure modifications led to the development of a fine, thick, and dense membrane. The increasing loading of Pd-nanoparticles causes the membrane mechanism to shift from molecular sieve/Knudsen diffusion to solution diffusion due to sponge-like structure change into a dense structure. This observation due to the rapid growth of the nuclei in the polymer matrix. The larger number of nuclei present in the polymer matrix contributed to reducing the polymer matrix, which ultimately led to the restraint of the movement of polysulfone segments across the main bonds of the chain and the forming of denser frameworks due to this at separation performance of membranes enhanced. The permeability of

Table 1 – Comparison of the properties of polymeric, inorganic, and MMMs.

Property	Fabrication Cost	Separation Performance	Strength	Swelling Problem	Thermal and chemical stability	Reference
Polymer membrane	Less	Moderate	Good	Yes	Moderate	[49]
Inorganic membrane	High	Excellent	Poor	No	Good	[11,49]
Mixed matrix membrane	Moderate	Moderate	Excellent	No	Excellent	[49,50]

Table 2 – Advantages and disadvantages of inorganic material used for preparing hydrogen separation MMMs.

Inorganic material	Advantages	Disadvantages	References
Zeolite	<ul style="list-style-type: none"> Enhanced the permeability and selectivity as compared to polymer membranes Thermally and chemically stable Easy processibility of polymers Success for exceeding the Robeson's upper bound 	<ul style="list-style-type: none"> Decreased permeability compared to their pure zeolite membrane Poor phase separation of particles with polymer matrix Agglomeration structural defects 	[55,56]
Silica	<ul style="list-style-type: none"> Low production cost Thermally, mechanically and chemically stable. Excellent permeability with small size molecules moderate-to-high selectivity 	<ul style="list-style-type: none"> Agglomeration with polymer matrix silica particles fail to alter semi-crystalline polymers' mechanical properties at a maximum load of 15–20 wt%. unstable in the presence of steam 	[40,57,58]
Carbon	<ul style="list-style-type: none"> Good exceptional mechanical, thermal, and electrical property Extremely high aspect ratios Excellent permeability and selectivity for small gas pairs Success for exceeding the Robeson's upper bound 	<ul style="list-style-type: none"> The difficulty for aligned CNTs fabrication Agglomeration 	[59]
Metallic	<ul style="list-style-type: none"> The high solubility of hydrogen higher durability and stability Success for exceeding the Robeson's upper bound 	<ul style="list-style-type: none"> Hydrogen-embrittlement High cost Agglomeration 	[54,60]

hydrogen at 2 wt% loading of Pd-nanoparticles obtained 3124 barrers, and the selectivity of H_2/CO_2 and H_2/N_2 are 6.2 and 20. Nevertheless, the dense structure of membranes decreases after 3 wt % Pd-loading, due to cell development in the polymer-rich phase, caused by the diffusional flow of solvent from the surrounding polymer solution. At this stage, agglomeration of Pd nanoparticles start due to this a membrane performance decrease [66]. Another investigation of Ahmad & Hågg prepared polyvinyl acetate/titanium membranes for hydrogen separation. Titanium nanoparticles were added in PVA to improve the membrane's morphological, thermal, and gas separation properties. Different amounts of nanocomposite are incorporated into the polymer matrix. The findings show that the addition of titanium up to 10% increased the permeability and selectivity of the MMMs. The hydrogen permeability levels increased by 62%, and selectivity H_2/N_2 has increased by 26.5%. Enhance the amount of nanocomposite cause of aggregation in the membrane, cause membrane performance decline. In this case, the void channels are developed between the polymeric matrix and non-porous inorganic nanocomposites. The gas transfers thru the polymer matrix, interface voids, and void channels. For this reason, the gas permeation rate through the membrane increased caused selectivity decreases [67]. The incorporation of Pd-nanoparticles in a polymer matrix is an important technique for improving hydrogen separation performance, and functionalities of membrane pore walls help to integrate the desired nanomaterial into the pore walls [59]. The reduction of nanocomposite agglomeration in a polymer matrix, a

functionalized track-etched polymeric membrane was reported by Kamakshi et al. (2016) these types of membranes are a good alternative for implementation in gas separation due to its tunable pores size, shape, and ion preference. During the process of ion irradiation, ion fluid is the key element of increasing porosity in a controllable manner. These types of membranes have high mechanical strength, good thermal resistance, and inertness. Such membranes result in less permeability as go for enhanced selectivity. Another investigation of Kumar et al. (2018) reported interactions between functional PET monitor etched membranes and palladium nanoparticles attached on the surface of the membrane that enhanced the membrane's performance. The presence of Pd-nanoparticles on the wall surface creates dense structure due to this solution diffusion mechanism, and the molecular sieve mechanism simultaneously worked. The selectivity of H_2/CO_2 obtained 3.34 [68]. Functionalized membrane pore is an important technique. For attachment of nanoparticles on the surface of the membrane pore wall, another investigation by Kumar et al. (2017) reported PET functionalization membrane with Pd nanoparticles that drastically enhanced the hydrogen selectivity from CO_2 and N_2 . Functionalization of the pore wall helps attach Pd-nanoparticles due to this H_2 gas permeability enhanced, and other gasses permeability decreases. Due to this, the selectivity of hydrogen increased as compared to the polymeric membranes. The molecular sieve and solution diffusion mechanism simultaneously work. The selectivity of H_2/CO_2 and H_2/N_2 was 6.05, and 3.72 were obtained [69]. Metal-MMMs membrane was suitable for the

separation of hydrogen due to its low cost compared to pure metallic membranes and excellent separation performance. The modification in the polymer membranes like membrane pores' functionalization reduces the agglomeration problem in the MMMs. Nevertheless, more modification is required for enhanced the membrane performance of metal-based MMMs to reach commercialization purposes.

Zeolite-based MMMs

Zeolites are microporous crystalline aluminosilicate structure with uniform pores and channels. Therefore utilized in different fields, such as the petrochemical industry as a catalyst and preparing gas separation membranes [70]. The incorporation of the polymer matrix and zeolite sieve has gained considerable interest in membrane gas separation technology due to many benefits like improving the selectivity of gas molecules, enhancing the thermal and mechanical stability of a polymeric matrix as well as molecular sieving properties, thermal resistance, and chemical stability of zeolite practical also increased [71]. A crucial factor in the production of MMMs is a material selection for both the matrix and sieve phases. Many researchers work to integrate a variety of zeolites with polymers matrix to enhance the hydrogen separation performance. The zeolite sieving molecular differentiate by practical size and shape discrimination. The particle size of the zeolite is shown in Table 4. The zeolites with three-dimensional networks are typically favored for gas separation with glassy polymers, as they provide less restricted diffusion paths. They usually exhibit high permeability and low selectivity and drive the overall performance of MMMs significantly below the upper bond trading curve.

For gas separation through zeolite-base MMMs, Glassy polymeric material appropriate choice due to its strong mechanical characteristics, influence commercial membrane separations, and high gas separation performance. Glassy polymeric such as polyimide (PI), polycarbonate (PC), polybenzimidazole (PBI), cellulose acetate (CA), polyester (PE), polysulfone (PSF), polyetherimide (PEI), commonly studied for gas separation [72,73]. Performance of zeolite-based MMMs shown in Table 3. The most thoroughly studied polymer materials for hydrogen separation are polyimide and polyethersulfone for zeolite-based MMMs. In the zeolite filler, the gas transport mechanism started from adsorption in the pore, spreading around the pore's surface and in the end, desorbing the permeate. Both adsorption and diffusion effect work simultaneously for the transportation of gasses [43,74]. Due to the intermolecular forces of attraction between the gas molecules and pore surface, gas molecules adsorb within zeolite pores. All the other characteristics are equally important, like adsorption's heat is higher with more massive dipole moments [43,74]. In zeolite-based MMMs, gas transport consists of various mechanisms at the same time.

In polymer membranes, zeolite used as an inorganic filler, change the permeability of membranes for various gasses. The separation performance of the membrane described by the Maxwell equation (Eq. (10)) is introduced here as the zeolite's facilitation ratio. By enhancing the zeolite loading, gas separation performance move towards the zeolite molecular sieving mechanism [75]. The investigator Peydayesh et al. (2017) developed polyimide matrimid 5218/Deca-dodecanol 3R zeolite MMMs for separation of H_2 from CH_4 . By increasing the zeolite loading increases the H_2 permeability and decreases the CH_4 permeability because the mechanism shift from

Table 3 – Zeolite and silica MMMs Membrane.

Polymer	Zeolite form	Hydrogen Permeability (Barrer)	Selectivity			References
			H_2/N_2	H_2/CO_2	H_2/CH_4	
Matrimid/Pd	ZIF-8	—	95.21	5.82	228.2	[78]
Polyimide	ZIF-7	3.0×10^{-7} a	—	91.5	128.4	[82]
carboxymethyl cellulose	ZIF-L	—	21.54	10.62	—	[85]
PDMS	zeolite 4A	12,000–13000	—	3–4	8–9	[19]
Polyimide	ZIF-302	4.25	62.6	—	42.3	[86]
PBI	ZIF-8	470.5	26.2	—	—	[87]
PES	SAPO-34	—	—	—	61.02	[88]
HMA/PES	SAPO-34	—	—	—	175.8	[88]
BTDA-MDA polyimide	Sodalite (Sod-N)	8	281	—	—	[89]
polysulfone Udel and polyimide	hollow silicalite-1 spheres	38.4	—	—	180	[90]
Matrimid						
poly (phenylene oxide)/carbon/ Al_2O_3	SBA-15	50–100	38.9	—	50.9	[91]
polysulfone	ITQ-29	21.9	—	—	118	[92]
polysulfone	Nu-6 (2)	35.8–47.5	—	—	73–398	[93]
Polysulfone	Zeolite 3A	15.10	—	3.57	—	[94]
Polysulfone	Zeolite 5A	58.91	—	1.67	—	[94]
GUS	BEA	10.7–57.3	74–267	—	—	[95]
Teflon AF 1600	MFI	3580–5590	4.6–4.9	—	—	[96]
polyetherimide	HSSZ-13	48–63.8	7.7–8.2	—	39.6–43.9	[97]
Matrimid	ZIF-8	47.2	78.6	3.33	124	[74]
Matrimid	ZIF-90	19	—	9.5	—	[32]
polymethyl phenyl siloxane	ZIF-8	103	—	—	1	[31]

a = $\text{molm}^{-2} \text{s}^{-1} \text{Pa}^{-1}$.

solution diffusion to molecular sieving [76]. In other studies of Ahmad & Hägg et al. (2013) also work on different zeolite loading in matrimid polymer matrix, which showed that an increase in zeolite loading in a polymeric matrix enhanced H_2 gas permeability because of the pores of zeolite larger than the hydrogen molecules. However, selectivity decreases due to the clogged when zeolite loading increases. The permeability and selectivity of hydrogen gas are directly affected by incorporating zeolite inorganic particles into the polymeric matrix, the crystallinity of the polymer matrix reduces by incorporating inorganic filler, which favors enhanced the permeability of smaller gas molecules corresponding decreases the selectivity [77]. However, as per Maxwell's model (Eq. (10)), the incorporation of zeolite to polymer matrix should substantially enhance selectivity, with a slight reduction in permeability. This is only feasible when zeolite micropores are accessible open during diffusion and thin and defect-free membranes are developed. Therefore, it is a concern in MMMs since zeolite pores are usually clogged at low temperature, or partly-clogged [67]. The manufacture of thin and defect-free membranes is also affected by the size of zeolite commercially available.

Zeolite-based MMMs development is difficult due to defects caused by poor contact with the molecular sieve/polymer interface, synthesis process complexity, identification of compatible inorganic particles, and structural defects [78]. Therefore, the zeolite immobile framework (ZIF) material with the different polymeric matrix is used to separate the membrane effectively. ZIF is one type of metallic organic framework (MOFs). Due to the organic-inorganic porous structure, MOFs can associate more readily with a polymeric matrix to reduce interfacial void problems in MMMs [51]. ZIF is used to separate hydrogen in various forms like ZIF-7, ZIF-8, ZIF-11, ZIF-6, ZIF 64, and ZIF-L. Table 4 indicates the size of the components of the zeolite. ZIF is a promising material for hydrogen separation from a gas mixture due to its properties such as controllable pore size, large surface area, high porosity, and incorporated with polymeric matrix to provide excellent film-forming property [79].

Polyimide (PI) and PBI is the most promising polymer with ZIF for preparing a hydrogen separation membrane, and many researchers work on these polymeric materials. Yang et al. (2012) prepared a ZIF-8-PBI/Matrimid membrane for H_2 separation from CO_2 . Different loading of ZIF -8 incorporated in the polymer matrix at 10% loading of ZIF in the matrix provide ideal selectivity were obtained 11.5, and this selectivity decreased 39% by enhanced the ZIF loading up to 33%. But these membranes generally showed significantly decreased permeability than their pure zeolite membrane due to the polymer matrix's low permeation rate. This issue could be

resolved if MMMs changed from polymer-rich to zeolite-rich composition. When loading of ZIF, enhanced ZIF partial allocation occurs due to this separation performance of membranes reduced [55]. High ZIF-8 loading does not result in a high selectivity of H_2/CO_2 . The homologous recombination factor is also because sizeable ZIF-8 charging in the solutions is much more viscous than less ZIF-8 charging. The distribution of ZIF-8 nanocomposite in the matrix is not as strong as in less ZIF loaded membranes. As a result, defects were created, which cause for reduction of the selectivity of H_2/CO_2 [80]. Another study by Etxeberria-Benavides et al. (2020) developed an MMMs using ZIF-8 use as a filler in PBI polymer for hydrogen separation from CO_2 having 300 nm thickness. Due to the incorporation of ZIF-8 in the polymeric matrix, hydrogen permeability increases from 65 GTU to 107 GTU at 105 °C. The ideal selectivity of H_2/CO_2 obtained 18. In this study, 10 wt% ZIF-8 loading is used, and it gives better performance compared to the previous study [81]. Ma et al. (2019) prepared a ZIF-7 and polyimide membrane for hydrogen separation from a gas mixture. This membrane show hydrogen permeability $3.0 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and the ideal selectivity of H_2/CO_2 and H_2/CH_4 are 91.5 and 128.4, respectively [82]. According to the previous studies, both PBI and polyimide polymer material provides better dispersion of ZIF at low loading but interfacial voids are present in the ZIF-MMMs.

For improving the interfacial void problem Wu et al. (2018) fabricated a membrane by incorporate ZIF-64 into polymer intrinsic microporosity (PIM-1). PIM is that polymer in which all rotary independence is stripped from the backbone of polymer structure but which has a molecular structure that is arbitrarily contoured. Due to changes in the structure of the polymer, the solubility of ZIF and polymer matrix improves. Resultant, interfacial void less created. The PIM-1/ZIF-67 MMMs show that the ideal selectivity of H_2/CH_4 increases by 86.96% [83]. To the improvement of the interfacial void problem Kim et al. (2019) using a thermally rearranged polymer with ZIF-8. The TR method can contribute to blocking the interfacial voids between polymer chains and ZIF-8 nanoparticles. As shown in Fig. 4(a–f), Compared to the HPI MMMs, the cross-section of the TR ZIF-8 MMMs has become more regular. In the SEM photos, ZIF-8 nanoparticles can still be distinguished, but the nanoparticles were well attached to the polymer phase and created less interfacial voids compared to HPI [84]. The TR ZIF-8 MMMs displayed 1206 Barrer H_2 permeability, 22.3 H_2/N_2 selectivities, and 25.7 H_2/CH_4 selectivities, respectively. Researcher continuous work for improving the hydrogen separation performance.

For enhanced membrane separation performance, Mirzaei et al. (2020) developed MMMs using Pd@ZIF-8 was incorporated into a Matrimid membrane. This membrane showed more effective hydrogen separation performance than matrimid/ZIF-8 membrane, as shown in Fig. 5. Metallic nanoparticles help to exceed the Robeson upper bound [78]. In this molecular sieve and solution diffusion, both mechanisms work and adsorption of hydrogen also occur due to the presence of Pd-nanoparticles in the matrix. Hydrogen molecules are adsorbed by the Pd-nanoparticles due to this permeability of hydrogen gas molecules reduced, resultant selectivity enhanced.

Table 4 – Zeolite partial size.

Inorganic material	Partials	Pore size	References
Zeolite	Zeolite-A	3.2–4.3	[98]
	ZSM-5	5.1–5.5	
	ZIF-7	3	
	ZIF-8	3.4	
	ZIF-11	3.10	

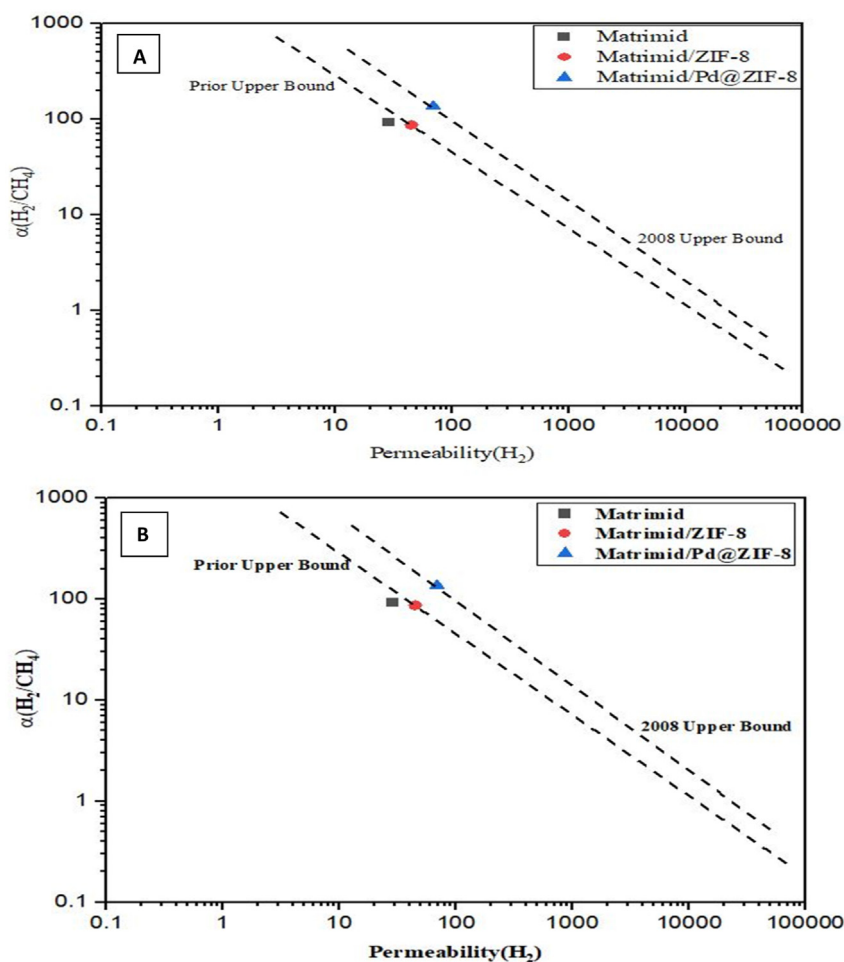


Fig. 5 – Trade off limit of Matrimid, Matrimide/ZIF-8 and Pd-Matrimide/ZIF-8 [78].

Pd-nanoparticles with ZIF, provide outstanding hydrogen separation performance. Despite this, these membranes are not commercialized because these membranes face limitations like weak-moderate interfacial compatibility of the zeolite with the polymer, leading to unselective voids in the membrane agglomeration of the nanoparticle. So, for the elimination of these drawbacks, improvement is needed.

Carbon-based MMMs

The concern about the carbon-based membrane increases for hydrogen separation due to its property like high thermal stability, chemical stability, and its sieving property, making it a highly hydrogen-selective membrane compared to the pure polymeric membrane.

These membranes facing many problems such as 1) very delicate and flexible results need careful treatment, 2) its manufacturing is difficult that leads to high production costs, 3) these membranes require a purification to eliminate residues of vapors with high absorbance, which can clog the pores. The high-temperature range used to avoid this problem, 4) They show increased selectivity only for particularly gasses those of a molecular size less than 4–5 Å. Therefore, they need to improve for hydrogen separation.

The development of hydrogen separation membranes, carbon-based MMMs shows more interest. The polymer

membranes have many disadvantages and carbon-membranes are not cost-effective to overcome these drawbacks of both the membranes carbon-based mixed matrix membranes innovated by the researcher. Numerous polymeric materials are used to develop carbon-based MMMs such as Polycarbonate, Polyimide, Polysulfone, Polyethylene, Polystyrene, Cellulose acetate, Polyetherimide. Among these polyimides (PI) promising polymeric material. CMS with optimum molecular dimension pore openings and a large volume of pores can react to high selectivity and permeability of hydrogen. CMS Produced by the pyrolysis of several thermosetting polymers [99]. Pure CMS membranes have a high fabrication cost. Extensive work of CMS-based MMMs, are used for hydrogen separation from a gas mixture application. The pore dimensions of carbon depend on the organic precursor morphology and pyrolysis chemistry [100]. Analysis of molecular sieve carbon adsorbents has shown that the molecular sieving effect of non-graphitizing carbons is precise and customizable to the discrimination range 2.8–5.2 Å thru mild activation and sintering steps [100]. In CMS, the molecular sieve mechanism works, the separation phenomenon depends on the molecular size of gas molecules. In carbon-based MMMs, two mechanisms simultaneously work: molecular sieve mechanism for carbon molecule and solution diffusion mechanism for dense polymeric membrane or Knudsen diffusion, surface diffusion, capillary condensation

for porous members. The mechanism of carbon-based MMMs total depends on the selection of polymer and type of carbon-based material. Junior et al. developed carbon black/PDMS MMMs that efficiently separated H_2 from CH_4 [101]. Different amount of carbon-black (2%, 6%, 10%, and 15%) loading incorporated in PDMS. By increasing the carbon-black loading, diffusion of H_2 also increases because carbon seems to have an affinity with H_2 gas molecules. The optimal condition for almost total blocking of CH_4 diffusion, while permitting the passage of H_2 , was obtained at 6 wt% of carbon-black loading.

Above 6 wt% carbon-black loading, the resultant blockage of both the gasses' passage due to this membrane separation performance reduces. To improve CMS-based membrane separation performance, Sazali et al. (2020) developed a PI/carbon membrane for hydrogen separation using a different type of thermally labile additive like PVP, NCC, and MCC. Thermally labile polymer controls the pore size of the carbon membrane. This blockage of the pore at a high loading of carbon partials in the membranes reduces, resulting in membrane gas separation performance. Among the three additives, NCC gives the membrane optimized physicochemical properties because of its nano-crystalline structure as well as it gives high gas separation performance [100]. As per the author's knowledge, a molecular sieve mechanism occurs due to the presence of microspores in the membranes. H_2 molecule has a high affinity toward the carbon particles, cause H_2 gas molecules to diffused through the membranes. N_2 gas partials have a large size compared to H_2 gas molecules, restrict the transportation of N_2 gas molecule through the membranes due to this enhanced the selectivity of H_2/N_2 was 434.68 ± 1.39 . However, the existence of additives induces the creation of fractures in the membrane during the carbonization process. Attempts to improve the performance of MMMs, polymer, and molecular sieves have resulted in blocking of the sieve pores, hampering the efficiency of hydrogen separation. These are the main drawback of CMS-based MMMs.

Another type of hydrogen separation membrane is carbon nanotubes (CNTs) based membrane. CNTs are of two types 1) single-wall CNTs 2) multi-wall CNTs. CNTs tend to be suitable inorganic fillers for developing high-performance polymer nanocomposite membrane structures through correct processing and manufacturing parameters monitoring. Table 6 describes the property of CNTs. In MMMs for high gas separation performance, the appropriate inorganic filler is those that have a large pore diameter than the kinetic size of target gas molecules (CO_2 , CH_4 , and N_2) [102]. Table 5 shows the kinetic Diameter of gas molecules. Among various inorganic fillers, CNTs are promising materials due to their property like high thermal and mechanical properties [103]. Due to its advantages, various researchers work on CNTs-based MMMs

Table 5 – Kinetic diameter of gas partials.

Gas	Kinetic Diameter of gas particles(Å)	References
Hydrogen (H_2)	2.890	[17,85]
Nitrogen (N_2)	3.64	[17,85]
Carbon dioxide (CO_2)	3.3	[17,85]
Methane (CH_4)	3.758	[17]

Table 6 – Physical property of carbon-based material [107].

Property	MWCNT	SWCNT
Electrical conductivity [Scm^{-1}]	10^3 – 10^5	10^2 – 10^6
Thermal stability in the air [$^{\circ}C$]	>600	>600
Specific gravity [gcm^{-3}]	1.8	0.8
Thermal conductivity [WmK^{-1}]	2000	6000
Coefficient of thermal expansion [K^{-1}]	nil	Nil
Electron mobility [$cm^2V^{-1}s^{-1}$]	10^4 – 10^5	10^6

such as Nour et al. (2013) prepared a CNTs/PDMS composite membrane to separate H_2 and CH_4 . In these composite membranes, CNTs works on the molecular sieve mechanism. The CNTs/PDMS membranes with 1% MWCNTs levels improved selectivity to H_2 gas by 94.8%. When the amount of MWCNTs in the membranes increases, the membrane mechanism shifts toward the molecular sieve, which helps separate molecules according to their size. According to the author's knowledge, above 1% loading of SWCNTs gradually decreases the CH_4 permeability due to mechanism shift toward the molecular sieve, and up to 5% loading of SWCNTs blocked the CH_4 permeation was obtained. According to the author, above 5% loading of SWCNTs H_2 permeability also reduced due to the agglomerates of SWCNTs and other problem is the alignment of SWCNTs. As a result, the membranes produced can be an efficient and low-cost solution for extracting H_2 from more giant gas molecules such as CH_4 up to the specific amount of SWCNTs [103]. Another study by Surya Murali et al. (2010) investigated the integration of MWCNTs into Pebax-1657 membranes for hydrogen separation from other large gas molecules. In this work, the pure hydrogen permeation was investigated by adding a different percentage of MWCNTs during the membrane's preparation. They found MWCNTs integration induced changes in the volume of the free membrane. The result shows that 2% MWCNTs/Pebax MMMs demonstrated promise for gas separation applications due to the high selectivity obtained for H_2/N_2 . MWCNTs in the polymer membranes may boost their commercial viability for applications that separate the gas. Selectivity can be reductions in binary or multi-component mixtures because of their coupling effect [104]. The CNTs-MMMs membranes suffer many problems, such as create agglomerates or bundles instead of individual tubes due to Vander wall attraction forces between CNTs. They also have very poor solubility in solvents and prefer to stay like enmeshed agglomerates. Due to these drawbacks, these types of membranes are not suitable for industrial purposes. These problems motivated the researcher to improving CNTs based membranes. CNT-MMMs efficiency depends on the dispersion of CNTs in the polymer matrix and on the interfacial relationships between CNT and polymer. CNT functionalization is an essential means of avoiding CNT agglomerates, resulting in better dispersion and stability of CNTs in the polymer matrix.

As already stated, the dispersion and coordination of CNTs in the polymer matrix is very difficult. CNTs functionalization is an effective way to eliminate the accumulation of CNTs and increase their dispersion in the polymer matrix. There are many methods to CNTs functionalization, including covalent methods and non-covalent storage. Covalent

functionalization is dependent on the covalent interaction of carbon with other functional groups. The functionalization of CNTs occurs at the defects and on the side walls [105]. Covalent methods of functionalization increase the solubility of solvents with diverse chemical structures. The most popular and traditional use of functionalizing is by treating the surface with strong inorganic acids. The associated functional groups may be small groups such as $-\text{COOH}$, $-\text{OH}$, $-\text{F}$, or $-\text{NH}_2$ (Kim et al., 2011). Several other studies have shown that the functionalization of CNTs can improve the solubility and homogeneous dispersion in MMMs. The hydrophobic character of the CNTs is modified to hydrophilic due to the addition of polar functional groups. The functionalized CNTs are soluble in a wide variety of organic solvents. Awasthi et al. (2014) functionalization of the MWCNTs associated with $-\text{carboxylic}$ and amino group by acid treatment. Functionalized MWCNTs uniformly dispersed in track-etched poly (ethylene terephthalate) (PET) membranes for hydrogen separation [25]. The Functionalization of MWCNTs leads to uniform distribution and prevents aggregation. Random distribution of CNTs into polymeric matrix not very useful for hydrogen separation. So, improving the hydrogen selectivity alignment of CNTs is needed. Performance of aligned and random distribution of CNTs in a polymer matrix shown in Fig. 7.

The alignment can be considered as a particular case of CNT dispersion. CNT electric field alignment and magnetic field allow for the possibility of positioning CNTs at unique positions. Oriented CNTs in a polymer matrix have some benefits owing to their anisotropic form and improved alignment properties. For improvising hydrogen separation Weng et al. fabricated a CNTs/polymer-based membrane for hydrogen separation. CNTs (MWCNTs/SWCNTs) alignment in a Polycarbonate polymeric matrix used 500 V/cm DC electric field. It is necessary to have CNTs aligned in polymer matrices to take advantage of their anisotropic structure and have enhanced properties in the alignment direction. The technique of electric field alignment is important since nanotubes can be placed more simply at specific locations to realize functional devices and circuits [106]. Many researchers used a magnetic field for the alignment of CNTs in the polymer matrix. Sharma et al. (2009) prepared a CNTs/polycarbonate matrix for hydrogen separation. In this work, MWCNTs and SWCNTs are used to improve the selectivity and permeability of hydrogen. It also showed that the gas permeation rate higher in SWCNTs/polycarbonate than MWCNTs/polycarbonate [107].

For enhancing the separation performance of CNTs-MMMs metallic nanoparticles incorporated with the matrix for hydrogen separation from a gas mixture, Pd and Pd alloys are promising metallic materials because these materials have high hydrogen affinity [7]. Kumar et al. (2016) developed a composite membrane with functionalized MWCNTs with Pd nanoparticles that were dispersed in a polycarbonate (PC) membrane of thickness 25 μm to improve selectivity and permeability of the polymeric membrane. The permeability of hydrogen in the PC + MWCNT membrane obtained the 1763 barrier. It improves by using functionalized MWCNTs, and Pd nanoparticles dispersed in the membrane were found 4758 barriers. Functionalized change in the surface morphology of

MWCNTs, due to this aggregation of MWCNTs reduces. Fig. 7 shows attachments of Pd-nanoparticles from the functionalized CNTs. As per the author's knowledge, uniform distribution of functionalized MWCNTs shift the gas separation mechanism toward the molecular sieve due to this H_2 permeability enhanced and the permeability of other gases reduces. The selectivity of H_2/N_2 and H_2/CO_2 was 4.19 and 7.96, respectively [59].

Fig. 6 shows MWCNTs incorporated with the PC membrane to enhance the hydrogen separation performance of the membrane. It shows that the random distribution of MWCNTs does not exceed the Robeson upper bound. The random distribution of MWCNTs (functionalized and unfunctionalized) blocks membrane pores. For this permeability of all the gasses pass thru, the membrane reduces. The Pd-nanoparticles are easily attached to the functionalized walls of MWCNTs due to this CNTs functionalization is an efficient way to prevent aggregation of CNTs, thereby improving their dispersion in polymer matrices. Because of this, the hydrogen separation performance of the membrane from the other gases is enhanced. Table 7 indicated the performance of carbon-based MMMs.

Fig. 7 describes the schematic illustration of the MMMs prepared by using MWCNTs and Pd nanoparticles dispersed in PC matrix for H_2 separation. Fig. 7(a) shows the random distribution of MWCNTs in PC membranes. Fig. 7(b) aligned MWCNTs in PC membrane, aligned MWCNTs creates a passage in the membrane for transportation of H_2 . The permeability mechanism entails (i) high-pressure dissolution (sorption), (ii) membrane diffusion, and (iii) lower-pressure desorption. It is expected that aligned MWCNTs in polymer matrix provided more dissolution in comparison to randomly distributed MWCNTs. Fig. 7(c) aligned MWCNTs with Pd-nanoparticles dispersed in PC membrane. Nanoparticles still have better absorption properties due to their high surface-to-volume ratio and palladium is one of the most absorbing metals for H_2 gas [7]. Fig. 7(d) aligned functionalized MWCNTs dispersed in PC membrane and Fig. 7(e) aligned functionalized MWCNTs in membrane with Pd-nanoparticles, Pd-nanoparticles easily attached functionalized MWCNTs due to presence of COOH group, which leads to improving membrane performance for H_2 separation from other gases. Functionalized MWCNTs and, deposition of nanoparticles is a much more advantageous approach for improving selectivity with permeability in the H_2 gas separation process [108].

Various types of materials are used for developing mixed matrix membranes for hydrogen separation. Silica-based, metallic-based, and zeolite-based materials provide better gas separation performance but an agglomeration of nanoparticles and the interfacial void created between the polymer and inorganic material are a major problem associated with these membranes. However, Functionalized aligned CNTs with Pd-nanoparticles are an effective way to prevent agglomeration of CNTs due to this uniform dispersion occur and the presence of Pd-nanoparticles enhancing the hydrogen separation performance of the membranes. These types of membranes mainly consist of molecular sieve (CNTs) and solution diffusion (Pd-nanoparticles) mechanism.

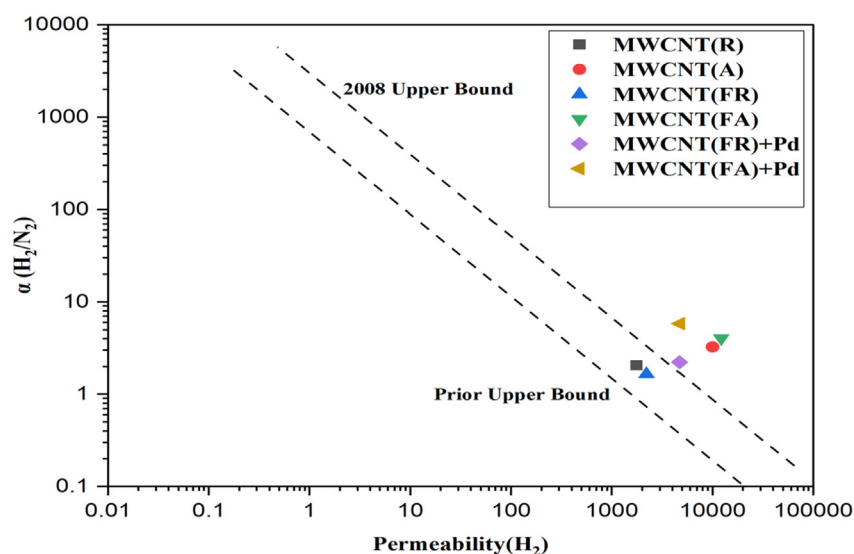


Fig. 6 – Performance of hydrogen separation of PC membrane with MWCNT. (R) Random, (A) Aligned, (FR) Functionalized and random, (FA) Functionalized and Aligned [59].

Principle and mechanism of hydrogen separation

Hydrogen selective membrane materials cover the III-V group of the periodic table consists of metal and metal alloys [114], organic polymers and their composites [72], and inorganic components [11]. These materials consist of intrinsic properties like thermal, chemical, and mechanical properties. Every membrane category provides its specific advantages and disadvantages to hydrogen separation shown in Table 1.

Hydrogen separation membranes are of two types: dense and porous. The transport phenomenon of hydrogen separation for both types of membrane are different as shown in Fig. 1: (a) Knudsen diffusion, (b) surface diffusion, (c) capillary condensation, (d) molecular sieving, and (e) solution diffusion [115]. In hydrogen separation membranes, gas transport occurs mainly due to the solubility and diffusivity of gases [23].

Hydrogen molecules behavior modeled using Knudsen diffusion (Fig. 8(a)) as they move through nanometre pores. This type of flow occurs when the mean free path between molecular collisions coincided by a molecule is greater than the pores' size, resulting in repetitive collisions with the pore walls. Knudsen diffusion is the dominant mode of transport for pores size from 2 to 50 nm [116]. The Knudsen number (Kn) defined as the gas molecules' ratio, means free path and a representative physical length scale.

$$Kn = \lambda/R \quad (1)$$

Using the pore radius as a standard physical length, the mean free path lengths at knudsen numbers higher than ten are considerably higher than the pore radii. The conclusion is that the smaller molecules permeate mainly pass through the pores. Nevertheless, selectivity is restricted and can be measured using the square root ratio of the molar masses of

the gasses involved [115]. In smaller knudsen value, increasing the pores and decrease the selectivity. The selectivity of separation originates from the varying retention times of the diffused gases. Gas molecules of a smaller scale collide with the pore walls more often than other gas molecules [117]. Surface diffusion (Fig. 8(b)) may proceed along the side of knudsen diffusion, as gas molecules can spread adsorbent along the pore walls. Permeability should be high for gas molecules quickly adsorbed onto pores walls. However, this will show less permeation of gas molecules that cannot adsorb on the walls while increasing selectivity. It will inevitably contribute to a reduction in the effective diameter of the pores.

Gas molecules adsorb onto the pore walls and then pass from one site to another under a rising concentration gradient [118]. Kajama et al. (2016) prepared composite inorganic membranes by impregnation of silica and platinum (Pt). In this membrane, H₂ gas is separated from other gasses by using the Knudsen diffusion and surface diffusion mechanism. N₂ gas separated from H₂ by the knudsen diffusion through silica particle and He, gas is separation from H₂ occurs through Pt-particles by surface diffusion mechanism [117]. The Capillary condensation (Fig. 8(c)) happens as a partly condensed phase fills the pores. In this case, only those components permeated that are soluble in the condensed phase. Usually, permeability and selectivity are very high in this mode of gas transportation, but this is strongly dependent on the uniformity of pores, pore size, and composition of the gas. It occurs under very particular conditions when the gas molecules condense to produce capillary forces inside a pore [119]. Bagher et al. (2019) prepared polymer/fiber membranes. The incorporation of fiber nanocomposite in the polymer matrix provides a continuous diffusion pathway. The researcher observed that at high fiber loading, show capillary condensation for more permeable gas [119].

Molecular sieving (Fig. 8(d)) will occur when the pore sizes are small enough. The pore size must be between 0.3 and

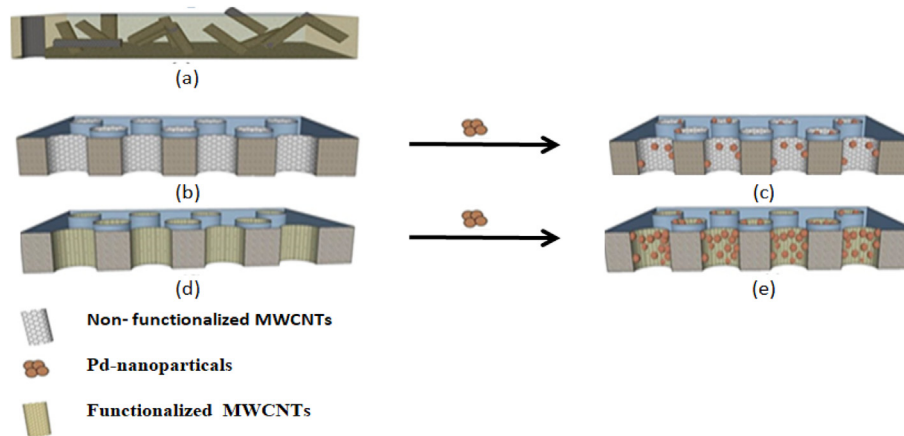


Fig. 7 – Schematic diagram of the MMMs preparation by using MWCNTs and Pd nanoparticles dispersed in polymer matrix a) random distribution of MWCNTs in PC membranes, b) aligned non-functionalized MWCNTs in PC membrane, c) aligned non-functionalized MWCNTs with Pd-nanoparticles dispersed in PC membrane, d) aligned functionalized MWCNTs in PC membrane, e) aligned functionalized MWCNTs in PC membrane with Pd-nanoparticles [108].

Table 7 – Performance of carbon-based MMMs.

Polymer precursor	Carbon form	Hydrogen Permeability (Barrer)	Selectivity			References
			H ₂ /N ₂	H ₂ /CO ₂	H ₂ /CH ₄	
Polyimide	CMS	1226.61 ± 4.12 _a	398.25 ± 2.31	–	–	[109]
Polyimide	CMS	908.5	40.7	–	–	[110]
Polyimide	CMS/attapulgit	2255.8	26.1	–	–	[110]
Polycarbonate	MWCNTs/Pd	4758	–	7.96	–	[108]
Polyimide	CMS/SBI-15	1468.4 ± 125.6	7.3 ± 3.1	–	5.2 ± 2.7	[111]
PBNPI	MWCNTs	14.31 ± 3.07	–	–	8–10	[106]
Polyimide	CMS	39–54	156–247	–	–	[112]
Polycarbonate	SWCNTs	40	–	–	–	[107]
Polycarbonate	SWCNTs	–	–	6.5	–	[113]
Polycarbonate	MWCNTs	13	–	–	–	[107]
Polycarbonate	SWCNTs	350	–	–	–	[107]
PEBAX	MWCNTs	2.50	–	7	–	[104]

a = GTU.

1 nm. It works by filtering and sorting gas molecules of different kinetic diameters. Ultimately, only gas molecules small enough to fit in the pores can permeate through the membrane. This mechanism happens when the sizes of the gas molecules and the pore are relatively similar [103,120]. Molecular sieving mechanisms generally occur in CMS, zeolite, silica molecular sieve, and polymers (depend on pore size). CMS-based membrane prepared by Xu et al. (2020), in which CMS used having a diameter of 3.49 Å. In this membrane molecular sieving mechanism due to CMS diameter, it transfers H₂ gas and restricted other gasses like CH₄ and N₂, resulting in high hydrogen separation performance [121].

Solution-diffusion (Fig. 8(e)) is the most widely used concept for understanding gas transport by dense membranes. In this, desorption and adsorption phenomena are used for gas separation. In metallic-based membranes, due to dense structure, the solution-diffusion mechanism occurs. Pd-based membrane prepared by Nayeboossadri et al. (2019) allows H₂ gas to impregnate or to adsorb in the palladium metal. Due to pressure differences, H₂ gas is separated from natural gas [122]. In this separation, the solution-diffusion

mechanism occurs. This separation mechanism depends on the mobility of the gas molecule and the solubility in the membrane [72].

Mechanism governing mixed matrix membrane

To improve the polymer membranes' performance, the inorganic material is incorporated in the polymer matrix called MMMs. The MMMs use both types of inorganic filler: porous structure (zeolite, silica, carbon molecular sieve, and CNTs) and dense structure (metal nanoparticles). The existence of pores in membranes offers various gas transport mechanisms that can be observed simultaneously (Fig. 8), depending on the pore size of membranes.

In Non-porous (Dense) polymeric membrane gas transport through the solution-diffusion mechanism. In this gas transport under the influence of a driving force (pressure force), penetrant gas molecules dissolve in an upstream phase (high pressure) of the membrane and diffuse through the downstream phase (low pressure) of the membrane. Diffusion is a rate-controlling step in penetrating permeation. The gas

diffusion through the polymeric membrane describe by the Fick's First law:

$$J = -D \left(\frac{dC}{dx} \right) \quad (2)$$

where J is the flux of hydrogen through the membrane; D is a diffusion coefficient; $\frac{dC}{dx}$ is the concentration gradient of gas over the membrane. The diffusion coefficient of different gasses in the polymeric membrane decreases with the increasing amount of molecules. The solubility of gases in the polymeric membrane is generally significantly low. Under such conditions, the diffusion coefficient does not depend on the concentration and diffusion of various gas mixture components flows separately. Diffusion coefficients of relatively large organic molecules may be relatively high because of polymers swelling. Generally, the diffusion-coefficient increase with the change in concentration. At steady-state condition diffusion coefficient is constant then Eq. (1) written as:

$$J = -D \frac{(C' - C'')}{T} \quad (3)$$

where C' is the upstream concentration of gas; C'' is the downstream concentration of gas; T is the thickness of the membrane.

At very low-pressure, Henry's law adequate for expressing the concentration of gas in the membrane:

$$C = Sp \quad (4)$$

where S is the solubility constant; p is the gas partial pressure. Concentration is represented in the form of partial pressure with the help of Henry's law. So, substituting Eq. (3) in Eq. (2) we get.

$$J = DS \frac{(p' - p'')}{T} \quad (5)$$

Therefore, in the being consideration case, the permeability (π) of gas defines as the product of diffusivity (D) and solubility (S) of gas in the membrane:

$$\pi = DS \quad (6)$$

So, Eq. (4) can be written as:

$$J = \pi \frac{(p' - p'')}{T} \quad (7)$$

In membrane gas separation, selectivity is described as the measure of the permeability of individual gases. The ideal selectivity of the membrane is based on the single gas permeability of "A" and "B." It can be written as.

$$\alpha = \frac{\pi_A}{\pi_B} \quad (8)$$

$$\alpha = \frac{D_A S_A}{D_B S_B} \quad (9)$$

Thus, selectivity is a result of variations in the solubility and diffusivity coefficients of the two gasses. The permeability and selectivity are associated with the performance of the membrane. The variation in permeability arises not only from the difference in diffusivity of different gas molecules but also from the change of the physical and chemical interconnection of gas molecules with the polymeric matrix, which defines the quantity per unit volume of the polymer matrix [115]. The balance between the solubility and the diffusivity of gas molecules determines the selective transport of gasses from a feed mixture. The selectivity improved by changing the polymer structure to improve one component's solubility in a gas mixture or by adding other cross-linking agents that can change membrane morphology.

The MMMs, where inorganic nanoparticles are dispersed in a consistent polymer phase, were thoroughly researched since the combined effect of the specific characteristic of polymers and inorganic nano-fillers produces synergistic

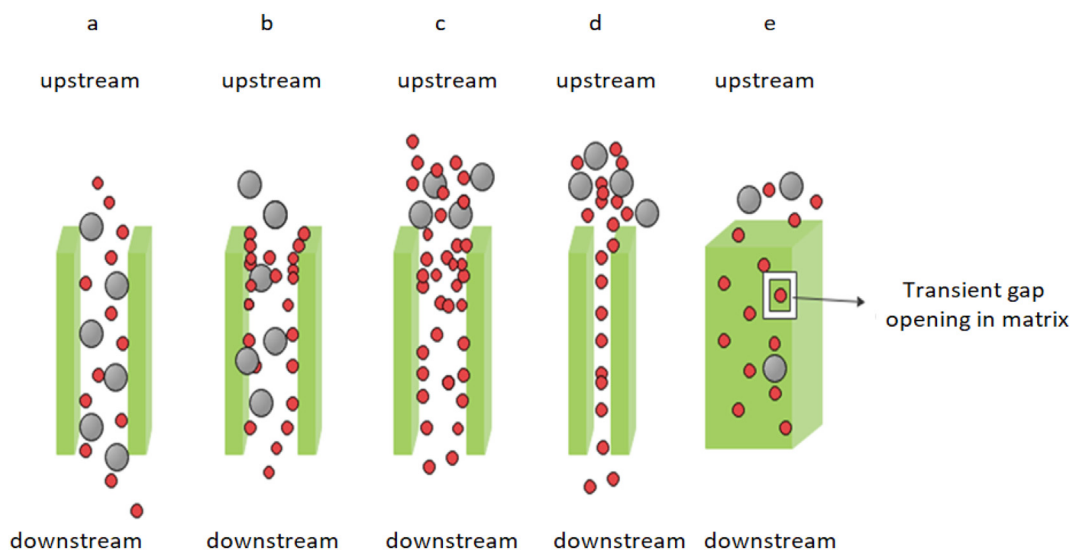


Fig. 8 – Mechanism of hydrogen separation membranes (dense and porous). a) Knudsen diffusion, (b) surface diffusion, (c) capillary condensation, (d) molecular sieving, and (e) solution diffusion.

effects. This principle incorporates the advantages of each phase: higher disperse filler selectivity, favorable mechanical characteristics, and inexpensive polymer processability. Most inorganic fillers are porous, such as zeolites, silica, and molecular carbon sieves. The mechanism in MMMs is very complex due to the combining effect of polymer and inorganic fillers [9]. So, the gas separation performance of MMMs was evaluated using the modified Maxwell model.

$$\frac{\pi}{\pi_M} = \frac{1 + 2\Phi \left(\frac{(\lambda_p - 1)}{(\lambda_p + 2)} \right)}{1 + \Phi \left(\frac{(\lambda_p - 1)}{(\lambda_p + 2)} \right)} \quad (10)$$

where π is the permeability of filler species; π_M is the permeability of polymeric membrane species; Φ volume fraction of inorganic filler partials; and λ_p is the permeability ratio $\frac{\pi_i}{\pi_M}$ where π_i is the permeability of species in the dispersion phase. The Lewis-Nielsen model adapted to permeability is:

$$\frac{\pi}{\pi_M} = \frac{1 + 2\Phi \left(\frac{(\lambda_p - 1)}{(\lambda_p + 2)} \right)}{1 + \psi \Phi \left(\frac{(\lambda_p - 1)}{(\lambda_p + 2)} \right)} \quad (11)$$

where:

$$\psi = 1 + \frac{1 - \Phi_V}{\Phi_V^2} \Phi \quad (12)$$

where Φ_V is the maximum packing volume fraction of inorganic filler particles. A modified Felske model (Felske, 2004) was introduced by Pal (2008).

$$\frac{\pi}{\pi_M} = \frac{1 + 2\Phi \left(\frac{(\beta - \gamma)}{(\beta + 2\gamma)} \right)}{1 + \psi \Phi \left(\frac{(\beta - \gamma)}{(\beta + 2\gamma)} \right)} \quad (13)$$

With:

$$\beta = (2 + \delta^3)\lambda_p - 2(1 - \delta^3)\lambda_D \quad (14)$$

$$\gamma = 1 + 2\delta^3 - (1 - \delta^3)\lambda_{p,D} \quad (15)$$

where δ is the ratio of the interfacial shell outer radius to the core radius, λ_D is the permeability ratio $\frac{\pi_D}{\pi_M}$ (π_D is the permeability of species in the interface), and $\lambda_{p,D}$ is the permeability ratio $\frac{\pi_p}{\pi_D}$.

The contact between polymer matrix and inorganic nanocomposites is an essential factor during the membrane's preparation, as unwanted channels are formed between both phases if the polymer matrix does not associate fully with the inorganic filler particles [123]. Classification defined as fillers separating from the polymeric membrane due to inconsistency and creating separate filling layers during the formulation of MMMs can impair the membrane's performance for hydrogen separation. Fig. 9 shows the different nanoscale polymer/particle interface structures. Case 1 describes an ideal morphology, which corresponds to the good predictions of the Maxwell model. Case 2 illustrates the separation of polymer chains from the inorganic sieve surface and creating interface voids. Case 3 Shows that the polymer chains in direct contact with the inorganic sieve surface may be stiffer than the polymer chains in bulk [115]. The creating of these

non-selective voids at the interface allows gasses to be bypassed due to the MMMs selectivity deteriorates [9]. To resolve this challenge, a bridging agent's existence to encourage better interfacial interaction is of crucial importance. The approaches involving alteration of surface hydrophobicity, the presence of surface roughness, and the variation of particle structure and pore architecture are also investigated. Another challenge addressed during the development of MMMs is the partial blockage of the filler pores by polymer chains that render the role of the filler integrated [106]. One of the most critical tasks to be tackled is the uniform dispersion and inclusion of inorganic particles as individuals in the polymer matrix to mitigate the adverse impact and overcome the above problems. In such cases, the particles' surface chemistry may need to be changed using different treatment approaches.

Fig. 10 displays a schematic diagram of the mixed matrix membranes' framework and the associated mechanism of gas transport. There are four kinds of gas transport pathways, including Cases 1, 2, 3, and 4, if inorganic nanocomposites are uniformly distributed in the membrane. Case 1 represents an interface voids between the polymer matrix and the incorporated inorganic nanocomposites. In this case, gas transfers through the polymeric matrix as well as interface voids. Due to this separation efficiency of the membrane reduces in Case 2, where there are interface craters between the polymer matrix and dispersed inorganic nanocomposite. Gas can transfer through the polymer matrix, interface voids, and porous inorganic nanocomposite. Case 3 presenting, no interface voids created between the polymer matrix and the non-porous inorganic nanocomposites. In this case, gas transfers through the polymeric matrix. Gas transfers through polymeric material and porous inorganic nanocomposite. As shown in Case 4, there are no interface voids created between the polymer matrix and the porous inorganic nanocomposite. The porous inorganic nanocomposite plays a role in diminishing the direction of gas transport.

The inorganic nanocomposite agglomerate in a membrane. In this situation, other forms of gas transfer mechanisms through the matrix are shown in cases 5, 6, 7, 8, 9, and 10, respectively. As shown in Case 5, the void channels are created between the polymeric matrix and non-porous inorganic nanocomposites. In this respect, gas-transfers through the polymer matrix, interface voids, and void channels [124]. In Case 6, the void channels develop between the polymer matrix and the porous inorganic composites. In this case, gas can transfer through the polymeric matrix, porous inorganic nanocomposites, void channels, and interface voids. As provided in Cases 7 and 9, no interface voids develop between the polymeric matrix and the non-porous inorganic nanocomposites. In this case, gas transfers thru the polymeric matrix. As demonstrated in Case 8, gas can transfer via polymeric matrix and porous inorganic nanocomposite. In this case, no interface voids develop between them. The porous inorganic nanocomposite plays a role in reducing the path of gas transfer. As seen in case 10, no interface voids develop between the polymeric matrix and the porous inorganic nanocomposites. In this case, forms continuous gas transfer channels across the matrix due to this gas can be transfer thru the polymeric matrix and porous inorganic nanocomposite [115].

Fabrication methods for hydrogen separation membrane

A variety of methods have been employed in the preparation of MMMs. The most common methods are coating, sol-gel, and phase-inversion, and these are described below.

Phase inversion

The phase inversion process comprises three components: polymer, solvent, and non-solvent. The polymer dissolves in a sufficient solvent. The resulting polymer solution is cast on adequate support and is immersed in a non-solvent (usually water) coagulation bath. The solvent penetrates the non-solvent into the polymer solution. The exchange happens until demixing takes place. A homogeneous polymer mixture is two phases. One is the polymer-rich phase, a membrane with an asymmetric structure, and the other is the phase with a high liquid material. The following are factors that are influential on the structure and size of the polymeric membrane are 1) polymeric concentration, 2) choice of solvent and non-solvent, 3) The type of additive, 4) Precipitation time, 5) bath temperature. Phase inversion by immersion precipitation is one of the most commonly used methods for successfully manufacturing defect-free membranes [63]. Several studies have investigated that successfully fabricated defect-free polymeric membranes for gas separation using phase inversion. The investigator Zhang et al. (2010) prepared the PEI membrane defect-free membrane with formamide as an additive, and the 153 separation factors for H_2/N_2 were achieved using phase-inversion. Separation factors 107 for H_2/N_2 have also been reported using a coating technique for PEI membrane coated with Poly [1-(trimethylsilyl)-1-propyne] (PTMSP) [125]. These studies show that Phase –inversion process more efficient for preparing hydrogen separation membranes as compared to the membranes prepared by the coating process. Table 8 indicated the advantages and disadvantages of membrane preparation methods.

PDMS/PEI defect-free membranes for H_2/CH_4 separation developed by Arabi & Kargari et al. (2013). Non-solvent used during the membrane preparation also affects membrane performance. Different types of non-solvent are used like water, ethanol, isopropanol, and methanol. Among these, non-solvent water gives high H_2/CH_4 selectivity was 27.99 [126]. In another study, Arabi et al. (2013) also prepared a defect-free PEI asymmetric membrane for H_2/CH_4 separation using the phase inversion process. In this study effect of different non-solvent used in previous study shows. Among these, water as a non-solvent shows high gas separation performance. The selectivity of H_2/CH_4 was obtained at 32.73. These two studies show that the immersed precipitation process successfully developed a defect-free membrane, and gas separation through the membranes directly depends on the selection of non-solvents, choice of polymeric membranes, and other parameters [127].

Itta et al. (2010) develop a carbon molecular sieve membrane using dry/wet phase inversion process on alumina support and polyetherimide (PEI) use as a procurer. Using this process, an extremely thin layer produces on the membrane's surface due to the membrane's performance-enhanced [128]. Gas permeability performance was observed in the capacity of molecular sieve in a CSM membrane at different pyrolysis temperatures. The results indicated that permeability of H_2 , CO_2 , and O_2 increases with increasing temperature from 550 to 600 °C, where N_2 and CH_4 permeability decreases. Accordingly, the ideal selectivity of H_2/CH_4 , H_2/CO_2 , H_2/N_2 increased at a temperature range of 550–600 °C and decreased at 650 °C. CSM molecules can perform molecular sieve mechanisms and enable significantly high gas permeability through the membranes due to the enhanced selectivity of gasses. In a wet phase, this phenomenon might become due to the high temperatures that result in loss of carbon content in the membrane and the impact of the membrane's final soaking time and temperature. In the wet phase, there is a prolonged duration from the preliminary phase transition to the full dry of the membrane wall during the membrane development. A longer time favors more growth of the nascent macro voids

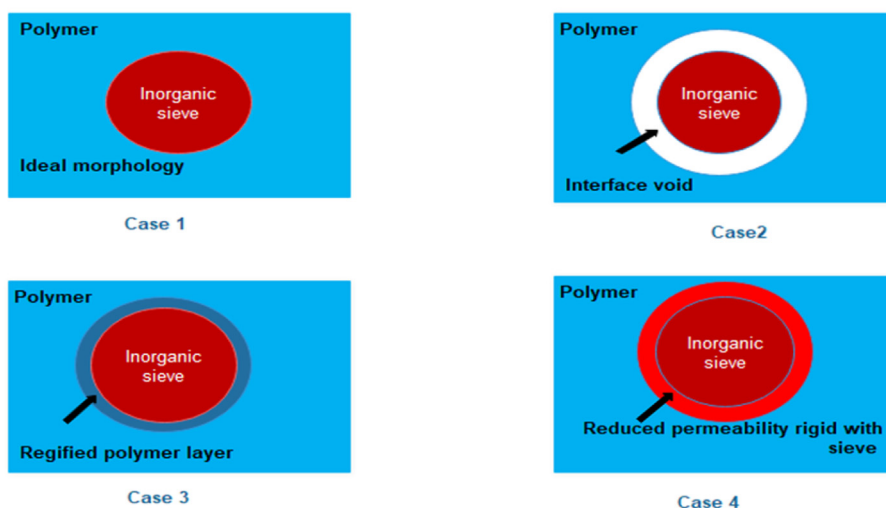


Fig. 9 – The schematic diagram of Nanoscale morphology of various mixed matrix membrane (MMMs).

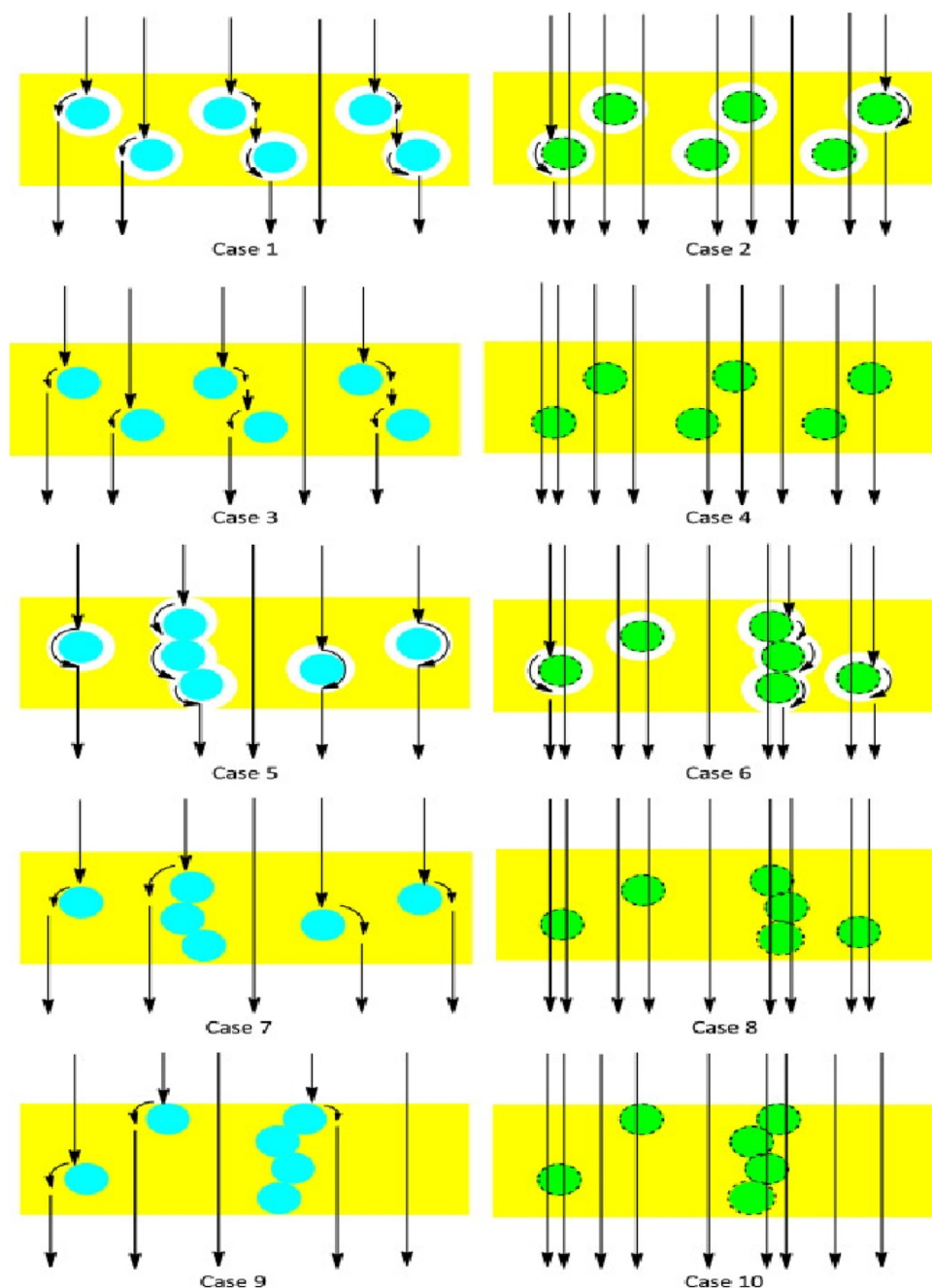


Fig. 10 – Schematic diagram of the mixed matrix membranes' framework and the associated mechanism of gas transport [124].

formed in the lean polymer process, thereby expanding the finger-like voids towards the outer skin layer. The delay in drying appears to generate large micro-events. By contrast, fast-drying prevents the alteration of polymer aggregate particles and the agglomeration of the nascent voids created by the growth of spinodal or nucleation [128]. Therefore, membrane morphology is directly affected by the polymer choice, processing time, solvent choice and non-solvents, and temperature. This process successfully developed defect-free and microporous membranes due to this selectivity of smaller molecules (H_2) enhanced.

Coating

Firstly, in a dip-coating process, the substrate is immersed in the precursor solution for significant material formation. Once the material has been dispersed, the substance can be excluded by evaporation, resulting in distinctive layer thickness. The main forces used for the dip-coating process are surface tension, Inertia force, gravitational force, and viscous force. Dip coating has several advantages: control membrane thickness, easy process, Suitable for complex structure, and low-cost process. Many studies investigated the effects of

Table 8 – Advantages and disadvantages of membrane preparation methods.

Method	Advantages	Disadvantages	References
Sol-gel	<ul style="list-style-type: none"> • Less energy consumption • Better homogeneity • Versatile • No need for expensive equipment • Simplest, homogeneity, low cost, reliability, reproducibility, controllability • devised to control the nano-structuring of inorganic material in MMMs, 	<ul style="list-style-type: none"> • Hard to control porosity • time taking process 	[53]
Phase inversion	<ul style="list-style-type: none"> • Easy fabrication • Homogenous dispersion of inorganic sieve • Less energy consumption • Extremely thin membranes can be prepared 	<ul style="list-style-type: none"> • High load of nanoparticles offers agglomeration • Membrane surface defect 	[134]
Dip-Coating	<ul style="list-style-type: none"> • low cost • layer thickness can be easily controlled. 	<ul style="list-style-type: none"> • Slow and time-consuming • Block the pores of the membrane 	[135]

coating parameters on membrane performance, like coating type of solvent, solution concentration, temperature, and numbers of coating surfaces [129].

Appropriate coating material also an essential parameter for preparing high separation performance membranes. Zhang et al. (2011) developed a PEI/PTFPMS composite membranes, but the coating layer showed poor performance for H₂/CH₄ separation [130]. Arabi and Kargari et al. (2013) prepared a PEI/PDMS composite membrane. These membranes are very effective for gas separation due to PDMS unique properties such as siloxane backbone stability, low intermolecular forces between the methyl groups, and high siloxane bonding ability. They were using different coating solvents such as water, ethanol, methanol, isopropanol, and water-isopropanol. Among these, water made a dense structure of membranes, and isopropanol forms a sponge-like structure. The dense structure of the membrane enhanced the separation performance of hydrogen. The selectivity of H₂/CH₄ 27.99 was achieved. Coagulant bath temperature also affects the structure of the membrane, increasing temperature makes membranes denser. Enhancing membrane separation efficiency by increasing the number of sequential coatings may reflect an increase in membrane thickness. Owing to thick layers of the skin and hence improved sealing of surface pores and defects, the decline in gases permeability increases the selectivity of gas [131]. Arabi and Kargari et al. (2013) reported with an increase in the number of coating of PDMS, the selectivity of H₂/CH₄ enhanced [126]. The swelling problem maybe occurs with increasing the number of coating on the membrane because the previous layer can be redissolved by the solvent in the new coating layer cause Swelling [131].

Sol-gel

The sol-gel process is a wet-chemical method used in both glassy and ceramic materials manufacturing. The sol (or solution) slowly evolves in this cycle into the development of a gel-like network containing both a liquid phase and a solid phase. This method allows for better control of the entire reactions involved during solids synthesis. Homogeneous multi-component systems can be easily acquired; generally homogeneous mixed oxides have been developed by mixing

solutions of molecular precursors. The sol-gel technique involves the formulation of a precursor mix (a sol or a solution), which has transformed into a final product via a stage that may include drying, chemical reactions, precursor gelation, and curing (often by heat). The benefits of sol-gel techniques provide lower processing temperatures, high purity levels, dopant concentration control, and the ability to synthesize multi-component formulations in different product types. For developing MMMs, various problems arise like inorganic fillers spread badly in the polymer matrix cause aggregates during the membrane formation. This created non-selective gaps between the two phases and reduced the efficiency of the gas separation [132]. To resolve the drawbacks of MMM's various enhancements, techniques have been suggested and developed. These processes include chemical modification, the priming method. Therefore, these methods involve the addition of agents for alteration procedures to raise the operating costs and the planning process complexity. On the side, many studies successfully developed well-mixed organic-inorganic composite membranes via an in-situ sol-gel process.

The inorganic liquid precursors were mixed in a polymer due to this uniform dispersion of material into the matrix. The liquid mixture of inorganic material generally increases the filler's nano-dispersion and reduces the phase difference between the organic and inorganic phases [133]. This approach also monitors the nanostructure of inorganic material dispersed in MMMs, such as tailoring the porous texture of inorganic material, pore size distribution, and surface area. Zhuang et al. (2014) have been developed PPO-silica-based MMMs using the sol-gel method through hydrolytic polycondensation for hydrogen separation from CO₂. The hydrolytic polycondensation reaction is directly affected by the base/acid medium. In catalytic conditions, dense clusters produced quick polycondensation and gradual hydrolysis. Opposite, in acidic catalytic conditions, small cluster aggregates have produced that lead to a small pore. In this study, a liquid precursor was used due to this good dispersion of inorganic material into the polymeric matrix. Due to the production of small pore size <2 nm and good dispersion of inorganic material caused enhanced the small size gas molecules (H₂) separation performance [53]. Nevertheless, the sol-gel process is time they are consuming when membranes are

in the process of calcination. To avoid crack formation, this process is often carried out very slowly, with time intervals covering one day to several days for one single sheet.

Future prospective of polymeric membrane

For hydrogen separation, mostly glassy polymers are used. Glassy polymers lose efficiency much faster than other membrane materials like inorganic and metallic. The acidic gasses (CO_2) plasticized the specific skin surface of the membrane in the presence of even small quantities of hydrocarbons. Due to this, the gas separation efficiency decreased with time. Physical aging resulted in the polymer due to the incremental reduction of unrelaxed additional free volume within their glass transition temperature to the stable equilibrium. Aging is more intense for the thin film membrane than bulk material and leads to a widespread reduction in permeability. Polymeric material facing a problem like low mechanical, thermal stability, and swelling property can be resolved by cross-linking. The cross-linking reduces the permeability of gasses as compared to the original one. To enhance the selectivity of polymeric membranes, the dispersion of inorganic particles is a good alternative (MMMs). The MMMs facing some problems like improvement in durability and agglomeration of the nanocomposite. So, need a new polymeric material which durable, non-toxic, and environment friendly as well as suitable for gas separation.

Currently, many membranes separation technology take advantage of membranes manufactured from organic polymers because their form and structure can be adapted to the requirements of an application with modular manufacturing processes such as solution casting and phase separation, coating, and interfacial polymerization. Organic membranes not a novel membrane material but is of growing attention for their renewable character. Organic membranes have various advantages such as 1) soluble in a large variety of solvent; this is due to quite complex processing, 2) biodegradable due to this its environment friendly. Guar gum, one of the organic materials with high film-forming property and environmentally friendly polymer, can be used to prepare the hydrogen separation membrane. Guar gum is a promising material that can use as a replacement for other conventional polymeric membranes. It is the naturally existing polymers like galactomannan acquired from *Cyamopsis tetragonolobus* through ground endosperm. It is a member of the Leguminosae family. Due to the existence of various functional groups that facilitate easy chemical or biochemical modification.

Conclusions

To improve the hydrogen separation performance of polymeric membranes, various types of MMMs were developed as reported in the literature. MMMs contain two or more compounds. In MMMs the polymeric matrix is a continuous phase and inorganic material dispersed in it as a filler. Generally, MMMs containing inorganic partial provide higher H_2 permeability compared to their pure polymeric membranes

due to increasing fraction free volume and the interaction between the active site with penetrant molecules. A trade-off relationship still exists with MMMs containing inorganic material with only a few combinations of polymer-inorganic membranes able to achieve high hydrogen separation performance that exceeds Robeson's upper bound. In MMMs two or more gas transport mechanisms simultaneously work. The hydrogen transport mechanism, inorganic partially controlled mainly by the Knudsen diffusion, surface diffusion, solution diffusion, and molecular sieve mechanism. The adjustment between these mechanisms balances the hydrogen permeability and selectivity of the resultant MMMs and disrupts Robeson's trade-off relationship. Various porous (zeolite, carbon molecular sieve, and CNTs) and non-porous (metals nanoparticles) inorganic filler are used for developing MMMs. In MMMs, agglomeration of nanocomposite at high loading in the matrix is the major problem. CNTs are a promising material for MMMs because of weak van der Waals forces of attraction between CNTs; the focus goes to avoiding the development of agglomerates or CNTs in packets. But, the low solubility of CNTs in solvents was the focus of many researchers. The efficiency of CNT-MMMs depends on the dispersion of the CNTs in the polymer membrane and interfacial interactions between polymeric membranes and CNTs. CNT functionalization is an essential way of preventing CNT aggregation, leading to greater dispersion and stabilization of CNTs in the polymer matrix. Functionalized CNTs can improve the characteristics, solubility, and homogeneous dispersion of CNTs in MMMs. To enhance the H_2 separation performance, Pd-nanoparticles are used with functionalized CNTs. Pd-nanoparticles easily attached to the surface of functionalized CNTs due to this hydrogen separation ability from the other gas molecules enhanced. The alignment of CNTs also an essential aspect of improving H_2 separation performance. Random dispersion of CNTs blocked the pores of the membrane; due to this MMMs performance declined. So, for the alignment of CNTs, electric, or magnetic field are required. These membranes exceed Robeson's trade-off limit but use functionalized CNTs with Pd-nanoparticle dispersed in polymeric membranes in industrial applications improving comprehensive research addressing the current alignment of CNTs at low cost. High voltage is required for the alignment of CNTs, which directly affects the cost of membranes. For preparing MMMs, various fabrication methods are used, such as sol-gel, phase-inversion, and coating, etc. Among these sol-gel processes provided good quality membranes for hydrogen separation due to creating a small pore size <2 nm. The good dispersion of inorganic material caused enhanced the small size gas molecules (H_2) separation performance.

In future perspectives, research on MMMs should be focused on the following aspects. 1) investigators should develop new polymers and fillers to create high-performance MMMs for hydrogen separation, 2) Researchers, developed cost-effective and environment-friendly MMMs with high gas separation performance. The Organic polymer material one of the best options for preparing MMMs because these polymer materials highly soluble in a large variety of solvents as well as these materials are biodegradable.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

REFERENCES

- [1] Rahimpour MR, Samimi F, Babapoor A, Tohidian T, Mohebi S. Palladium membranes applications in reaction systems for hydrogen separation and purification: a review. *Chem Eng Process Process Intensif* 2017;121:24–49. <https://doi.org/10.1016/j.cep.2017.07.021>.
- [2] Rahimpour MR, Bayat M. Production of ultrapure hydrogen via utilizing fluidization concept from coupling of methanol and benzene synthesis in a hydrogen-permselective membrane reactor. *Int J Hydrogen Energy* 2011;36:6616–27. <https://doi.org/10.1016/j.ijhydene.2011.02.095>.
- [3] Bhattacharyya R, Bhanja K, Mohan S. Simulation studies of the characteristics of a cryogenic distillation column for hydrogen isotope separation. *Int J Hydrogen Energy* 2016;41:5003–18. <https://doi.org/10.1016/j.ijhydene.2016.01.106>.
- [4] Liemberger W, Groß M, Miltner M, Harasek M. Experimental analysis of membrane and pressure swing adsorption (PSA) for the hydrogen separation from natural gas. *J Clean Prod* 2017;167:896–907. <https://doi.org/10.1016/j.jclepro.2017.08.012>.
- [5] Sazali N, Norharyati W, Salleh W, Ismail AF. Chapter 12 - synthetic polymer-based membranes for hydrogen separation. Elsevier Inc.; 2020. <https://doi.org/10.1016/B978-0-12-818485-1.00012-5>.
- [6] Weber M, Drobek M, Rebi B, Charmette C, Cartier J, Julbe A, et al. Hydrogen selective palladium-alumina composite membranes prepared by Atomic Layer Deposition, vol. 596; 2020. <https://doi.org/10.1016/j.memsci.2019.117701>.
- [7] Pal N, Agarwal M, Maheshwari K, Solanki YS. A review on types, fabrication and support material of hydrogen separation membrane. *Mater Today Proc* 2020;28:1386–91. <https://doi.org/10.1016/j.matpr.2020.04.806>.
- [8] Shiraz HG, Shiraz MG. Palladium nanoparticle and decorated carbon nanotube for electrochemical hydrogen storage. *Int J Hydrogen Energy* 2017;42:11528–33. <https://doi.org/10.1016/j.ijhydene.2017.03.129>.
- [9] Goh PS, Ismail AF, Sanip SM, Ng BC, Aziz M. Recent advances of inorganic fillers in mixed matrix membrane for gas separation, vol. 81; 2011. p. 243–64. <https://doi.org/10.1016/j.seppur.2011.07.042>.
- [10] Robeson LM. The upper bound revisited. *J Membr Sci* 2008;320:390–400. <https://doi.org/10.1016/j.memsci.2008.04.030>.
- [11] Cardoso SP, Azenha IS, Lin Z, Portugal I, Rodrigues AE, Silva CM. Inorganic membranes for hydrogen separation. *Separ Purif Rev* 2018;47:229–66. <https://doi.org/10.1080/15422119.2017.1383917>.
- [12] Wang H, Dong X, Lin YS. Highly stable bilayer MFI zeolite membranes for high temperature hydrogen separation. *J Membr Sci* 2014;450:425–32. <https://doi.org/10.1016/j.memsci.2013.08.030>.
- [13] Grainger D, Ha M. The recovery by carbon molecular sieve membranes of hydrogen transmitted in natural gas networks. *Int J Hydrogen Energy* 2008;33:2379–88. <https://doi.org/10.1016/j.ijhydene.2008.03.001>.
- [14] Kajiwarra M, Uemiya S, Kojima T, Kikuchi E. Hydrogen permeation properties through composite membranes of platinum supported on porous alumina 2000;56:65–73.
- [15] Yun S, Oyama ST. Correlations in palladium membranes for hydrogen separation: a review. *J Membr Sci* 2011;375:28–45. <https://doi.org/10.1016/j.memsci.2011.03.057>.
- [16] Abate S, Genovese C, Perathoner S, Centi G. Performances and stability of a Pd-based supported thin film membrane prepared by EPD with a novel seeding procedure. Part 1- Behaviour in H₂/N₂ mixtures. *Catal Today* 2009;145:63–71. <https://doi.org/10.1016/j.cattod.2008.06.024>.
- [17] Dong G, Chen V. Challenges and opportunities for mixed-matrix membranes for gas separation. 2013. p. 4610–30. <https://doi.org/10.1039/c3ta00927k>.
- [18] Ashtiani S, Khoshnamvand M, Bouša D, Šturala J, Sofer Z, Shaliutina-Kolešová A, et al. Surface and interface engineering in CO₂-philic based UiO-66-NH₂-PEI mixed matrix membranes via covalently bridging PVP for effective hydrogen purification. *Int J Hydrogen Energy* 2021;46:5449–58. <https://doi.org/10.1016/j.ijhydene.2020.11.081>.
- [19] Riasat H, Amirkhani F, Ahmad S, Rezakazemi M. Mass transfer through PDMS/zeolite 4A MMMs for hydrogen separation: molecular dynamics and grand canonical Monte Carlo simulations. *Int Commun Heat Mass Tran* 2019;108:104259. <https://doi.org/10.1016/j.icheatmasstransfer.2019.05.005>.
- [20] Zornoza B, Esekhiile O, Koros WJ, Téllez C, Coronas J. Hollow silicalite-1 sphere-polymer mixed matrix membranes for gas separation. *Separ Purif Technol* 2011;77:137–45. <https://doi.org/10.1016/j.seppur.2010.11.033>.
- [21] Bernardo P, Drioli E, Golemme G. *Ind Eng Chem Res* 2009;48:4638–63. *Gas Sep State of the art Bernardo et al.pdf* 2009:4638–63.
- [22] Lamb KE, Dolan MD, Kennedy DF. Ammonia for hydrogen storage; A review of catalytic ammonia decomposition and hydrogen separation and purification. *Int J Hydrogen Energy* 2019;44:3580–93. <https://doi.org/10.1016/j.ijhydene.2018.12.024>.
- [23] Ahn J, Chung W, Pinnau I, Guiver MD. Polysulfone/silica nanoparticle mixed-matrix membranes for gas separation. *J Membr Sci*; 2008. <https://doi.org/10.1016/j.memsci.2008.01.031>.
- [24] Vijay YK, Wate S, Acharya NK, Garg JC. The titanium-coated polymeric membranes for hydrogen recovery. *Int J Hydrogen Energy* 2002;27:905–8. [https://doi.org/10.1016/S0360-3199\(01\)00188-4](https://doi.org/10.1016/S0360-3199(01)00188-4).
- [25] Awasthi K, Choudhury S, Komber H, Simon F, Formanek P, Sharma A, et al. Functionalization of track-etched poly (ethylene terephthalate) membranes as a selective filter for hydrogen purification. *Int J Hydrogen Energy* 2014;39:9356–65. <https://doi.org/10.1016/j.ijhydene.2014.03.240>.
- [26] Cardoso SP, Azenha IS, Lin Z, Rodrigues AE, Silva CM, Cardoso SP, et al. Ce pt ed t. *Separ Purif Rev* 2017. <https://doi.org/10.1080/15422119.2017.1383917>. 0.
- [27] Caro J, Noack M. Zeolite membranes - recent developments and progress. *Microporous Mesoporous Mater* 2008;115:215–33. <https://doi.org/10.1016/j.micromeso.2008.03.008>.
- [28] Jaffar Al-Mulla EA, Issam AM, Al-Janabi KWS. A novel method for the synthesis of biodiesel from soybean oil and urea. *Compt Rendus Chem* 2015;18:525–9. <https://doi.org/10.1016/j.crci.2013.12.012>.
- [29] Kumbharkar SC, Karadkar PB, Kharul UK. Enhancement of gas permeation properties of polybenzimidazoles by systematic structure architecture. *J Membr Sci*

- 2006;286:161–9. <https://doi.org/10.1016/j.memsci.2006.09.030>.
- [30] Chem JM, Rodr A, Ibarra L, Gonz L, Valent JL. Overcoming the disadvantages of fumed silica as filler in elastomer composites. *J Mater Chem* 2011;7381. <https://doi.org/10.1039/c1jm10410a>. –92.
- [31] Diestel L, Liu XL, Li YS, Yang WS, Oxane Caro J. Comparative permeation studies on three supported membranes: pure ZIF-8 pure polymethylphenylsil and mixed matrix membranes. *Microporous and Mesoporous Mater* 2014;189:210–5. <https://doi.org/10.1016/j.micromeso.2013.09.012>.
- [32] Diestel L, Wang N, Schulz A, Steinbach F, Caro J. Matrimid-based mixed matrix Membranes: interpretation and correlation of experimental findings for zeolitic imidazolate frameworks as fillers in H₂/CO₂ separation. <https://doi.org/10.1021/ie504096j>; 2015.
- [33] Sazali N, Salleh WNW, Ismail AF, Kadirgama K, Othman FEC, Ismail NH. Impact of stabilization environment and heating rates on P84 co-polyimide/nanocrystalline cellulose carbon membrane for hydrogen enrichment. *Int J Hydrogen Energy* 2019;44:20924–32. <https://doi.org/10.1016/j.ijhydene.2018.06.039>.
- [34] Chung TS, Shao L, Tin PS. Surface modification of polyimide membranes by diamines for H₂ and CO₂ separation. *Macromol Rapid Commun* 2006;27:998–1003. <https://doi.org/10.1002/marc.200600147>.
- [35] Aberg CM, Ozcam AE, Majikes JM, Seyam MA, Spontak RJ. Extended chemical crosslinking of a thermoplastic polyimide: macroscopic and microscopic property development. *Macromol Rapid Commun* 2008;29:1461–6. <https://doi.org/10.1002/marc.200800230>.
- [36] Shishatskiy S, Nistor C, Popa M, Nunes SP, Peinemann KV. Polyimide asymmetric membranes for hydrogen separation: influence of formation conditions on gas transport properties. *Adv Eng Mater* 2006;8:390–7. <https://doi.org/10.1002/adem.200600024>.
- [37] Naderi A, Asadi Tashvigh A, Chung TS, Weber M, Maletzko C. Molecular design of double crosslinked sulfonated polyphenylsulfone/polybenzimidazole blend membranes for an efficient hydrogen purification. *J Membr Sci* 2018;563:726–33. <https://doi.org/10.1016/j.memsci.2018.06.033>.
- [38] Pesiri DR, Jorgensen B, Dye RC. Thermal optimization of polybenzimidazole meniscus membranes for the separation of hydrogen, methane, and carbon dioxide. *J Membr Sci* 2003;218:11–8. [https://doi.org/10.1016/S0376-7388\(03\)00129-7](https://doi.org/10.1016/S0376-7388(03)00129-7).
- [39] Kumbharkar SC, Liu Y, Li K. High performance polybenzimidazole based asymmetric hollow fibre membranes for H₂/CO₂ separation. *J Membr Sci* 2011;375:231–40. <https://doi.org/10.1016/j.memsci.2011.03.049>.
- [40] Cardoso SP, Azenha IS, Lin Z, Rodrigues AE, Silva CM, Cardoso SP, et al. Inorganic membranes for hydrogen separation inorganic membranes for hydrogen separation. *Separ Purif Rev* 2018;47:229–66. <https://doi.org/10.1080/15422119.2017.1383917>.
- [41] Gu Y, Hacırlıoğlu P, Oyama ST. Hydrothermally stable silica-alumina composite membranes for hydrogen separation. *J Membr Sci* 2008;310:28–37. <https://doi.org/10.1016/j.memsci.2007.10.025>.
- [42] Lee D, Oyama ST. Gas permeation characteristics of a hydrogen selective supported silica membrane 2002;210:291–306.
- [43] Kanezashi M, Brien-abraham JO, Lin YS. Gas permeation through DDR-type zeolite membranes at high temperatures, vol. 54; 2008. <https://doi.org/10.1002/aic>.
- [44] Hong M, Falconer JL, Noble RD. Modification of zeolite membranes for H₂ separation by catalytic cracking of methyl-diethoxysilane. 2005. p. 4035–41.
- [45] Ngamou PHT. High-performance carbon molecular sieve membranes for hydrogen purification and pervaporation dehydration of organic solvents, vol. 14; 2019. <https://doi.org/10.1039/c8ta09504c>.
- [46] Dolan MD. Non-Pd BCC alloy membranes for industrial hydrogen separation. *J Membr Sci* 2010;362:12–28. <https://doi.org/10.1016/j.memsci.2010.06.068>.
- [47] Tosto E, Alique D, Martinez-Diaz D, Sanz R, Calles JA, Caravella A, et al. Stability of pore-plated membranes for hydrogen production in fluidized-bed membrane reactors. *Int J Hydrogen Energy* 2019;45:7374–85. <https://doi.org/10.1016/j.ijhydene.2019.04.285>.
- [48] Weber M, Drobek M, Rebière B, Charmette C, Cartier J, Julbe A, et al. Hydrogen selective palladium-alumina composite membranes prepared by Atomic Layer Deposition. *J Membr Sci* 2020;596. <https://doi.org/10.1016/j.memsci.2019.117701>.
- [49] Ismail AF, Goh PS, Sanip SM, Aziz M. Transport and separation properties of carbon nanotube-mixed matrix membrane. *Separ Purif Technol* 2009;70:12–26. <https://doi.org/10.1016/j.seppur.2009.09.002>.
- [50] Strugova DV, Zadorozhnyy MY, Berdonosova EA, Yablokova MY, Konik PA, Zheleznyi MV, et al. Novel process for preparation of metal-polymer composite membranes for hydrogen separation. *Int J Hydrogen Energy* 2018;43:12146–52. <https://doi.org/10.1016/j.ijhydene.2018.04.183>.
- [51] Kim S, Shamsaei E, Lin X, Hu Y, Simon GP, Geun J, et al. The enhanced hydrogen separation performance of mixed matrix membranes by incorporation of two-dimensional ZIF-L into polyimide containing hydroxyl group. *J Membr Sci* 2018;549:260–6. <https://doi.org/10.1016/j.memsci.2017.12.022>.
- [52] Celik E, Park H, Choi H, Choi H. Carbon nanotube blended polyethersulfone membranes for fouling control in water treatment. *Water Res* 2010;45:274–82. <https://doi.org/10.1016/j.watres.2010.07.060>.
- [53] Zhuang G, Tseng H, Wey M. ScienceDirect Preparation of PPO-silica mixed matrix membranes by in-situ sol-gel method for H₂/CO₂ separation. *Int J Hydrogen Energy* 2014;39:17178–90. <https://doi.org/10.1016/j.ijhydene.2014.08.050>.
- [54] Kamakshi Kumar R, Saraswat VK, Kumar M, Awasthi K. Palladium nanoparticle binding in functionalized track etched PET membrane for hydrogen gas separation. *Int J Hydrogen Energy* 2017;42:16186–94. <https://doi.org/10.1016/j.ijhydene.2017.05.040>.
- [55] Rezakazemi M, Shahidi K, Mohammadi T. Hydrogen separation and purification using crosslinkable PDMS/zeolite A nanoparticles mixed matrix membranes. *Int J Hydrogen Energy* 2012;37:14576–89. <https://doi.org/10.1016/j.ijhydene.2012.06.104>.
- [56] Zhang X, Xiong G, Yang W. A modified electroless plating technique for thin dense palladium composite membranes with enhanced stability. *J Membr Sci* 2008;314:226–37. <https://doi.org/10.1016/j.memsci.2008.01.051>.
- [57] Flanagan TB, Wang D. Hydrogen permeation through fcc Pd-Au alloy membranes. *J Phys Chem C* 2011;115:11618–23. <https://doi.org/10.1021/jp201988u>.
- [58] Setiawan WK, Chiang K. Silica applied as mixed matrix membrane inorganic filler for gas separation. *Review* 2019;1:1–21.
- [59] Kumar R, Kumar M, Awasthi K. ScienceDirect Functionalized Pd-decorated and aligned MWCNTs in polycarbonate as a selective membrane for hydrogen

- separation. *Int J Hydrogen Energy* 2016;41:23057–66. <https://doi.org/10.1016/j.ijhydene.2016.09.008>.
- [60] Weber M, Drobek M, Rebière B, Charmette C, Cartier J, Julbe A, et al. Hydrogen selective palladium-alumina composite membranes prepared by Atomic Layer Deposition. *J Membr Sci* 2020;596. <https://doi.org/10.1016/j.memsci.2019.117701>.
- [61] Sanip SM, Ismail AF, Goh PS, Soga T, Tanemura M, Yasuhiko H. Gas separation properties of functionalized carbon nanotubes mixed matrix membranes. *Separ Purif Technol* 2011;78:208–13. <https://doi.org/10.1016/j.seppur.2011.02.003>.
- [62] Patel AK, Acharya NK. Thermally rearranged (TR) HAB-6FDA nanocomposite membranes for hydrogen separation. *Int J Hydrogen Energy* 2019. <https://doi.org/10.1016/j.ijhydene.2019.07.052>.
- [63] Aroon MA, Ismail AF. Performance studies of mixed matrix membranes for gas separation: a review. *Separ Purif Technol* 2010;75:229–42. <https://doi.org/10.1016/j.seppur.2010.08.023>.
- [64] Pacheco Tanaka DA, Medrano JA, Viviente Sole JL, Gallucci F. Metallic membranes for hydrogen separation. Elsevier Inc.; 2020. <https://doi.org/10.1016/b978-0-12-818332-8.00001-6>.
- [65] Khanlari S, Tofighy MA, Mohammadi T. Transport phenomena through nanocomposite membranes. Elsevier Inc.; 2020. <https://doi.org/10.1016/b978-0-12-816710-6.00004-3>.
- [66] Suhaimi HSM, Khir MNIM, Leo CP, Ahmad AL. Preparation and characterization of polysulfone mixed-matrix membrane incorporated with palladium nanoparticles dispersed in polyvinylpyrrolidone for hydrogen separation. *J Polym Res* 2014;21:1–8. <https://doi.org/10.1007/s10965-014-0428-1>.
- [67] Ahmad J, Hågg MB. Polyvinyl acetate/titanium dioxide nanocomposite membranes for gas separation. *J Membr Sci* 2013;445:200–10. <https://doi.org/10.1016/j.memsci.2013.04.052>.
- [68] Kumar R, Kamakshi Shisodia S, Kumar M, Awasthi K. Effect of UV irradiation on PC membrane and use of Pd nanoparticles with/without PVP for H₂ selectivity enhancement over CO₂ and N₂ gases. *Int J Hydrogen Energy* 2018;21690–8. <https://doi.org/10.1016/j.ijhydene.2018.06.094>.
- [69] Kumar R, Saraswat VK, Kumar M. ScienceDirect Palladium nanoparticle binding in functionalized track etched PET membrane for hydrogen gas separation. *Int J Hydrogen Energy* 2017;42:16186–94. <https://doi.org/10.1016/j.ijhydene.2017.05.040>.
- [70] Chaikittisilp W, Okubo T. Zeolite and zeolite-like materials. *Handb Solid State Chem* 2017:97–119. <https://doi.org/10.1002/9783527691036.hsscvol4013>.
- [71] Bastani D, Esmaili N, Asadollahi M. Polymeric mixed matrix membranes containing zeolites as a filler for gas separation applications: a review. *J Ind Eng Chem* 2013;19:375–93. <https://doi.org/10.1016/j.jiec.2012.09.019>. *Journal of Industrial and Engineering Chemistry*.
- [72] Cheng Z. Hydrogen separation membranes of polymeric materials. <https://doi.org/10.1007/978-3-662-53514-1>; 2017.
- [73] Michalkiewicz B, Koren ZC. Zeolite membranes for hydrogen production from natural gas: state of the art. *J Porous Mater* 2015;22:635–46. <https://doi.org/10.1007/s10934-015-9936-6>.
- [74] Ordoñez MJC, Balkus KJ, Ferraris JP, Musselman IH. Molecular sieving realized with ZIF-8/Matrimid® mixed-matrix membranes. *J Membr Sci* 2010;361:28–37. <https://doi.org/10.1016/j.memsci.2010.06.017>.
- [75] Kumar A, Yadav N, Bhatt M, Mishra NK, Chaudhary P, Singh R. Sol-gel derived nanomaterials and it's Applications : a review 2015;5:98–105.
- [76] Peydayesh M, Mohammadi T, Bakhtiari O. Effective hydrogen purification from methane via polyimide Matrimid 5218- deca-dodecasil 3R zeolite mixed matrix membrane. *Energy* 2017. <https://doi.org/10.1016/j.energy.2017.11.101>.
- [77] Ahmad J, Hågg M. Development of matrimid/zeolite 4A mixed matrix membranes using low boiling point solvent. *Separ Purif Technol* 2013;115:190–7. <https://doi.org/10.1016/j.seppur.2013.04.049>.
- [78] Mirzaei A, Navarchian AH, Tangestaninejad S. Mixed matrix membranes on the basis of Matrimid and palladium - zeolitic imidazolate framework for hydrogen separation. *Iran Polym J (Engl Ed)* 2020. <https://doi.org/10.1007/s13726-020-00812-w>.
- [79] Liu J, Liu C, Huang A. Co-based zeolitic imidazolate framework ZIF-9 membranes prepared on α -Al₂O₃ tubes through covalent modification for hydrogen separation. *Int J Hydrogen Energy* 2020;45:703–11. <https://doi.org/10.1016/j.ijhydene.2019.10.230>.
- [80] Yang T, Shi GM, Chung TSC. Symmetric and asymmetric zeolitic imidazolate frameworks (ZIFs)/Polybenzimidazole (PBI) nanocomposite membranes for hydrogen purification at high temperatures. *Adv Energy Mater* 2012;2:1358–67. <https://doi.org/10.1002/aenm.201200200>.
- [81] Etxeberria-Benavides M, Johnson T, Cao S, Zornoza B, Coronas J, Sanchez-Lainez J, et al. PBI mixed matrix hollow fiber membrane: influence of ZIF-8 filler over H₂/CO₂ separation performance at high temperature and pressure. *Separ Purif Technol* 2020;237:116347. <https://doi.org/10.1016/j.seppur.2019.116347>.
- [82] Ma X, Wu X, Caro J, Huang A. Polymer composite membrane with penetrating ZIF-7 sheets displays high hydrogen permselectivity. *Angew Chem Int Ed* 2019;58:16156–60. <https://doi.org/10.1002/anie.201911226>.
- [83] Wu X, Liu W, Wu H, Zong X, Yang L, Wu Y, et al. Nanoporous ZIF-67 embedded polymers of intrinsic microporosity membranes with enhanced gas separation performance. *J Membr Sci* 2018;548:309–18. <https://doi.org/10.1016/j.memsci.2017.11.038>.
- [84] Kim JS, Moon SJ, Wang HH, Kim S, Lee YM. Mixed matrix membranes with a thermally rearranged polymer and ZIF-8 for hydrogen separation. *J Membr Sci* 2019;582:381–90. <https://doi.org/10.1016/j.memsci.2019.04.029>.
- [85] Nanosheets NZ. Mixed membranes comprising carboxymethyl cellulose as capping agent and gas barrier matrix. <https://doi.org/10.3390/polym10121340>; 2018.
- [86] Ghanem AS, Ba-shammakh M, Usman M, Khan MF, Dafallah H, Habib MAM, et al. High gas permselectivity in ZIF-302/polyimide self-consistent mixed- matrix membrane, vol. 48513; 2019. p. 1–11. <https://doi.org/10.1002/app.48513>.
- [87] Yang T, Chung TS. High performance ZIF-8/PBI nanocomposite membranes for high temperature hydrogen separation consisting of carbon monoxide and water vapor. *Int J Hydrogen Energy* 2013;38:229–39. <https://doi.org/10.1016/j.ijhydene.2012.10.045>.
- [88] Karatay E, Kalipçılar H, Yilmaz L. Preparation and performance assessment of binary and ternary PES-SAPO 34-HMA based gas separation membranes. *J Membr Sci* 2010;364:75–81. <https://doi.org/10.1016/j.memsci.2010.08.004>.
- [89] Li D, Zhu HY, Ratnac KR, Ringer SP, Wang H. Synthesis and characterization of sodalite-polyimide nanocomposite membranes. *Microporous Mesoporous Mater*

- 2009;126:14–9. <https://doi.org/10.1016/j.micromeso.2009.05.014>.
- [90] Zornoza B, Téllez C, Coronas J. Mixed matrix membranes comprising glassy polymers and dispersed mesoporous silica spheres for gas separation. *J Membr Sci* 2011;368:100–9. <https://doi.org/10.1016/j.memsci.2010.11.027>.
- [91] Weng TH, Tseng HH, Wey MY. Fabrication and characterization of poly(phenylene oxide)/SBA-15/carbon molecule sieve multilayer mixed matrix membrane for gas separation. *Int J Hydrogen Energy* 2010;35:6971–83. <https://doi.org/10.1016/j.ijhydene.2010.04.024>.
- [92] Casado-Coterillo C, Soto J, Jimaré MM, Valencia S, Corma A, Téllez C, et al. Preparation and characterization of ITQ-29/polysulfone mixed-matrix membranes for gas separation: effect of zeolite composition and crystal size. *Chem Eng Sci* 2012;73:116–22. <https://doi.org/10.1016/j.ces.2012.01.024>.
- [93] Gorgojo P, Uriel S, Téllez C, Coronas J. Development of mixed matrix membranes based on zeolite Nu-6(2) for gas separation. *Microporous Mesoporous Mater* 2008;115:85–92. <https://doi.org/10.1016/j.micromeso.2007.11.046>.
- [94] Basu S, Khan AL, Cano-Odena A, Liu C, Vankelecom IFJ. Membrane-based technologies for biogas separations. *Chem Soc Rev* 2010;39:750–68. <https://doi.org/10.1039/b817050a>.
- [95] Kumbar SM, Selvam T, Gellermann C, Storch W, Ballweg T, Breu J, et al. ORMOCERS (organic-inorganic hybrid copolymers)-zeolite Beta (BEA) nanocomposite membranes for gas separation applications. *J Membr Sci* 2010;347:132–40. <https://doi.org/10.1016/j.memsci.2009.10.014>.
- [96] Golemme G, Bruno A, Manes R, Muoio D. Preparation and properties of superglassy polymers - zeolite mixed matrix membranes. *Desalination* 2006;200:440–2. <https://doi.org/10.1016/j.desal.2006.03.396>.
- [97] Husain S, Koros WJ. Mixed matrix hollow fiber membranes made with modified HSSZ-13 zeolite in polyetherimide polymer matrix for gas separation. *J Membr Sci* 2007;288:195–207. <https://doi.org/10.1016/j.memsci.2006.11.016>.
- [98] Gong X, Wang Y, Kuang T. ZIF-8-Based membranes for carbon dioxide capture and separation. <https://doi.org/10.1021/acssuschemeng.7b03613>; 2017.
- [99] Borghei M, Laocharoen N, Kibena-pöldsepp E, Johansson L. Applied Catalysis B: Environmental Porous N, P-doped carbon from coconut shells with high electrocatalytic activity for oxygen reduction: alternative to Pt-C for alkaline fuel cells. *Appl Catal B Environ* 2017;204:394–402. <https://doi.org/10.1016/j.apcatb.2016.11.029>.
- [100] Szali N, Mamat R, Siregar JP, Gunawan T, Salleh WNW, Nordin NAHM. PI/NCC carbon membrane: effect of additives loading towards hydrogen separation. *IOP Conf Ser Mater Sci Eng* 2020;736. <https://doi.org/10.1088/1757-899X/736/2/022002>.
- [101] Bucior BJ, Chen DL, Liu J, Johnson JK. Porous carbon nanotube membranes for separation of H₂/CH₄ and CO₂/CH₄ mixtures. *J Phys Chem C* 2012;116:25904–10. <https://doi.org/10.1021/jp3098022>.
- [102] Skoulidas AI, Sholl DS, Johnson JK. Adsorption and diffusion of carbon dioxide and nitrogen through single-walled carbon nanotube membranes. *J Chem Phys* 2006;124. <https://doi.org/10.1063/1.2151173>.
- [103] Nour M, Berean K, Balendhran S, Ou JZ, Du Plessis J, McSweeney C, et al. CNT/PDMS composite membranes for H₂ and CH₄ gas separation. *Int J Hydrogen Energy* 2013;38:10494–501. <https://doi.org/10.1016/j.ijhydene.2013.05.162>.
- [104] Surya Murali R, Sridhar S, Sankarshana T, Ravikumar YVL. Gas permeation behavior of pebax-1657 nanocomposite membrane incorporated with multiwalled carbon nanotubes. *Ind Eng Chem Res* 2010;49:6530–8. <https://doi.org/10.1021/ie9016495>.
- [105] Mittal G, Dhand V, Rhee KY, Park SJ, Lee WR. A review on carbon nanotubes and graphene as fillers in reinforced polymer nanocomposites. *J Ind Eng Chem* 2015;21:11–25. <https://doi.org/10.1016/j.jiec.2014.03.022>.
- [106] Weng TH, Tseng HH, Wey MY. Preparation and characterization of multi-walled carbon nanotube/PBNPI nanocomposite membrane for H₂/CH₄ separation. *Int J Hydrogen Energy* 2009;34:8707–15. <https://doi.org/10.1016/j.ijhydene.2009.08.027>.
- [107] Sharma A, Kumar S, Tripathi B, Singh M, Vijay YK. Aligned CNT/Polymer nanocomposite membranes for hydrogen separation. *Int J Hydrogen Energy* 2009;34:3977–82. <https://doi.org/10.1016/j.ijhydene.2009.02.068>.
- [108] Kumar R, Kamakshi Kumar M, Awasthi K. Functionalized Pd-decorated and aligned MWCNTs in polycarbonate as a selective membrane for hydrogen separation. *Int J Hydrogen Energy* 2016;41:23057–66. <https://doi.org/10.1016/j.ijhydene.2016.09.008>.
- [109] Series IOPC, Science M. PI/NCC carbon Membrane : effect of additives loading towards hydrogen separation PI/NCC carbon Membrane : effect of additives loading towards hydrogen separation. <https://doi.org/10.1088/1757-899X/736/2/022002>; 2020.
- [110] Wang F, Zhang B, Liu S, Wu Y, Wang T, Qiu J. Investigation of the attapulgite hybrid carbon molecular sieving membranes for permanent gas separation. *Chem Eng Res Des* 2019;151:146–56. <https://doi.org/10.1016/j.cherd.2019.09.011>.
- [111] Tseng HH, Shiu PT, Lin YS. Effect of mesoporous silica modification on the structure of hybrid carbon membrane for hydrogen separation. *Int J Hydrogen Energy* 2011;36:15352–63. <https://doi.org/10.1016/j.ijhydene.2011.08.060>.
- [112] Geiszler VC, Koros WJ. Effects of polyimide pyrolysis conditions on carbon molecular sieve membrane properties. *Ind Eng Chem Res* 1996;35:2999–3003. <https://doi.org/10.1021/ie950746j>.
- [113] Kumar S, Sharma A, Tripathi B, Srivastava S, Agrawal S, Singh M, et al. Enhancement of hydrogen gas permeability in electrically aligned MWCNT-PMMA composite membranes. *Micron* 2010;41:909–14. <https://doi.org/10.1016/j.micron.2010.05.016>.
- [114] Al-mufachi NA, Rees NV. Hydrogen selective membranes: a review of palladium-based dense metal membranes. *Renew Sustain Energy Rev* 2015;47:540–51. <https://doi.org/10.1016/j.rser.2015.03.026>.
- [115] Wang M, Wang Z, Zhao S, Wang J, Wang S. Chinese Journal of Chemical Engineering Recent advances on mixed matrix membranes for CO₂ separation ☆. *Chin J Chem Eng* 2017;25:1581–97. <https://doi.org/10.1016/j.cjche.2017.07.006>.
- [116] Malek K, Coppens MO. Knudsen self- and Fickian diffusion in rough nanoporous media. *J Chem Phys* 2003;119:2801–11. <https://doi.org/10.1063/1.1584652>.
- [117] Kajama MN, Nwogu NC, Gobina E. ScienceDirect Preparation and characterization of inorganic membranes for hydrogen separation. *Int J Hydrogen Energy* 2016;41:8221–7. <https://doi.org/10.1016/j.ijhydene.2015.11.179>.
- [118] Lee KH, Hwang ST. The transport of condensable vapors through a microporous vycor glass membrane. *J Colloid Interface Sci* 1986;110:544–55. [https://doi.org/10.1016/0021-9797\(86\)90407-8](https://doi.org/10.1016/0021-9797(86)90407-8).

- [119] Karimi MB, Hassanajili S, Khanbabaie G. Capillary condensation mechanism for gas transport in fiber reinforced poly (ether-b-amide) membranes. *Chem Eng Res Des* 2019;148:180–90. <https://doi.org/10.1016/j.cherd.2019.06.002>.
- [120] Nenoff* Nwo and TM. Membranes for hydrogen separation nathan. *Trans Am Soc Artif Intern Organs* 2007;8:373–7. <https://doi.org/10.1097/00002480-196204000-00075>.
- [121] Li MP, Zhang X, Zhang H, Liu WL, Huang ZH, Xie F, et al. Hydrophilic yolk-shell ZIF-8 modified polyamide thin-film nanocomposite membrane with improved permeability and selectivity. *Separ Purif Technol* 2020;247:116990. <https://doi.org/10.1016/j.seppur.2020.116990>.
- [122] Nayeboossadri S, Speight JD, Book D. Hydrogen separation from blended natural gas and hydrogen by Pd-based membranes. *Int J Hydrogen Energy* 2019;44:29092–9. <https://doi.org/10.1016/j.ijhydene.2019.03.044>.
- [123] Ahmad AL, Jawad ZA, Low SC, Zein SHS. A cellulose acetate/multi-walled carbon nanotube mixed matrix membrane for CO 2/N 2 separation. *J Membr Sci* 2014;451:55–66. <https://doi.org/10.1016/j.memsci.2013.09.043>.
- [124] Wang M, Wang Z, Li N, Liao J, Zhao S, Wang J, et al. Relationship between polymer-filler interfaces in separation layers and gas transport properties of mixed matrix composite membranes. *J Membr Sci* 2015;495:252–68. <https://doi.org/10.1016/j.memsci.2015.08.019>.
- [125] Zhang L, He G, Zhao W, Tan M, Li X. Effect of formamide additive on the structure and gas permeation performance of polyetherimide membrane. *Separ Purif Technol* 2010;73:188–93. <https://doi.org/10.1016/j.seppur.2010.03.024>.
- [126] Arabi A, Kargari A. ScienceDirect Preparation , characterization and gas permeation properties of PDMS/PEI composite asymmetric membrane for effective separation of hydrogen from H₂/CH₄ mixed gas. *Int J Hydrogen Energy* 2013;39:1410–9. <https://doi.org/10.1016/j.ijhydene.2013.11.004>.
- [127] Arabi A, Kargari A, Bahrami M, Laki S. Journal of industrial and engineering chemistry separation of hydrogen from methane by asymmetric PEI membranes. *J Ind Eng Chem* 2013;19:1680–8. <https://doi.org/10.1016/j.jiec.2013.02.006>.
- [128] Itta AK, Tseng HH, Wey MY. Effect of dry/wet-phase inversion method on fabricating polyetherimide-derived CMS membrane for H₂/N₂ separation. *Int J Hydrogen Energy* 2010;35:1650–8. <https://doi.org/10.1016/j.ijhydene.2009.12.069>.
- [129] Peng F, Liu J, Li J. Analysis of the gas transport performance through PDMS/PS composite membranes using the resistances-in-series model. *J Membr Sci*; 2003. [https://doi.org/10.1016/S0376-7388\(03\)00293-X](https://doi.org/10.1016/S0376-7388(03)00293-X).
- [130] Zhang L, He G, Zhao W, Nie F, Li X, Tan M. Studies on the coating layer in a PTFPMS/PEI composite membrane for gaseous separation. *J Membr Sci* 2011;371:141–7. <https://doi.org/10.1016/j.memsci.2011.01.027>.
- [131] Ji P, Cao Y, Jie X, Li M, Yuan Q. Impacts of coating condition on composite membrane performance for CO 2 separation71; 2010. p. 160–7. <https://doi.org/10.1016/j.seppur.2009.11.015>.
- [132] Mohshim DF, Mukhtar H, Man Z, Nasir R. Latest development on membrane fabrication for natural gas purification review. 2013. p. 2013.
- [133] Gaowen Z, Jiuxin J, Liu Jianing. High proton conducting SPEEK/SiO 2/PWA composite membranes for direct methanol fuel cells. 2011. p. 417–21. <https://doi.org/10.1007/s11595-011-0241-1>.
- [134] Gohil JM, Choudhury RR. Chapter 2 - introduction to nanostructured and nano-enhanced polymeric membranes: preparation, function, and application for water purification. Elsevier Inc.; 2019. <https://doi.org/10.1016/B978-0-12-813926-4.00038-0>.
- [135] Sahoo SK, Manoharan B. Introduction: why perovskite and perovskite solar Cells? Elsevier Inc.; 2018. <https://doi.org/10.1016/B978-0-12-812915-9.00001-0>.