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Review Paper

Polymer Membranes for Energy-Efficient Separation and Clean Energy Applications: Materials Design, Performance Trade-Offs, and Future Perspectives

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Abstract: The low energy requirement, modularity, operational flexibility, and tunable transport properties of polymer membranes make them promising technologies for energy-efficient separation and clean energy applications. Compared with conventional thermal separation processes, membrane systems significantly reduce energy consumption and carbon emissions while enabling compact and scalable process integration. Recent advances in polymer chemistry and nanocomposite fabrication have expanded membrane applications in gas separation, desalination, wastewater treatment, solvent recovery, fuel cells, electrolyzers, and electrochemical energy storage systems. This review critically examines the structure-function relationships of membranes in relation to transport phenomena and key performance characteristics, including permeability, selectivity, conductivity, stability, and fouling resistance. Particular attention is given to high-performance materials such as polymers of intrinsic microporosity (PIMs), thermally rearranged polymers, ion-conductive polymers, and mixed-matrix membranes incorporating metal-organic frameworks, covalent organic frameworks, and two-dimensional nanofillers. Recent strategies to overcome the conventional permeability–selectivity trade-off are reviewed together with challenges related to physical aging, plasticization, chemical degradation, and large-scale manufacturability. In addition to material innovation, this review highlights recent developments in advanced fabrication techniques, machine learning-assisted membrane discovery, and sustainable circular manufacturing approaches. Unlike previous reviews focusing on individual applications, this work provides an integrated perspective connecting separation technologies and clean energy systems through common membrane design principles. The development of durable, scalable, and intelligent membrane platforms will be essential for advancing decarbonization, water security, and sustainable industrial production worldwide.

Keywords: Batteries; Clean energy; Fuel cells; Gas separation; Polymer membranes.

1. Introduction

The current context of the global push to lower greenhouse gas emissions, enhance resource efficiency and shift to more sustainable industrial systems, advanced technologies with potential for reduced energy consumption, while maintaining productivity, are in high demand. Despite their widespread use in modern chemical and environmental industries, the conventional separation processes, like distillation, evaporation, absorption, and cryogenic fractionation, are still one of the most energy-demanding unit operations [1]. The processes represent a significant portion of energy use and carbon dioxide emissions in industrial applications, and there is therefore significant motivation for seeking alternative, more efficient, and environmentally friendly processes [2]. One of

the most promising technologies to address this challenge is membrane technology. Membrane processes typically do not involve bulk phase changes, as opposed to traditional thermal separations, decreasing the amount of energy needed and streamlining the process design. Other benefits include small equipment footprint, modularity, operational flexibility, lower capital costs in specific applications and compatibility with continuous manufacturing systems [3]. Membranes are now more and more utilized in gas purification, desalination, wastewater reclamation, solvent recovery, pharmaceutical processing, and food production. Polymer materials are the leading choice of materials used for membranes due to their low density, ease of scaling up, mechanical flexibility, tunable molecular structure, and low cost [4]. The development of asymmetric membranes with hollow fibres, thin-film composites, nanofibrous structures, and ion-conductive films has been achieved using a variety of fabrication methods, such as phase inversion, electrospinning, coating, stretching, and interfacial polymerization, depending on the needs and requirements of the respective industries [5]. The transport performance of polymers can be engineered through molecular design, which enables manipulation of polymer chain rigidity, polarity, free volume, hydrophilicity, charge density, and crosslinking behavior. These properties have led to the use of polymer membranes in new applications such as clean energy [6]. In proton exchange membrane fuel cells (PEMFCs) and anion exchange fuel cells (AEMFCs), as well as water electrolyzers, redox flow batteries, lithium-based energy storage systems, and emerging electrochemical conversion devices, polymer membranes now play vital role [7]. In these systems, membranes not only serve as a separation medium but also act as an active transportation medium and have a significant impact on the efficiency, durability, and safety. Although their versatility is well-known, the traditional polymer membranes still have a number of limitations. Many materials can be shown to have an inherent permeability – selectivity trade-off as in gas separation, and this is typically depicted by the Robeson upper bound [8], [9]. Fouling, scaling, chlorine sensitivity, and mechanical compaction are among the many limitations that water-treatment membranes have. Under extreme operating conditions, electrochemical membranes can be chemically degraded, have gas crossover, change dimensions, and become less conductive [10], [11]. Other issues are related to physical aging in high free volume polymers, swelling in aggressive solvents, and difficulty in ensuring long-term performance under industrial stress [12-15]. Achieving this, significant research has been undertaken to develop next-generation membranes and architectures [15-19]. These include polymers of intrinsic microporosity, thermally rearranged polymers, block copolymers, mixed-matrix membranes (with porous fillers), nanocomposite thin films, responsive membranes, and advanced ionomers [20-25]. The mechanism of conventional membrane separation is given in Figure 1.

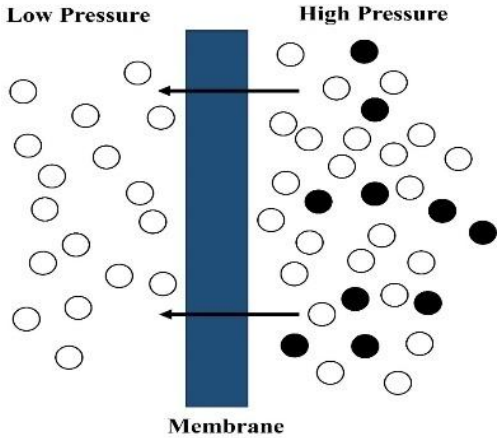

Figure 1. Schematic diagram of Conventional Membrane separation.

The efforts in these developments seek to break this conventional performance trade-off and enhance the stability and manufacturability. While there has been considerable progress in recent years, a great deal of the literature is still segregated by application sector. Most of the existing reviews are dedicated to gas separation membranes, desalination membranes, fuel-cell electrolytes, or battery separators. This specialization has resulted in valuable depth, but sometimes it loses sight of common scientific principles that connect these technologies. Nearly every membrane system has to address the following challenges: transport selectivity, morphology control, interface engineering, degradation resistance, and scalable membrane fabrication.

The novelty of the review is in its integrated and critical approach across different sectors for energy-efficient separations and clean energy applications, using polymer membranes. The review does not focus on any single field, but rather links the various categories of fields together by a shared structure–property relationship, a shared mechanism of transport, a shared method of fabrication, and a shared barrier to commercialization. Comparative performance analysis, recurrent trade-offs, advanced materials that are just coming out, and future research directions are highlighted. Thus, the most basic polymer membrane science of transport and performance is first reviewed. It then examines significant applications such as gas processing, desalination, and solvent recovery applications, before discussing the issues of membranes in fuel cells, electrolyzers, batteries, and other clean energy applications. Advanced materials and fabrication techniques are then assessed and discussed, followed by a discussion of larger-scale commercialization issues, sustainability issues, and future opportunities.

This review offers a more comprehensive navigation map for the next generation of polymer membrane technologies that are durable, scalable, and energy efficient for global decarbonization, water security, and sustainable industrial production, by combining knowledge from different fields of research that often work in isolation.

2. Fundamentals of Polymer Membrane Science

Transport mechanisms, membrane morphology, and polymer chemistry all play a role in the performance of membranes that are composed of polymers. The design of membranes, which need to be highly permeable, highly selective, durable during operation, and with low energy consumption, requires a thorough knowledge of these relationships. While strong progress has been achieved by empirical development of materials, future advances rely more and more on predictive understanding of relationships between structure and properties, as well as realistic assessment of the process-level trade-offs.

2.1 Separation Mechanisms

Membrane separations use a selectively permeable membrane to separate species passing through to a driving force, which may be one or a combination of pressure, concentration gradient, electrical potential, or temperature difference. The transport can take place in several different ways, but often by a combination of different mechanisms, depending on membrane structure and operating conditions.

2.1.1 Solution–Diffusion

Solution–diffusion model is the most widely accepted theory for the transport process in dense polymer membranes in gas separation, reverse osmosis, pervaporation, and polymer electrolytes [26-34]. Here, the molecules first sorb into the polymer matrix, then diffuse through transient free-volume elements, and finally desorb on the downstream side [26-29]. Permeability is typically expressed in terms of the product of diffusivity and solubility. This correlation poses an important design challenge since polymers with high free volume typically have good diffusion rates but poor molecular

discrimination, and polymers with strong interactions have good sorption selectivity at the expense of flux. This makes it difficult to optimize productivity as well as separation efficiency for many membrane materials [30-34]. The solution–diffusion model is still very popular, but in highly microporous polymers, swollen membranes, and mixed-matrix systems, for which non-classical transport pathways may occur, the model can be misleadingly simple. Polymer membranes are designed to selectively allow one type of species to permeate but block another type of species, as illustrated in Figure 2.

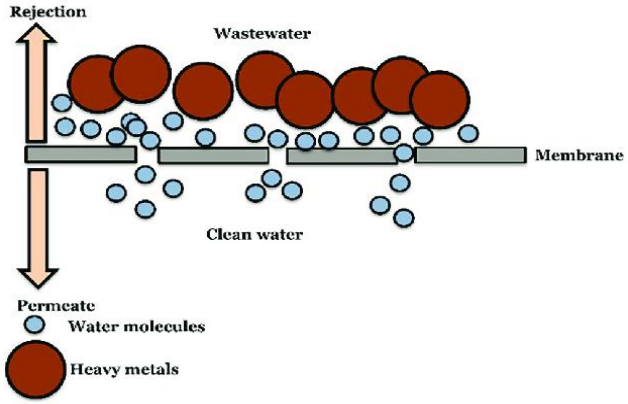

Figure 2. Separation Mechanisms [35]

2.1.2 Size Exclusion

In ultrafiltration, nanofiltration, and in some desalination processes, the separation of species occurs mainly due to steric hindrance, which occurs because of the porous membranes. Larger molecules get rejected, and smaller ones get through easily [36-38]. When pore size is on the sub-nanometer scale, the rejection performance may change by a very small amount due to changes in the pore size distribution, pore connectivity, and pore hydration [38–43]. This mechanism can allow for a greater flux than dense membranes, as there is less transport resistance. But in the presence of water or a solvent, the polymer may swell, leading to a widening of pore-size distributions and eventual loss of selectivity during extended use. This means that dimensional stability is of as much importance as the nominal pore size for the application.

2.1.3 Facilitated Transport

The facilitated transport membranes have reversible carrier sites that selectively bind the target molecules, like carbon dioxide, protons, lithium ions, or hydroxide ions [45-49]. The carriers exhibit transport properties that are enhanced over those observed for the simple solution–diffusion process and can, in part, bypass traditional permeability–selectivity considerations [50-54], [55]. These include amine functional membranes for CO_2 capture, proton-conducting ionomers for proton exchange membrane fuel cells, and hydroxide-conducting polymers for alkaline electrochemical systems. Although the membranes are promising, they often have problems due to degradation of the carrier, leaching of the carrier by the feed stream, humidity sensitivity, and degradation when the feed stream is contaminated. These stability problems are still hindering commercialization [56-59].

2.1.4 Ion Exchange and Donnan Exclusion

Ion exchange membranes have fixed charged groups which attract counter-ions and repel co-ions, allowing for selective ionic transport to occur. The Donnan exclusion effect plays a key role in electrodialysis, fuel cells, electrolyzers, and redox flow batteries [60-62]. Proton exchange membranes are mainly based on sulfonated polymers, and anion exchange membranes are extensively investigated with quaternary ammonium and other cationic chemistries [63], [64], [65]. One of the common problems in these materials is the trade-off between conductivity and dimensional stability. There is a positive correlation between the higher the ion exchange capacity, the higher the

conductivity, but also the higher the water absorbency, water swelling, and weakening of mechanical properties. So there needs to be a compromise between functional ionic groups and structural strength [66-69].

2.1.5 Coupled and Mixed Mechanisms

Modern membrane systems increasingly combine multiple transport mechanisms. Thin-film composite desalination membranes may display dense-layer solution–diffusion behavior alongside support-layer pore transport. Mixed-matrix membranes consist of polymer diffusion pathways along with molecular sieving provided by porous particles, like metal-organic frameworks or covalent organic frameworks [69–72]. The hybrid mechanisms open possibilities to overcome the drawbacks of the conventional polymers. They also make the modeling of transport more complicated and make scale-up more challenging, as the multiple resistances and interface effects have to be controlled simultaneously.

2.2 Key Performance Metrics

Polymer membrane performance is assessed based on a number of critical factors such as permeability, selectivity, flux, energy consumption, chemical resistance, and lifetime under typical operating conditions.

2.2.1 Permeability and Diffusivity

Permeability (P) is an intrinsic property of a species that is determined by both sorption and diffusion and is the ability of that species to pass through a membrane material. Permeability is typically used in gas separations in Barrer, and liquid systems are often reported per unit membrane thickness and driving force [74-76]. Permeability is desirable because it will allow a lower membrane area to be used to achieve the desired throughput, lowering the module size and capital costs. However, industrial success depends less on record permeability values than on stable permeance under mixed-feed and long-duration operating conditions.

2.2.2 Selectivity

Another important requirement in applications like carbon capture, hydrogen purification, desalination, and separation of ions is the ability to select one species over another, which is defined as the selectivity of the membrane [77], [78]. High selectivity can lower the costs required to polish the effluent downstream and increase the purity of the product [79]. However, the selectivity values obtained at ideal laboratory conditions may not reflect the actual selectivity during operation, as competitive sorption effects, moisture, impurities, and concentration polarization can have a considerable influence on the transport under practical operation conditions.

2.2.3 Flux and Productivity

Flux is the quantity of material that is transferred through the membrane area per unit time, and plays a crucial role in the productivity of plants, especially in water treatment and solvent recovery systems [46], [80]. Technologies to improve flux include the use of thinner selective layers, more porous supports, and better surface hydrophilicity of the supports. However, the high initial flux might lead to fouling, compaction, and degradation of the membrane. This is why a long-term average productivity is more useful than the lab flux value in the short term [81], [82].

2.2.4 Energy Efficiency

One of the key benefits of membrane technology is the energy saving over thermal separations. The efficiency in practice, however, is reliant on the pressure drop, pumping requirements, concentration polarization, recovery ratio, and membrane resistance [83-85]. For electrochemical systems, the influence of ionic conductivity, ohmic losses, gas crossover, and water management is

also an important consideration for efficiency [86], [87]. Therefore, low theoretical energy demand does not necessarily translate into good practical performance if auxiliary energy needs or burden for fouling control are ignored [86], [87].

2.2.5 Robeson Upper Bound and Trade-Offs

The Robeson upper bound represents the empirical correlation among permeability and selectivity found among various families of polymers for gas separations [88], [89], [90]. Materials beyond this boundary are of great interest as they represent some degree of decoupling of conventional transport constraints. Several types of polymers that have been introduced as a new class of materials have exhibited potential to overcome the inherent limitations: polymers of intrinsic microporosity, thermally rearranged polymers, carbon molecular sieve membranes, facilitated transport systems, and mixed-matrix membranes [13-91] But, just surpassing the upper bound is not enough to make it industrially relevant unless it has the processability, durability, and the possibility of scaling up the manufacturing process [92].

Commercial membranes have to be able to operate for an extended period of time when subjected to thermal, chemical, and mechanical stresses [88-90]. Plasticization, physical aging, chlorine attack, biofouling, radical degradation, hydration cycling, and shrinkage and penetration by dendrites are all challenges for gas separation membranes, water-treatment membranes, fuel-cell membranes, and battery separators, respectively [13-91]. A material that has a good initial performance but a long service life can be more economical than a material that has a high initial performance and is rapidly degraded over a short service life [92].

2.3 Structure–Property Relationships

Membrane transport properties are intrinsically related to molecular structure, shape, and manufacturing process. There is a need for rational design, which imposes the requirement for an understanding of the translation of polymer chemistry to their macroscopic separation performance.

2.3.1 Polymer Chemistry

Chain packing and free volume are strongly affected by backbone rigidity, side group functionality, polarity, branching, and crosslink density [15-94]. The rigid contorted backbones give PIMs a high internal free volume, and the sulfonic acid groups aid proton conduction [15], [93], [94]. Often, fluorinated segments will enhance the resistance to chemical attack, while crosslinking will help to reduce swelling and solvent attack [15], [93], [94]. But there are often disadvantages to chemical modification that affect not all properties [95-97]. For instance, an increase in charge density improves conductivity but may also lead to higher water uptake and dimensional instability.

2.3.2 Morphology and Free Volume

Nanoscale free-volume elements are the pathways for transport of small molecules and gases, and their size distribution and connectivity are important factors that influence both diffusivity and selectivity [98]. The semi-crystalline domains typically enhance mechanical properties, but decrease permeability, whereas the amorphous regions have the opposite characteristics of higher permeability and lower mechanical properties. Morphology is not static; it is dynamic. Free volume and membrane performance could change with time in various ways, including aging, hydration, annealing, pressure history, and exposure to solvents [99].

2.3.3 Polymer Blends and Mixed-Matrix Membranes

Complementary properties not obtainable in single-component systems can be obtained by blending polymers or using porous fillers. These include metal-organic frameworks, covalent organic frameworks, zeolites, silica, and graphene derivatives, and they have been extensively studied [100-

102]. The main drawback of mixed matrix membranes is usually the poor polymer/filler compatibility, even though the most promising laboratory results have been achieved [103], [104]. When poor interfacial adhesion occurs, non-selective voids can develop, which can negatively affect separation performance.

2.3.4 Processing and Fabrication Effects

The properties of the membrane are very sensitive to the fabrication route. The pore structure, chain packing, and defect density can be significantly affected by the choice of solvent or its evaporation rate, coagulation conditions, curing temperature, and/or the annealing history [46], [105-108]. Various techniques like "phase inversion", "electrospinning", "interfacial polymerization", "coating", and "additive manufacturing" allow the precise control of the structure [109], [110], [111]. Several reported material breakthroughs are, in part, processing breakthroughs. It's important to differentiate the improvements that are chemistry-driven versus fabrication when comparing to the literature.

3. Polymer Membranes for Energy-Efficient Separations

In recent years, membrane-based separations have become important because industries look to move away from energy-intensive, greenhouse gas-emitting, and process-complex traditional thermal separation processes. Distillation, evaporation, and cryogenic separation are also effective, but often have to be repeated, which consumes energy. In contrast, membrane processes normally do not involve a bulk phase transition and therefore offer lower specific energy demand, modular design, smaller footprint, and are easier to integrate with continuous manufacturing processes. Polymer materials are the most present materials available because they are not only tunable, but cost-effective, and compatible with various industrial streams, and can also be scaled up during fabrication. Despite these advantages, membrane separations are not considered universally superior. The feed composition, product purity required, pressure ratio, fouling tendency, and membrane life are important factors affecting their economic and technical performance. Therefore, moderate selectivity and low energy requirement are the most desirable features when using membranes, especially when compared to more energy-intensive thermal processes that produce higher purity. As a result, the most successful uses of membranes are those in which moderate selectivity and low energy consumption can outperform highly pure but energy-intensive thermal routes.

3.1 Gas Separation

Gas separation is one of the most developed and market-ready membrane applications. The polymeric membranes have been widely used for hydrogen recovery, natural gas sweetening, generation of nitrogen and oxygen, and recently for CO_2 capture [17]. In these systems, transport usually occurs by the mechanism of solution diffusion, and the gas permeability is thus controlled by both solution diffusion and condensation. The mechanical strength and processability have been achieved by the conventional glassy polymers like polysulfone, cellulose acetate, and polyimides, which have been widely used in industries. Both cellulose acetate membranes and polyimides are still useful as materials for natural gas treatment because they have relatively balanced selectivity and cost, and have higher thermal resistance and separation performance in more severe environments, respectively [17]. Table 1 shows a comparative performance trend of some polymer membranes in gas separation.

Table 1. Comparative Performance Trends of Polymer Membranes in Gas Separation

Membrane Type	Typical Target Separation	Relative Permeability	Relative Selectivity	Stability Under Pressure	Commercial Readiness	Priority
Cellulose acetate	CO_2/CH_4	Moderate	Moderate	Good	High	Plasticization resistance
Polyimide	H_2/CO_2, CO_2/CH_4	Moderate to high	High	Moderate	High	Aging control
Polysulfone	H_2/N_2, air separation	Moderate	Moderate	Good	High	Flux enhancement
PIM membranes	CO_2/N_2, CO_2/CH_4	Very high	Moderate to high	Low to moderate	Medium	Aging suppression
Thermally rearranged polymers	CO_2/CH_4, H_2/CO_2	High	High	High	Medium	Lower-cost fabrication
Mixed-matrix membranes	CO_2 capture, H_2 purification	High	High	Variable	Medium	Interface engineering
Carbon molecular sieve membranes	H_2 separation	Moderate to high	Very high	High	Low to medium	Defect-free scale-up

Conventional polymers are, however, limited by the widely known permeability–selectivity dilemma. High throughput of gas often means less purity, while highly selective membranes may need excessive area to produce industrially. Furthermore, under high pressure of carbon dioxide or condensable hydrocarbons, exposure can lead to plasticization, which will lead to chain relaxation and decreasing selectivity over time [109-111]. In recent years, advanced materials like polymers of intrinsic microporosity, thermally rearranged polymers, carbon molecular sieve precursors, and mixed-matrix membranes have thus been the focus of research. These materials have rigid or highly contorted structures that form interconnected pathways of free volume that can frequently allow for permeability in excess of conventional polymers [109-111].. However, in a few cases, the good laboratory results are not accompanied by industrial viability due to physical aging, brittleness, or processability limitations of many high free-volume polymers.

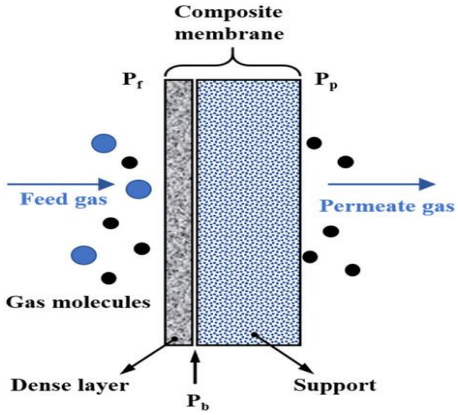

Figure 3. Gas Separation Applications [112]

The mixed-matrix membranes (MMMs) with different kinds of inorganic materials and polymers have received special attention, as they try to achieve the advantages of polymer processability and inorganic selectivity [113]. Most of the studies reported good gas transport, but the reproducibility is difficult because of the presence of voids between the interfaces, particle agglomeration and

inconsistency of the filler dispersion, which often affect the quality of the membrane [15]. A more significant aspect from a commercial point of view may be the ability of the gas separation membranes to provide stable multi-year performance under a contaminated mixed-gas feed and realistic pressure cycling conditions rather than the highest reported permeability [114].

3.2 Carbon Capture and Carbon Dioxide Separation

Separation of CO_2 is emerging as a priority area since CO_2 separation is required for decarbonization of power generation, cement, steel and chemical production and requires scalable separation technologies. These features make polymeric membranes appealing for use in this application, as they can be used continuously, are exempt from solvent regeneration penalties, and can be packaged into modular capture units [114].

The post-combustion capture from flue gas is still a challenge due to the low partial pressure of CO_2 in the flue gas, moisture, oxygen, sulphur compounds, and particulates in the flue gas. In this dilute regime, membranes need to have high CO_2 permeability and high CO_2/NF selectivity. Facilitated transport membranes with amines or ionic carriers have been demonstrated to work well, due to the selective interaction with CO2 that can lead to higher fluxes than simple diffusional transport [115]. These are typically less attractive options, due to the higher partial pressure of CO2 than in pre combustion, and the higher concentration of CO_2 than in natural gas sweetening. For these types of systems, the following membranes are still highly relevant: polyimides, cellulose acetate and mixed-matrix membranes [115]. The main challenge to the adoption of membranes is not only their performance, but also their economic competitiveness. Cost competitiveness is strongly influenced by compression energy, complexity of multi-stage design, tolerance of impurities, and frequency of membrane replacement, when compared to absorption processes. Thus, the advancement will not only rely on the new polymer chemistry but also on the process engineering.

3.3 Water and Wastewater Treatment

Table 2. Some Polymer Membranes for Water Treatment, Desalination, and Wastewater Reuse

Membrane Process	Typical Polymer Materials	Separation Range	Main Advantages	Main Challenges	Industrial Maturity
Microfiltration	PVDF, PP, PES	Suspended solids, bacteria	High flux, pretreatment value	Fouling, wetting	Very high
Ultrafiltration	PES, PSf, PVDF	Colloids, proteins, macromolecules	Low-pressure operation	Organic fouling	Very high
Nanofiltration	Polyamide composites	Divalent salts, dyes, organics	Lower pressure than RO, selective ion removal	Scaling, chlorine sensitivity	High
Reverse osmosis	Thin-film composite polyamide	Monovalent salts, seawater desalination	High rejection, mature technology	Fouling, energy demand	Very high
Membrane distillation	PTFE, PVDF, PP	High-salinity water	Uses low-grade heat, near-complete rejection	Wetting, heat loss	Medium
Forward osmosis	CTA, TFC membranes	Water extraction	Lower hydraulic pressure	Draw solution regeneration	Medium

Water treatment is one of the largest membrane markets globally. For reverse osmosis, nanofiltration, ultrafiltration, and microfiltration systems for seawater desalination, wastewater reuse, industrial water recovery and production of drinking water, the polymeric membranes are the predominant choice. Figure 4 illustrate a typical membrane design for waste water treatment. Despite

the development of new membranes, the thin-film composite (TFC) polyamide membranes continue to set the standard in RO due to their high salt rejection and acceptable water permeance (see Table 2) [116]. They have also demonstrated the relevance of the asymmetric membrane architecture consisting of an ultrathin selective layer supported by a porous substrate with reduced transport resistance [117]. Nanofiltration membranes are a unique intermediate technology between reverse osmosis and ultrafiltration, and are able to selectively remove multivalent ions, organic micropollutants, dyes and hardness species [118]. In systems where full desalination is not required, nanofiltration can offer useful energy savings because typically it is run at lower operating pressure than reverse osmosis [119]. One of the major problems with water-treatment membranes is fouling. Reduced flux, higher pressure demand and/or shorter membrane life due to organic matter, colloids, microorganisms and inorganic scale [120]. Various approaches have been tried to reduce fouling, including surface hydrophilization, zwitterionic coatings, incorporation of nanoparticles and smoother selective layers [121].

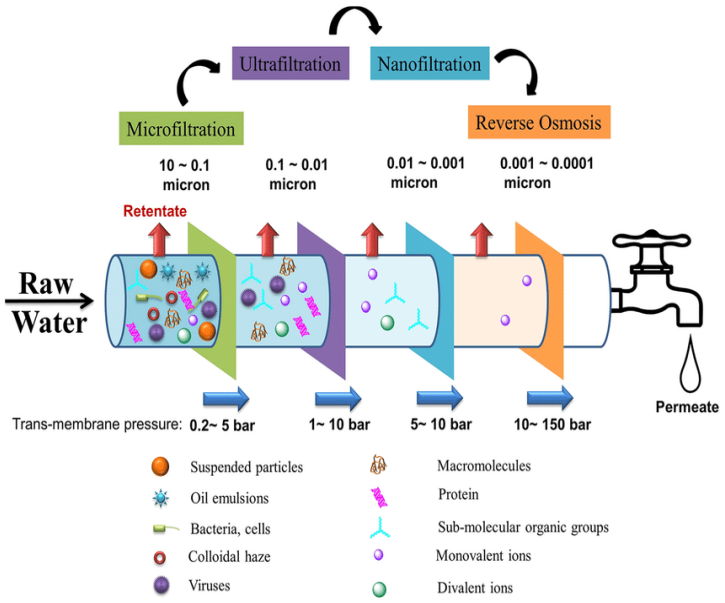

Figure 4. Wastewater Treatment Membrane [122].

Many anti-fouling modifications, however, are tested under simplified laboratory conditions which are not chemically complex wastes. This means that long term field validation is a key area of need between academic innovation and industrial deployment [123].

3.4 Organic Solvent Separations

Pervaporation membranes are used in a range of applications that include recovery of organics from dilute streams, drying of alcohols, and separation of azeotropic mixtures which are difficult to separate by distillation [110], [124-126]. Liquid feed is in contact with the membrane and the permeate is removed as vapour under vacuum or sweep gas conditions. A hydrophilic membrane is typically used to remove water from an alcohol mixture while an organophilic membrane is used to remove volatile organic from the mixture [127]. The less energy intensive part of pervaporation as compared to whole-stream vaporation is due to the fact that only the permeating fraction goes through a phase transition [124]. The most promising hybrid systems might include membrane/adsorption or membrane/distillation systems. In many instances, membranes have been found to be most cost-

effective when applied as a debottlenecking or polishing step in the current process, instead of being used as a full replacement process [128].

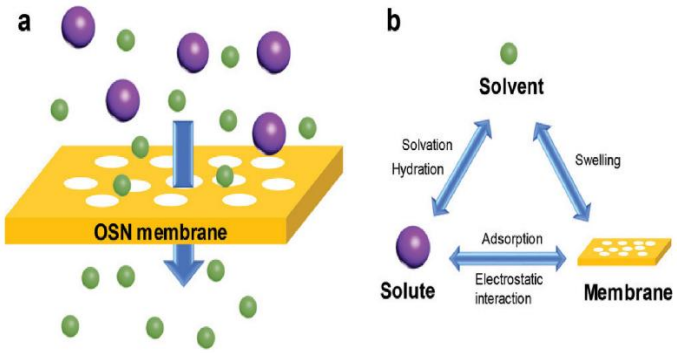

Figure 5. Organic Solvent Separations [129]

3.5 Pervaporation and Hybrid Separations

Pervaporation membranes are used in a range of applications that include the recovery of organics from dilute streams, the drying of alcohols, and the separation of azeotropic mixtures, which are difficult to separate by distillation [66], [130], [131]. In these systems, liquid feed contacts the membrane while permeate is removed as vapor under vacuum or sweep gas conditions [66], [130], [131]. A hydrophilic membrane is typically used to remove water from an alcohol mixture, while an organophilic membrane is used to remove volatile organic compounds from the mixture. Because only the permeating fraction undergoes phase transition, pervaporation can be substantially less energy-intensive than whole-stream vaporization [66], [130], [131]. The most promising hybrid systems include membrane/adsorption or membrane/distillation systems. In many instances, membranes have been found to be most cost-effective when applied as a debottlenecking or polishing conventional process, instead of being used as a full replacement process

3.6 Comparative Performance and Industrial Perspective

Across separation sectors, no single membrane material is universally optimal. Gasoline separations often prioritize permeability, selectivity, and pressure resistance. Water treatment emphasizes flux, fouling resistance, and chemical durability. Solvent systems require swelling resistance, while pervaporation requires powerful sorption selectivity. A recurring lesson throughout all sectors is that academic performance records often overemphasize intrinsic transport metrics while underemphasizing manufacturability, defect regulation, module layout, and lifetime economics. Commercial success relies more on balanced functionality than extreme laboratory values.

4. Polymer Membranes for Clean Energy Applications

In addition to molecular separations, polymer membranes have become vital parts of the current clean energy technologies. They are important for fuel cells, electrolyzers, batteries, and new electrochemical conversion systems because they can selectively transport ions, gases, or solvents, while providing mechanical separation between different environments. In many applications, it is the failure of the membrane that ultimately affects the operation of the device, its longevity, and its value. As a result, membrane science is now placed in a strategic state in process engineering and is also playing a key role in the global energy transition. Unlike conventional separation processes, clean energy systems often operate under coupled electrochemical, thermal, and mechanical stresses. Membranes must therefore satisfy a more demanding combination of conductivity, selectivity, chemical resistance, dimensional stability, and interfacial compatibility. These multi-parameter

requirements explain why progress in clean energy membranes is often slower than progress in simpler pressure-driven separations.

Table 3. Polymer Membranes in Fuel Cells, Electrolyzers, Batteries, and Flow Batteries

Energy System	Membrane Role	Common Materials	Key Performance Requirement	Principal Failure Mode	Future Opportunity
Proton exchange fuel cell	Proton transport, gas separation	Nafion, SPEEK, PBI	High conductivity, durability	Radical degradation, dehydration	Low-cost hydrocarbon PEMs
Anion exchange fuel cell	Hydroxide transport	Functionalized hydrocarbon polymers	Alkaline stability, conductivity	Cation degradation, swelling	Stable cation chemistry
PEM electrolyzer	Proton transport, gas barrier	PFSA membranes	Low resistance, gas purity	Oxidative thinning	Lower noble-metal systems
AEM electrolyzer	Hydroxide transport	Functionalized AEM polymers	Conductivity, durability	Chemical instability	Low-cost green hydrogen
Redox flow battery	Ion transport, crossover control	Nafion, hydrocarbon IEMs	Selectivity, low resistance	Vanadium crossover	Low-cost selective membranes
Lithium-ion battery	Separator	PE, PP, ceramic-coated polyolefins	Safety, porosity, wettability	Thermal shrinkage, dendrites	Safer high-energy cells
Solid-state battery	Solid electrolyte membrane	PEO, composite polymers	Ionic conductivity, interface contact	Interfacial resistance	Lithium metal compatibility

4.1 Fuel Cells

4.1.1 Proton Exchange Membrane Fuel Cells

Proton exchange membrane fuel cells (PEMFCs) have received substantial attention for transportation, portable, and stationary applications due to their ability to generate electricity from hydrogen with high efficiency and minimal local emissions [66], [130], [131]. In such systems, proton transfer is allowed to happen from anode to cathode across the membrane, whereas electron transfer is not allowed, and the amount of fuel crossover is limited [66], [130], [131]. Perfluorosulfonic acid membranes, especially the Nafion type, are still the industry standard because they have high proton-conducting capabilities, are resistant to chemicals, and have well-established processing methods. They have a phase-separated morphology, which allows fast proton transport under certain humidity conditions [3].

However, there are also a number of drawbacks to this. The proton conductivity will drop in low humidity and high temperature, the membrane cost is still high, and in long-term cycling, the polymer structure can be broken down by radical attack [132-137]. Furthermore, the presence of hydrogen crossover and changes in dimensions during hydration cycles may lead to lower durability. These difficulties have encouraged scientists to develop alternative materials based on hydrocarbons like sulfonated poly(ether ether ketone), sulfonated polyimides, polybenzimidazole systems, and composite membranes filled with inorganic materials [132-137]. Numerous alternatives are available that have lower cost or better thermal stability, but it is not easy to obtain the same combined conductivity and durability as the existing fluorinated membranes [132-137]. One of the most common

lessons that have been learned in this area is that conductivity alone is insufficient [132-137]. The long-term performance is also dependent on catalyst layer compatibility, water management, and repeated start-stop cycling.

4.1.2 Anion Exchange Membrane Fuel Cells

AEMFCs have become very popular due to the ability to utilize non-precious metal catalysts under alkaline conditions, and thus become less expensive [132-137]. In these devices, hydroxide ions are the mobile charge carrier instead of protons [132-137]. The functional groups generally used in polymer design in this area are cationic quaternary ammonium, imidazolium, piperidinium or phosphonium species linked to stable polymer backbones. There has been significant research effort in the pursuit of high hydroxide conductivity and low fuel crossover [132-137].

Alkaline degradation is the major problem, however. Under strong basic conditions, many cationic groups will react with nucleophiles, lose water (Hofmann) or undergo backbone degradation, particularly at high temperature. Water management is also complicated as a need for sufficient water is required for ion transport and too much swelling would compromise mechanical integrity [132-137]. Conductivity is no longer the primary tradeoff in anion exchange membranes but conductivity combine with long-term alkaline stability. It continues to be one of the most dynamic areas of polymer membrane research. Figure 6 explains the challenges which should be addressed to overcome the problems of proton transport and water balances in the polymer electrolyte membrane (PEM) fuel cells. In a different way, AEMFCs today attract the vast majority of consumers as they offer the use of low-cost non-platinum catalysts.

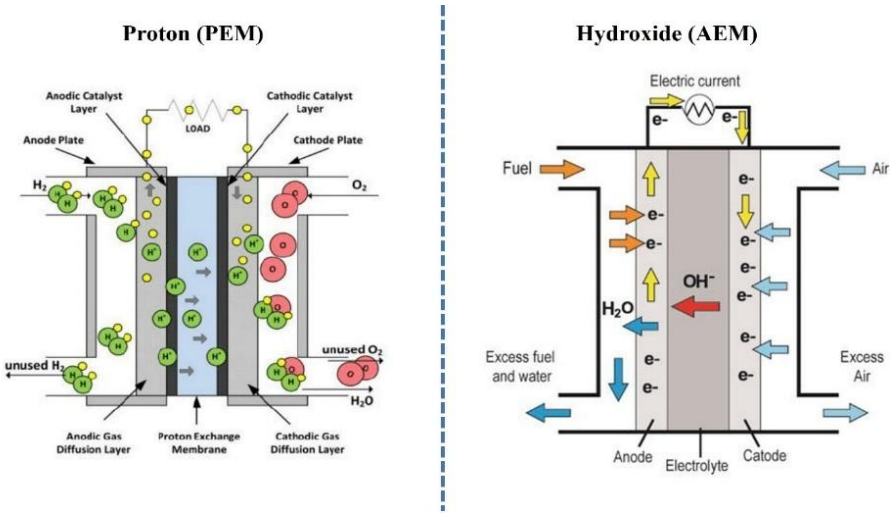

Figure 6. Proton (PEM) and hydroxide (AEM) conduction pathways, highlighting water management and degradation mechanisms [138], [139]

4.2 Water Electrolyzers

In water electrolyzers, the polymer membranes play a significant role as they separate product gases and transport ions between electrodes during the production of hydrogen [140-142]. The efficiency, purity of generated gases, and lifetime of the stack are strongly influenced by membrane performance. Perfluoro sulfonic acid membranes are typically used in proton exchange membrane electrolyzers due to their high conductivity and small size, operating at high current density [140-142]. These systems can respond rapidly to intermittent renewable electricity, making them attractive for green hydrogen production [140-142]. The alkaline and anion exchange membrane electrolyzers are designed to minimize the use of precious metals and expensive fluorinated materials. These systems, however, have similar issues involving membrane degradation and gas crossover, and lower

conductivity relative to proton-conducting analogs [140-142]. In electrolyzers, the membrane is usually treated as a passive separator, but in actively controlling ohmic resistance, water balance, and gas purity [140-142]. The economic value of improvements in membrane durability may thus be as significant as improvements in catalyst activity.

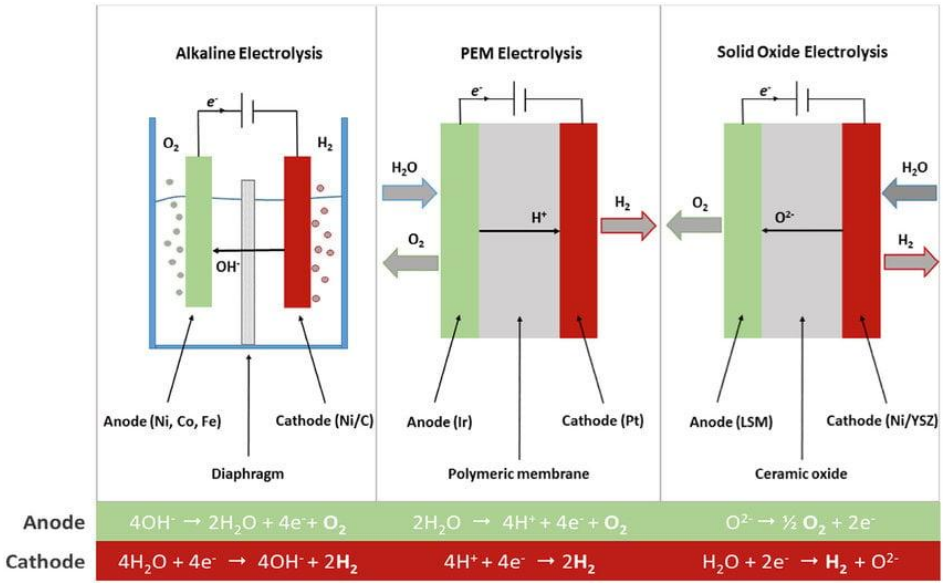

Figure 7. Comparative schematic of alkaline, PEM (proton-exchange membrane) and solid oxide water electrolysis [143]

4.3 Energy Storage

4.3.1 Redox Flow Batteries

Redox flow batteries are promising for large-scale stationary storage because energy capacity and power output can be independently scaled. These systems involve polymer membranes that separate electrolytes and allow the selective transport of ions to maintain charge balance [144-146]. Historically, perfluorinated ion exchange membranes (IEMs) have been the major choice for application in vanadium redox flow batteries due to their excellent conductivity and chemical stability [144-146]. However, high cost and undesired vanadium crossover made it necessary to search for a cost-effective hydrocarbon and composite alternative [144-146]. Suppression of the crossover of the active species is the major challenge in the flow battery membranes [144-146]. Excess crossover decreases the coulombic efficiency and leads to electrolyte imbalance, while excessive transport resistance results in a decrease in voltage efficiency [144-146]. This means that, in fact, the highest value commercial membranes are not necessarily the ones with the best conductivity, but rather the highest efficiency over the entire membrane system life cycle – thousands of charge/discharge cycles.

4.3.2 Lithium Batteries and Advanced Electrochemical Storage

In lithium-ion batteries, polymer membranes are commonly employed as porous separators that are electrically insulating but allow the passage of ions in a liquid electrolyte [144-146]. Polyethylene (PE) and polypropylene (PP) separators are still commercially predominant due to their low cost and good mechanical properties. However, they face some challenges such as thermal shrinkage, flammability, poor wettability, and dendrite penetration, particularly for high-energy cells [147], [148]. Thus, ceramic-coated separators, electrospun nanofibrous membranes, gel polymer electrolytes, and fully solid polymer electrolytes have been developed [147], [148]. The use of solid polymer electrolytes is particularly attractive as it can be used to enhance safety and allow lithium metal anodes [149]. But

the major impediments to the widespread use are the room temperature ionic conductivity and interfacial resistance. The battery sector is a good example of a principle that is used in many other contexts: the membrane principle. Materials that have remarkable intrinsic transport properties can be an engineering success or an engineering failure because of manufacturing complexity, safety certification, and interface engineering issues.

4.3.3 Emerging Electrochemical Conversion Systems

Recently, the use of polymer membranes in carbon dioxide electrolysis, ammonia synthesis, direct methanol fuel cells, and other innovative conversion platforms has been extensively investigated [149]. In these types of systems, the membranes control product selectivity, local pH gradients, ionic conduction, and reactant crossover. The membrane requirements are not yet completely standardized due to the fact that these technologies are still being developed [149]. However, durability under mixed chemical environments and contamination resistance are emerging as decisive factors. It implies that innovation in the membrane must proceed alongside device engineering rather than isolated materials exercise.

Fuel cells, electrolyzers, batteries, and flow batteries are very different, but have similar design challenges with membranes. A higher conductivity may lead to increased swelling. Thinner membranes decrease resistance, but increase cross-over risk. Strong chemical functionality improves transport but can increase the rate of degradation. Lower-cost hydrocarbon materials may sacrifice the durability of fluorinated benchmarks. Consistent with these trade-offs, future development will require more than just optimization of a single metric and will be more driven by multifunctional performance balance based on each device architecture.

4.4 Bioenergy Systems

Bioenergy systems have increasingly relied on polymer membranes for efficient conversion of renewable feedstock, collection of valuable products, and reduction of the energy demand in the process. They play a particularly important role in the purification of biogas, bioethanol production, biofuel production (biodiesel), and selective separation processes in integrated circular biorefineries, which are typically operated under relatively mild process conditions [150]. Membrane technology is used extensively for capturing CO2 from methane-rich biogas streams produced in anaerobic digestion processes in the area of biogas upgrading. This upgrading is necessary due to the fact that raw biogas is usually contaminated with significant amounts of carbon dioxide, water vapor, and trace contaminants, which affect the calorific value or direct grid/fuel application [150]. Selective removal of carbon dioxide has been studied with polyimides, cellulose acetate, facilitated transport membranes, and polymers of intrinsic microporosity, which possess good transport properties [150]. Mixed-matrix membranes containing inorganic fillers have also received increasing attention since the incorporation of inorganic fillers can lead to an improvement in the selectivity, but at the same time creates resistance to plasticization by carbon dioxide.

Even though membrane upgrading is more energy efficient than the traditional scrubbing method, its long-term performance is affected by impurities such as hydrogen sulfide, siloxanes, moisture, and varying feed composition. Membranes are also employed in the production of biofuel, especially biodiesel, where glycerol separation, catalyst recovery, water removal, and methanol recovery are achieved, reducing washing steps, distillation strength, and wastewater generation, although fouling is still a challenge. In bioethanol production, pervaporation membranes, specifically hydrophilic poly(vinyl alcohol) based membranes, are effective for ethanol dehydration and decreasing separation energy demand. The current polymer membranes support circular bioenergy systems through resource recovery and reuse, but future research needs to concentrate on developing

materials that resist fouling, solvent-resistant fabrics, hybrid membrane reactors, and low-cost modules for sustainable bioenergy production.

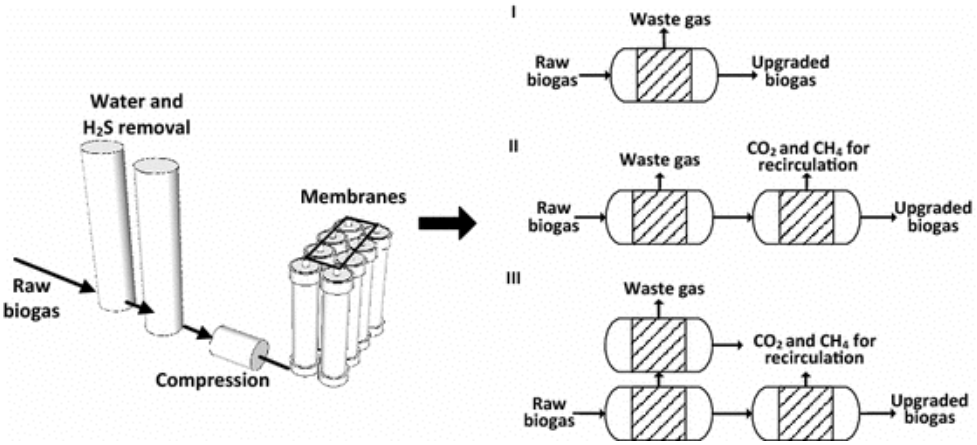

Figure 8. Polymer membranes in bioenergy processes, including biogas upgrading and ethanol dehydration pathways [151]

5. Advanced Materials and Fabrication Strategies for Next-Generation Polymer Membranes

Although significant advances have been made in separation science and clean energy technologies by conventional polymer membranes, many of these materials have been approaching their intrinsic performance limits [13], [15], [152]. Researchers need to develop new membrane materials and better production methods because existing membranes fail to work properly due to their permeability–selectivity trade-off, chemical degradation, fouling, physical aging, and their limited operational conditions [13], [15], [152]. Current research has shifted away from using basic modifications of polymer materials to developing membrane systems that involve an optimization of chemistry, morphology, and processing. The organization of transport pathways, its interfacial quality, the nanoscale free volume, and defect control are usually the decisive factors for the success or failure of the realization of a promising material [13], [15], [152]. This shift is important because membrane performance is not dependent on composition alone. The success or failure of a material in practical use depends on its transport pathway arrangement, interfacial quality, and nanoscale free volume and defect control.

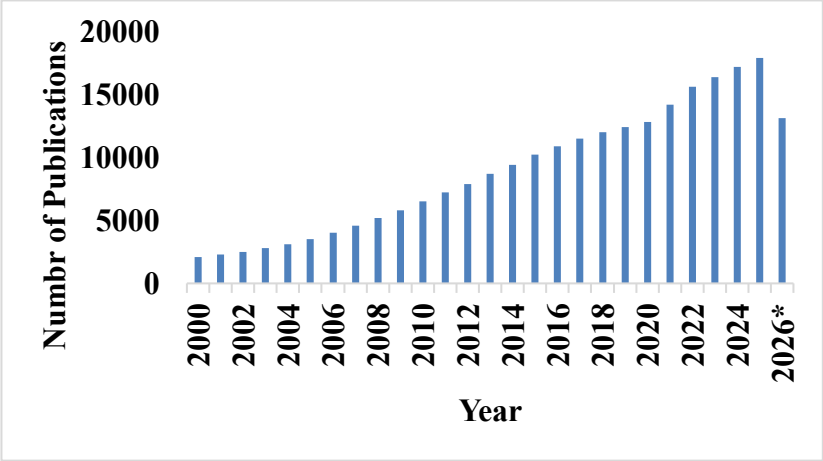

Figure 9. Growth of advanced membrane materials from 2000 to 2026.

Figure 9 illustrates research development in advanced polymer membrane classes from 2000 to 2026. Interest has expanded from traditional membranes toward mixed matrix membranes, PIMs, nanocomposites, ionomers, smart membranes, and machine learning assisted membrane design.

5.1 Thermally Rearranged and Carbon-Derived Polymers

Thermal rearrangement of precursor polyimides to polybenzoxazole structures is an important step that has been made in the development of high-performance membranes. Thermally rearranged (TR) polymers have stiff backbones and higher internal free volume, resulting in high thermal and chemical stability with rapid molecular transport. These properties are responsible for their high interest in demanding separation processes, such as CO_2 capture, hydrogen recovery, and hydrocarbon purification under extreme industrial conditions [153-156]. Block copolymers have also proven to be useful membrane materials as they form well-defined nanostructures on their own, which can create well-defined transport channels for water and ions. In desalination and ion conductive applications, these ordered morphologies are especially advantageous because they contain pathways that can be used to maximize the efficiency of the material to transport ions while rejecting contaminants [157]. With regard to electrochemical energy systems, advanced ionomers with functional groups such as sulfonic acid, phosphonium, quaternary ammonium, or other ionic groups have been shown to have better conductivity and compatibility with the interfaces. The alkaline and acidic degradation of membranes has also been improved significantly in recent years with cationic group chemistry [157]. Another emerging trend is the design of biomimetic membrane architectures. The selective transport behaviour of biological membranes is mimicked in these systems, which are constructed using peptide-based scaffolds, hydrogen-bonding networks or channel-inspired nanostructures. Many bio-inspired membranes possess excellent fouling resistance in addition to good selectivity, offering potential for use in advanced water treatment and selective separation processes[157].

These advances reflect the shift in membrane science from "passive" membranes to highly engineered membranes featuring controlled transport pathways, chemical durability, and adaptability.

5.2 Mixed Matrix Membranes

Advanced polymers and inorganic or porous nanofillers have provided a new avenue for the development of nanofillers of polymer–nanofillers, which can overcome the inherent permeability–selectivity tradeoffs of purely polymeric membranes [158-164]. Mixed-matrix membranes (MMMs) are membranes that are comprised of a continuous polymer matrix and dispersed fillers that can be metal-organic frameworks (MOFs), covalent organic frameworks (COFs), zeolites, graphene derivatives, silica nanoparticles, and MXenes. The combination of the processability of polymers and the molecular sieving ability of porous solids is the goal of MMMs in order to achieve properties exceeding those of the Robeson upper bound without compromising mechanical integrity [103], [165]. MOFs have received special attention among the various possible fillers due to their extremely porous structures as well as their tunable surface chemistry and environments. The resultant properties allow for the design of selective pathways for the transport of gases like carbon dioxide, hydrogen, and methane. But the major determinant of MMM performance is not determined by the filler itself, rather by the quality of the polymer–filler interface. If the adhesion is not good enough, non-selective voids can be formed, which can cause a decrease in separation efficiency [148-169]. In addition to increasing the loading of the fillers, current research increasingly considers the surface functionalization, the suppression of defects, and the enhancement of the compatibility of the different phases [148], [165], [166-169] . COFs provide a new platform of porous filler materials that have covalent bonds, chemical stability, and ordered pore channels. They are also structurally sound, and hence they are appealing in extreme nanofiltration and solvent separation applications [158--164]. Zeolites remain highly relevant, especially for thermally stable processes with well-defined microporous channels like natural

gas sweetening and hydrocarbon purification [158-164]. The advent of two-dimensional fillers such as graphene oxide, reduced graphene derivatives, and MXenes has provided new avenues in the design of membranes. They have a high aspect ratio and their interlayer spacing can be controlled, which can make highly tortuous diffusion pathways that promote molecular sieving and strengthen the stiffness of the membrane. In many systems, low filler loading can significantly improve selectivity and mechanical strength [158-164].

Although good laboratory advances have been made in hybrid membranes, the commercialization of these membranes is hindered by issues of reproducibility, consistent dispersion of fillers, long-term interfacial stability, and scalable fabrication [28], [170]. The paradigm is thus moving from finding new filler chemistries to developing well-established manufacturing procedures and control of nanoscale orientation. The different fabrication methods for MOFs, COFs, and 2D materials have reached advanced stages of development, which Figure 10 demonstrates.

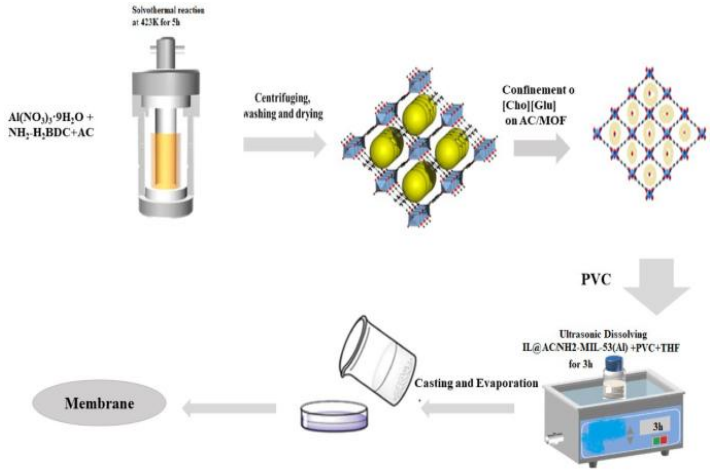

Figure 10. Integrating various fillers into polymer matrices to create MMMs [171]

5.3 Advanced Manufacturing

In addition to the chemistry of the materials, the method of fabrication can affect the performance of a membrane. Nanoscale control of the morphology, pore structure, thickness, and surface functionality can be realized using modern manufacturing methods, which have a significant impact on the transport behavior and durability [172-177]. Nanofibrous membranes made using electrospinning have successfully developed an interconnected pathway and a large surface area, which is very conducive to the formation of highly porous membranes [172-177]. The bacteria separator, the support for thin film composites, filtration media, and scaffolds for catalytic coatings are some of the applications for which electrospun structures are currently being utilized [186]. Their surface can be modified with hydrophilic/hydrophobic or antifouling layers, further extending their use in water treatment and bioenergy applications. Three-dimensional printing opens up new pathways for the fabrication of membranes with the ability to geometrically control channels, graded porosity, and integrated module architectures [172-177]. While the selective ultrafine nanopores are not directly formed by the usual printing techniques, hybrid approaches of printing and coating or post-treatment are developing rapidly [172-177]. Additive manufacturing could prove to be more impactful on spacers, supports, and module design than on selective layers themselves, in the near term [172-177]. Thin Film Composite membranes are the most commonly used in the industry for reverse osmosis, nanofiltration, and solvent separations, and the most common method for production is by the process of interfacial polymerization [172-177]. Some recent innovations currently include the use of more

environmentally friendly solvent systems, the use of more advanced monomers, more controlled reaction kinetics and the introduction of nanofillers during the reaction process [194]. The result of these developments has led to enhanced permeability, chlorine resistance and fouling tolerance. A significant development of this idea is the use of nanoparticles, like MOFs, COFs, silica, or graphene, as part of the selective polyamide layer of thin-film nanocomposite membranes [172-177]. These membranes are usually found to have better water flux, salt rejection, and fouling resistance than conventional thin film composite membranes [196–200]. With a view to the future, the most promising membranes might arise not from new polymers, but rather manufacturing approaches capable of producing defect-free, ultra-thin, and scalable membrane architectures.

The inventive fabrication techniques, including electrospinning, 3D printing, and interfacial polymerization for the new generation of membranes, can be seen in Figure 11.

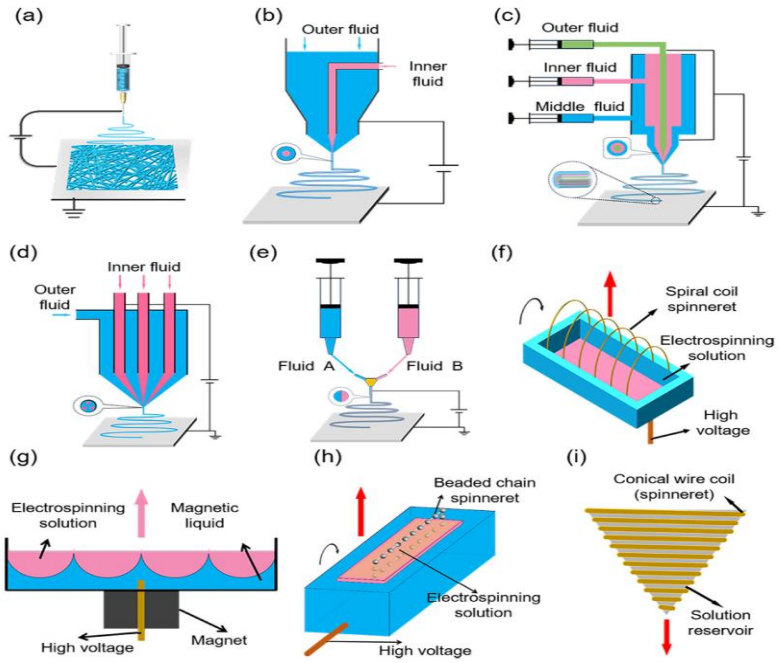

Figure 11. Advanced membrane fabrication techniques: electrospinning nanofibers, 3D-printed architectures, and thin-film nanocomposite assembly [178]

5.4 Data-Driven Material Discovery

The use of computation has greatly sped up the discovery of new membrane materials and optimization of processes [179-182]. Atomistic understanding of free-volume distribution, polymer chain mobility, sorption behavior, and interfacial transport phenomena, which are hard to investigate experimentally, is offered by molecular dynamics (MD) and density functional theory (DFT) simulation studies of these systems [179-182]. The prediction of permeability, selectivity, conductivity and mechanical properties using machine learning approaches with descriptor structures of polymers is gaining increasing traction. In these approaches, the need for trial and error experimentation with slow speed is reduced, and large chemical design spaces are screened very fast [179-182] [12], [141], [206–211]. Recently, new approaches using generative artificial intelligence and high-throughput screening methods have been introduced that suggest completely new polymer chemistries and optimal combinations of nanoparticles with polymers for hybrid membranes [179-182]. These approaches can also significantly reduce lead-time for concept development to experimental testing [179-182]. AI is being used in the production of membranes, too. By applying predictive algorithms,

parameters, such as interfacial polymerization time, solvent selection, curing temperature, and annealing process, can be optimized to achieve consistency and performance of membranes [179-182]. But the quality of data is a critical factor to determine the effectiveness of data-driven approaches. There are inconsistencies in the data for testing conditions, missing durability data, and reporting formats in many of the published membrane datasets. Therefore, future advancements need closer integration of simulation, machine learning, and rigorous experimental testing.

In the end, computational approaches are unlikely to replace experimental membrane science, but they are increasingly becoming essential tools for accelerating innovation through faster, smarter and more efficient innovation paths. The data-driven workflow for the integration of the molecular, ML, and the experimental validation in the membrane design process is presented in Figure 12.

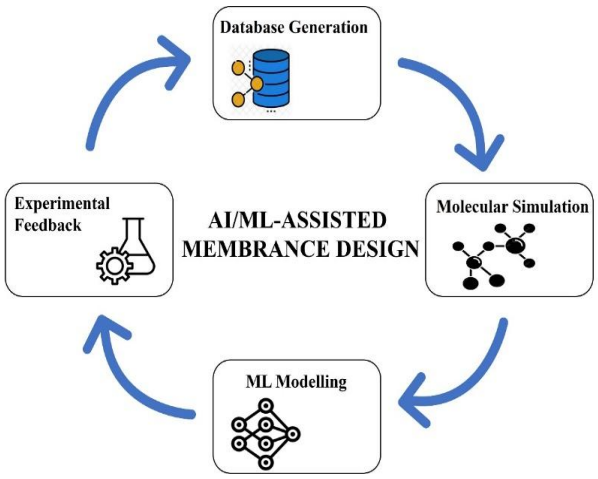

Figure 12. Schematic of AI/ML-assisted membrane design workflow: database generation, molecular simulation, ML modeling, and experimental feedback loops (created by the author).

6. Challenges and Outlook

6.1 Major Challenges

Polymer membranes are now crucial in fields such as clean energy systems and energy-efficient separations, but several scientific and engineering obstacles limit their broader application. Polymer membranes have come a long way since their inception and are increasingly embraced as the material of choice for energy-intensive separations and clean energy systems, but several scientific and engineering challenges remain. The permeability–selectivity trade-off, exemplified by the Robeson upper bound, is one of the most persistent challenges [91], [183-185]. However, materials like polymers of intrinsic microporosity, thermally rearranged polymers, and mixed-matrix membranes have significantly gotten closer to and/or surpassed this limit, and fundamental limitations for molecular transport still play a role [100], [186-190]. Therefore, further advances rely on the ability to achieve the highest permeability and selectivity in the laboratory, and to be able to operate them in realistic industrial feeds, mixed contaminants, pressure cycling, and extended operating times. This means innovative development at the molecular level (new polymer chemistries) and at the process level (optimized module and system integration). Simultaneous innovation at the molecular level by developing new polymer chemistries and at the process level by optimization of the module and system integration is required.

Another limitation is its durability in extreme conditions. The membranes in carbon capture systems are subjected to high levels of acidic and plasticizing gases, desalination membranes are subjected to oxidants and biological foulants, and fuel-cell membranes are subjected to repeated

humidity and temperature cycling [191-198]. Combined chemical, thermal, and mechanical stress can cause performance degradation. While some of the metrics for stability may be improved, that may also result in compromising other metrics, and multi-year service life becomes difficult target to achieve [191-198]. Fouling is still the major challenge in aqueous membrane separation. The accumulation of mineral scaling, deposits of colloidal materials, and biofilm formation are potential causes of increased hydraulic resistance, decreased permeate flux, and higher cleaning costs [191-198]. Although hydrophilic coatings and antimicrobial surfaces have improved resistance, fouling behavior remains highly feed-dependent and difficult to predict over long operating periods [191-198]. Combined advances in materials science, microbiology, and process control are thus necessary requirements for the effective solutions. Economic scalability is also equally important. The high-performance membranes are often based on specialty monomers, complex synthesis routes or manufacturing processes that involve a large number of solvents and are hard to commercialize [191-198]. For commodity separations, where the cost is the most important factor, new membranes have to be competitive not only technically, but also economically with mature thermal methods such as distillation [191-198]. Table 4 summarizes some major scientific, current mitigation strategies, and future directions.

Table 4. Major Scientific Challenges, Current Mitigation Strategies, and Future Directions

Challenge	Affected Applications	Current Mitigation Strategy	Remaining Gap	Future Direction
Permeability–selectivity trade-off	Gas separation	PIMs, MMMs, TR polymers	Aging, scale-up	Data-driven polymer design
Membrane fouling	Water treatment	Surface coating, hydrophilization, cleaning cycles	Long-term field durability	Self-cleaning smart surfaces
Chemical degradation	Fuel cells, electrolyzers	Stabilized backbones, antioxidants	Lifetime under cycling	Durable non-fluorinated ionomers
Swelling and dimensional instability	Ion-exchange membranes	Crosslinking, reinforcement	Conductivity loss	Nanophase control
Plasticization and aging	CO_2 separations	Thermal treatment, crosslinking	Long-term retention	Stable microporous polymers
Filler agglomeration	Mixed-matrix membranes	Surface functionalization	Batch reproducibility	Interface-by-design manufacturing
High fabrication cost	Advanced membranes	Thin-film composites, scalable casting	Specialty monomer cost	Green low-cost synthesis
End-of-life disposal	All sectors	Limited recycling efforts	Circularity gap	Recyclable membrane platforms

6.2 Sustainability and Lifecycle Considerations

Sustainability has become a core design principle with the transition of membrane technologies from niche applications to mainstream industrial applications [199-203]. The environmental impact will largely depend on the life cycle of the membrane separation processes, including how the membranes are produced, utilized, and disposed of, although membrane separations may require less energy than thermal processes [199-203]. Studies on environmentally-friendly production techniques such as solvent-free extrusion, aqueous-phase casting, the use of renewable feedstocks, and curing at lower

temperatures have become more prevalent. These strategies are designed to minimize the amount of hazardous solvents used, manufacturing emissions, and energy use during the manufacturing process. Another emerging concern is that of recyclability. The majority of traditional membranes feature a cross-linked network, multilayer composites, or additives, which make it difficult to recycle the membrane after use. Future circular material systems could utilize emerging dynamic covalent chemistry and thermally reversible crosslinks to disassemble, reprocess, and reuse membranes [199-203]. Membrane systems have less energy use during operation than distillation or evaporation systems, as revealed by lifecycle assessment studies. The advantages of these are offset if the energy-intensive synthesis or use of toxic solvents or short replacement cycles are required to produce membranes. Hence, the evaluation of sustainability needs to take into account the entire life cycle of a product, from raw material to end-of-life management [199-203].. Durability and reparability should be added to the list of sustainability indicators. A moderately successful membrane that lasts many years could have less environmental impact than a very successful membrane that needs to be replaced often.

6.3 Emerging Trends and Future Directions

The field of polymer membranes is moving to a new era of opportunities for transformative progress through integrated innovations, despite ongoing challenges. The potential for designing smart and stimulus-responsive membranes that can reversibly switch between different states of wettability, charge, selectivity, and permeability in response to external stimuli like pH changes, temperature, light, electrical fields, or chemical signals [28], [88], [204], [205], [206]. These include temperature-responsive block copolymers with tunable pore size and electrically-conductive polymers that can enable controlled ion transport. The applications of these systems include cyclic adsorption processes, Water Treatment Systems that respond to the water, and Renewable-energy based desalination systems. Membranes are also becoming increasingly important in future energy infrastructures. They play a crucial role in green hydrogen generation, CO_2 conversion to synthetic fuels, redox flow batteries, and next-generation lithium-based energy storage technologies [207-211]. This convergence demonstrates the growing trend of membranes to become the key element for integrated energy platforms beyond conventional separation applications. Rapid machine learning, AI, and high-throughput screening for membrane discovery and optimization is another major trend. Researchers may now be able to predict promising polymer structures, simulate transport behavior, and optimize fabrication conditions by data-driven methods, rather than performing trial-and-error experiments [12], [179], [212], [213]. Together with molecular simulations and automation of experimentation, these tools can significantly speed up innovation. Meanwhile, there is an increasing interest in coupling the membrane technology with the principles of the circular economy. Future materials should be fabricated with biodegradable polymers, recyclable composites, modular elements, and components that can be disassembled or reconditioned easily. This will need to be done not only by developing new chemistry, but by developing supportive policy frameworks and industrial redesign [191]. The progress presented here suggests that no one should expect membrane technology to remain a step-by-step advancement; instead, new applications are expected. The future generation of membranes will be intelligent and digitally optimized, energy-efficient, scalable and eco-friendly systems connected to other industrial and clean energy systems.

7. Conclusion

Polymer membranes have become key strategic technologies for separation and are now finding applications in a variety of water security, clean energy, and sustainable industry applications. They are highly useful in gas purification, carbon capture, desalination, water/solvent recovery, fuel cells, electrolyzers, batteries, and emerging electrochemical conversion platforms because of their

capability to operate on a selective transport and require a relatively low energy consumption for use. Global demand to decarbonize industrial activity and optimize resource efficiency will substantially increase the relevance of membrane technologies. This review has demonstrated that the polymer chemistry, nanoscale morphology, transport mechanism, and the fabrication process are the fundamental parameters that dictate membrane performance. Advances in rigid microporous polymers, ion-conductive materials, mixed-matrix membranes, thin-film composites, nanofibrous supports, and data-assisted materials discovery have significantly expanded the boundaries of what polymer membranes can achieve. In many applications, recent materials have approached or exceeded historical limitations in permeability, selectivity, conductivity, and resistance to degradation. Recent materials have reached or even surpassed historical limits in permeability, selectivity, conductivity, and degradation resistance in many applications. The common findings in all application areas show that high intrinsic performance alone is rarely sufficient for real-world success. Mixed feeds and pressure cycling are two challenges for gas separation membranes. Water-treatment membranes must withstand chemical attack and fouling. Membranes in fuel cells and electrolyzers should exhibit high electrochemical stability over a long period of time. The battery membranes must combine safety, transport efficiency, and robustness to endure the stresses of everyday use. These challenges highlight that the true benchmark of future membrane technologies cannot be best measured by maximum performance measured in the laboratory, but by sustained multifunctional performance under realistic operating conditions.

Another main finding is that there are numerous scientific trade-offs that many membrane fields face. Higher permeability will result in less selectivity. Increased conductivities can lead to increased swelling or crossover. Thinner selective layers may improve the flux, but increase the defect risk. Strong chemical functionality can improve transport capability but can also lead to degradation. The next stage of membrane innovation will likely be driven by integrated strategies rather than isolated material discoveries. A combination of advanced polymer synthesis, interface engineering, scalable manufacturing, digital process optimization, machine learning, and lifecycle sustainability assessment will be required. Processability, reusability, and industrialization should be considered from the initial stages of materials design. In conclusion, polymer membranes are poised to play a key role in a low-carbon and sustainable future. Their greatest contribution will no longer come from isolated record-setting materials but from robust, scalable, cost-effective systems that can be readily adopted across all industries and infrastructures. Future progress, therefore, depends on aligning membrane science with practical engineering realities, sustainability priorities, and long-term societal needs.

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