



Mass transport in carbon membranes

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Carbon molecular sieve membranes (CMSMs) are inorganic membranes produced by carbonization of a thermosetting polymer. The selection of the adequate polymer, the conditions of carbonization and post-carbonization treatment allow the production of a large variety of porous structures. The mass transport of species through these porous structures is not easy to model in detail. This review reports the last developments in the field of mass transport through CMSMs. The membrane production is also briefly touched upon, followed by the definition of transport equations and a description of detailed models for these membranes.

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Introduction

Carbon membranes have attracted an increasing amount of interest during the last few decades. This is due to their potential for a higher permeability, permselectivity, thermal-, and chemical stability [1,2]. Moreover, carbon membranes are produced from low-cost materials, generally by carbonization of a thermosetting polymer precursor coupled to pre- and post-treatment steps, all of which influence the final membrane properties. Not surprisingly, a wide variety of potential applications for

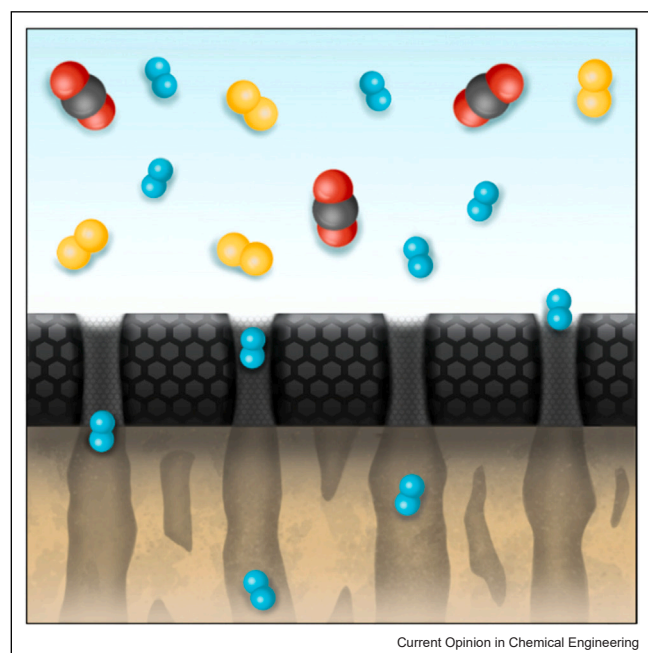
carbon membranes have emerged in fields such as biogas upgrading, H₂ purification, micro-/ultra- and nanofiltration, pervaporation, vapor permeation, and membrane reactors. The preparation of carbon molecular sieve membranes (CMSMs) for H₂ separation and tailoring its nanopore size and porosity is reported by Hu et al. [3]. In the wastewater treatment field, a SiO₂ composite microfiltration carbon membrane was prepared by Yao et al. for separation of oil–water mixtures [4]. Hydrophilic CMSMs suitable for bioethanol dehydration through pervaporation were developed by Rahimalimamaghani et al. [5]. These examples showcase the flexibility of carbon membranes. Within the carbon membrane realm, CMSMs are of particular interest for gas separations due to the tailorable pore-size distribution (PSD), which is tuned by optimizing the fabrication parameters (e.g. precursor type, carbonization temperature, and post treatment methods). The plethora of different applications for carbon membranes, which span from small to large molecules and from liquid to gas processes, hints to the fact that the transport phenomena occurring in carbon nanopores are complex, diverse, and intertwined. Accordingly, further development of carbon membranes requires an improved understanding of mass transport fundamentals and of the key parameters that control such phenomena.

With this work, we provide an up-to-date overview of mass transport within carbon membranes that aims at highlighting current knowledge and gaps in this field. We therefore discuss (i) mass transport theory for carbon membranes, (ii) common synthesis and characterization techniques in light of mass transport parameters, and (iii) modeling of mass transport inside carbon membranes. Moreover, promising new modeling approaches are identified that have the potential to improve fundamental understandings of transport phenomena in carbon membranes.

Mass transport theory

Carbon membranes are porous membranes that separate molecules, thanks to the nature and distribution of pores. Flow through porous media is largely controlled by the pore dimensions: among the many material parameters, this is the critical one that identifies the dominating transport mechanism. Figure 1 depicts selective transport through such pores. The pore dimensions and gas densities within those pores affect the rate of particle–particle collisions with respect to particle–wall

Figure 1



Schematic representation of selective transport through pores.

collisions. These in turn influence the characteristics of the prevailing transport mechanics. The frequency of these collisions is often described using the mean-free path (λ), defined as the average length a particle travels between collisions. Notably, the ratio between this mean-free path and the characteristic length of the physical system is defined as the Knudsen number. For porous media, this characteristic dimension is the pore diameter, therefore resulting in

$$Kn = \frac{\lambda}{d_p} \quad (1)$$

The gas kinetic theory applied to hard spheres provides a useful expression for the mean-free path:

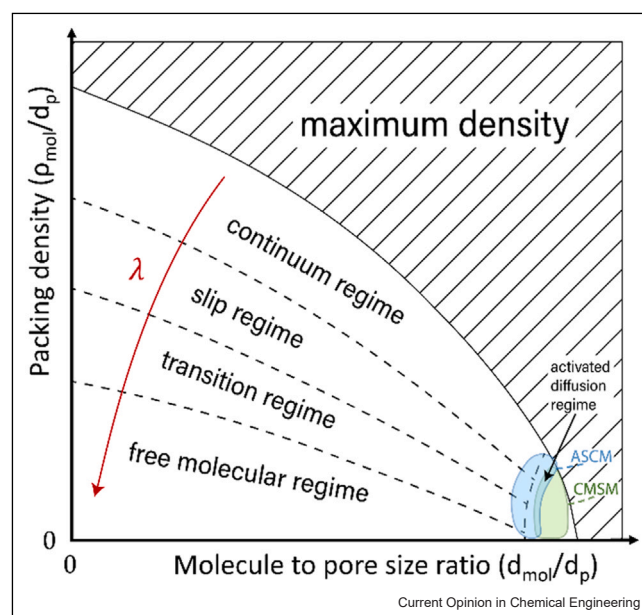
$$\lambda = \frac{RT}{\sqrt{2} \pi d_{col}^2 N_A p} \quad (2)$$

where d_{col} is the collision diameter. The Knudsen number is a key parameter in rarefied gas dynamic theory that quantifies the degree of gas rarefaction [6]. Based on characteristic ranges of Knudsen numbers, three to four flow regimes are generally accepted based on increasing the degree of gas rarefaction: they are typically identified as 'continuum flow', 'slip flow', 'transition flow', and 'free molecular flow' [7]. At $Kn \ll 1$, the gas behaves like a continuous fluid; particle-particle collisions prevail over particle-wall collisions and there is effective transfer of these. Moreover, at the pore wall, the velocity is generally zero (no-slip boundary). For

flows that have small but not negligible Knudsen number, rarefaction phenomena start occurring: a finite tangential velocity is observed near the pore wall called the 'slip' phenomenon [7]. Molecules are trapped near the wall in lesser degree due to rarefaction, which reduces the collision frequency of these trapped molecules. The resulting decrease in momentum loss due to these collisions contributes to the generation of a slip velocity. As the Knudsen number becomes even larger, these rarefaction effects start dominating and a transition regime is observed. At $Kn \gg 1$, extremely rarefied flow effects dominate, and particle-wall collisions govern the mass transport resulting in a free molecular regime. The mean-free path within this regime is larger than the pore diameter and there is very limited transfer of momentum between molecules at which point the gas is completely devoid of continuum properties.

Figure 2 shows a schematic representation of the flow regimes in porous media discussed above as a function of the 'packing density' (y axis) and kinetic diameter of the permeating molecules relative to the pore diameter (x axis). The packing density is defined here as the molar density relative to the pore diameter (ρ_{mol}/d_p). The schematic is a qualitative illustration of the underlying concept and correlations between these regimes as a result of particle (packing) density and relative molecular size. The mean-free path is a function of both the kinetic diameter ($\lambda \propto d_{mol}^{-2}$) and the molar density ($\lambda \propto \rho_{mol}^{-1}$) as becomes clear from Equation (2). For ideal pure gasses, the collisional diameter is equal to the kinetic diameter of a

Figure 2



Schematic representation of flow regimes in porous media as a function of packing density and molecule size relative to pore size.

molecule and the molar density is defined as $\rho_{\text{mol}} = \frac{p}{RT}$. Therefore, the largest mean-free path is achieved at the lowest molar density and lowest molecular diameter for a given pore diameter. As the molar density or the molecule size increases, particle–particle interaction frequency increases, leading to larger momentum transfer and therefore in a shift in the flow regime. It is worth noting that a maximum density exists, as the structural integrity of the porous medium is compromised past certain pressures imposed by the permeating species. It is important to note that the precise (quantitative) shape and proportions of the flow regimes are a function of the properties of the permeating fluid and the system (e.g. porosity, tortuosity, porous material, multicomponent interactions, and surface affinity). For gas separation applications, the leading carbon membrane types are either CMSMs or ASCMs (adsorption-selective carbon membranes). They generally have extremely narrow pore sizes of 3–5 Å and 5–7 Å, respectively [8]. They operate mostly in an activated diffusion regime as shown in Figure 2, where CMSMs are depicted by the green region and ASCMs are depicted by the blue region.

Within the defined flow regimes, different mass transport mechanisms occur. The following 7 mass transport mechanisms are generally distinguished for permeation through (carbon) membranes:

1. Viscous flow and/or molecular diffusion for continuum fluid transport.
2. Transition- and slip flow in the transition and slip regime where slip effects on the pore walls start occurring.
3. Knudsen diffusion in the free molecular regime where particle-wall collisions govern the transport.
4. Surface diffusion where molecules move along a surface through continuous adsorption and desorption processes.
5. Capillary condensation where the partial pressure of a condensable permeating component is sufficient to facilitate condensation (and thereafter displacement) inside the porous network.
6. Activated diffusion (also referred to as configurational diffusion or molecular sieving) where pore dimensions start approaching molecule sizes. Interaction potentials overlap considerably, creating a much stronger potential for trapped gas molecules, which introduces a series of activation barriers that the molecules must overcome [9,10].
7. Solution diffusion through a dense solid layer where transport of particles is considered to go through transient gaps within the solid matrix rather than through a fixed porous network.

In principle, transport of species could go through both the porous network and the solid matrix. However,

carbon membranes are currently considered refractory porous solids and transport through the transient gaps of the solid carbon matrix can be assumed negligible compared with transport through the pores [2,11]. For permeation of noncondensable gases, transport through means of capillary condensation is often considered negligible with respect to other gaseous and surface transport mechanisms for permeation of simple gases. The specific contribution of each mechanism and the transition points between transport mechanisms is a function of the material properties, PSD, operating conditions, and inlet composition [12]. Surface diffusion often occurs in parallel with other transport mechanisms such as Knudsen diffusion or molecular sieving [13]. Studies on porous media often attempt to define transition points between these mechanisms. However, the complex way these mechanisms interact makes the identification of clear-cut transition points challenging. No consensus is reached in literature, and they cannot be considered generally applicable to the wide range of porous carbon membranes. Table 1 gives an overview of transition points found in literature between mass transport mechanisms based on pore sizes or dimensionless numbers (Knudsen, Reynolds, and Mach) within different fields related to rarefied flows and porous media. Some authors neglect activated transport (e.g. surface diffusion and molecular sieving) when defining flow- and mass transport regimes while others neglect transitional transport (e.g. slip flow and transition flow). The lower bound for molecular sieving lies between nano- and subnanoscale depending on the author. For works defining a lower boundary for Knudsen diffusion, this boundary is overall agreed to be 2 nm. The upper boundary varies, but works using the Knudsen number agree on a value of $\text{Kn} > 10$. There is no clear agreement on boundaries for other flow regimes. Furthermore, the boundary for viscous flow differs strongly per author.

Not every mass transport mechanism contributes to permselectivity of membranes. Gas separation within a porous membrane can generally be based on four mechanisms out of the previously defined seven [14]. These are based on molecular weight due to Knudsen diffusion, selective adsorption to pore walls followed by surface diffusion, capillary condensation of components and subsequent selective transport, and last interaction potential in terms of kinetic diameter through activated diffusion or molecular sieving. The mechanism(s) dominating the transport in carbon membranes depend on the pore network and functional groups on the walls, which in turn are affected by the pre- and post-treatment as well as the specific production steps adopted in the synthesis. For example, selection of precursor, oligomer molecular weight, degree of polymerization (DP), pyrolysis temperature, heating rate, atmosphere, and thermal soaking time are critical factors for the PSD and

Table 1

Transition points between mass transport phenomena as found in literature.

	Viscous flow	Slip flow	Transition flow	Knudsen diffusion	Surface diffusion	Molecular sieving
Hamm et al. [18] (gas separation in supported carbon membranes)	$d_p > 50\text{nm}$	-	-	$2 < d_p < 50\text{nm}$	$0.6 < d_p < 2\text{nm}$	$d_p < 0.6\text{nm}$
Ma [19] (shale pores)	$\text{Kn} < 0.01$	$0.01 < \text{Kn} < 0.1$	$0.1 < \text{Kn} < 10$	$\text{Kn} > 10$	-	-
Chen et al. [20] (shale nanopores)	$\text{Kn} < 0.001$	$0.001 < \text{Kn} < 0.1$	$0.1 < \text{Kn} < 10$	$\text{Kn} > 10$	-	-
Chambre and Schaaf [7] (rarefied gas flow theory)	$\frac{\text{Ma}}{\sqrt{\text{Re}}} < 0.01$	$0.01 < \frac{\text{Ma}}{\sqrt{\text{Re}}} < 0.1$ for $\text{Re} > 1$ $0.01 < \frac{\text{Ma}}{\text{Re}} < 0.1$ for $\text{Re} < 1$	$0.01 < \frac{\text{Ma}}{\sqrt{\text{Re}}} < 3$	$\frac{\text{Ma}}{\text{Re}} > 3$	-	-
Keizer et al. [21] (gas separation in inorganic membranes)	$d_p > 50\text{nm}$	-	-	$d_p > 2\text{nm}$	$2\text{nm} < d_p < 50\text{nm}$	$d_p < 2\text{nm}$
Li [22] (ceramic membranes) based on Liepmann [23] and Kong and Li [24]	$\text{Kn} < 0.167$	$0.167 < \text{Kn} < 10$	-	$\text{Kn} > 10$	-	-
Choi et al. [25] (porous media)	$d_p > 20\text{nm}$	-	-	$2 < d_p < 100\text{nm}$	-	$d_p < 1.5\text{nm}$
	$\text{Kn} = \lambda/d_p$	$\text{Kn} = \lambda/d_p$			$\text{Ma} = v/c$	

for the functional groups in the porous structure of the fabricated carbon membranes [1,2]. These production parameters can be fine-tuned to achieve specific separations and reaction performances [15].

During operation, several aspects can severely affect mass transport inside carbon membranes. When operating above the carbonization temperature, permeating species as well as existing functional groups become reactive. The membrane structure becomes more dynamic and eventually changes permanently, which influences the mass transport. Another factor that could impact permeation performance is the presence of organic contaminants, which is discussed by Jones and Koros [16]. Carbons generally have nonpolar surfaces that can adsorb organic contaminants as low as 0.1 ppm, thus leading to pore blocking and deterioration of the membrane performance. A similar pore blocking effect is observed in the presence of water, where the interaction of water molecules with functional groups containing oxygen effectively reduces the pore size. This effect was shown by Llosa et al. [17]: they demonstrated an increase in O_2/N_2 permselectivity with a reduced permeance due to the oxygen chemisorption and water physical adsorption. The presence of adsorbing fluids strongly affects the mass transport of other permeating species inside carbon membranes.

The adsorption and condensation of fluids inside pores is however a reversible process. These species are desorbed by increasing temperature, which is referred to as the membrane activation temperature [1]. The rate of desorption depends on the interaction of the water molecules with functional groups on the wall as well as the operating conditions. Membranes carbonized at intermediate

temperatures will retain more functional groups on the walls from the original precursor, resulting in more water adsorption. Carbonization at higher temperatures removes more functional groups, reducing the interaction strength of the water molecules with the pore walls. The required membrane activation temperature is lowered as a result. The exposure to higher temperatures can lead to a shift in dominant transport mechanism due to the change in effective pore size as water adsorbs or desorbs. An alternative solution proposed by Jones and Koros is the implementation of a hydrophobic barrier layer on the carbon membrane to avoid adsorption of water [26]. It is to be noted that the adsorption of water in these ultramicropores has not been described as capillary condensation. This is because the ultramicropore regime does not facilitate a continuum fluid regime with classical hydrodynamics. The size of the pores only facilitates singular water molecules in a very restricted passage. Coasne et al. [27] describe such critical capillarity effects in detail.

Synthesis and characterization techniques

Carbon membrane synthesis starts with precursor selection based on parameters such as price, glass transition temperature, high aromatic carbon content, required functional groups, the required PSD, and porosity of the structure after carbonization. Phenolic resins, polyimides, cellulose acetate, polyfurfuryl alcohol, polypyrrolidone, and polyphenylene oxide are the most commonly used precursors for carbon membrane synthesis [28]. In terms of structure of the carbon membranes, it could be supported or self-supported. In case of supported carbon membranes, with the mechanical stability of the support, the membrane's thickness could be minimized (1–17 μm) to enhance the permeance of the membrane reducing the resistance of transport [29,30].

Higher permeance will be beneficial in terms of lower required membrane areas, leading to reduction in the construction and operational costs.

After the selection of precursor and appropriate support, the precursor is dissolved in an organic solvent to result in a solution to be coated on the support. The coating could be done via technologies such as CVD, dip coating, spin coating, ultrasonic coating, and other new techniques. Normally after the coating, the membrane is dried/polymerized for a short time and then carbonized. In the polymerization step, the DP plays a critical role in determining the final PSD in the CMSMs [31]. The chosen carbonization temperature, generally above the glass transition temperature, determines the final PSD, electronic structure, and functional groups present in the membrane. Usually, in membranes synthesized from phenol-formaldehyde resins (Novalac), the porous structure appears in carbonization temperatures starting from 400°C. The porosity and diameter of the pores increase up to 650°C. In carbonization temperatures higher than 650°C, the pores start to shrink and most of the functional groups leave the membrane structure, resulting in reduction of hydrophilicity and average pore size. For separation processes containing molecules with similar kinetic diameter but different dipole moments, the membrane could be tuned accordingly. This is done with precursor selection and carbonization temperature to contain and retain certain functional groups to increase the interaction of the desired molecule with the porous structure. In carbonization temperatures higher than 1100°C, the amorphous carbon structure shifts toward a graphite-layered structure and most of the pores diminish [32].

Post treatment of the carbon membranes could be done via reversible or irreversible methods. Aging of the carbon membrane in an atmosphere containing water molecules is a reversible process. However, carbon membrane post treatment with oxygen or fluorinated gas molecules is an irreversible chemical post treatment that changes the affinity of the membrane toward polar or nonpolar molecules permanently [33].

For characterization of carbon membranes, analysis techniques such as SEM, TEM, FTIR NMR, XPS, XRD, TGA, Raman, and permoporometry could be utilized. FTIR NMR, XRD, Raman, and XPS will determine the type of functional groups and the carbon structure in the membrane, while SEM, TEM, TGA, and permoporometry are used to measure the selective layer thickness, PSD, hydrophilicity, and the affinity of the carbon membranes toward molecules.

Mathematical modeling

Understanding the behaviour of the separation mechanisms and mass transport mechanisms is crucial to

the development of carbon membranes. Mathematical modeling is a key tool to aid this development. Currently, few models exist that accurately describe carbon membranes. Moreover, reproducibility of carbon membranes with the same characteristics is currently limited. While the several degrees of freedom available for carbon membrane synthesis are advantageous for fine-tuning, they prevent the adoption of a uniform model for mass transfer.

The implementation of the solution-diffusion model for gas permeation in carbon membranes has been discussed by Ismail [2]. The solution-diffusion model describes overall permeation in a simplified flux equation. It is derived from a chemical potential balance across the membrane interface between a compressible fluid and an incompressible membrane. Ismail further discusses the implementation of the solution-diffusion model for binary mixtures as opposed to single gasses, first proposed by Chen and Yang [34]. Their equations describe the flux through a membrane for binary mixtures, considering both binary diffusion and self-diffusion.

Another popular approach is to use Fick's first law on individual transport phenomena, which are then summed according to a set of assumptions. Gilron and Soffer implemented this methodology considering several simultaneous phenomena [35]. Their model accounts for Knudsen diffusion, surface diffusion, and molecular sieving. They rewrite the transport in terms of permeance ($P_i = J_i/\Delta p$), and investigate with a parallel resistance model and a resistance-in-series model. The parallel resistance model assumes that the transport mechanisms occur in parallel inside the pores and are therefore additive, $P_{\text{tot}} = \sum_i P_i$. They compare this approach to a resistance-in-series model, where pores are assumed to change width along their axial direction and the dominant transport mechanism depends on the width of the pore section. The mass transport mechanisms are summed in series as follows: $P_{\text{tot}} = \sum_i 1/P_i$. They find the parallel resistance model to predict a surprisingly high tortuosity and unrealistic affinity of helium to the carbon surface through fitting of temperature-permeance data. Their resistance-in-series model predicts a more realistic tortuosity and activation energies for the permeating gases they investigate.

Rangarajan et al. proposed a modeling method for asymmetric porous membranes similar to the parallel resistance model [36]. This model differs from the model by Gilron and Soffer as it considers the simultaneous occurrence of mass transport phenomena with a PSD as a weight factor instead of summing them up directly. This was adapted by Li to ceramic membranes and carbon membranes [22]. Pirouzfar and Omidkhan attempted to implement a genetic algorithm to fit this model to experimental data for a CMSM with a sum-

squared error function for the permeability [37]. Their methodology is promising, but they lump their fitting parameters together to improve fitting that decreases the physical relevance of the fit. An interesting approach could be to separate the quantifiable fitting parameters and enforce realistic physical boundaries, so as to draw more meaningful conclusions from the resulting fits. Owing to the shortcoming of Fick's law for multi-component systems, multiple models have been developed that take multicomponent interactions into account. The Wilke and Maxwell–Stefan diffusion flux models assume bulk diffusion, whereas the Dusty Gas Model describes the combined bulk and Knudsen diffusion fluxes in rarefied gas flow regimes [38]. The Dusty Gas Model is generally suited for macro- and mesopores, which is seen in the supports of carbon membranes. Krishna proposed an implementation of Maxwell–Stefan equations for binary mixtures in zeolites and other crystalline materials [39,40]. The Maxwell–Stefan equation as well as the Dusty Gas Model have been applied to carbon membranes by multiple works [41–45].

Mass transfer through porous media depends on the topology of pores. Ranging from macropores where bulk behavior dominates, to nanoporous materials where surface- and confinement effects lead to complex dynamics. The structure of membrane materials is often heterogeneous. Moreover, in the case of carbon membranes, experimental determination of structure and dynamics at the molecular length scale is a challenging task. Simulation techniques such as molecular dynamics and Monte Carlo provide an excellent alternative. They can help to elucidate general trends, refine existing laws, and to explore the limits of phenomenological models. Monte Carlo is especially popular for equilibrium studies in porous materials. In the Grand Canonical Ensemble (fixed μ , V , and T), it provides insights into adsorption or condensation. For example, Monte Carlo simulation of condensation in cylindrical corresponds well to experimental data [46]. Pore-filling pressures of a broad range of adsorbate–adsorbent combinations are shown to follow simple general laws based on fluid density and surface tension. Fluid behavior in simple geometries such as slits or cylindrical pores is well understood. However, these geometries may fail to paint a complete picture of mass transfer through the ill-defined topologies of carbon membranes. In that case, building representative structures is pivotal to the success of any simulation approach. Reactive force fields have been developed to aid this process. For example, the Reactive Empirical Bond Order potential was used by Bousige et al. to create a range of carbon structures [47]. By cooling down a box of randomly placed atoms, they created disordered porous structures of varying density, porosity, and mean pore diameter. Applying various simulation techniques, they show that diffusion in such

media is governed by subsequent surface adsorption and relocation. Although the geometry is much more complex than, for example, a simple slit diffusion, it still obeys relatively simple laws.

Instead of starting from a collection of atoms, reactive force fields that capture the effects of carbonization of polymer precursors are also available. Reactive molecular dynamics force field (ReaxFF) is one of the most prominent approaches. Recently, the CHON-2019 parameterization has been published [48]. Aptly named, it was developed to describe the carbonization of polymer precursors that contain C, H, O, or N atoms. It has been used to, for example, study less expensive alternatives to existing carbon fiber precursors and to develop hybrid materials with interesting electrical properties [49].

Conclusions

Carbon membranes are promising for a wide variety of applications. Improving the fundamental understanding on its transport behavior is of paramount importance for carbon membrane development. In this work, mass transport through carbon membranes was reviewed and promising research directions were identified. First, rarefied flows and mass transport in porous media show a range of flow regimes based on the mean-free path of permeating species. Within these flow regimes, seven different transport mechanisms are defined for porous media. These transport mechanisms were discussed in the context of carbon membranes. Pore blocking, its causes, and possible regeneration procedures were identified. We gave an overview of the main synthesis- and characterization techniques for carbon membranes and their effects on the membrane properties. Last, multiple simplified approaches were discussed in modeling works on carbon membranes. These simplified models have limited applicability to diffusion in complex nanoporous structures. Molecular simulation techniques can be used to gain additional insight into the applicability and limitations of these models, as well as develop new ones. Future applications will greatly benefit from a better understanding of the porous structure and dynamic behavior of carbon membranes. Advancements will be driven by a multitude of fields such as experimental characterization techniques, phenomenological models for process design and optimization, and molecular simulation methods. Specifically, future research should focus on exploring pore blocking and the behavior of water with surface-functional groups by means of molecular simulation. Interaction potentials and thermodynamic properties could be obtained through calculations rather than costly experimental methods. Simulations could enable and optimize the predictive synthesis of membranes and fine-tune parameters such as hydrophilicity and PSD. In conclusion, coupling molecular simulations, targeted experiments,

and larger-scale models, such as phenomenological permeability models and computational fluid dynamics, would be key for advancing carbon membrane modules.

Data availability

Data will be made available on request.

Declaration of competing interest

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

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