SUSTAINABLE ENGINEERING

(eISSN:3083-8231)
Review
Volume 3, 2026
https://doi.org/10.51200/susten.v3i1.7682

Mixed Matrix Membrane for Hydrogen Recovery: Development, Challenges and Future Outlooks

Nor Azwana Ariana Ibrahim[1], Nur Hazmiera Puteri Hazmy[1], Dg Nur Aliyah Jainuddin[1], Nureyn Hameesya Aqilah Mohd Haizam[1], Laura Fabrick[1], Noor Maizura Ismail[1*]

[1] Faculty of Engineering, Universiti Malaysia Sabah Jalan UMS, 88400 Kota Kinabalu Sabah
*Correspondence: maizura@ums.edu.my

*ORCID ID: 0000-0002-4469-0993
Received: 19 May 2026, Accepted: 15 July 2026

Abstract: Hydrogen is widely seen as a clean and sustainable energy option but extracting and recovering it efficiently still poses significant challenges. In recent years, membrane separation has gained attention as an effective method for purifying hydrogen due to its promising performance and potential for practical application. Mixed-matrix membranes (MMMs) have gained significant attention among membrane types because of their potential to improve separation performance. This review examines recent progress in innovative MMM materials tailored to enhance hydrogen recovery efficiency. Researchers blend polymers with advanced inorganic fillers like zeolites, metal-organic frameworks (MOFs), and carbon-based materials. The discussion begins with an overview of hydrogen purification and existing MMM technologies. The evolution of material selection and integration of advanced inorganic fillers with compatible polymers was also discussed. This review highlighted the complex interactions between fillers and polymer matrices which play an important role in determining the membrane morphology, stability, and selectivity. Few of MMMs technology separation performance were compared in terms of hydrogen selectivity across various fillers and polymers. Lastly, this work addresses existing challenges such as high temperature, pressure and the presence of contaminants can lead to instability.

Keywords: mixed-matrix membrane; hydrogen recovery; zeolites; metal-organic frameworks; carbon-based; selectivity

1. Introduction

The global energy transition seeks to address climate change and environmental degradation and is propelled by technological developments and political agreements [1]. To address the gap between supply and demand, hydrogen has become a vital energy source, especially when used alongside renewable energy. Recovering hydrogen from industrial waste streams presents a valuable opportunity to meet the rising demand for this fuel [2]. Currently, up to 0.5 Mt of hydrogen with concentrations above 60 vol% are either released or underused in streams like coke oven gas, methanol purge gas (MPG), and ammonia purge gas (APG). While recovering hydrogen from these industrial waste streams holds great potential, its economic feasibility is limited by high separation costs, which can account for as much as 70% of the total production expenses [3]. Therefore, it is crucial to create low-footprint, efficient technologies in order to lower these expenses. A possible solution is membrane technologies, which use less energy and operate more freely than conventional gas separation techniques [4].

The concept of hydrogen recovery emerged from the need to efficiently capture and purify hydrogen produced as a by-product in industrial processes like steam methane reforming and gasification. Despite their effectiveness, conventional techniques for hydrogen separation including pressure swing adsorption (PSA) and cryogenic distillation are costly and require a large amount of energy to operate. PSA works by adsorbing contaminants at high pressures to produce pure hydrogen, but because it is cyclic, it has low recovery rates (65–90%) and high operating costs. Despite its potential for greater recovery, cryogenic distillation necessitates extremely low temperatures, which limits the recovered hydrogen purity to 99% and increases energy costs. These limitations have prompted research into membrane-based systems, which provide scalable and energy-efficient hydrogen recovery methods [5]. The cost-effectiveness, energy efficiency, and modular design of membrane separation make it an attractive technology for hydrogen purification and supporting carbon capture, storage, and utilisation (CCSU) initiatives for hydrogen recovery. This allows for simple installation of existing plants [6].

MMMs provide an efficient and economical solution for hydrogen separation, outperforming traditional techniques like PSA and cryogenic distillation. This membrane works through a solution-diffusion process, allowing hydrogen to pass through without changing phases. By integrating inorganic fillers such as zeolites, metal-organic frameworks (MOFs), and graphene, MMMs address the typical compromise between permeability and selectivity found in purely polymer-based membranes [5]. The fillers improve separation efficiency by enhancing hydrogen permeability and selectively blocking other gases. Additionally, using binary filler combinations in MMMs generates synergistic effects that further optimize performance. In contrast to PSA and cryogenic distillation, which require large, custom-built infrastructure, MMMs are modular and can be easily integrated into existing systems.

Recent research on mixed matrix membranes (MMMs) has focused on enhancing hydrogen separation performance through advanced filler engineering and improved interfacial compatibility, particularly using high-aspect-ratio nanofillers [37], functionalized MOFs, and hybrid systems to improve dispersion, reduce defects, and strengthen polymer–filler interactions [38]. This study offers an integrated view of MMMs for hydrogen recovery by highlighting the intricate filler–polymer interactions controlling morphology, stability, and selectivity, in contrast to earlier reviews that primarily target particular fillers or polymer systems. It also highlights the limited comparative studies under consistent conditions and the fragmented treatment of operational challenges such as high temperature, pressure, and contaminants, thereby consolidating these aspects to better link material design with real-world hydrogen separation performance and future application needs.

2. Tailored Materials for Functional Mixed Matrix Membranes (MMMs)

Mixed matrix membranes (MMMs) have become a promising technology for hydrogen recovery by combining polymeric matrices with high-performance fillers to improve gas separation performance [7]. These composite membranes leverage the unique characteristics of both the polymer matrix and fillers, such as zeolites, metal-organic frameworks (MOFs), and carbon nanotubes, to enhance hydrogen permeability and selectivity ([8-10]). The polymer matrix in a mixed matrix membrane (MMMs) is the continuous organic phase that forms the

main body of the membrane. It is typically a processable polymer that provides mechanical strength, flexibility, and processability.

The polymer matrix is the medium in which the inorganic fillers are dispersed to create the MMMs structure [7]. An inorganic filler is a solid material integrated into the polymer matrix to enhance membrane performance. These fillers can be porous or molecular sieve materials, such as zeolites, metal-organic frameworks (MOFs), or porous organic frameworks (POFs). Their role is to augment gas separation by providing additional selective paths for gas molecules, improving permeability and/or selectivity to a level beyond what is possible with the polymer alone [11].

Figure 1 represents the process of gas transportation through a mixed matrix membrane (MMM). The structure of the MMM is unique and includes a combination of a continuous polymer matrix and dispersed inorganic fillers such as zeolites, MOFs, carbon, or silica [42]. The feed gas comes into the membrane from the top side of the membrane and consists of various gas components. Fast-permeable gases like H_2, He, and CO_2 can penetrate through the membrane faster due to their low molecular size, diffusivity, or affinity with the material of the membrane [39]. In case of hydrogen recovery, H_2 has the ability to penetrate faster due to its low molecular size, which means that it can diffuse through the polymer free volume and selective pores of the inorganic fillers.

At the same time, slow-permeable gases such as N_2 and CH_4 move slower due to high molecular size, diffusivity, or affinity with the material of the membrane. That is why their permeation is limited and only a small number of molecules penetrate to the permeate side. The unique structure of MMM is essential since the polymer matrix serves as the primary medium for diffusion, while the inorganic fillers act as selective pathways for small molecules such as H_2 [40]. The inorganic fillers facilitate the movement of hydrogen at a fast pace but make it difficult for larger or slower gases to move through.

Another critical factor that influences the diffusion process in MMM is the interface region between the polymer and filler. The existence of good polymer–filler interactions enhance selective gas transfer, while poor interaction leads to the presence of nonselective defects in the membrane structure [41]. Additionally, thinner membranes enhance gas transfer, whereas thick membranes increase resistance. In hybrid structures of polymer and inorganic filler, H_2 molecules have easy access and can be captured as the permeate gas, while other molecules such as N_2 and CH_4 experience resistance. Therefore, MMM is an ideal choice for hydrogen recovery.

There is a significant amount of sustainability value in the development of MMM for hydrogen recovery, as this kind of technology can offer an opportunity for a greener and energy-efficient method of separation compared to other existing technologies used for hydrogen recovery. Technologies such as pressure swing adsorption, cryogenic separation, and chemical absorption normally work at high pressures or cryogenic temperatures or need chemical solvents. This can result in energy inefficiency, increased cost, and increased environmental footprint [43]. In comparison, MMM allows the separation of hydrogen using membranes. One of the most significant benefits of MMMs related to sustainability is the possibility of energy savings. Being a membrane process that does not involve phase change or very low temperatures, energy consumption may be lower than cryogenic purification

processes [43, 44]. The use of fillers in polymer membranes can also help increase the selectivity and permeability of hydrogen, thereby ensuring that hydrogen passes through and large gas molecules such as carbon dioxide, methane, or nitrogen do not penetrate.

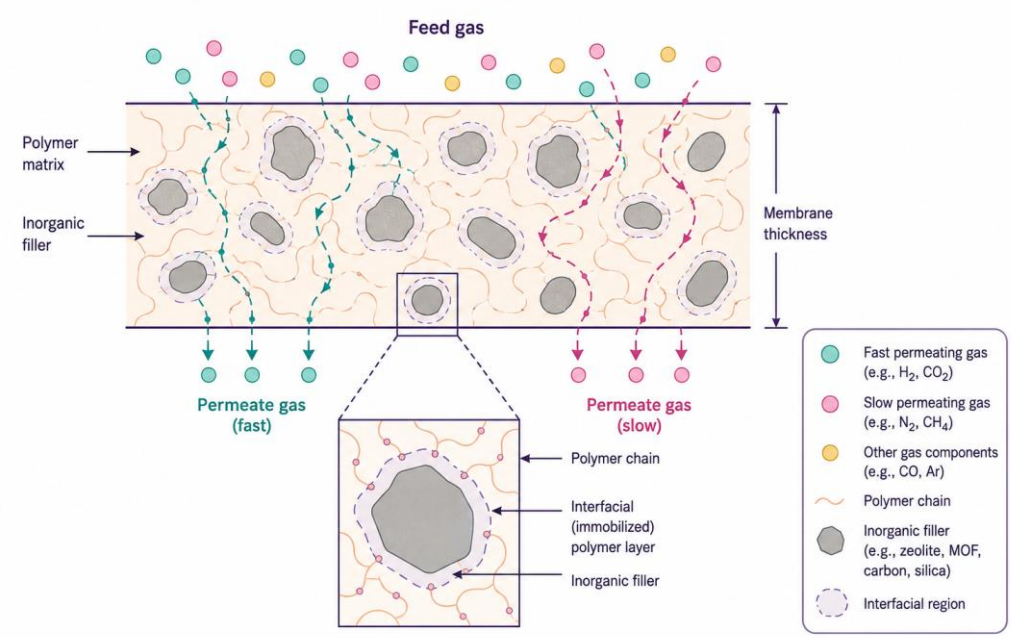

Figure 1: Schematic illustration of gas transport through mixed matrix membrane (MMM)

From an environmental perspective, MMMs could play an important role in reducing greenhouse gases due to the reduced amount of energy needed for the hydrogen purification process. Lower energy consumption implies less fuel usage and therefore reduces the carbon footprint in industries that produce or purify hydrogen from gas mixtures [45]. Moreover, MMMs could lower the use of chemicals that serve as solvents in other conventional processes, thus decreasing pollution from these chemicals. The development of better MMM stability, compatibility between filler and membranes, and their performance over time would facilitate this process.

2.1 Polymer matrix

One of the polymer matrix materials widely used due to its good selectivity and mechanical properties for hydrogen separation is Matrimid®. Pure Matrimid® membranes, however, often require optimization to improve permeability and selectivity to reach industrial purity levels (Ortiz et al., 2021). There are also sophisticated polymers such as 6FCl-APAF that have been synthesized and thermally rearranged to improve hydrogen permeability and selectivity, especially when incorporated with porous polymer networks (PPNs)[11]. This polymer undergoes a thermal rearrangement process that reorganizes its molecular structure, improving the permeability of hydrogen and selectivity [12].

Other than that, polyetherimide (PEI) is another polymer commonly used as a base material for MMMs for hydrogen separation [8]. Due to its high thermal and mechanical stability, PEI is resistant to high temperatures and mechanical stress without degrading. These properties are appropriate for harsh industrial environments where membranes need to be functional for long periods of time. Polysulfone is widely utilized as a polymer matrix in

MMMs due to its high-performance thermoplastic properties [13]. Due to its outstanding mechanical strength, thermal stability, and resistance to oxidation and hydrolysis, it is an ideal material for use in harsh chemical and thermal environments. Polysulfone membranes are applied in gas separation applications on an industrial scale since they possess good processability and stable operation under operating conditions.

2.2 Inorganic Filler

ZIF-8 and ZIF-90 are metal-organic framework (MOF) forms that are hugely applied as inorganic fillers for MMMs [5]. The frameworks are made up of metal ions bound by organic linkers, leading to a highly porous framework. The distinctive morphology of zeolites (very small, uniform pores) makes them suitable as sieves that selectively adsorb, and separate gases depending on the shape and size of molecules [14]. Metal hydrides like LaNI5, are another class of inorganic fillers used in MMMs for hydrogen separation [15]. Metal hydrides are metal salts like lanthanum (La) and nickel (Ni) that absorb and desorb hydrogen based on the environment [16]. When incorporated into Matrimid® membranes, these fillers enhance hydrogen uptake and membrane performance overall by enabling more efficient separation of hydrogen.

Porous polymer networks (PPNs) are also utilized as fillers in mixed matrix membranes. PPNs are polymer networks that have high porosity, making it easier to have improved gas transport properties [9]. The membrane's overall permeability is enhanced as gases can pass through it easily. Alumina nanoparticles are commonly used as inorganic fillers in mixed matrix membranes because of their mechanical strength, thermal stability, and high surface area [17]. On dispersion in the polymer matrix, alumina nanoparticles create an extremely effective interface that enhances the overall performance of the membrane. Recent progress has focused on material selection and fabrication optimization to improve hydrogen permeability without sacrificing or even with improved selectivity. The choices of polymer materials and fillers are critical in possessing good hydrogen permeation and rejecting larger gas molecules. These are the material choices and developments for the recent advancement of MMMs for hydrogen recovery. Table 1 shows the latest research works involving MMM for hydrogen separation.

Table 1: Recent works for mixed matrix membrane for hydrogen separation

Polymer Matrix + inorganic Filler	**H_2 permeability permeance**	**Selectivity (H_2/CO_2)**	**Development**	**References**
6FCl-APAF (hydroxy-polyamide) + Porous Polymer Network (PPN)	Increased with PPN load up to (30%)	Good for H_2/CH_4 and H_2/N_2; selectivity drops for H_2/CO_2 after thermal rearrangement	Thermal rearrangement increases permeability but reduces H_2/CO_2 selectivity; surpasses Robeson upper bounds	[9], [12]

Matrimid® + LaNi5 metal hydride	107 Barrer	14.5	Metal hydride filler selectively absorbs H_2, enhancing permeability and selectivity	[3], [15]
Polyetherimide (PEI) + Alumina nanoparticles	H_2 permeance 1065 GPU (units of GPU)	not specified	Hollow fiber MMMs with filler size-dependent permeation; good separation performance	[8], [10], [18]
Polysulfone + Zeolite-based fillers	Improved over pure polysulfone	H_2/N_2 selectivity up to 105	Zeolite fillers enhance permeability and selectivity, molecular sieving effect	[5], [14]

Based on Table 1, recent advances in MMMs for hydrogen recovery have revolved around several polymers such as 6FCl-APAF, Matrimid®, polyetherimide (PEI) and polysulfone with various inorganic fillers to enhance the separation performance. All these developments highlight the importance of optimizing polymer-filler compatibility, filler content, and membrane structure to balance permeability and selectivity to facilitate the realistic use of MMMs for efficient hydrogen purification. These advancements in MMMs combine the high permeability and selectvitity of inorganic fillers with the mechanical stability and processability of polymers to develop membranes that surpass the limitation of traditional polymer performance. Such membranes show great potential for industrial hydrogen recovery, provifing energy-efficient and cost-effective alternatives to common separation methods like cryogenic distillation and PSA.

3. Interfacial Interactions Between Inorganic Fillers and Polymer Matrices

In industrial applications like petrochemical refining, fuel cells and ammonia production, hydrogen recovery is a critical gas separation process. It involves the separation and recovery of hydrogen gas (H_2) from gas mixtures, so that it can be reused instead of being wasted or lost. This contributes to both economic efficiency and environmental sustainability. Over the past decade, the performance of hydrogen recovery systems has significantly increased with the invention of mixed matrix membranes (MMMs). MMMs combine the processability and mechanical flexibility of polymeric matrices with enhanced gas selectivity, permeability and thermal stability provided by the inorganic fillers. This synergy provides considerable advantages under harsh conditions such as high operating temperatures or the separation of complex multicomponent mixtures. However, the MMMs effectiveness is largely dependent on the interfacial interaction between the inorganic fillers and polymer matrix. Poor compatibility at the interface, resulting in defects such as interfacial voids or filler aggregation should be minimized, as it compromises the membrane's selectivity and permeability.

Therefore, it is crucial to comprehend the interaction between inorganic fillers and polymers to achieve greater hydrogen recovery performance by MMMs.

Several common inorganic fillers used in MMMs include calcium carbonate, zeolites, carbon nanotubes, calcium hydroxide (lime), metal organic frameworks (MOFs) and portland cement [19]. These fillers enhance physical properties and create a preferred permeation pathway for selective permeability by blocking non-selective permeation routes [20]. The ordered pore structures funtions as molecular sieves, permitting smaller hydrogen molecules to pass through while blocking larger gas molecules like CO_2 and CH_4 [5]. Meanwhile, polymeric membranes are made primarily from synthetic or natural polymers, which are designed to separate gas components based on molecular size, charge, and chemical affinity. Common polymers used for gas-separation include Polysulfone (PSF), Polyethersulfone (PESf), Polyetherimide (PEI) and Polyimide (PI), all known for their excellent permeability and selectivity [21].

In MMMs, the polymer serves as the support matrix that provides mechanical flexibility and processability, supports uniform filler dispersion, and enables efficient membrane fabrication. For MMMs designed for hydrogen recovery, the interfacial interactions between inorganic fillers and polymer matrices play a critical role in determining membrane performance by influencing permeability, selectivity and long-term stability. These interactions include chemical bonding, physical adhesion and van der Waals force. For chemical bonding, strong covalent bonding is formed when the fillers are functionalized and chemically react with the polymer chains. For instance, metal-organic framework (MOFs) coated with polydopamine (PDA) form strong covalent bonds with polyimide, effectively eliminating interfacial voids and ensuring uniform filler dispersion. On the other hand, physical adhesion involves non-specific mechanical interlocking where the polymer adheres to the surface of the filler without forming chemical bonds. Simple and weak adhesion can lead to defects and reduced membrane performance. Additionally, van der Waals forces, common between polar polymers and functional groups on filler surfaces, offer moderate compatibility but may degrade at elevated temperatures or humidity. Balancing these interactions through surface functionalization, coupling agents, or optimized polymer selection is essential to minimize defects, ensuring controlled gas diffusion, and achieving efficient hydrogen recovery.

These common interface issues such as interfacial voids, rigidified polymer layer or poor filler dispersion should be minimized to maintain membrane performance as it may hinder the effectiveness of MMMs in hydrogen recovery. Interfacial voids, or gaps between the inorganic filler and polymer matrix, form non-selective pathways that reduce gas selectivity. Meanwhile, rigidified polymer layer refers to a region of limited polymer chain mobility near the filler surface, often caused by strong filler-polymer interactions. This dense layer restricts gas diffusion and reduces overall permeability. Additionally, aggregation of fillers within the polymer matrix leads to non-uniform structure and defects consequently compromises the separation efficiency. Uniform filler dispersion is essential to maintain consistent gas separation properties across the membrane. Hence, it is vital to address these interfacial issues through filler surface modification, optimized fabrication techniques, and post-treatment processes, for enhancing the effectiveness of MMMs in hydrogen recovery.

Several studies have demonstrated how polymer-filler interactions impact hydrogen recovery performance in MMMs. Chuah et al. (2021) showed that embedding the ZIF-8 particles coated with polydopamine (ZIF-8@PDA) into a polyimide matrix resulted in higher

hydrogen permeability and H_2/CO_2 selectivity compared to unmodified ZIF-8 MMMs [5]. The PDA layer formed covalent bonds with the polymer, eliminating interfacial defects effectively and improving structural integrity, which led to better selectivity and enhanced stability under harsh operating conditions. Moreover, Soto et al. (2021) developed high performance MMMs for hydrogen recovery by incorporating porous polymer networks (PPN) into an o-hydroxy polyamide (HPA) matrix (6FCI-APAF), followed by thermal rearrangement at 375 ℃ to form a polybenzoxazole framework [12]. These membranes preserved the PPN structure and exceeded the Robeson upper bound for hydrogen separation, demonstrating that strong filler–polymer synergy can significantly enhance performance under extreme conditions. Notably, even without rearrangement, the HPA-PPN MMM showed a favorable selectivity–permeability balance, while the thermal rearrangement further increases throughput and reduces the required membrane area. Furthermore, Kim et al., (2023) reported that the MMMs containing 20 wt% Zeolitic Imidazolate Framework-8 nanoplates (NZIF-8) achieved excellent separation performance, with hydrogen permeability of 1451 barrer and H_2/C_3H_8 separation factor of 283 [22]. These membranes exhibited greater mechanical properties with high thermal stability up to 300 ℃, highlighting the effectiveness of optimized filler-polymer combinations in demanding hydrogen recovery operations.

In brief, MMMs offer a viable approach for effective hydrogen recovery by combining the polymer's flexibility with the superior selectivity and stability of inorganic fillers. The compatibility and interaction at the polymer-filler interface, particularly through covalent bonding, thermal rearrangement and optimized dispersion are critical to the success of MMMs, especially in challenging industrial environments.

4. Improved Separation Efficiency in Mixed Matrix Membranes (MMMs)

Among a variety of membranes, MMMs are one of the most well-studied and promising techniques [23]. The advantage in the permeability-selectivity tradeoff has been shown by MMMs as they not only exceed the Robeson upper bound limit from 1991 but also approach or exceed the limit from 2008 in difficult gas pairs such as H_2/CH_4 and H_2/N_2 [12]. Improvements in the performance of MMMs include advancements in techniques to bypass the natural barriers and achieve increased efficiency in separation. To enhance the interaction between fillers and polymers in MMMs, researchers have been experimenting with advanced fillers, including MOFs, PAFs, and POCs, along with techniques of surface modification and structural change [24]. Additionally, careful selection of inorganic filler is also crucial for high-performance MMMs [25**].**

The effectiveness of zeolites in gas separation depends on their structure, composition, and integration with polymers. The narrow pores of most zeolites make them ideal for H_2-selective membranes. For instance, the addition of 20 wt% DDR zeolite leads to a higher permeability of hydrogen gas at 34.90 Barrer and a H_2/CH_4 selectivity of 375.27. This is because the pore size of 3.6 Å to 4.4 Å found in the DDR zeolite will ensure that small-sized H_2 gas molecules at 2.89 Å can pass through easily without the passage of large-sized CH_4 molecules at 3.8 Å [26]. Similarly, it was discovered that zeolite 4A, which has a pore diameter of 3.8 Å, could greatly improve the MMMs' H2/N2 and H2/CH4 selectivity. However, Esmaeili *et al.* addressed interfacial compatibility issues in MMMs by employing nanosizing and silanisation of zeolite 4A particles [27]. This approach increased the interaction between zeolite

4A and the PVAc matrix, which reduced particle agglomeration, promoted better filler dispersion and enhanced the microstructure of the membranes.

However, MOFs belong to one category of porous hybrid materials made up of organic ligands and metal ions or clusters in comparison to pure inorganic zeolites [28]. For instance, the application of NH_2-functionalised CAU-1-NH2 was used as a filler in poly(methyl methacrylate) (PMMA) membranes by Cao et al. (2013) [29]. With a pore size of 8Å, CAU-1 helped in the separation of H2 molecules of about 2.9 Å and larger CO2 molecules of about 3.3 Å. Hydrogen bonds interaction of hydrogen bonds between CAU-1-NH2 and the PMMA matrix made the formed MMMs have an ultrahigh H2 permeability (> 1 × 10-10 barrer) and H_2/CO_2 selectivity (>10). MMM containing 20% ZIF-L-Co had the greatest H2 permeability at 1986 barrer. Bi et al. show that embedded Co-benzenedicarboxylate MOF nanosheets (CBMNs) in a 6FDA-Durene-DABA matrix provide great H_2/CH_4 and H_2/CO_2 separation performance and increase the selectivity of H_2/CH_4 to 42 [30]. Apart from changing the filler material, post-synthetic modification of the membranes' production process helps in addressing polymer-filler interface problems. Xiang et al. prove that layer-by-layer assembled PAA/(PVP + MOF) membranes display exceptional hydrogen gas separation with 20.3 selectivity of H_2/CO_2 [31].

Recently, much attention has been directed towards the use of covalent organic frameworks (COFs) because of their remarkable features like high porosity, adjustable pore size, and stability. The investigation of COFL and COFM (Figure 2), possessing large surface area (about 441-452 m^2/g) and a pore size ranging from 1.85nm helps to enhance membrane performance. However, COFP has a lower surface area (125 m^2/g) but similar pore size exhibits stronger interactions with PVAm, leading to enhanced membrane stability and achieving a higher H_2/CO_2 selectivity of 22.2 [32].

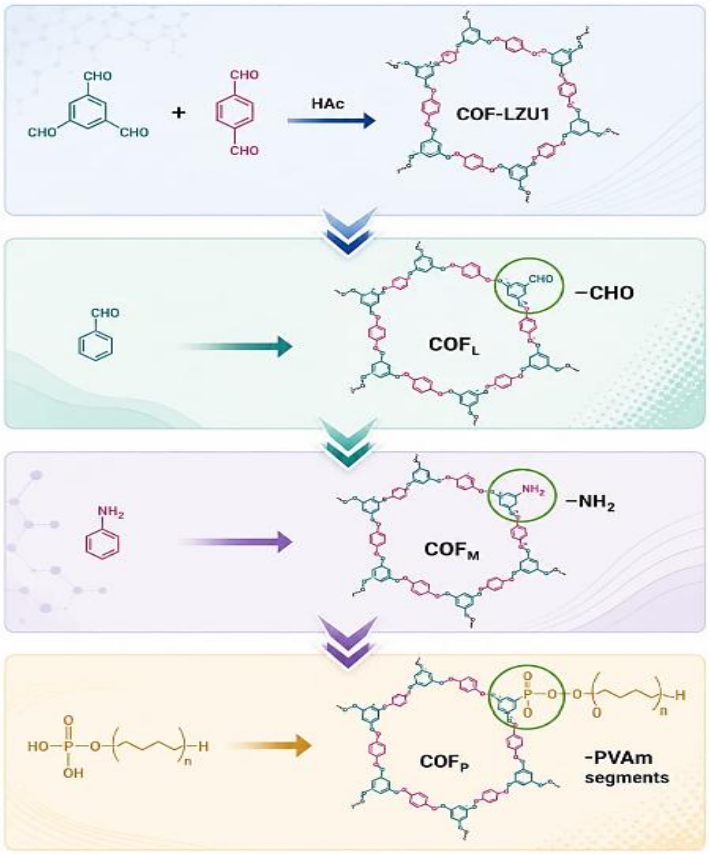

Figure 2: Synthesis of functionalized COFL, COFM, and COFP [5]

Most COFs possess 2D lamellar structures which can readily peel off into high aspect ratio nanosheets to enhance membrane selectivity [33]. Kang *et al.* reported that adding 20wt% of the 2D COF NUS-2 into a PBI membrane (Figure 3) boosted its hydrogen separation capabilities and increase the H_2/CO_2 selectivity from the 9.5 in pure PBI membrane to 31.4 in MMMs [34]. Furthermore, COFs are increasingly used to improve the selectivity and resistance to physical aging in highly permeable glassy polymers. Hou *et al.* demonstrates that the incorporation of 10 wt% of hyper-cross-linked polymer additives (PAF-1, *ρ*-DCX and V-125) into MMMs enhanced the hydrogen gas selectivity [35]. PAF-1 improves H_2/CO_2, H_2/CH_4, and H_2/N_2 selectivities while increasing permeability. ρ-DCX offers moderate selectivity gains with enhanced interfacial compatibility. PBI/ZIF-8 provides excellent H_2/CO_2 selectivity increases up to 18.7 without compromising permeability [2]. Table 2 summarizes the performance benchmarks of improved MMMs for gas separation based on recent literature.

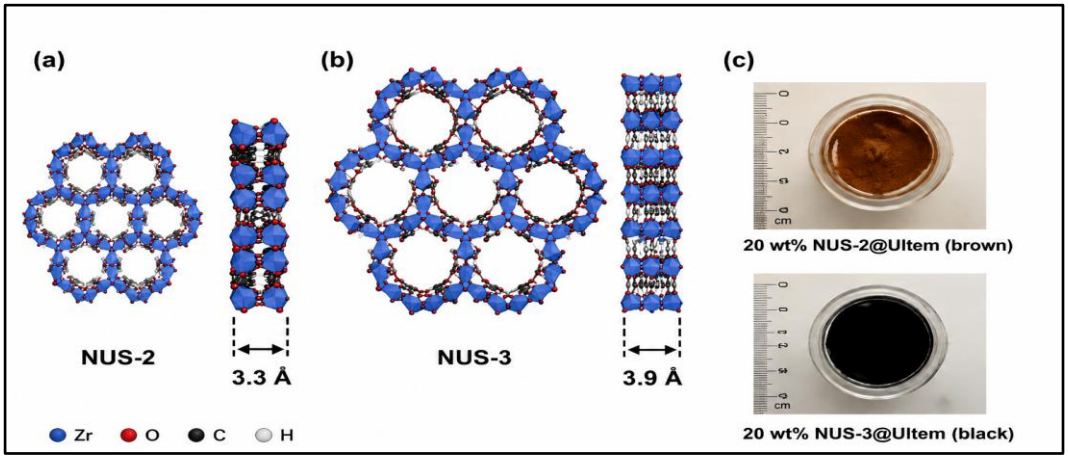

Figure 3: Crystal structures showing a pore size of (a) NUS-2 as compared to (b) NUS-3 and (c) photo images of 20 wt% NUS-2@Ultem (brown) and 20wt% NUS-3@Ultem (black) [5]

5. Challenges and Future Outlooks

Mixed matrix membranes (MMMs) have been introduced as an exciting approach for separating hydrogen as an alternative to conventional polymers and inorganic membranes, although some inherent problems hinder their widespread application. Poor compatibility between the polymer matrix and the dispersed filler remains one of the most critical factors affecting the performance of MMMs. This problem may be illustrated by using MOFs, COFs, PPNs, zeolites, carbon nanotubes, and graphene-based compounds. Such incompatibilities most often cause inferior filler dispersion and interfacial voids, non-specific flaws that provide leakage channels, degrading useful molecular sieving capabilities, and lowering selectivity. In others, polymer-filler interaction may additionally introduce rigidified zones that are obstructive to gas transport. The issue mentioned above also ties into the famous permeability/selectivity compromise, according to which an increase in one characteristic entails a decrease in the other, when trying to surpass the Robeson maximum point [36].

MMMs also encounter significant challenges when operating in actual industrial conditions. The separation of hydrogen in industry takes place at high temperatures and pressures, in addition to being conducted in an environment where there is water vapor, carbon

dioxide, or H_2S present. The majority of polymeric matrices and porous fillers are chemically and thermally unstable under these conditions and undergo degradation, plasticization, or swelling. For example, MOFs can hydrolyze, and polymer chains can deform or break due to thermal or mechanical cycling. In thermally rearranged MMMs, such as those from poly (o-hydroxyamide) (HPA) rearranged to polybenzoxazole (β-TR-PBO), the rearrangement is a high-temperature process of greater than 350 °C [12]. While this enhances permeability and selectivity, it is energetically intensive and challenging to up-scale. Most MMMs remain processed in lab scale by solution casting methods challenging up-scale to reproducible high-throughput processes. Scale-up problems such as inhomogeneous filler distribution, membrane cracking, and delamination generally pose a problem in the majority of scenarios while influencing the consistency of performance and reliability of operation.

(eISSN:3083-8231)

Table 2: The performance benchmarks of improved MMMs for gas separation based on recent literature

	Membrane			Performance			
Filler type	**Polymer matrix**	**Test Condition**	**Permeation Area (cm^2)**	**Selectivity**			**Ref.**
				H_2/CO_2	**H_2/CH_4**	**H_2/N_2**	
DD3R (20 wt%)	Matrimid® 5218	1 Bar, 25 C	11.95	-	375	-	[26]
Zeolite 4A (15 wt%)	PVAc	0.75 Bar, 30 C	-	5.3		117	[27]
Modified Zeolite 4A (15 wt%)	PVAc	0.75 Bar, 30 C	-	6.1		143	[27]
CAU-1-NH2 (15 wt%)	PMMA	3 Bar, 25 C	0.02	13	-	-	[29]
CBMN (2 wt%)	6FDA-Durene-DABA	3 Bar, 25 C	-	1.2	29	42	[30]
UiO-66-PA	PAA/PVP	3 Bar, 40 C	-	20.3	-	-	[31]
COFL	PVAm/mPSF	2 Bar	-	16.1	-	-	[32]
COFM	PVAm/mPSF	2 Bar	-	17.2	-	-	[32]
COFP	PVAm/mPSF	2 Bar	-	22.2	-	-	[32]
NUS-2 (20 wt%)	Ultem	2 Bar, 35 C	-	4.6	103	-	[34]
NUS-2 (20 wt%)	PBI	2 Bar, 35 C	-	31.4	-	-	[34]
NUS-3 (20 wt%)	Ultem	2 Bar, 35 C	-	2.2	63	-	[34]
NUS-3 (20 wt%)	PBI	2 Bar, 35 C	-	8.9	-	-	[34]
PAF-1 (10 wt%)	PTMSP	2 Bar, 25 C	-	0.7	4.8	8.3	[35]
ρ-DCX (10 wt%)	PTMSP	2 Bar, 25 C	-	0.7	2.8	5.0	[35]
ZIF-7 (80 wt%)	PBI	-	-	18.7	-	-	[2]

There have been recent publications describing extra operational and material problems related to MMMs with Matrimid and zeolitic imidazolate frameworks (ZIFs) such as ZIF-8 and ZIF-90. These membranes exhibit higher hydrogen permeability and selectivity than the parent polymer; for example, hydrogen permeability was increased by over 100% while H_2/CO_2 selectivity was increased by 76% for Matrimid/ZIF-8 and 138% for Matrimid/ZIF-90 at 30 °C [15]. At higher temperatures, however, improved performance degrades because increasing mobility of polymer chains lowers filler-polymer interfacial integrity and increases bulk gas diffusion, reducing selectivity by up to 30% from 30 °C to 80 °C. CO_2 is a particularly difficult impurity due to its high solubility and plasticizing effect on polymers, which reduces hydrogen purity in mixed gas streams such as methanol purge gas (MPG) or coke oven gas (COG). Furthermore, the study by Moral et al. (2023) revealed that while increased ZIF loading improves selectivity, it negatively impacts mechanical strength and processability due to filler agglomeration and loss of polymer integrity [15]. High loading also reduces permeability by blocking transport channels. In addition, current membranes are fabricated in the shape of flat sheets using solvent casting, which reduces the membrane area and scaling up constraints. The small surface area is a contributor to the low hydrogen recoveries (≈0.5%) and makes the technology impractical for industrial use subject to significant design enhancements. Long-term operating experience is lacking, and true performances under multicomponent gas streams ($H_2/N_2/CO/CH_4/CO_2$) are unknown.

However, the future of MMMs for hydrogen separation is promising if breakthroughs and priority research topics are attained. To begin with, interfacial compatibility among the fillers and the polymers has to be increased. This can be achieved by surface functionalization of fillers (integration of amine, carboxyl, or silane groups), in-situ polymerization of fillers in the matrix of the polymer, or mediator action of computerizing agents of chemical interaction. New fillers with specifically engineered particle sizes, fabricated pore sizes, and chemical and thermal stability will equally be crucial. Greater focus on binary and hybrid filler systems, two different fillers blended to harness synergistic properties, already seems to be able to prevent the permeability–selectivity trade-off and to achieve greater mechanical strength. Data-based material design practices will also be likely to accelerate the development of MMMs. Methods like the filler enhancement index (F index), machine learning, and molecular simulation can forecast membrane performance from structure parameters and direct synthesis to an application.

On the processing level, scalable manufacture methods like phase inversion, interfacial polymerization, 3D printing, and roll-to-roll need to be modified for MMMs with retention of filler distribution and avoidance of defect formation [5]. No less important is the need to test MMMs under conditions simulating reality, including longer-term performance testing and mixed-gas tests simulating the complexity of industrial feeds. The Matrimid/ZIF study highlights the necessity of testing under multicomponent conditions and the optimization of feed composition and operating conditions (temperature, pressure, flow rate) to achieve high H_2 purity and recovery. Additional development into hollow fiber membrane configurations and integration into hybrid systems such as MMM-PSA or MMM-distillation cascades can increase recovery efficiency considerably and reduce system footprint. Integration of the green chemistry principles of solvent-free processing, biodegradable materials usage, and low-energy

processes can also align MMM development with sustainable global goals. Lastly, interdisciplinary research efforts among materials scientists, process engineers, and industry colleagues must bridge the gap between university discovery and commercial deployment. Through joint research and continued innovation, MMMs can be developed as a clean hydrogen generation and carbon capture base technology and enabling other gas separation technology necessary for a low-carbon economy.

6. Conclusions

The reviewed articles present an extensive analysis of current advances in mixed matrix membranes (MMMs) for hydrogen recovery and their potential to become a future replacement for existing separation methods like PSA and cryogenic distillation. By introducing inorganic fillers such as zeolites, MOFs, COFs, and carbon materials into various high-performance polymer matrices (Matrimid, PEI, polysulfone), MMMs have shown remarkable hydrogen permeability and selectivity enhancement. The material compensates for the intrinsic trade-off limitations of common polymeric membranes. Filler-polymer compatibility and interface design are highlighted in the report to overcome major performance barriers. Surface modification, thermal reorganization, and nano-scale dispersion approaches play a critical role in defect reduction like interfacial voids and rigidified polymer films. The article recorded research that established that modified fillers and hybrid systems (ZIF-8@PDA, CAU-1-NH_2, PPN-enhanced MMMs) have the capability to overcome Robeson upper limits, especially for H_2/CH_4 and H_2/N_2 separations.

However, the mass production of MMMs has been prevented by various challenges such as material degradation in harsh operating conditions, low long-term stability, and scalable fabrication processes. Impurities like CO_2 that lead to plasticization and the low mechanical strength at high filler loadings were the primary disadvantages. Future research efforts should be directed towards the development of stable interfacial chemistries, hybrid filler systems, and scalable, defect-free manufacturing methods such as 3D printing or roll-to-roll processing. Performance evaluation under real, multi-component gas streams is equally important to bring MMMs out of the lab and into the field. In conclusion, while MMMs are replete with promise for effective hydrogen recovery in alignment with decarbonization goals, commercial viability will depend on interdisciplinary collaboration, scalable applications of engineering, and extreme long-term performance testing under realistic industrial conditions.

Funding

This research received no external funding.

Acknowledgments

The authors would like to thank Universiti Malaysia Sabah, particularly the Faculty of Engineering for the support in terms of resources and facilities provided during the preparation of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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